

LECTURE

4

CHE 415

Chemical Engineering Thermodynamics II

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**Properties of
Two-Phase Systems
and Phase
Equilibrium**



Learning Objectives for today's lecture

- At the end of this week's lecture, you should be able to:
 - Use thermodynamic tables to calculate thermodynamic properties of two-phase systems.
 - Develop thermodynamic relations for multi-component systems
 - Conceptualize the various criteria for phase equilibria.



Two-Phase Liquid/Vapour Systems

□ When a system consists of saturated vapour and saturated liquid phases coexisting in equilibrium, the total value of any extensive property of the two-phase system is the sum of the total properties of the phases.

□ For volume,

$$\square \quad nV = n^L V^L + n^V V^V \quad 2-24$$

□ Where V is the system molar volume and n , the total number of moles

$$n = n^L + n^V$$

□ Dividing eqn.2-24 by n , yields

$$\square \quad V = x^L V^L + x^V V^V$$

□ where x^L and x^V represent the fractions of the total system that are liquid (or moisture) and vapour (or quality, dryness fraction).

□ Since $x^L = 1 - x^V$

$$\square \quad V = (1-x^V)V^L + x^V V^V$$

□ x^V is called the quality of the mixture.

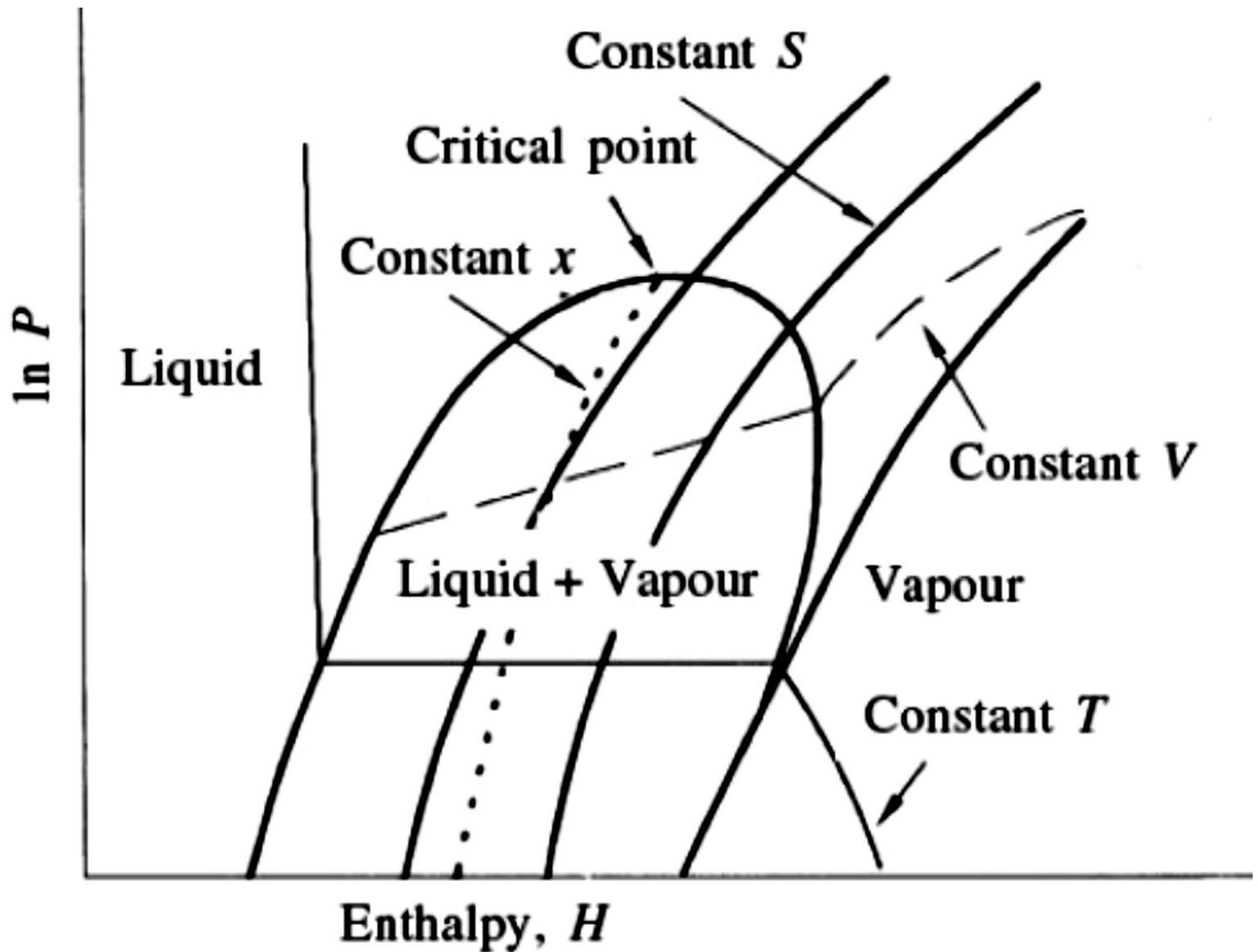
□ Analogous eqn can be written for the other extensive thermodynamic properties (U,H,S etc),

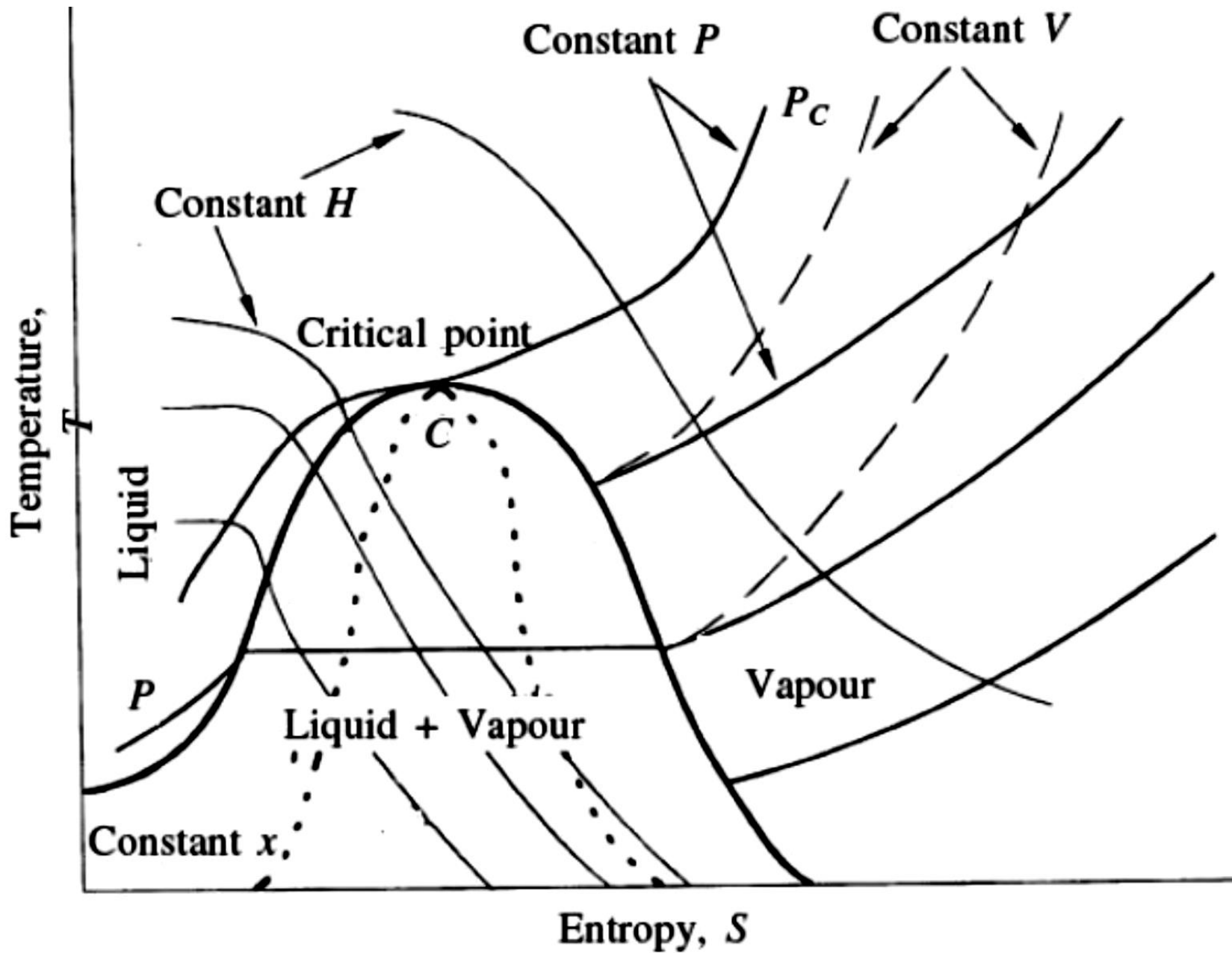
$$\square \quad M = (1-x^V)M^L + x^V M^V$$

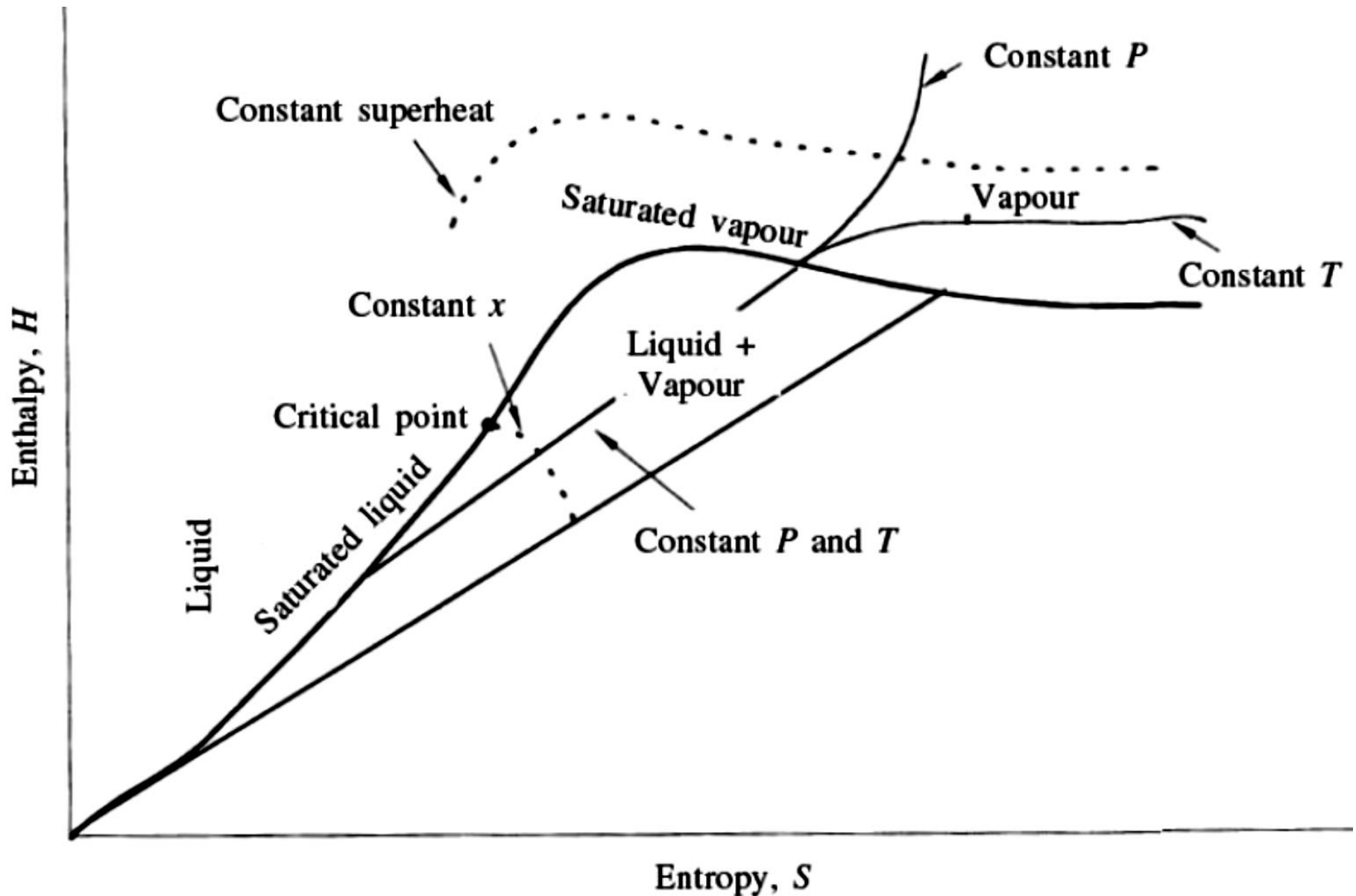
Two-Phase Liquid/Vapour Systems

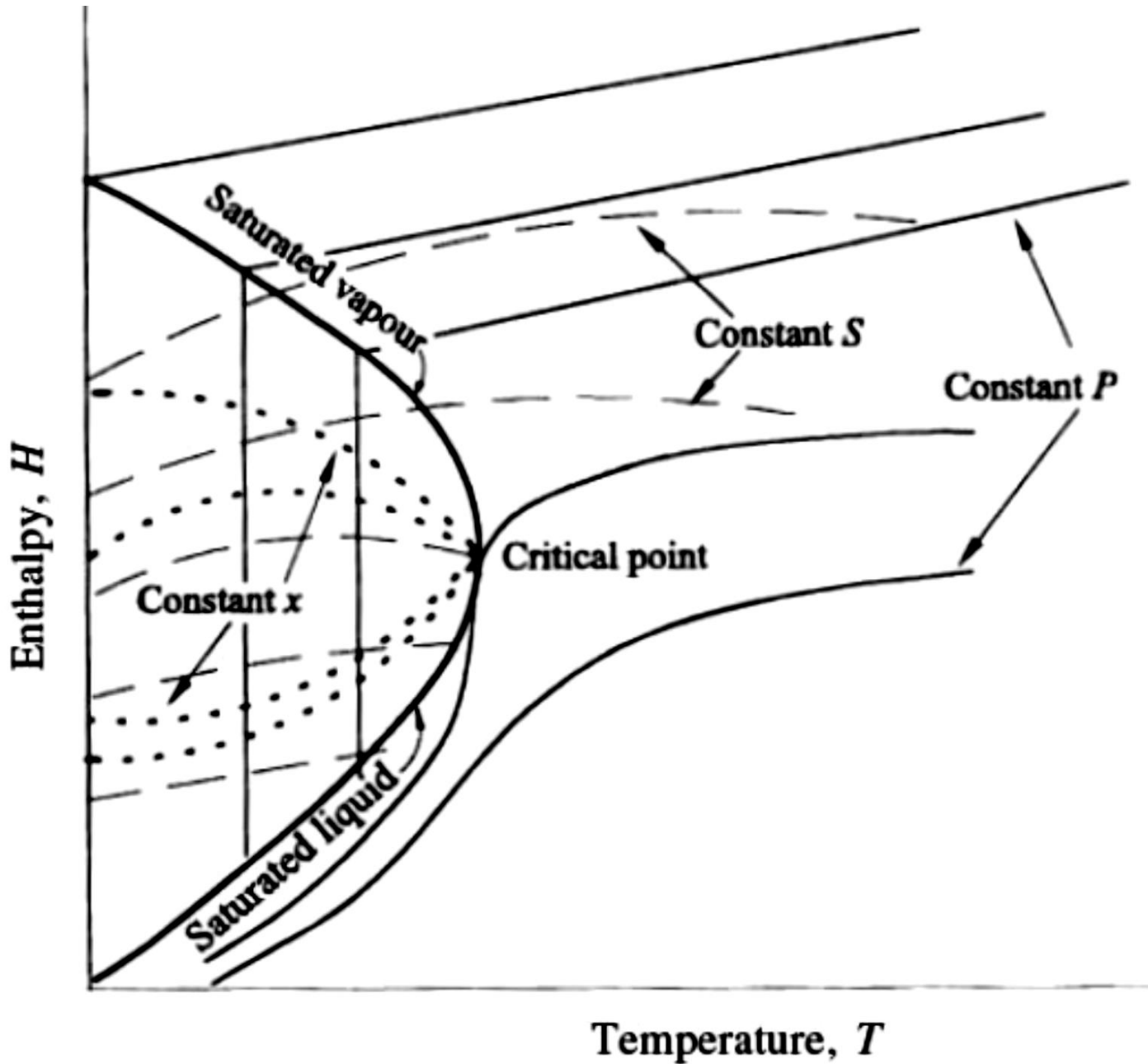
- ❑ Thermodynamic charts and tables are used to present values of these thermodynamic properties at varying conditions of temperature and pressure.
- ❑ The charts/tables represent the T,P,V,U,H and S properties of a substance on a single plot.
- ❑ The most common ones are:
 - ✓ [T-S chart](#)
 - ✓ [P-H chart](#)
 - ✓ [H-S \(Mollier diagram\)](#)
 - ✓ [H-T chart](#) etc.
- ❑ The Steam table is the thermodynamic property tables for saturated water and steam.

- ❑ **NOW: OPERATION SHOW ME YOUR STEAM TABLE. IF YOU DON'T HAVE, COME AND SIT ON THE FLOOR IN FRONT OF THE CLASS OR YOU LEAVE THE CLASS NOW.**
- ❑ **HOW DO WE USE THE [STEAM TABLE](#)?**











Two-Phase Liquid/Vapour Systems

EXAMPLE:

Superheated steam originally at 1000 kPa and 260°C expands through a nozzle to an exhaust pressure 200 kPa. Assuming the process is reversible and adiabatic and that equilibrium is attained, determine the state of the steam at the exit of the nozzle.

- ❑ Solution:
- ❑ NB: Reversible and adiabatic process implies constant entropy, hence $dS = 0$, i.e. $S_2 = S_1$
- ❑ Properties of initial condition include
- ❑ $T_1 = 260^\circ\text{C}$, $P_1 = 1000$ kPa. From the steam table we read the values for H_1 and S_1
- ❑ $H_1 = 2965.2$ kJ/kg and $S_1 = 6.9680$ kJ/kgK
- ❑ Condition at the exit of the nozzle, only P_2 is known. We need to determine S_2 , H_2 and x^V
- ❑ Since the process is reversible and adiabatic, $S_2 = S_1$: 6.968 kJ/kgK, But at $P_2 = 200$ kPa, entropy value is greater than S_2 , thus the final state is in the 2-phase region.

Two-Phase Liquid/Vapour Systems

- ❑ So we carry out an entropy balance for the system;
- ❑
$$S = (1-x^V)S^L + x^V S^V$$
- ❑ From the steam table, find values for S^L and S^V
- ❑ (these are entropy values for saturated liquid and vapour at 200 kPa)
- ❑ $S^L = 1.5301$ kJ/kgK, $S^V = 7.1268$ kJ/kgK:
- ❑ Substituting in the entropy balance expression,
- ❑
$$6.9680 = 1.5301(1 - x^V) + x^V(7.1268)$$
- ❑
$$x^V = 0.9716$$
- ❑ This implies that the system is a mixture of liquid and vapour with 97.16% vapour and 2.84% liquid
- ❑ To obtain the enthalpy, we write the enthalpy balance expression,
- ❑
$$H = (1-x^V)H^L + x^V H^V$$
- ❑ Similarly we read the values of H^L and H^V which are the enthalpy values for the saturated liquid and vapour at 200 kPa respectively.
- ❑ $H^L = 504.7$ kJ/kg and $H^V = 2706.7$ kJ/kg
- ❑ Substituting for all known values in the enthalpy balance expression,
- ❑
$$H = (1 - 0.9716)*504.7 + 0.9716 * 2706.7$$
- ❑
$$H = 2644.2$$
 kJ/kg
- ❑ What will T_2 value be???

SOME PRACTICE QUESTIONS

1. Steam at 2,100 kPa and 260°C expands at constant enthalpy (as in a throttling process) to 125 kPa. What is the temperature of the steam in its final state and what is its entropy change? What would be the final temperature and entropy change for an ideal gas?
2. A vessel contains 1 kg of H₂O as liquid and vapor in equilibrium at 1,000 kPa. If the vapor occupies 70% of the volume of the vessel, determine H and S for the 1 kg of H₂O.
3. A vessel of 0.15-m³ volume containing saturated-vapor steam at 150°C is cooled to 30°C. Determine the final volume and mass of *liquid* water in the vessel.
4. Wet steam at 1,100 kPa expands at constant enthalpy (as in a throttling process) to 101.33 kPa, where its temperature is 105°C. What is the quality of the steam in its initial state?
5. Wet steam at 230°C has a density of 0.025 g cm⁻³. Determine x , H , and S .
6. Superheated steam at 500 kPa and 300°C expands isentropically to 50 kPa. What is its final enthalpy?
7. A two-phase system of liquid water and water vapor in equilibrium at 8,000 kPa consists of equal volumes of liquid and vapor. If the total volume $V^f = 0.15$ m³, what is the total enthalpy H^f and what is the total entropy S^f ?



PHASE EQUILIBRIA

- A system is said to be in *equilibrium* if no changes occur within the system when it is isolated from its surroundings.
- An isolated system is in
 - *mechanical equilibrium* if no changes occur in pressure,
 - *thermal equilibrium* if no changes occur in temperature,
 - *phase equilibrium* if no transformations occur from one phase to another,
 - *chemical equilibrium* if no changes occur in the chemical composition of the system.
- The conditions of mechanical and thermal equilibrium are straightforward, but the conditions of chemical and phase equilibrium can be rather involved.



Thermodynamic Property Relations for Homogenous Mixtures (Solution Thermodynamics)

- ❑ Thermodynamics can be applied to multi-component systems of either gaseous or liquids mixtures..
- ❑ Multi-component systems undergo composition changes as a result of:
 - ❑ mixing or separation processes,
 - ❑ transfer of species from one phase to another (diffusion/mass transfer),
 - ❑ chemical reaction
- ❑ Properties of such system, therefore depend on composition as well as temperature and pressure.
- ❑ The fundamental property relation for homogenous system of variable compositions as given earlier is:
 - ❑ $d(nU) = Td(nS) - Pd(nV) + \sum[\mu_i]dn_i$ **1**
 - ❑ Based on the definitions of H, A and G, we could have
 - ❑ $d(nH) = Td(nS) + (nV)dP + \sum[\mu_i]dn_i$ **2**
 - ❑ $d(nA) = -(nS)dT - Pd(nV) + \sum[\mu_i]dn_i$ **3**
 - ❑ $d(nG) = -(nS)dT + (nV)dP + \sum[\mu_i]dn_i$ **4**
- ❑ Eqn.4 is the foundation eqn. upon which the structure of solution thermodynamics (i.e. phase equilibrium) is built.



Solution Thermodynamics....

- When $n = 1$ and $n_i = x_i$, eqn.4 becomes,

- $$dG = VdP - SdT + \sum[\mu_i]dx_i \quad 5$$

- hence, $G = G(P, T, x_1, x_2, \dots, x_i, \dots)$

- NB, $\sum_i x_i = 1$, as earlier done, it thus imply from Eqn.5 that

- $$S = - \left[\frac{\partial G}{\partial T} \right]_{P, x} \quad \text{and} \quad V = \left[\frac{\partial G}{\partial P} \right]_{T, x}$$

- For a 2-phase closed system in equilibrium, from eqn.4, we have

- $$d(nG)^\alpha = (nV)^\alpha dP - (nS)^\alpha dT + \sum_i \mu_i^\alpha dn_i^\alpha \quad 6$$

- and
$$d(nG)^\beta = (nV)^\beta dP - (nS)^\beta dT + \sum_i \mu_i^\beta dn_i^\beta \quad 7$$

- Where α and β identify the phases.

- Expressing the total system property by an equation of the form

- $$nM = (nM)^\alpha + (nM)^\beta \quad 8$$

- The summation of (6) and (7) is given by

- $$d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i^\alpha dn_i^\alpha + \sum_i \mu_i^\beta dn_i^\beta \quad 9$$

- For a closed system

- $$d(nG) = (nV)dP - (nS)dT$$

- Hence
$$\sum_i \mu_i^\alpha dn_i^\alpha + \sum_i \mu_i^\beta dn_i^\beta = 0 \quad 10$$



Solution Thermodynamics....

❑ For mass conservation,

$$\text{❑} \quad dn_i^\alpha = - dn_i^\beta \quad 11$$

❑ Since they result from mass transfer between the phases

$$\text{❑} \quad \sum_i (\mu_i^\alpha - \mu_i^\beta) dn_i^\alpha = 0 \quad 12$$

❑ For eqn 12 to be true, $\mu_i^\alpha - \mu_i^\beta = 0$, and

$$\text{❑} \quad \mu_i^\alpha = \mu_i^\beta \text{ for } (i = 1, 2, \dots, N) \quad N = \text{no of species.}$$

❑ Generally, the equality of chemical potential for π -phases is

$$\text{❑} \quad \mu_i^\alpha = \mu_i^\beta = \dots = \mu_i^\pi \text{ for } (i = 1, 2, \dots, N)$$

❑ Hence, **multiple phases at the same temperature and pressure are in equilibrium when the chemical potential of each species is the same in all phases.**



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