The observed pressure dependence of T_d can be obtained from the curves of Fig. 3. If the phonon term were not present in the expression for second sound velocity, the velocity would go to zero with the square root of the temperature.[1,2] The ratio $c_2/T^{\frac{1}{2}}$ therefore exhibits a horizontal straight line at higher temperature but somewhat below the lambda-point, which may be easily extrapolated to low temperature. The deviation from the extrapolated line is then taken from the rising part of the curve at low temperature. Lines of constant deviation are shown for various values of the deviation. The corresponding values of dT_d/dP are plotted against the amount of deviation in Fig. 4. The values of dT_d/dP and $(1/T_d)\ dT_d/dP$ are nearly the same because T_d is near 1°K. The extrapolated value at zero deviation is in good agreement with the value computed above.

This agreement supports the hypothesis that the phonons contribute to the normal fraction of fluid only and are responsible for the rise of second sound velocity at low temperature. The phonons do not, however, combine linearly with the Bose-Einstein excitations, unless the Bose-Einstein spectrum is greatly different from what has been assumed heretofore.

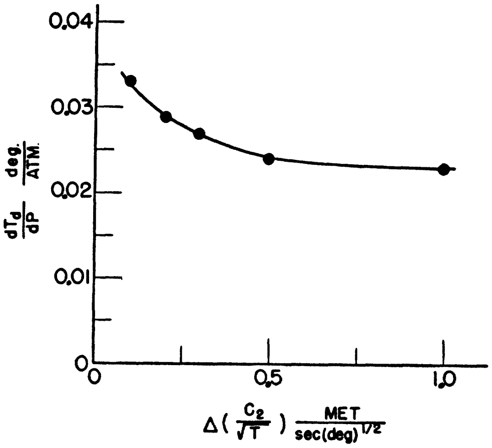

FIG. 4. Pressure derivative of the temperature of constant deviation, (dT_d/dP), as a function of the amount of deviation, $\Delta(c_2/T^{\frac{1}{2}})$, taken from Fig. 3. Since T_d is near 1°K, dT_d/dP is nearly the same as $(1/T_d)dT_d/dP$. The value expected from the phonon contribution to the normal fluid flow at small deviations is about 0.037.

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A Contribution to the Theory of Bose-Einstein Liquids

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Smoothed potential models for liquid He^4 and liquid He^3 in which each are considered as ideal Bose-Einstein and Fermi-Dirac gases situated in potential wells of potential $-\chi_4{}^0$ and $-\chi_3{}^0$, respectively, are considered. It is shown that the degeneracy temperature, T_0 of pure liquid He^4 on this model can be deduced and that the λ-transition temperatures, T_λ, of solutions of such liquids can be calculated. The calculated values of T_λ as a function of concentration of He^3 appear to be in satisfactory agreement with the observed values. From these considerations, predictions are made regarding the behavior of solutions of two Bose-Einstein liquids; e.g., He^6 in He^4. It is shown, moreover, that solutions of such model liquids obey the third law of thermodynamics.

Detailed calculations have been made of the vapor pressures of such smoothed potential liquid models of He^4 and He^3 both in the pure state and in solution. The results for the vapor pressures of the solutions indicate that, in the temperature range above 1°K for solutions of not too high concentration of He^3, the total vapor pressure would be higher than that given by Raoult's law for temperatures both above and below the λ-temperature of the solution. In this way the experimental results for the vapor pressure of such solutions, first emphasized by Taconis, *et al.*, can be explained, and good agreement between theory and experiment is evident. Explicit formulas are given for further numerical evaluation.

Finally the results of calculations of the total vapor pressure of model solutions of He^3 in He^4 in which the He^3 Fermi-Dirac liquid model is extremely degenerate are discussed. It would appear that at very low temperatures (<0.5°K) the partial vapor pressure of He^3 in such solutions of He^3 in He^4 and the distribution coefficient, C_v/C_L should become *smaller* than the values calculable from Raoult's law.

I. MODEL FOR A BOSE-EINSTEIN LIQUID

IN 1938 F. London[1] calculated in detail the behavior of a perfect Bose-Einstein gas in the degenerate state and suggested that the anomalous properties of liquid He II could be understood, at least qualitatively, by considering the λ-transition in liquid helium as a Bose-Einstein degeneration. Such a possible significance of the statistics in determining the behavior of liquid helium has recently been the subject of study owing to the availability of the rarer isotope of helium, He^3. The preliminary experiments of Daunt and others,[2]

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[1] F. London, Nature **141**, 643 (1938); Phys. Rev. **54**, 947 (1938); J. Phys. Chem. **43**, 1 (1939).

[2] Daunt, Probst, Johnston, Aldrich, and Nier, Phys. Rev. **72**, 502 (1947). Daunt, Probst, and Johnston, J. Chem. Phys. **15**, 759 (1947).

followed by those of Lane and his co-workers,[3] on the flow properties of solutions of He^3 in liquid He^4, which showed that He^3 did not partake in superfluid flow in solution, lent strong support to the theory of London. The more recent flow measurements on pure liquid He^3 by Osborne, Weinstock, and Abraham[4] and those on 90 percent He^3 solutions by Daunt and Heer[5] have shown that pure He^3, obeying Fermi-Dirac statistics, does not show superfluidity even down to 0.25°K, and hence the importance of the statistics seems to be firmly established.

In order to investigate theoretically the change of λ-temperature of solutions of He^3 in He^4 with concentration changes and to study the vapor pressures of such solutions, we have developed the properties of a model of a Bose-Einstein liquid which is the Bose-Einstein analog of a free-electron gas in a metal. The model adopted here treats tentatively liquid He^4 as a perfect Bose-Einstein gas in a potential well, of potential $\chi_4{}^0$. This smoothed potential model assumes that the volume of the liquid, V, can be written as

$$V = NV_4{}^0, \tag{1.1}$$

where N is the number of particles and $V_4{}^0$ the atomic volume per atom. The free energy of such a liquid can be written as

$$F = -kTZ + N_4 kT \ln\lambda_4, \tag{1.2}$$

where Z is given by:[6]

$$Z = \sum_r \tilde{\omega}_r \ln[1 - \lambda_4 \exp(-\epsilon_r/kT)]^{-1},$$

where the energy ϵ is written as $\epsilon = (p^2/2m_4) - \chi_4{}^0$ and where λ_4 is determined by the general condition for maintaining a constant number of particles, as discussed below.

For the situation below the condensation temperature, T_0, of the Bose-Einstein system, the term Z can be written in two parts, as has been pointed out by London,[1] the first of which concerns the number of particles which are "condensed." One can therefore write the free energy, F_4, as

$$\begin{aligned} F_4 = -kT\Big\{ & -\ln[1 - \lambda_4 \exp(\chi_4{}^0/kT)] \\ & - N_4 \ln\lambda_4 - N_4 V_4{}^0 2\pi \left(\frac{2m_4 kT}{h^2}\right)^{\frac{3}{2}} \\ & \times \int_0^\infty \ln\left[1 - \lambda_4 \exp\left(\frac{\chi_4{}^0}{kT} - y\right)\right] y^{\frac{1}{2}} dy \Big\}. \end{aligned} \tag{1.3}$$

For this model, therefore, the onset of extreme degeneracy will be determined when the term

$$\lambda_4{}^* \equiv \lambda_4 \exp(\chi_4{}^0/kT) \simeq 1. \tag{1.4}$$

On this simple model the introduction of the potential well does not affect the condensation temperature T_0 of the system in first approximation.[7]

The conservation of the total number of particles requires as is pointed out by Fowler and Guggenheim,[8] that:

$$\left(\frac{\partial F_4}{\partial \lambda_4}\right)_{TV} = 0 = \left(\frac{\partial F}{\partial \lambda_4{}^*}\right)_{TNV_4{}^0} \tag{1.5}$$

a condition which evaluates $\lambda_4{}^*$. If one now introduces, as is general in the two fluid theories of liquid He II, a parameter, x, defining the fraction of noncondensed particles, given by

$$x = (1/N_4)(\text{number of uncondensed particles}) = N_4{}^n/N_4$$

and putting with London[9]

$$\lambda_4{}^* = 1 - \frac{1}{(1-x)N_4}, \tag{1.6}$$

then one finds from Eqs. (1.3), (1.4), (1.5), and (1.6) that the temperature T_0, at which almost all the particles are noncondensed, is given by

$$T_0 = (h^2/2\pi m_4 k)(1/2.612 V_4{}^0)^{\frac{2}{3}}, \tag{1.7}$$

which is the same value of the degeneracy temperature as that given by London[1] for a perfect Bose-Einstein gas. When $\mathfrak{N} V_4{}^0$ is taken to be 27.6 cc, the numerical value of T_0 calculated in this way[1] is 3.13°K.

From Eqs. (1.5) and (1.6) it will be seen that the very general statistical requirement given by Eq. (1.5), which is the requirement of constant number of particles, can in the case of our *liquid* model be written

$$(\partial F_4/\partial \lambda_4)_{TV} = 0 = (\partial F_4/\partial \lambda_4{}^*)_{TNV_4{}^0} \simeq (\partial G_4/\partial x)_{Tp} \tag{1.8}$$

hence showing that the equilibrium evaluation of G, given when $(\partial G/\partial x)_{Tp} = 0$ as used in Gorter's treatment,[10] follows directly from the statistics provided the pressures are small, a condition necessary for Eq. (1.8) to hold.

Examination of Eqs. (1.3), (1.5), and (1.8) indicates that in any experiment on a degenerate Bose-Einstein liquid which attempts to count the total number of particles; i.e., the number given by the total mass, an operation equivalent to $(\partial F/\partial \lambda)$ is performed and the number of particles contributing is the same as the total number of atoms. For experiments which do not

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[3] Lane, Fairbank, Aldrich, and Nier, Phys. Rev. **73**, 256 (1948).

[4] Osborne, Weinstock, and Abraham, Phys. Rev. **75**, 988 (1949).

[5] J. G. Daunt and C. V. Heer, Phys. Rev. **79**, 46 (1950).

[6] The notation is the same as that used by Fowler in Statistical Mechanics (Cambridge University Press, London, 1936). See for example this reference, p. 72.

[7] Variations in $\chi_4{}^0$ with variation in volume V will, however, give further (second order) variations in T_0. See footnote 16 for further discussion of this.

[8] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, London, 1936), p. 62.

[9] See also E. Schrödinger, *Statistical Thermodynamics* (Cambridge University Press, London, 1946), p. 77.

[10] C. J. Gorter, Physica **15**, 523 (1949).

depend on the operation $(\partial F/\partial\lambda)$, e.g., specific heat measurements, the term $\ln(1-\lambda_4^*)$ can be neglected, and hence the free energy F, and the entropy, S, and etc., will appear to depend only on some number N_4^n; i.e., on the number of active particles. Such measurements would appear to include viscosity experiments, for which, therefore, only the number of normal atoms would be active and take part in producing a viscous term.

II. SOLUTIONS OF He^3 IN THE BOSE-EINSTEIN LIQUID AND THEIR LAMBDA-TEMPERATURES

In order to investigate the change in lambda-temperature of He^3 and He^4 solutions the treatment given in Sec. I of a Bose-Einstein liquid is extended to include a solution composed of such a Bose-Einstein liquid model and a similar but statistically independent Fermi-Dirac liquid model.

For calculation of the properties of such a solution the molar volume of He^3 is taken as $\mathfrak{N}V_3^0$, and of He^4 as $\mathfrak{N}V_4^0$, and we assume potential wells of depth $-\chi_3^0$, and $-\chi_4^0$ for the He^3 and He^4, respectively. In addition, the assumptions regarding ideal solutions are made; i.e., that the total volume of such a solution is assumed to be

$$V=N_3V_3^0+N_4V_4^0. \tag{2.1}$$

Moreover, the values of the χ^0's are assumed to be unaffected by the mixing process. Mixing therefore will affect only the statistical properties of the mixture.

Using Eq. (1.2), the free energy of the Fermi-Dirac liquid can be expressed as

$$F_3=-kT\left\{4\pi\left(\frac{2m_3kT}{h^2}\right)^{\frac{3}{2}}N_3V_3^0\int_0^\infty \ln\left[1+\lambda_3\exp\left(\frac{\chi_3^0}{kT}-y\right)\right]y^{\frac{1}{2}}dy-N_3\ln\lambda_3\right\}, \tag{2.2}$$

where the statistical weight of each level is for a known spin[11] of ½ for He^3. Combining this with Eq. (1.3) for the free energy of the Bose-Einstein liquid, the free energy of the solution is written as:

$$\begin{aligned}F&=F_3+F_4=F_3^0+F_4^0+\Delta F\\&=-kT\left\{4\pi\left(\frac{2m_3kT}{h^2}\right)^{\frac{3}{2}}(N_3V_3^0+N_4V_4^0)\right.\\&\qquad\times\int_0^\infty \ln[1+\lambda_3\exp(\chi_3^0/kT-y)]y^{\frac{1}{2}}dy\\&\qquad-N_3\ln\lambda_3-\ln(1-\lambda_4^*)-N_4\ln\lambda_4\\&\qquad-2\pi\left(\frac{2m_4kT}{h^2}\right)^{\frac{3}{2}}(N_3V_3^0+N_4V_4^0)\\&\qquad\qquad\left.\times\int_0^\infty \ln(1-\lambda_4^*e^{-y})y^{\frac{1}{2}}dy\right\}\cdots,\end{aligned} \tag{2.3}$$

where λ_4^* is given by Eq. (1.4), F_3^0 and F_4^0 are the free energies in the unmixed state, and ΔF is the free energy of mixing.

The conservation of the total number of particles requires that

$$(\partial F/\partial\lambda_3)_{TV_3^0V_4^0N_3N_4\lambda_4}=0, \tag{2.41}$$

$$(\partial F/\partial\lambda_4)_{TV_3^0V_4^0N_3N_4\lambda_3}=0, \tag{2.42}$$

and so λ_3 and λ_4 are determined from Eqs. (2.41) and (2.42). For $\lambda_4^*\simeq1$, this leads to

$$\frac{\lambda_4^*}{1-\lambda_4^*}-N_4+\left(\frac{2\pi m_4kT}{h^2}\right)^{\frac{3}{2}}\times(N_3V_3^0+N_4V_4^0)(2.612)=0. \tag{2.5}$$

Defining $\lambda_4^*=1-1/(1-x)N_4$ as in Eq. (1.6), where xN_4 is the number of He^4 atoms in the noncondensed state, the temperature at which condensation begins is given by

$$T_\lambda=\frac{h^2}{2\pi m_4k}\left(\frac{N_4}{N_3V_3^0+N_4V_4^0}\right)^{\frac{2}{3}}\left(\frac{1}{2.612}\right)^{\frac{2}{3}}. \tag{2.6}$$

By combining Eq. (2.6) with Eq. (1.7) one obtains

$$T_\lambda/T_0=[N_4V_4^0/(N_3V_3^0+N_4V_4^0)]^{\frac{2}{3}} \tag{2.7}$$

as the equation of the λ-line for solutions of He^3 and He^4.

In terms of the concentration of He^3 atoms in He^4, $C_3=N_3/(N_3+N_4)$, Eq. (2.7) can be written:

$$T_\lambda/T_0=\left[\frac{1-C_3}{1+C_3(V_3^0/V_4^0-1)}\right]^{\frac{2}{3}}. \tag{2.8}$$

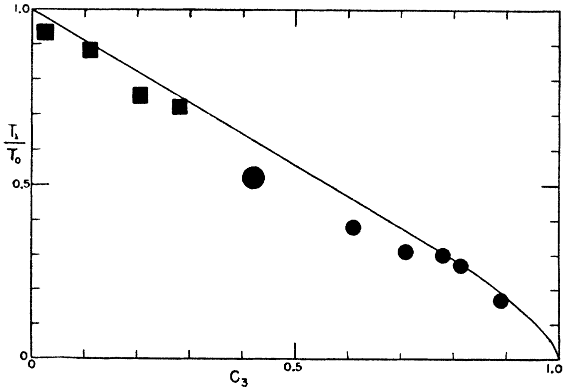

FIG. 1. Plot of the λ-temperature, T_λ, of solutions of He^3 in He^4 (as a fraction of the λ-temperature, T_0, of pure liquid He^4) against He^3 concentration, C_3. The full curve is the theoretical evaluation (Eq. (2.8)). The points marked with circles are the experimental results of Daunt and Heer (reference 5). The points marked with squares are the experimental results of Abraham, Weinstock, and Osborne (reference 14).

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[11] H. L. Anderson, Phys. Rev. **76**, 1460 (1949).

In order to estimate T_λ numerically, the molar volumes $\mathfrak{N}V_4^0$ and $\mathfrak{N}V_3^0$ of liquid He^4 and liquid He^3, respectively, have been taken to be[12,13] 27.6 cc and 37.6 cc. Using these values, and putting $T_0=2.18$°K, the experimentally determined[12] λ-point of pure liquid He^4, rather than the theoretical value of 3.13°K, the calculated variation of T_λ for the solutions according to Eq. (2.8) has been plotted against C_3 in Fig. 1.

Experimental observations have been made of the lambda-temperatures, T_λ, of He^3 solutions by Abraham, Weinstock, and Osborne[14] in the concentration range C_3 up to 28 percent and by Daunt and Heer[5] in the concentration range C_3 up to 89 percent. The observations are also shown in Fig. 1, and it will be seen that, except for the point at $C_3=42$ percent, there is good agreement with the theoretical values deduced from Eq. (2.8) as has been previously briefly pointed out.[5,15] The observed point at $C_3=42$ percent, however, was open to considerable error of observation (see Daunt and Heer, reference 5).[15a]

It might be concluded, therefore, that the assumptions made earlier, namely that we are dealing with perfect solutions of smoothed potential liquid models may in first approximation be applicable and that the change in T_λ with change in C_3 is due largely to the effect of the accompanying changes in the number density of the Bose-Einstein gas, rather than by the potential of the liquid well in which it is contained.[16]

These considerations also lead to the conclusion that a solution of two Bose-Einstein liquids, e.g., He^6 in He^4, should show two lambda-points (if each separately in the pure phase shows a lambda-transition), the T_λ for each concentration being given by Eq. (2.8). For very dilute solutions the lambda-temperature of the solute (e.g., He^6) would not be reached at temperatures of 1°K up, and hence one would not expect the solute to take part in superflow.[17] On such a model, therefore, an observed lack of superfluidity of Bose-Einstein particles in *dilute* solution could be taken as a strong support of the original thesis of London.[1]

III. ENTROPY AND FREE ENERGY OF MIXING OF DEGENERATE BOSE-EINSTEIN AND FERMI-DIRAC LIQUID MODELS

Assuming the models for Bose-Einstein and Fermi-Dirac liquids outlined in Secs. I and II above, the free energy of mixing can be written:

$$\begin{aligned}\Delta F=-kT\Bigg\{&4\pi\left(\frac{2m_3kT}{h^2}\right)^{3/2}\bigg[(N_3V_3^0+N_4V_4^0)\\&\times\int_0^\infty \ln[1+\lambda_3\exp(\chi_3^0/kT-y)]y^{\frac{1}{2}}dy\\&-N_3V_3^0\int_0^\infty \ln[1+\lambda_3^0\exp(\chi_3^0/kT-y)]y^{\frac{1}{2}}dy\bigg]\\&-N_3\ln\lambda_3/\lambda_3^0-\ln\left(\frac{1-\lambda_4^*}{1-\lambda_4^{0*}}\right)-N_4\ln\lambda_4/\lambda_4^0\\&-2\pi\left(\frac{2m_4kT}{h^2}\right)^{3/2}\bigg[(N_3V_3^0+N_4V_4^0)\\&\times\int_0^\infty \ln(1-\lambda_4^*e^{-y})y^{\frac{1}{2}}dy\\&-N_4V_4^0\int_0^\infty \ln(1-\lambda_4^{0*}e^{-y})y^{\frac{1}{2}}dy\bigg]\Bigg\}\cdots\quad(3.1)\end{aligned}$$

It can be shown that only in the completely classical case; i.e., far from degeneracy, where $\lambda_3\exp(\chi_3^0/kT)\ll1$ and $\lambda_4\exp(\chi_4^0/kT)\ll1$ that the expression (3.1) reduces to the more familiar formulation.[18]

$$\Delta F=-kT\left\{N_3\ln\frac{N_3+N_4}{N_3}+N_4\ln\frac{N_3+N_4}{N_4}\right\}.\quad(3.2)$$

At sufficiently low temperatures it can be assumed that in the case of He^3 and He^4 solutions, both the Fermi-Dirac and the Bose-Einstein liquids will be very degenerate, and in this situation Eq. (3.1) leads to the

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[12] W. H. Keesom, *Helium* (Elsevier Publishing Company, Inc., New York, 1942).

[13] Grilly, Hammel, and Sydoriak, Phys. Rev. **75**, 1103 (1949).

[14] Abraham, Weinstock, and Osborne, Phys. Rev. **76**, 864 (1949).

[15] Other theoretical evaluations of the λ-line for solutions of He^3 in He^4 have been made by deBoer [Phys. Rev. **76**, 852 (1949)], deBoer and Gorter [Phys. Rev. **77**, 569 (1950)], Stout [Phys. Rev. **76**, 864 (1949)], and by Engel and Rice [Phys. Rev. **78**, 55 (1950)]. These previous evaluations have considered classical statistics only, such as would involve a localized model of the liquid phase and have obtained numerical results by making *ad hoc* assumptions regarding the free energy of pure liquid He^4. A fuller discussion of these theoretical evaluations in the light of the experimental results has been given elsewhere (reference 5).

[15a] *Note added in proof.* One measurement on the change in lambda-temperature for a 1.5 percent solution of He^3 in He^4 has recently been reported by B. N. Eselson and B. G. Lazarew [Doklady Akad. Nauk S. S. S. R. **72**, 265 (1950)], and this gives a result which is somewhat nearer our theoretical curve (see Fig. 1) than the point at 2.4 percent He^3 concentration reported by Abraham, Weinstock, and Osborne (reference 14).

[16] Such a model, however, can be taken only as a first approximation, since it is well known (reference 12) that an increase in the external pressure decreases the lambda-point of pure liquid He^4. Since the external pressure is made up of two terms, one a "kinetic" term calculable from the statistics and the other a statical pressure due to variation of χ_4^0 with volume, one must conclude that $\partial\chi(V^0)/\partial V^0$ must in second approximation for our model affect T_0. Such a difficulty is a natural consequence for any smoothed potential model in which the gas-like quality of the liquid is emphasized. See for example Fowler and Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, London, 1949), p. 486.

[17] This conclusion has been arrived at by Landau and Pomeranchuk [Compt. rend. acad. sci. U.R.S.S. **59**, 669 (1948)] starting from different initial assumptions.

[18] The resolution to this form requires the usual assumption that the difference between the arithmetic mean and the geometric mean of the molar volumes is small: i.e.,

$$\frac{N_3V_3^0+N_4V_4^0}{N_3+N_4}\cong[(V_3^0)^{N_3}(V_4^0)^{N_4}]^{1/(N_3+N_4)}.$$

following value for the entropy of mixing, ΔS:

$$\Delta S=-\left(\frac{\partial\Delta F}{\partial T}\right)=-\frac{\partial}{\partial T}\left[\tfrac{3}{5}N_3(\epsilon^{0*}-\epsilon^*)+O(T^2)\right] \quad (3.3)$$

where ϵ^* and ϵ^{0*} are the Fermi-Dirac degeneracy energies in the mixed and unmixed states respectively. Equation (3.3) shows that the entropy of mixing ΔS tends to zero as $T\rightarrow 0$, in conformity with the third law, a result which does not hold for the classical expression derivable from Eq. (3.2). Thus the models postulated herewith for liquid He^3 and He^4 indicate an "unmixing" as $T\rightarrow 0$.

IV. VAPOR PRESSURES OF SOLUTIONS OF He^3 IN THE BOSE-EINSTEIN LIQUID ABOVE AND BELOW THE LAMBDA-TEMPERATURE

A. Below the Lambda-Temperature

The partial vapor pressures of He^3 and He^4 in equilibrium with a solution of He^3 and He^4 can be computed by equating the partial potentials $\mu_3{}^L$, $\mu_4{}^L$ in the liquid phase to the partial potentials in the vapor phase $\mu_3{}^v$ and $\mu_4{}^v$.

The Gibbs function G for the liquid is

$$G=F+pV=F+p(N_3V_3{}^0+N_4V_4{}^0)\simeq F$$

at ordinary pressures. With this approximation the partial potentials are given by

$$\mu_3{}^L=\left(\frac{\partial G}{\partial N_3}\right)_{Tp}=\left(\frac{\partial G}{\partial N_3}\right)_{TV_3{}^0V_4{}^0}\simeq\left(\frac{\partial F}{\partial N_3}\right)_{TV_3{}^0V_4{}^0}, \quad (4.1)$$

etc.

In the first instance the He^3 liquid model, pure and diluted, will be considered as essentially Boltzmannian in the temperature region above 1°K. Using Eqs. (1.3), (2.2), and (2.3) the partial potentials become, for the pure liquids He^3 and He^4 separately:

$$\mu_3{}^{0L}=-\chi_3{}^0-kT-kT\ln V_3{}^0-kT\ln 2\left(\frac{2\pi m_3kT}{h^2}\right)^{\frac{3}{2}} \quad (4.2)$$

$$\mu_4{}^{0L}=-\chi_4{}^0-0.514\left(\frac{2\pi m_4kT}{h^2}\right)^{\frac{3}{2}}(2.612)V_4{}^0kT \quad (4.3)$$

and for the solutions:

$$\begin{aligned}\mu_3{}^L=-\chi_3{}^0&-\frac{N_3V_3{}^0kT}{N_3V_3{}^0+N_4V_4{}^0}\\ &-kT\ln 2\left(\frac{2\pi m_3kT}{h^2}\right)^{\frac{3}{2}}+kT\ln\frac{N_3}{N_3V_3{}^0+N_4V_4{}^0}\\ &-\left(\frac{2\pi m_4kT}{h^2}\right)^{\frac{3}{2}}(1.341)V_3{}^0kT \quad (4.4)\end{aligned}$$

$$\begin{aligned}\mu_4{}^L=-\chi_4{}^0&-\frac{N_3V_4{}^0kT}{N_3V_3{}^0+N_4V_4{}^0}\\ &-(1.341)\left(\frac{2\pi m_4kT}{h^2}\right)^{\frac{3}{2}}V_4{}^0kT. \quad (4.5)\end{aligned}$$

Applying the condition of equilibrium, i.e., the partial potential in the vapor phase is equal in each case to the partial potential in the liquid phase, we obtain, assuming the vapor to be a perfect gas,

$$\begin{aligned}\mu_3{}^L-\mu_3{}^{0L}&=\mu_3{}^v-\mu_3{}^{0v}=kT\ln(p_3/p_3{}^0)\\ \mu_4{}^L-\mu_4{}^{0L}&=\mu_4{}^v-\mu_4{}^{0v}=kT\ln(p_4/p_4{}^0)\end{aligned} \quad (4.6)$$

where the superscripts v refer to the vapor phase, and where p_3 and p_4 are the *partial* vapor pressures and $p_4{}^0$ and $p_4{}^0$ the full vapor pressures of liquid He^3 and He^4 respectively.[19]

Combining Eqs. (4.2) to (4.6) the partial vapor

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[19] Adopting the same equilibrium conditions, the smoothed potential models of liquid He^4 and liquid He^3 allow immediate calculation of the vapor pressures, $p_4{}^0$ and $p_3{}^0$, of the pure liquids. *At sufficiently low temperatures*, where the effect of degeneracy predominates, the vapor pressure formulas can be written as:

For the He^4 liquid model

$$\ln p_4{}^0=-\chi_4{}^0/kT+5/2\ln T-0.514(T/T_0)^{\frac{3}{2}}+\ln(2\pi m_4/h^2)^{\frac{3}{2}}k^{5/2},$$

i.e.,

$$\log_{10}p_4{}^0(\mathrm{cm})=-U_4{}^0/RT+2.5\log_{10}T-0.069T^{\frac{3}{2}}+1.196.$$

This equation is similar to the equations put forward by Bleaney and Simon and by Lingac and Kistemaker (see H. Van Dijk, Proceedings of International Conference on the Physics of Very Low Temperatures. M.I.T. 1949, p. 117, for a discussion of vapor pressure data). The third (specific heat) term in the above equation however gives a variation of T to the three halves power, rather than to higher powers of T (three or six) as previously assumed.

For the He^3 liquid model.

$$\ln p_3{}^0=-\frac{(\chi_3{}^0-\frac{3}{5}\epsilon^{0*})}{kT}+\frac{5}{2}\ln T-\frac{\pi^2}{4}\frac{kT}{\epsilon^{0*}}+\ln 2\left(\frac{2\pi m_3}{h^2}\right)^{\frac{3}{2}}k^{5/2}$$

or

$$\log_{10}p_3{}^0(\mathrm{cm})=-\frac{U_3{}^0}{RT}+2.5\log_{10}T-0.511T+1.31.$$

For He^3 the smoothed potential model leads to an additional factor of 2 in the vapor pressure constant due to the spin. The coefficient of the third (specific heat) term in the above equation has been calculated assuming that the degeneracy temperature of the liquid He^3 is the same (4.85°K) as that for a perfect Fermi-Dirac gas with the liquid density. However it is expected that the degeneracy temperature would be somewhat lower, as in the case of He^4, and consequently the term in T would require slight modification. It should be emphasized moreover, that strictly the vapor pressure formula given above would be accurate only for *temperatures less than one quarter of the degeneracy temperature.* The chief differences between the above equation and that first proposed by deBoer and Lunbeck [Physica **14**, 510 (1948)] are (a) the inclusion of the spin in the vapor pressure constant, as has previously been adopted for the smoothed potential model of electrons in metals and (b) the inclusion here of a specific heat term proportional to T. This term may remain important even at low temperatures due to its slow dependence on T. For a limited temperature range above 1°K, it is reasonable to allow for the conditions being nearer the degeneracy temperature by reducing the coefficient in the specific heat term. If this specific heat term in the vapor pressure formula given above is put equal to $0.170T$ and if $U_3{}^0$ is put equal to $1.16R$, a value in agreement with that proposed by deBoer and Lunbeck, the calculated vapor pressures are within 2.5 percent of the observed values given in the preliminary measurements of Sydoriak, Grilly, and Hammel (reference 23), up to 1.8°K. Modifications should, of course, be made to the above formulations for the non-ideality of the vapor [see Kranendonk, Compaan, and deBoer, Phys. Rev. **76**, 1728 (1949)] but in view of the approximate character of our liquid models this has not been considered worth while.

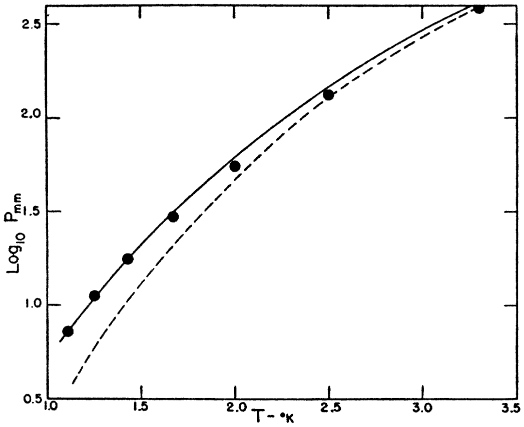

FIG. 2. Plot of the vapor pressure of a 20 percent solution of He^3 in liquid He^4 against temperature. The full curve is the theoretical evaluation [Eqs. (4.13) to (4.16)]. The dashed curve is the result of assuming Raoult's law. The points marked with circles are the experimental results of measurement of a 20.3 percent mixture of He^3 in He^4 by Weinstock, Osborne, and Abraham (reference 21).

pressures ratios can be expressed as

$$p_3/p_4=C_3'p_3^0/p_4^0\exp\left\{C_3'V_4^0/V_3^0+C_4'-0.514\frac{N_4^nV_3^0}{N_3V_3^0+N_4V_4^0}\right\}\cdots,\quad (4.7)$$

where

$$C_4'=\frac{N_4V_4^0}{N_3V_3^0+N_4V_4^0}\text{ and }C_3'=\frac{N_3V_3^0}{N_3V_3^0+N_4V_4^0}\cdots,\quad (4.8)$$

and where N_4^n is the number of "normal" (uncondensed) He^4 atoms, given for the perfect Bose-Einstein fluid by:

$$N_4^n=(T/T_0)^{\frac{3}{2}}N_4.$$

For dilute solutions, $N_4 \gg N_3$, formulas (4.7) can be written, as:

$$\frac{C_v}{C_L}=(V_3^0/V_4^0)(p_3^0/p_4^0)\times\exp\left[1-0.514\left(\frac{T}{2.18}\right)^{\frac{3}{2}}\frac{V_3^0}{V_4^0}\right],\quad (4.9)$$

where the concentration in the liquid phase is given by $C_L=N_3/N_4$ and the concentration in the vapor phase by $C_v=N_3^v/N_4^v=p_3/p_4$. This result, as will be discussed later, gives values of C_v/C_L higher than those obtained from Raoult's law, such as has been experimentally observed by Taconis *et al.*[20]

B. Above the Lambda-Temperature

Following the procedure adopted in Sec. IVA, similar calculations for the vapor pressure ratios above the lambda point have been made.

The equation for the free energy above the λ-point is given by London.[1]

$$F_4=-N_4\chi_4^0-N_4kT\ln(T/T_\lambda)^{\frac{3}{2}}-N_4kT(1-\ln2.612)$$
$$-0.462N_4kT(T_\lambda/T)^{\frac{3}{2}}-0.108N_4kT(T_\lambda/T)^3\cdots\quad (4.10)$$

where T_λ is given by Eq. (2.6).

Applying the conditions of equilibrium to the liquid and gaseous phases, the latter being assumed perfect, the vapor pressure equation, for example, for the dilute model solutions reduces to

$$p_3/p_4=(p_3^0/p_4^0)(N_3V_3^0/N_4V_4^0)$$
$$\times\exp[1-V_3^0/V_4^0+0.462(V_3^0/V_4^0)(T_0/T)^{\frac{3}{2}}$$
$$+0.022(V_3^0/V_4^0)(T_0/T)^3+\cdots],\quad (4.11)$$

or in terms of the concentrations,

$$C_v/C_L=(V_3^0/V_4^0)\exp\{1-V_3^0/V_4^0$$
$$+0.462(V_3^0/V_4^0)(T_0/T)^{\frac{3}{2}}$$
$$+0.022(V_3^0/V_4^0)(T_0/T)^3+\cdots\}.\quad (4.12)$$

These results for the model solutions indicate that p_3, dp_3/dT, and C_v/C_L are continuous across the λ-point, even for concentrated solutions which are discussed in more detail below.

C. Discussion of Vapor Pressure Results

Numerical evaluations have been made of the total vapor pressures (p_3+p_4) of two model solutions of He^3 and He^4 as a function of temperature using the following formulas from which formulas (4.7) and (4.11) were obtained:

Above T_λ

$$p_3/p_3^0=C_3'\exp\left\{\left(1-\frac{V_3^0}{V_4^0}\right)C_4'+0.462\left(\frac{V_3^0}{V_4^0}\right)\left(\frac{T_\lambda}{T}\right)^{\frac{3}{2}}C_4'+0.022\left(\frac{V_3^0}{V_4^0}\right)\left(\frac{T_\lambda}{T}\right)^3C_4'+\cdots\right\},\quad (4.13)$$

$$p_4/p_4^0=C_4'\exp\left\{\left(1-\frac{V_4^0}{V_3^0}\right)C_3'-0.462\left[1+C_3'-\frac{1}{C_4'}\right]\left(\frac{T_\lambda}{T}\right)^{\frac{3}{2}}-0.011\left[1+2C_3'-\frac{1}{(C_4')^2}\right]\left(\frac{T_\lambda}{T}\right)^3-\cdots\right\}.\quad (4.14)$$

Below T_λ

$$p_3/p_3^0=C_3'\exp\left\{C_4'-0.514\left(\frac{V_3^0}{V_4^0}\right)\left(\frac{T}{T_\lambda}\right)^{\frac{3}{2}}C_4'\right\},\quad (4.15)$$

$$p_4/p_4^0=\exp\left[-\left(\frac{V_4^0}{V_3^0}\right)C_3'\right].\quad (4.16)$$

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[20] Taconis, Beenakker, Nier, and Aldrich, Physica 15, 733 (1949).

The two solution concentrations chosen for calculation were with C_3 of 20 and 25.5 percent. These values were chosen because experiments have been made by Weinstock, Osborne, and Abraham[21] on the vapor pressures of such solutions. The result of our computations, giving the vapor pressure ($p=p_3+p_4$) plotted against temperature for the 20 percent solution is given in Fig. 2 by the full curve. The dashed line indicates the vapor pressure curve calculated from Raoult's law. The experimental points[21] for a 20.3 percent He^3 mixture are shown by the circled points in Fig. 2, and it will be seen that their agreement with our calculation is good, particularly below the lambda-temperature (calculated $T_\lambda=1.79$). The deviations of the experimental points from the full curve at the higher temperatures are in a direction which would be expected, since experimentally at the higher temperatures the quantity of He^3 in the vapor increases and consequently the concentration, C_3, in the liquid phase becomes smaller than that (20.3 percent) for the unrefrigerated gas. The general agreement between theory and experiment for the vapor pressures of the 25.5 percent concentration solution is as good as that shown for the 20 percent solution of Fig. 2. It is concluded that Eqs. (4.13) to (4.16) are adequate in first approximation to account for the vapor pressure of strong or dilute solutions above or below their lambda-temperatures. It is to be noticed moreover that Eqs. (4.13) and (4.14), as is shown in Fig. 2, indicate that even *above* T_λ Raoult's law is inadequate, as has been noticed experimentally by Weinstock, Osborne, and Abraham[21] and by Lane and his co-workers.[22]

It would be of interest to have more detailed measurements of the vapor pressures, or of the distribution coefficient C_v/C_L, above the lambda-temperatures of the solutions concerned.

Although it is considered that many of the measurements of the distribution coefficient, C_v/C_L, for He^3 in He^4 do not have the accuracy of a direct vapor pressure, measurement, it was thought worth while to calculate numerically C_v/C_L for the case of very dilute solutions, since the experimental work on the measurement of C_v/C_L has been carried out so far using only dilute solutions. ($C_3<1$ percent.) A numerical evaluation therefore has been made of C_v/C_L for dilute model solutions using Eqs. (4.9) and (4.12) for below and above the λ-temperature respectively. In the calculations it was assumed that the He^3 concentration, C_3, in the solution was so small that $T_\lambda \simeq T_0=2.18$°K, and the measured values of the vapor pressures $p_3{}^0$ and $p_4{}^0$ of the pure-components were adopted (see Sydoriak, Grilly, and Hammel[23] for vapor pressures of liquid He^3 and Van Dijk and Shoenberg[24] for vapor pressure of liquid He^4). The result of this computation is given by the full curve of Fig. 3.

Also in Fig. 3, the dashed curve gives the calculated value of C_v/C_L, obtained by assuming Raoult's law, being given by

$$C_v/C_L=p_3{}^0/p_4{}^0. \tag{4.17}$$

It will be seen that the values of C_v/C_L for our model lie at all temperatures above those given by Eq. (4.17). Below the lambda-temperature, experiments have shown that, in conditions where the He^3 was well mixed in the liquid phase, the observed values of C_v/C_L, also lie well above the values calculated from Eq. (4.17), as has been demonstrated by Taconis[20] *et al.* and by Lane and his co-workers,[25] and as is indicated by the points plotted in Fig. 3.[26]

It has been suggested[20] by Taconis that formula (4.17) could be modified to fit the observations *below* the lambda-temperature by assuming that the He^3 dissolves in the "normal" fraction ($N_4{}^n$) of the liquid He^4 only. Such a postulate would leave the theoretical evaluation of C_v/C_L *above* the lambda-temperature as being determined with good approximation by Eq.

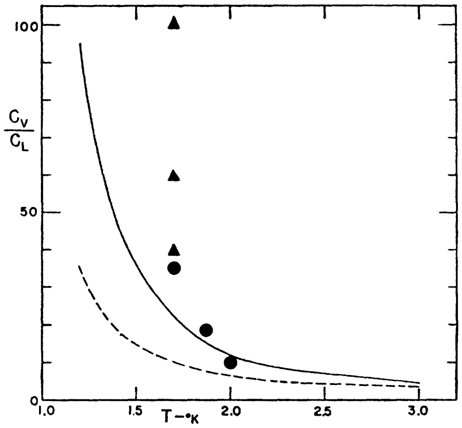

FIG. 3. Plot of the distribution coefficient, C_v/C_L, for dilute solutions ($C_3 \leq 1$ percent) of He^3 in liquid He^4 against temperature. The full curve is the theoretical evaluation [Eqs. (4.9) and (4.12)]. The dashed curve is the result of assuming Raoult's law [Eq. (4.17)]. The points marked with circles are the measurements of Taconis and co-workers (reference 20). The triangular points are the measurements of Lane and co-workers (reference 25).

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[21] Weinstock, Osborne, and Abraham, Phys. Rev. **77**, 400 (1950).

[22] Fairbank, Reynolds, Lane, McInteer, Aldrich, and Nier, Phys. Rev. **74**, 345 (1948).

[23] Sydoriak, Grilly, and Hammel, Phys. Rev. **75**, 303 (1949). See also Abraham, Osborne, and Weinstock, Phys. Rev. **80**, 366 (1950).

[24] H. Van Dijk and D. Shoenberg, Nature **169**, 151 (1949).

[25] Lane, Fairbank, Aldrich, and Nier, Phys. Rev. **75**, 46 (1949).

[26] The results of measurement of C_v/C_L by Taconis *et al.* (reference 20) lie between the extremes presented on the one hand by the work of Daunt and others (reference 27) and of Lane and co-workers [Phys. Rev. **73**, 729 (1948)] and on the other hand by Rollin and Hatton [Phys. Rev. **74**, 508 (1948)] and by Lane and co-workers (reference 25). This is largely due to the improved method of stirring the solution adopted by Taconis whereby strong concentration gradients within the liquid were avoided. (See Daunt and Heer, reference 5, for further discussion of this point.) It has been suggested (reference 5) that these difficulties of observation of equilibrium values of C_v/C_L would be largely avoided by measurement on solutions with higher He^3 concentration, and further experiments with $C_3>1$ percent would be of value.

(4.17). In our model, however, C_v/C_L should lie above the values calculated by the simple theory of Eq. (4.17) even *above* the lambda-temperature.

The measurements below the lambda-temperature of C_v/C_L are in moderate agreement with our calculations, as is shown in Fig. 3. Too great a reliance, however, cannot be placed on the accuracy of the existing experimental data, as is evident from the large scatter of the results (see also footnote 26). The direct vapor pressure measurements of more concentrated solutions provides, as is indicated earlier, a more satisfactory test of the adequacy of the calculations.

Above the lambda-temperature there are indications in the work of Lane and co-workers[22] and of Weinstock *et al.*[21] that discrepancies exist between the observations of C_v/C_L and the simple theory [Eq. (4.17)]; although the older results[27,28] on extremely dilute solutions do not permit a conclusion to be made. It would be valuable to have further measurements of C_v/C_L above the lambda-temperature in order to check whether the high values of C_v/C_L can be explained in the manner outlined above.[28a]

D. The Vapor Pressures of Solutions Where Both He³ and He⁴ Are Degenerate

Finally some discussion of the effect of the degree of degeneracy of the Fermi-Dirac component on the calculation of the partial vapor pressures should be made. In the calculations outlined in Secs. IVA and IVB above, it has been assumed that the He^3 was nondegenerate both as pure liquid and in solution. If, however, it is assumed that as a pure liquid the He^3 is degenerate, then the results for the vapor pressures of the solutions need modification. To carry out the necessary calculations two paths have been followed. In the first (a) it has been assumed that the liquid He^3 model is degenerate in the pure state and nondegenerate in solution. This might be a situation reflecting the properties of dilute solutions at sufficiently low temperatures. Under these conditions it can be shown that:

$$p_3/p_3^0 = C_3'(4/3(\pi)^{\frac{1}{2}})(\epsilon^{0*}/kT)^{\frac{3}{2}} \times\exp\{-\tfrac{3}{5}(\epsilon^{0*}/kT)+\pi^2/4(kT/\epsilon^{0*}) -C_3'-0.514(T/T_\lambda)^{\frac{3}{2}}C_4'(V_3^0/V_4^0)\}. \quad (4.18)$$

At sufficiently low temperatures the term $\exp[-\frac{3}{5}(\epsilon^{0*}/kT)]$ predominates and results in a reduction of the partial vapor pressure even below the value calculable from Raoult's law. If the degeneracy temperature of the pure Fermi-Dirac liquid model, $T^{0*}=\epsilon^{0*}/k$, were equal to 4.85°K, i.e., the value calculable for a perfect gas of He^3 with the liquid density, the value of p_3/p_3^0, as given by Eq. (4.18), would already be less than the value predicted by Raoult's law at 1°K. The experimental results however (see Fig. 2) for the measured vapor pressures indicate that down to 1°K values are obtained in good agreement with our theory on the basis of nondegeneracy of the Fermi-Dirac liquid, as given in Sec. IVA. It must in consequence be assumed that $T^{0*}<4.85°K$ (see footnote 19) and moreover it can be shown from Eq. (4.18) that for $T^{0*}\leq 2°K$, the non-degenerate evaluation of p_3/p_3^0 given in Eq. (4.15) is an adequate approximation down to the lowest temperatures to which measurements have been made, i.e. down to 1°K.

The evaluation of C_v/C_L under the degenerate conditions assumed above involves not only (4.18) for p_3/p_3^0 but also a knowledge of p_3^0/p_4^0. It can be shown that, if the known vapor pressure formulas for He^4 (Bleaney and Simon[29]) and for He^3 (Sydoriak, Grilly, and Hammel[23]) are extrapolated below 1°K, then the distribution coefficient C_v/C_L will always continue to increase with decreasing temperature. This is due to the fact that the ratio of the vapor pressure of He^3 to that of He^4 increases with decreasing temperature more rapidly than the ratio of the partial vapor pressures p_3/p_4. Nevertheless C_v/C_L would in these circumstances be below the values calculable from Raoult's law [Eq. (4.17)]. It would appear therefore that the results given in Sec. IVA, which showed that the partial vapor pressure of He^3 in model solutions of He^3 and He^4 and the value of the distribution coefficient, C_v/C_L, were greater than the values given by Raoult's law, are limited to a temperature range above some critical temperature which is estimated to be about 0.5°K.

The second case of interest (b) would occur when both the pure liquid He^3 and the He^3 in solution are degenerate. In this case the general results are the same as for case (a), i.e. values for p_3 and C_v/C_L less than those calculable from Raoult's law are obtained. This situation is probably of less importance than the case (a) above, since at easily attainable temperatures it would involve only strong solutions of He^3. The value of p_3 which has been obtained for case (b) is given by:

$$\ln p_3/p_3^0 = 3/5(1/kT)(\epsilon^*-\epsilon^{0*}) - \frac{\pi^2}{4}\left(\frac{1}{\epsilon^*}-\frac{1}{\epsilon^{0*}}\right)kT + 2/5(\epsilon^*/kT)C_4' - \frac{\pi^2}{6}\frac{kT}{\epsilon^*}C_4' - 0.514\left(\frac{T}{T_\lambda}\right)^{\frac{3}{2}} C_4'\frac{V_3^0}{V_4^0}. \quad (4.19)$$

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[27] Daunt, Probst, and Smith, Phys. Rev. **74**, 495 (1948).

[28] Fairbank, Lane, Aldrich, and Nier, Phys. Rev. **71**, 911 (1947).

[28a] *Note added in proof.* We have recently carried out experimental measurements of C_v/C_L above and below the λ-temperature of a one percent He^3 solution in He^4 and find results in close agreement with our theoretical evaluations given in this paper, even *above* the λ-temperature. Details of this work will be published shortly. We note also that recent experimental values of C_v/C_L quoted by Taconis, Beenakker, and Dokoupil [(Phys. Rev. **78**, 171 (1950)] for He^3 in He^4 solutions varying from 0.11 to 0.22 percent He^3 concentration average about a value of C_v/C_L equal to 75 at 1.38°K. This is in moderate agreement with our calculated value of 50 at the same temperature, whereas Taconis' empirical solubility law (reference 20) predicts a value of C_v/C_L equal to 300 at this temperature.

[29] B. Bleaney and F. Simon, Trans. Faraday Soc. **35**, 1205 (1939).