Sharif University of Technology
School of Mechanical Engineering
Center of Excellence in Energy Conversion

Advanced Thermodynamics

Lecture 19

Dr. M. H. Saidi

2011

Translational P. F.

- Monoatomic ideal gas:
  - They only have e_e and e_t.
  - e_e is at the base level for them, they are non-degenerate.
  - The electronic ground level degeneracy, g_{e0}, may be subtracted from the total partition functions.

$$Z = g_{e0} \sum_j g_{jt} e^{-\frac{e_{jt}}{KT}} = g_{e0} Z_t$$

Translational partition function

$$\bar{S} = \bar{S}_t + \bar{S}_{e0} = \underbrace{\bar{R}\left[\ln\left(\frac{Z_t}{N}\right) + 1\right] + \frac{U_t}{T}}_{\bar{S}_t} + \underbrace{\bar{R}\ln g_{e0}}_{\bar{S}_{e0}}$$

$$Z_t = \sum_{\text{levels}} g_j e^{-\frac{e_j}{KT}} \text{ or } Z = \sum_{\text{quantum states}} e^{-\frac{e_j}{KT}}$$

- The energy of each quantum state due to Schrodinger Wave Eq.:

$$e_j = \frac{h^2}{8m}\left(\frac{K_x^2}{a^2} + \frac{K_y^2}{b^2} + \frac{K_z^2}{c^2}\right)$$

- K_x, K_y, and K_z are quantum numbers

$$Z_t = \sum_{K_x=1}^{\infty}\sum_{K_y=1}^{\infty}\sum_{K_z=1}^{\infty} e^{-\left(\frac{h^2}{8mKT}\right)\left(\frac{K_x^2}{a^2}+\frac{K_y^2}{b^2}+\frac{K_z^2}{c^2}\right)}$$

K_x, K_y, and K_z are such huge numbers $\rightarrow$

$$Z_t = \left[\int_0^{\infty} e^{-\left(\frac{h^2}{8mKT}\right)\left(\frac{K_x^2}{a^2}\right)} dK_x\right]\left[\int_0^{\infty} e^{-\left(\frac{h^2}{8mKT}\right)\left(\frac{K_y^2}{b^2}\right)} dK_y\right]\left[\int_0^{\infty} e^{-\left(\frac{h^2}{8mKT}\right)\left(\frac{K_z^2}{c^2}\right)} dK_z\right]$$

$$\int_0^{\infty} e^{-x^2} dx = \frac{1}{2}\sqrt{\frac{p}{a}} \Rightarrow Z_t = V\left(\frac{2p\, mKT}{h^2}\right)^{\frac{3}{2}}$$

Monoatomic Ideal Gas

$$\ln Z_t = \ln V + \frac{3}{2}\ln T + \frac{3}{2}\ln\left(\frac{2\pi mK}{h^2}\right)$$

- Pressure of monoatomic ideal gas

$$P = NKT\left(\frac{\partial \ln Z}{\partial V}\right)_T = \frac{\mathrm{NKT}}{\mathrm{V}}$$

- Energy of monoatomic ideal gas

$$U = NKT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V = \frac{3}{2}\mathrm{NKT}$$

- Entropy of monoatomic ideal gas

$$S = NKT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V = \mathrm{NK}\left[\frac{3}{2}\ln T + \ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi mK}{h^2}\right) + \frac{5}{2}\right]$$

For one mole $\longrightarrow \bar{s} = \frac{3}{2}\bar{R}\ln T + \bar{R}\ln v + \underbrace{\frac{\bar{R}}{N_0}\left[\frac{3}{2}\ln\left(\frac{2\pi mK}{h^2}\right) + \frac{5}{2}\right]}_{s_0}$

$$\Rightarrow \boxed{\bar{s} = \bar{c}_V \ln T + \bar{R}\ln v + s_0}$$

For monoatomic ideal gas:

$$\ln Z_t = \ln V + \ln C + \frac{3}{2}\ln T$$

$$\left(\frac{\partial \ln Z_t}{\partial T}\right)_V = \frac{3}{2}T$$

$$\bar{U}_t = \frac{3}{2}\bar{R}T \,,\ \bar{h}_t = \frac{5}{2}\bar{R}T$$

$$\bar{c}_{V0} = \bar{c}_{Vt} = \frac{3}{2}\bar{R},\ \bar{c}_{P0} = \bar{c}_{Pt} = \frac{5}{2}\bar{R}$$

$$\bar{s}_t = \bar{R}\left[\ln\left(\frac{Z_t}{N}\right)+1\right]+\frac{\bar{U}_t}{T} = \bar{R}\left[\ln\left(\frac{Z_t}{N}\right)+\frac{5}{2}\right]$$

- In addition to s, s_0 will be calculated in statistical thermodynamics.

- Find Entropy of monoatomic Nitrogen at $25^0 C$ and $0.1\ MPa$

Given: $M = 14.0067$ and $g_{e_0} = 4$

For monoatomic ideal gas:

$$\frac{Z_t}{N} = 2.5944 \frac{M^{3/2} T[K]^{5/2}}{P[KPa]} = 2.087 \times 10^6$$

$$\bar{s}_t = \bar{R}\left[\ln\left(\frac{Z_t}{N}\right) + 1\right] + \frac{\bar{U}_t}{T} = \bar{R}\left[\ln\left(\frac{Z_t}{N}\right) + \frac{5}{2}\right] = 141.73\ \frac{KJ}{Kmole\ K}$$

$$\bar{s}_{e_0} = \bar{R}\ln g_{e_0} = 11.526\ \frac{KJ}{Kmole\ K}$$

$$\rightarrow \boxed{s = \bar{s}_t + \bar{s}_{e_0} = 153.298\ \frac{KJ}{Kmole\ K}}$$

Example 2

- The validity of $e^{a} >> 1 \rightarrow g_{j} >> N_{j}$

For He:

$$e^{a} = \frac{Z}{N} = \frac{Z_{t}+1}{N} = 2.5944\frac{M^{3/2}T[K]^{5/2}}{P[KPa]} = 2.5944\frac{(4.0076)^{3/2}T^{5/2}}{100}$$

He ia an inert gas (g_{e_0} =1).

T=5K (around C.P.)

$$\rightarrow e^{a} = 1.1014 \text{ (It's better not to use C.B.M.)}$$

T=50K (cryogenic temp.)

$$\rightarrow e^{a} = 367.26 \text{ (C.B.M ??)}$$

T=500K

$$\rightarrow e^{a} = 116155.64 \text{ (C.B.M. is properly valid at this condition)}$$

- Find $N_{j\ \text{M.P.}}$ for the Fermi-Dirac distribution function.

$$w_{F.D.} = \prod_j \left[\frac{g_j!}{(g_j - N_j)!N_j!} \right] \rightarrow \ln w = \sum_j \left[\ln g_j! - \ln(g_j - N_j)! - \ln N_j! \right]$$

$$\Rightarrow \ln w = \sum_j \left[g_j \ln g_j - (g_j - N_j)\ln(g_j - N_j) - N_j \ln N_j \right]$$

At fixed U, V, and N $\rightarrow$

$$d \ln w = \sum_j \left[dN_j + \ln(g_j - N_j)dN_j - dN_j - \ln N_j dN_j \right] =$$

$$\sum_j \left[-\ln\left(\frac{g_j - N_j}{N_j} \right) + a + b\, e_j \right] dN_j = 0 \rightarrow$$

$$\boxed{N_{j\ \text{M.P.}} = \frac{g_j}{e^a e^{b\, e_j} + 1}} \qquad \left(\text{for B.M.} = \frac{g_j}{e^a e^{b\, e_j}} \text{ and for B.E.} = \frac{g_j}{e^a e^{b\, e_j} - 1} \right)$$