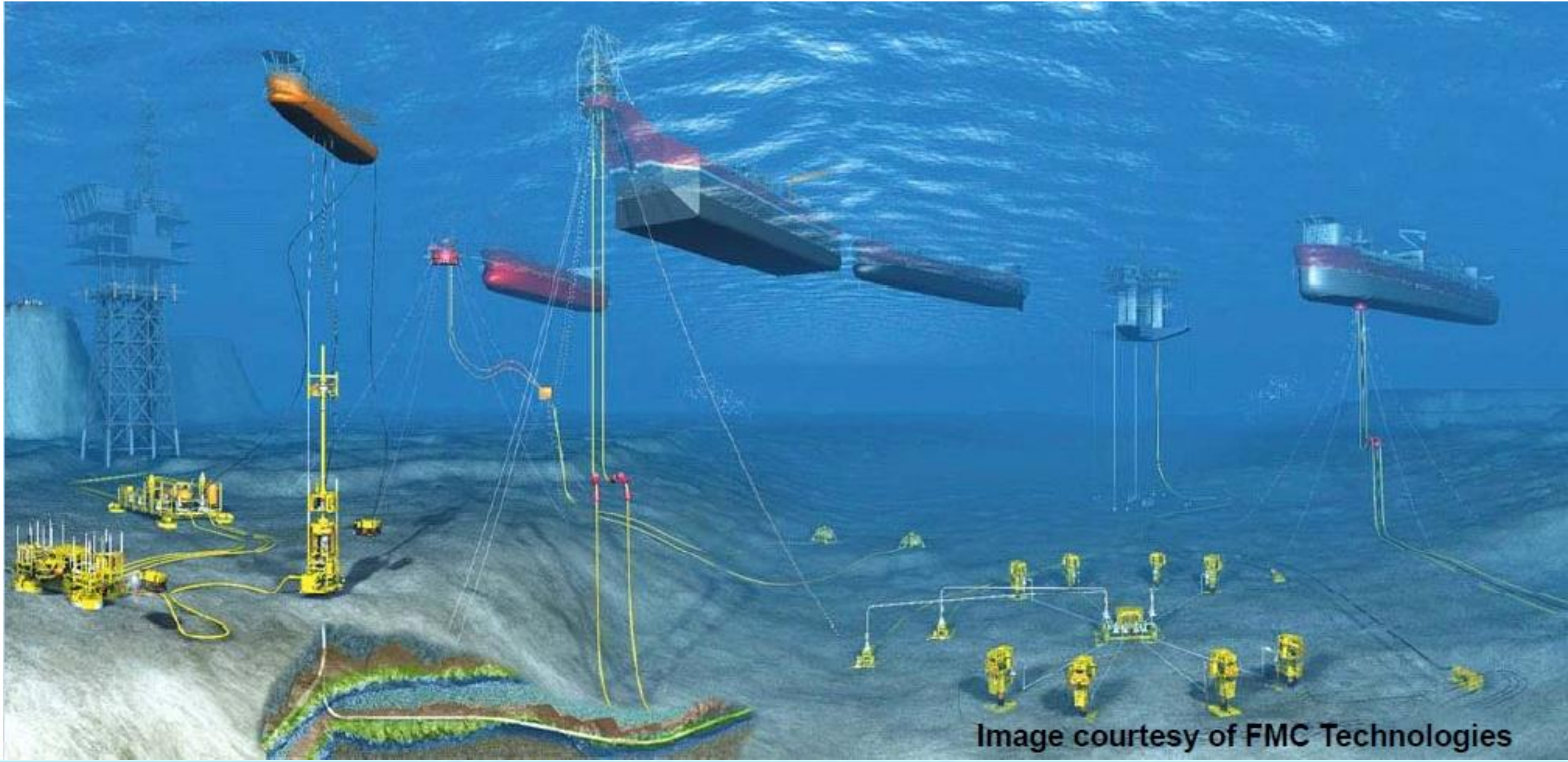


Image courtesy of FMC Technologies

Introduction to Offshore Platform Engineering

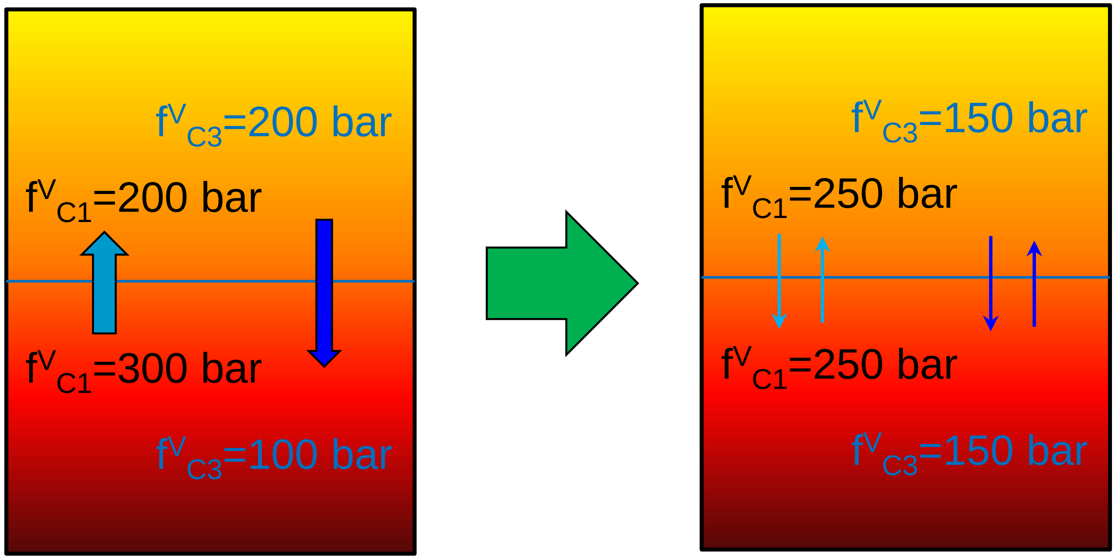
Yutaek Seo

Vapor – Liquid Equilibrium (VLE)

- List of petroleum production systems that involve VLE
  - Separators
  - Reservoir
  - Pipelines
  - Wellbore
  - LNG Processing
  - NGL Processing
  - Storage
  - Oil and LNG Tankers
- Vapor/liquid equilibrium pertains to all aspects of petroleum production with which we are concerned
- Depends on the production conditions, phase changes would affect the design and operation of each production system. Ex)retrograde condensation, bubble/dew point, phases fraction

Phase equilibrium

- At equilibrium all components will have the same fugacity (f_i) in all phases.
- Fugacity may be understood as effective partial pressures taking into account non-ideal interactions with other molecules



Non-equilibrium

Equilibrium

Types of VLE problems

- In a typical problem of liquid and vapor coexistence, we are usually required to know one or more of the following:
    - The phase boundaries,
    - The extent of each phase,
    - The quality of each phase.

- The main emphasis is on the quantitative prediction of the above. These three represent the three basic types of VLE problems.

Phase boundary determination

- These types of problems are either a bubble-point or a dew-point calculation. They are mathematically stated as follows:

   1. Bubble-point T calculation: Given liquid composition (x_i) and pressure (P), determine the equilibrium temperature (T),
   2. Bubble-point P calculation: Given liquid composition (x_i) and temperature (T), determine the equilibrium pressure (P),
   3. Dew-point T calculation: Given vapor composition (y_i) and pressure (P), determine the equilibrium temperature (T),
   4. Dew-point P calculation: Given vapor composition (y_i) and temperature (T), determine the equilibrium pressure (P).

Fundamentals of Equilibrium - Fugacity

- For a closed system, the Gibbs energy is related to pressure and temperature as follows:

$$dG = VdP - SdT$$

- For a constant temperature process,

$$dG = VdP \qquad \text{at constant T}$$

- For an ideal gas,

$$dG = \frac{RT}{P}dP \qquad \text{at constant T}$$

- This expression by itself is strictly applicable to ideal gases. However, Lewis, in 1905, suggested extending the applicability of this expression to all substances by defining a new thermodynamic property called fugacity, f, such that:

$$dG = RTd\,ln\ f \qquad \text{at constant T}$$

- This definition implies that for ideal gases, 'f' must be equal to 'P'.
- For mixtures, this expression is written as:

$$d\overline{G}_i = RTdlnf_i \qquad \text{at constant T}$$

- where G_i and f_i are the partial molar Gibbs energy and fugacity of the i-th component, respectively.
- The definition of fugacity in terms of chemical potential becomes:

For a component in a mixture,

$$dlnf_i = \frac{d\mu_i}{RT} \qquad \text{at const T}$$

$$\lim_{P \to 0} f_i = y_i P$$ = partial pressure (ideal gas limit)

- The fugacity coefficient (Φ_i) is defined as the ratio of fugacity to its value at the ideal state. Hence, for pure substances:

$$\phi = \frac{f}{P}$$

for a component in a mixture,

$$\phi_i = \frac{f_i}{y_i P}$$

- The fugacity coefficient takes a value of unity when the substance behaves like an ideal gas. Therefore, the fugacity coefficient is also regarded as a *measure of non-ideality*;
- The closer the value of the fugacity coefficient is to unity, the closer we are to the ideal state.

- Let’s recall, $$dlnf_i = \frac{d\mu_i}{RT}$$
- Previous expressions can be integrated for the change of state from liquid to vapor at saturation conditions to obtain:

$$\int_l^v dlnf_i = \frac{1}{RT}\int_l^v d\mu_i$$

$$ln\ f_i^{(v)} - ln\ f_i^{l} = \frac{1}{RT}(\mu_i^v - \mu_i^l)$$

- For equilibrium, $\mu_i^v = \mu_i^l$, hence

$$ln\left(\frac{f_i^v}{f_i^l}\right)_i = 0$$

VLE calculation

- Consider a liquid-vapor in equilibrium. As we have discussed previously, a condition for equilibrium is that the chemical potential of each component in both phases are equal, thus:

$$\mu_i^v = \mu_i^l$$

- We showed that this is equivalent to:

$$f_i^v = f_i^l$$

- For a system to be in equilibrium, the fugacity of each component in each of the phases must be equal as well.
- The fugacity of a component in a mixture can be expressed in terms of the fugacity coefficient.

Flash calculation

- Relative phase quantity determination

: In this type of problem, overall composition (z_i), pressure (P), and temperature (T) are given, and the extent of the phases (molar fractions of gas and liquid) are required.

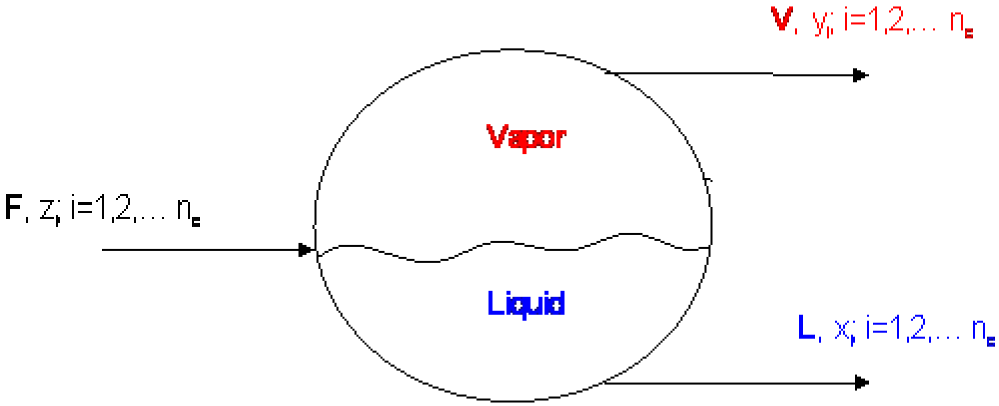
- Phase quality determination

: In this type of problem, overall composition (z_i), pressure (P), and temperature (T) are given, and the composition of the liquid and vapor phases is required.

- These two problems are referred to as *flash calculation* problems
- All three are problems that we encounter in oil and gas production engineering (Phase boundary, volume, composition)

Formulation of the VLE problem

- Consider a hydrocarbon fluid made up of known components or grouped components, for instance a certain percentage of CO2, N2 , C1, C 2-3 , C 4-6, C 7-10, C 11-15, C 16-20 and C20+.
- Place this mixture in a container such as a PVT cell, a grid block, or any other volume. Fix both the temperature and the pressure within the container. Allow enough time to reach equilibrium.
- We know the total composition {zi} of the hydrocarbon mixture. We know the pressure P and the temperature T of the mixture. What we want to know is whether there are one or two hydrocarbon phases present and what the properties of the phases are:



Where, F = L + V

- If the mixture forms a single phase, then its composition is known and it’s properties can be calculated.
- If the mixture forms two hydrocarbon phases then we need to first calculate how much is liquid and vapor (the mole fractions L and V). As part of this calculation we also calculate the relative concentration of moles in each phase (the K-values (Ki=yi/xi)). From these we can work out the compositions of each phase {xi} and {yi} and from the compositions we work out the properties of each phase.
- The same flash calculations can be used to work out the bubble point P^{bub} or dew point P^{dew} of a mixture, or more generally the saturation pressure P^{sat}. In this case we know total composition {zi} of the hydrocarbon mixture and the temperature T of the mixture. By definition, we also know that at the saturation pressure is the lowest pressure at which either (L=1 and V=0) or (L=0 and V=1). We can then solve for the K-values {Ki}) and the pressure $P=P^{sat}$.

Equilibrium ratio - K

- A distribution coefficient used to express the ratio of the mole fraction in one phase to the mole fraction of the same component in another phase

  Vapor – Liquid: $K_i = \dfrac{y_i}{x_i}$

  where y_i and x_i are the mole fractions of component i in the phases vapor and liquid, respectively
- The values of the ratio K_i are correlated empirically or theoretically in terms of temperature, pressure and phase compositions in the form of equations, tables or graph such as the DePriester charts

Equilibrium ratio estimation

- We assumed that we knew all the equilibrium ratios. But usually we don't. Actually, if we happen to know Ki's, the VLE problem is soluble
- Ki value is a function of P, T, and the composition of each of the phases. If they were known, the VLE calculation would be performed by solving the Rachford-Rice objective function
- Ki's are fairly independent of the phase composition. Numerous correlations have been developed to estimate the value of K' for hydrocarbon component as a function of P and T.
- DePriester charts
- Wilson's empirical correlation

$$K_i = \frac{1}{P_{r,i}} \exp\left(5.37(1+\varpi_i)(1-\frac{1}{T_{r,i}}) \right)$$

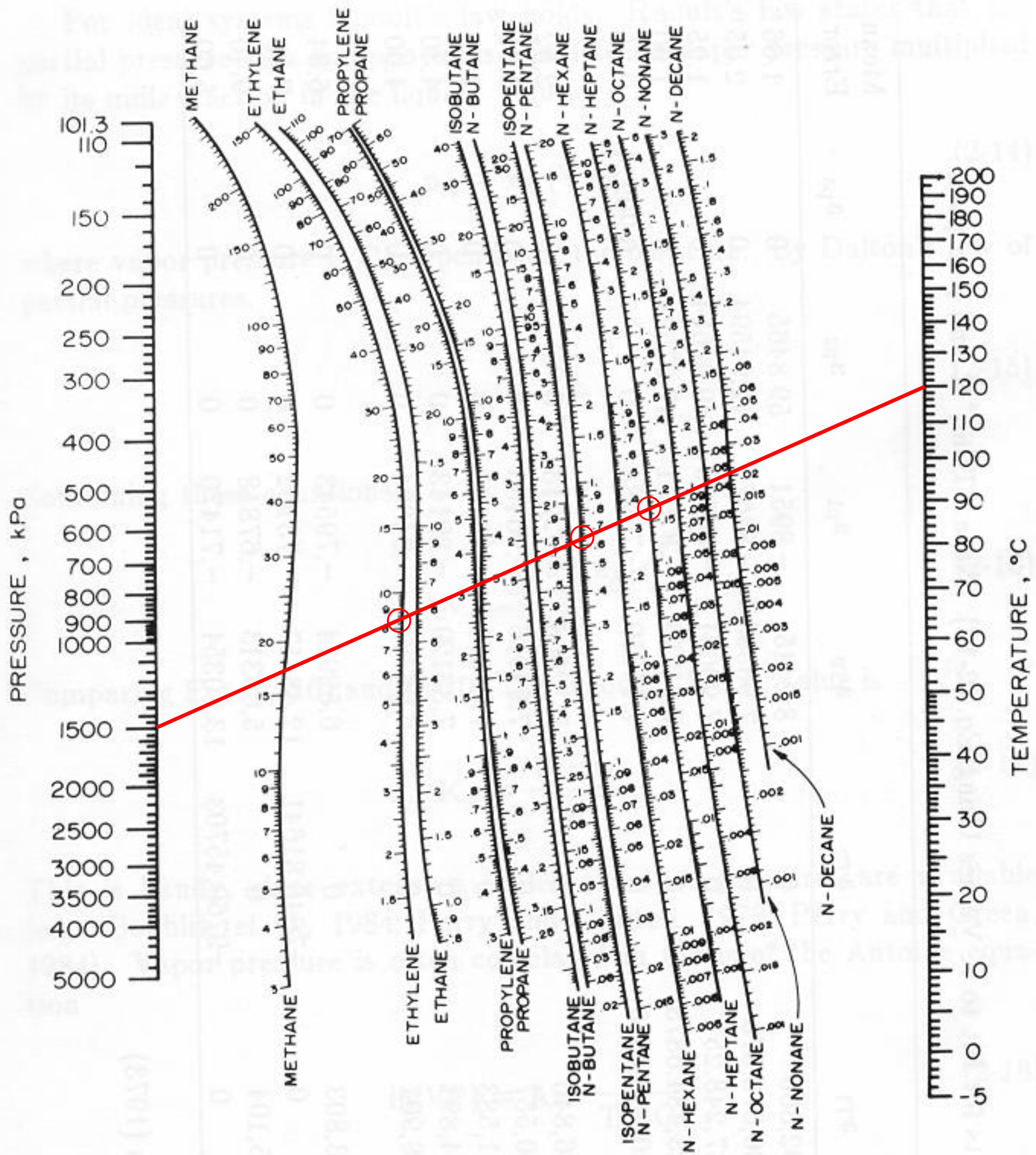


Figure 2-12. Modified DePriester chart at high temperatures. From D.B. Dadyburjor, *Chem. Eng. Prog.*, 85, April 1978. Copyright 1978, AIChE. Reproduced by permission of the American Institute of Chemical Engineers.

- at T = 120 °C and P =1500 kPa. K, are:

Ethylene	8.5
n-Pentane	0.64
n-Heptane	0.17

.

- When use K ?

- Calculate the bubble point temperature of a liquid mixture given the total pressure and liquid composition
- Calculate the dew point temperature of a vapor mixture given the total pressure and vapor composition
- Calculate the composition of the vapor and liquid, and their respective quantities, when a liquid is partially vaporized at a given temperature and pressure
- Calculate the related equilibrium vapor-liquid compositions over the range of mole fractions from 0 to 1 as a function of temperature given the total pressure

Equilibrium and K_i

- The fugacity of a component in either phase can be written as:

$$f_i^v = y_i \phi_i^v P$$

$$f_i^l = x_i \phi_i^l P$$

- At equilibrium,

$$y_i \phi_i^v P = x_i \phi_i^l P$$

- This equilibrium condition can be written in terms of the equilibrium ratio $K_i = y_i/x_i$, to get:

$$K_i = \frac{y_i}{x_i} = \frac{\phi_i^l}{\phi_i^v}$$

Flash equations

- Rachford-Rice equation

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

Where, N = number of components

Zi = overall composition, or composition of the feed

Ki = Equilibrium ratio of each components of the mixture

V = vapor fraction in the system

- This equation is a non-linear equation in one variable. The Newton Raphson procedure is usually implemented to solve it.

Newton’s method

- we could try to overcome this problem by “guessing” those compositions, and proceed by solving equations for K_i.
- With this “rough” estimate for K_i, we could solve for “α_v” with the Newton-Raphson Procedure. Once “α_v” is known, we could back calculate the compositions of the phases using equations.
- If we were correct, those compositions would match each other (the “guessed” ones with respect to the “back-calculated”). More than likely, this would not happen, and we would have to make a new “guess.” This is, fundamentally, an iterative procedure. Although this is not what we do, it does illustrate that this problem is solvable by implementing the appropriate iterative scheme.
- As you see, everything that we have studied is completely interlinked. That’s one of the main ideas of solving the VLE problems.

Flash cacluation

Type	Known information	Variables to be calculated	Equation to use
Bubble point T	P_{total}, x_i	T, y_i	(1)
Dew point T	P_{total}, y_i	T, x_i	(2)
Bubble point P	T, x_i	P_{total}, y_i	(1)
Dew point P	T, y_i	P_{total}, x_i	(2)
Flash	P_{total}, T, z_i	L/F, y_i, x_i	(3)

$$(1) \qquad 1 = K_1 x_1 + K_2 x_2$$

$$(2) \qquad 1 = \frac{y_1}{K_1} + \frac{y_2}{K_2}$$

$$(3) \qquad 1 = \frac{z_1}{1 - \frac{L}{F}\left(1 - \frac{1}{K_1}\right)} + \frac{z_2}{1 - \frac{L}{F}\left(1 - \frac{1}{K_2}\right)}$$

Equation of States - Ideal gases

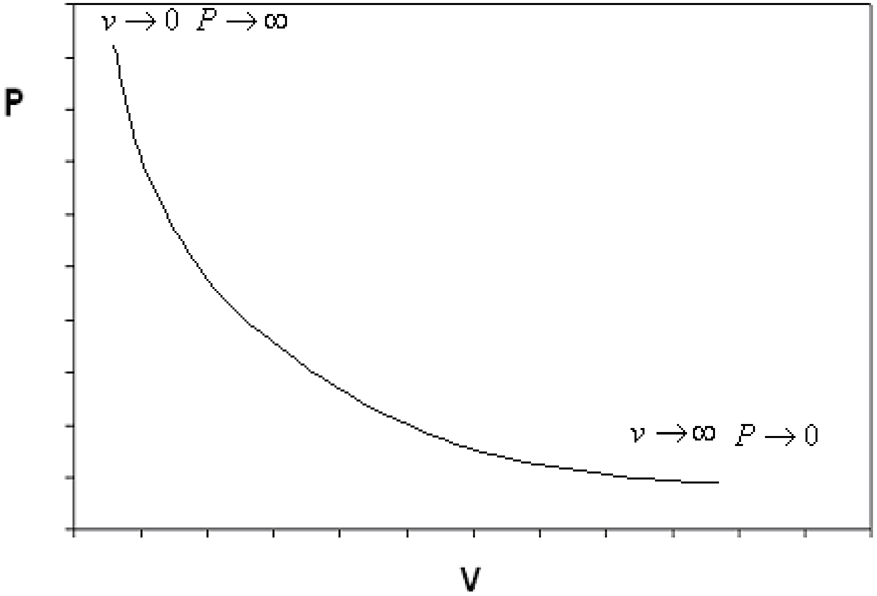
- An ideal gas is an *imaginary* gas that satisfies the following conditions

  : Negligible interactions between the molecules,

  : Its molecules occupy no volume (negligible molecular volume),

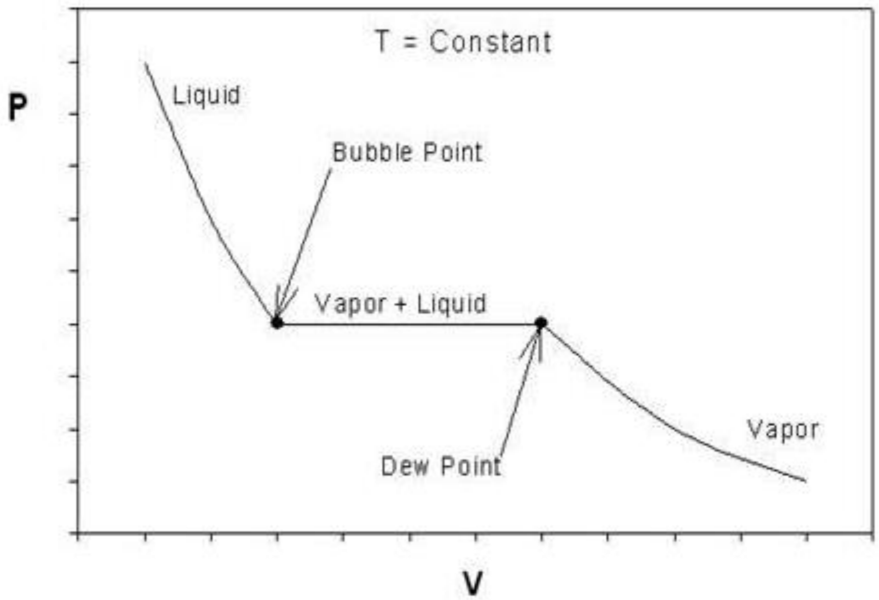
  : Collisions between molecules are perfectly elastic (no energy is lost after colliding)

- If we construct the P-v diagram for an ideal gas at a given temperature, we end up with the isotherm shown as follows,



Real gases

- Typical P-V behavior of a pure substance.



- For a real substance, as pressure increases, there **must** be a point of discontinuity that represents the phase change.
- *Ideal gas will not condense, no matter what pressure it is subjected to, regardless of the temperature of the system*. In other words, we cannot hope to reproduce the above P-v behavior using the ideal equation since no discontinuity is to be found

Cubic EOS

- If we multiply the EOS by V^2 and expand the factorized product by applying the distributive law,

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT \longrightarrow V^3-\left(b+\frac{RT}{P}\right)V^2+\left(\frac{a}{P}\right)V-\frac{ab}{P}=0$$

- This is a third order polynomial in V i.e. it is cubic in molar volume.
- Thus van der Waals EOS is referred to as *cubic* because it is a polynomial of order 3 in molar volume. In general, any equation of state that is cubic in volume and explicit in pressure is regarded as a *cubic equation of state.*
- All the transformations and modifications that it has undergone during the more than one hundred years since its publication are also *cubic EOS* including RK, SRK, and PR.

van der Waals EOS (1873)

- Capable of handling the transition from vapor to liquid

$$P = \frac{RT}{(V-b)} - \frac{a}{V^2} \rightarrow \left(P + \frac{a}{V^2}\right)(V-b) = RT$$

$$a = \frac{27}{64}\frac{R^2 T_c^2}{P_c},\ b = \frac{1}{8}\frac{RT_c}{P_c},\ then\, V_c = \frac{3}{8}\frac{RT_c}{P_c}$$

Modern cubic EOS

- SRK (1972)

$$P = \frac{RT}{(V-b)} - \frac{\alpha\, a}{V(V+b)} \rightarrow \left(P + \frac{\alpha\, a}{V(V+b)}\right)(V-b) = RT$$

$$a = 0.42748\frac{R^2T_c^2}{P_c},\ b = 0.08664\frac{RT_c}{P_c}$$

$$\alpha = \left(1 + m\left(1 - T_R^{1/2}\right)\right)^2, m = 0.48508 + 1.55171\cdot\varpi - 0.1561\cdot\varpi^2$$

- PR (1976)

$$P = \frac{RT}{(V-b)} - \frac{\alpha\, a}{V(V+b)+b(V-b)} \rightarrow \left(P + \frac{\alpha\, a}{V(V+b)+b(V-b)}\right)(V-b) = RT$$

$$a = 0.45724\frac{R^2T_c^2}{P_c},\ b = 0.07780\frac{RT_c}{P_c}$$

$$\alpha = \left(1 + m\left(1 - T_R^{1/2}\right)\right)^2, m = 0.37464 + 1.5422\cdot\varpi - 0.26992\cdot\varpi^2$$

Comparison of SRK and PR EOS

- RK EOS

- Generally good for gas phase properties, but poor for liquid phase properties

- Better when used in conjunction with a correlation for liquid phase behavior.

- SRK and PR EOS

- Serve similar functions as RK EOS but require more parameters

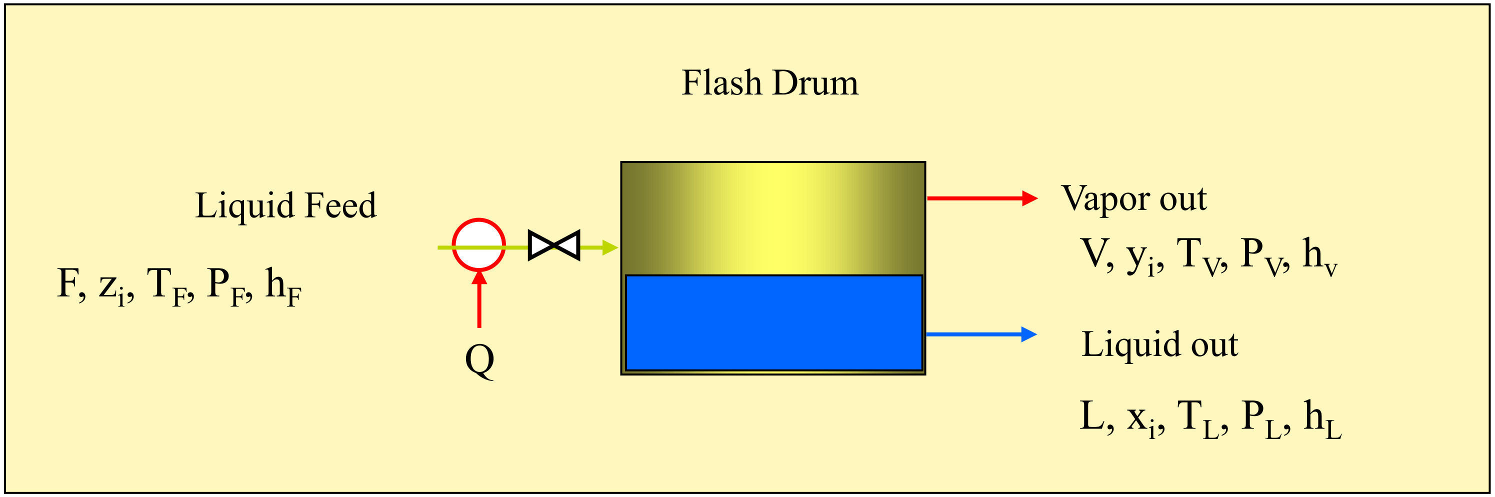
- PR obtains better liquid densities than SRK

- Overall, PR does a better job, slightly, for gas and condensate then SRK. However for polar systems, SRK always makes a better prediction, but in the petroleum industry, we do not usually deal with those.

- Peng and Robinson (Uni. Of Calgary) was trying to develop an EOS specifically focused on natural gas systems. PR EOS shows a slightly better behavior at the critical point. This slightly better performance around critical conditions makes the PR EOS somewhat better suited to gas condensate systems.

Isothermal FlashConfiguration

Consider the following operation which produces a liquid-vapor equilibrium from a liquid feed:



For each stream:

n: molar flow rate: F, L, V

z_i: composition variables: x,y,z

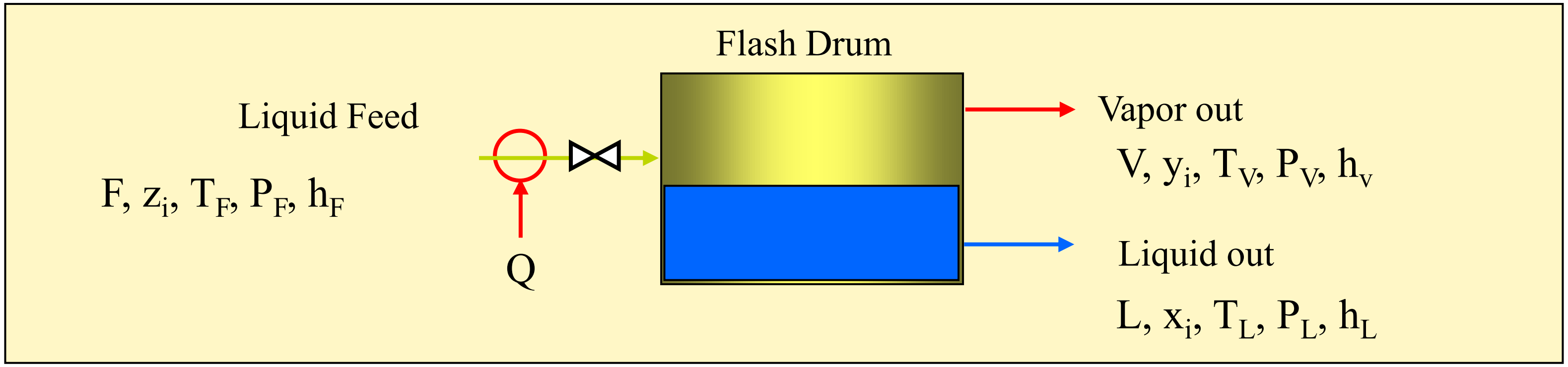
T: temperature

P: pressure

h: enthalpy

Q: heat transfer

Isothermal Flash Variables



For this system there are 3C+10 variables: $F, V, L, T_F, P_F, T_V, P_V, T_L, P_L, Q, \{x_i, y_i, z_i\}_C$

If we specify F, z_i, T_F, P_F we have specified (C+3) variables and we can specify two additional variables.

Common Specifications:

T_V, P_V	Isothermal Flash
$V/F=0, P_L$	Bubble-Point Temperature
$V/F=1, P_V$	Dew-Point Temperature
$V/F=0, T_L$	Bubble-Point Pressure
$V/F=1, T_V$	Dew-Point Pressure
$Q=0, P_V$	Adiabatic Flash
Q, P_V	Non adiabatic flash
$V/F, P_V$	Percent Vaporization Flash

Isothermal Flash Equations

The assumption of thermal and mechanical equilibrium in the drum.

$$T_L = T_V \qquad P_L = P_V$$

We have total material balance: $F = V + L$

We have component material balances, one for each component:

$$FZ_i = VY_i + LX_i$$

We have the mole fraction summations for each phase (or stream):

$$\sum_i X_i = 1 \qquad \sum_i Y_i = 1 \qquad \sum_i Z_i = 1$$

In equilibrium, we have a K-value relationship for each component:

$$k_i^{L,V} = \frac{Y_i^V}{X_i^L}$$

Rachford Rice Derivation

It is convenient to define the Vapor Fraction as follows:

$$\psi = \frac{V}{F}$$

Substituting into our total material balance:

$$L = F - \psi F$$

For the component material balances:

$$FZ_i = VY_i + LX_i \longrightarrow Z_i = \frac{V}{F} Y_i + \frac{F - \psi F}{F} X_i \longrightarrow Z_i = \psi Y_i + X_i - \psi X_i$$

Using the K-Value and solving for the liquid phase mole fraction:

$$\begin{tikzcd}
Z_i = \psi Y_i + X_i - \psi X_i \arrow[r] & Z_i = \psi K_i X_i + X_i - \psi X_i \arrow[r] & X_i = \dfrac{Z_i}{\psi K_i + 1 - \psi} \arrow[d] \\
Y_i = K_i X_i \arrow[u] \arrow[urr] & & Y_i = \dfrac{K_i Z_i}{\psi K_i + 1 - \psi}
\end{tikzcd}$$

We use the K-Value to get:

Rachford Rice Equations

We use the mole fraction summations:

$$\sum_i X_i = 1 \qquad \sum_i Y_i = 1 \qquad \longrightarrow \qquad \sum_i \left(Y_i - X_i\right) = 0$$

Substituting in our expressions for the mole fractions:

$$X_i = \frac{Z_i}{\psi K_i + 1 - \psi} \qquad Y_i = \frac{K_i Z_i}{\psi K_i + 1 - \psi}$$

Gives us the Rachford-Rice Equation:

$$\sum_i \left(\frac{K_i Z_i}{\psi K_i + 1 - \psi} - \frac{Z_i}{\psi K_i + 1 - \psi} \right) = 0 \qquad \longrightarrow \qquad f(\psi) = \sum_i \frac{Z_i\left(K_i - 1\right)}{\psi K_i + 1 - \psi} = 0$$

The roots of this equation give us the compositions, and vapor fraction of the Isothermal Flash operation.

To solve this equation, we need to use some procedure for finding the roots:

- Iterative
- Graphical

Newton’s Iterative Method

To solve the Rachford-Rice equation we can use Newton’s method to find ψ:

Newton’s method estimates a better root using the last guess and the ratio of the function to its derivative at that guess:

$$\psi^{k+1} = \psi^{k} - \frac{f\left(\psi^{k}\right)}{f'\left(\psi^{k}\right)}$$

For the Rachford-Rice Equation this becomes:

$$\psi^{k+1} = \psi^{k} + \frac{\sum_{i} \frac{Z_i\left(K_i - 1\right)}{\psi^{k}\left(K_i - 1\right) + 1}}{\sum_{i} \frac{Z_i\left(K_i - 1\right)^2}{\left(\psi^{k}\left(K_i - 1\right) + 1\right)^2}}$$

Rachford-Rice Procedure

The Rachford-Rice procedure using Newton's method is then:

Step 1: $T_L = T_V$ Thermal equilibrium

Step 2: $P_L = P_V$ Mechanical equilibrium

Step 3: Solve Rachford-Rice for V/F where the K-values are determined by T_L, and P_L.

$$\sum_i \frac{Z_i(K_i - 1)}{\psi K_i + 1 - \psi} = 0$$

Can use Newton's method here.

Step 4: $V = F\psi$ Determine V

Steps 5 and 6: $X_i = \dfrac{Z_i}{\psi K_i + 1 - \psi}$ $Y_i = \dfrac{K_i Z_i}{\psi K_i + 1 - \psi}$

Step 7: $L = F - \psi F$ Determine L

Step 8: $Q = Vh_v + Lh_l - Fh_f$ Determine Q

Example: Rachford-Rice

A flash chamber operating at 50ºC and 200kPa is separating 1000 kg moles/hr of a feed that is 30 mole %propane, 10 % n-butane, 15 % n-pentane, and 45 % n-hexane.

What are the product compositions and flow rates?

1) Using the Depriester Chart we determine that:

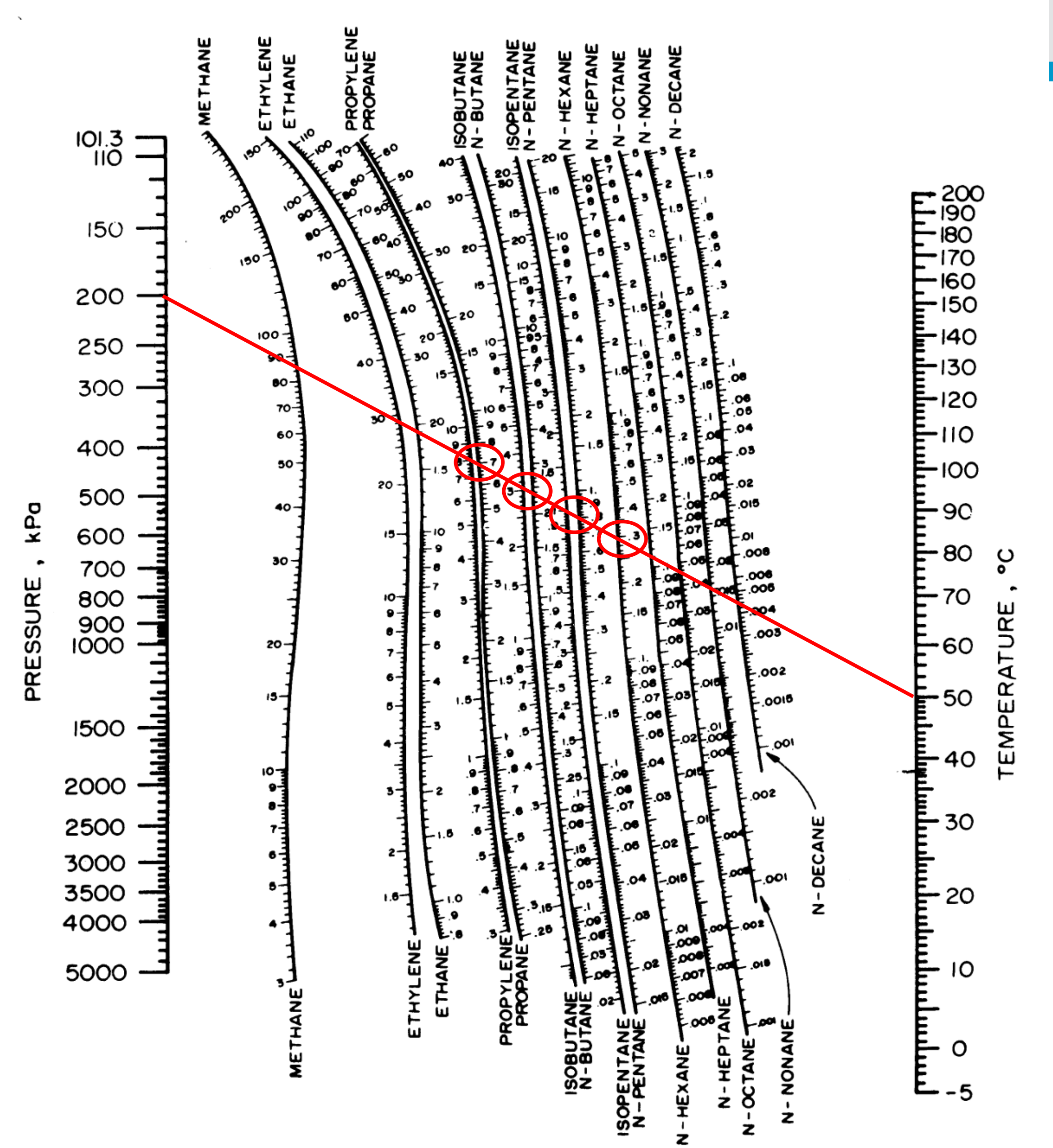
K_1 (propane) = 7.0
K_2 (n-butane) = 2.4
K_3 (n-pentane) = 0.80
K_4 (n-hexane) = 0.30

2) We first write the Rachford-Rice Equation and substitute in the composition and K-values:

$$f\left(\frac{V}{F}\right) = \sum_i \frac{Z_i\left(K_i - 1\right)}{\psi\left(K_i - 1\right) + 1}$$

$$f\left(\frac{V}{F}\right) = \frac{0.3(7.0-1)}{\psi(7.0-1)+1} + \frac{0.1(2.4-1)}{\psi(2.4-1)+1} + \frac{0.15(0.8-1)}{\psi(0.8-1)+1} + \frac{0.45(0.3-1)}{\psi(0.3-1)+1}$$

Depriester Determination of K Values



Example: Rachford-Rice

We can either plot the Rachford-Rice Equation as a function of V/F or use Newton's method:

$$f\left(\frac{V}{F}\right) = \sum_i \frac{Z_i(K_i - 1)}{\psi(K_i - 1) + 1}$$

$$f\left(\frac{V}{F}\right) = \frac{0.3(7.0-1)}{\psi(7.0-1)+1} + \frac{0.1(2.4-1)}{\psi(2.4-1)+1} + \frac{0.15(0.8-1)}{\psi(0.8-1)+1} + \frac{0.45(0.3-1)}{\psi(0.3-1)+1}$$

Guess V/F=0.1

$$f(0.1) = \frac{0.3(7.0-1)}{0.1(7-1)+1} + \frac{0.1(2.4-1)}{0.1(2.4-1)+1} + \frac{0.15(0.8-1)}{0.1(0.8-1)+1} + \frac{0.45(0.3-1)}{0.1(0.3-1)+1} = 0.8785$$

To obtain a new guess we need the derivative of the RR equation:

$$f'\left(\frac{V}{F}\right) = \frac{0.3(7.0-1)^2}{[\psi(7-1)+1]^2} + \frac{0.1(2.4-1)^2}{[\psi(2.4-1)+1]^2} + \frac{0.15(0.8-1)^2}{[\psi(0.8-1)+1]^2} + \frac{0.45(0.3-1)^2}{[\psi(0.3-1)+1]^2}$$

$$f'(0.1) = \frac{0.3(7.0-1)^2}{[0.1(7-1)+1]^2} + \frac{0.1(2.4-1)^2}{[0.1(2.4-1)+1]^2} + \frac{0.15(0.8-1)^2}{[0.1(0.8-1)+1]^2} + \frac{0.45(0.3-1)^2}{[0.1(0.3-1)+1]^2} = 4.631$$

Example: Rachford-Rice

So our next guess is

$$\psi^2 = 0.1 + \frac{0.879}{4.631} = 0.29$$

$$f(0.29) = \frac{0.3(7.0-1)}{0.29(7-1)+1} + \frac{0.1(2.4-1)}{0.29(2.4-1)+1} + \frac{0.15(0.8-1)}{0.29(0.8-1)+1} + \frac{0.45(0.3-1)}{0.29(0.3-1)+1} = 0.329$$

To obtain a new guess we need the derivative of the RR equation:

$$f'(0.29) = \frac{0.3(7.0-1)^2}{[0.29(7-1)+1]^2} + \frac{0.1(2.4-1)^2}{[0.29(2.4-1)+1]^2} + \frac{0.15(0.8-1)^2}{[0.29(0.8-1)+1]^2} + \frac{0.45(0.3-1)^2}{[0.29(0.3-1)+1]^2} = 1.891$$

$$\psi^3 = 0.29 + \frac{0.329}{1.891} = 0.46$$

$$f(0.46) = 0.066 \qquad f'(0.46) = 1.32$$

$$\psi^4 = 0.46 + \frac{0.066}{1.32} = 0.51$$

$$f(0.51) = 0.00173$$

Example: Rachford-Rice

So: $V/F = 0.51$ $V = 510 kg/hr$

Using:

$$X_i = \frac{Z_i}{\psi K_i + 1 - \psi}$$

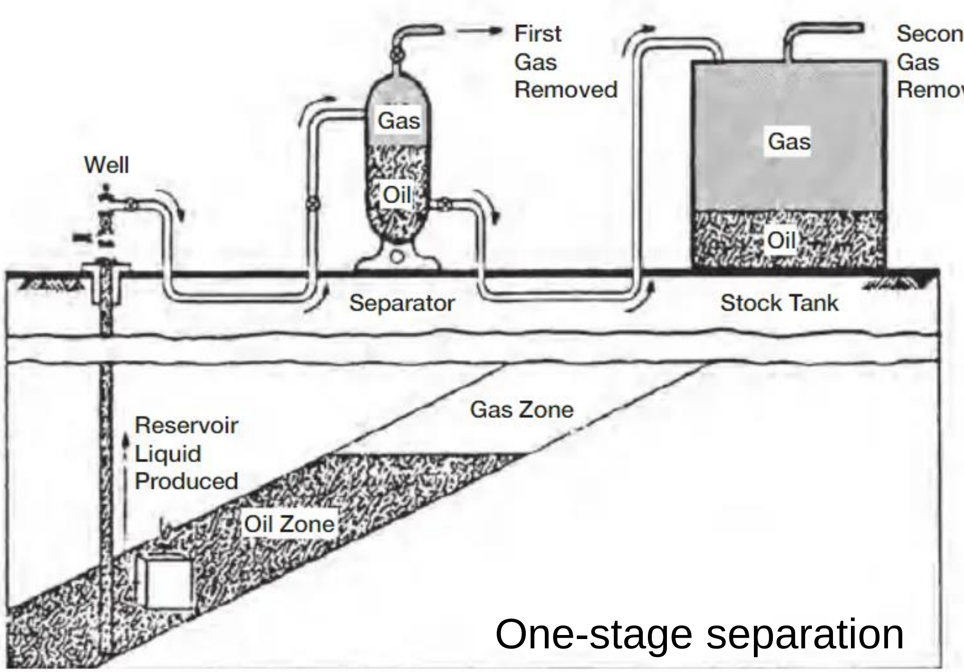
$$Y_i = \frac{K_i Z_i}{\psi K_i + 1 - \psi}$$

X_1 (propane) = 0.0739
X_2 (n-butane) = 0.0583
X_3 (n-pentane) = 0.1670
X_4 (n-hexane) = 0.6998

Y_1 (propane) = 0.5172
Y_2 (n-butane) = 0.1400
Y_3 (n-pentane) = 0.1336
Y_4 (n-hexane) = 0.2099

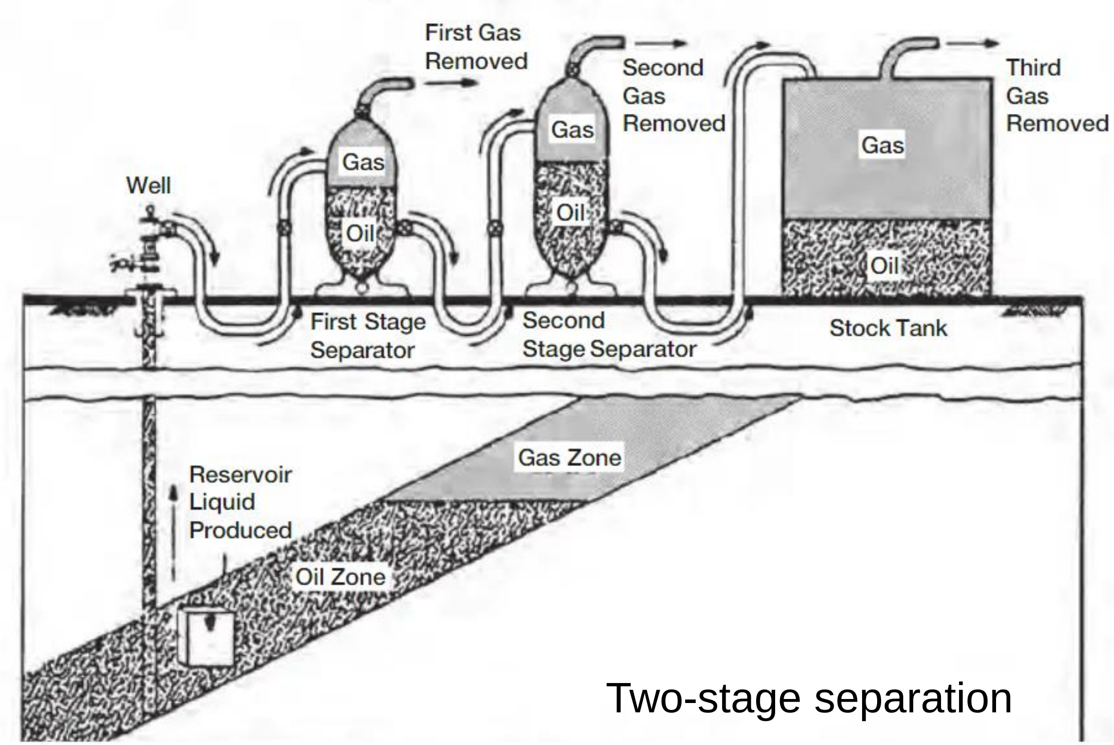
Separator calculation

- Produced reservoir fluids are complex mixtures of different physical characteristics. As a well stream flows from the high-temperature, high-pressure reservoir, it experiences pressure and temperature reductions.
- Gases evolve from the liquids and the well stream changes in character. The physical separation of these phases is by far the most common of all field-processing operations and one of the most critical.
- The manner in which the hydrocarbon phases are separated at the surface influences the stock-tank oil recovery.



One-stage separation

- The principal means of surface separation of gas and oil is the conventional stage separation.
- Stage separation is a process in which gaseous and liquid hydrocarbons are flashed(separated) into vapor and liquid phases by two or more separators. These separators usually are operated in a series at consecutively lower pressures. Each condition of pressure and temperature at which hydrocarbon phases are flashed is called a stage of separation.



Two-stage separation

Differential vs. Flash separation

- Traditionally, the stock tank is considered a separate stage of separation. Mechanically, there are two types of gas/oil separation: *differential* and *flash* or *equilibrium* separation.
- To explain the various separation processes, it is convenient to define the composition of a hydrocarbon mixture by three groups of components.

  : The very volatile components, the “*lights*,” such as nitrogen, methane, and ethane.

  : The components of intermediate volatility, that is, “*intermediates*,” such as propane through hexane.

  : The components of less volatility, the “*heavies*,” such as heptane and heavier components
- In the *differential* separation, the liberated gas (which is composed mainly of lighter components) is removed from contact with the oil as the pressure on the oil is reduced.
- As pointed out by Clark (1960), when the gas is separated in this manner, the maximum amount of heavy and intermediate components remain in the liquid, and there is minimum shrinkage of the oil, and therefore, greater stock-tank oil recovery.
- This is due to the fact that the gas liberated earlier at higher pressures is not present at lower pressures to attract the intermediate and heavy components and pull them into the gas phase

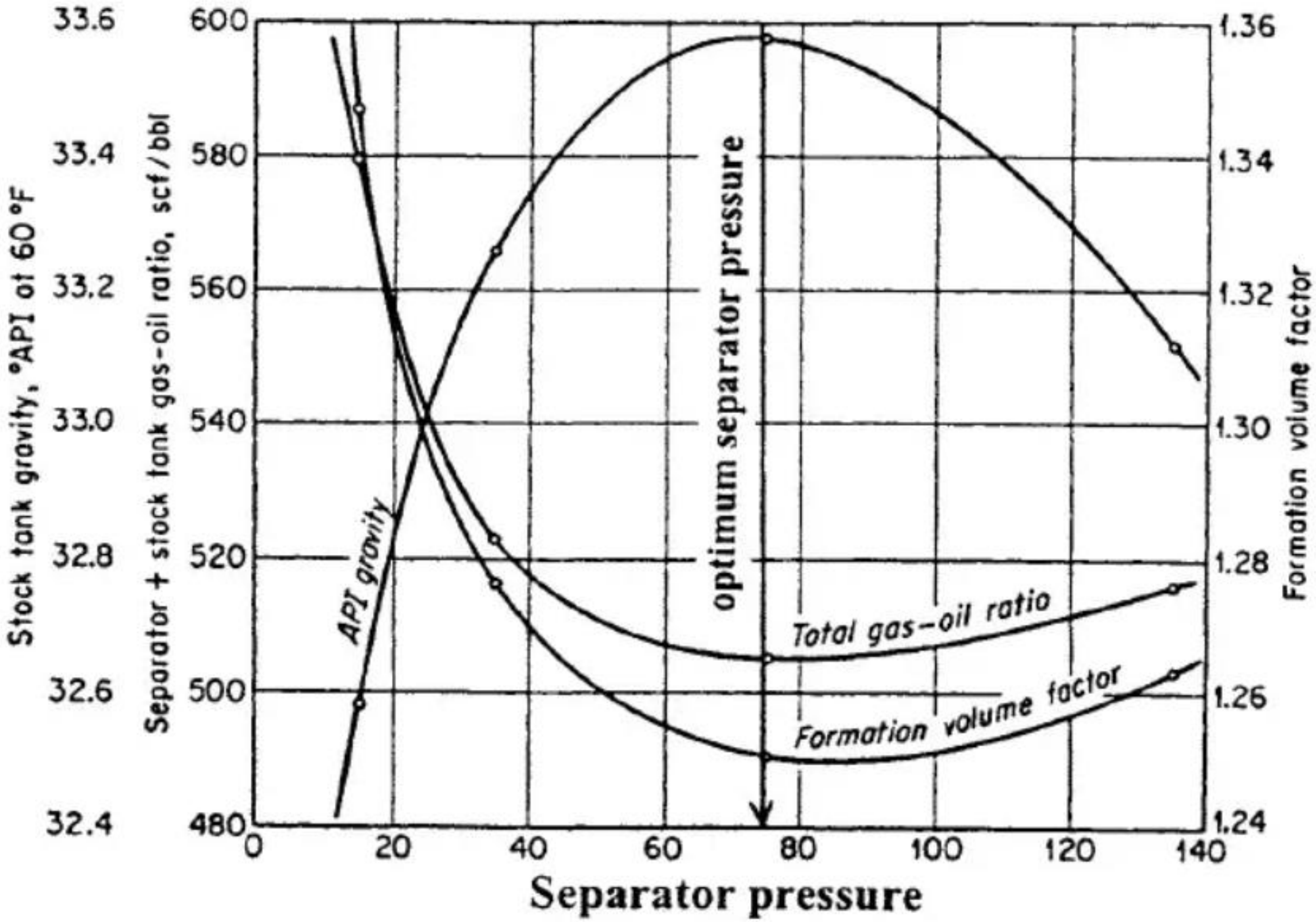
- In the *flash (equilibrium)* separation, the liberated gas remains in contact with the oil until its instantaneous removal at the final separation pressure.
- A maximum proportion of intermediate and heavy components are attracted into the gas phase by this process, and this results in maximum oil shrinkage and, therefore, lower oil recovery.
- In practice, the differential process is introduced first in field separation, when gas or liquid is removed from the primary separator. In each subsequent stage of separation, the liquid initially undergoes a flash liberation followed by a differential process as actual separation occurs. As the number of stages increases, the differential aspect of the overall separation becomes greater.
- The purpose of stage separation then is to reduce the pressure on the produced oil insteps so that more stock-tank oil recovery results.
- Separator calculations are basically performed to determine
    - Optimum separation conditions: separator pressure and temperature.
    - Composition of the separated gas and oil phases.
    - Oil formation volume factor.
    - Producing gas/oil ratio
    - API gravity of the stock-tank oil

- Note that, if the separator pressure is high, large amounts of light components remain in the liquid phase at the separator and are lost along with other valuable components to the gas phase at the stock tank.
- On the other hand, if the pressure is too low, large amounts of light components are separated from the liquid, and they attract substantial quantities of intermediate and heavier components.
- An intermediate pressure, called the optimum separator pressure, should be selected to maximize the oil volume accumulation in the stock tank.
- This optimum pressure also yields

  : A maximum in the stock-tank API gravity.

  : A minimum in the oil formation volume factor (i.e., less oil shrinkage).

  : A minimum in the producing gas/oil ratio (gas solubility).
- The concept of determining the optimum separator pressure by calculating the API gravity, Bo, and Rs is shown graphically,



Effect of separator pressure on API, Bo, and GOR.

Source: After J. M. Amyx, D. M. Bass, and R. Whiting, Petroleum Reservoir Engineering—Physical Properties. New York: McGraw-Hill, 1960.

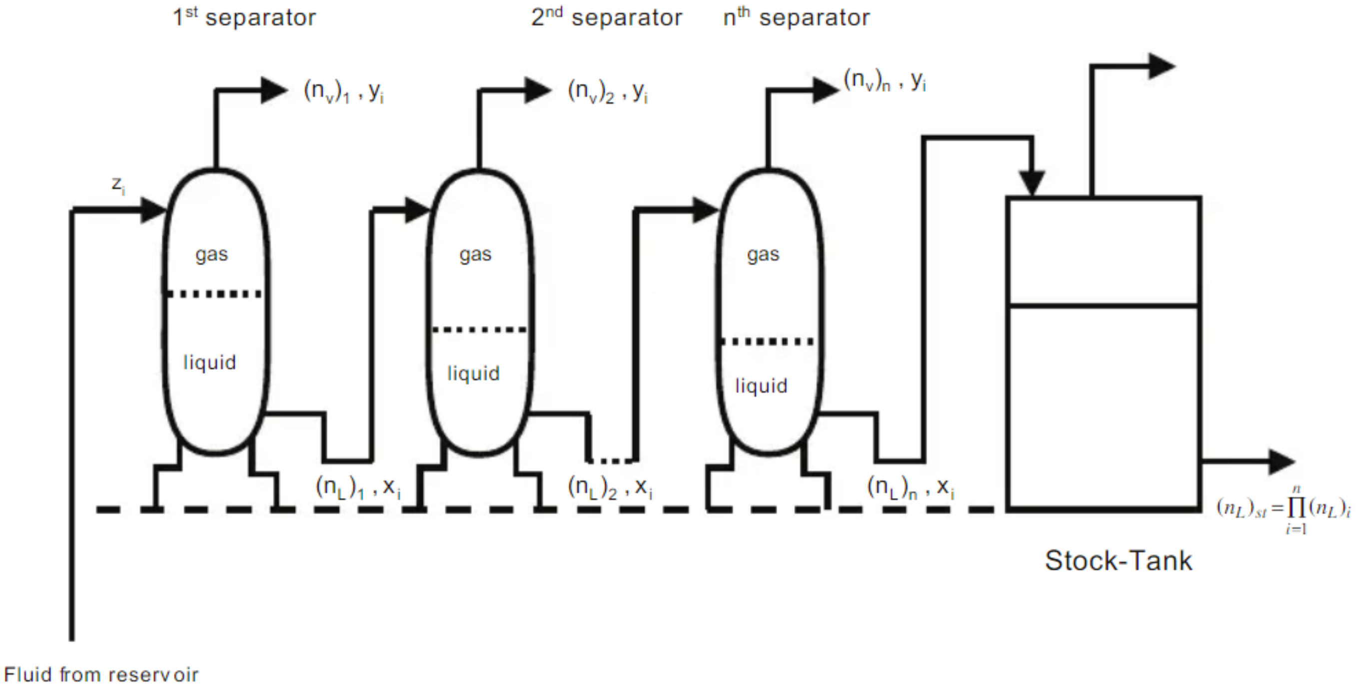
Example: Stage separation

- The following figure shows a bubble-point reservoir flowing into a surface separation unit consisting of n-stages operating at successively lower pressures.

<u>Step 1</u>

- Calculate the volume of oil occupied by 1 lb-mole of the crude oil at the reservoir pressure and temperature. This volume, denoted Vo, is calculated by the equation that defines the number of moles, to give

$$n = \frac{\rho_o V_o}{M_a} = 1$$



$$V_o = \frac{M_a}{\rho_o}$$

Where,

V_o = volume of 1 lb-mole of the crude oil at reservoir conditions, ft^3/mole

M_a = apparent molecular weight

ρ_o = density of the reservoir oil, lb/ft^3

Step 2

- Given the composition of the feed stream, z_i, to the first separator and the operating conditions of the separator (separator pressure and temperature), calculate the equilibrium ratios of the hydrocarbon mixture.

Step 3

- Assuming a total of 1 mole of the feed entering the first separator and using the preceding calculated equilibrium ratios, perform flash calculations to obtain the compositions and quantities, in moles, of the gas and the liquid leaving the first separator.
- The actual number of moles of the gas and the liquid leaving the first separation stage are

$$[n_{v1}]_a = (n)(n_v)_1 = (1)(n_v)_1$$
$$[n_{L1}]_a = (n)(n_L)_1 = (1)(n_L)_1$$

Step 4

- Using the composition of the liquid leaving the first separator as the feed for the second separator, that is, zi = xi, calculate the equilibrium ratios of the hydrocarbon mixture at the prevailing pressure and temperature of the separator.

Step 5

- Based on 1 mole of the feed, perform flash calculations to determine the compositions and quantities of the gas and liquid leaving the second separation stage. The actual number of moles of the two phases then is calculated from

$$[n_{v2}]_a = [n_{L1}]_a (n_v)_2 = (1)(n_L)_1 (n_v)_2$$

$$[n_{L2}]_a = [n_{L1}]_a (n_L)_2 = (1)(n_L)_1 (n_L)_2$$

where,

$[n_{v2}]_a, [n_{L2}]_a = actual\ moles\ of\ gas\ and\ liquid\ leaving\ separator\ 2$

$(n_v)_2, (n_L)_2 = moles\ of\ gas\ and\ liquid\ as\ determined\ from\ flash\ calculation$

Step 6

- The previously outlined procedure is repeated for each separation stage, including the stock-tank storage, and the calculated moles and compositions are recorded. The total number of moles of gas given off in all stages then are calculated as,

$$(n_v)_t = (n_v)_1 + \sum_{i=2}^{n}\left[(n_v)_i \prod_{j=1}^{i-1} (n_L)_j \right]$$

where

$(n_v)_t$ = total moles of gas given off in all stages, lb−mole/mole of feed

n = number of separation stages

The total moles of liquid remaining in the stock tank can be calculated as

$$(n_L)_{st} = \prod_{i=1}^{n} (n_L)_j$$

Step 7 (V_g)

- Calculate the volume in scf of all the liberated solution gas from

$$V_g = 379.4\ (n_v)_t$$

V_g = total volume of the liberated solution gas scf/mole of feed

Step 8 $(V_o)_{st}$

- Determine the volume of stock tank oil occupied by $(n_L)_{st}$ moles of liquid from

$$(V_o)_{st} = \frac{(n_L)_{st}(M_a)_{st}}{(\rho_o)_{st}}$$

where

$(V_o)_{st}$= volume of stock-tank oil, ft^3/mole of feed

$(M_a)_{st}$= apparent molecular weight of the stock tank oil

$(\rho_o)_{st}$= density of the stock tank oil, lb/ft^3

Step 9 (γ_o)

- Calculate the specific gravity and the API gravity of the stock-tank oil by applying the expression

$$\gamma_o = \frac{(\rho_o)_{st}}{62.4}$$

Step 10 GOR

- Calculate the total gas/oil ratio (or gas solubility, R_f)

$$GOR = \frac{V_g}{(V_o)_{st}/5.615} = \frac{(5.615)\,(379.4)(n_v)_t}{\frac{(n_L)_{st}(M_a)_{st}}{(\rho_o)_{st}}} = \frac{2130.331\,(n_v)_t(\rho_o)_{st}}{(n_L)_{st}(M_a)_{st}}$$

Step 11 B_o

- Calculate the oil formation volume factor from the relationship

$$B_o = \frac{V_o}{(V_o)_{st}} = \frac{M_a(\rho_o)_{st}}{\rho_o(n_L)_{st}(M_a)_{st}}$$

Where

B_o=oil formation volume factor, bbl/STB

M_a = apparent molecular weight of the feed

$(M_a)_{st}$=apparent molecular weight of the stock-tank oil

ρ_o = density of crude oil at reservoir conditions, lb/ft^3

The optimum pressure can be found by calculating the API gravity, GOR, and B_o at different assumed pressures.

Thank you!