

Chapter 2

The Equilibrium Stage

Problem Solutions

2.1 A hydrocarbon stream is separated into vapor and liquid streams in a flash drum maintained at 27°C and 1035 kPa. The feed composition and component K -values (assumed composition-independent) are given below. Calculate the vapor rate as a fraction of the feed, and the vapor and liquid compositions.

i	Component	Z_i	K_i
1	Ethane	0.40	2.90
2	Propane	0.35	0.95
3	n-Butane	0.15	0.33
4	n-Pentane	0.10	0.11

Solution

Equation 2.14 is solved for the vapor fraction ψ by trial and error:

i	Z_i	K_i	$f(\psi)$		
			$\psi=0.5$	$\psi=0.6$	$\psi=0.575$
1	0.40	2.90	0.3897	0.3551	0.3632
2	0.35	0.95	-0.0179	-0.0180	-0.0180
3	0.15	0.33	-0.1511	-0.1681	-0.1635
4	0.10	0.11	-0.1604	-0.1910	-0.1823
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	1.00		0.0603	-0.0220	-0.0006

The third trial, $\psi=0.575$, is determined by linear interpolation between $\psi=0.5$ and $\psi=0.6$ for $f(\psi)=0$. The calculated result is within acceptable tolerance. Equations 2.13a and 2.13b are now used to calculate X_i and Y_i :

i	Z_i	K_i	X_i	Y_i
1	0.40	2.90	0.1912	0.5544
2	0.35	0.95	0.3604	0.3423
3	0.15	0.33	0.2440	0.0805
4	0.10	0.11	0.2048	0.0225
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	1.00		1.0004	0.9997

2.2 A stream containing ethane, butane, and pentane is fed to a temperature-controlled vessel where phase separation takes place between the vapor and the liquid. The vessel pressure is maintained at 690 kPa. The K -values, assumed composition-independent, are given by the equation

$$\ln K_i = A_i - B_i/(1.8T + C_i)$$

where T is in degrees Kelvin. The feed composition and the equation constants are given below:

		<u>Z_i</u>	<u>A_i</u>	<u>B_i</u>	<u>C_i</u>
1	Ethane	0.27	5.75	2155	-30.3
2	n-Butane	0.34	6.21	3386	-60.1
3	n-Pentane	0.39	6.52	3973	-72.9

Determine the bubble point and dew point temperatures at 690 kPa, and the vapor fraction and temperature that results in a maximum n-butane mole fraction in the vapor.

Solution

The bubble point and dew point are calculated from Equations 2.16 and 2.17 by iterating on the temperature. After two trials, subsequent trials may be determined by linear interpolation or extrapolation.

Bubble point: $\sum K_i Z_i = 1$

i	Z_i	<u>$T=278K$</u>		<u>$T=283K$</u>		<u>$T=279K$</u>	
		K_i	$K_i Z_i$	K_i	$K_i Z_i$	K_i	Z_i
1	0.27	3.1962	0.8630	3.5170	0.9496	3.2906	0.8885
2	0.34	0.2260	0.0768	0.2682	0.0912	0.2381	0.0810
3	0.39	0.0619	0.0241	0.0766	0.0299	0.0660	0.0258
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	1.00		0.9639		1.0707		0.9953

Dew point: $\sum (Z_i/K_i) = 1$

i	Z_i	<u>$T=350K$</u>		<u>$T=356K$</u>		<u>$T=351K$</u>	
		K_i	Z_i/K_i	K_i	Z_i/K_i	K_i	Z_i/K_i
1	0.27	8.6412	0.0312	9.1658	0.0295	8.6930	0.0311
2	0.34	1.3081	0.2599	1.4493	0.2346	1.3218	0.2572
3	0.39	0.5425	0.7189	0.6152	0.6339	0.5495	0.7098
	-----		-----		-----		-----
	1.00		1.0100		0.8980		0.9981

The vapor fraction and temperature that maximize the n-butane mole fraction in the vapor are determined by carrying out flash calculations at increments of the vapor fraction ψ . At each ψ , the temperature is determined that satisfies Equation 2.14. For each vapor fraction, the temperature is calculated iteratively. After two trials, subsequent trials are determined by linear interpolation or extrapolation. The liquid and vapor compositions are calculated by Equations 2.13a and 2.13b.

$\psi=0.20$									
i	Z_i	$T=311\text{K}$		$T=306\text{K}$		$T=304\text{K}$		$T=304\text{K}$	
		K_i	$f(\psi)$	K_i	$f(\psi)$	K_i	$f(\psi)$	X_i	Y_i
1	0.27	5.3745	0.6300	4.9698	0.5975	4.8908	0.5908	0.1518	0.7424
2	0.34	0.5693	-.1602	0.4958	-.1907	0.4819	-.1965	0.3793	0.1828
3	0.39	0.1947	-.3744	0.1641	-.3914	0.1584	-.3947	0.4689	0.0742
1.00		0.0954		0.0154		0.0004		1.0000	0.9995
$\psi=0.40$									
i	Z_i	$T=322\text{K}$		$T=324\text{K}$		$T=325\text{K}$		$T=325\text{K}$	
		K_i	$f(\psi)$	K_i	$f(\psi)$	K_i	$f(\psi)$	X_i	Y_i
1	0.27	6.2319	0.4567	6.4109	0.4617	6.4560	0.4629	0.0848	0.5475
2	0.34	0.7388	-.0992	0.7764	-.0835	0.7860	-.0796	0.3718	0.2922
3	0.39	0.2685	-.4033	0.2855	-.3902	0.2899	-.3868	0.5447	0.1579
1.00		-.0458		-.0120		-.0035		1.0013	0.9976
$\psi=0.60$									
i	Z_i	$T=333\text{K}$		$T=339\text{K}$		$T=337\text{K}$		$T=337\text{K}$	
		K_i	$f(\psi)$	K_i	$f(\psi)$	K_i	$f(\psi)$	X_i	Y_i
1	0.27	7.1514	0.3541	7.6336	0.3596	7.4874	0.3580	0.0552	0.4133
2	0.34	0.9403	-.0210	1.0539	0.0178	1.0189	0.0064	0.3362	0.3426
3	0.39	0.3615	-.4037	0.4160	-.3506	0.3990	-.3666	0.6099	0.2434
1.00		-.0706		0.0268		-.0022		1.0013	0.9993
$\psi=0.80$									
i	Z_i	$T=344\text{K}$		$T=350\text{K}$		$T=345\text{K}$		$T=345\text{K}$	
		K_i	$f(\psi)$	K_i	$f(\psi)$	K_i	$f(\psi)$	X_i	Y_i
1	0.27	8.1303	0.2872	8.6412	0.2901	8.1808	0.2875	0.0400	0.3272
2	0.34	1.1764	0.0526	1.3081	0.0840	1.1892	0.0559	0.2953	0.3512
3	0.39	0.4762	-.3516	0.5425	-.2814	0.4825	-.3444	0.6655	0.3211
1.00		-.0118		0.0927		-.0010		1.0008	0.9995

The n-butane mole fraction in the vapor is at a maximum of about 0.35 at around 345K and a vapor fraction of 0.80.

2.3 The starting conditions of a given hydrocarbon stream are 38°C and 690 kPa. The stream is heated in an exchanger where 23,200 kJ/kmol are transferred to the stream. Calculate the temperature, vapor fraction, and vapor and liquid compositions at the exchanger outlet. Assume the pressure remains constant at 690 kPa. Stream composition:

		Z_i
1	Ethane	0.25
2	n-Butane	0.35
3	n-Pentane	0.40

Use the K -values given in Problem 2.2. The enthalpies may be calculated on the assumption of ideal solution (zero excess enthalpy). The following data are given for the component enthalpies: $H(\text{kJ/kmol}) = 2.32[a + b(1.8T(^{\circ}\text{C}) + 32)]$

		<u>Liquid</u>		<u>Vapor</u>	
		a	b	a	b
1	Ethane	2160	22.0	7200	13.5
2	n-Butane	2668	32.5	12590	20.0
3	n-Pentane	2880	40.0	15150	28.5

Solution

Calculate the phase separation and enthalpy of the inlet stream at 38°C and 690 kPa. Solve Equation 2.14 for ψ and Equations 2.13a and 2.13b for X_i and Y_i .

i	Z_i	K_i	<u>$f(\psi)$</u>			<u>$\psi=0.22$</u>	
			$\psi=0.3$	$\psi=0.2$	$\psi=0.22$	X_i	Y_i
1	0.25	5.3745	0.4729	0.5833	0.5573	0.1274	0.6847
2	0.35	0.5693	-.1731	-.1650	-.1665	0.3866	0.2201
3	0.40	0.1947	-.4247	-.3840	-.3915	0.4861	0.0946
1.00			-.1249	0.0343	-.0007	1.0001	0.9994

The inlet enthalpy, using the given equation at 38°C, and assuming $H^{ex} = 0$,

$$H_{\text{in}} = 16,692 \text{ kJ/kmol}$$

The outlet enthalpy:

$$H_{\text{out}} = 16,692 + 23,200 = 39,892 \text{ kJ/kmol}$$

The outlet temperature is calculated iteratively: At each outlet temperature trial, a flash calculation is made to determine the phase separation and the enthalpy. The object is to match the

specified outlet enthalpy. Prior to this, a dew point calculation is made to check if the outlet stream is mixed phase or all vapor.

Dew point calculation: $\Sigma(Z_i/K_i) = 1$

<i>i</i>	<i>Z_i</i>	<i>T</i> =356 K		<i>T</i> =350 K		<i>T</i> =352 K	
		<i>K_i</i>	<i>Z_i/K_i</i>	<i>K_i</i>	<i>Z_i/K_i</i>	<i>K_i</i>	<i>Z_i/K_i</i>
1	0.25	9.1658	0.0273	8.6412	0.0289	8.7971	0.0284
2	0.35	1.4493	0.2415	1.3081	0.2676	1.3495	0.2594
3	<u>0.40</u>	0.6152	<u>0.6502</u>	0.5425	<u>0.7373</u>	0.5636	<u>0.7097</u>
	1.00		0.9190		1.0338		0.9975

The dew point temperature is $T = 352 \text{ K} = 79^\circ\text{C}$.

The enthalpy at this temperature calculated by the given enthalpy equation,

$$H = 37,199 \text{ kJ/kmol}$$

Since the specified outlet enthalpy is higher than the dew point enthalpy, the outlet stream must be superheated vapor. The outlet temperature is calculated from the enthalpy equation, rearranged:

$$T(^{\circ}\text{C}) = (H/2.32 - \Sigma Z_i a_i) / (1.8 \Sigma Z_i b_i) - 18 = 91^{\circ}\text{C}$$

2.4 Derive equations to calculate the K -values and composition of a vapor at equilibrium with a binary liquid solution having a given composition and a given relative volatility α_{12} , or ratio of K -values. Calculate the composition of the vapor at equilibrium with a liquid having 0.40 mole fraction n-hexane and 0.60 mole fraction n-heptane. The relative volatility of n-hexane to n-heptane is 3.40.

Solution

$$X_1 + X_2 = 1$$

$$Y_1 + Y_2 = 1$$

$$K_1 = Y_1/X_1$$

$$K_2 = Y_2/X_2$$

$$\alpha_{12} = K_1/K_2$$

Substituting,

$$\begin{aligned}\alpha_{12} &= (Y_1/X_1)/(Y_2/X_2) \\ &= (X_2/X_1)(Y_1)/(1-Y_1) \\ &= (X_2/X_1)(1-Y_2)/Y_2\end{aligned}$$

Rearrange to calculate Y_1 and Y_2 :

$$Y_1 = \alpha_{12} / (X_2/X_1 + \alpha_{12})$$

$$Y_2 = X_2/X_1 / (X_2/X_1 + \alpha_{12})$$

$$K_1 = Y_1/X_1 = (\alpha_{12}/X_1) / (X_2/X_1 + \alpha_{12})$$

$$K_2 = Y_2/X_2 = (1/X_1) / (X_2/X_1 + \alpha_{12})$$

The results may be checked to verify that $Y_1 + Y_2 = 1$ and $\alpha_{12} = K_1/K_2$. For the n-hexane and n-heptane mixture,

$$Y_1 = 3.40/(0.6/0.4 + 3.40) = 0.6939$$

$$Y_2 = (0.6/0.4)/(0.6/0.4 + 3.40) = 0.3061$$

$$K_1 = 0.6939/0.4 = 1.7348$$

$$K_2 = 0.3061/0.6 = 0.5102$$

2.5 A vapor mixture of n-hexane, n-heptane, and water is condensed at 100 kPa. The hydrocarbon K -values are given by the equation

$$\ln K_i = A_i - B_i/1.8T$$

where T is in degrees Kelvin. The mixture composition and the values of the constants are as follows:

		Z_i	A_i	B_i
1	n-Hexane	0.62	11.08	6821
2	n-Heptane	0.05	11.29	7545
3	Water	0.33	—	—

Assuming water and the hydrocarbons are immiscible,

- Calculate the water and hydrocarbon dew point temperatures and equilibrium compositions.
- Outline an algorithm for calculating the temperature and phase compositions of a hydrocarbon–water mixture at given total pressure P , when the fraction of the hydrocarbons condensed is β . Assume composition-independent K -values. Do the calculations for $P=100$ kPa, $\beta=0.5$.

Solution

a. The water dew point occurs when its partial pressure equals its vapor pressure. The hydrocarbon dew point occurs when $\sum Y_i/K_i = 1$. Depending on the overall composition and the K -values, the water dew point may be either higher or lower than the hydrocarbon dew point. The dew point that occurs at the higher temperature is calculated on the basis that the total mixture is in the vapor phase.

If the water dew point is at the higher temperature, then

$$p_3^0 = Y_3 P = (0.33)(100) = 33 \text{ kPa}$$

The water dew point is the saturation temperature at this pressure, obtained from the steam tables, $T = 72.7^\circ\text{C}$ (345.9 K). If the hydrocarbon dew point is the higher temperature, it is calculated iteratively as follows:

i		Z_i	$T=333.3 \text{ K}$		$T=334.4 \text{ K}$		$T=333.4 \text{ K}$	
			K_i	Z_i/K_i	K_i	Z_i/K_i	K_i	Z_i/K_i
1	n-hexane	0.62	0.7495	0.8272	0.7784	0.7965	0.7524	0.8240
2	n-heptane	0.05	0.2767	0.1807	0.2885	0.1733	0.2778	0.1800
3	water	0.33	---	0.0*	---	0.0*	---	0.0*

1.00

1.0067

0.9698

1.0040

* Since water is assumed insoluble in the hydrocarbon liquid, its K-value is taken as infinity.

The calculated hydrocarbon dew point is 333.4 K = 60.2°C. However, since this temperature is lower than the water dew point, some water would have condensed, and the hydrocarbon dew point must be calculated based on the corrected vapor composition.

At 60.2°C (333.4K) the vapor pressure of water is 20.1 kPa. The water mole fraction in the vapor,

$$Y_3 = 20.1/100 = 0.201$$

The hydrocarbon mole fraction,

$$Y_1 + Y_2 = 1 - 0.201 = 0.799$$

$$Y_1 = Z_1/(Z_1 + Z_2) (0.799) = (0.62)(0.799)/(0.62 + 0.05) = 0.739$$

$$Y_2 = (0.05)(0.799)/(0.62 + 0.05) = 0.0596$$

The results are tabulated below. Iterating on the temperature, the hydrocarbon dew point is 337.3K (64.1°C).

		$T=337.3\text{K}; p_3^0 = 24.05 \text{ kPa}$		
i		Y_i	K_i	Y_i/K_i
1	n-hexane	0.7056	0.8561	0.8242
2	n-heptane	0.0569	0.3205	0.1775
3	water	0.2375	---	0.0
		1.0000		1.0017

b. Given the total pressure P (assumed constant), the total mixture moles N , and the overall composition:

$Z_i \quad i = 1, \dots, C$ Hydrocarbon mole fractions

Z_w Water mole fraction

Assume immiscible liquids, and composition-independent K -values.

1. Calculate the total hydrocarbon mole fraction:

$$Z_C = \sum Z_i \quad i = 1, \dots, C$$

$$Z_C + Z_w = 1$$

The hydrocarbon liquid moles are calculated from β , the specified fraction of the hydrocarbons condensed:

$$N_{LC} = NZ_C \beta$$

The hydrocarbon vapor moles:

$$N_{VC} = NZ_C (1 - \beta)$$

2. Assume temperature T .

3. Determine p_w^0 , the vapor pressure of water at T (from steam tables).

4. Calculate the saturation water mole fraction in the vapor:

$$Y_w^s = p_w^0 / P$$

5. If $Y_w^s \geq Z_w$, there is no liquid water.

Water vapor moles, $N_{Vw} = NZ_w$

Water liquid moles, $N_{Lw} = 0$

If $Y_w^s < Z_w$, liquid water exists. If N_V is the total number of vapor moles, then the number of water vapor moles is

$$N_{Vw} = N_V Y_w^s$$

The number of hydrocarbon vapor moles,

$$N_{VC} = N_V (1 - Y_w^s)$$

Eliminating N_V ,

$$N_{Vw} = N_{VC} Y_w^s / (1 - Y_w^s)$$

The number of water liquid moles,

$$N_{Lw} = NZ_w - N_{Vw}$$

6. Calculate the overall composition on a liquid water-free basis:

$$Z_i' = NZ_i / (N - N_{Lw}) \quad i = 1, \dots, C$$

$$Z_w' = N_{Vw} / (N - N_{Lw})$$

7. Calculate the vapor fraction on a liquid water-free basis:

$$\psi = (N_{VC} + N_{Vw}) / (N - N_{Lw})$$

8. Calculate K_i , $i = 1, \dots, C$, at the assumed temperature. Since water is assumed insoluble in the hydrocarbon liquid, $K_w = \infty$.

9. By extending Equation 2.14 to include water, calculate $f(\psi)$:

$$f(\psi) = \sum_{i=1}^C \frac{Z'_i(K_i - 1)}{1 + \psi(K_i - 1)} + \frac{Z'_w(K_w - 1)}{1 + \psi(K_w - 1)}$$

The water term approaches the limit of Z_w/ψ as K_w goes to infinity.

10. At solution, $f(\psi) = 0$. If this is not satisfied, the problem is solved iteratively by assuming a new temperature and going back to step 2. Subsequent temperatures are estimated by some convergence technique. A simple method is to calculate the next temperature estimate by linear interpolation or extrapolation of the last two temperatures versus the calculated values of $f(\psi)$.

Once the temperature is determined, the compositions of the hydrocarbon liquid and of the vapor are calculated by Equations 2.13a and 2.13b.

With $\beta = 0.5$ and using a basis of total moles $N = 1$, the calculations proceed as follows:

$$Z_C = 0.62 + 0.05 = 0.67$$

$$N_{LC} = 1 \times 0.67 \times 0.5 = 0.335$$

$$N_{VC} = 1 \times 0.67 \times (1 - 0.5) = 0.335$$

Iterating on the temperature, convergence is reached at $T = 63.1^\circ\text{C} = 336.2\text{ K}$ where the water vapor pressure $p_3^0 = 23.07\text{ kPa}$. The saturation water mole fraction in the vapor,

$$Y_3^s = 23.07/100 = 0.2307$$

Since $Y_3^s < Z_3$, liquid water exists. The number of water vapor moles,

$$N_{V3} = 0.335 \times 0.2307 / (1 - 0.2307) = 0.1005$$

The number of water liquid moles,

$$N_{L3} = 1 \times 0.33 - 0.1005 = 0.2295$$

The overall composition on a liquid water-free basis is calculated, followed by flash calculations, giving the following results:

	Z'_i	K_i	X'_i	Y'_i
1. n-Hexane	0.80639	0.82596	0.89422	0.73858
2. n-Heptane	0.06503	0.30803	0.10669	0.03286
3. Water	0.12857	∞	0.00000	0.22785

2.6 A stream of hydrofluoric acid (1) in water (2) at 120°C and 200 kPa contains 12% mole hydrofluoric acid (HF). It is proposed to concentrate the HF in solution by partial vaporization in a single stage, by means of temperature and pressure control. Calculate the resulting liquid composition and the fraction vaporized at 120°C and 135 kPa. Can this process be used to concentrate the liquid for any starting composition? Use the van Laar equation for liquid activity coefficients and assume ideal gas behavior in the vapor phase. The vapor pressures of HF and water at 120°C are 1693 kPa and 207 kPa, respectively, and the van Laar constants are $A_{12} = -6.0983$, $A_{21} = -6.9658$ (see Problems 1.10 and 1.11).

Solution

The VLE calculations involve composition dependent K -values, and should follow a procedure similar to the basic algorithm described in Section 2.3.1 with a few modifications. In Step 1 assume the starting liquid composition to be the same as the overall composition. Calculate the K -values from the following equation, derived from Equation 1.29:

$$K_i = \gamma_i p_i^0 / P$$

The activity coefficient γ_i is calculated by Equation 1.34. Steps 4 and 5 are replaced by a check on the constancy of the K -values. If the difference from the previous iteration is greater than a certain tolerance, the calculations are restarted at Step 1 by calculating new K -values. Since the relationship between activity coefficients and composition is highly nonlinear, the liquid composition may change considerably from iteration to iteration. To stabilize the calculations, the activity coefficients may be calculated based on an average composition of the current and last iteration. The calculations are tabulated below for the first three iterations.

$$T = 120^\circ\text{C}, P = 135 \text{ kPa}$$

i		Z_i	p_i^0 (kPa)	A_{ij}
1	HF	0.12	1693	- 6.0983
2	H ₂ O	0.88	207	- 6.9658

Iteration 1

i	X_i^*	γ_i	K_i	$f(\psi)$			X_i
				$\psi=0.6$	$\psi=0.7$	$\psi=0.658$	
1	0.12	0.007697	0.0946	-0.2379	-0.2967	-0.2688	0.2968
2	0.88	0.9238	1.3875	0.2767	0.2682	0.2717	0.7012
				-----	-----	-----	-----
				0.0388	-0.0285	0.0029	0.9980

* Assume $X_i = Z_i$

Iteration 2

i	X_i^*	γ_i	K_i	$f(\psi)$			X_i
				$\psi=0.50$	$\psi=0.48$	$\psi=0.45$	
1	0.2084	0.01785	0.2193	-0.1537	-0.1498	-0.1444	0.1850
2	0.7906	0.7828	1.1758	0.1422	0.1427	0.1434	0.8155
				-----	-----	-----	-----
				-0.0115	-0.0071	-0.0010	1.0005

* Average of starting and final values in iteration 1.

Iteration 3

i	X_i^*	γ_i	K_i	$f(\psi)$		X_i
				$\psi=0.50$	$\psi=0.52$	
1	0.1967	0.0160	0.1966	-0.1611	-0.1656	0.2061
2	0.8030	0.8048	1.2088	0.1644	0.1657	0.7938
				-----	-----	-----
				0.0053	0.0001	0.9999

* Average of starting and final values in iteration 2.

If the overall HF concentration in the feed is higher than the azeotropic composition (Problem 1.10), evaporation would result in lowering the HF concentration in the liquid and raising it in the vapor.

2.7 In a single equilibrium stage absorber at 25°C and 100 kPa, water is used to reduce the amount of acetone in 1000 kmol/h air from 2% mole to 0.5% mole. Assuming the flow rates of air and water leaving the absorber to be the same as the inlets, calculate the required water flow rate. The following information may be used:

Acetone vapor pressure at 25°C = 30.5 kPa

Activity coefficient of acetone at low concentrations (infinite dilution) at 25°C = 6.5

Water vapor pressure at 25°C = 3.2 kPa

Assuming ideal gas behavior in the vapor, and that air is insoluble in water–acetone, use the calculated inlet water rate to determine the compositions of the outlet streams when the assumption of constant liquid and gas rates is dropped.

Solution

The K -value of acetone (Equation 1.29, ideal gas vapor phase, low pressure),

$$K(\text{acetone}) = \gamma p^0 / P = (6.5)(30.5) / 100 = 1.9825$$

The K -value of water ($\gamma=1$, since the liquid is almost entirely water),

$$K(\text{water}) = 3.2 / 100 = 0.032$$

Designate the liquid and gas rates, assumed constant, as L and G . By material balance on the acetone,

$$(0.0L + 0.02G)_{\text{in}} = (LX + GY)_{\text{out}}$$

$$Y = 0.005$$

$$X = Y / K(\text{acetone}) = 0.005 / 1.9825 = 0.00252$$

$$G = 1000 \text{ kmol/h}$$

$$(1000)(0.02) = 0.00252L + (0.005)(1000)$$

$$L = 5952 \text{ kmol/h}$$

The combined feed composition Z_i is computed and an isothermal flash calculation is carried out (Section 2.3.1, Equations 2.14, 2.13a, 2.13b). The K -value of air is infinity since it is assumed insoluble in the liquid. The results are tabulated as follows:

i	kgmole/hr	Z_i	K_i	$f(\psi)$			X_i	Y_i
				$\psi=0.15$	$\psi=0.145$	$\psi=0.1478$		
1 Air	980.0	0.1410	∞^*	0.9493	0.9821	0.9635	0.0000	0.9635
2 Acetone	20.0	0.0029	1.9825	0.0024	0.0024	0.0024	0.0025	0.0049
3 Water	5952.0	0.8561	0.0320	-0.9684	-0.9629	-0.9659	0.9975	0.0315
	6952.0	1.0000		-0.0167	0.0216	0.0000	1.0000	0.9999

$$* \lim_{K_1 \rightarrow \infty} Z_1(K_1 - 1) / \{1 + \psi(K_1 - 1)\} = Z_1 / \psi, K_1 = \infty$$

$$\lim_{K_1 \rightarrow \infty} X_1 = Z_1 / \{1 + \psi(K_1 - 1)\} = 0, K_1 = \infty$$

$$\lim_{K_1 \rightarrow \infty} Y_1 = Z_1 K_1 / \{1 + \psi(K_1 - 1)\} = Z_1 / \psi, K_1 = \infty$$

2.8 The separation of benzene (1) and cyclohexane (2) by distillation is complicated due to the formation of an azeotrope (Example 2.5). Vapor-liquid equilibrium data for this binary are required for the design of a workable separation process. As a first step, find the azeotropic composition and temperature at 100 kPa pressure. Use the van Laar equation for activity coefficients with parameters $A_{12} = 0.147$, $A_{21} = 0.165$. The computations may be made with assumptions consistent with low pressure conditions. The vapor pressures of benzene and cyclohexane may be represented by the Antoine equation (2.19) with the following constants: $A_1 = 13.88$, $B_1 = 2788.5$, $C_1 = -52.36$, $A_2 = 13.74$, $B_2 = 2766.6$, $C_2 = -50.30$, where T is in K and p_i^0 is in kPa.

Solution

At the azeotropic conditions the liquid and vapor compositions are identical; hence,

$$K_1 = K_2 = 1$$

From Equation 1.29a,

$$K_1 = \frac{\gamma_1 p_1^0}{P} = 1$$

$$K_2 = \frac{\gamma_2 p_2^0}{P} = 1$$

It follows that

$$\gamma_1 p_1^0 = \gamma_2 p_2^0 = P$$

Using the van Laar equation (1.34) and the Antoine equation (2.19),

$$\exp\left(A_1 - \frac{B_1}{T + C_1}\right) \times \exp\left[A_{12} \left(\frac{A_{21} X_2}{A_{12} X_1 + A_{21} X_2}\right)^2\right] = P$$

$$\exp\left(A_2 - \frac{B_2}{T + C_2}\right) \times \exp\left[A_{21} \left(\frac{A_{12} X_1}{A_{12} X_1 + A_{21} X_2}\right)^2\right] = P$$

These equations may be rewritten as

$$A_1 - \frac{B_1}{T + C_1} + A_{12} \left(\frac{A_{21} X_2}{A_{12} X_1 + A_{21} X_2}\right)^2 = \ln P$$

$$A_2 - \frac{B_2}{T + C_2} + A_{21} \left(\frac{A_{12} X_1}{A_{12} X_1 + A_{21} X_2}\right)^2 = \ln P$$

Define F_1 and F_2 as follows and rearrange:

$$F_1 = \frac{A_{21} X_2}{A_{12} X_1 + A_{21} X_2} = \frac{A_{21} - A_{21} X_1}{A_{21} - (A_{21} - A_{12}) X_1}$$

$$F_2 = \frac{A_{12}X_1}{A_{12}X_1 + A_{21}X_2} = \frac{A_{12}X_1}{A_{21} - (A_{21} - A_{12})X_1}$$

The temperature may be derived from either of the above equations:

$$T = f_1(X_1) = \frac{B_1 - C_1(A_1 + A_{12}F_1^2 - \ln P)}{A_1 + A_{12}F_1^2 - \ln P}$$

$$T = f_2(X_1) = \frac{B_2 - C_2(A_2 + A_{21}F_2^2 - \ln P)}{A_2 + A_{21}F_2^2 - \ln P}$$

The equation

$$f_1(X_1) - f_2(X_1) = 0$$

is solved iteratively for X_1 , then T is calculated directly, giving the azeotropic conditions:

$$P = 100 \text{ kPa}$$

$$T = 351.65 \text{ K} = 78.5^\circ\text{C}$$

$$X_1 = Y_1 = 0.55657$$

$$X_2 = Y_2 = 0.44343$$

2.9 A three-component feed stream is flashed at 390 K to recover most of component 3 in the liquid product, with 18% of that component leaving with the vapor product. The feed flow rate is 250 kmol/h and its composition and vapor pressures of the components at the flash temperature are as follows:

	Z_i	p_i^0 , kPa
1.	0.24	1800
2.	0.43	800
3.	0.33	400

Using the simultaneous method, calculate the flash pressure required for this separation, and the product rates and compositions. Assume Raoult's law applies at the problem conditions.

Solution

The problem equations are the flash equation (2.14) and the specification equation, with ψ and P as the independent variables:

$$f_1(\psi, P) = \sum_{i=1}^c \frac{Z_i(K_i - 1)}{1 + \psi(K_i - 1)} = 0$$

$$f_2(\psi, P) = V_k - F\psi Y_k$$

$$= V_k - \frac{FZ_k\psi K_k}{1 + \psi(K_k - 1)} = 0$$

where V_k is the specified flow rate of component k in the vapor. The K -values are calculated by Raoult's law (Equation 1.27):

$$K_i = p_i^0 / P$$

The partial derivatives for the Jacobian matrix are

$$\frac{\partial f_1}{\partial \psi} = - \sum_{i=1}^c \frac{Z_i(K_i - 1)^2}{[1 + \psi(K_i - 1)]^2}$$

$$\frac{\partial f_1}{\partial P} = \sum_{i=1}^c \frac{Z_i[1 + \psi(K_i - 1)] - Z_i(K_i - 1)\psi}{[1 + \psi(K_i - 1)]^2} \frac{dK_i}{dP} = - \frac{1}{P^2} \sum_{i=1}^c \frac{Z_i p_i^0}{[1 + \psi(K_i - 1)]^2}$$

$$\frac{\partial f_2}{\partial \psi} = - \frac{FZ_k K_k}{[1 + \psi(K_k - 1)]^2}$$

$$\frac{\partial f_2}{\partial P} = \frac{-FZ_k\psi + FZ_k\psi^2}{[1 + \psi(K_k - 1)]^2} \frac{dK_k}{dP} = \frac{p_k^0 FZ_k (\psi - \psi^2)}{P^2 [1 + \psi(K_k - 1)]^2}$$

The corrections to the variables, ΔP and $\Delta\psi$, are calculated from the equations

$$\frac{\partial f_1}{\partial \psi} \Delta\psi + \frac{\partial f_1}{\partial P} \Delta P + f_1 = 0$$

$$\frac{\partial f_2}{\partial \psi} \Delta\psi + \frac{\partial f_2}{\partial P} \Delta P + f_2 = 0$$

With initial estimates of $P = 700$ kPa and $\psi = 0.5$, the calculations converged as follows:

Iteration	P , kPa	ψ
0	700.0	0.5
1	802.4807	0.3382
2	817.7356	0.3106
3	818.1063	0.3099
4	818.1065	0.30985

The converged value of ψ is used to calculate the product compositions (Equations 2.13a and 2.13b), and the product rates:

<i>Component</i>	<i>Vapor</i>		<i>Liquid</i>	
	Y_i	kmol/h	X_i	kmol/h
1.	0.3849	29.816	0.1749	30.184
2.	0.4234	32.797	0.4330	74.703
3.	<u>0.1917</u>	<u>14.850</u>	<u>0.3921</u>	<u>67.650</u>
	1.0000	77.463	1.0000	172.537

2.10 The stream defined below is heated to 100°C to be partially vaporized in a flash drum before entering a distillation column. The fraction vaporized is controlled by the flash drum pressure. Calculate the required pressure at 100°C to have 20% mole vaporization, assuming Raoult's law applies. What are the products' flow rates and compositions? The constants for the Antoine equation (2.19) are given for each component, with the pressure in kPa and the temperature in K.

	Feed stream kmol/h	A_i	B_i	C_i
1. Benzene	210	13.86	2773.8	-53.0
2. Toluene	75	14.01	3103.0	-53.4
3. n-Heptane	<u>30</u>	13.86	2911.3	-56.5
	315			

Solution

It is required to find the pressure that satisfies the flash equation (2.14) at the specified T and ψ :

$$f(P) = \sum \frac{Z_i(K_i - 1)}{1 + \psi(K_i - 1)} = 0$$

$$T = 100^\circ\text{C} = 373.15 \text{ K}$$

$$\psi = 0.2$$

The K -values are calculated as

$$K_i = \frac{p_i^0}{P} = \frac{1}{P} \exp\left(A_i - \frac{B_i}{T + C_i}\right)$$

The feed composition,

$$Z_1 = 210/315 = 0.6667$$

$$Z_2 = 75/315 = 0.2381$$

$$Z_3 = 30/315 = 0.0952$$

The pressure is calculated iteratively using the correction ΔP obtained from the equation

$$\frac{df}{dP} \Delta P + f = 0 \quad \Delta P = -\frac{f}{df/dP} \quad P^{k+1} = P^k + \Delta P$$

The derivative is expressed as

$$\frac{df}{dP} = \sum \frac{df}{dK_i} \frac{dK_i}{dP} = -\frac{1}{P^2} \sum \frac{Z_i \exp\left(A_i - \frac{B_i}{T + C_i}\right)}{[1 + \psi(K_i - 1)]^2}$$

Starting with an initial estimate of $P = 100 \text{ kPa}$, the iterations converge as follows:

Iteration	0	1	2	3	4
P , kPa	100	133.9554	144.318	144.976	144.979

The product compositions are as follows:

	L_i , kmol/h	V_i , kmol/h
1. Benzene	160.1444	49.8556
2. Toluene	66.5015	8.4985
3. n-Heptane	<u>25.3541</u>	<u>4.6459</u>
	252.0000	63.0000

2.11 A hydrocarbon vapor stream is cooled in a heat exchanger where the outlet pressure is 100 kPa. What is the required outlet temperature that would result in 75% mole condensation of the stream? The feed stream composition and the components' Antoine equation (2.19) constants (p^0 in kPa, T in K) are given below. Raoult's law may be assumed valid at the problem conditions.

	Z_i	A_i	B_i	C_i
1. n-Pentane	0.12	13.82	2447.1	-39.9
2. n-Hexane	0.47	12.81	2154.3	-79.0
3. n-Heptane	0.41	13.86	2911.3	-56.5

Solution

The flash equation (2.14) must be solved for T at the specified values of P and ψ .

$$P = 100 \text{ kPa}$$

$$\psi = 0.25$$

$$f(T) = \sum \frac{Z_i(K_i - 1)}{1 + \psi(K_i - 1)} = 0$$

where

$$K_i = \frac{p_i^0}{P} = \frac{1}{P} \exp\left(A_i - \frac{B_i}{T + C_i}\right)$$

The temperature is calculated iteratively using the correction ΔT obtained from the equation

$$\frac{df}{dT} \Delta T + f = 0 \quad \Delta T = -\frac{f}{df/dT} \quad T^{k+1} = T^k + \Delta T$$

The derivative is expressed as

$$\begin{aligned} \frac{df}{dT} &= \sum \frac{df}{dK_i} \frac{dK_i}{dT} \\ \frac{df}{dK_i} &= \frac{Z_i}{[1 + \psi(K_i - 1)]^2} \\ \frac{dK_i}{dT} &= \frac{1}{P} \frac{B_i}{(T + C_i)^2} \exp\left(A_i - \frac{B_i}{T + C_i}\right) \\ \frac{df}{dT} &= \frac{1}{P} \sum \frac{Z_i B_i}{[1 + \psi(K_i - 1)]^2 (T + C_i)^2} \exp\left(A_i - \frac{B_i}{T + C_i}\right) \end{aligned}$$

Starting with an initial estimate of $T = 300$ K, the calculations converged in 4 iterations:

Iteration	0	1	2	3	4
T , K	300	375.0151	347.2763	346.5921	346.5904

The resulting liquid and vapor streams are as follows, based on 100 kmol/h feed:

	L_i , kmol/h	V_i , kmol/h
1. n-Pentane	5.5892	6.4108
2. n-Hexane	33.8405	13.1595
3. n-Heptane	<u>35.5703</u>	<u>5.4297</u>
	75.0000	25.0000

2.12 The mixture given below is sent to a flash drum for a crude separation into a vapor product with 0.05 mole fraction n-pentane and a liquid product with 0.05 mole fraction ethane. Find the flash temperature and pressure required to achieve this separation. The K -values may be calculated according to Raoult's law with vapor pressures from the Antoine equation (2.19) using the constants provided, p^0 in kPa, T in K.

	Z_i	A_i	B_i	C_i
1. Ethane	0.18	13.551	1459.7	-20.998
2. Propane	0.27	13.439	1728.4	-34.898
3. n-Butane	0.36	13.692	2140.8	-36.504
4. n-Pentane	0.19	14.246	2714.8	-27.294

Solution

The problem equations are the flash equation (2.14) and the specification equations. The independent variables are ψ , T , and P :

$$f_1(\psi, T, P) = \sum_{i=1}^c \frac{Z_i(K_i - 1)}{1 + \psi(K_i - 1)} = 0$$

$$f_2(\psi, T, P) = X_{1S} - \frac{Z_1}{1 + \psi(K_1 - 1)} = 0$$

$$f_3(\psi, T, P) = Y_{4S} - \frac{Z_4 K_4}{1 + \psi(K_4 - 1)} = 0$$

where X_{1S} and Y_{4S} are the specified mole fractions. The K -values are given by the equation

$$K_i = \frac{1}{P} \exp \left(A_i - \frac{B_i}{T + C_i} \right)$$

The above equations are solved by Newton's method, with the following partial derivatives for the Jacobian matrix:

$$\frac{\partial f_1}{\partial \psi} = - \sum \frac{Z_i(K_i - 1)^2}{[1 + \psi(K_i - 1)]^2}$$

$$\frac{\partial f_1}{\partial T} = \sum \frac{\partial f_1}{\partial K_i} \frac{\partial K_i}{\partial T} = \frac{1}{P} \sum \frac{B_i Z_i}{(T + C_i)^2 [1 + \psi(K_i - 1)]^2} \exp \left(A_i - \frac{B_i}{T + C_i} \right)$$

$$\frac{\partial f_1}{\partial P} = \sum \frac{\partial f_1}{\partial K_i} \frac{\partial K_i}{\partial P} = - \frac{1}{P^2} \sum \frac{Z_i}{[1 + \psi(K_i - 1)]^2} \exp \left(A_i - \frac{B_i}{T + C_i} \right)$$

$$\begin{aligned}
\frac{\partial f_2}{\partial \psi} &= \frac{Z_1(K_1 - 1)}{[1 + \psi(K_1 - 1)]^2} \quad \frac{\partial f_2}{\partial T} = \frac{\partial f_2}{\partial K_1} \frac{\partial K_1}{\partial T} = \frac{Z_1 \psi}{[1 + \psi(K_1 - 1)]^2} \frac{B_1}{P(T + C_1)^2} \exp\left(A_1 - \frac{B_1}{T + C_1}\right) \\
\frac{\partial f_2}{\partial P} &= \frac{\partial f_2}{\partial K_1} \frac{\partial K_1}{\partial P} = -\frac{Z_1 \psi}{[1 + \psi(K_1 - 1)]^2} \frac{1}{P^2} \exp\left(A_1 - \frac{B_1}{T + C_1}\right) \\
\frac{\partial f_3}{\partial \psi} &= \frac{Z_4 K_4 (K_4 - 1)}{[1 + \psi(K_4 - 1)]^2} \\
\frac{\partial f_3}{\partial T} &= \frac{\partial f_3}{\partial K_4} \frac{\partial K_4}{\partial T} = -\frac{Z_4(1 - \psi)}{[1 + \psi(K_4 - 1)]^2} \frac{B_4}{P(T + C_4)^2} \exp\left(A_4 - \frac{B_4}{T + C_4}\right) \\
\frac{\partial f_3}{\partial P} &= \frac{\partial f_3}{\partial K_4} \frac{\partial K_4}{\partial P} = \frac{Z_4(1 - \psi)}{[1 + \psi(K_4 - 1)]^2} \frac{1}{P^2} \exp\left(A_4 - \frac{B_4}{T + C_4}\right)
\end{aligned}$$

The following equations are solved for the corrections $\Delta\psi$, ΔT , ΔP :

$$\begin{aligned}
\frac{\partial f_1}{\partial \psi} \Delta\psi + \frac{\partial f_1}{\partial T} \Delta T + \frac{\partial f_1}{\partial P} \Delta P + f_1 &= 0 \\
\frac{\partial f_2}{\partial \psi} \Delta\psi + \frac{\partial f_2}{\partial T} \Delta T + \frac{\partial f_2}{\partial P} \Delta P + f_2 &= 0 \\
\frac{\partial f_3}{\partial \psi} \Delta\psi + \frac{\partial f_3}{\partial T} \Delta T + \frac{\partial f_3}{\partial P} \Delta P + f_3 &= 0
\end{aligned}$$

The solutions are

$$\begin{aligned}
\Delta\psi &= \frac{(c_1 f_2 - c_2 f_1)(b_1 c_3 - b_3 c_1) - (c_1 f_3 - c_3 f_1)(b_1 c_2 - b_2 c_1)}{(a_1 c_2 - a_2 c_1)(b_1 c_3 - b_3 c_1) - (a_1 c_3 - a_3 c_1)(b_1 c_2 - b_2 c_1)} \\
\Delta T &= \frac{(c_1 f_2 - c_2 f_1) - (a_1 c_2 - a_2 c_1) \Delta\psi}{b_1 c_2 - b_2 c_1} \\
\Delta P &= \frac{-f_1 - a_1 \Delta\psi - b_1 \Delta T}{c_1}
\end{aligned}$$

where $a_i \equiv \partial f_i / \partial \psi$

$b_i \equiv \partial f_i / \partial T$

$c_i \equiv \partial f_i / \partial P$

Starting with initial estimates of $T = 300$ K, $P = 750$ kPa, $\psi = 0.5$, the calculations converged in four iterations:

<i>Iteration</i>	0	1	2	3	4
T, K	300	323.5131	318.4070	318.3980	318.3963
P, kPa	750	934.7872	822.5905	827.4335	827.3963
ψ	0.5	0.45447	0.44432	0.44433	0.44433

The resulting products are as follows, based on 100 kmol/h feed:

	X_i	$L_i, \text{kmol/h}$	Y_i	$V_i, \text{kmol/h}$
1. Ethane	0.0500	2.7783	0.34257	15.2217
2. Propane	0.19495	10.8327	0.36386	16.1673
3. n-Butane	0.45310	25.1772	0.24357	10.8228
4. n-Pentane	<u>0.30195</u>	<u>16.7783</u>	<u>0.05000</u>	<u>2.2217</u>
	1.0	55.5665	1.0	44.4335

2.13 Acetone and chloroform form an azeotrope and cannot be separated by conventional distillation. In extractive distillation the separation is enhanced by adding benzene as a solvent. In a preliminary evaluation of the effectiveness of the solvent, calculations are made on a single equilibrium stage. The main feed stream is at a rate of 100 kmol/h with 50% mole acetone and 50% mole chloroform. The equilibrium stage is controlled at 70°C and 110 kPa. Determine the effect of adding 45, 50 and 60 kmol/h benzene on the separation.

Use the Wilson equation for activity coefficients and assume ideal gas behavior in the vapor phase, with component vapor pressures calculated by the Antoine equation (2.19). The constants for this equation are consistent with pressure in kPa and temperature in Kelvin. The following data are given:

Antoine equation constants				
	A_i	B_i	C_i	liq. mol. vol, V_i cm ³ /mol
1. Acetone	14.636	2940.5	-35.9	77
2. Chloroform	16.055	3977.5	13.44	81
3. Benzene	13.886	2788.5	-52.4	94

The Wilson equation parameters are given below in cal/mol.

$$\begin{array}{lll} \lambda_{12} - \lambda_{11} = -72.20 & \lambda_{13} - \lambda_{11} = 494.92 & \lambda_{23} - \lambda_{22} = -204.22 \\ \lambda_{12} - \lambda_{22} = -332.23 & \lambda_{13} - \lambda_{33} = -167.91 & \lambda_{23} - \lambda_{33} = 141.62 \end{array}$$

Solution

The combined composition of the main feed with the solvent at each of the given rates is flashed at the specified temperature and pressure. The activity coefficients are calculated as in Example 1.6A, and the flash calculations follow the procedure described in Example 2.7. The results are tabulated herewith.

	Feed kmol/h	Solvent kmol/h	Z_i	K_i	X_i	Y_i
1. Acetone	50	0	0.34483	1.39793	0.26565	0.37136
2. Chloroform	50	0	0.34483	0.99091	0.34719	0.34403
3. Benzene	0	45	0.31034	0.73519	0.38713	0.28461
1. Acetone	50	0	0.33333	1.40801	0.26857	0.37815
2. Chloroform	50	0	0.33333	0.98561	0.33619	0.33135
3. Benzene	0	50	0.33333	0.73514	0.39519	0.29052
1. Acetone	50	0	0.3125	1.42752	0.27386	0.39094
2. Chloroform	50	0	0.3125	0.97372	0.31523	0.30695
3. Benzene	0	60	0.3750	0.73541	0.41088	0.30216

The calculations show that adding increasing amounts of benzene results in higher acetone to

chloroform relative volatilities or K -value ratios.

2.14 Benzene (1) and water (2) form a heterogeneous azeotrope at 450 K and 2000 kPa. The benzene-rich liquid phase has 95.7% mole benzene, the water-rich phase has 97.7% mole water and the vapor phase has 48% mole benzene. Use these data to determine the van Laar parameters for the benzene-rich and the water-rich phases. An approximation of ideal gas behavior in the vapor phase may be assumed. The vapor pressures at 450 K are 936 kPa for water and 978 kPa for benzene.

Solution

$$T = 450 \text{ K}, P = 2000 \text{ kPa}$$

Benzene-rich liquid phase:	$X'_1 = 0.957$	$X'_2 = 0.043$
Water-rich liquid phase:	$X''_1 = 0.023$	$X''_2 = 0.977$
Vapor phase:	$Y_1 = 0.48$	$Y_2 = 0.52$
Vapor pressures at 450 K, kPa:	$p_1^0 = 978$	$p_2^0 = 936$

From Equation 2.24,

$$\gamma'_1 X'_1 = \gamma''_1 X''_1 = Y_1 P / p_1^0 = 0.48 \times 2000 / 978 = 0.9816$$

$$\gamma'_2 X'_2 = \gamma''_2 X''_2 = Y_2 P / p_2^0 = 0.52 \times 2000 / 936 = 1.1111$$

$$\gamma'_1 = 0.9816 / X'_1 = 0.9816 / 0.957 = 1.0257$$

$$\gamma'_2 = 1.1111 / X'_2 = 1.1111 / 0.043 = 25.8398$$

$$\gamma''_1 = 0.9816 / X''_1 = 0.9816 / 0.023 = 42.6780$$

$$\gamma''_2 = 1.1111 / X''_2 = 1.1111 / 0.977 = 1.1373$$

The van Laar parameters (See Problem 1.9),

$$A'_{12} = \ln \gamma'_1 \left(1 + \frac{X'_2 \ln \gamma'_2}{X'_1 \ln \gamma'_1} \right)^2 = 1.1590$$

$$A'_{21} = 4.4795$$

$$A''_{12} = 22.6350$$

$$A''_{21} = 0.3661$$

2.15 The stream described below is flashed at 2026.5 kPa. It is required to determine its two-phase temperature range. Calculate the equilibrium temperature, and vapor and liquid compositions at vapor fractions of 0.001 (bubble point), 0.25, 0.50, 0.75, and 0.999 (dew point). Use the Wilson equation for activity coefficients and the truncated virial equation for the fugacity coefficients. (See Example 2.7A).

Component	Feed		P_{Ci} , kPa	ω_i	Liquid molar volume V_i , cm ³ /mol
	Z_i	T_{Ci} , K			
1. Acetone	0.3	508.1	4701	0.309	73.52
2. 2-Butanone	0.3	535.6	4154	0.329	89.57
3. Ethylacetate	0.4	523.2	3830	0.363	97.79

Pseudo critical pressures, kPa, $P_{C12} = 4408$, $P_{C13} = 4053$, $P_{C23} = 3830$

Antoine constants (Equation 2.19), T in K, p_i^0 in kPa,

	A_i	B_i	C_i
1.	14.63615	2940.46	-35.93
2.	14.58345	3150.42	-36.65
3.	14.13645	2790.50	-57.15

Wilson exponential parameters, δ_{ij} , cal/mol,

$\delta_{11} = 0$	$\delta_{12} = 1371.31$	$\delta_{13} = -292.975$
$\delta_{21} = -650.152$	$\delta_{22} = 0$	$\delta_{23} = -405.21$
$\delta_{31} = 644.481$	$\delta_{32} = 2704.427$	$\delta_{33} = 0$

Solution

The following calculations are at convergence, for $T = 468.9$ K, $P = 2026.5$ kPa, and $\psi = 0.001$. The converged compositions are

	X_i	Y_i
1.	0.3	0.3784
2.	0.3	0.2942
3.	0.4	0.3274

The pseudo critical temperatures,

$$T_{C12} = (508.1 \times 535.6)^{0.5} = 521.67 \text{ K}$$

$$T_{C13} = 515.60 \text{ K}$$

$$T_{C23} = 529.36 \text{ K}$$

The second virial coefficients,

$$\begin{aligned}
 B_{11}^0 &= 0.083 - 0.422/(468.9/508.1)^{1.6} = -0.3968 \\
 B_{11}^1 &= 0.139 - 0.172/(468.9/508.1)^{4.2} = -0.10198 \\
 B_{11} &= (8314 \times 508.1/4701)[-0.3968 + 0.309(-0.10198)] = -384.9 \\
 B_{22} &= -527.6 \\
 B_{33} &= -531.9 \\
 B_{12} &= -451.7 \\
 B_{13} &= -473.4 \\
 B_{23} &= -552.0
 \end{aligned}$$

The mixture second virial coefficient,

$$\begin{aligned}
 B &= (0.3784)^2(-384.9) + (0.2942)^2(-527.6) + (0.3274)^2(-531.9) \\
 &+ 2[(0.3784)(0.2942)(-451.7) + (0.3784)(0.3274)(-473.4) + (0.2942)(0.3274)(-552.0)] \\
 &= -482.0
 \end{aligned}$$

Vapor pressures,

$$\begin{aligned}
 p_1^0 &= \exp\left(14.63615 - \frac{2940.46}{468.9 - 35.93}\right) = 1939.39 \text{ kPa} \\
 p_2^0 &= 1472.96 \text{ kPa} \\
 p_3^0 &= 1570.70 \text{ kPa}
 \end{aligned}$$

Pure component fugacity coefficients,

$$\begin{aligned}
 \phi_1^V &= \exp[-384.9 \times 2026.5 / (8314 \times 468.9)] = 0.8187 \\
 \phi_2^V &= 0.7601 \\
 \phi_3^V &= 0.7584
 \end{aligned}$$

Partial fugacity coefficients,

$$\begin{aligned}
 \hat{\phi}_1^V &= \exp\left[\left(\frac{2026.5}{8314 \times 468.9}\right)\{-2(0.3784 \times 384.9 + 0.2942 \times 451.7 + 0.3274 \times 473.4) + 482.0\}\right] \\
 &= 0.8186 \\
 \hat{\phi}_2^V &= 0.7585 \\
 \hat{\phi}_3^V &= 0.7516
 \end{aligned}$$

Activity Coefficients

Wilson binary interaction parameters (equation before Equation 1.36),

$$A_{11} = \frac{73.52}{73.52} \exp \left[\frac{0}{8314 \times 468.9} \right] = 1.0$$

$$A_{12} = \frac{89.57}{73.52} \exp \left[-\frac{1371.31}{1.987 \times 468.9} \right] = 0.2769$$

$$A_{13} = 1.8216$$

$$A_{21} = 1.6493$$

$$A_{22} = 1.0$$

$$A_{23} = 1.6866$$

$$A_{31} = 0.3764$$

$$A_{32} = 0.0503$$

$$A_{33} = 1.0$$

Denominators,

$$D_1 = (0.3)(1.0) + (0.3 \times 0.2769) + (0.4 \times 1.8216) = 1.1125$$

$$D_2 = 1.4694$$

$$D_3 = 0.5281$$

$$\ln \gamma_1 = 1 - \ln(1.1125) - 0.3 \times 1.0/1.1125 - 0.3 \times 1.6493/1.4694 - 0.4 \times 0.3764/0.5281$$

$$= 0.00188$$

$$\gamma_1 = 1.0018$$

$$\gamma_2 = 1.3465$$

$$\gamma_3 = 1.0466$$

$$K_1 = 1.0018 \times 2552.37 \times 0.8187 / (0.8186 \times 2026.5) = 1.2619$$

$$K_2 = 0.9808$$

$$K_3 = 0.8186$$

These K -values are consistent with the vapor and liquid compositions shown above from the latest iteration, indicating convergence. The complete results are summarized below.

T, K	P, kPa	ψ	X_i	Y_i
468.9	2026.5	0.001	0.3000	0.3784
			0.3000	0.2942
			0.4000	0.3274
469.4	2026.5	0.25	0.2809	0.3572
			0.3005	0.2985
			0.4186	0.3443
469.9	2026.5	0.50	0.2630	0.3370
			0.2990	0.3010
			0.4380	0.3620

470.4	2026.5	0.75	0.2462	0.3179
			0.2956	0.3014
			0.4582	0.3806

470.9	2026.5	0.999	0.2303	0.3000
			0.2894	0.3000
			0.4795	0.4000

2.16 Compare the van Laar and Wilson equations by solving the problem in Example 2.7A using the van Laar equation for activity coefficients. Ideal gas behavior may be assumed for the vapor phase. Use the feed composition and vapor pressure data from Example 2.7A, and calculate the temperature and phase compositions at the pressure and vapor fraction in that example. The following are the binary van Laar constants:

$$A_{12} = 0.243, A_{21} = 0.243, A_{13} = 0.89, A_{31} = 0.65, A_{23} = 0.36, A_{32} = 0.22.$$

Solution

Following the procedure used in Example 2.7B, Equations 1.35a are used to calculate the activity coefficients based on a liquid composition estimate identical to the feed composition. This is followed by calculating the K -values from Equation 1.29a, and solving the flash equation (2.14) at 150 kPa and the vapor fraction of 0.38558 from Example 2.7A. The new liquid composition is used to recalculate the activity coefficients and the calculations are repeated until convergence is reached. The final results at convergence are shown below:

$$P = 150 \text{ kPa}, T = 359.55 \text{ K}, \psi = 0.38558$$

	Z_i	γ_i	p_i^0 , kPa	K_i	X_i	Y_i
1. Acetone	0.2	1.5505	259.80	2.6855	0.1212	0.3255
2. Methanol	0.3	1.0824	227.19	1.6394	0.2407	0.3945
3. Water	0.5	1.0716	61.43	0.4388	0.6381	0.2800

2.17 In an ethyl acetate (1) – ethyl alcohol (2) separation process, it is required to determine if this mixture forms an azeotrope. If it does, it is required to determine the azeotropic temperature and composition as a function of the azeotropic pressure between 70 kPa and 120 kPa at 10 kPa intervals. Solve for the composition and temperature by doing a single computation operation at each pressure value. Additionally, for any one of the pressure points determine if the azeotrope is minimum- or maximum-boiling. Use the van Laar equation for the liquid activity coefficients and assume ideal gas behavior for the vapor phase. The following data are given:

van Laar parameters: $A_{12} = 0.855$, $A_{21} = 0.753$

Antoine constants (Equation 2.19, p_i^0 in kPa, T in °C):

$$A_1 = 14.3376, B_1 = 2866.624, C_1 = 217.881$$

$$A_2 = 15.4540, B_2 = 2950.989, C_3 = 193.768$$

Solution

If an azeotrope exists, $K_i = 1$, and the following equations must be satisfied:

$$\gamma_1 p_1^0 = P$$

$$\gamma_2 p_2^0 = P$$

$$X_1 + X_2 = 1$$

For a given value of P , these equations are solved for X_1 , X_2 , and T , with the constraints $0 \leq X_i \leq 1$, and with reasonable upper and lower temperature bounds. A spreadsheet solver may be used to solve the equations. The following are the azeotropic conditions:

P , kPa	T , °C	X_1
70	62.88	0.593
80	66.27	0.575
90	69.32	0.559
100	72.10	0.545
110	74.66	0.533
120	77.03	0.522

Bubble point calculations at $P = 100$ kPa around the azeotropic composition indicate that this is a minimum-boiling azeotrope:

$T, ^\circ\text{C}$	X_1	Y_1
72.37	0.4	0.4569
72.22	0.45	0.4878
72.13	0.5	0.5180
72.11	0.55	0.5483
72.14	0.6	0.5795
72.25	0.65	0.6124
72.44	0.7	0.6478

2.18 One hundred kmol/h of a hydrocarbon stream is flashed at 25 °C and 10 atm. The stream composition and vapor pressures at these conditions are given below. Assuming Raoult's law applies, calculate the number of kmol/h of propane in the liquid product. It is estimated that the total liquid product is between 20 and 30 kmol/h.

	Z_i	p_i^0 , atm
Ethane	0.40	28
Propane	0.35	9
n-Butane	0.25	4

Solution

By Raoult's law, $K_i = p_i^0/P$

Iterating on ψ , convergence is achieved at $\psi = 0.743$.

$$f(\psi) = \sum \frac{Z_i(K_i - 1)}{1 + \psi(K_i - 1)}$$

	Z_i	p_i^0	K_i	$f(\psi)$
Ethane	0.40	28	2.8	0.3080
Propane	0.35	9	0.9	-0.0378
n-Butane	0.25	4	0.4	<u>-0.2707</u>
				-0.0005

$$X_i = \frac{Z_i}{1 + \psi(K_i - 1)}$$

$$X(\text{propane}) = 0.35/[1 + 0.743(0.9 - 1)] = 0.378$$

$$L = 100(1 - \psi) = 100(1 - 0.743) = 25.7 \text{ kmol/h}$$

$$l(\text{propane}) = LX(\text{propane}) = (25.7)(0.378) = 9.715 \text{ kmol/h}$$

2.19 A liquid solution of isopropanol (1) and water (2) at 90°C contains 30% mole isopropanol and 70% mole water. The van Laar constants are $A_{12} = 1.042$ and $A_{21} = 0.492$. The vapor pressures of isopropanol and water at 90°C are $p_1^0 = 201.3$ kPa and $p_2^0 = 70.0$ kPa. The vapor phase may be assumed an ideal gas. Calculate the activity coefficients of isopropanol and water in this solution and its bubble point pressure at 90°C.

Solution

$$\ln \gamma_1 = A_{12} \left[\frac{A_{21} X_2}{A_{12} X_1 + A_{21} X_2} \right]^2 = 1.042 \left[\frac{(0.492)(0.7)}{(1.042)(0.3) + (0.492)(0.7)} \right]^2 = 0.2863$$

$$\gamma_1 = 1.3315$$

$$\ln \gamma_2 = 0.492 \left[\frac{(1.042)(0.3)}{(1.042)(0.3) + (0.492)(0.7)} \right]^2 = 0.11138$$

$$\gamma_2 = 1.1178$$

$$K_1 = \gamma_1 p_1^0 / P$$

$$K_2 = \gamma_2 p_2^0 / P$$

$$Y_1 + Y_2 = 1 = K_1 X_1 + K_2 X_2 = (1/P)(X_1 \gamma_1 p_1^0 + X_2 \gamma_2 p_2^0)$$

$$P_{bp} = X_1 \gamma_1 p_1^0 + X_2 \gamma_2 p_2^0 = (0.3)(1.3315)(201.3) + (0.7)(1.1178)(70.0) = 135.18 \text{ kPa}$$

2.20 A stream flowing at the rate of 100 kmol/h separates in a flash drum at 80°C and 115 kPa into a vapor stream and a liquid stream at equilibrium. The overall stream composition and the component vapor pressures at 80 C are given below:

	Z_i	p_i^0 , kPa
1. Acetone	0.45	195.75
2. Acetonitrile	0.35	97.84
3. Nitromethane	0.20	50.32

Assuming Raoult's law applies, calculate the rate of nitromethane flowing in the vapor.

Solution

$$f(\psi) = \sum \frac{Z_i(K_i - 1)}{1 + \psi(K_i - 1)} = 0$$

By trial and error, $f(0.58) = 0$, $\psi = 0$.

	Z_i	$K_i = p_i^0/P$	$f(\psi)$	X_i	Y_i
1. Acetone	0.45	1.7022	0.2245	0.3198	0.5443
2. Acetonitrile	0.35	0.8508	-0.0571	0.3831	0.3260
3. Nitromethane	<u>0.20</u>	0.4376	<u>-0.1668</u>	<u>0.2967</u>	<u>0.1300</u>
	1.00		0.0006	0.9996	1.0003

$$X_i = Z_i / [1 + 0.58(K_i - 1)]$$

$$Y_i = K_i X_i$$

$$\text{Nitromethane in the vapor} = (100)\psi Y_3 = (100)(0.58)(0.1300) = 7.54 \text{ kmol/h}$$

2.21 A single-stage process is used to separate a binary mixture of ethyl alcohol (1) and cyclohexane (2) at 45 C. The following infinite dilution liquid activity coefficient data are given:

$$\text{At } X_1 = 0, \quad \gamma_1 = 8.9$$

$$\text{At } X_2 = 0, \quad \gamma_2 = 3.9$$

The vapor pressures at 45 C are $p_1^0 = 21.3$ kPa, $p_2^0 = 40.0$ kPa. Using the Margules liquid activity coefficient equation, calculate the activity coefficients of ethyl alcohol and cyclohexane, the total pressure, and the vapor composition if the ethyl alcohol mole fraction in the liquid is 0.30. Assume ideal gas behavior in the vapor phase.

Solution

$$\text{At } X_1 = 0, X_2 = 1, \log \gamma_1 = 2A_{21} - A_{12} + 2A_{12} - 2A_{21} = A_{12}$$

$$A_{12} = \log \gamma_1 = \log 8.9 = 0.949$$

$$\text{At } X_1 = 1, X_2 = 0, \log \gamma_2 = A_{21}$$

$$A_{21} = \log \gamma_2 = \log 3.9 = 0.591$$

$$\text{At } X_1 = 0.3, X_2 = 0.7,$$

$$\log \gamma_1 = (2 \times 0.591 - 0.949)(0.7)^2 + 2(0.949 - 0.591)(0.7)^3 = 0.3598, \gamma_1 = 2.290$$

$$\log \gamma_2 = (2 \times 0.949 - 0.591)(0.3)^2 + 2(0.591 - 0.949)(0.3)^3 = 0.0983, \gamma_2 = 1.254$$

$$K_i = \frac{\gamma_i f_i^L}{\phi_i^V P}$$

If the vapor behaves as an ideal gas, $f_i^L = p_i^0$, $\phi_i^V = 1$, $K_i = \gamma_i p_i^0 / P$

$$Y_1 P + Y_2 P = P = \gamma_1 p_1^0 X_1 + \gamma_2 p_2^0 X_2 = (2.290)(21.3)(0.3) + (1.254)(40.0)(0.7) = 49.75 \text{ kPa}$$

$$Y_1 = (2.290)(21.3)(0.3)/49.75 = 0.294$$

$$Y_2 = (1.254)(40.0)(0.7)/49.75 = 0.706$$

2.22 The following vapor-liquid equilibrium data are given for benzene (1) / cyclohexane (2) at 100 kPa:

$T, ^\circ\text{C}$	X_1	Y_1	γ_1	γ_2
77.8	0.399	0.421	1.135	1.056
77.6	0.545	0.545	1.078	1.101
77.8	0.700	0.677	1.038	1.177

- Calculate the relative volatility at each temperature and identify the azeotropic point, if one exists.
- Calculate the van Laar constants for this binary based on the azeotropic composition.
- For a liquid with 60% mole benzene and 40% mole cyclohexane at 80°C and assuming ideal gas behavior in the vapor phase, calculate the bubble point pressure and the equilibrium vapor composition. The component vapor pressures are given by the equation $\ln p_i^0 = A_i - B_i/(T+C_i)$, where p^0 is in kPa and T is in K. The equation constants are given:

	A_i	B_i	C_i
1	15.904	4088.766	9.043
2	12.819	2247.980	-79.742

Solution

a)

$T, ^\circ\text{C}$	$X_2 = 1 - X_1$	$Y_2 = 1 - Y_1$	$K_1 = Y_1/X_1$	$K_2 = Y_2/X_2$	$\alpha_{12} = K_1/K_2$
77.8	0.601	0.579	1.055	0.963	1.0955
77.6	0.455	0.455	1.000	1.000	1.000
77.8	0.300	0.323	0.967	1.077	0.8979

A minimum boiling azeotrope exists at 77.6°C.

b)

$$A_{12} = \ln \gamma_1 \left[1 + \frac{X_2 \ln \gamma_2}{X_1 \ln \gamma_1} \right]^2 = \ln 1.078 \left[1 + \frac{0.455 \ln 1.101}{0.545 \ln 1.078} \right]^2 = 0.322$$

$$A_{21} = \ln \gamma_2 \left[1 + \frac{X_1 \ln \gamma_1}{X_2 \ln \gamma_2} \right]^2 = \ln 1.101 \left[1 + \frac{0.545 \ln 1.078}{0.455 \ln 1.101} \right]^2 = 0.360$$

c)

$$T = 80^\circ\text{C} = 353.15 \text{ K}$$

$$\ln p_1^0 = 15.904 - 4088.766/(353.15 + 9.043) = 4.61508, \quad p_1^0 = 100.9959 \text{ kPa}$$

$$\ln p_2^0 = 12.819 - 2247.980/(353.15 - 79.742) = 4.59690, \quad p_2^0 = 99.1764 \text{ kPa}$$

$$Y_1 + Y_2 = 1 = (X_1\gamma_1p_1^0 + X_2\gamma_2p_2^0)/P$$

$$P = X_1\gamma_1p_1^0 + X_2\gamma_2p_2^0$$

$$\ln \gamma_1 = A_{12} \left[\frac{A_{21}X_2}{A_{12}X_1 + A_{21}X_2} \right]^2 = 0.322 \left[\frac{0.360 \times 0.40}{0.322 \times 0.60 + 0.360 \times 0.40} \right]^2 = 0.05872$$

$$\gamma_1 = 1.06048$$

$$\ln \gamma_2 = A_{21} \left[\frac{A_{12}X_1}{A_{12}X_1 + A_{21}X_2} \right]^2 = 0.360 \left[\frac{0.322 \times 0.60}{0.322 \times 0.60 + 0.360 \times 0.40} \right]^2 = 0.11818$$

$$\gamma_2 = 1.12540$$

$$P = (0.60)(1.06048)(101.00) + (0.40)(1.12540)(99.18) = 108.91 \text{ kPa}$$

$$Y_1 = X_1\gamma_1p_1^0/P = (0.60 \times 1.06048 \times 101.00)/108.91 = 0.59$$

$$Y_2 = X_2\gamma_2p_2^0/P = (0.40 \times 1.12540 \times 99.18)/108.91 = 0.41$$

2.23 Streams 1 and 2, defined below, are mixed together in a vessel where the temperature is controlled at 300 K. The mixed stream leaving the vessel must be saturated vapor. What should be the pressure in the vessel? Raoult's law may be assumed, with vapor pressures calculated as in Problem 1 using the constants given below.

	Stream 1 kmol/h	Stream 2 kmol/h	A_i	B_i	C_i
1. Propane	30	5	13.439	1728.4	-34.989
2. n-Butane	55	25	13.692	2140.8	-36.504
3. n-Pentane	29	67	14.246	2714.8	-27.294

Solution

$$p_1^0 = \exp[13.439 - 1728.4/(300 - 34.989)] = 1009.29 \text{ kPa}$$

$$p_2^0 = \exp[13.692 - 2140.8/(300 - 36.504)] = 261.75 \text{ kPa}$$

$$p_3^0 = \exp[14.246 - 2714.8/(300 - 27.294)] = 73.04 \text{ kPa}$$

<u>Mixed stream</u>	<u>kmol/h</u>	<u>$Y_i = Z_i$</u>
1	30 + 5 = 35	0.1659
2	55 + 25 = 80	0.3791
3	29 + 67 = 96	0.4550
<hr/>		
	211	1.0000

Saturated vapor at its dew point,

$$\sum X_i = 1 = \sum Y_i/K_i = \sum P Y_i/p_i^0$$

$$P(0.1659/1009.29 + 0.3791/261.75 + 0.4550/73.04) = 1,$$

$$P = 127.52 \text{ kPa}$$

2.24 Phase equilibrium data are required for a process involving a binary mixture of ethanol (1) and benzene (2) at 40°C. The infinite dilution liquid activity coefficients are given:

$$\text{At } X_1 = 0, \quad \gamma_1 = 9.025$$

$$\text{At } X_2 = 0, \quad \gamma_2 = 4.055$$

The vapor pressures at 40°C are $p_1^0 = 20$ kPa, $p_2^0 = 37.3$ kPa. Using the van Laar liquid activity equation, calculate the K -values of ethanol and benzene at 40°C when the ethanol mole fraction in the liquid is 0.25, and determine the bubble point pressure. Assume ideal gas behavior in the vapor phase.

Solution

From the van Laar equation (1.34),

$$\text{At } X_1 = 0, \ln \gamma_1 = \ln 9.025 = 2.20 = A_{12}$$

$$\text{At } X_2 = 0, \ln \gamma_2 = \ln 4.055 = 1.40 = A_{21}$$

$$\text{At } X_1 = 0.25, X_2 = 0.75,$$

$$\ln \gamma_1 = 2.20 \left[\frac{1.40 \times 0.75}{2.20 \times 0.25 + 1.40 \times 0.75} \right]^2 = 0.9475 \quad \gamma_1 = 2.579$$

$$\ln \gamma_2 = 1.40 \left[\frac{2.20 \times 0.25}{2.20 \times 0.25 + 1.40 \times 0.75} \right]^2 = 0.1654 \quad \gamma_2 = 1.180$$

$$K_i = \frac{Y_i}{X_i} = \frac{\gamma_i p_i^0}{P}$$

At the bubble point,

$$\sum Y_i = 1 = \frac{1}{P} (\gamma_1 p_1^0 X_1 + \gamma_2 p_2^0 X_2)$$

$$\begin{aligned} P &= \gamma_1 p_1^0 X_1 + \gamma_2 p_2^0 X_2 \\ &= (2.579 \times 20.0 \times 0.25) + (1.180 \times 37.3 \times 0.75) = 45.9 \text{ kPa} \end{aligned}$$

$$K_1 = \frac{2.579 \times 20.0}{45.9} = 1.123$$

$$K_2 = \frac{1.180 \times 37.3}{45.9} = 0.959$$

$$Y_1 = K_1 X_1 = 1.123 \times 0.25 = 0.28075$$

$$Y_2 = K_2 X_2 = 0.959 \times 0.75 = 0.71925$$

2.25 Isobutane and 1-butene are close-boilers and are difficult to separate by conventional distillation. Using a single stage, a 100 kmol/h stream containing 50% mole isobutane and 50% mole 1-butene is flashed at 480 kPa, producing a 50 kmol/h vapor stream. With no solvent added, the vapor composition is about the same as the feed. Furfural, which is less volatile than both components, is now added as a solvent to alter the isobutane-1-butene relative volatility by depressing the 1-butene K -value relative to that of isobutane.

It is required to determine the effect of the furfural rate on the separation. The multi-component Van Laar equation is used to calculate the liquid activity coefficients, and the vapor phase is assumed to behave as an ideal solution. Solvent rates of 0, 100, 200, and 400 kmol/h are to be considered. Vapor pressure data are calculated by the Antoine equation (2.19) with the constants given below (p_i^0 in kPa and T in K):

	A_i	B_i	C_i
1. Isobutane	14.853	2796.78	12.470
2. 1-Butene	15.249	3071.37	22.853
3. Furfural	17.339	5705.99	13.576

Van Laar constants are given for the isobutane-furfural and 1-butene-furfural binaries. The isobutane-1-butene binary constants are set to zero because these components are assumed to form an ideal solution with each other, so that

$$\gamma_1^\infty = 1 \text{ and } \gamma_2^\infty = 1 \quad (A_{12} = \ln \gamma_1^\infty \text{ and } A_{21} = \ln \gamma_2^\infty)$$

$A_{12} = 0$	$A_{13} = 1.142$	$A_{23} = 0.842$
$A_{21} = 0$	$A_{31} = 1.310$	$A_{32} = 1.029$

Note: In order to avoid division by zero, small and equal values for A_{12} and A_{21} may be used ($A_{12} = A_{21} = 0.001$).

For the 400 kmol/h solvent rate, in order to determine the recovery of furfural in the liquid from the extractive separation stage, the liquid is sent to an equilibrium separation stage at 480 kPa and 350°C. Find the product rates and compositions for this stage.

Solution

The Van Laar Equation for a three-component system (Equations 1.35a)

$$\log \gamma_1 = \frac{X_2^2 A_{21}^2 / A_{12} + X_3^2 A_{31}^2 / A_{13} + X_2 X_3 A_{21} A_{31} (A_{12} + A_{13} - A_{32} A_{13} / A_{31}) / (A_{12} A_{13})}{(X_1 + X_2 A_{21} / A_{12} + X_3 A_{31} / A_{13})^2}$$

$$\log \gamma_2 = \frac{X_3^2 A_{32}^2 / A_{23} + X_1^2 A_{12}^2 / A_{21} + X_3 X_1 A_{32} A_{12} (A_{23} + A_{21} - A_{13} A_{21} / A_{12}) / (A_{23} A_{21})}{(X_2 + X_3 A_{32} / A_{23} + X_1 A_{12} / A_{21})^2}$$

$$\log \gamma_3 = \frac{X_1^2 A_{13}^2 / A_{31} + X_2^2 A_{23}^2 / A_{32} + X_1 X_2 A_{13} A_{23} (A_{31} + A_{32} - A_{21} A_{32} / A_{23}) / (A_{31} A_{32})}{(X_3 + X_1 A_{13} / A_{31} + X_2 A_{23} / A_{32})^2}$$

The K -values are calculated from Equation 1.29a, $K_i = \gamma_i p_i^0 / P$. The liquid activity coefficients are calculated from the 3-component formulation of the Van Laar equation.

If the furfural rate is S , the fraction vapor is $\psi = V / (F + S) = 50 / (100 + S)$. For each value of ψ (corresponding to each solvent rate), the flash equation (2.14) is solved by iterating on the flash temperature. The component mole fractions in the combined feed are calculated as

$$Z_1 = 50 / (100 + S) \quad Z_2 = 50 / (100 + S) \quad Z_3 = S / (100 + S)$$

Since the liquid activity coefficients are functions of the liquid composition, this composition must be updated during the iterations:

1. Assume a liquid composition (use the feed composition as an initial guess).
2. Calculate the activity coefficients.
3. Assume a flash temperature.
4. Calculate the K -values.
5. Solve the flash equation (2.14) by adjusting the temperature in Step 3.
6. Calculate the equilibrium vapor and liquid compositions.
7. If the calculated liquid composition does not match the values in Step 1, restart with the calculated liquid composition. Repeat until the liquid composition stabilizes.

The results are summarized as follows (p_i^0 in kPa, T in K, S in kmol/h):

$S = 0$						$S = 100$					
$T = 312.7$						$T = 311.5$					
	γ_i	p_i^0	K_i	X_i	Y_i		γ_i	p_i^0	K_i	X_i	Y_i
1.	1.000	519.0	1.082	0.480	0.520		3.828	502.8	4.010	0.143	0.572
2.	1.000	444.0	0.926	0.519	0.481		2.496	429.7	2.234	0.191	0.427
3.	14.73	0.861	0.026	0.0	0.0		1.263	0.808	0.002	0.666	0.001

$S = 200$						$S = 400$					
$T = 314.5$						$T = 325.0$					
	γ_i	p_i^0	K_i	X_i	Y_i		γ_i	p_i^0	K_i	X_i	Y_i
1.	6.175	544.2	7.001	0.083	0.583		8.722	710.2	12.90	0.046	0.589
2.	3.652	466.2	3.547	0.117	0.415		4.808	613.7	6.148	0.066	0.406
3.	1.083	0.948	0.002	0.800	0.002		1.024	1.626	0.003	0.889	0.003

S , kmol/h	0	100	200	400
Y_1/Y_2	1.0812	1.3403	1.4065	1.4516