Question ?

Electron-Energy Distribution: The Bose-Einstein and Fermi-Dirac distribution functions both reduce to the Maxwell-Boltzmann function when $e^{\alpha}e^{\epsilon/kT} >> 1$. For energies in the neighborhood of kT, this approximation holds if $e^{\alpha} >> 1$. Helium atoms have spin 0 and so obey Bose-Einstein statistics. Verify that $f(\epsilon) \approx 1/e^{\alpha}e^{\epsilon/kT} \approx Ae^{-\epsilon/kT}$ is valid for He at STP ($20°C$ and atmospheric pressure, when the volume of 1 *kmol* of any gas is $\approx 22.4\,m^3$) by showing that $A << 1$ under these circumstances.

A He atom does not have the two spin states, hence using

$$g(\epsilon)d\epsilon = \frac{4\sqrt{2}\pi V m^{3/2}}{h^3}\sqrt{\epsilon}\,d\epsilon \quad \text{(Eq 9.55)}$$

and employing the approximation, find A from the normalization condition $\int_0^{\infty} n(\epsilon)d\epsilon = N$ where N is the total number of atoms in the sample. (A *kmol* of HE contains Avogadro's number N_0 of atoms, the atomic mass of He is 4.00 u, and $\int_0^{\infty}\sqrt{x}e^{-ax}\,dx = \sqrt{\pi/a}/2a$.)

Solution

If $e^{\alpha} >> 1$ the Bose-Einstein distribution clearly reduces Maxwell-Boltzmann

$$f_{BE}(\epsilon) = \frac{1}{e^{\alpha}e^{\epsilon/kT} - 1} \approx Ae^{-\epsilon/kT} = f_{MB}(\epsilon)$$

Hence using the normalisation condition

$$\begin{aligned}
N &= \int_0^{\infty} n(\epsilon)d\epsilon \\
&= \int_0^{\infty} g(\epsilon)f(\epsilon)d\epsilon \\
&= \int_0^{\infty} \frac{4\sqrt{2}\pi V m^{3/2}}{h^3}\sqrt{\epsilon}\,Ae^{-\epsilon/kT}d\epsilon \\
&= \frac{4A\sqrt{2}\pi V m^{3/2}}{h^3}\int_0^{\infty}\sqrt{\epsilon}\,e^{-\epsilon/kT}d\epsilon \\
&= \frac{4A\sqrt{2}\pi V m^{3/2}}{h^3}\,\frac{\sqrt{\pi kT}}{2/kT} \\
&= \frac{AV}{h^3}(2\pi mkT)^{3/2} \\
A &= \frac{Nh^3}{V}(2\pi mkT)^{-3/2}
\end{aligned}$$

Subs for He at $293\,K$ $\quad N = 6.022\times 10^{26}\,/kmol \quad V = 22.4\,m^3$

$$\begin{aligned}
A &= \frac{(6.022\times 10^{26})(6.626\times 10^{-34})^3}{22.4}\left(2\pi(4\times 1.66\times 10^{-27})(1.381\times 10^{-23})(293)\right)^{-3/2} \\
&= (7.821\times 10^{-75})(1.688\times 10^{-46})^{-3/2} \\
&= 3.56\times 10^{-6}
\end{aligned}$$

Since $A << 1$ the approximation $f(\epsilon) \approx Ae^{-\epsilon/kT}$ is valid for He at STP.