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

Advanced Thermodynamics

Lecture 9

Dr. M. H. Saidi

2011

Maxwell Relations

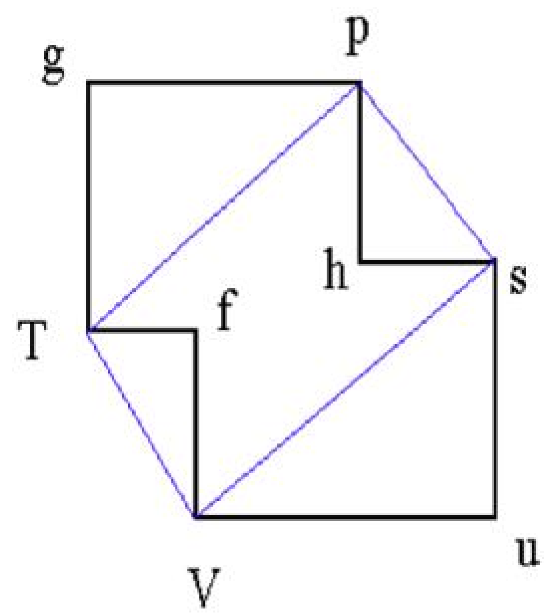
- The Maxwell relations may be represented as:

$$U = U[S, V] \Longrightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

$$H = H[S, p] \Longrightarrow \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$F = F[T, V] \Longrightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

$$G = G[T, p] \Longrightarrow \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$



Massieu Functions

- The fundamental relation may be considered in energy or entropy representation.
- The transforms of the energy are the thermodynamic potentials, where as the transforms of the entropy are called Massieu functions.
- The most common Massieu functions are

$$S[1/T] \equiv S - \frac{1}{T}U = -\frac{F}{T}$$

$$S[P/T] \equiv S - \frac{P}{T}V$$

$$S[1/T, P/T] \equiv S - \frac{1}{T}U - \frac{P}{T}V = -\frac{G}{T}$$

- These functions are useful in theory of irreversible thermodynamics.

Potentials Minimum Principles

- Reformulation of the basic extremum principles, Energy Minimum and entropy maximum, in forms of appropriate to the Legendre transformed representations are important.
- In the energy representation, the energy is minimum for constant entropy. Hence, each Legendre transform of the energy is minimum for constant values of the transformed (intensive) variables.
- **Helmholtz Potential Minimum Principle:** The equilibrium value of any unconstrained internal parameter in a system in diathermal contact with a heat reservoir minimizes the Helmholtz Potential at constant temperature (equal to that of the heat reservoir).

- **Enthalpy Minimum Principle:** The equilibrium value of any unconstrained internal parameter in a system in contact with a pressure reservoir minimizes the enthalpy at constant pressure (equal to that of the pressure reservoir).
- **Gibbs Function Minimum Principle:** The equilibrium value of any unconstrained internal parameter in a system in contact with a temperature and a pressure reservoirs minimizes the Gibbs function at constant temperature and pressure (equal to those of the respective reservoirs).

Massieu Functions

- In the energy representation, the energy is minimum for constant entropy.
- Hence, each Legendre transform of the energy is minimum for constant values of the transformed (intensive) variables.
- In contrast, in the entropy representation, the entropy is maximum for constant energy.
- Hence, each Legendre transform of the entropy is maximum for constant values of the transformed (intensive) variables.
- For some Massieu functions, due to direct relation to potential functions, the maximum principles can be readily obtained.