Sharif University of Technology
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Center of Excellence in Energy Conversion

Advanced Thermodynamics

Lecture 8

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Legendre Transformation

$Y = Y(X)$	$y = y(P)$
$P = \frac{dY}{dX}$	$-X = \frac{dy}{dP}$
$y = -PX + Y$	$Y = XP + y$
Elimination of X and Y yields	Elimination of P and y yields
$y = y(P)$	$Y = Y(X)$

- $Y = Y(X)$ is a fundamental relation in Y-representation.
- $y = y(P)$ is a fundamental relation in y-representation.
- The generalization of the Legendre Transformation to functions of more than a single independent variable is straightforward. It may be applied for a (t+2)-dimensional hyper-surface $Y = Y(X_0, X_1, \ldots, X_t)$

General Legendre Transform.

$$Y = Y(X_0, X_1, \ldots, X_t) \quad \text{Eq.(1)}$$

$$P_k = \frac{\partial Y}{\partial X_k}$$

$$y = -PX + Y$$

$$dY = \sum_0^t P_k \, dX_k$$

$$Y[P_0, \ldots, P_n] = Y - \sum_0^n P_k X_k$$

Elimination of Y and $X_0, X_1, \ldots, X_n$ from Eqs. (2), (4), and the first *n+1* Eqs. of (3) yields the transformed fundamental relation.

$$Y = Y[P_0, P_1, \ldots, P_n] = \text{function of}$$

$$P_0, P_1, \ldots, P_n, X_{n+1}, \ldots, X_t \quad \text{Eq.(2)}$$

Eq.(2) is obtained by making transformation W.R.T. $X_0, X_1, \ldots, X_n$ on the Eq. (1).

$$\begin{cases} -X_k = \dfrac{\partial Y[P_0, \ldots, P_n]}{\partial P_k}, & k \le n \\ P_k = \dfrac{\partial Y[P_0, \ldots, P_n]}{\partial X_k}, & k > n \end{cases} \quad \text{Eq.(3)}$$

$$dY[P_0, \ldots, P_n] = -\sum_0^n X_k \, dP_k + \sum_{n+1}^t P_k \, dX_k$$

$$Y = Y[P_0, \ldots, P_n] + \sum_0^n P_k X_k \quad \text{Eq.(4)}$$

Elimination of $Y[P_0, \ldots, P_n]$ and $P_0, P_1, \ldots, P_n$ from Eqs. (2), (4), and first *n+1* Eqs. of (3) yields the original fundamental relation.

- The Legendre transformations may be applied into physical applications, such as the thermodynamics, Lagrangian, and Hamiltonian mechanics.

- Application of Legendre transformations to thermodynamic:

  - Fundamental relation, $Y = Y(X_0, X_1, ..., X_t)$, may be interpreted as $U = U(S,\ V,\ N_1, ...,\ N_t)$

  - Derivatives $P_0, P_1, ..., P_t$ correspond to the intensive parameters $T,\ -P,\ m_1,\ m_2, ...,\ m_t$

  - The Legendre transformed functions are called thermodynamic potentials, such as the Helmholtz, enthalpy, and Gibbs functions.

Helmholtz Free Energy

- Helmholtz potential (Helmholtz free energy), *F* or *A*, is that partial Legendre transform of *U* replaces the entropy by the temperature as independent variable.

- With the previous notation $F \equiv U[T]$

$U = U(S,\ V,\ N_1, \ldots,\ N_t)$	$F = F(T,\ V,\ N_1, \ldots,\ N_t)$
$T = \dfrac{\partial U}{\partial S}$	$-S = \dfrac{\partial F}{\partial T}$
$F = U - T\,S$	$U = F + T\,S$
Elimination of *U* and *S* yields	Elimination of *F* and *T* yields
$F = F(T,\ V,\ N_1, \ldots,\ N_t)$	$U = U(S,\ V,\ N_1, \ldots,\ N_t)$

$$dF = -S\ dT - P\,dV + \sum_{i=1}^{t} m_i\ dN_i$$

Enthalpy

- Enthalpy, *H*, is a partial Legendre transform of *U* which replaces the volume by the pressure as independent variable.
- With the previous notation $H \equiv U[P]$

$U = U(S,\ V,\ N_1,...,\ N_t)$	$H = H(S,\ P,\ N_1,...,\ N_t)$
$-P = \dfrac{\partial U}{\partial V}$	$V = \dfrac{\partial H}{\partial P}$
$H = U + PV$	$U = H - PV$
Elimination of *U* and *V* yields	Elimination of *H* and *P* yields
$H = H(S,\ P,\ N_1,...,\ N_t)$	$U = U(S,\ V,\ N_1,...,\ N_t)$

$$dH = T\,dS + V\,dP + \sum_{i=1}^{t} m_i\ dN_i$$

Gibbs Free Energy

- Gibbs function (Gibbs free energy), *G*, is partial Legendre transform which simultaneously replaces the entropy by the temperature and the volume by the pressure as independent variables, $G \equiv U[T, P]$

$U = U(S,\ V,\ N_1, \ldots,\ N_t)$	$G = G(T,\ P,\ N_1, \ldots,\ N_t)$
$T = \partial U / \partial S$	$-S = \partial G / \partial T$
$-P = \partial U / \partial V$	$V = \partial G / \partial P$
$G = U - T\,S + P\,V$	$U = G + T\,S - P\,V$
Elimination of *U*, *S*, and *V* yields $G = G(T,\ P,\ N_1, \ldots,\ N_t)$	Elimination of *G*, *T*, and *P* yields $U = U(S,\ V,\ N_1, \ldots,\ N_t)$

$$dG = -S\ dT + V\ dP + \sum_{i=1}^{t} m_i\ dN_i$$

Another Potential

- A thermodynamic potential, which is useful in statistical mechanical theory, may be introduced for a single component simple system as $U[T, m]$

$U = U(S, V, N)$	$U[T, m] =$ function of T, V, and m
$T = \partial U / \partial S$	$-S = \partial U[T, m] / \partial T$
$m = \partial U / \partial N$	$-N = \partial U[T, m] / \partial m$
$U[T, m] = U - TS - mN$	$U = U[T, m] + TS + mN$
Elimination of *U*, *S*, and *N* yields	Elimination of $U[T, m]$, T and m
$U[T, m]$ as a function of T, V, and m	yields $U = U(S, V, N)$

$$dU[T, m] = -S\,dT - P\,dV - N\,dm$$