CBEg 6162- Advanced Chemical Engineering Thermodynamics

Gibbs-Duhem Relations and Energy Minimum Principles

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CBEg 6162-ADCHENTD-Outline

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CHAPTER-3- Gibbs-Duhem Relations and Energy Minimum Principles

- *The Euler relations*
- *The Gibbs-Duhem relations*
- *Fundamental surface*
- *Energy minimum principles*
- *The equivalence of entropy maximum and energy minimum principles*

- It is known that ***the fundamental relation is a homogenous first order function** of the extensive parameters*. The fundamental relation in the entropy representation for a single component system is

$$\textbf{S=S(U,V,N)...............................(3.1)}$$

- Since S is homogeneous first order function of U,V,N

$$\textbf{S(nU,nV,nN) = nS(U,V,N).......(3.2)}$$ (for any n = no of subsystems)

- Differentiating equation (3.2) with respect to

$$\frac{\partial\, S(nU,nV,nN)}{\partial(nU)} * \frac{\partial(nU)}{\partial(n)} + \frac{\partial\, S(nU,nV,nN)}{\partial(nV)} * \frac{\partial(nV)}{\partial(n)} + \frac{\partial\, S(nU,nV,nN)}{\partial(nN)} * \frac{\partial(nN)}{\partial(n)} = S(U,V,N)$$

- This equation is true for all values of n. if n is taken as equal to 1.

$$\frac{\partial\, S(U,V,N)}{\partial(U)} *U + \frac{\partial\, S(U,V,N)}{\partial(V)} *V + \frac{\partial\, S(U,V,N)}{\partial(N)} *N = S(U,V,N)$$

But, $\dfrac{\partial S}{\partial U} = \dfrac{1}{T}$, $\quad \dfrac{\partial S}{\partial V} = \dfrac{P}{T}$ and $\dfrac{\partial S}{\partial N} = \dfrac{-\mu}{T}$,

substituting all these terms in the above equation

$$(1/T)U + (P/T)V - (\mu/T)N = S \ldots\ldots\ldots\ldots\ldots\ldots\ldots(3.3)$$

- Equation (3.3) is the *Euler relation in entropy representation.*

- It is stated as *the sum of the products of the extensive parameters* and their corresponding *intensive parameters* is equal to *entropy (S)*.

- The Euler relation in energy representation can also be found as follows:-
We know that, $U = U(S,V,N)$.................................(3.4)

- And since U is homogeneous first order function of S,V and N

$$U(nS,nV,nN) = nU(S,V,N)....................(3.5)$$

- Differentiating with respect to n

$$\frac{\partial\, U(nS,nV,nN)}{\partial(nS)}*\frac{\partial(nS)}{\partial(n)}+\frac{\partial\, U(nU,nV,nN)}{\partial(nV)}*\frac{\partial(nV)}{\partial(n)}+\frac{\partial\, U(nU,nV,nN)}{\partial(nN)}*\frac{\partial(nN)}{\partial(n)} = U(U,V,N)$$

But, $\frac{\partial(nS)}{\partial(n)} = n\,\frac{\partial(S)}{\partial(n)} + S\frac{\partial(n)}{\partial(n)} = S$, like the same wise others will give us V & N

- Then, substitute the simplifications and letting n=1, we will get

$$\frac{\partial\,U(U,V,N)}{\partial(S)}*S + \frac{\partial\,U(U,V,N)}{\partial(V)}*V + \frac{\partial\,U(U,V,N)}{\partial(N)}*N = S(U,V,N)$$

- But, $\frac{\partial U}{\partial S} = T$, $\frac{\partial S}{\partial V} = -P$ and $\frac{\partial S}{\partial N} = \mu$, substitute in the above equation

$$\text{TS} - \text{PV} + \mu\text{N} = \text{U}...(3.6)$$

   Equation (3.6) is the *Euler relation in energy representation.*

- It is stated as *the sum of the products of the extensive parameters* and their corresponding *intensive parameters* for the given representation is equal to *internal energy(U).*

- If the equation of state of the thermodynamic system is known *in the entropy and energy representation*, **the fundamental relation** for that system in the entropy and energy representation can be *obtained by making use of equation (3.3) and (3.6).*

Example 1

- *Express the following fundamental Relation in **the Euler form***

$$U = CS3/NV$$

- This is another consequence of *the homogeneous first order property of the fundamental relations*. It determine the explicit relationship between *intensive parameters.*

- Knowledge of the exact fundamental relation is required. However we can *use the Euler relation*.

- From equation (3.3) $(1/T)U + (P/T)V - (\mu/T)N = S$;   Then the differential of S can be written as: $- (1/T)\, dU + U\, d(1/T) + (P/T)\, dV + V\, d(P/T) - (\mu/T)\, dN - N\, d(\mu/T) = dS$ ....**(3.7)**

    And from equation (3.1) we can obtain the differential of S

    $$(1/T)\, dU + (P/T)\, dV - (\mu/T)\, dN = dS \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(3.8)}$$

    Subtracting equation (3.7) from (3.8) will give us

    $$0 = U\, d(1/T) + V\, d(P/T) - N\, d(\mu/T), \text{ this can be written us}$$

    $$\mathbf{d(\mu/T) = u\ d\,(1/T) + v\ d(P/T)}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(3.9)}$$

- Equation (3.9) is *Gibbs-Duhem relation in entropy representation.*

Similarly, from the Euler relation of energy representation: - $U = TS - PV + \mu N$

Its differential is : $du = T\,dS + S\,dT - P\,dV - VdP + \mu\,dN + N\,d\mu$**....(3.10)**

And the differential of the fundamental relation of equation (3.4) is

$$du = T\,dS - P\,dV + \mu\,dN \dotfill \textbf{(3.11)}$$

Subtracting equation (3.10) from (3.11) will give us

$0 = S\,dT - V\,dP + N\,d\mu$, it can be written as

$$\textbf{d}\mu = \textbf{-}\,\textbf{s}\,\textbf{dT} + \textbf{v}\,\textbf{dP} \dotfill \textbf{(3.12)}$$

Equation (3.12) is *the Gibbs-Duhem relation in energy representation*.

Gibbs-Duhem relations equation (3.9) and (3.12) state that *the sum of the products of extensive parameters* and *the derivative of their corresponding intensive parameters is equal to zero.*

For a multi-component system, they have the form of: -

$$U \, d(1/T) + V \, d(P/T) - \Sigma N_i \, d(\mu_i/T) = 0 \qquad \text{(entropy representation)}$$

$$S \, dT - V \, dP + \Sigma \, N_i \, d\mu_i = 0 \qquad \text{(energy representation)}$$

Conclusion

- *If two equations of state of a system are known* *the third equation of state* can be determined *by making use of the Gibbs-Duhem relation*. Then the **three equations of states** can be substituted in *the Euler relation* to determine the fundamental relation.

- Alternatively one can substitute the known two equations of states in the differential forms of the *fundamental relations, (equations(3.8)and (3.11))* and *integrate them to obtain the fundamental relation.*

Example 2 and 3

Example 2

A particular thermodynamic system obeys the following equations of state

$$T = 3CS^2/NV \text{ and } P = CS^3/NV^2$$

Where C is a positive constant. Determine the fundamental relation

Example 3

Find the fundamental relation for a thermodynamic system which obeys the equations of state given in example 2. Use the alternative procedure of obtaining the fundamental relation by direct integration of the deferential form

Example 4

- *An ideal monotonic gas is described by the two equations of state:* **PV = NRT and U = (3/2)NRT**. *Determine the fundamental relation for an ideal monotonic gas.*

If Y is a functional of *two variables X1 and X2*, then it needs three dimensional *coordinate plane Y- X1- X2*.

The fundamental surface corresponding to *S=S(u,v)* in the thermodynamic configuration space for a single component system
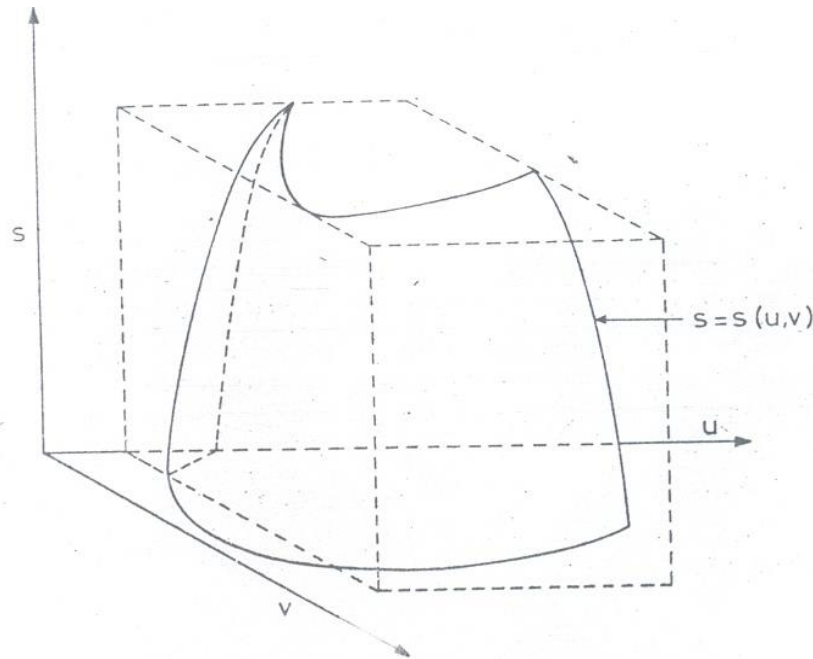
The fundamental surface corresponding the fundamental relation *S=S(U, X₁, X₂, ... Xc₊₁)* for fixed values of all X_i except i=k is similar to a fundamental relation of *single component system S=S (u, v), diagrammatically,*
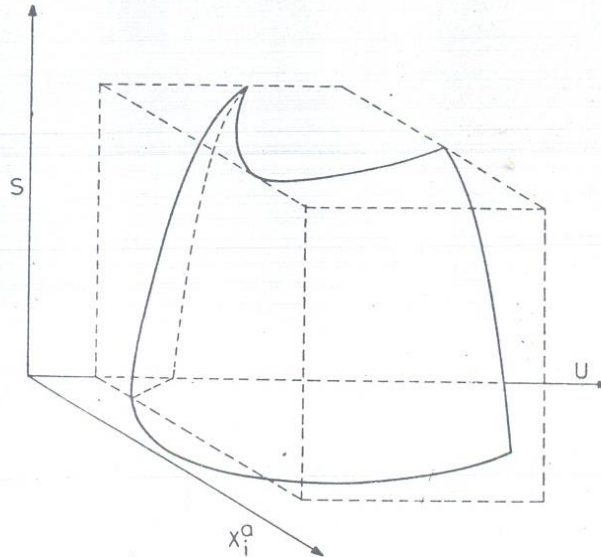
The hyper surface which represents the fundamental relations of a thermodynamic system is known as *fundamental surface.*
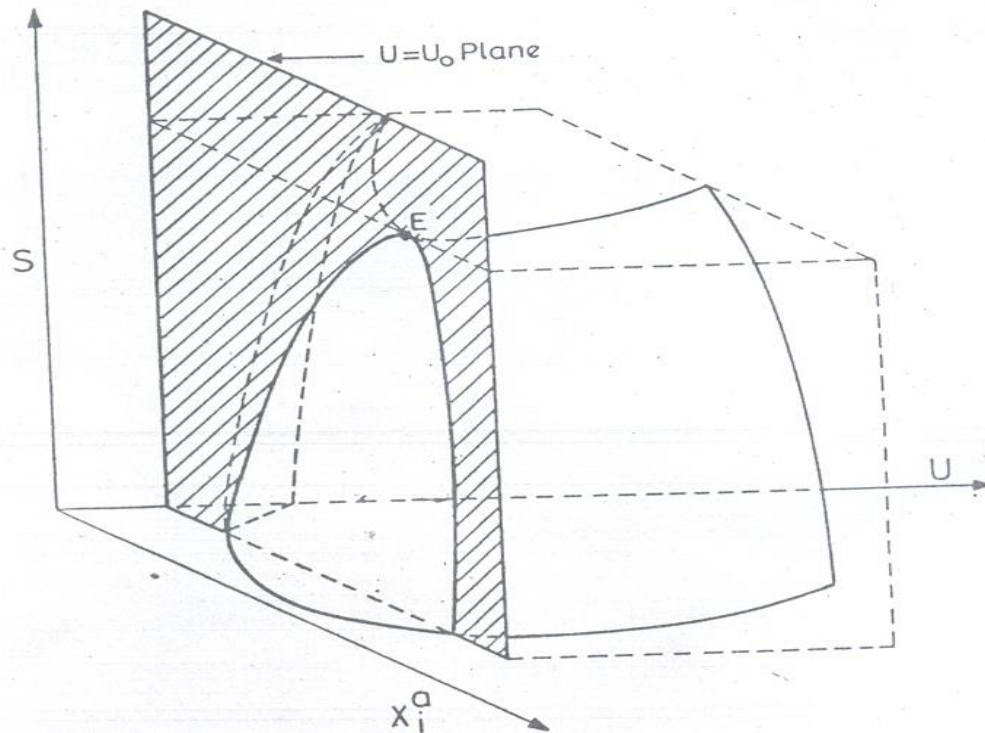
- **Energy minimum principle**: - in the equilibrium state the value of the *unconstrained extensive parameters is such as to minimize the total internal energy of the composite system* for a given value of total entropy.

- **Entropy maximum principle:-** in the equilibrium state the values of the *unconstrained extensive parameters is such as to maximize the total entropy of the composite system* for a given value of total internal energy.

- Since *energy minimum principle* is obtained by *inverting the entropy maximum principle*, the equilibrium state satisfies both principles
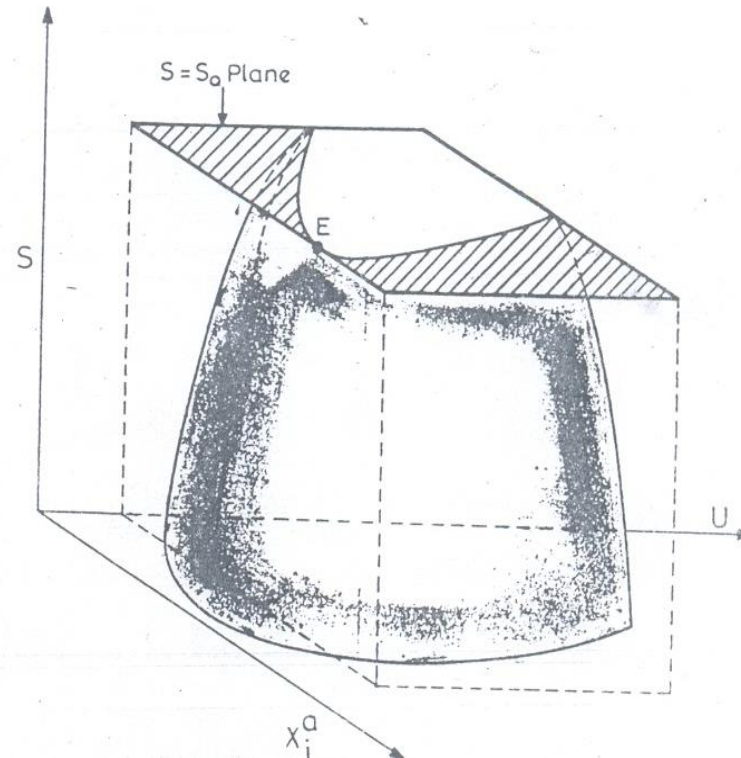
- The composite system moves along *the curve of intersection of U = U_O plane and fundamental surface* until the *entropy reaches a maximum value.*

- the composite system moves along the curve of *intersection of S=S$_o$ plane and fundamental surface* till the *energy reaches a minimum value.*

- **Entropy Maximum principle:** In a state of equilibrium the unconstrained extensive parameter assume such value as to *maximize the entropy of a composite system* for a given value of total internal energy of the system.

$$\left(\frac{\partial S}{\partial X}\right)_U = 0$$

$$\left(\frac{\partial^2 S}{\partial X^2}\right)_U < 0$$

- **Energy minimum principle:** In a state of stable system the unconstrained extensive parameter assume such value as *to minimize the total energy of the system.*

$$\left(\frac{\partial U}{\partial X} \right)_S = 0$$

$$\left(\frac{\partial^2 U}{\partial X^2} \right)_S > 0$$

The equivalence of these two principles can be proven mathematically as follows

Cyclic equation

$$\left(\frac{\partial S}{\partial U}\right)_X \left(\frac{\partial U}{\partial X}\right)_S \left(\frac{\partial X}{\partial S}\right)_U = -1$$

For instance, if x = V,

$$\left(\frac{\partial S}{\partial U}\right)_X \left(\frac{\partial U}{\partial V}\right)_S \left(\frac{\partial V}{\partial S}\right)_U = \left(\frac{1}{T}\right)\left(-P\right)\left(\frac{T}{P}\right) = -1$$

$$\left(\frac{\partial U}{\partial X}\right)_S = -\left(\frac{\partial U}{\partial S}\right)_X \left(\frac{\partial S}{\partial X}\right)_U = -T\left(\frac{\partial S}{\partial X}\right)_U = 0$$

Since,
$$\left(\frac{\partial S}{\partial X}\right)_U = 0$$

$$\left(\frac{\partial^2 U}{\partial X^2}\right)_s = \left[\frac{\partial}{\partial X}\left(\frac{\partial U}{\partial X}\right)_s\right]_S = \left(\frac{\partial m}{\partial X}\right)_S$$

Where, m = $\left(\frac{\partial U}{\partial X}\right)_S$

Considering, m = m (U, X), then, derivative of m, that is

$$dm = \left(\frac{\partial m}{\partial U}\right)_x du + \left(\frac{\partial m}{\partial X}\right)_U dX$$

$$\left(\frac{\partial m}{\partial X}\right)_S = \left(\frac{\partial m}{\partial U}\right)_X \left(\frac{\partial U}{\partial X}\right)_S + \left(\frac{\partial m}{\partial X}\right)_U \left(\frac{\partial X}{\partial X}\right)_S = \left(\frac{\partial m}{\partial X}\right)_u$$

- Substituting $\left(\dfrac{\partial U}{\partial X}\right)_S = -\left(\dfrac{\partial U}{\partial S}\right)_X \left(\dfrac{\partial S}{\partial X}\right)_U$ and m=$\left(\dfrac{\partial U}{\partial X}\right)_S$

$$\left(\frac{\partial^2 U}{\partial X^2}\right)_S = -\left(\frac{\partial U}{\partial S}\right)_X \left(\frac{\partial^2 S}{\partial X^2}\right)_U - \left(\frac{\partial S}{\partial X}\right)_U \left(\frac{\partial}{\partial X}\left[\frac{\partial U}{\partial S}\right]_X\right)_U$$

$$\left(\frac{\partial^2 U}{\partial X^2}\right)_S = -T\left[\frac{\partial^2 S}{\partial X^2}\right]_U > 0$$

Hence, *the energy minimum principle and entropy maximum principle are equivalent.*

- Consider *an isolated composite system* consisting of two subsystems, separated *by rigid, adiabatic and impermeable boundary.*

- Suppose the *internal boundary in made movable.*

- According *to entropy maximum principle* the rigid boundary can be *suddenly made to move* allowing the system to undergo a spontaneous change.

- The *energy of the system is constant and the entropy increase*. In the final equilibrium state *the pressure in both the subsystems will be identical.*

$$dU = dQ - dW$$

$$0 = (TdS) - VdP$$

dU=0, dQ= TdS, dw = d(PV)=VdP (Contant volume)

- According to *energy minimum principle*, the internal boundary can be *made to move*, while doing work on an external agent, allowing the system to undergo *a reversible and adiabatic process*. And *(isentropic system) and (constant volume)*

$$dU = dQ - dW \qquad\qquad dU = -VdP$$

$$dQ = TdS = 0$$

$$dW = VdP$$

- During the *entropy of the system remains constant and its energy decrease* by the amount of work done on the external agent. *In the final equilibrium state, the gas pressure in both the subsystem will be equal.*

Example 5

- ***An isolated composite system consisting of two subsystems a and b*** *which are separated from each other by **a rigid, adiabatic and impermeable boundary**. The extensive parameters of the subsystems are **Ua = 7.2 MJ, Va = 1m3, Na = 1 kmol, Ub = 6 MJ; Vb = 1m3, Nb = 1 kmol**. The fundamental relation **U=Uo(Vo/V)2/3*(No/N)-5/3 exp(-2So/3NoR) exp(2S/3NR)** where R = 8.314 kJ/kmol K and the subscript zero denotes reference state values, is valid for both the subsystems. If the internal boundary is made **diathermal**, **determine the equilibrium temperature**.*