On the Bose-Einstein Liquid Model for Liquid Helium, III

_Further Considerations regarding Vapour Pressures of He³-He⁴ Mixtures_

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Discontinuities at the \( \lambda \)-point in the temperature derivatives of vapour pressures of a He³-He⁴ mixture, which were predicted by deBoer and Gorter, have been thought not to be found in the existing experimental results. Re-examination of these data, however, reveals that the partial vapour pressure of He³ has a break when it is plotted as a function of temperature. Both the deBoer - Gorter - Taconis and the "modified Bose-Einstein liquid" theories agree with experiment with respect to this point, in contrast to the Heer and Daunt theory. Below the \( \lambda \)-temperature, the "modified B. E. liquid" theory gives the partial pressure of He³ in qualitatively good agreement with experiment, but above this temperature neither theory agrees with experiment even qualitatively. The temperatures at which experimental these discontinuities occur, are however always considerably higher than the \( \lambda \)-temperatures expected from the experiment on superflow in mixtures.

§ 1. Introduction

In the previous two papers\(^{1,2} \) of this series (referred to hereinafter as Papers (I) and (II) respectively), the "modified Bose-Einstein liquid" theory was developed and applied to various problems on He³-He⁴ mixtures and those on pure liquid He⁴ under high pressures. The vapour pressure in the He³-He⁴ mixture, which has already been partly discussed in Paper (I), will be further discussed in this paper, since it is a problem in purely static equilibrium, independent of the somewhat ambiguous dynamical behaviours of He³ and He⁴ atoms in the mixture, and consequently the study of it enables one to select among various possible ways, a most justifiable one to construct the thermodynamic functions of He³-He⁴ liquid mixtures. deBoer and Gorter\(^3 \) used the thermodynamic functions of a mixture of ideal classical liquids under Taconis' assumption, and Heer and Daunt\(^4 \) used those of a mixture of a nondegenerate ideal Fermi-Dirac gas (liquid He³) and a degenerate ideal Bose-Einstein gas (liquid He⁴) in respective potential wells. The present author presented a theory, in which Heer and Daunt's ideal B. E. gas was replaced by a "modified B. E. gas" with an excitation energy proportional to the number density of He⁴ particles, whose individual mass is chosen as 8.8 times as large as the mass of a He⁴ atom, independently of He³ concentration. In § 2, the relation between the vapour

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pressure and temperature is considered. Among the above mentioned theories, those of deBoer and Gorter and the author predict breaks in the vapour pressure versus temperature curve at the \( \lambda \)-temperature, while Heer and Daunt's theory does not. In the experimental data of Weinstock et al.\(^7\) and Sommers\(^6\), in which no breaks have been thought to be found, breaks are shown to exist when the partial vapour pressure of He\(^3\) is plotted as a function of temperature\(^*\). It is found, however, that the breaks in these experimental plots are always less marked than the theoretical ones, and are located at considerably higher temperatures than those expected from the experimental results of superflow in mixtures. The general features of \( p_3-T \) curves below the \( \lambda \)-temperatures in the "modified B.E. liquid" theory agree with those of experimental plots, though the agreement above these temperatures is not good. The results of the deBoer-Gorter-Taconis theory does not seem to agree with experiment even qualitatively. In \( \S \) 3, the vapour pressure versus He\(^3\) concentration relations at constant temperature are discussed.

\( \S \) 2. Partial vapour pressure of He\(^3\) versus temperature relation

From purely thermodynamic considerations assuming the transition of the second order, deBoer and Gorter\(^7\) showed that the temperature derivatives of the total and partial vapour pressures in the He\(^3\)-He\(^4\) mixture should have discontinuities at the \( \lambda \)-temperature. It has been thought that in the experiments of both Weinstock et al. and Sommers no such discontinuities were observed. The author evaluated, from their data of total vapour pressure, the values of the partial pressure of He\(^3\), \( p_3 \), and plotted them as a function of temperature. Breaks in \( p_3-T \) plots are then clearly found in the four following cases:

Sommers' 9.49 and 13.0\% solutions and Weinstock et al.'s 20.3 and 25.5\% solutions. In the case of Sommers' more dilute solutions, no breaks are found. The reason why the breaks appear clearly in the \( p_3-T \) plots, but not in the \( p-T \) plots seems obvious: in solutions with relatively small He\(^3\) concentrations, the relative amount of discontinuity in \( dP_3/dT \) is large and that in \( dP_4/dT \) is small, but, as the absolute value of \( dP_3/dT \) is much larger than that of \( dP_4/dT \), the relative amount of discontinuity in \( dP/dT (=dP_3/dT +dP_4/dT) \) becomes small.

The partial vapour pressure of He\(^3\), \( p_3 \), can be derived from experimental values of total vapour pressure, \( p \), by applying

\[
p_3 = p X_v
\]

and the empirical equation

\[
X_v = \frac{\Delta p}{p} \left[ 1 + 0.080 \left( T-1.100 + 0.600 \left( \frac{\Delta p}{p} \right)^2 \right) \right],
\]

where \( X_v \) is the mole concentration of He\(^3\) in vapour, and \( \Delta p \) the total vapour pressure of a solution minus the vapour pressure of pure He\(^4\) at the same temperature. This formula was presented by Sommers\(^6\) in order to represent his experimental results for

\* In a lecture given in Kyoto on Sept. 22, 1953, Gorter reported that in very recent Leiden observations a discontinuity is found in the temperature derivative of the vapour to liquid concentration ratio at the \( \lambda \)-point.
$0 \leq X_e \leq 1.00$ and in the temperature range $1.3\degree \leq T \leq 2.2\degree$K. In this paper this formula is used up to temperatures a little higher than 2.2\degree K.

Fig. 1. The partial vapour pressure of He$^3$ plotted as a function of temperature. Experimental points are derived from the unsmoothed data of Sommers$^6$ for the total vapour pressure. The arrows indicate the expected $λ$-temperatures. (Note added in proof: The positions of the arrows are erroneous. The expected $λ$-temperatures should nearly coincide with the break points of the uppermost (solid) curves.)
In Fig. 1, the values of $P_3$ derived from Sommers' unsmoothed data are plotted as a function of $T$. The plots for 9.49 and 13.0% solutions are clearly seen to have breaks, though the number of experimental points near the break-temperatures are too small to locate them definitely. Thus, the prediction by deBoer and Gorter may be said to be experimentally confirmed. The break for a 9.49% solution is situated at a temperature higher than 2.0°K, and that for 13.0% solution at a temperature higher than 1.95°K, as is seen in the figure. A remarkable fact is that no indications of breaks are found at the $\lambda$-temperatures expected from the experiment of Abraham et al. on superflow through the superleak immersed in solutions, and that the break-temperatures found in the present plots are considerably higher than the expected $\lambda$-temperatures, 1.94° and 1.86°K (indicated by arrows in the figure*). Fig. 2 shows the similar plots for 20.3 and 25.5% solutions of Weinstock et al. As they did not present numerical values of $P$, the points in the

![Graph](https://example.com/graph.png)

Fig. 2. The partial vapour pressure of He\(^3\) plotted as a function of temperature. Experimental points are derived from the log $\beta$ versus $1/T$ plots of Weinstock et al\(^9\). (a) 20.3% He\(^3\), (b) 25.5% He\(^3\). The arrows indicate the expected $\lambda$-temperatures.

* Note added in proof: The positions of the arrows in Fig. 1 are erroneous.
figure are derived by reading the experimental points in their log $p$ versus $1/T$ graph. Breaks are also found in these cases, at about 1.85' K for the 20.3% solution and at about 1.75' K for the 25.5% solution. They are again considerably higher than the expected $\lambda$-temperatures, 1.65' and 1.55' K respectively (indicated by arrows in the figure).

Now the results are compared with theories. Since experimental results clearly show jumps in $dp_*/dT$ at $\lambda$-temperatures, those theories alone are considered, which are in accord with experiment with respect to this point. In Figs. 1 and 2, the results from the deBoer-Gorter-Taconis theory are shown by dot-dashed curves, and those from the "modified B.E. liquid" theory by solid curves. The formulae for vapour pressures in both theories, which are used to draw these curves, are found in Paper (I) (eqs. (34)-(43)). The dotted curves indicate the results of calculation from the "modified B.E. liquid" theory when the He$^3$ concentrations in solutions are taken somewhat smaller than those reported by the original authors. The agreement below the theoretical $\lambda$-temperatures can be made satisfactory by this adjustment of the values of concentration. Deviations above the $\lambda$-temperatures, however, still remain. It should further be noted that the breaks in the empirical $P_3-T$ plots are still located at temperatures considerably higher than the theoretical $\lambda$-points for the solutions of adjusted concentrations.

The above discrepancies between the transition temperatures obtainable from the two kinds of measurement, i.e., the vapour pressure and the rate of superflow, appear to be too large to be ascribed to experimental errors in the determination of He$^3$ concentration in either of these experiments. If one assumes the determination of concentration in Abraham et al.'s superflow experiment not seriously erroneous, the 20.3% solution of Weinstock et al. should have contained only about 13% He$^3$, and the 25.5% solution about 17% He$^3$. These values are still lower than those of concentrations which must be assumed, in the "modified B.E. liquid" theory, in order to obtain the agreement with experiment below the $\lambda$-temperatures. (See Fig. 2) If the discrepancies were not caused by the experimental errors in the determination of concentration of the original gas, one is led to assume that the vapour on the solution does not exhibit the true equilibrium pressure corresponding to the liquid concentration, say, on account of the decrease of He$^3$ concentration on the liquid or in the film on the wall. This possibility might be tested by an experiment, in which the vapour pressure and the rate of superflow through the superleak immersed in a solution are simultaneously observed.

The quite different features of theoretical and experimental plots above the $\lambda$-temperature appear to suggest that the "modified B.E. liquid" theory is no longer valid in this temperature region. This suggestion seems to be supported also by the following fact: the specific heat of pure He$^4$ evaluated from this theory is about seven times smaller than the experimentally obtained value just above the $\lambda$-temperature, though it is in satisfactory agreement with experiment below this temperature. The low values of the theoretical specific heat above the $\lambda$-temperature is obviously caused by the assumption of small particle number, i.e. $1/\nu$ times the number of atoms ($\nu=8.8$, c.f. Paper (I)). It is noticeable that, if one takes the particle number equal to the number of atoms, the theoretical specific heat above the $\lambda$-temperature is of the same order of magnitude as that
experimentally obtained, though assuming different values for \( \nu \) above and below the \( \lambda \)-temperature introduces complications in the explanation of the \( \lambda \)-transition as the B.E. gas condensation.

§ 3. Vapour pressure versus He\(^3\) concentration relation

There have been so far no experimental studies on vapour pressures of solutions containing more than 25.5 % He\(^3\). From the theoretical point of view, the investigations of these cases seem to be interesting, in particular those of the case of pure liquid He\(^3\) containing small amount of He\(^4\). The two theories discussed in the preceding section predict quite different features in this concentration region. This is clearly shown in Fig. 3, in which the total vapour pressure is plotted as functions of He\(^3\) concentration. The results of calculation from the Heer and Daunt "ideal B.E. liquid" theory are also

![Graph of vapour pressure versus He\(^3\) concentration](image)

Fig. 3. The total vapour pressures of He\(^3\)-He\(^4\) mixtures plotted as a function of He\(^3\) concentration. The insert shows in large scale the feature in the neighbourhood of pure He\(^3\).
included, together with the experimental points in the low concentration region. The difference between the deBoer-Gorter-Taconis and the "modified B.E. liquid" theories are drastic in the neighbourhood of 100% He³. (See the insert in Fig. 3). The peculiar feature of the curve, which is seen, in the case of the "modified B.E. liquid" theory, in the neighbourhood of pure He³, originates clearly from the decrease of the number of He⁴ particles in the liquid state due to clustering (c.f. eq. (39) in Paper (I)). The validity of this assumption of small particle number in liquid state is open to question above the λ-temperature as was discussed in the preceding section, and consequently so is also this characteristic deviation from Raoult's law at extremely high He³ concentrations. The solution of the problem is left to future experiments.

§ 4. Conclusion

In concluding this series of papers, it may be said that the "modified B.E. liquid" model of liquid He⁴ with the mass factor, ν, and the excitation energy, λ, satisfying the relations

\[ \lambda = a_n \frac{n/\nu}{n_0/\nu_0} \left( \frac{M_4}{M_0} \right)^{1/4}, \]  
\[ \nu = \frac{M_4}{m_4} = \nu_0 + 0.15(\rho - \rho_0), \]  

represents reasonably well the real properties of liquid He⁴, pure and diluted with He³, under high pressures as well as under its saturated vapour pressures, at least below the λ-temperatures.** It should be remarked, however, that eq. (1) has been set forth in order to reproduce as well as possible the empirical relation between λ-temperature and He³ concentration, and that whether it is correct or not depends strongly on the accuracy of this experiment. Consequently possible future revisions of eqs. (1) and (2) are reserved until more precise experiments on superflow in solution will appear, since, on account of the scattering of the experimental points in existing observations, one cannot consider these results as most conclusive.

References


* Here \( n \) is the number density of He⁴ atoms, \( M_4 \) the particle mass, \( m_4 \) the mass of a He⁴ atom, and \( \rho \) the pressure in atmosphere. The suffix zero means the pure He⁴. cf. Paper (II).

** The properties bearing on the equation of states, such as the thermal expansion and compressibility, are excluded, because they depend on the properties of the potential well, which is assumed rigid in the present model.