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

Advanced Thermodynamics

Lecture 18

Dr. M. H. Saidi

2011

- What is the relation between Entropy, S, and thermodynamics probability, w :
- w is an multiplicative property
- Properties of S :
  - S is an additive property
  - Randomness
  - Lack of information
  - Uncertainty
  - Disorder

$$w_{Total} = \sum_{d} w_d \rightarrow \ln w_{Total} = \ln \sum_{d} w_d$$

$$w_{Total} >> w_{M.P.} \rightarrow \ln w_{Total} = K \ln w_{M.P.}$$

$$\Rightarrow S = K \ln w_{M.P.}$$

$$\left.\begin{aligned} N_{j\ \text{M.P.}} &= \frac{N}{Z} g_j e^{-b e_j} \\ w_{\text{M.P., Cor Bol}} &= \prod_j \left[\frac{g_j^{N_{j\ \text{M.P.}}}}{N_{j\ \text{M.P.}}!} \right] \end{aligned}\right\} \Rightarrow$$

$$\underrightarrow{S = K \ln w_{\text{M.P.}}}\quad S = NK\left[\ln\left(\frac{N}{Z}\right) + 1\right] + K bU = f(N, b, U)$$

$$dS = \frac{NK}{Z} dZ + KUd b$$

$$U = -\frac{N}{Z}\left(\frac{\partial Z}{\partial b}\right),\ Z = \sum g_j e^{-b e_j},\ \text{and } N_{j\ \text{M.P.}} = \frac{N}{Z} g_j e^{-b e_j}$$

$$\rightarrow dS = K b dU - K b \sum N_{j\ \text{M.P.}} d e_j$$

- For a quasi-static process

$$\left.\begin{aligned} dS &= K\,b\,dU - K\,b\sum N_{j\ \text{M.P.}}\,de_j \\ \sum N_{j\ \text{M.P.}}\,de_j &= dW_{rev} \end{aligned}\right\} \rightarrow dS_{rev} = K\,b\,[dW_{rev} + dU\,] = \frac{dQ}{T}$$

$$\text{Integrity Factor} \equiv K\,b = \frac{1}{T}$$

- where, K is the Boltzmann Factor

$$PV = n\bar{R}T = \frac{N}{b} \qquad\qquad NK = n\bar{R}$$

$$\text{Mole No. } n = \frac{N}{N_0} \rightarrow b = \frac{N_0}{\bar{R}T} \text{ and } K = \frac{\bar{R}}{N_0}$$

$$\bar{R} = 8.314\ \text{KJ}/\text{KMole K} \text{ and } N_0 = \text{Awoogadro No.}$$

$$Z = Z(b, V) \neq Z(N)$$

$$S = NK\left[\ln\left(\frac{Z}{N}\right)+1\right]+KbU$$

$$U = U(S, V, N) \rightarrow dU = \frac{1}{Kb}dS - PdV + m dN$$

- Helmholtz function:

$$N\left(\frac{\partial A}{\partial N}\right)_{b,V} = -\frac{N}{b}\ln\left(\frac{Z}{N}\right) = A + \frac{N}{b}$$

$$A = U - TS = U - \frac{S}{Kb} = -\frac{N}{b}\left[\ln\left(\frac{Z}{N}\right)+1\right]$$

Properties of P. F.

$$Z=\sum_j g_j e^{-\frac{e_j}{KT}} \text{ and } PV=-\frac{N}{Z}\sum_j g_j e^{-\frac{e_j}{KT}} de_j$$

$$PdV=\frac{NKTdZ}{Z}=NKTd(\ln Z)$$

- At constant T:

$$dZ=\frac{-1}{KT}\sum_j g_j e^{-\frac{e_j}{KT}} de_j$$

- At equilibrium:

$$P=NKT\left(\frac{\partial \ln Z}{\partial V}\right)_T \text{ and } PV=NKT \rightarrow \ln V=\ln Z+C(T)\rightarrow Z=V\,f(T)$$

- The partition function dependency to V and T is separable.

$$\ln V = \ln Z + C(T) \rightarrow Z = V f(T)$$

$$\left(\frac{\partial \ln Z}{\partial T}\right)_V = \frac{d \ln\left[f(T)\right]}{dT}$$

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

- Macrostate numbers are related to N and U.
- Microstate numbers are related to V.

$$e_e = \text{ Electrical Energy}$$

$$e_t = \text{ Translational Kinetic Energy } (V_X, V_Y, V_Z)$$

$$e_r = \text{ Rotational Modes Energy}$$

$$e_v = \text{ Vibrational Modes Energy}$$