

Lecture 34

Statistical Thermodynamics

Conditions for Equilibrium



A. K. M. B. Rashid
Professor, Department of MME
BUET, Dhaka

Topics to Discuss

- Conditions for Equilibrium in Statistical Thermodynamics
- Calculation of macroscopic properties from Partition Function

Conditions for Equilibrium in Statistical Thermodynamics

- ◆ In statistical thermodynamics, a process is described by a change in the macrostate for the system.
 - ❑ the number of particles in some or all of the energy states changes or the particles redistribute over the energy levels in the system.
 - ❑ the number of particles in some energy levels increases while those in others decrease.

- ◆ In statistical thermodynamics, the equilibrium state is that particular macrostate which has maximum entropy when it is isolated.
 - ❑ the equilibrium state is a particular set of values of the number of particles that define macrostates: $(n_1, n_2, \dots, n_r)_{eq}$.

General strategy for finding a constrained maximum of entropy

1. Write a differential expression for the change in entropy.
2. Write differential expressions for the constraints.
3. Use the isolation constraints to eliminate dependent variables.
4. Set the coefficients of each of the differentials in the new expression of dS equal to zero.

$$S = k \ln \Omega \quad \Omega = \frac{N_0!}{n_1! n_2! \dots n_r!}$$

$$S = k \ln \left(\frac{N_0!}{n_1! \cdot n_2! \dots n_r!} \right)$$

$$S = k \left(\ln N_0! - \sum_{i=1}^r \ln (n_i!) \right)$$

Stirling's approximation :

$$\ln x! \cong x \ln x - x$$

$$S = k \left((N_0 \ln N_0 - N_0) - \sum_{i=1}^r (n_i \ln n_i - n_i) \right)$$

$$S = k \left((N_0 \ln N_0 - N_0) - \sum_{i=1}^r (n_i \ln n_i - n_i) \right)$$

$$S = k \left(N_0 \ln N_0 - N_0 - \sum_{i=1}^r n_i \ln n_i + \sum_{i=1}^r n_i \right)$$

$$S = k \left(\sum_{i=1}^r n_i \ln N_0 - \sum_{i=1}^r n_i \ln n_i \right)$$

$$N_0 = \sum_{i=1}^r n_i$$

$$S = k \sum_{i=1}^r n_i \left(\ln N_0 - \ln n_i \right)$$

$$S = -k \sum_{i=1}^r n_i \ln \left(\frac{n_i}{N_0} \right)$$

- ◆ This is the general expression for the entropy of a system with a given macrostate.

- ◆ During a process, the particles will redistribute themselves over the energy levels in the system and the number of particles in a given energy level will change.

☐ the number of particles in some energy levels will increase while in other decrease.

- ◆ Mathematically, a process can be represented by a collection of changes in the n_i terms:

$$(\Delta n_1, \Delta n_2, \dots, \Delta n_i, \dots, \Delta n_r)$$

- ◆ For an infinitesimal change in the macrostate, these finite changes can be replaced with infinitesimal changes:

$$(dn_1, dn_2, \dots, dn_i, \dots, dn_r)$$

$$S = -k \sum_{i=1}^r n_i \ln \left(\frac{n_i}{N_0} \right)$$

- ◆ The change in entropy for any arbitrary change in state

$$dS = -k d \left\{ \sum_{i=1}^r n_i \ln \left(\frac{n_i}{N_0} \right) \right\}$$

$$dS = -k \sum_{i=1}^r d \left\{ n_i \ln \left(\frac{n_i}{N_0} \right) \right\}$$

- ◆ Simplification of the equation will yield

$$dS = -k \sum_{i=1}^r \ln \left(\frac{n_i}{N_0} \right) dn_i$$

This describes the changes in entropy for any process through which the system may be taken.

◆ The constraint equations for the isolating systems :

- **number of atoms** of the system will not change during the process

$$dN_0 = d\left(\sum_{i=1}^r n_i\right) = \sum_{i=1}^r dn_i = 0$$

- **internal energy** of the system will not change during the process

$$dU = d\left(\sum_{i=1}^r \varepsilon_i n_i\right) = \sum_{i=1}^r \varepsilon_i dn_i = 0$$

$d\varepsilon_i = 0$, since ε_i does not change during a process

- ◆ For problems containing a large number of variables, a direct substitution of the constraint equations in the entropy function to eliminate dependent variables cannot be applied.

Lagrange multipliers

- ◆ In this method, the differential constraint equations are multiplied by multipliers and then added to the entropy equation.

$$dS + \alpha dN_0 + \beta dU = 0 \quad (10.12)$$

α and β are Lagrange multipliers

- ◆ Substituting dS , dN_0 , and dU :

$$-k \sum_{i=1}^r \ln\left(\frac{n_i}{N_0}\right) dn_i + \alpha \sum_{i=1}^r dn_i + \beta \sum_{i=1}^r \varepsilon_i dn_i = 0$$

$$-k \sum_{i=1}^r \ln \left(\frac{n_i}{N_0} \right) dn_i + \alpha \sum_{i=1}^r dn_i + \beta \sum_{i=1}^r \varepsilon_i dn_i = 0$$

◆ Collecting terms:

$$\sum_{i=1}^r \left\{ -k \ln \left(\frac{n_i}{N_0} \right) + \alpha + \beta \varepsilon_i \right\} dn_i = 0$$

◆ Then, the conditions for equilibrium:

$$-k \ln \left(\frac{n_i}{N_0} \right) + \alpha + \beta \varepsilon_i = 0 \quad (10.14)$$

$$\left(\frac{n_i}{N_0} \right) = e^{\alpha/k} \cdot e^{\beta \varepsilon_i/k} \quad (i = 1, 2, \dots, r)$$

◆ Here, the Lagrange multipliers, α and β , need to be evaluated.

$$\left(\frac{n_i}{N_0} \right) = e^{\alpha/k} \cdot e^{\beta \varepsilon_i/k} \quad N_0 = \sum_{i=1}^r n_i$$

$$\sum_{i=1}^r \frac{n_i}{N_0} = 1 = \sum_{i=1}^r e^{\alpha/k} \cdot e^{\beta \varepsilon_i/k} = e^{\alpha/k} \sum_{i=1}^r e^{\beta \varepsilon_i/k}$$

$$e^{\alpha/k} = \frac{1}{\sum_{i=1}^r e^{\beta \varepsilon_i/k}} = \frac{1}{\mathcal{P}}$$

$$\mathcal{P} = \sum_{i=1}^r e^{\beta \varepsilon_i/k} \quad \mathcal{P} = \text{the partition function}$$

$$\frac{n_i}{N_0} = \frac{1}{\mathcal{P}} e^{\beta \varepsilon_i/k}$$

$$dS = -k \sum_{i=1}^r \ln \left(\frac{n_i}{N_0} \right) dn_i = -k \sum_{i=1}^r \ln \left(\frac{1}{\mathcal{P}} e^{\beta \varepsilon_i / k} \right) dn_i$$

$$dS = -k \sum_{i=1}^r \left[(\beta \varepsilon_i / k) - \ln \mathcal{P} \right] dn_i$$

$$dS = -\beta \sum_{i=1}^r \varepsilon_i dn_i + k \ln \mathcal{P} \sum_{i=1}^r dn_i$$

$$dS = -\beta dU + k \ln \mathcal{P} dN_0$$

$$dS = -\beta dU + k \ln \mathcal{P} dN_0$$

$$dU = T dS - P dV + \mu dN_0$$

$$dS = (1/T) dU + (P/T) dV - (\mu/T) dN_0$$

$$\beta = -1/T$$

$$\left(\frac{n_i}{N_0} \right) = e^{\alpha/k} \cdot e^{\beta \varepsilon_i / k}$$

$$\left(\frac{n_i}{N_0} \right) = (1/\mathcal{P}) \cdot e^{-\varepsilon_i / kT}$$

$$\frac{n_i}{N_0} = \frac{1}{\mathcal{P}} e^{-(\varepsilon_i/kT)} \quad (i = 1, 2, \dots, r) \quad (10.15)$$

$$\mathcal{P} = \sum_{i=1}^r e^{-(\varepsilon_i/kT)} \quad \mathcal{P} = \text{the partition function}$$

- ◆ Eq. (10.15), containing a set of r number of equations, constitutes the conditions for equilibrium in the statistical description of thermodynamic behaviour.

Calculation of Macroscopic Properties from Partition Function

$$S = -k \sum_{i=1}^r n_i \ln \left(\frac{n_i}{N_0} \right) \quad \frac{n_i}{N_0} = \frac{1}{\mathcal{P}} e^{-(\varepsilon_i/kT)}$$

$$S = -k \sum_{i=1}^r n_i \ln \left(\frac{1}{\mathcal{P}} e^{-(\varepsilon_i/kT)} \right)$$

$$S = \sum_{i=1}^r \varepsilon_i n_i / T + k \ln \mathcal{P} \sum_{i=1}^r n_i$$

$$S = U/T + k N_0 \ln \mathcal{P} \quad (10.17)$$

$$S = U/T + k N_0 \ln \mathcal{P}$$

$$F = U - TS = U - T \left[U/T + k N_0 \ln \mathcal{P} \right]$$

$$F = -kT N_0 \ln \mathcal{P}$$

$$-S = \left(\frac{\partial}{\partial T} (-kT N_0 \ln \mathcal{P}) \right)_V$$

$$dF = -SdT - PdV + \mu dN_0$$

$$-S = \left(\frac{\partial F}{\partial T} \right)_{V, N_0}$$

$$S = k N_0 \ln \mathcal{P} + kT N_0 \left(\frac{\partial \ln \mathcal{P}}{\partial T} \right)_{V, N_0}$$

$$U = F + TS = kT^2 N_0 \left(\frac{\partial \ln \mathcal{P}}{\partial T} \right)_{V, N_0}$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$U = kT^2 N_0 \left(\frac{\partial \ln \mathcal{P}}{\partial T} \right)_V$$

$$C_V = 2kT N_0 \left(\frac{\partial \ln \mathcal{P}}{\partial T} \right)_{V, N_0} + kT^2 N_0 \left(\frac{\partial^2 \ln \mathcal{P}}{\partial T^2} \right)_{V, N_0}$$

Next Class

Lecture 35

Review Class