

Course exercises

Chapter 9

1. We consider the 7-component mixture investigated in Figure 8.1, and use the values for the component critical properties given in the Cubic EOS computer program. It is assumed that the Wilson K -factor expression provides for an adequate expression of the equilibrium factors. The K -factors are thus considered to be only functions of T and P .

Write a general computer subprogram to solve the *Rachford-Rice* equation,

$$\sum_{i=1}^{NC} z_i \frac{K_i - 1}{1 - \beta + \beta K_i} = 0$$

using the feed mole fractions of Figure 8.1. Use the Rachford-Rice equation to calculate the phase boundaries and compare to the ‘exact’ results obtained with the SRK-equation and listed in Table 11.1.

2. Extend your Rachford-Rice solver to handle the ‘negative flash’, i.e. a solution for β outside the physically permitted interval $[0,1]$. Show that a unique real-valued solution is found whenever the smallest and the largest K -value, K_{\min} and K_{\max} , satisfy $K_{\min} < 1$, $K_{\max} > 1$, with the proper solution satisfying

$$-\frac{1}{K_{\max} - 1} < \beta < \frac{1}{1 - K_{\min}}$$

A value of $\beta < 0$ indicates a subcooled liquid, and a value > 1 a superheated vapour.

3. For the 7-component mixture investigated above, initiate flash calculations with the Wilson K -factors and continue with K -factors based on calls to your thermodynamic subprogram with the compositions of the previous iteration. Repeat calculations until the change in component fugacities is smaller than 10^{-7} (relative). Investigate the convergence behaviour at various (T, P) , in particular in the vicinity of the critical point. You may also try to converge the ‘negative flash’ in this manner.
4. Next, use the Dominant Eigenvalue Method to accelerate convergence. Compare the performance of the unaccelerated method to that when

acceleration is used. Verify that reliability is not adversely affected, and apply checks on G to ensure that the extrapolations are appropriate. Check whether inadequate initial estimates from the Wilson K -factors cause incorrect convergence to the trivial solution.

Investigate in addition whether the General Dominant Eigenvalue Method with two terms leads to any improvements. You may finally investigate Newton's method, or a Newton-based minimization procedure.

5. Supplement your flash program with stability analysis by successive substitution according to the guidelines given in the text for the two-phase flash. Use the Wilson K -factors to generate initial estimates for the stability analysis. Try to characterize your feed as either a vapour or a liquid and investigate whether a stability analysis, where you look for only the 'missing' phase is adequate. Test the reliability and performance of the routine in the critical region.

Implement an accelerated convergence procedure and compare the performance of the unaccelerated, relative to the accelerated procedure.

6. Suppose that you are required to perform a series of flash calculations at conditions that do not vary very much. This is usually the case in connection with compositional simulations, where the material composition in any given 'grid block' changes slowly with time. Let us here for simplicity consider the case where the overall feed is assumed to be of constant composition, where we keep constant pressure and where the temperature increases by the same amount, 0.25 K, for each run. Start at 4 MPa and 180 K and consider a total of 250 flash calculations where the temperature in each is increased by 0.25 K relative to the previous.

Modify your algorithm such that it is capable of taking advantage of initial estimates and note the increase in efficiency. Your algorithm must, of course, be capable of also handling *bad* initial estimates.

7. Assume that the gas mixture we have investigate above contains water in such amounts that a liquid water phase might precipitate. Neglect the solubility of the hydrocarbons in the water phase. Modify your programs for flash calculation and stability analysis to take care of this situation.
8. Consider a 3-component mixture containing methane (50%), carbon dioxide (10%) and hydrogen sulphide (40%). This mixture can, at low

temperatures, form 3 phases in a fairly narrow pressure range. The presence of immiscible liquid phases can often be detected by means of only an ordinary two-phase flash program. Set the temperature to 180 K and try to locate the bubble line by doing flash calculations. If your program does ‘full’ stability analysis it should return a two-phase liquid-liquid solution at pressures slightly above the apparent (false) bubble point pressure.

Chapter 10

1. A mixture containing hydrocarbons and substantial amounts of hydrogen sulphide may form two liquid phases: A methane-rich liquid phase and a hydrogen sulphide rich liquid phase. The two liquid phases are only found in a narrow temperature/pressure range. It is generally difficult to create initial estimates for the fugacity coefficients for the liquid phases. The Wilson approximation cannot distinguish between immiscible liquids, and specific modifications are needed. For the current example we use the Wilson K -factor approximation with the following modifications:

- (a) The methane rich liquid phase: $\ln K_{\text{H}_2\text{S}} = \ln K_{\text{Wilson}} + 1$;
- (b) The hydrogen sulphide rich liquid phase: $\ln K_{\text{CH}_4} = \ln K_{\text{Wilson}} + 1$;

Hydrogen sulphide is thus given a higher volatility in the methane phase and methane is assumed to be more volatile in the hydrogen sulphide phase.

Consider a mixture of the following composition: C_1 : 66%; C_2 : 3%; C_3 : 1%; CO_2 : 5%, H_2S : 25%, at $T=201$ K, $P = 4.0$ MPa.

Write a multiphase Rachford-Rice program to calculate the phase distribution predicted using the modified Wilson K -factors under these conditions (3 phases should result).

2. Use the SRK equation of state to model the above mixture and solve the flash using successive substitution. Incorporate acceleration using the Dominant Eigenvalue Method.
3. Incorporate stability analysis in your three-phase flash, where you test 3 different initial estimates for the trial phase, liquid hydrogen sulphide, liquid methane and an ideal gas. Converge the stability equations by successive substitution or by the Dominant Eigenvalue Me-

thod. Note that your code must be capable of handling cases where a phase is removed in the course of iterations.

4. Add solid carbon dioxide and solid hydrogen sulphide as possible phases. You will need to get data for the melting points and the heats of fusion for these compounds. Use these to calculate properties of the pure solids at other conditions, assuming that the volume change on solidification is zero and that the heat of fusion is temperature independent.
5. Extend your approach with a more general scheme for the stability analysis, where you do not rely on specific knowledge regarding the mutual miscibility of the components. Also, incorporate in your algorithm a minimization approach and second order methods where this is necessary.

Chapter 11

1. Write an algorithm for calculating the bubble point pressure (given T) or temperature (given P) and the composition of the incipient phase, using the successive substitution approach with the Wilson K -factor initial estimates. Test your algorithm on the 7-component mixture. Monitor the convergence behaviour and plot:

- (a) The error in $\ln K_6$ vs. the iteration number, and
- (b) The error in $\ln T$ vs. the iteration number.

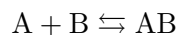
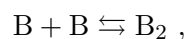
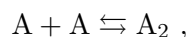
With specified P , investigate how close you can get to the critical point.

2. Extend the algorithm to the calculation of dewpoint temperature and pressure. Investigate, with pressure specified, how close you can get to the maximum pressure.
3. Program a full Newton method to perform the calculation. You may use successive substitution to initialize calculations. The Newton routine should also be able to provide you with sensitivities with respect to the specified variable, T or P .
4. Extend the Newton approach to incorporate one of the K -factors as the specified variable, including calculation of sensitivities.

5. You are now in a position to construct a full phase envelope calculation program. Start with a low pressure bubble point calculation and *manually* specify the next point to be calculated. You have succeeded when you can return to your initial P on the dewline.
6. Automate the selection of stepsize and the choice of specification variable in 5).

Chapter 12

Organic acids like acetic acid and propionic acid form dimers and cross-dimers in the vapour phase,



Assume that the vapour phase is ideal and that the equilibrium constants for the dimerisation reactions are given by (for compound A)

$$K_A P = \frac{y_{A_2}}{y_A^2}$$

where K_A is a temperature function of the form:

$$\log_{10} K ((\text{mm Hg})^{-1}) = K_1 + \frac{K_2}{T}$$

where T is the Kelvin temperature. Values of K_1 and K_2 , taken from Fredenslund et al. (1977) are given in the table below:

Component	K_1	K_2
A (Formic acid)	-10.743	3083
B (Acetic acid)	-10.421	3166
C (Propionic acid)	-10.843	3316
D (Butyric acid)	-10.136	3079

For cross-dimers,

$$K_{AB} P = \frac{y_{AB}}{y_A y_B}$$

assume that $K_{AB} = 2\sqrt{K_A K_B}$. Consider a gas mixture containing the four components A, B, C and D together with an inert, I. Write a program

that, given temperature, pressure and overall composition in terms of the monomers calculates the ‘true’ equilibrium composition and the apparent fugacity coefficients in the mixture. Relevant values of the temperature and the pressure are 350 K, 0.1 MPa, but your program should of course work correctly in a wider temperature and pressure range.

It is advisable that you test your program by doing calculation at low pressures where the degree of dimerisation is modest. This enables you to generate accurate initial estimates.