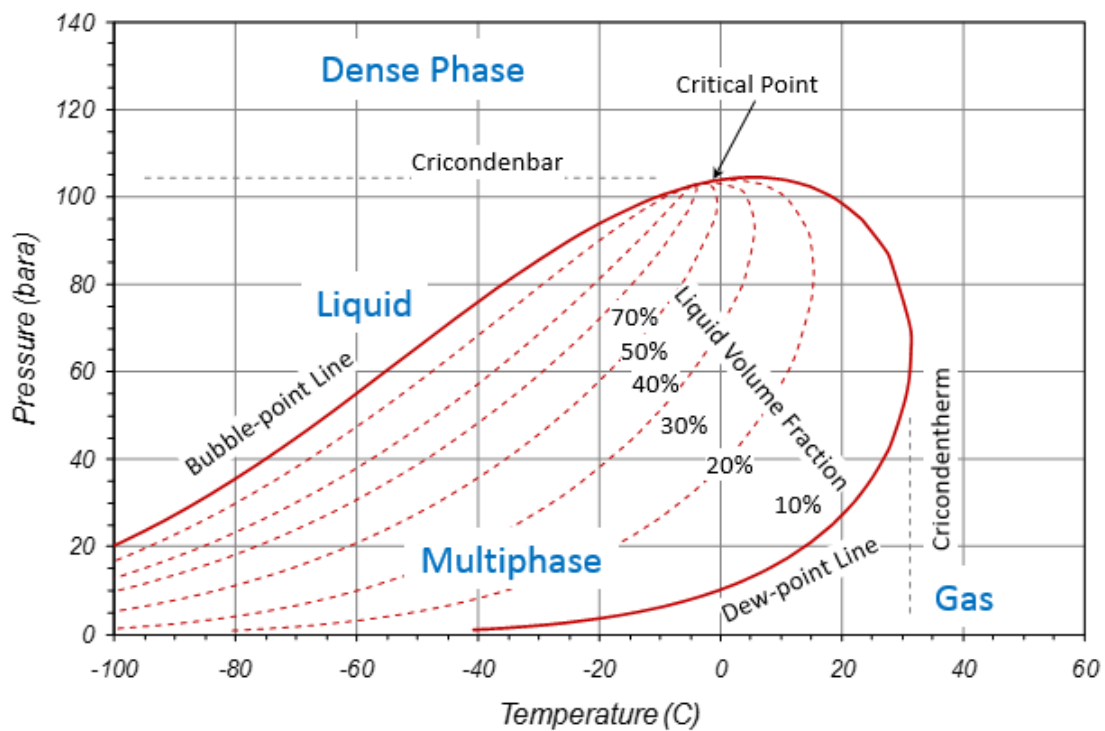


Phase Behaviour and Physical Properties



1	Introduction	3
2	Oil and Gas Components.....	3
2.1	Paraffins	3
2.2	Aromatics	3
2.3	Naphthenes	4
2.4	Sulphur	4
2.5	Nitrogen.....	5
2.6	Carbon Dioxide	5
2.7	Water	5
2.8	Mercury	5
3	Reservoir Oil and Gas	6
3.1	Phase Diagrams	7
3.1.1	Single Phase Fluid	7
3.1.2	Multicomponent Fluid.....	7
3.1.3	Phase Behaviour for differing Reservoir types	8
4	Fluid Sampling	13
4.1	Drill Stem Test	13
4.2	Extended Well Testing	13
5	Fluid Modelling.....	14
5.1	Black Oil	14
5.2	Compositional	14
5.2.1	Pseudo-Component	15
5.3	Equilibrium Ratios	17
5.3.1	Bubble Point Calculation	18
5.3.2	Dew Point Calculation	18
5.3.3	Flash Calculation Procedure.....	18
5.4	Equations of State.....	24
5.4.1	Van der Waals	24
5.4.2	Soave-Redlich-Kwong (SRK).....	25
5.4.3	Peng-Robinson	28
5.5	Property Package Selection.....	30
5.5.1	BWRS.....	33
5.5.2	CPA Model – Polar Fluids	34
5.5.3	Activity Models.....	35
5.5.4	Modelling Summary.....	37
5.5.5	CO2 Modelling.....	40
5.6	The Mollier Chart.....	40
5.7	Crude Assay	43
6	Physical Properties	45
6.1	Critical and Reduced Temperature and Pressure	46
6.2	Liquid Density.....	46
6.3	Gas Compressibility	50
6.4	Viscosity.....	53
6.4.1	Liquid	53
6.4.2	Gas.....	54
6.5	Specific Heat Capacity	56
6.6	Thermal Conductivity	56
6.7	Surface Tension.....	56
6.8	Vapour Pressure	57
7	Key Learnings	58
8	Reference books	58

1 Introduction

Accurate predicting of phase behaviour, and thermodynamic and physical properties is a prerequisite of process design and rating calculations. This module sets out a range of common methods used in practice.

2 Oil and Gas Components

Naturally occurring oil and gas reservoirs contain a wide range of hydrocarbon compounds and other species.

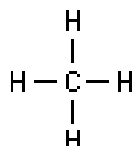
2.1 Paraffins

The paraffinic series of hydrocarbon compounds have the general formula C_nH_{2n+2} and can be either straight chains (normal) or branched chains (isomers) of carbon atoms. Paraffinic hydrocarbons are commonly referred to as alkanes.

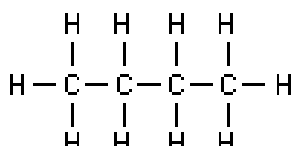
Methane is the simplest paraffin molecule:

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

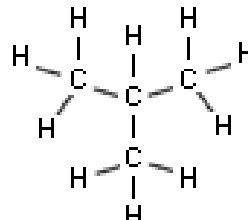
Methane (CH_4)



Butane (C_4H_{10})



Isobutane (C_4H_{10})



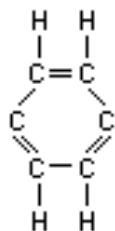
2.2 Aromatics

Aromatics are unsaturated ring-type (cyclic) compounds. All aromatics have at least one benzene ring (a single-ring compound characterized by three double bonds alternating with three single bonds between six carbon atoms) as part of their molecular structure.

Naphthalenes are fused double-ring aromatic compounds. The most complex aromatics are the polycyclic aromatic hydrocarbons (PAH), also referred to as polynuclear hydrocarbons, with three or more fused aromatic rings and they typically are found in the heavier fractions of petroleum crude oil. PAH are generally toxic to most organisms.

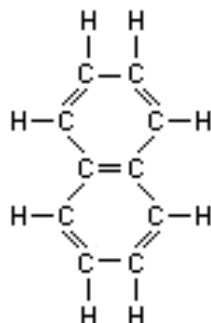
Example of simple aromatic compound:

Benzene ($C_6 H_6$)



Example of simple double-ring aromatic compound:

Naphthalene ($C_{10} H_8$)



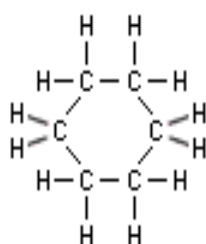
2.3 Naphthenes

Naphthenes are saturated hydrocarbon compounds having the general formula of $C_n H_{2n}$, arranged in the form of closed rings. Naphthenes are also commonly referred to as cycloparaffins or cycloalkanes.

Single-ring naphthenes (monocycloparaffins) with five and six carbon atoms predominate, with two-ring naphthenes (dicycloparaffins) found in the heavier ends of the naphtha fraction of petroleum crude oil.

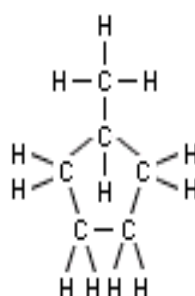
Example of a typical single-ring naphthenic:

Cyclohexane



Example of naphthene with same chemical formula ($C_6 H_{12}$) but with a different molecular structure:

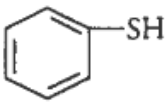
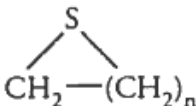
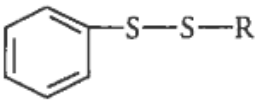

Methylcyclopentane ($C_6 H_{12}$)



2.4 Sulphur

Sulphur compounds occur to some extent in most naturally occurring oil and gases. They are unwanted as sulphur compounds are poisons for many catalytic processes used within refinery operations. In the presence of water they are corrosive. When burned/flared the sulphur oxidises to sulphur dioxide – an atmospheric pollutant.

Typical sulphur species are shown below.

Hydrogen Sulfide	H_2S
Mercaptans	
Aliphatic	$\text{R}-\text{SH}$
Aromatic	
Sulfides	
Aliphatic	$\text{R}-\text{S}-\text{R}$
Cyclic	
Disulfides	
Aliphatic	$\text{R}-\text{S}-\text{S}-\text{R}$
Aromatic	
Polysulfides	$\text{R}-\text{S}_n-\text{R}$
Thiophene and Homologs	

2.5 Nitrogen

Nitrogen is present in many oil and gas fields. Note that nitrogen can significantly effect phase behaviour characteristics with consequent impacts on processing requirements.

2.6 Carbon Dioxide

Like Nitrogen, carbon dioxide is a feature of most reservoirs. In combination with water it is corrosive.

2.7 Water

Water is a ubiquitous component of almost oil naturally occurring hydrocarbon reservoirs. Its presence and composition can significantly impact the process plant configuration as will be discussed later.

2.8 Mercury

Mercury is found in many oil and gas fields. It is a concern for metallurgy particularly Aluminium. It is also a health hazard.

3 Reservoir Oil and Gas

Reservoir oil is conditioned to allow for pipeline transportation or as a suitable feedstock for a refinery. The components of the unprocessed fluids and the refined products are shown.

	SUBSTANCE	USES
●	gases	Propane and butane gas for lighter fuel & camping stoves
●	naphtha	Chemicals for medicines, plastics, paints, cosmetics & clothing materials
●	gasoline	Petrol for vehicles
●	kerosene	Jet fuel and paraffin
●	diesel oils	Diesel fuel
●	Lubricating oils	Machine oil, waxes and polishes
●	Fuel oil	Fuel for ships and central heating
●	residue	Bitumen for road surfaces and roofing materials



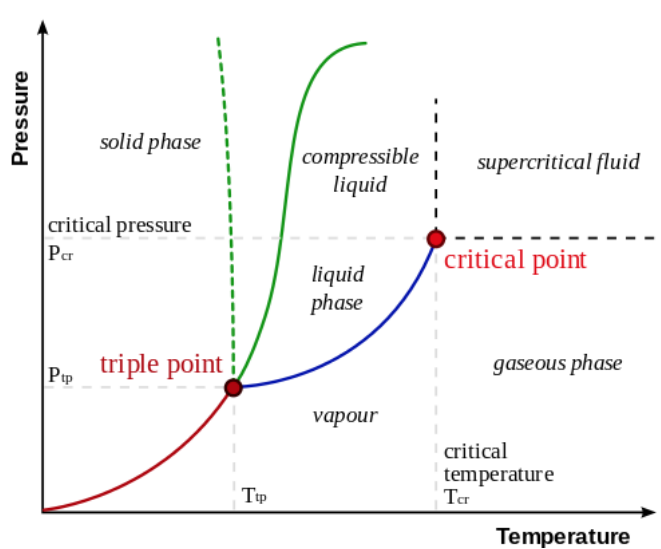
Like oil, gas is conditioned into a form suitable for transportation and sale. It should be noted that there is no typical oil or gas composition. Each field is different due to the geochemical formation processes which produced the hydrocarbons.

3.1 Phase Diagrams

An ability to predict the phase state of the fluids to be processed is an essential step in any process design. Inaccurate prediction will lead to a flawed design of the associated process equipment.

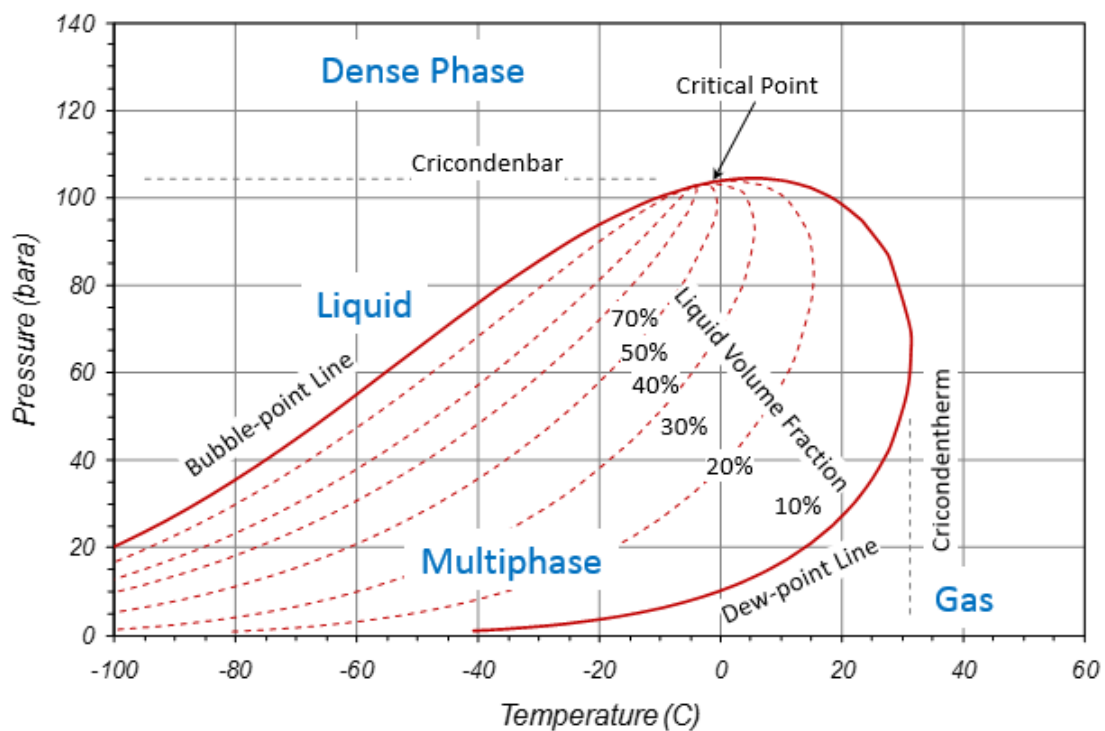
3.1.1 Single Phase Fluid

Consider the phase characteristics of water.



As can be seen the phase transition from all liquid to all vapour occurs at a single point. This is not the case for a multicomponent mixture such as a naturally occurring oil or gas.

3.1.2 Multicomponent Fluid



Here a different behaviour is seen – at a given pressure the transition from liquid to vapour occurs across a temperature range as the heavier molecular weight components change phase from liquid to vapour.

Key aspects of this phase behaviour plot are:

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

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 where the slope of the quality line changes from negative to positive.

3.1.3 Phase Behaviour for differing Reservoir types

Jargon used in the oilfield often categorises reservoirs into four types with a characteristic phase behaviour as follows. There is no clear definition categorising the differing types – black oil, volatile oil, condensate or gas. Typical compositions and phase characteristics are shown.

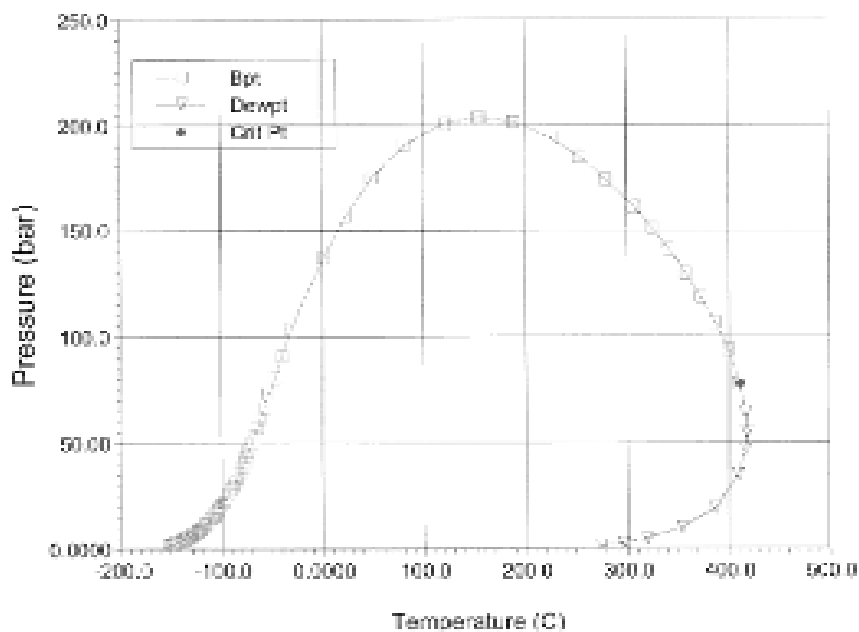
Black Oil

Component	Mol %
Methane (CH ₄)	48.83
Ethane (C ₂ H ₆)	2.75
Propane (C ₃ H ₈)	1.93
Butanes (C ₄ H ₁₀)	1.6
Pentanes (C ₅ H ₁₂)	1.15
Hexane (C ₆ H ₁₄)	1.59
C7+	42.15
Molecular Weight of C7+	225
GOR (scf/bbl)	625
Oil Gravity (° API)	34.3
Colour	Black

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

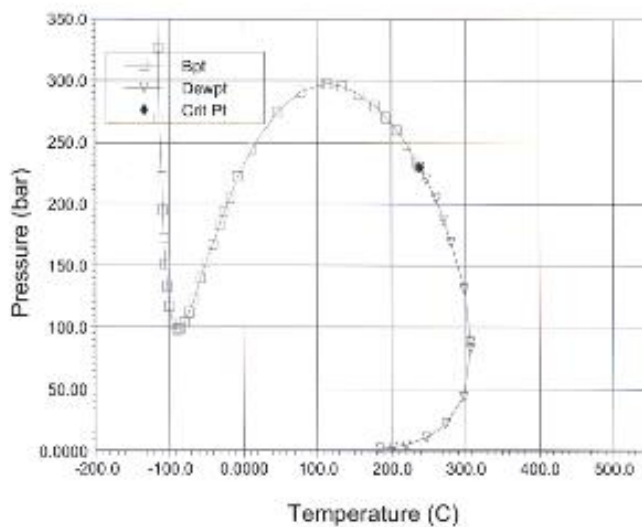
GOR – gas oil ratio, volume ratio of gas to liquid oil.

API – liquid density



Volatile Oil

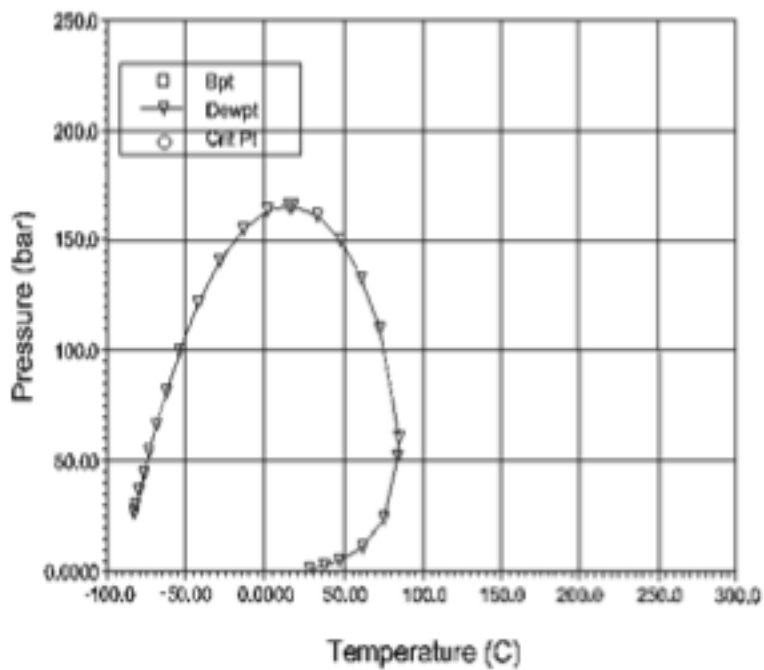
Component	Mol %
Methane (CH ₄)	64.36
Ethane (C ₂ H ₆)	7.52
Propane (C ₃ H ₈)	4.74
Butanes (C ₄ H ₁₀)	4.12
Pentanes (C ₅ H ₁₂)	2.97
Hexane (C ₆ H ₁₄)	1.38
C7+	14.91
Molecular Weight of C7+	181
GOR (scf/bbl)	2000
Oil Gravity (° API)	50.1
Colour	Brown



Note the kick up in the envelope. This is not a real situation; it is a function of the determined mathematical solution. This is a useful reminder that not everything generated by a computer is correct.

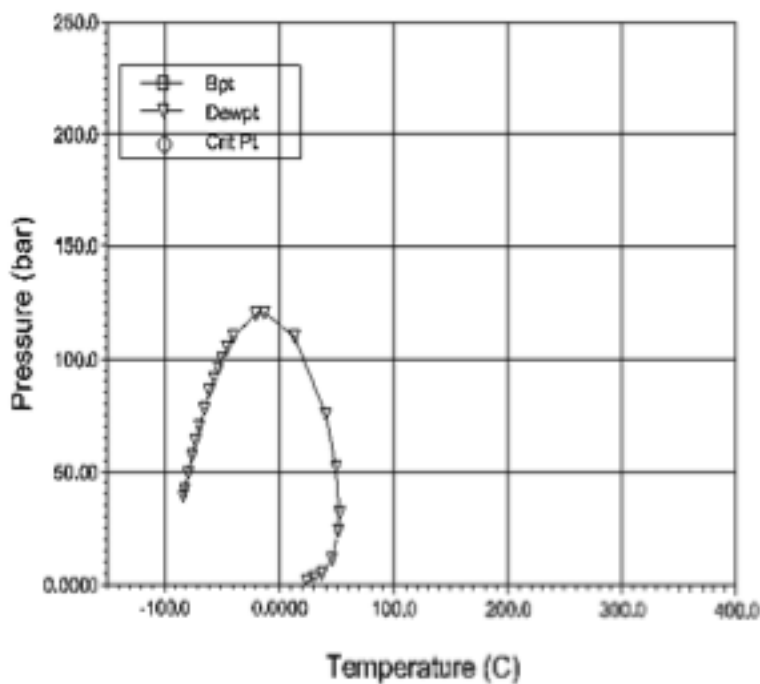
Gas Condensate

Component	Mol %
Methane (CH ₄)	87.07
Ethane (C ₂ H ₆)	4.39
Propane (C ₃ H ₈)	2.29
Butanes (C ₄ H ₁₀)	1.74
Pentanes (C ₅ H ₁₂)	0.83
Hexane (C ₆ H ₁₄)	0.6
C7+	3.8
Molecular Weight of C7+	112
GOR (scf/bbl)	18200
Oil Gravity (° API)	60.8
Colour	Straw



Gas

Component	Mol %
Methane (CH ₄)	95.85
Ethane (C ₂ H ₆)	2.67
Propane (C ₃ H ₈)	0.34
Butanes (C ₄ H ₁₀)	0.52
Pentanes (C ₅ H ₁₂)	0.08
Hexane (C ₆ H ₁₄)	0.12
C7+	0.42
Molecular Weight of C7+	157
GOR (scf/bbl)	105000
Oil Gravity (° API)	125
Colour	White



On inspection of the four phase envelopes the transition, temperature difference from the bubble point to the dew point reduces from black oil to gas. The gas composition is dominated by methane hence the system is behaving more like a single component. In the extreme, if the gas were 100% methane the phase behaviour would be a single line.

4 Fluid Sampling

Representative samples of the reservoir have to be obtained to allow for phase behaviour modelling. This is generally facilitated by a Drill Stem Test.

4.1 Drill Stem Test

This is a procedure to determine the productive capacity, pressure, permeability or extent (or a combination of these) of a hydrocarbon reservoir. A three phase separator is provided on the test vessel which measures the quantity of each phase – generally oil and gas but sometimes water too. Samples are taken of each phase and the composition determined by chromatography at an onshore laboratory. Knowing the rate and composition of each phase a recombined mass balance is used to determine the reservoir fluid composition.

This type of sampling may omit components which could deposit within the test well or react with the iron in the well wall. For that reason downhole samples are taken – a fluid sample is taken at reservoir rockface thus ensuring the fluid has all the compositional species.

A drill stem test may last for a day or two during which time the oil and gas are burned. The longer the test the more informative is the data received. This has to be balanced against cost, as the longer the vessel is on station the greater the expense.

4.2 Extended Well Testing

Contrary to the aforementioned, some oil fields may be subject to an extended test – many months. This can arise where the field geology and reservoir flow characteristics are very complex and a long duration test can provide additional information to offset potential risks and uncertainties. Nowadays extended well tests are less common due to the environmental impact of prolonged flaring/burning.

5 Fluid Modelling

The choice of thermodynamic model is critical when evaluating phase behaviour. Fluid phase behaviour and properties can be predicted using either a 'Black Oil' model or a 'Compositional' model. Compositional models are now custom and practice in Process Engineering.

5.1 Black Oil

Not to be confused with the previous Black Oil Reservoir - Black Oil models are generally used for simple, multiphase modelling in flowlines and wellbores. They predict phase behaviour and bulk properties for varying conditions by relating the fluid volumetric properties at the surface (e.g. GOR, Oil Gravity and Gas Gravity) to the system conditions. No detailed knowledge of fluid composition is required. Black oil models are clearly not recommended for preparing heat and mass balances.

With the development of equations of state (see later), black oil models are now seldom used for Process Design. They are used for reservoir analysis where detailed compositional data is not required.

Compositional models are used for rigorous heat and mass balance work. They use a property package and a composition specified in terms of individual components which are available in the package database or component library. If required, pseudo-components can be specified for non-library components or for boiling point cuts. Binary interaction parameters for components pairs are used to give improved VLE property predictions.

Modern simulation packages generally have several property packages available for selection including both equations of state and activity models.

5.2 Compositional

Compositional fluid modelling is a method for describing a stream based upon its pure components. An equation of state will be used to predict VLE (vapour liquid equilibria), gas and liquid enthalpies, gas and liquid densities, gas and liquid viscosities, surface tension and thermal properties - thermal conductivity.

It is not practical to model every component of a reservoir fluid due to the large numbers of components that are present. Generally, for acceptable phase behaviour prediction, it is sufficient to specify the mole fractions of the main light end paraffins, typically C1 to C10 for black oils. If dealing with gas condensate systems, however, more rigorous compositional data may be required, particularly if modelling retrograde behaviour. Heavier components are handled as pseudo or hypothetical components.

For the heavier components in a reservoir fluid mix one or more pseudo-components (or hypothetical components) can be used. Pseudo-components are a mixture of many components with different properties but modelled as one component with generalised/average properties.

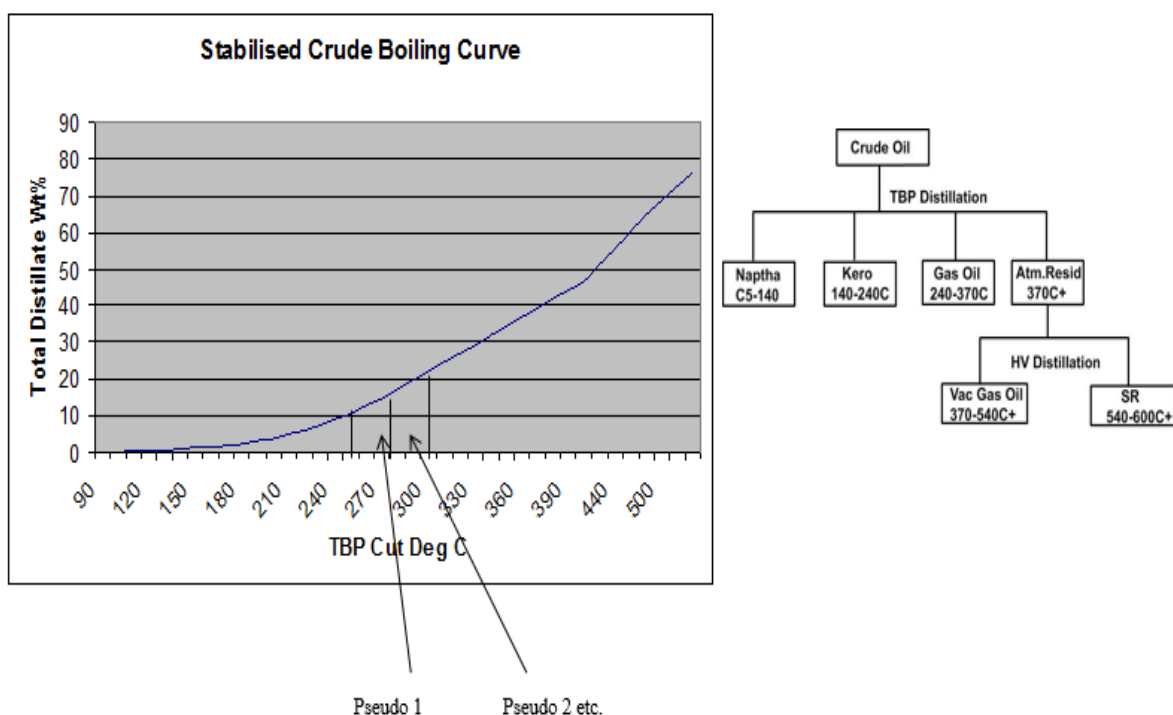
5.2.1 Pseudo-Component

Pseudo-Components are normally defined either by the critical properties or by average molecular weight, specific gravity and normal boiling point. For most computer simulations a minimum of two of these must be specified. Acentric factors and binary interaction parameters can also be entered; most simulation packages will estimate these if not supplied by the user.

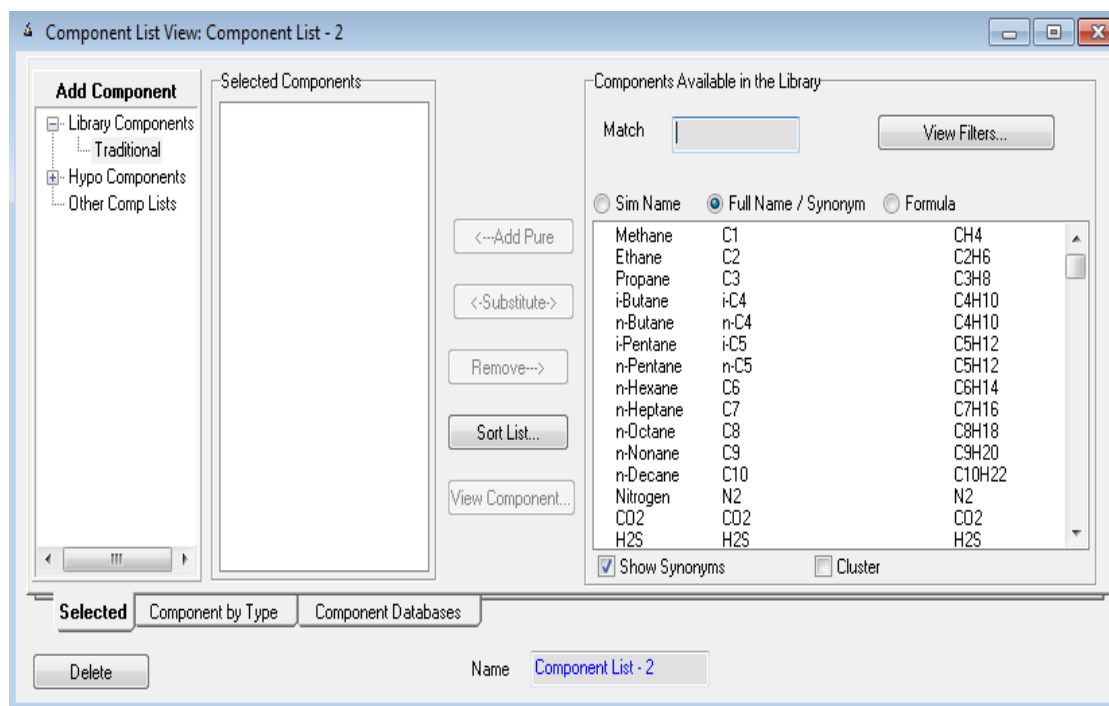
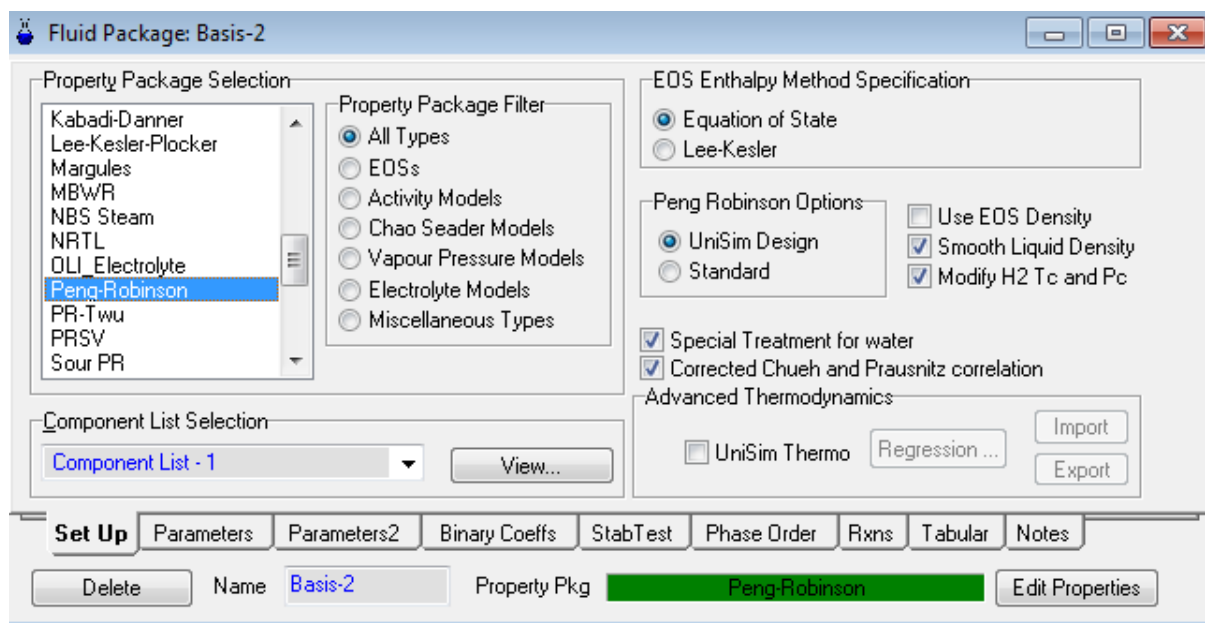
Prediction of heavy end physical properties is important for accurate prediction of phase behaviour; incomplete or inaccurate data can radically affect phase calculations, for example the prediction of bubble and dew points.

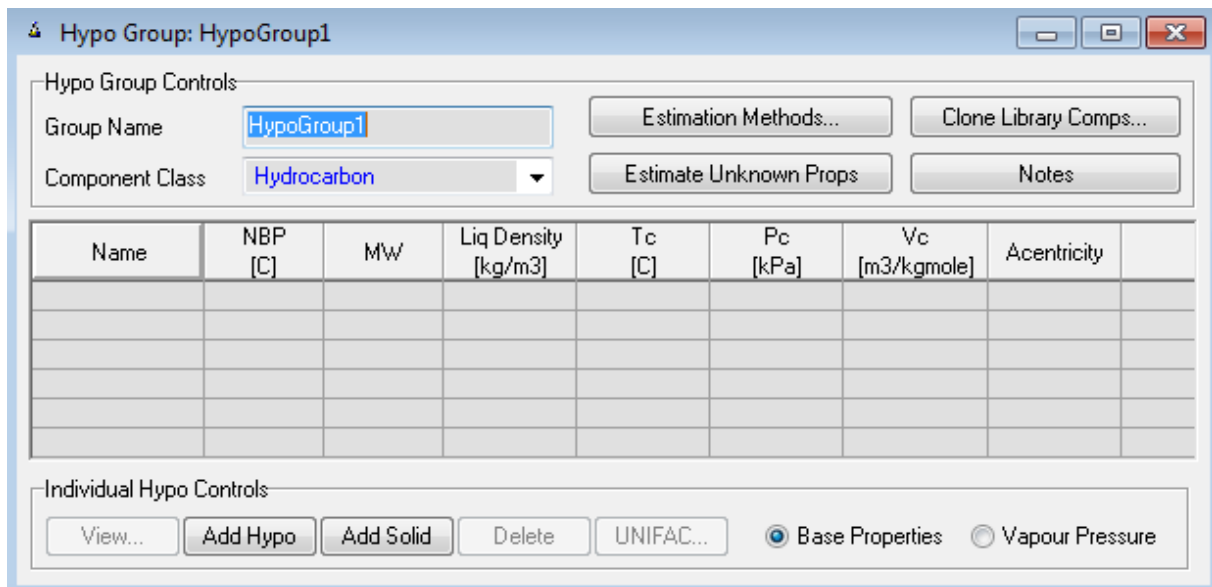
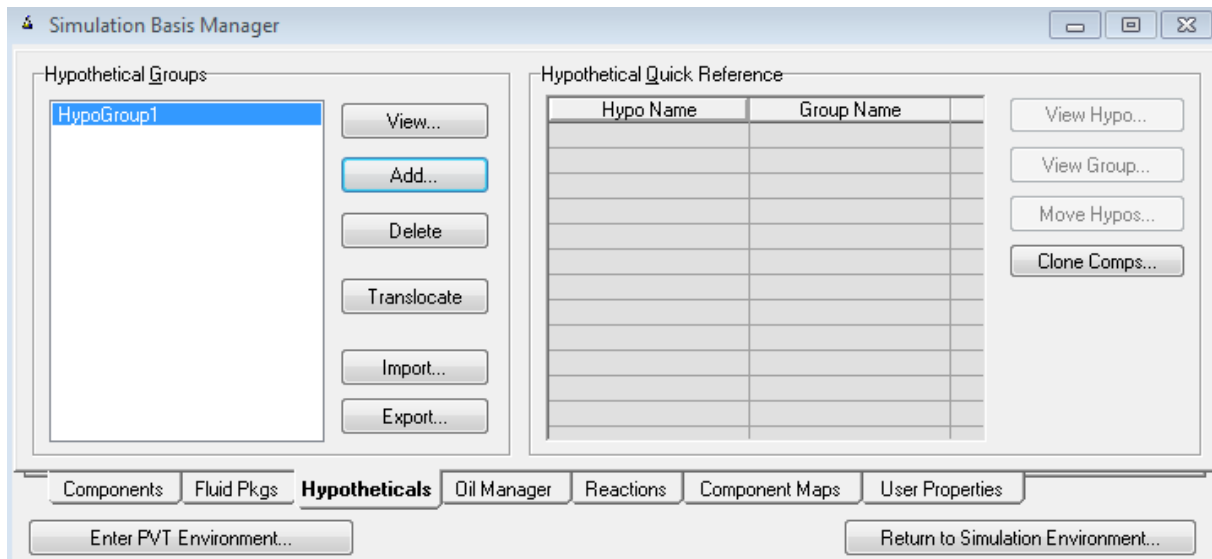
Standard fractional distillation tests can be used to produce boiling point curves and physical properties allowing the heavy ends to be split into a number of pseudo components.

Some simulation packages have the facility to take in distillation test data directly and to produce the pseudo-components automatically. Some 'tuning' may be required to match the properties of the modelled reservoir fluids to well test data.



Commercial heat and mass balance simulators require an equation of state to be selected then normal and hypothetical component properties are added as shown.





5.3 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:

$$K_i = y_i / x_i$$

Use of Equilibrium Ratios is key to the preparation of oil and gas processing heat and mass balances. The application of K values allows for the calculation of dew points, bubble points and the vapour-liquid behaviour inside the phase envelope (flash calculations).

5.3.1 Bubble Point Calculation

The following criteria is met;

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

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 $\sum K_i x_i = 1.0$.

5.3.2 Dew Point Calculation

The following criteria is met;

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

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.

5.3.3 Flash Calculation Procedure

By an overall and component mass balance the following is readily developed.

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

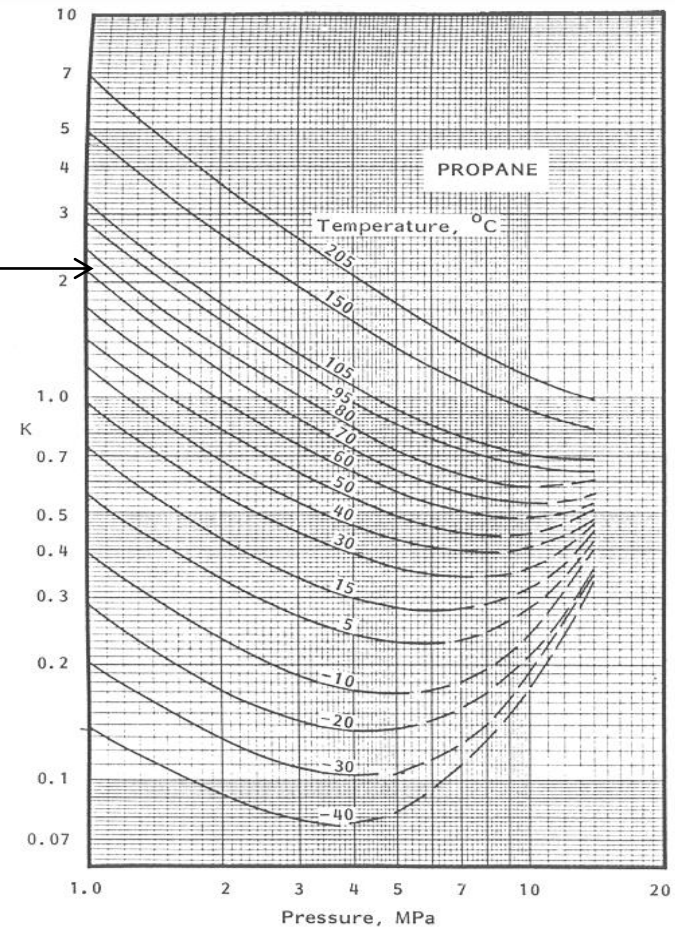
- For a specific pressure and temperature K_i can be determined
- Flash calculation solution is iterative
- Guess V and calculate L
- Calculate all y_i all x_i
- Test $\sum x_i$ or $\sum y_i = 1.0$ then a solution has been obtained
- If not re-initialise L or V

Using K value charts (available in many text books) the following are worked examples of the three types of calculation.

Bubble Point Estimate

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

	x_i	K_i	$K_i x_i$	K_i	$K_i x_i$
Component	Mole Frac.	70 °C		80 °C	
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 $T = 70\text{ °C}$ and find K values from charts.

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

2. Assume $T = 80\text{ °C}$ 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 Pont Estimate

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

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

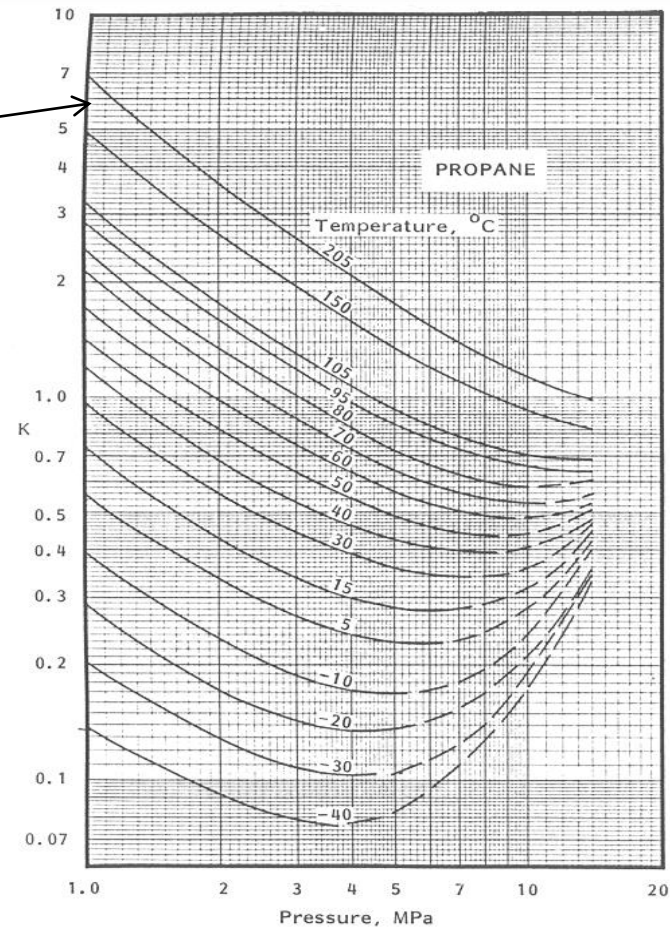
1. Assume $T = 180\text{ °C}$ and find K from charts.

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

2. Assume $T = 190\text{ °C}$ and find K from charts.

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

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



Flash Calculation

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

$\sum y_i - x_i$

Component	Z_i	K_i	$V = 0.5$	$V = 0.4$	$V = 0.3$
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		$\Sigma = -0.298$	$\Sigma = -0.153$	$\Sigma = -0.02$

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

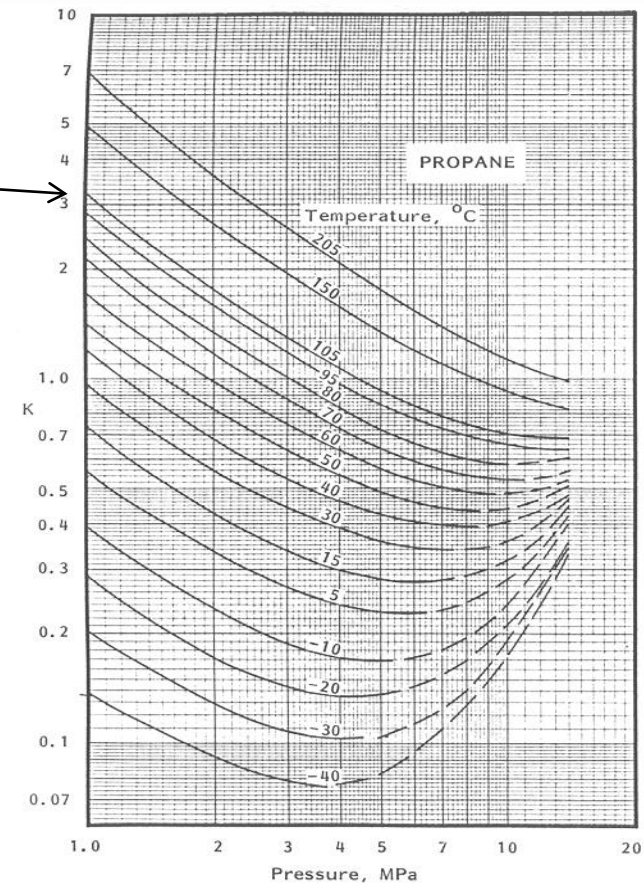
$$\sum y_i - x_i = -0.298 \Rightarrow \text{toohigh}$$

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

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

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

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

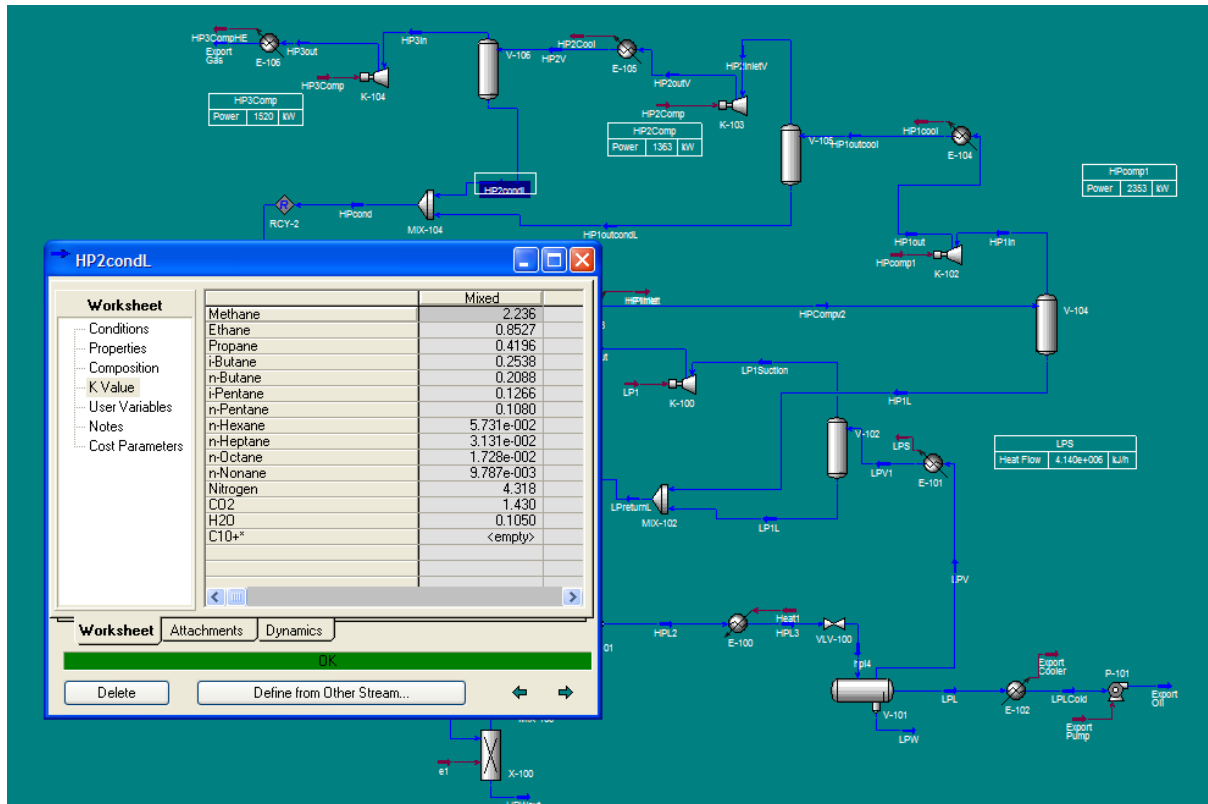


Vapour and Liquid Composition for V=0.3

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

Component	Z _i	K _i	y _i - x _i	x _i	y _i
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		Σ = -0.02	Σ = 1.005	Σ = 0.98

K values can be found from simulation packages as shown.



K values can also be estimated from the following – *Wilson, A Modified Redlich-Kwong EOS, AIChE National Meeting*. The expression is a curve fit of the K value charts.

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

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

ω_i - Acentric factor component i (discussed later)

5.4 Equations of State

Whilst the K value method is useful and provide insight for the student, more accurate calculations are provided by the use of Equations of State

5.4.1 Van der Waals

An equation of state is a thermodynamic equation describing the state of matter under a given set of physical conditions. 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 as:

Also written as:

$$\begin{aligned} a &= 3p_c V_c^2 & a &= \frac{27(R T_c)^2}{64p_c} \\ b &= \frac{V_c}{3} & b &= \frac{R T_c}{8p_c} \end{aligned}$$

The van der Waals equation of state was one of the first to perform markedly better than the ideal gas law. In this landmark equation a is the attraction parameter and b the repulsion parameter or the effective molecular volume. While the equation is definitely superior to the ideal gas law and does predict the formation of a liquid phase, the agreement with experimental data is limited for conditions where liquid forms. While the van der Waals equation is commonly referenced in text books and papers for historical reasons, it is now obsolete. Other modern equations of only slightly greater complexity are much more accurate. One such equation is SRK.

5.4.2 Soave-Redlich-Kwong (SRK)

SRK is robust and well proven equation of state, ideal for use in oil & gas and refinery applications. It is suitable for cryogenic conditions and pressures up to 300 bara. Binary interaction parameters (BIP, symbol k_{ij}) for component pairs are used to improve accuracy with correlations used to generate binary interaction parameters for pseudo-components. BIPs are obtained from experimental data which is regressed for EOS use in simulators.

In common with many EOS, SRK is not considered suitable where accuracy is required for systems with polar compounds.

Liquid compressibility predictions are sufficiently accurate for fugacity calculations but not for accurate liquid densities (can be 10 - 20% low).

SRK can predict phase behaviour in the critical region although calculations are somewhat unstable. Furthermore SRK is not considered to be particularly accurate for heavy end VLE prediction and vacuum systems.

Redlich, O. and Kwong, J. N. S. (1949). On the Thermodynamics of Solutions. V: An Equation of State. Fugacities of Gaseous Solutions. Chem. Rev., 44, 233-244.

Soave, G. (1972). Equilibrium Constants from a Modified Redlich-Kwong Equation of State. Chem. Eng. Sci., 27, 1197-1203.

5.4.2.1 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 chemical potential hence at equilibrium species fugacity will be equal.

The fugacity coefficient for a pure component is defined as:

$$F_i = \frac{f_i}{P}$$

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

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

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

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

Classical thermodynamics shows;

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

Each equation of state provides a related solution to the above integral as will be shown in the following information on SRK.

Properties and parameters used;

a	Attraction parameter
b	Residual volume parameter
W	SRK Parameter (numerical co-efficient)
A	Derived parameter
B	Derived parameter
z	= PV/RT, compressibility factor
\hat{f}_i	Partial fugacity of species i
k_{ij}	Binary Interaction Parameter
F	= f_i/P , Fugacity Coefficient
W	Acentric Factor
ρ	Molar Density

Subscripts

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

Superscripts

0	property of a standard state
---	------------------------------

SRK Standard Form

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

The variables 'a' and 'b' are derived from the Van-der-Waals equation, which was based on a model where molecules were represented by hard spheres which behaved in a classical and predictable fashion

The parameter 'b' represents the hard-sphere volume of the molecules

The parameter 'a' represents the intermolecular attraction

Polynomial Compressibility Form – (the cubic equation)

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

Parameters

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

$$B = (b P)/(RT) = 0.08664P_r/T_r$$

$$a = W_a R^2 T_c^2 / P_c = 0.42748 R^2 T_c^2 / P_c$$

$$b = W_b R T_c / P_c = 0.08664 R T_c / P_c$$

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

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

Fugacity Coefficient

$$\ln \bar{F} = Z - 1 - \ln(Z - B) - A/B \ln(1 + B/Z)$$

Mixtures

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

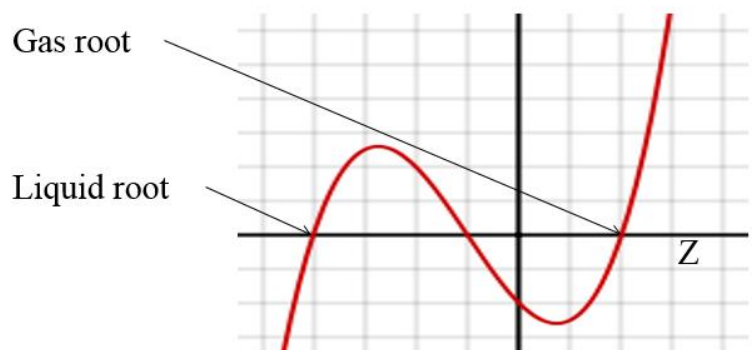
$$b = \sum y_i b_i$$

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

$$B = \sum y_i B_i$$

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

The system is in equilibrium if the phase fugacities at roots are equal.



5.4.3 Peng-Robinson

Peng-Robinson is robust and well proven, generally ideal for use in oil & gas and refinery applications. It is similar to SRK in performance however it is generally accurate over a wider range of conditions. Specifically;

- 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, vacuum distillation and glycol dehydration.

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

PR Standard Form

$$P = \frac{RT}{(V-b)} - \frac{a\alpha}{(V^2 + 2bV - b^2)}$$

Polynomial Compressibility Form

$$z^3 - (1-B)z^2 + (A - 3B^2 - 2B)z - (AB - B^2 - B^3) = 0$$

Parameters

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

$$b = 0.07780 RT_c/P_c$$

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

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

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

Fugacity Coefficient

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

Mixtures

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

$$b = \sum y_i b_i$$

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

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

$$B = \sum y_i B_i$$

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

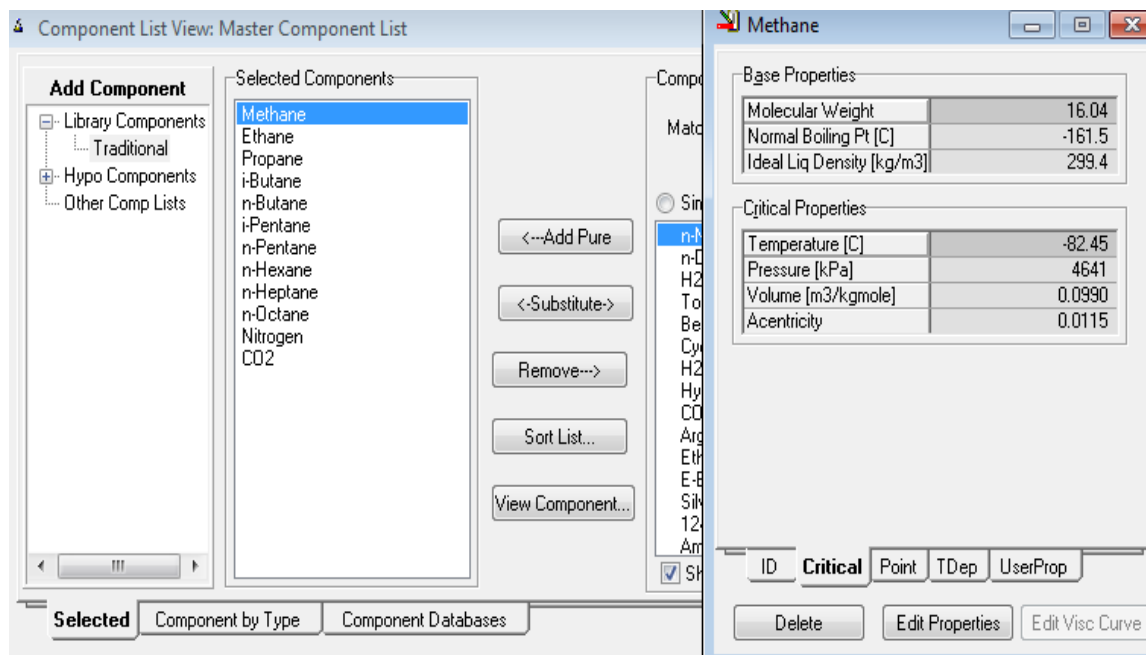
Acentric Factor

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

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

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

Acentric factors can also be found in simulation packages.



SRK worked example

Calculation of the saturation pressure (boiling point) of n-Pentane at 100 °C using SRK.

The experimentally determined vapour pressure is 5.86 atm

Critical properties of n-Pentane are:

$$T_c = 469.7 \text{ K}, P_c = 33.25 \text{ bar}, w = 0.251$$

Using S-R-K :

$$\sqrt{\alpha} = 1 + m(1 - \sqrt{Tr}) \text{ where } m = 0.48 + 1.574\omega - 0.172\omega^2$$

$$\sqrt{\alpha} = 1 + \left(0.48 + (1.574 \times 0.251) - (0.172 \times 0.251^2)\right) \left(1 - \sqrt{\frac{373}{469.6}}\right) = 1.094$$

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:

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

$$f_v = f_v/P_v \text{ and } f_L = f_L/P_v$$

At equilibrium, $f_v = f_L$ therefore $f_v = f_L$

	z		f		
P	Vapour	Liquid	Vapour	Liquid	Ratio
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

At equilibrium, the fugacity of the liquid and vapour phases is equal.

Trial and error is conducted from 4 to 7 atm. By interpolation of the above table, the predicted saturation pressure is 6.01 atm

5.5 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 equipment applications.

The PR and SRK equations of state give accurate modelling for systems containing up to 5% N₂, CO₂ or H₂S. For systems with greater than 5% N₂, CO₂ or H₂S 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 for the particular simulation 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. These utilise a combination of an EOS to predict vapour phase fugacity coefficients and an activity coefficient model for the liquid phase.

The following is the modelling output for a simple system where the gas rate to compressors is a key issue. Two EOS are used – Peng-Robinson and Zudevitch Joffe. As can be seen similar gas from the higher pressure separator are predicted by both EOS. However for the lower pressure separator a difference of around 30% is shown. This difference could be very significant when considering the design of the low pressure compressor. The question is what is correct? That is a key skill for the engineer – the selection of the most accurate EOS for the particular application.

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., Joffe, 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

	PR	ZJ
MW	22.89	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

1.1 barg
53 C

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

5.5.1 BWRS

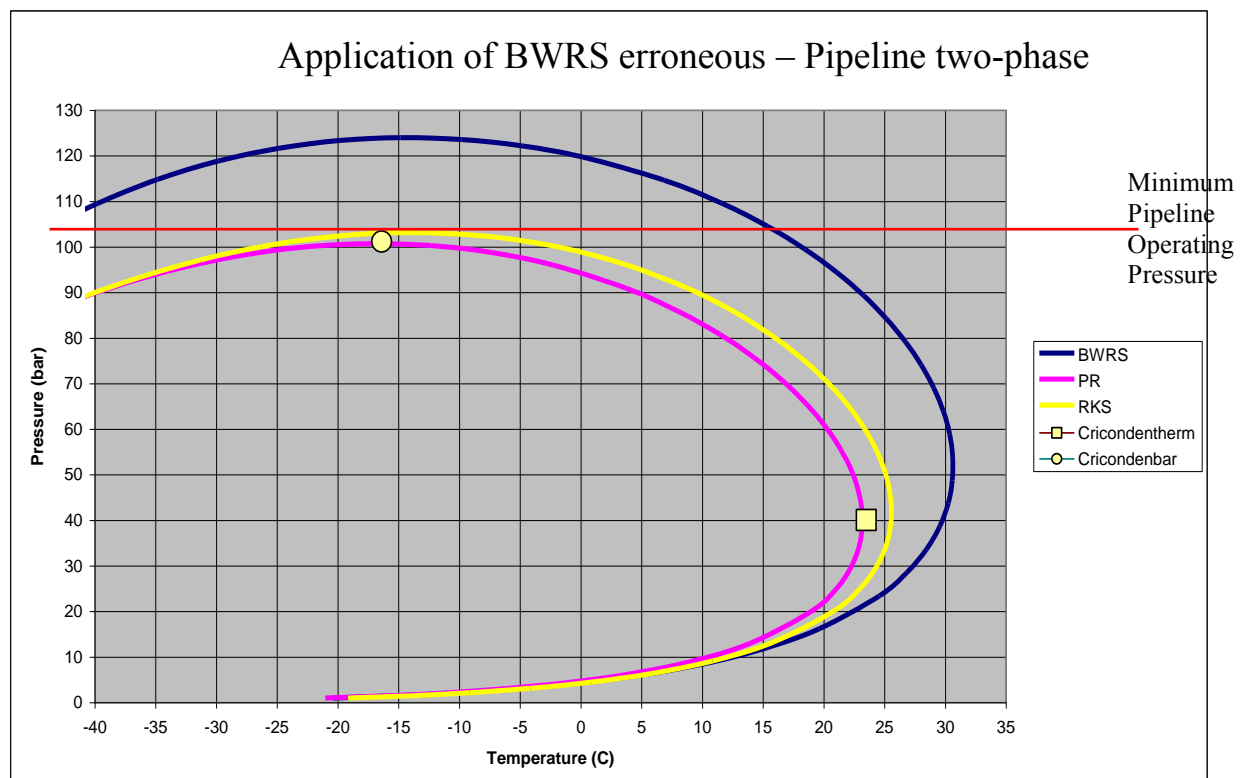
This is the Benedict-Webb-Rubin equation of state modified by Professor Kenneth E. Starling of the University of Oklahoma:

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

ρ = 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. The following phase envelope shows BWRS, PR and SRK results with measured values of cricondentherm and cricondenbar for a specific gas. As can be seen PR and SRK are very accurate whereas BWRS is significantly different. If BWRS were assumed to be accurate for this application significantly more process plant would be required to achieve the pipeline cricondenbar. Once again reinforcing the requirement for appropriate package selection.



5.5.1.1 Limitations of Phase Behaviour Prediction

All phase behaviour methods assume an equilibrium is reached. 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 fluid shear rates which disperses water in the oil phase, water will carry over into the oil phase. Also liquid droplets may be entrained into the gas phase. EOS do not accurately predict phase behaviour at the critical point.

5.5.2 CPA Model – Polar Fluids

The cubic equation of state is the most widely used thermodynamic models for phase equilibrium calculation and physical property estimation in the petroleum industry. As stated earlier, 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

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

Property Package Type	Typical Application
Equations of State,	Ideal hydrocarbon systems
Activity Models,	Polar or non-ideal systems
Chao Seader Models	Systems containing mainly liquid or vapour H ₂ O or high H ₂ 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.

5.5.3 Activity Models

As previously stated, 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 an EOS for property predictions. For example, they cannot be used as reliably as the equations of state for generalised application or extrapolating into untested operating conditions. Their tuning parameters should be fitted against a representative sample of experimental data and their application should be limited to moderate pressures. Consequently, more caution should be exercised when selecting these models for simulation.

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: γ_i = liquid phase activity coefficient of component i

f_i° = standard state fugacity of component i

P = system pressure

ϕ_i = vapour phase fugacity coefficient of component i

5.5.3.1 NRTL

The NRTL (Non-Random-Two-Liquid) equation was proposed by Renon and Prausnitz in 1968, is an extension of the original Wilson equation. It uses statistical mechanics and the liquid cell theory to represent the liquid structure.

The NRTL equation contains five adjustable parameters (temperature dependent and independent) for fitting per binary pair.

The NRTL equation has the form shown.

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

where: γ_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)

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

The five adjustable parameters for the NRTL equation are the a_{ij} , a_{ji} , b_{ij} , b_{ji} , and α_{ij} terms. The equation uses parameter values stored in the simulator or user supplied value for further fitting the equation to a given set of data.

The best results are produced when an activity model is applied in the operating region for which the parameters apply.

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

5.5.4 Modelling Summary

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 ₂ 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 ₂ 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 where appropriate to check that the most appropriate property package has been selected.

In summary for oil, gas and petrochemical applications, the Peng-Robinson EOS is generally the recommended property package. Enhancements to this equation of state enable it to be accurate for a variety of systems over a wide range of conditions. It rigorously solves most

single, two-phase or three-phase system with a high degree of efficiency and reliability, and is applicable over a wide range of conditions.

The PR equation of state is enhanced to yield accurate phase equilibrium calculations for systems ranging from low temperature cryogenic systems to high temperature, high pressure reservoir systems. The same equation of state predicts component distributions for heavy oil, aqueous glycol, and CH₃OH systems.

PR equation of state recommendation is largely due to the preferential attention that is given to it by modelling packages. Although the Soave-Redlich-Kwong (SRK) equation also provides comparable results to the PR in many cases, it is known that its range of application is significantly limited and it is not as reliable for non-ideal systems. For example, it should not be used for systems with CH₃OH or glycols.

As an alternate, the CPA or PRSV equation of state should also be considered. It can handle the same systems as the PR equation with equivalent, or better accuracy, plus it is more suitable for handling moderately non-ideal systems.

Activity Models, which handle highly non-ideal systems, are much more empirical in nature when compared to the property predictions in the hydrocarbon industry. Polar or non-ideal chemical systems are traditionally handled using dual model approaches. In this type of approach, an equation of state is used for predicting the vapor fugacity coefficients and an activity coefficient model is used for the liquid phase. Since the experimental data for activity model parameters are fitted for a specific range, these property methods cannot be used as reliably for generalized application.

The CS and GS methods, though limited in scope, may be preferred in some instances. For example, they are recommended for problems containing mainly steam/water systems because they include special correlations that accurately represent the steam tables. The Grayson-Streed correlation is recommended for use with systems having a high concentration of H₂ because of the special treatment given to H₂ in the development of the model. This correlation may also be slightly more accurate in the simulation of vacuum towers.

The vapor Pressure K models, Antoine, BraunK10 and EssoK models, are designed to handle heavier hydrocarbon systems at lower pressures. These equations are traditionally applied for heavier hydrocarbon fractionation systems and consequently provide a good means of comparison against rigorous models. They should not be considered for VLE predictions for systems operating at high pressures or systems with significant quantities of light hydrocarbons.

Typical simulator default combinations are as indicated;

Property Method	VLE Calculation	Enthalpy/Entropy Calculation
Equations of State		
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

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

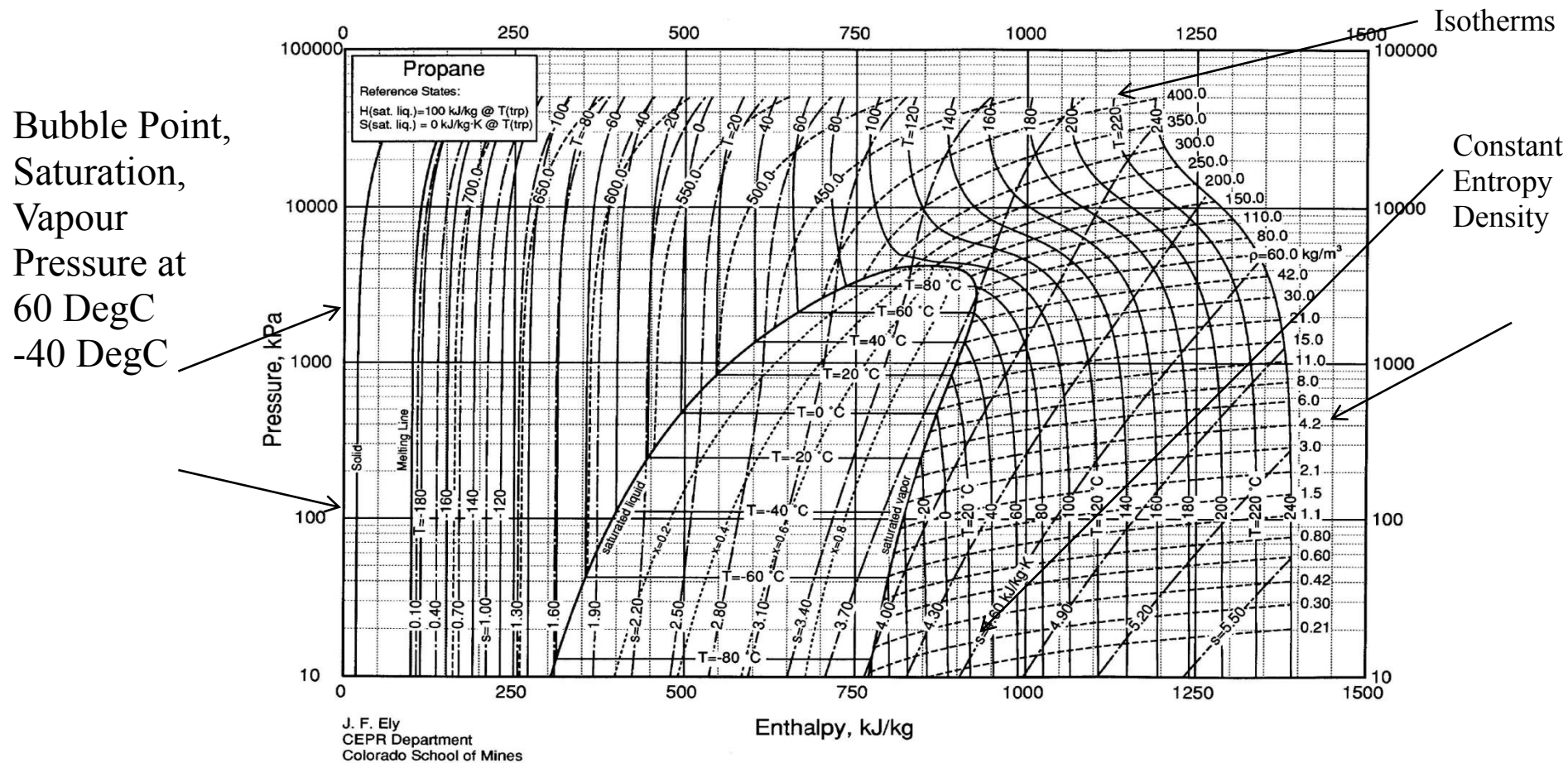
Semi-Empirical Models		
Chao-Seader	CS-RK	Lee-Kesler
Grayson-Streed	GS-RK	Lee-Kesler
vapor Pressure Models		
Mod Antoine	Mod Antoine-Ideal Gas	Lee-Kesler
Braun K10	Braun K10-Ideal Gas	Lee-Kesler
Esso K	Esso-Ideal Gas	Lee-Kesler
Miscellaneous - Special Application Methods		
Amines	Mod Kent Eisenberg (L), 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

5.5.5 CO₂ Modelling

Interest in Carbon Capture and Storage has focussed attention on accurate CO₂ modelling. The EOS of Span and Wagner is recommended.

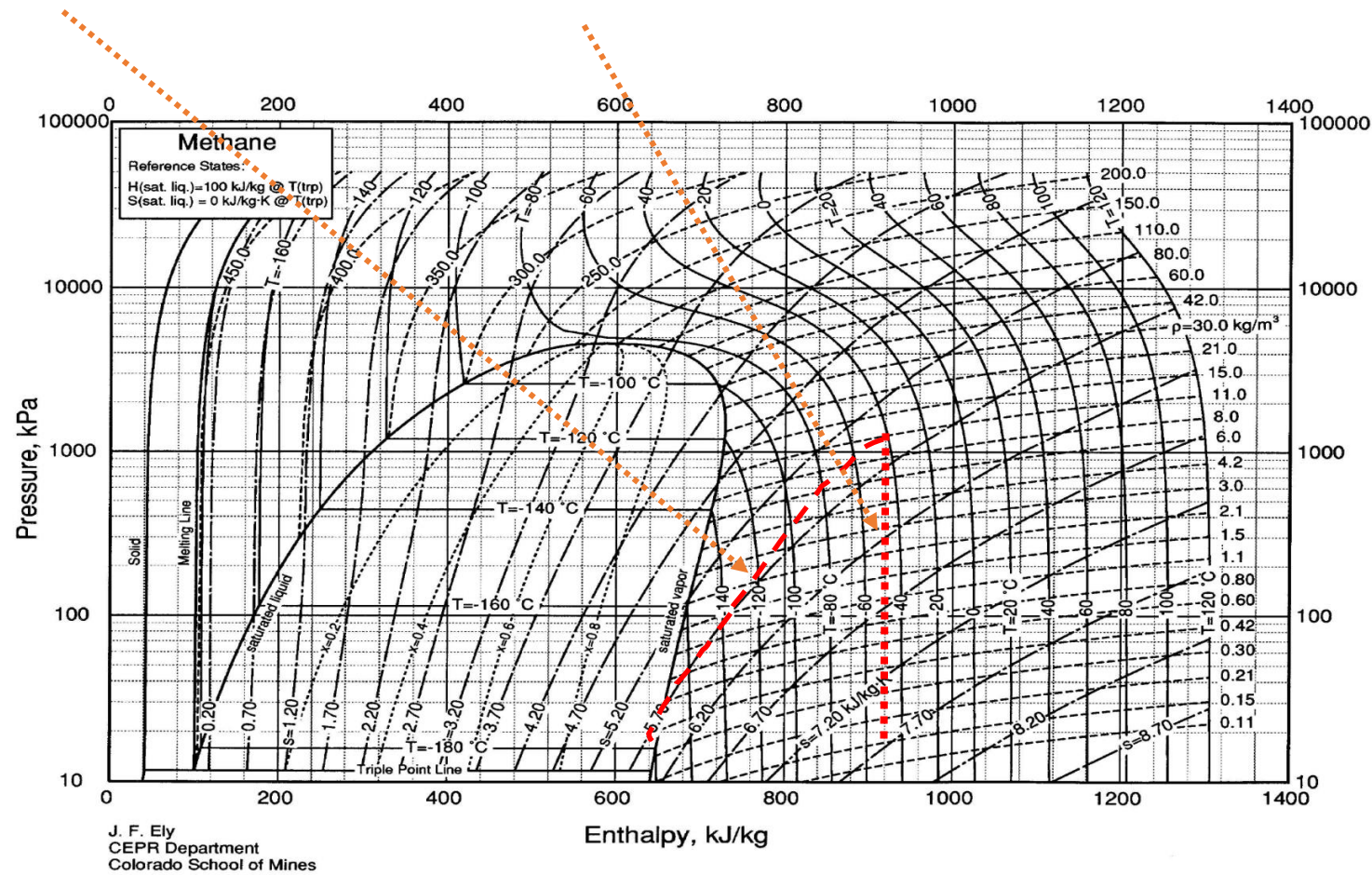
5.6 The Mollier Chart

The Mollier Chart is a convenient representation of the phase behaviour and thermodynamics of a fluid. The charts are very useful for preliminary calculations. Key features are shown.

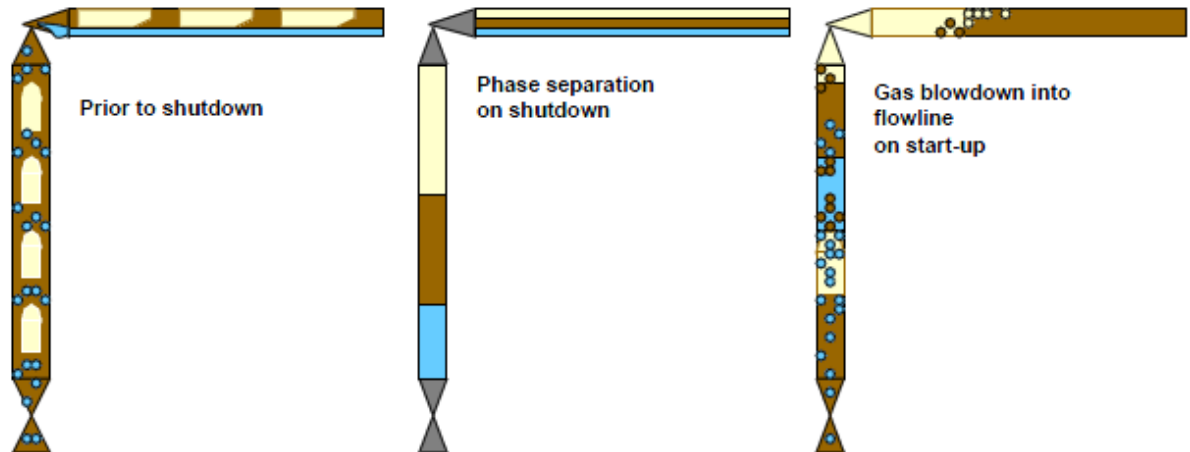


Constant entropy

Constant enthalpy



The Mollier chart can be used for as a first approximation gas expansion across a valve follows an isenthalpic path. Gas expansion can result in downstream temperatures considerably below the ambient temperature. Low temperatures can result in ice and hydrate formation furthermore; materials have to be designed to handle low temperatures where appropriate. A typical application is the opening of a closed well. Here the formed gas cap expands isenthalpically.



5.7 Crude Assay

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 ₂ 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 ₂ - C ₄	C5 - 175° F	175° - 250° F	250° - 375° F	375° - 530° F	530° - 650° F	650° - 1050° F	650° 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 ₂ 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

* = calculated from gas chromatographic data

6 Physical Properties

Accurate physical properties are required for system and equipment design. They underpin Chemical Engineering calculations and errors here will result in a flawed design or perhaps an unsafe design. The student should not blindly assume that the physical property output from a simulation is accurate and verification should be undertaken.

A typical heat exchanger data sheet follows, as can be seen key physical properties are essential for the design to proceed.

GENERAL INFORMATION									
1	APPLICABLE TO:	T PROPOSAL	μ PURCHASE	μ AS BUILT					
2	Item No.:	HBG-3540							
3	Site:	BP Clair Platform / UK Continental Shelf, West of Shetlands							
4	Service:	HP Compressor Discharge Cooler			Serial Number 32016-1				
5	Size:	508-4877	Type:	NEN	Shells/Unit:	One (1)			
6	Surface/Unit:	90.4 (m ²)	Surface/Shell (Eff):	90.4 (m ²)					
7	Manufacturer:	Allards International Ltd			Connected In:	λ Series	μ Parallel		
PERFORMANCE OF ONE UNIT									
8	Fluid Allocation			Shell Side			Tube Side		
9	Fluid Circulated			Cooling Medium (35% TEG & Water)			Hydrocarbon Gas		
10	Fluid Quantity, Total (kg/hr)			87,273			44710		
11				In Out			In Out		
12	Vapor	(kg/hr)					44710	44710	
13	Liquid	(kg/hr)	87,273	87,273					
14	Steam	(kg/hr)							
15	Water	(kg/hr)							
16	Non-condensable	(kg/hr)							
17	Operating Temperature	(°C)	24	49			113	54	
18	Density, (L/V)	(kg/m ³)	1059	1037			188	247	
19	Viscosity (L/V)	(cP)	3.0	1.5			0.03	0.03	
20	Molecular Weight (L/V)		26	26			21.7	21.7	
21	Molecular Weight, Non-condensable								
22	Specific Heat (L/V)	(kJ/kg·°C)	3.78	3.81			3.13	3.31	
23	Thermal Conductivity (L/V)	(W/m·°C)	0.43	0.44			0.07	0.08	
24	Latent Heat	(MJ/kg @ °C)							
25	Inlet Pressure	(bar (g))		3.45			242		
26	Velocity	(m/sec)		0.414			1.909		
27	Pressure Drop (Allow/Calc.)	(bar)	1	0.3			1	0.1	
28	Fouling Resistance	(m ² ·°C/W)		0.00035			0.00018		
29	Heat Load:	2300 (kW)			Corrected LMTD:		44.39 (°C)		
30	Heat Transfer Rate	Service: 573.2 (W/m ² ·°C)			Clean:		920.5 (W/m ² ·°C)		
CONSTRUCTION									
31	Fluid Allocation			Shell Side			Tube Side		
32	Pressure Design/ Test	(bar(g))	12	17.16			270	386.1	
33	Maximum Allowable Working Pressure	(bar(g))		12			270		
34	Temperature Design/Minimum	(°C)	175	-6			175	-6	
35	No. of Passes			1			1		
36	Corrosion Allowance	(mm)		3.0			3.0		
37	Nozzles: (No.) & Size (In/Out)	Note (9)	8"	8"			8"	8"	
38	Nozzles: Flange Type & Rating		RF 150#			RTJ 2500#			
39	Tubes: No.:	389	OD: 16.2 (mm)	BWG: 12 min.	Length: 4877 (mm)		Pitch: 22.23 mm, 30°		
40	Tube Material:	SA-789 UNS 31803, Note (1)		Tube Type: μ Seamless λ Welded					
41	Shell:	SA-516-70	IU: μ BU8	UU: μ	Impact Plate: CS				
42	Shell Cover:	--	μ Integral	μ Removable	Floating Head Cover:				
43	Channel:	SA-516-70	Channel Cover:	SA-516-70 or SA-350-LF2					
44	Tubesheets: λ Stationary μ Floating		Impingement Protection: λ Yes μ No	Type					
45	Tubesheets Material:	SA-350-LF2		Impinge. Protection Mat'l: CS Baffle Mat'l CS					
46	Baffles CS, Note (7) λ Cross μ Long	Type: Segment λ Vertical μ Horizontal		μ Others					
47	% Cut 20 (Dia.) Spacing: C/C 24 / 1	Inlet: 508	Seal type: μ	Tube Supports: μ					
48	Gaskets: Shell Side: Tube Side: RTJ, 316 SS, solid Note (4)		λ Exp. Joint	Type: 316L SS, Note (6)					
49	Code Requirements: λ ASME Sec. VIII, DIV. 1 μ Code Stamp λ TEMA Class: R		μ Others						
50	Weights: Shell (kg) Bundle: (kg)		Full of Water: (kg)	μ Insulation Thk. (mm)					
51	Notes								
52	(1) Strength weld tube to tube sheet. (2) 100 % RT on channel side. (3) 8" pressure relief connection in shell								
53	(4) 316 SS spiral wound gasket, style CGI (w/ inner and outer ring) on shell nozzles; tube nozzle, solid 316 SS for RTJ								
54	(5) Expansion joint, flanged and flued, designed for 1000 cycles, with 1/2" plugged vent and drain. The expansion shall be based on:								
55	a. Shell fluid flowing at -6 °C and tube fluid entering at 113 °C								
56	b. Normal operating condition								
57	(6) Both ends of channel require insulation, or personnel protection heat shields. (7) 1/ crosspaths shell side (16 baffles)								
58	(8) Deleted								
59	(9) Two (2) 8" 150# nozzles shall be provided at 1/3 point and 2/3 point on top of shell for rupture pin valve.								

6.1 Critical and Reduced Temperature and Pressure

Critical and reduced pressure and temperature are often used as correlating parameters. As the critical temperature is approached, the properties of gas and liquid phases approach one another, resulting in only one phase at the critical point: a homogeneous supercritical fluid. The heat of vaporization is zero at and beyond this critical point, hence there is no distinction between the two phases. Above the critical temperature a liquid cannot be formed by an increase in pressure, but with enough pressure a solid may be formed. The critical pressure is the vapour pressure at the critical temperature. Critical properties vary from material to material, just as is the case for the melting point and boiling point. Critical properties for many pure substances are readily available in the literature. Obtaining critical properties for mixtures is somewhat more problematic.

The critical point for a multicomponent mixture is referred to as the state of pressure and temperature at which all intensive properties of the gas and liquid phases are equal.

Reduced Properties

Like critical properties, reduced properties are often used as correlating parameters and properties in thermodynamics. Reduced properties are temperature and pressure divided by their respective critical property.

6.2 Liquid Density

Liquid density is required for the design of numerous items of process plant. Common liquid densities are as shown.

Compound	Density @ 15 °C (kg/m ³)
Water	1000
Ethyl alcohol	785
Butane	563.2
Octane	706.7
Heavy Crude	903
Medium Crude	859
Light Gas Condensate	734
Steel	Approx. 7800
Concrete	Approx. 2300

One of the simplest calculation methods is the API corresponding states method which uses a correlation to obtain a correction factor that adjusts the density at standard conditions to the actual conditions.

$$v_m = \sum \frac{M_i x_i}{\rho_i}$$

$$M_m = \sum x_i M_i$$

$$\rho_{\text{actual}} = \rho_{\text{standard}} \left(\frac{C1}{C2} \right)$$

Where:

v - Molar Volume (m³/kmol)

ρ - density (kg/m³)

M - Molecular weight (kg/kmol)

x - Mole fraction

C1 & C2 - Correlation factors for density correction

m - mixed compound

Example:

Calculate the liquid density of a saturated mixture of 70% ethane, 20% propane and 10 %butane at 100 bara and 25°C.

Obtain the density of components at standard conditions, here data is given relative to water.

$$\left. \begin{array}{l} C_2 - \gamma = 0.3581 \quad \therefore \rho = 358.1 \text{ kg/m}^3, \quad M = 30.07 \\ C_3 - \gamma = 0.5083 \quad \therefore \rho = 508.3 \text{ kg/m}^3, \quad M = 44.097 \\ C_4 - \gamma = 0.5637 \quad \therefore \rho = 563.7 \text{ kg/m}^3, \quad M = 58.124 \end{array} \right\}$$

Using volume mixing equation

$$v_m = \frac{30.07 \times 0.7}{358.1} + \frac{44.097 \times 0.2}{508.3} + \frac{58.124 \times 0.1}{563.7} = 0.0865 \text{ m}^3 / \text{kmol}$$

$$M_m = (30.07 \times 0.8) + (44.097 \times 0.2) + (58.124 \times 0.1) = 35.68 \text{ kg/kmol}$$

$$\rho_{m \text{ standard}} = \frac{M_m}{v_m} = \frac{38.69}{0.0864} = 412.6 \text{ kg/m}^3 \quad \text{@ Standard Conditions}$$

Now find the correlation factors to adjust the standard density to the actual conditions.

Taking Critical Properties from standard databooks

$$P_{cm} = \sum x_i P_{ci} = (0.7 \times 48.8) + (0.2 \times 42.49) + (0.1 \times 36.49) = 46.31 \text{ bara}$$

$$T_{cm} = \sum x_i T_{ci} = (0.7 \times 305.43) + (0.2 \times 369.82) + (0.1 \times 408.13) = 328.6 \text{ K}$$

@ Standard Conditions (15 C & 1 bara)

$$P_{r \text{ standard}} = \text{Saturated Liquid} \quad T_{r \text{ standard}} = \frac{288}{328.6} = 0.876$$

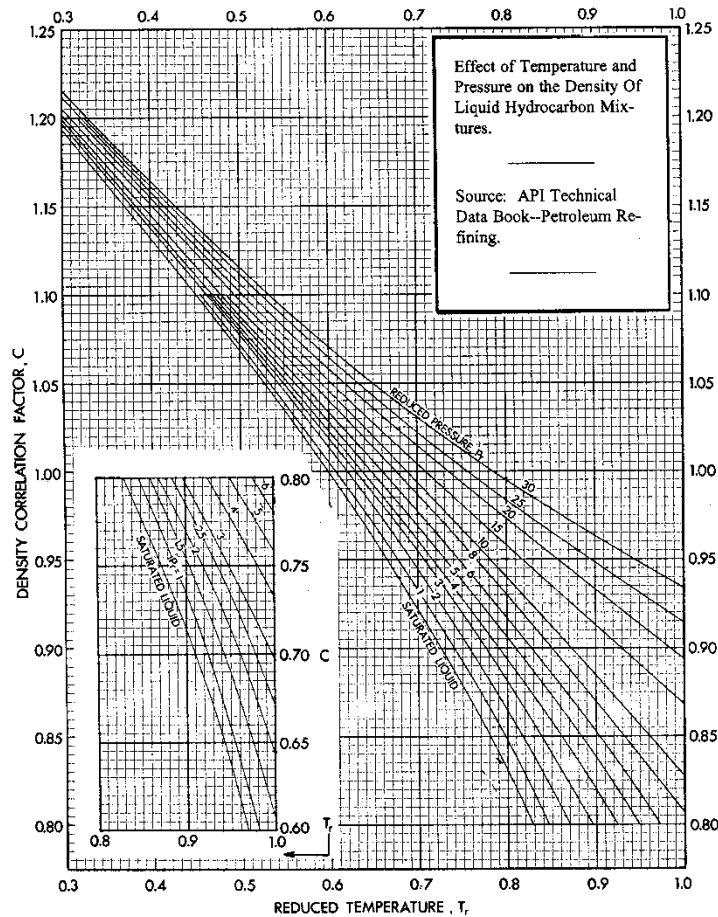
From Correlation chart C1 = 0.745

@ Actual Conditions (25 C & 100 barg)

$$P_{r \text{ actual}} = \frac{100}{46.31} = 2.16 \quad T_{r \text{ actual}} = \frac{298}{328.6} = 0.907$$

From Correlation Chart C2 = 0.764

$$\text{So } \rho_{\text{actual}} = \rho_{\text{standard}} \left(\frac{C2}{C1} \right) = 412.6 \left(\frac{0.764}{0.745} \right) = 423.11 \text{ kg/m}^3$$



API Correction Factor Chart

Comparing the above with the simulation Unisim. Equation of State generally use the Hawkinson, Brombst & Thomson method - referred to as COSTALD because it uses Corresponding Standard Liquid Tables.

$$\frac{V_s}{V^*} = V_R^0 [1 - \omega_{SRK} V_R^\delta]$$

$$V_R^0 = 1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + c(1 - T_r) + d(1 - T_r)^{4/3} \quad 0.25 < T_r < 0.95$$

$$V_R^\delta = [e + fT_r + gT_r^2 + hT_r^3] / (T_r - 1.00001) \quad 0.25 < T_r < 1.0$$

Where

V_s – Saturated Liquid Volume

V_R^0, V_R^δ – Functions of T_r

T_r – Reduced Temperature

V^* – Molar Volume

ω_{SRK} – Acentric factor

} Found in COSTALD tables

$$\begin{aligned}
 a &= -1.52816 & b &= 1.43907 \\
 c &= -0.81446 & d &= 0.190454 \\
 e &= -0.296123 & f &= 0.386914 \\
 g &= -0.0427258 & h &= -0.0480645
 \end{aligned}$$

The mixing rules for the variables in the previous equations are as follows:

$$\begin{aligned}
 T_{cm} &= \frac{\sum_{i=1}^n \sum_{j=1}^n x_i x_j V_{ij}^* T_{cij}}{V_m^*} \\
 V_m^* &= \frac{1}{4} \left[\sum x_i V_i^* + 3 \left(\sum x_i V_i^{*2/3} \right) \left(\sum x_i V_i^{*1/3} \right) \right] \\
 V_{ij}^* T_{cij} &= \left(V_i^* T_{ci} V_j^* T_{cj} \right)^{1/2} \\
 \omega_{SRK_m} &= \sum x_i \omega_{SRK_i} \quad \text{Acentric Factor (shape sensitive)} \\
 P_{cm} &= \frac{(0.291 - 0.80 \omega_{SRK_m}) R T_{cm}}{V_m^*}
 \end{aligned}$$

This is a much more complicated method and is not suitable for hand calculations.

Using the liquid density calculation in Unisim returns a density of 456.5 kg/m³.

Using the API method a value of 423.11 kg/m³ was calculated.

6.3 Gas Compressibility

The term "compressibility" is also used in thermodynamics to describe the deviance in the thermodynamic properties of a real gas from those expected from an ideal gas. The compressibility factor is defined by the familiar expression as;

$$Z = \frac{P V_m}{RT}$$

where

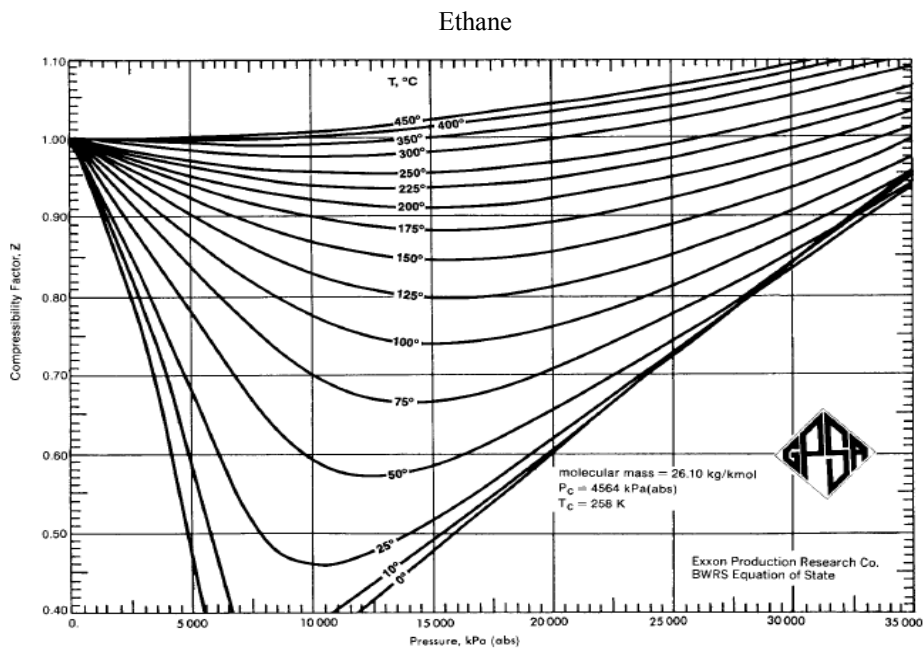
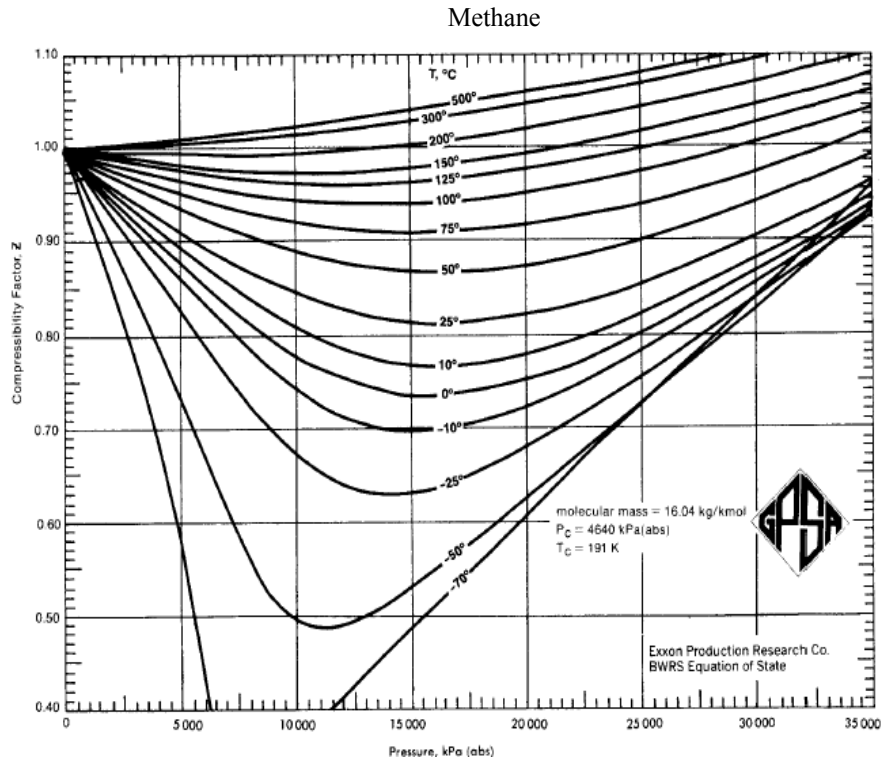
P is the pressure of the gas

T is its temperature

V_m is molar volume. In the case of an ideal gas

Note, Z can be either greater or less than unity for a real gas.

The deviation from ideal gas behavior tends to become particularly significant near the critical point, or in the case of high pressure or low temperature. In these cases, a generalized compressibility chart or an alternative equation of state better suited to the problem can be utilised to produce accurate results.



Typical gas densities at 15 C and 1 bara

Compound	Vapour Density (kg/m ³)
Air	1.21
Oxygen	1.335
Carbon dioxide	1.873
Methane	0.6784
Propane	1.865

The main parameter in calculating vapour density is the compressibility. This can be calculated by either the appropriate equation of state or activity model, or by generalised compressibility charts.

Example calculation using compressibility charts;

Mixed critical properties are calculated using Kay's rule and databook tables :

$$P_{cm} = \sum y_i P_{ci} \quad , \quad T_{cm} = \sum y_i T_{ci} \quad \text{where } y_i \text{ is mole fraction of vapour component}$$

Reduced properties (Pr, Tr) are calculated

$$P_{rm} = \frac{P}{P_{cm}} \quad , \quad T_{rm} = \frac{T}{T_{cm}}$$

Use the reduced properties with a compressibility chart to obtain the compressibility, Z.

The Mean molecular mass is then calculated $M_m = \sum y_i M_i$

$$\text{and Density is calculated} \quad \rho_m = M_m P / ZRT$$

Calculate the density of the following vapour at 15 bara pressure and 25 C temperature. At these conditions the mixture is single phase gas. Watch units MPa.

Component	Yi	Tci (K)	YTci	Pci (MPa)	YPci	M	Myi		
C2	0.7	305	213.5	4.88	3.416	30.07	21.049		
C3	0.2	370	74	4.25	0.85	44.097	8.8194		
C4	0.1	408	40.8	3.65	0.365	58.124	5.8124		
Sum			328.3		4.631		35.681		

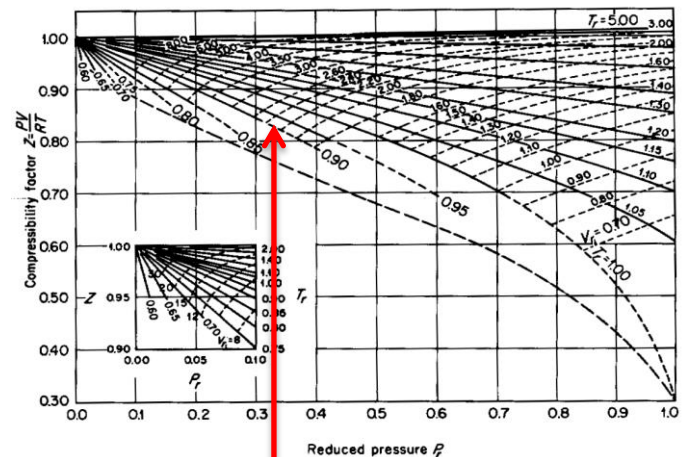
We have the mixtures critical properties, next calculate the reduced properties

$$P_r = \frac{P}{P_c}$$

$$T_r = \frac{T}{T_c}$$

$$P_r = 15 / 46.3 = 0.324$$

$$T_r = 298.15 / 328.3 = 0.907$$



From generalized compressibility charts $Z = 0.84$

$$\begin{aligned}\rho_m &= M_m P / ZRT \\ &= 35.68 \times 1500 / (0.84 \times 8.314 \times 298.15) \\ &= 25.7 \text{ kg/m}^3\end{aligned}$$

6.4 Viscosity

6.4.1 Liquid

Component viscosities can be found by using viscosity charts. The charts are in many data books along with co-ordinates which relate to different compounds. There are separate charts for gases and liquids.

For viscosity estimation of liquid mixtures the following rule can be used

$$\mu_m = \left[\sum x_i (\mu_i)^{1/3} \right]^3$$

where

μ_m – mixture viscosity,

x_i – component mole fraction

μ_i – component viscosity

Example:

Using the viscosity chart estimate the viscosity of a mixture of 30% Pentane and 70% Octane at 25 °C and 1 bar.

Find the co-ordinates for Pentane and Octane to be used with the chart.

Pentane - X=14.9, Y=5.2

Octane - X=13.7, Y=10

from the chart

μ (mPa) = 0.23 for pentane and 0.54 for octane (note: cP = mPas)

$$\begin{aligned}\mu_m &= \left[\left(0.3 * (0.23)^{1/3} \right) + \left(0.7 * (0.54)^{1/3} \right) \right]^3 \\ &= [0.1838 + 0.5700]^3 \\ &= 0.428 \text{ cP}\end{aligned}$$

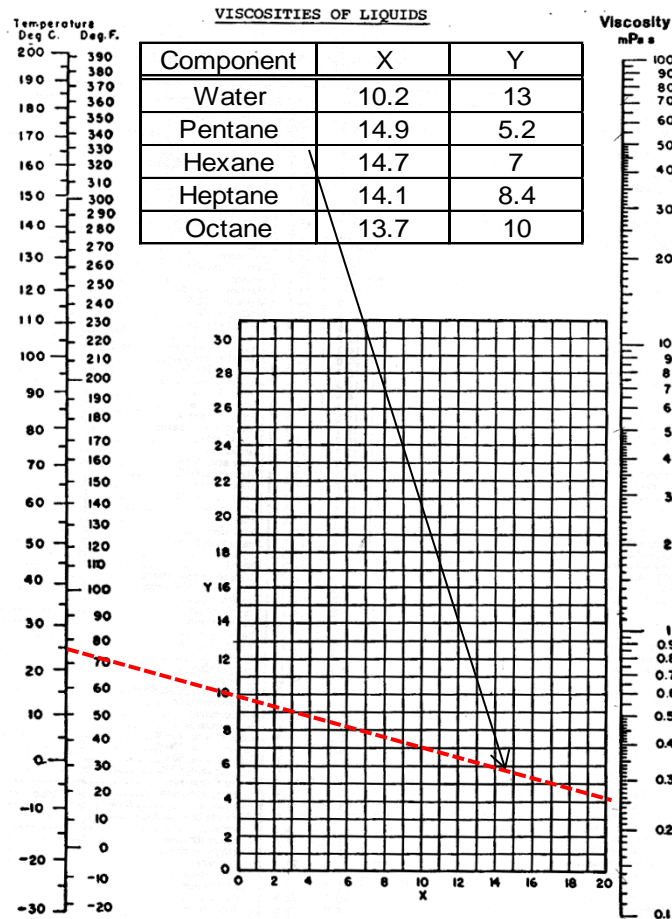


FIG. 3-43. Viscosities of liquids at 1 atm. For coordinates, see Table 3-266.

Note Unisim returns a liquid viscosity of 0.416 cP

6.4.2 Gas

For viscosity estimation of gases the following rule can be used

$$\mu_m = \frac{\sum \mu_i y_i \sqrt{M_i}}{\sum y_i \sqrt{M_i}}$$

where;

μ_m - Mixture viscosity,

μ_i - Component viscosity

y_i - Mole fraction of component

M_i - Component molecular weight

Viscosities are found from viscosity charts. The charts give the viscosity at 1 atmosphere and the required temperature. Correction for pressure and temperature

can be made by using a viscosity correction chart. This requires the reduced P & T from Kay's rule.

Example:

Estimate the viscosity of a gas with composition 40% methane & 60% propane at 25°C and 5 bara pressure.

Calculated the viscosity of the gas at 1 atmosphere and the required temperature

Using co-ordinates: Methane - X= 9.9, Y= 15.5: Propane - X= 9.7, Y= 12.9

From chart μ (mPa) = 0.011 for methane

= 0.0084 for propane

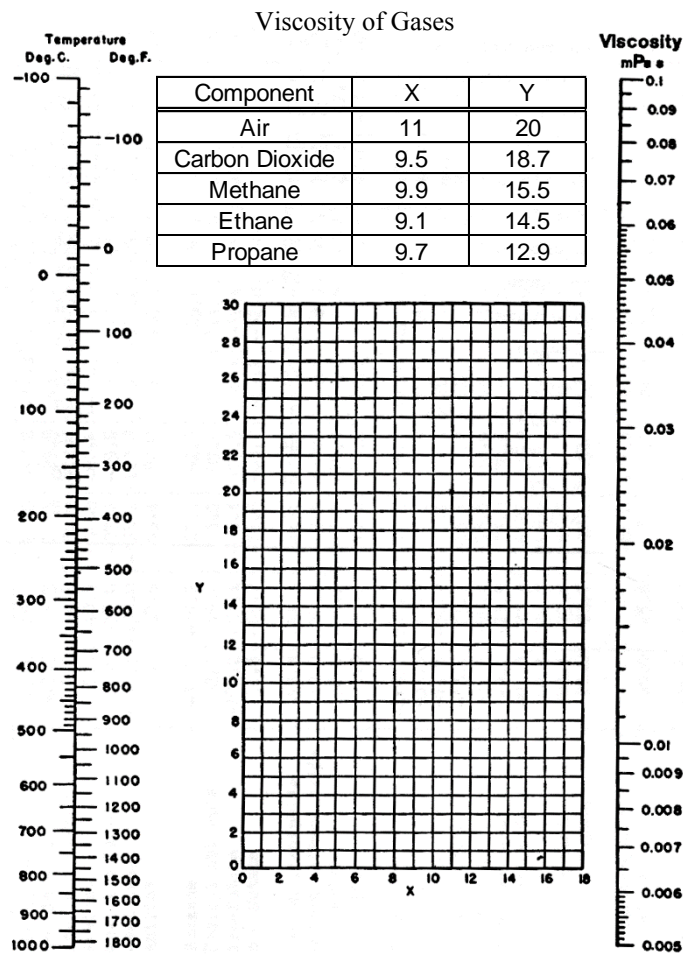


FIG. 3-42. Viscosities of gases at 1 atm. For coordinates, see Table 3-263.

$$\mu_m = \frac{0.011 * 0.4 * \sqrt{16.043} + 0.0084 * 0.6 * \sqrt{44.097}}{0.4 * \sqrt{16.043} + 0.6 * \sqrt{44.097}}$$

$$= \frac{0.0176 + 0.0335}{1.602 + 3.984} = 0.00915 \text{ (cP)}$$

6.5 Specific Heat Capacity

Typical values are given. Note the high heat capacity of water compared to hydrocarbons.

Gas / solid Compound	Isobaric Heat Capacity, C_p (J/kgK)	Liquid Compound	Isobaric Heat Capacity, C_p (kJ/kgK)
Air	0.996	Water	4.187
Propane	2.467	Octane	2.177
		Decane	1.758
Steel	0.502	Heavy Crude	1.718
		Medium Crude	1.750
		Gas Condensate	2.077

The AIChE method can be applied for both gases and liquids. A correction factor is used to adjust the ideal value.

A simple weight fraction average can be used as a first approximation

6.6 Thermal Conductivity

Typical values are given for some common fluids and solids.

Gas / solid Compound	Thermal Conductivity (W/m ² K)	Liquid Compound	Thermal Conductivity (W/m ² K)
Methane	0.0286	Water	0.569
Propane	0.1181	Octane	0.144
		Heavy crude	0.164
Carbon steel	51.9	Medium crude	0.146
Stainless steel	16.3	Gas condensate	0.132

Most simulators use the general guidelines of Reid, Prausnitz & Poling to determine which model best suits each class of component.

- Hydrocarbon systems use the corresponding states method of Ely & Hanley
- Glycols & Acids are calculated by Sato-Reidel method
- Esters, alcohols and light hydrocarbons by Latini

6.7 Surface Tension

A molecule on the surface of a liquid is subject to an inward force as a result of the attraction between molecules. This surface molecule tends to adjust itself to a

minimum surface area causing the droplet to assume a spherical shape. Work is required to extend this surface or to bring molecules from the bulk of the liquid into the surface.

The units of surface tension are therefore force/unit length – N/m. However, most surface tension values are presented as dyne/cm – where 1 dyne – 10^{-5} Newton.

Component	Surface Tension (dyne/cm)
Water	73.82
Octane	25.05
Heavy crude	30.27
Medium crude	27.32
Gas condensate	23.39

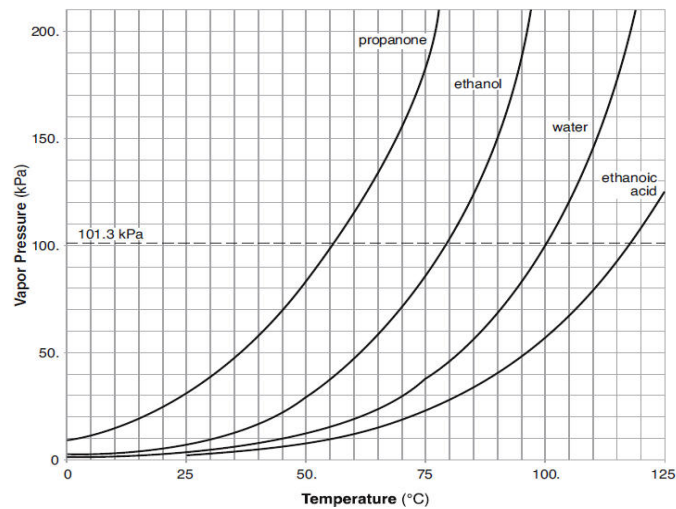
6.8 Vapour Pressure

The vapor pressure of a liquid, is the pressure exerted by its vapor when the liquid and vapor are in dynamic equilibrium. Vapor pressure is the pressure of a vapor in equilibrium with its non-vapor phases. All solids and liquids have a tendency to evaporate to a gaseous form, and all gases have a tendency to condense back. At any given temperature, for a particular substance, there is a partial pressure at which the gas of that substance is in dynamic equilibrium with its liquid or solid forms. This is the vapor pressure of that substance at that temperature. In meteorology, the term vapor pressure is used to mean the partial pressure of water vapor in the atmosphere, even if it is not equilibrium, and the equilibrium vapor pressure is specified as such. Vapor pressure is an indication of a liquid's evaporation rate. It relates to the tendency of molecules and atoms to escape from a liquid or a solid. A substance with a high vapor pressure at normal temperatures is often referred to as volatile. The higher the vapor pressure of a material at a given temperature, the lower the boiling point.

The vapor pressure of any substance increases non-linearly with temperature according to the Clausius-Clapeyron relation. The boiling point of a liquid is the temperature where the vapor pressure equals the ambient atmospheric pressure. At the boiling temperature, the vapor pressure becomes sufficient to overcome atmospheric pressure and the liquid forms bubbles inside the bulk of the substance.

Vapour pressure of common liquids. Note bubble point and

saturation pressure are commonly utilised to describe vapour pressure.



7 Key Learnings

Features of mixed hydrocarbon Phase Envelope – dew point etc.

Pseudo/hypothetical components

Concept of fugacity

Application of K values

Application of Peng-Robinson/SRK EOSs

Application of Activity Models

Importance of EOS selection

Importance of physical property prediction

Vapour pressure

8 Reference books

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

