

LECTURE

3

CHE 415

Chemical Engineering Thermodynamics II

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**Thermodynamic
Properties of
Two-Phase Systems**



Learning Objectives for today's lecture

- At the end of this week's lecture, you should be able to:
 - develop the Clapeyron equation and determine the enthalpy of vaporization from P , v , and T measurements alone.
 - Develop general relations for c_v , c_p , du , dh , and ds that are valid for all pure substances.



Application of Maxwell Equations

EXAMPLE: The molar volume of an organic liquid at 300 K and 1 bar is 0.1 m³/kmol and its coefficient of expansion is 1.25 x10⁻³ K⁻¹. What would be the change in entropy if the pressure is increased to 20 bar at 300 K?

Solution The coefficient of volume expansion is defined as

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

Since, this is equal to 1.25 x 10⁻³ K⁻¹,

$$\left(\frac{\partial V}{\partial T} \right)_P = 1.25 \times 10^{-3} V = 1.25 \times 10^{-4} \text{ m}^3/\text{kmol K}$$

Consider Maxwell's relation which gives

$$dS = - \left(\frac{\partial V}{\partial T} \right)_P dP$$

The change in entropy is

$$\Delta S = -1.25 \times 10^{-4} (P_2 - P_1) = -1.25 \times 10^{-4} (20.0 - 1.0) \times 10^5 = -237.5 \text{ J/kmol K}$$



Enthalpy and Entropy as functions of T and P.

- In expressing H and S as functions of T and P, the following derivatives are very useful:

- $\left(\frac{\partial H}{\partial T}\right)_P, \left(\frac{\partial S}{\partial T}\right)_P, \left(\frac{\partial H}{\partial P}\right)_T$ and $\left(\frac{\partial S}{\partial P}\right)_T$

- Since $dH = C_p dT$, it may be expressed as

- $$\left(\frac{\partial H}{\partial T}\right)_P = C_p \quad 2-1$$

- Also, we know that $dH = TdS + VdP$ 2-2

- Dividing Eqn.2-2 by dT and restricting the result to constant P,

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

- Combining this with Eqn.3-1 gives

- $$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T} \quad 2-3$$

- And from one of the Maxwell eqn. we have, $\left[\frac{\partial S}{\partial P}\right]_T = -\left[\frac{\partial V}{\partial T}\right]_P$

- The corresponding derivatives for the enthalpy is obtained by dividing Eqn.2-2 by dP and restriction to constant T

- $$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V \quad 2-4$$



Enthalpy and Entropy as functions of T and P...

□ Substituting * in Eqn.2-4 yields,

- $$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \quad 2-5$$

- Also if the fundamental relations chosen for H and S is given by

- $H = f(T, P)$ and $S = f(T, P)$,

- It follows that

- $$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

- $$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

- Substituting for the partial derivatives in these equations from previous derivations, we get

- $$dH = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P \right] dP \quad 2-6$$

- and
$$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

- But $\left(\frac{\partial V}{\partial T}\right)_P$ has the same meaning as volume expansivity for a compressible fluid, hence $\left(\frac{\partial V}{\partial T}\right)_P = \beta V$

- Hence
$$dS = \frac{C_P}{T} dT - \beta V dP \quad 2-7$$



Enthalpy and Entropy as functions of T and P.....

- and
$$dH = CPdT + [1 - \beta T]VdP$$
- Similarly,
$$\left(\frac{\partial S}{\partial P}\right)_T = -\beta V$$
- and
$$\left(\frac{\partial H}{\partial P}\right)_T = (1 - \beta T)V \quad 2-8$$
- These are general relations relating the enthalpy and entropy of homogenous fluids of constant composition to temperature and pressure.
- The pressure dependence of the internal energy can be obtained by differentiation of the equation $U = H - PV$
- $$\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T - V$$
- For $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$
- $$\left(\frac{\partial U}{\partial P}\right)_T = (\kappa P - \beta T)V \quad 2-9$$
- Where κ is the isothermal compressibility.
- Eqns.2-6 to 2-9 which require values of β and κ , are usually applied only to liquids.



Internal Energy and Entropy as functions of T and V

- ❑ T and V are more convenient independent variables than do T and P.
- ❑ The most useful property relations for U and S are the derivatives of
- ❑ $\left(\frac{\partial U}{\partial T}\right)_V$, $\left(\frac{\partial S}{\partial T}\right)_V$, $\left(\frac{\partial U}{\partial V}\right)_T$ and $\left(\frac{\partial S}{\partial V}\right)_T$
- ❑ Since $dU = TdS - PdV$
- ❑ Dividing through by dT and restricting to constant volume yields
- ❑ $\left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V$
- ❑ and dividing through by dV and restricting to constant T yields
- ❑ $\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P$
- ❑ From first law expression for closed system at constant volume
- ❑ $C_V = \left(\frac{\partial U}{\partial T}\right)_V$
- ❑ Hence, $\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$ 2-10
- ❑ Also from one of Maxwell equation $\left[\frac{\partial P}{\partial T}\right]_V = \left[\frac{\partial S}{\partial V}\right]_T$
- ❑ Thus, $\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$ 2-11



Internal Energy and Entropy as functions of T and V

- Also if the fundamental relations chosen for U and S is given by
- $H = f(T,V)$ and $S = f(T,V)$,
- It follows that

- $$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

- $$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

- Substituting for the partial derivatives in these equations from previous derivations, we get

- $$dU = C_V dT + \left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right] dV \quad 2-12$$

- and
$$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV \quad 2-13$$

- But $\left(\frac{\partial P}{\partial T}\right)_V$ has the same meaning as volume expansivity for a compressible fluid, hence $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa}$

- Hence
$$dS = \frac{C_V}{T} dT + \frac{\beta}{\kappa} dV \quad 2-14$$

- And
$$dU = C_V dT + \left[T \frac{\beta}{\kappa} - P \right] dV \quad 2-15$$



Thermodynamic Properties of Two-Phase Systems

- ❑ From PVT diagram, a phase transition at constant T and P occurs whenever the phase boundaries is crossed, hence the values of the extensive properties (V, U, H, S) changes abruptly.
- ❑ The values of these properties for a saturated liquid is very different from that for saturated vapour at the same T and P, except G.
- ❑ G for a pure specie remains the same during a phase transition.
- ❑ Hence for system at equilibrium, $dG = 0$. this is a necessary condition.
- ❑ For two phases α and β of a pure specie co-existing at equilibrium,
- ❑
$$G^\alpha = G^\beta \quad 2-16$$
- ❑ Where G^α and G^β are molar Gibbs energies of the individual phases.
- ❑ If the temperature of a 2-phase system is changed, the pressure must also change in accordance with the relation between vapour pressure and temperature for the system to remain in equilibrium,
- ❑ Hence
$$dG^\alpha = dG^\beta \quad 2-17$$
- ❑ But $dG = VdP - SdT$
- ❑ Substituting the expression for $dG^\alpha = dG^\beta$ we have
- ❑
$$V^\alpha dP^{\text{sat}} - S^\alpha dT = V^\beta dP^{\text{sat}} - S^\beta dT \quad 2-18$$



Thermodynamic Properties of Two-Phase Systems

- Upon rearrangement, Eqn.2-18 becomes,
- Substituting the expression for $dG^\alpha = dG^\beta$ we have

$$\square \quad \frac{dP^{sat}}{dT} = \frac{s^\beta - s^\alpha}{V^\beta - V^\alpha} = \frac{\Delta S^{\alpha\beta}}{\Delta V^{\alpha\beta}} \quad 2-19$$

- $\Delta S^{\alpha\beta}$ and $\Delta V^{\alpha\beta}$ are the changes which occur when a unit amount of a pure chemical specie is transferred from phase α to phase β at the equilibrium T and P.

$$\square \quad \text{Also since} \quad dH = TdS + VdP$$

- Integrating this equation for a phase transition yields the latent heat

$$\square \quad \Delta H^{\alpha\beta} = T\Delta S^{\alpha\beta} \quad \text{and} \quad \Delta S^{\alpha\beta} = \frac{\Delta H^{\alpha\beta}}{T} \quad 2-20$$

- Substituting in eqn.2-19 yields,

$$\square \quad \frac{dP^{sat}}{dT} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}} \quad 2-21$$

- Eqn.2-21 is called **the Clapeyron equation**. It provides vital connection between properties of different phases.

- For phase transition from liquid (l) to vapour (v), the Clapeyron equation is written as

$$\square \quad \frac{dP^{sat}}{dT} = \frac{\Delta H^{lv}}{T\Delta V^{lv}} \quad 2-22$$



Thermodynamic Properties of Two-Phase Systems

- If the vapour phase is assumed to be an ideal gas, and the molar volume of the liquid is negligible compared with that of the vapour, the Clapeyron equation is modified as thus,

- $$\Delta V^{\text{vap}} = V^{\text{g}} \Delta V^{\text{vap}} = V^{\text{g}} = \frac{RT}{p^{\text{sat}}}$$

- Eqn.2-22 then becomes,

- $$\frac{dp^{\text{sat}}}{dT} = \frac{\Delta H^{\text{vap}}}{RT^2/p^{\text{sat}}} \quad 2-22a$$

- $$\frac{dp^{\text{sat}}/p^{\text{sat}}}{dT/T^2} = \frac{\Delta H^{\text{vap}}}{R} \quad 2-22b$$

- $$\Delta H^{\text{vap}} = -R \frac{d \ln p^{\text{sat}}}{d(1/T)} \quad 2-22c$$

- Eqn.2-22c is called **the Clausius-Clapeyron equation**. It relates the latent heat of vapourization directly to the vapour pressure vs T curve.

- $$d \ln p^{\text{sat}} = \frac{\Delta H^{\text{vap}}}{R} d \left(\frac{1}{T} \right) \quad 2-22d$$

- A plot of $\ln p^{\text{sat}}$ vs $1/T$ gives the value of the slope as $\Delta H^{\text{vap}}/R$.
- Integration of Eqn.2-22d yields,



Thermodynamic Properties of Two-Phase Systems

$$\ln\left(\frac{P_2}{P_1}\right)_{\text{sat}} \cong \frac{h_{fg}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)_{\text{sat}}$$

- where $h_{fg} = \Delta H^{\text{vap}}$
- Other correlations of Eqn.2-22d are
- $$\ln P^{\text{sat}} = A - \frac{B}{T} \quad 2-23a$$
 - ✓ A and B are constants for specific species (though less accurate)
- There is also
$$\ln P^{\text{sat}} = A - \frac{B}{T+C} \quad 2-23b$$
 - ✓ A, B and C are constants
- This is the Antoine equation provides a more satisfactory form, and it is more widely used.
- For high accuracy, we have
- $$\ln P^{\text{sat}} = A - \frac{B}{T+C} + DT + E \ln T, \quad 2-23c$$
 - ✓ A, B, C, D and E are constants (difficult to evaluate)
- ✓ These Eqns are used to estimate the saturation vapour pressure of a substance.



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