STATISTICAL THERMODYNAMICS OF MIXTURE OF BOSE-EINSTEIN AND FERMI-DIRAC 'LIQUIDS'

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1. Introduction

Recent experiments of Abraham, Osborne and Weinstock (1949a) and of Daunt and Heer (1950) indicate that He^3 does not show superfluid properties even down to $0.25°K$. unlike He^4 which becomes superfluid at about $2.19°K$. This seems to confirm London's (1938) hypothesis that the peculiar phase transition in Helium (i.e. He^4) can be interpreted as the 'condensation' phenomenon exhibited by an ideal Bose gas so that no transition would be expected in the case of He^3, which obeys Fermi statistics. Hence, it is now generally held that the difference in the Behaviour of He^3 and He^4 arises from the different statistics that they obey.

Heer and Daunt (1951) have proposed 'smoothed' potential models for considering mixtures of Bose and Fermi liquids. They have assumed that the 'Fermi liquid' can be regarded as an ideal Fermi gas in a constant potential well $-\chi_F^0$, and the 'Bose liquid' as an ideal Bose gas with a constant potential well $-\chi_B^0$. In the case of the mixture they have assumed that the liquids are incompressible and form statistically independent systems. Thus they have written for the total volume V, and the total potential χ, of the mixture the expressions

$$V = N_F V_F^0 + N_B V_B^0 .$$

$$\chi = N_F \chi_F^0 + N_B \chi_B^0 ,$$

respectively, where V_F^0 and V_B^0 are the respective atomic volumes. Further, they have assumed the vapours to be perfect gases. Heer and Daunt (1951) and more recently Daunt, Tseng and Heer (1952) have applied this model to calculate the partial vapour pressures and the distribution coefficients of their 'model solutions'. They find that the theoretical predictions are in good agreement with the observed properties of He^3-He^4 mixtures.

The present paper is concerned with a detailed discussion of the thermodynamic properties of mixtures of Bose-Einstein and Fermi-Dirac liquids when the distribution laws are of the more general type:

$$N_B(\epsilon)\, d\epsilon = \frac{N_B V_B^0 C_B \epsilon^{s_B-1} d\epsilon}{\dfrac{1}{A_B^0}\exp\left[\dfrac{\epsilon}{kT}-\dfrac{\chi_B^0}{kT}\right]-1}, \qquad \qquad \qquad (1)$$

$$N_F(\epsilon)\, d\epsilon = \frac{N_F V_F^0 C_F \epsilon^{s_F-1} d\epsilon}{\dfrac{1}{A_F^0}\exp\left[\dfrac{\epsilon}{kT}-\dfrac{\chi_F^0}{kT}\right]+1}, \qquad \qquad \qquad (2)$$

for a Bose and a Fermi 'liquid' respectively. In the sequel we shall refer to them as Liq. B and Liq. F. Clearly, our results would reduce to those of Daunt and Heer when

$$s_B = s_F = \frac{3}{2},$$

and

$$C = \frac{2\pi g(2m)^{\frac{3}{2}}}{h^3},$$

where g is the weight factor, being 1 for He^4 and 2 for He^3. As usual, the conditions for the onset of extreme degeneracy are

$$A_B^0 \exp\left(\frac{\chi_B^0}{kT}\right) \equiv A_B^{0*} = 1,$$

$$A_F^0 \exp\left(\frac{\chi_F^0}{kT}\right) \equiv A_F^{0*} \gg 1.$$

Kothari and Singh (1941, 1942) have studied the properties of pure Bose and Fermi gases obeying general distribution laws of the type given above. Wherever possible, we shall use their notation.

In the sequel we shall consider the following cases of mixtures of Liq. B and Liq. F:

> (i) Liq. F Boltzmannian $\left(A_F^* \to 0\right)$,
>
> (ii) Liq. F Non-degenerate $\left(A_F^* \ll 1\right)$, and
>
> (iii) Liq. F Degenerate $\left(A_F^* \gg 1\right)$.

In each of these cases we distinguish between two ranges of temperature, viz., (a) below the λ-temperature and (b) above the λ-temperature, of the mixture. It is of interest to do so because below T_λ Liq. B is degenerate $\left(A_B^* = 1\right)$ and above T_λ Liq. B is non-degenerate $\left(A_B^* \ll 1\right)$.

2. The Pure Liquids

The generalized distribution laws lead to the following expressions for the Helmholtz free energy :—

$$F_B^0 = -N_B \chi_B^0 - N_B kT \left[1 - \log A_{0B}^{0*} + b_2 A_{0B}^{0*} + \frac{b_3}{2}\left(A_{0B}^{0*}\right)^2 + \ldots\right], \quad \ldots \quad (3)$$

$$F_F^0 = -N_F \chi_F^0 - N_F kT \left[1 - \log A_{0F}^{0*} - b_2 A_{0F}^{0*} - \frac{b_3}{2}\left(A_{0F}^{0*}\right)^2 - \ldots\right], \quad \ldots \quad (4)$$

of non-degenerate and

$$F_B^0 = -N_B \chi_B^0 - \frac{N_B kT}{A_{0B}^{0*}} \zeta\left(s_B + 1\right), \qquad \ldots \qquad \ldots \qquad \ldots \qquad \ldots \quad (5)$$

$$F_F^0 = -N_F \chi_F^0 + \frac{s_F}{s_F + 1} N_F \xi_0^0 \left[1 - \frac{\pi^2}{6}\left(s_F + 1\right)\left(\frac{kT}{\xi_0^0}\right)^2\right], \qquad \ldots \quad (6)$$

of degenerate Bose and Fermi liquids, respectively. Here ξ_0^0 is the Fermi degeneracy energy for pure Liq. F^* and

$$A_0^{0*} = \sum_n \left\{ \frac{(A^{0*})^n}{n^S} \right\} = \frac{N}{C\Gamma(S)\,(kT)^S\,N\,V^0},$$

$$b_2 = \frac{1}{2^{S+1}},\; b_3 = \frac{2}{3^{S+1}} - \frac{1}{4^S}.$$

Following London (1938) we have for the degeneracy temperature of Liq. B the expression

$$T_0 = \frac{1}{k} \left[\frac{1}{C_B V_B^0 \Gamma(s_B)\,\zeta(s_B)} \right]^{\frac{1}{s_B}}. \qquad .. \qquad .. \qquad .. \qquad (7)$$

For completely non-interacting systems (Heer and Daunt's case) $s_B = \frac{3}{2}$ and

$$C_B = \frac{2\pi(2m)^{3/2}}{h^3}$$

and eq. (7) reduces to the well-known expression due to London. Eq. (7) shows that the introduction of the potential well does not, in the first approximation†, modify the degeneracy temperature. It may be noted that in this paper the degeneracy temperature will always refer to the condensation temperature of the Bose assembly, unless otherwise specified.

3. THE λ-TEMPERATURE

We shall now consider the case of a mixture of Liq. F and Liq. B. Since they are assumed to form statistically independent assemblies the modification of the degeneracy temperature is purely due to the change in the volume of the Bose assembly. We shall therefore get the degeneracy temperature, T_λ, of the Bose assembly (Liq. B) in the mixture by replacing the volume $N_B V_B^0$ of pure Liq. B in eq. (7) by the volume $\left(N_F V_F^0 + N_B V_B^0\right)$ of the mixture, thus giving

$$T_\lambda = \frac{1}{k} \left[\frac{N_B}{N_F V_F^0 + N_B V_B^0} \cdot \frac{1}{C_B \Gamma(s_B)\zeta(s_B)} \right]^{\frac{1}{s_B}}, \qquad .. \qquad .. \qquad (8)$$

This, on combination with eq. (7), leads to

$$\frac{T_\lambda}{T_0} = \left[\frac{N_B V_B^0}{N_F V_F^0 + N_B V_B^0} \right]^{\frac{1}{s_B}} = \left[\frac{1 - X_F}{1 + X_F \left(\frac{V_F^0}{V_B^0} - 1 \right)} \right]^{\frac{1}{s_B}}, \qquad .. \qquad .. \qquad (9)$$

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* Throughout this paper the superscript zero (0) is used to indicate quantities referring to the pure liquids.

† Our model must be regarded as a first approximation in so far as the variation in χ^0, with volume, has been neglected. In practice it is well-known that the λ-temperature of He⁴ depends upon the external pressure. Since contributions to the pressure will come from (i) a kinetic term and (ii) a statical term due to the variation of χ^0, we expect that in the second approximation, i.e., when $\dfrac{\partial \chi^0}{\partial V^0}$ is taken into account, T_0 would be modified by the introduction of χ^0.

whence

$$\frac{\partial T_\lambda}{\partial X_F} = -\frac{T_0}{s_B} \cdot \frac{(1-X_F)^{\frac{1}{s_B}-1}}{\left[1+X_F\left(\frac{V_F^0}{V_B^0}-1\right)\right]^{\frac{1}{s_B}+1}} \cdot \frac{V_F^0}{V_B^0}, \qquad .. \qquad .. \quad (10)$$

where $X_F = \dfrac{N_F}{N_F+N_B}$ and $X_B = \dfrac{N_B}{N_F+N_B}$ are, respectively, the concentrations

of Liq. F and Liq. B in the mixture.

4. PROPERTIES OF MIXTURES IN CASE (i)

As pointed out in Sec. 1 we shall get two sets of expressions according as the temperature is above or below the λ-point of the mixture.

(a) Below the λ-point.

For a mixture of volume $(N_F V_F^0 + N_B V_B^0)$ eqs. (4) and (5) lead to the following expression for the free energy :—

$$F = -N_F \chi_F^0 - N_B \chi_B^0 + N_F kT \log A_{0F}^* - C_B \Gamma(s_B)(kT)^{s_B+1} \zeta(s_B+1) \times$$
$$\times (N_F V_F^0 + N_B V_B^0), \quad .. \quad (11)$$

whereas, the free energy of mixing, $\Delta F = F - F_F^0 - F_B^0$ will be given by

$$\Delta F = N_F kT \log \frac{A_{0F}^*}{A_{0F}^{0*}} - C_B \Gamma(s_B)(kT)^{s_B+1} \zeta(s_B+1) N_F V_F^0, \qquad .. \quad (12)$$

where all terms of the order of A_{0F}^* have been neglected corresponding to the Boltzmannian case.

It is usual to assume, for a liquid, that $G \approx F$, G being the Gibbs free energy. In our model the 'liquids' are actually gases with certain potential wells. It is, therefore, of interest to note that if this assumption is not introduced the pressure values so obtained are higher by about 20 per cent for low temperatures and by about 10 per cent for high temperatures (Bhagat and Katti 1954a). However, following Daunt and Heer we assume that

$$G = F + P(N_F V_F^0 + N_B V_B^0),$$
$$\approx F,$$

for sufficiently small pressures. Then, using the usual thermodynamic relations we obtain for the thermodynamic potentials the expressions

$$\mu_F^0 = -\chi_F^0 - kT - kT \log \left\{ C_F \Gamma(s_F) V_F^0 (kT)^{s_F} \right\}, \qquad .. \qquad .. \quad (13)$$

$$\mu_B^0 = -\chi_B^0 - C_B V_B^0 (kT)^{s_B+1} \Gamma(s_B) \zeta(s_B+1), \qquad .. \qquad .. \quad (14)$$

for the pure liquids and

$$\mu_F = -\chi_F^0 - X_F' kT + kT \log \frac{X_F'}{V_F^0} - kT \log C_F \Gamma(s_F)(kT)^{s_F}$$

$$- C_B V_F^0 (kT)^{s_B+1} \Gamma(s_B)\zeta(s_B+1), \quad \cdots \quad (15)$$

$$\mu_B = -\chi_B^0 - C_B V_B^0 (kT)^{s_B+1} \Gamma(s_B)\zeta(s_B+1) \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad (16)$$

for the liquids in the mixture. · Since the vapours are assumed to be perfect gases we use the relations:

$$\mu_F - \mu_F^0 = kT \log \frac{p_F}{p_F^0},$$

$$\mu_B - \mu_B^0 = kT \log \frac{p_B}{p_B^0},$$

and obtain for the partial vapour pressures

$$\frac{p_F}{p_F^0} = X_F' \exp\left[-\frac{V_F^0}{V_B^0} \frac{\zeta(s_B+1)}{\zeta(s_B)} X_B' \left(\frac{T}{T_\lambda}\right)^{s_B} + X_B' \right], \quad \cdots \quad \cdots \quad (17)$$

$$\frac{p_B}{p_B^0} = \exp\left[-\frac{V_B^0}{V_F^0} X_F' \right], \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad (18)$$

where

$$X_F' = \frac{N_F V_F^0}{N_F V_F^0 + N_B V_B^0} \quad \text{and} \quad X_B' = \frac{N_B V_B^0}{N_F V_F^0 + N_B V_B^0}.$$

Further, the total energy U, entropy S, and specific heat C are obtained from the expression for the free energy by using the well-known thermodynamic relations

$$U = F - T\left(\frac{\partial F}{\partial T}\right), \quad S = -\left(\frac{\partial F}{\partial T}\right), \quad \text{and} \quad C = \left(\frac{\partial U}{\partial T}\right),$$

whence,

$$U = X_F s_F T - \frac{1}{R}\left[N_F \chi_F^0 + N_B \chi_B^0\right] + C_B \Gamma(s_B+1)(kT)^{s_B+1} \frac{(X_F V_F^0 + X_B V_B^0)}{k}, \quad \cdots \quad (19)$$

$$S = X_F(s_F+1) - X_F \log A_{0F}^* + \frac{C_B}{s_B} \Gamma(s_B+2)\zeta(s_B+1)(kT)^{s_B}(X_F V_F^0 + X_B V_B^0), \quad (20)$$

$$C = X_F s_F - C_B \Gamma(s_B+2)(kT)^{s_B}\zeta(s_B+1)(X_F V_F^0 + X_B V_B^0), \quad \cdots \quad \cdots \quad \cdots \quad (21)$$

in units of $R (= k(N_F + N_B))$.

(b) *Above the λ-point.*

Combining eqs. (3) and (7) we obtain the free energy of non-degenerate Liq. B in the form

$$F_B^0 = -N_B \chi_B^0 - N_B kT\left[1 - \log \zeta(s_B) + \log\left(\frac{T}{T_0}\right)^{s_B} + b_2 \zeta(s_B)\left(\frac{T_0}{T}\right)^{s_B} + \right.$$

$$\left. + \frac{b_3}{2}[\zeta(s_B)]^2 \left(\frac{T_0}{T}\right)^{2s_B} + \dots \right], \quad \cdots \quad (22)$$

whence the thermodynamic potential of pure Liq. B becomes

$$\mu_B^0 = -\chi_B^0 - kT\left[1 - \log \zeta(s_B) + \log\left(\frac{T}{T_0}\right)^{s_B} + b_2\,\zeta(s_B)\left(\frac{T_0}{T}\right)^{s_B}\right.$$
$$\left. + \frac{b_3}{2}\,[\zeta(s_B)]^2\left(\frac{T_0}{T}\right)^{2s_B} + \ldots\right], \qquad \ldots \quad (23)$$

On combining the expressions for the free energies of Liq. B and Liq. F we obtain for the free energy of the mixture and the free energy of mixing (for $T > T_0$) the expressions:

$$F = -N_F\,\chi_F^0 - N_B\,\chi_B^0 - N_F\,kT\log A_{0F}^* - N_B\,kT\left[1 - \log\zeta(s_B) + \log\left(\frac{T}{T_\lambda}\right)^{s_B} + \right.$$
$$\left. + b_2\zeta(s_B)\left(\frac{T_\lambda}{T}\right)^{s_B} + \frac{b_3}{2}\,[\zeta(s_B)]^2\left(\frac{T_\lambda}{T}\right)^{2s_B} + \ldots\right], \qquad \ldots \quad (24)$$

$$\Delta F = -kT\left[-N_F\log\frac{A_{0F}^*}{A_{0F}^{0*}} + N_B\log\left(\frac{T_0}{T_\lambda}\right)^{s_B} + b_2 N_B\,\frac{\zeta(s_B)}{T^{s_B}_\lambda}\,(T^{s_B}_\lambda - T_0^{s_B}) + \right.$$
$$\left. + \frac{b_3}{2}\left[\frac{\zeta(s_B)}{T^{S_B}_\lambda}\right]^2(T^{2s_B}_\lambda - T_0^{2s_B}) + \ldots\right]. \qquad \ldots \quad (25)$$

Thence the potentials in the mixed state take the form

$$\mu_F = -\chi_F^0 - X_F'\,kT + kT\log A_{0F}^* - X_B'\,\frac{V_F^0}{V_B^0}\,kT\left[1 - b_2\zeta(s_B)\left(\frac{T_\lambda}{T}\right)^{s_B} - b_3\,[\zeta(s_B)]^2\times\right.$$
$$\left. \times\left(\frac{T_\lambda}{T}\right)^{2s_B} - \ldots\right], \qquad \ldots \quad (26)$$

$$\mu_B = -\chi_B^0 - X_F'\,\frac{V_F^0}{V_B^0}\,kT - kT\left[X_B' - \log\zeta(s_B) + \log\left(\frac{T}{T_\lambda}\right)^{s_B} + (1 + X_F')\,b_2\zeta(s_B)\left(\frac{T_\lambda}{T}\right)^{s_B}\right.$$
$$\left. + (1 + 2X_F')\,\frac{b_3}{2}\,[\zeta(s_B)]^2\left(\frac{T_\lambda}{T}\right)^{2s_B} + \ldots\right], \qquad \ldots \quad (27)$$

which when combined with the expressions for the potentials of the pure liquids, eqs. (13) and (23), give for the partial vapour pressures

$$\frac{p_B}{p_B^0} = X_B'\exp\left[-X_B' - X_F'\,\frac{V_B^0}{V_F^0} + \log\left(\frac{T_0}{T}\right)^{s_B} + \frac{\zeta(s_B+1)}{\zeta(s_B)}\left(\frac{T}{T_0}\right)^{s_B} + \log\zeta(s_B)\right.$$
$$\left. - (1 + X_F')\,b_2\zeta(s_B)\left(\frac{T_\lambda}{T}\right)^{s_B} - (1 + 2X_F')\,\frac{b_3}{2}\,[\zeta(s_B)]^2\left(\frac{T_\lambda}{T}\right)^{2s_B} - \ldots\right], \qquad \ldots \quad (28)$$

for $T_\lambda < T \leqslant T_0$,

$$\frac{p_B}{p_B^0} = X_B'\exp\left[\left(1 - \frac{V_B^0}{V_F^0}\right)X_F' - b_2\zeta(s_B)\left(1 + X_F' - \frac{1}{X_B'}\right)\left(\frac{T_\lambda}{T}\right)^{s_B} - \right.$$
$$\left. - \frac{b_3}{2}\,[\zeta(s_B)]^2\left(1 + 2X_F' - \frac{1}{(X_B')^2}\right)\left(\frac{T_\lambda}{T}\right)^{2s_B} - \ldots\right], \qquad \ldots \quad (28')$$

for $T > T_0$, and

$$\frac{p_F}{p_F^0} = X'_F \exp\left[\left(1 - \frac{V_F^0}{V_B^0}\right)X'_F + X'_B\frac{V_F^0}{V_B^0}\left\{b_2\zeta(s_B)\left(\frac{T_\lambda}{T}\right)^{s_B}\right.\right.$$
$$\left.\left. + b_3[\zeta(s_B)]^2\left(\frac{T_\lambda}{T}\right)^{2s_B} + \dots\right\}\right]. \quad \dots (29)$$

It is important to note here that the distinction between the two temperature ranges $T_\lambda < T < T_0$ and $T > T_0$ above, as well as in the following sections, has to be introduced only because the partial pressures have been expressed in terms of the saturated pressures. Otherwise, the pressure of Liq. B in the mixture is given by the same expression both above and below the degeneracy temperature, T_0, of pure Liq. B.

The expression for the free energy of the mixture when substituted in the thermodynamic relations quoted above gives for the energy U, entropy S, and specific heat C, in units of R, the expressions

$$U = -\frac{1}{R}\left[N_F\chi_F^0 + N_B\chi_B^0\right] + (s_F X_F + s_B X_B)T -$$
$$- s_B X_B T\left[b_2\zeta(s_B)\left(\frac{T_\lambda}{T}\right)^{s_B} + b_3[\zeta(s_B)]^2\left(\frac{T_\lambda}{T}\right)^{2s_B} + \dots\right], \quad \dots (30)$$

$$S = 1 - X_F \log A_{0F}^{\bullet} - X_B \log \zeta(s_B) + X_B \log\left(\frac{T}{T_\lambda}\right)^{s_B} + (s_F X_F + s_B X_B) -$$
$$- \left[b_2 X_B(s_B - 1)\left(\frac{T_\lambda}{T}\right)^{s_B}\zeta(s_B) + \frac{b_3}{2}X_B(2s_B - 1)\left(\frac{T_\lambda}{T}\right)^{2s_B}[\zeta(s_B)]^2 + \dots\right], \quad (31)$$

$$C = (s_F X_F + s_B X_B) + X_B\left[b_2 s_B(s_B - 1)\zeta(s_B)\left(\frac{T_\lambda}{T}\right)^{s_B} +\right.$$
$$\left. + b_3 s_B(2s_B - 1)[\zeta(s_B)]^2\left(\frac{T_\lambda}{T}\right)^{2s_B} + \dots\right]. \quad \dots (32)$$

From eqs. (32) and (21) we obtain for the jump in the specific heat at the λ-temperature of the mixture the expression

$$\Delta C = X_B s_B\left[1 + b_2\zeta(s_B)(s_B - 1) + b_3[\zeta(s_B)]^2(2s_B - 1) + \dots\right] -$$
$$- C_B\Gamma(s_B + 2)(kT_\lambda)^{s_B}(X_F V_F^0 + X_B V_B^0)\zeta(s_B + 1). \quad \dots (33)$$

5. LIQ. F NON-DEGENERATE

In our considerations so far Liq. F has been regarded as essentially Boltzmannian in character. We shall now study the case when Liq. F is considered to be a non-degenerate 'Fermi liquid'. For this purpose we shall have to include the higher order terms in the series expression for the free energy of Liq. F, i.e., eq. (4). The results of the preceding section then take the generalized form given below:

(a) *Below the λ-point*: the free energy expression becomes

$$F = -N_F\chi_F^0 - N_B\chi_B^0 - C_B\Gamma(s_B)\zeta(s_B + 1)(N_F V_F^0 + N_B V_B^0)(kT)^{s_B+1} -$$
$$- N_F kT\left[1 - \log A_{0F}^{\bullet} - b_2 A_{0F}^{\bullet} - \frac{b_3}{2}(A_{0F}^{\bullet})^2 - \dots\right], \quad \dots (34)$$

which gives, on combination with eqs. (8) and (9), for the free energy of mixing, $\triangle F$,

$$\triangle F = -N_F kT \left[\log \frac{A_{0F}^{\bullet}}{A_{0F}^{0\bullet}} + b_2(A_{0F}^{0\bullet} - A_{0F}^{\bullet}) + \frac{b_3}{2}\left\{(A_{0F}^{0\bullet})^2 - (A_{0F}^{\bullet})^2\right\} + \cdots \right] -$$
$$- C_B \Gamma(s_B)\zeta(s_B+1)N_F V_F^0 (kT)^{s_B+1}. \quad \cdots \quad (35)$$

In this case the thermodynamic potentials of Liq. F take the form

$$\mu_F^0 = -\chi_F^0 - kT \left[\log A_{0F}^{0\bullet} + A_{0F}^{0\bullet} + \frac{b_3}{2}(A_{0F}^{0\bullet})^2 + \cdots \right], \quad \cdots \quad (36)$$

when pure, and

$$\mu_F = -\chi_F^0 - C_B V_F^0 (kT)^{s_B+1}\zeta(s_B+1) + kT \left[\log A_{0F}^{\bullet} + 2b_2 A_{0F}^{\bullet} + \frac{3b_3}{2}(A_{0F}^{\bullet})^2 + \cdots \right] -$$
$$- X_F' kT \left[1 + b_2 A_{0F}^{\bullet} + b_3 (A_{0F}^{\bullet})^2 + \cdots \right], \quad \cdots \quad \cdots \quad (37)$$

when in solution.   Also, the potential of Liq. B, when in solution, takes the form

$$\mu_B = -\chi_B^0 - C_B(kT)^{s_B+1} V_B^0 \zeta(s_B+1) -$$
$$- kT X_F' \left[\frac{V_B^0}{V_F^0} + b_2 A_{0F}^{\bullet} + \frac{b_3}{2} 2 (A_{0F}^{\bullet})^2 + \cdots \right]. \quad \cdots \quad \cdots \quad (38)$$

These then give for the partial vapour pressures the expressions

$$\frac{p_B}{p_B^0} = \exp \left[-\frac{V_B^0}{V_F^0} X_F' - X_F'\left(b_2 A_{0F}^{\bullet} + b_3 (A_{0F}^{\bullet})^2 + \cdots \right) \right], \quad \cdots \quad (39)$$

$$\frac{p_F}{p_F^0} = X_F' \exp \left[X_B' \frac{V_F^0}{V_B^0}\frac{\zeta(s_B+1)}{\zeta(s_B)}\left(\frac{T}{T_\lambda}\right)^{s_B} + X_B'\left\{1 + b_2 A_{0F}^{\bullet} + b_3 (A_{0F}^{\bullet})^2 + \cdots \right\} + \right.$$
$$\left. + \left\{b_2(A_{0F}^{\bullet} - A_{0F}^{0\bullet}) + \frac{b_3}{2}\left([A_{0F}^{\bullet}]^2 - [A_{0F}^{0\bullet}]^2\right) + \cdots \right\} \right]. \quad \cdots \quad (40)$$

The expressions for the energy, entropy and specific heat (all in units of R) will, from eq. (34), come out to be

$$U = -\frac{1}{R}\left(N_F \chi_F^0 + N_B \chi_B^0\right) + C_B \Gamma(s_B+1)\zeta(s_B+1)(kT)^{s_B+1}\frac{X_F V_F^0 + X_B V_B^0}{k} +$$
$$+ X_F s_F \left[T + b_2 A_{0F}^{\bullet} + b_3 (A_{0F}^{\bullet})^2 + \cdots \right], \quad \cdots \quad \cdots \quad (41)$$

$$S = \frac{C_B}{s_B}\Gamma(s_B+2)\zeta(s_B+1)(kT)^{s_B}(X_F V_F^0 + X_B V_B^0) +$$
$$+ X_F \left[1 + s_F - \log A_{0F}^{\bullet} + b_2(s_F-1)A_{0F}^{\bullet} + \frac{b_3}{2}(2s_F-1)(A_{0F}^{\bullet})^2 + \cdots \right], \quad (42)$$

$$C = C_B \Gamma(s_B+2)\zeta(s_B+1)(kT)^{s_B}(X_F V_F^0 + X_B V_B^0) +$$
$$+ \frac{X_F s_F^2}{T}\left[\frac{T}{s_F} - b_2 A_{0F}^{\bullet} - 2b_3 (A_{0F}^{\bullet})^2 - \cdots \right]. \quad \cdots \quad (43)$$

(b) *Above the λ-temperature*: each expression will involve two series since both Liq. F and Liq. B (in solution) are non-degenerate in character. Thus the free energy of the mixture and the free energy of mixing $(T > T_0)$* will be given by

$$F = -N_F \chi_F^0 - N_B \chi_B^0 - N_F kT \left[1 - \log \overset{*}{A}_{0F} - b_2 \overset{*}{A}_{0F} - \frac{b_3}{2} \left(\overset{*}{A}_{0F} \right)^2 - \ldots \right] -$$

$$- N_B kT \left[1 - \log \zeta(s_B) + \log \left(\frac{T}{T_\lambda} \right)^{s_B} + b_2 \zeta(s_B) \left(\frac{T_\lambda}{T} \right)^{s_B} + \right.$$

$$\left. + \frac{b_3}{2} [\zeta(s_B)]^2 \left(\frac{T_\lambda}{T} \right)^{2s_B} + \ldots \right], \quad \ldots \quad (44)$$

$$\Delta F = -N_B kT \left[\log \left(\frac{T_0}{T_\lambda} \right)^{s_B} + \frac{b_2 \zeta(s_B)}{T^{s_B}} \left(T_\lambda^{s_B} - T_0^{s_B} \right) + \right.$$

$$\left. + \frac{b_3}{2} \left\{ \frac{\zeta(s_B)}{T^{s_B}} \right\}^2 \left(T_\lambda^{2s_B} - T_0^{2s_B} \right) + \ldots \right] -$$

$$- N_F kT \left[\log \frac{\overset{0}{A}{}^*_{0F}}{\overset{*}{A}_{0F}} - b_2 \left(\overset{*}{A}_{0F} - \overset{0}{A}{}^*_{0F} \right) - \frac{b_3}{2} \left\{ \left(\overset{*}{A}_{0F} \right)^2 - \left(\overset{0}{A}{}^*_{0F} \right)^2 \right\} - \ldots \right]. \quad \ldots \quad (45)$$

Eq. (44) gives for the thermodynamic potentials the expressions

$$\mu_F = -\chi_F^0 + kT \left[\log \overset{*}{A}_{0F} - X_F' + b_2 \left(2 - X_F' \right) \overset{*}{A}_{0F} + b_3 \left(\frac{3}{2} - X_F' \right) \left(\overset{*}{A}_{0F} \right)^2 + \ldots \right] -$$

$$- X_B' \frac{V_F^0}{V_B^0} kT \left[1 - b_2 \zeta(s_B) \left(\frac{T_\lambda}{T} \right)^{s_B} - b_3 [\zeta(s_B)]^2 \left(\frac{T_\lambda}{T} \right)^{2s_B} - \ldots \right]. \quad \ldots \quad (46)$$

$$\mu_B = -\chi_B^0 - X_F' \left[\frac{V_B^0}{V_F^0} kT + b_2 \overset{*}{A}_{0F} + b_3 \left(\overset{*}{A}_{0F} \right)^2 + \ldots \right] -$$

$$- kT \left[X_B' + \log \left(\frac{T}{T_\lambda} \right)^{s_B} + (1 + X_F') b_2 \zeta(s_B) \left(\frac{T_\lambda}{T} \right)^{s_B} + \right.$$

$$\left. + (1 + 2X_F') \frac{b_3}{2} [\zeta(s_B)]^2 \left(\frac{T_\lambda}{T} \right)^{2s_B} + \ldots \right], \quad \ldots \quad (47)$$

which, applying the usual method, give for the partial pressures

$$\frac{p_B}{p_B^0} = X_B' \exp \left[-X_B' - X_F' \frac{V_B^0}{V_F^0} - X_F' \left\{ b_2 \overset{*}{A}_{0F} + b_3 (\overset{*}{A}_{0F})^2 + \ldots \right\} + \frac{\zeta(s_B + 1)}{\zeta(s_B)} \left(\frac{T'}{T_\lambda} \right)^{s_B} - \right.$$

$$- \left\{ \log \left(\frac{T}{T_0} \right)^{s_B} + b_2 \zeta(s_B) (1 + X_F') \left(\frac{T_\lambda}{T} \right)^{s_B} + \right.$$

$$\left. \left. + \frac{b_3}{2} [\zeta(s_B)]^2 (1 + 2X_F') \left(\frac{T_\lambda}{T} \right)^{2s_B} + \ldots \right\} \right]. \quad \ldots \quad (48)$$

---

* It may be noted that here, as elsewhere, the range $T > T_0$ has to be specified because in the range $T_\lambda < T \leqslant T_0$ pure Liq. B is degenerate and therefore the expression for ΔF will be different according as $T > T_0$ or $T_\lambda < T \leqslant T_0$.

for $T_\lambda < T \leqslant T_0$,

$$\frac{p_B}{p_B^0} = X_B' \exp\left[X_F'\left\{1-\frac{V_B^0}{V_F^0}-b_2 A_{0F}^{\bullet}-b_3\left(A_{0F}^{\bullet}\right)^2-\ldots\right\}-\right.$$

$$-\left\{b_2\zeta(s_B)\left(1+X_F'-\frac{1}{X_B}\right)\left(\frac{T_\lambda}{T}\right)^{s_B}+\frac{b_3}{2}\left[\zeta(s_B)\right]^2\left(1+2X_F'-\frac{1}{(X_B')^2}\right)\times\right.$$

$$\left.\left.\times\left(\frac{T_\lambda}{T}\right)^{2s_B}+\ldots\right\}\right], \quad \ldots \text{(48')}$$

for $T > T_0$ and,

$$\frac{p_F}{p_F^0} = X_F' \exp\left[X_B'\left\{1-\frac{V_F^0}{V_B^0}+b_2\zeta(s_B)\left(\frac{T_\lambda}{T}\right)^{s_B}+\frac{b_3}{2}\left[\zeta(s_B)\right]^2\left(\frac{T_\lambda}{T}\right)^{2s_B}+\ldots\right\}+\right.$$

$$+X_B'\left\{b_2 A_{0F}^{\bullet}+b_3(A_{0F}^{\bullet})^2+\ldots\right\}+b_2\left\{(A_{0F}^{\bullet}-A_{0F}^{0\bullet})+\right.$$

$$\left.\left.+\frac{b_3}{2b_2}\left[(A_{0F}^{\bullet})^2-(A_{0F}^{0\bullet})^2\right]+\ldots\right\}\right]. \quad \ldots \text{(49)}$$

Using eq. (44) we obtain for the other thermodynamic properties of the mixture the relations

$$U = -\frac{1}{R}\left(N_F \chi_F^0+N_B \chi_B^0\right)+X_F s_F\left[T+b_2 A_{0F}^{\bullet}+b_3\left(A_{0F}^{\bullet}\right)^2+\ldots\right]-$$

$$-s_B X_B T\left[-1+b_2\zeta(s_B)\left(\frac{T_\lambda}{T}\right)^{s_B}+b_3\left[\zeta(s_B)\right]^2\left(\frac{T_\lambda}{T}\right)^{2s_B}+\ldots\right], \quad \ldots \text{(50)}$$

$$S = X_B\left[1+s_B-\log\,\zeta(s_B)-b_2(s_B-1)\zeta(s_B)\left(\frac{T_\lambda}{T}\right)^{s_B}-\right.$$

$$\left.-\frac{b_3}{2}\left(2s_B-1\right)\left[\zeta(s_B)\right]^2\left(\frac{T_\lambda}{T}\right)^{2s_B}-\ldots\right]+$$

$$+X_F\left[1+s_F-\log A_{0F}^{\bullet}+b_2(s_F-1)A_{0F}^{\bullet}+\frac{b_3}{2}\left(2s_F-1\right)\left(A_{0F}^{\bullet}\right)^2+\ldots\right], \quad \ldots \text{(51)}$$

$$C = \frac{X_F s_F^2}{T}\left[\frac{T}{s_F}-b_2\,A_{0F}^{\bullet}+\frac{b_3}{2}\left(A_{0F}^{\bullet}\right)^2+\ldots\right]+s_B X_B\left[1+b_2(s_B-1)\zeta(s_B)\left(\frac{T_\lambda}{T}\right)^{s_B}+\right.$$

$$\left.+\frac{b_3}{2}\left(2s_B-1\right)\left[\zeta(s_B)\right]^2\left(\frac{T_\lambda}{T}\right)^{2s_B}+\ldots\right]. \quad \ldots \text{(52)}$$

From eqs. (52) and (43) we get for the jump in the specific heat at the λ-temperature of the mixture

$$\Delta C = X_B s_B\left[1+b_2\zeta(s_B)\left(s_B-1\right)+b_3[\zeta(s_B)]^2\left(2s_B-1\right)+\ldots\right]-$$

$$-C_B \Gamma(s_B+2)\left(kT_\lambda\right)s_B\left(X_F V_F^0+X_B V_B^0\right)\zeta(s_B+1). \quad \ldots \text{(53)}$$

6. Liq. F Degenerate in the Pure State and Non-degenerate when in the Mixture

Evidently, this case is of interest only for very dilute mixtures at temperatures below the Fermi degeneracy temperature, 4·85°K., for the pure Fermi gas (with liquid density). Also it is important only in so far as it is customary to express the partial pressures of the liquids in the mixture in terms of their saturated pressures. As regards the partial pressures themselves they would still be the same as in the previous case. As in the previous case we shall obtain two sets of expressions according as the remperature is above or below the λ-temperature of the mixture. Now, we have for the thermodynamic potential of pure Liq. F

$$\mu_F^0 = -\chi_F^0 + \frac{s_F}{s_F+1}\, \xi_0^0 \left[1-(s_F+1)\frac{\pi^2}{6}\left(\frac{kT}{\xi_0^0}\right)^2\right]. \qquad .. \qquad .. \quad (54)$$

The other thermodynamic potentials are unaltered and therefore only the expressions for $\dfrac{p_F}{p_F^0}$ would be modified. Combining eq. (54) with eqs. (37) and (46) we obtain

(a) *for temperatures below the λ-point*:

$$\frac{p_F}{p_F^0} = \frac{X_F'}{\Gamma(S_F+1)}\left(\frac{\xi_0^0}{kT}\right)^{s_F} \times$$

$$\times \exp\left[-X_F'-\frac{\zeta(s_B+1)}{\zeta(s_B)}\frac{V_F^0}{V_B^0}\left(\frac{T}{T_\lambda}\right)^{s_B}-\frac{s_F}{s_F+1}\frac{\xi_0^0}{kT}\left\{1-(s_F+1)\frac{\pi^2}{6}\left(\frac{kT}{\xi_0^0}\right)^2\right\}+\right.$$

$$\left.+\left\{b_2(1+X_F')\,A_{0F}^{\bullet}+b_3(\tfrac{1}{2}+X_F')(A_{0F}^{\bullet})^2+\ldots.\right\}\right], \qquad .. \quad (55)$$

and (b) *for temperatures above the λ-point*:

$$\frac{p_F}{p_F^0} = \frac{X_F'}{\Gamma(s_F+1)}\left(\frac{\xi_0^0}{kT}\right)^{s_F} \times$$

$$\times \exp\left[-X_F'+X_B'\frac{V_F^0}{V_B^0}\left\{-1+b_2\zeta(s_B)\left(\frac{T_\lambda}{T}\right)^{s_B}+b_3[\zeta(s_B)]^2\left(\frac{T_\lambda}{T}\right)^{2s_B}+\ldots.\right\}+\right.$$

$$+\left\{b_2(1+X_B')\,A_{0F}^{\bullet}+\frac{b_3}{2}(1+2X_B')(A_{0F}^{\bullet})^2+\ldots\right\}-$$

$$\left.-\frac{s_F}{s_F+1}\frac{\xi_0^0}{kT}\left\{1-(s_F+1)\frac{\pi^2}{6}\left(\frac{kT}{\xi_0^0}\right)^2\right\}\right]. \qquad .. \qquad .. \quad (56)$$

Further, the expressions for the other thermodynamic quantities are left un-altered since the expression for the free energy of the mixture is the same as in Sec. 5.

In the extreme (Boltzmannian) case $A_F^* \to 0$ and eqs. (55) and (56) reduce to the form

$$\frac{p_F}{p_F^0} = \frac{X_F'}{\Gamma(s_F+1)} \left(\frac{\xi_0^0}{kT}\right)^{s_F} \exp\left[-X_F' - \frac{s_F}{s_F+1} \frac{\xi_0^0}{kT} \left\{ 1-(s_F+1)\frac{\pi^2}{6}\left(\frac{kT}{\xi_0^0}\right)^2 \right\} - \right.$$
$$\left. - \frac{\zeta(s_B+1)}{\zeta(s_B)} \frac{V_F^0}{V_B^0} X_B' \left(\frac{T_\lambda}{T}\right)^{s_B} \right], \qquad .. \quad (55')$$

and

$$\frac{p_F}{p_F^0} = \frac{X_F'}{\Gamma(s_F+1)} \left(\frac{\xi_0^0}{kT}\right)^{s_F} \times$$
$$\times \exp\left[-X_F' + X_B' \frac{V_F^0}{V_B^0} \left\{ -1 + b_2\zeta(s_B)\left(\frac{T_\lambda}{T}\right)^{s_B} + b_3[\zeta(s_B)]^2 \left(\frac{T_\lambda}{T}\right)^{2s_B} + \ldots . \right\} - \right.$$
$$\left. - \frac{s_F}{(s_F+1)} \frac{\xi_0^0}{kT} \left\{ 1-(s_F+1)\frac{\pi^2}{6}\left(\frac{kT}{\xi_0^0}\right)^2 \right\} \right], \qquad .. \quad .. \quad .. \quad (56')$$

respectively.

7. LIQ. F DEGENERATE

Now we deal with the other extreme case $(A_F^* \gg 1)$. It is expected that this case will be of importance for mixture with very high Liq. F concentration, that is, mixtures in which the density of Liq. F is comparable with the density of pure Liq. F. We shall obtain two sets of expressions according as $T > T_\lambda$ or $T_\lambda < T \leqslant 4.85°K$. For $T > 4.85°K$. the expressions derived in Sec. 5 would apply. Hence, we find that

(a) *Below the λ-point*: the expressions for the free energy of the mixture and the free energy of mixing get modified to

$$F = -N_F\chi_F^0 + \frac{s_F}{s_F+1} N_F\xi_0 \left[1-(s_F+1)\frac{\pi^2}{6}\left(\frac{kT}{\xi_0}\right)^2 \right] -$$
$$- N_B\chi_B^0 - C_B\Gamma(s_B)\zeta(s_B+1)(N_FV_F^0 + N_BV_B^0)(kT)^{s_B+1}, \qquad .. \quad (57)$$

and

$$\Delta F = \frac{s_F}{s_F+1} N_F\left(\xi_0-\xi_0^0\right) + s_FN_F(kT)^2\left[\frac{1}{\xi_0^0} - \frac{1}{\xi_0}\right]\frac{\pi^2}{6}$$
$$- C_B\Gamma(s_B)(kT)^{s_B+1}\zeta(s_B)N_FV_F^0, \qquad .. \quad (58)$$

respectively. Consequently, the thermodynamic potentials of Liq. F and Liq. B, when in the mixture, take the form

$$\mu_F = \frac{s_F+X_B'}{s_F+1}\xi_0\left[1-\frac{\pi^2}{6}(s_F+1)\left(\frac{kT}{\xi_0}\right)^2\right] - \chi_F^0 - \frac{\zeta(s_B+1)}{\zeta(s_B)} X_B' \frac{V_F^0}{V_B^0} kT \left(\frac{T}{T_\lambda}\right)^{s_B}, \qquad (59)$$

$$\mu_B = -\chi_B^0 - C_BV_B^0(kT)^{s_B+1}\Gamma(s_B)\zeta(s_B+1)$$
$$- \frac{X_F'}{s_F+1}\frac{V_B^0}{V_F^0}\frac{\xi_0}{kT}\left[1+\frac{\pi^2}{6}(s_F+1)\left(\frac{kT}{\xi_0}\right)^2\right]. \qquad .. \quad (60)$$

These relations, when combined with the expressions for the potentials of pure Liq. F and Liq. B, give for the partial vapour pressures

$$\frac{p_B}{p_B^0} = \exp\left[-\frac{X'_F}{s_F+1}\frac{V_B^0}{V_F^0}\frac{\xi_0}{kT}\left\{1+(s_F+1)\frac{\pi^2}{6}\left(\frac{kT}{\xi_0}\right)^2\right\}\right], \quad .. \quad .. \quad (61)$$

$$\log\frac{p_F}{p_F^0} = \frac{X'_B+s_F}{1+s_F}\cdot\frac{\xi_0}{kT}\left[1-(s_F+1)\frac{\pi^2}{6}\left(\frac{kT}{\xi_0}\right)^2\right] - \frac{s_F}{s_F+1}\frac{\xi_0^0}{kT}\left[1-(s_F+1)\frac{\pi^2}{6}\left(\frac{kT}{\xi_0^0}\right)^2\right]$$

$$-\frac{\zeta(s_B+1)}{\zeta(s_B)}X'_B\frac{V_F^0}{V_B^0}\left(\frac{T}{T_\lambda}\right)^{s_B}. \quad .. \quad (62)$$

Again, the modified expression for the free energy, Eq. (57), gives for the other thermodynamic properties (in units of R) the expressions

$$U = -\frac{1}{R}(N_F\chi_F^0+N_B\chi_B^0) + \frac{X_F s_F}{1+s_F}\frac{\xi_0}{kT}\left[1+(1+s_F)\frac{\pi^2}{6}\left(\frac{kT}{\xi_0}\right)^2\right] +$$

$$+ C_B\Gamma(s_B+1)\zeta(s_B+1)\frac{(X_F V_F^0+X_B V_B^0)}{k}(kT)^{s_B+1}, \quad .. \quad (63)$$

$$S = \frac{\pi^2}{3}s_F X_F\frac{kT}{\xi_0} + \frac{C_B}{s_B}\Gamma(s_B+2)\zeta(s_B+1)(kT)^{s_B}(X_F V_F^0+X_B V_B^0), \quad .. \quad .. \quad (64)$$

$$C = \frac{\pi^2}{3}s_F X_F\frac{kT}{\xi_0} + C_B\Gamma(s_B+2)\zeta(s_B+1)(kT)^{s_B}(X_F V_F^0+X_B V_B^0), \quad .. \quad .. \quad (65)$$

and (b) *Above the λ-point*: Liq. B, when in the mixture, must be considered as non-degenerate so that the free energy of the mixture will be given by

$$F = -N_F\chi_F^0 - N_B\chi_B^0 + \frac{s_F}{1+s_F}\xi_0\left[1-(1+s_F)\frac{\pi^2}{6}\left(\frac{kT}{\xi_0}\right)^2\right] -$$

$$- N_B kT\left[1-\log\zeta(s_B)+\log\left(\frac{T}{T_\lambda}\right)^{s_B}+b_2\zeta(S_B)\left(\frac{T_\lambda}{T}\right)^{s_B}+\right.$$

$$\left. +\frac{b_3}{2}\{\zeta(s_B)\}^2\left(\frac{T_\lambda}{T}\right)^{2s_B}+......\right]. \quad .. \quad .. \quad (66)$$

·In the temperature range $T > T_0$ the free energy of mixing will take the form

$$\Delta F = N_F s_F\frac{\pi^2}{6}(kT)^2\left[\frac{1}{\xi_0^0}-\frac{1}{\xi_0}\right] + \frac{s_F}{1+s_F}N_F(\xi_0-\xi_0^0)$$

$$-N_B kT\left[\log\left(\frac{T_0}{T_\lambda}\right)^{s_B}+b_2\frac{\zeta(s_B)}{T^{s_B}}(T_\lambda{}^{s_B}-T_0{}^{s_B})+\right.$$

$$\left. +\frac{b_3}{2}\left\{\frac{\zeta(s_B)}{T^{s_B}}\right\}^2(T_\lambda{}^{2s_B}-T_0{}^{2s_B})+,....\right]. \quad .. \quad (67)$$

Eq. (66) gives for the potentials in the mixed state

$$\mu_F = -\chi_F^0 - \frac{X_B' + s_F}{1 + s_F} \cdot \xi_0 \left[1 - (s_F + 1) \frac{\pi^2}{6} \left(\frac{kT}{\xi_0} \right)^2 \right] -$$

$$- X_B' \frac{V_F^0}{V_B^0} kT \left[1 - b_2 \zeta(s_B) \left(\frac{T_\lambda}{T} \right)^{s_B} - b_3 \{ \zeta(s_B) \}^2 \left(\frac{T_\lambda}{T} \right)^{2s_B} + \dots \right], \quad \dots \quad (68)$$

$$\mu_B = -\chi_B^0 - \frac{X_F'}{1 + s_F} \frac{V_B^0}{V_F^0} \cdot \xi_0 \left[1 + (s_F + 1) \frac{\pi^2}{6} \left(\frac{kT}{\xi_0} \right)^2 \right] -$$

$$- kT \left[X_B' - \log \zeta(s_B) + \log \left(\frac{T}{T_\lambda} \right)^{s_B} + b_2 \zeta(s_B) \left(1 + X_F' \right) \left(\frac{T_\lambda}{T} \right)^{s_B} \right.$$

$$+ \frac{b_3}{2} \left. \{ \zeta(s_B) \}^2 \left(1 + 2X_F' \right) \left(\frac{T_\lambda}{T} \right)^{2s_B} + \dots \right]. \quad \dots \quad \dots \quad (69)$$

Combining, as before, with the expressions for the pure liquids we have

$$\frac{p_B}{p_B^0} = X_B' \exp \left[-X_B' - \frac{X_F'}{s_F + 1} \frac{V_B^0}{V_F^0} \frac{\xi_0}{kT} \left\{ 1 + (1 + s_F) \frac{\pi^2}{6} \left(\frac{kT}{\xi_0} \right)^2 \right\} + \frac{\zeta(s_B + 1)}{\zeta(s_B)} \left(\frac{T}{T_\lambda} \right)^{s_B} - \right.$$

$$- \left\{ b_2 \zeta(s_B)(1 + X_F') \left(\frac{T_\lambda}{T} \right)^{s_B} + \frac{b_3}{2} [\zeta(s_B)]^2 (1 + 2X_F') \left(\frac{T_\lambda}{T} \right)^{2s_B} + \dots \right\} \right]$$

for $\quad T_\lambda < T \leqslant T_0, \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (70)$

$$\frac{p_B}{p_B^0} = X_B' \exp \left[X_F' - \frac{X_F'}{s_F + 1} \frac{V_B^0}{V_F^0} \frac{\xi^0}{kT} \right\} 1 + (s_F + 1) \frac{\pi^2}{6} \left(\frac{kT}{\xi_0} \right)^2 \right\} -$$

$$- \left\{ b_2 \zeta(s_B) \left(1 + X_F' - \frac{1}{X_B'} \right) \left(\frac{T_\lambda}{T} \right)^{s_B} + \right.$$

$$+ \frac{b_3}{2} [\zeta(S_B)]^2 \left(1 + 2X_F' - \frac{1}{(X_B')^2} \right) \left(\frac{T_\lambda}{T} \right)^{2s_B} + \dots \left. \right\} \right], \quad (70')$$

for $\quad T > T_0$ and,

$$\log \frac{p_F}{p_F^0} = \frac{s_F + X_B'}{1 + s_F} \frac{\xi_0}{kT} \left[1 - \frac{\pi^2}{6} (s_F + 1) \left(\frac{kT}{\xi_0} \right)^2 \right] - \frac{s_F}{s_F + 1} \frac{\xi_0^0}{kT} \left[1 - (s_F + 1) \frac{\pi^2}{6} \left(\frac{kT}{\xi_0} \right)^2 \right] -$$

$$- X_B' \frac{V_F^0}{V_B^0} \left[1 - b_2 \zeta(s_B) \left(\frac{T_\lambda}{T} \right)^{s_B} - b_3 [\zeta(s_B)]^2 \left(\frac{T_\lambda}{T} \right)^{2s_B} - \dots \right]. \quad \dots \quad (71)$$

Further, eq. (66) gives for U, S and C (all in terms of R) the expressions

$$U = - \frac{1}{R} \left(N_F \chi_F^0 + N_B \chi_B^0 \right) + \frac{s_F}{1 + s_F} X_F \frac{\xi_0}{k} \left[1 + (1 + s_F) \frac{\pi^2}{6} \left(\frac{kT}{\xi_0} \right)^2 \right] +$$

$$+ X_B s_B T \left[1 - b_2 \zeta(s_B) \left(\frac{T_\lambda}{T} \right)^{s_B} - b_3 [\zeta(s_B)]^2 \left(\frac{T_\lambda}{T} \right)^{2s_B} - \dots \right], \quad \dots \quad (72)$$

3B

$$S = \frac{\pi^2}{3} s_F X_F \frac{kT}{\xi_0} + X_B \left[s_B + \log \left(\frac{T}{T_\lambda} \right)^{s_B} - b_2 (s_B - 1) \zeta(s_B) \left(\frac{T_\lambda}{T} \right)^{s_B} - \right.$$

$$\left. - \frac{b_3}{2} (2s_B - 1) [\zeta(s_B)]^2 \left(\frac{T_\lambda}{T'} \right)^{2s_B} - \dots \right], \quad \dots \quad (73)$$

$$C = \frac{\pi^2}{3} s_F X_F \frac{kT}{\xi_0} + X_B s_B \left[1 + b_2(s_B - 1) \zeta(s_B) \left(\frac{T_\lambda}{T} \right)^{s_B} \right.$$

$$\left. + b_3(2s_B - 1) [\zeta(s_B)]^2 \left(\frac{T_\lambda}{T} \right)^{2S_B} + \dots \right]. \quad \dots \quad (74)$$

The last equation together with eq. (65) leads to the following expression for the jump in the specific heat of the mixture at its λ-point

$$\Delta C = X_B s_B \left[1 + b_2(s_B - 1) \zeta(s_B) + b_3(2s_B - 1) [\zeta(s_B)]^2 + \dots \right] -$$

$$- C_B \Gamma (s_B + 2) \zeta(s_B + 1) (X_F V_F^0 + X_B V_B^0) (kT_\lambda)^{s_B}. \quad \dots \quad (75)$$

As expected, eqs. (33), (53) and (75) show that the specific heat jump at the λ-temperature of the mixture is the same whether Liq. F is Boltzmannian, non-degenerate or degenerate. The discontinuity in the specific heat is a property of the Bose assembly alone and therefore there is no question of it being affected by the nature of the Fermi assembly. The difference in the ΔC for pure Liq. B and the ΔC for Liq. B in the mixture arises purely from the difference in the volumes of the Bose assembly in the two cases.

8. DISCUSSION OF RESULTS

Recently, Bhagat and Katti (1954b) have calculated the saturated vapour pressures of Liq. He⁴ and Liq. He³ on the basis of smoothed potential models of ideal Bose and Fermi gases. They find that the theoretical results are in good agreement with the observed pressures. On the other hand, there are many pronounced discrepancies between the theoretical predictions for an ideal Bose gas and the observed properties of Liq. He⁴. For instance, we have for the specific heat of an ideal Bose gas the expression $C \propto T^{1.5}$ as opposed to the observed relation $C \propto T^6$ ($T \geqslant 0.6°K.$) for liquid He⁴. This discrepancy may be due to the complete neglect of the interactions between the molecules in the liquid state. As pointed out by Dingle (1952) a considerable improvement in the theory is obtained by the introduction of a 'self-consistent' field, that is, by assuming that each molecule is moving in a field due to its neighbours. Thus, the ideal-gas spectrum, $\epsilon = \frac{p^2}{2m}$, is replaced by an ad hoc spectrum, $\epsilon = Bp^{3/s}$. This modification is assumed to take account of the interactions between the molecules. We do not wish to insist here on the details of this concept, which is certainly open to much criticism. It may, however, lead to a somewhat better description of the properties of mixtures of the liquids. The modification in the energy spectrum leads to distribution laws of the more general type:

$$N(\epsilon) \, d\epsilon = \frac{V C \epsilon^{S-1}}{\frac{1}{A} \exp \left(\frac{\epsilon}{kT} \right) \pm 1}.$$

Next, following Heer and Daunt, we introduce constant or smoothed potential wells. In other words, we consider the 'liquid' as being a Bose or a Fermi gas in a constant potential well, each particle of the assembly being subject to a self-consistent field due to its neighbours. Thus we have written the distribution laws in the form:

$$N(\epsilon)\, d\epsilon = \frac{VC\epsilon^{S-1}}{\dfrac{1}{A}\exp\left(\dfrac{\epsilon}{kT} - \dfrac{\chi^0}{kT}\right) \pm 1}.$$

This single-particle approximation to the liquids stresses the rôle of statistics, obeyed by them, in the behaviour of their mixtures. It may, therefore, be expected that when a large amount of experimental data become available our discussion would be of great importance for testing the influence of statistics of the two components on the properties of their mixtures.

Below we discuss some of the important results obtained in the previous sections:

(a) *Variation of the λ-temperature with Concentration.*

Three values of s_B, namely, 3/2, 5 and 6, were used for computing $\dfrac{T_\lambda}{T_0}$ from eq. (9). The molar volumes, as usual, were taken to be 27·6 c.c. and 37·6 c.c. for He⁴ (Liq. B) and He³ (Liq. F), respectively. The results are plotted in Fig. 1 as a function of the He³ concentration, X_F. Measurements of the λ-temperature of He³-He⁴ mixtures have been carried out by Daunt and Heer (1950) and by Abraham *et al.* (1949). Their results are also shown in Fig. 1. It is seen that the
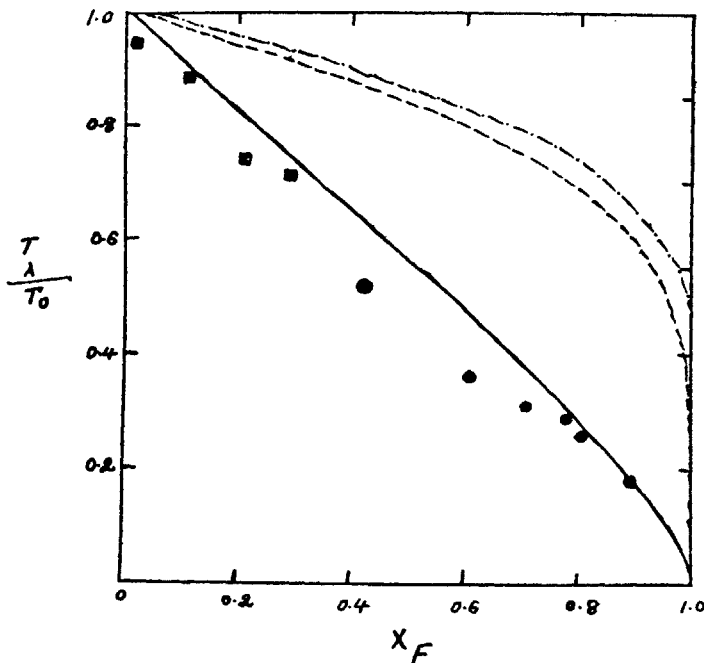
Fig. 1. Plots of the λ-temperature, T_λ, against concentration, X_F, of He³ in He⁴ mixtures. The curves are computed from eq. (9) with $s_B = 3/2$ (————), $s_B = 5$ (– – – –) and $s_B = 6$ (—·—·—·—·—). Experimental results are indicated by dots (Daunt *et al.*) and by squares (Abraham *et al.*).

experimental points are represented fairly closely by the curve for $S_B = 3/2$, (which corresponds to the ideal gas case). For higher values of S_B the theoretical curve deviates more and more from the experimental values.

The slope of the T_λ vs. X_F curve for very low concentrations of He (i.e. $X_F \to 0$) becomes, from eq. (10),

$$\frac{\partial T'_\lambda}{\partial X_F} = -\frac{T_0}{s_B}\frac{V_F^0}{V_B^0}$$

$$= -1{\cdot}986 \text{ for } s_B = \tfrac{3}{2},$$

$$= -0{\cdot}496 \text{ for } s_B = 6.$$

These values may be compared with those obtained by de Boer and Gorter (1950), $-2{\cdot}78$, and by Stout (1949), $-3{\cdot}50$, whereas the observed value is $\sim -2{\cdot}8$.

For very high concentrations (i.e. $X_F \to 1$)

$$\frac{\partial T_\lambda}{\partial X_F} \to \infty \text{ since } s_B > 1.$$

Hence the curve should approach the abscissae vertically in each case. The experimental points also indicate such a behaviour.

(b) The Vapour Pressures

Using observed values for the saturated pressures p_F^0 and p_B^0, the total vapour pressure $(p_F + p_B)$ over a 20 per cent mixture was computed from the theoretical expressions in the following cases:—

    (i) when Liq. F is Boltzmannian, with $s_B = 3/2$,
    (ii) when Liq. F is non-degenerate, with $s_B = 3/2$,
    (iii) when Liq. F is degenerate and $s_B = 3/2$, and
    (iv) when Liq. F is Boltzmannian and $s_B = 6$.

In calculating the values of p_B for temperatures above T_λ no distinction was made between the regions $T_\lambda < T \leqslant T_0$ and $T > T_0$, in fact, the expression for the latter region were used throughout the range $T > T_\lambda$. The results are plotted in Fig. 2 as a function of temperature. Weinstock *et al.* (1950) have observed the total pressure over a 20·3 per cent He³-He⁴ mixture. We have included their results in Fig. 2 for the sake of comparison. Clearly there is very little difference between the curves I$_A$ and II, corresponding, respectively, to cases (i) and (ii). However, curve I$_B$ (case iv) has a discontinuity at the λ-point, whereas curve III (case iii) is much lower than the experimental values. The agreement between the theoretical predictions in the first two cases and the observed pressures may not, however, be stressed. As pointed out in Sec. 4 the assumption $G \approx F$ entails a considerable error (Bhagat and Katti, 1954a).

In Fig. 2a are shown the plots of eqs. (28) and (28'), curves I and II respectively. In obtaining Fig. 2, as already mentioned, we used for p_B, throughout the range $T > T_\lambda$, an expression which is valid only for $T > T_0$. Fig. 2a shows, in the representative Boltzmannian case, how far this approximation is valid.
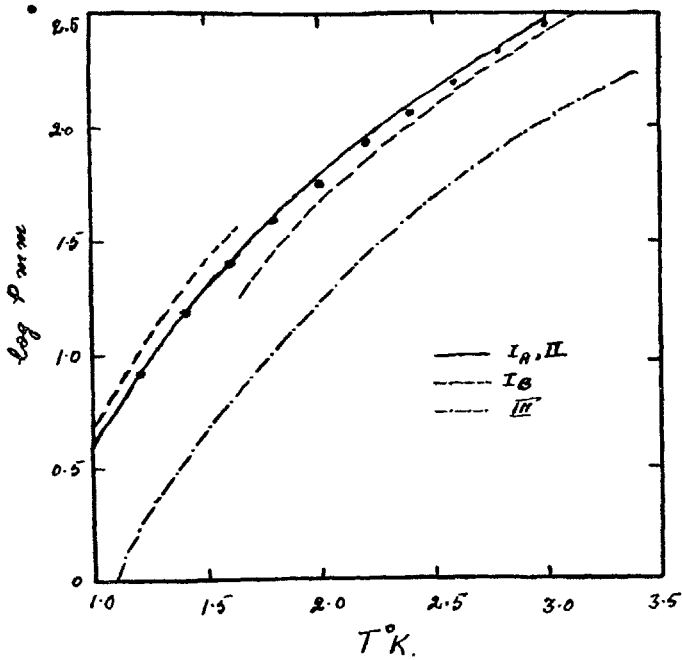
FIG. 2. Plots of the computed values of the total vapour pressure over a 20% He³ in He⁴ mixture. Curve I$_A$ is for Liq. F Boltzmannian and $s_B = 3/2$, curve I$_B$ for Liq. F Boltzmannian and $s_B = 6$, curve II for Liq. F non-degenerate and $s_B = 3/2$, and curve III for Liq. F degenerate and $s_B = 3/2$. Experimental points (indicated by circles) are due to Weinstock *et al.*
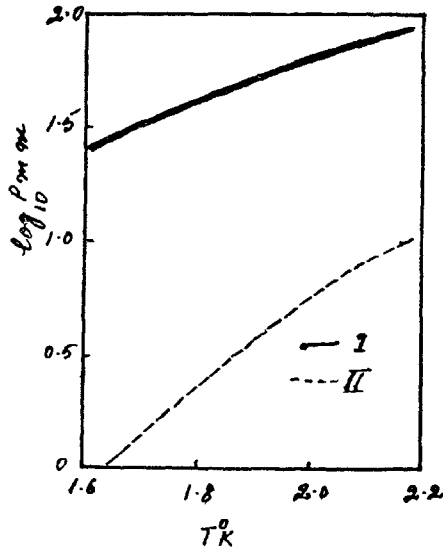

FIG. 2a. Plots of the total vapour pressures above a 20% He³ in He⁴ mixture in the temperature range $T_\lambda < T \leqslant T_0$, as computed from eq. (28), curve I, and eq. (28'), curve II.

(c) The Distribution Coefficient.

From eqs. (17) and (18) and (27) and (28′) we have, for dilute solutions (i.e. $N_F \ll N_B$),

$T \leqslant T_\lambda$

$$\frac{X_V}{X_L} = \frac{V_F^0}{V_B^0} \cdot \frac{p_F^0}{p_B^0} \exp\left[1 - \left(\frac{T}{2 \cdot 186}\right)^{s_B} \frac{\zeta(s_B+1)}{\zeta(s_B)} \cdot \frac{V_F^0}{V_B^0}\right], \qquad \ldots \qquad \ldots \qquad (76)$$

$T \geqslant T_\lambda$

$$\frac{X_V}{X_L} = \frac{V_F^0}{V_B^0} \cdot \frac{p_F^0}{p_B^0} \left[\exp\left\{ 1 - \frac{V_F^0}{V_B^0}\left(1 - b_2\zeta(s_B)\right)\left(\frac{2 \cdot 186}{T}\right)^{s_B} \right. \right.$$
$$\left. \left. - b_3[\zeta(s_B)]^2 \left(\frac{2 \cdot 186}{T}\right)^{2s_B}\right) \right\} \right], \qquad \ldots \qquad (77)$$

where X_V and X_L are the relative concentrations in the vapour and the liquid phases and for $T_\lambda \approx T_0$ we have taken the observed value of $2 \cdot 186°$K. In obtaining

(76) and (77) it has been assumed that $X_V = \frac{p_F}{p_B}$. This relation would hold also

in the non-perfect gas approximation to the vapours provided that the partial
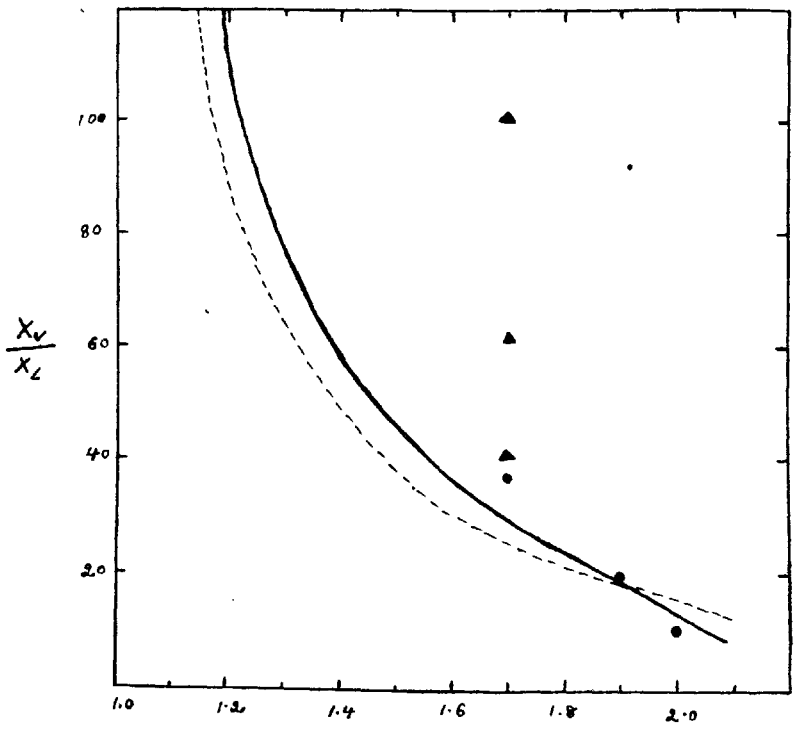
Fig. 3. Plots of the relative concentration $\frac{X_V}{X_L}$ for very low concentrations $(X_F \ll 1)$ as computed from eqs. (76) and (77). Experimental points are due to Taconis et al. (circles) and to Lane et al. (triangles).

pressures are thought of as fugacities. Values of $\left(\dfrac{X_V}{X_L}\right)$ have been calculated from eqs. (76) and (77) for two values of S_B, namely, 3/2 and 6. The results are shown in Fig. 3. Measurements of the distribution coefficient of dilute solutions of He³ in He⁴ have been carried out by Taconis et al. (1949) and by Lane and his co-workers (1949). Their results have also been shown in Fig. 3. The percentage error in the experimental results is so large that no decision can be made as to which law is preferable. However, considering more concentrated solutions Daunt, Tseng and Heer (1952) have reported good agreement between the 3/2 law and the experimental results.

(d) The Specific Heat.

In this case no experimental data are available for comparison. Theoretical values of the specific heat (in units of $R = k \ (N_F + N_B)$) have been computed for a 20 per cent mixture in the following cases:—

  (i) Liq. *F* Boltzmannian,
  (ii) Liq. *F* non-degenerate Fermi liquid, and
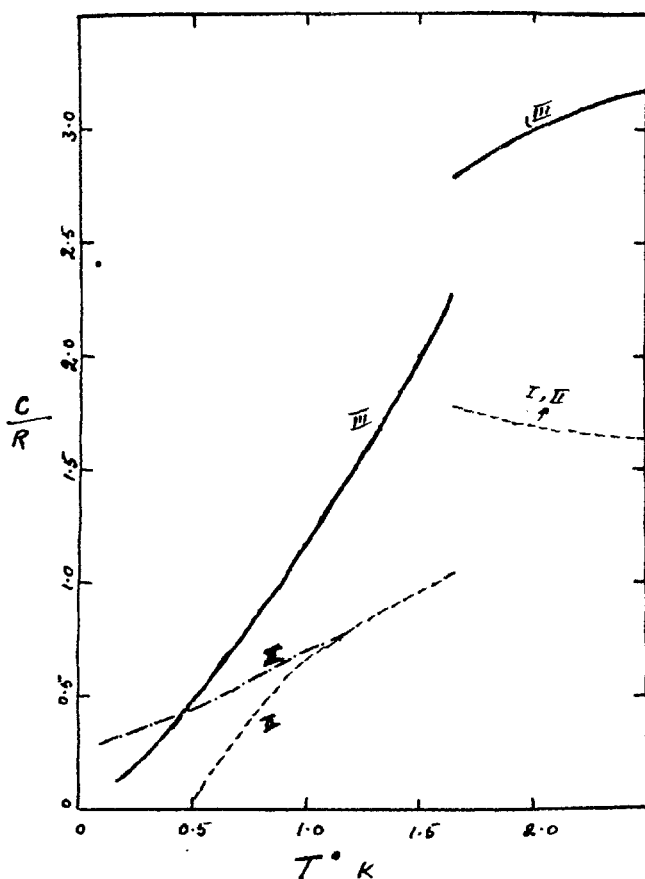 (iii) Liq. *F* degenerate Fermi liquid.

FIG. 4. Plots of the computed values of the specific heat, C/R, of a 20% He³ in He⁴ mixture against temperature. Curve I is for Liq. *F* Boltzmannian, Curve III for Liq. *F* degenerate and Curve II for Liq. *F* non-degenerate.

In each case we have taken $s_B = s_F = 3/2$. The results are represented by curves I, II and III, respectively, in Fig. 4.

In case (i) as the temperature decreases from higher values towards the λ-temperature ($\sim 1\cdot63°$K.) C increases slowly from $1\cdot5$ to $1\cdot6$. At $1\cdot63°$K. it drops discontinuously to the value $1\cdot15$ and decreases slowly to $0\cdot3$ as the absolute zero is approached. For temperatures above about $1°$K. the curve for case (ii) follows very closely the curve for case (i). Below $1°$K. they deviate appreciably from each other and the former drops to zero nearabout $0\cdot5°$K. For case (iii) C tends to zero as the absolute zero is approached and above the λ-temperature it increases slowly with the rise of temperature.

Table I below shows the various relations for C at different concentrations. The relations clearly show that in the Boltzmannian case the specific heat increases with concentration at low temperatures. At temperatures above the λ-point, however, it has, more or less, a constant value, $\sim 1\cdot5\ R$, the temperature terms having little contribution. In the degenerate case $C \to 0$ as $T \to 0$ for temperatures below the λ-point whereas in the non-degenerate case C rapidly decreases to zero at $T \sim 0\cdot5°$K. Thus the behaviour of C for temperature below $1°$K. is very sensitive to the nature of Liq. F being considerably different according as Liq. F is Boltzmannian, non-degenerate or degenerate. Experimental measurements of the specific heat in this region would therefore give an indication as to the nature of He³.

In passing, we may point out that recent experiments of Fairbank et al. (1953) on the magnetic susceptibility of He³ indicate that He³ behaves as a classical liquid even down to the lowest temperatures.

(e) The Entropy of Mixing.

In the case where Liq. F is taken to be a degenerate Fermi liquid we obtain for the entropy of mixing, from eq. (58), the expression

$$\Delta S = -\frac{\partial(\Delta F)}{\partial T} = -\frac{\partial}{\partial T}\left[\frac{s_F}{s_F+1}(\xi_0 - \xi_0^0) + \text{terms involving temperature}\right]. \qquad \qquad (78)$$

As already pointed out by Daunt and Heer (1951) we note that $\Delta S \to 0$ as the absolute zero is approached. This leads us to expect an unmixing of the liquids as the absolute zero is approached. This may be in accordance with Taconis' hypothesis that He³ mixes only with the normal part of He⁴ so that at the absolute zero, where no normal He⁴ atoms are present, there would be a complete unmixing of the liquids. Also, it is clear that eq. (78) is in accordance with Nernst's theorem. The classical expression for ΔS, however, does not show such a behaviour, that is, ΔS does not vanish at the absolute zero.

SUMMARY

Smoothed potential models of the type used by Heer and Daunt are considered when the distribution laws have the generalized form introduced by Kothari and Singh. In the mixture the liquids are assumed to form statistically independent systems. The thermodynamic properties of mixtures (both above and below their λ-points) are derived when the 'Fermi liquid' is (i) Boltzmannian, (ii) Non-degenerate and (iii) Degenerate. Comparison with observed properties of He³-He⁴ mixtures is carried out. The behaviour of the specific heat, below $1°$K., is found to be very sensitive to the nature of the Fermi liquid.

TABLE I

Theoretical expressions for the specific heat C/R.

Concentration X%	Liq. F Boltzmannian		Liq. F' Degenerate	
	Below λ-point	Above λ-point	Below λ-point	Above λ-point
0·5	$0{\cdot}0075 + 0{\cdot}3555\,T$	$1{\cdot}5 + \dfrac{0{\cdot}0049}{T^{\frac{3}{2}}} + \dfrac{0{\cdot}0030}{T^3}$	$0{\cdot}001\,T + 0{\cdot}3555\,T^{\frac{3}{2}}$	$1{\cdot}49 + 0{\cdot}0100\,T + \dfrac{0{\cdot}0049}{T^{\frac{1}{2}}} + \dfrac{0{\cdot}0030}{T^3}$
3·0	$0{\cdot}045 + 0{\cdot}3589\,T$	$1{\cdot}5 + \dfrac{0{\cdot}02789}{T^{\frac{3}{2}}} + \dfrac{0{\cdot}0166}{T^3}$	$0{\cdot}0605\,T + 0{\cdot}3589\,T^{\frac{3}{2}}$	$1{\cdot}44 + 0{\cdot}0605\,T + \dfrac{0{\cdot}02789}{T^{\frac{1}{2}}} + \dfrac{0{\cdot}0166}{T^3}$
20·0	$0{\cdot}300 + 0{\cdot}3806\,T$	$1{\cdot}5 + \dfrac{0{\cdot}5352}{T^{\frac{3}{2}}} + \dfrac{0{\cdot}2287}{T^3}$	$0{\cdot}403\,T + 0{\cdot}3608\,T^{\frac{3}{2}}$	$1{\cdot}20 + 0{\cdot}403\,T + \dfrac{0{\cdot}5352}{T^{\frac{1}{2}}} + \dfrac{0{\cdot}2287}{T^3}$
60·0	$0{\cdot}900 + 0{\cdot}4320\,T$	$1{\cdot}5 + \dfrac{0{\cdot}0946}{T^{\frac{3}{2}}} + \dfrac{0{\cdot}0143}{T^3}$	$1{\cdot}010\,T + 0{\cdot}4320\,T^{\frac{3}{2}}$	$0{\cdot}60 + 1{\cdot}010\,T + \dfrac{0{\cdot}0946}{T^{\frac{1}{2}}} + \dfrac{0{\cdot}0140}{T^3}$

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