VLE-EOS_EtOH/Water ---- H.C. Van Ness; January 2005

VLE for Ethanol(1)/Water(2) at 90 deg C. Calculations with Peng/Robinson EOS. Activity coefs. by the van Laar Equation. This is a BUBL P calculation illustrating in detail the procedure described on pp. 569-572 of "Introduction to Chemical Engineering Thermodynamics," 7th ed., McGraw-Hill, 2005, by Smith, Van Ness, & Abbott.

Temperatures in kelvins; Pressures in bars. $R := 83.14$

Data: $T := 363.15$ $\quad x_1 := 0.2464$ $\quad x_2 := 1 - x_1$

$$Tc := \begin{pmatrix} 513.9 \\ 647.1 \end{pmatrix} \quad Pc := \begin{pmatrix} 61.48 \\ 220.55 \end{pmatrix} \quad \omega := \begin{pmatrix} 0.645 \\ 0.345 \end{pmatrix} \quad Psat := \begin{pmatrix} 1.57892 \\ 0.70124 \end{pmatrix}$$

$$Tr := \overrightarrow{\frac{T}{Tc}} \qquad Tr = \begin{pmatrix} 0.7067 \\ 0.5612 \end{pmatrix}$$

Table 3.1: $\varepsilon := 1 - \sqrt{2}$ $\quad \sigma := 1 + \sqrt{2}$ $\quad \Psi := 0.45724$ $\quad \Omega := 0.07780$

$$\alpha := \overrightarrow{\left[1 + \left(0.37464 + 1.54226\cdot\omega - 0.26992\cdot\omega^2\right)\cdot\left(1 - \sqrt{Tr}\right) \right]^2} \qquad \alpha = \begin{pmatrix} 1.4408 \\ 1.4870 \end{pmatrix}$$

$$a := \overrightarrow{\frac{\Psi\cdot\alpha\cdot R^2\cdot Tc^2}{Pc}} \quad \textbf{(3.45)} \qquad b := \overrightarrow{\frac{\Omega\cdot R\cdot Tc}{Pc}} \quad \textbf{(3.46)}$$

The following are final parameter values that do not change:

$$a = \begin{pmatrix} 1.9561 \times 10^7 \\ 8.9227 \times 10^6 \end{pmatrix} \qquad b = \begin{pmatrix} 54.0673 \\ 18.9782 \end{pmatrix}$$

$$b_{liq} := x_1\cdot b_1 + x_2\cdot b_2 \quad \textbf{(14.42)} \qquad b_{liq} = 27.6241$$

van Laar eqn. parameters (Table 14.4): $A_{12} := 1.7720$ $\quad A_{21} := 0.9042$

Liquid-phase activity coefficients:

$$lngam_1 := A_{12}\cdot\left(1 + \frac{A_{12}\cdot x_1}{A_{21}\cdot x_2}\right)^{-2} \qquad lngam_2 := A_{21}\cdot\left(1 + \frac{A_{21}\cdot x_2}{A_{12}\cdot x_1}\right)^{-2} \quad \textbf{(12.17)}$$

$$\gamma := \overrightarrow{e^{lngam}} \qquad lngam = \begin{pmatrix} 0.6582 \\ 0.1379 \end{pmatrix} \qquad \gamma = \begin{pmatrix} 1.9314 \\ 1.1479 \end{pmatrix}$$

FIND q-VALUES FROM VAPOR-PRESSURE DATA FOR PURE SPECIES.
This insures that the pure-species vapor pressures are reproduced as part of the results.

Preliminary values: $q := \overrightarrow{\frac{a}{b \cdot R \cdot T}}$ **(14.34)** **(Used for initial iteration)**

$$q = \begin{pmatrix} 11.9832 \\ 15.5722 \end{pmatrix}$$

Updated values used in iteration:

$q_1 := 12.0364$ $q_2 := 15.4551$ **(These are the final converged values from iteration.)**

For calculations at P=Psat:

$\beta := \overrightarrow{\frac{b \cdot Psat}{R \cdot T}}$ **(14.33)** $\beta = \begin{pmatrix} 2.8275 \times 10^{-3} \\ 4.4078 \times 10^{-4} \end{pmatrix}$

Solve blocks with initial estimates: $Zliq := \beta_1$ $Zvap := 1$
(Species 1)

Given $Zvap = 1 + \beta_1 - q_1 \cdot \beta_1 \cdot \frac{Zvap - \beta_1}{(Zvap + \varepsilon \cdot \beta_1) \cdot (Zvap + \sigma \cdot \beta_1)}$ **(14.36)**

$zvap_1 := Find(Zvap)$

Given $Zliq = \beta_1 + (Zliq + \varepsilon \cdot \beta_1) \cdot (Zliq + \sigma \cdot \beta_1) \cdot \frac{1 + \beta_1 - Zliq}{q_1 \cdot \beta_1}$ **(14.35)**

$zliq_1 := Find(Zliq)$

Solve blocks with initial estimates: $Zliq := \beta_2$ $Zvap := 1$
(Species 2)

Given $Zvap = 1 + \beta_2 - q_2 \cdot \beta_2 \cdot \frac{Zvap - \beta_2}{(Zvap + \varepsilon \cdot \beta_2) \cdot (Zvap + \sigma \cdot \beta_2)}$ **(14.36)**

$zvap_2 := Find(Zvap)$

Given $Zliq = \beta_2 + (Zliq + \varepsilon\cdot\beta_2)\cdot(Zliq + \sigma\cdot\beta_2)\cdot\frac{1 + \beta_2 - Zliq}{q_2\cdot\beta_2}$ **(14.35)**

$zliq_2 := Find(Zliq)$

$zliq = \begin{pmatrix} 3.5536\times10^{-3} \\ 5.1894\times10^{-4} \end{pmatrix}$ $zvap = \begin{pmatrix} 0.9680 \\ 0.9936 \end{pmatrix}$ **(At P=Psat)**

$Iliq := \overrightarrow{\left(\frac{1}{\sigma-\varepsilon}\cdot\ln\left(\frac{zliq + \sigma\cdot\beta}{zliq + \varepsilon\cdot\beta}\right)\right)}$ **(6.65b)** $Iliq = \begin{pmatrix} 0.5203 \\ 0.5476 \end{pmatrix}$

$Ivap := \overrightarrow{\left(\frac{1}{\sigma-\varepsilon}\cdot\ln\left(\frac{zvap + \sigma\cdot\beta}{zvap + \varepsilon\cdot\beta}\right)\right)}$ **(6.65b)** $Ivap = \begin{pmatrix} 2.9125\times10^{-3} \\ 4.4343\times10^{-4} \end{pmatrix}$

$q := \overrightarrow{\frac{(zvap - zliq) + \ln\left(\frac{zliq-\beta}{zvap-\beta}\right)}{Ivap - Iliq}}$ **(14.37)** $q = \begin{pmatrix} 12.0364 \\ 15.4551 \end{pmatrix}$ **FINAL VALUES**

Subsequent calculations require values of Z and I for the PURE LIQUID species at system pressure P. Because P is to be determined, an iterative procedure is initiated by a starting value for P. A logical initial choice is the sum of the pure-species vapor pressures at the known temperature T, each weighted by its known liquid-phase mole fraction.

CURRENT VALUE OF PRESSURE: $P := 1.3576$ **(Shown is the final converged value)**

$\beta := \overrightarrow{\frac{b\cdot P}{R\cdot T}}$ **(14.40)** $\beta = \begin{pmatrix} 2.4311\times10^{-3} \\ 8.5335\times10^{-4} \end{pmatrix}$

Solve block with initial estimate: (Species 1) $Zliq := \beta_1$

Given $Zliq = \beta_1 + (Zliq + \varepsilon\cdot\beta_1)\cdot(Zliq + \sigma\cdot\beta_1)\cdot\frac{1 + \beta_1 - Zliq}{q_1\cdot\beta_1}$ **(14.35)**

$zliq_1 := Find(Zliq)$

Solve block with initial estimate: $Zliq := \beta_2$
(Species 2)

$$\text{Given} \quad Zliq = \beta_2 + (Zliq + \varepsilon\cdot\beta_2)\cdot(Zliq + \sigma\cdot\beta_2)\cdot\frac{1 + \beta_2 - Zliq}{q_2\cdot\beta_2} \qquad \textbf{(14.35)}$$

$$zliq_2 := \text{Find}(Zliq)$$

$$Iliq := \overrightarrow{\left(\frac{1}{\sigma - \varepsilon}\cdot\ln\left(\frac{zliq + \sigma\cdot\beta}{zliq + \varepsilon\cdot\beta}\right)\right)} \qquad \textbf{(6.65b)}$$

$$zliq = \begin{pmatrix} 3.0556 \times 10^{-3} \\ 1.0047 \times 10^{-3} \end{pmatrix} \qquad Iliq = \begin{pmatrix} 0.5203 \\ 0.5476 \end{pmatrix} \qquad \textbf{(At pressure P)}$$

CALCULATION OF PARTIAL q-VALUES:
Liquid phase first; vapor phase second

$$\beta_{liq} := \frac{b_{liq}\cdot P}{R\cdot T} \qquad \textbf{(14.40)} \qquad \beta_{liq} = 1.2421 \times 10^{-3}$$

$$q_{liq} := x_1\cdot q_1 + x_2\cdot q_2 \qquad q_{liq} = 14.6127 \quad \textbf{(initial estimate)}$$

Must update q_{liq} as calculation progresses:

$$q_{liq} := 13.9175 \qquad \textbf{(converged value)}$$

Solve block with initial estimate: $Z_{liq} := \beta_{liq}$

Given

$$Z_{liq} = \beta_{liq} + (Z_{liq} + \varepsilon\cdot\beta_{liq})\cdot(Z_{liq} + \sigma\cdot\beta_{liq})\cdot\left(\frac{1 + \beta_{liq} - Z_{liq}}{q_{liq}\cdot\beta_{liq}}\right) \qquad \textbf{(14.38)}$$

$$z_{liq} := \text{Find}(Z_{liq}) \qquad z_{liq} = 1.4978 \times 10^{-3}$$

$$I_{liq} := \frac{1}{\sigma - \varepsilon}\cdot\ln\left(\frac{z_{liq} + \sigma\cdot\beta_{liq}}{z_{liq} + \varepsilon\cdot\beta_{liq}}\right) \qquad \textbf{(6.65b)} \qquad I_{liq} = 0.5374$$

$$qbar_{liq} := \overrightarrow{\left[\frac{1}{I_{liq}}\cdot\left[1 - zliq + \frac{b}{b_{liq}}\cdot(z_{liq} - 1) - \ln\left(\frac{z_{liq} - \beta_{liq}}{zliq - \beta}\right) + q\cdot Iliq - lngam\right]\right]} \qquad \textbf{(14.57)}$$

$$qbar_{liq} = \begin{pmatrix} 10.3080 \\ 15.0975 \end{pmatrix} \qquad q_{liq} := x_1 \cdot qbar_{liq_1} + x_2 \cdot qbar_{liq_2} \quad \textbf{(14.58)}$$

$q_{liq} = 13.9174$ **(update value)**

$$\ln\phi hat_{liq} := \overrightarrow{\left[\frac{b}{b_{liq}} \cdot (z_{liq} - 1) - \ln(z_{liq} - \beta_{liq}) - qbar_{liq} \cdot I_{liq}\right]} \quad \textbf{(14.50)}$$

$$\phi hat_{liq} := e^{\overrightarrow{\ln\phi hat_{liq}}} \qquad \phi hat_{liq} = \begin{pmatrix} 2.1752 \\ 0.5894 \end{pmatrix}$$

Repeat these calculations for a LIQUID phase with the VAPOR composition. This is done by duplicating the preceding calculation with the xs changed to ys. THE ONLY PURPOSE IS TO GET VALUES FOR q and qbar for the VAPOR phase. These calculations require knowledge of the vapor composition, which is yet to be determined. Iteration is again indicated, with starting values for the ys. They could be found from Raoult's law or by assuming ideal solutions in both phases. The properties of this special phase are denoted here by subscript lv:

Current value of y: $y_1 := .5496$ **(Shown is the final converged value.)**

$y_2 := 1 - y_1$

$b_{lv} := y_1 \cdot b_1 + y_2 \cdot b_2$ **(14.42)** $\qquad b_{lv} = 38.2631$

$q_{vap} := y_1 \cdot q_1 + y_2 \cdot q_2$ **(initial value)** $\qquad q_{vap} = 13.5761$

Must update q_{vap} as calculation progresses:

$q_{vap} := 12.5616$ **(converged value)**

$$\beta_{lv} := \frac{b_{lv} \cdot P}{R \cdot T} \quad \textbf{(14.40)} \qquad \beta_{lv} = 1.7205 \times 10^{-3}$$

Solve block with initial estimate: $Z_{lv} := \beta_{lv}$

Given

$$Z_{lv} = \beta_{lv} + (Z_{lv} + \varepsilon \cdot \beta_{lv}) \cdot (Z_{lv} + \sigma \cdot \beta_{lv}) \cdot \left(\frac{1 + \beta_{lv} - Z_{lv}}{q_{vap} \cdot \beta_{lv}}\right) \quad \textbf{(14.38)}$$

$$z_{lv} := \mathrm{Find}(Z_{lv}) \qquad z_{lv} = 2.1338\times10^{-3}$$

$$I_{lv} := \frac{1}{\sigma-\varepsilon}\cdot\ln\left(\frac{z_{lv}+\sigma\cdot\beta_{lv}}{z_{lv}+\varepsilon\cdot\beta_{lv}}\right) \qquad \textbf{(6.65b)} \qquad I_{lv} = 0.5258$$

$$qbar_{vap} := \overrightarrow{\left[\frac{1}{I_{lv}}\cdot\left[1 - zliq + \frac{b}{b_{lv}}\cdot(z_{lv}-1) - \ln\left(\frac{z_{lv}-\beta_{lv}}{zliq-\beta}\right) + q\cdot Iliq - lngam\right]\right]} \qquad \textbf{(14.59)}$$

$$qbar_{vap} = \begin{pmatrix}10.6591\\14.8830\end{pmatrix} \qquad q_{vap} := y_1\cdot qbar_{vap_1} + y_2\cdot qbar_{vap_2} \qquad \textbf{(14.60)}$$

$$q_{vap} = 12.5615 \qquad \textbf{(update value)}$$

For the REAL vapor phase by (14.42) & (14.40):

$$b_{vap} := y_1\cdot b_1 + y_2\cdot b_2 \qquad \beta_{vap} := \frac{b_{vap}\cdot P}{R\cdot T} \qquad \beta_{vap} = 1.7205\times10^{-3}$$

Solve block with initial estimate: $Z_{vap} := 1$

Given

$$Z_{vap} = 1 + \beta_{vap} - q_{vap}\cdot\beta_{vap}\cdot\frac{Z_{vap}-\beta_{vap}}{(Z_{vap}+\varepsilon\cdot\beta_{vap})\cdot(Z_{vap}+\sigma\cdot\beta_{vap})} \qquad \textbf{(14.39)}$$

$$z_{vap} := \mathrm{Find}(Z_{vap}) \qquad z_{vap} = 0.9798$$

$$I_{vap} := \frac{1}{\sigma-\varepsilon}\cdot\ln\left(\frac{z_{vap}+\sigma\cdot\beta_{vap}}{z_{vap}+\varepsilon\cdot\beta_{vap}}\right) \qquad \textbf{(6.65b)} \qquad I_{vap} = 1.7529\times10^{-3}$$

$$\ln\phi hat_{vap} := \overrightarrow{\left[\frac{b}{b_{vap}}\cdot(z_{vap}-1) - \ln(z_{vap}-\beta_{vap}) - qbar_{vap}\cdot I_{vap}\right]} \qquad \textbf{(14.50)}$$

$$\phi hat_{vap} := \overrightarrow{e^{\ln\phi hat_{vap}}} \qquad \phi hat_{vap} = \begin{pmatrix}0.9752\\0.9862\end{pmatrix}$$

$$K := \overrightarrow{\frac{\phi hat_{liq}}{\phi hat_{vap}}}$$ **(14.53)** $$K = \begin{pmatrix} 2.2305 \\ 0.5977 \end{pmatrix}$$

$$\Sigma := x_1 \cdot K_1 + x_2 \cdot K_2$$ $\Sigma = 1.0000$ **(converged value)** **(14.52)**

The value of Σ is the key to the correct value of P. If $\Sigma > 1$, then P is too low; if $\Sigma < 1$, then P is too high. Adjust P (back on page 3) so that $\Sigma = 1$.

$$y_1 := \frac{x_1 \cdot K_1}{\Sigma}$$ **(normalize)** $y_1 = 0.5496$

Update y first and then P. Final converged values are:

$y_1 = 0.5496$ $P = 1.3576$

Experimental value of Pemberton and Mash (footnote 11; p. 573). Vapor-phase compositions were not measured.

$P(exp) = 1.3564$

NOTE THAT THIS CALCULATION IS RIGOROUS, EXCEPT FOR THE MIXING RULE USED FOR b. The mixing rule used for q is the summability equation, which is exact.