Specific Heat of Liquid He³†*

MYRON STRONGIN,‡ GEORGE O. ZIMMERMAN, AND HENRY A. FAIRBANK§

Physics Department, Yale University, New Haven, Connecticut

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The specific heat of liquid He³ has been measured at saturated vapor pressure and at three elevated pressures in the temperature range 0.054 to 0.3°K. No evidence of a transition to a correlated superfluid phase was found. At the lowest temperatures the specific heat was nearly proportional to T in agreement with other recent measurements. Entropy values are calculated at each pressure. Measurements at pressures above the minimum in the melting curve show no anomalous behavior. Measurement of the expansion coefficient of the liquid below 0.1°K confirms that the expansion coefficient is negative.

INTRODUCTION

IN this paper we report specific-heat measurements of liquid He³ in the temperature range from 0.054 to 0.3°K, and at pressures from saturated vapor pressure to pressures above the minimum in the melting curve.[1–3] Measurements of the properties of liquid He³ are of particular interest near 0°K, where quantum effects are important and where the existing theories should apply. Previous measurements of Brewer, Daunt, and Sreedhar[4] extending to 0.085°K indicated that the liquid specific heat appeared to be proportional to the temperature in the region below about 0.1°K, which is the behavior predicted from the Fermi liquid theories,[5–7] and the theory of Goldstein[8] near 0°K.

At the time our measurements were undertaken, several investigators had indicated that if He³ were, indeed, a Fermi liquid, a cooperative transition to a superfluid phase should occur at about 0.08°K.[9,10] In going from the normal to the superfluid state a discontinuous increase in the specific heat of about a factor of 2 was predicted. This would make the specific heat a very sensitive test for such a transition. No indication of a transition was found in any of our measurements. Measurements at the University of Illinois have now established that at saturated vapor pressure no transition is present in the liquid down to 0.008°K.[11,12]

From our specific-heat data and the data of Anderson *et al.*, we have been able to calculate the entropy of the liquid. The entropy values obtained by us are in good agreement with those obtained by other investigators at higher temperatures.[13]

APPARATUS

Figure 1 shows the low-temperature part of the apparatus, which is immersed in liquid He⁴. Initial cooling of the apparatus to about 0.4°K is provided by the He³ cryostat, from which the rest of the specific-heat apparatus is suspended, and final cooling of the sample

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‡ Present address: MIT, Lincoln Laboratory, Lexington, Massachusetts.

§ Present address: Duke University, Durham, North Carolina.

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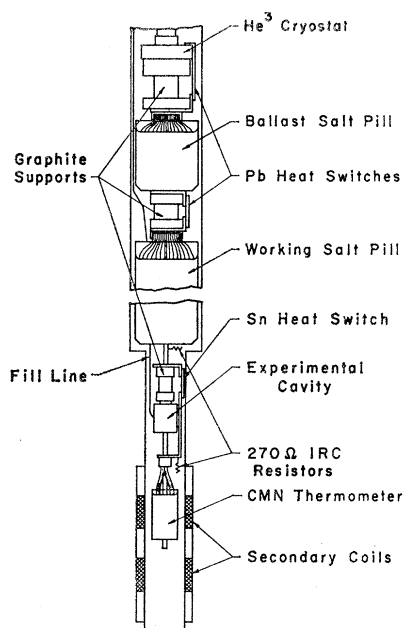
FIG. 1. The specific-heat apparatus. Shown is the part of the apparatus immersed in a liquid He^4 bath.

chamber is obtained by adiabatic demagnetization of two chromic methylammonium alum (CMA) salt pills. These pills were constructed by tamping a powder of chromic methylammonium alum into a nylon container with about ten thousand 0.003-in.-diam copper wires inside. To provide good contact between the paramagnetic salt and the copper wires, Castolite, a cold-setting plastic whose favorable contact properties at low temperatures have previously been demonstrated,[14,15] was sucked into the packed salt. Then pressure up to 200 psi was applied to the salt-Castolite mixture to make sure that the plastic impregnated the interstices in the salt pill. The upper salt pill, consisting of about 50 g of CMA, serves as a ballast for the heat leak coming from the He^3 cryostat. The working pill, containing 150 g of CMA, serves as the refrigerant to cool the sample cavity. The salt pills and cavity were mounted in a rigid assembly by means of graphite supports. Graphite has been shown to be a very poor thermal conductor at these low temperatures.[16] The copper systems of the salt pills are thermally linked to the He^3 cryostat and to each other by means of superconducting Pb heat switches, and the specific-heat cavity is linked to the copper system of the working salt by means of a Sn heat switch.

The cavity is depicted in detail in Fig. 2. Inside the

He^3 container, made of electrolytic copper, ten thousand 0.003-in.-diam bare copper wires were silver soldered to the bottom of the calorimeter to provide good thermal contact between the He^3 and the calorimeter. Two thousand bare 0.003-in.-diam copper wires were silver soldered to the bottom of the He^3 container and were embedded in the thermometer pill which contained about 10 g of cerium magnesium nitrate (CMN). This pill was made in a similar way to the CMA pills, and the thermal contact between the wires and salt was again provided by Castolite. For the specific-heat measurements under vapor pressure, the cap of the cavity was soft soldered to the rest of the cavity, while for the measurements of the specific heat at higher pressures the cap was fastened to the calorimeter by means of twelve 2-56 screws, and the seal was made by means of a Pb O-ring. In both cases the heater, which consisted of a length of 0.003-in. "Advance" wire, was wound on the outside of the calorimeter in one layer, and was thermally bound to the calorimeter with Castolite.

The times of the heat pulses, which varied from 1 to 10 sec, were measured with a Hewlett Packard counter, and the power was measured with a potentiometer. The calorimeter assembly described above is enclosed in a brass vacuum can into which He^4 exchange gas could be introduced.

The susceptibility of our CMN thermometer salt pill was measured by means of an ac mutual inductance bridge similar to the one described by Pillinger, Jastram,
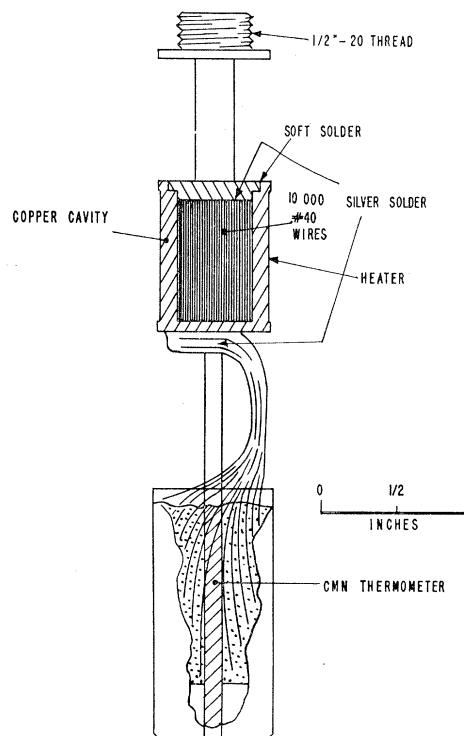
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FIG. 2. The He^3 calorimeter and attached cerium magnesium nitrate thermometer.

and Daunt.[17] The secondary coils of the cryostat mutual inductance are shown in Fig. 1.

The He³ used in this experiment was purified by pumping back 2/3 of a given amount of He³ at 0.4°K (starting purity, 99.9%). This process was carried out twice, giving an He⁴ concentration estimated to be less than one part in 10⁵. No trace of He⁴ was found using a mass spectrometer capable of detecting an He⁴ concentration of 0.003%.

EXPERIMENTAL PROCEDURE

After filling the outer Dewar with liquid He⁴, the bath was kept at about 4.2°K and the exchange gas was pumped out of the exchange gas can for times ranging from 15 min to 1 h. On some runs no exchange gas was used at all; on these runs we obtained our smallest heat leak, which was about 6 ergs/min. However, it was usually found that pumping out the He⁴ at 4.2°K was extremely effective, and the bother of waiting about 12 h for the salt pills to cool to 4.2°K when no exchange gas was used was not justified.

After pumping out the exchange gas, the surrounding He⁴ bath was slowly pumped down to about 1.1°K, and the He³ gas was introduced into the low-temperature part of the He³ refrigerator. The heat exchange provided by this He³ gas was sufficient to cool all the apparatus inside the exchange gas can to about 1.1°K in a time of about 15 min.

The salt pills were demagnetized after the apparatus was cooled to about 0.4°K by the He³ refrigerator. Initially, the magnetic field was rapidly reduced to a value below the critical field of the lead heat switches, causing the lead to become superconducting, and thereby isolating the salt pills and calorimeter from the He³ cryostat. The magnet was then lowered until the poles were around the tin heat switch and the magnetic field was slowly decreased to a value slightly higher than the critical field of tin. The time to cool about 0.03 mole of liquid He³ to its lowest temperature was usually from 1 to 2 h. The magnet was then removed slowly by means of a mechanical drive.
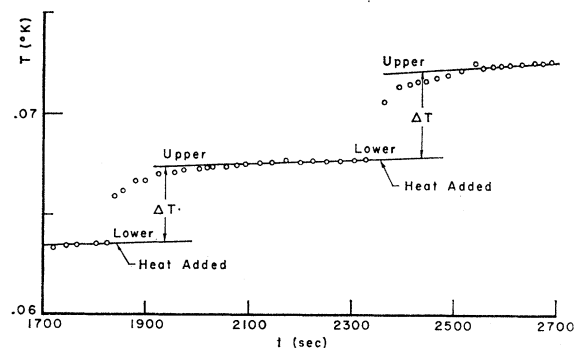

FIG. 3. A typical record of the temperature of the calorimeter vs time, during a warmup showing the temperature increase ΔT resulting from a heat input of ΔQ.

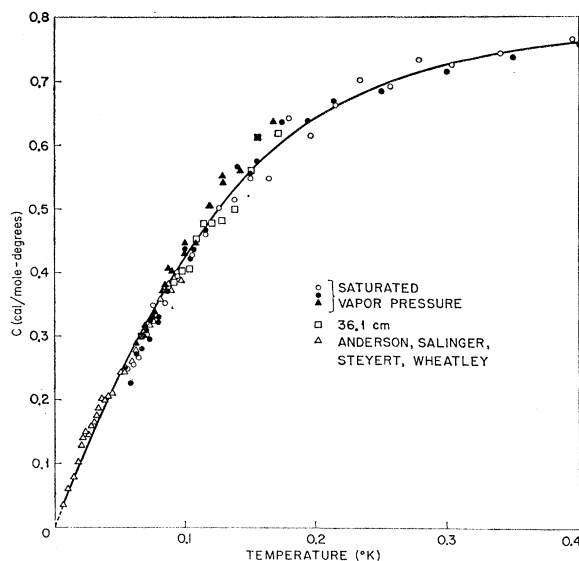[17] W. L. Pillinger, P. S. Jastram, and J. G. Daunt, Rev. Sci. Instr. 92, 159 (1958).

FIG. 4. The specific heat of liquid He³ at saturated vapor pressure vs temperature. The results of Anderson et al. at a pressure of 0.12 atm are also shown.

In Fig. 3 a typical warmup curve which includes two heat pulses is shown. After the magnetic field was completely removed, the heat leak was determined by observing the quiescent warmup. On the particular warmup shown, the heat leak was about 0.5 erg/sec. At intervals of about 4 to 10 min heat pulses were applied which ranged in time from 1 to 10 sec and in power from 300 to 5000 erg/sec. The relaxation time of about 20 sec is typical.

The change in temperature ΔT due to an applied heat pulse ΔQ was then determined in the way shown in Fig. 3, and the heat capacity $\Delta Q/\Delta T$ was calculated. The heat capacity of the liquid He³ sample was then obtained by subtracting out the calculated heat capacity of the empty calorimeters (always less than 2% of the total).

To obtain the molar specific heat, it was necessary to know the amount of He³ in the cavity. For the vapor pressure measurements the cavity was partially filled and the He³ metered out carefully by means of a calibrated Toeppler pump. For the determinations at higher pressure, where the cavity was completely filled, the amount of He³ was determined from the volume of the cavity and the known density of the liquid[18] (see Error Section).

Before and after each series of experiments, and whenever we let exchange gas into the vacuum jacket around the apparatus, the susceptibility of the CMN thermometer was calibrated against the vapor pressure of the He⁴ bath, between 1.1 and 2°K. At the end of the series of elevated pressure measurements reported in this paper, the He³ cryostat and the CMN ther-

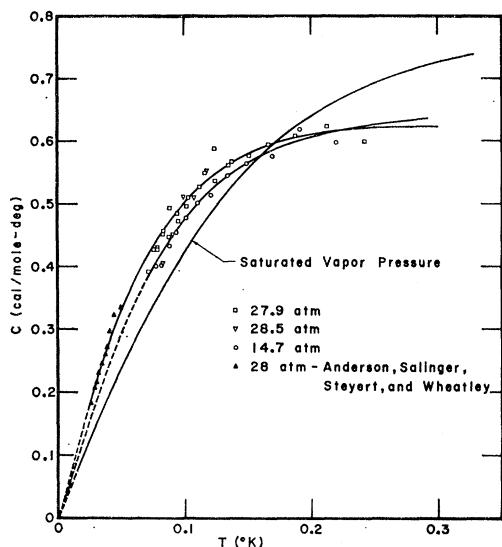[18] R. H. Sherman and F. J. Edeskuty, Ann. Phys. (New York) 9, 522 (1960).

FIG. 5. The specific heat of liquid He[3] vs temperature
at several pressures.

mometer were linked by a copper strip and the CMN susceptibility was calibrated against He[3] vapor pressure at temperatures between 0.4 and 1.1°K. The calibrations agreed within the experimental error. Extrapolation to lower temperatures was made by assuming that the susceptibility varied linearly with $1/(T-\Delta)$ where Δ is approximately 0.0005°K for the pill used.

RESULTS AND DISCUSSION

The results at saturated vapor pressures are shown in Fig. 4, along with the data of Anderson et al.[12] It is seen that there is no evidence of any cooperative transition. In the region near 0°K the Landau[5,6] and Brueckner-Gammel[7] theories give $C=C_f m^*/m$, where C_f, the specific heat of an ideal Fermi gas of mass m, is proportional to T, and m^*/m, the ratio of the effective mass of He[3] to the mass of an He[3] atom, is a constant.

The combined data confirm the approximate behavior predicted. The lowest temperature data of Anderson et al. would seem to join on to our data with a slight jog in the curve at about 0.05°K. Whether or not this jog is real is not clear. In drawing the smooth curve in Fig. 4 we have chosen to ignore it and assume that a slight curvature remains in the C vs T curve to very low temperatures. A straight line drawn through the origin and our lowest temperature points in Fig. 4 gives a value of $m^*/m=2.19\pm0.13$. However, the limiting low-temperature value of m^*/m from the lower temperature data of Anderson et al.[12] is given by them as 2.82±10%. The value of C/T, corresponding to the above value of m^*/m, is in good agreement with the spin specific-heat theory of Goldstein.[8]

The results at elevated pressures, along with the smoothed curve of the saturated vapor pressure data, are shown in Fig. 5. It is seen that in the low-tempera-

ture region the specific heat increases with pressure, in agreement with the measurements of Brewer, Daunt, and Sreedhar.[4] Our measurements agree reasonably well with recent results of Brewer and Keyston,[19] and the data of Anderson et al.[12] at lower temperatures are seen to join on well to ours.

By combining all the specific-heat data we have been able to obtain a reasonable extrapolation to 0°K. The entropy at temperature T was then calculated from the equation

$$S = \int_0^T \frac{C}{T} dT.$$

The entropy values obtained in this way are shown in Fig. 6. Above 0.23°K the results can be compared with the entropy values of Weinstock, Abraham, and Osborne,[13] who calculated the liquid entropy from the entropy of the vapor and heat of vaporization at 1.5°K, and the liquid specific-heat values from 0.23 to 1.5°K. The agreement is excellent. At saturated vapor pressure and 0.23°K we obtain for the liquid entropy 0.95±0.04 cal/mole-deg; Weinstock et al. report 0.96±0.03 cal/mole-deg.

At the minimum in the melting curve, according to the Clapeyron equation, the entropies of the solid and liquid are equal, and since the lattice entropy of the solid is very small at this temperature, the entropy of the solid should be $R\ln2$, the entropy of the unaligned nuclear spin system. Measurements of the nuclear susceptibility show classical Curie law behavior down to temperatures below that of the melting curve minimum.[20] From the entropy curve at 27.9 atm, and the entropy of compression values of Lee, Fairbank, and
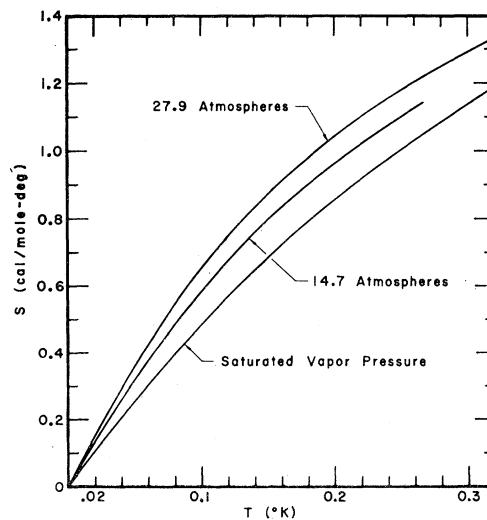

FIG. 6. The entropy of liquid He[3] vs temperature
at three pressures.

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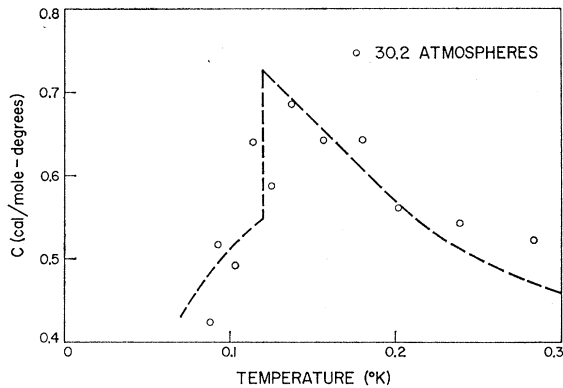
FIG. 7. The apparent specific heat of He³ vs temperature at a starting pressure 30.2 atm. The circles are experimental points. The dashed curve is that calculated for a molar volume of 25.75 cm³ and shows the sharp rise as freezing commences.

Walker,[21] we obtain 1.34±0.04 cal/mole-deg for the entropy at the melting curve minimum; in good agreement with the expected value of $R \ln 2$.

Pressure Above $P_{\min}$

Recently, particular attention has been given to measurements at pressures above the pressure of the melting curve minimum $P_{\min}$. At these pressures and temperatures below about 0.1°K, Wheatley and his co-workers at Illinois[12,22,23] observed a sudden change in the behavior of the liquid which suggested the possibility of a new phase. Recently, one of us[24] suggested the possibility of nonideal blocking of the capillary going to the experimental chamber, which makes it possible for the liquid to be at a higher density than was supposed. The anomalous behavior can be explained on the basis of this assumption, as the expected properties of a mixture of solid and liquid. Thus, the drop in specific heat below about 0.04°K, observed by the Illinois group, was interpreted not as the property of a new phase, but as the expected apparent specific heat of a solid-liquid mixture given by

$$C = x_s C_s + x_L C_L + L dx/dT, \qquad (1)$$

where C_s and C_L are the solid and liquid specific heats, x_s and x_L are the fraction of liquid and solid, and L is the latent heat of fusion.

In Fig. 7 we present our measurements of specific heat at a starting pressure of 30.2 atm. The broken curve is the behavior calculated from Eq. (1), following the method outlined in reference 24, assuming that nearly ideal blockage of the capillary (0.004-in. i.d.) occurred, leaving the He³ sample at a volume of 25.75

cm³/mole. It is seen that, although there is more scatter in the data than at pressures below $P_{\min}$, the behavior agrees essentially with the behavior calculated from the above formula. The jump in the specific heat occurs at the transition from the liquid to the solid-liquid mixture, and reflects the initial contribution of the $L dx/dT$ term. More precise evidence for this type of behavior has been obtained recently by Edwards et al.[25] Recent measurements of the nuclear susceptibility and spin-lattice relaxation time T_1 in this region of the phase diagram confirm also that the properties of the liquid and solid in the vicinity of the melting curve minimum are not anamalous.[26,27]

EXPANSION COEFFICIENT MEASUREMENTS

Measurements of the expansion coefficient α of liquid He³ have also been made in order to clarify the disagreement between recent measurements from other laboratories.[19,28] From measurements of the dielectric constant, Rives and Meyer[28] indicated that the expansion coefficient of the liquid becomes positive at a pressure above 20 atm and at temperatures below 0.1°K. Brewer and Keyston,[19] on the other hand, find α to be approximately proportional to T and negative in this same temperature and pressure range. With the method of Brewer and Keyston[19] we measured the change in temperature ΔT resulting from an adiabatic change of pressure ΔP and then calculated α from the equation

$$\alpha = (C/TV)(\Delta T/\Delta P)_s.$$

The values of the expansion coefficient obtained in the range of temperature 0.07 to 0.135°K and at average pressures from 21.3 to 27.7 atm are in good agreement with those of Brewer and Keyston (the estimated error is about 50% in both sets of measurements). In every case heating was observed on expansion and cooling on compression, indicating a negative α.

ANALYSIS OF ERRORS

The greatest contribution to the error in the specific-heat values arises from the error in the calibration of the CMN thermometer above 1.1°K. The estimated error in the calibration is ±2.5%. In the region where the specific heat is proportional to T such an error would produce an error in the slope of the C vs T curve of 5%.

The errors in the specific heat arising from uncertainties in the amount of heat that was absorbed by the He³ are considerably smaller than the above. The error in the time of a pulse was less than 0.1%, and the error in the power was also about 0.1%. In the initial specific-

[21] D. M. Lee, H. A. Fairbank, and E. J. Walker, Phys. Rev. 121, 1258 (1961).
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heat apparatus superconducting heater leads were not used; we estimate an uncertainty of about 1% in the value of ΔQ on these runs.

In the specific-heat runs at saturated vapor pressure the cavity was not filled completely, and the amount of gas which entered the cavity was accurately determined with a Toeppler pump which was previously calibrated. We estimate that the error in the amount of gas was less than 1%. On the high-pressure runs the cavity has to be completely filled; hence, in these runs it was important to know accurately the volume of the cavity. The cavity volume was obtained by measuring the weight of the cavity with and without acetone.

Because of the O-ring flange incorporated in the cavity design, it was possible to accurately fill the cavity with no danger of air spaces. We estimate that the error in the determination of the cavity volume was 1%. The error in pressure on the elevated pressure runs was ± 0.25 atm.

Back Diffusion of Electrons in Nitrogen, Hydrogen, and Argon*

JOHN A. DAHLQUIST
Department of Physics, Washington University, St. Louis, Missouri
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The back diffusion of electrons to an emitting surface results in the decrease of i_0, the current leaving the cathode, to i, the current arriving at the anode in the presence of a gas. The ratio of i/i_0 is a function of the random thermal velocity and the drift velocity, and these velocities in turn are functions of E/p, the electric field strength-to-pressure ratio. An experiment was performed which controlled these velocities independently over wide ranges in the gases nitrogen, hydrogen, and argon. In accordance with theoretical prediction, the value of i/i_0 was found to decrease with increasing thermal velocity and to increase with increasing drift velocity. Typical measured values of i/i_0 for both thermal velocity and drift velocity appropriate to E/p of 2 V/cm per mm Hg were 0.06 in N_2, 0.075 in H_2, and 0.05 in Ar, indicating the low probability of escaping back diffusion at this value of E/p.

THE study of back diffusion of electrons to an emitting surface dates back to the early work of Thomson.[1] Thomson, by using a kinetic theory approximation, derived a formula for the ratio of the electron current with gas present to the current in vacuum:

$$\frac{i}{i_0} = \frac{1}{1+(c/4v)}, \qquad (1)$$

where c is interpreted as the average speed of the electrons at the cathode, and v is the drift velocity appropriate to the electric field and pressure.

Varney[2] solved the one-dimensional diffusion equations, using standard techniques. Briefly, his procedure was to take the diffusion equation with a superimposed drift velocity, separate variables, solve the resulting ordinary differential equation, determine eigenvalues to satisfy initial conditions, and to set a sum of linear orthogonal solutions to satisfy the boundary conditions. In the semi-infinite case with zero concentration at $x=0$,

the diffusion equation is solved by setting up an image solution. Integration over time of the flux crossing the plane $x=0$ results in the equation,

$$n_c = n_0 e^{-\alpha v/D}, \qquad (2)$$

where n_c is the number of particles out of an initial delta function of n_0 particles at $x=\alpha$ which return to the cathode.

Varney assumed that the injected electrons travel a free path in a normal manner before entering the diffusion process and so the delta function is replaced by a normal free-path distribution,

$$\phi(\alpha)d\alpha = (n_0/L)e^{-\alpha/L}d\alpha. \qquad (3)$$

Integration then gives

$$n_c = \frac{n_0}{L} \int_0^X e^{-\alpha/L}e^{-\alpha v/D}d\alpha. \qquad (4)$$

The symbol X, introduced as the upper limit of integration, takes on one of two values, whichever is less. Either it is the distance to the anode at which the electrons are again removed or it is the mean distance to the first inelastic impact the electrons may experience. In

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[2] R. N. Varney, Seventh Annual Gaseous Electronics Conference, New York University, October 14, 1954 (unpublished).