TOPIC : FRACTION OF MONOATOMIC GASES AT DIFFERENT ELECTRONIC LEVELS

Pages (15-16)

APRIL 9, 2020

Dr. R. K. Hazra

$$Z(N,V,T) = \left(q_{trans}\, q_e\, q_{nucl}\right)^N / N!$$

$$q_{electronic} = q_e = \sum \omega_{ei} e^{-\beta \varepsilon_i}$$

Can be modified by setting Ground-state energy $\varepsilon_1 = 0$, as:

$$q_e = \omega_{e1} + \omega_{e2} e^{-\beta \Delta\varepsilon_{12}} + \omega_{e3} e^{-\beta \Delta\varepsilon_{13}} + \cdots$$

$$\Rightarrow \left(q_e / q_e\right) = 1 = f_1 + f_2 + f_3 + \cdots + \infty$$

$f_k \equiv$ Fraction of Molecules at k-th electronic level

$$\Rightarrow f_k = \left(\omega_{ek} / q_e\right)$$

E.g.,

$$f_2 = \omega_{e2} \Big/ \left(\omega_{e1} + \omega_{e2} e^{-\beta \Delta\varepsilon_{12}} + \omega_{e3} e^{-\beta \Delta\varepsilon_{13}} + \cdots\right)$$

$$f_1 = \omega_{e1} \Big/ \left(\omega_{e1} + \omega_{e2} e^{-\beta \Delta\varepsilon_{12}} + \cdots\right)$$

Problem :- Calculate "f_2" of He-atoms at 300°K and 3000°K

McQuarrie, Page 84, Statistical Mechanics.

Comparison between Molecular-states-density and Particle-density of Monoatomic gases

No. of Molecular states of Monoatomic gas confined in 3-D box (Non-interacting)

$$\Phi(\varepsilon) = \frac{1}{8}\left(\frac{4}{3}\pi R^3\right) \quad \because R^2 = n_x^2 + n_y^2 + n_z^2 = \left(\frac{8ma^2\varepsilon}{h^2}\right)$$

$$= \frac{\pi}{6}\left(\frac{8ma^2\varepsilon}{h^2}\right)^{\frac{3}{2}}$$

Assuming equipartition of energy

$$\varepsilon = \frac{3}{2} k_B T$$

Substituting in above equation

$$\Rightarrow \Phi(\varepsilon) = \frac{\pi}{6}\left(\frac{12 m k_B T}{h^2}\right)^{\frac{3}{2}} a^3$$

$$\Rightarrow \Phi(\varepsilon) = \frac{\pi}{6}\left(\frac{12 m k_B T}{h^2}\right)^{3/2} V$$

$$\Rightarrow \text{Density of Molecular states} = \left(\frac{\Phi(\varepsilon)}{V}\right) = \frac{\pi}{6}\left(\frac{12 m k_B T}{h^2}\right)^{\frac{3}{2}}$$

Thus Non-Interacting quantum gas behaving as ideal classical gas requires $\Phi(\varepsilon) \ggg N$

i.e., Nearly Infinite dilution

$$\Rightarrow \left(\Phi(\varepsilon)/V\right) \ggg (N/V) \text{ (Density of gas)}$$

$$\Rightarrow \frac{\pi}{6}\left(\frac{12 m k_B T}{h^2}\right)^{3/2} \ggg \left(\frac{N}{V}\right)$$