Final course problem examples

1. One of the first (primitive) algorithms to calculate tricritical points in ternary mixtures (Michelsen, Fluid Phase Equilib., **30**, p. 15, 1986) was based on the 'method of shrinking triangles'. Initially, 3 equilibrium phases are determined, and these are moved through conditions, where the *shape* of the triangle is preserved while the *size* shrinks to a point. Write a program based on these principles and verify the code using some of the examples of the article.

2. Binary mixtures for which liquid-liquid as well as vapour-liquid equilibrium can occur are capable of 3-phase equilibrium. The equilibrium curve defines a line in $T - P$ space like the vapour pressure curve for pure components.

   Write a program that can generate the equilibrium line for such mixtures. Exemplify by constructing the equilibrium curves for water and hydrocarbons (C_5 and higher), and for the methane-hydrogen sulphide mixture.

3. Correlation of VLE frequently require the calculation of the equilibrium curve for binary mixtures at fixed temperature (Pxy-curves) or at fixed pressure (Txy-curves). Write a program for automatic calculation of such equilibrium curves. The program should be capable of calculating the equilibrium curve for mixtures in which one of the pure components is supercritical.

4. Successive substitution is the 'workhorse' in many PT-flash algorithms. Its popularity can be ascribed to its simple implementation and to the fact that is almost always converges (even though many iterations may be required).

5. Recently, Heidemann and Michelsen (I&EC Research, 1995) described a variety of mixtures for which successive substitution can be divergent. Such mixtures are characterized by strong negative deviations from Raoult's law. One example is the Flory polymer model used by Sandler et al. Develop a flash program that is capable of solving the flash for the example considered by Sandler et al. and investigate its performance.

6. In connection with oil production processes phase equilibrium calculations where the presence of a water rich phase must be taken into

account in addition to the hydrocarbon liquid and the hydrocarbon vapour are of important.

Extend a two-phase PT-flash to account for a potential third water-rich phase. One may use as a simplifying assumption that the water phase does not contain dissolved components (whereas water solubility in the hydrocarbon phases is accounted for), or one may consider the case where all components are allowed to distribute in all phases. You should investigate both.

7. Chemical reaction equilibrium calculations for non-ideal mixtures are of importance in connecting with reactive distillation. Construct an algorithm capable of calculating phase equilibrium at specified P and T for such mixtures. The vapour phase can be assumed ideal, and the liquid phase is described by an activity coefficient model. As examples you can use the cases studied by Doherty and Ung (Chem. Eng. Sci., 1996)

8. The Wong-Sandler model is one approach for combining excess Gibbs energy models with an Equation of State. In this problem you should write a subroutine based on the Wong-Sandler approach for calculation compressibility factor and fugacity coefficients, where the Soave-Redlich-Kwong equation is the base Equation of State and where UNIFAC, UNIQUAC, WILSON and NRTL are the excess Gibbs energy models that can be used. Existing activity coefficient modules can be utilized. Your subroutine should be verified for thermodynamic consistency.

9. The *first contact miscibility pressure* (FCMP) is the pressure (at a specified temperature) at which two mixtures (typically a reservoir oil and an injection gas). become miscible in all proportions. The FCMP can be determined by calculating the saturation pressure in dependence of the proportion of one of the mixtures, the maximum pressure on the coexistence curve being equal to the FCMP.

   Write a program for the constuction of such saturation curves and demonstrate its applicability for typical reservoir/oil - injection gas pairs.

10. The *multiple contact minimum miscibility pressure* (MMP) is the pressure where two mixtures at specified temperature become miscible after repeated contacts. Under certain conditions a simple determination is possible by calculating equilibrium compositions with the property

that the tie line passing through the equilibrium compositions extend through one of the two specified phase compositions. MMP occurs when this tieline becomes critical. Write a program for calculating this 'tieline' MMP.

11. Specifications of pressure and enthalpy, or pressure and entropy, are of importance in flow calculations for heat exchangers and compressors. Write a flash program that solves the PH and the PS-flash. You are free to choose your method but it should be based entirely on your own flash code, and it should be able to handle narrow-boiling as well as wide-boiling mixtures.

12. The oil composition varies with depth due to gravitational effects. Assume that the pressure, temperature and oil composition is known at a given depth in an oil reservoir, and assume that the temperature does not vary with depth.

    Write a computer program that can determine the oil composition and the pressure above and below the reference point and which is able to determine whether the oil becomes saturated.

13. Extend a 2-phase PT-flash program to incorporate the possible formation of (multiple) pure solid phases. The properties of the solid phase (i.e. the fugacity) is assumed given by a simple expression that enables calculation of the fugacity as a function of temperature and pressure, assuming a constant heat of melting and a constant volume change associated with the phase transition.

14. The first computationally efficient procedure to calculate critical points directly is that of Heidemann and Khalil (AIChE J., 1980). Temperature and volume are used as the independent variables, and the iteration procedure is based on nested loops, where the first stability condition is solved for T in the inner loop, and the second solved for V in the outer loop.

    Write a program that uses the method of Heidemann and Khalil, in which the triple sum is replaced by the numerical determination described by Michelsen. Investigate the examples presented in the Heidemann-Khalil paper.

15. Successive substitution is the 'workhorse' in many PT-flash algorithms. Its popularity can be ascribed to its simple implementation and to the

fact that is almost always converges (even though many iterations may be required).

Recently, Heidemann and Michelsen (I&EC Research, 1995) described a variety of mixtures for which successive substitution can be divergent. Such mixtures are characterized by strong negative deviations from Raoult's law. One example is the Flory polymer model used by Sandler et al. Develop a flash program that is capable of solving the flash for the example considered by Sandler et al. and investigate its performance.