

PROCESS MODELLING
SELECTION OF
THERMODYNAMIC METHODS

by
John E. Edwards
jee@pidesign.co.uk

Download available from www.pidesign.co.uk



P & I Design Ltd
2 Reed Street, Thornaby, UK, TS17 7AF
Tel: 00 44 (1642) 617444
Fax: 00 44 (1642) 616447
www.pidesign.co.uk

MNL031 05/01
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1.0 INTRODUCTION

The selection of a suitable thermodynamic model for the prediction of enthalpy (H) and phase equilibrium (K) is fundamental to process modelling. Selection of an inappropriate model will result in convergence problems and erroneous results.

The selection process is driven by considering the following:-

- Process species and compositions.
- Pressure and temperature ranges.
- Phase systems involved.
- Nature of the fluids.
- Availability of data.

There are four categories of thermodynamic models:-

- Equations-of-State (E-o-S)
- Activity coefficient (γ)
- Empirical
- Special system specific

This paper is not intended to be a rigorous analysis of the methods available and their selection but is offered as an aide memoire to the practicing engineer who is looking for rapid, realistic results from his process models.

The study of complex systems invariably involves extensive research and expenditure of considerable manpower effort by specialists. There are extensive sources of data available from data banks run by DECHEMA, DIPPR and others.

This paper presents practical selection methods and suggests techniques to test the validity of the thermodynamic model selected.

2.0 THERMODYNAMIC FUNDAMENTALS

2.1 Thermodynamic Energies⁽¹⁾

The thermodynamic fundamentals of fluid states in relation to energies and phase behaviour needs to be thoroughly understood.

Four thermodynamic variables determine six thermodynamic energies

Intensive variables
Pressure (**P**)
Temperature (**T**)

Extensive variables (capacity)
Volume (**V**)
Entropy (**S**)

We define thermodynamic energy as follows

$$\text{Energy} = \text{Intensity variable } \begin{matrix} \mathbf{P} \text{ or } \mathbf{T} \end{matrix} \times \text{Extensive variable } \begin{matrix} \mathbf{V} \text{ or } \mathbf{S} \end{matrix}$$

TS represents internal bound energy isothermally unavailable.

PV represents external free energy.

Helmholtz free energy (**F**) is the internal energy available for work and is part of the internal energy (**U**)

We have the following energy relationships

$$\begin{aligned} \text{Internal energy} \quad \mathbf{U} &= \mathbf{T} \mathbf{S} + \mathbf{F} \\ \text{Gibbs free energy} \quad \mathbf{G} &= \mathbf{F} + \mathbf{P} \mathbf{V} \\ \text{Enthalpy} \quad \mathbf{H} &= \mathbf{T} \mathbf{S} + \mathbf{F} + \mathbf{P} \mathbf{V} \\ \mathbf{H} &= \mathbf{U} + \mathbf{P} \mathbf{V} \end{aligned}$$

When considering chemical reactions we have

Chemical energy = chemical potential factor x capacity factor

$$dU = (\mathbf{m}_i - \mathbf{m}_i^0) dn_i$$

Where dn_i is change in species **i** moles
 \mathbf{m}_i is chemical potential species **i**

$$dU = T dS - P dV + \sum_i \mathbf{m}_i dn_i$$

For equilibrium $\sum_i \mathbf{m}_i dn_i = 0$

$$\begin{aligned} \text{Other equilibrium conditions} \quad dF &= 0 \quad (\text{constV \& T}) & dG &= 0 \quad (\text{constP \& T}) \\ dU &= 0 \quad (\text{constS \& V}) & dH &= 0 \quad (\text{constS \& P}) \end{aligned}$$

It can be shown that $\mathbf{G} = \sum_i \mathbf{m}_i n_i$

2.3 Enthalpy

Enthalpy is the sum of the internal energy (U) and the external free energy (PV)

$$H = U + P V$$

The heat supplied is given by

$$dQ = dU + P dV$$

The sign convention should be noted and is + for heat added and dU gain in internal energy

$$dU = C_v dT$$

The specific heat at constant pressure C_p is related to heat input

$$dQ = C_p dT$$

The adiabatic index or specific ratio γ is defined

$$\gamma = \frac{C_p}{C_v}$$

It can be shown that the following relationship holds

$$C_p - C_v = R$$

The heating of a liquid at constant pressure e.g. water is considered in Figure 2

This shows the relationships between the enthalpies in the different phases namely the sensible heat in the liquid phase, the latent heat of vaporisation during the vapour liquid equilibrium phase and the superheat in the gas phase.

Enthalpy is calculated using Latent Heat (LATE) in the liquid and vle phases and Eo-S (SRK) in the superheated or gas phase.

Appendix I reviews the calculation methods adopted in CHEMCAD.

A standard reference state of 298°K for the liquid heat of formation is used providing the advantage that the pressure has no influence on the liquid C_p

The enthalpy method used will depend on the K-value method selected as detailed in Appendix II with the following exceptions

Peng Robinson (PR)	H value PR
Benedict-Webb-Ruben-Starling (BWRS)	H value BWRS
Grayson Streed (GS) and ESSO	H value Lee Kessler
Amine	H value Amine

Special methods are used for

Enthalpy of water steam tables (empirical)
Acid gas absorption by DEA and MEA
Solid components

3.0 SYSTEM PHASES

There are three phase states namely solid, liquid and gas. Processes comprise either single phase or multiphase systems with separation processes involving at least two phases.

Processes involving solids such as filtration and crystallisation, solid – liquid systems and drying, solid – gas system are special cases and receive no further consideration here.

The primary area of interest for thermodynamic model selection involve two phases. Liquid – liquid systems, such as extraction and extractive distillation, where liquid – liquid equilibrium (LLE) is considered and vapour liquid systems, such as distillation, stripping and absorption, where vapour – liquid equilibrium (VLE) is considered.

Figure 3 shows the inter-relationships between the system phases for a series of isotherms based on the E-o-S due to van-der-Waal. This figure provides the first indication of the validity of making a thermodynamic model selection for the K-value on the basis of the system phases namely single phase gas by E-o-S and VLE by activity coefficient.

3.1 Single Phase Gas⁽²⁾

An E-o-S relates the quantity and volume of gas to the temperature and pressure.

The **ideal gas** law is the simplest **E-o-S**

$$P V = n R T$$

Where	P	=	absolute pressure of gas
	V	=	volume or volume of rate of flow
	n	=	number of moles or molar flowrate
	R	=	gas constant in consistent units
	T	=	absolute temperature

In an **ideal gas mixture** the individual components and the mixture as a whole behave in an ideal manner which yields for component **i** the following relationships

$$P_i V = n_i R T$$

$$\frac{P_i}{P} = \frac{n_i}{n} = y_i \quad \text{where } y_i \text{ is mole fraction of } i \text{ in gas}$$

$$P_i = y_i P$$

$$\sum_i P_i = P \quad \text{where } P \text{ is the total system pressure}$$

$$m_i = m_i^0 + R T \ln p_i$$

Note that when $p_i = 1$ we have $m_i = m_i^0$ the reference condition

As the system temperature decreases and the pressure increases deviations from the ideal gas E-o-S result. There are many equation of state ⁽³⁾ available for predicting non-ideal gas behaviour and another method incorporates a **compressibility factor** into the ideal gas law.

3.1 Single Phase Gas (Cont.)

To predict real gases behaviour the concept of fugacity f is introduced giving

$$m_i = m_i^0 + R T \ln f_i$$

All gases tend to ideal behaviour at low pressures where $f \approx p$

Fugacity is of importance when considering processes exhibiting highly non-ideal behaviour involving vapour liquid equilibrium.

Virial Equation of State is given by the following

$$\frac{P V}{R T} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} +$$

Where $B(T)$ is the second virial coefficient

$C(T)$ is the third virial coefficient

Note if $B = C = 0$ the equation reduces to the ideal gas law.

Benedict–Webb–Rubin (BWR) Equation of State

This E-o-S is in the same form as the above equation extended to a fifth virial coefficient. BWR is accurate for gases containing a single species or a gas mixture with a dominant component eg natural gas, and provides considerable precision.

Cubic Equations of State

This represents an E-o-S linear in pressure and cubic in volume and is equivalent to the virial equation truncated at the third virial coefficient.

One of the first E-o-S was that due to **van der Waals** (University of Leiden), developed in 1873, which is shown in Figure 4. This was based on two effects

- 1 The volume of the molecules reduces the amount of free volume in the fluid $(V-b)$
- 2 Molecular attraction produces additional pressure. The fluid pressure is corrected by a term related to the attraction parameter a of the molecules $(P+a/V^2)$

The resulting equation is

$$P = \left(\frac{R T}{V - b} \right) - \frac{a}{V^2}$$

It can be shown from relationship $V = R T \frac{d(\ln f)}{dp}$ that for van der Waals equation

$$\ln f = \ln \left(\frac{R T}{V - b} \right) + \frac{b}{V - b} - \frac{2 a}{R T V}$$

3.1 Single Phase Gas (Cont.)

The most widely used cubic E-o-S is the **Soave** modifications of **Redlich-Kwong (SRK)** equation which is a modification to van der Waals original equation.

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

Where \hat{a} , a and b are system parameters. Parameters a and b are determined from the critical temperature T_c and critical Pressure P_c

Parameter \hat{a} is determined from a correlation based on experimental data which uses a constant called the **Pitzer acentric factor**.⁽³⁾

At the critical point the two phases (gas and liquid) have exactly the same density (technically one phase). If $T > T_c$ no phase change occurs.

Compressibility Factor Equation of State

The Compressibility Factor E-o-S retains the simplicity of the ideal gas law but is applicable over a much wider range of conditions.

$$P V = z n R T \quad \text{Where } Z \text{ is the compressibility factor.}$$

The compressibility factor, dependent on the gas temperature and pressure, varies for different gases and is determined from reference data⁽⁵⁾.

If data is not available for the specific gas **generalised compressibility charts** can be used which require the critical temperature and critical pressure of the gas

For single phase gas systems the following guidelines for thermodynamic model selection are proposed

Process Application	K-Value Method	Enthalpy H
Hydrocarbon systems Pressure > 10 bar	Soave-Redlick-Kwong (SRK)	SRK or LATE
Non-polar hydrocarbons Pressure < 200 bar Temperature -18°C to 430°C	Grayson-Streed-Choa-Seeder(GS)	Lee Kessler(LK)
Hydrocarbon systems Pressure > 10 bar Good for cryogenic systems	Peng Robinson (PR)	PR
Single species gas system Gas compression	Benedict-Webb-Rubin-Starling(BWRS)	Lee Kessler(LK)

3.2 Liquid Phase

On systems involving liquid phases thermodynamic K-value selection is driven by the nature of the solution. Appendix II provides a summary of thermodynamic selection criteria considered in this section.

The following five categories are considered

Ideal solution

These solutions are non-polar and typically involve hydrocarbons in the same homologous series.

Non-ideal solution – regular

These solutions exhibit mildly non ideal behaviour and are usually non-polar in nature.

Polar solutions – non electrolyte

These exhibit highly non-ideal behaviour and will use activity coefficient or special K-value models.

Polar solutions – electrolyte

Electrolytes are not considered in detail here.

However, it should be noted that in modelling they can be treated as true species (molecules and ions) or apparent species (molecules only)

There are two methods

MNRTL	uses	K-value	NRTL	H	LATE
Pitzer method has no restrictions					

Binary interaction parameters (BIPs) are required by both methods for accurate modelling.

Special

Special models have been developed for specific systems.

In **non-polar** applications, such as hydrocarbon processing and refining, due to the complex nature of the mixtures and the large number of species **pseudo components** are created based on average boiling point, specific gravity and molecular weight. The alternative is to specify all species by molecular formula i.e. **real components**.

3.2 Liquid Phase Gas (Cont.)

Ideal Solutions⁽³⁾

In an ideal solution the chemical potential μ_i for species i is of the form

$$\mu_i = \mu_i^0 + R T \ln (x_i)$$

where μ_i^0 is the chemical potential of pure component i

If an ideal solution is considered in equilibrium with a perfect gas the phase rule demonstrates that the two phases at a given T and P are not independent.

Raoult's Law describes the distribution of species i between the gas and the liquid phases

$$p_i = y_i P = x_i p_i^0 \quad \text{at temperature } T$$

Raoult's Law is valid when x_i is close to 1 as in the case of a single component liquid and over the entire composition range for mixtures with components of similar molecular structure, size and chemical nature.

The members of homologous series tend to form ideal mixtures in which the activity coefficient γ is close to 1 throughout the concentration range.

The following systems can be considered suitable for Raoult's Law.

1 Aliphatic hydrocarbons

Paraffins C_nH_{2n+2}	n-hexane (C_6H_{14})	n-heptane (C_7H_{16})
Olefines C_nH_{2n}		
Alcohols $C_nH_{2n+1} \cdot OH$	methanol ($CH_3 \cdot OH$)	ethanol ($C_2H_5 \cdot OH$)

2 Aromatic hydrocarbons

benzene (C_6H_6) toluene ($C_6H_5 \cdot CH_3$)

For ideal liquid systems the following guidelines for thermodynamic model selection are proposed

K – Value	Enthalpy
Ideal Vapour Pressure(VAP)	SRK

In dilute solutions when x_i is close to 0 and with no dissociation, ionisation or reaction in the liquid phase **Henry's law** applies where

$$p_i = y_i P = x_i H_i \quad \text{at temperature } T$$

Henry's law constants H_i for species i in given solvents are available. Typical applications include slightly soluble gases in aqueous systems.

3.2 Liquid Phase (Cont.)

Non-ideal solutions⁽³⁾

In a non ideal solution the chemical potential μ_i for species i is of the form:-

$$\mu_i = \mu_i^0 + R T \ln (g_i x_i)$$

Where g_i is the activity coefficient and component activity $a_i = g_i x_i$

Consider a non ideal solution in equilibrium with a perfect gas we can derive an equation of the form

$$p_i = k_i g_i x_i$$

Raoult's law when $g_i \rightarrow 1$ and $x_i \rightarrow 1$ $k_i = p_i^0$ giving $g_i = \frac{p_i}{p_i^0 x_i} = 1$

Henry's law when $g_i \rightarrow 1$ and $x_i \rightarrow 0$ giving $k_i = H_i$

For vapour liquid equilibrium at temperature T and pressure P the condition of thermodynamic equilibrium for every component i in a mixture is given by

$$f_{vi} = f_{li}$$

Where the fugacity coefficient $f_i = \frac{f_{vi}}{y_i P}$ note $f_i = 1$ for ideal gases

The fugacity of component i in the liquid phase is related to the composition of that phase by the activity coefficient g_i as follows

$$g_i = \frac{a_i}{x_i} = \frac{f_{li}}{x_i f_i^0}$$

The standard state fugacity f_i^0 is at some arbitrarily chosen P and T and in non electrolyte systems is the fugacity of the pure component at system T and P

3.2 Liquid Phase (Cont.)

Regular solutions

Regular solutions exhibit mildly non ideal behaviour and occur in non-polar systems where the component molecular size, structure and chemical nature do not differ greatly. These systems can be modelled using E-o-S.

K-values are calculated from the following relationships using fugacity coefficients

$$K_i = \frac{y_i}{x_i} = \frac{f_{li}}{f_{vi}} \quad \text{where fugacity coefficients } f_{vi} = \frac{f_{vi}}{P} \quad \text{and} \quad f_{li} = \frac{f_{li}}{x_i P}$$

Process Application	K-value	Enthalpy H
General hydrocarbon (same homologous series) System pressure > 10 bar	PR	PR
Branch chained hydrocarbon System pressure > 10 bar	SRK	SRK
Heavy end hydrocarbons System pressure < 7 bar Temperature 90C to 430C	ESSO	LK
Branch-chained and halogenated hydrocarbon Some polar compounds	MSRK	SRK

Polar-nonelectrolyte solutions

These are systems where the liquid phase non-idealities arise predominantly from molecular associations. These systems must be modelled using activity coefficient methods which generally require binary interaction parameters for accuracy.

The vapor phase is taken to be a regular solution giving

$$K_i = \frac{y_i}{x_i} = \frac{f_{li}}{f_{vi}} = \frac{g_i f_{li}^0}{f_{vi} P}$$

Where f_{li}^0 standard fugacity comp i
 f_{vi} fugacity coefficient vapour comp i
 g_i activity coefficient

Models covered by the activity coefficient method include

NRTL, UNIQUAC, Wilson, UNIFAC, Hiranuma, Van Laar, Margules and GMAC.

In making a selection the following should be considered

Wilson, NRTL, and UNIQUAC
UNIFAC

When sufficient data is available (>50%)
When data is incomplete (<50%)

3.3 Vapour Liquid Equilibrium⁽⁴⁾

VLE diagrams provide a very useful source of information in relation to the suitability of the K-value selected and the problems presented for the proposed separation. Having selected a K-value method test the Txy and VLE diagrams against known data for the pure components and azeotropes if present.

Figure 5 in the attachments shows the VLE diagrams for N-Hexane systems.

N-Hexane(1)/N-Heptane(2) can be considered close to representing ideal behaviour which is indicated by the curve symmetry ($\gamma \cong 1$). The different binary systems presented in Figure 5 demonstrate the effect of an increasing α and its influence on ease of separation. We can investigate the effect of γ on α by considering the following

$$p_1 = g_1 x_1 p_1^0 \quad \text{and} \quad p_2 = g_2 x_2 p_2^0$$

$$a = \frac{g_1 p_1^0}{g_2 p_2^0} = a^0 \frac{g_1}{g_2} \quad \text{where } a^0 \text{ is the ideal mixture value}$$

Since $\gamma > 1$ is the usual situation, except in molecules of a very different size, the actual relative volatility is very often much less than the ideal relative volatility particularly at the column top.

Values of γ can be calculated throughout the concentration range using van Laar's equation

$$\ln g_1 = A_{12} \frac{x_2^2}{x_1 + A_{12} x_2} \quad \text{where} \quad A_{12} = \ln g_1^{\infty} \quad \text{with } \infty \text{ representing infinite dilution}$$

An extensive data bank providing values of parameter A_{xy} are available from Dechema.

Values of γ can also be calculated at an azeotrope which can be very useful due to the extensive azeotropic data available in the literature.

At an azeotrope we have $x_1 = y_1$ giving $y_1 P = x_1 g_1 p_1^0$ resulting in $g_1 = \frac{P}{p_1^0}$

Figure 6 in the attachments shows the VLE diagrams for N-Hexane(1)/Ethyl Acetate(2) system.

CHEMCAD Wizard selected K-value NRTL and H Latent Heat and it can be seen that the model is reasonably accurate against known data. The γ values are shown and their influence seen at the column bottom and top.

Figure 7 in the attachments shows the VLE diagrams for Ethanol(1)/Water(2) using K-value method NRTL and SRK which clearly demonstrates the importance of model selection. To achieve convergence for high purity near the azeotropic composition it is recommended to start the simulation with "slack" parameters which can be loaded as initial column profile (set flag) and then tighten the specification iteratively.

4.0 Summary

CHEMCAD provides a K-Value Wizard as an aide to thermodynamic model selection. The selection is essentially based on the component list and operating temperature and pressure ranges. The Wizard decides which model to use between E-o-S, activity coefficient, empirical and special. If inadequate BIP data is available for the activity coefficient method the Wizard defaults to UNIFAC. The key decision paths in the method are shown in Figure 8 in the attachments.

If using the Wizard exclude utility streams from the component list as the presence of water for example will probably lead to an incorrect selection.

The following additional points should to be considered when setting the K-Value

Vapour phase association	typical systems acetic acid, formic acid, acrylic acid
Vapour fugacity correction	set when using an activity coefficient method $P > 1$ bar
Water/hydrocarbon solubility	immiscibility valid only for non activity coefficient methods for which water is assumed to be miscible
Salt	considers effect of dissolved salts when using the Wilson method

In the attachments can be found summary tables providing a basis for model selection. A thermodynamic model decision tree based on system phases is shown in Figure 9.

A synopsis on Thermodynamic Model Selection is presented in Appendix II

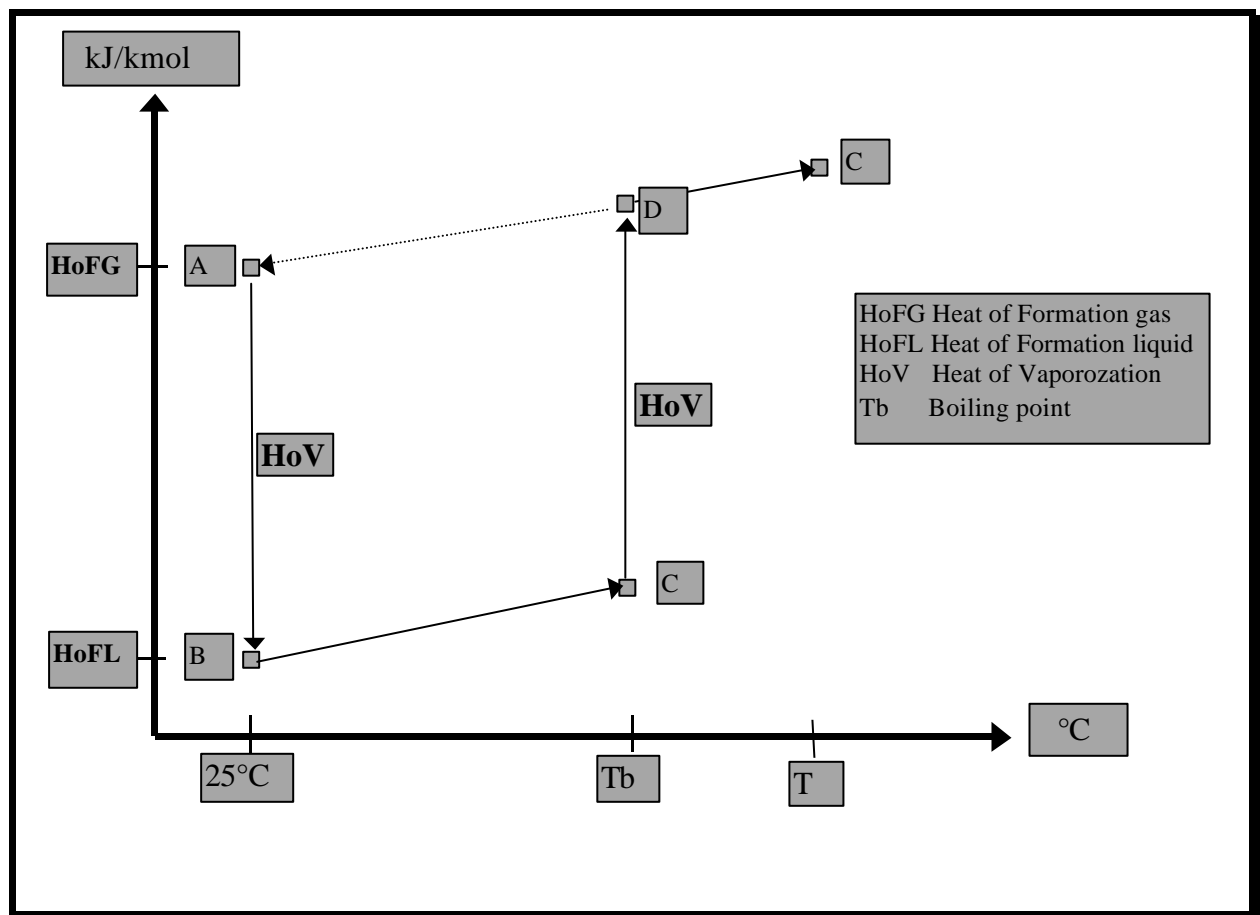
Enthalpy calculation in CHEMCAD

Stream enthalpy by latent heat modell:

CHEMCAD calculates the stream enthalpy beginning at the ideal gas heat of formation (25°C, 1 atm, gas) [A], subtracts the heat of vaporization at 25°C and 1 atm [HoV], which gives the ideal liquid heat of formation at 25°C, 1 atm. With C_p liquid the liquid enthalpy from 25°C to the desired temperature is calculated next. This temperature can be the stream temperature, if the stream is liquid. In that case the enthalpy calculation is done.

If the stream is vapor, the calculation of liquid enthalpy goes until the boiling point [C] and the heat of vaporization at this temperature is added to come to the gas state [D]. From here C_p ideal Gas is used to come to the stream temperature [E], if this is not equal the boiling point.

In the graphic it is assumed, that this temperature is greater than the boiling point.



Enthalpy diagram of the stream enthalpy

Using the liquid heat of formation as a starting point instead of the gas heat of formation has the advantage, that the pressure has no influence to C_p liquid. If the stream is liquid that should be the best way. If the stream is gas there will be still a small problem if the stream pressure is high, because C_p gas is measured for ideal gas only and there is no pressure correction available.

Stream enthalpy by equation of state modell:

The gas enthalpy can also be calculated using the equation of state. CHEMCAD begins in that case with the ideal gas heat of formation. This has the advantage for the gas phase that the pressure is part of the enthalpy. The gas models are SRK, PR, Lee Kessler etc. In the liquid phase these models are not so good as the C_p liquid calculation using the latent heat model. In the case the liquid is highly non ideal the user should select the latent heat model and not an equation of state for enthalpy calculation. This is the reason why the thermodynamic expert selects NRTL, or UNIQUAC or UNIFAC together only with latent heat as the best enthalpy model

A check:

Calculating the stream enthalpy at 25°C, 1 atm which means the user goes from A to B to C to D to A. this should give the ideal gas heat of formation at 25°C, 1 atm. Theoretically the thermodynamic rules says that, but because of errors in the measured physical properties, which are used here, there will be a small deviation in comparison to the data of the databank if the modell is latent heat.

A good decision:

A great number of systems where checked until CHEMSTATIONS decided to calculate the stream enthalpy in the described way. However, we are in discussion with our users about enthalpy.

Reactor enthalpy calculation

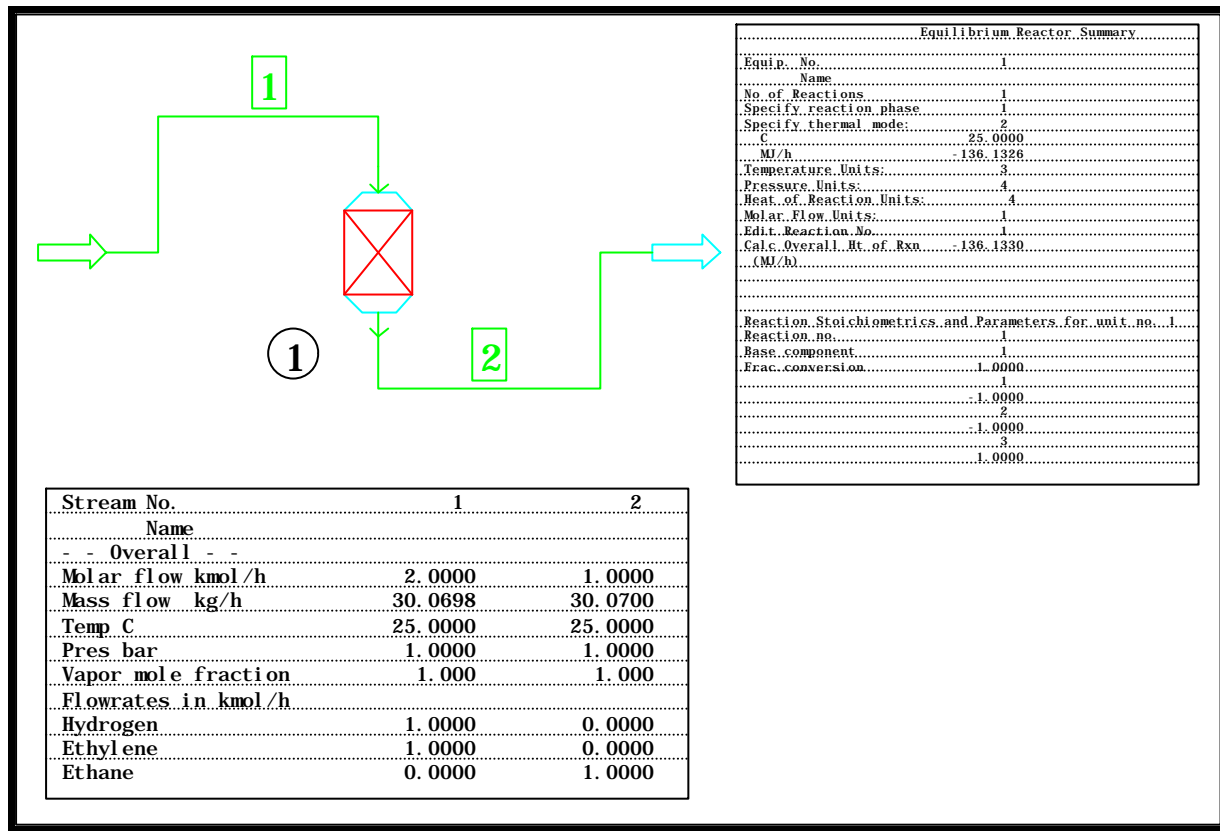
The calculation of enthalpy in the CHEMCAD reactors are discussed now. We will begin with an easy example of a gas reaction.

This is the gas reaction which we will investigate first:

a) Reaction $\text{C}_2\text{H}_4 + \text{H}_2 = \text{C}_2\text{H}_6$ at 25°C

EREA reactor examples, Job file: EREA2

This gas reaction shows a simple example to check the enthalpy balance. The reaction works in the gas phase. That makes the enthalpy calculation easy.



Flowsheet with data

Stream data:

Stream No.	1	2
Stream Name		
Temp C	25.0000*	25.0000
Pres bar	1.0000*	1.0000
Enth MJ/h	52.256	-83.906
Vapor mole fraction	1.0000	1.0000
Total kmol/h	2.0000	1.0000
Total kg/h	30.0698	30.0700
Total std L m3/h	0.1091	0.0845
Total std V m3/h	44.83	22.41
Flowrates in kmol/h		
Hydrogen	1.0000	0.0000
Ethylene	1.0000	0.0000
Ethane	0.0000	1.0000

The enthalpy balance (str.2 - str.1): $-83.9 - 52.2 = -136.1$ MJ/h

Reactor data:

Equip. No.	1
Name	
No of Reactions	1
Specify reaction phase	1
Specify thermal mode:	2
C	25.0000
MJ/h	-136.1326
Temperature Units:	3
Pressure Units:	4
Heat of Reaction Units:	4
Molar Flow Units:	1
Edit Reaction No.	1
Calc Overall Ht of Rxn	-136.1330
(MJ/h)	

Reaction Stoichiometrics and Parameters for unit no. 1

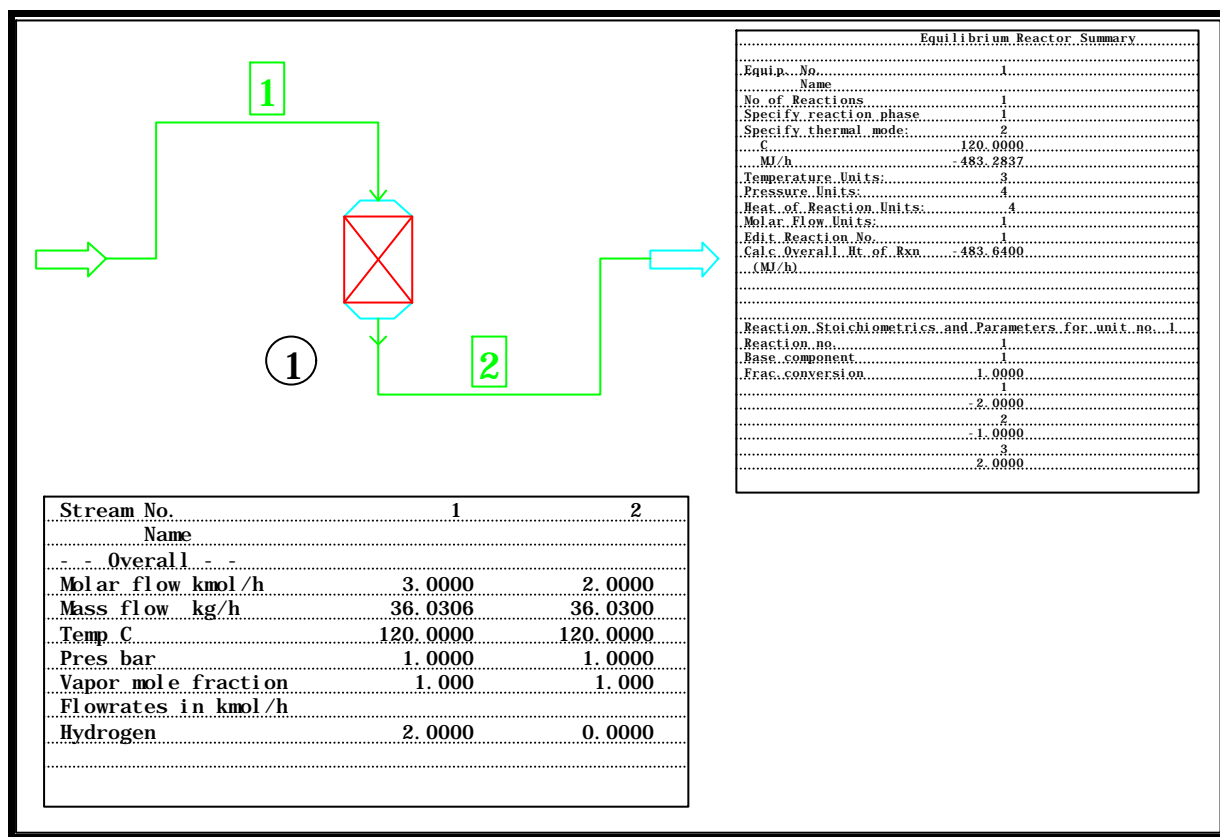
Reaction no.	1
Base component	1
Frac.conversion	1.0000
	1
	-1.0000
	2
	-1.0000
	3
	1.0000

The heat of reaction is -136.13 MJ/h, the heat duty also is -136.13 MJ/h. Because the flowrate is 1 kmol/h, the heat of reaction is -136.13 kJ/kmol. This result can be checked using the heat of formation in the databank.

b) Reaction $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ at 120°C

Job file: EREA3

The reaction is at 120°C in a vapor phase. Therefore we can ignore the heat of condensation.



Flowsheet and data

Stream data:

Stream No.	1	2
Stream Name		
Temp C	120.0000*	120.0000
Pres bar	1.0000*	1.0000
Enth MJ/h	8.2364	-477.95
Vapor mole fraction	1.0000	1.0000
Total kmol/h	3.0000	2.0000
Total kg/h	36.0306	36.0300
Total std L m3/h	0.0861	0.0361
Total std V m3/h	67.24	44.83
Flowrates in kmol/h		
Hydrogen	2.0000	0.0000
Oxygen	1.0000	0.0000
Water	0.0000	2.0000

The enthalpy balance gives the heat duty: $(\text{str.2} - \text{str.1}) \text{ dH} = -477.9 - 8.2 = -486.1 \text{ MJ/h}$

The reactor data

Equip. No.	1
Name	
No of Reactions	1
Specify reaction phase	1
Specify thermal mode:	2
C	120.0000
MJ/h	-483.2837
Temperature Units:	3
Pressure Units:	4
Heat of Reaction Units:	4
Molar Flow Units:	1
Edit Reaction No.	1
Calc Overall Ht of Rxn	-483.6400
(MJ/h)	

Reaction Stoichiometrics and Parameters for unit no. 1

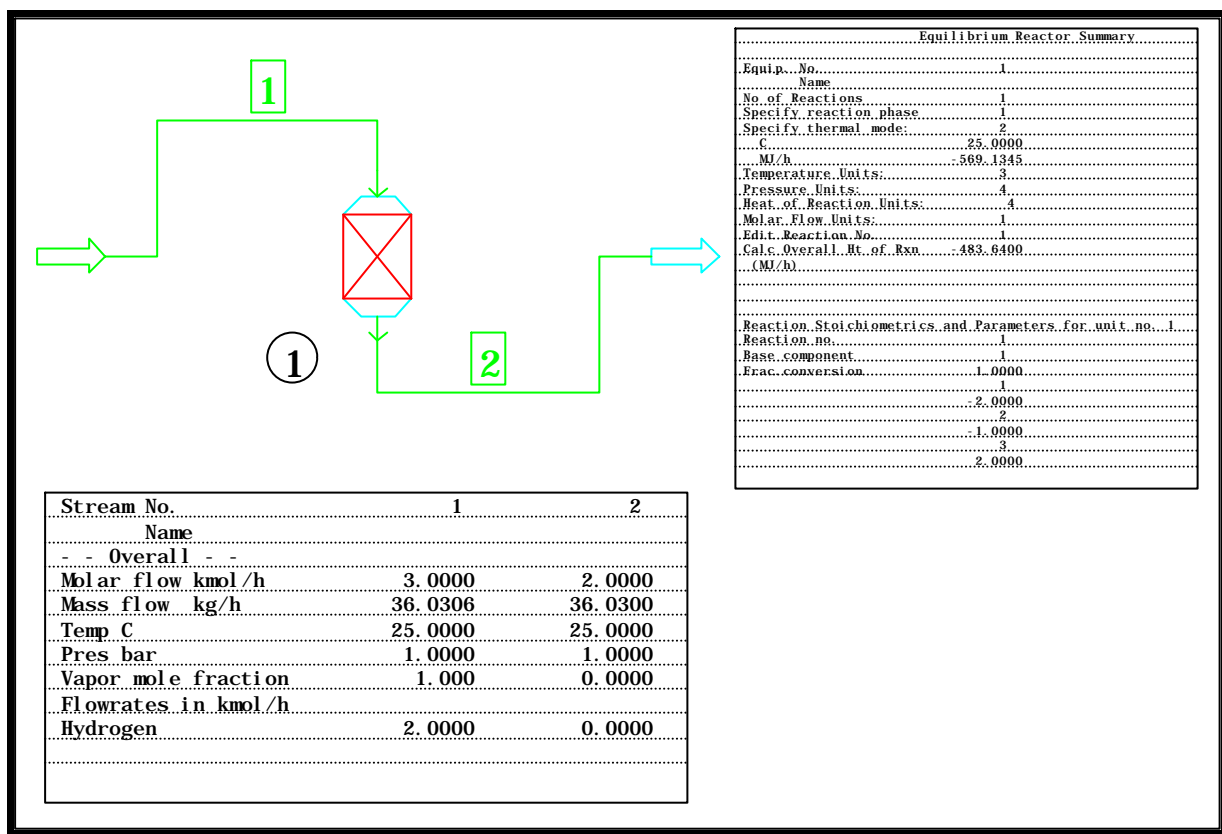
Reaction no.	1
Base component	1
Frac.conversion	1.0000
	1
	-2.0000
	2
	-1.0000
	3
	2.0000

The heat of reaction is -483.64 MJ/h. The heat duty of the reactor is $dH = -483.28$ MJ/h. There is a small difference between the reactor heat duty and the heat duty calculated as the enthalpy difference of the two streams, which was calculated by hand above.

c) Reaction $2 \text{H}_2 + \text{O}_2 = 2 \text{H}_2\text{O}$ at 25°C .

Job file: EREA3

In this example the product stream is liquid. Therefore CHEMCAD calculates the heat of condensation.



Flowsheet and data

Stream data:

Stream No.	1	2
Stream Name		
Temp C	25.0000*	25.0000
Pres bar	1.0000*	1.0000
Enth MJ/h	-0.00459418	-572.04
Vapor mole fraction	1.0000	0.00000
Total kmol/h	3.0000	2.0000
Total kg/h	36.0306	36.0300
Total std L m3/h	0.0861	0.0361
Total std V m3/h	67.24	44.83
Flowrates in kmol/h		
Hydrogen	2.0000	0.0000
Oxygen	1.0000	0.0000
Water	0.0000	2.0000

The enthalpy balance gives the heat duty $dH = -572.0 - 0 = -572.0$ MJ/h

Because water is under 25°C liquid, the enthalpy of condensation must be included. The heat of condensation at 1 bar is ca. 40.6 MJ/kmol.

The reactor data:

Equilibrium Reactor Summary

Equip. No.	1
Name	
No of Reactions	1
Specify reaction phase	1
Specify thermal mode:	2
C	25.0000
MJ/h	-569.1345
Temperature Units:	3
Pressure Units:	4
Heat of Reaction Units:	4
Molar Flow Units:	1
Edit Reaction No.	1
Calc Overall Ht of Rxn	-483.6400
(MJ/h)	
Reaction Stoichiometrics and Parameters for unit no. 1	
Reaction no.	1
Base component	1
Frac.conversion	1.0000
	1
	-2.0000
	2
	-1.0000
	3
	2.0000

The enthalpy balance of the reaction at 25°C under the ideal gas condition the enthalpy gives -483.6 MJ/h, which is equal to the ideal gas heat of reaction and is the same as in the previous example. Because the heat of condensation is included the heat duty is now: -569.1 MJ/h, which is similar to the enthalpy difference of the output and input stream (572 MJ/h). The small difference will be discussed below.

Comments.

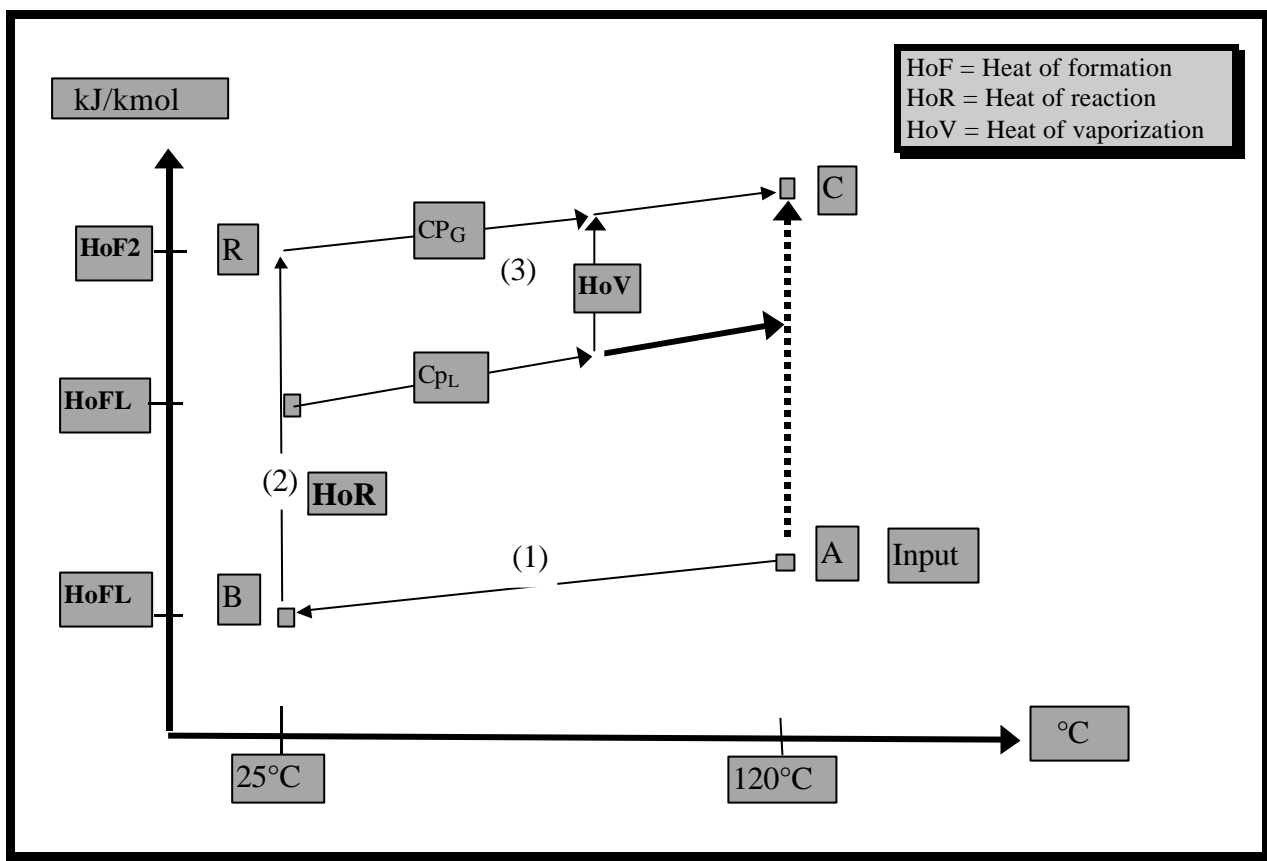
There may occur a little difference from time to time between the hand calculated **heat duty** which is the enthalpy difference of the output and input stream on one side and the **heat duty** calculated by the reactor on the other side. The reason is that the reactor calculates the heat duty different than the hand calculation is done. Under the rules of thermodynamic there should never be any difference between enthalpy calculation because the way has no influence to a result as long as both starts and goals are the same.

To understand the enthalpy calculation which the reactor use the following graphics shows the calculation of the heat duty by the reactor and by hand.

The reactor calculates the heat duty so:

We assume the input and output stream are gas.

- 1) With the input composition and input temperature and pressure (**A**) to 25°C gas and 1 atm (**B**), which are the conditions of the ideal gas heat of formation.
- 2) + heat of reaction at 25°C at 1 atm (**R**)
- 3) with the output composition from 25°C and 1 atm to the output temperature and pressure (**C**).



Enthalpy diagram of an isothermal reaction

So the way is from A to B to R to C. The heat duty result is therefore $C - A$. In the case the output stream vaporized CHEMCAD has to calculate the heat of vaporization, which is shown in the diagram.

The heat of reaction is the heat of formation of all products (output)- heat of formation of all educts (input) at 25°C, 1 atm.

The hand calculation of the heat duty is so:

Heat duty = enthalpy of the output stream (C)- enthalpy of the input stream (A), which is $C - A$.

Theoretically the hand calculation should give the same heat duty as the reactor heat duty, because in both cases we calculate $C - A$.

But if one stream is gas and one stream is liquid than one stream vaporized and the heat of vaporization must be calculated. This heat of vaporization can be calculated at the normal boiling point or at the stream temperature or at 25°C or at the stream temperature. All these three ways will give 3 different results because of errors of the measured data. These different ways or drawn in the diagram. There are some more possibilities to go from A to C if we have a change of phases.

Summary:

However, if all physical property data are consistent no enthalpy difference should occur. But unfortunately this is not the case. Therefore from time to time we will have this problem of

enthalpie difference, but it will be small. In that case we will check the data and the way of calculation again.

But in any case for the process simulation the way CHEMCAD uses to calculates the enthalpy seems to be the best way of all other ways. This was checked for a great number of cases. In the case physical properties are not available in the databank CHEMCAD has to change the way of calculation to come to a result, which means that the enthalpy difference may occur greater or smaller depending by the selected way.

Remark:

This problem description is a comment and not an official description of CHEMSTATIONS Inc. USA.

THERMODYNAMIC MODEL SELECTION

VAPOUR LIQUID EQUILIBRIUM

The primary consideration when selecting a thermodynamic model is to consider the liquid phase.

We classify liquid solutions into five categories

- **Ideal**
- **Regular**
- **Polar -nonelectrolyte**
- **Electrolytes**
- **Special**

1 Ideal Solutions are systems where the vapor phase behaves essentially as an ideal gas. Pressure will be low (<1bar), all the molecules in the liquid phase virtually the same size and no intermolecular forces exist.

VAP model for K-value and SRK for enthalpy are proposed

Vapor-liquid equilibrium is according to **Raoult's law**

$$K_i = \frac{y_i}{x_i} = \frac{p_i^0}{P} \quad \text{where } p_i^0 \text{ is pure component vapour pressure}$$

2 Regular Solutions are systems where the non-idealities stem from moderate physical interactions due to the differences in size and shape of the molecules with minimal intermolecular associations. Both the vapor and the liquid phases are assumed to form regular solutions mildly non-ideal. The following should be considered when making a selection

PR and SRK	All non-polar hydrocarbon systems for pressures >10 bar
GS	Certain wide boiling range hydrocarbon processes –18C to 430C
ESSO	Processes with heavy end hydrocarbons at pressures < 7bar
	Temperatures in the range 90C to 200C
MSRK	Chemicals such as branch-chained hydrocarbons, halogenated hydrocarbons and some polar compounds

K-values are calculated from the following relationships using fugacity coefficients

$$K_i = \frac{y_i}{x_i} = \frac{f_{li}}{f_{vi}} \quad \text{where fugacity coefficients } f_{vi} = \frac{f_{vi}}{P} \text{ and } f_{li} = \frac{f_{li}}{x_i P}$$

3 Polar -nonelectrolyte solutions are systems where the liquid phase non-idealities arise predominantly from molecular associations. These systems must be modelled using activity coefficient methods which generally require BIPs for accuracy.

The vapor phase is taken to be a regular solution giving

$$K_i = \frac{y_i}{x_i} = \frac{f_{li}}{f_{vi}} = \frac{g_i f_{li}^0}{f_{vi} P}$$

where f_{li}^0 = standard fugacity comp i f_{vi} fugacity coefficient vapour comp i g_i activity coefficient

Models covered by the activity coefficient method include NRTL, UNIFAC, UNIQUAC, Wilson, T.K.Wilson, Hiranuma, Van Laar, Margules and GMAC. The following should be considered

Wilson, NRTL, and UNIQUAC	When sufficient data is available (>50%)
UNIFAC	When data is incomplete (<50%)

4 Electrolytes are described elsewhere

5 Special Systems are provided for the simulation of applications specific processes

THERMODYNAMIC MODEL SELECTION

RECOMMENDATION BY APPLICATION

HYDROCARBONS		
K-VALUE METHOD	APPLICATION	H-ENTHALPY
Soave-Redlich-Kwong (SRK)	Pressure >1bar General hydrocarbon	SRK
API SRK	Pressure >1bar General hydrocarbon	SRK
Peng-Robinson (PR)	Pressure >1bar Cryogenics <-70C	PR
Benedict-Webb-Ruben-Starling (BWRS)	Pressure>1bar Single species	BWRS
Grayson-Streed (GS)	Moderate P >7bar <200bar Temperature – 18C to 430C Heavy end hydrocarbons	Lee-Kessler (LK)
ESSO	Pressure <7bar Temperature 90-200C Heavy end hydrocarbons	Lee-Kessler (LK)
Maxwell-Bonnell K-charts	Low P Heavy end hydrocarbons	
Elliott,Suresk,Donohue (ESD)	Hydrocarbon –water Hydrocarbon-gases	SRK
SAFT	Hydrocarbon –water Hydrocarbon-gases	SRK
MSRK	Halogenated aliphatics	SRK

THERMODYNAMIC MODEL SELECTION

RECOMMENDATION BY APPLICATION

CHEMICALS		
K-VALUE METHOD	APPLICATION	H-ENTHALPY
Vapor Pressure (VAP) ⁽³⁾	Ideal solutions	SRK
UNIFAC ⁽²⁾	P (0-4atm) T(275-475K) Non-ideal & 2 liquid phases Heterogeneous azeotrope Group Contribution Predictive	LATE
Wilson ⁽²⁾	Highly non-ideal Homogeneous azeotrope	LATE
NRTL ⁽²⁾	Highly non-ideal & 2 liquid phases Heterogeneous azeotrope	LATE
UNIQUAC ⁽²⁾	Highly non-ideal & 2 liquid phases Heterogeneous azeotrope	LATE
Margules ⁽²⁾	Highly non-ideal & 2 liquid phases Homogeneous azeotrope	LATE
T. K. Wilson ⁽²⁾	Highly non-ideal & 2 liquid phases Homogeneous azeotrope	LATE
Hiranuma (HRNM)	Highly non-ideal & 2 liquid phases	LATE
Regular Solution ⁽²⁾	Moderately non-ideal (Predictive)	SRK
van Laar ⁽²⁾	Moderately non-ideal Homogeneous azeotrope	LATE
Modified SRK (MSRK) ⁽¹⁾ (4 parameter)	Polar compounds in regular solutions	SRK
Predictive SRK (PSRK) ⁽¹⁾	Polar compounds in non-ideal solutions Better than UNIFAC at high pressures	LATE
Wilson	Non-ideal solutions with dissolved salts	LATE

(1) Equation of State Model

(2) Activity Coefficient Model

(3) Empirical Method

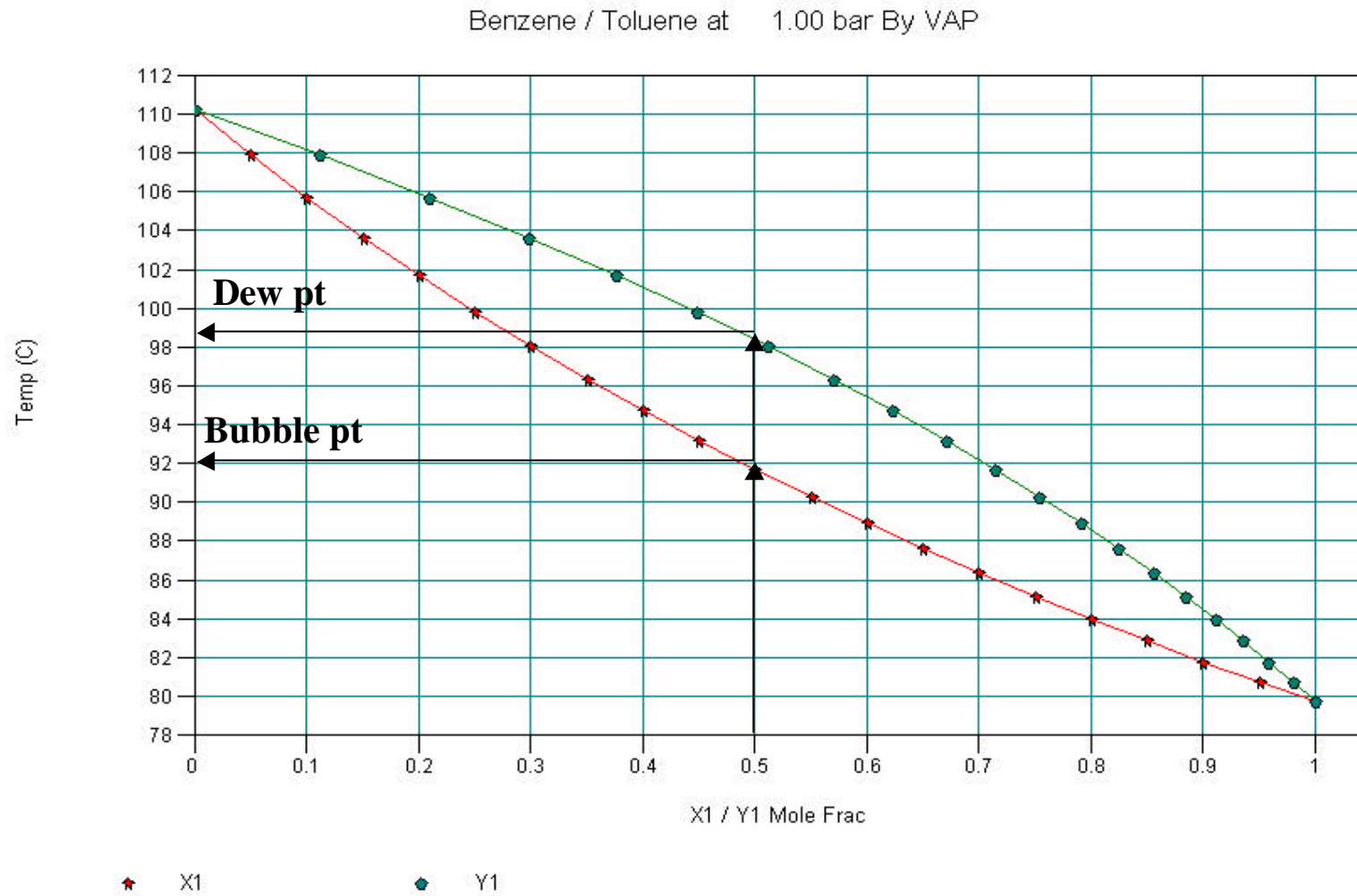
THERMODYNAMIC MODEL SELECTION

RECOMMENDATION BY APPLICATION

SPECIAL MODELS		
K-VALUE METHOD	APPLICATION	H-ENTHALPY
Henry's Gas Law	Gases dissolved in water	
Amine	Gas sweetening H ₂ S-MEA -DEA	Amine
Sour Water	H ₂ S-CO ₂ - NH ₃ dissolved in H ₂ O	SRK
TSRK	Methanol system particularly with light gases	SRK
PPAQ	Ionic compounds which dissolve in water and disassociate eg HCl, NH ₃ , HNO ₃	SRK or LATE
TEG	Dehydration of hydrocarbon streams Using tri-ethylene-glycol	SRK
Flory-Huggins (FLOR)	Method for polymers	LATE
UPLM	UNIFAC for polymers	LATE
ESD	Hydrogen bonding Hydrogen bonding at high pressure	SRK
SAFT	Hydrogen bonding Hydrogen bonding at high pressure	SRK
ACTX	User specified activity coefficients	LATE
K Tables	User specified K-value	
Polynomial	User specified K-value	
User-Added Subroutine	User specified K-value	

IDEAL SOLUTION T_{xy} DIAGRAM Figure 1

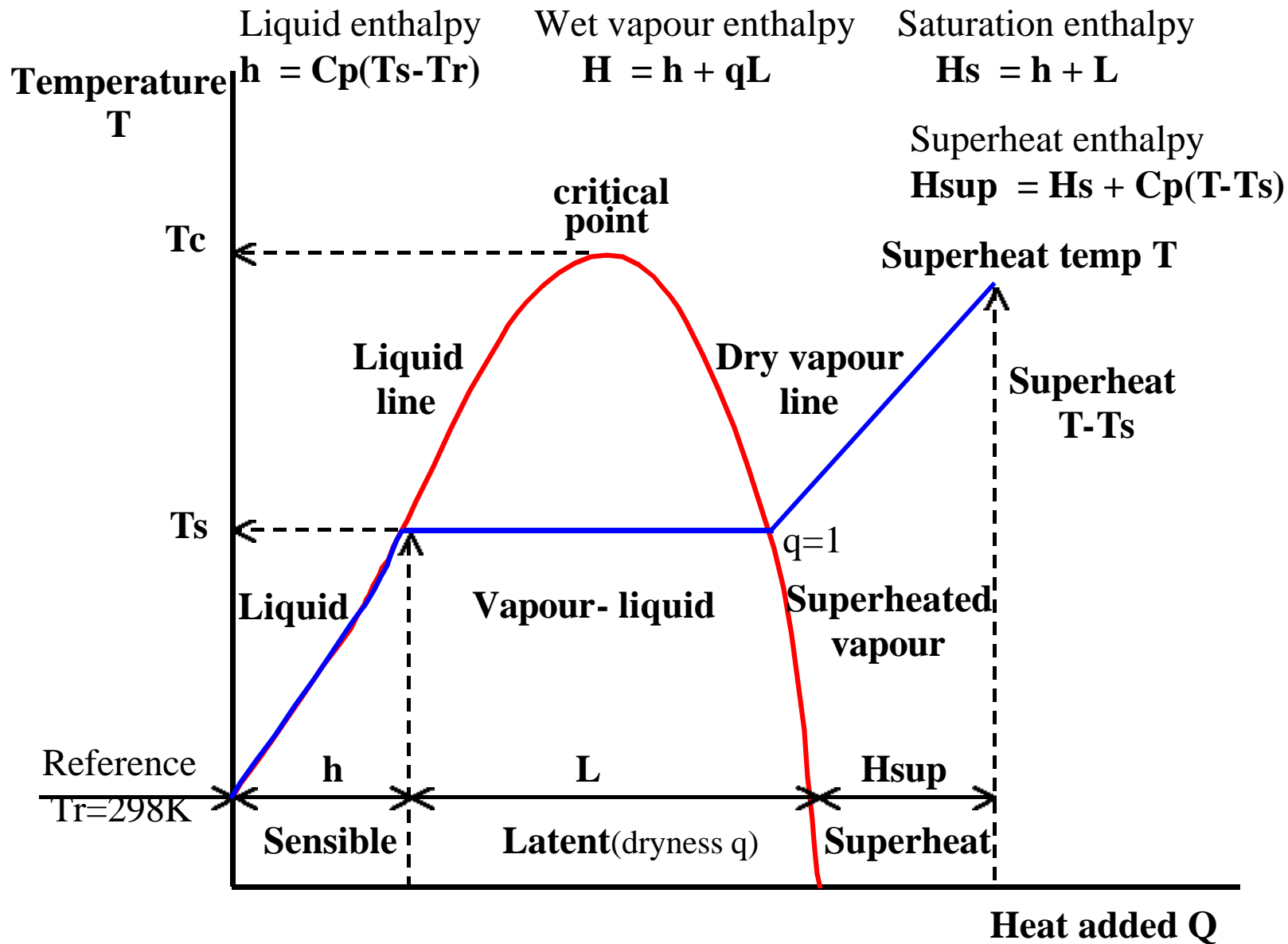
Raoult's Law $p_i = y_i P = x_i p_i^0$ at system temperature **T**



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03/11/2001
Time: 10:35:57

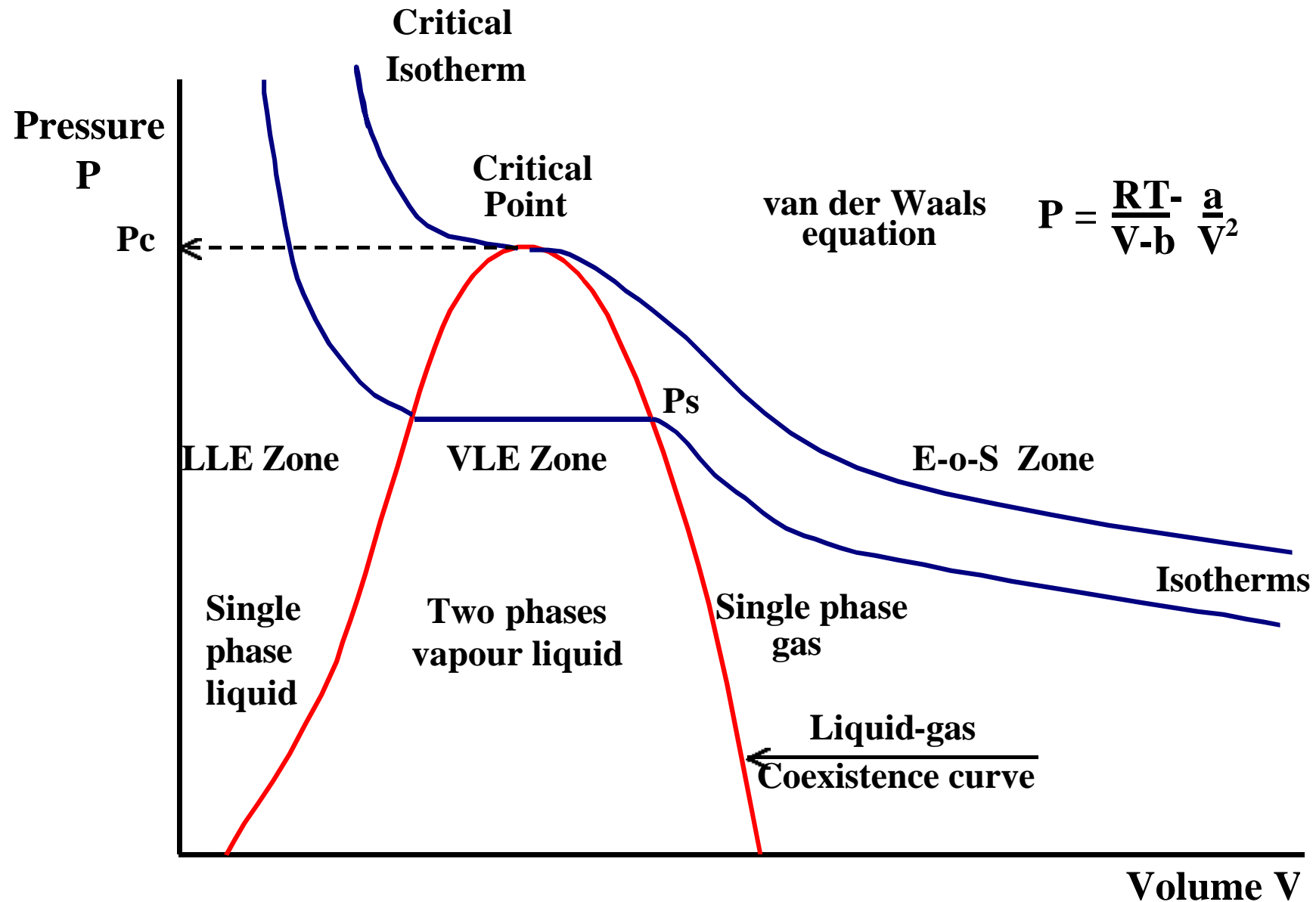
ENTHALPY ISOBAR

Figure 2



THERMODYNAMIC PHASES

Figure 3



van der Waals EQUATION of STATE Figure 4

COMPONENT	MW	BP	T _c	P _c	V _c	STATE CONSTANTS	
	kg/kmol	degC	degK	bar	cm ³ /gmol	a	b
HYDROGEN	2.0158	-252.76	33.12	12.9595	65	2.4685E+05	2.6561E+01

van der Waals equation

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

where we have

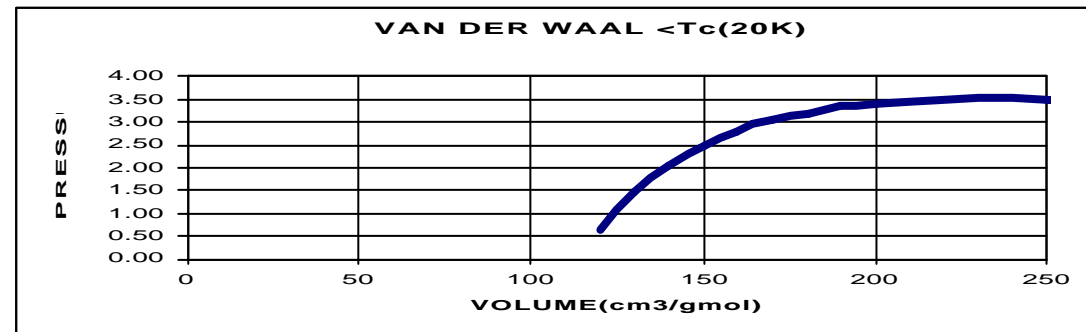
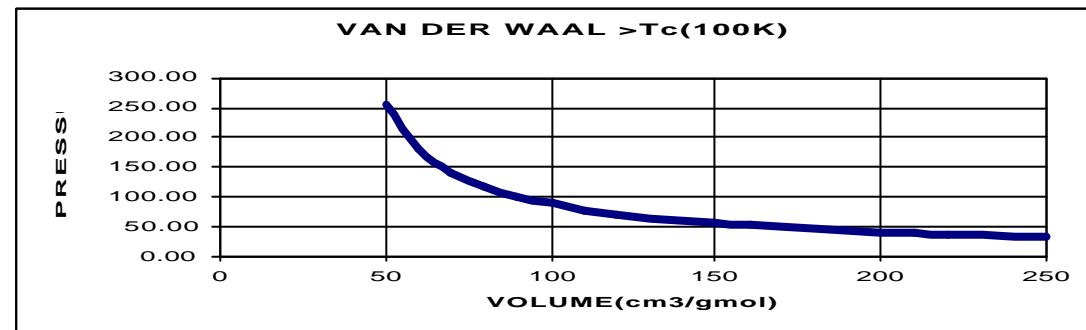
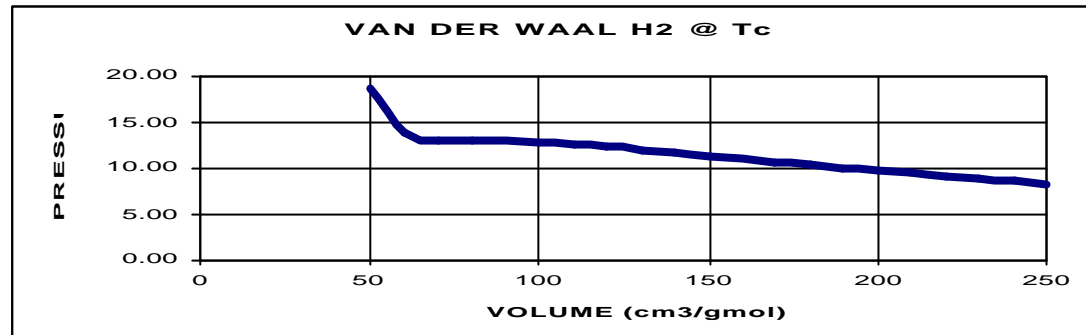
$$a = \frac{27}{64} \frac{(R^2)(T_c^2)}{P_c}$$

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

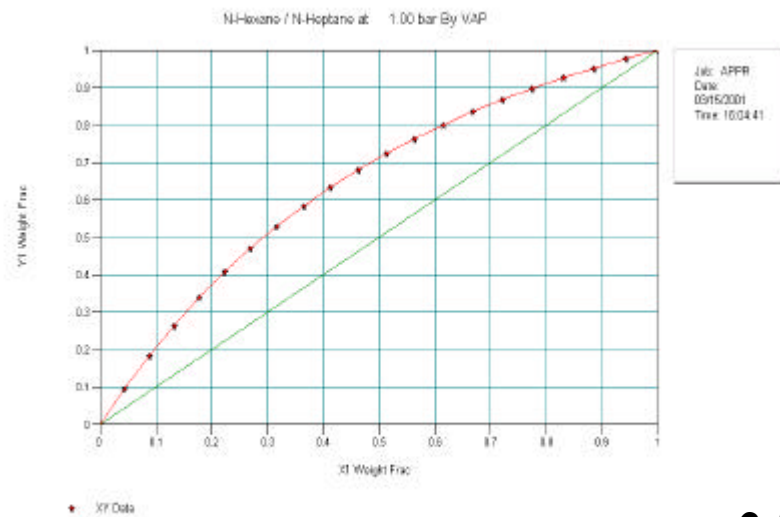
$$R = 83.144 \text{ (bar.cm}^3\text{)/(mol.K)}$$

Reference:

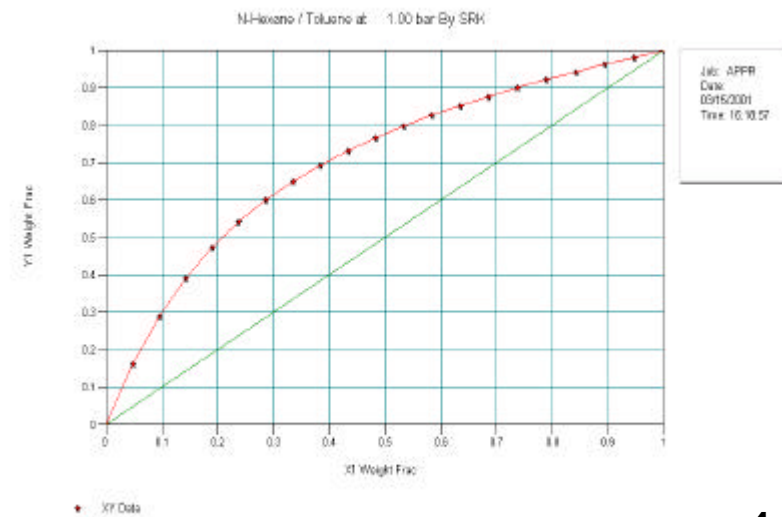
Reid, Prausnitz, Poling
Properties Gases Liquids
Table 3-5 p42



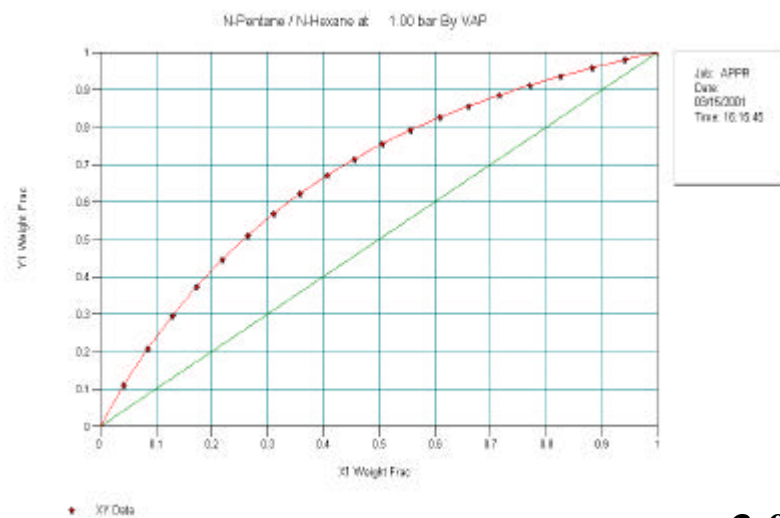
RELATIVE VOLATILITY IN VLE DIAGRAM Figure 5



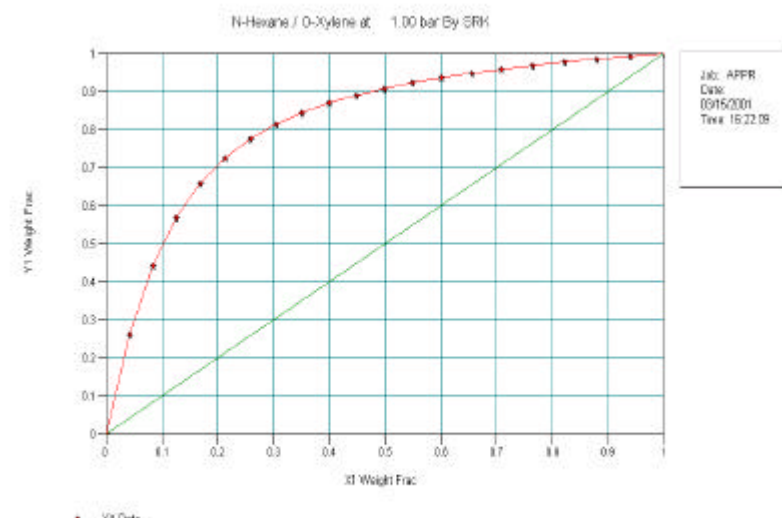
$a = 2.5$



$a = 4.0$



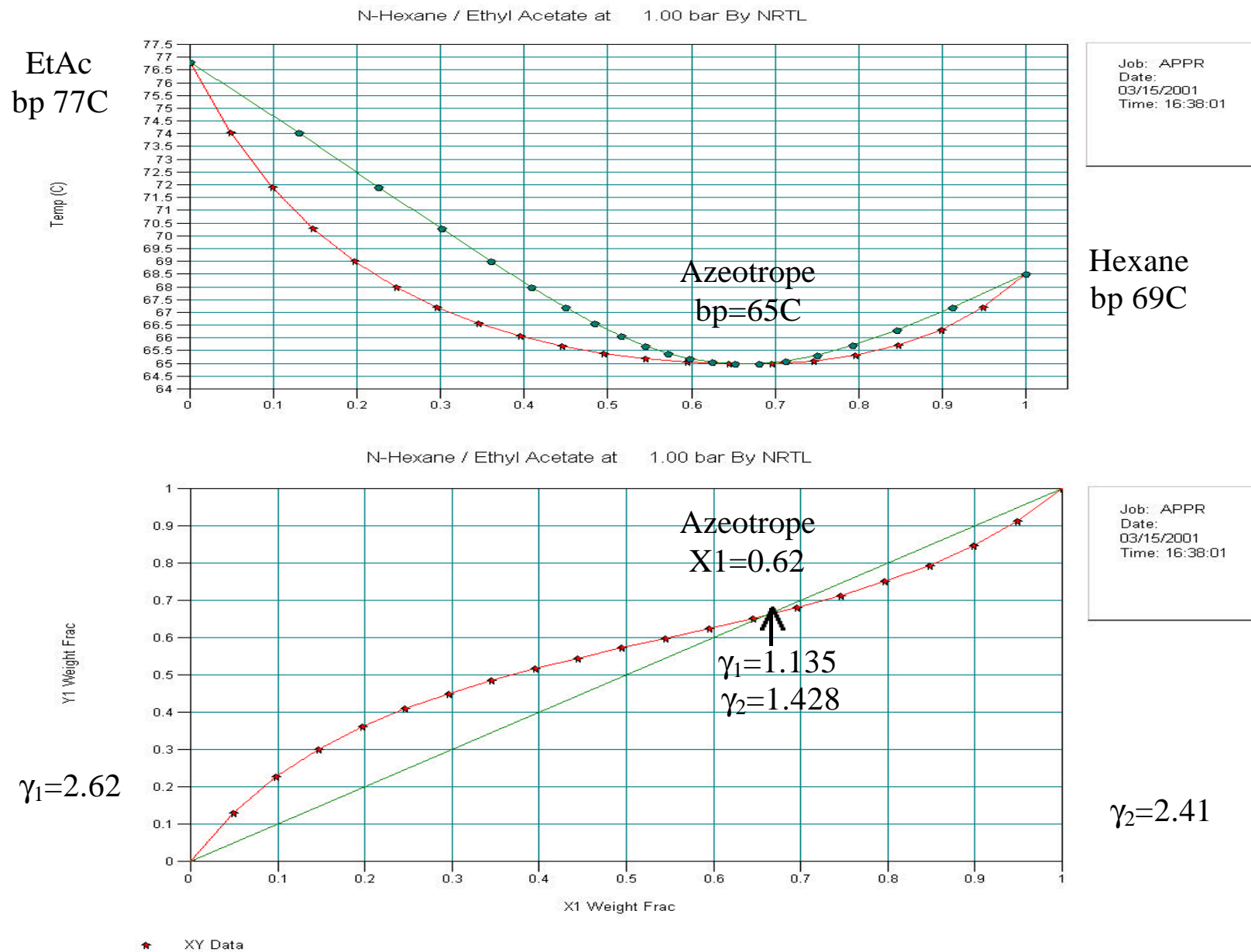
$a = 3.0$



$a = 10$

AZEOTROPE γ VALUE IN VLE DIAGRAM

Figure 6

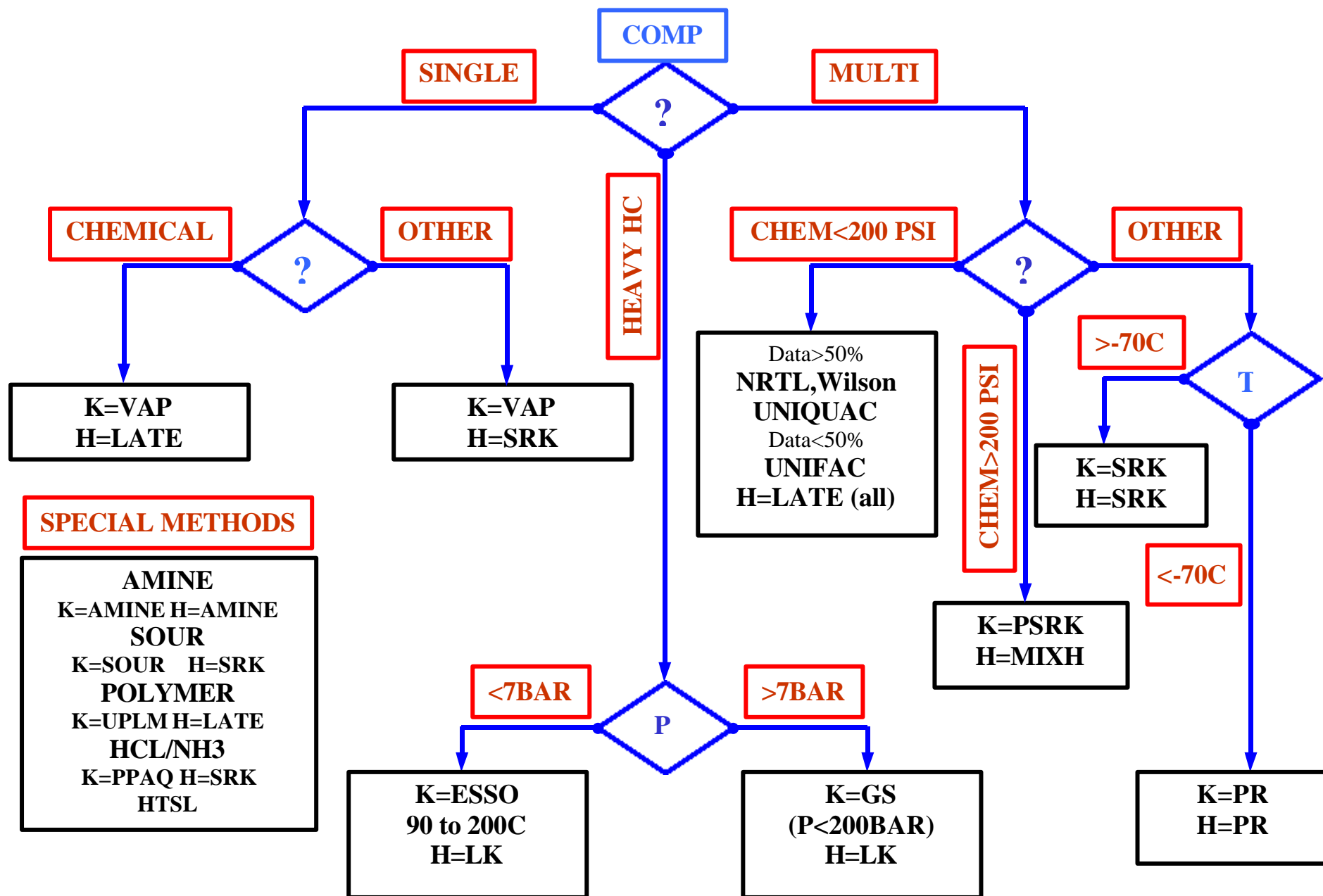


VLE DIAGRAM AND CONVERGENCE EFFECTS Figure 7

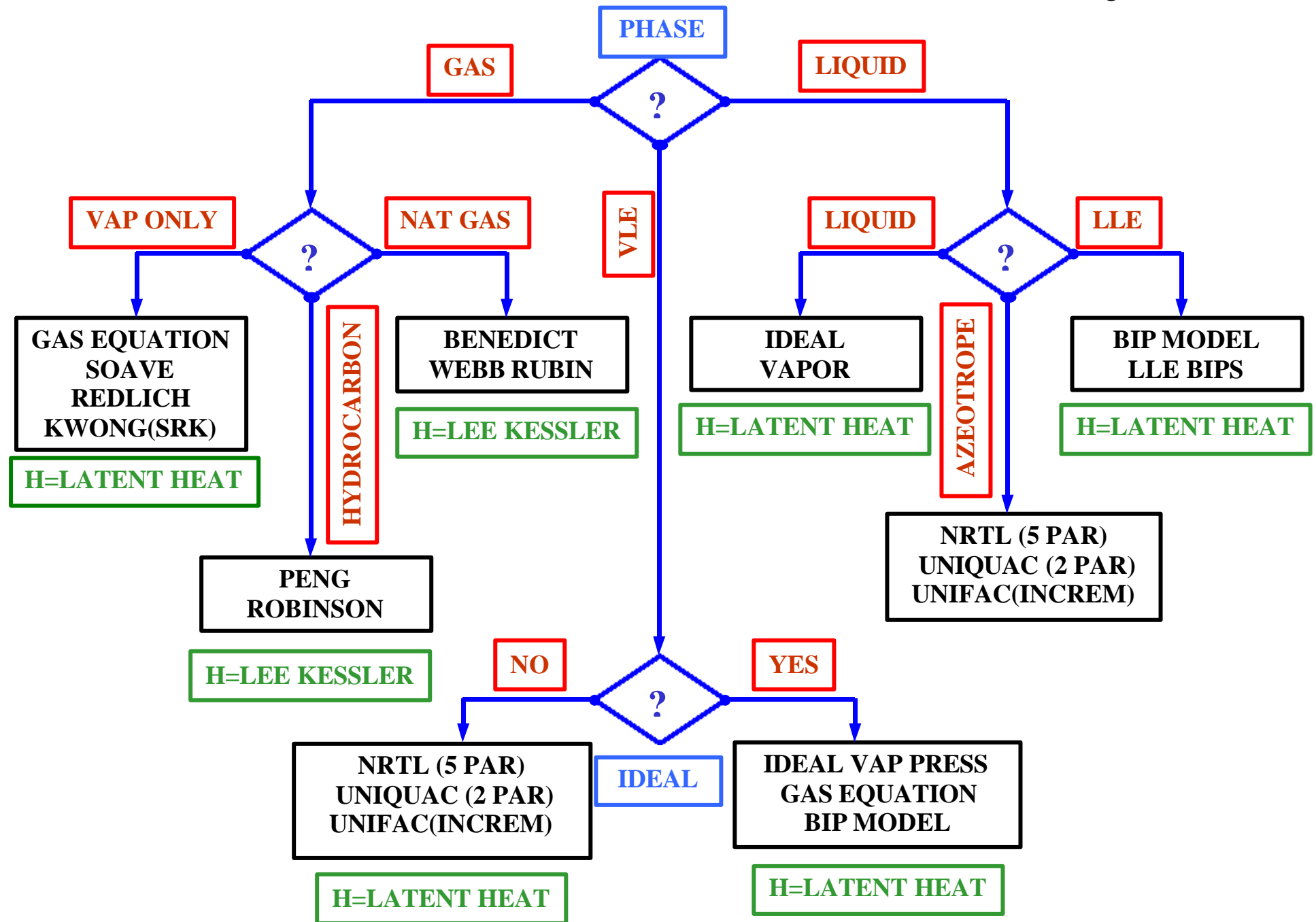


CHEMCAD K AND H VALUES WIZARD

Figure 8



THERMODYNAMIC MODEL DECISION TREE Figure 9



SET THERMODYNAMIC MODEL Figure 10

K value and Enthalpy Models Selection Basis

Thermodynamic Model Selection based on System Phases						
Parameter	Solid component	Liquid only	Vapor only	VLE Ideal	VLE None Ideal	LLE
K value Enthalpy Solid	VAP (liquid/solid) SRK (gas/solid) Latent Heat Pick Solid, but no Solid Liquid Equilibrium	Ideal Vapour Pressure(VAP) Latent Heat	Gas equation Lee Kessler(LK)	VAP, Gas equation (gas solubility), BIP model Latent Heat, Gas equation	BIP model Latent heat	BIP model with LLE BIPS Latent Heat

Gas Model based on Application					
Description	General	HC (Hydrocarbon)		Gas	Enthalpy
Equation of State	Soave Redlich Kwong(SRK)	Peng Robinson(PR)	Grayson Streed Choa Seader(GS)	Benedict Webb Rubin(BWR)	Lee Kessler(LK)

Liquid Model(BIP,Gamma) based on Application						
Description	NRTL	UNIQUAC	UNIFAC (UNIQUAC)	Wilson	van Laar	Margules
Heterogeneous Azeotrope Parameters	Yes 5	Yes 2	Yes Increments	No 2	No 2	No 2

Enthalpy			
Description	Total	Liquid	Gas
Latent heat	$H = H_f + H_{liq} + H_{vap} + H_{gas}$ (H_f =Heat of formation @ 25DegC)	$H_{liq} = \text{Integral } (Cp_{liq} dT)$	$H_{gas} = \text{Integral } (Cp_{gas} dT)$