CBEg 6162- Advanced Chemical Engineering Thermodynamics

Alternative Fundamental Relations-Thermodynamic potentials

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CHAPTER-4-Alternative Fundamental Relations-Thermodynamic potentials

- *Legendre Transformation*
- *Partial Legendre Transformation*
- *Thermodynamic Potentials*
- *Massieu Functions*
- *Thermodynamic Potential Minimum Principles*
- *Massieu Function Extremum Principle*

Objectives of the Chapter

- To obtain ***fundamental relation that is convenient to measure*** and control and contain ***maximum amount of information***.
- In fundamental relation of ***energy and entropy representation extensive parameters appears as independent variable*** and ***intensive parameters derived from the relation***.
- For instance, consider ***the extensive parameter entropy, S***, and the ***corresponding intensive parameter***, Temperature, T, in the energy representation.
- It is easy to ***measure and control temperature than entropy***. There are number of devices to measure and control temperature but ***none to measure and control entropy.***

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- Is it possible to obtain ***the fundamental relations*** with ***intensive parameters as an independent variable*** and ***derive the extensive variables*** from the fundamental relations?
- To answer the question ***Legendre transformation technique*** is used to formulate the fundamental relation
- From a practical point of view it is convenient to have ***the fundamental relation with intensive parameter as independent variables.***
- The ***Legendre transformation*** provides a means of ***replacing the extensive parameters by their corresponding intensive parameters*** and yields several alternative fundamental relations.

Legendre Transformation

- For purely mathematical convenience, consider the following fundamental relation which is ***a function of a single independent variable x.***
- Let Y=Y(X) is fundamental relation which is the function of single independent X, and let ***X is extensive parameter***.
- The Intensive parameter corresponding to the independent variable X is given by

$$\frac{dY}{dX} = m = m(X)$$

- It is possible to eliminate X from the above two equation to obtain Y=Y(m) but it does not represent fundamental relation Y=Y(X).

Steps in Legendre transformation

- Given fundamental relation $Y = Y(X)$
- The ***intensive parameter (derivative)*** corresponding to the independent variable x is given by
$$\frac{dY}{dX} = m = m(X)$$
- It is possible to eliminate x from the above two equations to obtain ***y=y(m)***. A moment's reflection on the representation of a curve in geometry will greatly help in finding a suitable procedure of transformation. ***Slope or derivative with respect to independent variable***
- Legendre transformation relation $C = Y - mX$

Legendre…cont'd

- Each straight line in a two dimensional space can be described by ***its slope m and intercept C on the y-axis.*** Suppose the relation ***c = c(m)*** selects a subset of all possible straight lines in a two dimensional space such that the envelope of these lines gives the required ***curve y = y (x).*** Then the relation ***c = c (m)*** can be used to construct ***the curve y = y(x),*** since a curve in a two-dimensional space can be viewed as a locus of all the points satisfying the relation y = y(x) or as envelop of a family of tangent lines.

Legendre…cont'd

- It is possible to eliminate x and y from among the relations ***y = y (x)*** ***and c = y - mx*** and ***obtain the relation c = c (m)*** which is the required alternative fundamental relation in which ***the slope m (intensive parameter) plays the role of independent variable***. The relation is ***c= y - mx may be considered as the basic defining equation for Legendre transformation.***
- Therefore, the relation c=c(m) contains all the information that is present in the relation y = y(x). Hence c = c(m) is also an equally valid fundamental relation. That is a knowledge of the intercept c on the y-axis as a function of slope m, constitutes a fundamental relation which is equivalent to the given ***fundamental relation***

  y = y(x).

Legendre…cont'd

- $y = y(x)$ is a fundamental relation in the y-representation and

  $c = c(m)$ is a fundamental relation in the c representation.

- Now, the problem of finding an alternative fundamental relation reduced to the determination of the relation $c = c(m)$ from the given relation $y = y(m)$. Any tangent line to the curve representing the relation $y = y(x)$ can be represented as $y = mx + c$ or $c = y - mx$.

- The elimination of x and y is possible only if $dy/dx=m=m(x)$. That is only if $\frac{d^2Y}{dX^2} \neq 0$ In thermodynamics this criterion is must always satisfied.

- Suppose the Legender transformed function c = c (m) is given and it is required to obtain the original function

  y = y (x). From the relation c = y - mx, one can write

  dc = dy - mdx - xdm = -xdm or . That is the first derivative of c with respect to m (intensive parameter) yields the negative of the original independent variable x (extensive parameter).

Straight forward elimination of c and m from among the relation c=c(m), c = y - mx and $-X = \frac{dC}{dm} = -X(m)$ yields y = y(x). This elimination is possible only if $\left(\frac{d^2C}{d^2m}\right) \neq 0$ which is always guaranteed by the stability of a thermodynamic system.

Legendre…cont'd

- Thus it is seen that a given fundamental relation of a single independent variable can be transformed without any loss of information by the Legender transformation and the inverse transformation also can be carried out to regenerate the original fundamental relation.
- The Legender transformation and the inverse transformation for a function is given as follows
- Given fundamental relation Y=Y(X)
- The slope or derivative with respect to independent variable X yields intensive parameter $\frac{dY}{dX} = m = m(X)$

Legender trasformation relation $C = Y - mX$

Elimination of x and y from the above equations yields the Legender transform of y $C = C(m)$

Inverse transformation

- Given fundamental relation $C = C(m)$
- Slope or derivative with respect to independent variable m yields the negative of the extensive paramenter $-X = \frac{dC}{dm} = -X(m)$
- Legendre transformation relation

Elimination of c and m from the above relations yields the fundamental relation $C = Y - mX$

$$Y = Y(X)$$

Legendre transformation for more than one independent variable

- Given relation $Y = Y(X_1, X_2, ...), X_{c+2}$
- Intensive parameters (Partial derivatives of Y with respect to Xi)

$$(\frac{\partial Y}{\partial X})_{xj} = mi$$

- Legendre transformation relation:
- Elimination of Y and X_i from the above equation yields

$$C = Y - \sum_{i=1}^{c+2} m_i X_i \qquad \mathrm{C} = \mathrm{C}(m_1, \mathrm{m}_2, \ldots, \mathrm{m}_{c+2}$$

Inverse transformation

- Given relation $\mathrm{C} = \mathrm{C}(m_1, \mathrm{m}_2, \ldots, \mathrm{m}_{c+2})$
- Intensive parameters (Partial derivatives of C with respect to m_i) $-Xi = \left(\frac{\partial C}{\partial m}\right)_{m_j}$
- Legendre transformation relation: $C = Y - \sum_{i=1}^{c+2} m_i X_i$
- Elimination of C and m_i from the above equation yields $Y = Y(X_1, X_2, \ldots, X_{c+2})$

Partial Legendre transformation

- Legendre transformation of all the extensive Parameters by the corresponding intensive parameters will reduce to zero. Therefore we need to work with partial derivative
- Given relation $Y = Y(X_1, X_2, \dots, X_{c+2}$
- Intensive parameter $(\partial Y/\partial X_i)_{xj} = mi$
- Legendre transformation relation

$$C[m_{1,}m_2, \dots, m_{n+2}] = Y - \sum_{i=1}^{n+2} m_i X_i$$

$$Y, X_1, \dots, X_{n+2}$$

Elimination of

$C[m_{1,}m_2, \dots, m_{n+2}] =$ A function of $m_{1,}m_{2,} \dots, X_{n+3}, \dots, X_{c+2}$

Inverse transformation

- Given relation: $c[m_1, m_2, \ldots, m_{n+2}] =$ A function of

$$m_1, m_2, \ldots, X_{n+3}, \ldots, X_{c+2}$$

- Extensive parameter $-X_i = \dfrac{\partial C[m_1, \ldots, m_{n+2}]}{\partial m_i}$
- Legendre transformation relation:

$$c[m_1, m_2, \ldots, m_{n+2}] = Y - \sum_{i=1}^{n+2} m_i X_i$$

- Elimination of $C[m_1, m_2, \ldots, m_{n+2}]$ $, m_1, m_2 \ldots m_{n+2}$ from the above relation yields

$$Y = Y(X_1, X_2, \ldots, X_{c+2}$$

Thermodynamic Potentials

- The partial Legendre transforms of the fundamental relation in the energy representation are called ***thermodynamic potentials.***
- The widely used ***thermodynamic potentials*** are
  - ***Internal Energy***
  - ***Helmholtz free energy (A)***
  - ***Enthalpy (H) and***
  - ***Gibbs free energy (G)***
  - ***Grand canonical potential***

Internal Energy

- Thermodynamic system may ***exchange energy*** with its surrounding through ***heat and work***. The surrounding may perform work / transfer heat on/to the system and vice versa.
- Work done by the system on surrounding can be conventionally considered as positive and work done by the surrounding on the system as negative. Similarly energy transferred as heat from the system to the surrounding as positive and energy transferred from the surrounding to the system as negative

Internal Energy… cont'd

$$du = dQ - dW \text{ or } \Delta u = Q - W$$

Q-energy transferred as heat to the system

W-work done by the system

If the boundary to the system is ***adiabatic the relation*** will reduce to; - $\Delta u = W$

The work done during adiabatic process is equal to the decrease in the internal energy of the system. Therefore, internal energy represents the potential to do work by system during adiabatic process. ***Hence, internal energy is thermodynamic potential***

Helmholtz potential

- It is ***the partial Legendre transform of U (S,V,N)*** in which the ***extensive parameter entropy's is replaced by the corresponding intensive parameter temperature (T)***. It is denoted by A and is equal to U [T]. The independent variables of A are T,V,N or A = A (T, V, N). Since A = A (T,V,N) is an alternative fundamental relation it contain all ***the thermodynamic information present in U (S, V, N)***

Partial Legendre transformation to obtain A=U[T]

- Given relation: $U = U(S, V, N_1 \ldots Nc)$
- Intensive parameter $T = \left(\frac{\partial U}{\partial S}\right)_{v,Ni}$
- Partial Legendre transformation relation

  $A = U[T] = U - TS$

- Elimination of U and S from above three equation yields $A = A(T, V, N_1, \ldots Nc)$
- The differential of A can be written as

  $$\mathbf{dA = -SdT - PdV + \sum m_i dN_i}$$

Inverse transformation

- **to obtain U from A (T, V, N_1 … N_c)**
- Given relation : A = A (T, V, N_1, … Nc)
- Partial derivative: $-S = \left(\frac{\partial A}{\partial T}\right)_{v,N\mathrm{i}}$
- Partial Legender transformation relation A = U - TS
- Elimination of A and T from the three equation yields U = U (S, V, N1 …. Nc)
- The work done by a system a given process in which the initial and final temperature of the system are equal to that of the surroundings, is less than or equal to the decrease in the Helmholtz free energy of the system. i.e. $\mathbf{W \leq A_1 - A_2}$

… Cont’d

- The maximum work that can be obtained from a system during a given process in which the initial and final temperature of the system are the same as the surrounding temperature, ***is equal to the decrease in the Helmholtz free energy of the system.***
- If work is performed on the system then the minimum work to be done on the system is given by ***the increase in the Helmholtz free energy.***
- This shows that ***the Helmholtz free energy represents the potential to do work by a system*** which is in diathermal contact with its surrounding and ***hence, Helmholtz free energy is a thermodynamic potential***

Enthalpy (H)

- It is the partial Legendre transform of U (S, V, N1, Ni) in which ***the extensive parameter V is replaced by the corresponding intensive parameter (-P).*** Therefore, ***H = U [-P]*** . The independent variables of the thermodynamic potential enthalpy are ***S, P, N_1 ... N_c***. The partial Legendre transformation to obtain $H(S,P,N_1 \ldots N_c)$ from $U(S,V,N_1 \ldots N_c)$ and inverse transformation are as follows;

Enthalpy (H)-Partial Legendre transformation

to obtain H = U [- P]

- Given relation : U = U (S, V, N, … Nc)
- Intensive parameter*:* ***- P =(au/av)$_{S,Ni}$***
- Partial Legendre transformation relation
- ***H = U [-P] = U + PV***
- Elimination of U and V from the above relation yields
- ***H = H (S, P, N… Nc)***
- The differential of H can be written as

$$dH = TdS + VdP + \sum m_i dN_i$$

Enthalpy (H)-Inverse transformation

to obtain U from H (S, P, N_1… N_c)

- Given relation: H = H (S, P, N_1 … Nc)
- ***Partial derivative - V =*** $\left(\frac{\partial H}{\partial(-P)}\right)_{S, Ni}$
- Partial Legendre transformation relation:
- H = U + PV
- Elimination of H and P from the above equation yield ***U = U (S, V, N_1… Nc)***

The Gibbs Free Energy (G)

- It is the partial Legendre transform of U (S, V, N_1… N_c) in which ***the extensive parameters entropy and volume are simultaneously replaced by their corresponding intensive parameters temperature and pressure respectively***. i.e. ***G = U [T, -P]*** . The natural variables of the thermodynamic potential of Gibbs free energy are T,P,N_1 …… Nc. The partial Legendre transformation of ***U (S, V, N_1 … N_c)*** to obtain ***G (T, P, N_1 ….. N_c)***

The Gibbs Free Energy (G)-Partial Legendre transformation

- Given relation: $U = U(S, V, N_1 \ldots\ldots N_c)$
- Intensive parameters $T = \left(\frac{\partial U}{\partial S}\right)_{V, Ni}$
- $-P = \left(\frac{\partial U}{\partial V}\right)_{S, Ni}$
- Partial Legendre transformation relation
- $G = U[T, -P] = U - TS + PV$
- ***Elimination of U, S and V*** among the relations the above equations yields
- $G = G(T, P, N_1 \ldots N_c)$
- The differential of G is given by

$$\mathbf{dG = -SdT + VdP + \sum_{i=1}^{c} \mu_i dN_i}$$

The Gibbs Free Energy (G)-Inverse transformation

- **U from G (T, P N_1 …… N_c),** Given relation G = G (T, P N_1 … N_c)

  Partial derivatives $-S = \left(\frac{\partial G}{\partial T}\right)_{P,Ni}$

  $$-V = \left(\frac{\partial G}{\partial(-P)}\right)_{T,Ni}$$

- Partial Legendre transformation relation ***G = U - TS + PV***
- Elimination of G, T and P from the above relation yields

  $U = U (S, V, N_1 \ldots. N_c)$

Grand Canonical Potential

- It is the partial Legendre transformation of U(S,V,N) in which ***the extensive parameters S and N are simultaneously replaced by their corresponding intensive parameters T and μ.*** i.e. the grand canonical potential is U[T,μ]. The natural variables of this potential are ***T,V and μ .***
- Usually the grand canonical potential is not used in classical thermodynamics and hence no special symbol was given to it.

- **to obtain U [T, μ]**
- Given relation : U = u (S, V, N)
- Intensive parameters T = $\left(\frac{\partial U}{\partial S}\right)_{V,N}$
- μ= $\left(\frac{\partial U}{\partial N}\right)_{S,V}$
- Partial Legender transformation relation

  U [T, μ] = U - TS - μN
- Elimination of U,S and N these relations yields

  U [T, μ] = A function of T, V, μ
- The differential of U [T, μ] can be written as

  dU [T, μ] = -SdT - PdV – Ndμ

to obtain U from U [T, μ]

- Given relation U [T, μ] = A function of T,V, μ
- Partial derivatives $-S = \left\{\frac{\partial U(T,\mu)}{\partial T}\right\}_{V,\mu}$

  $-N = \left\{\frac{\partial U(T,\mu)}{\partial \mu}\right\}_{T,V}$
- Partial Legender transformation relation U[T,μ]=U-TS-μN
- Elimination of U[T,μ], T and μ among the relations yields U=U(S,V,N)

Massieu function

- Partial Legendre transforms of the fundamental relation in the entropy representation provides additional *alternative fundamental relations*. These alternative fundamental relations are called ***Massieu functions***
- These Massieu functions *are rarely used in classical thermodynamics* and hence they were not given special names and symbols. Some of the common Massieu functions are presented in the next slides

Massieu function S [1/T]

- It is partial Legendre transform of S (U, V, N_1 ... Nc) in which the extensive parameter U is replaced by the corresponding intensive parameter 1/T. Its natural variables are 1/T, V, N_1, N_2.. N_c its partial Legendre and inverse transformation are shown below

Partial Legendre transformation -to obtain S [1/T]

- Given relation: S = S (U, V, N)
- Intensive parameter 1/T = $\left(\frac{\partial S}{\partial U}\right)_{V,N}$
- Partial Legender transformation relation

$$S\,[1/T] = S - [1/T]\,U$$

- Elimination of S and U from the two equations yields

S [1/T] = A function of 1/T, V, N

- The differential of S [1/T] can be written as

$$dS\,[1/T] = -U d\,(1/T) + (P/T)\,dV - (\mu/T)\,dN$$

Massieu function S [1/T]…

Inverse transformation

to obtain S (U, V, N) from S [1/T]

- Given relation : S [1/T] = A function of 1/T, V, N
- Extensive parameter -U = $\left\{\frac{\partial S(1/T)}{\partial(1/T)}\right\}_{V.N}$
- Legendre transformation relation S[1/T] = S - (1/T)U
- Elimination of S[1/T] and 1/T from equations yields

  S = S (U, V, N)

Massieu function S [P/T]

- It is the partial Legendre transform of S (U, V, N) in which the extensive parameter V is replaced by the corresponding intensive parameter p/T. Its natural variables are U, P/T, and N

Partial Legendre transformation to obtain S [P/T]

- Given relation S = S (U, V, N)
- Intensive parameter P/T = $\left(\frac{\partial S}{\partial V}\right)_{U,N}$
- Partial Legendre transformation relation S [P/T] = S - [P/T] V
- Elimination of S and V from equations yields
- S [P/T] = A function of U, P/T, N
- The differential of S [P/T] can be written as

dS[P/T] = [1/T] dU - Vd [P/T] - [μ/T] dN

Inverse transformation

to obtain S (U, V, N) from S [P/T]

- Given relation S[P/T] = A function of U, P/T, N
- Extensive parameter - V = $\left\{\frac{\partial S(P/T)}{\partial (P/T)}\right\}_{U,N}$
- Legendre transformation relation

  S [P/T] = S - [P/T]V
- Elimination of S [P/T] and P/T from equations. yields S = S (U,V,N)

Massieu function S [1/T, P/T]

- It is the partial Legendre transform of S (U, V N) in which the extensive parameters U and V are simultaneously replaced by their corresponding intensive parameters 1/T and P/T respectively. Its natural variables are 1/T, P/T, and N

Legendre transformation to obtain S [1/T, P/T]

- Given relation: S = S (U, V,N)
- Intensive parameters 1/T= $\left(\frac{\partial S}{\partial U}\right)_{V,N}$

  P/T = $\left(\frac{\partial S}{\partial V}\right)_{U,N}$
- Partial Legender transformation relation S [1/T, P/T] = S - (1/T) U - (P/T) V)
- Elimination of S,U and V from the equations yields
- S [1/T, P/A] = A function of 1/T, P/T N
- The difference of S [1/T, P/T] can be written as

dS [1/T, P/T] = - Ud (1/T) - Vd (P/T) - (μ/T) dN

Massieu function S [1/T, P/T]…

Inverse transformation

- **to obtain S (U, V, N) from S [1/T, p/T]**
- Given relation S [1/P, p/T] = A function of 1/T, p/T , N
- Extensive parameters

$$-U = \left\{\frac{\partial S(1/T, P/T)}{\partial(1/T)}\right\}_{P/T,N}$$

$$-V = \left\{\frac{\partial S(1/T, P/T)}{\partial(P/T)}\right\}_{1/T,N}$$

- Legendre transformation relation

  S [1/T, P/T] = S - (1/T)U - (P/T) V
- Elimination of S [1/T, p/T], 1/T and P/T from the above equations yields
- S = S (U, V, N)

Thermodynamic potential minimum principles

- The energy minimum principle can be recast in terms of ***the thermodynamic potentials.***

The Helmholtz free energy minimum principle

- States that in a state of equilibrium the unconstrained extensive parameter in a system which is in contact with a constant temperature reservoir assumes such values as to minimize the Helmholtz free energy at constant temperature. That is the equilibrium state as a system in diathermal contact with a constant temperature reservoir is characterized as ***a state of minimum Helmholtz free energy.***

Helmholtz Free Energy Minimum Principle…

- Consider composite system and temp. reservoir:

Energy mini. principle $d\,(U+U^{r)} = 0$

Given constraints $dS = dS^a + dS^b = -dS^r$

$dV^a + dV^b = 0$ or $dV^a = -dV^b$

$dN_i^b + dN_i^a = 0$

$$d\,(U+U^r) = dU + dU^r = (T^a dS^a + T^b dS^b + T^r dS^r) - P^a dV^a - P^b dV^b + \sum \mu_i dN_i^a + \sum \mu_i dN_i^b = 0$$

Substituting the constraints and we will obtain

$$d\,(U+U^r) = dU + dU^r = [T^a dS^a + T^b dS^b - T^r (dS^a + dS^b)] - \ldots = 0$$

Therefore $T^a = T^b = T^r$

To express energy min. principle in terms of TD potentials

$$d\,(U+U^{r)} = dU + dU^r = dU + T^r dS^r = 0$$

$$du - TdS = d(U-TS) = dA = 0$$

The enthalpy minimum principle

States that in a state of equilibrium the unconstrained internal parameter in a system which is in contact with a pressure reservoir assumes such values as to minimize the enthalpy at constant pressure. That is the equilibrium state of a system which is in contact with a pressure reservoir is characterized ***as a state of minimum enthalpy.***

Consider composite system and pressure reservoir

Energy mini. principle $d(U+U^{r}) = 0$

Constraint $dV^{a} + dV^{b} + dV^{r} = 0$

$$d(U+U^{r}) = dU + dU^{r} = TdS - PdV + \sum \mu_i dN_i - P^{r}dV^{r} = 0$$

$$= T^{a}dS^{a} + T^{b}dS^{b} - P^{a}dV^{a} - P^{b}dV^{b} + \ldots - P^{r}dV^{r} = 0$$

$P^{a} = P^{b} = P^{r}$

$d(U+U^{r}) = dU + dU^{r} = dU - P^{r}dV^{r} = dU + PdV = d(U+PV) = dH = 0$

Gibbs free energy minimum principle

- The Gibbs free energy minimum principle states that in a state of equilibrium the unconstrained internal parameter in a system which is in simultaneous contact with a constant temperature reservation and a constant temperature and pressure. That is, the equilibrium state of a system at constant temperature and pressure is characterized ***as a state of minimum Gibbs free energy.***

Consider composite system and pressure and temp. reservoir:

Energy mini. principle $d(U+U^r) = 0$

$$d(U+U^r) = dU + dU^r = dU + T^r dS^r - P^r dV^r = 0$$

$$= T^a dS^a + T^b dS^b - P^a dV^a - P^b dV^b + T^r dS^r - P^r dV^r = 0$$

Gibbs free energy minimum principle…

Constraints

$$dS^a + dS^b + dS^r = 0 \text{ or } dS = dS^a + dS^b = -dS^r$$

$$dV = -dV^r \text{ or } dV^a + dV^b = -dV^r$$

$$= (T^a - T^r)\, dS^a + (T^b - T^r)\, dS^b - (P^a - P^r)\, dV^a - (P^b - P^r)\, dV^b = 0$$

$$T^a = T^b = T^r \text{ or } P^a = P^b = P^r$$

Consider again energy min. principle

$$d\,(U + U^r) = dU + dU^r = dU - T^r dS + P^r dV$$

$$= dU - TdS + PdV = 0$$

$$= d(U - TS + PV) = dG = 0$$

Thermodynamic potential minimum principles

- The thermodynamic potential minimum principles can be stated in more general way as follows. In a state of equilibrium, the unconstrained internal parameters in a system in contact with a set of reservoirs with intensive parameters m_i, m_j, assume such values as to minimize the thermodynamic potential U [m_i, m_j] at constant mi, m_j.

- In short the extremum principles characterize the equilibrium state as a state for which
  - ✓ *S is Maximum at constant U and V*
  - ✓ *N is Minimum at constant S and V*
  - ✓ *A is Minimum at constant T and V*
  - ✓ *H is Minimum at constant S and P*
  - ✓ *G is Minimum at constant T and P*

Massieu function extremum principles

- The partial Legendre transforms of the fundamental relation in the entropy representation are called the Massieu functions. The entropy maximum principle can be rephrased in terms of the Massieu functions.

Massieu function S [1/T] maximum principle

- The Massieu function S [1/T] maximum principles states that in a state of equilibrium, the unconstrained internal parameter in a system in contact with a reservoir with internal parameter in a system in contact with a reservoir with intensive parameter 1/T. assumes such values as to maximize S[1/T] at constant 1/T.

Massieu function extremum principles

The Massieu function S [1/T, p/T] maximum principle

- The Massieu function S [1/T, p/T] maximum principle state that in a state or equilibrium the unconstrained internal parameter in a system in contact with a set of reservoirs with intensive parameters 1/T and p/T assumes such values as to maximize the Massieu function s[1/T], p/T] at constant 1/T and P/T.
- Partial Legendre transformation of fundamental relation in entropy representation is called massieu function
- Massieu function $S\left[\frac{1}{T}\right]$ is Partial Legendre transformation of S(U,V, Ni) in which U is replaced by $\frac{1}{T}$

Massieu function extremum principles

Partial Legendre transformation

- given relation S= S(U, V, N)
- Legendre transformation relation $S\left[\frac{1}{T}\right]$ =S - ($\frac{1}{T}$)U
- elimination of U and S yield $S\left[\frac{1}{T}\right]$ = A function of $\frac{1}{T}$,V and N

Inverse transformation

Given relation $S\left[\frac{1}{T}\right]$ =A function of $\frac{1}{T}$,V, N

- Extensive parameter - $U = \left(\frac{\partial S}{\partial \frac{1}{T}}\right)_{V, N_i}$
- Legendre transformation relation

$S\left[\frac{1}{T}\right]$= S - ($\frac{1}{T}$)U

- Elimination of $S\left[\frac{1}{T}\right]$ & Yields $\frac{1}{T}$

S= S (U, V,N)