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The Free Energy of Electron Gas

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The energy and free energy of a semi-degenerate gas obeying the Fermi statistics are computed as functions of temperature and concentration. The significance of the deviation of the free energy from the limiting high temperature value is illustrated by calculating the degree of thermal ionization of potassium vapor under conditions of high electron concentration.

IT has long been known that the translational partition function for a gas obeying either the Bose-Einstein or the Fermi statistics approaches asymptotically with increasing temperature the limiting value given by the Sackur-Tetrode equation. In general this approach is to all intents complete within a few degrees of absolute zero, but in the case of an electron gas (owing to the small mass of the particle) the deviation from the classical value persists to much higher temperatures. Sommerfeld[1] in a well-known paper has derived expressions defining the translational energy, free energy, entropy etc. of a gas obeying the Fermi statistics, with special consideration of the case in which, owing to high concentration and moderate temperature, the deviations from the classical values are particularly great ("complete degeneracy"); and Mott[2] has recently computed the energy, heat capacity and magnetic susceptibility for a few points in the "semi-degenerate" range. In dealing with the equilibria involved in problems of thermal ionization, however, it is the free energy that is of primary importance, and the present paper deals with the calculation of this and related thermodynamic quantities for an electron gas when temperature and concentration are not such as to permit the conventional Sackur-Tetrode expression to be used.

Sommerfeld has shown that for a gas containing $N=6.06\times10^{23}$ electrons in V cc at T°K,

$$N=2\pi VG\cdot\frac{(2mkT)^{\frac{3}{2}}}{h^3}\cdot\int_0^\infty\frac{u^{\frac{1}{2}}\cdot du}{e^{\alpha}\cdot e^{u}+1}, \qquad (1)$$

where G (the spin weight of the electron) $=2$, $\alpha=-F/RT$, F is the free energy of one "mole" of the gas, m is the mass of the electron, and the other symbols have their conventional meanings. Eq. (1) can be written

$$Q^*=e^{\alpha}/I_{1/2}(\alpha), \qquad (2)$$

where Q^*, the classical expression for the partition function, is equal to

$$(2\pi MkT)^{3/2}\cdot VG/N^{5/2}h^3$$

$M=Nm=1/1838$, and $I_m(\alpha)$ is defined by

$$I_m(\alpha)=\int_0^\infty\frac{u^m\cdot du}{e^{u}+e^{-\alpha}}\Big/\Gamma(m+1). \qquad (3)$$

Similarly, the energy of one mole of the gas is given by

$$E=(3/2)NkT\cdot I_{3/2}(\alpha)/I_{1/2}(\alpha), \qquad (4)$$

while $pV/NkT=I_{3/2}(\alpha)/I_{1/2}(\alpha)$. For large values of α, i.e., large T or V, it is easily verified that both $I_{1/2}(\alpha)$ and $I_{3/2}(\alpha)$ approach unity, i.e., $\alpha(=-F/RT)=\ln Q^*$, etc.

Table I gives the values of $I_{1/2}(\alpha)$ and of $I_{3/2}(\alpha)$ for $-1<\alpha<6$, and Table II gives α as a function of $\ln Q^*$ for $-0.4<\ln Q^*<8.0$. For $\alpha\geqslant0.3$, $I_m(\alpha)$ was computed by the obvious relation

$$I_m(\alpha)=\sum_{n=0}^{\infty}(-1)^n\cdot e^{-n\alpha}/(n+1)^{m+1}. \qquad (5)$$

For $\alpha<0.3$, the range of integration was split; for $0<u<0.3$, e^u was expanded and the integrand reduced to a power series in which could be integrated term by term. For $0.3<u<2.0$, the integrals were evaluated by tabular integration, while for $2.0<u<\infty$, the contribution to $I_{1/2}(\alpha)$ was computed by the rapidly converging series

[1] Sommerfeld, Zeits. f. Physik **47**, 1 (1928).
[2] Mott, Proc. Camb. Phil. Soc. **32**, 108 (1936).

TABLE I.

$$I_{1/2}(\alpha)=\frac{2}{\sqrt{\pi}}\cdot\int_0^\infty \frac{u^{\frac{1}{2}}\cdot du}{e^u+e^{-\alpha}};\qquad I_{3/2}(\alpha)=\frac{4}{3\sqrt{\pi}}\cdot\int_0^\infty \frac{u^{\frac{3}{2}}\cdot du}{e^u+e^{-\alpha}}.$$

α	$I_{1/2}(\alpha)$	$I_{3/2}(\alpha)$	α	$I_{1/2}(\alpha)$	$I_{3/2}(\alpha)$
−1.0	0.57965	0.73659	+0.8	0.87138	0.93126
0.9	.59976	.75206	0.9	.88154	.93702
0.8	.61968	.76704	1.0	.89104	.94236
0.7	.63935	.78152	1.2	.90815	.95185
0.6	.65871	.79547	1.4	.92292	.95990
0.5	.67769	.80886	1.6	.93556	.96669
0.4	.69624	.82169	1.8	.94631	.97240
0.3	.71431	.83395	2.0	.95539	.97718
0.2	.73184	.84562	2.2	.96303	.98116
−0.1	.74880	.85670	2.4	.96942	.98447
0	.76515	.86720	2.6	.97475	.98721
+0.1	.78085	.87712	2.8	.97919	.98948
0.2	.79588	.88646	3.0	.98286	.99135
0.3	.81022	.89524	3.5	.98950	.99472
0.4	.82386	.90347	4.0	.99359	.99678
0.5	.83679	.91116	4.5	.99610	.99804
0.6	.84901	.91835	5.0	.99763	.99881
+0.7	0.86054	0.92504	5.5	.99856	.99928
			+6.0	0.99913	0.99956

$$\frac{2}{\sqrt{\pi}}\int_2^\infty \frac{u^{\frac{1}{2}}\cdot du}{e^u+e^{-\alpha}}=e^\alpha\sum_{n=1}^{\infty}(-1)^{n+1}\cdot e^{-n\alpha}\left[2\left(\frac{2}{\pi}\right)^{\frac{1}{2}}\cdot\frac{e^{-2n}}{n}+\frac{P(2n)}{n^{\frac{3}{2}}}\right],\quad (6)$$

where $$P(t^2)=(2/\sqrt{\pi})\cdot\int_t^\infty e^{-y^2}\cdot dy,$$

with a similar relation for $I_{3/2}$.

In dealing with electron concentrations, it is convenient to define a fictive pressure P^* such that $P^*V=NkT$; in terms of this new quantity, $\ln Q^*=-14.239+\ln T^{5/2}/P^*$ where P^* is measured in atmospheres. It is evident from Table II, that for $\ln Q^*>3.6$, i.e., $(5/2)\log T-\log P^*>7.75$, F may be replaced by $-RT\ln Q^*$ without introducing an error greater than $0.01RT$; Table II shows that in this case $P=P^*$ within one-half of one percent or less. This condition implies that T must be greater than 1250° for $P^*=1$ atmosphere, and greater than 20,000° for $P^*=1000$ atmospheres.

TABLE II.

$\ln Q^*$	α	$\ln Q^*$	α	$\ln Q^*$	α
−0.4	−0.9169	+0.7	+0.5256	+2.6	+2.5738
0.3	0.7686	0.8	0.6421	2.8	2.7785
0.2	0.6247	0.9	0.7571	3.0	2.9824
−0.1	0.4849	1.0	0.8706	3.5	3.4893
0	0.3488	1.2	1.0940	4.0	3.9935
+0.1	0.2160	1.4	1.3131	4.5	4.4961
0.2	−0.0862	1.6	1.5288	5.0	4.9976
0.3	+0.0408	1.8	1.7417	5.5	5.4986
0.4	0.1652	2.0	1.9522	6.0	5.9991
0.5	0.2874	2.2	2.1609	7.0	6.9997
+0.6	+0.4074	+2.4	+2.3680	+8.0	+7.9999

For smaller values of $\ln Q^*$, however, the use of such approximations may introduce appreciable errors. To take an extreme case (selected from Russell's tables[3] of metal ionization in stellar atmospheres) consider the ionization of potassium at 5000°K under an electron concentration such that $P^*=1000$ atmospheres; $\ln Q^*$ is then $+0.1462$, $\alpha=-0.1557$, and $P=(J_{3/2}/J_{1/2})P^*=1150$ atmospheres. From spectroscopic data,[4] it follows that if x be the fraction of potassium ionized, $\log x=-4.76$; had the Sackur-Tetrode approximation to the free energy of the electrons been used, the result would have been $\log x=-4.63$.

[3] Russell, Astrophys. J. **75**, 337 (1932).

[4] Bacher and Goudsmit, *Atomic Energy States* (1932), p. 245. In computing the State Sum for neutral potassium, only the low lying states up to and including ^2F were taken into account.