LECTURE

2

CHE 415
Chemical Engineering Thermodynamics II

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Maxwell Equations

Learning Objectives for today's lecture

- At the end of this week's lecture, you should be able to:
  - Develop fundamental relations between commonly encountered thermodynamic properties
  - Express the properties that cannot be measured directly in terms of easily measurable properties.

Thermodynamic Property Relations for Open System

- For a single phase open system,

  nU = n(nS, nV, n_1, n_2, ……., n_i, …..),

  where n_i is the no. of moles of the chemical species, since materials may be added or taken from the system.
- The total differential of nU for the open system is therefore given by:

$$d(nU) = \left[\frac{\partial(nU)}{\partial(nS)}\right]_{nV,n} d(nS) + \left[\frac{\partial(nU)}{\partial(nV)}\right]_{nS,n} d(nV) + \sum\left[\left[\frac{\partial(nU)}{\partial(n_i)}\right]_{nS,nVnj}\right] dn_i \quad 25$$

  where the summation is over all species present in the system and subscript nj indicates that all mole numbers except the ith are held constant

- Setting $\mu = \left[\frac{\partial(nU)}{\partial(n_i)}\right]_{nS,nVnj}$
- By direct substitution of eqns.17 – 20 in eqn. 25, we have

$$\boldsymbol{d(nU) = \mathrm{T}d(nS) - Pd(nV) + \sum[\mu_i]dn_i} \quad \mathbf{26}$$

- Eqn.26 is **the fundamental property relation for a single phase fluid system, applicable to system of constant or variable mass and constant or variable composition.**

Relationships among the Thermodynamic Properties

- For a simple case of n = 1, Eqn. 26 becomes

$$dU = \mathrm{T}dS - PdV + \sum[\mu_i]dn_i \qquad 27$$

- Eqn.27 arrived at by purely formal manipulations, is **the Euler equation**, an equation that relates seven thermodynamic variables
- The quantity μ_i is called the chemical potential of component i, and it plays a vital role in phase and chemical equilibria.
- Similar relations could be derived for the other energy properties (i.e. H, A, and G) of an open system homogeneous fluid.

CLASS ACTIVITY 1

- Let's derive the Euler equation for the other energy properties of a fluid in an open system, i.e. for H, A and G. What would they look like. Bring out the similarities between them.

Maxwell Equation

- The equations that relate the partial derivatives of properties *P, v, T,* and *s* of a simple compressible system to each other are called the ***Maxwell relations***.
- For a 1 mole homogenous fluid of constant composition (i.e. n=1), we already established their fundamental property relation as

$$dU = TdS - PdV \qquad 28$$
$$dH = TdS + VdP \qquad 29$$
$$dA = -PdV - SdT \qquad 30$$
$$dG = VdP - SdT \qquad 31$$

- The total differentials of Eqns. 28 – 31 can also be given by
- $$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$
- $$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$
- $$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT$$
- $$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$$

Term-by term comparison of the pairs of Equation for dU, dH, dA and dG shows that

Maxwell Equation

- $\left[\frac{\partial(U)}{\partial(S)}\right]_V = \left[\frac{\partial(H)}{\partial(S)}\right]_P$ = T

and $\left[\frac{\partial(U)}{\partial(V)}\right]_S = \left[\frac{\partial(A)}{\partial(V)}\right]_T$ = - P

and $\left[\frac{\partial(H)}{\partial P}\right]_S = \left[\frac{\partial(G)}{\partial P}\right]_T$ = V

and $\left[\frac{\partial(A)}{\partial T}\right]_V = \left[\frac{\partial(G)}{\partial T}\right]_P$ = –S

Applying the reciprocating criterion for an exact differential equation:

If z = f(x,y), then the total differential of z is

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Or dz = Mdx + Ndy 32

Where $M = \left(\frac{\partial z}{\partial x}\right)_V$ and $N = \left(\frac{\partial z}{\partial y}\right)_x$

Further differentiation of M and N yields,

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial y \partial x} \quad \text{and} \quad \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial x \partial y}$$

Thus, $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$ 33

Maxwell Equation

- It is known that when the differential expression on the RHS of an equation of the form of Eqn.32 satisfies Eqn.33, it is said to be exact, and z can be expressed as a function of x and y.
- Application of Eqn.33 to eqns.28 – 31 (which are exact differential expressions), yields **the Maxwell Equations**.
- $$\left[\frac{\partial T}{\partial V}\right]_S = - \left[\frac{\partial P}{\partial S}\right]_V \qquad 34$$

and $$\left[\frac{\partial T}{\partial P}\right]_S = \left[\frac{\partial V}{\partial S}\right]_P \qquad 35$$

and $$\left[\frac{\partial P}{\partial T}\right]_V = \left[\frac{\partial S}{\partial V}\right]_T \qquad 36$$

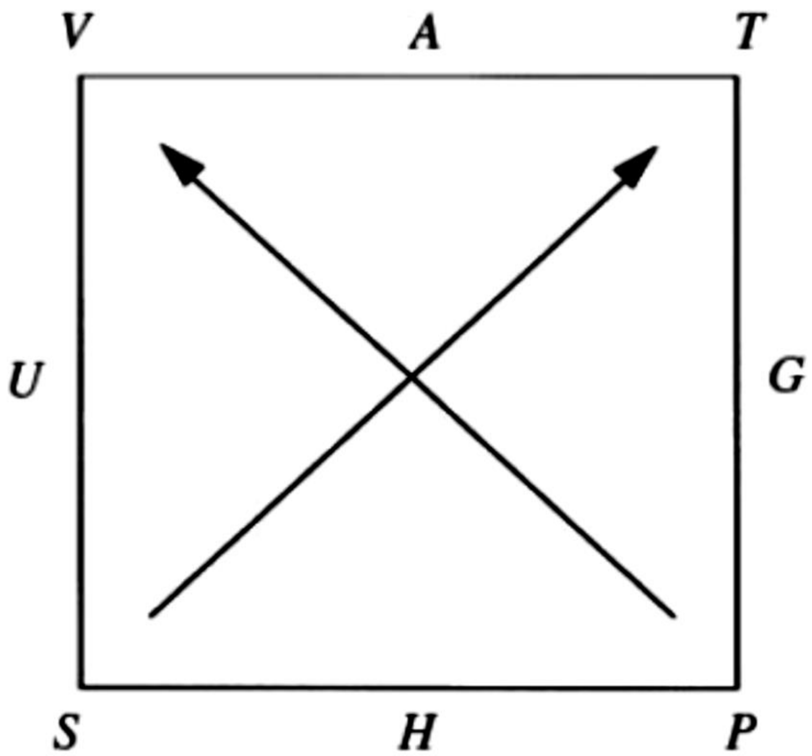
and $$\left[\frac{\partial V}{\partial T}\right]_P = - \left[\frac{\partial S}{\partial P}\right]_T \qquad 37$$

- *Maxwell's equations* are useful
  - ✓ in replacing unmeasurable quantities appearing in thermodynamic equations by measurable quantities.
  - ✓ Using these relations, the partial derivatives of entropy with respect to pressure and volume are expressed as derivatives possessing easily identifiable physical meaning.

Maxwell Equations and Mnemonic Diagram

CLASS ACTIVITY 2

Let’s show how the Maxwell Equation is arrived from first principle.



Mnemonic Diagram

- ✓ The sides of the squares are labelled with the energy properties in alphabetical order (*A, G, H,* and *U*) starting with the topside.
- ✓ The corners are labelled with the canonical variables of the energy properties in such a way that each energy property is flanked by its canonical variables.

Maxwell Equations and Mnemonic Diagram

The Mnemonic diagram can be used as a convenient tool for writing the differential equations for the energy properties as well as the Maxwell's equations.

- The differential equations contain the differentials of its natural variables and their coefficients.
- The differentials are obtained from the variables adjacent to the energy property under consideration, and the coefficients are obtained from the variables that are diametrically opposite to these variables.
- The sign of the coefficient is to be decided from the direction in which the arrows are pointing.
    - ✓ If the arrow is pointing away from the canonical variable, the coefficient is positive and
    - ✓ if the arrow is pointing towards the canonical variable, the coefficient is negative.

Maxwell Equations and Mnemonic Diagram

- To get Maxwell's equations from the Mnemonic diagram.
- Consider the topside of the square.
  - ✓ The partial derivative is formed by the canonical variables e.g. $(\partial T/\partial V)$.
  - ✓ The suffix to be used is the variable that is diametrically opposite to the first variable, i.e. S. Yielding $(\partial T/\partial V)_S$.
  - ✓ The other derivative is obtained from the opposite side of the square in a similar way, i.e. $(\partial P/\partial S)_V$.
  - ✓ Since the direction of arrows being opposite, i.e. towards T and away from P, the sign of the derivatives will be opposite.

CLASS ACTIVITY 3

Let's do some examples using the Mnemonic Diagram to the write the differential equations for the energy properties as well as derive the Maxwell's equations for a 1 mole homogenous fluid of constant composition..

THANK YOU

FOR

YOUR

ATTENTION!

ANY QUESTIONS?