

# Upstream Process Engineering Course

## 1. Hydrocarbon Phase Behaviour

# Oil and Gas Components

Alkanes (Paraffins).

Methane (CH<sub>4</sub>)

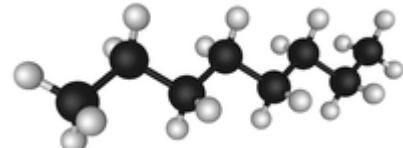
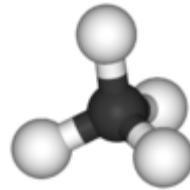
Ethane

Propane

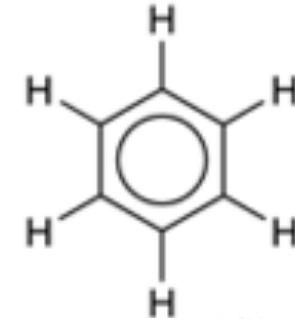
Butane

.....

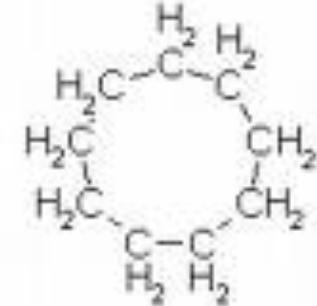
Octane (C<sub>8</sub>H<sub>18</sub>)



Aromatics -  
Benzene



Cycloparaffins -  
one or more  
cyclic structures

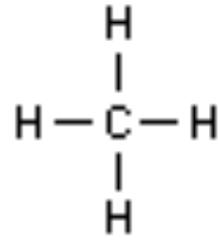


Naphthenates -  
one or more  
cyclic structures

# Oil and Gas Components

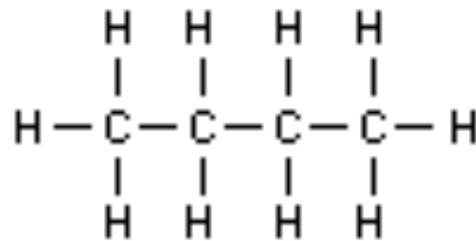
Methane is the simplest paraffin molecule:

Methane ( $\text{CH}_4$ )

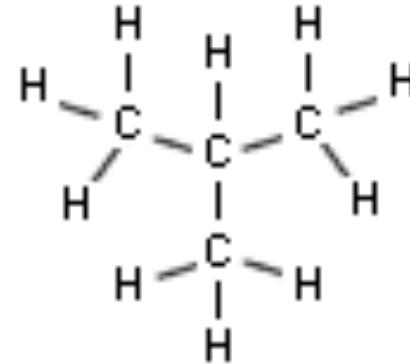


Examples of straight chain paraffin molecule (Butane) and branched paraffin molecule (Isobutane) with same chemical formula of:

Butane ( $\text{C}_4\text{H}_{10}$ )



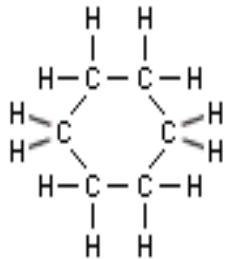
Isobutane ( $\text{C}_4\text{H}_{10}$ )



# Oil and Gas Components

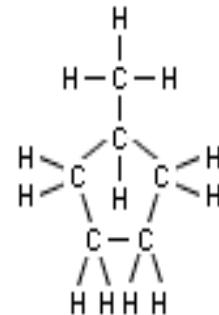
Example of a typical single-ring naphthenic:

Cyclohexane



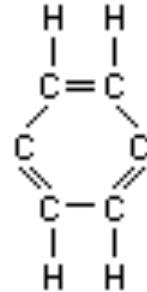
Example of naphthene with same chemical formula ( $C_6H_{12}$ ) but with a different molecular structure:

Methylcyclopentane ( $C_6H_{12}$ )



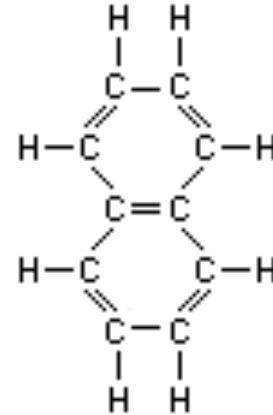
Example of simple aromatic compound:

Benzene ( $C_6H_6$ )



Example of simple double-ring aromatic compound:

Naphthalene ( $C_{10}H_8$ )



# Oil and Gas Components

## Sulphur

Sulphur compounds occur to some extent in most naturally occurring oil and gases. Sulphur compounds are poisons for many catalytic processes used within refinery operations. They also cause corrosion. When burned/flared the sulphur oxidise to sulphur dioxide – an atmospheric pollutant. Typical sulphur species are shown opposite.

## Nitrogen

Nitrogen is present in many oil and gas fields. Nitrogen can significantly impact phase behaviour .

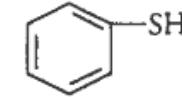
Hydrogen Sulfide



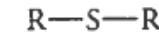
Mercaptans  
Aliphatic



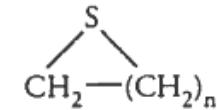
Aromatic



Sulfides  
Aliphatic



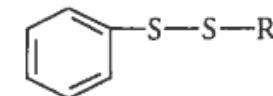
Cyclic



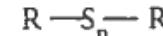
Disulfides  
Aliphatic



Aromatic



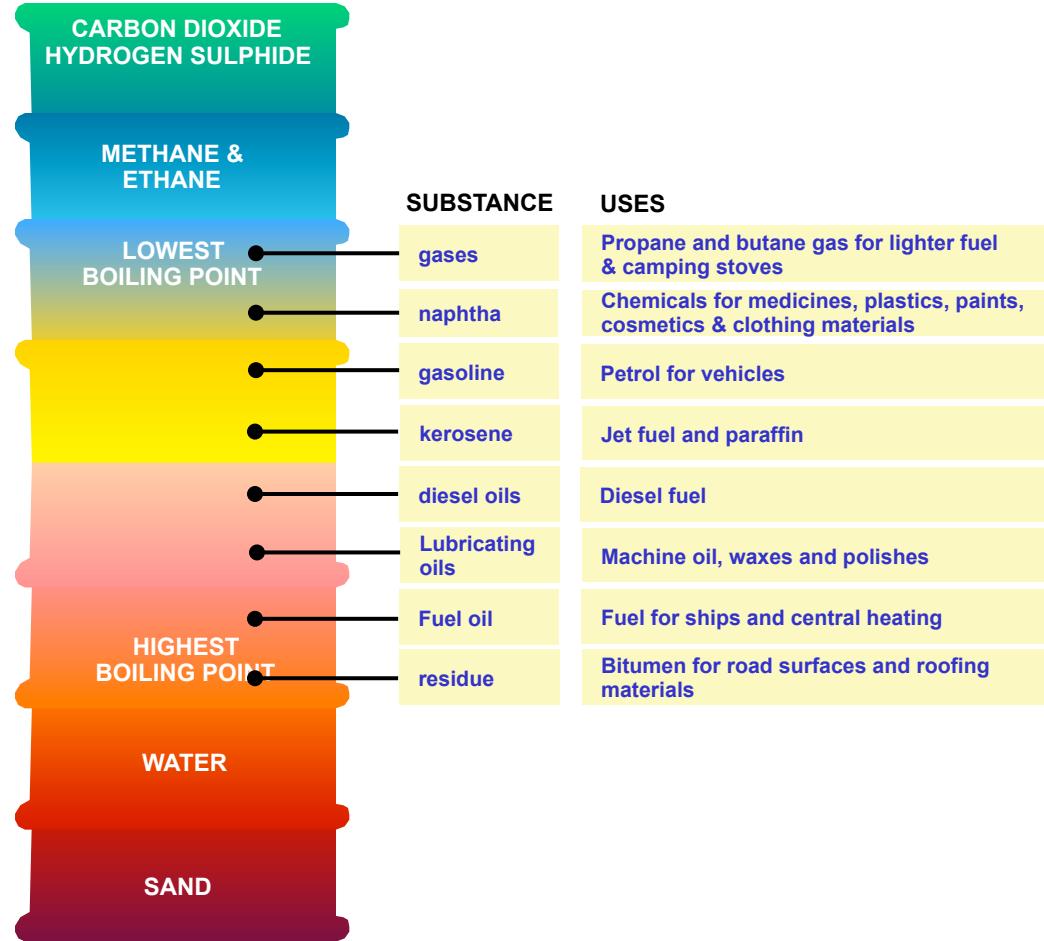
Polysulfides



Thiophene and  
Homologs



# Reservoir Barrel - Oil



Other components which may require treatment/consideration are;

- Hydrogen Cyanide (HCN)
- Carbonyl Sulphide (COS)
- Carbon Disulphide ( $CS_2$ )
- Mercaptans (RSH)
- Nitrogen ( $N_2$ )
- Sulphur Dioxide ( $SO_2$ )
- Mercury

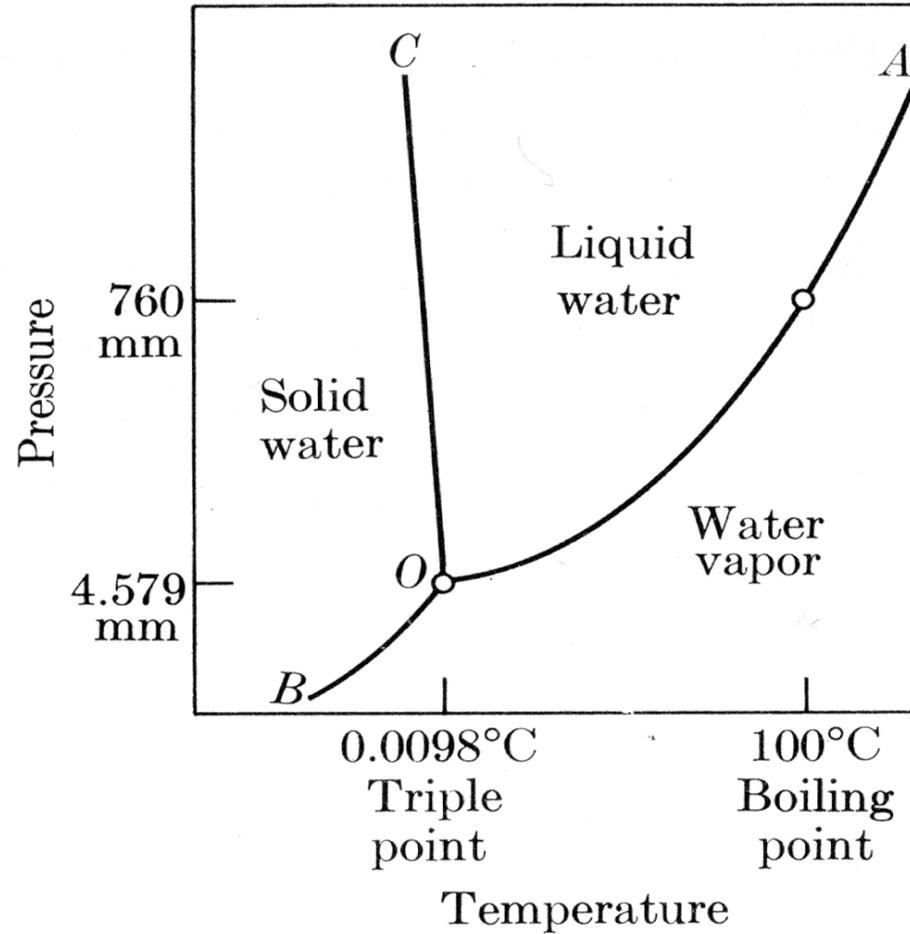
# Reservoir Barrel - Gas



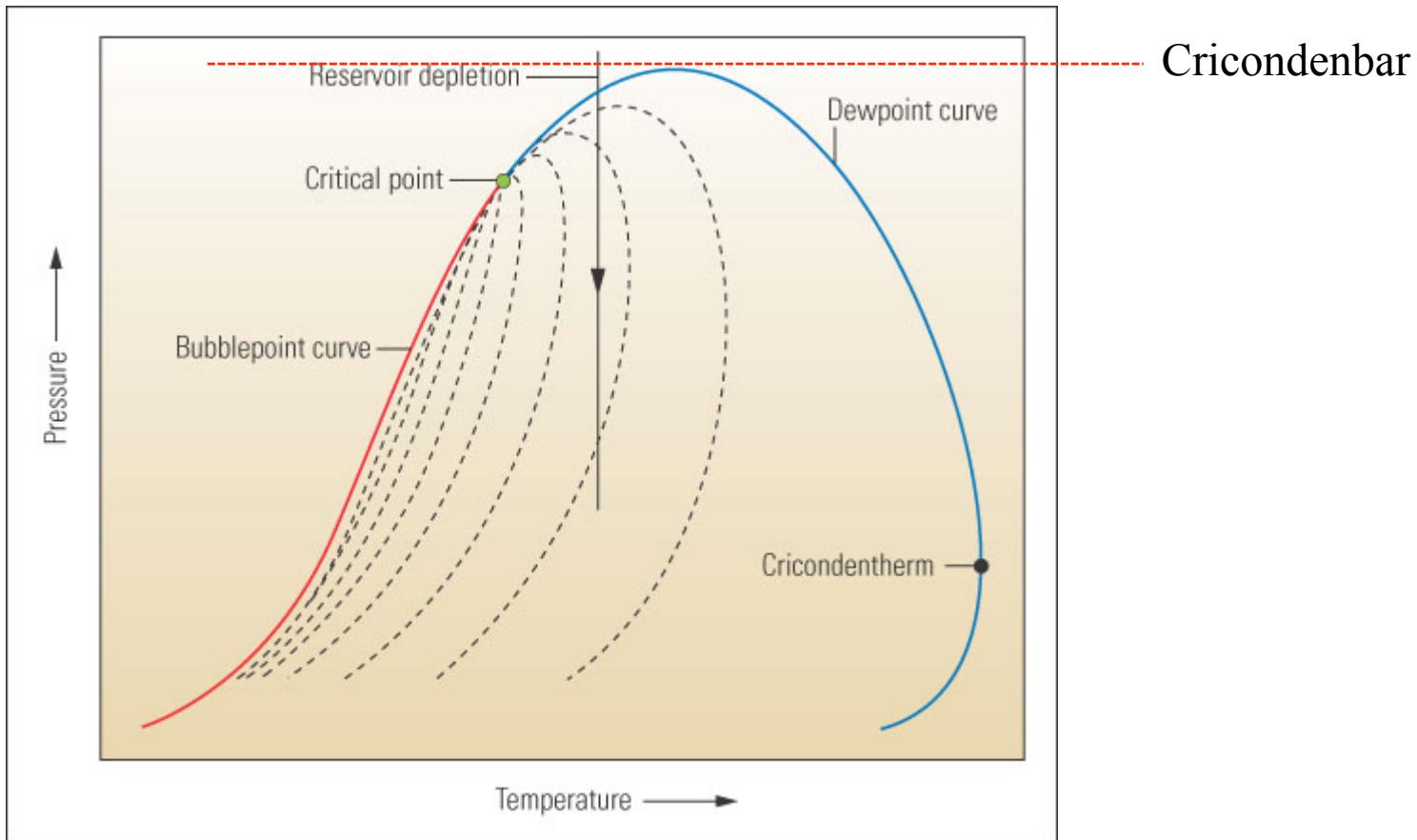
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- Nitrogen ( $N_2$ )
- Sulphur Dioxide ( $SO_2$ )
- Mercury

# Phase Diagram - Water



# Phase Envelope – multi-component hydrocarbon



# Phase Equilibrium Definitions

## Phase Diagram

A record of the effects of temperature, pressure and composition on the kinds and numbers of phases that can exist in equilibrium with each other

## Bubble Point

The point at which the first infinitesimally small vapour bubble appears in a liquid system. The bubble point curve on a phase diagram represents 0% vapour

## Dew Point

The point at which the first infinitesimally small droplet of condensation forms in a gaseous system. The dew point curve on a phase diagram represents 0% liquid

## Phase Envelope

The area on a pressure-temperature phase diagram for a mixture enclosed by the bubble and dew point curves. This area represents the set of conditions for the mixture where vapour and liquid phases co-exist in equilibrium.

## Cricondenbar

The maximum pressure at which vapour and liquid can co-exist in equilibrium

# Phase Equilibrium Definitions

## Cricondentherm

The maximum temperature at which vapour and liquid can co-exist in equilibrium.

## Critical Point

At the critical point, liquid and vapour phases of a fluid have identical physical properties.

## Quality Lines

Lines through the two-phase region showing a constant percentage of liquid and vapour.

## Retrograde

The name given to phase behaviour above the critical temperature and pressure where vapour and liquid phases coexist and the amount of vaporisation or condensation changes with pressure and temperature in the opposite direction to normal behaviour.

## Equation of State

An equation which describes the relationship between pressure, temperature and molar volume of any homogenous fluid at equilibrium

# Phase Equilibrium Definitions

## Fugacity

A thermodynamic concept arising from the consideration of the change in Gibbs free energy with changes in pressure and temperature for non-ideal mixtures and substances. Three types of fugacity can be defined: pure component fugacity, mixture fugacity, partial fugacity. Fugacity must have the same units as pressure by definition but will only be equal to pressure under ideal conditions (e.g. low pressure gases).

## Binary Interaction Coefficient

A constant which accounts for the deviation from ideality for component pairs in mixtures. These are specific to one equation of state as they are calculated by the regression of measured data. The coefficients used in a liquid activity method are essentially regression constants used to calculate the liquid activity coefficient

## Liquid Activity Coefficient

The ratio of the partial fugacity of a component in a mixture to its pure component fugacity at the same physical conditions, divided by its mole fraction in the mixture.

# Reservoir Fluid Types

Reservoir fluids are sometimes categorised into four types;

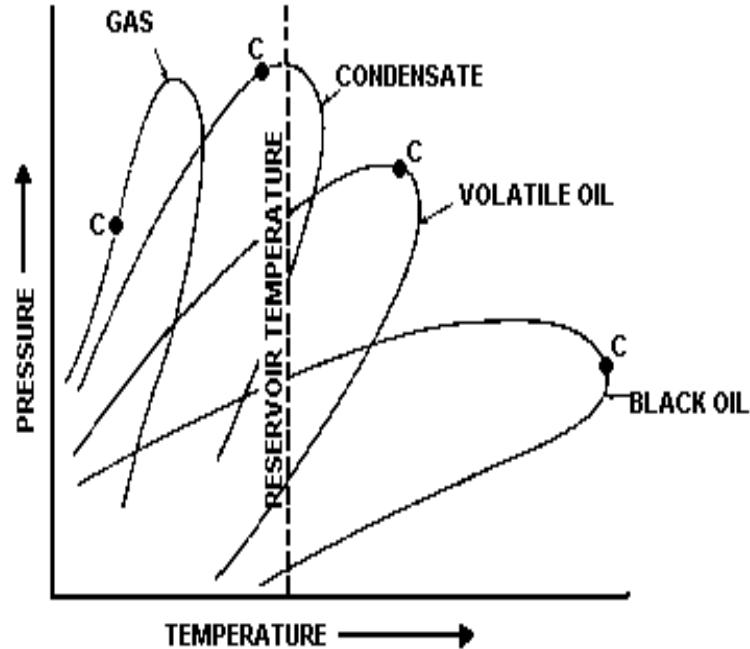
Black Oil - Forties

Volatile Oil - Gyda

Condensate - Brae

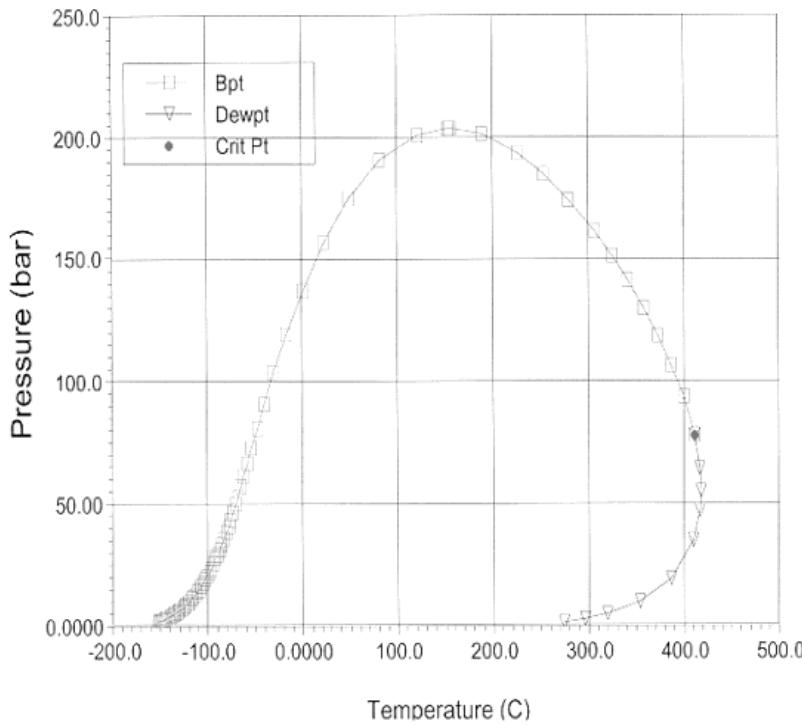
Gas – Viking

No clear definition of transition from one type to another.



Typical P-T diagrams – Phase Envelopes

# Typical ‘Black Oil’



Component	Mol %
Methane ( $\text{CH}_4$ )	48.83
Ethane ( $\text{C}_2\text{H}_6$ )	2.75
Propane ( $\text{C}_3\text{H}_8$ )	1.93
Butanes ( $\text{C}_4\text{H}_{10}$ )	1.6
Pentanes ( $\text{C}_5\text{H}_{12}$ )	1.15
Hexane ( $\text{C}_6\text{H}_{14}$ )	1.59
C7+	42.15
Molecular Weight of C7+	225
GOR (scf/bbl)	625
Oil Gravity ( $^{\circ}$ API)	34.3
Colour	Black

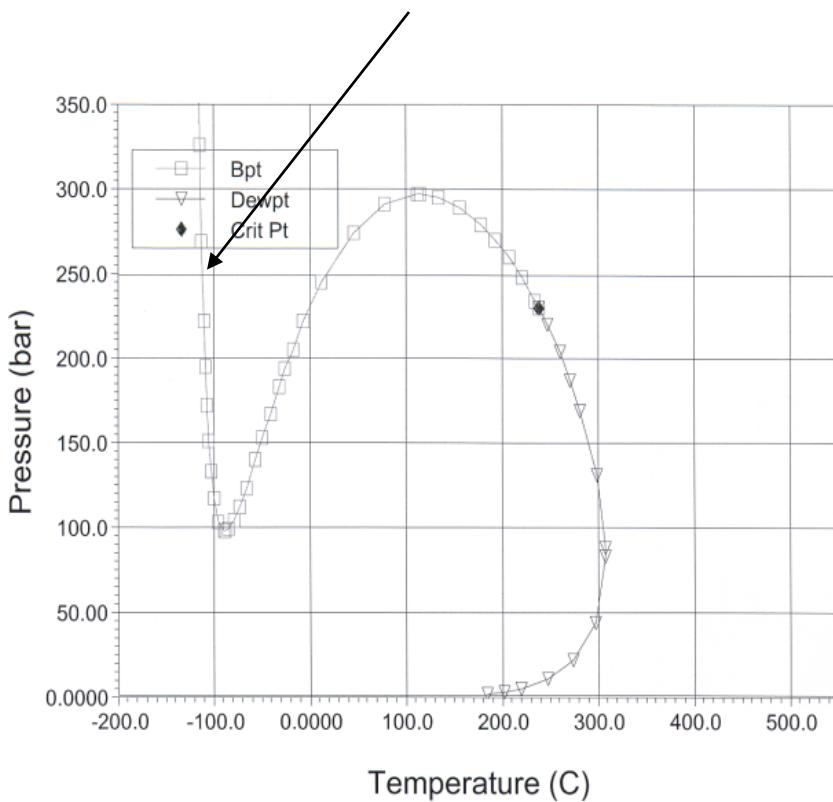
C7+ is a pseudo/hypothetical component representing an average of all species C7 and greater.

GOR – gas oil ratio, volume ratio of of gas to liquid oil.

API – liquid density – see lecture 1.

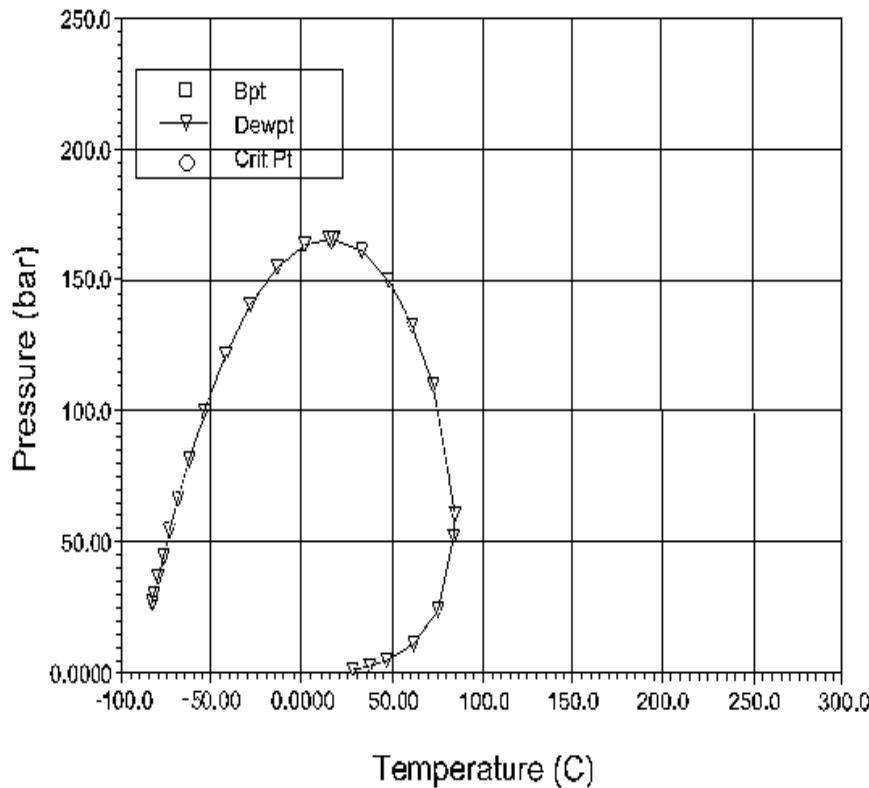
# Typical ‘Volatile Oil’

Is this real?



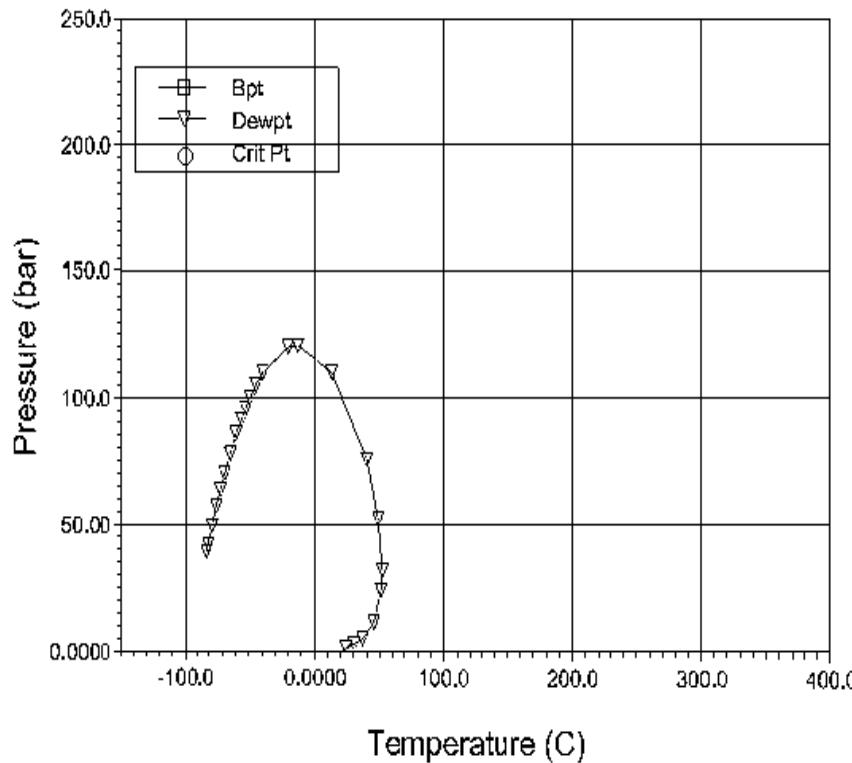
Component	Mol %
Methane ( $\text{CH}_4$ )	64.36
Ethane ( $\text{C}_2\text{H}_6$ )	7.52
Propane ( $\text{C}_3\text{H}_8$ )	4.74
Butanes ( $\text{C}_4\text{H}_{10}$ )	4.12
Pentanes ( $\text{C}_5\text{H}_{12}$ )	2.97
Hexane ( $\text{C}_6\text{H}_{14}$ )	1.38
C7+	14.91
Molecular Weight of C7+	181
GOR (scf/bbl)	2000
Oil Gravity ( $^{\circ}$ API)	50.1
Colour	Brown

# Typical ‘Gas Condensate’



Component	Mol %
Methane ( $\text{CH}_4$ )	87.07
Ethane ( $\text{C}_2\text{H}_6$ )	4.39
Propane ( $\text{C}_3\text{H}_8$ )	2.29
Butanes ( $\text{C}_4\text{H}_{10}$ )	1.74
Pentanes ( $\text{C}_5\text{H}_{12}$ )	0.83
Hexane ( $\text{C}_6\text{H}_{14}$ )	0.6
C7+	3.8
Molecular Weight of C7+	112
GOR (scf/bbl)	18200
Oil Gravity (° API)	60.8
Colour	Straw

# Typical ‘Dry Gas’



Component	Mol %
Methane ( $\text{CH}_4$ )	95.85
Ethane ( $\text{C}_2\text{H}_6$ )	2.67
Propane ( $\text{C}_3\text{H}_8$ )	0.34
Butanes ( $\text{C}_4\text{H}_{10}$ )	0.52
Pentanes ( $\text{C}_5\text{H}_{12}$ )	0.08
Hexane ( $\text{C}_6\text{H}_{14}$ )	0.12
C7+	0.42
Molecular Weight of C7+	157
GOR (scf/bbl)	105000
Oil Gravity ( ${}^{\circ}\text{ API}$ )	125
Colour	White

# Fluid Sampling

## Drill Stem Tests

Carried out on appraisal wells to provide sub-surface information and data for facilities design – fluid composition and physical properties

Laboratory and field measurements made

Basis for verifying simulation models

## Extended Well Test

Testing over many months

Sub-surface uncertainty reduced

Opportunities to undertake extensive facilities testing

Environmental implications require to be evaluated

## Topsides Samples

Regular samples are taken to maintain product quality and ensure levels of chemical treatment are sufficient

Pressurised samples are taken of crude at normal operating conditions for laboratory analysis and atmospheric samples

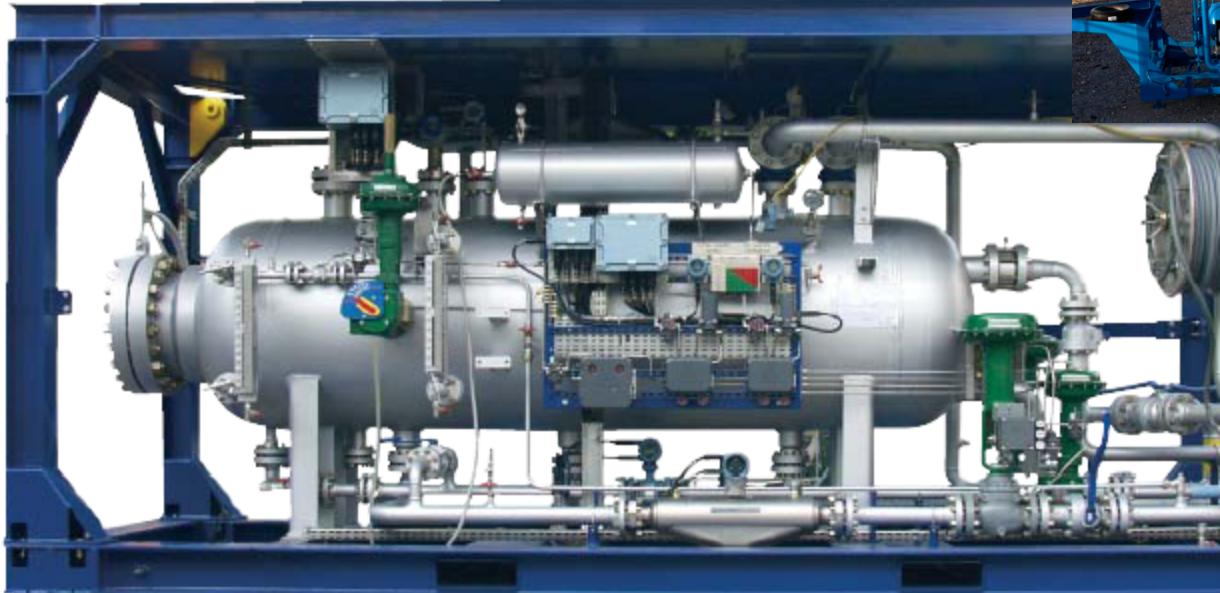


## Bottom Hole Samples

Downhole sampling involves capturing reservoir fluid samples at reservoir conditions. To obtain accurate compositional and PVT analyses of these samples, the recovered samples must remain in downhole conditions. Special chambers compensate for the pressure drop as the samples are returned to the surface.

QA for drilling fluid contamination  
For fast track development sometimes only sample

# Test Separator and Burner



Test separator is a fixed or mobile unit which is connected to a well where the oil, gas and water flows are measured. Fluid samples are also taken to allow for composition determination.

# Fluid Modelling

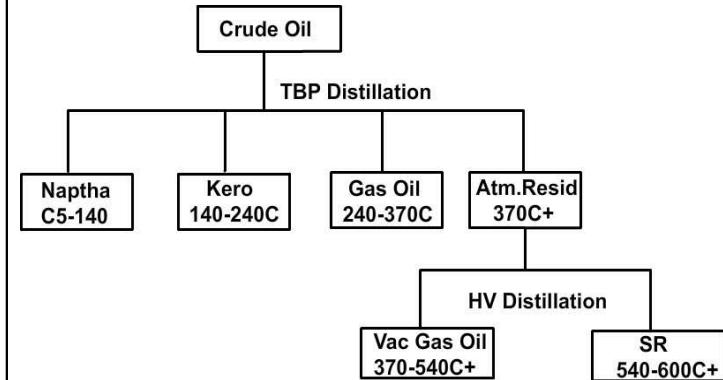
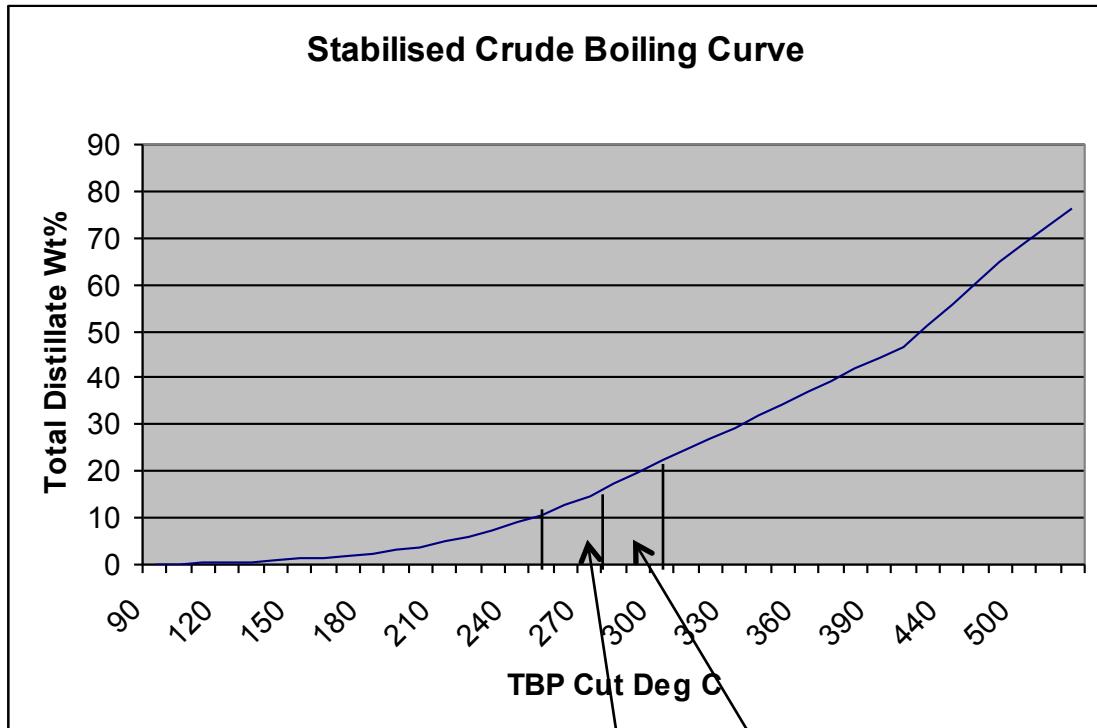
The choice of thermodynamic model is critical when evaluating phase behaviour.

Black Oil – simple correlations

Compositional – required for equation of state and generally more accurate than black oil.

# Heavy End Fluid Characterisation

## Pseudo components/Hypotheticals



# Simulator EOS Set Up

**Fluid Package: Basis-2**

**Property Package Selection**

- Kabadi-Danner
- Lee-Kesler-Plocker
- Margules
- MBWR
- NBS Steam
- NRTL
- OLI\_Electrolyte
- Peng-Robinson**
- PR-Twu
- PRSV
- Sour PR

**Property Package Filter**

- All Types
- EOSs
- Activity Models
- Chao Seader Models
- Vapour Pressure Models
- Electrolyte Models
- Miscellaneous Types

**EOS Enthalpy Method Specification**

- Equation of State
- Lee-Kesler

**Peng Robinson Options**

- Use EOS Density
- UniSim Design
- Smooth Liquid Density
- Modify H<sub>2</sub> T<sub>c</sub> and P<sub>c</sub>

Special Treatment for water

Component List View: Component List - 2

**Component List Selection**

Component List - 1

**Set Up** **Parameters** **Parameters2** **Binary Coeffs** **StabTest**

Delete Name **Basis-2** Property Pkg **Selected**

**Add Component**

- Library Components
  - Traditional
- + Hypo Components
- Other Comp Lists

**Selected Components**

**Components Available in the Library**

Match  View Filters...

<input type="radio"/> Sim Name	<input checked="" type="radio"/> Full Name / Synonym	<input type="radio"/> Formula
Methane	C1	CH <sub>4</sub>
Ethane	C2	C <sub>2</sub> H <sub>6</sub>
Propane	C3	C <sub>3</sub> H <sub>8</sub>
i-Butane	i-C <sub>4</sub>	C <sub>4</sub> H <sub>10</sub>
n-Butane	n-C <sub>4</sub>	C <sub>4</sub> H <sub>10</sub>
i-Pentane	i-C <sub>5</sub>	C <sub>5</sub> H <sub>12</sub>
n-Pentane	n-C <sub>5</sub>	C <sub>5</sub> H <sub>12</sub>
n-Hexane	C <sub>6</sub>	C <sub>6</sub> H <sub>14</sub>
n-Heptane	C <sub>7</sub>	C <sub>7</sub> H <sub>16</sub>
n-Octane	C <sub>8</sub>	C <sub>8</sub> H <sub>18</sub>
n-Nonane	C <sub>9</sub>	C <sub>9</sub> H <sub>20</sub>
n-Decane	C <sub>10</sub>	C <sub>10</sub> H <sub>22</sub>
Nitrogen	N <sub>2</sub>	N <sub>2</sub>
CO <sub>2</sub>	CO <sub>2</sub>	CO <sub>2</sub>
H <sub>2</sub> S	H <sub>2</sub> S	H <sub>2</sub> S

Show Synonyms  Cluster

**Selected** **Component by Type** **Component Databases**

Name **Component List - 2**

**Delete**

# Simulator EOS Set Up

**Simulation Basis Manager**

**Hypothetical Groups**

- HypoGroup1 (selected)
- Add...**
- Delete**
- Translocate**
- Import...**
- Export...**

**Hypothetical Quick Reference**

Hypo Name	Group Name

**View Hypo...**

**View Group...**

**Move Hypos...**

**Clone Comps...**

**Hypo Group: HypoGroup1**

**Hypo Group Controls**

Group Name: **HypoGroup1**

Component Class: **Hydrocarbon**

**Estimation Methods...**

**Clone Library Comps...**

**Enter PVT Environment...**

**Notes**

Name	NBP [C]	MW	Liq Density [kg/m3]	Tc [C]	Pc [kPa]	Vc [m3/kgmole]	Acentricity

**Individual Hypo Controls**

**View...** **Add Hypo** **Add Solid** **Delete** **UNIFAC...**

**Base Properties**  **Vapour Pressure**

# Fugacity

Fugacity is key to the understanding of the solution of an equation state and the principles of equilibrium. To recap earlier thermodynamic lectures, fugacity is a conceptual term which is related to Gibb's free energy, temperature, volume and pressure. The units of fugacity are the same as pressure. Although fugacity has the same units as pressure it will only be equal to pressure under ideal conditions.

For a system of phases to be in equilibrium there must be no mechanical, thermal or chemical driving force. At constant temperature and pressure the chemical potential of every species must be equal. Thus there is no driving force for species to move from one phase to another. Fugacity is directly related to chemical potential hence at equilibrium species fugacity will be equal.

# Fugacity

For a component in a gas and liquid mixture, the fugacity coefficient is:

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

$$\Phi_i = \frac{f_i}{x_i P}$$

Where  $y_i$  and  $x_i$  is the mole fraction of component  $y$  in the vapour and liquid phase.

Classical thermodynamics shows;

$$\ln \Phi_i = \int_0^P \left[ \frac{z_i - 1}{P} \right] dP$$

# Equilibrium Ratios

The vapour-liquid equilibrium constant ( $K$ ) is defined as the mole fraction of any component in the vapour phase divided by the mole fraction of the same component in the liquid phase:

$$K_i = y_i / x_i$$

An equation of state can be used to calculate accurate  $K$  values when the vapour and liquid phases co-exist in equilibrium

Use of Equilibrium Ratios is key to the preparation of oil and gas processing heat and mass balances.  $K$  value charts can be used to provide the required ratios.

# Application of K Values

The basic application of K values is the calculation of dew points, bubble points and the vapour-liquid behaviour inside the phase envelope (flash calculations)

## Bubble Point Calculation

$$\sum K_i x_i = \sum y_i = 1.0$$

Assume a temperature for the known pressure (or assume pressure if temperature is known)

Find  $K_i$  at pressure and temperature known and assumed

Multiply  $K_i$  by the corresponding  $x_i$

If summation of values is 1.0, then pressure and temperature is correct, if not repeat until  $\sum K_i x_i = 1.0$ , within accuracy limits

## Dew Point Calculation

$$\sum (y_i/K_i) = \sum x_i = 1.0$$

The steps involved in a dew point calculation are the same as for the bubble point calculation.

A dew point calculation is less exact than a bubble point calculation, especially for lean gases containing a small amount of heavy ends.

# Flash Calculation

Flash calculations determine the amount of vapour and liquid in a two phase system

- $F = V + L$  (Overall)
- $F z_i = V y_i + L x_i$  (For each component)
- Where

$F$  = mols of total feed

$V$  = mols of gas leaving system for  $F$  mols of feed

$L$  = mols of liquid leaving system for  $F$  mols of feed

$z_i$  = mols of component ‘ $i$ ’ in the feed stream per mol total feed

$y_i$  = mol fraction of component ‘ $i$ ’ in the gas stream ( $V$ )

$x_i$  = mol fraction of component ‘ $i$ ’ in the liquid stream ( $L$ )

- Let  $F = 1$  and substitute  $y_i = K_i x_i$ , then

$$x_i = \frac{z_i}{(L + VK_i)} \quad \text{and} \quad y_i = \frac{z_i}{\left(V + \frac{L}{K_i}\right)}$$

# Flash Calculation Procedure

$$\sum x_i = \sum \frac{z_i}{(L + VK_i)} = 1.0 \quad \sum y_i = \sum \frac{z_i}{\left(V + \frac{L}{K_i}\right)} = 1.0$$

- For a specific pressure and temperature  $K_i$  can be determined
- Flash calculation solution is iterative
- Guess V and calculate L
- Calculate all  $y_i$  all  $x_i$
- Test  $\sum x_i$  or  $\sum y_i = 1.0$  then a solution has been obtained
- If not re-initialise L or V

# Bubble Point – Worked Example

## Refer to handout example

Given the following mixture composition, determine the bubble point at 10 bara.

Component	Mole Frac.	70 °C		80 °C	
		x <sub>i</sub>	K <sub>i</sub>	x <sub>i</sub>	K <sub>i</sub>
Propane	0.4	2.1	0.84	2.4	0.96
Butane	0.05	0.78	0.039	0.96	0.048
Pentane	0.1	0.32	0.032	0.4	0.04
Hexane	0.17	0.12	0.02	0.165	0.028
Octane	0.28	0.02	0.006	0.027	0.0076
Total	1.0		0.94		1.08

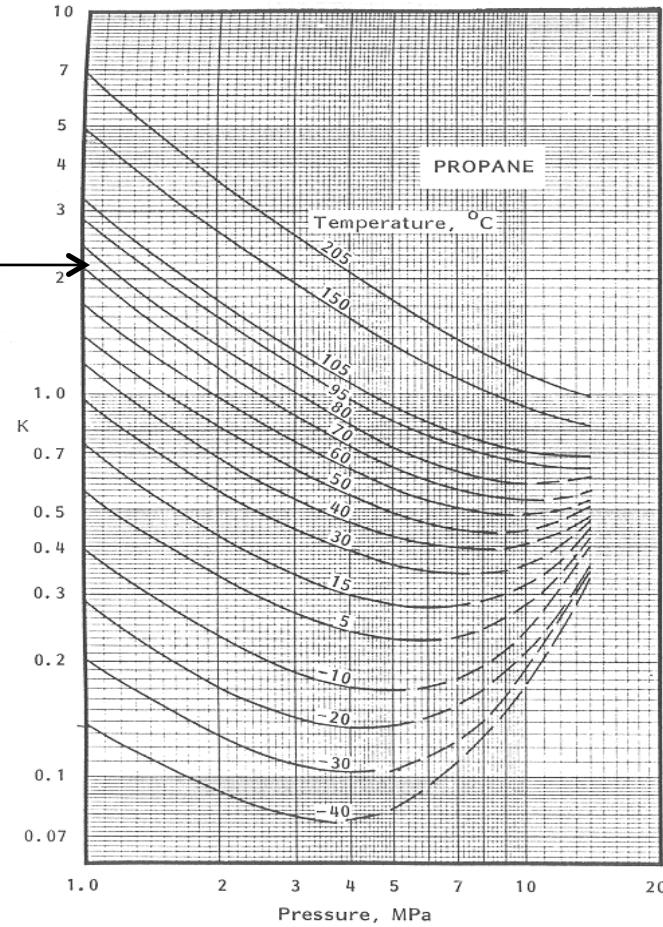
1. Assume T = 70 °C and find K values from charts.

$$\sum Kx_i = 0.94 \Rightarrow \text{too low}$$

2. Assume T = 80 °C and find K values from charts.

$$\sum Kx_i = 1.08 \Rightarrow \text{too high}$$

3. Interpolate between 70 and 80 °C to find bubble point = 74 °C



# Dew Point – Worked Example

Given the same composition, determine the dew point at 10 bara.

Component	Mole Frac.	$y_i$	$K_i$	$y_i/K_i$	$K_i$	$y_i/K_i$
		180 °C	190 °C	180 °C	190 °C	180 °C
Propane	0.4	5.9	6.25	0.068	0.064	
Butane	0.05	3.2	3.4	0.016	0.015	
Pentane	0.1	2.0	2.2	0.05	0.045	
Hexane	0.17	1.0	1.15	0.17	0.148	
Octane	0.28	0.35	0.42	0.8	0.67	
Total	1.0			1.104		0.94

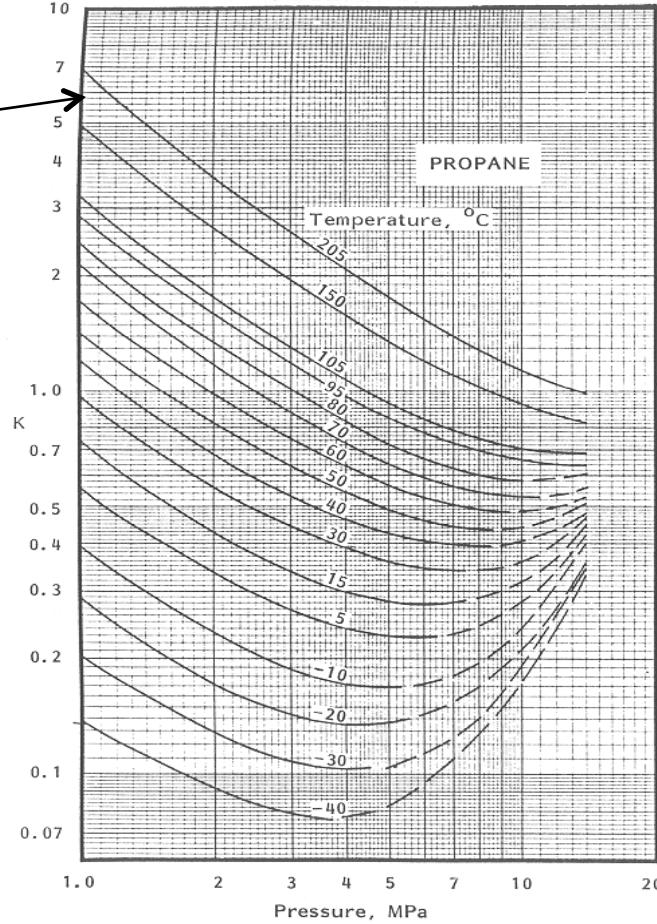
- Assume T = 180 °C and find K from charts.

$$\sum y_i/K_i = 1.104 \Rightarrow \text{too high}$$

- Assume T = 190 °C and find K from charts.

$$\sum y_i/K_i = 0.94 \Rightarrow \text{too low}$$

- Interpolate between 180 °C and 190 °C to find the dew point = 186.5 °C

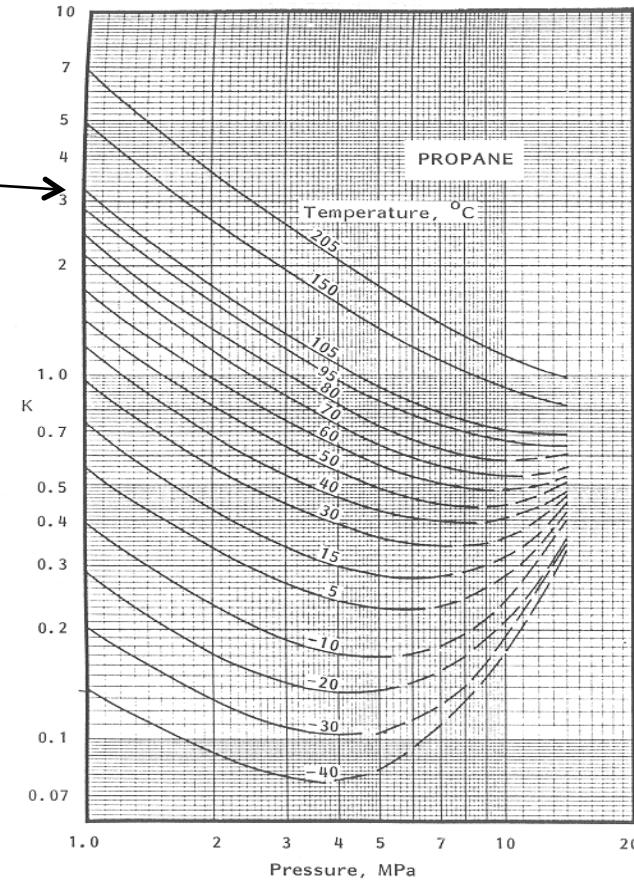


# Flash Calculation – Worked Example

Calculate the vapour Liquid split for the same fluid at 100 °C and 10 bara.

Component	$Z_i$	$K_i$	$V_i = 0.5$	$V = 0.4$	$V = 0.3$
Propane	0.4	3.1	0.409	0.457	0.51
Butane	0.05	1.4	0.016	0.02	0.026
Pentane	0.1	0.62	-0.046	-0.045	-0.04
Hexane	0.17	0.3	-0.182	-0.165	-0.15
Octane	0.28	0.062	-0.494	-0.42	-0.366
Total	1.0		$\Sigma = -0.298$	$\Sigma = -0.153$	$\Sigma = -0.02$

$$\sum y_i - x_i$$



1. Assume  $V=0.5$  and  $L=0.5$  ( $L+V=1$ ) and calculate  $x_i$  and  $y_i$  as in next slide.

$$\sum y_i - x_i = -0.298 \Rightarrow \text{too high}$$

2. Assume  $V=0.4$  and  $L=0.6$

$$\sum y_i - x_i = -0.153 \Rightarrow \text{too high}$$

3. Assume  $V=0.3$  and  $L=0.7$  – convergence achieved.

$$\sum y_i - x_i = -0.02$$

# Flash Calculation – Worked Example

**Vapour and Liquid Composition for V=0.3**

$$\sum x_i = \sum \frac{z_i}{(L + VK_i)} = 1.0 \quad \sum y_i = \sum \frac{z_i}{\left(V + \frac{L}{K_i}\right)} = 1.0$$

Component	Z <sub>i</sub>	K <sub>i</sub>	y <sub>i</sub> - x <sub>i</sub>	x <sub>i</sub>	y <sub>i</sub>
Propane	0.4	3.1	0.51	0.25	0.76
Butane	0.05	1.4	0.026	0.04	0.0625
Pentane	0.1	0.62	-0.04	0.11	0.069
Hexane	0.17	0.3	-0.15	0.215	0.06
C7+	0.28	0.062	0.366	0.390	0.024
Total	1.0		$\Sigma = -0.02$	$\Sigma = 1.005$	$\Sigma = 0.98$

# K Values

K values can be estimated from the following – (Wilson, A Modified Redlich-Kwong EOS, AIChE National Meeting).

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

P - absolute pressure

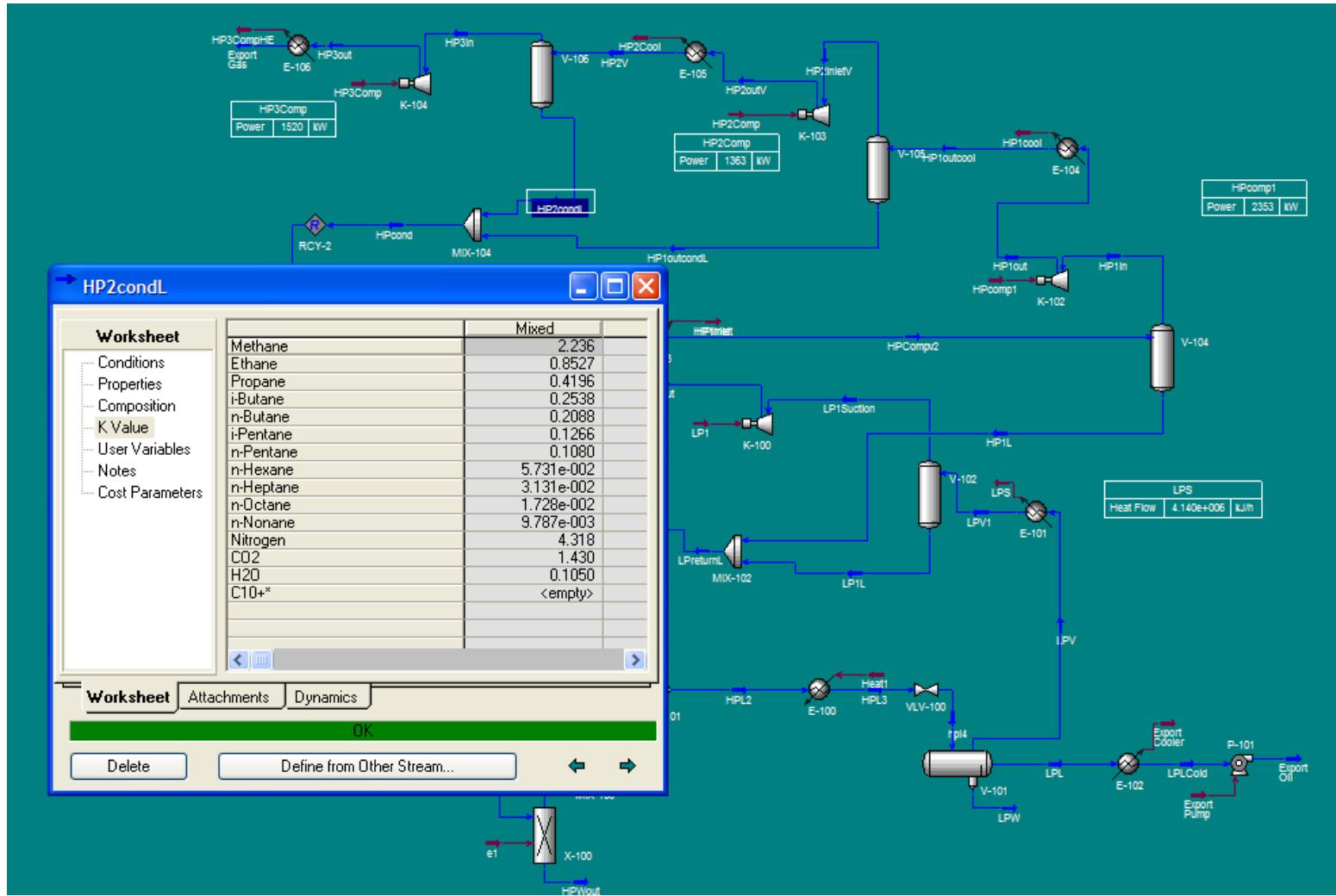
$P_{ci}$  – component i critical pressure in same units as P

T – absolute temperature

$T_{ci}$  – component i critical temperature in same units as T

$\omega_i$  - Acentric factor component i (discussed later)

# EOS in UniSim provides accurate K values



# Equations of State – Van der Waals

In 1873, J. D. van der Waals introduced the first equation of state derived by the assumption of a finite volume occupied by the constituent molecules. His new formula revolutionized the study of equations of state, and was most famously continued via the Redlich–Kwong equation of state and the Soave modification of Redlich-Kwong.

The Van der Waals equation of state may be written:

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

where  $V_m$  is molar volume, and  $a$  and  $b$  are substance-specific constants  
 $a$  and  $b$  can be calculated from the critical properties  $p_c$ ,  $T_c$  and  $V_c$

# Soave-Redlich-Kwong

## Standard Form

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

## Polynomial Compressibility Form

$$z^3 - z^2 + (A - B - B^2)z - AB = 0$$

## Parameters

$$A = (a\alpha P)/(R^2 T^2) = 0.42748 \alpha P_r / T_r^2$$

$$B = (b P)/(R T) = 0.08664 P_r / T_r$$

$$a = \Omega_a R^2 T_c^2 / P_c = 0.42748 R^2 T_c^2 / P_c$$

$$b = \Omega_b R T_c / P_c = 0.08664 R T_c / P_c$$

$$\sqrt{\alpha} = 1 + m(1 - Tr^{0.5}) \text{ where}$$

$$m = 0.48 + 1.574\omega - 0.172\omega^2$$

## Fugacity Coefficient

$$\ln \phi = z - 1 - \ln(z - B) - A/B \ln(1 + B/z)$$

## Mixtures

$$a\alpha = \sum \sum y_i y_j (a\alpha)_{ij}$$

$$b = \sum y_i b_i$$

$$A = \sum \sum y_i y_j A_{ij}$$

$$B = \sum y_i B_i$$

$$(a\alpha)_{ij} = (1 - k_{ij})[(a\alpha_i)(a\alpha_j)]^{0.5}$$

# Notation

## Definitions

$a$	Attraction parameter
$b$	Residual volume parameter
$\Omega$	SRK Parameter (numerical coefficient)
$A$	Derived parameter
$B$	Derived parameter
$z$	$= PV/RT$ , compressibility factor
$a_i$	$= \hat{f}_i/f^0$ , activity of a species in a mixture
$\hat{f}_i$	Partial fugacity of species $i$
$k_{ij}$	Binary Interaction Parameter (values of $k_{ij}$ for around 100 pairs are available)
$a_{ij}$	Cross-parameter

## Symbols

$\alpha$	Parameter
$\alpha_{ij}$	Volatility of species $i$ relative to that of species $j$
$\phi$	$= f_i/P$ , Fugacity Coefficient
$\omega$	Acentric Factor
$\rho$	Molar Density
$\gamma$	$= a_i/x_i$ , Activity Coefficient of species $i$

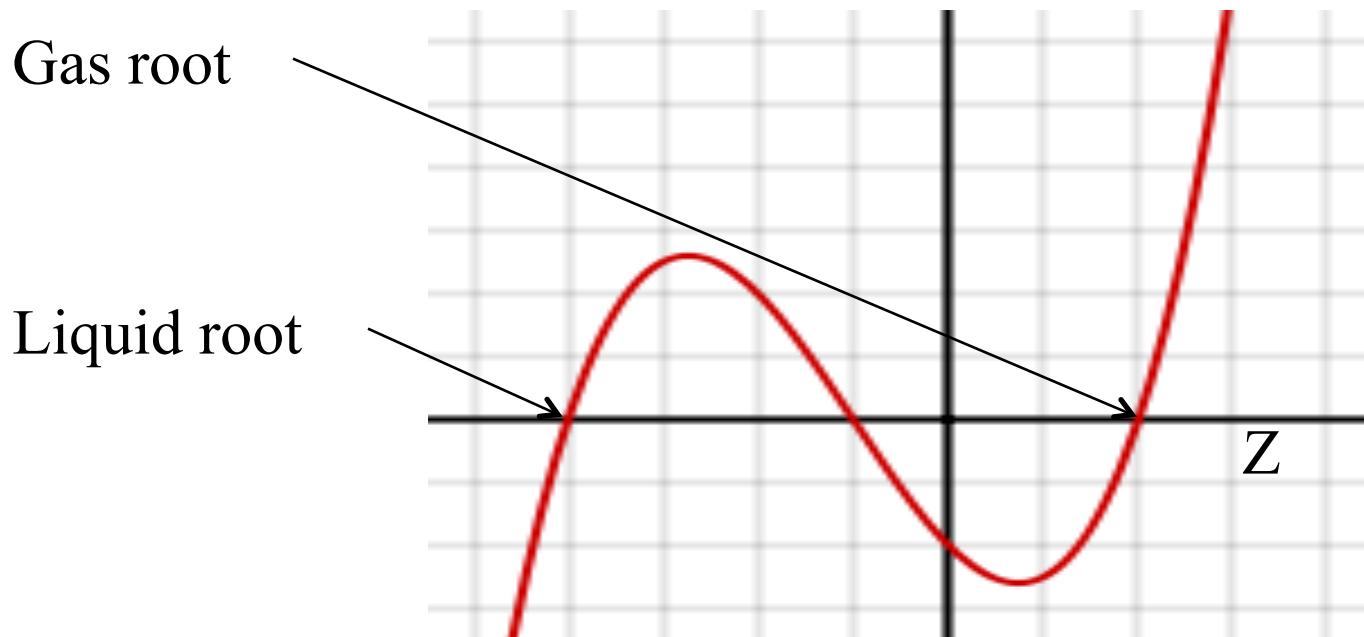
## Subscripts

$c$	Value of any variable at the critical point
$r$	Reduced Value
$pc$	Pseudo-critical value

## Superscripts

$0$	property of a standard state, e.g. $f^0$
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# Cubic Equation



# Peng-Robinson

Peng-Robinson is robust and well proven, ideal for use in oil & gas and refinery applications. It is generally similar in performance and applicability to SRK except as follows.

It is generally accurate over a wider range of conditions.

It is more accurate around the critical point.

Liquid phase density prediction is more accurate.

Adapted PR packages can be used for heavy end VLE prediction and vacuum distillation.

*Peng, D. Y. and Robinson, D. B., (1976). A New Two-Constant Equation of State. Ind. Eng. Chem. Fundam., 15, 59-64.*

# Peng-Robinson

## Standard Form

### Polynomial Compressibility Form

$$z^3 - \frac{RT}{(1-B)^2} + \frac{aa}{(\sqrt{A} - 2b\sqrt{B})^2} - 2B)z - (AB - B^2 - B^3) = 0$$

### Parameters

$$a = 0.45724 [(R^2 T_c^2)/P_c]$$

$$b = 0.07780 RT_c/P_c$$

$$\alpha = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1-T_r^{0.5})]^2$$

$$A = (a\alpha P)/(R^2 T^2) = 0.45724 \alpha P_r / T_r^2$$

$$B = (bP)/(RT) = 0.0778 P_r / T_r$$

### Fugacity Coefficient

$$\ln \phi = z - 1 - \ln(z - B) - [A/2(2B)^{0.5}] \ln [(z+2.414B)/(z-0.414B)]$$

### Mixtures

$$a\alpha = \sum \sum y_i y_j (a\alpha)_{ij}$$

$$b = \sum y_i b_i$$

$$(a\alpha)_{ij} = (1 - k_{ij}) [(a\alpha)_i (a\alpha)_j]^{0.5}$$

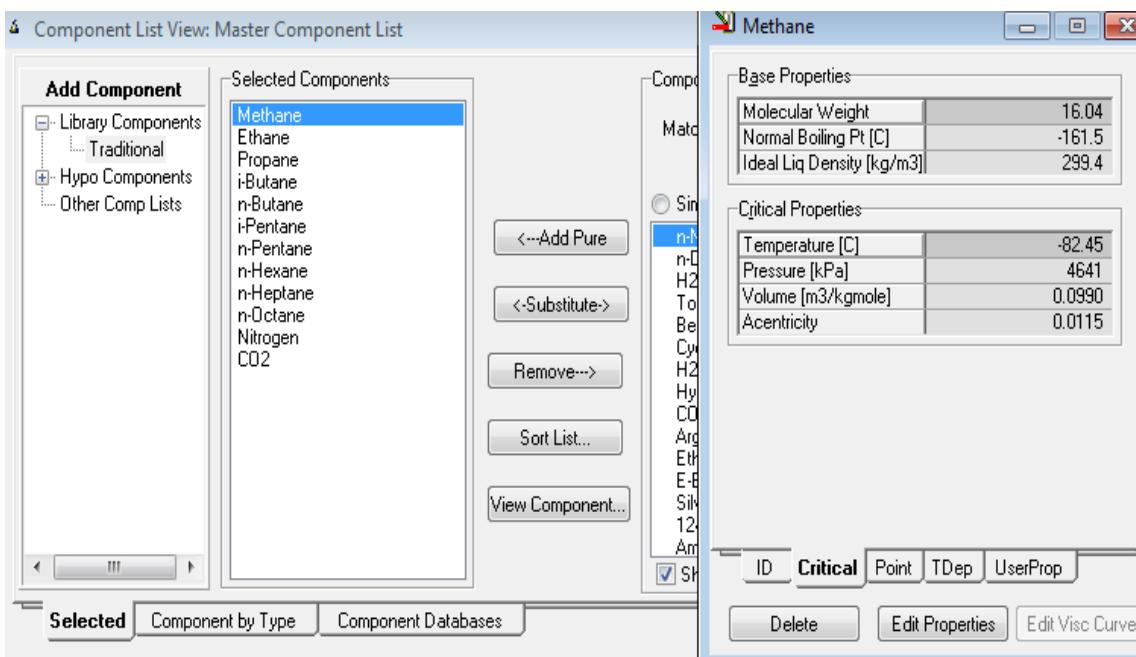
$$A = \sum \sum y_i y_j A_{ij}$$

$$B = \sum y_i B_i$$

$$A_{ij} = (1 - k_{ij})(A_i A_j)^{0.5}$$

# Acentric Factor

The acentric factor ( $\omega$ ) describes the change in the intermolecular attraction component,  $a$  with temperature.

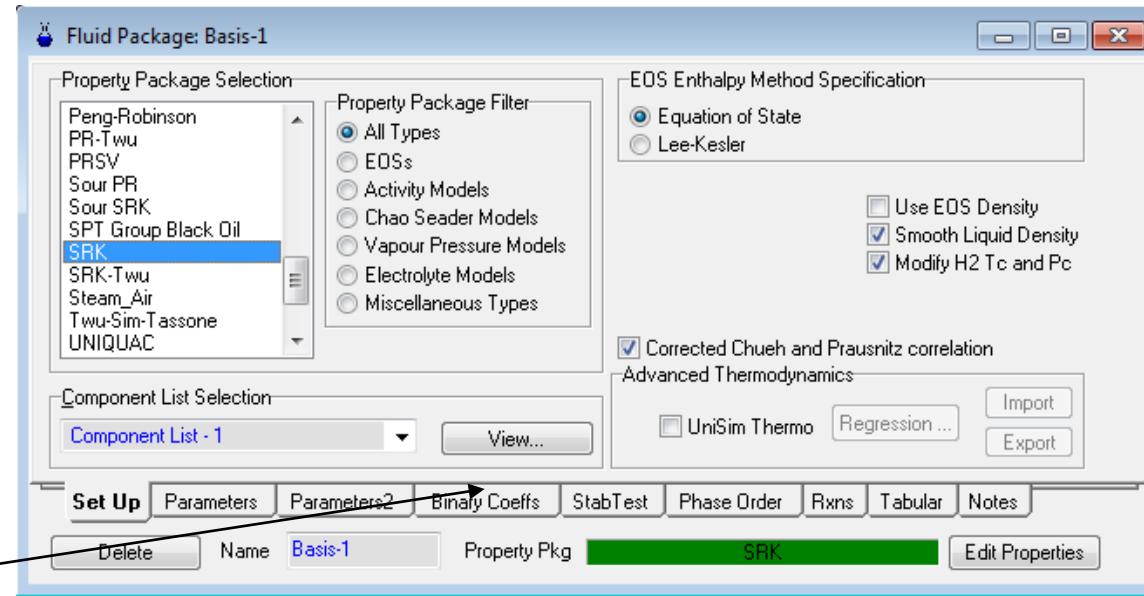


The screenshot shows a software application for managing component lists. On the left, a 'Component List View: Master Component List' window displays a tree view of components under 'Add Component' categories like Library Components, Traditional, Hypo Components, and Other Comp Lists. A 'Selected Components' list on the right contains Methane, Ethane, Propane, i-Butane, n-Butane, i-Pentane, n-Pentane, n-Hexane, n-Heptane, n-Octane, Nitrogen, and CO2. The 'Methane' component is selected, and its detailed properties are shown in a modal window titled 'Methane'. The 'Base Properties' section includes Molecular Weight (16.04), Normal Boiling Pt [C] (-161.5), and Ideal Liq Density [kg/m3] (299.4). The 'Critical Properties' section includes Temperature [C] (-82.45), Pressure [kPa] (4641), Volume [m3/kgmole] (0.0990), and Acentricity (0.0115). Below the modal are tabs for ID, Critical, Point, TDep, and UserProp, with 'Critical' being the active tab. At the bottom are buttons for Delete, Edit Properties, and Edit Visc Curve.

Compound	Acentric Factor
Nitrogen	0.039
Carbon Dioxide	0.224
Methane	0.011
Ethane	0.099
Butane	0.119
Hexane	0.299
Octane	0.398
Decane	0.489

The table shows typical acentric factors, the value increases with the size of the molecule and polarity.

# Binary Interaction Parameters



## Equation of State Interaction Parameters

	Methane	Ethane	Propane	i-Butane	n-Butane	i-Pentane	n-Pentane	n-Hexane	n-Heptane	n-Octane	Nitrogen	CO2
Methane	...	0.00224	0.00683	0.01311	0.01230	0.01763	0.01793	0.02347	0.02886	0.03416	0.03120	0.09560
Ethane	0.00224	...	0.00126	0.00457	0.00410	0.00741	0.00761	0.01141	0.01532	0.01932	0.03190	0.14010
Propane	0.00683	0.00126	...	0.00104	0.00082	0.00258	0.00270	0.00514	0.00789	0.01085	0.08860	0.13680
i-Butane	0.01311	0.00457	0.00104	...	0.00001	0.00035	0.00039	0.00157	0.00322	0.00521	0.13150	0.13680
n-Butane	0.01230	0.00410	0.00082	0.00001	...	0.00050	0.00055	0.00187	0.00365	0.00575	0.05970	0.14120
i-Pentane	0.01763	0.00741	0.00258	0.00035	0.00050	...	0.00000	0.00044	0.00146	0.00288	0.09300	0.12970
n-Pentane	0.01793	0.00761	0.00270	0.00039	0.00055	0.00000	...	0.00039	0.00137	0.00276	0.09360	0.13470
n-Hexane	0.02347	0.01141	0.00514	0.00157	0.00187	0.00044	0.00039	...	0.00030	0.00107	0.16500	0.14200
n-Heptane	0.02886	0.01532	0.00789	0.00322	0.00365	0.00146	0.00137	0.00030	...	0.00024	0.07999	0.10920
n-Octane	0.03416	0.01932	0.01085	0.00521	0.00575	0.00288	0.00276	0.00107	0.00024	...	0.07999	0.13500
Nitrogen	0.03120	0.03190	0.08860	0.13150	0.05970	0.09300	0.09360	0.16500	0.07999	0.07999	...	-0.01710
CO2	0.09560	0.14010	0.13680	0.13680	0.14120	0.12970	0.13470	0.14200	0.10920	0.13500	-0.01710	...

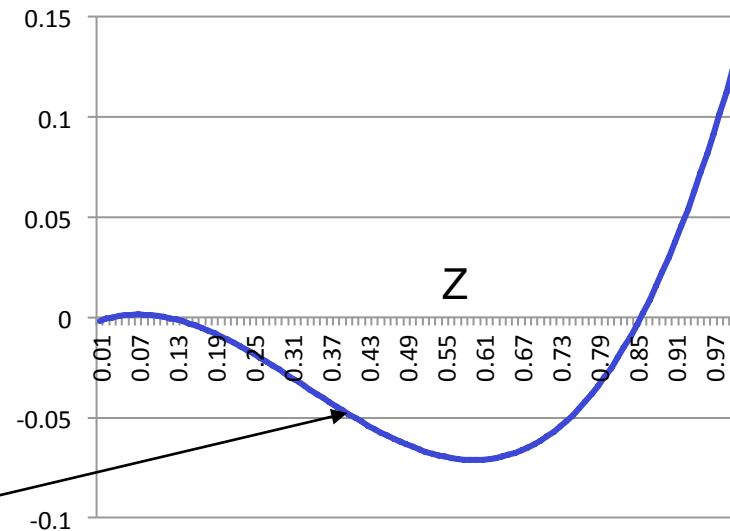
# SRK Example

Calculation of the saturation pressure of n-Pentane at 100 °C using an Equation of State

- At equilibrium, the fugacity of the liquid and vapour phases is equal
- The experimentally determined vapour pressure is 5.86 atm
- Critical properties of n-Pentane are:  
 $T_c = 469.7 \text{ K}$ ,  $P_c = 33.25 \text{ atm}$ ,  $\omega = 0.251$
- Using S-R-K :
$$\sqrt{\alpha} = 1 + m(1 - \sqrt{Tr}) \text{ where } m = 0.48 + 1.574\omega - 0.172\omega^2$$

$$\sqrt{\alpha} = 1 + (0.48 + (1.574 \times 0.251) - (0.172 \times 0.251^2)) \left(1 - \sqrt{\frac{373}{469.6}}\right) = 1.094$$
- Calculate A & B
$$A = 0.42747\alpha(P/P_c)(T_c/T)^2 = 0.0224P$$

$$B = 0.08664(P/P_c)(T_c/T) = 0.0033P$$
- Substitute values of A & B into the polynomial compressibility equation:  
 $Z^3 - Z^2 + (A - B - B^2)Z - AB = 0$
- Solve to find Z for liquid and vapour phases
- Calculate the fugacity of the vapour and liquid phases:  
 $\ln \phi_v = z - 1 - \ln(z - B) - A/B \ln(1 + B/z)$   
 $\phi_v = f_v/P_v \text{ and } \phi_l = f_l/P_l$
- At equilibrium,  $f_v = f_l$  therefore  $\phi_v = \phi_l$



P	z		f		Ratio
	Vapour	Liquid	Vapour	Liquid	
4	0.8943	0.0184	3.665	5.196	
5	0.8647	0.0229	4.4774	5.2287	0.8563
6	0.831	0.0275	5.2482	5.2512	0.9994
7	0.7955	0.0321	5.9775	5.2807	1.132

By interpolation of the above table, the predicted vapour pressure is 6.01 atm

# Property Package Selection

Selection of the property package must take into account the components and the operating conditions

For most purposes, Peng Robinson (PR), Soave-Redlich-Kwong (SRK), or a modified version of these methods, will provide sufficiently accurate modelling for oil and gas flow applications.

The PR and SRK equations of state give accurate modelling for systems containing up to 5% N<sub>2</sub>, CO<sub>2</sub> or H<sub>2</sub>S. For systems with greater than 5% N<sub>2</sub>, CO<sub>2</sub> or H<sub>2</sub>S these equations of state are still recommended if the system does not include free water. It may be advisable, however, to utilise user defined binary interaction parameters if available. This will depend upon the simulation/flash package being used and the quality of the data in its components library. It is recommended to consult the user guide (or help desk) for the particular package being used.

Polar compounds can be problematic for EOS methods - methanol, glycol and water - empirical correction factors are often required to improve accuracy. Most simulation packages offer specialised property packages to handle such systems which utilise a combination of an EOS to predict vapour phase fugacity coefficients and an activity coefficient model for the liquid phase.

# EOS Comparison: Peng Robinson v Zudkevitch Joffee

Peng Robinson  
Zudevitch Joffe

Q flowrate in  
million standard  
cubic feet per day

	PR	ZJ
MW	18.53	18.43
Q (mmscfd)	15.0	14.6
C1 (mol%)	88.57	88.94
C2 (mol%)	7.17	6.87
C3 (mol%)	0.13	0.12

Zudkevitch, D., Joffee, J. "Correlation and Prediction of Vapor-Liquid Equilibria with the Redlich-Kwong Equation of State", AIChE Journal, Volume 16, No. 1, 112-119, (1970).

GOR	PR	ZJ
1st Stage (scf/bbl)	299	292
2nd Stage (scf/bbl)	19	24
Overall (scf/bbl)	318	316

Reservoir  
Fluids

9 barg  
54 C

1.1 barg  
53 C

The skill of the Chemical/  
Petroleum Engineer is to select  
the appropriate equation of state.

	PR	ZJ
MW	22.09	21.54
Q (mmscfd)	0.9	1.2
C1 (mol%)	74.75	76.34
C2 (mol%)	16.33	15.80
C3 (mol%)	0.45	0.41

A modification of the Benedict-Webb-Rubin equation of state by Professor Kenneth E. Starling of the University of Oklahoma:

$$P = \rho RT + \left( B_0 RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4} \right) \rho^2 + \left( bRT - a - \frac{d}{T} \right) \rho^3 + \alpha \left( a + \frac{d}{T} \right) \rho^6 + \frac{c\rho^3}{T^2} (\beta + \gamma\rho^2) \exp(-\gamma\rho^2)$$

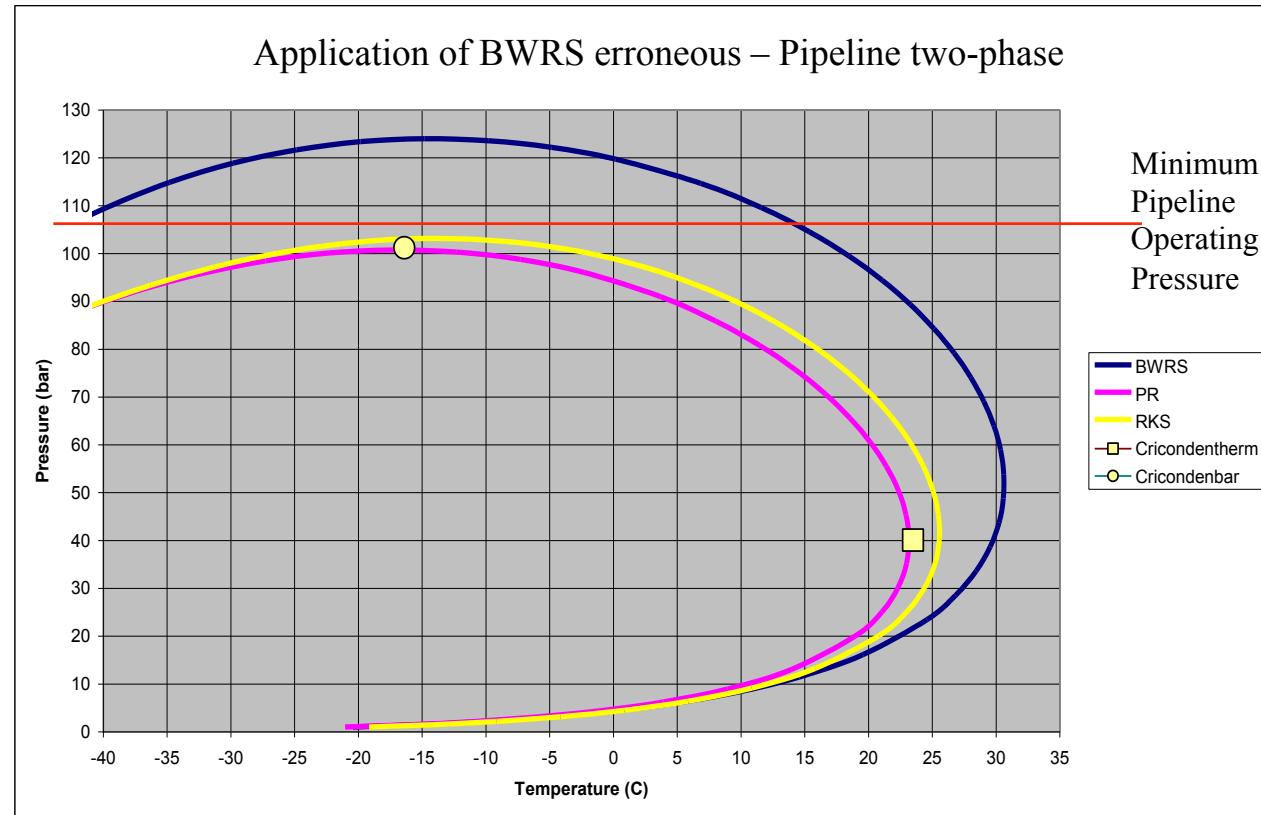
$\rho$  = the molar density.

Values of the various parameters for 15 substances can be found in K.E. Starling, Fluid Properties for Light Petroleum Systems. Gulf Publishing Company (1973).

The BWRS is favoured by some gas pipeline designers.

# Phase Behaviour – Pipeline Gas

Components	Gas A
C1	86.5473
C2	7.30256
C3	2.01471
IC4	0.475166
NC4	0.566198
IC5	0.213075
NC5	0.230081
C6	0.120042
C7	0.100035
C8	0.060021
N2	0.880308
CO2	1.49052
SUM	100
Molar weight	19.1
HC dewpoint (Cricondentherm)	23.5 °C @ 40.1 bara
HC dewpoint (Cricondenbar)	101.2 bara @ -16.4 °C



# Limitations of Phase Behaviour Prediction

All phase behaviour methods assume an equilibrium is reached, this is an idealised situation and in reality equilibrium is not always achieved.

EOS can not be used to predict water/hydrocarbon separation.

Phase behaviour prediction deals with mass transfer effects and therefore does not take into account bulk fluid flow. In practice there is almost inevitably some bulk transfer of fluids between the phases: emulsions may be formed due to high shear rates across control valves and the addition of corrosion inhibitor which holds water in the oil phase, oil will carry over into the oil phase, liquid droplets carry over into the gas phase.

Prediction methods are generally only valid over a particular range of conditions and for particular components.

EOS do not accurately predict phase behaviour at the critical point.

# Polar Fluids – CPA Model

Cubic equation of state (EoS) is the most widely used thermodynamic models for phase equilibrium calculation and physical property estimation in the petroleum industry. Peng-Robinson was developed originally for hydrocarbon mixtures and can have limitations when there are associating molecules present e.g. water, methanol, glycol. The Cubic Plus Association model is gaining interest as a useful EOS for handling associating molecules. It is a modified SRK model introducing an association term.

SRK

$$p = \frac{NRT}{V - b} + \frac{a}{V(V + b)}$$

CPA

$$p = \frac{NRT}{V - b} + \frac{a}{V(V + b)} + \frac{\sum_i n_i F_i (1 - X_i)}{V - 0.45b}$$

*Kontogeorgis GM, Voutsas EC, Yakoumis IV, Tassios DP. An equation of state for associating fluids. Ind Eng Chem Res. 1996*

# Property Package Selection

Within simulators the available property packages are generally grouped under the types detailed;

<b>Property Package Type</b>	<b>Typical Application</b>
Equations of State,	Ideal hydrocarbon systems
Activity Models,	Polar or non-ideal systems
Chao Seader Models	Systems containing mainly liquid or vapour H <sub>2</sub> O or high H <sub>2</sub> contents
Vapour Pressure Models	Heavy hydrocarbon systems at low pressures (increasing light hydrocarbons results in decreasing accuracy)
Miscellaneous Type	Acid gas systems, steam systems, non-volatile oils, aqueous electrolyte systems

Non-ideal components include alcohols, acids, glycols and other non-ideal or polar chemicals. The more non-ideal components present, the less ideal the mixture.

# Activity Models

Although equation of state models have proven to be very reliable in predicting properties of most hydrocarbon based fluids over a large range of operating conditions, their application has been limited to primarily non-polar or slightly polar components.

Polar or non-ideal chemical systems have traditionally been handled using dual model approaches. In this approach, an equation of state is used for predicting the vapour fugacity coefficients and an activity coefficient model is used for the liquid phase. Although there is considerable research being conducted to extend equation of state applications into the chemical arena (e.g., the PRSV equation), the state of the art of property predictions for chemical systems is still governed mainly by Activity Models.

Activity Models are much more empirical in nature when compared to the property predictions (equations of state) typically used in the hydrocarbon industry

# Activity Models

The phase separation or equilibrium ratio  $K_i$  for component i, defined in terms of the vapour phase fugacity coefficient and the liquid phase activity coefficient, is calculated from the following expression:

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i f_i^\circ}{P\phi_i}$$

*where:  $\gamma_i$  = liquid phase activity coefficient of component i*

*$f_i^\circ$  = standard state fugacity of component i*

*$P$  = system pressure*

*$\phi_i$  = vapour phase fugacity coefficient of component i*

$$\ln \gamma_i = \frac{\sum_{j=1}^n \tau_{ji} x_j G_{ji}}{\sum_{k=1}^n x_k G_{ki}} + \sum_{j=1}^n \frac{x_j G_{ij}}{\sum_{k=1}^n x_k G_{kj}} \left( \tau_{ij} - \frac{\sum_{m=1}^n \tau_{mj} x_m G_{mj}}{\sum_{k=1}^n x_k G_{kj}} \right)$$

where:  $\gamma_i$  = activity coefficient of component  $i$

$$G_{ij} = \exp[-\tau_{ij}\alpha_{ij}]$$

$$\tau_{ij} = \frac{a_{ij} + b_{ij}T}{RT}$$

$x_i$  = mole fraction of component  $i$

$T$  = temperature (K)

$n$  = total number of components

$a_{ij}$  = non-temperature dependent energy parameter between components  $i$  and  $j$  (cal/gmol)

$b_{ij}$  = temperature dependent energy parameter between components  $i$  and  $j$  (cal/gmol-K)

$\alpha_{ij}$  = NRTL non-randomness constant for binary interaction  
note that  $\alpha_{ij} = \alpha_{ji}$  for all binaries

# Activity Models

Activity Models are suitable for highly non-ideal systems and are empirical in nature. They are based on experimental data which is generated over a specific range and therefore can not be used reliably for generalised applications

The best results are produced when an Activity Model is applied in the operating region for which the interaction parameters apply. Caution should therefore be taken when selecting an Activity Model for a simulation

The table below shows when the different Activity Models can be used

Application	Margules	van Laar	Wilson	NRTL	UNIQUAC
Binary Systems	A	A	A	A	A
Multicomponent Systems	LA	LA	A	A	A
Azeotropic Systems	A	A	A	A	A
Liquid-Liquid Equilibria	A	A	N/A	A	A
Dilute Systems	?	?	A	A	A
Self-Associating Systems	?	?	A	A	A
Polymers	N/A	N/A	N/A	N/A	A
Extrapolation	?	?	G	G	G

A = Applicable; N/A = Not Applicable; ? = Questionable; G = Good; LA = Limited Application

# Property Package Selection

The table below summarises recommended property packages for various systems commonly encountered in oil and gas/ petrochemical simulations.

Type of System	Recommended Property Methods
TEG Dehydration	PR
Sour Water	Sour PR
Cryogenic Gas Processing	PR, PRSV, TST
Air Separation	PR, PRSV, TST
Atm Crude Towers	PR, PR Options, GS, TST
Vacuum Towers	PR, PR Options, GS (<10 mm Hg), Braun K10, Esso K, TST
Ethylene Towers	Lee Kesler Plocker
High H <sub>2</sub> Systems	PR, ZJ, GS, TST
Reservoir Systems	PR, PR Options, TST
Steam Systems	Steam Package, CS or GS
Hydrate Inhibition	PR
Chemical systems	Activity Models, PRSV
HF Alkylation	PRSV, NRTL*
TEG Dehydration with Aromatics	PR*
Hydrocarbon systems where H <sub>2</sub> O solubility in HC is important	Kabadi Danner
Systems with select gases and light hydrocarbons	MBWR

Validation of simulation against real data should be carried out to check that the most appropriate property package has been selected.

# Property Package Selection

Typical simulator default combinations are as indicated;

Property Method	VLE Calculation	Enthalpy/Entropy Calculation
<b>Equations of State</b>		
PR	PR	PR
PR LK ENTH	PR	Lee-Kesler
SRK	SRK	SRK
SRK LK ENTH	SRK	Lee-Kesler
Kabadi Danner	Kabadi Danner	SRK
Lee Kesler Plocker	Lee Kesler Plocker	Lee Kesler
PRSV	PRSV	PRSV
PRSV LK	PRSV	Lee-Kesler
Sour PR	PR & API-Sour	PR
SOUR SRK	SRK & API-Sour	SRK
Zudkevitch-Joffee	Zudkevitch-Joffee	Lee-Kesler

# Property Package Selection

Typical simulator default combinations are as indicated;

Activity Models		
Liquid		
Chien Null	Chien Null	Cavett
Extended and General NRTL	NRTL	Cavett
Margules	Margules	Cavett
NRTL	NRTL	Cavett
UNIQUAC	UNIQUAC	Cavett
van Laar	van Laar	Cavett
Wilson	Wilson	Cavett
vapor		
Ideal Gas	Ideal	Ideal Gas
RK	RK	RK
Virial	Virial	Virial
Peng Robinson	Peng Robinson	Peng Robinson
SRK	SRK	SRK

# Property Package Selection

Typical simulator default combinations are as indicated;

Semi-Empirical Models		
Chao-Seader	CS-RK	Lee-Kesler
Grayson-Streed	GS-RK	Lee-Kesler
vapor Pressure Models		
Mod Antoine	Mod Antoine-Ideal Gas	Lee-Kesler
Braun K10	Braun K10-Ideal Gas	Lee-Kesler
Esso K	Esso-Ideal Gas	Lee-Kesler
Miscellaneous - Special Application Methods		
Amines	Mod Kent Eisenberg (L), PR (V)	Curve Fit
Steam Packages		
ASME Steam	ASME Steam Tables	ASME Steam Tables
NBS Steam	NBS/NRC Steam Tables	NBS/NRC Steam Tables
MBWR	Modified BWR	Modified BWR

# CO<sub>2</sub> Modelling

Interest in Carbon Capture and Storage has focussed attention on accurate CO<sub>2</sub> modelling. The EOS of Span and Wagner is recommended.

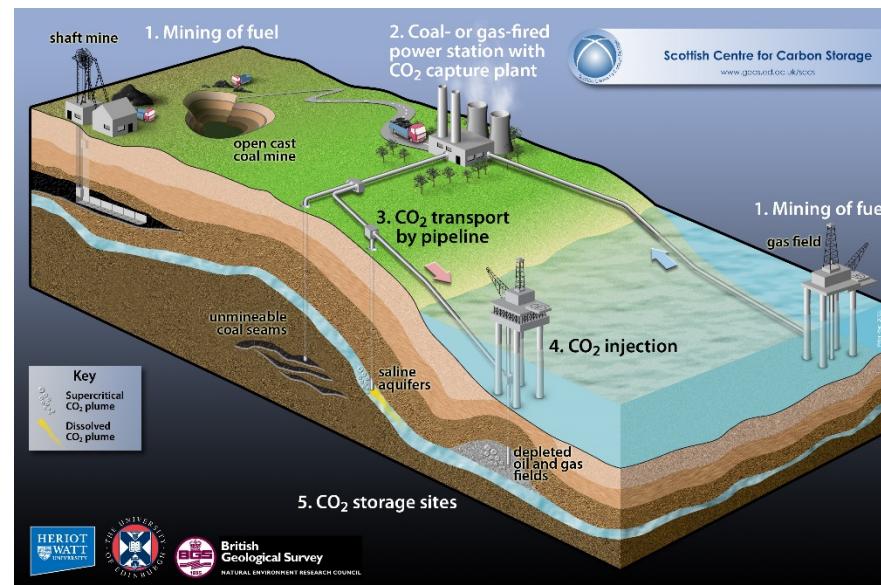
## A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa

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Received 25 May 1994

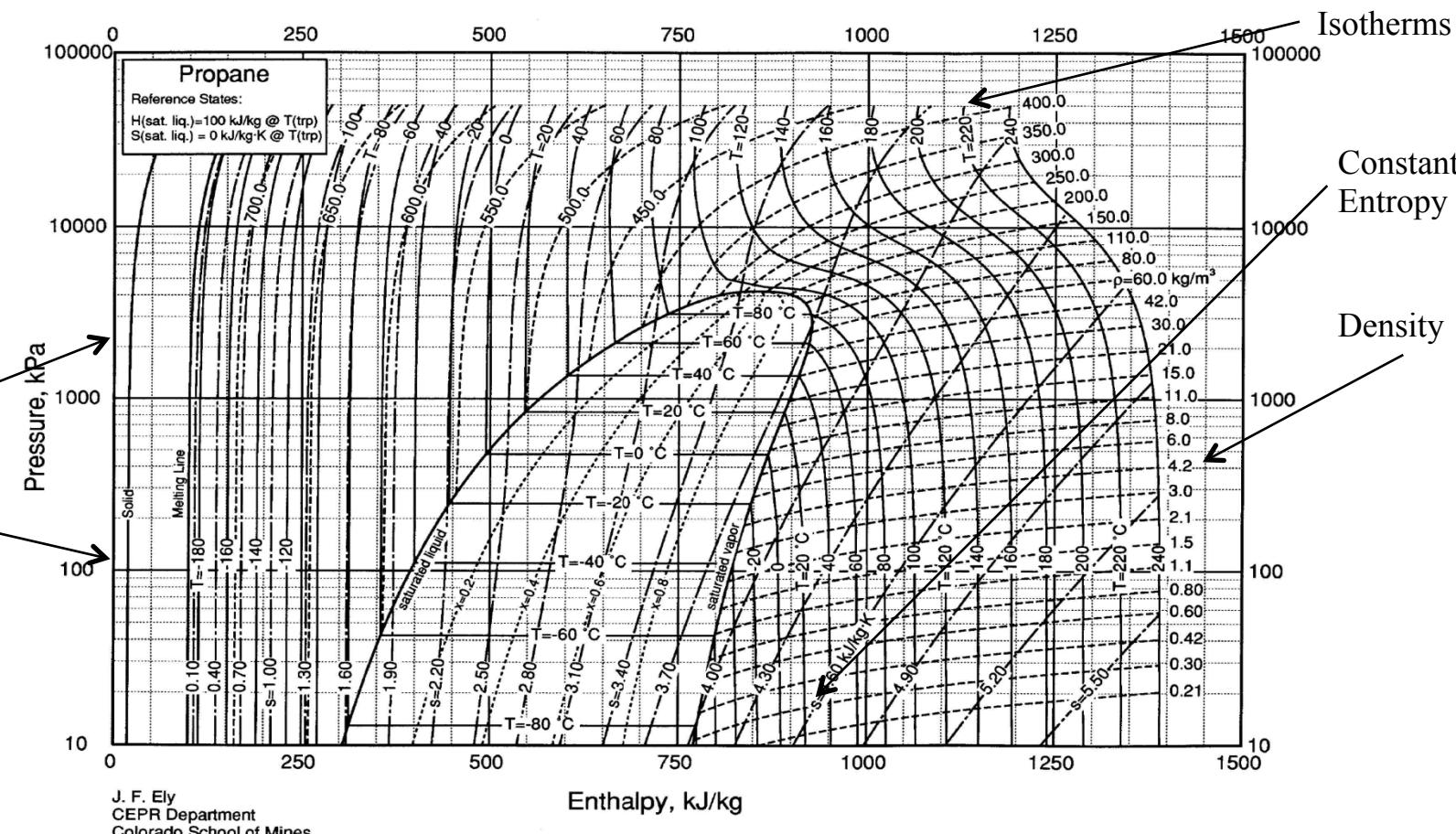
This work reviews the available data on thermodynamic properties of carbon dioxide and presents a new equation of state in the form of a fundamental equation explicit in the Helmholtz free energy. The function for the residual part of the Helmholtz free energy was fitted to selected data of the following properties: (a) thermal properties of the single-phase region ( $p, \rho, T$ ) and (b) of the liquid-vapor saturation curve ( $p_s, \rho', \rho''$ ) including the Maxwell criterion, (c) speed of sound  $w$  and (d) specific isobaric heat capacity  $c_p$  of the single phase region and of the saturation curve, (e) specific isochoric heat capacity  $c_v$ , (f) specific enthalpy  $h$ , (g) specific internal energy  $u$ , and (h) Joule-Thomson coefficient  $\mu$ . By applying modern strategies for the optimization of the mathematical form of the equation of state and for the simultaneous nonlinear fit to the data of all these properties, the resulting formulation is able to represent even the most accurate data to within their experimental uncertainty. In the technically most important region up to pressures of 30 MPa and up to temperatures of 523 K, the estimated uncertainty of the equation ranges from  $\pm 0.03\%$  to  $\pm 0.05\%$  in the density,  $\pm 0.03\%$  to  $\pm 1\%$  in the speed of sound, and  $\pm 0.15\%$  to  $\pm 1.5\%$  in the isobaric heat capacity. Special interest has been focused on the description of the critical region and the extrapolation behavior of the formulation. Without a complex coupling to a scaled equation of state, the new formulation yields a reasonable description even of the caloric properties in the immediate vicinity of the critical point. At least for the basic properties such as pressure, fugacity, and enthalpy, the equation can be extrapolated up to the limits of the chemical stability of carbon dioxide. Independent equations for the vapor pressure and for the pressure on the sublimation and melting curve, for the saturated liquid and vapor densities, and for the isobaric ideal gas heat capacity are also included. Property tables calculated from the equation of state are given in the appendix. © 1996 American Institute of Physics and American Chemical Society.



# Single Component Thermodynamics

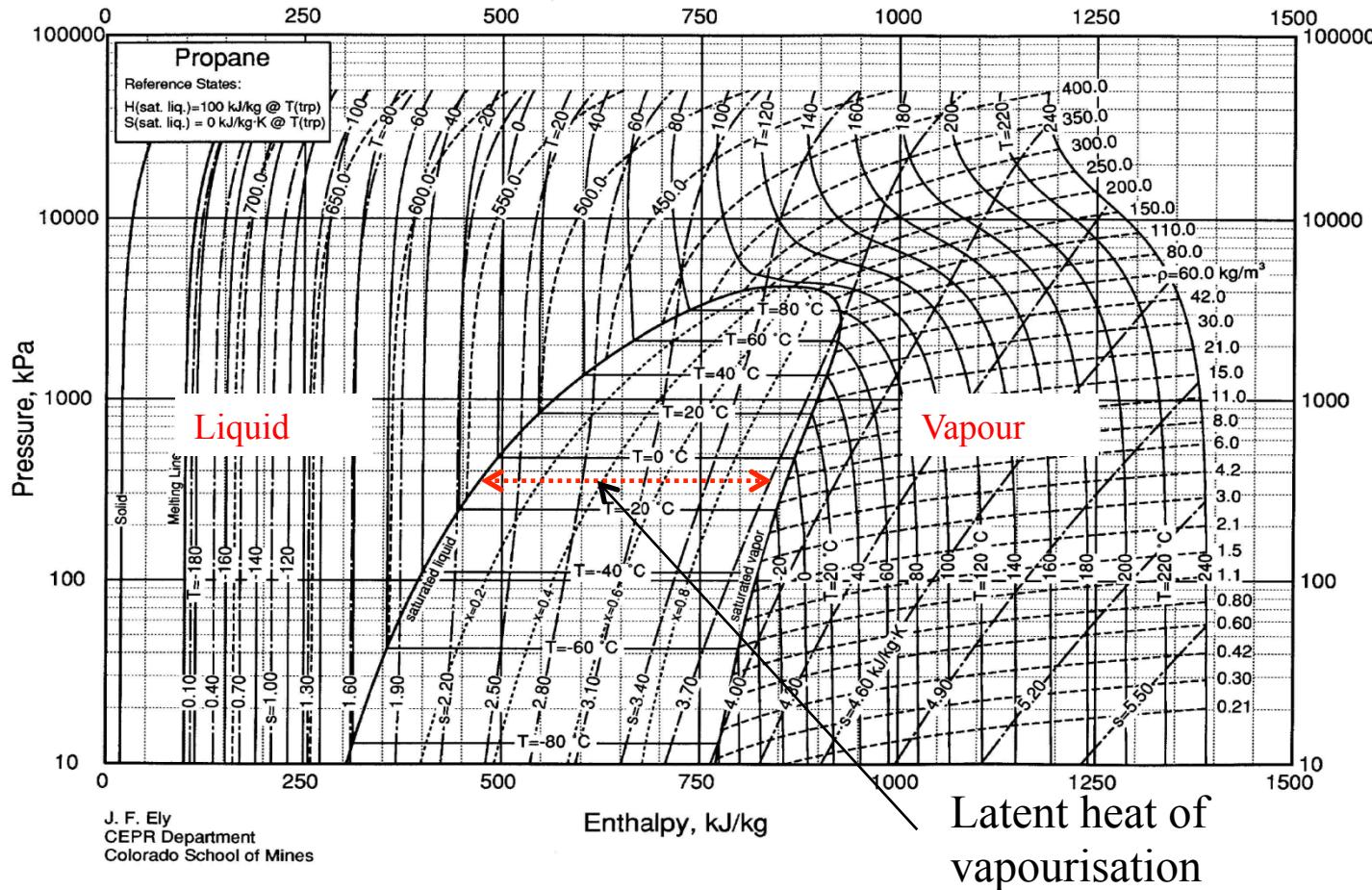
## Phase Behaviour – Mollier Chart

Bubble Point,  
Saturation,  
Vapour  
Pressure at



# Single Component Thermodynamics

## Phase Behaviour – Mollier Chart



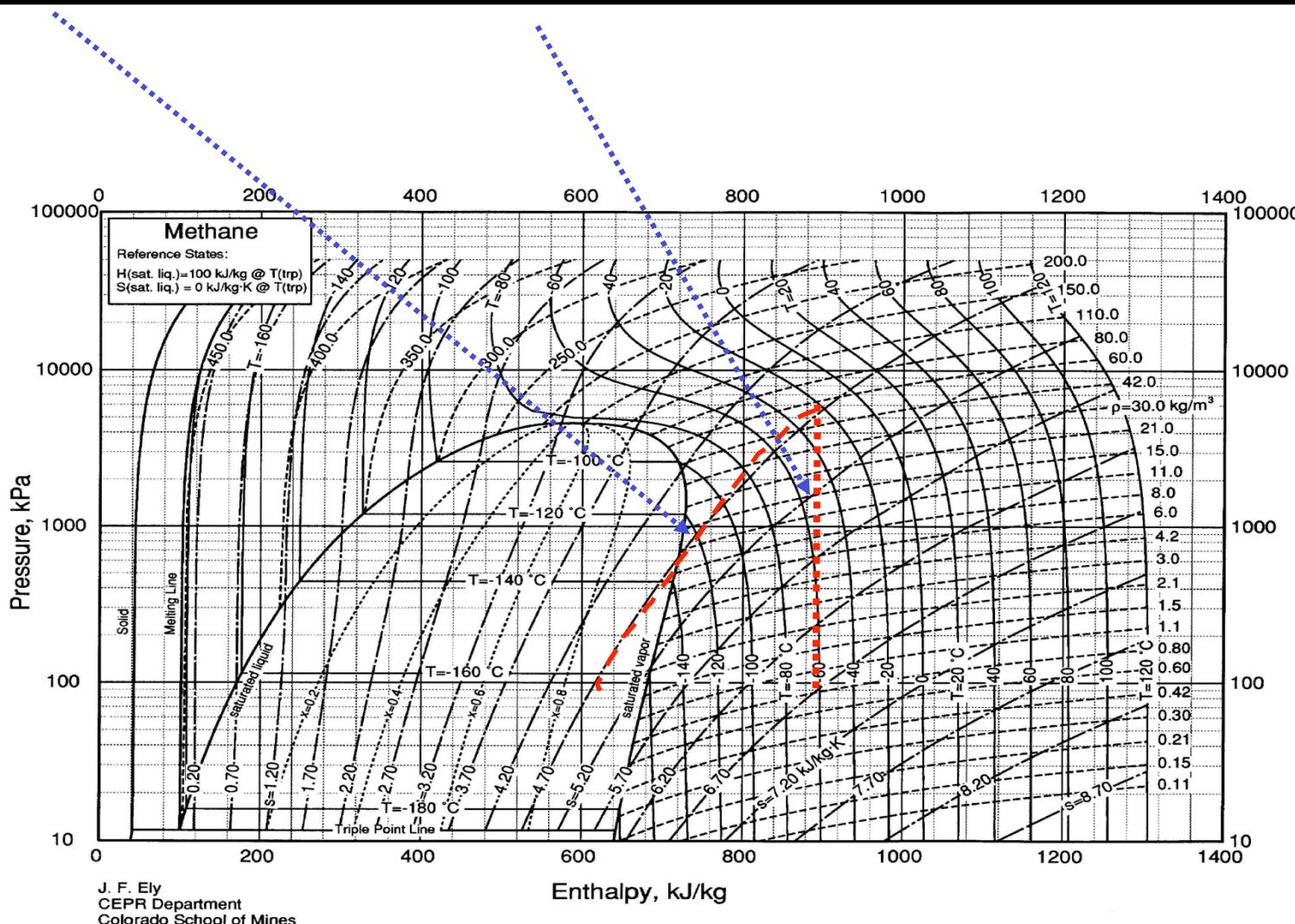
# Joule Thomson Expansion

As a gas expands, the average distance between molecules grows. Because of intermolecular attractive expansion causes an increase in the potential energy of the gas. If no external work is extracted in the process and no heat is transferred, the total energy of the gas remains the same because of the conservation of energy. The increase in potential energy thus implies a decrease in kinetic energy and therefore in temperature.

A second mechanism has the opposite effect. During gas molecule collisions, kinetic energy is temporarily converted into potential energy. As the average intermolecular distance increases, there is a drop in the number of collisions per time unit, which causes a decrease in average potential energy. Again, total energy is conserved, so this leads to an increase in kinetic energy (temperature). Below the Joule–Thomson inversion temperature, the former effect (work done internally against intermolecular attractive forces) dominates, and free expansion causes a decrease in temperature. Above the inversion temperature, gas molecules move faster and so collide more often, and the latter effect (reduced collisions causing a decrease in the average potential energy) dominates: Joule-Thomson expansion causes a temperature increase.

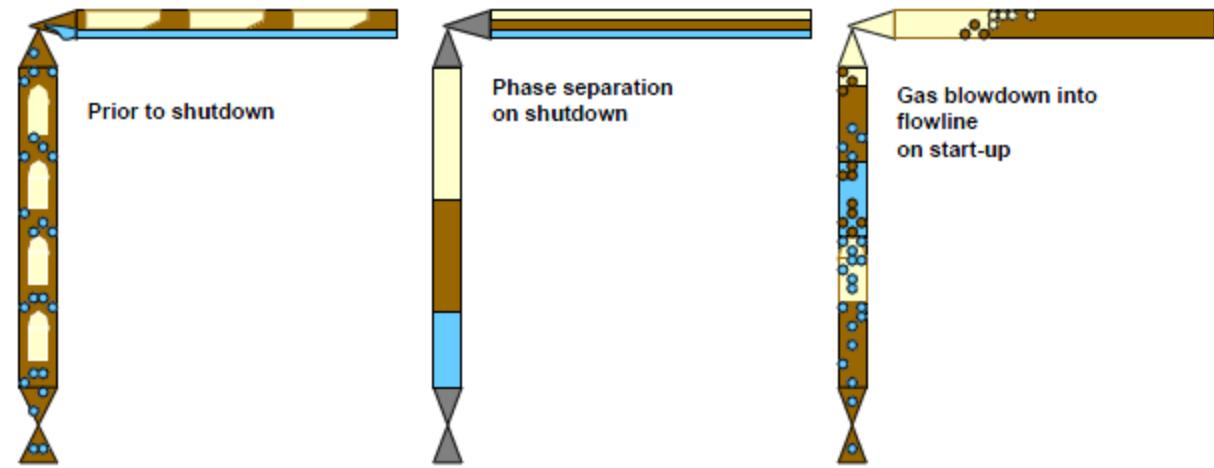
# Basic Thermodynamics

## ISENTROPIC and ISENTHALPIC Paths



# Well Choke Valve

As a first approximation gas expansion across a valve follows an isenthalpic path. Gas expansion can result in choke downstream temperatures considerably below the ambient temperature. Low Temperatures can result in ice and hydrate formation. Materials have to be designed to handle low temperatures where appropriate.



# Crude Assays

An Assay is a detailed fluid analysis of crude oil, sampled under strictly controlled conditions

Assay reports include the quantities and properties of distillates used for crude valuation purposes, the quantity of waxes, heavy metals, salt and sulphur and physical properties of the fluid such as viscosity

Assay samples are taken periodically for the purposes of crude valuation purposes and annually for crudes being exported via a pipeline shared with other fields

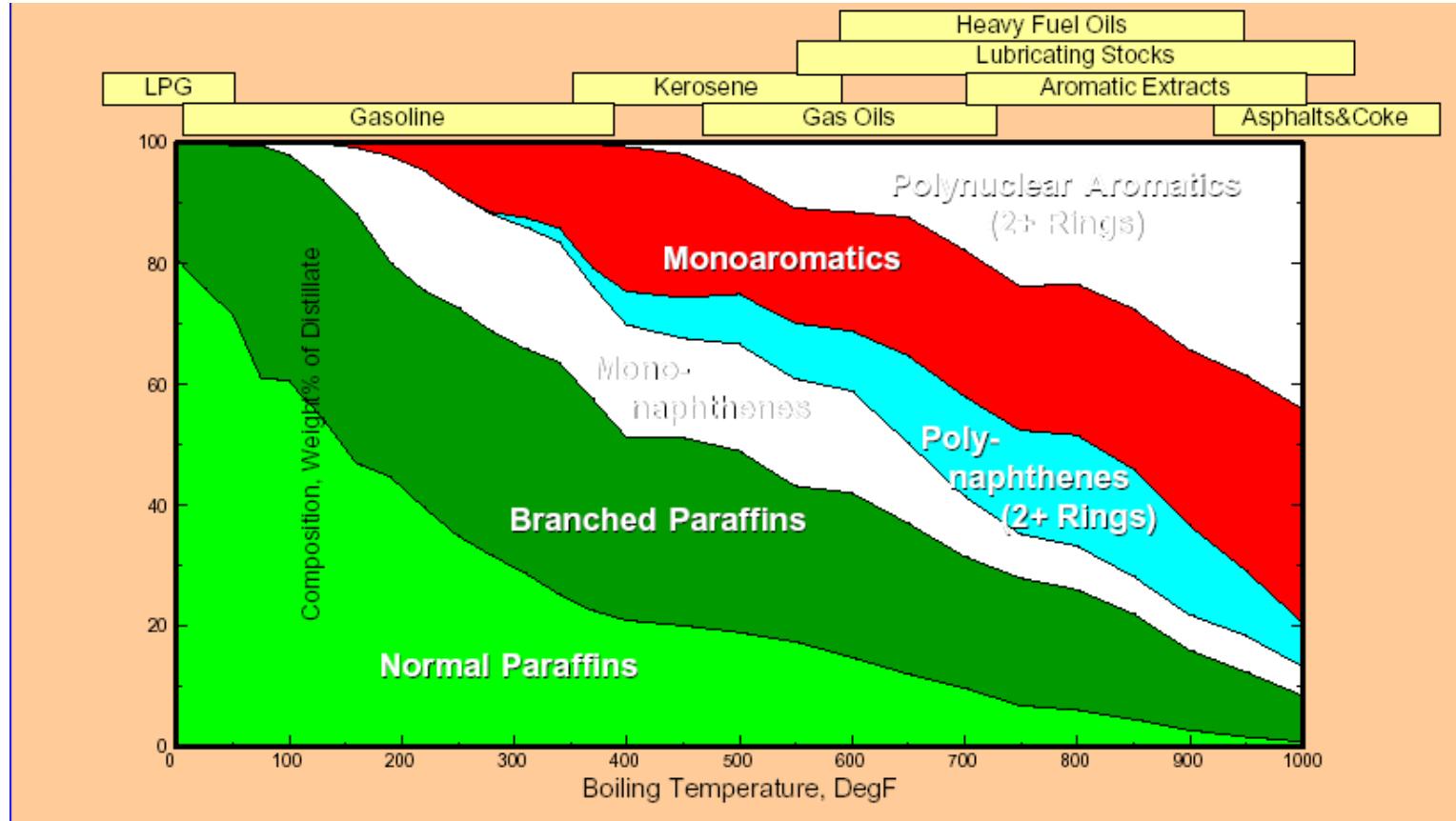
## SPR CRUDE OIL COMPREHENSIVE ANALYSIS

Sample ID BAYOU CHOCTAW SWEET Date of Assay 18/09/2000

Crude					
Specific Gravity, 60/60° F	0.8447	Ni, ppm	3.50	RVP, psi @ 100° F	4.62
API Gravity	36.0	V, ppm	5.49	Acid number, mg KOH/g	0.084
Sulfur, Wt. %	0.36	Fe, ppm	0.844	Mercaptan Sulfur, ppm	7.021
Nitrogen, Wt. %	0.114			H <sub>2</sub> S Sulfur, ppm	0
Micro Car. Res., Wt. %	2.22	Org. Cl, ppm	0.3	Viscosity: 77° F	6.874 cSt
Pour Point, °F	31	UOP "K"	11.94	100° F	4.623 cSt

Fraction	Gas	1	2	3	4	5	6	Residuum	Residuum
Cut Temp.	C <sub>2</sub> - C <sub>4</sub>	C <sub>5</sub> - 175° F	175° - 250° F	250° - 375° F	375° - 530° F	530° - 650° F	650° - 1050° F	1050° F+	1050° F+
Vol. %	1.7	7.3	8.1	14.2	16.3	10.0	31.8	42.4	10.7
Vol. Sum %	1.7	9.0	17.1	31.3	47.6	57.6	89.3	100.0	100.0
Wt. %	1.2	5.8	7.1	13.1	15.9	10.1	34.3	47.0	12.7
Wt. Sum %	1.2	7.0	14.1	27.1	43.0	53.1	87.4	100.0	100.0
Specific Gravity, 60/60° F	0.6730	0.7396	0.7763	0.8240	0.8526	0.9116	0.9349	1.004	
API Gravity	78.8	59.8	50.8	40.2	34.5	23.7	19.9	9.4	
Sulfur, Wt. %	0.0043	0.0040	0.0123	0.07	0.21	0.57	0.69	1.04	
Molecular Weight	97	111	136	184	246	425			
Hydrogen, Wt. %	15.89	14.65	na				12.99	10.61	
Mercaptan Sulfur, ppm	14.6	10.1	22.5	17.4					
H <sub>2</sub> S Sulfur, ppm	0.03	0.8	0.7	0.02					
Organic Cl, ppm	2.1	0.5	0.5	0.6					
Research Octane Number*	68.4	61.1	42.3						
Motor Octane Number*	66.5	58.6	40.0						
Flash Point, ° F			77	171	246	303			
Aniline Point, ° F			122.4	144.1	164.3	193.3			
Acid Number, mg KOH/g				0.03	0.10				
Cetane Index				47.1	53.2				
Diesel Index			62.2	58.0	56.6				
Naphthalenes, Vol. %				4.42	8.20				
Smoke point, mm				20.3	16.8				
Nitrogen, Wt. %				0.0015	0.006	0.108	0.240	0.603	
Viscosity, cSt	77° F			2.473					
	100° F			1.951	4.795				
	130° F					3.312	37.03	95.3	
	180° F						14.22	28.28	5671
	210° F								1722
	275° F								249.3
Freezing Point, °F				-28.54					
Cloud Point, °F					24.0	106			
Pour Point, °F					19.9	102	75		
Ni, ppm							7.539	26.2	
V, ppm							11.81	41.0	
Fe, ppm							3.856	13.87	
Micro Car. Res., Wt. %							5.07	18.17	

# Crude Oil Composition Schematic



# Key Learnings

- Features of mixed hydrocarbon Phase Envelope – dew point etc.
- Pseudo components
- Concept of fugacity
- Application of K values
- Application of Peng-Robinson/SRK EOSs
- Application of Activity Models
- Importance of property package selection
- Importance of physical property prediction

# Reading List

- 1. GPSA Engineering Data Book (Gas Processors Association)**
- 2. Phase Equilibria in Chemical Engineering, Stanley M Walas**
- 3. Chemical and Engineering Thermodynamics, S.I Sandler**