

LECTURE

1

CHE 415

Chemical Engineering Thermodynamics II

Department of Chemical Engineering
College of Science and Engineering
Landmark University, Omu-Aran,
Kwara State.



**Thermodynamic
Properties of
Fluids**



Learning Objectives for today's lecture

- At the end of this lecture, students 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.

Review of ChE Thermodynamics I

- ❖ Recalling from CHE 325 on Properties of pure substances.
 - ❖ What is a pure substances?
- ❖ Review of the [PVT behaviour of pure substances](#).
- ❖ What can we remember?
 - ❖ [PV, TV and PT](#) curves of substances. What are there features?
- ❖ Equation of state of ideal and real gases
 - ❖ Cubic EOS
 - ❖ Van der Waal equation,
 - ❖ Benedict-Webb-Rubin equation,
 - ❖ Redlich-Kwong equation
 - ❖ Virial EOS (2nd and 3rd term truncations)
 - ❖ Generalized correlations
 - ❖ Generalised compressibility factor correlation
 - ❖ Generalised 2nd virial coefficient correlations
- ❖ First and Second laws of thermodynamics



Thermodynamic Properties of Fluids

❖ The why of thermodynamic Properties of Fluids

- ❖ Some thermodynamic properties can be measured directly, but many others cannot, (Give examples).
- ❖ It is necessary to develop some relations between these two groups so that the properties that cannot be measured directly can be evaluated.
- ❖ The derivations are based on the fact that properties are **point functions**, and the state of a simple, compressible system is completely specified by any two independent, **intensive properties**.



Thermodynamic Properties of Fluids

Thermodynamic properties of fluids can be classified into three broad groups:

□ Reference or fundamental Properties

- ✓ Also known as *primary properties*, these properties are the ones that are used to define the state of the system. They have absolute values, as against energy properties, which are measured relative to some arbitrary reference state. E.g. temperature, pressure, volume, entropy and composition (for solutions).

□ Energy Properties

- ✓ The four energy properties are the internal energy (U), enthalpy (H), the Helmholtz free energy (A), and the Gibbs free energy (G). All are extensive thermodynamic properties and are known relative to some reference state.

□ Derived Properties

- ✓ These are partial derivatives of energy properties or the reference properties. Examples include specific heat (C), coefficient of expansion (β), and coefficient of compressibility (k).
- ✓ Among the four energy properties, the internal energy and enthalpy were introduced in CHE 325. In CHE 415, **the Helmholtz work function and the Gibbs free energy** will be defined.



Relationships among the Thermodynamic Properties

- The 1st law for a closed system of n moles is given by:

$$d(nU) = dQ + dW \quad 1$$

- for a reversible process, $dW_{rev} = -Pd(nV)$ and $dQ = Td(nS)$

- It then follows that:

$$d(nU) = Td(nS) - Pd(nV) \quad 2$$

- Eqn.2 is applicable to reversible and irreversible processes, likewise the 1st and 2nd laws of thermodynamics are reflected.

- Other similar relations to Eqn.2 can be derived from the energy properties.

- ✓ Enthalpy was defined as: $H = U + PV \quad 3$

- ✓ Helmholtz energy: $A = U - TS \quad 4$

- ✓ And Gibbs energy as: $G = H - TS \quad 5$

- For n moles, Eqn.3 becomes $nH = nU + P(nV) \quad 6$

- Differentiating 6 yields

$$d(nH) = d(nU) + Pd(nV) + (nV)dP \quad 7$$

- Substituting (2) into (7) yields,

$$d(nH) = Td(nS) + (nV)dP \quad 8$$

Relationships among the Thermodynamic Properties

- Similarly from Eqns.4 and 5, we have:

$$d(nA) = -Pd(nV) - (nS)dT \quad 9$$

and

$$d(nG) = (nV)dP - (nS)dT \quad 10$$

- For a base case of $n = 1$ of a homogeneous fluid of constant composition, Eqn.2,8,9 and 10 simplify to:

$$dU = TdS - PdV \quad 11$$

$$dH = TdS + VdP \quad 12$$

$$dA = -PdV - SdT \quad 13$$

$$dG = VdP - SdT \quad 14$$

- Eqns. 11 – 14 are called the **Fundamental property relations** for a homogeneous fluid of constant composition.

- They are applicable to non reacting single liquid or gaseous phase systems.

- From eqn.2, $nU = n(nS, nV) \quad 15$

- The total differential of nU by definition is:

$$d(nU) = \left[\frac{\partial(nU)}{\partial(nS)} \right]_{nV,n} d(nS) + \left[\frac{\partial(nU)}{\partial(nV)} \right]_{nS,n} d(nV) \quad 16$$



Relationships among the Thermodynamic Properties

□ Comparing Eqns.2 and 16, it can be shown that:

$$\left[\frac{\partial(nU)}{\partial(nS)} \right]_{nV,n} = T \quad \text{and} \quad \left[\frac{\partial(nU)}{\partial(nV)} \right]_{nS,n} = P$$

□ Deriving similar relations, for Eqn.8 we have that:

$$\left[\frac{\partial(nH)}{\partial(nS)} \right]_{P,n} = T \quad \text{and} \quad \left[\frac{\partial(nH)}{\partial P} \right]_{nS,n} = V$$

For Eqn.9 we have that:

$$\left[\frac{\partial(nA)}{\partial(nV)} \right]_{T,n} = -P \quad \text{and} \quad \left[\frac{\partial(nA)}{\partial T} \right]_{nV,n} = -S$$

For Eqn.10 we have that:

$$\left[\frac{\partial(nG)}{\partial P} \right]_{T,n} = V \quad \text{and} \quad \left[\frac{\partial(nG)}{\partial T} \right]_{P,n} = -S$$

Thus, $\left[\frac{\partial(nU)}{\partial(nS)} \right]_{nV,n} = \left[\frac{\partial(nH)}{\partial(nS)} \right]_{P,n} = T$ 17

and $\left[\frac{\partial(nU)}{\partial(nV)} \right]_{nS,n} = - \left[\frac{\partial(nA)}{\partial(nV)} \right]_{T,n} = P$ 18

and $\left[\frac{\partial(nH)}{\partial P} \right]_{nS,n} = \left[\frac{\partial(nG)}{\partial P} \right]_{T,n} = V$ 19

and $\left[\frac{\partial(nA)}{\partial T} \right]_{nV,n} = \left[\frac{\partial(nG)}{\partial T} \right]_{P,n} = -S$ 20



Relationships among the Thermodynamic Properties

- For a single phase closed system, where $n = 1$, eqns.17 – 20 becomes

Thus,
$$\left[\frac{\partial U}{\partial S} \right]_V = \left[\frac{\partial H}{\partial S} \right]_P = T \quad 21$$

and
$$\left[\frac{\partial U}{\partial V} \right]_S = - \left[\frac{\partial A}{\partial V} \right]_T = P \quad 22$$

and
$$\left[\frac{\partial H}{\partial P} \right]_S = \left[\frac{\partial G}{\partial P} \right]_T = V \quad 23$$

and
$$\left[\frac{\partial A}{\partial T} \right]_V = \left[\frac{\partial G}{\partial T} \right]_P = -S \quad 24$$

For a single phase open system,

$$nU = n(nS, nV, n_1, n_2, \dots, n_i, \dots),$$

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:

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

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



**THANK YOU
FOR
YOUR
ATTENTION!
ANY QUESTIONS?**