

## AUTOMATIC PLOTTING OF MULTIPLE PHASE BOUNDARIES AND FLASH CALCULATIONS

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- Shows complex phase behaviour of multicomponent mixtures
- Can also trace other thermodynamic properties
- Plots can be produced in minutes for particular mixtures
- Simple and effective visual tool for process engineers

## Introduction

Tracing vapour-liquid phase boundaries is a well understood problem, but that is not the case if more phases are involved. In the algorithm proposed by Michelsen, the variables are the component K-values, the temperature and the pressure. The equations describing the vapour-liquid equilibrium are the conditions of equal fugacity for each component in both phases:

$$x_i f_i^L = y_i f_i^V$$

with the usual notation. In addition there is the Rachford-Rice equation that expresses the condition of phase equilibrium for a specified vapour phase fraction  $\alpha$ :

$$\sum_i \frac{(K_i - 1)z_i}{\alpha(K_i - 1) + 1} = 0$$

The liquid and vapour mole fractions follow from basic definitions.

There is one more variable than the number of constraining equations; a solution therefore requires that one variable is specified by the user. Tracing a phase line can then be performed automatically by incrementing one of the variables to obtain the next point on the line, etc.

The procedure above can be generalised to cover any number of phases in equilibrium provided that a suitable thermodynamic model is implemented to calculate the fugacity coefficients for each phase. For each additional phase there is a new set of K-values which are balanced by a new set of equal fugacity constraints for the components. There is also an additional phase fraction, in this case unconstrained, which is balanced by an additional Rachford-Rice equation. For example, the Rachford-Rice equations generalised for three phases become:

$$\sum_i \frac{(K_i^{(1)} - 1)z_i}{\alpha^{(1)}(K_i^{(1)} - 1) + \alpha^{(2)}(K_i^{(2)} - 1) + 1} = 0$$

$$\sum_i \frac{(K_i^{(2)} - 1)z_i}{\alpha^{(1)}(K_i^{(1)} - 1) + \alpha^{(2)}(K_i^{(2)} - 1) + 1} = 0$$

As the formulation is now valid for any number of phases, the number of phases must be checked for each calculated point. If one of the phase fractions goes to zero or a negative value, that phase must be eliminated. It is also necessary to check if an additional phase must be added by performing a phase stability analysis.

The method can be modified to correspond to any type of flash calculation. For example, to trace isenthalpic lines, an additional constraint is added that the calculated enthalpy equals the specified enthalpy. This requires the relaxation of the problem by the introduction of one more variable, namely the phase fraction that was previously fixed.

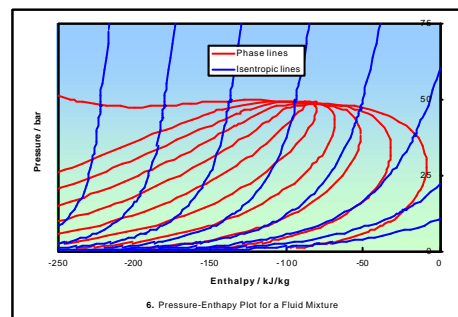
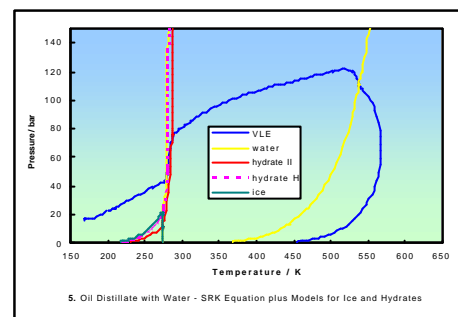
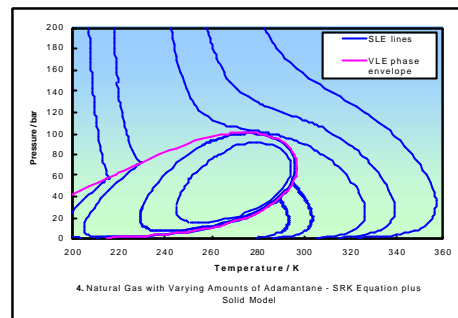
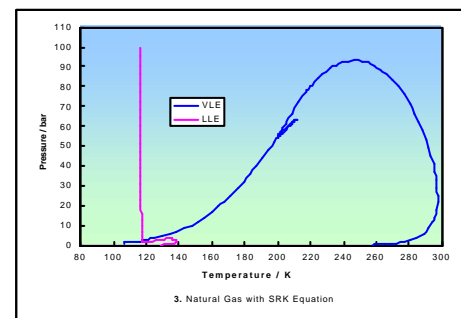
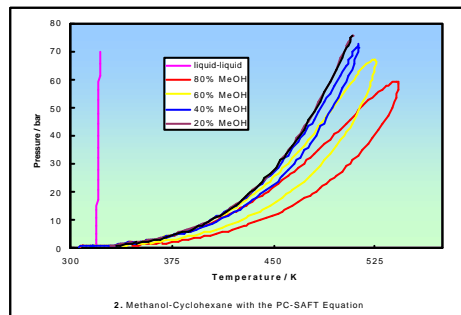
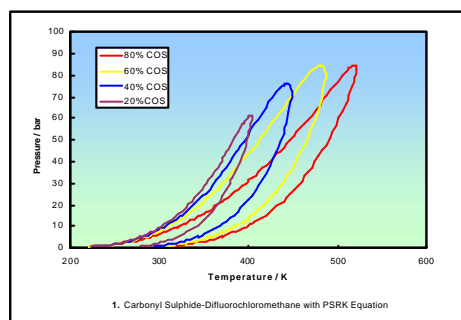
Other extensions are possible. The pressure or temperature variable could be replaced by an overall composition variable, thereby extending the technique to cover binary and possibly ternary phase diagrams.

## Results

Phase envelope tracing has usually been used to plot the vapour-liquid phase envelopes of hydrocarbon mixtures. However, the robust nature of this algorithm means it can be used with a variety of models. Figure 1 shows the PSRK equation and Figure 2 the PC-SAFT equation. Figure 2 also shows that liquid-liquid boundaries can also be plotted.

Even with cubic equations, phase behaviour can be more complex than expected. Figure 3 shows that the SRK equation can predict the presence of 3-phase lobes projecting off the vapour-liquid phase envelope. We do not believe they are quantitatively correct, but this type of behaviour has been observed experimentally. As with Figure 2, the boundary of the liquid-liquid region is plotted; here it crosses the bubble point line.

Low temperatures solutions for fluid phases tend to be artificial as in reality components will solidify. Figure 4 introduces solids: the system is a natural gas with varying amounts of dissolved adamantane, a compound that occurs naturally in some gas fields. The adamantane will precipi-



tate out as a pure solid at various conditions (cf. supercritical extraction). Note the interesting island phase boundaries for solid adamantane.

Figure 5 shows the phase behaviour for a mixture of oil distillate and water. The solid phases are ice and two gas hydrate phases of structure II and structure H. The result is a very complex diagram with a number of points with five coexisting phases. Note how the hydrate and water lines have a major impact on the shape of the hydrocarbon bubble point line; also the water dew point line joins at low temperature into the water 'disappearance' line in the vicinity of the hydrate lines.

Finally Figure 6 illustrates how the technique can be used to trace lines corresponding to other types of phase equilibria, in this case isentropic lines. Also it shows that the results can be displayed in plots other than of pressure v. temperature. A whole range of plots for thermal properties are possible, e.g. Mollier diagrams.

More examples are on our web site [www.infochemuk.com](http://www.infochemuk.com)