K:DMP

Sent by regd airmail

19th August, 1952.

Professor N. F. Mott,
H. H. Wills Physical Laboratory,
University of Bristol,
Royal Fort,
BRISTOL 8. ENGLAND.

Dear Professor Mott,

Herewith I am enclosing a short note by Dr. Klemens and myself on the temperature variation of the therm~~ionic~~odynamic potential of a degenerate electron gas. If you think the results are correct, and are worth getting into print, may I request you to consider the note for publication in the Correspondence Section of the Philosophical Magazine. If accepted for publication the proofs may kindly be sent to me to ~~at~~ my New Delhi address.

I came to Australia as a delegate to U.R.S.I. Conference and to the meetings of the Australian and New Zealand Association for the Advancement of Science, and I expect to be back in India early in September.

With kind regards,
Yours sincerely,

(P.M. 711)
8/52 Communicated by the Author Received Aug 25, 1952
No fig
22 SEP 1952

# THE TEMPERATURE VARIATION OF THE ~~THERMIONIC~~ THERMODYNAMIC POTENTIAL OF A DEGENERATE ELECTRON GAS

by

Sir K. S. Krishnan, F.R.S., National Physical Laboratory of India, New Delhi, and P. G. Klemens, Division of Physics, Commonwealth Scientific and Industrial Research Organization, Sydney.*

In the Fermi-Dirac distribution function, namely

zeta

$$f(E) = \frac{1}{e^{(E-\zeta)/kT}+1} \tag{1}$$

zeta

$\zeta$, as is well known, is the thermodynamic potenti~~ce~~al, or the free energy at constant pressure, per electron, and is given by

$$\zeta = u - Ts + pv, \tag{2}$$

where the letters have their usual significance. Obviously $\zeta$ is a function of the temperature, and is determined by the equation

$$n = 2\int_0^\infty N(E)\,f(E)\,dE, \tag{3}$$

where $n$ is the number of electrons per unit volume, and $N(E)$ is the density of energy states. For an almost completely degenerate gas, i.e. at temperatures $T \ll T_o$, where

$$T_o = \zeta_o/k = \frac{h^2}{2mk}\left(\frac{3n}{8\pi}\right)^{2/3} \tag{4}$$

pi

is the degeneracy-temperature, the integration of (3) yields to a first approximation

gamma

$$\zeta = \zeta_o(1-\gamma T^2/6), \tag{5}$$

where

$$\gamma = \pi^2 k^2/2\zeta^2. \tag{6}$$

~~Corrected copy to be substituted for page 2 of original typescript.~~

Zeta



Since the second term in (5) is merely a correction term, $\zeta$ appearing in the denominator of (6) may be replaced by $\zeta_0$, or by $\zeta_0^*$, which we shall define presently, which are both of nearly the same magnitude as $\zeta$.

In expression (5) $\zeta_0$ is frequently referred to as the value of $\zeta$ at $\underline{T} = 0$, and for that reason is sometimes regarded as independent of $\underline{T}$, and hence the temperature variation of $\zeta$ is taken to be determined completely by the second term, which involves $\underline{T}$ explicitly. It is the main purpose of this note to emphasise that this will be the case only if the density of electrons n is kept constant, whereas at constant pressure the density n, and hence also $\zeta_0$ as will be seen from (4), will vary with the temperature. In other words $\zeta_0$ will not represent the free energy at the same pressure at T = 0. The latter energy will be given by

gamma

$$\zeta_0^* = \zeta_0(1+\gamma \underline{T}^2/3), \tag{7}$$

and the expression for the temperature variation of $\zeta$ at constant pressure will therefore be given by

$$\zeta = \zeta_0^*(1-\gamma \underline{T}^2/2) \tag{8}$$

Physically $\zeta_0^*-\zeta$ has the following significance. ~~If~~ Let $\varphi_T$ ~~is~~ be the thermionic work function, as usually defined, of a metal at temperature $\underline{T}$, then the temperature variation of $\varphi$ due to the temperature variation of $\zeta$ will be given by

If the electrons in the metal, i.e. in the condensed phase can be regarded as an almost completely degenerate assemblage, having a finite extent [illegible] separation,

$$\varphi_T - \varphi_0 = \zeta_0^* - \zeta. \tag{9}$$

Incidentally it may be mentioned that thermodynamically

$$\zeta_0^* - \zeta = \underline{T}\int_0^{\underline{T}} \frac{c_p}{\underline{T}}\,d\underline{T} - \int_0^{\underline{T}} c_p\,d\underline{T}, \tag{10}$$

$c_p$ is the specific heat of the electrons in the condensed phase at constant pressure. In view of (8) and (10) one obtains

gamma

$$c_p = \gamma T, \tag{11}$$

which is the same expression as for $c_v$.

It should be mentioned here that if the electronic structure of the metal, instead of corresponding to a nearly empty parabolic band, as we have taken it to be till now, corresponds to a nearly full parabolic band, the expressions for $c_p$ and $c_v$ will remain the same as before, but will now refer to the holes, and hence $\zeta_o^* - \zeta$ in equations (8), (9) and (10) should be replaced by $\zeta - \zeta_o^*$. In other words $\zeta$ will now increase with the increase of the temperature, though the specific heats remain positive, as they should.

That in a highly degenerate electron gas, the specific heat at constant pressure should be the same as that at constant volume can also be demonstrated otherwise. At higher temperatures naturally $c_p$ will increase more rapidly than $c_v$, and they will tend to the values $\frac{5}{2}k$ and $\frac{3}{2}k$ respectively.

KSK:DMP

Professor N. F. Mott,
H.H. Wills Physical Laboratory,
University of Bristol,
BRISTOL. 8 ENGLAND.

27th August, 1952.

Dear Professor Mott,

After sending the note by Dr. Klemens and myself on "The Temperature Variation of the Thermodynamic Potential of a Degenerate Electron Gas" I noticed an error on page 2 of the typescript. The second, third and fourth lines after equation (8) should read

"$\varphi_T$ is the thermionic work-function, as usually defined, of a metal at temperature T, then the"

in place of

"$\varphi_T$ is the latent heat of evaporation of the electrons from a metal at temperature T and at the saturation vapour pressure of the electron gas in equilibrium with the metal, then the"

Herewith I am enclosing a copy of page 2 of the original typescript with the corrections made on it in red ink, and a clean copy of page 2 which may kindly be substituted for the one previously sent.

With kind regards,
Yours sincerely,

KSK.