

# **PVT introduction**

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# Outline

- ✓ Phase diagram
- ✓ Equation of states
- ✓ Flash calculation

# Phase Diagrams

*A picture is worth a thousand words!*

1) Pure-component systems

graphical method

2) Mixtures

large amount of information

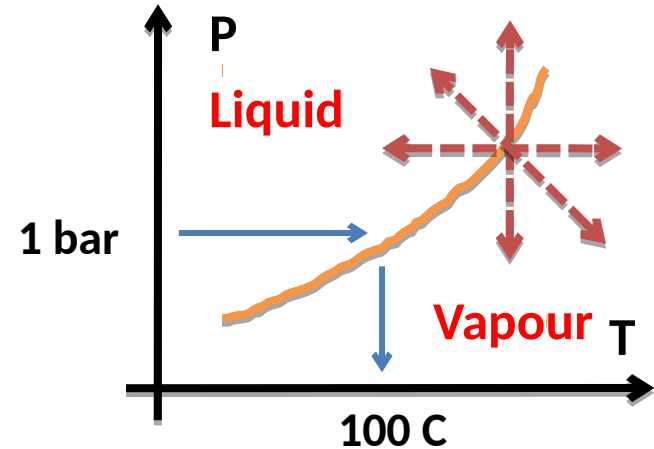
more components, more the complexity

**P-T**    **P-V**

# Phase Diagrams - Pure component

– Water! behavior at different conditions?

- $T_b \uparrow \rightarrow P_b \uparrow$
- dew point curve and the bubble point curve



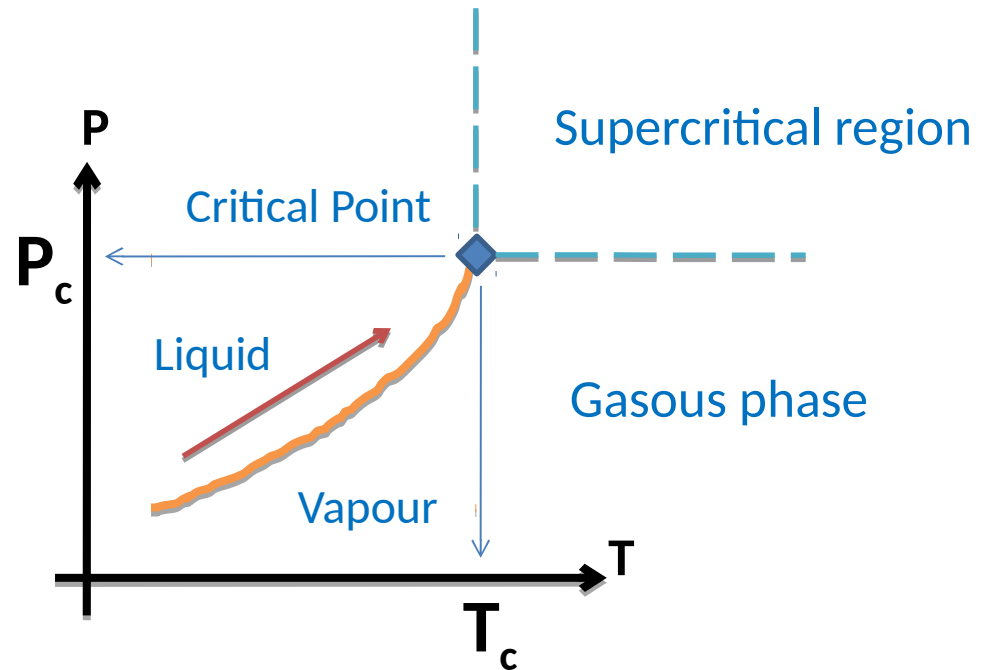
**Dew Point:** The pressure and temperature condition at which a droplet exists in equilibrium with a vapor system.

**Bubble Point:** The pressure and temperature condition at which the system is all liquid, and in equilibrium with a bubble of gas.

# Phase Diagrams - Pure component

## - Critical point

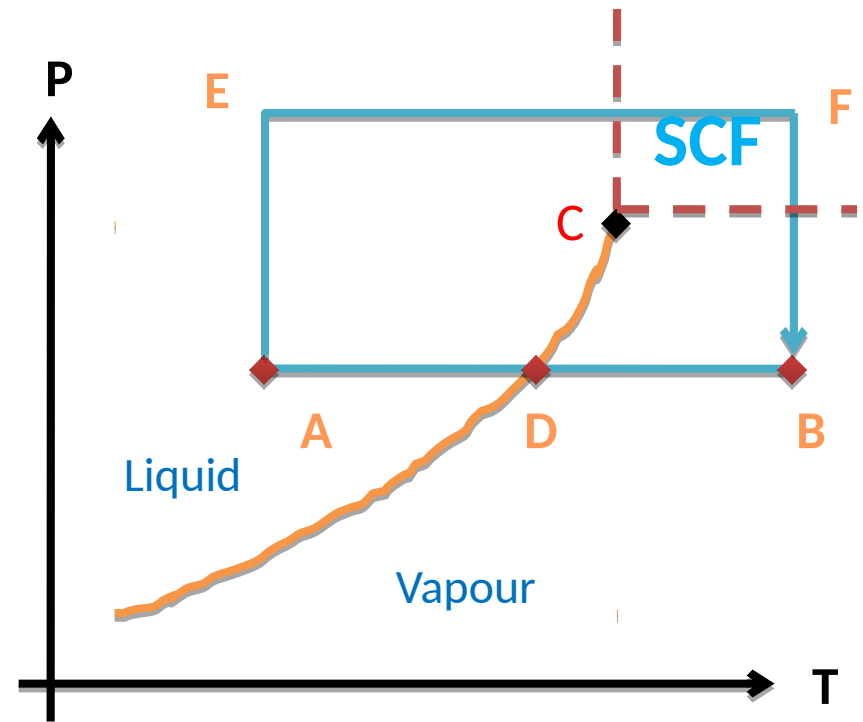
liquid and gas are in equilibrium along the vapor pressure curve.



✓ Temperature and pressure for which liquid and vapor are no longer distinguishable.

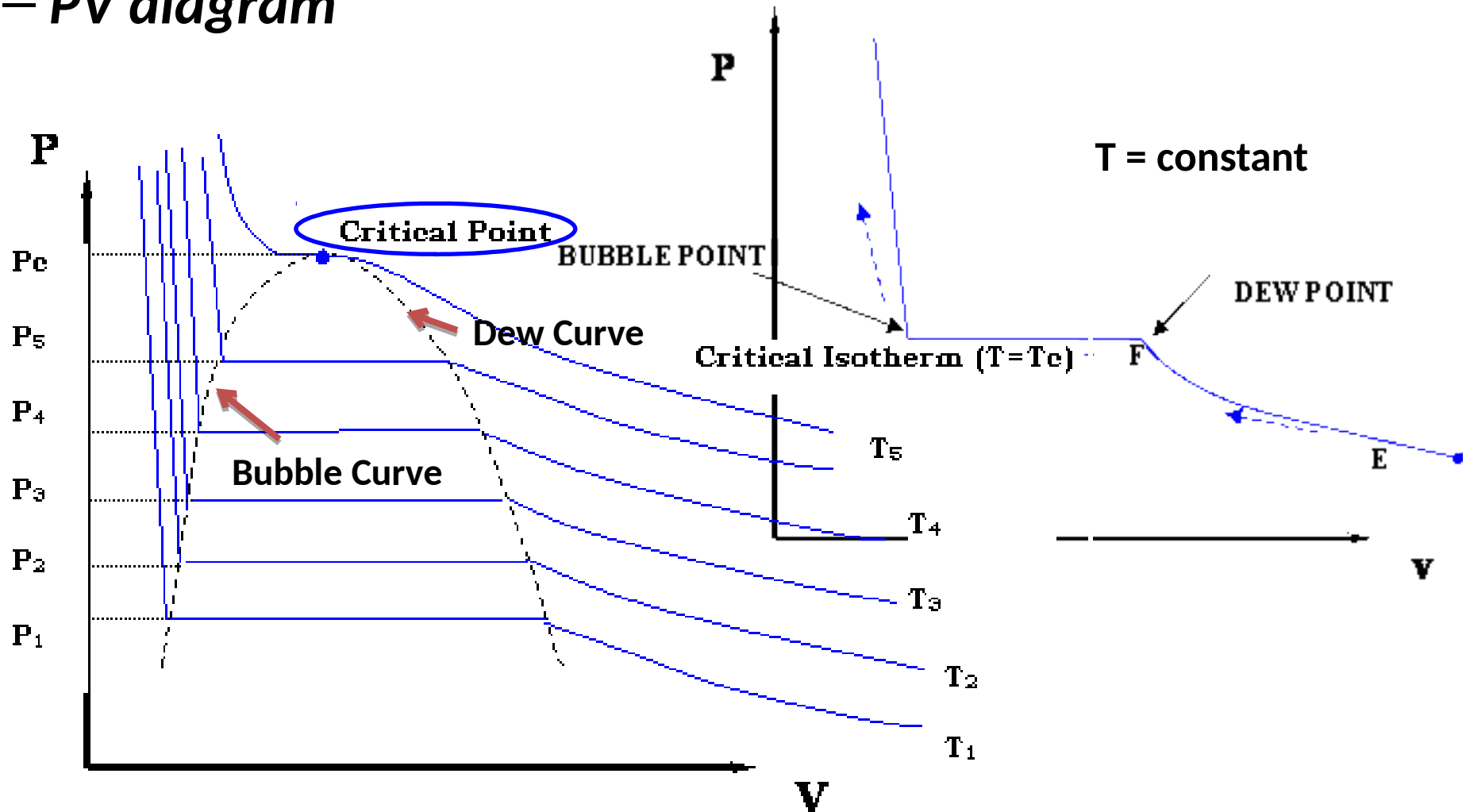
# Phase Diagrams - Pure component

- *Isobaric heating*
- *A path without phase change*
  - *liquid, or high-density (A) to a gas, or low-density (B)*
- *Supercritical fluid (SCF)*
- **CO<sub>2</sub>**
  - **31 °C, 73.8 bar**
  - *expanding to fill its container like a gas but with a density like that of a liquid!*
  - SC-CO<sub>2</sub> may act **differently!!** when neighboring hydrocarbon

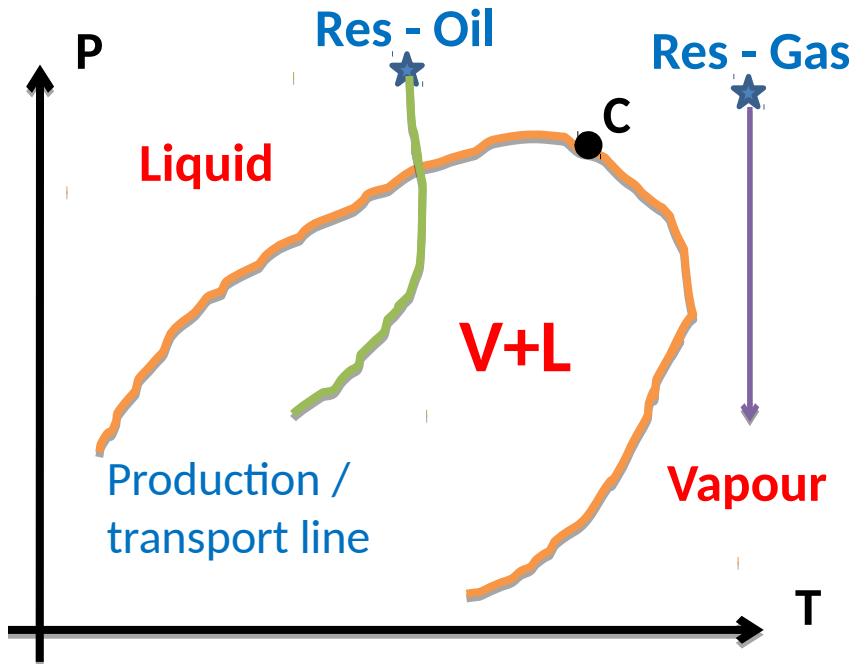


# Phase Diagrams - Pure component

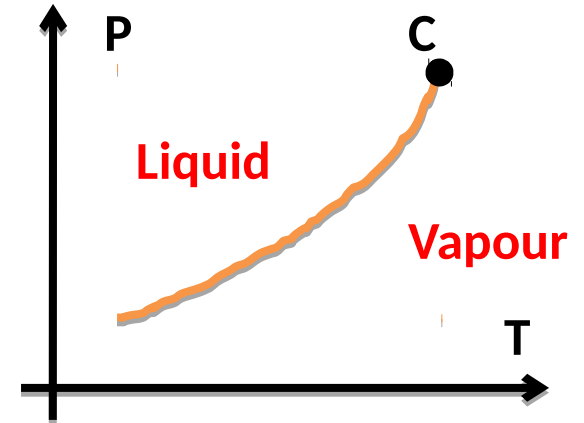
- *PV diagram*



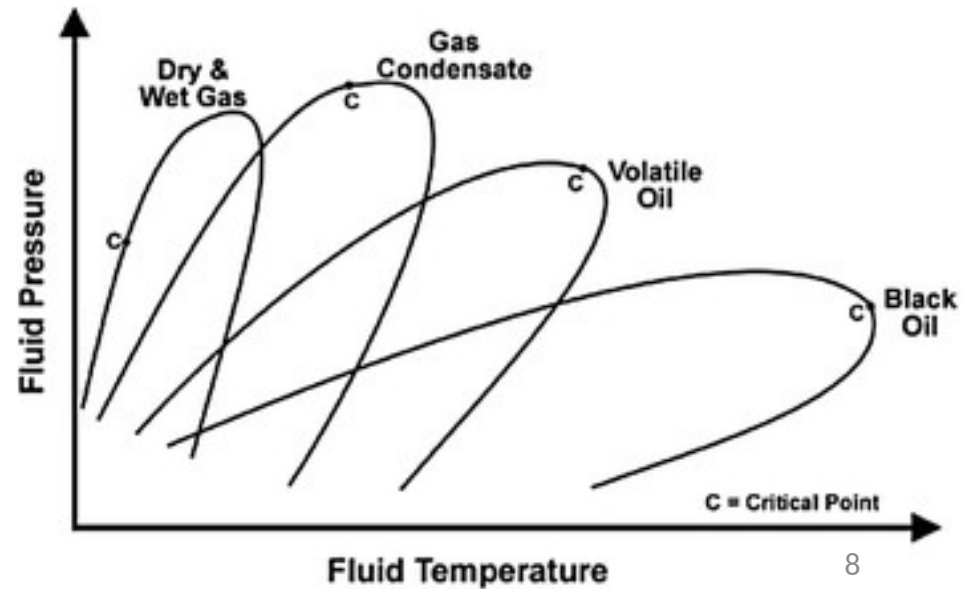
# Phase Diagrams - mixture



← mixture



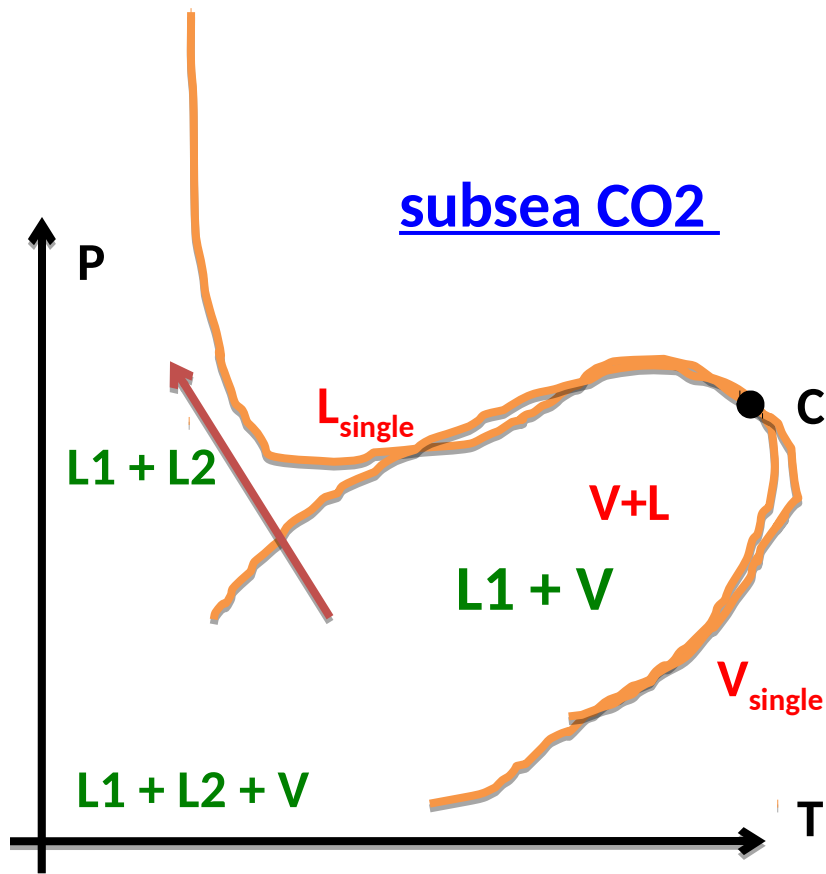
Fluid	Composition
Dry gas	C1
Wet gas	C1-C6
Gas condensate	C1-C8
Volatile oil	C1-C12
Black oil	C1-C20+
Heavey oil	> C20+





# Phase Diagrams ?

? Is this wrong, and it is just not converged?  
Do we have such a this fluid system?



Hydrocarbon/ $\text{CO}_2$   
high content

oil phase (L1)

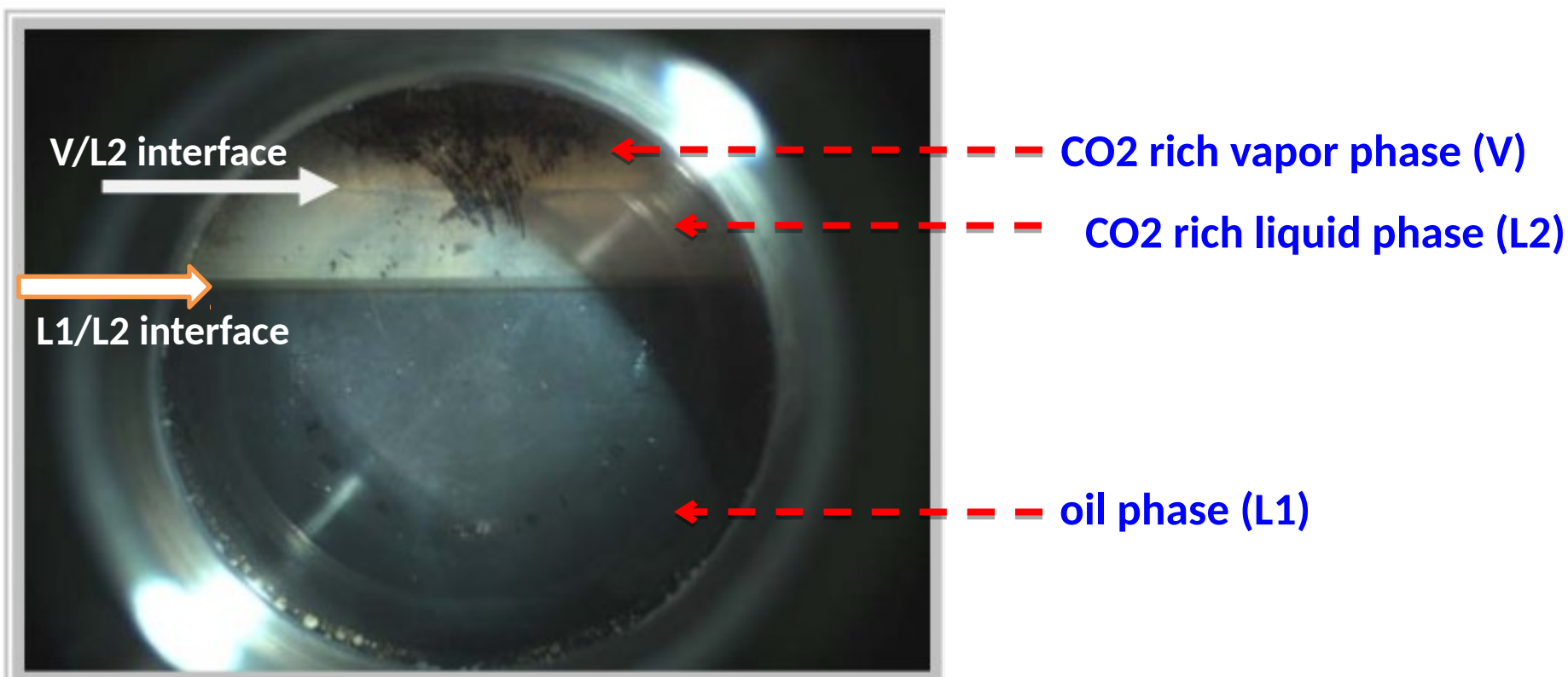
CO2 rich vapor phase (V)

CO2 rich Liquid phase (L2)

SPE 166270

### Investigation of Miscibility Behavior of CO<sub>2</sub> rich Hydrocarbon Systems – With Application for Gas Injection EOR

Niels Lindeloff, Kristian Mogensen, Mærsk Oil, Karen Schou Pedersen, Peter Tybjerg, Calsep, Rashed Noman, Qatar Petroleum



**Figure 2** Example of observed three-phase behavior at 1,315 psia and 100 °F for Oil B with 225% CO<sub>2</sub> added. Arrow indicate vapor - liquid interface.

# Equations of State

- The principal thermodynamic models are the equations of state (EoS).
- **Phase behavior data:** Laboratory measurements, expensive; Field data, you would lose valuable resources or have to stop operations to make your observations.
- Why do we need an Equation of State? To define the *state of the system* and to determine the *properties* of the system *at that state*.
- Given a fluid, with EOS, possible to predict its behavior at any condition of pressure, temperature and volume (P-V-T).
- In other words, we want to describe the P-V-T behavior *of fluids* in general.

# Equations of State - ideal

- Negligible interactions between the molecules,
- Its molecules occupy no volume (negligible molecular volume),
- Collisions between molecules are perfectly elastic — this is, no energy is lost after colliding.
- ideal behavior may be approached by real gases at low P and high T, where the distance between any pair of gas molecules is great.

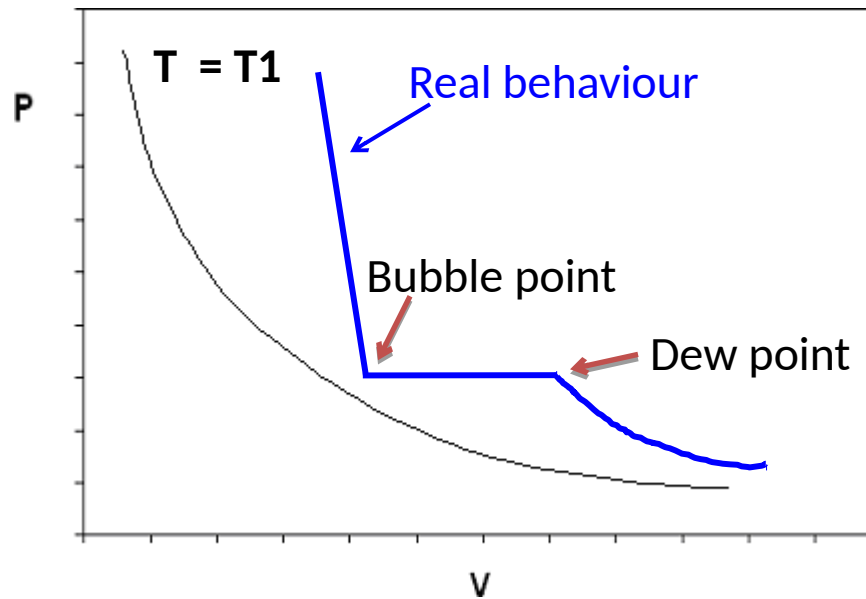
$$Pv = nRT$$

$$v \propto \frac{1}{P} \text{ (at constant temperature)}$$

$$v \propto T \text{ (at constant pressure)}$$

$$\rho = \frac{P}{RT}$$

# Equations of State - ideal

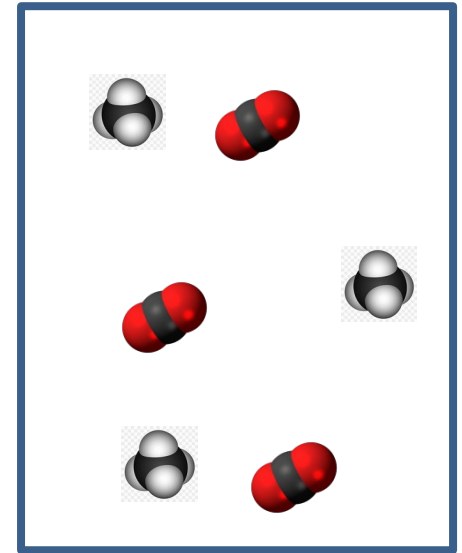


# Equations of State - Cubic Behavior

~~Dimensionless point!~~

~~Particles do not interact when they collide (elastic collision)~~

HP - LT



**a** Depends on the strength of the attraction

**b** Correction for the volume occupies by the molecule itself

van der Waals<sup>3</sup> (vdW)

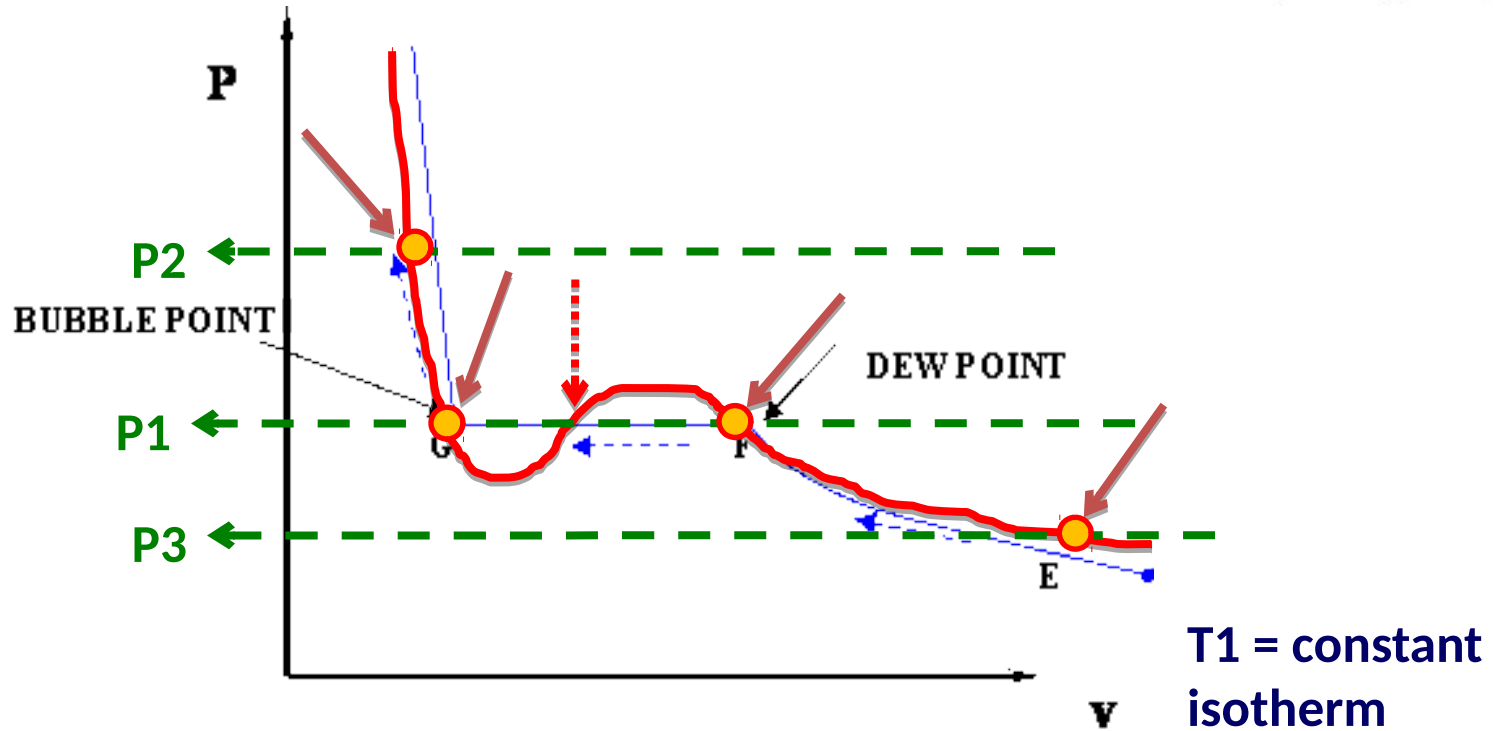
$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$a = \frac{27 (RT_c)^2}{64 P_c}$$

$$b = \frac{1 RT_c}{8 P_c}$$

# Equations of State - Cubic Behavior

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$



# Equations of State – Cubic EOS

Soave–Redlich–Kwong (SRK)

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)}$$

$$a_c = 0.42748 \frac{(RT_c)^2}{P_c}$$

$$b = 0.08664 \frac{RT_c}{P_c}$$

Soave<sup>5</sup>

$$a(T) = a_c [1 + m(1 - \sqrt{T_r})]^2$$

$$m = 0.48 + 1.574\omega - 0.176\omega^2$$

Peng–Robinson (PR)

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + b(V-b)}$$

$$a_c = 0.45724 \frac{(RT_c)^2}{P_c}$$

$$b = 0.07780 \frac{RT_c}{P_c}$$

Peng and Robinson<sup>6</sup>

$$a(T) = a_c [1 + m(1 - \sqrt{T_r})]^2$$

$$m = 0.37464 + 1.54226\omega$$

$$-0.26992\omega^2$$

$$\omega = -\log P_r^{sat} |_{T_r=0.7} - 1.00$$

where  $P_r^{sat}$  is the reduced vapor pressure ( $= P^{sat}/P_c$ ).

$$a = \sum_{i=1}^n \sum_{j=1}^n x_i x_j a_{ij}$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij})$$

CO<sub>2</sub> / hydrocarbon

$$b = \sum_{i=1}^n x_i b_i$$

mixing rules



# Advantages of cubic EoS

- ✓ They are simple models capable of fast calculations.
- ✓ They are applicable over a wide range of pressures and temperatures.
- ✓ They are capable of describing properties of compounds in both liquid and vapor phases, and can therefore be used to predict phase equilibrium properties, such as vapor pressure.
- ✓ There is no need, in most cases, for more than one interaction parameter for gas-hydrocarbons and good correlations for such mixtures are obtained.
- ✓ Satisfactory results are obtained both for low- and high-pressure VLE.
- ✓ Often good multicomponent VLE prediction is achieved for mixtures containing hydrocarbons, gases and other non-polar compounds (using interaction parameters from binary data).
- ✓ Many existing databases and correlations are available for kij.

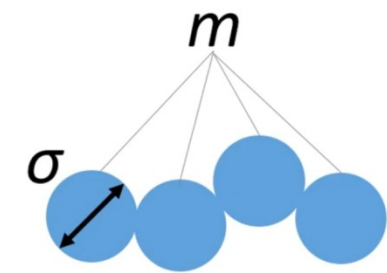
# Shortcoming of cubic EoS

- ✓ Calculations may, in some cases, be sensitive to the interaction parameter,  $k_{ij}$ , especially for gas– hydrocarbons.
- ✓ Interaction parameters, often  $k_{ij}$ , depend on temperature.
- ✓ Cubic EoS do not yield liquid volumes in good agreement with experimental values, unless a volume translation is used.
- ✓ Results are poor for complex, multicomponent VLE and LLE, especially in the presence of associating compounds and water.
- ✓ LLE of highly immiscible systems is not correlated satisfactorily. In most cases, a single interaction parameter cannot represent both solubilities in such systems. In general, LLE is not very well correlated with cubic EoS even for non-polar systems, e.g. **CO<sub>2</sub>–decane** at low temperatures.

# Advanced EOS

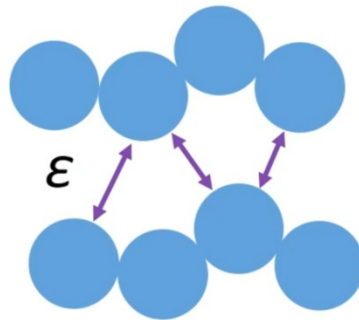
- **Statistical Associating Fluid Theory (SAFT)**
  - perturbed-chain SAFT (PC-SAFT)
  - .....
- **Cubic-Plus-Association EoS (CPA)**

## SAFT parameters

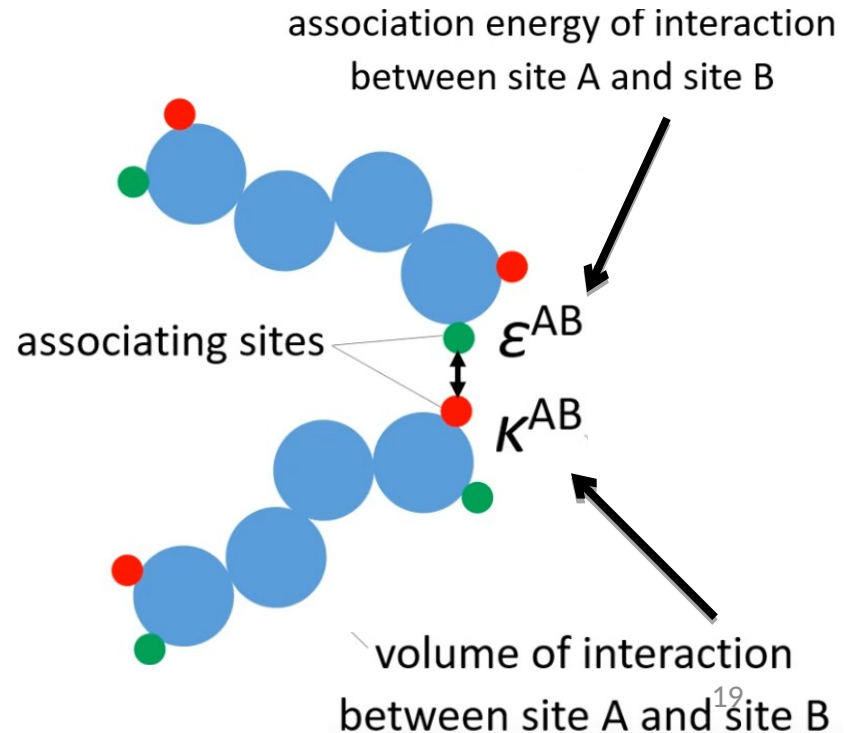


$m$  - number of segments in a chain

$\sigma$  - diameter of segments

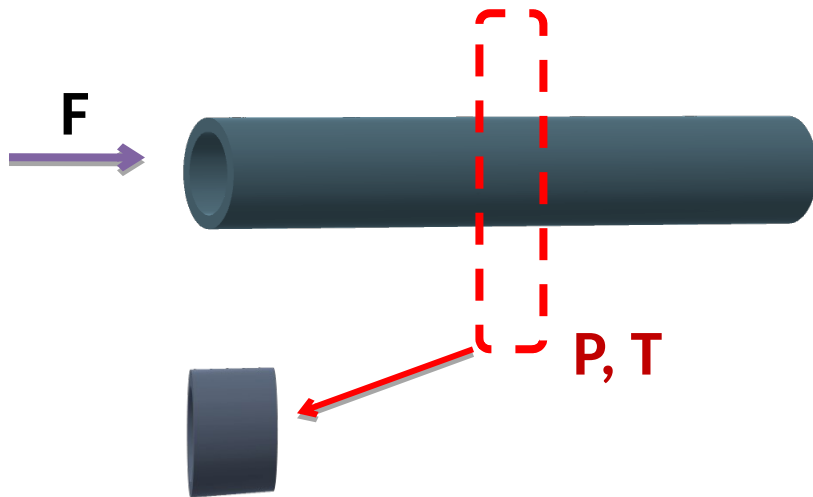


$\epsilon$  - dispersion energy of interaction between segments



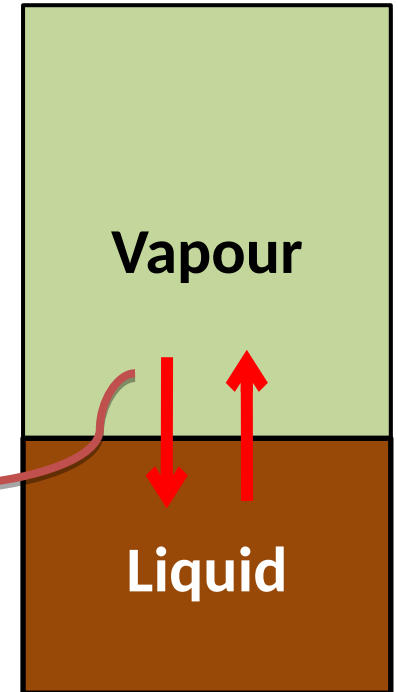
# Some tips and concepts...

- ✓ Thermodynamic equilibrium



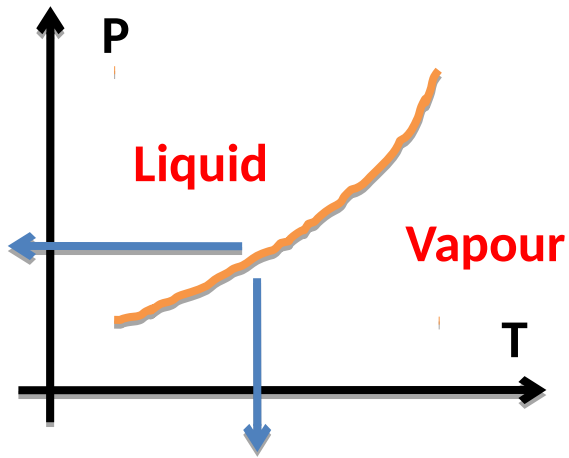
But we have  
heat transfer!!

Net  $Q = 0$



# Some tips and concepts...

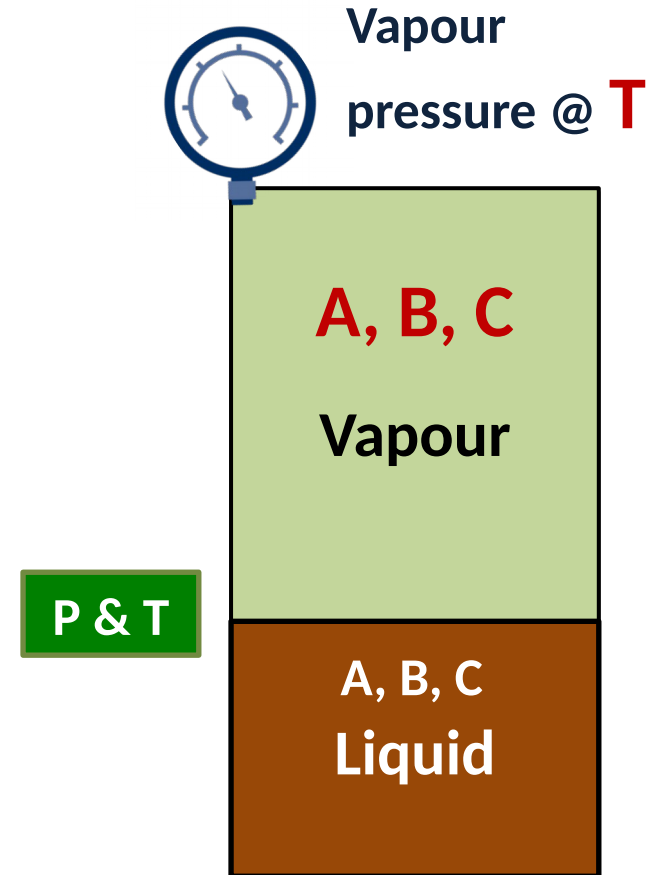
- ✓ Saturation Pressure & Temperature
- ✓ Vapor pressure
- ✓ Partial pressure



$$P_{\text{total}} = P_A + P_B + P_C$$

$$P_A = y_A \times P_{\text{total}}$$

$$P_A = x_A \times P_A^*$$



# Some tips and concepts...

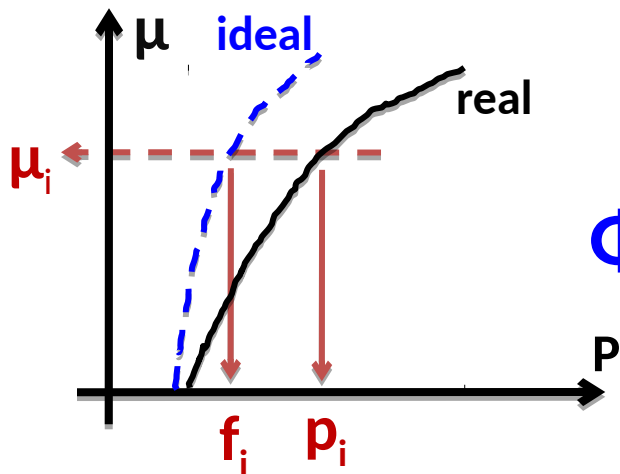
- ✓ Chemical potential ( $\mu$ )
- ✓ Fugacity ( $f$ )
- ✓ Fugacity coefficient ( $\Phi$ )



Equilibrium

chemical potential ( $\mu$ ) of a species is energy that can be absorbed or released due to a change

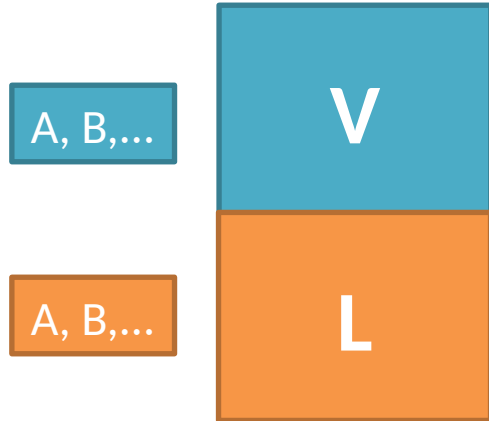
**Fugacity: Tendency to escape**



$$\Phi_i = f_i / p_i$$

$$\mu_B^V = \mu_B^L$$

$$\mu_A^V = \mu_A^L$$

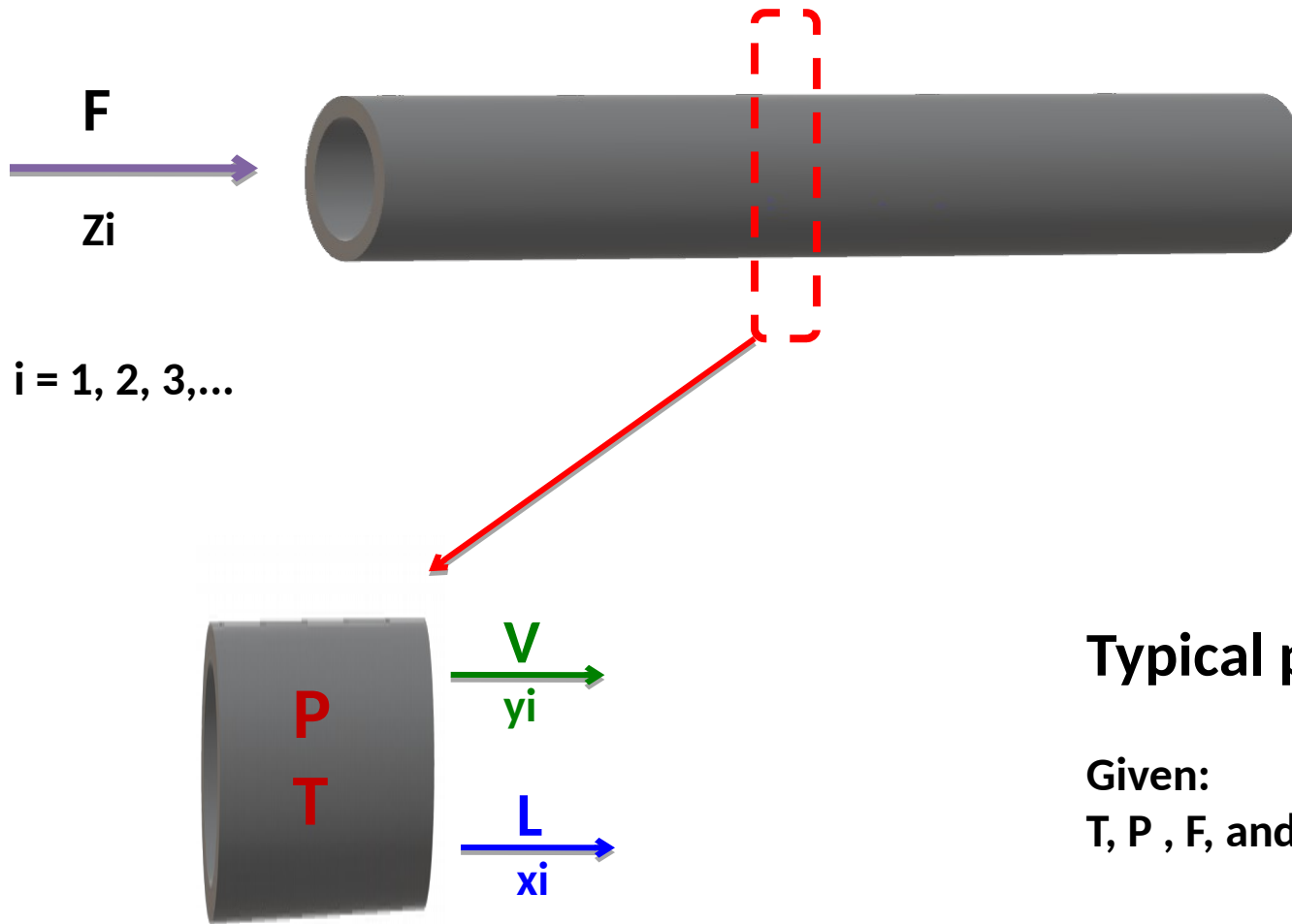


Thermodynamic equations...

$$f_B^V = f_B^L$$

$$f_A^V = f_A^L$$

# Flash Calculation



**Typical problem to solve:**

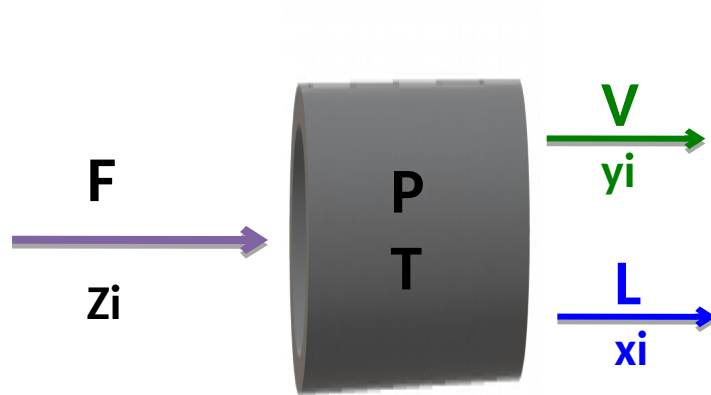
**Given:**

$T, P, F,$  and  $Z_i$

**Find:**

$V, y_i, L, x_i$

# Flash Calculation



$$F = L + V$$

$$F \cdot z_i = L \cdot x_i + V \cdot y_i$$

$$y_i = K_i \cdot x_i \quad \text{VLE}$$

$$\sum y_i = 1$$

$$\sum x_i = 1$$

$$x_i = z_i / [1 + (K_i - 1)(V/F)]$$

$$y_i = K_i \cdot z_i / [1 + (K_i - 1)(V/F)]$$



# Flash Calculation

$$x_i = z_i / [1 + (K_i - 1)(V/F)]$$

$$\sum y_i = 1$$

$$\sum x_i = 1$$

$$y_i = K_i \cdot z_i / [1 + (K_i - 1)(V/F)]$$

$$\sum_{i=1}^C \frac{z_i(1 - K_i)}{1 + (V/F)(K_i - 1)} = 0$$

Rachford Rice equation

(1)  $K_i = P_i^* / P_t$     $\Rightarrow$    (2)  $V/F$     $\Rightarrow$    (3)  $x_i$  and  $y_i$

Dalton and Raoult's laws  
Ideal gas & solution



Different methods to calculate...

# K-values

$$K_i = \frac{y_i}{x_i}$$

Function of T, P and  $z_i$

✓ Experimental

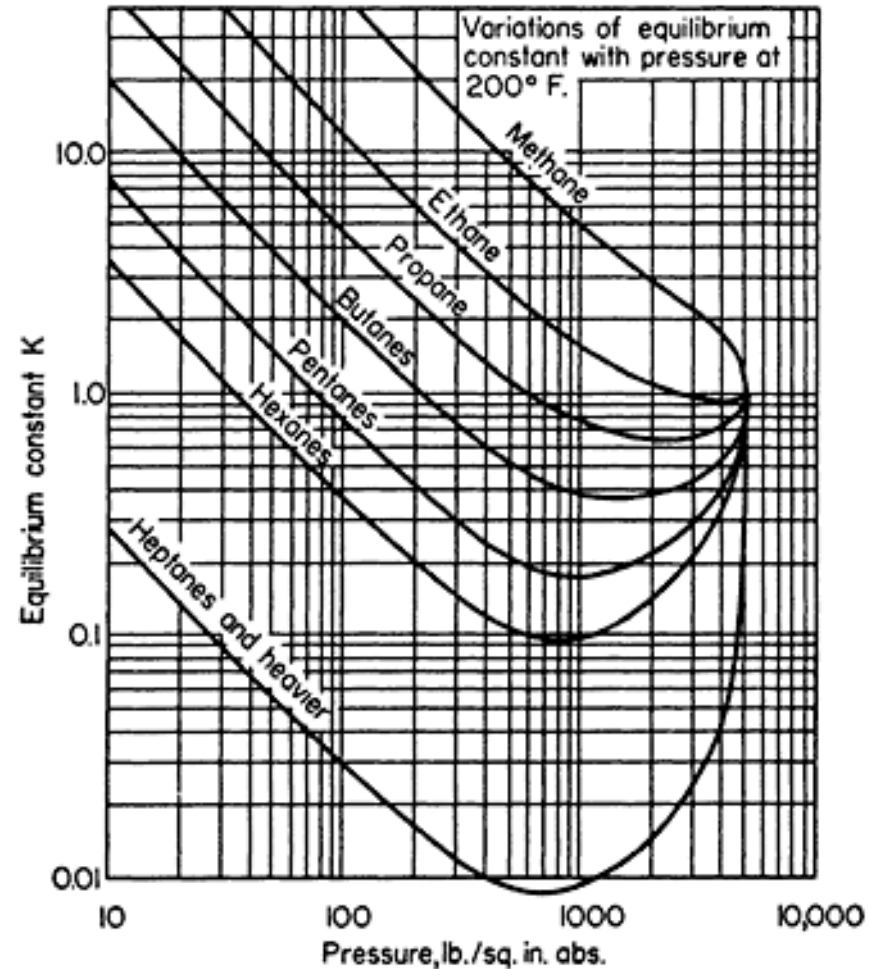
✓ K-value charts

-light hydrocarbon  
-limited pressure

-numerous curve fitted available  
for calculation of K-values.

- Wilson eq. is an example:

$$K_i = \frac{P_{C_i}}{P} \exp \left[ 5.37(1 + \omega_i) \left( 1 - \frac{T_{C_i}}{T} \right) \right]$$



# K-values

$$K_i = \frac{y_i}{x_i}$$

- ✓ Experimental
- ✓ K-value charts
- ✓ **Raoult's Law**

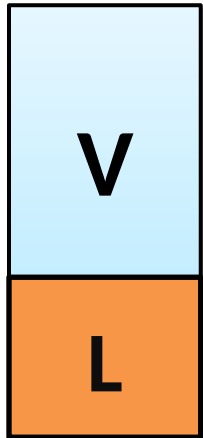
vapor phase behaves as an ideal gas and the liquid phase is an ideal solution.

$$y_i P = x_i P_i^{Sat} \quad \text{or} \quad K_i = \frac{P_i^{Sat}}{P}$$

# K-values

- ✓ Experimental
- ✓ K-value charts
- ✓ Raoult's Law
- ✓ **EoS Approach**

$$K_i = \frac{y_i}{x_i}$$



$$\mu_i^L = \mu_i^V \longrightarrow f_i^L = f_i^V \longrightarrow$$

$$\begin{aligned} f_i^L &= P \phi_i^L x_i \\ f_i^V &= P \phi_i^V y_i \end{aligned}$$

$$y_i = \frac{\phi_i^L}{\phi_i^V} x_i$$

$$K_i = \frac{\phi_i^L}{\phi_i^V}$$

$$\longrightarrow \phi_i^L = \phi_i^L(P, T, x_i)$$

$$\longrightarrow \phi_i^V = \phi_i^V(P, T, y_i)$$

# Fugacity Coefficient

$$K_i = \frac{\phi_i^L}{\phi_i^V} \longrightarrow \text{Flash Calc.}$$

## Equations of State - EoS

$$\ln \phi = \int_0^P \left\{ \frac{\bar{v}}{RT} - \frac{1}{P} \right\} dP = \int_0^P \left\{ \frac{Z - 1}{P} \right\} dP \quad \text{Pure component}$$

$$\ln \phi_i = \int_0^P \left\{ \bar{Z}_i - 1 \right\} \frac{dP}{P} \quad \bar{Z}_i = \frac{P\bar{V}_i}{RT} \quad \text{Mixture}$$

# Flash Calculation

$$\sum_{i=1}^C \frac{z_i(1 - K_i)}{1 + (V/F)(K_i - 1)} = 0$$

Rachford Rice equation

$$K_i = f(P, T, x_i, y_i)$$



$$V/F$$



$$x_i, y_i, L, V$$

$$K_i = \frac{\phi_i^L}{\phi_i^V}$$

$$K_i = f(T, P, x_i, y_i)$$

appropriate iterative scheme...

# Flash Calculation

## Successive Substitution Method (SSM)

$$K_i = \frac{\phi_i^L}{\phi_i^V} = \frac{f_i^L / (x_i P)}{f_i^V / (y_i P)} = \frac{y_i}{x_i} \left( \frac{f_i^L}{f_i^V} \right)$$

$$K_i^{n+1} = \left( \frac{y_i}{x_i} \right)^n \left( \frac{f_{li}}{f_{gi}} \right)^n$$

$$K_i^{n+1} = K_i^n \left( \frac{f_{li}}{f_{gi}} \right)^n$$

$$f_G = ? f_L$$

Known: **T, P, F, and Zi**

Guess **Ki**  
ex. Wilson eq.

**Ki**

$$\sum_{i=1}^C \frac{z_i(1 - K_i)}{1 + (V/F)(K_i - 1)} = 0$$

**V**

$$x_i = z_i / [1 + (K_i - 1)(V/F)]$$

$$y_i = K_i \cdot z_i / [1 + (K_i - 1)(V/F)]$$

**xi, yi**

Using EoS  
calculate fugacity (**f<sub>G</sub>**)

Using EoS  
calculate fugacity (**f<sub>L</sub>**)

**f<sub>G</sub>, f<sub>L</sub>**

Next step: [Any other suggestions?](#)

Knowing the behavior of the CO<sub>2</sub>/hydrocarbon system is important for us.

I would suggest to gather the PVT data on this system available in the literature, with the aim of:

- ✓ Analysing the behaviour of CO<sub>2</sub>/hydrocarbon system at different conditions and different fluids.
- ✓ The PVT data would help us in validating the models and codes in our project.