Chemical Thermodynamics for Process Simulation
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Example 05.12 VLE of N2 - CH4 Using SRK (First Iteration Step)

problem: With the help of the Soave-Redlich-Kwong equation of state the system pressure and vapor phase composition for the binary system nitrogen(1) - methane(2) for a liquid mole fraction of nitrogen x_1 = 0.2152 at 144.26 K should be calculated.

general constants and definitions:

$$R_{gas} := 8.31433 \frac{J}{K \cdot mol} \qquad bar := 10^5 Pa \qquad dm := 0.1m \qquad kmol := 1000mol$$

input data

$$n_{comp} := 2 \qquad i := 1 .. n_{comp}$$

Critical data and acentric factor:

$$T_c := \begin{pmatrix} 126.192 \\ 190.564 \end{pmatrix} K \qquad P_c := \begin{pmatrix} 33.958 \\ 45.992 \end{pmatrix} bar \qquad \omega := \begin{pmatrix} 0.0372 \\ 0.0114 \end{pmatrix}$$

Binary parameter k_{SRK}: $$k_{SRK} := \begin{pmatrix} 0 & 0.0267 \\ 0.0267 & 0 \end{pmatrix}$$

Conditions for calculation: $T := 144.26K \qquad x_1 := 0.2152 \qquad x_2 := 1 - x_1$

Estimated values for first iteration: $P := 20bar \qquad y_1 := 0.6 \qquad y_2 := 1 - y_1$

Solution

1) As most equations use the reduced value of temperature, this is calculated first:

$$T_{r_i} := \frac{T}{T_{c_i}} \qquad T_r = \begin{pmatrix} 1.143 \\ 0.757 \end{pmatrix}$$

2) From the values of T_r it can be seen that the first component (nitrogen) is already supercritical. In the next step, those pure component and mixture parameters of the SRK-EOS are calculated, which do not depend on phase composition:

$$\alpha_{SRK_i} := \left[1 + \left[0.48 + 1.574 \cdot \omega_i - 0.176 \cdot (\omega_i)^2\right] \cdot \left[1 - (T_{r_i})^{0.5}\right]\right]^2 \qquad \alpha_{SRK} = \begin{pmatrix} 0.927 \\ 1.134 \end{pmatrix}$$

$$a_{SRK_{i,i}} := 0.42748 \cdot \frac{R_{gas}^{2} \cdot \left(T_{c_i}\right)^2}{P_{c_i}} \cdot \alpha_{SRK_i} \qquad a_{SRK} = \begin{pmatrix} 1.284459 & 0 \\ 0 & 2.644974 \end{pmatrix} \frac{\left(dm^3\right)^2 bar}{mol^2}$$

$$b_{SRK_i} := 0.08664 \cdot \frac{R_{gas} \cdot T_{c_i}}{P_{c_i}} \qquad b_{SRK} = \begin{pmatrix} 0.026769 \\ 0.029847 \end{pmatrix} \frac{dm^3}{mol}$$

$i := 1..2 \qquad j := 1..2$

$$a_{SRK_{i,j}} := \sqrt{a_{SRK_{i,i}} \cdot a_{SRK_{j,j}}} \cdot \left(1 - k_{SRK_{i,j}}\right) \qquad a_{SRK} = \begin{pmatrix} 1.284459 & 1.79398 \\ 1.79398 & 2.644974 \end{pmatrix} \frac{\left(dm^3\right)^2 bar}{mol^2}$$

3) Now the mixture parameters for the liquid phase can be calculated. As the mixture phase composition is fixed, this calculation is not required again in the iterative solution.

$$a_{SRKm} := \sum_i \sum_j x_i \cdot x_j \cdot a_{SRK_{i,j}} \qquad a_{SRKm} = 2.29452 \frac{\left(dm^3\right)^2 bar}{mol^2}$$

$$b_{SRKm} := \sum_i x_i \cdot b_{SRK_i} \qquad b_{SRKm} = 0.029185 \frac{dm^3}{mol}$$

4) At this point all required values are available to calculate the liquid volume by solving the following equation at the estimated pressure:

$$P_{SRK}(v,T) := \frac{R_{gas} \cdot T}{v - b_{SRKm}} - \frac{a_{SRKm}}{v \cdot \left(v + b_{SRKm}\right)}$$

The solution of the cubic equation is found using the root-function with a starting value for v not too far above the closest packing volume b_{SRKm}:

$$v := 1.5 \cdot b_{SRKm} \qquad v_L := \mathrm{root}\left(P_{SRK}(v,T) - P, v\right) \qquad v_L = 0.047859 \frac{dm^3}{mol}$$

5) With the liquid volume available, the fugacity coefficients can now be calculated:

$$\ln\phi_{L_i} := \ln\left(\frac{v_L}{v_L - b_{SRKm}}\right) - \frac{2 \cdot \sum_j x_j \cdot a_{SRK_{j,i}}}{R_{gas} \cdot T \cdot b_{SRKm}} \cdot \ln\left(\frac{v_L + b_{SRKm}}{v_L}\right) \ldots$$
$$+ \frac{b_{SRK_i}}{\left(v_L - b_{SRKm}\right)} - \ln\left(\frac{P \cdot v_L}{R_{gas} \cdot T}\right) \ldots$$
$$+ \frac{a_{SRKm} \cdot b_{SRK_i}}{R_{gas} \cdot T \cdot b_{SRKm}^{2}} \cdot \left(\ln\left(\frac{v_L + b_{SRKm}}{v_L}\right) - \frac{b_{SRKm}}{v_L + b_{SRKm}}\right)$$

$$\phi_{L_i} := \exp\left(\ln\phi_{L_i}\right) \qquad \phi_L = \begin{pmatrix} 2.474348 \\ 0.376459 \end{pmatrix}$$

6) Now the calculations performed in step 3 to 5 are repeated for the vapor phase using the estimated pressure and the estimated vapor phase composition:

$$a_{SRKm} := \sum_i \sum_j y_i \cdot y_j \cdot a_{SRK_{i,j}} \qquad a_{SRKm} = 1.746711 \frac{\left(dm^3\right)^2 bar}{mol^2}$$

$$b_{SRKm} := \sum_i y_i \cdot b_{SRK_i} \qquad b_{SRKm} = 0.028 \frac{dm^3}{mol}$$

The SRK pressure function has to be re-defined here. Otherwise the function would use the parameters for the liquid phase above as the vapor phase parameters were defined after the function definition.

$$P_{SRK}(v,T) := \frac{R_{gas} \cdot T}{v - b_{SRKm}} - \frac{a_{SRKm}}{v \cdot \left(v + b_{SRKm}\right)}$$

$$v := \frac{R_{gas} \cdot T}{P} \qquad v_V := \mathrm{root}\left(P_{SRK}(v,T) - P, v\right) \qquad v_V = 0.459471 \frac{dm^3}{mol}$$

$$\ln\phi V_i := \ln\left(\frac{v_V}{v_V - b_{SRKm}}\right) - \frac{2 \cdot \sum_j y_j \cdot a_{SRK_{j,i}}}{R_{gas} \cdot T \cdot b_{SRKm}} \cdot \ln\left(\frac{v_V + b_{SRKm}}{v_V}\right) \ldots$$
$$+ \frac{b_{SRK_i}}{\left(v_V - b_{SRKm}\right)} - \ln\left(\frac{P \cdot v_V}{R_{gas} \cdot T}\right) \ldots$$
$$+ \frac{a_{SRKm} \cdot b_{SRK_i}}{R_{gas} \cdot T \cdot b_{SRKm}^2} \cdot \left(\ln\left(\frac{v_V + b_{SRKm}}{v_V}\right) - \frac{b_{SRKm}}{v_V + b_{SRKm}}\right)$$

$$\phi V_i := \exp\left(\ln\phi V_i\right) \qquad \phi V = \begin{pmatrix} 0.882969 \\ 0.708955 \end{pmatrix}$$

7) Using the fugacity coefficients for the liquid and vapor phase, a new estimate for the vapor composition can now be found. As both pressure and vapor phase composition were only guessed, the summation condition is not fulfilled:

$$y_i := x_i \cdot \frac{\phi L_i}{\phi V_i} \qquad y = \begin{pmatrix} 0.603 \\ 0.417 \end{pmatrix} \qquad S := \sum_i y_i \qquad S = 1.019789$$

8) New and better estimates for pressure and vapor phase composition can be generated by scaling the vapor phase compositions calculated via the fugacity coefficients and the liquid composition to observe the summation condition:

$$y_i := \frac{y_i}{S} \qquad y = \begin{pmatrix} 0.591 \\ 0.409 \end{pmatrix} \qquad \sum_i y_i = 1$$

In a similar way, the pressure estimate is rescaled:

$$P := S \cdot P \qquad P = 20.396\,\text{bar}$$

These improved estimated values can now be copied to the top of this calculation yielding a value of S closer to 1. A few iterations like this lead to the final result that compares well with the experimental findings:

$$P := 20.733\text{bar} \qquad y_1 := 0.5893$$

$$P_{exp} := 20.684 \qquad y_{exp_1} := 0.5804$$

At low reduced temperatures and near the critical point, some numeric problems can arise:
Near the critical point, the pressure range in which three real solutions of the equation of state can be found becomes rather small. If only one real solution is found for an estimated pressure and phase composition, the algorithm fails. This can be corrected by breaking the calculation for this iteration step and starting the iteration with better estimates. A good idea in this case is to limit the allowed change in pressure and phase composition.
At low reduced temperatures, small changes in the liquid volume result in very large pressure changes. This can lead to convergence problems, even when the calculation is performed using double precision. If the changing pressure from one iteration to the next has a neglible effect on the liquid volume and liquid fugacity coefficients, the values of the last iteration should be kept and recalculation of the liquid phase can be skipped.