

Chapter 5 solutions

WARM-UPS

P5.1

Crystallization: differences in freezing point

Adsorption: differences in binding to solid

Extraction: differences in solubility in 2 immiscible liquids

Distillation: differences in volatility

Membrane filtration: differences in size

Absorption: difference in solubility of gas in liquid

P5.2

Flash vaporization, condensation, and distillation all involve vapor-liquid equilibrium and the use of an energy separating agent. In flash vaporization, a liquid feed is heated to evaporate part or all of the material. In condensation, a vapor feed is cooled to condense part or all of the material. In distillation, a feed (liquid and/or vapor) is repeatedly condensed and vaporized in multiple stages, resulting in two product streams of different composition.

Adsorption, absorption, and solvent extraction all require the addition of a material separating agent. In adsorption, a multicomponent fluid (gas or liquid) is contacted with a solid separating agent; some components of the fluid stick to the solid whereas others do not. In absorption, a multicomponent gas is contacted with a liquid; some components of the gas dissolve in the liquid while others do not. In solvent extraction, a multicomponent liquid is contacted with another immiscible liquid; some components of the first liquid dissolve in the second while others do not.

P5.3

Antoine equation for water from 60 to 150 °C:

$$\log_{10} P_w^{sat} = 7.96681 - \frac{1668.21}{228 + T(^{\circ}\text{C})}$$

At boiling point, $P = P^{sat}$.

At $P = 1 \text{ atm} = 760 \text{ mmHg}$

$$\log_{10}(760) = 7.96681 - \frac{1668.21}{228 + T(^{\circ}\text{C})}, \text{ or } T = 100^{\circ}\text{C}$$

At $P = 2.5 \text{ atm} = 1900 \text{ mmHg}$

$$\log_{10}(1900) = 7.96681 - \frac{1668.21}{228 + T(^{\circ}\text{C})}, \text{ or } T = 128^{\circ}\text{C}$$

P5.4

150 psig = 164.7 psia = 8515 mm Hg. From Figure 5.10, we follow across at 8.5×10^3 mm Hg pressure until we reach the vapor-liquid coexistence curve, then read down to the Temperature axis. I read a temperature of about 180°C.

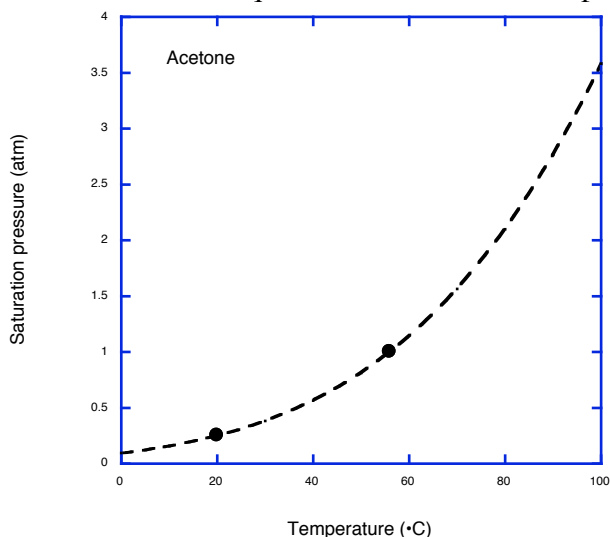
Another way to find the temperature of saturated steam at this pressure is to use Antoine's equation

$$\log_{10}(8515) = 7.96681 - \frac{1668.21}{228 + T(^{\circ}\text{C})}, \text{ or } T = 185^{\circ}\text{C}$$

A third way will be learned in Chapter 6, when we are introduced to steam tables.

P5.5

Two data points are shown. The general shape comes from knowing that the vapor pressure increases faster than linearly with temperature (which we can see for example from the Antoine equation or from the water phase diagram).

**P5.6**

Refer to Figure 5.12, or to Table B.9. A saturated solution of benzene and naphthalene at 45°C contains about 48 mol% naphthalene and about 52 mol% benzene. The solid phase formed upon cooling is pure naphthalene.

P5.7

$$x_E = 0.09, y_E = 0.41, x_W = 0.91, y_W = 0.59$$

$$\text{From inverse lever rule, } \frac{n_V}{n_L} = \frac{0.3 - 0.09}{0.41 - 0.3} = 1.90, \text{ or about 65.5\% is vaporized.}$$

P5.8

The mixture is 20 wt% acetic acid, 60 wt% water, and 20 wt% MIBK. This composition clearly falls in the two-phase (shaded) domain of Figure 5.15. To find the compositions

of the two liquid phases we follow the dashed tie line to the curve. The water-rich phase contains about 21 wt% acetic acid, 4 wt% MIBK, and the remainder water. The extract phase contains about 17 wt% acetic acid, 74 wt% MIBK, and the remainder water.

The Gibbs phase rule is $F = C + 2 - \Pi$. For our situation, $F = 3 + 2 - 2 = 3$. The temperature is specified (25°C) so there are 2 additional degrees of freedom. These are satisfied by specifying two compositions (e.g., % acetic acid and % MIBK).

P5.9

$y_{SO_2} = 0.09$. At 760 mm Hg, $p_{SO_2} = 0.09(760) = 68.4$. From table B.6 at 20°C this corresponds to about 1.15 kg SO₂/100 kg water, or $x_{SO_2} = 0.011$. At 3040 mm Hg, $p_{SO_2} = 273.6$. Evaluating data in table B.6, $x_{SO_2} = 0.057$.

P5.10

Neither – Raoult's and Henry's law do not apply to liquid-solid equilibrium.

Henry's – CO₂ is a “noncondensable” gas

Neither – there are not two phases, so you can't apply a phase equilibrium relationship.

Raoult's – these compounds form both vapor and liquid phases, and are chemically similar and relatively non-interacting.

Neither – acetic acid and water participate in hydrogen bonding which makes Raoult's law inappropriate.

P5.11

Because the air in the room is multicomponent, not single component. From Antoine equation for water at 22°C, $P_w^{sat} = 19.7$ mm Hg. Maximum water content is if air is saturated; from Raoult's law this occurs at

$$\begin{aligned}x_w P_w^{sat} &= y_w P \\1(19.7) &= y_w (760) \\y_w &= 0.026\end{aligned}$$

P5.12

The Henry's law constant for oxygen in water increases with increasing temperature (e.g., 32,700 atm at 10°C and 47,500 atm at 30°C). Assuming the oxygen content of the air is constant at 0.21 mol fraction, and the pressure is 1 atm, then the mole fraction of oxygen dissolved in the water at 10°C is

$$x_{O_2} = \frac{y_{O_2} P}{H_{O_2}} = \frac{0.21(1 \text{ atm})}{32700 \text{ atm}} = 6.4 \times 10^{-6}$$

and at 30°C the mole fraction of oxygen dissolved in water is only

$$x_{O_2} = \frac{y_{O_2} P}{H_{O_2}} = \frac{0.21(1 \text{ atm})}{47,500 \text{ atm}} = 4.4 \times 10^{-6}$$

There is more oxygen dissolved in the cooler waters, so that is where the fish go.

P5.13

Colored dye partitions into the hexane layer, because like dissolves like, and oil is more like hexane than like water. The colored dye is in the top layer, because hexane is less dense than water.

P5.14

(1) Add stages. Multistaging reduces the solvent requirements but increases the cost of building the equipment. (2) Add a chemical to the water that complexes with the H_2S , such as DEA or MEA. (3) Increase the operating pressure or decrease the operating temperature.

DRILLS AND SKILLS

P5.15

Antibiotics: extraction (difference in solubility in liquid, can't use high temperatures, want to selectively pluck out one component at low concentration from complex mixture)

Isopropanol-air: condensation (large difference in volatility)

Limestone: sedimentation (two phases so use mechanical, large difference in density)

Soybean oil: leaching

Colored impurities: adsorption (want to selectively remove component at low concentration)

Methane: vaporization (methane is gas at ambient T and P, manure isn't)

CO_2 and H_2 : absorption (both gases at ambient, need to go too cold for distillation),

Ethylbenzene and styrene: distillation (boiling points are different and not much higher than ambient)

Yeast: filtration (two phases so use mechanical) filtration

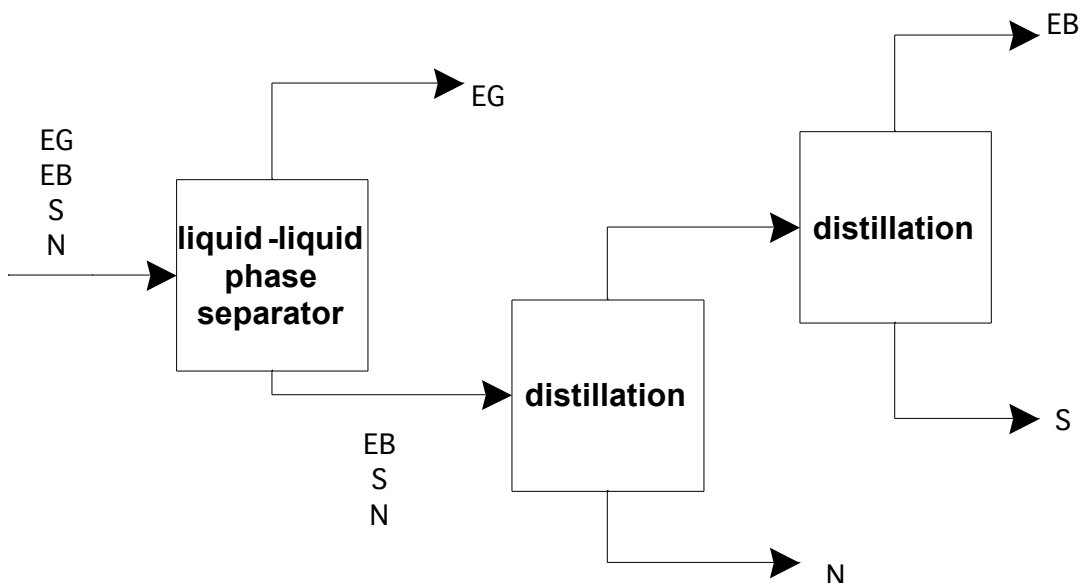
Potassium nitrate: crystallization (if cooled with form solid phase plus liquid solution)

Sedimentation and filtration are mechanical separations; others are equilibrium-based.

P5.16

For selection of separation technology, we consider the heuristics on p. 373-374. Given the solubility information, it is possible that ethylene glycol is insoluble not just in benzene but also in ethylbenzene, styrene, and naphthalene. (In fact the data in Table B.14 supports the idea that ethylene glycol is only sparingly soluble in styrene and ethylbenzene). If there are 2 liquid phases, we can simply mechanically separate, into one phase that is mainly ethylene glycol and another phase that is a mixture of the 3 benzene-like compounds. We will next consider equilibrium-based separations (heuristic 2). All compounds have normal boiling points at un-exotic temperatures but all but one have below-ambient melting points. Therefore, separations based on differences in relative volatility (e.g., distillation) are better than crystallization (heuristics 4 and 5). The differences in boiling points are large enough to make distillation feasible (heuristic 4), so although we *could* separate based on differences in solubility, we don't *need* to, thereby avoiding addition of a foreign species (heuristic 6).

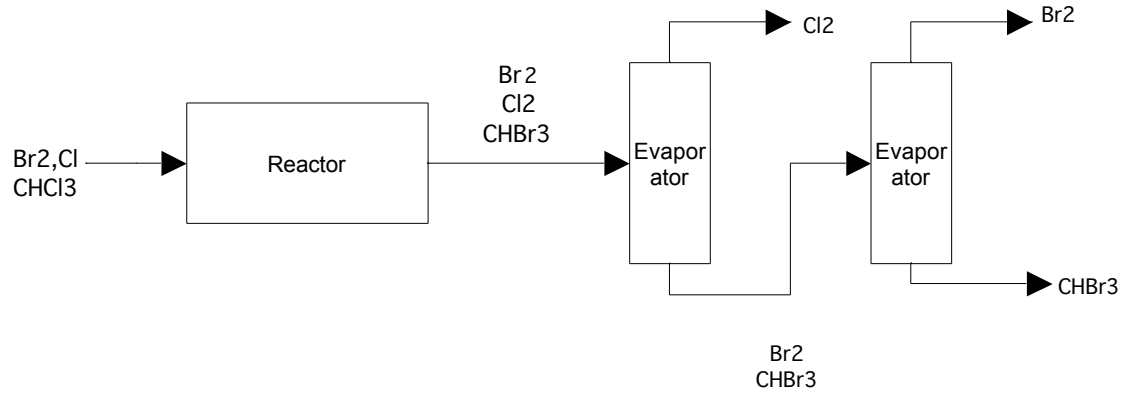
For sequencing of separation units, we consider the heuristics on p. 377-378. If the mixture forms 2 liquid phases including one phase that is mostly ethylene glycol, then we are left with distillation for the remaining 2 separations. We note that the order of relative volatility is ethylbenzene > styrene > naphthalene. The most difficult separation (approximated as the smallest difference between boiling point temperatures) is ethylbenzene from styrene. Based on separating the components present in the greatest quantities first (heuristic 2), we would first remove styrene, but based on saving difficult separations for last (heuristic 3), we would first remove naphthalene. Since the difference in quantity is relatively smaller than the difference in volatility, heuristic 3 probably wins out. Our block flow diagram might look like this:



What if there is insufficient phase separation between ethylene glycol and the benzene-like compounds to give the required purities? We might still use the liquid-liquid phase separator to get an initial “cut”, then further purify the ethylene glycol product by distillation (to remove the lower boiling styrene and ethylbenzene) and by crystallization (to remove the naphthalene).

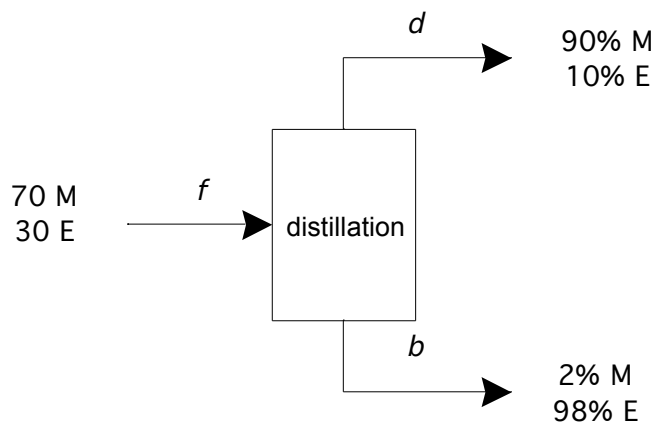
P5.17

Strategy: there is only a small amount of CHCl_3 , so use the Br_2 to convert CHCl_3 to CHBr_3 . The boiling point differences are now much larger so the separation is easier.



P5.18

Use M for methane and E for ethane. Flows are given in gmol/min, and compositions as mol%. Use f , d , and b to indicate feed, distillate (or overhead), and bottoms streams, respectively. The flow diagram is



The 2 material balance equations are;

$$70 = \dot{n}_{Md} + \dot{n}_{Mb} = 0.90\dot{n}_d + 0.02\dot{n}_b$$

$$30 = \dot{n}_{Ed} + \dot{n}_{Eb} = 0.10\dot{n}_d + 0.98\dot{n}_b$$

We combine and solve to find

$$\dot{n}_d = 77.3 \text{ gmol/min}$$

$$\dot{n}_b = 22.7 \text{ gmol/min}$$

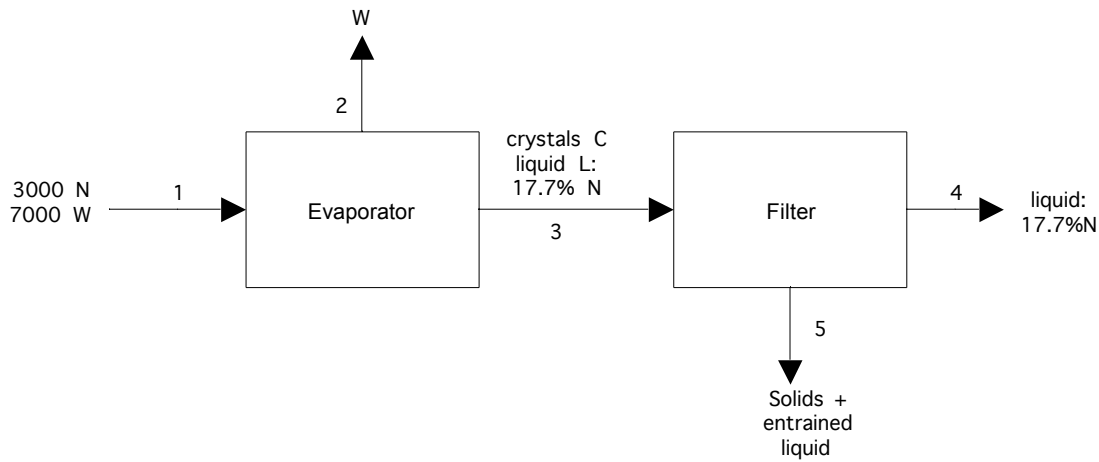
From the definitions we calculate the fractional recoveries of each component;

$$f_{RMd} = \frac{\dot{n}_{Md}}{\dot{n}_{Mf}} = \frac{0.90(77.3)}{70} = 0.994$$

$$f_{REb} = \frac{\dot{n}_{Eb}}{\dot{n}_{Ef}} = \frac{0.98(22.7)}{30} = 0.74$$

P5.19

Use *N* for sodium carbonate and *W* for water. Streams are numbered as shown on flow diagram. Use *c* for crystal phase and *l* for liquid phase. All flows in lb/h.



Material balance on evaporator:

$$\dot{m}_{N1} = 3000 = \dot{m}_{c3} + 0.177\dot{m}_{l3}$$

$$\dot{m}_{W1} = 7000 = \dot{m}_{W2} + \dot{m}_{W3} = \dot{m}_{W2} + 0.823\dot{m}_{l3}$$

From system performance specification on evaporator:

$$\dot{m}_{W2} = 0.4 \times 7000 = 2800$$

therefore

$$\dot{m}_{W3} = 4200 = 0.823\dot{m}_{l3}, \text{ or } \dot{m}_{l3} = 5103 \text{ and } \dot{m}_{c3} = 2097.$$

Material balance on filter:

$$3000 = 0.177\dot{m}_{l4} + 0.177\dot{m}_{l5} + \dot{m}_{c5} \text{ (assuming entrained solution is same composition as liquid filtrate)}$$

$$4200 = 0.823\dot{m}_{l4} + 0.823\dot{m}_{l5}$$

Also from entrainment specification,

$$\frac{\dot{m}_{c5}}{\dot{m}_{l5}} = 3.5$$

$$\dot{m}_{c5} = 2097$$

Combine and solve to find: $\dot{m}_{l5} = 599$

$$\dot{m}_{l4} = 4504$$

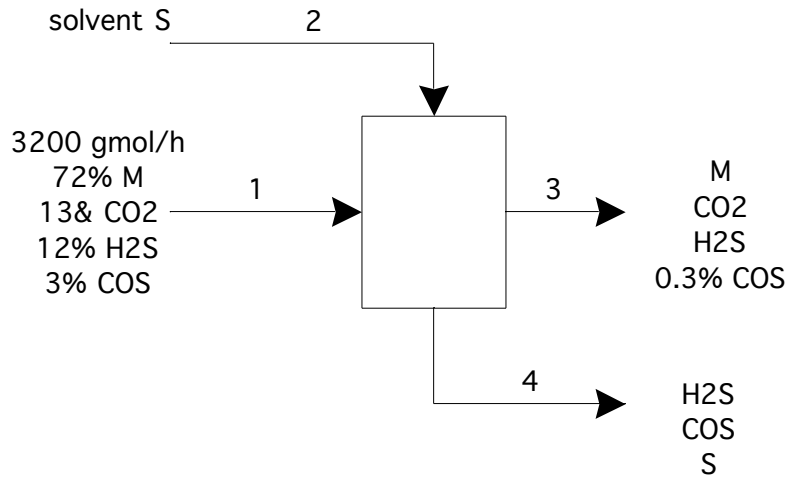
(a) filter cake production = $2097 + 599 = 2696$ lb/h

(b) filter cake purity = $(2097 + 0.177(599)) / 2696 = 0.817$

(c) fractional recovery = $(2097 + (0.177(599))) / 3000 = 0.73$

P5.20

The flow diagram is



with M for methane and S for the solvent. We also know that the gas:solvent ratio is 3:1 and the solvent absorbs 97.2% of the H_2S fed.

DOF analysis

Number of variables		
Stream variables	12	4 in stream 1, 1 in stream 2, 4 in stream 3, 3 in stream 4
System variables	0	No reaction, assumed steady state
Number of constraints		
Specified flows	2	Stream 1 = 3200 gmol/h Stream 2 = 1067 gmol/h
Specified compositions	4	3 in stream 1, 1 in stream 3
System performance specifications	1	97.2% recovery of H_2S
Material balances	5	

$$DOF = 12 - (2 + 4 + 1 + 5) = 12 - 12 = 0.$$

The material balances for methane and CO_2 are simple because each appears in only one input and one output stream.

$$\dot{n}_{M1} = \dot{n}_{M3} = 0.72(3200) = 2304 \text{ gmol/h}$$

$$\dot{n}_{CO_2,1} = \dot{n}_{CO_2,3} = 0.13(3200) = 416 \text{ gmol/h}$$

From the system performance specification for H_2S we know

$$f_{R,H_2S,4} = 0.972 = \frac{\dot{n}_{H_2S,4}}{\dot{n}_{H_2S,1}} = \frac{\dot{n}_{H_2S,4}}{0.12(3200)}$$

$$\dot{n}_{H_2S,4} = 373.25 \text{ gmol/h}$$

Now from material balance on H₂S we find

$$\dot{n}_{H_2S,3} = \dot{n}_{H_2S,1} - \dot{n}_{H_2S,4} = 384 - 373.25 = 10.75 \text{ gmol/h}$$

From the specified stream composition of the exiting gas,

$$0.003 = \frac{\dot{n}_{COS,3}}{\dot{n}_3} = \frac{\dot{n}_{COS,3}}{\dot{n}_{COS,3} + 2304 + 416 + 10.75}$$

$$\dot{n}_{COS,3} = 8.2 \text{ gmol/h}$$

From material balance on COS we find

$$\dot{n}_{COS,4} = \dot{n}_{COS,1} - \dot{n}_{COS,3} = 96 - 8.2 = 87.8 \text{ gmol/h}$$

The solvent in streams 2 and 4 is 1067 gmol/h.

From these calculations we find that the exit gas flow rate is 2739 gmol/h and the gas contains 84.1 mol% CH₄, 15.2 mol% CO₂, 0.4 mol% H₂S and 0.3 mol% COS. The liquid stream flow rate is 1528 gmol/h; it contains 24.4 mol% H₂S and 5.75 mol% COS in addition to the solvent.

P5.21

Consider 3 components: dry air, H₂O, and dry popcorn. The popcorn production is 50 kg/h total. At 10 wt% moisture, the popcorn product is therefore 45 kg/h dry popcorn and 5 kg/h water. Therefore, the wet popcorn, at 25% moisture, must contain 15 kg/h water (plus 45 kg/hr dry popcorn), and 10 kg/h water are removed in the hot air stream, or 555.6 gmol/h.

Since the wet air is modeled as an ideal gas, mol fraction = volume fraction. A steady-state material balance on water, with the entire process as the system, is

$$0.02\dot{n}_{gas,in} + 555.6 = 0.15\dot{n}_{gas,out} \text{ where the gas includes both dry air and water vapor.}$$

A steady-state material balance on air is:

$$0.98\dot{n}_{gas,in} = 0.85\dot{n}_{gas,out}$$

Solving 2 equations in 2 unknowns gives $\dot{n}_{gas,in} = 3633 \text{ gmol/h}$, or, converting to a volumetric flow rate assuming ideal gas behavior:

$$\dot{V}_{gas,in} = \frac{\dot{n}RT}{P} = \frac{(3633)(.082057)(80 + 273)}{1} = 105,230 \text{ L/h}$$

The recycle flow rate is 4 times the gas feed rate, or 14532 gmol/h. The recycle gas contains 15 mol% water – because there is simply a splitter on the exit air stream. From

this we can then do a material balance on the mixer, where the hot air feed is mixed with the recycle stream.

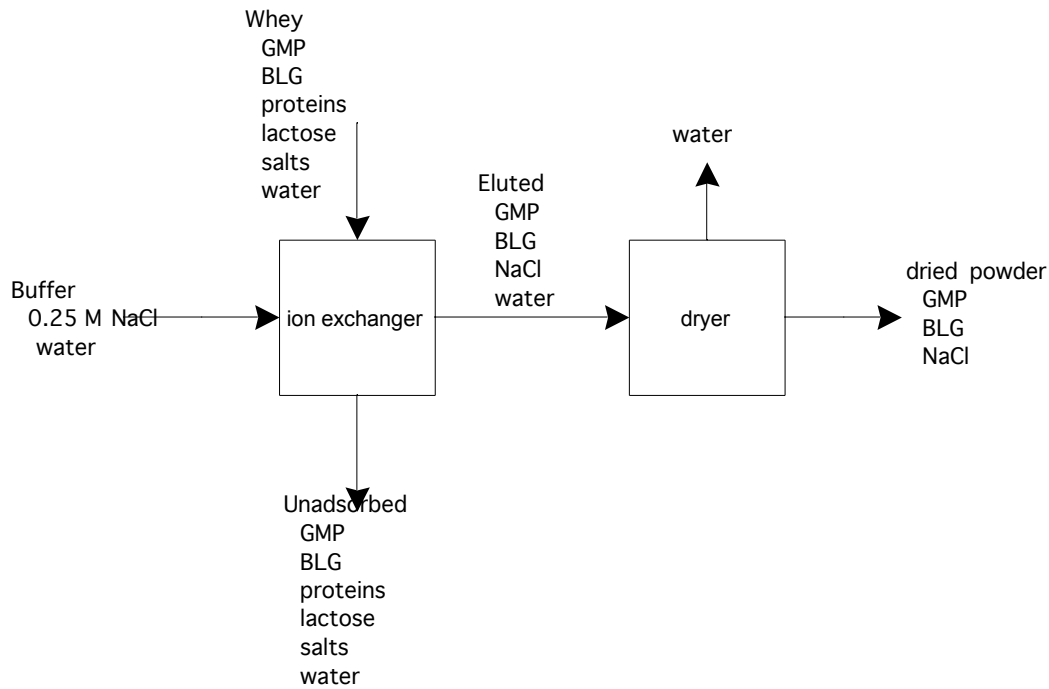
$$\text{Water: } 0.02(3633) + 0.15(14532) = \dot{n}_{\text{water},\text{to dryer}} = 2252.5 \text{ gmol/h}$$

$$\text{Total: } 3633 + 14532 = \dot{n}_{\text{gas},\text{to dryer}} = 18165 \text{ gmol/h}$$

Therefore, the moisture content of the gas to the dryer is $2252.5/18165$, or 0.124.

P5.22

This is a semi-batch process. We can consider the ion exchanger as a separation unit that achieves recovery of GMP and BLG by adding the separating agent, salt. The flow diagram shows what is accomplished by the ion exchanger in the two steps of adsorption and elution.



(a) During the first 30 minutes: consider the ion exchanger as the system. Whey is pumped at a steady flow rate (150 mL/min) onto the ion exchanger unit, GMP and BLG accumulate in the system, and unadsorbed materials leave the system at a steady flow rate. There is no NaCl in this part of the process. We write integral material balance equations because we are interested in what happens over a specified time interval. The material balance equation for GMP is:

$$\begin{aligned}
 m_{\text{GMP},\text{sys},f} - m_{\text{GMP},\text{sys},0} &= \int_0^{30} (1.2 \text{ g/L} \times 0.15 \text{ L/min}) dt - \int_0^{30} \dot{m}_{\text{GMP},\text{out}} dt \\
 &= 5.4 \text{ g} - 30\dot{m}_{\text{GMP},\text{out}}
 \end{aligned}$$

We also have a system performance specification for fractional recovery of GMP – expressed as the fraction GMP accumulated onto the resin:

$$f_{R,GMP,sys} = 0.89 = \frac{m_{GMP,sys,f} - m_{GMP,sys,0}}{\int_{t_0}^{t_f} \dot{m}_{GMP,in} dt} = \frac{m_{GMP,sys,f} - m_{GMP,sys,0}}{5.4 \text{ g}}$$

$$m_{GMP,sys,f} - m_{GMP,sys,0} = 0.89(5.4) = 4.8 \text{ g}$$

The total quantity of GMP that exits in the “unadsorbed” stream is 5.4 – 4.8 or 0.6 g.

A similar analysis leads to the conclusion that 3.6 g of BLG are fed to the system, 0.86 g adsorb to the resin and accumulate in the system, and 2.74 g exit in the “unadsorbed” stream.

(b) During the next 10 minutes, the high-salt buffer is pumped through the system and all the material initially adsorbed to the resin is eluted, so that none remains in the system at the end of the 10 minute interval. No protein enters the system, so the material balance is

$$m_{GMP,sys,f} - m_{GMP,sys,0} = 0 - 4.8 = - \int_0^{10} (c_{GMP,eluted} \times 0.15 \text{ L/min}) dt$$

$$- 4.8 = -1.5 c_{GMP,eluted}$$

$$c_{GMP,eluted} = 3.2 \text{ g/L}$$

The total quantity of GMP eluted is 4.8 g, and the total volume of the elution stream is 1.5 L. (The GMP is 2.67 times more concentrated in the elution stream than it was in the whey.)

Similarly, we find that the total quantity of BLG eluted is 0.86 g, and the concentration of BLG in the elution stream is 0.57 g/L. (The BLG is less concentrated in the elution stream than it was in the whey.)

NaCl does not accumulate on the resin; rather it simply enters and leaves the system at a steady state. The total quantity of NaCl that enters the system equals the quantity leaving the system, and is equal to

$$\int_0^{10} \left(\frac{0.25 \text{ moles NaCl}}{\text{L}} \times \frac{58.5 \text{ g NaCl}}{\text{mole NaCl}} \times \frac{0.15 \text{ L}}{\text{min}} \right) dt = 21.9 \text{ g NaCl}$$

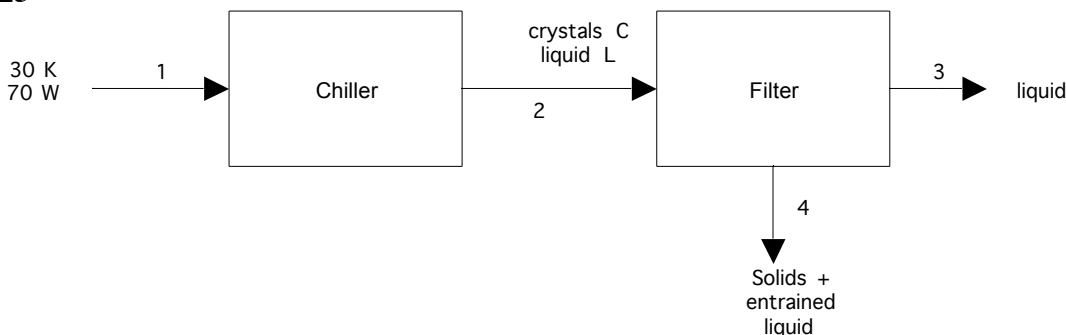
(c) During drying: the dryer is the system, nothing accumulates inside the dryer, and all water is removed while all NaCl, all GMP, and all BLG exits in the “dried powder” stream. The material balance is simply IN = OUT, or the dried powder contains 4.8 g GMP, 0.86 g BLG, and 21.9 g NaCl.

The total quantity of powder product is 27.56 g, and the purity is only $(4.8/27.56) \times 100\%$ or 17%. The majority of the impurity is salt. On a salt-free (protein-only) basis, the product is $(4.8/(4.8+0.86)) \times 100\%$ or 85% GMP.

The two product streams are the eluted and the unadsorbed materials. The separation factor for the separation of GMP and BLG between these two streams is:

$$\frac{m_{\text{GMP,eluted}}}{m_{\text{GMP,unadsorbed}}} \times \frac{m_{\text{BLG,unadsorbed}}}{m_{\text{BLG,eluted}}} = \frac{4.8 \text{ g}}{0.6 \text{ g}} \times \frac{2.74 \text{ g}}{0.86 \text{ g}} = 25.5$$

P5.23



From Figure 5.11, at 5°C , saturated solution is 15 wt% KNO_3 . If we call ES the entrained solution, C the crystals in the filter cake, and L the filtrate liquid, and assume that the composition of ES is the same as that of L, and that both are saturated solutions, then material balances around the entire system yield:

$$\text{Water: } 70 = 0.85\dot{m}_L + 0.85\dot{m}_{ES}$$

$$\text{KNO}_3: 30 = 0.15\dot{m}_L + 0.15\dot{m}_{ES} + \dot{m}_C$$

Also, we know that $\frac{\dot{m}_{ES}}{\dot{m}_C} = \frac{1}{19}$ from entrainment. This gives 3 equations in 3 unknowns.

Solving:

$$\dot{m}_C = 17.65 \text{ kg/h}$$

$$\dot{m}_{ES} = 0.93 \text{ kg/h}$$

$$\dot{m}_L = 81.42 \text{ kg/h}$$

$$\text{Purity of cake: } \frac{17.65 + 0.15(0.93)}{17.65 + 0.93} = 0.957$$

$$\text{Fractional recovery: } \frac{17.65 + 0.15(0.93)}{30} = 0.59$$

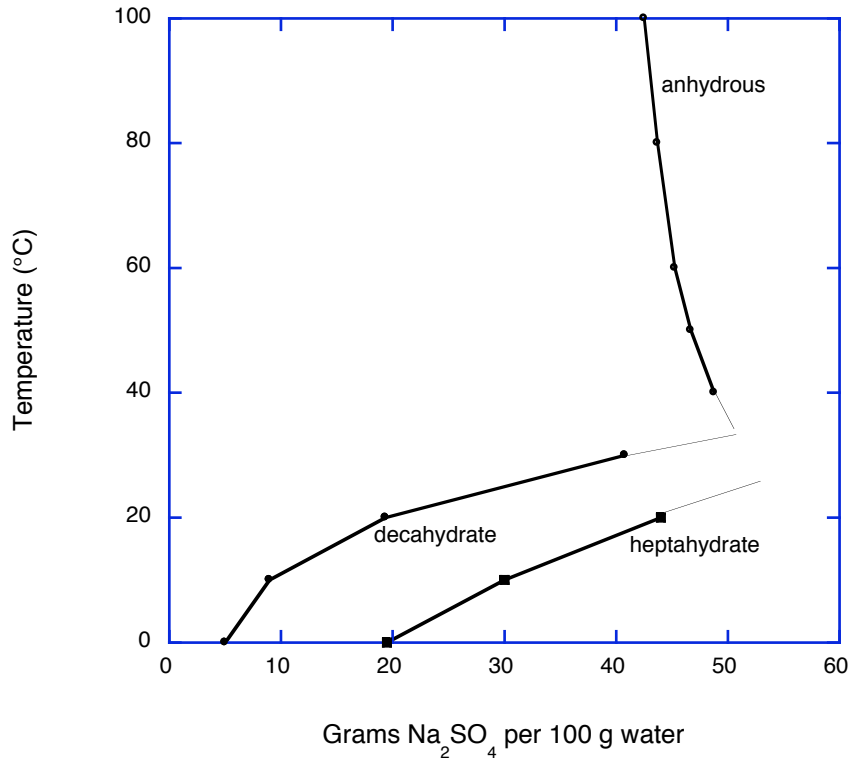
$$\text{Separation factor: } \alpha_{KW} = \frac{0.957}{0.043} \frac{0.85}{0.15} = 126$$

Recycling won't help. The salt concentration in the liquid is fixed by phase equilibrium, and the solid:liquid ratio in the cake is fixed by the entrainment specification. Since these

are fixed, and we still need to satisfy the material balance equation, the purity, recovery, and separation factor can't change.

P5.24

The data in Table B.8 were plotted to generate a phase diagram:



The curves show the salt form at different concentrations and temperatures. We extrapolated the data a bit (light lines) so the curves would meet up.

A 30 wt% solution is 30 g Na₂SO₄ per 100 g *solution*. We need to convert to g Na₂SO₄/100 g *water* to use the diagram:

$$\frac{30 \text{ g Na}_2\text{SO}_4}{70 \text{ g H}_2\text{O}} = \frac{x \text{ g Na}_2\text{SO}_4}{100 \text{ g H}_2\text{O}}$$

$$x = 42.9 \text{ g Na}_2\text{SO}_4$$

(a) Reading from the diagram, at 42.9 g Na₂SO₄ per 100 g H₂O, a solid phase of the decahydrate form appear at about 32°C. Thus, the solution should be cooled to below 32°C to allow crystallization.

(b) If 50% of the Na_2SO_4 is crystallized, then 15 g of Na_2SO_4 out of the original 100 g solution is crystallized. The remaining solution therefore contains

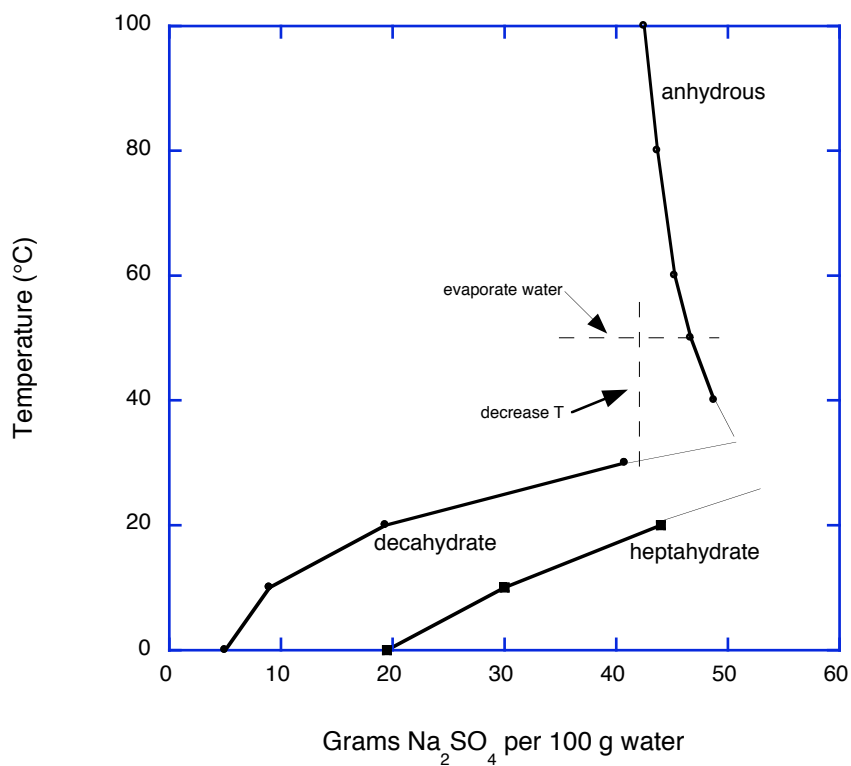
$$\frac{30 \text{ g} - 15 \text{ g } \text{Na}_2\text{SO}_4}{70 \text{ g } \text{H}_2\text{O}} = \frac{21.4 \text{ g } \text{Na}_2\text{SO}_4}{100 \text{ g } \text{H}_2\text{O}}$$

The solution must be cooled to 21°C .

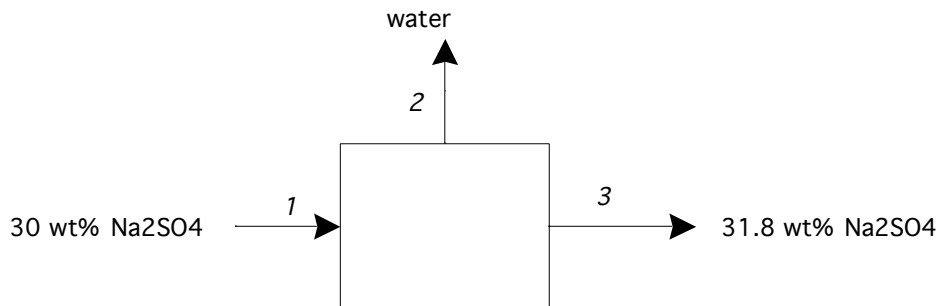
(c) By reading from the diagram, or using the table, we find that at 50°C , a solid phase appears if the salt concentration exceeds 46.7 g Na_2SO_4 per 100 g H_2O , or

$$\frac{46.7 \text{ g } \text{Na}_2\text{SO}_4}{100 \text{ g } \text{H}_2\text{O} + 46.7 \text{ g } \text{Na}_2\text{SO}_4} \times 100\% = 31.8 \text{ wt}\% \text{Na}_2\text{SO}_4.$$

Case (a) and (c) are illustrated by the dashed lines on the figure:



To determine the quantity of water that must be evaporated we sketch a flow diagram and complete material balance calculations:



Choosing as a basis 100 g/h in stream 1 (fed to the evaporator), we find by material balance on Na_2SO_4 (denoted by S for salt):

$$0.30(100) = 0.318\dot{m}_3$$

$$\dot{m}_3 = 94.3 \text{ g/h}$$

The water material balance is:

$$0.70(100) = 0.682(94.3) + \dot{m}_2$$

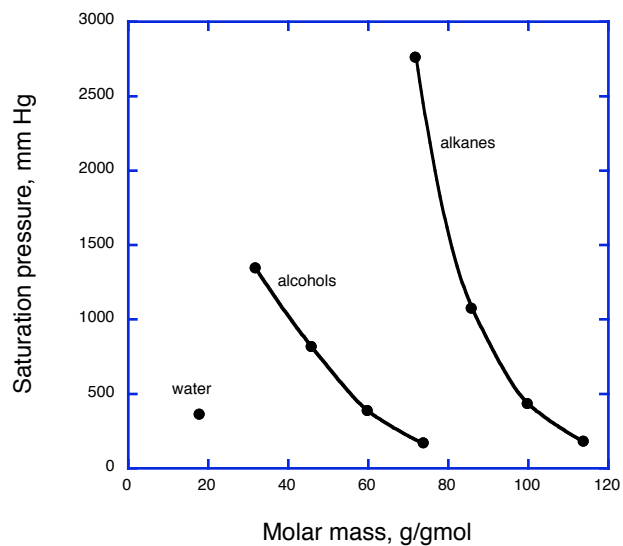
$$\dot{m}_2 = 5.7 \text{ g/h}$$

Since the water feed rate is 70 g/h, then 5.7/70 or 8.1% of the water fed must be evaporated to just begin to see solid phase formation.

P5.25

The saturation pressures at 80°C are tabulated and plotted.

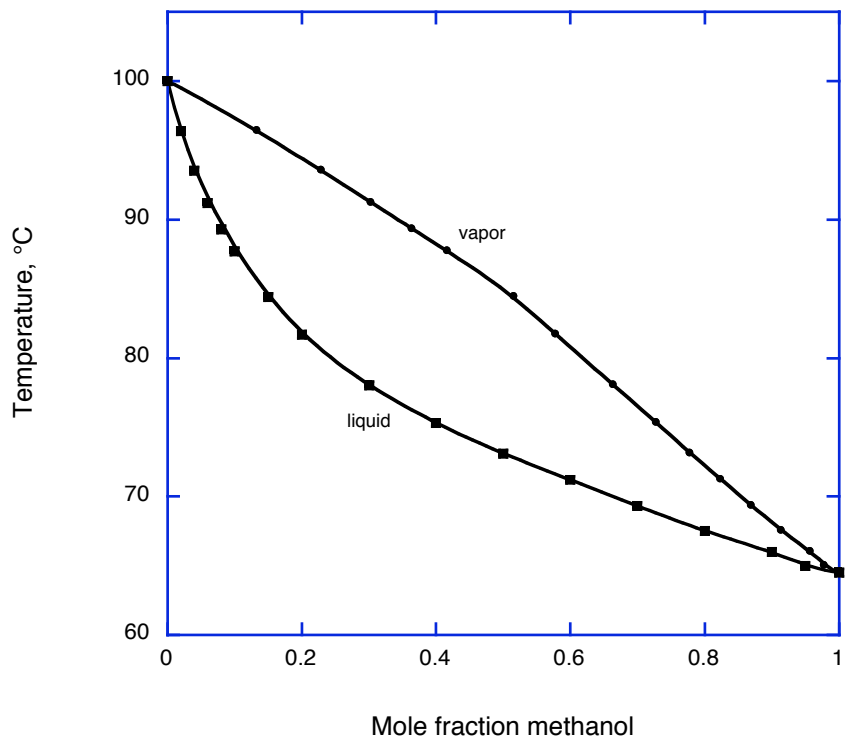
Compound	P^{sat} (mm Hg)	M_w
Alkanes: n-C5	2724	72
n-C6	1068	86
n-C7	428	100
n-C8	175	114
Alcohols: n-C1	1350	32
n-C2	811	46
n-C3	381	60
n-C4	163	74
Water	355	18



Saturation pressure drops rapidly as molar mass increases. The alkanes have the highest saturation pressure at a given molar mass. This is because attractive hydrogen bonding interactions for the alcohols keep them in the liquid phase compared to the alkanes, which have only weaker van der Waals and similar forces to hold together the liquid phase. Water is a very anomalous compound due to its strong hydrogen bonding.

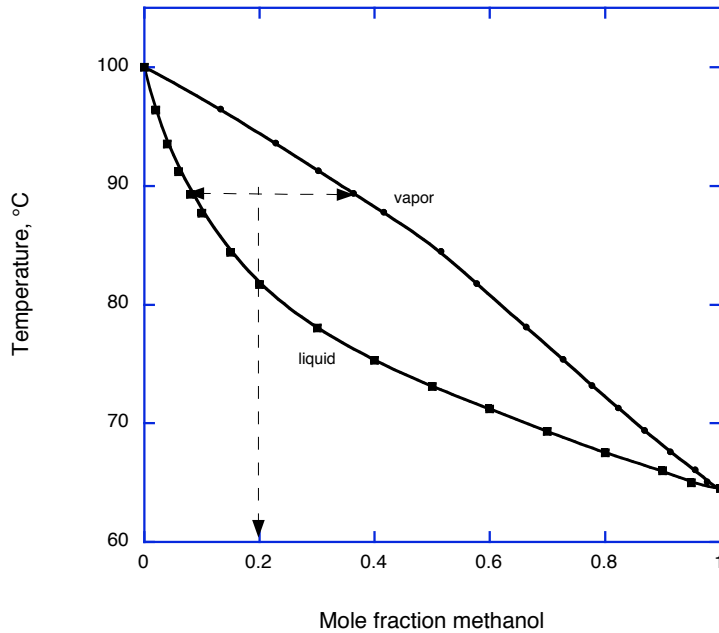
P5.26

The data are plotted.



(a) The boiling point of methanol is the temperature corresponding to $x_{meth} = y_{meth} = 1$, or 64.5°C. The boiling point of water is the temperature corresponding to $x_{meth} = y_{meth} = 0$, or 100°C. For a mixture of 50% methanol/50% water, the dewpoint corresponds to the temperature at which $y_{meth} = 0.5$, or about 85°C. The bubblepoint corresponds to the temperature at which $x_{meth} = 0.5$, or 73.1°C. At 95°C, this mixture is above its dewpoint so it is all vapor.

(b) A 20% methanol mixture at 89.3°C clearly falls in the two-phase region, as shown:



At 89.3°C, the saturated vapor contains 36.5 mol% methanol (63.5 mol% water) and the saturated liquid contains 8.0 mol% methanol (92 mol% water). By material balance on methanol (using as a basis 100 gmol/h feed):

$$0.2(100) = 0.365\dot{n}_V + 0.08\dot{n}_L$$

Also, from a total mole balance equation:

$$100 = \dot{n}_V + \dot{n}_L$$

We solve simultaneously to find

$$\dot{n}_V = 42 \text{ gmol/h}$$

or, 42% of the feed is vaporized.

The fractional recovery of methanol in the vapor stream is

$$f_{RMV} = \frac{y_{meth}\dot{n}_V}{z_{meth}\dot{n}_F} = \frac{0.365(42)}{0.2(100)} = 0.77$$

The separation factor is

$$\alpha_{M-W} = \frac{y_{meth}}{x_{meth}} \frac{x_w}{y_w} = \left(\frac{0.365}{0.08} \right) \frac{0.92}{0.635} = 6.6$$

P5.27

$$(a) \log_{10}(1500) = 7.14016 - \frac{1574.51}{T + 224.09}, \text{ or } T_b = 173.1^\circ\text{C}.$$

$$(b) \log_{10}(1500) = 6.95719 - \frac{1424.255}{T + 213.21}, \text{ or } T_b = 163.5^\circ\text{C}.$$

(c) At $P = 2 \text{ bar} = 1500 \text{ mm Hg}$
from Eq. 5.12, at *bubblepoint*

$$1500 = 0.5P_s^{sat} + 0.5P_{eb}^{sat}$$

$$1500 = 0.5 \times 10^{7.14016 - \frac{1574.51}{T + 224.09}} + 0.5 \times 10^{6.95719 - \frac{1424.255}{T + 213.21}}$$

Solving in Excel gives $T = 168.1^\circ\text{C}$. at bubblepoint.

From Eq. 5.13 at *dewpoint*

$$\frac{1}{1500} = \frac{0.5}{P_s^{sat}} + \frac{0.5}{P_{eb}^{sat}}$$

Solving in Excel gives $T = 168.6^\circ\text{C}$ at dewpoint.

(Temperatures lie outside the range given in Table B.4, so the solution should be used with caution.)

P5.28

For ethylene glycol, the Antoine equation is

$$\log_{10}(P^{sat}) = 8.0908 - \frac{2088.9}{T + 203.5}$$

and for water we will use

$$\log_{10}(P^{sat}) = 7.96681 - \frac{1668.21}{T + 228}$$

where T is in $^\circ\text{C}$.

(a) 260°F is equivalent to 126.7°C , at which (from the Antoine equations) we find $P^{sat} = 58.2 \text{ mm Hg}$ for ethylene glycol and 1835 mm Hg for water. We want the composition of the ethylene glycol-water mixture that gives a *bubblepoint* of 126.7°C . From Eq. 5.12 (assuming Raoult's Law behavior – which may not be a great assumption), at the bubblepoint

$$x_e P_e^{sat} + x_w P_w^{sat} = P$$

$$x_e(58.2) + x_w(1835) = 760 \text{ mm Hg}$$

Also,

$$x_e + x_w = 1$$

Solving simultaneously, we find

$$x_e = 0.605$$

The mixture should contain at least 60.5 mol% ethylene glycol or

$$\frac{x_e M_e}{x_e M_e + x_w M_w} \times 100\% = \frac{0.605(62)}{0.605(62) + 0.395(18)} 100\% = 84.1 \text{ wt}\%$$

(b) We return to the bubblepoint equation from part (a), except now we know the mole fractions and total pressure (15 psig, or 1535 mm Hg) but not the saturation pressures:

$$0.605 P_e^{sat} + 0.395 P_w^{sat} = 1535 \text{ mm Hg}$$

We substitute in our Antoine equations, arriving at a single equation in the unknown variable T , and solve to find $T = 150^\circ\text{C}$ or 302°F .

P5.29

$$(a) \log_{10}(7600) = 6.90565 - \frac{1211.033}{T + 220.79}, \text{ or } T = 179.6^\circ\text{C}.$$

(b) From Antoine's equation, at 202°C ,

$$\text{benzene: } \log_{10} P_b^{sat} = 6.90565 - \frac{1211.033}{202 + 220.79}, \text{ or } P_b^{sat} = 10,997 \text{ mm Hg}$$

$$\text{toluene: } \log_{10} P_t^{sat} = 6.95464 - \frac{1344.8}{202 + 219.48}, \text{ or } P_t^{sat} = 5790 \text{ mm Hg}$$

(This temperature lies outside the range given in Table B.4, so the results should be used with caution.)

Material balances:

$$\text{Benzene: } 40 = y_b n_V + x_b n_L$$

$$\text{Total: } 100 = n_V + n_L$$

Phase equilibrium from Raoult's law:

$$y_b = \frac{10997}{7600} x_b$$

$$n_V = 32$$

$$n_L = 68$$

Solving, we get:

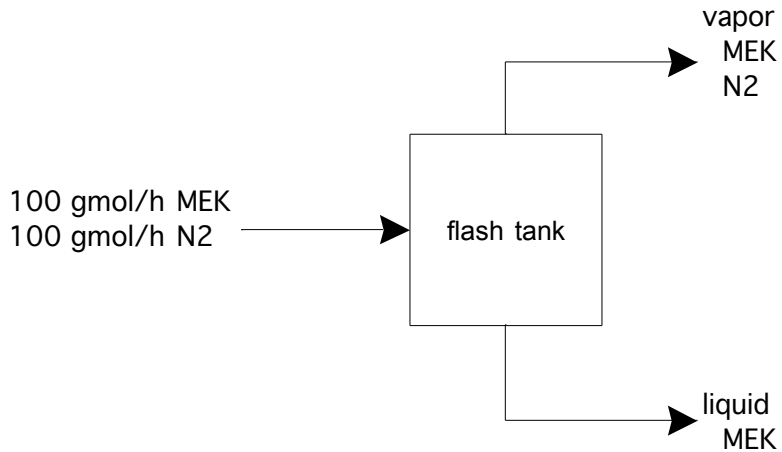
$$y_b = 0.506, y_t = 0.494$$

$$x_b = 0.35, x_t = 0.65$$

To check answer, use Raoult's law on toluene.

P5.30

We'll postulate that at any operating conditions N_2 is noncondensable and only MEK will appear in the liquid stream. The flow diagram is



The Antoine equation for methyl ethyl ketone (MEK), from Table B.4, is

$$\log_{10}(P^{sat}) = 6.97 - \frac{1210}{T + 216}$$

(a) At 80°C, P^{sat} for MEK is calculated to be 762 mm Hg. We have only one phase equilibrium relationship, which we get from Raoult's law:

$$y_{MEK}P = x_{MEK}P_{MEK}^{sat}$$

$$y_{MEK} = \frac{(1.0)762}{3050} = 0.25$$

The vapor is 25 mol% MEK and 75 mol% N₂. Liquid is pure MEK. From the material balance equations we find the vapor and liquid flow rates:

$$100 = y_{N_2}\dot{n}_V = 0.75\dot{n}_V$$

$$100 = x_{MEK}\dot{n}_L + y_{MEK}\dot{n}_V = 1.0\dot{n}_L + 0.25\dot{n}_V$$

$$\dot{n}_V = 133 \text{ gmol/h}$$

$$\dot{n}_L = 67 \text{ gmol/h}$$

(b) We maintain the pressure at 3050 mm Hg but increase the temperature until just all the liquid is gone – in other words, to the dewpoint temperature. Since all the MEK and all the N₂ goes to the vapor, then we know that $y_{MEK} = z_{MEK} = 0.5$. At the dewpoint we postulate the existence of a tiny droplet of liquid, which in this case will be pure MEK. From Raoult's law

$$y_{MEK}P = x_{MEK}P_{MEK}^{sat}$$

$$0.5(3050) = P_{MEK}^{sat} = 1525 \text{ mm Hg}$$

We insert this value into the Antoine equation to find the dewpoint temperature:

$$\log_{10}(1525) = 6.97 - \frac{1210}{T + 216}, \text{ or } T = 103.5^\circ\text{C}$$

The flash tank must operate at temperatures of at least 103.5°C to ensure complete vaporization of the feed stream.

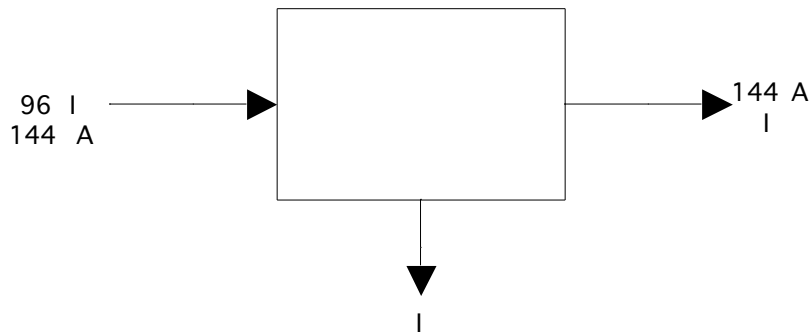
(c) Now we maintain a constant temperature (80°C) and vary the pressure. Raoult's law is

$$y_{MEK}P = x_{MEK}P_{MEK}^{sat}$$

$$0.5P = 762 \text{ mm Hg, or } P = 1524 \text{ mm Hg}$$

The maximum tank pressure at which full vaporization can occur at 80°C is 1524 mm Hg.

P5.31



(a)

I is isopropanol and A is air, known flows are given in gmol/min. Condensate is assumed to be pure isopropanol. *v* is vapor product, *l* is liquid product.

At 25°C, from Antoine equation for isopropanol,

$$\log_{10} P_I^{sat} = 8.1178 - \frac{1580.92}{25 + 219.61} \text{ or } P_I^{sat} = 45.16 \text{ mm Hg}$$

Using Raoult's law we find

$$y_I = \frac{45.16}{760}(1) = 0.059 = \frac{n_{Iv}}{n_{Iv} + n_{Av}} = \frac{n_{Iv}}{n_{Iv} + 144}$$

$$n_{Iv} = 9.03 \text{ gmol/min}$$

Vapor is 5.9% isopropanol, 94.1 mol% air, 153 gmol/min total. Liquid condensate is calculated from material balance on isopropanol: $96 - 9.03 = 87$ gmol/min, 100% isopropanol. Percent recovery is $87/96 \times 100 = 90.5\%$.

(b) At 98% recovery, the liquid condensate flow rate 0.98×96 or 94.1 gmol/min, and isopropanol flow in the vapor is 1.9 gmol/min, so the vapor is 1.3 mol% isopropanol, and the partial pressure is 9.9 mm Hg. Now we just use Antoine's equation to find the temperature at which the saturation pressure of isopropanol = 9.9 mm Hg.

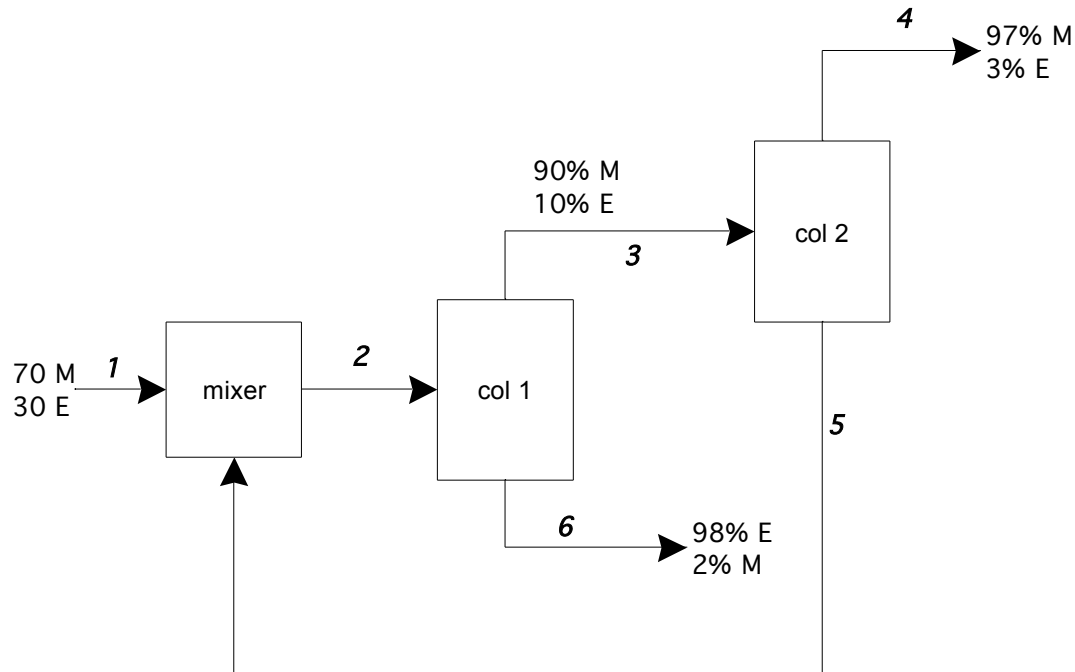
$$\log_{10}(9.9) = 8.1178 - \frac{1580.92}{T + 219.61}$$

$$T = 2.3^{\circ}\text{C}$$

Brrr!!

P5.32

The flow diagram is shown, with E for ethane and M for methane.



Flows are given in gmol/min, compositions in mol%, and we assume steady-state operation. We write material balances on all 3 process units. We will use mole fractions and total molar flow rates as variables, because of the nature of the information provided.

Mixer:

$$70 + x_{M5}(100) = x_{M2}\dot{n}_2$$

$$30 + x_{E5}(100) = x_{E2}\dot{n}_2$$

Column 1:

$$x_{M2}\dot{n}_2 = 0.9\dot{n}_3 + 0.02\dot{n}_6$$

$$x_{E2}\dot{n}_2 = 0.1\dot{n}_3 + 0.98\dot{n}_6$$

Column 2:

$$0.90\dot{n}_3 = 0.97\dot{n}_4 + x_{M5}(100)$$

$$0.10\dot{n}_3 = 0.03\dot{n}_4 + x_{E5}(100)$$

We also have

$$x_{M5} + x_{E5} = 1$$

$$x_{M2} + x_{E2} = 1$$

We have 8 equations in 8 unknowns. We can proceed by simultaneously solving all 8 equations (using an equation-solving package such as EES), or by setting up the matrices as we learned in Chapter 3 and solving using a matrix function on a calculator.

Alternatively, we can first group all 3 units into a single system and derive 2 equations in 2 unknowns:

$$70 = 0.97\dot{n}_4 + 0.02\dot{n}_6$$

$$30 = 0.03\dot{n}_4 + 0.98\dot{n}_6$$

(or, we use one of these balances plus a total mole balance equation). We solve by substitution and elimination to find

$$\dot{n}_4 = 71.6 \text{ gmol/min}$$

$$\dot{n}_6 = 28.4 \text{ gmol/min}$$

From a total mole balance around column 2, we find

$$\dot{n}_3 = \dot{n}_4 + \dot{n}_5 = 71.6 + 100 = 171.6 \text{ gmol/min}$$

This result inserted into the component balance equations on column 2 tells us

$$x_{M5} = 0.85$$

$$x_{E5} = 0.15$$

Now we move backwards to column 1 balances:

$$x_{M2}\dot{n}_2 = 0.9(171.6) + 0.02(28.4) = 155 \text{ gmol/min}$$

$$x_{E2}\dot{n}_2 = 0.1(171.6) + 0.98(28.4) = 45 \text{ gmol/min}$$

or

$$\dot{n}_2 = 200 \text{ gmol/min}$$

$$x_{M2} = 0.775$$

$$x_{E2} = 0.225$$

The flowrate of the desired product, stream 4, is 71.6 gmol/min. The recycled stream, stream 5, is 85% methane and 15% ethane. The fractional recoveries of methane and ethane are:

$$f_{RM4} = \frac{x_{M4}\dot{n}_4}{x_{M1}\dot{n}_1} = \frac{0.97(71.6)}{0.70(100)} = 0.992$$

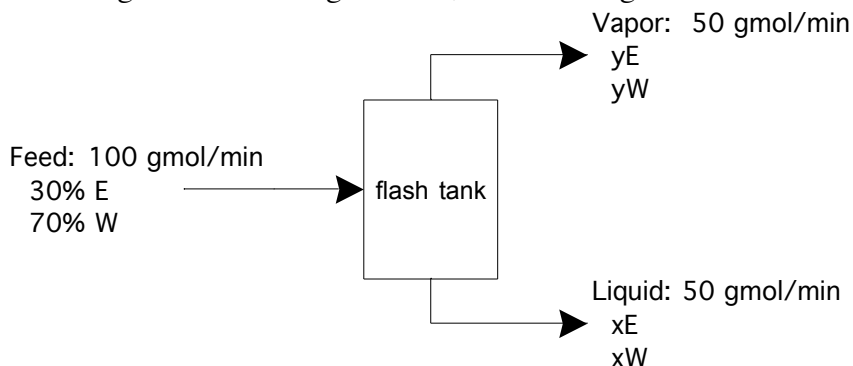
$$f_{RE6} = \frac{x_{E6}\dot{n}_6}{x_{E1}\dot{n}_1} = \frac{0.98(28.4)}{0.30(100)} = 0.928$$

P5.33

- (a) The dewpoint temperature corresponds to the saturated vapor at $y_E = 0.3$, or 92°C .
 (b) Reading across from $y_E = 0.3$, at 92°C , we find $x_E = 0.05$
 (c) The bubblepoint temperature corresponds to the saturated liquid at $x_E = 0.3$, or 82°C .
 (D) Reading across from $x_E = 0.3$, at 82°C , we find $y_E = 0.57$

P5.34

Assuming a basis of 100 gmol/min, the flow diagram is



where we've used E for ethanol and W for water; compositions are given in mole fractions.

The material balance equations are

$$0.3(100) = 30 = y_E(50) + x_E(50)$$

$$0.7(100) = 70 = y_W(50) + x_W(50)$$

We also know of course that

$$y_E + y_W = 1.0$$

$$x_E + x_W = 1.0$$

Figure 5.13 (and Table B.11) provides the phase equilibrium relationships (relating y_E to x_E , and y_W to x_W). Since the information is in graphical rather than equation form, we are stuck with a trial-and-error approach: guess a temperature, find y_E and x_E from the graph, insert values into the material balance equation and see if the equation is satisfied.

Try $T = 84.1^\circ\text{C}$: $y_E = 0.5089$ and $x_E = 0.1661$ (Table B.11). In material balance;

$$y_E(50) + x_E(50) = 0.5089(50) + 0.1661(50) = 33.75 \neq 30$$

Try $T = 85.3^\circ\text{C}$: $y_E = 0.4704$ and $x_E = 0.1238$ (Table B.11). In material balance;
 $y_E(50) + x_E(50) = 0.4704(50) + 0.1238(50) = 29.7 \sim 30$

This is close enough – a temperature of about 85°C will vaporize 50% of the feed stream and produce a vapor of 47 mol% ethanol and a liquid of 12.4 mol% ethanol.

The fractional recoveries and separation factors are:

$$f_{REv} = \frac{y_E \dot{n}_v}{z_{Ef} \dot{n}_f} = \frac{0.47(50)}{0.30(100)} = 0.78$$

$$f_{RWl} = \frac{x_W \dot{n}_l}{z_{Wf} \dot{n}_f} = \frac{0.876(50)}{0.70(100)} = 0.626$$

$$\alpha_{E-W} = \frac{y_E}{x_E} \frac{x_W}{y_W} = \left(\frac{0.47}{0.124} \right) \left(\frac{0.876}{0.53} \right) = 6.26$$

P5.35

From the Antoine equation constants for benzene and toluene:

$$\log_{10}(P_b^{sat}) = 6.90565 - \frac{1211.033}{130 + 220.790}$$

$$P_b^{sat} = 2840 \text{ mm Hg}$$

$$\log_{10}(P_t^{sat}) = 6.95464 - \frac{1344.8}{130 + 219.48}$$

$$P_t^{sat} = 1278 \text{ mm Hg}$$

The minimum pressure to have two phases is the dewpoint (maximum is the bubblepoint). Using Raoult's law,

$$y_b = 0.3 = \frac{2840x_b}{P}$$

$$y_t = 0.7 = \frac{1278x_t}{P}$$

Also, $x_b + x_t = 1$.

Solving, we find $P = 1530 \text{ mm Hg}$ for dewpoint. (The bubblepoint pressure is found in a similar manner to be 1747 mm Hg .)

Using as a basis 100 gmol mixture fed to the distillation column, and using the specifications of 96% recovery of toluene in the bottoms product and a 98% purity in this product, we find by material balance that the distillate must contain 28.63 gmol benzene

and 2.8 gmol toluene while the bottoms must be 67.2 gmol toluene and 1.37 gmol benzene. Assuming operation at 130 °C, from the Fenske equation

$$N_{\min} = \frac{\log\left[\left(\frac{28.63}{2.8}\right)\left(\frac{67.2}{1.37}\right)\right]}{\log\left[\frac{2840}{1278}\right]} = 7.78$$

or, about 8 stages are the minimum needed.

P5.36

To convert partial pressures to mole fraction H_2S in the vapor phase, we simply use

$$y_{H_2S} = \frac{p_{H_2S}}{P} = \frac{p_{H_2S}}{760}$$

where p_{H_2S} is the partial pressure of H_2S in mm Hg.

To convert moles H_2S per mole MEA solution to mole fraction H_2S in the liquid phase, we use

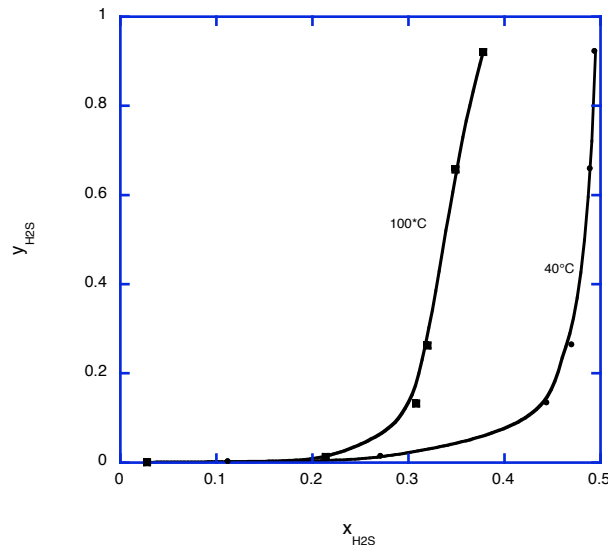
$$x_{H_2S} = \frac{n_{H_2S}}{n_{H_2S} + 1}$$

where n_{H_2S} is the moles of H_2S per mole of MEA solution.

The results are:

y_{H_2S}	x_{H_2S} at 40°C	x_{H_2S} at 100°C
0.0013	0.113	0.028
0.013	0.272	0.214
0.132	0.445	0.308
0.263	0.471	0.320
0.658	0.490	0.349
0.921	0.495	0.378

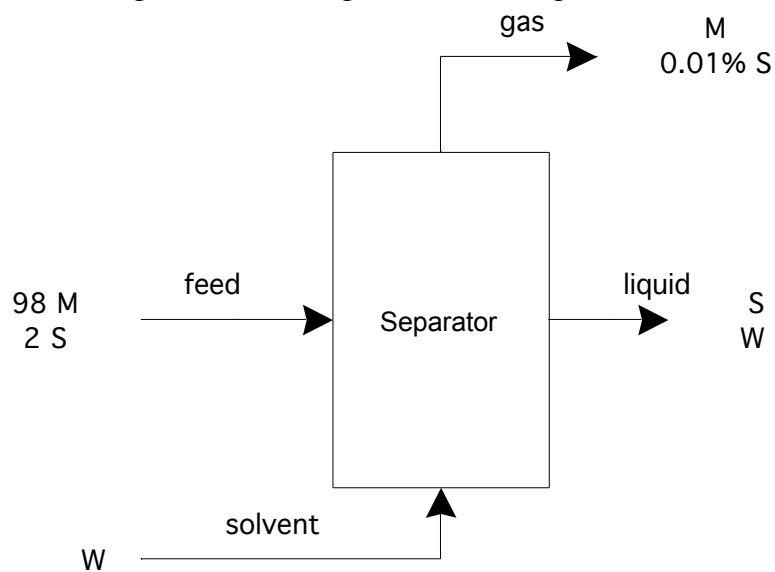
The data are plotted:



The data are clearly highly nonlinear, and cannot be described by Henry's law. This is not surprising – MEA is a good solvent for H_2S because there are strong noncovalent (acid-base) interactions.

P5.37

(a) From the problem statement, and assuming no methane is absorbed into the water, and no water evaporates into the gas, the flow diagram is



where M = methane and $S = H_2S$. From the process stream specification on the outlet

$$0.0001 = \frac{\dot{n}_{S,gas}}{\dot{n}_{S,gas} + \dot{n}_{M,gas}} = \frac{\dot{n}_{S,gas}}{\dot{n}_{S,gas} + 98}$$

$$\dot{n}_{S,gas} = 0.0098$$

By material balance, then $\dot{n}_{S,liq} = 1.9902$ kmol/h. For dilute solutions of H_2S in water, we can use Henry's law to model the gas-liquid equilibrium. At 40°C , from App. B, $H_{H_2S} = 745$ atm and

$$y_{H_2S}P = 0.0001(5) = x_{H_2S}H_{H_2S} = 745x_{H_2S}$$

$$x_{H_2S} = 6.71 \times 10^{-7} = \frac{\dot{n}_{H_2S,liq}}{\dot{n}_{H_2S,liq} + \dot{n}_{W,liq}} = \frac{1.9902}{1.9902 + \dot{n}_{W,liq}}$$

$$\dot{n}_{W,liq} = 2.97 \times 10^6 \text{ kmol/h!}$$

(b) At $T = 10^\circ\text{C}$, by linear interpolation, $H_{H_2S} = 367$ atm. With the change in temperature and pressure we find

$$y_{H_2S}P = 0.0001(40) = x_{H_2S}H_{H_2S} = 367x_{H_2S}$$

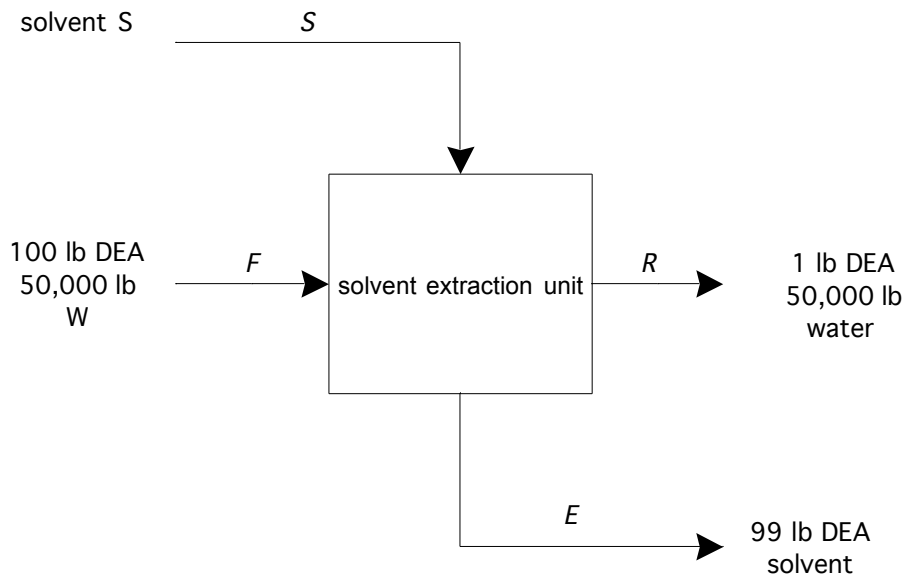
$$x_{H_2S} = 1.09 \times 10^{-5} = \frac{\dot{n}_{H_2S,liq}}{\dot{n}_{H_2S,liq} + \dot{n}_{W,liq}} = \frac{1.9902}{1.9902 + \dot{n}_{W,liq}}$$

$$\dot{n}_{W,liq} = 1.82 \times 10^5 \text{ kmol/h}$$

A big improvement.

P5.38

The flow diagram for the clean-up unit is



The streams are labeled as feed F , solvent S , raffinate R and extract E .

The solvent choices listed in Table B.15 for the DEA-water system are chloroform, benzene, toluene, and xylene. Chloroform has the highest K_D , indicating that DEA will

partition best into chloroform. In the absence of any other considerations (e.g., safety, cost), chloroform is the best choice.

We'll assume that the chloroform does not partition into the raffinate (aqueous) phase.

There is one equilibrium relationship relating the concentration of DEA in the extract and raffinate phases (the exiting streams):

$$x_{DEA,E} = K_D x_{DEA,R}$$

$$\frac{99}{99 + m_S} = 2.2 \left(\frac{1}{1 + 50000} \right) = 4.4 \times 10^{-5}$$

$$m_S = 2.25 \times 10^6 \text{ lb}$$

P5.39

We find the mixture point on Fig. 5.15 and then follow along the tie lines to find extract and raffinate compositions:

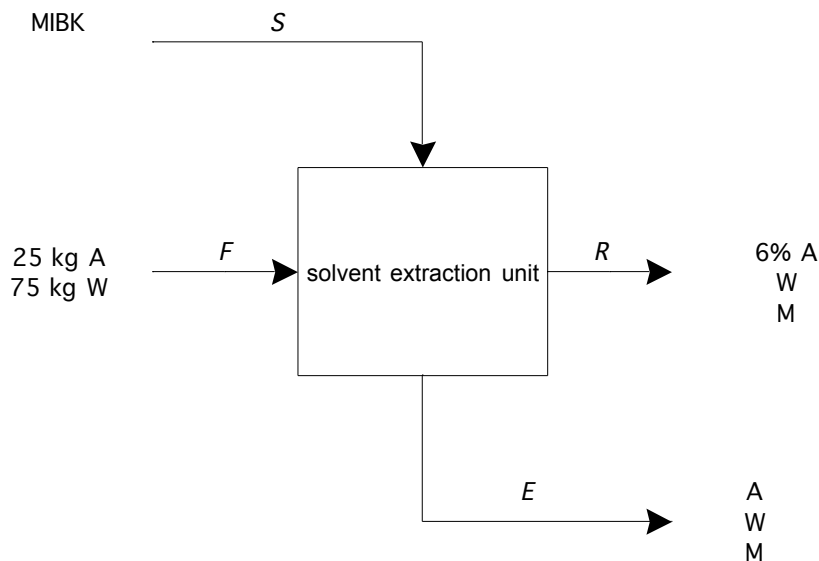
Extract: 11% acetic acid, 84% MIBK, 5% water

Raffinate: 14% acetic acid, 3% MIBK, 83% water.

By either using the inverse lever rule, or solving the material balance equations, we find that the extract quantity is 1160 kg and the raffinate quantity is 840 kg.

P5.40

The flow diagram is shown, using as a basis 100 kg/h feed. Compositions are given as wt%.



The raffinate R and extract E stream compositions are related by the phase equilibrium information in Figure 5.15 (and Table B.13).

Reading from the phase envelope in Figure 5.15, we see that a saturated water-rich solution containing 6 wt% acetic acid would also have ~2% MIBK and 92 wt% water. Following along an imaginary tie-line that falls in-between the two dashed tie lines in Figure 5.15, we estimate that this solution would be in equilibrium with an organic phase of 5 wt% acetic acid, 92 wt% MIBK and 3 wt% water. Thus, we find

Raffinate: 6 wt% acetic acid, 2 wt% MIBK, 92 wt% water

Extract: 5 wt% acetic acid, 92 wt% MIBK, 3 wt% water

We write material balances on all 3 components:

$$25 = 0.06\dot{m}_R + 0.05\dot{m}_E$$

$$75 = 0.92\dot{m}_R + 0.03\dot{m}_E$$

$$\dot{m}_S = 0.02\dot{m}_R + 0.92\dot{m}_E$$

We solve the first two equations simultaneously to find:

$$\dot{m}_E = 387 \text{ kg/h} \quad (\text{at our chosen basis of 100 kg/h feed})$$

$$\dot{m}_R = 69 \text{ kg/h}$$

Then we find the solvent flow rate from the 3rd equation:

$$\dot{m}_S = 357 \text{ kg/h}$$

Now we do a final check by using the total mass balance equation:

$$\dot{m}_S + \dot{m}_F = \dot{m}_E + \dot{m}_R \quad (?)$$

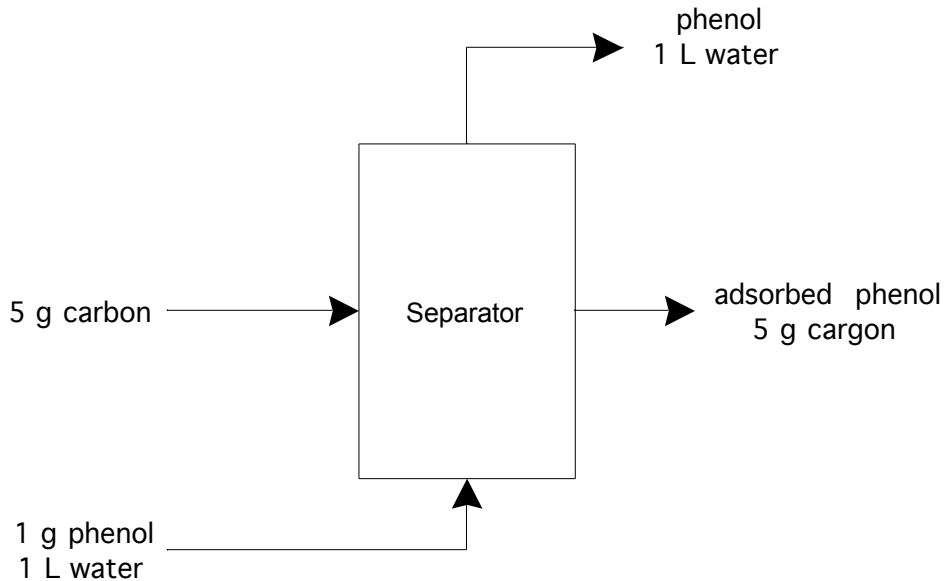
$$357 + 100 = 387 + 69 \quad (?)$$

$$457 = 456 \text{ (close enough)!}$$

Thus, we need 3.57 kg solvent per kg feed.

P5.41

We can draw a flow diagram as



To use the phase diagram, we need to convert to mmol: 1 g phenol ($\text{C}_6\text{H}_5\text{OH}$) = 10.638 mmol. Letting c_P = phenol concentration (mmol/L) in the liquid, and q_P = the phenol adsorbed (mmol/g) on the carbon, the material balance equation is simply

$$10.638 = c_P(1 \text{ L}) + q_P(5 \text{ g})$$

Now we need to find, by trial and error, the point (c_P , q_P) that lies on the curve and that satisfies the material balance equation. These two conditions are satisfied at $c_P \sim 0.6$ mmol/L, where $q_P = 2$ mmol/g.

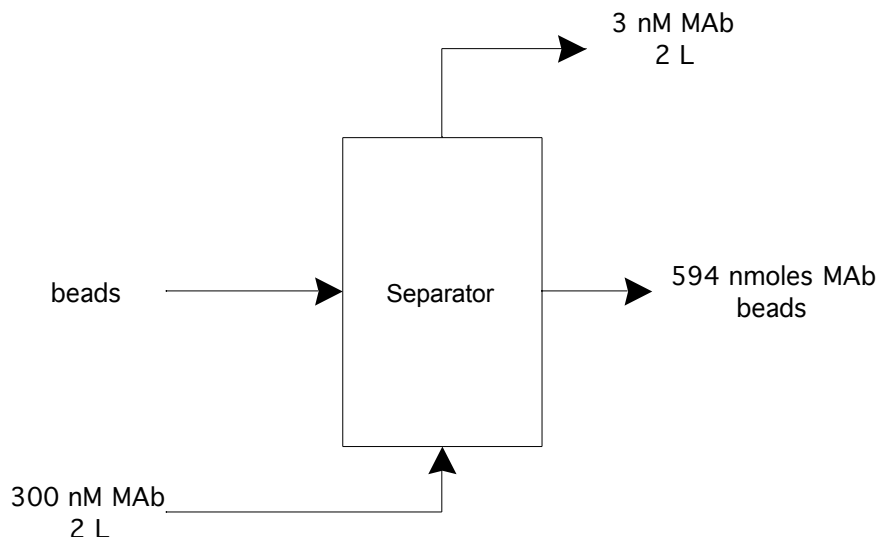
$$\% \text{ removal} = \frac{2 \times 5}{10.638} \times 100\% = 95\%$$

P5.42

The water leaving the vessel must contain 5 mmol phenol, and there will be 10 L, so the concentration is 0.5 mmol/L. This is in equilibrium with the adsorbed phenol, which we read directly off the chart as 1.8 mmol/g activated carbon. The total quantity of phenol to be removed comes from a material balance: $200 - 5 = 195$ mmol. Thus, the grams of activated carbon required is $195/1.8$, or 108.3 g.

P5.43

Since 99% of the MAb fed should be adsorbed, then 1%, or 3 nmoles/liter (nM) MAb, are left in the liquid phase. There are a total of 300×2 or 600 nmoles MAb fed, so by material balance there must be 594 nmoles adsorbed to the beads. This information is shown on the flow diagram.



From the phase equilibrium diagram, a fluid at 3 nM MAb is in equilibrium with 60 nmoles/g adsorbed MAb. Therefore, the total grams of beads required is 594/60, or just under 10 grams beads.

P5.44

Some possibilities: Sugar melts on a stove top (but it does brown) while salt does not. The solubility of sugar in water is much higher than that of salt. Students may try other solvents (ethanol seems to be a popular choice).

P5.45

Some possibilities:

- (a) food manufacture: drying, crystallization (sugars)
- (b) petroleum refining: distillation
- (c) pharmaceutical manufacturing: crystallization (synthetic drugs), solvent extraction (antibiotics made by fermentation), adsorption chromatography (protein therapeutics)
- (d) photographic film manufacture: drying
- (e) water purification: membrane filtration, reverse osmosis

P5.46

Technology	Category	Feed phase(s)	Product phase(s)	Property exploited	Separating agent
Drying of solids	Equilibrium	Moist solid	Vapor and solid	Differences in volatility	Heat
Adsorption	Equilibrium	Fluid	Fluid + solid	Differences in affinity for solid	Solid adsorbent

Electrophoresis	Rate	Liquid	Liquid	Differences in ion mobility in an electric field	Electric field (+ gel, paper, or other support media)
Distillation	Equilibrium	Liquid or vapor	Vapor + liquid	Differences in volatility	Heat
Crystallization	Equilibrium	Liquid	Liquid + solid	Differences in freezing	Cooling, or heating to evaporate
Absorption	Equilibrium	Gas	Gas + liquid	Differences in gas solubility in liquid	Liquid solvent
Settling	Mechanical	Solids (suspended) + liquid	Solids + liquid	Differences in density	Gravity
Reverse osmosis	Rate	Liquid	Liquid	Differences in diffusivity through a porous membrane	Pressure gradient + membrane

P5.47

Some general ideas:

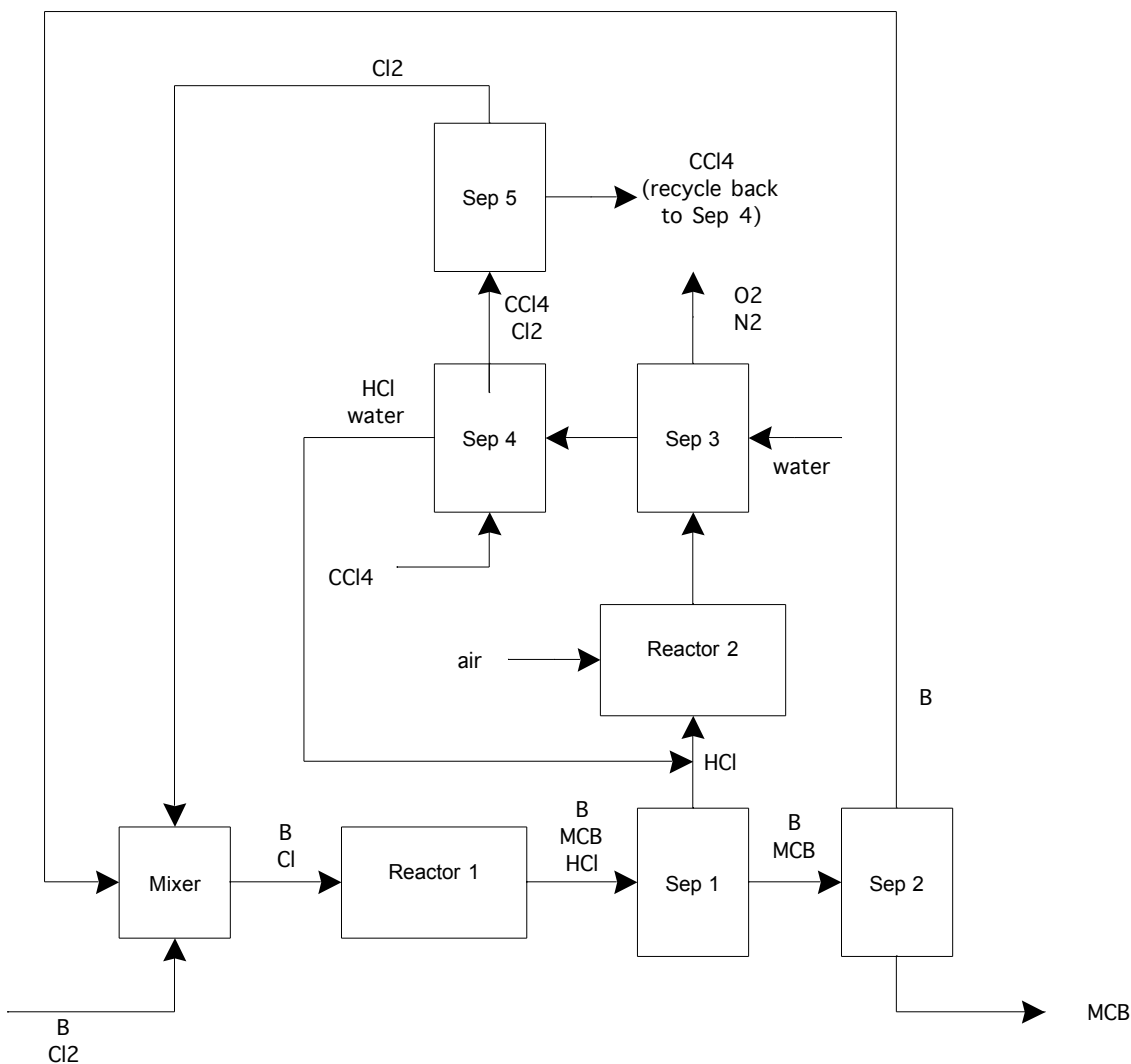
- (1) There's a lot of water that should be removed early on, to reduce the volume that needs to be processed in other separation steps downstream. Evaporating off all that water would be energy intensive.
- (2) We need to remove the salt from the solution and discard it. Ion exchange adsorption is a good choice because it scales with the volume of salt to be removed (small) rather than volume of water to be processed (large)).
- (3) Proteins are sensitive to temperature – a technology that requires high temperatures would not be a good choice. Lactic acid, lactose, and protein are all relatively large in molecular size compared to water, and are at relatively low concentrations. Proteins are much larger than lactose and lactic acid. A size-dependent separation (e.g., ultrafiltration) is attractive. Solubilities of lactic acid and lactose in solvents is likely to be different.

From this, we propose the following: first, remove salt by ion exchange adsorption, then concentrate lactic acid, lactose, and protein by reverse osmosis filtration (to remove water), then, ultrafilter to separate proteins from lactic acid and lactose. Don't want to remove all the water yet, because solutions are easier to process than solids. If lactic acid is not marketable, could try running the ion exchanger at a pH where the lactic acid is ionized, so that some/all of it adsorbs as well. Alternatively, if lactic acid is a useful

The dried protein product is 91 wt% protein and 9 wt% lactose. The dried lactose product is pure.

P5.48

Here is one reasonable scheme. Notice how much effort is expended to recover and recycle Cl_2 !



In this scheme, fresh benzene (B) and chlorine (Cl) are mixed with recycled streams and fed to Reactor 1. All the chlorine but only a fraction of the B react, since Cl is by far the limiting reactant. B and monochlorobenzene (MCB) are easily separated from HCl by cooling and condensing in Separator 1, because the boiling points of B (80°C) and MCB are much higher than that of HCl (-85°C). Benzene and MCB are separated by distillation in Separator 2; their relative volatilities are significantly different and distillation is fairly easy.. The MCB is taken off as product and benzene is recycled.

HCl is mixed with air (oxygen and nitrogen) and fed to Reactor 2, where the HCl is partially converted back to Cl_2 , with water as a byproduct. HCl and Cl_2 are both quite soluble in water whereas oxygen and nitrogen are relatively insoluble in water. Therefore, water is used as an inexpensive solvent in Separator 3, which is an absorption tower. (The Reactor 2 outlet will likely be cooled prior to feeding it to Separator 3.) Oxygen and nitrogen gas is discharged to the atmosphere (or to a flare, just in case of a process upset.) The HCl and Cl_2 dissolved in water is sent to Separator 4, which is a liquid-liquid contactor. Carbon tetrachloride is added, and much of the Cl_2 partitions into this phase. (Carbon tetrachloride is essentially immiscible with water – see Table B.15.) The boiling point of carbon tetrachloride is 77°C , so it is readily separated from Cl_2 by heating in Separator 5. The chlorine is recycled back to the mixer, and the carbon tetrachloride is recycled back to Separator 4. HCl and water (along with some Cl_2 that remains in the aqueous phase) is fed back to Reactor 2. (Some purge of this stream, not shown on the flow diagram, will be necessary to remove the water made by reaction. It may not be necessary to add much if any water to Separator 3, as it can be recycled.)

P5.49

Notice the following features of this problem:

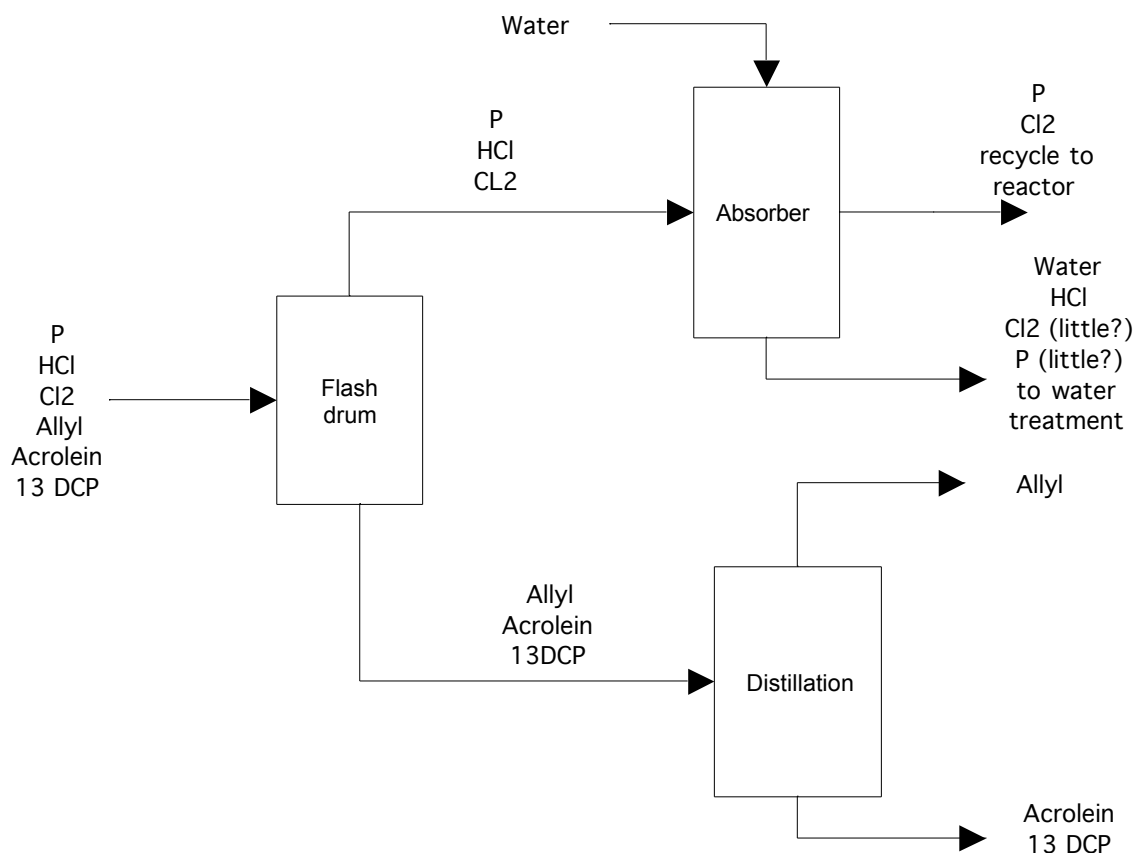
- (1) Propylene and HCl are the major components of stream.
- (2) HCl and Cl_2 are both corrosive.
- (3) Propylene, HCl, Cl_2 all boil at very low temperatures, and are significantly different in boiling point than the chlorinated hydrocarbons.
- (4) Want to recycle propylene and Cl_2 to reactor feed but not the HCl. Therefore we need to separate Cl_2 from HCl, but we don't necessarily need to separate propylene and Cl_2 .
- (5) HCl is highly soluble in water.
- (6) 1,3-dichloropropane and acrolein chloride need to be separated from the product allyl chloride, but there is no need to separate these two byproducts from each other.

Removing the HCl early would be suggested by the heuristic “remove corrosives early”, but so is Cl_2 . So it makes sense to apply the heuristic “do the easy separation first” and the heuristic “separate large quantities first”.

Distillation to separate propylene and Cl_2 from HCl doesn't make sense because it would have to operate at very low temperatures (violates “avoid very high or very low temperatures and pressures” heuristic). Absorption into water takes advantage of the differences in solubility.

Distillation would work well to separate allyl chloride from the chlorinated waste products, because allyl chloride is more volatile than the byproducts.

A reasonable flow sketch is shown:



P5.50

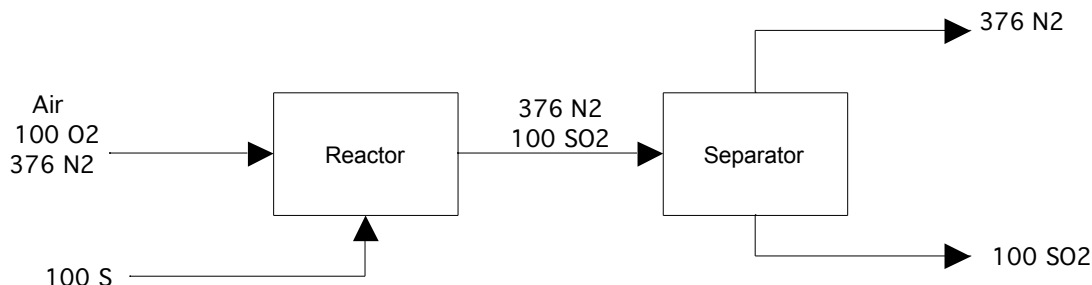
We picked chloroform to extract diethylamine. The boiling point of chloroform is 61°C while that of DEA is 58°C . Distillation might be an option, although these are pretty close so many stages may be required. The melting points are -63.6 and -93°C , respectively. These are pretty different, but are so low that it would be very expensive to try to exploit crystallization as a separation method. Maybe there is another solvent we could add, but that doesn't seem to be getting us anywhere! Diethylamine is a strong base. One possibility might be to use adsorption with an ion exchange resin (with acid groups immobilized on the resin). Chloroform would not adsorb to this resin, so it could be recycled back to the solvent extraction unit. The diethylamine could accumulate on the resin until it is saturated, then recovered by flowing an elution solvent across the resin. Now of course the DEA is dissolved in the new solvent...but it is at least more concentrated than the initial contaminated water.

It might be worth a look at a solvent other than chloroform for the original extraction. Benzene, for example, is almost as good at extracting DEA from water as chloroform ($K_D = 1.8$ vs 2.2), but its boiling point is much more different than DEA (80°C), so distillation would be a relatively easy way to separate benzene from DEA. (One concern

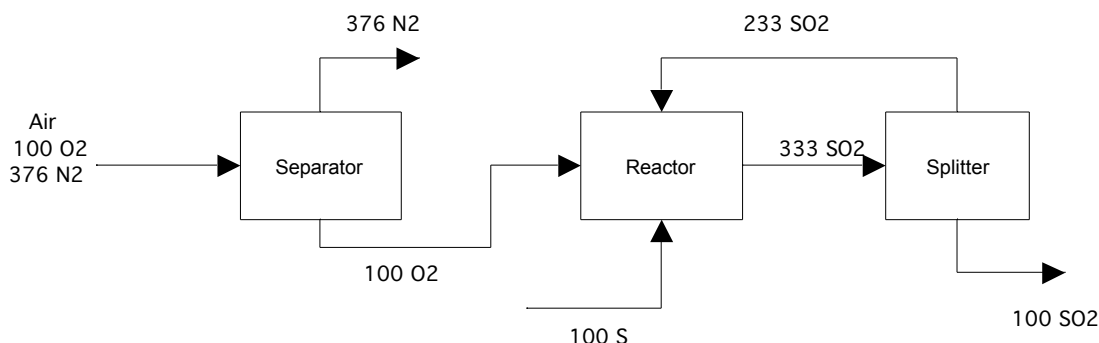
with benzene is that it is not completely immiscible in water; we might be substituting one pollution problem with another!) Still, this illustrates how, in separation processes that require the addition of a foreign species, the choice of that species depends not only on its performance in the main separation step, but also on the ease of recovering and re-using the material.

P5.51

Scheme A: Flow rates are shown in molar units, with a basis of 100 gmol/min S fed. The inert:oxygen ratio in the mix fed to the reactor is 476:100 which is greater than 7:3.



Scheme B: Recycle of SO₂ to the reactor is required to maintain the inert:oxygen ratio in the mix fed to the reactor at 7:3.



Scheme A has a lot going for it. It avoids an expensive separation (N₂/O₂) and adds a much easier separation (N₂/SO₂). (SO₂ differs significantly from N₂ in its boiling point, size, and its solubility in water, any of which difference could potentially be used as a basis for separation.) It also uses nitrogen as the diluent, avoiding the need for recycle. Finally, if not all the O₂ is consumed by reaction, with the separator after the reactor you can easily remove traces of O₂ from SO₂ in this scheme.

P5.52

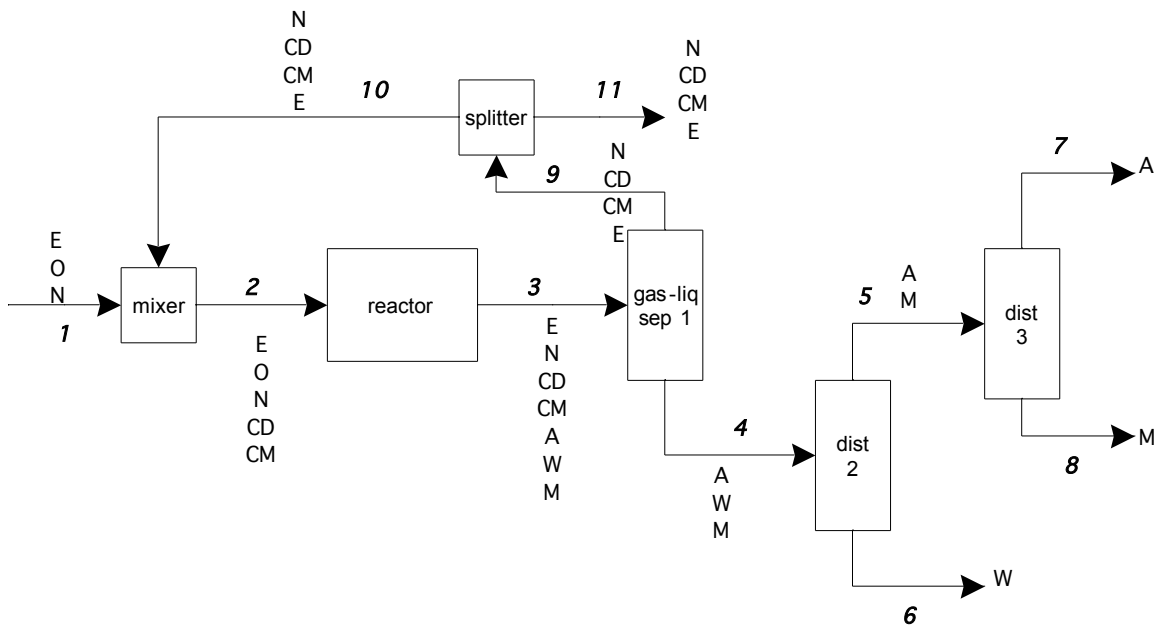
This problem reviews material from Chapters 3 and 4 and adds some new material from Chapter 5.

The ethane:oxygen reactor feed is maintained at 6:1 molar ratio, so oxygen is the limiting reactant. This is done to reduce excess oxidation of ethanol to methanol, CO, and CO₂.

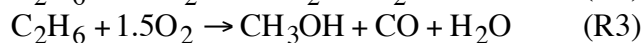
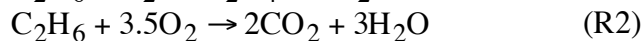
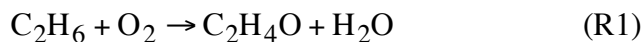
Because air is the source of the oxygen, the nitrogen in air must be removed from the system somewhere. It is expensive to separate nitrogen from other gases (CO₂, CO), so it makes more sense simply to purge this stream rather than try to recover all the ethane.

Separating the gases from the liquids first in Separator 1 makes a lot of sense. This is an easy separation (following the heuristic – save the difficult separations for last), and it splits the reactor outlet into roughly equal flows. The boiling points of acetaldehyde, methanol and water are 20°C, 65°C, and 100°C, all at or slightly above ambient and fairly widely separated. Distillation, since it operates at pressure and temperature at which vapor and liquid phases can co-exist, and because it exploits differences in relative volatility, makes sense. The sequence shown is reasonable; an equally reasonable sequence would be to have distillation column separate into water + methanol and acetaldehyde, followed by a methanol-water separation. This alternative sequence might be preferable if methanol is sold as a byproduct (following the heuristic – take products off as distillates one-by-one). More detailed analysis is required to make a final choice.

The flow diagram is sketched below (we assume that the separators are perfect). Components are named as E (ethane), O (oxygen), N (nitrogen), CD (carbon dioxide), CM (carbon monoxide), A (acetaldehyde), M (methanol), W (water). Streams are numbered as shown.



Reactions:



DOF Analysis

No. of stream variables	35	Counting components in each stream and summing: 3 + 5 + 7 + 3 + 2 + 1 + 1 + 1 + 4 + 4 + 4
No. of reaction variables	3	
No. of specified flows	2	Ethane and air fed in stream 1
No. of stream composition specifications	4	1 in stream 1 (N ₂ :O ₂ = 79:21) 1 in stream 2 (E:O = 6:1) 2 in stream 11 (10% E, CD:CM = 2:1)
No. of system performance specifications	0	
No. of splitter restrictions	3	4 components in splitter
No. of material balance equations	29	5 in mixer + 8 in reactor + 7 in sep 1 + 3 in sep 2 + 2 in sep 3 + 4 in splitter
DOF		(35+3) – (2+4+3+29) = 38 – 38 = 0

We start by lumping together all the units in a single system and writing overall material balance equations. We assume steady-state operation. All flows are in gmol/h.

Material balance equations:

$$\dot{n}_{N11} = \dot{n}_{N1} = 0.79(30952) = 24452$$

$$\dot{n}_{O11} = 0 = \dot{n}_{O1} - \dot{\xi}_1 - 3.5\dot{\xi}_2 - 1.5\dot{\xi}_3 = 6500 - \dot{\xi}_1 - 3.5\dot{\xi}_2 - 1.5\dot{\xi}_3$$

$$\dot{n}_{E11} = \dot{n}_{E1} - \dot{\xi}_1 - \dot{\xi}_2 - \dot{\xi}_3 = 6000 - \dot{\xi}_1 - \dot{\xi}_2 - \dot{\xi}_3$$

$$\dot{n}_{CM11} = \dot{\xi}_3$$

$$\dot{n}_{CD11} = 2\dot{\xi}_2$$

$$\dot{n}_{A7} = \dot{\xi}_1$$

$$\dot{n}_{M8} = \dot{\xi}_3$$

$$\dot{n}_{W6} = \dot{\xi}_1 + 3\dot{\xi}_2 + \dot{\xi}_3$$

From stream composition specifications:

$$\frac{\dot{n}_{CM11}}{\dot{n}_{CD11}} = 0.5$$

$$\frac{\dot{n}_{E11}}{\dot{n}_{E11} + \dot{n}_{CM11} + \dot{n}_{CD11} + 24452} = 0.10$$

Excluding the nitrogen material balance, we have 9 equations in 9 variables. We can use an equation solving package like EES, or a spreadsheet with Solver, to find a solution.

$$\dot{\xi}_1 = 468$$

$$\dot{\xi}_2 = \dot{\xi}_3 = 1206$$

Purge gas: 31,190 gmol/h: 10% ethane, 78.4% nitrogen, 3.9% CO, 7.7% CO₂.

The overall conversion of ethane is

$$f_{CE} = \frac{\dot{\xi}_1 + \dot{\xi}_2 + \dot{\xi}_3}{\dot{n}_{E1}} = \frac{468 + 1206 + 1206}{6000} = 0.48$$

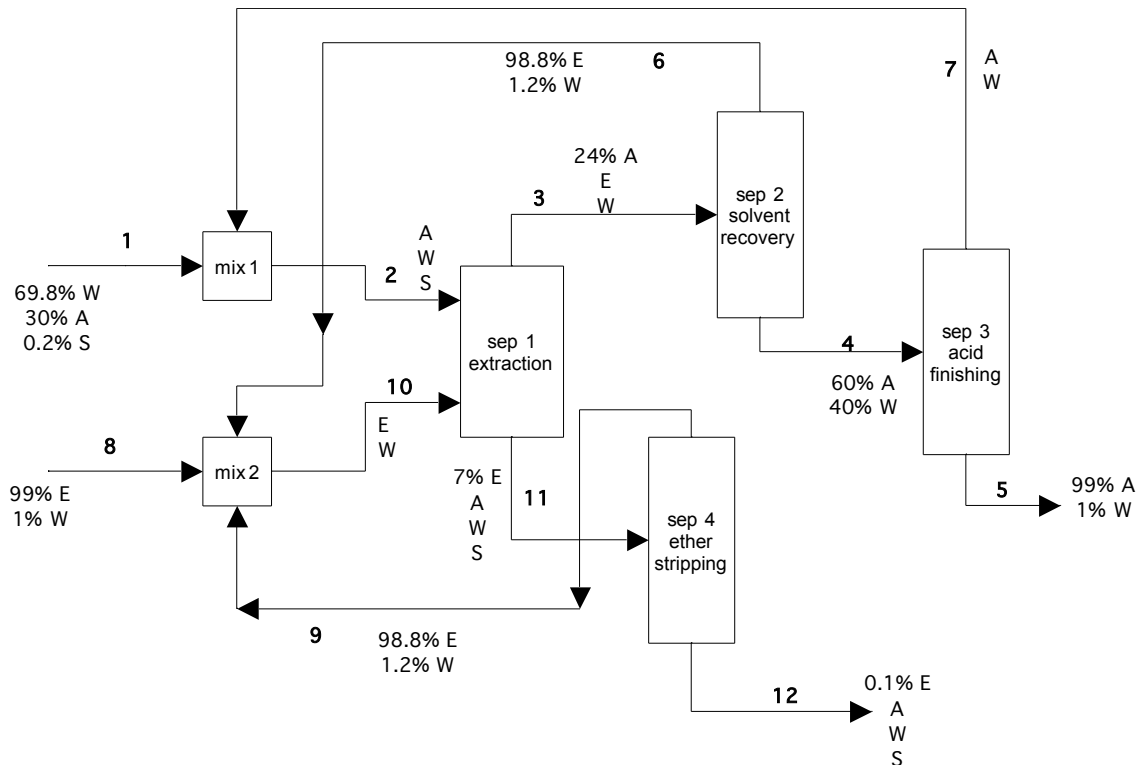
The overall yield and selectivity for converting ethane to acetaldehyde are:

$$y_{E \rightarrow A} = \frac{\dot{\xi}_1}{\dot{n}_{E1}} = \frac{468}{6000} = 0.078$$

$$s_{E \rightarrow A} = \frac{\dot{\xi}_1}{\dot{\xi}_1 + \dot{\xi}_2 + \dot{\xi}_3} = \frac{468}{468 + 1206 + 1206} = 0.1625$$

P5.53

- (a) Cellulose acetate is a polymer made from wood pulp and acetic anhydride. It is used for example in textiles, photographic film, absorbent disposable materials, and filters.
- (b) There are four separation steps. Extraction separates acetic acid from sulfuric acid and water. It is used instead of distillation because acetic acid boils at a temperature in between water and sulfuric acid, yet we want to separate it from these two in one step. Extraction is placed first in the sequence to get rid of the corrosive acid early, in line with the heuristics. The other 3 steps are all distillation: the solvent recovery column separates ether from the acetic acid/water mix; the acid finishing separates acetic acid from water, and the ether stripping separates ether from water.
- (c) The flow diagram is shown, with W for water, S for sulfuric acid, A for acetic acid, and E for diethyl ether.



DOF Analysis

No. of stream variables	31	Counting components in each stream and summing: 3 + 3 + 3 + 2 + 2 + 2 + 2 + 2 + 2 + 2 + 4 + 4
No. of reaction variables	0	
No. of specified flows	0	
No. of stream composition specifications	11	2 in stream 1 + 1 in stream 3 + 1 in stream 4 + 1 in stream 5 + 1 in stream 6 + 1 in stream 8 + 1 in stream 9 + 1 in stream 11 + 1 in stream 12 2.3:1 ratio of acetic acid in stream 7:stream 1
No. of system performance specifications	1	67.5% recovery of acetic acid
No. of material balance equations	18	3 in mix 1 + 2 in mix 2 + 4 in sep 1 + 3 in sep 2 + 2 in sep 3 + 4 in sep 4
DOF		$31 - (11+1+18) = 1$

If we choose a basis, the system is correctly specified. We'll choose 1000 lb/h in stream 1 as the basis. Then we write the 19 material balance equations, the 11 composition specifications, and the 1 performance specification equations, and solve. Sulfuric acid balances are solved first. After that, acetic acid is the component that is the easiest to work with first because we have the most information. Once the acetic acid flows are calculated, there is sufficient stream composition information to get several of the water and ether flows. The equations and solution are summarized.

Material balance equations:

Sulfuric acid: $\dot{m}_{S1} = \dot{m}_{S2} = \dot{m}_{S11} = \dot{m}_{S12} = 2$

$$300 + \dot{m}_{A7} = \dot{m}_{A2} = \dot{m}_{A3} + \dot{m}_{A11}$$

Acetic acid: $\dot{m}_{A11} = \dot{m}_{A12}$

$$\dot{m}_{A3} = \dot{m}_{A4} = \dot{m}_{A5} + \dot{m}_{A7}$$

$$698 + \dot{m}_{W7} = \dot{m}_{W2}$$

$$\dot{m}_{W10} + \dot{m}_{W2} = \dot{m}_{W3} + \dot{m}_{W11}$$

Water: $\dot{m}_{W3} = \dot{m}_{W6} + \dot{m}_{W4}$

$$\dot{m}_{W4} = \dot{m}_{W5} + \dot{m}_{W7}$$

$$\dot{m}_{W11} = \dot{m}_{W9} + \dot{m}_{W12}$$

$$\dot{m}_{W8} + \dot{m}_{W9} + \dot{m}_{W6} = \dot{m}_{W10}$$

$$\dot{m}_{E8} + \dot{m}_{E6} + \dot{m}_{E9} = \dot{m}_{E10}$$

Ether: $\dot{m}_{E10} = \dot{m}_{E3} + \dot{m}_{E11}$

$$\dot{m}_{E11} = \dot{m}_{E9} + \dot{m}_{E12}$$

$$\dot{m}_{E3} = \dot{m}_{E6}$$

System performance specifications:

$$\dot{m}_{A5} = 0.675\dot{m}_{A4}$$

Stream composition specifications:

$$\dot{m}_{A7} = \frac{1}{2.3}(300) = 130.4$$

plus wt% information shown on diagram.

Flows are all given in lb/h.

	1	2	3	4	5	6	7	8	9	10	11	12
S	2	2									2	2
W	698	962.8	279.5	267.5	2.7	12	264.8	0.007	0.65	12.6	696	695
A	300	430.4	401.2	401.2	270.8		130.4				29.2	29.2
E			991			991		0.7	53.7	1045	54.7	1
sum	1000	1395	1672	669	274	1003	395	1	54	1058	782	727

90.3% of acetic acid fed is recovered in concentrated product.

P5.54

Let's look at the boiling points of the 4 components:

Pentane: 36°C

Benzene: 80°C

Toluene: 110.6°C

o-xylene: 144°C

Based on simply the differences in boiling points, the easiest separation is between pentane and benzene, followed by toluene and *o*-xylene, and the most difficult (although still not particularly difficult) is between benzene and toluene. It would be a little better to calculate the saturation pressures from Antoine's equation, and then compare the ratios of saturation pressures as a measure of the relative volatility. Using the data in Table B.4, and arbitrarily choosing a temperature of 100°C for comparison, we find saturation pressures of:

Pentane: 4520 mm Hg

Benzene: 1350 mm Hg

Toluene: 556 mm Hg

o-xylene: 198 mm Hg

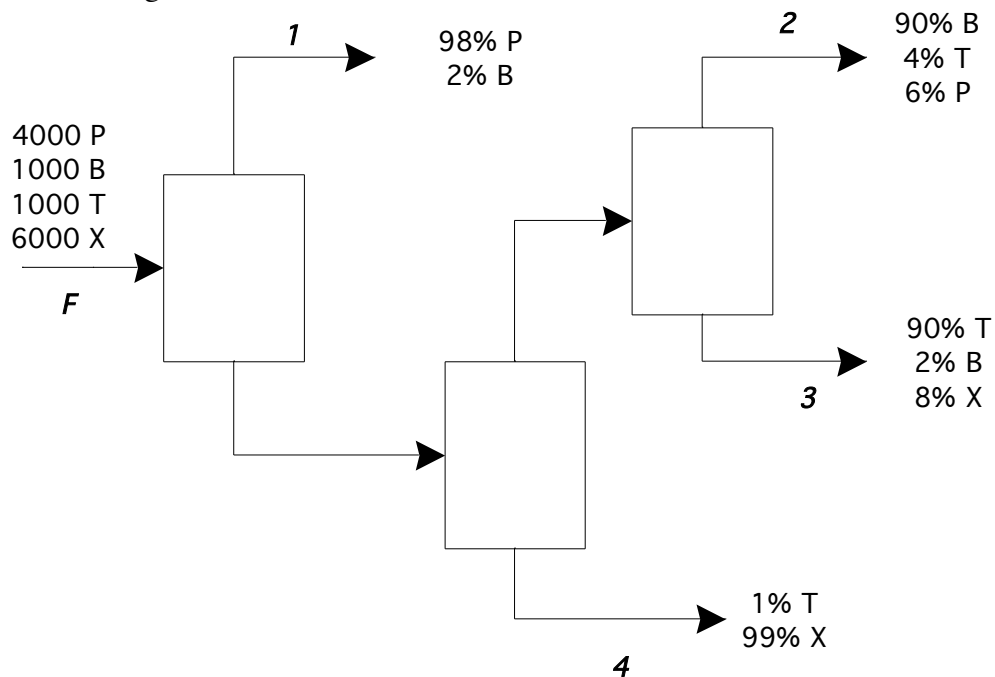
The ratio of saturation pressures is in the order of 3.35 (pentane/benzene) > 2.81 (toluene/xylene) > 2.43 (benzene/toluene) – same as what we concluded by looking at

differences in boiling point temperatures. The proposal from the supervisor follows this sequence exactly.

Based on the heuristics of separating into equal amounts and removing the largest quantities first, one might argue for doing the o-xylene – toluene separation first, then the pentane-benzene separation, and finally the benzene-toluene separation.

The supervisor's design is quite reasonable, but there is also a reasonable alternative. Since he's the boss, I'd probably just agree with him!

The labeled flow diagram is



The material balance equations are straightforward to set up.

$$4000 = 0.98\dot{n}_1 + 0.06\dot{n}_2$$

$$1000 = 0.02\dot{n}_1 + 0.90\dot{n}_2 + 0.02\dot{n}_3$$

$$1000 = 0.04\dot{n}_2 + 0.90\dot{n}_3 + 0.01\dot{n}_4$$

$$6000 = 0.08\dot{n}_3 + 0.99\dot{n}_4$$

This is easy to set up and solve as a matrix equation. The solution is

$$\begin{bmatrix} \dot{n}_1 \\ \dot{n}_2 \\ \dot{n}_3 \\ \dot{n}_4 \end{bmatrix} = \begin{bmatrix} 4020 \\ 1000 \\ 1000 \\ 5980 \end{bmatrix} \text{ with all flows in gmol/h}$$

The fractional recoveries of each component in their respective product stream are

$$f_{RP1} = \frac{0.98(4020)}{4000} = 0.985$$

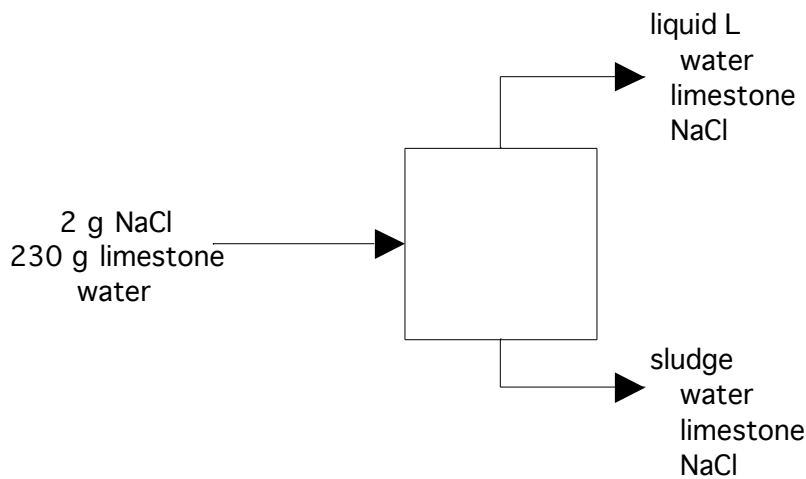
$$f_{RB2} = \frac{0.90(1000)}{1000} = 0.90$$

$$f_{RT3} = \frac{0.9(1000)}{1000} = 0.90$$

$$f_{RX4} = \frac{0.99(5979)}{6000} = 0.987$$

P5.55

The flow diagram is shown.



In the clear liquid L, the maximum concentrations of limestone and NaCl are set at their solubility limits of 0.015 and 300 g/l, respectively. If there is no limestone or no NaCl in the solid phase, then the concentration may be below the solubility limit.

The sludge is (10/36) or 27.8% of the total volume, or 278 ml.

The clean liquid is the remainder, or 722 ml.

The limestone solubility limit is very low, so some of it will be in the solid phase, thus we can pin the liquid concentration at 0.015 g/ml. From material balance:

$$230 \text{ g} = 0.015 \text{ g/L} \times 0.722 \text{ L} + m_{LS,S}$$

$$m_{LS,S} = 229.99 \text{ g limestone in the sludge}$$

the concentration of limestone in the sludge is therefore 827 g/l.

For NaCl, let's assume that it is at its solubility limit in the liquid

$$2 \text{ g} = 360 \text{ g/L} \times 0.722 \text{ L} + m_{NaCl,S}$$

$$m_{NaCl,S} = -257.9 \text{ g?? the negative sign shows us that our assumption was wrong,}$$

NaCl is below its solubility limit – none of it goes into the solid phase; it is in the clear liquid as well as the entrained solution in the sludge.

To calculate the volume of entrained solution vs. solid phase in the sludge, I need the density of limestone – 2.7 g/ml. The total volume of solid limestone is therefore $229.99/2.7$, or 85.2 ml. The sludge volume is 278 ml, so the entrained liquid is $278 - 85.2$ or 192.8 ml.

Thus, the total liquid (clear liquid plus entrained solution) is $192.8 + 722 = 915$ ml. The NaCl concentration is therefore 2 g/915 ml, or 2.19 g/L. Therefore the sludge contains 2.19×0.193 L or 0.42 g NaCl, and the clear liquid has 1.58 g NaCl.

The thickener is designed to separate NaCl from limestone. Limestone fractional recovery is $229.99/230 = 0.99996$. NaCl product recovery is $1.58/2 = 0.79$. Sludge product “purity” = $229.99/(229.99+192.8) \times 100\% = 54.4\%$ (assuming the liquid density is 1 g/ml). The clear liquid is 0.219% NaCl. Finally, the separation factor is

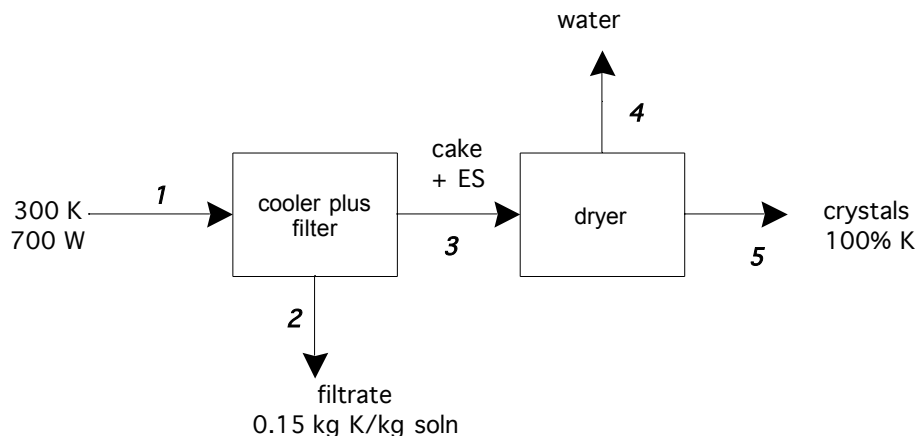
$$\alpha_{LS-NaCl} = \frac{229.99}{0.01} \frac{1.58}{0.42} = 86,500 \text{ (approx.)}$$

P5.56

Let’s start by considering phase behavior of potassium nitrate – water system. If the solution is cooled to 5°C, from Figure 5.11 we find that the saturated solution is 0.15 kg KNO₃/kg solution. At 90°C, the solubility is very high – about 0.65 kg KNO₃/kg solution.

The vacuum evaporator alone won’t do the trick, because its maximum salt is still below the solubility limit. But, if we cool the solution we will get some crystals forming.

Can we accomplish the necessary separation with just the cooler, rotary drum filter, and drum dryer? The flow diagram is



For material balance purposes, we’ve lumped together the cooler plus rotary drum filter. The entrained solution (ES) is 0.15 kg KNO₃/kg solution, and there is 1 kg solution

entrained per 19 kg cake (which is pure KNO_3). The material balance equation on KNO_3 around the cooler/filter is

$$300 = 0.15\dot{m}_2 + \dot{m}_{C3} + 0.15\dot{m}_{ES3}$$

where we have distributed the flow in stream 3 between cake C and entrained solution ES . We also know from the performance specification on the filter that

$$\dot{m}_{C3} = 19\dot{m}_{ES3}$$

and the material balance on water gives:

$$700 = 0.85\dot{m}_2 + 0.85\dot{m}_{ES3}$$

We solve 3 equations in 3 unknowns to find

$$\dot{m}_{C3} = 176.5$$

$$\dot{m}_{ES3} = 9.3$$

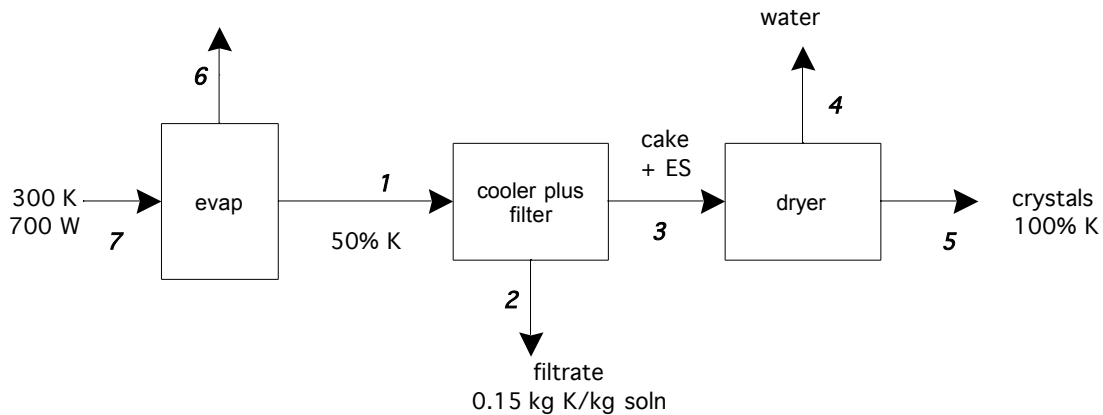
$$\dot{m}_2 = 814.2$$

with flows all in kg/h. Assuming all the water from stream 3 is removed in the dryer, then a material balance around the dryer yields

$$\dot{m}_5 = \dot{m}_{C3} + 0.15\dot{m}_{ES3} = 176.5 + 1.4 = 177.9 \text{ kg/h}$$

well below the target production rate of 245 kg/h.

What if we evaporate some of the water first, to raise the feed solution to the cooler/filter up to 50 wt% KNO_3 ?



A material balance around the evaporator reveals that

$$\dot{m}_{K1} = 300$$

$$\dot{m}_{W1} = 700$$

The material balance equations around the cooler/filter are slightly modified:

$$300 = 0.15\dot{m}_2 + \dot{m}_{C3} + 0.15\dot{m}_{ES3}$$

$$\dot{m}_{C3} = 19\dot{m}_{ES3}$$

$$700 = 0.85\dot{m}_2 + 0.85\dot{m}_{ES3}$$

We solve 3 equations in 3 unknowns to find

$$\dot{m}_{C3} = 247$$

$$\dot{m}_{ES3} = 13$$

$$\dot{m}_2 = 340$$

with flows all in kg/h. The material balance around the dryer yields

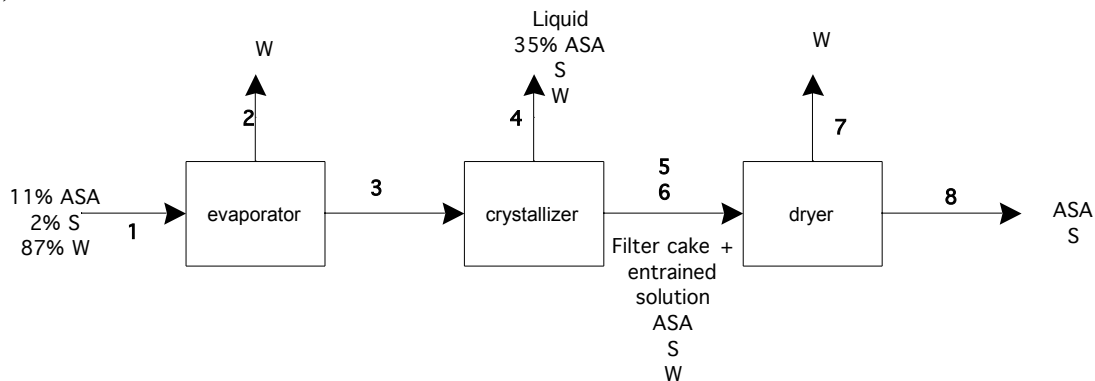
$$\dot{m}_5 = \dot{m}_{C3} + 0.15\dot{m}_{ES3} = 247 + 2 = 249 \text{ kg/h}$$

Let's go shopping!

P5.57

(a) Product purity is $\frac{11}{11+2} \times 100\% = 84.6\text{wt}\%$ if just the water is removed. Component recovery is 100%.

(b)



We've used S for sodium acetate and W for water. We've denoted two streams 5 and 6 as the solid phase and the entrained liquid solution, respectively. The entrained solution is assumed to be at the solubility limit of ASA, that is, 35% ASA. The filter cake contains no salt. Given 100 kg in the feed to the evaporator, there are 11 kg ASA fed to the process ($m_{A3} = 11 \text{ kg}$), and half is recovered as dried product in stream 8

($m_{A8} = 5.5 \text{ kg}$). From this we write a material balance equation around the dryer

$$5.5 = m_5 + 0.35m_6 \quad (\text{the solid phase is pure ASA since sodium acetate is considered infinitely soluble})$$

From the entrainment specification,

$$m_5 = 4m_6$$

Therefore

$$m_5 = 5.056$$

$$m_6 = 1.264$$

Since half of the ASA leaves the dryer as dried product, the other half leaves the system in stream 4, as liquid filtrate:

$$m_{A4} = 5.5$$

This is 35 wt% ASA, so

$$m_4 = \frac{5.5}{0.35} = 15.71$$

The 2 kg sodium acetate is at the same concentration in stream 4 and stream 5

$$\frac{2}{15.71 + 1.264} = 0.118 \text{ kg S/kg solution}$$

Since there is 1.264 kg entrained solution fed to the dryer, there is $0.118(1.264)$ or 0.149 kg sodium acetate fed to the dryer, all of which ends up in the dried product. Therefore, the final product purity is better in the alternative process:

$$\frac{5.5}{5.5 + 0.149} \times 100\% = 97.36 \text{ wt\% ASA}$$

The total mass balance around the filter yields:

$$m_3 = m_4 + m_5 + m_6 = 15.71 + 1.264 + 5.057 = 22.03$$

The total feed to the evaporator is 100 kg, therefore the water removed in the evaporator must be $100 - 22.03$ or 78 kg.

(c) As we've seen from parts (a) and (b), product purity increases as component recovery decreases. The impurity is due to the sodium acetate in the entrained solution. In terms of our stream variables:

$$\text{product purity (\%)} = \frac{m_{A8}}{m_{A8} + m_{S8}} \times 100\%$$

where we use A for acetylsalicylic acid and S for sodium acetate. The fractional recovery is

$$f_{RA} = \frac{m_{A8}}{m_{A1}}$$

Therefore, product purity is related to fractional recovery and feed rate by

$$\text{product purity (\%)} = \frac{f_{RA} m_{A1}}{f_{RA} m_{A1} + m_{S8}} \times 100\%$$

Our job is derive a general expression for m_{S8} . We know that

$$m_{S8} = m_{S6}$$

and that

$$m_{S6} + m_{S4} = m_{S1}$$

The crystallizer/filter acts essentially as a splitter for sodium acetate:

$$\frac{m_{S4}}{m_{S6}} = \frac{m_4}{m_6}$$

From the phase equilibrium information on ASA and the entrainment specification, plus a material balance on ASA,

$$m_{A8} = m_5 + 0.35m_6 = 4.35m_6$$

$$m_6 = \frac{m_{A8}}{4.35} = \frac{f_{RA}m_{A1}}{4.35}$$

Also

$$m_{A1} = m_{A3} = 0.35m_4 + m_{A8} = 0.35m_4 + f_{RA}m_{A1}$$

$$m_4 = \frac{(1 - f_{RA})m_{A1}}{0.35}$$

Combining this with previous results:

$$\frac{m_{S4}}{m_{S6}} = \frac{m_4}{m_6} = \frac{4.35}{0.35} \frac{(1 - f_{RA})}{f_{RA}}$$

and the material balance equations on sodium acetate:

$$m_{S6} = m_{S1} - m_{S4} = m_{S1} - \frac{4.35}{0.35} \frac{(1 - f_{RA})}{f_{RA}} m_{S6}$$

$$m_{S6} = \frac{m_{S1}}{\left[1 + \frac{4.35}{0.35} \frac{(1 - f_{RA})}{f_{RA}}\right]} = m_{S8}$$

Now we can write purity in terms of fractional recoveries and feed quantities:

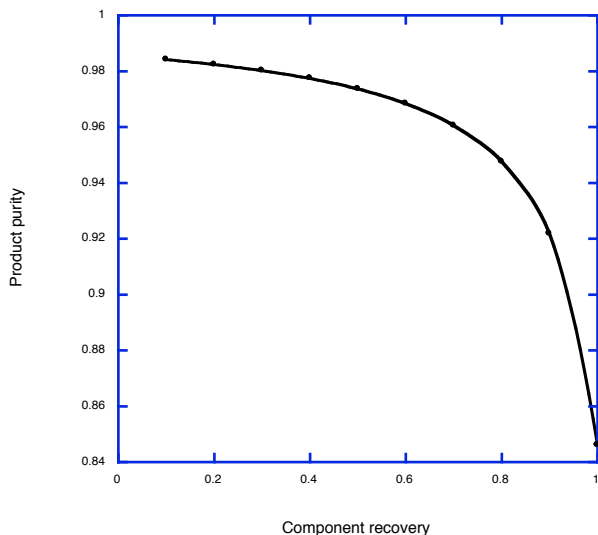
$$\text{product purity (\%)} = \frac{f_{RA}m_{A1}}{f_{RA}m_{A1} + \frac{m_{S1}}{\left[1 + \frac{4.35}{0.35} \frac{(1 - f_{RA})}{f_{RA}}\right]}} \times 100\%$$

We check the expression against the two points that we previously calculated:

$$f_{RA} = 1.0 \Rightarrow \text{product purity} = 84.6\% \quad \text{check!}$$

$$f_{RA} = 0.5 \Rightarrow \text{product purity} = 97.4\%$$

The equation (at the given feed rates) plots as

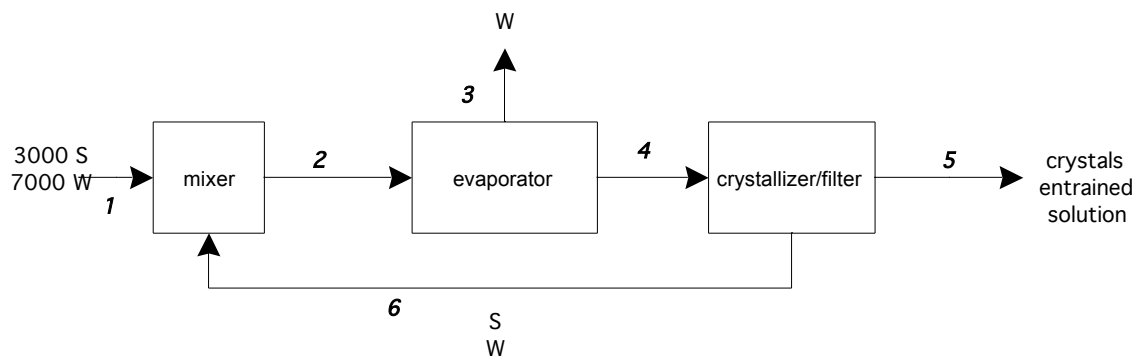


At 90% recovery, we calculate a purity of 92.2wt%, while 10% recovery gives us 98.4 wt% purity. The purity drops slowly as recovery increases to about 50%, then precipitously as recovery increases further.

(d) The best change to make would be to install a separation device upstream that could remove the sodium acetate, if possible. Alternatively, the quantity of entrained solution is rather high, installing a better filter would improve purity (or improve recovery at equal purity).

P5.58

The labeled flow diagram, with components indicated by S for sodium carbonate, and W for water, is shown. Flow rates are in lb/h. We will distinguish between crystals and entrained solution in stream 5 by subscripts C5 and ES5, respectively.



The mass fraction of salt in the entrained and recycle solution is 0.177. Considering the entire process as the system operating at steady-state, we write the material balance equations:

$$3000 = \dot{m}_{C5} + 0.177\dot{m}_{ES5} \quad (\text{sodium carbonate})$$

$$7000 = \dot{m}_{W3} + 0.823\dot{m}_{ES5} \text{ (water)}$$

We are also given the system performance specification

$$\dot{m}_{C5} = 3.5\dot{m}_{ES5}$$

We solve this set of 3 equations in 3 unknowns to find

$$\dot{m}_{C5} = 2856 \text{ lb/h}$$

$$\dot{m}_{ES5} = 816 \text{ lb/h}$$

$$\dot{m}_{W3} = 6328 \text{ lb/h}$$

The product stream includes the crystals (100% sodium carbonate) plus entrained solution (17.7wt% sodium carbonate), so the product purity is

$$\frac{2856 + 0.177(816)}{2856 + 816} \times 100\% = 81.7\text{wt}\%$$

From the performance specification on the evaporator, that 40% of the water fed to the evaporator is evaporated, we find

$$\dot{m}_{W2} = \frac{6328}{0.4} = 15820 \text{ lb/h}$$

This is the total feed to the evaporator, which includes both fresh (7000 lb/h) and recycled. Therefore, the recycle flow rate of water must be

$$\dot{m}_{W4} = 15820 - 7000 = 8820 \text{ lb/h}$$

Since the recycle stream is 82.3 wt% water, then the total recycle flow rate is

$$\dot{m}_4 = \frac{\dot{m}_{W4}}{0.823} = \frac{8820}{0.823} = 10716 \text{ lb/h}$$

Therefore, the ratio of recycle to fresh feed is $10716/10000 = 1.07$.

(a) The recovery is already at 100%, so no improvement is possible. If the concentration of salt in the entrained solution remains constant, and the amount of entrained solution (kg solution/kg crystals) remains the same, then the purity must remain the same. Therefore, the evaporator remains underutilized (you can't change the water evaporation rate).

(b) Increasing the temperature at which the evaporator operates (and removing more water in the evaporator) might help. Most salt solubilities increase with temperature, so this would increase the concentration of salt in the entrained solution, thus reducing the amount of water in the product. Improvements in the filter operation that reduce the amount of entrained solution would help product purity. Alternatively, installation of a dryer to remove the remaining water would also increase purity. Recovery remains at 100%.

P5.59

(This is a hard problem – students may need some suggestions to get them thinking in the right direction.)

First, solvent-extraction is useless – benzene B and naphthalene N are chemically very similar.

Let's next examine crystallization. We can go as low as 12°C. The phase diagram in Figure 5.12 is in mol fraction, so we need to convert: 60 wt% benzene/40 wt% naphthalene is equivalent of 71 mol% B/29 mol% N. From the phase diagram in Figure 5.12, a 29 mol% N solution cooled to 12°C would phase separate into a pure N solid phase and a liquid phase of about 21 mol% N (or 30 wt% N). We have a drum filter that entrains 1 lb solution per 10 lb solids. Material balances around such a filter, along with this performance specification and the phase equilibrium information, are

$$\begin{aligned}600 &= 0.7\dot{m}_L + 0.7\dot{m}_{ES} \text{ (benzene)} \\400 &= 0.3\dot{m}_L + 0.3\dot{m}_{ES} + \dot{m}_C \text{ (naphthalene)} \\ \dot{m}_C &= 10\dot{m}_{ES}\end{aligned}$$

where L , C , and ES indicate liquid, crystal, and entrained solution flows, in lb/h, respectively. Solving by substitution and elimination, we find:

$$\begin{aligned}\dot{m}_C &= 143 \text{ lb/h} \\ \dot{m}_{ES} &= 14.3 \text{ lb/h} \\ \dot{m}_L &= 842.7 \text{ lb/h}\end{aligned}$$

The filter product (crystal plus entrained solution) purity is

$$\frac{143 + 0.3(14.3)}{143 + 14.3} \times 100\% = 93.6\text{wt}\% \text{ which is below our target of 96 wt\%}.$$

The filtrate (liquid from filter) is only 70 wt% B, much below our target of 99%.

What about the distillation column? To prevent formation of tarry materials, the bottoms temperature can be no greater than 150°C. The higher the pressure, the higher the temperature, so we want to operate at the minimum allowable pressure – 1 atm. What we need to do is calculate the bubblepoint composition if the temperature is fixed at 150°C. This sets the composition of the bottoms product from the distillation column.

From Antoine equations, we calculate that at 150°C

$$\begin{aligned}P_B^{sat} &= 5.74 \text{ atm} \\ P_N^{sat} &= 0.1585 \text{ atm}\end{aligned}$$

The bubblepoint equation is

$$x_B P_B^{sat} + x_N P_N^{sat} = 5.74x_B + 0.1585x_N = (y_B + y_N)P = P = 1$$

And it is also true that:

$$x_B + x_N = 1$$

We combine and find that, at 150°C and 1 atm pressure, the bottoms product from the distillation column is 15 mol% benzene and 85 mol% naphthalene (9.7 wt% B/90.3 wt% N). This isn't pure enough to meet our product requirements.

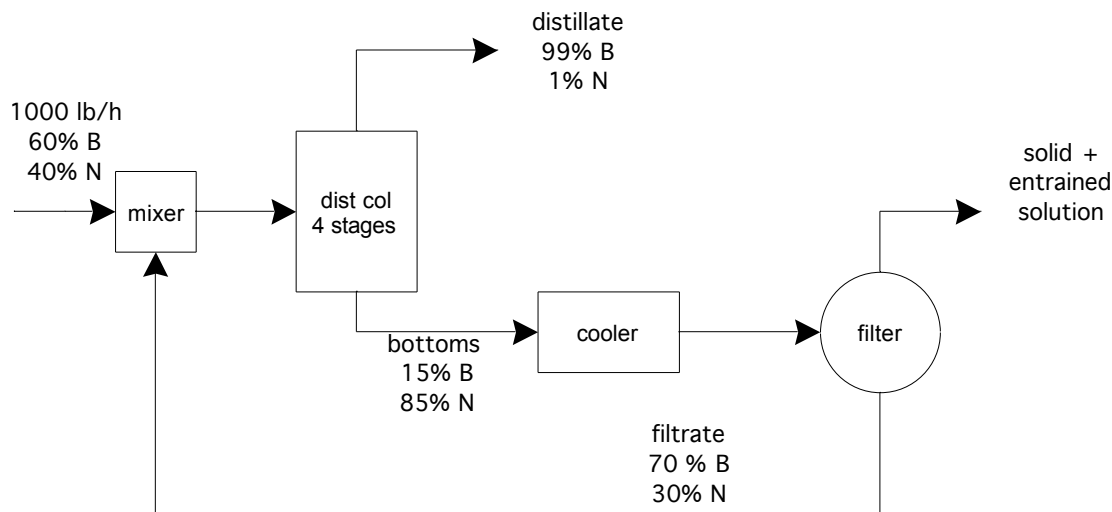
But, what if we still operated the distillation column, and produced a distillate that met our purity specifications for benzene (99%), and an impure bottoms product of 85 mol% N? Can the distillation column available handle that separation? (Reminder: the vapor phase in equilibrium with the bottoms product is NOT the same as the distillate if we have a multistage column!)

From the Fenske equation, a distillation column producing a 99% benzene distillate and a 85% naphthalene bottoms requires

$$N_{\min} = \log \frac{\left(\frac{0.99}{0.01}\right)\left(\frac{0.85}{0.15}\right)}{\log\left(\frac{5.74}{0.1585}\right)} \approx 2$$

A minimum of 2 stages is required, so the 4 stage distillation column available should be about right.

Now we could feed the bottoms from the distillation column to the crystallizer/filter instead of the raw feed, and recycle the filtrate solution back to the distillation column feed:



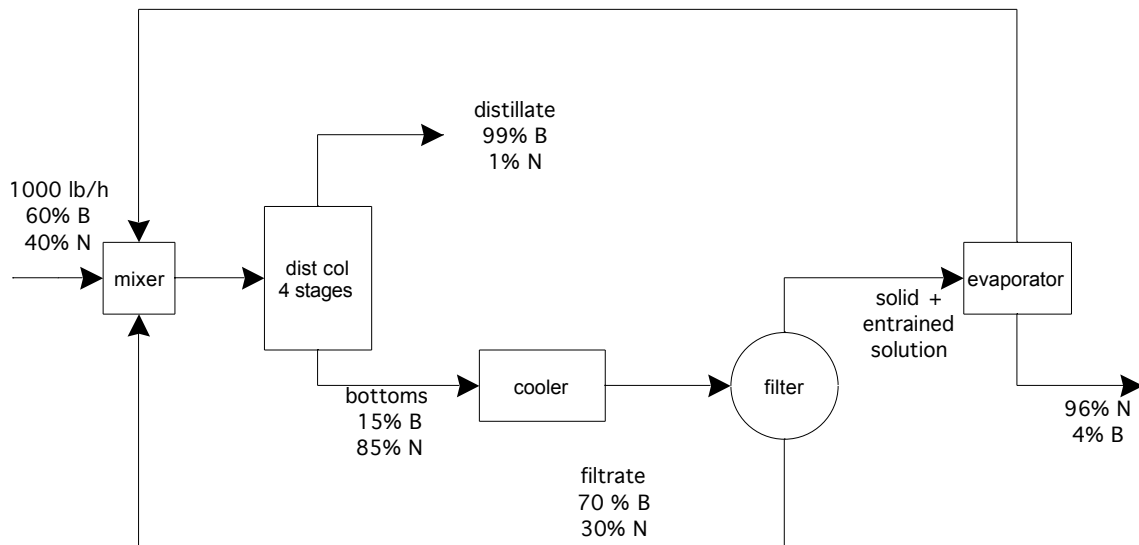
Now we have a process that makes a sufficiently pure benzene product, but the filter cake (solids + entrained solution), at 93.6 wt% N, is still below our target. We haven't used the vacuum evaporator yet – what if we heat the filter cake to melt the solids and then send to the evaporator to remove sufficient benzene? The final desired product is 96 wt% N (94 mol%). The vacuum evaporator would, hopefully, produce a liquid product of this composition plus a vapor enriched in benzene. We can use Raoult's law to model operation of this single-stage evaporator:

$$x_N P_N^{sat} + x_B P_B^{sat} = 0.94 P_N^{sat} + 0.06 P_B^{sat} = P$$

The maximum operating temperature of the evaporator is 250°C, but we may still want to keep the temperature at or below 150°C to avoid tarry polymer formation. Can we get the separation we need in the evaporator? To find out, we plug the saturation pressures of benzene and naphthalene into the equation, calculate P, and compare to 300 mm Hg (0.39 atm)

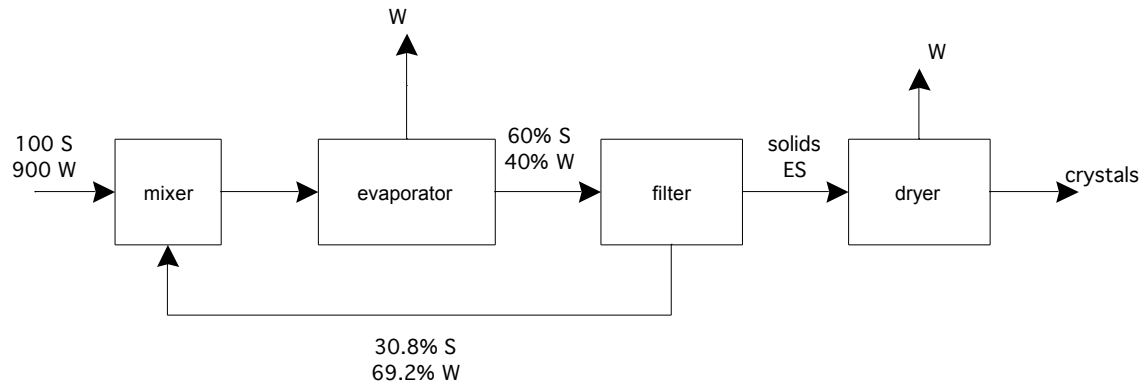
$$0.94(0.1585) + 0.06(5.74) = 0.49 \text{ atm}$$

We can operate the evaporator at 0.49 atm and 150°C, well within its operating range, and obtain the purity we need. We'll recycle the bit of vapor from the evaporator back to the feed. The final design is



P5.60

We have a couple of considerations based on the solubility data. Na_2SO_4 is pretty soluble in water. At 40°C, the solubility is at a maximum of 48.8 g/100 g water, and the solid in equilibrium with this saturated solution is anhydrous Na_2SO_4 . At cooler temperatures, we get lower solubility – this means more crystals produced, but the crystals are not anhydrous and any entrained solution is lower in salt concentration. So the dryer has to work harder if we operate the filter at a lower temperature. We want to remove as much water as possible in the evaporator compared to the dryer, and recover as much of the salt as possible. One way to accomplish this is to skip the cooler all together, and recycle the filtrate back to the evaporator. We should operate the vacuum evaporator at 70°C, by interpolation of the data in App. B we estimate that the solubility of Na_2SO_4 at this temperature is 44.5 g/100 g (30.8 wt%). The proposed flow diagram, with flows in kg/h and compositions in wt%, is shown.



Process flow calculations proceed using the usual combination of material balances, performance specifications, and phase equilibrium. We'll simply summarize the results:

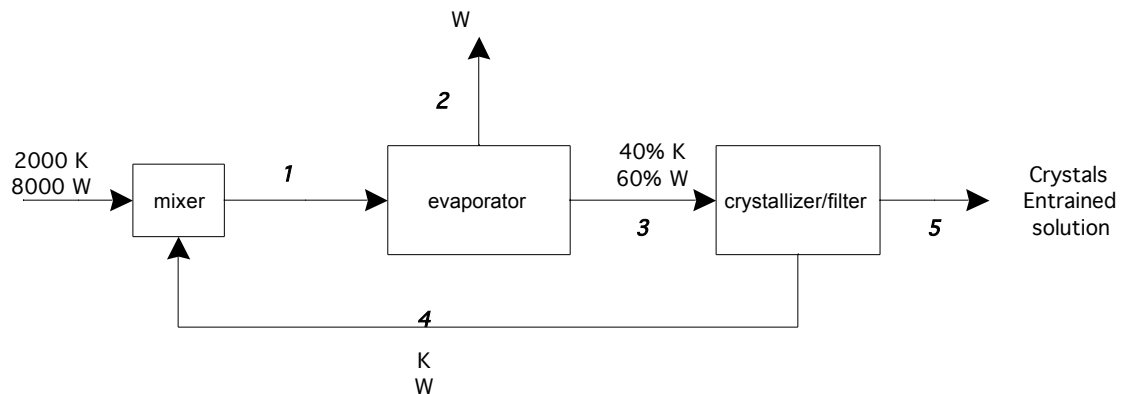
Flows (kg/h)	Fresh feed	To evap	Water from evap	To filter	Filtrate (recycle)	Cake (solids + soln)	Water from dryer	Crystals
Na ₂ SO ₄	100	139.9		139.9	39.9	100		100
H ₂ O	900	989.7	896.4	93.3	89.7	3.58	3.58	
total	1000	1129.6	896.4	233.2	129.6	103.58	3.58	100

100% product recovery is achieved with this design, and the dryer does very little water removal.

P5.61

At 40°C, from Table B.8, the solubility of K₂SO₄ in water is 14.76 g salt/100 g water, or 12.9 g salt per 100 g solution (0.129 mass fraction).

(a) The labeled flow diagram is shown, with components potassium sulfate K and water W. Stream 5 includes both crystals C (pure K) and entrained solution ES (saturated solution of K and W); flows are in lb/h.



Considering the entire process as a system, the material balance on K is

$$2000 = \dot{m}_{C5} + 0.129\dot{m}_{ES5}$$

From the entrainment specification

$$\dot{m}_{C5} = 10\dot{m}_{ES5}$$

Solving

$$\dot{m}_{C5} = 1975 \text{ lb/h}$$

Crystal production rate

$$\dot{m}_{ES5} = 197 \text{ lb/h}$$

The balance equation for water (again with the entire process as system), is

$$8000 = \dot{m}_2 + 0.871\dot{m}_{ES5} = \dot{m}_2 + 0.871(197)$$

Water evaporation rate

$$\dot{m}_2 = 7828 \text{ lb/h}$$

Now let's lump the mixer + evaporator together as our system. Material balance equations are

$$2000 + 0.129\dot{m}_4 = 0.4\dot{m}_3 \quad (\text{K balance})$$

$$8000 + 0.871\dot{m}_4 = 7828 + 0.6\dot{m}_3 \quad (\text{W balance})$$

We solve simultaneously to find

$$\dot{m}_3 = 6345 \text{ lb/h}$$

$$\dot{m}_4 = 4170 \text{ lb/h}$$

Recycle rate

(b) The lower temperature would produce a filtrate with a lower concentration of salt. However, without the water evaporation step this could not be recycled – because the water must be removed somewhere. This solution would result in a significantly lower recovery of salt in the filter cake product. Not a good idea.

(c) If we assume that the operation of the crystallizer/filter remains at 40°C, and the entrained solution remains at 1 lb/10 lb crystals, then the purity of the product must stay the same. This is because the salt concentration in the saturated liquid solution remains at 0.129 g/g. But, if less water is evaporated, then the feed rate to the process must decrease.

Let's look at the case where the water evaporation rate is 6000 lb/h. Now we allow the feed rate to vary. The balances around the entire system are:

$$0.8\dot{m}_F = \dot{m}_2 + 0.871\dot{m}_{ES5} = 6000 + 0.871\dot{m}_{ES5}$$

$$0.2\dot{m}_F = \dot{m}_{C5} + 0.129\dot{m}_{ES5}$$

It is still true that

$$\dot{m}_{C5} = 10\dot{m}_{ES5}$$

Solving, we find that the feed and production rates at the new lower evaporation rate are

$$\dot{m}_F = 7665 \text{ lb/h} \quad \text{Feed rate}$$

$$\dot{m}_{C5} = 1510 \text{ lb/h} \quad \text{Crystal production rate}$$

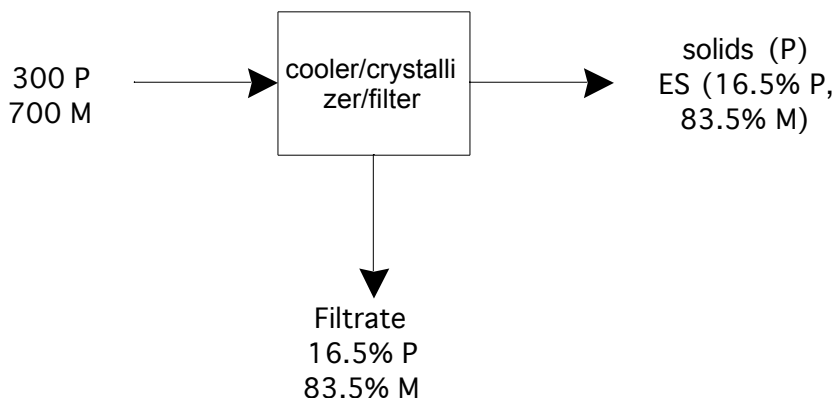
$$\dot{m}_{ES5} = 151 \text{ lb/h}$$

The feed rate drops linearly with the drop in the water evaporation rate, as does the crystal production rate. Further calculations would show that the recycle rate also drops linearly with water evaporation rate. This is because all the equations involved are linear.

(d) If the fresh feed rate is maintained constant while the water evaporation rate decreases, then by overall material balance some of the filtrate must be split off and discarded – it can't all be recycled. It seems like a dumb idea – the net effect of what the superintendent is proposing is to simply feed material in and then discard it. (Of course, one would be more polite in responding to the superintendent!)

P5.62

The crystallizer operates at -50°F (-45°C). From Table B.10 we see that this temperature produces a liquid phase containing 16.5 mol% *p*-xylene/83.5 mol% *m*-xylene, and a solid *p*-xylene phase. The process is shown, with flows in gmol/h and compositions in mol%



The material balance equations are (with S for solids, ES for entrained solution, and F for filtrate)

$$300 = \dot{n}_S + 0.165\dot{n}_{ES} + 0.165\dot{n}_F \quad (p\text{-xylene})$$

$$700 = 0.835\dot{n}_{ES} + 0.835\dot{n}_F \quad (m\text{-xylene})$$

The entrainment specification gives us a final equation:

$$\dot{n}_S = 19\dot{n}_{ES}$$

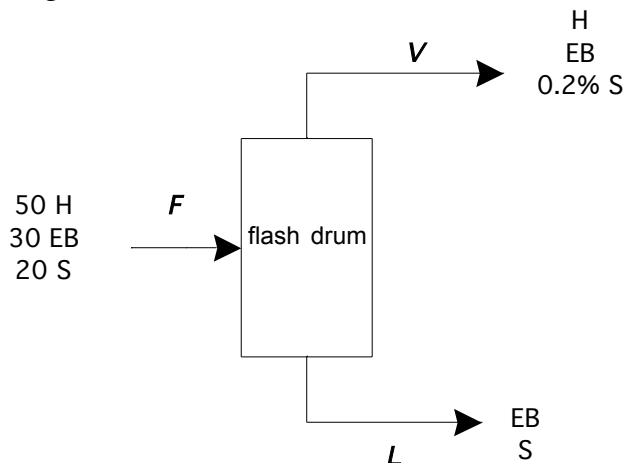
Solution by substitution and elimination is straightforward. The filtrate is 16.5 mol% *p*-xylene/83.5 mol% *m*-xylene at a flow rate of 830 gmol/h. The filter cake is 161.7 gmol/h pure *p*-xylene solids plus 8.5 gmol/h entrained solution. The cake is therefore 95.8 mol% *p*-xylene. The fractional recovery of *p*-xylene in the cake is $163.1/300$ or 0.544.

If *p*-xylene is the more valuable product, the addition of the isomerization reactor is a great idea. It allows eventually almost all of the feed to be converted to the desired product. This is achieved through the coupling of reaction and separation. Since this is an

isomerization, the reaction is reversible, and reaction alone could not achieve complete conversion of *m*-xylene to *p*-xylene.

P5.63

The flow diagram for the flash drum is



where flows are in kgmol/h and compositions in mol%. We have made an assumption that hydrogen *H* does not condense at any reasonable operating conditions for the drum, and therefore appears only in the vapor (V) phase. We have assumed that ethylbenzene *EB* and styrene *S* are in both vapor and liquid phases. Since the flash drum operates as a single equilibrium stage, V and L are in equilibrium. Since EB and S are chemically similar compounds, Raoult's law is an appropriate model for phase equilibrium:

$$x_{EB}P_{EB}^{sat} = y_{EB}P$$

$$x_S P_S^{sat} = y_S P$$

We do not write an equilibrium expression for hydrogen – all of it is in the vapor phase. We do write material balance equations for all three components:

$$50 = y_H \dot{n}_V$$

$$30 = y_{EB} \dot{n}_V + x_{EB} \dot{n}_L$$

$$20 = y_S \dot{n}_V + x_S \dot{n}_L$$

The pressure is specified at 760 mm Hg, and the styrene content of the vapor stream $y_S = 0.002$. We also know that mole fractions in each stream must sum to 1:

$$y_H + y_{EB} + y_S = 1$$

$$x_{EB} + x_S = 1$$

Finally, we have two Antoine equations that relate saturation pressures to temperature:

$$\log_{10} P_{EB}^{sat} = 6.95719 - \frac{1424.255}{213.21 + T}$$

$$\log_{10} P_S^{sat} = 7.14016 - \frac{1574.51}{224.09 + T}$$

We solve this system of equations in an equation-solving program:

$$T = 15.9^\circ\text{C}$$

$$y_{EB} = 0.0043$$

Note that there is a short-cut we can take to solve this problem. Very little ethylbenzene and styrene are in the vapor phase, and their saturation pressures are not that different, so to a good approximation we can say that the EB:S ratio in the feed is the same as that in the liquid product. With this approximation, we estimate that $x_{EB} = 0.6$, $x_S = 0.4$, and we can immediately use these values in the Raoult's law equations (plus the Antoine expressions) to find the desired operating temperature and the mole fraction ethylbenzene the vapor phase.

P5.64

For methanol and water, Antoine equations are

$$\log_{10} P_m^{sat} = 7.97328 - \frac{1515.14}{T + 232.85}$$

$$\log_{10} P_w^{sat} = 7.96681 - \frac{1668.21}{T + 228}$$

Our procedure will be to set $P = 1$ atm, pick a temperature, calculate the bubblepoint composition by satisfying

$$x_m P_m^{sat} + x_w P_w^{sat} = P$$

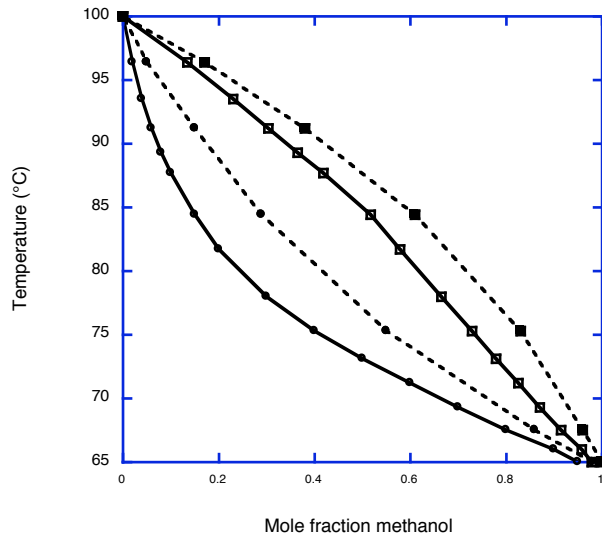
then calculating the vapor composition in equilibrium with that liquid at the calculated T from Raoult's law. We can do this easily by recognizing that the bubblepoint equation can be re-arranged to

$$x_m = \frac{P - P_w^{sat}}{P_m^{sat} - P_w^{sat}}$$

Calculations are then carried out in a spreadsheet, results are tabulated and plotted below. (Note that we choose the temperature range from the methanol boiling point to the water boiling point.)

T	P_m^{sat}	P_w^{sat}	x_m	x_w	y_m	y_w
65.00	769.76	187.61	0.98	0.02	1.00	0.00
67.50	848.59	209.62	0.86	0.14	0.96	0.04
75.30	1138.65	292.83	0.55	0.45	0.83	0.17
84.40	1575.52	423.48	0.29	0.71	0.61	0.39
91.20	1984.47	550.29	0.15	0.85	0.38	0.62

96.40	2352.27	667.36	0.05	0.95	0.17	0.83
100.00	2637.91	759.98	0.00	1.00	0.00	1.00



The solid lines are the data and the dashed lines are the calculations from Raoult's law. This system exhibits significant deviations from Raoult's law. This is not surprising because methanol and water are both good hydrogen bonders. Raoult's law should NOT be used to model methanol-water vapor-liquid equilibrium.

P5.65

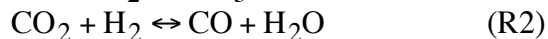
Water and methanol are the most condensable. If these were pure at 200°C and 4000 kPa, would they be liquid or vapor? We can estimate this from the Antoine equation (although the accuracy is not great, as 200°C is outside the range of the constants in Table B.4).

$$\text{Water: } \log_{10} P_w^{sat} = 7.96681 - \frac{1668.21}{T + 228} \quad P_w^{sat} = 11725 \text{ mm Hg at } 200^\circ\text{C}$$

$$\text{Methanol: } \log_{10} P_m^{sat} = 7.97328 - \frac{1515.14}{T + 232.85} \quad P_m^{sat} = 29,709 \text{ mm Hg at } 200^\circ\text{C}$$

4000 kPa = 39.5 atm = 30,000 mm Hg. Since $P > P^{sat}$ for both compounds, if these compounds were pure they would be liquid.

The two reactions are:



From the Gibbs energy and enthalpy of formation (Table B.3) assuming all gas phase, we calculate:

$$\Delta \hat{G}_{R1} = -25.05 \text{ kJ/gmol}$$

$$\Delta \hat{H}_{R1} = -90.41 \text{ kJ/gmol}$$

$$\Delta \hat{G}_{R2} = +28.51 \text{ kJ/gmol}$$

$$\Delta \hat{G}_{R2} = +41.14 \text{ kJ/gmol}$$

At $T = 200^\circ\text{C} = 473 \text{ K}$, we calculate

$$K_{a1} = 0.0338$$

$$K_{a2} = 0.0047$$

These are related to extents of reaction as:

$$K_{a1} = 0.0338 = \frac{y_m}{y_{CO}(y_{H2})^2} \frac{1}{P^2} = \frac{\xi_1 (700 - 2\xi_1)^2}{(300 - \xi_1 + \xi_2)(300 - 2\xi_1 - \xi_2)^2} \frac{1}{(39.5)^2}$$

$$K_{a1} = 0.0047 = \frac{y_{CO}y_w}{y_{CO2}y_{H2}} = \frac{(300 - \xi_1 + \xi_2)\xi_2}{(100 - \xi_2)(300 - 2\xi_1 - \xi_2)}$$

(We convert pressure to atm to be in agreement with standard state for the Gibbs energy data.)

The solution is $\xi_1 = 123.8$
 $\xi_2 = 0.14$

The reactor outlet flow is:

Methanol:	123.8 gmol/s
CO:	176.3 gmol/s
CO ₂ :	99.9 gmol/s
H ₂ :	52.2 gmol/s
H ₂ O:	0.14 gmol/s

The mole fraction of methanol in the outlet is 123.8/452.3 or 0.274. The mole fraction of water in the outlet is 0.14/452.3 or 0.0003. Is this above the dewpoint of the mixture? (we can assume the other components are not condensable). We'll use Raoult's law as a crude measure: *if* the mixture is at its dewpoint then

$$x_w = \frac{y_w P}{P_w^{sat}} = \frac{0.0003(30000)}{11725} = 0.0008$$

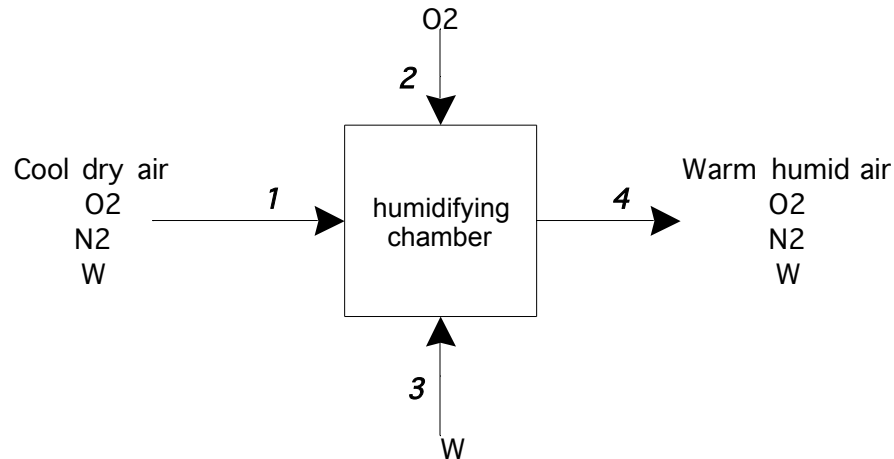
$$x_m = \frac{y_m P}{P_m^{sat}} = \frac{0.274(30000)}{29709} = 0.277$$

Since $x_w + x_m \ll 1$, then this mixture is NOT condensing, it is above its dewpoint, and the mixture is all vapor, consistent with our original assumption. (One could calculate the

dewpoint temperature of the mixture and see how far we are from having a liquid phase present.)

P5.66

The flow diagram is



The inlet air (stream 1) is at 20% relative humidity, or

$$0.20 = \frac{y_{W1}P}{P_W^{sat}}$$

From Antoine's equation we calculate that at 20°C $P_W^{sat} = 17.5$ mm Hg. Since the total pressure is 1 atm (760 mm Hg)

$$y_{W1} = \frac{0.20(17.5)}{760} = 0.0046$$

The outlet air is at 100% relative humidity and 37°C. We calculate

$$y_{W4} = \frac{1(47.1)}{760} = 0.062$$

Now we write material balances on our 3 components

$$\begin{aligned} 0.0046\dot{n}_1 + \dot{n}_3 &= 0.062\dot{n}_4 && \text{(water)} \\ \dot{n}_{O1} + \dot{n}_2 &= 0.40\dot{n}_4 && \text{(oxygen)} \\ \dot{n}_{N1} = \dot{n}_{N4} &= (1 - 0.062 - 0.4)\dot{n}_4 = 0.538\dot{n}_4 && \text{(nitrogen)} \end{aligned}$$

Also

$$\begin{aligned} \dot{n}_{N1} &= 3.76\dot{n}_{O1} \\ \dot{n}_{N1} + \dot{n}_{O1} &= 0.9954\dot{n}_1 \end{aligned}$$

The volumetric flow rate of warm humid air serves as our basis. To convert to a molar flow rate, we use the ideal gas law

$$\dot{n}_4 = \frac{P\dot{V}}{RT} = \frac{(1 \text{ atm})(2000 \text{ ft}^3/\text{min})(28.32 \text{ L/ft}^3)}{(0.082057 \text{ atm L/gmol K})(273 + 37)} = 2226 \text{ gmol/min}$$

Now working back:

$$\dot{n}_{N1} = 0.538\dot{n}_4 = 0.538(2226) = 1197.6 \text{ gmol/min}$$

$$\dot{n}_{O1} = \frac{\dot{n}_{N1}}{3.76} = 318.5 \text{ gmol/min}$$

$$\dot{n}_1 = \frac{\dot{n}_{N1} + \dot{n}_{O1}}{0.9954} = 1523 \text{ gmol/min}$$

$$\dot{n}_{W1} = 0.0046\dot{n}_1 = 7 \text{ gmol/min}$$

$$\dot{n}_2 = 0.40(2226) - 318.5 = 572 \text{ gmol/min}$$

$$\dot{n}_3 = 0.062(2226) - 0.0046(1523) = 131 \text{ gmol/min}$$

Now that we have all the molar flow rates, we convert to mass flow rates (through molar masses) and volumetric flow rates (through ideal gas law for air and O₂, using liquid density of 1 g/cm³ for liquid water).

Results:

Air in: 1523 gmol/min, 43.8 kg/min, 1290 ft³/min

Pure oxygen in: 572 gmol/min, 18.3 kg/min, 486 ft³/min (at 20°C and 1 atm)

Liquid water in: 131 gmol/min, 2.36 kg/min, 0.083 ft³/min

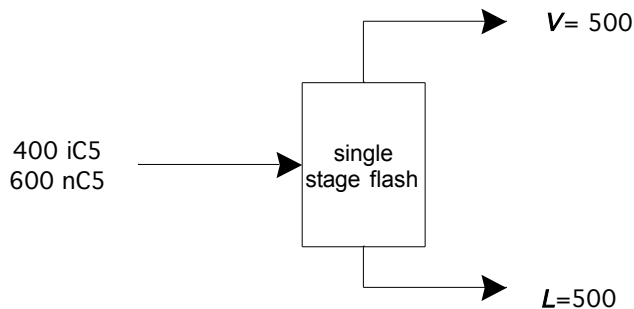
P5.67

Antoine equations for isopentane (i) and n-pentane (n) are

$$\log_{10} P_i^{sat} = 6.78967 - \frac{1020.012}{233.097 + T}$$

$$\log_{10} P_n^{sat} = 6.85221 - \frac{1064.63}{233.01 + T}$$

(a) The pressure is 350 kPa = 2625 mm Hg. For equal-sized vapor and liquid products (assuming an arbitrary basis of 1000 gmol/s)



Raoult's law is appropriate as a model of vapor-liquid equilibrium for this similar compounds.

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

$$y_n P = x_n P_n^{sat}$$

Material balance equations are

$$400 = 500y_i + 500x_i$$

$$600 = 500y_n + 500x_n$$

Also

$$y_i + y_n = 1$$

$$x_i + x_n = 1$$

Solving this set of equations simultaneously in EES, Excel, or other tool, we find

$$T = 74.1^\circ\text{C}$$

(at which $P_i^{sat} = 2991$ mm Hg and $P_n^{sat} = 2404$ mm Hg. Notice that one saturation pressure lies above the total pressure and the other lies below. This is a good check on the calculated temperature.)

Also we find

$$x_i = 0.376 \quad y_i = 0.423$$

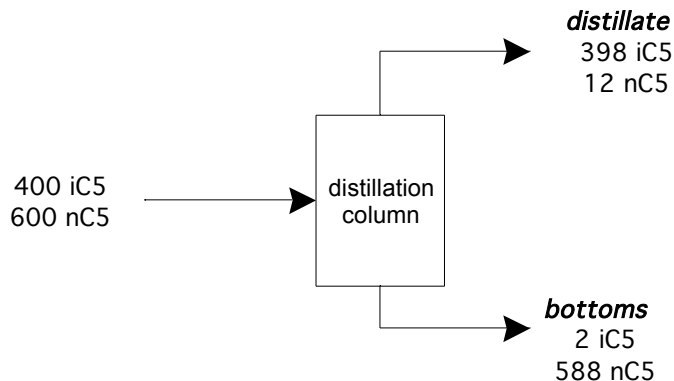
$$x_n = 0.623 \quad y_n = 0.577$$

from which we calculate fractional recoveries

$$f_{RiV} = \frac{0.426(500)}{0.4(1000)} = 0.53$$

$$f_{RnL} = \frac{0.626(500)}{0.6(1000)} = 0.52$$

(b) A single stage flash cannot achieve the desired recoveries. The column flow diagram should be



where distillate and bottoms flows are calculated from the specified component recoveries of 99.5% for isopentane and 98% for n-pentane. At this flows,

$$x_{iB} = \frac{2}{590} = 0.00339 \quad y_{iD} = \frac{398}{410} = 0.9707$$

$$x_{nB} = \frac{588}{590} = 0.9966 \quad y_{nB} = \frac{12}{410} = 0.0293$$

Saturation pressures at 60°C are 2039.6 and 1654.9 mm Hg for isopentane and n-pentane, respectively. From the Fenske equation

$$N_{min} = \frac{\log\left[\left(\frac{0.9707}{0.0293}\right)\left(\frac{0.9966}{0.00339}\right)\right]}{\log\left[\frac{2039.6}{1654.9}\right]} = 44 \text{ stages}$$

(c) The distillate is almost pure isopentane, so the temperature should be roughly the saturation pressure of isopentane at 350 kPa. From Antoine's equation:

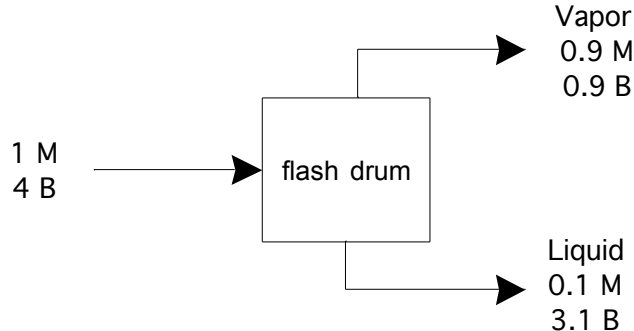
$$\log_{10}(2625) = 6.78967 - \frac{1020.012}{233.097 + T}$$

$$T = 69.5^{\circ}\text{C}$$

(Temperature would be slightly higher due to the presence of the n-pentane.)

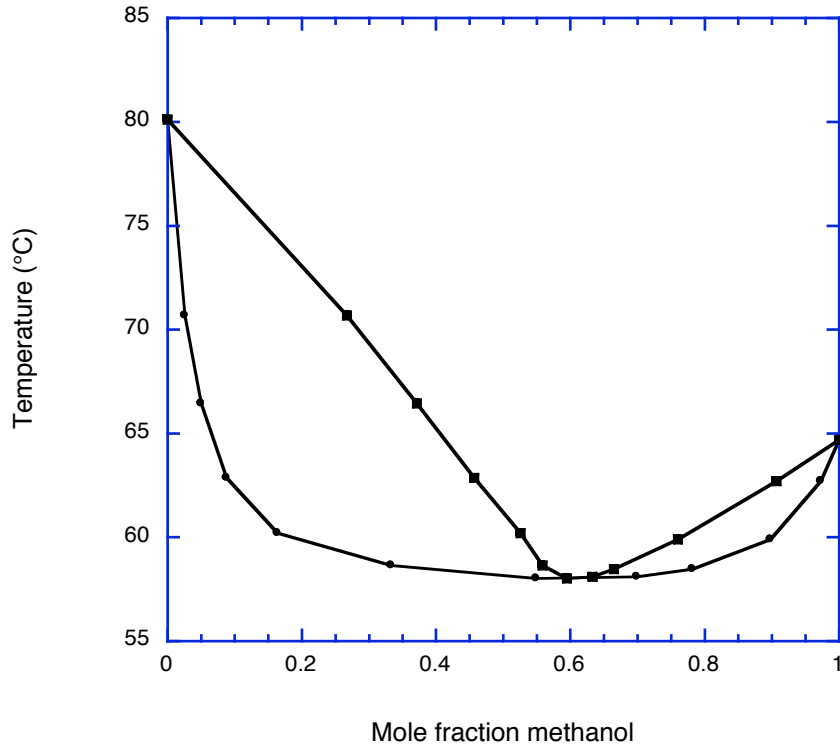
P5.68

The desired operation is



with flows in gmol/min and calculated from the recovery and purity specifications.

To determine if this is achievable in a single equilibrium stage, we examine the vapor-liquid phase diagram (Table B.12, plotted here along with the pure component boiling point data).



This system forms an azeotrope and is clearly nonideal. Raoult's law cannot be used to model its behavior!

(a) Reading from the diagram, the vapor contains 50% methanol at $\sim 61^\circ\text{C}$ and is in equilibrium with a liquid of $\sim 13\text{ mol}\%$ methanol. From the inverse lever rule or from completing the material balance equations:

$$1 = 0.5\dot{n}_V + 0.13\dot{n}_L$$

$$4 = 0.5\dot{n}_V + 0.87\dot{n}_L$$

we find that if we meet purity specifications by operating at 61°C , $\dot{n}_V = 0.95$, $\dot{n}_L = 4.05$ and $f_{RMV} = 0.5(0.95)/1 = 0.475$, well below the desired fractional recovery of 0.90.

(b) To ensure that we meet the recovery specification, we require that

$$y_M \dot{n}_V = 0.90$$

$$x_M \dot{n}_L = 0.10$$

and that

$$\dot{n}_V + \dot{n}_L = 5$$

We resort to trial-and-error: guess y_M , find x_M from the phase diagram, calculate \dot{n}_V and \dot{n}_L , and see if the total mass balance equation is satisfied. Some iterations are tabulated:

T °C	y_M	x_M	\dot{n}_V	\dot{n}_L	$\dot{n}_V + \dot{n}_L$
------	-------	-------	-------------	-------------	-------------------------

66.44	0.371	0.050	2.43	2	4.43 (too low)
70.67	0.267	0.026	3.37	3.38	7.21 (too high)
67.5	~0.345	~0.044	2.61	2.27	4.88 (a little low)

~67.6°C would produce the desired recovery, but the purity of the vapor would be only ~34 mol% methanol.

P5.69

(Note to instructor: Students are likely to need some guidance to make appropriate assumptions, which are necessary to solve this problem.)

From Table B.20, we find that the boiling point temperatures are

Ethylbenzene: 136.2°C

p-xylene: 138.4°C

m-xylene: 139.1°C

o-xylene: 144.4°C

We also need Antoine equation data:

$$\log_{10} P_{EB}^{sat} = 6.95719 - \frac{1424.255}{213.21 + T}$$

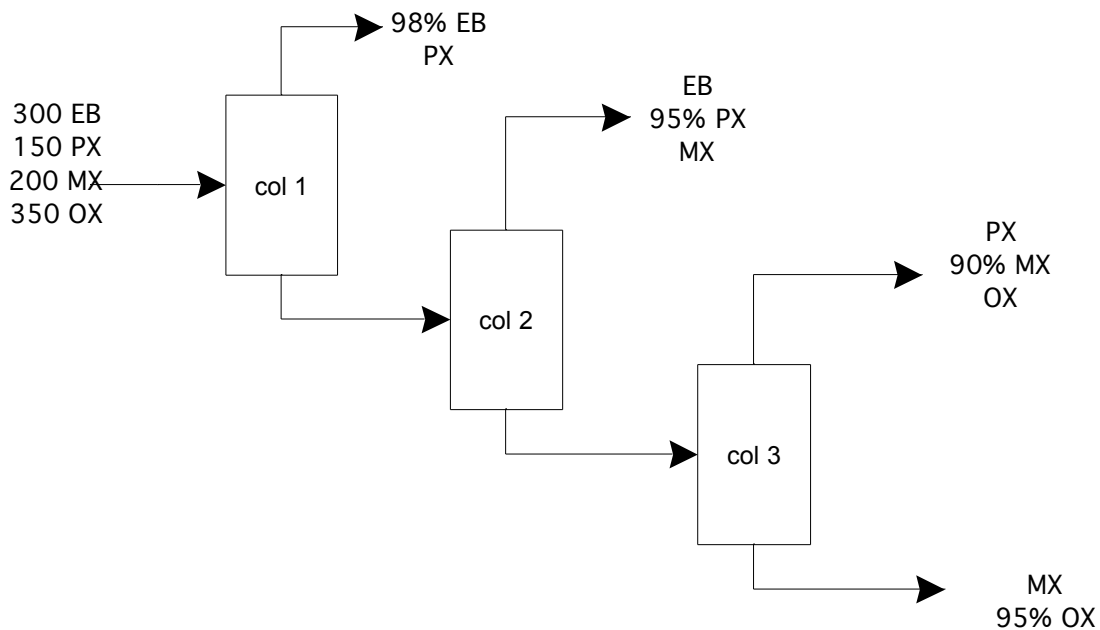
$$\log_{10} P_{PX}^{sat} = 6.99052 - \frac{1453.43}{215.31 + T}$$

$$\log_{10} P_{MX}^{sat} = 7.00908 - \frac{1462.266}{215.11 + T}$$

$$\log_{10} P_{OX}^{sat} = 6.99891 - \frac{1474.679}{213.69 + T}$$

Our heuristics would argue for first separating OX, then EB, then finally PX from MX. But we will consider several different configurations. We'll assume that the only impurities in each product are the compounds with adjacent volatilities. Where there are 2 impurities we simply assumed they were in equal quantities.

Configuration 1:



Approximate flows (basis: 1000 gmol/h):

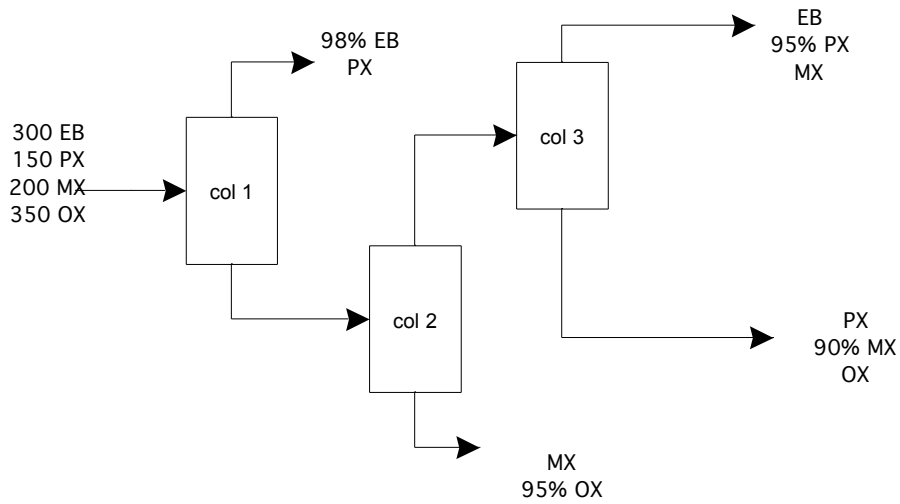
	Feed	Col 1 distillate	Col 1 bottoms	Col 2 distillate	Col 2 bottoms	Col 3 distillate	Col 3 bottoms
EB	300	297	3	3			
PX	150	6	144	134	10	10	
MX	200		200	4	196	178	18
OX	350		350		350	10	340
total	1000	303	697	141	556	198	358
$T(^{\circ}\text{C})$		136	142	138	142	139	144

To determine the approximate temperatures of each column, we calculate the dewpoint temperature of the distillate and the bubblepoint temperature of the bottoms, using Eqs. 5.12 and 5.13. We'll postulate operation at 1 atm (760 mm Hg), and assume that Raoult's law is adequate to model vapor-liquid equilibrium. The results were added to the table.

Minimum stages are calculated from the Fenske equation, using the compositions in the table and separation factors calculated from the ratio of the saturation pressures (1.059 for EB/PX, 1.02 for PX/MX, and 1.155 for MX/OX). Results are summarized in the table, assuming the actual number of stages equals twice the minimum.

	Nmin	N	Q	\$ (relative)
Col 1	135	270	1000	8,540
Col 2	328 (!)	655	697	17,290
Col 3	40	80	556	1,890
total				\$27,720

Configuration 2:

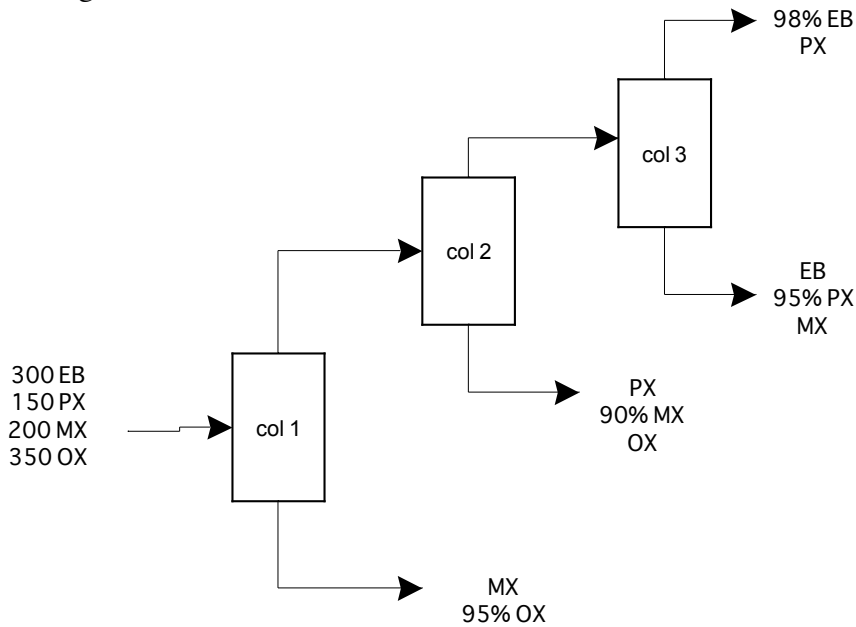


Approximate flows (basis: 1000 gmol/h):

	Feed	Col 1 distillate	Col 1 bottoms	Col 2 distillate	Col 2 bottoms	Col 3 distillate	Col 3 bottoms
EB	300	297	3	3		3	
PX	150	6	144	144		134	10
MX	200		200	182	18	4	178
OX	350		350	10	340		10
total	1000	303	547	339	358	141	198
$T(^{\circ}\text{C})$		136	142	139	144	138	139

	Nmin	N	Q	\$ (relative)
Col 1	135	270	1000	8,540
Col 2	41	82	697	2,165
Col 3	323	645	339	11,875
total				\$22,580

Configuration 3:



Approximate flows (basis: 1000 gmol/h):

	Feed	Col 1 distillate	Col 1 bottoms	Col 2 distillate	Col 2 bottoms	Col 3 distillate	Col 3 bottoms
EB	300	300		300		297	3
PX	150	150		140	10	6	134
MX	200	182	18	4	178		4
OX	350	10	340		10		
total	1000	642	358	444	198	303	141
$T (^{\circ}\text{C})$		138	144	137	139	136	138

	Nmin	N	Q	\$ (relative)
Col 1	41	82	1000	2,595
Col 2	323	646	642	16,368
Col 3	134	268	444	5645
total				\$24,610

Configuration 2 is the cheapest, because it saves the most difficult separation for last, and requires the least total flows through all the columns.

P5.70

We'll use Raoult's law to model the phase equilibrium behavior for both benzene and toluene.

$$y_b P = x_b P_b^{sat}$$

$$y_t P = x_t P_t^{sat}$$

Also

$$y_b + y_t = 1$$

$$x_b + x_t = 1$$

Adding together the two Raoult's law equations and then substituting:

$$y_b P + y_t P = x_b P_b^{sat} + x_t P_t^{sat}$$

$$(y_b + y_t)P = P = P_b^{sat} + (1 - x_b)P_t^{sat}$$

We re-arrange to get our desired relationship:

$$x_b = \frac{P - P_t^{sat}}{P_b^{sat} - P_t^{sat}} \quad \text{Eq. (1)}$$

which, if Antoine's expressions are substituted in ,gives x_b as a function of P and T .

The material balance equations for benzene and total moles are:

$$z_b \dot{n}_F = y_b \dot{n}_V + x_b \dot{n}_L$$

$$\dot{n}_F = \dot{n}_V + \dot{n}_L$$

Combining:

$$z_b (\dot{n}_V + \dot{n}_L) = y_b \dot{n}_V + x_b \dot{n}_L$$

$$z_b \left(\frac{\dot{n}_V}{\dot{n}_L} + 1 \right) = y_b \left(\frac{\dot{n}_V}{\dot{n}_L} \right) + x_b$$

$$(z_b - y_b) \left(\frac{\dot{n}_V}{\dot{n}_L} \right) = x_b - z_b$$

$$\frac{\dot{n}_V}{\dot{n}_L} = \frac{x_b - z_b}{z_b - y_b} \quad \text{Eq. (2)}$$

which is simply the equation behind the inverse lever rule.

We set $P = 100$ atm and $\dot{n}_F = 100$. The minimum temperature is the bubblepoint temperature, and the maximum is the dewpoint. We calculate saturation pressures from Antoine's equation

$$\log_{10} P_b^{sat} = 6.90565 - \frac{1211.033}{T + 220.79}$$

$$\log_{10} P_t^{sat} = 6.95464 - \frac{1344.8}{T + 219.48}$$

Now we combine Eqs. 1 and 2 along with Antoine equation and Raoult's law to complete the calculations. These are most easily carried out in a spreadsheet. Results are summarized.

(i) $z_b = 0.2$

	T	\dot{n}_V	\dot{n}_L	x_b	y_b
Minimum	102.1	0	100	0.2	0.377
Maximum	106.3	100	0	0.095	0.20
Halfway	104.2	36.5	63.5	0.147	0.292

(ii) $z_b = 0.5$

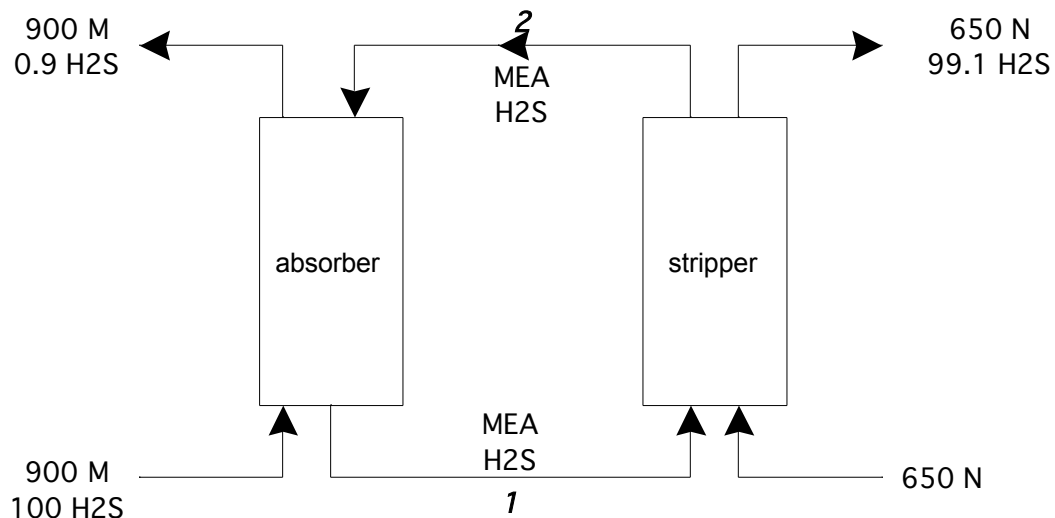
	T	\dot{n}_V	\dot{n}_L	x_b	y_b
Minimum	92.1	0	100	0.5	0.714
Maximum	98.8	100	0	0.291	0.5
Halfway	95.5	50	50	0.389	0.610

(iii) $z_b = 0.8$

	T	\dot{n}_V	\dot{n}_L	x_b	y_b
Minimum	84.4	0	100	0.8	0.911
Maximum	88.9	100	0	0.614	0.8
Halfway	86.6	61.4	31.6	0.706	0.859

P5.71

Best operation for absorbers is high P, low T; for strippers it is low P, high T. Given the limitations, we therefore pick for the absorber $P = 10,000$ mm Hg and $T = 40^\circ\text{C}$, and for the stripper, $P = 760$ mm Hg and $T = 100^\circ\text{C}$. The flow diagram is



with all flows given in kmol/h, and H₂S flows calculated from the stream composition specifications and an overall material balance.

Each unit operates as a single equilibrium stage. The gas leaving the absorber is in equilibrium with the liquid, stream 1, leaving the absorber. The mole fraction of H₂S in the gas leaving the absorber is 0.001. The absorber pressure is 10,000 mm Hg, therefore,

$$p_{H_2S} = y_{H_2S}P = 0.001(10000) = 10 \text{ mm Hg}$$

From the data, at 40°C (the operating temperature of the absorber) the liquid in equilibrium with this gas is at 0.374 moles H₂S per mole MEA, or

$$\frac{\dot{n}_{H_2S,1}}{\dot{n}_{MEA,1}} = 0.374$$

The partial pressure of H₂S in the gas leaving the stripper is

$$p_{H_2S} = y_{H_2S}P = \frac{99.1}{99.1 + 650}(760) = 100 \text{ mm Hg}$$

From the data at 100 °C (stripper operating temperature)

$$\frac{\dot{n}_{H_2S,2}}{\dot{n}_{MEA,2}} = 0.279$$

From an MEA balance around the absorber

$$\dot{n}_{MEA,1} = \dot{n}_{MEA,2}$$

and from the H₂S balance around the stripper

$$\dot{n}_{H_2S,2} + 99.1 = \dot{n}_{H_2S,1}$$

We have 4 equations in 4 unknowns that we can solve to find that the MEA flow rate is 1043 kmol/h.

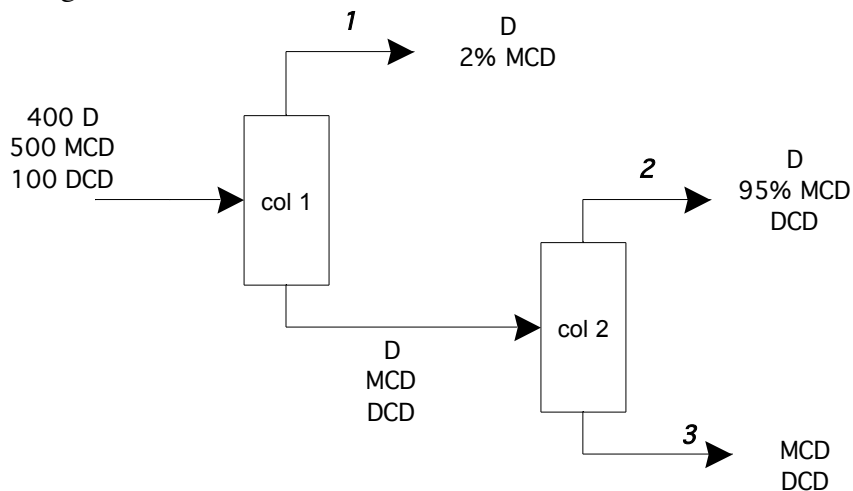
If the N₂ flow rate decreased while solvent flows and operating *T* and *P* remained constant, the molar flow rate of H₂S would have to decrease because *y*_{H₂S} would remain constant. Not as much H₂S would be removed from the MEA solution, so not as much could be picked up in the absorber. The mole fraction of H₂S in the gas leaving the absorber would increase above its specification. (Think of what would happen if the nitrogen stream was shut off entirely!)

P5.72.

Differences in solubility in water could be used to separate Cl₂ and HCl from the decanes. However, the decanes have similar insolubility in water, and are chemically similar so their solubility in other solvents is also likely to be similar and therefore not a basis for separation. Their melting points are below ambient, making crystallization unattractive.

Boiling points are all above ambient, but are not unusually high, so distillation is a reasonable separation technology.

Configuration 1:



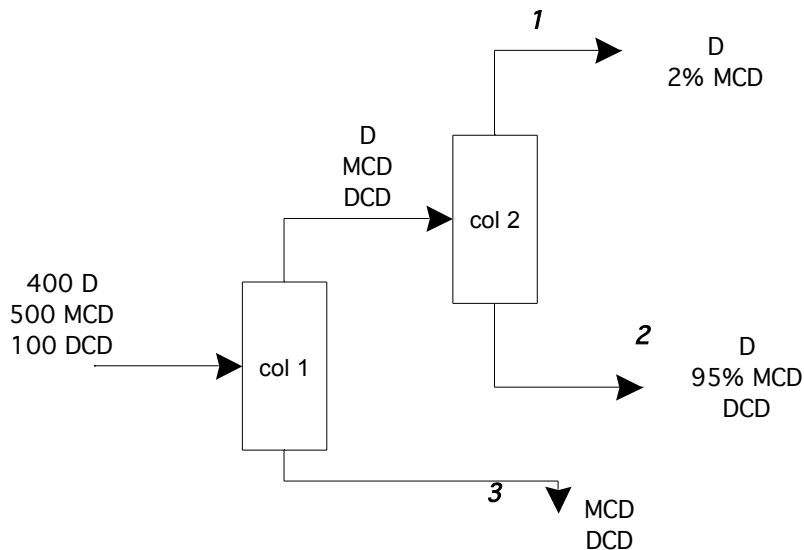
The two key components in column 1 are decane and MCD, while the key components in column 2 are MCD and DCD.

DOF analysis

Number of variables		
Stream variables	13	3+2+3+3+2
System variables	0	No reaction, assumed steady state
Number of constraints		
Specified flows	1	Stream 1 = 1000 gmol/min
Specified compositions	4	2 in feed, 1 in product 1, 1 in product 2 (we use the max 2% and minimum 95% as specifications.)
System performance specifications	2	97% recovery of decane 99% recovery of MCD
Material balances	6	3+3

DOF = 13 – (1+4+2+6) = 13 – 13 = 0. Correctly specified.

Configuration 2:



Key components in column 1 are MCD and DCD, and in column 2 the key components are decane and MCD.

DOF analysis is the same.

Flow rates are calculated from stream composition and system performance specifications as well as material balance equations.

Configuration 1 (all flows in gmol/min)

	Intermediate stream	Product 1	Product 2	Product 3
Decane	12	388	12	0
MCD	<495	<8	495	?
DCD	100		14	86
total	<607	<396	521	>86

Notice that Product 1 must contain less than 2 mol% MCD based on material balances and the very high recovery of MCD in product 2! Because we don't know how much less, we have 1 fewer constraint than we counted and so the problem is not completely specified.

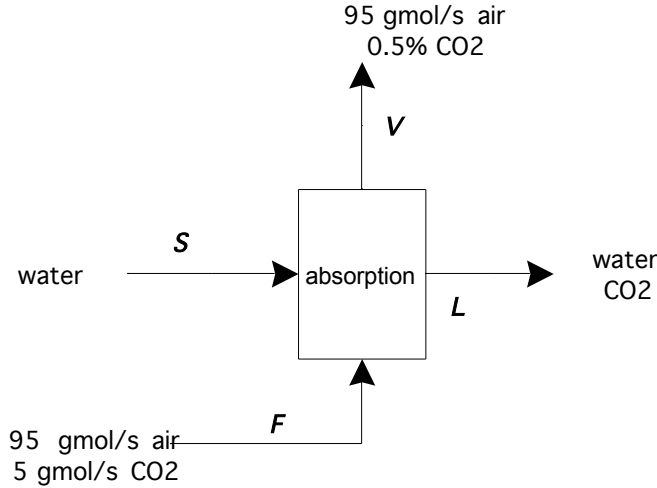
Configuration 2 (all flows in gmol/min)

	Intermediate stream	Product 1	Product 2	Product 3
Decane	400	388	12	0
MCD	>495	<8	495	?
DCD	14		14	86
total	>909	<396	521	>86

Based on these calculations, Configuration 1 is more attractive because the feed rate to the second column is lower, which reduces the cost of the column. Based on the difference in boiling point temperature as a rough measure of the difficulty of separation, the MCD/DCD split is more difficult than the decane/MCD split. Configuration 1 is also better in that the easier separation is done first.

P5.73

(a) If the air is insoluble and the water nonvolatile, then the single absorption stage is sketched as



where the streams are labeled solvent S, feed F, vapor V and liquid L. V and L are in equilibrium, which Henry's law describes.

$$y_{CO_2}P = x_{CO_2}H_{CO_2}$$

The Henry's law constant for CO_2 at $40^\circ C$ in water is 2330 atm, the operating pressure is 26 atm, and $y_{CO_2} = 0.005$:

$$x_{CO_2} = \frac{y_{CO_2}P}{H_{CO_2}} = \frac{0.005(26)}{2330} = 5.58 \times 10^{-5}$$

The flow rate of CO_2 in the vapor stream is calculated from

$$y_{CO_2} = 0.005 = \frac{\dot{n}_{CO_2,V}}{\dot{n}_{CO_2,V} + 95} \Rightarrow \dot{n}_{CO_2,V} = 0.48 \text{ gmol/s}$$

Therefore by material balance

$$\dot{n}_{CO_2,L} = 5 - 0.48 = 4.52 \text{ gmol/s}$$

The water flow rate is calculated from

$$x_{CO_2} = 5.58 \times 10^{-5} = \frac{\dot{n}_{CO_2,L}}{\dot{n}_{CO_2,L} + \dot{n}_{W,L}} = \frac{4.52}{4.52 + \dot{n}_{W,L}} \Rightarrow \dot{n}_{W,L} = 81,000 \text{ gmol/s}$$

The water feed rate is 81,000 gmol/s, to treat 100 gmol/s gas!

(b) Is air insoluble? Model N_2 and O_2 dissolved in water using Henry's law, assume N_2 mol fraction in gas stream is same as in air.

$$x_{N_2} = \frac{y_{N_2} P}{H_{N_2}} = \frac{0.79(26)}{104,000} = 1.97 \times 10^{-4}$$

Total N_2 lost from air stream is

$$x_{N_2} = 1.97 \times 10^{-4} = \frac{\dot{n}_{N_2,L}}{\dot{n}_{N_2,L} + \dot{n}_{W,L}} = \frac{\dot{n}_{N_2,L}}{\dot{n}_{N_2,L} + 81,000} \Rightarrow \dot{n}_{N_2,L} = 16 \text{ gmol/s}$$

(out of 75 gmol/s N_2 fed to the absorber – significant!)

A similar calculation for O_2 reveals that about 8 gmol/s O_2 leaves in the liquid stream – about 40% of the O_2 in the air feed stream!

The assumption that air is insoluble is not good in this case, because there is so much water.

Is water nonvolatile? The saturation pressure of water at 40°C is calculated from Antoine equation to be 0.073 atm. Raoult's law is used to estimate the mole fraction of water vapor

$$y_W = \frac{x_W P_W^{sat}}{P} = \frac{1(0.073)}{26} = 0.0028$$

The flow rate of water leaving in the vapor stream is

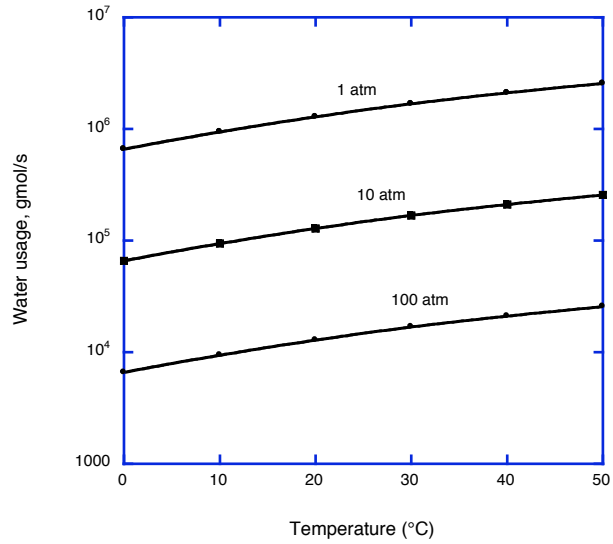
$$y_W = 0.0028 = \frac{\dot{n}_{W,V}}{\dot{n}_{W,V} + \dot{n}_{N_2,V} + \dot{n}_{O_2,V} + \dot{n}_{CO_2,V}} = \frac{\dot{n}_{W,V}}{\dot{n}_{W,V} + 59 + 12 + 0.48} \Rightarrow \dot{n}_{W,V} = 0.2 \text{ gmol/s}$$

Relatively insignificant.

(c) We return to the assumptions of part (a). We use Henry's law to model the phase behavior, and we combine that with a material balance equation on CO_2 and the stream composition specifications.

$$x_{CO_2} = \frac{\dot{n}_{CO_2,L}}{\dot{n}_{CO_2,L} + \dot{n}_{W,L}} = \frac{4.52}{4.52 + \dot{n}_{W,L}} = \frac{y_{CO_2} P}{H_{CO_2}} = \frac{0.005 P}{H_{CO_2}}$$

Given T , we find H_{CO_2} from the data in App. B. Given T and P we use the above equation to find $\dot{n}_{W,L}$ at 0, 10, 20, 30, 40 and 50°C, and at 1, 10 and 100 atm. Results are plotted (Notice the log scale). Water usage decreases with increasing pressure and decreasing temperature. Within this range, I would choose 0°C and 100 atm.



(d)

To use the KSB equation,

$$\text{fractional recovery} = \frac{4.52}{5} = 0.904$$

$$K = \frac{x_{CO_2}}{y_{CO_2}} = \frac{P}{H_{CO_2}} = \frac{100}{728} = 0.137 \text{ at } 0^\circ\text{C and } 100 \text{ atm}$$

Then the KSB equation is

$$0.904 = \frac{(0.137 \dot{n}_S / \dot{n}_F)^{N+1} - (0.137 \dot{n}_S / \dot{n}_F)}{(0.137 \dot{n}_S / \dot{n}_F)^{N+1} - 1}$$

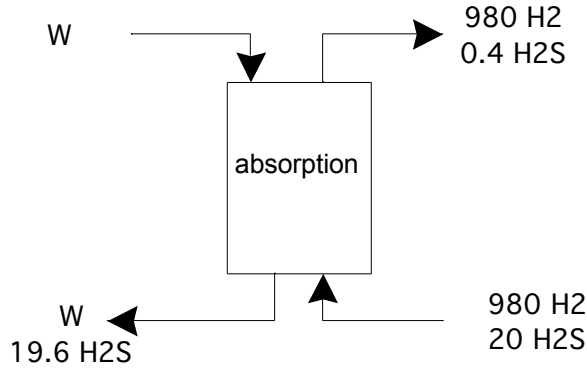
The ratio of solvent to feed flow is calculated for different number of stages; results are summarized

No. of stages	1	2	5	10
Solvent/feed	69	19.2	8.9	7.2

There is an enormous advantage to increasing from 1 to 2 stages. Increasing stages much above 5 does not seem very helpful.

P5.74

The flow diagram is



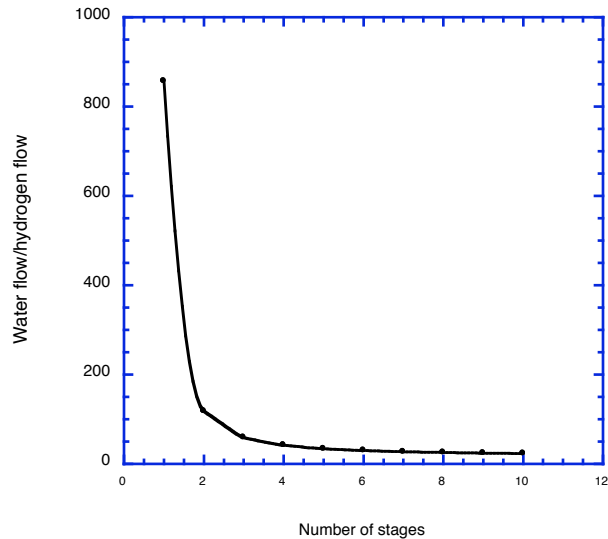
with a basis chosen as 1000 gmol/min and flows calculated from stream composition and system performance specifications. We'll use Henry's law to model the phase equilibrium. At 10°C, $H_{H_2S} = 367$ atm, therefore

$$K_{H_2S} = \frac{x_{H_2S}}{y_{H_2S}} = \frac{P}{H_{H_2S}} = \frac{20}{367} = 0.0545$$

(b) From the KSB equation, with 98% recovery,

$$0.98 = \frac{(0.0545 \dot{n}_S / \dot{n}_F)^{N+1} - (0.0545 \dot{n}_S / \dot{n}_F)}{(0.0545 \dot{n}_S / \dot{n}_F)^{N+1} - 1}$$

We find the solution in Excel at various values of N ; the results are plotted:



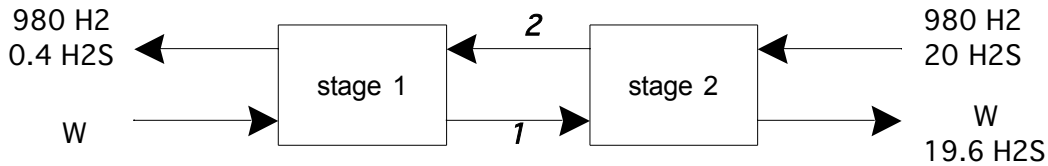
There is a huge advantage to increase from 1 to 2 stages. Although solvent flow requirements continue to drop as N increases, the decrease becomes less and less interesting. About 3-4 stages might be right.

(a) The stagewise calculations are set up: for each stage we have a material balance equation and a Henry's law equation relating the two exit streams. For $N = 1$, the combination simplifies to:

$$\frac{19.6}{19.6 + \dot{m}_W}(367) = \frac{0.4}{980.4}(20)$$

$$\dot{m}_W = 882,000 \text{ (versus 857,000 from KSB)}$$

For $N = 2$,



The equations are

$$\frac{\dot{m}_{H_2S,1}}{\dot{m}_{H_2S,1} + \dot{m}_W}(367) = \left(\frac{0.4}{980.4}\right)(20)$$

$$\dot{m}_{H_2S,2} = 0.4 + \dot{m}_{H_2S,1}$$

$$\frac{19.6}{19.6 + \dot{m}_W}(367) = \left(\frac{\dot{m}_{H_2S,2}}{980 + \dot{m}_{H_2S,2}}\right)(20)$$

$$\dot{m}_{H_2S,1} + 20 = \dot{m}_{H_2S,2} + 19.6$$

This can be solved to find: $\dot{m}_W = 117,500$ (vs 118,000 from KSB)

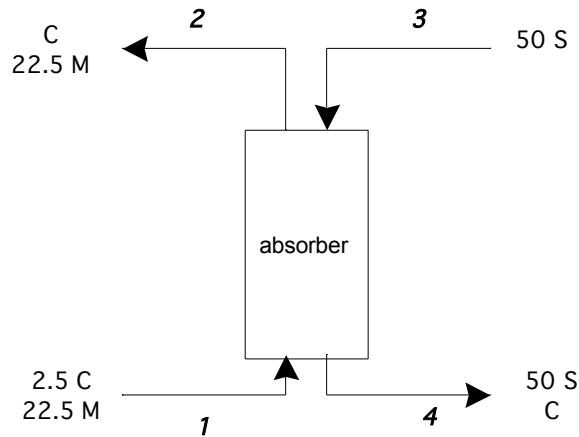
The procedure continues to $N = 10$ in a similar manner. The assumption that the water flow is constant simplifies the solution somewhat. Solutions from the stagewise calculations are very similar to those obtained from the KSB equation, because the assumptions that went into the KSB equation are good for this situation – but the solutions are obtained with much less tedium with the KSB equation.

P5.75

(a) The exit liquid stream is in equilibrium with the entering gas stream. From material balance and the system performance specification that 80% of the CO_2 fed is recovered in the aqueous stream, we calculate that the flow rate of CO_2 in the aqueous stream is 2 gmol/min. From this, the equilibrium constant is

$$K_D = \frac{\text{moles CO}_2/\text{moles liquid}}{\text{moles CO}_2/\text{moles gas}} = \frac{2/(50 + 2)}{2.5/(22.5 + 2.5)} = 0.385$$

(b) The flow diagram is



where C = carbon dioxide, M = methane, and S = the solvent (with additives). We've assumed that none of the methane dissolves in the solvent and that none of the solvent is vaporized. All flows are in gmol/min.

With Frannie's superadditive, the phase equilibrium relationship becomes

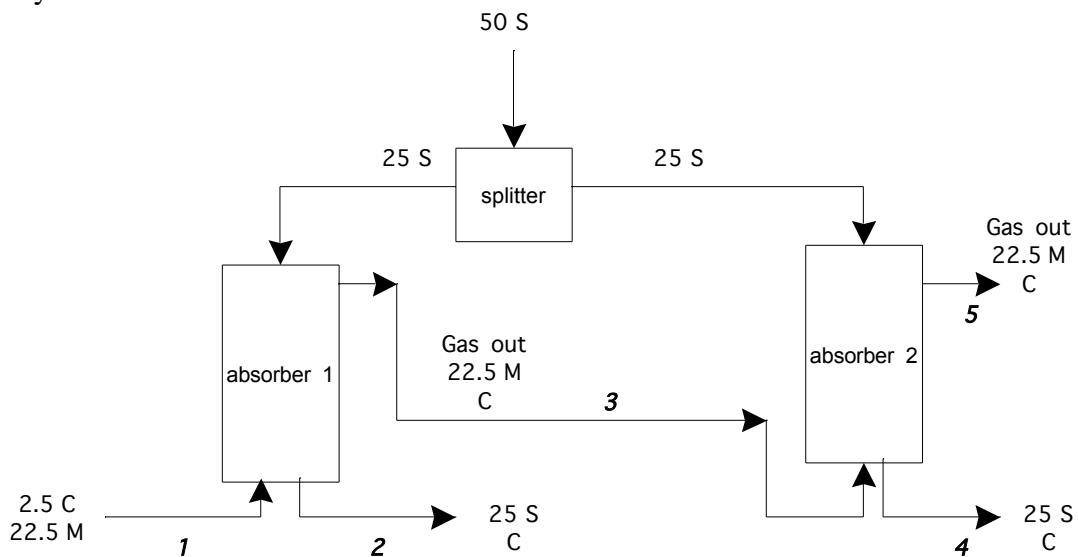
$$x_{C4} = 0.423y_{C1} = 0.423\left(\frac{2.5}{22.5 + 2.5}\right) = 0.0423 = \frac{\dot{n}_{C4}}{50 + \dot{n}_{C4}}$$

$$\dot{n}_{C4} = 2.208 \text{ gmol/min}$$

The % recovery is

$$\frac{2.208}{2.5} \times 100\% = 88.3\%$$

Zooey's idea is sketched below:



The exit liquid from absorber 1 (stream 2) is in equilibrium with the entering gas stream (stream 1)

$$x_{C2} = 0.385 y_{C1} = 0.385 \left(\frac{2.5}{2.5 + 22.5} \right) = 0.0385 = \frac{\dot{n}_{C2}}{\dot{n}_{C2} + 25}$$

$$\dot{n}_{C2} = 1.0 \text{ gmol/min}$$

By material balance we find that

$$\dot{n}_{C3} = 1.5 \text{ gmol/min}$$

The exit liquid from absorber 2 (stream 4) is in equilibrium with the entering gas stream (stream 3)

$$x_{C4} = 0.385 y_{C3} = 0.385 \left(\frac{1.5}{1.5 + 22.5} \right) = 0.0241 = \frac{\dot{n}_{C4}}{\dot{n}_{C4} + 25}$$

$$\dot{n}_{C4} = 0.616 \text{ gmol/min}$$

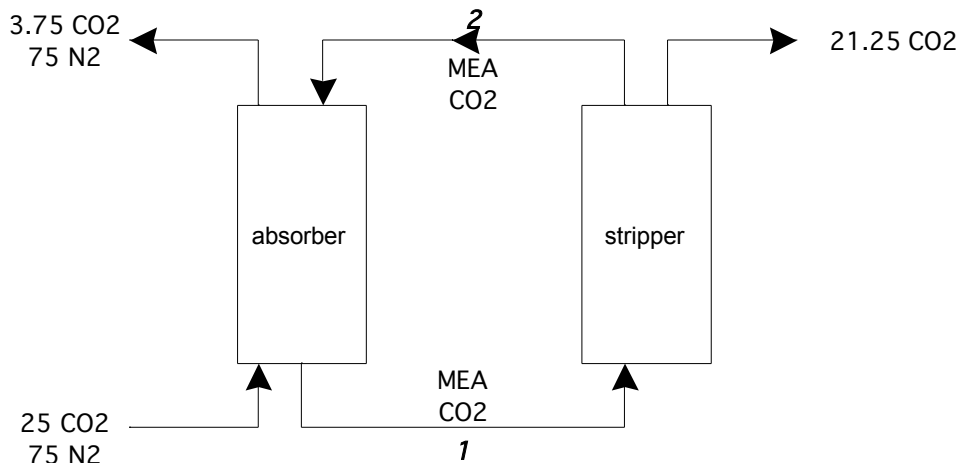
The total percent recovered from Zooey's idea is

$$\frac{1.0 + 0.616}{2.5} \times 100\% = 64.6\%$$

Frannie's idea is much better; Zooey's idea is actually worse than the base case!

P5.76

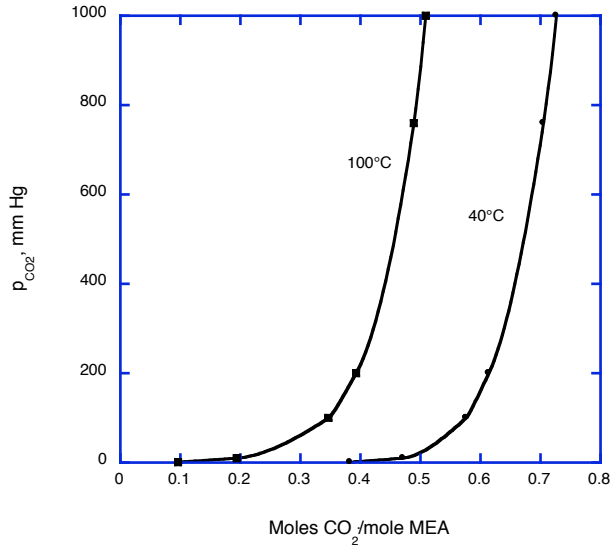
The proposed block flow diagram is shown, along with the flow rates (in kgmol/h) calculated from the specifications.



The absorber should be operated at highest allowable P – 20 atm - and lowest allowable T – 40°C since that's the data available. The gas leaving the absorber is in equilibrium with the liquid leaving the absorber (stream 1).

$$p_{CO_2} = y_{CO_2} P = \frac{3.75}{75 + 3.75} (20) (760/1) = 724 \text{ mm Hg}$$

The phase equilibrium data are plotted. The data are highly nonlinear, and linear interpolation to find the solubility corresponding to 724 mm Hg is dangerous – it is better to fit a nonlinear curve to the data (see App. A).



From this, we estimate that 724 mm Hg CO₂ is in equilibrium with 0.698 moles CO₂/mole MEA at the absorber conditions, or

$$\frac{\dot{n}_{CO_2,1}}{\dot{n}_{MEA,1}} = 0.698.$$

The stripper should be operated at the lowest possible pressure (1 atm) and the highest possible temperature (100°C). At these conditions,

$$p_{CO_2} = y_{CO_2}P = 760 \text{ mm Hg}$$

which is in equilibrium with stream 2. Reading from the graph:

$$\frac{\dot{n}_{CO_2,2}}{\dot{n}_{MEA,2}} = 0.489$$

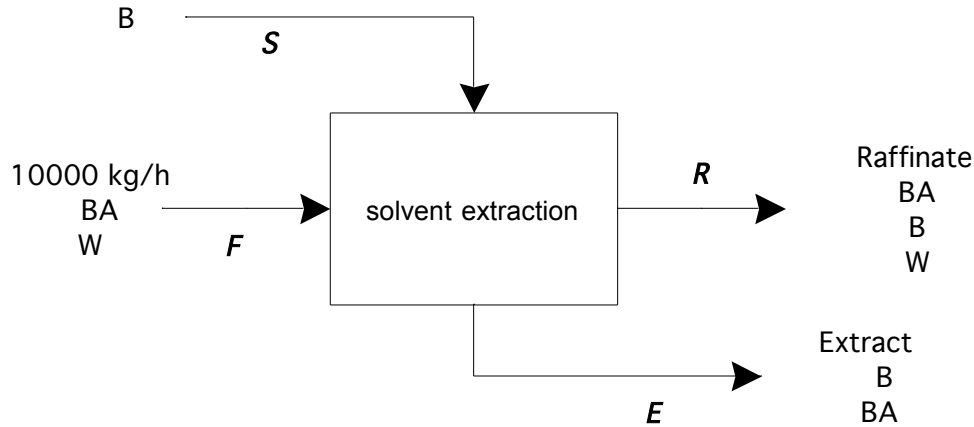
By material balance around the stripper,

$$21.25 = \dot{n}_{CO_2,1} - \dot{n}_{CO_2,2} = (0.698 - 0.489)\dot{n}_{MEA,2}$$

$$\dot{n}_{MEA,2} = 101.7 \text{ kgmol/h}$$

P5.77

The flow diagram is



with components labeled as B (benzene), W (water) and BA (benzoic acid), and streams labeled as feed F , solvent S , raffinate R and extract E .

From feed specifications,

$$\frac{\dot{m}_{BAF}}{\dot{m}_{WF}} = 0.02 \text{ and } \dot{m}_{WF} + \dot{m}_{BAF} = 10000$$

so

$$\dot{m}_{WF} = 9804 \text{ kg/h and } \dot{m}_{BAF} = 196 \text{ kg/h}$$

We know that all the water exits in the raffinate, therefore from a mass balance
 $\dot{m}_{WR} = \dot{m}_{WF} = 9804 \text{ kg/h}$

Benzoic acid concentrations in the raffinate and in the extract are related by the equilibrium distribution coefficient

$$K_D = 4 = \frac{\dot{m}_{BAE}/\dot{m}_{BE}}{\dot{m}_{BAR}/(\dot{m}_{WR} + \dot{m}_{BR})} = \frac{\dot{m}_{BAE}/\dot{m}_{BE}}{\dot{m}_{BAR}/(9804 + 0.07(9804))}$$

From material balances on benzoic acid and benzene

$$\dot{m}_{BAR} + \dot{m}_{BAE} = \dot{m}_{BAF} = 196 \text{ kg/h}$$

$$\dot{m}_{BR} + \dot{m}_{BE} = 0.07(9804) + \dot{m}_{BE} = \dot{m}_S$$

The net profit is

$$\text{\$} = \$1.35\dot{m}_{BAE} - \$0.03\dot{m}_S$$

To solve: we pick a value for the solvent flow rate \dot{m}_S , find

$\dot{m}_{BE} = \dot{m}_S - 0.07(9804) = \dot{m}_S - 686$, then combine material balance and phase equilibrium equation to find

$$\dot{m}_{BAE} = \frac{(4\dot{m}_{BE}/10490)196}{[1 + (4\dot{m}_{BE}/10490)]}$$

Finally, we solve for profit (per hour). Some calculations are tabulated:

\dot{m}_S	\dot{m}_{BE}	\dot{m}_{BAE}	Profit \$/h
1000	314	20.9	-1.73
1500	814	46.4	17.66
2000	1314	65.4	29.31
2500	1814	80.1	33.18
3000	2314	91.9	34.02
4000	3314	109.4	27.05
5000	4314	121.9	14.56
7500	6814	141.5	-33.94
10000	9314	152.9	-93.53

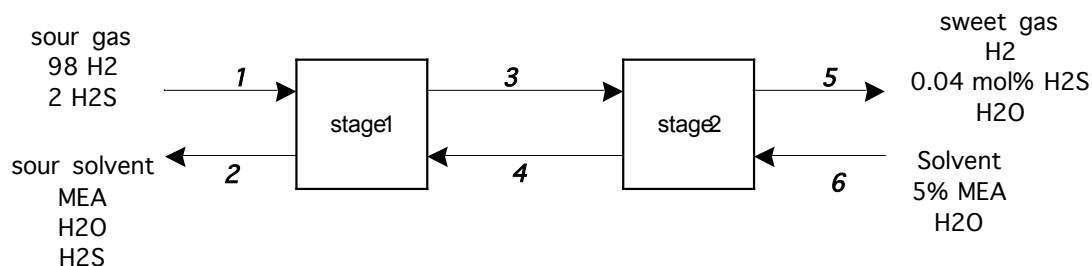
The most profit is around 2900 kg/h solvent flow rate. Greater solvent flow increases benzoic acid recovery, but the eventually the cost of the solvent outweighs the incremental value of the recovered benzoic acid.

P5.78

We'll use the sour gas composition listed on p. 452 and the MEA data given on p. 456. If there is some CO_2 in the sour gas, we would need to consider its solubility in MEA, which complicates this problem.) Some water will evaporate and leave in the sour gas stream. We'll assume that the hydrogen, as a nonpolar compound, has negligible solubility in the MEA solution. (A 15.3 wt% solution of MEA is a 5 mol% solution.) We'll also assume that none of the MEA evaporates, and that any small change in the MEA concentration in the liquid does not affect its solubility behavior. We'll use 40°C and 20 atm, as in the case study.

We'll use A for MEA, W for water, H for hydrogen, and S for hydrogen sulfide.

The flow diagram for the 2-stage countercurrent absorption unit is



The material balance equations are straightforward. We'll use 100 kgmol/h sour gas as the basis.

Stage 1

$$\begin{aligned}
 2 + \dot{n}_{S4} &= \dot{n}_{S2} + \dot{n}_{S3} && \text{(hydrogen sulfide)} \\
 98 &= \dot{n}_{H3} && \text{(hydrogen)} \\
 \dot{n}_{A4} &= \dot{n}_{A2} && \text{(MEA)} \\
 \dot{n}_{W4} &= \dot{n}_{W2} + \dot{n}_{W3} && \text{(water)}
 \end{aligned}$$

Stage 2

$$\begin{aligned}\dot{n}_{S3} &= \dot{n}_{S4} + \dot{n}_{S5} && \text{(hydrogen sulfide)} \\ \dot{n}_{H3} &= \dot{n}_{H5} && \text{(hydrogen)} \\ \dot{n}_{A6} &= \dot{n}_{A4} && \text{(MEA)} \\ \dot{n}_{W3} + \dot{n}_{W6} &= \dot{n}_{W4} + \dot{n}_{W5} && \text{(water)}\end{aligned}$$

We have a few stream composition specifications

$$\begin{aligned}\frac{\dot{n}_{S5}}{\dot{n}_{S5} + \dot{n}_{H5} + \dot{n}_{W5}} &= 0.0004 \\ \frac{\dot{n}_{A6}}{\dot{n}_{A6} + \dot{n}_{W6}} &= 0.05\end{aligned}$$

Finally, we need to consider phase equilibrium relationships. There are 2 components that partition between the 2 phases: hydrogen sulfide, and water. Streams 2 (liquid) and 3 (gas) are in equilibrium with each other, as are streams 4 (liquid) and 5 (gas). Thus, we will write (2 x 2) or 6 equilibrium relationships.

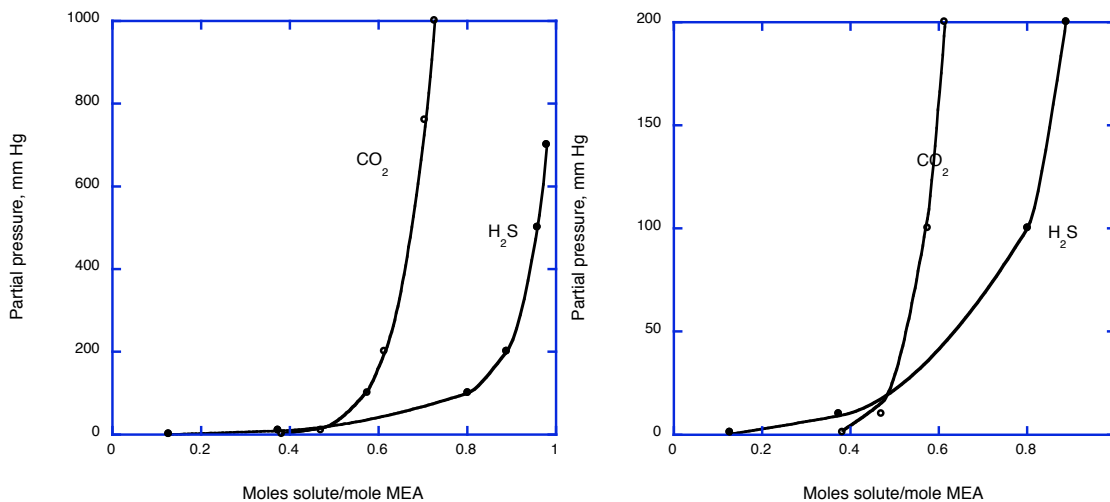
For water, we use Raoult's law (with the saturation pressure calculated from Antoine's equation to be 0.0728 atm at 40°C and P = 20 atm).

$$\begin{aligned}y_{W3} &= \frac{x_{W2}P_W^{sat}}{P} \quad \text{or} \quad \frac{\dot{n}_{W3}}{\dot{n}_{S3} + \dot{n}_{H3} + \dot{n}_{W3}} = \frac{0.0036\dot{n}_{W2}}{\dot{n}_{W2} + \dot{n}_{A2} + \dot{n}_{S2}} \\ y_{W5} &= \frac{x_{W4}P_W^{sat}}{P} \quad \text{or} \quad \frac{\dot{n}_{W5}}{\dot{n}_{S5} + \dot{n}_{H5} + \dot{n}_{W5}} = \frac{0.0036\dot{n}_{W4}}{\dot{n}_{W4} + \dot{n}_{A4} + \dot{n}_{S4}}\end{aligned}$$

For H₂S dissolved in 5 mol% MEA, we have phase equilibrium data but no simple equation. We have 2 choices: one is to guess a partial pressure, find the solubility from the data, and see if the material balance equations are satisfied. If not, we make a new guess and repeat. An alternative is to fit an empirical equation to the data and use that fitted equation. The equation is simply a mathematical tool for correlating data and does not describe any underlying theory, nor should it be used outside of the range of the data. Let's plot the data, and see if we can find a reasonable equation. (We did this in Kaleidagraph, see App. A for information on this graphing software. Just for fun we did this for both H₂S and CO₂.) After a few false starts we came up with 2 empirical equations:

$$\begin{aligned}P_{H_2S} &= y_{H_2S}P = 804(X_{H_2S})^{20} + 176(X_{H_2S})^3 \\ P_{CO_2} &= y_{CO_2}P = 21350(X_{CO_2})^{9.6}\end{aligned}$$

where X is the ratio (moles solute/mole MEA). The data along with the fitted equations are plotted; note that we must examine the fit closely over the entire range of the data, which is why we show in separate figures the low and high partial pressures.



Now we can describe the phase equilibrium for our particular case using these empirical equations

$$\frac{\dot{n}_{S3}}{\dot{n}_{S3} + \dot{n}_{H3} + \dot{n}_{W3}}(15200) = 804 \left(\frac{\dot{n}_{S2}}{\dot{n}_{A2}} \right)^{20} + 176 \left(\frac{\dot{n}_{S2}}{\dot{n}_{A2}} \right)^3$$

$$\frac{\dot{n}_{S5}}{\dot{n}_{S5} + \dot{n}_{H5} + \dot{n}_{W5}}(15200) = 804 \left(\frac{\dot{n}_{S4}}{\dot{n}_{A4}} \right)^{20} + 176 \left(\frac{\dot{n}_{S4}}{\dot{n}_{A4}} \right)^3$$

Now we are finally ready to proceed. (It wouldn't be a bad idea to check a DOF analysis first, just to make sure the problem is solvable!) Solution requires the use of an equation-solving program like EES, or a spreadsheet like EXCEL with a SOLVER.

From the solution, we find that the MEA required drops to only 2.35 kgmol/h! (Total solution flow is 47 kgmol/h).

The flows are:

Gas from stage 1: 0.80 kgmol/h H₂S, 0.3 kgmol/h H₂O, 98 kgmol/h H₂

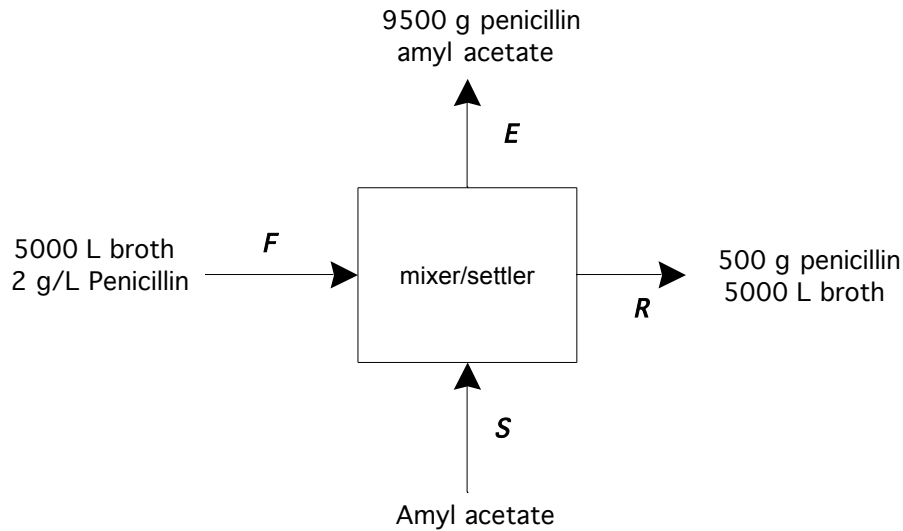
Gas from stage 2: 0.04 kgmol/h H₂S, 0.3 kgmol/h H₂O, 98 kgmol/h H₂

Liquid from stage 2: 0.76 kgmol/h H₂S, 2.35 kgmol/h MEA, 44.6 kgmol/h H₂O

Liquid from stage 1: 1.96 kgmol/h H₂S, 2.35 kgmol/h MEA, 44.3 kgmol/h H₂O

P5.79

(a) Given 95% recovery of penicillin in the extract, the flow diagram for a single-stage extraction is



where we indicate streams as feed F , solvent S , extract E and raffinate R . We also assume that the quantity of penicillin removed is small enough that the total volume of broth doesn't change. The concentration of penicillin P in the raffinate x is

$$x = \frac{500 \text{ g}}{5000 \text{ L}} = 0.1 \text{ g/L}$$

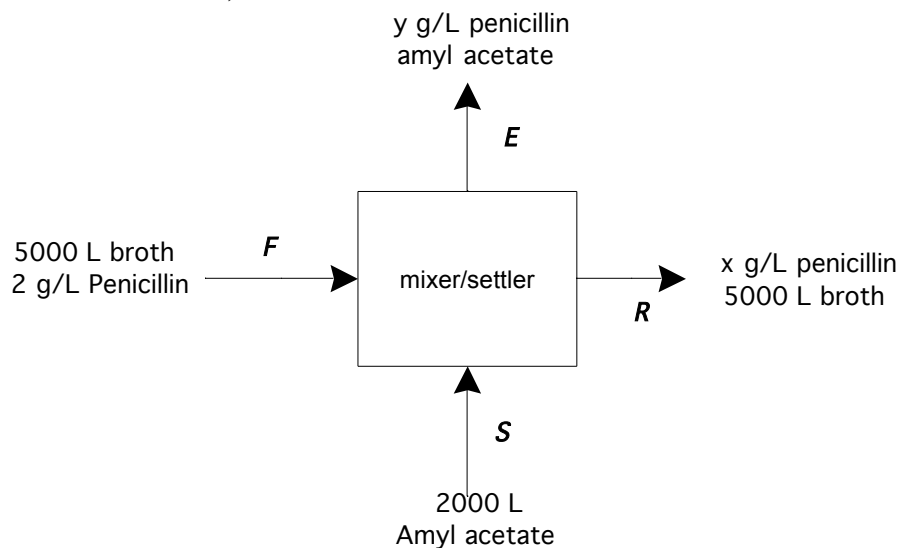
This is in equilibrium with the penicillin concentration y in the extract phase;

$$y = K_D x = 9(0.1) = 0.9 \text{ g/L}$$

Since there are a total of 9500 g penicillin in the extract,

$$\frac{9500 \text{ g}}{0.9 \text{ g/L}} = 10,555 \text{ L solvent required}$$

(b) With a 7000 Liter tank and 5000 L broth, we can add at most 2000 L solvent each step. In the first extraction,



The material balance equation for penicillin is

$$5000x + 2000y = 2(5000) = 10000 \text{ g}$$

This is coupled to the phase equilibrium equation;

$$y = 9x$$

We solve to find $x = 0.435 \text{ g/L}$, and $y = 3.91 \text{ g/L}$. The percent penicillin recovery in the solvent phase is

$$\frac{3.91(2000)}{10000} \times 100\% = 78.2\%$$

which is below the target of 95% recovery.

If we remove the penicillin-loaded solvent, and then add back 2000 L fresh solvent, we can recover more penicillin. There is less penicillin in the system, and the material balance equation is

$$5000x + 2000y = 0.435(5000) = 2175 \text{ g}$$

The phase equilibrium equation remains

$$y = 9x$$

We solve to find $x = 0.0948 \text{ g/L}$, and $y = 0.853 \text{ g/L}$. The percent penicillin recovery in the solvent phase in this step is

$$\frac{0.853(2000)}{2175} \times 100\% = 78\%$$

but, the total penicillin recovered in the two steps is

$$\frac{3.91(2000) + 0.853(2000)}{10000} \times 100\% = 95.3\%$$

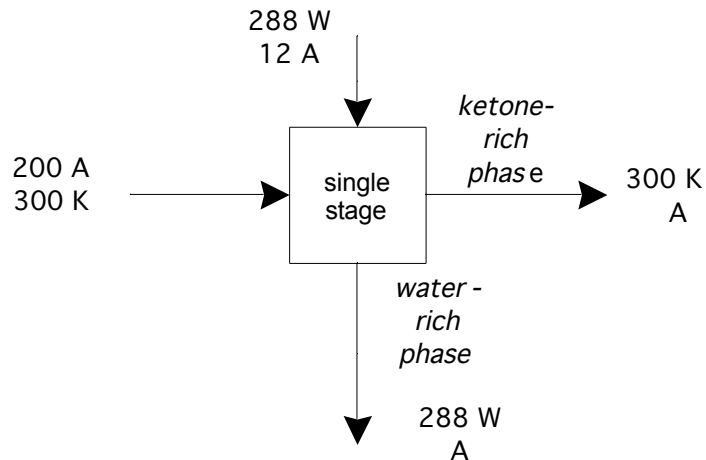
In two steps, we meet our performance objective, and we use only 4000 L total solvent (vs. 10,555 L for a single-step extraction). Furthermore, the penicillin concentration in the solvent is higher in the two-step process than in the single-step process, making further purification less costly.

It makes no sense at all to drain the broth and leave the solvent in the tank – the broth after the first step of equilibration still has enough penicillin in it to warrant a second contact with fresh solvent.

P5.80

(a)

For single-stage contacting, using the flows and compositions given, with all flows in kg/h:



The material balance plus phase equilibrium relationship allows us to calculate the quantity of alcohol A in each of the phases:

$$200 + 12 = \dot{m}_{AI} + \dot{m}_{AII}$$

$$K_D = 4 = \frac{x_{AII}}{x_{AI}} = \frac{\dot{m}_{AII} / (\dot{m}_{AII} + 288)}{\dot{m}_{AI} / (\dot{m}_{AI} + 300)}$$

The solution is

$$\dot{m}_{AI} = 32 \text{ kg/h}$$

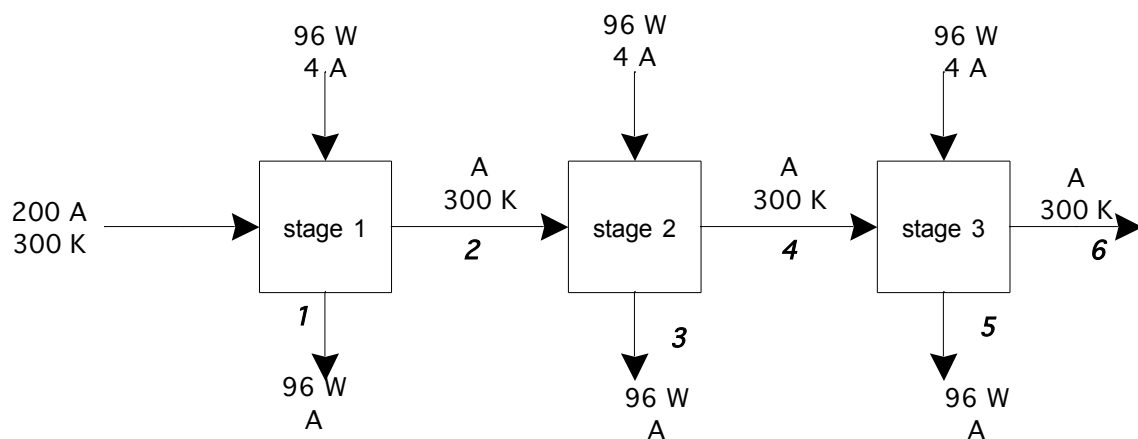
$$\dot{m}_{AII} = 180 \text{ kg/h}$$

The fractional removal of alcohol from the ketone-rich phase is

$$f_{RAII} = \frac{200 - 32}{200} = 0.84$$

(b)

Crosscurrent with 3 stages, with equal distribution of wash water among the 3 stages:



We write 1 material balance equation and 1 phase relationship for each stage:

Stage 1:

$$200 + 4 = \dot{m}_{A2} + \dot{m}_{A1}$$

$$K_D = 4 = \frac{x_{AII}}{x_{AI}} = \frac{\dot{m}_{A1}/(\dot{m}_{A1} + 96)}{\dot{m}_{A2}/(\dot{m}_{A2} + 300)}$$

Stage 2:

$$\dot{m}_{A2} + 4 = \dot{m}_{A4} + \dot{m}_{A3}$$

$$K_D = 4 = \frac{x_{AII}}{x_{AI}} = \frac{\dot{m}_{A3}/(\dot{m}_{A3} + 96)}{\dot{m}_{A4}/(\dot{m}_{A4} + 300)}$$

Stage 3:

$$\dot{m}_{A4} + 4 = \dot{m}_{A6} + \dot{m}_{A5}$$

$$K_D = 4 = \frac{x_{AII}}{x_{AI}} = \frac{\dot{m}_{A5}/(\dot{m}_{A5} + 96)}{\dot{m}_{A6}/(\dot{m}_{A6} + 300)}$$

We proceed with stagewise solution

$$\dot{m}_{A1} = 150$$

$$\dot{m}_{A2} = 54$$

$$\dot{m}_{A3} = 36$$

$$\dot{m}_{A4} = 22$$

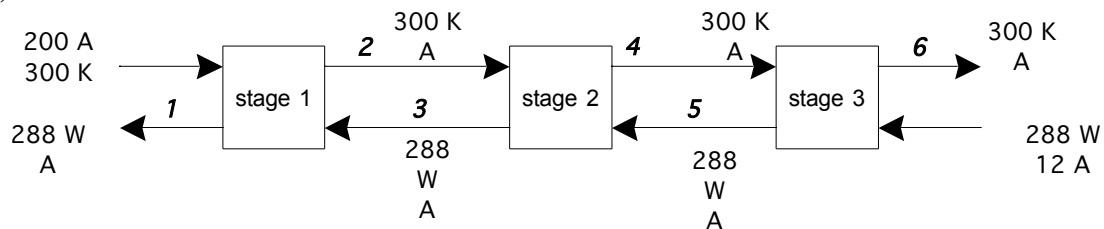
$$\dot{m}_{A5} = 15.3$$

$$\dot{m}_{A6} = 10.7$$

The fractional removal of alcohol from the ketone-rich phase is

$$f_{RAII} = \frac{200 - 10.7}{200} = 0.95$$

(c)



Again we write material balance equations and phase equilibrium equations:

We write one material balance equation and one phase relationship for each stage:

Stage 1:

$$200 + \dot{m}_{A3} = \dot{m}_{A2} + \dot{m}_{A1}$$

$$K_D = 4 = \frac{x_{AII}}{x_{AI}} = \frac{\dot{m}_{A1}/(\dot{m}_{A1} + 288)}{\dot{m}_{A2}/(\dot{m}_{A2} + 300)}$$

Stage 2:

$$\dot{m}_{A2} + \dot{m}_{A5} = \dot{m}_{A4} + \dot{m}_{A3}$$

$$K_D = 4 = \frac{x_{AII}}{x_{AI}} = \frac{\dot{m}_{A3}/(\dot{m}_{A3} + 288)}{\dot{m}_{A4}/(\dot{m}_{A4} + 300)}$$

Stage 3:

$$\dot{m}_{A4} + 12 = \dot{m}_{A6} + \dot{m}_{A5}$$

$$K_D = 4 = \frac{x_{AII}}{x_{AI}} = \frac{\dot{m}_{A5}/(\dot{m}_{A5} + 96)}{\dot{m}_{A6}/(\dot{m}_{A6} + 300)}$$

We proceed with simultaneous solution:

$$\dot{m}_{A1} = 207.6$$

$$\dot{m}_{A2} = 35$$

$$\dot{m}_{A3} = 42.7$$

$$\dot{m}_{A4} = 10$$

$$\dot{m}_{A5} = 17.6$$

$$\dot{m}_{A6} = 4.4$$

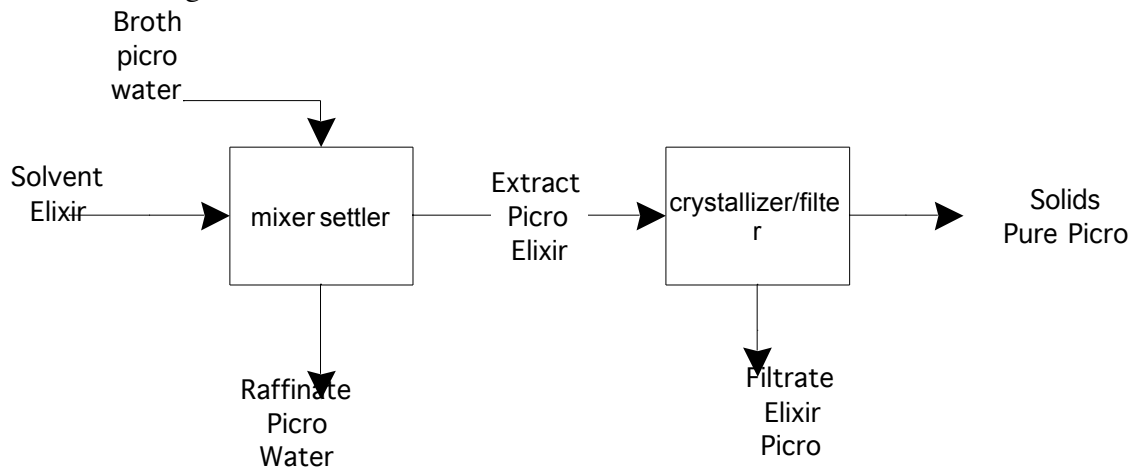
The fractional removal of alcohol from the ketone-rich phase is

$$f_{RAII} = \frac{200 - 4.4}{200} = 0.978$$

Countercurrent staging gives the best removal.

P5.81

Ima's flow diagram must look like this:



There are 3 components: Picro P, water (and other water-soluble components) W, and Elixir E.

(a) Start with a balance on the mixer-settler. Assuming no change in volume of the broth due to the loss of Picro, the Picro mass balance is

$$0.001053(10000) = 0.00001053(10000) - \dot{m}_{P,ex}$$

$$\dot{m}_{P,ex} = 10.425 \text{ g/day}$$

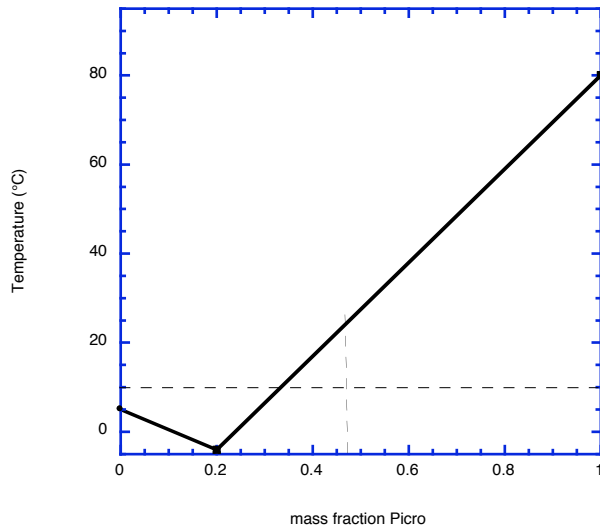
where “ex” indicates the extract stream. From the distribution coefficient

$$K_D = 45000 = \frac{\dot{m}_{P,ex} / \dot{m}_{ex}}{\dot{m}_{P,raff} / \dot{m}_{raff}} = \frac{10.425 / \dot{m}_{ex}}{0.00001053}$$

$$\dot{m}_{ex} = 22 \text{ g/day}$$

which is the total flow of both Picro and Elixir, Therefore, the Elixir flow rate must be 11.575 g/day.

(b) Now we need to estimate the liquid-solid phase equilibrium graph. We plot the two pure melting point temperatures and the eutectic temperature, and connect the dots with smooth curves. The dashed lines indicate the temperature of the crystallization unit and the mass fraction Picro of the feed to the crystallizer, (10.425/22 or 0.474). Operation at 10°C produces a pure Picro solid plus a saturated solution of about 32 wt% Picro.



Material balances around the crystallizer are:

$$10.425 = \dot{m}_{crystals} + 0.32\dot{m}_{filtrate}$$

$$11.575 = 0.68\dot{m}_{filtrate}$$

which we readily solve:

$$\dot{m}_{filtrate} = 17 \text{ g/day}$$

$$\dot{m}_{crystals} = 5 \text{ g/day}$$

The overall fractional recovery of Picro as crystals from the fermentation broth is

$$f_{RP} = \frac{5}{10.53} = 0.475$$

(c) The mixer-settler unit is very effective at extracting Picro, recovering 99% of the material in the broth. There is not much opportunity for improving this step. Most of the losses appear in the filtrate. Purchasing a new crystallizer that could operate at lower temperatures would improve this a bit, but we are limited to a minimum wt% of >20% Picro in the filtrate. Better would be an alternative method to partially remove some of the Elixir from the filtrate (perhaps by evaporation?) and then recycle the concentrated filtrate back to the crystallizer.