(1) The expansion for $\tan\eta_l$ converges until the phase shift corresponding to either + or − $|\lambda|V(r)$ becomes + or − $\pi/2$; but, when $ka \ll l+1$ [a = typical dimension of $V(r)$], the smallness of $|\eta_l|$ compared with $\pi/2$ is not a criterion for *rapid* convergence of the Born approximations.

(2) For any l, the existence of bound states implies failure of the Born approximations at zero energy and vice versa. However, even in the absence of bound states the Born series may diverge at some higher energy.

(3) For $l \geqslant 1$, λ_T and λ_S first decrease with increasing energy, before finally increasing. Both increase rapidly with l, like $l(l+1)$.

(4) At high energies, η remains almost proportional to λ up to large values of η, so that it is very effective to expand $\eta = \tan^{-1}(\tan\eta)$.

(5) λ_T and λ_S may differ substantially. Thus, for the $n-p$ ^3S potential, the series for $\tan\eta$ converges at 20 Mev and above, while that for $e^{2i\eta}$ only converges above ≈100 Mev.

(6) For $n-p$ scattering, the failure of the three-dimensional Born expansion at low energies is due entirely to the S-wave, the P-scattering being already convergent.

A detailed account, including illustrative examples, will be published in the near future.

It is a pleasure to express my gratitude to Professor Niels Bohr for the opportunity to work at his institute. I would also like to thank Dr. Res Jost for several very helpful remarks.

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* Postdoctoral N.R.C. fellow 1950–51; on leave of absence from Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

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Entropy and Specific Heat of Liquid He^3

K. S. Singwi
Physics Department, University of Illinois, Urbana, Illinois
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The formulas for the temperature dependence of viscosity, specific heat, and thermal conductivity of liquid He^3 were given by Singwi and Kothari[1] and later by other investigators,[2,3] on the assumption that the elementary excitations of He^3 are of the Fermi-Dirac type. This viewpoint has been confirmed by the experiments of Weinstock, Osborne, and Abraham[4] on the temperature variation of viscosity of pure liquid He^3. We, here, attempt to explain the entropy of liquid He^3, as calculated by Abraham *et al.*,[5] from their vapor pressure measurements. We have also calculated the specific heat of He^3 for which no experimental data are yet available.

TABLE I. Calculated entropy and specific heat as functions of the temperature.

η	Temp T (°K)	Entropy S (cal mole^{-1}, deg^{-1})	Specific heat C_v (cal mole^{-1}, deg^{-1})
20	0.24	0.50	0.48
10	0.48	0.98	0.96
8	0.60	1.20	1.16
7	0.68	1.36	1.28
6	0.79	1.56	1.44
5	0.94	1.82	1.64
4	1.15	2.18	1.86
3	1.47	2.68	2.12
2	2.01	3.38	2.38
1	2.96	4.36	2.68

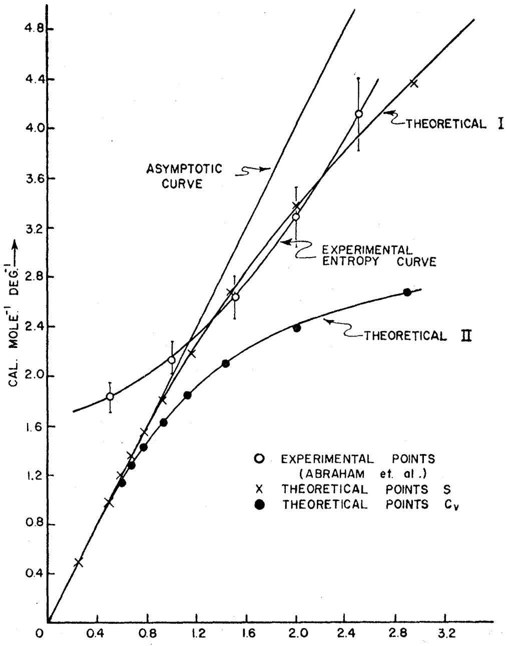

FIG. 1. Curve I: entropy S *versus* temperature T; curve II: specific heat C_v *versus* temperature T.

The degeneracy temperature of liquid He^3 is about 5°K. In the temperature range, so far investigated experimentally, He^3 is partially degenerate and, therefore, one has to use the exact rather than the asymptotic formulas for the thermodynamic quantities. For a system of particles, obeying F−D statistics, it can easily be shown that the entropy and the specific heat are, respectively, given by:

$$\frac{S}{R}=\frac{5}{2}\frac{\frac{2}{3}F_{3/2}(\eta)}{F_{1/2}(\eta)}-\eta, \tag{1a}$$

and

$$\frac{C_v}{R}=\frac{15}{4}\frac{\frac{2}{3}F_{3/2}(\eta)}{F_{1/2}(\eta)}-\frac{9}{4}\frac{F_{1/2}(\eta)}{\frac{d}{d\eta}F_{1/2}(\eta)}, \tag{2a}$$

where $F_k(\eta)$ are the well-known F−D functions and η is the degeneracy parameter. Using the asymptotic expansions of $F_k(\eta)$ for large values of η (i.e., $kT \ll \epsilon_0$), as given by McDougall and Stoner,[6] it can easily be shown that

$$S/R \approx 4.93(kT/\epsilon_0), \tag{1b}$$

and

$$C_v/R \approx 4.93(kT/\epsilon_0), \tag{2b}$$

where ϵ_0, the Fermi energy, is given by

$$\epsilon_0=(3/\pi)^{2/3}h^2\rho^{2/3}/8m^{5/3}. \tag{3}$$

ρ is the density of liquid He^3 and m is the mass of an He^3 atom.

Using (1a) and (2a) we have calculated the entropy and the specific heat of liquid He^3 for various temperatures and the results are given in Table I and also shown graphically in Fig. 1. The density[7] of liquid He^3 was taken as 0.08 g/cc at 0°K. For a given value of η, the temperature was calculated from the relation

$$\tfrac{2}{3}(\epsilon_0/kT)^{3/2}=F_{1/2}(\eta),$$

[see Eqs. (1-11), reference 6]. We have also plotted in Fig. 1 the entropy values given by Abraham *et al.*,[5] to which the nuclear spin entropy R log2 has been added. It will be seen from Fig. 1 that the experimental curve for entropy, in the entire temperature range from 1°K to 2.5°K, lies very close to the theoretical curve, calculated on the basis of an ideal F−D gas. It is not surprising that liquid He^3 behaves more like an ideal F−D gas than like a liquid because of its high zero-point energy.

No experimental data are available below 1°K. The experimental curve, however, shows a strong tendency to approach a constant value as $T \rightarrow 0$; the extrapolatal value of the entropy is 1.8 cal mole^{-1}, deg^{-1}, at 0°K. This has led Abraham and co-workers[5] to suggest that below 1°K liquid He^3 must undergo a transition to account for this excess entropy or there may be a hump in the heat capacity. In the absence of further experimental data below 1°K, it would be hard to say anything regarding the nature of this transition, yet it is not without interest to speculate on its nature. It is possible to account for this excess entropy on the basis of the following phenomenological picture. The liquid phase, presumably, near 1°K goes into a peculiar ordered state resembling somewhat a loose solid. It is a sort of a λ-transition. The specific heat of this ordered phase is no longer given by (2b) but by the Debye expression

$$C_v = 464.5\ (T/\theta)^3\ \text{cal mole}^{-1}\ \text{deg}^{-1}, \tag{4}$$

which gives

$$S = (C_v/T)dT = \tfrac{1}{3}\cdot 464.5(T/\theta)^3\ \text{cal mole}^{-1}\ \text{deg}^{-1}. \tag{5}$$

Using Eq. (5) and assuming that the λ-transition takes place at 1°K, we can explain the residual entropy if the value of the characteristic temperature θ is taken as 4.3°K. Expression (4) includes the contribution of both the transverse and the longitudinal waves; and if we assume that it is only the latter which contribute we shall require θ to be smaller still. One would like to ask whether such a low value of θ is compatible with our knowledge about He^4. Recently Kramers[8] has reported that, below 0.6°K, the specific heat of He^4II can be roughly represented by a T^3 law, with $\theta \approx 27$°K, in agreement with Landau's theoretical estimate which excludes the transverse waves. The characteristic temperature θ of solid He^4, as has been pointed out by Simon,[9] varies markedly with density. If the density changes by a factor 2, θ changes by a factor of 4. The observed density of liquid He^4 near the absolute zero is roughly twice the observed density of liquid He^3 at the same temperature. We, therefore, expect that for liquid He^3 θ will be about 7°K, if not smaller. If we use London's expression[10] to calculate the zero-point energy of He^3 corresponding to $\rho = 0.8$ g/cc, we find that $u_0 = 18$ cal mole^{-1}, giving $\theta = 8$°K. Thus a low value of θ is quite compatible with this theory. However, to account for the excess entropy of liquid He^3, we shall have to assume a value of θ about half the theoretically expected value.

It may be worth pointing out that a jump, if there is any, in the specific heat should show up as an angular point in the heat of vaporization *versus* temperature curve. No such jump is evident in the curve given by Abraham and co-workers.[5] It would be of great theoretical interest to extend the experimental investigation of the heat of vaporization below 1°K.

My thanks are due to Professor J. Bardeen and Dr. W. Heller for many interesting discussions.[11]

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[11] *Note added in proof.*—After this letter was submitted for publication, the author received from Dr. L. Goldstein of Los Alamos Scientific Laboratory his unpublished calculations on the entropy and specific heat of He^3, which agree with those of the author. Dr. Goldstein does not consider the residual entropy.

Magnetic Shielding Effects in Compounds of Vanadium*

H. E. Walchli and H. W. Morgan
Stable Isotope Research and Production Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

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Recent measurements to determine the gyromagnetic ratio of vanadium 50[1] in $VOCl_3$ and inconsistencies in the reported values[2–4] for vanadium 51 led to the desirability of checking for shifts due to magnetic shielding. Since V^{50} enriched compounds were not readily available and the signal of V^{50} is extremely weak in natural concentration (0.25 percent), compounds of V^{51} in normal abundance were used for all measurements. The nuclear magnetic resonance for V^{51} was observed in $VOCl_3$, and the measured value was found to differ from those previously reported for other compounds.[2–4] The metal powder and several compounds of V^{51} were then investigated and data are reported in Table I. Accurate frequency measurements were made with reference to sodium for the $NaVO_3$, $VOCl_3$, and V metal resonances. Other compounds were measured relative to the vanadium resonance in $VOCl_3$. The signal from solid $Pb(VO_3)_2$ was too broad for accurate determination of the resonance frequency. No signals were observed for V_2O_3, VOF_3, or VF_3, all in the solid state. All resonances were measured in saturated aqueous solutions except for $VOCl_3$ (liquid at room temperatures), V_2O_5, and $Pb(VO_3)_2$ (both dry powders). Care was exercised in the preparation of the chemical compounds to eliminate effects of possible admixtures. This was necessary since a great many of the vanadium compounds are unstable or decompose under the effects of light and heat. No magnetic catalysts were added to the samples.

Table I. Nuclear resonance data for vanadium compounds.

Compound	Valence	Observed line width in gauss[a]	$\nu(V^{51})/\nu(Na^{23})$	% field shift
$NaVO_3$	+5	0.35	0.993855 ±0.000025	0.00
Na_3VO_4	+5	0.35	0.993855 ±0.000035	0.00
NH_4VO_3	+5	0.35		
$VO(NO_3)_2$	+4	2.3		
$VO(SO_4)$	+4	1.1		
$K_2V_4O_9$	+4	1.4		
V_2O_5 powder	+5	10.1		
VCl_2	+2	2.0		
$VOCl_2$	+4	1.5		
$Pb(VO_3)_2$	+5	~16.1	See text	...
$VOCl_3$	+5	0.25	0.994358 ±0.000026	−0.05
V metal (powder)	...	8.5	0.999960 ±0.00001	−0.61

[a] $H^* = 6740$ gauss, frequency = 7550 kc.

All measurements were made at an identical position in the magnetic field. In cases where two compounds could not be mixed because of chemical considerations, one was sealed in a small spherical glass vial of 0.2-ml volume and the vial surrounded with the other compound. Magnetic field homogeneity over the entire coil volume is such that resonances have been observed with signal widths as narrow as 0.2 gauss. The shifts observed were at least 15 times this amount. The width of the signal resonance is given for points of maximum deflection of the derivative of the absorption curve for the value of magnetic field H^* at which the signal was observed. Our value for the line width of the metallic vanadium is smaller than that reported by Knight.[5] There appears to be no correlation of the shift observed for $VOCl_3$ with the valence state or the bonding orbitals in this molecule.

The resonance occurring at the highest value of externally applied field exhibits the least paramagnetic shielding.[6,7] Also, it has been shown[8] that the percent shift to be expected for different isotopes is the same for similar compounds of those isotopes. Thus, a small correction can be made in the data reported for V^{50}.[1] In addition, we report a direct measurement of the ratio of V^{51} in the two compounds $VOCl_3$ and $NaVO_3$. Using this value, the earlier value for V^{50}, the sodium-to-proton frequency ratio of 0.264518,[9,10] and the deuterium-to-proton frequency ratio of 0.1535059,[11] we report final values as listed in Table II.

The signs of both magnetic moments have been determined to be positive by comparison with known elements and are in agree-

Table II. Frequency ratios for vanadium isotopes.

$\nu(V^{51})/\nu(V^{51})$ in $(NaVO_3/VOCl_3)$	0.999491 ±0.000010
$\nu(V^{50})/\nu(D_2)$ in $(NaVO_3)$	0.649203 ±0.000012
$\nu(V^{50})/\nu(V^{51})$ in $(VOCl_3)$	0.379074 ±0.000017