PROCESS MODELLING

SELECTION OF

THERMODYNAMIC METHODS

by

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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 DECHHEMA, 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

<table>
<thead>
<tr>
<th>Intensive variables</th>
<th>Extensive variables (capacity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure ((P))</td>
<td>Volume ((V))</td>
</tr>
<tr>
<td>Temperature ((T))</td>
<td>Entropy ((S))</td>
</tr>
</tbody>
</table>

We define thermodynamic energy as follows

\[
\text{Energy} = \text{Intensity variable} \times \text{Extensive variable}
\]

\[
\text{TS} \quad \text{represents internal bound energy isothermally unavailable.}
\]

\[
\text{PV} \quad \text{represents external free energy.}
\]

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

\[
\text{Internal energy} \quad U = T \ S + F
\]

\[
\text{Gibbs free energy} \quad G = F + P \ V
\]

\[
\text{Enthalpy} \quad H = T \ S + F + P \ V
\]

\[
H = U + P \ V
\]

When considering chemical reactions we have

\[
\text{Chemical energy} = \text{chemical potential factor} \times \text{capacity factor}
\]

\[
dU = \left(\mu_i - \mu_i^0\right)dn_i
\]

Where

\[
dn_i \quad \text{is change in species } i \text{ moles}
\]

\[
\mu_i \quad \text{is chemical potential species } i
\]

\[
dU = T \ dS - P \ dV + \sum_i \mu_i dn_i
\]

For equilibrium

\[
\sum_i \mu_i dn_i = 0
\]

Other equilibrium conditions

\[
dF = 0 \ (\text{const}V \ & \ T) \quad dG = 0 \ (\text{const}P \ & \ T)
\]

\[
dU = 0 \ (\text{const}S \ & \ V) \quad dH = 0 \ (\text{const}S \ & \ P)
\]

It can be shown that

\[
G = \sum_i \mu_i n_i
\]
2.2 Gibbs Phase Rule

The variables that define a process condition are in two categories:

- **Extensive variables**: moles, mass, volume
- **Intensive variables**: temperature, pressure, density, specific volume, mass and mole fractions of components i.

The number of intensive variables that can be independently specified for a system at equilibrium is called the number of degrees of freedom $F$ and is given by the Gibbs Phase Rule. In a system involving no reactions this is given by

$$F = 2 + m - p$$

Where
- $m$ = no of chemical species
- $p$ = number of system phases

With $r$ independent reactions at equilibrium

$$F = 2 + m - r - p$$

When defining a stream condition in the model the phase rule applies.

Consider a single component liquid in equilibrium with its vapour and an inert.

Giving $m = 2$, $p = 2$, $F = 2$

Two variables $P$ and $T$ or Vapour fraction ($v$) with $T$ or $P$ will define the stream.

For a binary liquid system one degree of freedom is consumed by the composition leaving either $P$ or $T$ to be specified. In a VLE system it is preferable to specify $P$ which then allows system analysis using $Txy$ plots.

When setting up the FlashUnitOp applying the phase rule will ensure that relevant flash conditions are being set.

The stream flash calculation can be used to determine the boiling point and dew point of mixtures with and without inerts present by applying the following:

The bubble point of a liquid at the given pressure is determined by a flash calculation at a vapour fraction of 0.

The dew point of a vapour at the given pressure is determined by a flash calculation at a vapour fraction of 1.

For a pure component the bubble point and the dew point are identical so a flash calculation at a vapour fraction of 0 or 1 will yield the same result.

Figure 1 shows the $Txy$ diagram for Benzene/Toluene, a near ideal mixture. The bubble point for a given composition is read directly from the liquid curve and the dew point is read directly from the vapour curve.
2.3 Enthalpy

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

\[ H = U + PV \]

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 \( \gamma \) 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 E-o-S (SRK) in the superheated or gas phase.

Appendix I reviews the calculation methods adopted in CHEMCAD. A standard reference state of 298ºK 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

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

\[ P_i \ V = n_i R \ T \]

\[ \frac{P_i}{P} = \frac{n_i}{n} = y_i \]

where \( y_i \) is mole fraction of \( i \) in gas

\[ p_i = y_i P \]

\[ \sum p_i = P \]

\[ \mu_i = \mu_i^0 + R \ T \ln p_i \]

Note that when \( p_i = 1 \) we have \( \mu_i = \mu_i^0 \) 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 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

\[
\mu_i = \mu_i^0 + R \ T \ \ln f_i
\]

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

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

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 e.g. 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

\[
P = \frac{R \ T}{(V-b)} - \frac{a}{V^2}
\]

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

\[
\ln f = \ln \left( \frac{R \ T}{V-b} \right) + \frac{b}{V-b} - \frac{2a}{R \ T \ V}
\]
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 \( a, a \) and \( b \) are system parameters. Parameters \( a \) and \( b \) are determined from the critical temperature \( T_c \) and critical Pressure \( P_c \). Parameter \( \alpha \) 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.

\[ P \, V = Z \, n \, R \, T \]

Where \( Z \) 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**

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

<table>
<thead>
<tr>
<th>Method</th>
<th>K-value</th>
<th>NRTL</th>
<th>H</th>
<th>LATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>MNRTL</td>
<td>uses</td>
<td>K-value</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pitzer</td>
<td>method</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>method</td>
<td>has no</td>
<td></td>
<td>restrictions</td>
<td></td>
</tr>
</tbody>
</table>

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.
Ideal Solutions

In an ideal solution the chemical potential $\mu_i$ for species $i$ is of the form

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

where $\mu_i^0$ 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

$$p_i = y_i P = x_i \mu_i^0$$

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 $\gamma$ is close to 1 throughout the concentration range.

The following systems can be considered suitable for Raoult’s Law:

1. Aliphatic hydrocarbons
   - Paraffins $C_n \text{H}_{2n+2}$: n-hexane (C6H14), n-heptane (C7H16)
   - Olefines $C_n \text{H}_{2n}$
   - Alcohols $C_n \text{H}_{2n+1} \cdot \text{OH}$: methanol (CH3•OH), ethanol (C2H5•OH)

2. Aromatic hydrocarbons: benzene (C6H6), toluene (C6H5•CH3)

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

<table>
<thead>
<tr>
<th>$K$ – Value</th>
<th>Enthalpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal Vapour Pressure(VAP)</td>
<td>SRK</td>
</tr>
</tbody>
</table>

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

$$p_i = y_i P = x_i H_i$$

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 \(\mu_i\) for species \(i\) is of the form:

\[
\mu_i = \mu_i^0 + R \ T \ \ln \left( \gamma_i x_i \right)
\]

Where \(\gamma_i\) is the activity coefficient and component activity \(a_i = \gamma_i x_i\)

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

\[
p_i = k_i \gamma_i x_i
\]

Raoult’s law when \(\gamma_i \to 1\) and \(x_i \to 1\) \(k_i = p_i^0\) giving \(\gamma_i = \frac{p_i}{p_i^0} = 1\)

Henry’s law when \(\gamma_i \to 1\) and \(x_i \to 0\) 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 \(\phi_i = \frac{f_{vi}}{\gamma_i P}\) note \(\phi_i = 1\) for ideal gases

The fugacity of component \(i\) in the liquid phase is related to the composition of that phase by the activity coefficient \(\gamma\) as follows

\[
\gamma_i = \frac{a_i}{x_i} = \frac{f_{li}}{x_i f_i^0}
\]

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

\[ K_i = \frac{y_i}{x_i} = \frac{\phi_{li}}{\phi_{vi}} \]

where fugacity coefficients \( \phi_{vi} = \frac{f_{vi}}{P} \) and \( \phi_{li} = \frac{f_{li}}{x_i P} \)

<table>
<thead>
<tr>
<th>Process Application</th>
<th>K-value</th>
<th>Enthalpy H</th>
</tr>
</thead>
<tbody>
<tr>
<td>General hydrocarbon (same homologous series) System pressure &gt; 10 bar</td>
<td>PR</td>
<td>PR</td>
</tr>
<tr>
<td>Branch chained hydrocarbon System pressure &gt; 10 bar</td>
<td>SRK</td>
<td>SRK</td>
</tr>
<tr>
<td>Heavy end hydrocarbons System pressure &lt; 7 bar Temperature 90C to 430C</td>
<td>ESSO</td>
<td>LK</td>
</tr>
<tr>
<td>Branch-chained and halogenated hydrocarbon Some polar compounds</td>
<td>MSRK</td>
<td>SRK</td>
</tr>
</tbody>
</table>

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

\[ K_i = \frac{y_i}{x_i} = \frac{\phi_{li}}{\phi_{vi}} = \frac{\gamma_i f_{li}^0}{\phi_{vi} P} \]

Where

\( f_{li}^0 \) standard fugacity comp \( i \)
\( \phi_{vi} \) fugacity coefficient vapour comp \( i \)
\( \gamma_i \) 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

<table>
<thead>
<tr>
<th>Wilson, NRTL, and UNIQUAC</th>
<th>When sufficient data is available (&gt;50%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNIFAC</td>
<td>When data is incomplete (&lt;50%)</td>
</tr>
</tbody>
</table>
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 (γ ≈ 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

\[
p_1 = \gamma_1 x_1 p_1^0 \quad \text{and} \quad p_2 = \gamma_2 x_2 p_2^0
\]

\[
\alpha = \frac{\gamma_1 p_1^0}{\gamma_2 p_2^0} = \frac{\alpha^0}{\gamma_2}
\]

where \(\alpha^0\) 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 \(\gamma\) can be calculated throughout the concentration range using van Laar’s equation

\[
\ln \gamma_1 = A_{12} \left( \frac{1}{1 + A_{12} x_1 / A_{21} x_2} \right)^2
\]

where \(A_{12} = \ln \gamma_1^\infty\) with \(\infty\) representing infinite dilution

An extensive data bank providing values of parameter \(A_{xy}\) are available from Dechema. Values of \(\gamma\) 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 \(\gamma_1 p = x_1 \gamma_1 p_1^0\) resulting in \(\gamma_1 = \frac{p}{p_1^0}\)

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 \(\gamma\) 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 be considered when setting the K-Value:

- **Vapour phase association**
- **Vapour fugacity correction**
- **Water/hydrocarbon solubility**
- **Salt**

Vapour phase association: typical systems acetic acid, formic acid, acrylic acid.
Vapour fugacity correction: set when using an activity coefficient method P>1bar.
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 \([H_oV]\), 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 \([C]\), 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**

**Abbreviations:**
- \(HoFG\): Heat of Formation gas
- \(HoFL\): Heat of Formation liquid
- \(HoV\): Heat of Vaporization
- \(Tb\): Boiling point
- \(T\): Temperature
- \(kJ/kmol\): Kilojoules per kilomol
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 Cp 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 Cp 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 Cp 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 C2H4 + H2 = C2H6 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.

**Equilibrium Reactor Summary**

- **Equip. No.:** 1
- **Name:** Overall
- **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

The enthalpy balance (str.2-str1): -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:

<table>
<thead>
<tr>
<th>Stream No.</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stream Name</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temp °C</td>
<td>120.0000*</td>
<td>120.0000</td>
</tr>
<tr>
<td>Pres bar</td>
<td>1.0000*</td>
<td>1.0000</td>
</tr>
<tr>
<td>Enthalpy MJ/h</td>
<td>9.2364</td>
<td>-477.95</td>
</tr>
<tr>
<td>Vapor mole fraction</td>
<td>1.0000</td>
<td>1.0000</td>
</tr>
<tr>
<td>Total kmol/h</td>
<td>3.0000</td>
<td>2.0000</td>
</tr>
<tr>
<td>Total kg/h</td>
<td>36.0306</td>
<td>36.0300</td>
</tr>
<tr>
<td>Total std L m3/h</td>
<td>0.0861</td>
<td>0.0361</td>
</tr>
<tr>
<td>Total std V m3/h</td>
<td>67.24</td>
<td>44.83</td>
</tr>
<tr>
<td>Flowrates in kmol/h</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Water</td>
<td>0.0000</td>
<td>2.0000</td>
</tr>
</tbody>
</table>

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

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

Reaction Stoichiometrics and Parameters for unit no. 1

| Reaction no. | 1 |
| Base component | 1 |
| Frac.conversion | 1.0000 |
| 1 | 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.

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

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**

<table>
<thead>
<tr>
<th>Equip. No.</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td></td>
</tr>
<tr>
<td>No of Reactions</td>
<td>1</td>
</tr>
<tr>
<td>Specify reaction phase</td>
<td>1</td>
</tr>
<tr>
<td>Specify thermal mode:</td>
<td>2</td>
</tr>
<tr>
<td>C</td>
<td>25.0000</td>
</tr>
<tr>
<td>MJ/h</td>
<td>-569.1345</td>
</tr>
<tr>
<td>Temperature Units:</td>
<td>3</td>
</tr>
<tr>
<td>Pressure Units:</td>
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</tr>
<tr>
<td>Heat of Reaction Units:</td>
<td>4</td>
</tr>
<tr>
<td>Molar Flow Units:</td>
<td>1</td>
</tr>
<tr>
<td>Edit Reaction No.</td>
<td>1</td>
</tr>
<tr>
<td>Calc Overall Ht of Rxn</td>
<td>-483.6400 (MJ/h)</td>
</tr>
</tbody>
</table>

**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).
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 date 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
enthalpic 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

\[ K_i = \frac{y_i}{x_i} = \frac{P_i^0}{P} \]

where \( P_i^0 \) 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

\[ K_i = \frac{y_i}{x_i} = \frac{\phi_i}{\phi_{vi}} \]

where fugacity coefficients \( \phi_i = \frac{f_{vi}}{P} \) and \( \phi_{vi} = \frac{f_{vi}}{x_i P} \)

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

\[ K_i = \frac{y_i}{x_i} = \frac{\phi_i}{\phi_{vi}} = \frac{\gamma_i f_i^0}{\phi_{vi} P} \]

where \( f_i^0 \) = standard fugacity comp \( \phi_i \) fugacity coefficient vapour comp \( \gamma_i \) 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

<table>
<thead>
<tr>
<th>K-VALUE METHOD</th>
<th>APPLICATION</th>
<th>H-ENTHALPY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soave-Redlich-Kwong (SRK)</td>
<td>Pressure &gt;1bar General hydrocarbon</td>
<td>SRK</td>
</tr>
<tr>
<td>API SRK</td>
<td>Pressure &gt;1bar General hydrocarbon</td>
<td>SRK</td>
</tr>
<tr>
<td>Peng-Robinson (PR)</td>
<td>Pressure &gt;1bar Cryogenics &lt;-70°C</td>
<td>PR</td>
</tr>
<tr>
<td>Benedict-Webb-Ruben-Starling (BWRS)</td>
<td>Pressure &gt;1bar Single species</td>
<td>BWRS</td>
</tr>
<tr>
<td>Grayson-Streed (GS)</td>
<td>Moderate P &gt;7bar &lt;200bar Temperature –18C to 430C</td>
<td>Lee-Kessler (LK)</td>
</tr>
<tr>
<td>ESSO</td>
<td>Pressure &lt;7bar Temperature 90-200C Heavy end hydrocarbons</td>
<td>Lee-Kessler (LK)</td>
</tr>
<tr>
<td>Maxwell-Bonnell K-charts</td>
<td>Low P Heavy end hydrocarbons</td>
<td></td>
</tr>
<tr>
<td>Elliott,Suresk,Donohue (ESD)</td>
<td>Hydrocarbon-water Hydrocarbon-gases</td>
<td>SRK</td>
</tr>
<tr>
<td>SAFT</td>
<td>Hydrocarbon-water Hydrocarbon-gases</td>
<td>SRK</td>
</tr>
<tr>
<td>MSRK</td>
<td>Halogenated aliphatics</td>
<td>SRK</td>
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</tbody>
</table>
# THERMODYNAMIC MODEL SELECTION
## RECOMMENDATION BY APPLICATION

### CHEMICALS

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

---

(1) Equation of State Model  
(2) Activity Coefficient Model  
(3) Empirical Method
### THERMODYNAMIC MODEL SELECTION

**RECOMMENDATION BY APPLICATION**

<table>
<thead>
<tr>
<th>K-VALUE METHOD</th>
<th>APPLICATION</th>
<th>H-ENTHALPY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Henry's Gas Law</td>
<td>Gases dissolved in water</td>
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</tr>
<tr>
<td>Amine</td>
<td>Gas sweetening H2S-MEA-DEA</td>
<td>Amine</td>
</tr>
<tr>
<td>Sour Water</td>
<td>H2S-CO2- NH3 dissolved in H2O</td>
<td>SRK</td>
</tr>
<tr>
<td>TSRK</td>
<td>Methanol system</td>
<td>SRK</td>
</tr>
<tr>
<td></td>
<td>particularly with light gases</td>
<td></td>
</tr>
<tr>
<td>PPAQ</td>
<td>Ionic compounds which dissolve in water and disassociate eg HCl, NH3, HNO3</td>
<td>SRK or LATE</td>
</tr>
<tr>
<td>TEG</td>
<td>Dehydration of hydrocarbon streams</td>
<td>SRK</td>
</tr>
<tr>
<td></td>
<td>Using tri-ethylene-glycol</td>
<td></td>
</tr>
<tr>
<td>Flory-Huggins (FLOR)</td>
<td>Method for polymers</td>
<td>LATE</td>
</tr>
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<td>UPLM</td>
<td>UNIFAC for polymers</td>
<td>LATE</td>
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<td>ESD</td>
<td>Hydrogen bonding</td>
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<td>Hydrogen bonding at high pressure</td>
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<tr>
<td>SAFT</td>
<td>Hydrogen bonding</td>
<td>SRK</td>
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<td></td>
<td>Hydrogen bonding at high pressure</td>
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<td>ACTX</td>
<td>User specified activity coefficients</td>
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<td>K Tables</td>
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<td>Polynomial</td>
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<tr>
<td>User-Added Subroutine</td>
<td>User specified K-value</td>
<td></td>
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</table>
Raoult’s Law $p_i = y_i \, P = x_i \, p_i^0$ at system temperature $T$
**ENTHALPY ISOBAR**

**Figure 2**

- **Liquid enthalpy**: \( h = C_P(T_s - T_r) \)
- **Wet vapour enthalpy**: \( H = h + qL \)
- **Saturation enthalpy**: \( H_s = h + L \)
- **Superheat enthalpy**: \( H_{sup} = H_s + C_p(T - T_s) \)

- **Superheat temp**: \( T \)
- **Critical point**: \( T_c \)
- **Vapour-liquid point**: \( T_s \)
- **Liquid line**: \( h \)
- **Dry vapour line**: \( L \)
- **Superheating**: \( q=1 \)
- **Reference**: \( T_{ref} = 298 K \)
- **Sensible**: \( h \)
- **Latent**: \( L \)
- **Superheat**: \( H_{sup} \)

**Heat added**: \( Q \)
THERMODYNAMIC PHASES

Figure 3

Pressure $P$

$P_c$

LLE Zone

VLE Zone

E-o-S Zone

Single phase liquid

Two phases vapor liquid

Single phase gas

Liquid-gas Coexistence curve

van der Waals equation

$P = \frac{RT-a}{V-b} \frac{1}{V^2}$
van der Waals EQUATION of STATE

Figure 4

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>MW</th>
<th>BP</th>
<th>Tc</th>
<th>Pc</th>
<th>Vc</th>
<th>STATE CONSTANTS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kg/kmol</td>
<td>degC</td>
<td>degK</td>
<td>bar</td>
<td>cm³/gmol</td>
<td>a</td>
</tr>
<tr>
<td>HYDROGEN</td>
<td>2.0158</td>
<td>-252.76</td>
<td>33.12</td>
<td>12.9595</td>
<td>65</td>
<td>2.4685E+05</td>
</tr>
</tbody>
</table>

van der Waals equation

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

where we have

\[ a = \frac{(27/64)(R^2)(T_c^2)}{P_c} \]

\[ b = \frac{RT_c}{8P_c} \]

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

Reference:

Reid, Prausnitz, Poling
Properties Gases Liquids
Table 3-5 p42
RELATIVE VOLATILITY IN VLE DIAGRAM  

- \( \alpha = 2.5 \)  
- \( \alpha = 4.0 \)  
- \( \alpha = 3.0 \)  
- \( \alpha = 10 \)
**Figure 6**

**AZEOTROPE \( \gamma \) VALUE IN VLE DIAGRAM**

- **EtAc** bp 77°C
- **Hexane** bp 69°C

### N-Hexane / Ethyl Acetate at 1.00 bar By NRTL

- Azeotrope: \( \alpha = 0.62 \)
- \( \gamma_1 = 1.135 \)
- \( \gamma_2 = 1.428 \)
- \( \gamma_1 = 2.62 \)
- \( \gamma_2 = 2.41 \)

Job: APPR
Date: 03/15/2001
Time: 16:38:01
VLE DIAGRAM AND CONVERGENCE EFFECTS

Figure 7

Ethanol / Water at 15.00 psia By NRTL

Ethanol / Water at 15.00 psia By SRK
CHEMCAD K AND H VALUES WIZARD

Figure 8

COMP

SINGLE

MULTI

CHEMICAL

OTHER

CHEM<200 PSI

CHEM>200 PSI

HEAVY HC

<7BAR

>7BAR

K=VAP
H=LATE

K=VAP
H=SRK

Data>50%
NRTL,Wilson
UNIQUAC
Data<50%
UNIFAC
H=LATE (all)

SPECIAL METHODS

AMINE
K=AMINE H=AMINE
SOUR
K=SOUR H=SRK
POLYMER
K=UPLM H=LATE
HCL/NH3
K=PPAQ H=SRK
HTSL

K=ESSO
90 to 200°C
H=LK

K=GS
(P<200BAR)
H=LK

K=SRK
H=SRK

K=PSRK
H=MIXH

K=PR
H=PR

T

>-70°C

<-70°C
# SET THERMODYNAMIC MODEL

## Figure 10

### K value and Enthalpy Models Selection Basis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Solid component</th>
<th>Liquid only</th>
<th>Vapor only</th>
<th>VLE Ideal</th>
<th>VLE None Ideal</th>
<th>LLLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid</td>
<td>Pick Solid, but no Solid Liquid Equilibrium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Gas Model based on Application

<table>
<thead>
<tr>
<th>Description</th>
<th>General</th>
<th>HC (Hydrocarbon)</th>
<th>Gas</th>
<th>Enthalpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation of State</td>
<td>Soave-Redlich-Kwong(SRK)</td>
<td>Peng Robinson(PR)</td>
<td>Grayson-Bredt-Chao-Seader(GS)</td>
<td>Benedict Weiss Rubin(BWR)</td>
</tr>
</tbody>
</table>

### Liquid Model (BIP, Gamma) based on Application

<table>
<thead>
<tr>
<th>Description</th>
<th>NRTL</th>
<th>UNIQUAC</th>
<th>UNIFAC (UNIQUAC)</th>
<th>Wilson</th>
<th>van Laar</th>
<th>Margules</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heterogeneous Azeotrope Parameters</td>
<td>Yes 5</td>
<td>Yes 2</td>
<td>Yes Increments</td>
<td>No 2</td>
<td>No 2</td>
<td>No 2</td>
</tr>
</tbody>
</table>

### Enthalpy

<table>
<thead>
<tr>
<th>Description</th>
<th>Total</th>
<th>Liquid</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latent heat</td>
<td>( H = H_f + H_{\text{liq}} + H_{\text{vap}} + H_{\text{gas}} )</td>
<td>( H_{\text{liq}} = \text{Integral (} C_{\text{p, liq}} \text{ d}T )</td>
<td>( H_{\text{gas}} = \text{Integral (} C_{\text{p, gas}} \text{ d}T )</td>
</tr>
</tbody>
</table>