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

Advanced Thermodynamics

Lecture 9

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The Maxwell relations may be represented as:

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

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

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

\[
G = G[T, p] \implies \left( \frac{\partial S}{\partial p} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_p
\]
The fundamental relation may be considered in energy or entropy representation.

The transforms of the energy are the thermodynamic potentials, whereas the transforms of the entropy are called Massieu functions.

The most common Massieu functions are

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

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

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

These functions are useful in theory of irreversible thermodynamics.
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).
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.