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

Advanced Thermodynamics

Lecture 2

Dr. M. H. Saidi

2011

Thermodynamics Postulates

- **Postulate I:**
- There exist particular states, equilibrium states, of simple systems that, macroscopically, are characterized completely by the internal energy, U, the volume, V, and the mole numbers $N_1, N_2 \dots N_r$ of the chemical components of the system.

- **Postulate II:**
- There exists a function, the entropy (S), of the extensive parameters of any composite system, defined for all equilibrium states, and having the following property:
  - The values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium state.

- Postulates I & II $\longrightarrow$ Fundamental Equation (contains all thermodynamics information)

- **Postulate III:**
- The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous and differentiable and is a monotonically increasing function of the energy.

- Postulate III $\longrightarrow$ The entropy of a simple system is
  - a homogeneous first-order $S(aU, aV, aN_i) = a\,S(U, V, N_i)$
  - Continuous & differentiable

$$\partial S/\partial X \quad \textit{is finite} \quad \textit{for all } X \quad (X = U, V, N_i)$$

- **Postulate IV:**
- The entropy of any system vanishes in the state for which
  $(\partial S/\partial U)_{V,\ N_1,\ldots,\ N_r} = 0$ (that is, at the zero of temperature)
- Planck: the so-called Nernst postulate or third law of thermodynamics.

- Postulate IV $\longrightarrow$ $(\partial S/\partial U)_{V,\ N_1,\ldots,\ N_r} > 0$

- Intensive parameters:

$$\begin{cases} \left(\dfrac{\partial U}{\partial S}\right)_{V,\, N_1,\dots,\, N_r} \equiv T \quad \text{(the temperature)} \\ -\left(\dfrac{\partial U}{\partial V}\right)_{S,\, N_1,\dots,\, N_r} \equiv P \quad \text{(the pressure)} \\ \left(\dfrac{\partial U}{\partial N_i}\right)_{S,V,\, N_1,\dots,\, N_{j\neq i},\dots,\, N_r} \equiv m_i \quad \left(\begin{array}{l}\text{the electrochemical potential} \\ \text{of ith component}\end{array}\right) \end{cases}$$

- Entropic intensive parameters may be introduced as well by considering the fundamental relation in S representation.

- Equations of state: expressing intensive parameters in terms of the independent extensive parameters, are called Equations of state.

$$\begin{cases} T \equiv \left(\dfrac{\partial S}{\partial U}\right)_{V,\,N_j} \Rightarrow T = T(S, V, N_j) \\ P \equiv -\left(\dfrac{\partial S}{\partial V}\right)_{U,\,N_j} \Rightarrow P = P(S, V, N_j) \\ m_i \equiv \left(\dfrac{\partial S}{\partial N_i}\right)_{U,\,V,\,N_{j\neq i}} \Rightarrow m_i = m_i(S, V, N_j) \end{cases}$$

- For a single component

$$\begin{cases} T = T(S, V, N) = T(S, V) \\ P = P(S, V, N) = P(S, V) \\ m = m(S, V, N) = m(S, V) \end{cases}$$