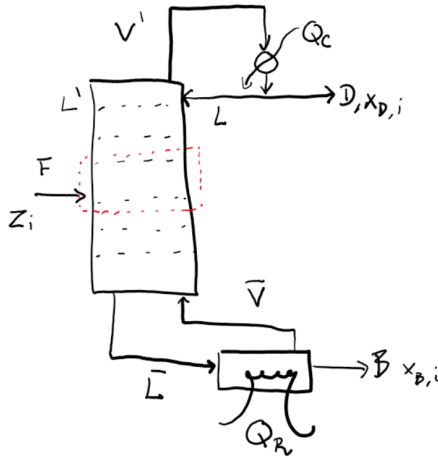


1)

a.



$$P = 101.325 \text{ kPa}$$

(1) Methanol, (2) Ethanol,

(3) n – Propanol, (4) n – Butanol

$$(x_1, x_2, x_3, x_4)_F = (0.30, 0.20, 0.15, 0.35)$$

$$d_2 = 0.95f_1$$

$$d_3 = 0.06f_2$$

$$q = 1.10$$

$$R = 3.0$$

$$F = 100 \text{ mol/hr}$$

**Assume:** CMO, ideal mixture**Solve:**The relevant physical properties of the feed are listed as follows <sup>1</sup>.**Table 1:** Physical properties of alcohols

			Critical Constants			Antoine Parameters		
Comp.	$i$	$T_{npb} \text{ (K)}$	$T_c \text{ (K)}$	$P_c \text{ (bar)}$	$\omega$	$A$	$B$	$C$
Methanol	1	337.9	512.6	80.97	0.564	16.5785	3638.27	239.500
Ethanol	2	351.4	513.9	61.48	0.645	16.8958	3795.17	230.918
n-Propanol	3	370.4	536.8	51.75	0.622	16.1154	3483.67	205.807
n-Butanol	4	390.8	563.1	44.23	0.594	15.3144	3112.43	182.739

The Antoine equation parameters are listed such that,

$$\ln(P_i^{sat}) = A_i - \frac{B_i}{T + C_i},$$

where  $P_i^{sat}$  is in kPa and  $T$  is in °C.Let methanol be the light key and ethanol be the heavy key. The material balance for a component,  $i$ , is then given by,

$$f_i = d_i + b_i.$$

<sup>1</sup>Smith, J.M., Van Ness, H.C., Abbot, M. M., Swihart, M. T., *Introduction to Chemical Engineering Thermodynamics*. 9th Ed., McGraw Hill, 2018.

For the light key,  $d_1 = 0.95f_1$  and for the heavy key,  $d_2 = 0.06f_2$ . We will further assume (as a first approximation) a perfect split such that all HHK components end up in the bottoms stream. Performing the material balances with these specifications yields the following table.

**Table 2:** Estimated material balance of alcohol feed

Comp.	$i$	$f_i$ (mol/hr)	$x_{F,i}$	$d_i$ (mol/hr)	$x_{D,i}$	$b_i$ (mol/hr)	$x_{B,i}$
Methanol	1	30.0	0.300	28.5	0.960	1.5	0.021
Ethanol	2	20.0	0.200	1.2	0.040	18.8	0.267
n-Propanol	3	15.0	0.150	0.0	0.000	15.0	0.213
n-Butanol	4	35.0	0.350	0.0	0.000	35.0	0.498
$\Sigma$		100.0	1.000	29.7	1.000	70.3	1.000

The mole fractions were calculated according to,

$$D = \sum_{i=1}^{N_c} d_i \quad , \quad B = \sum_{i=1}^{N_c} b_i,$$

along with,

$$x_{D,i} = \frac{d_i}{D} \quad , \quad x_{B,i} = \frac{b_i}{B}.$$

**b.**

From the compositions, we may estimate the temperature and relative volatilities of the distillate and bottoms. For the distillate, we assume it is leaving the first stage as a saturated vapor at the dew point. Since we have a total condenser, the distillate vapor composition leaving the first stage is same as the liquid composition of the distillate stream, i.e.  $y_i = x_{D,i}$ . The dew point temperature is then estimated by applying Raoult's law,

$$y_i P = x_i P_i^{sat},$$

and summing over  $i$ ,

$$P = \frac{1}{\sum_i y_i / P_i^{sat}}.$$

Since  $P$  and  $y_i$  are known and  $P_i^{sat} = P_i^{sat}(T)$ , this is a root finding problem for  $T$ ,

$$f(T) = P - \frac{1}{\sum_i y_i / P_i^{sat}(T)} = 0.$$

Since the distillate is mostly methanol, we use an initial guess of the pure boiling point of methanol. With Newton's method, this gives  $T_{dew} = T_{dist} = 338.6 \text{ K}$ . The  $K_i$  values are then back-calculated using,

$$K_i := \frac{y_i}{x_i} = \frac{P_i^{sat}(T)}{P},$$

where  $T = T_{dew}$  for the distillate. The  $(\alpha_{i,j})_D$  values are then (finally) calculated as,

$$(\alpha_{i,j})_D = \left( \frac{K_i}{K_j} \right)_D,$$

where we use  $j = 2$  for the heavy key. The bottoms follows essentially the same procedure as the distillate except that we are now performing a bubble point calculation. We now know the liquid mole fractions,  $x_i = x_{B,i}$ , and wish to calculate  $T_{bub} = T_{btm}$ . This is again done with a summed version of Raoult's law,

$$f(T) = P - \sum_{i=1}^{N_c} x_i P_i^{sat}(T) = 0,$$

and root solving for  $T$ . As a first guess, we assume,

$$T = \sum_{i=1}^{N_c} x_i T_i^{sat},$$

using this, Newton's method then converges to  $T_{bub} = T_{btm} = 368.9 \text{ K}$ . We then back-calculate  $K_i$  and  $(\alpha_{i,j})_B$  using  $T = T_{dew}$ ,

$$K_i = \frac{P_i^{sat}(T)}{P} \quad , \quad (\alpha_{i,j})_B = \left( \frac{K_i}{K_j} \right)_B.$$

The mean relative volatility is then given by the geometric mean,

$$\alpha_{i,j} = (\alpha_{i,j})_M = \sqrt{(\alpha_{i,j})_B (\alpha_{i,j})_D}.$$

Performing all of the previously explained calculations yields the following table.

**Table 3:** Estimated thermodynamics of distillate and bottoms (Ideal)

		Distillate				Bottoms				Mean
Comp.	$i$	$y_i$	$x_i$	$K_i$	$\alpha_{ij}$	$y_i$	$x_i$	$K_i$	$\alpha_{ij}$	$(\alpha_{ij})_M$
Methanol	1	0.960	0.931	1.030	1.746	0.065	0.021	3.031	1.565	1.653
Ethanol	2	0.040	0.068	0.590	1.000	0.518	0.267	1.936	1.000	1.000
n-Propanol	3	0.000	0.000	0.260	0.442	0.202	0.213	0.947	0.489	0.465
n-Butanol	4	0.000	0.000	0.106	0.179	0.215	0.498	0.433	0.223	0.200
$\Sigma$		1.000	1.000	$T_D \text{ (K):}$	338.6	1.000	1.000	$T_B \text{ (K):}$	368.9	-

**c.**

To get a better estimate of the distribution of the feed, we use the Fenske equation to estimate  $N_{min}$ . The Fenske equation in terms of flow rates is then given as,

$$\begin{aligned} N_{min} &= \frac{\ln \left( \left[ \frac{d_1}{d_2} \right] \left[ \frac{b_2}{b_1} \right] \right)}{\ln(\alpha_{12})} \\ &= \frac{\ln \left( \left[ \frac{28.5}{1.2} \right] \left[ \frac{18.8}{1.5} \right] \right)}{\ln(1.653)} \\ &= 11.33. \end{aligned}$$

Therefore,  $\boxed{N_{min} = 11 + 1}$  stages are required at total reflux. To estimate the composition of n-propanol in the bottoms, consider a rearranged form of the Fenske equation,

$$\frac{d_i}{b_i} = \frac{d_i}{f_i - d_i} = \frac{d_2}{b_2} \alpha_{i2}^{N_{min}},$$

or solving for  $d_i$ ,

$$d_i = \frac{f_i (d_2/b_2) \alpha_{i2}^{N_{min}}}{1 + (d_2/b_2) \alpha_{i2}^{N_{min}}}.$$

Therefore, using  $i = 3$  for n-propanol,

$$d_3 = \frac{(15.0 \text{ mol/hr})(1.2/18.8)(0.465)^{11.33}}{1 + (1.2/18.8)(0.465)^{11.33}} = 1.63 \times 10^{-4} \text{ mol/hr}.$$

Therefore, practically all of the n-propanol is recovered in the bottoms. A similar calculation is performed for n-butanol with  $i = 4$ ,

$$d_4 = \frac{(35.0 \text{ mol/hr})(1.2/18.8)(0.200)^{11.33}}{1 + (1.2/18.8)(0.200)^{11.33}} = 2.71 \times 10^{-8} \text{ mol/hr}.$$

Again, practically all of the n-butanol is recovered in the bottoms. The updated distillate and bottoms compositions are then calculated by,

$$D = \sum_{i=1}^{N_c} d_i \quad , \quad B = \sum_{i=1}^{N_c} b_i \quad , \quad x_{D,i} = \frac{d_i}{D} \quad , \quad x_{B,i} = \frac{b_i}{B},$$

which yields the following table.

**Table 4:** Corrected material balance of alcohol feed (Ideal)

Comp.	$i$	$f_i$ (mol/hr)	$x_{F,i}$	$d_i$ (mol/hr)	$x_{D,i}$	$b_i$ (mol/hr)	$x_{B,i}$
Methanol	1	30.0	0.300	28.5	0.960	1.5	0.021
Ethanol	2	20.0	0.200	1.2	0.040	18.8	0.267
n-Propanol	3	15.0	0.150	1.63E-04	5.49E-06	15.0	0.213
n-Butanol	4	35.0	0.350	2.71E-08	9.12E-10	35.0	0.498
$\Sigma$		100.0	1.000	29.7	1.000	70.3	1.000

d.

The Underwood equations are given as,

$$\sum_{i=1}^{N_c} \frac{(\alpha_{ij})_{\infty} x_{F,i}}{(\alpha_{ij})_{\infty} - \theta} = 1 - q,$$

$$\sum_{i=1}^{N_c} \frac{(\alpha_{ij})_{\infty} x_{D,i}}{(\alpha_{ij})_{\infty} - \theta} = 1 + R_{min},$$

for some  $\theta$ 's satisfying  $1 < \theta < \alpha_{ij}$ . Using  $q = 1.10$ , the given  $\alpha_{ij}$ 's, and the  $x_{F,i}$ , we may set up the Underwood root finding function,

$$f(\theta) = \frac{(1.653)(0.30)}{1.653 - \theta} + \frac{(1.0)(0.20)}{1.0 - \theta} + \frac{(0.465)(0.15)}{0.465 - \theta} + \frac{(0.200)(0.15)}{0.200 - \theta} - 1 + 1.10 = 0.$$

Plotting for the initial guess.

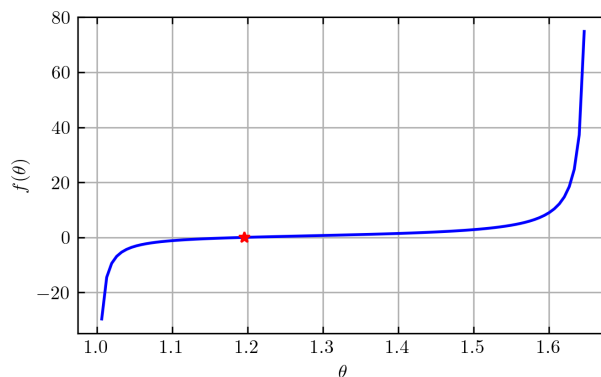


Figure 1: Graphical solution to the Underwood equation

With this, Newton's method gives  $\theta = 1.1962$ .  $R_{min}$  may now be calculated with this,

$$\begin{aligned} R_{min} &= \frac{(1.653)(0.960)}{1.653 - \theta} + \frac{(1.0)(0.040)}{1.0 - \theta} + \frac{(0.465)(5.49 \times 10^{-6})}{0.465 - \theta} + \frac{(0.200)(9.12 \times 10^{-10})}{0.200 - \theta} - 1 \\ &= \frac{(1.653)(0.960)}{1.653 - 1.196} + \frac{(1.0)(0.040)}{1.0 - 1.196} + \frac{(0.465)(5.49 \times 10^{-6})}{0.465 - 1.196} + \frac{(0.200)(9.12 \times 10^{-10})}{0.200 - 1.196} - 1 \\ &= 2.265. \end{aligned}$$

Thus, for the saturated vapor feed,  $R_{min} = 2.27$ .

The Gilliland correlation is given as,

$$Y = 1 - \exp \left( \left[ \frac{1 + 54.4X}{11 + 117.2X} \right] \left[ \frac{X - 1}{X^{0.5}} \right] \right),$$

where,

$$X = \frac{R - R_{min}}{R + 1} \quad , \quad Y = \frac{N - N_{min}}{N + 1}.$$

Since  $R = 3.0$ , we can directly calculate  $X$ ,

$$X = \frac{3.0 - 2.27}{3.0 + 1} = 0.184,$$

from which we find,  $Y = 0.475$ . Thus, we may solve for  $N$ ,

$$N = \frac{Y + N_{min}}{1 - Y} = \frac{0.475 + 11.33}{1 - 0.475} = 22.46,$$

meaning  $\boxed{N = 22 + 1}$  stages are required.

**e.**

The Kirkbride equation may now be used to estimate the feed location,  $N_F$ ,

$$\frac{N_R}{N_S} = \left[ \left( \frac{x_{HK,F}}{x_{LK,F}} \right) \left( \frac{x_{LK,B}}{x_{HK,D}} \right)^2 \left( \frac{B}{D} \right) \right]^{0.206}.$$

Numerically,

$$\frac{N_R}{N_S} = \left[ \left( \frac{0.30}{0.20} \right) \left( \frac{0.040}{0.021} \right)^2 \left( \frac{70.3}{29.7} \right) \right]^{0.206} = 0.844.$$

Since,

$$N = N_R + N_S + 1,$$

we have,

$$\frac{N - 1}{N_S} = \frac{N_R}{N_S} + 1 = 1.844,$$

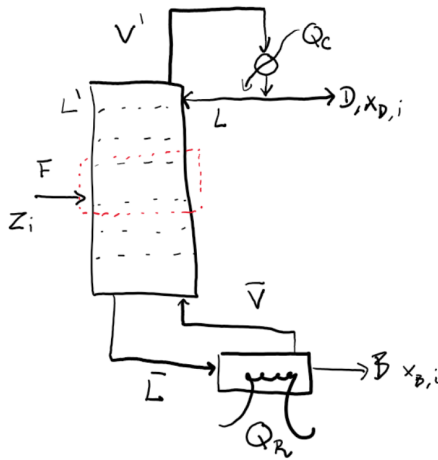
or,

$$N_S = \frac{1.844}{N - 1},$$

and since  $N = 22.46 \sim 23$ , this gives,  $N_S = 11.64 \sim 12$ , meaning,  $N_R = N - N_S - 1 = 9.83 \sim 10$ , and thus,  $\boxed{N_F = N_R + 1 = 11}$ .

2)

a.



$$P = 101.325 \text{ kPa}$$

(1) Methanol, (2) Ethanol,

(3) n - Propanol, (4) n - Butanol

$$(x_1, x_2, x_3, x_4)_F = (0.30, 0.20, 0.15, 0.35)$$

$$d_2 = 0.95 f_1$$

$$d_3 = 0.06 f_2$$

$$q = 1.10$$

$$R = 3.0$$

$$F = 100 \text{ mol/hr}$$

**Assume:** CMO, non-ideal mixture

**Solve:**

We will use the corrected material balance (Table 4) from the ideal calculation as an initial guess of the distribution of the components.

b.

For the improved thermodynamic model, the Soave-Redlich-Kwong (SRK) equation of state was used with van der Waals mixing rules. For an overview on the implementation of this, refer to the appendix.

From the compositions, we may estimate the temperature and relative volatilities of the distillate and bottoms. For the distillate, we assume it is leaving the first stage as a saturated vapor at the dew point. Since we have a total condenser, the distillate vapor composition leaving the first stage is same as the liquid composition of the distillate stream, i.e.  $y_i = x_{D,i}$ . The bottoms follows essentially the same procedure as the distillate except that we are now performing a bubble point calculation. We now know the liquid mole fractions,  $x_i = x_{B,i}$ , and wish to calculate  $T_{bub} = T_{btm}$ . As an initial guess for the SRK solver, the ideal compositions and temperatures were used. Running the solver yields the results in the following table.

**Table 5:** Estimated thermodynamics of distillate and bottoms (SRK)

		Distillate				Bottoms				Mean
Comp.	$i$	$y_i$	$x_i$	$K_i$	$\alpha_{ij}$	$y_i$	$x_i$	$K_i$	$\alpha_{ij}$	$(\alpha_{ij})_M$
Methanol	1	0.931	0.937	1.024	1.604	0.069	0.021	3.238	1.713	1.658
Ethanol	2	0.068	0.063	0.639	1.000	0.505	0.267	1.890	1.000	1.000
n-Propanol	3	5.49E-06	1.61E-05	0.340	0.532	0.201	0.213	0.940	0.498	0.514
n-Butanol	4	9.12E-10	4.94E-09	0.185	0.289	0.225	0.498	0.452	0.239	0.263
$\Sigma$		1.000	1.000	$T_D$ (K):	339.1	1.000	1.000	$T_B$ (K):	368.5	-

**c.**

To get a better estimate of the distribution of the feed, we use the Fenske equation to estimate  $N_{min}$ . The Fenske equation in terms of flow rates is then given as,

$$\begin{aligned}
 N_{min} &= \frac{\ln \left( \left[ \frac{d_1}{d_2} \right] \left[ \frac{b_2}{b_1} \right] \right)}{\ln(\alpha_{12})} \\
 &= \frac{\ln \left( \left[ \frac{28.5}{1.2} \right] \left[ \frac{18.8}{1.5} \right] \right)}{\ln(1.658)} \\
 &= 11.28.
 \end{aligned}$$

Therefore,  $\boxed{N_{min} = 11 + 1}$  stages are required at total reflux. To estimate the composition of n-propanol in the bottoms, consider a rearranged form of the Fenske equation,

$$d_i = \frac{f_i(d_2/b_2)\alpha_{i2}^{N_{min}}}{1 + (d_2/b_2)\alpha_{i2}^{N_{min}}}.$$

Therefore, using  $i = 3$  for n-propanol,

$$d_3 = \frac{(15.0 \text{ mol/hr})(1.2/18.8)(0.532)^{11.28}}{1 + (1.2/18.8)(0.532)^{11.28}} = 1.80 \times 10^{-5} \text{ mol/hr.}$$

Therefore, practically all of the n-propanol is recovered in the bottoms. A similar calculation is performed for n-butanol with  $i = 4$ ,

$$d_4 = \frac{(35.0 \text{ mol/hr})(1.2/18.8)(0.200)^{11.28}}{1 + (1.2/18.8)(0.200)^{11.28}} = 2.18 \times 10^{-8} \text{ mol/hr.}$$

Again, practically all of the n-butanol is recovered in the bottoms. The updated distillate and bottoms compositions are then calculated by,

$$D = \sum_{i=1}^{N_c} d_i \quad , \quad B = \sum_{i=1}^{N_c} b_i \quad , \quad x_{D,i} = \frac{d_i}{D} \quad , \quad x_{B,i} = \frac{b_i}{B},$$



which yields the following table.

**Table 6:** Corrected material balance of alcohol feed (SRK)

Comp.	$i$	$f_i$ (mol/hr)	$x_{F,i}$	$d_i$ (mol/hr)	$x_{D,i}$	$b_i$ (mol/hr)	$x_{B,i}$
Methanol	1	30.0	0.300	28.5	0.960	1.5	0.021
Ethanol	2	20.0	0.200	1.2	0.040	18.8	0.267
n-Propanol	3	15.0	0.150	5.36E-04	1.80E-05	15.0	0.213
n-Butanol	4	35.0	0.350	6.49E-07	2.18E-08	35.0	0.498
$\Sigma$		100.0	1.000	29.7	1.000	70.3	1.000

d.

Using  $q = 1.10$ , the given  $\alpha_{ij}$ 's, and the  $x_{F,i}$ , we may set up the Underwood root finding function,

$$f(\theta) = \frac{(1.658)(0.30)}{1.658 - \theta} + \frac{(1.0)(0.20)}{1.0 - \theta} + \frac{(0.514)(0.15)}{0.514 - \theta} + \frac{(0.263)(0.15)}{0.263 - \theta} - 1 + 1.10 = 0.$$

Plotting for the initial guess.

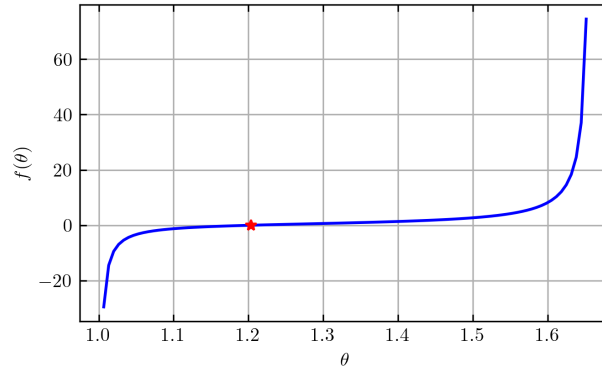


Figure 2: Graphical solution to the Underwood equation

With this, Newton's method gives  $\theta = 1.2032$ .  $R_{min}$  may now be calculated with this,

$$\begin{aligned} R_{min} &= \frac{(1.658)(0.96)}{1.658 - \theta} + \frac{(1.0)(0.04)}{1.0 - \theta} + \frac{(0.514)(1.80 \times 10^{-5})}{0.514 - \theta} + \frac{(0.263)(2.18 \times 10^{-8})}{0.263 - \theta} - 1 \\ &= \frac{(1.658)(0.96)}{1.658 - 1.203} + \frac{(1.0)(0.04)}{1.0 - 1.203} + \frac{(0.514)(1.80 \times 10^{-5})}{0.514 - 1.203} + \frac{(0.263)(2.18 \times 10^{-8})}{0.263 - 1.203} - 1 \\ &= 2.300. \end{aligned}$$

Thus, for the saturated vapor feed,  $R_{min} = 2.30$ .

Since  $R = 3.0$ , we can directly calculate  $X$  for the Gilliland correlation,

$$X = \frac{3.0 - 2.30}{3.0 + 1} = 0.175,$$

from which we find,  $Y = 0.482$ . Thus, we may solve for  $N$ ,

$$N = \frac{Y + N_{min}}{1 - Y} = \frac{0.482 + 11.28}{1 - 0.482} = 22.70,$$

meaning  $\boxed{N = 22 + 1}$  stages are required.

**e.**

The Kirkbride equation may now be used to estimate the feed location,  $N_F$ ,

$$\frac{N_R}{N_S} = \left[ \left( \frac{x_{HK,F}}{x_{LK,F}} \right) \left( \frac{x_{LK,B}}{x_{HK,D}} \right)^2 \left( \frac{B}{D} \right) \right]^{0.206}.$$

Numerically,

$$\frac{N_R}{N_S} = \left[ \left( \frac{0.30}{0.20} \right) \left( \frac{0.040}{0.021} \right)^2 \left( \frac{70.3}{29.7} \right) \right]^{0.206} = 0.844.$$

Since,

$$N = N_R + N_S + 1,$$

we have,

$$\frac{N - 1}{N_S} = \frac{N_R}{N_S} + 1 = 1.844,$$

or,

$$N_S = \frac{1.844}{N - 1},$$

and since  $N = 22.70 \sim 23$ , this gives,  $N_S = 11.77 \sim 12$ , meaning,  $N_R = N - N_S - 1 = 9.94 \sim 10$ , and thus,  $\boxed{N_F = N_R + 1 = 11}$ .

## Comparison of Results

The results predicted by the Raoult's law and the SRK equation are nearly the same. Of course, the thermodynamics changed *slightly* with the  $\alpha_{i,j}$  values, but this was not even enough to appreciably change  $N_{min}$ ,  $R_{min}$ , or  $N$ . Perhaps this is because the SRK equation is not capturing the non-ideality of the liquid in the system; inclusion of activity coefficients will likely give better results. - Was it worth the effort? Absolutely not! <sup>2</sup> However, at least I have a SRK K-value solver now, not a bad thing to have.

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<sup>2</sup>If you cannot tell, I was a little disappointed...

# Appendix

## Cubic EOS VLE

A general cubic EOS may be used to predict VLE based on the following equations <sup>3</sup>.

13.7. VLE from Cubic Equations of State

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**Table 13.9: VLE Calculations Based on Equations of State**

<b>A. Mixing and combining rules. Liquid phase.</b>	
$a^l = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2} \quad (i = j = 1, 2, \dots, N)$	
$b^l = \sum_i x_i b_i \quad (i = 1, 2, \dots, N)$	
2 equations; 2 variables: $a^l, b^l$	
<b>B. Mixing and combining rules. Vapor phase.</b>	
$a^v = \sum_i \sum_j y_i y_j (a_i a_j)^{1/2} \quad (i = j = 1, 2, \dots, N)$	
$b^v = \sum_i y_i b_i \quad (i = 1, 2, \dots, N)$	
2 equations; 2 variables: $a^v, b^v$	
<b>C. Dimensionless parameters. Liquid phase.</b>	
$\beta^l = b^l P / (RT) \quad q^l = a^l / (b^l RT)$	
$\bar{q}_i^l = q^l \left( 1 + \frac{\bar{a}_i^l}{a^l} - \frac{b_i}{b^l} \right) \quad (i = 1, 2, \dots, N)$	
2 + N equations; 2 + N variables: $b^l, q^l, \{\bar{q}_i^l\}$	
<b>D. Dimensionless parameters. Vapor phase.</b>	
$\beta^v = b^v P / (RT) \quad q^v = a^v / (b^v RT)$	
$\bar{q}_i^v = q^v \left( 1 + \frac{\bar{a}_i^v}{a^v} - \frac{b_i}{b^v} \right) \quad (i = 1, 2, \dots, N)$	
2 + N equations; 2 + N variables: $b^v, q^v, \{\bar{q}_i^v\}$	
<b>E. Equilibrium and related equations.</b>	
$y_i \hat{\phi}_i^v = x_i \hat{\phi}_i^l \quad (i = 1, 2, \dots, N)$	
$\ln \hat{\phi}_i^l = \frac{b_i}{b^l} (Z^l - 1) - \ln(Z^l - \beta^l) - \bar{q}_i^l I^l \quad (i = 1, 2, \dots, N)$	
$\ln \hat{\phi}_i^v = \frac{b_i}{b^v} (Z^v - 1) - \ln(Z^v - \beta^v) - \bar{q}_i^v I^v \quad (i = 1, 2, \dots, N)$	
$Z^p = 1 + \beta^p - q^p \beta^p \frac{Z^p - \beta^p}{(Z + \epsilon \beta^p)(Z + \sigma \beta^p)} \quad (p = v, l)$	
$I^p = \frac{1}{\sigma - \epsilon} \ln \left( \frac{Z^p + \sigma \beta^p}{Z^p + \epsilon \beta^p} \right) \quad (p = v, l)$	
4 + 3N equations; 4 + 2N variables: $\{\hat{\phi}_i^v\}, \{\hat{\phi}_i^l\}, I^l, Z^l, I^v, Z^v$	

<sup>3</sup>Smith, J.M., Van Ness, H.C., Abbot, M. M., Swihart, M. T., *Introduction to Chemical Engineering Thermodynamics*. 9th Ed., McGraw Hill, 2018.

In this assignment, the Soave-Redlich-Kwong equation was used which has  $\varepsilon = 0$  and  $\sigma = 1$ . Given the previous relations, we are left with  $N_c + 1$  unknowns to solve for, namely the liquid or vapor compositions and the temperature. Thus, we must supply  $N_c + 1$  equations. The first  $N_c$  equations come from the equilibrium constraints,

$$y_i - K_i x_i = 0,$$

where,

$$K_i = \frac{\hat{\phi}_i^L}{\hat{\phi}_i^V}.$$

The last equation comes from the material balance, stating that the mole fractions sum to 1,

$$1 - \sum_{i=1}^{N_c} K_i x_i = 0.$$

This constitutes a non-linear system of algebraic equations, we thus form a vector objective function,  $\mathbf{F}$ ,

$$\mathbf{F}(\mathbf{x}) = \mathbf{0},$$

where the first  $N_c$  components of  $\mathbf{F}$  are the equilibrium constraints and the last component is the material balance constraint. The unknown vector,  $\mathbf{x}$ , is given as,

$$\mathbf{x} = \begin{pmatrix} z_i \\ \vdots \\ z_{N_c} \\ T \end{pmatrix},$$

where the  $z_i$  are the liquid or vapor mole fractions depending on if a bubble or dew point calculation is being made. This system can be solved using MATLAB or Python's 'fsolve' function (or Excel's Goal Seek if you're feeling adventurous) which essentially solves the minimization problem <sup>4</sup>,

$$\arg \min_{\mathbf{x}} \|\mathbf{F}(\mathbf{x})\|^2,$$

by using successive quadratic approximations of  $\mathbf{F}$ . The results of the coded function were validated using the following online calculator:

<https://pjb10.user.srcf.net/thermo/mixture.html>.

A Python implementation of this algorithm is presented as follows.

---

<sup>4</sup>fsolve is essentially a beefed up Newton solver for multidimensional systems. I won't pretend like I know all the details, but it generally follows the 1D Newton algorithm, replacing the function derivative with a Jacobian approximation.

```

import numpy as np
from scipy.optimize import fsolve
from scipy.optimize import root_scalar
import matplotlib.pyplot as plt

# Auxiliary functions for cubic VLE calculations
def a_lv(x,a):
    xx = np.outer(x,x)
    aa = np.sqrt(np.outer(a,a))
    return np.sum(xx*aa)

def b_lv(x,b): return np.dot(x,b)

def beta_lv(b,P,R,T): return b*P/(R*T)

def q_lv(a_lv,b_lv,R,T): return a_lv/(b_lv*R*T)

def q_bar_lv(x,a,b,R,T,a_lv,b_lv,q_lv):
    aa = np.outer(a,a)**0.5
    for i in range(np.size(a)):
        aa[i,i] = 0
    a_bar = 2*aa*x + 2*a*x
    return q_lv*(a_bar/a_lv-b/b_lv)

def I_lv(sigma,eps,Z,beta):
    ans = np.log((Z+sigma*beta)/(Z+eps*beta))/(sigma-eps)
    return ans

def phi_lv(b,q,Z,beta,I,b_lv):
    ans = np.exp(b*(Z-1)/b_lv - np.log(Z-beta) - q*I)
    return ans

def Z_coeffs(beta,sigma,eps,q):
    ans = [1,beta*(sigma+eps)-(1+beta),
            (sigma*eps*beta+q-(1+beta)*(sigma+eps))*beta,
            -sigma*eps*beta**2*(1+beta)-q*beta**2]
    return ans

# -----
# Patrick Heng
# 03/21/25
# Objective function to find bubble point composition and temperature given
# liquid mole fractions and pressure
#
# INPUTS:
# XX: unknown vector, i.e. F(XX) = 0
# x: liquid phase mole fraction, vector
# P: system pressure, scalar
# w, Tc, Pc: critical constants, vectors
# R: Gas constant given in a consistent set of units, scalar
# optional:
# Omega, Psi, sigma, eps: Cubic EOS parameters, default are for SRK
# equation
# OUTPUTS:
# F: solution vector, first N components being the equilibrium constraints
# and the last component being the material balance constraint
#
# To get solution vector:
# sol = fsolve(obj_func_bub,x0=x0,args=(x,P,w,Tc,Pc,R))
# where x0 is the initial guess
# -----

def obj_func_bub(XX,x,P,w,Tc,Pc,R,Omega=0.08664,Psi=0.42748,sigma=1,eps=0):

    # Get physical variables from input vector
    N = np.size(x)
    y = XX[0:N]
    T = XX[-1]

    # Compute cubic EOS parameters
    b = Omega*R*Tc/Pc
    b1 = np.dot(x,b)
    a = Psi*(R**2*Tc**2/Pc)*(1+(0.480+1.574*w-0.176*w**2)*(1-(T/Tc)**0.5))**2
    al = a_lv(x,a)
    bl = np.dot(x,b)
    av = a_lv(y,a)
    bv = b_lv(y,b)
    ql = q_lv(al,b1,R,T)
    qv = q_lv(av,bv,R,T)
    betal = beta_lv(bl,P,R,T)

```

```

betav = beta_lv(bv,P,R,T)
q_bar_l = q_bar_lv(x,a,b,R,T,al,b1,q1)
q_bar_v = q_bar_lv(y,a,b,R,T,av,bv,qv)

# Compute cubic roots
# Zl -> liquid -> smallest root
coeffs = Z_coeffs(betal,sigma,eps,q1)
sol = np.roots(coeffs)
sol = np.min(sol[sol>0])
Zl = sol
# Zv -> vapor -> largest root
coeffs = Z_coeffs(betav,sigma,eps,qv)
sol = np.roots(coeffs)
sol = np.max(np.roots(coeffs))
Zv = sol

# More cubic EOS parameters...
Il = I_lv(sigma,eps,Zl,betal)
Iv = I_lv(sigma,eps,Zv,betav)
# Compute fugacities
phi_l = phi_lv(b,q_bar_l,Zl,betal,Il,b1)
phi_v = phi_lv(b,q_bar_v,Zv,betav,Iv,bv)
# Compute K values from fugacities (finally)
K = phi_l/phi_v

# Return equilibrium constraints
F = np.zeros(N+1)
F[0:N] = y-K*x
F[-1] = 1 - np.sum(K*x)
return F
# -----
# Patrick Heng
# 03/21/25
# Objective function to find dew point composition and temperature given
# vapor mole fractions and pressure
#
# INPUTS:
#     XX: unknown vector, i.e. F(XX) = 0
#     y: vapor phase mole fraction, vector
#     P: system pressure, scalar
#     w, Tc, Pc: critical constants, vectors
#     R: Gas constant given in a consistent set of units, scalar
#     optional:
#     Omega, Psi, sigma, eps: Cubic EOS parameters, default are for SRK
#                               equation
#
# OUTPUTS:
#     F: solution vector, first N components being the equilibrium constraints
#       and the last component being the material balance constraint
#
# To get solution vector:
#     sol = fsolve(obj_func_dew,x0=x0,args=(y,P,w,Tc,Pc,R))
# where x0 is the initial guess
# -----

def obj_func_dew(XX,y,P,w,Tc,Pc,R,Omega=0.08664,Psi=0.42748,sigma=1,eps=0):

    # Get physcial variables from input vector
    N = np.size(y)
    x = XX[0:N]
    T = XX[-1]

    # Compute cubic EOS parameters
    b = Omega*R*Tc/Pc
    b1 = np.dot(x,b)
    a = Psi*(R**2*Tc**2/Pc)*(1+(0.480+1.574*w-0.176*w**2)*(1-(T/Tc)**0.5))**2
    al = a_lv(x,a)
    b1 = np.dot(x,b)
    av = a_lv(y,a)
    bv = b_lv(y,b)
    q1 = q_lv(al,b1,R,T)
    qv = q_lv(av,bv,R,T)
    betal = beta_lv(b1,P,R,T)
    betav = beta_lv(bv,P,R,T)
    q_bar_l = q_bar_lv(x,a,b,R,T,al,b1,q1)
    q_bar_v = q_bar_lv(y,a,b,R,T,av,bv,qv)

    # Compute cubic roots
    # Zl -> liquid -> smallest root
    coeffs = Z_coeffs(betal,sigma,eps,q1)
    sol = np.roots(coeffs)

```

```

sol = np.min(sol[sol>0])
Zl = sol
# Zv -> vapor -> largest root
coeffs = Z_coeffs(betav,sigma,eps,qv)
sol = np.max(np.roots(coeffs))
Zv = sol

# More cubic EOS parameters...
Il = I_lv(sigma,eps,Zl,betal)
Iv = I_lv(sigma,eps,Zv,betav)
# Compute fugacities
phi_l = phi_lv(b,q_bar_l,Zl,betal,Il,b1)
phi_v = phi_lv(b,q_bar_v,Zv,betav,Iv,bv)
# Compute K values from fugacities (finally)
K = phi_l/phi_v

# Return equilibrium constraints
F = np.zeros(N+1)
F[0:N] = y-K*x
F[-1] = 1 - np.sum(y/K)
return F

```

### Example:

An example of the calculation of dew point K-values is shown as follows.

```

P = 101325 # Pa
Rg = 8.314 # J/mol-K

# Critical constants
Pc = np.array([80.97,61.48,51.75,44.23])*10**5 # Pa
Tc = np.array([512.6,513.9,536.8,563.1]) # K
w = np.array([0.564,0.645,0.622,0.594])

F = 100 # mol/hr
xF = np.array([0.30,0.20,0.15,0.35])

# LK, HK indices
LK = 0
HK = 1

# Feed flows
f = F*xF
# Initial guess at distillate flows, traces set to 1e-6*feed to allow for
# computation of K values for these components
d = np.array([0.95*f[0],0.06*f[1],1e-6*f[2],1e-6*f[3]])
b = f - d

# Initial mole fraction guess
xD = d/np.sum(d)
xB = b/np.sum(b)

N = np.size(x)

# Set up objective function for non-ideal system
T = dew_pt_T # (Calculated from Raoult's law)
y = xD
# Initial guess vector
x0 = np.zeros(N+1)
x0[0:N] = x # (Liquid composition calculated from Raoult's law)
x0[-1] = T
# Predict non-ideal compositions using SRK EOS
sol = fsolve(obj_func_dew,x0=x0,args=(y,P,w,Tc,Pc,Rg))
x = sol[0:N]
T = sol[-1]
K = y/x
a_ij_D = K/K[HK]

print('\n')
print('SRK Predicted Distillate VLE')
print('x = ')
print(x)
print('K = ')
print(K)
print('a_ij_D = ')
print(a_ij_D)
print('T = %0.3f' % T)

```