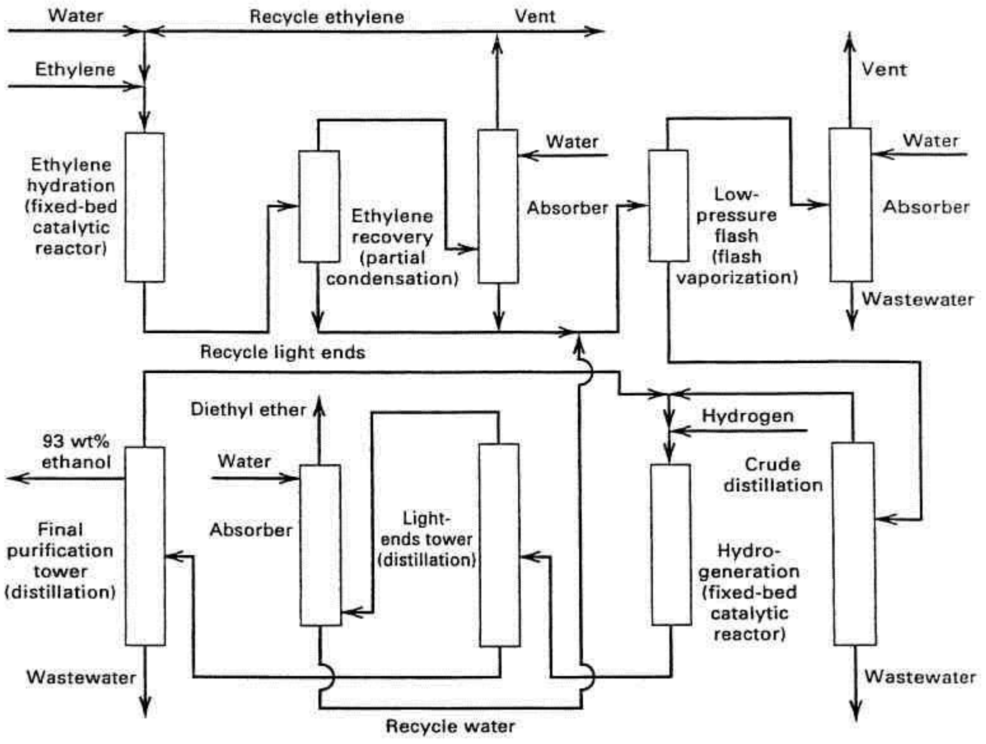
Exercise 1.1

Subject: Separation operations in an ethanol process.

Given: Flow sheet for the process.

Find: Operation in each block of the process

Analysis: The flow sheet is as follows:



Starting from the left side of the top row, number the equipment blocks 1-5. On the next row, number them from right to left as 6-10.

1. The feed to the reactor contains ethylene, propylene, and water. The very incomplete reaction effluent of gas contains, in addition:ethyl alcohol, diethyl ether, acetaldehyde, and isopropyl alcohol.
2. Most of the chemicals, except most of the ethylene, are condensed and sent to item 4. The remaining gas is sent to 3.
3. The ethylene is recovered from the small quantity of other chemicals in the absorber. Most of the ethylene is recycled to 1. The water and other chemicals are sent to 4.
4. Remaining ethylene is flashed off and sent to 5. The liquid contains most of the hydrocarbons and is sent to 6.

Exercise 1.1 (continued)

5. The small quantity of ethanol plus other chemicals is absorbed from the ethylene by water. The exit gas is vented. The liquid is wastewater that will have to be treated elsewhere.
6. The liquid from 4 is distilled to separate water from ethanol and other chemicals that are mostly diethyl ether and acetaldehyde. The bottoms is wastewater. The distillate is the organic chemicals that are sent to 7.
7. This unit is a fixed-bed catalytic reactor to convert acetaldehyde to ethanol. The reactor effluent is sent to 8.
8. Diethyl ether and small amounts of the ethanol and other chemicals are removed as vapor by distillation and sent to 9. The bottoms containing most of the ethanol is sent to 10.
9. The diethyl ether in the vapor from 8 is recovered by absorbing the other chemicals with water, which is recycled to 4.
10. The crude ethanol from 8 is distilled to obtain the near-azeotrope of ethanol and water. The bottoms is wastewater.

Exercise 1.2

Subject: Mixing vs. separation

Given: Thermodynamic principles.

Find: Explanation for why mixing and separation are different.

Analysis: Mixing is a natural, spontaneous process. It may take time, but concentrations of components in a single fluid phase will tend to become uniform, with an increase in entropy. By the second law of thermodynamics, a natural process tends to randomness. The separation of a mixture does not occur naturally or spontaneously. Energy is required to separate the different molecular species.

Exercise 1.3

Subject: Separation of a mixture requires a transfer of energy to it or the degradation of its energy.

Given: The first and second laws of thermodynamics.

Find: Explain why the separation of a mixture requires energy.

Analysis: As an example, consider the isothermal minimum (reversible) work of separation of an ideal binary gas mixture. Therefore, the change in enthalpy is zero. However, there is a change in entropy, determined as follows. From a chemical engineering thermodynamics textbook or Table 2.11, Eq. (4):

$$\begin{aligned} W_{\min} &= \sum_{out} n(h - T_0 s) - \sum_{in} n(h - T_0 s) \\ &= RT_0 \left\{ \sum_{out} n_k \sum y_{i,k} \ln\left(y_{i,k}\right) - \sum_{in} n_j \sum y_{i,j} \ln\left(y_{i,j}\right) \right\} \end{aligned}$$

It can be shown that regardless of values of y between 0 and 1, that $W_{\min}$ is always positive. This minimum work is independent of the process.

Exercise 1.4

Subject : Use of an ESA or an MSA to make a separations.

Given: Differences between an ESA and an MSA.

Find: State the advantages and disadvantages of ESA and MSA.

Analysis: With an MSA, an additional separator is needed to recover the MSA. Also, some MSA will be lost, necessitating the need for MSA makeup. If the MSA is incompletely recovered, a small amount of contamination may result. The use of an MSA can make possible a separation that cannot be carried out with an ESA. An ESA separation is easier to design.

Exercise 1.5

Subject : Distillation versus liquid-liquid extraction..

Find: State differences between the two separation operations.

Analysis:

1. Distillation involves both liquid and vapor phases. Extraction involves two liquid phases
2. Distillation uses an ESA. Extraction uses an MSA.
3. Distillation may occur over a wide range of temperature. Extraction usually occurs over a narrow range of temperature.
4. Mass transfer in distillation is relatively rapid. Mass transfer in extraction is relatively slow.
5. Distillation often uses more many stages. Extraction usually involves just several stages.
6. Distillation seldom requires mechanical agitation. Extraction is best carried out with mechanical agitation.

Exercise 1.6

Subject: Osmotic pressure for the separation of water from sea water by reverse osmosis with a membrane.

Given: Sea water containing 0.035 g of salt/cm^3 of sea water on one side of a membrane
Molecular weight of the salt = 31.5
Temperature = 298 K
Pure water on the other side of a membrane

Find: Minimum required pressure difference in kPa across the membrane

Analysis: The minimum pressure difference across the membrane is equal to the osmotic pressure of the sea water, since the osmotic pressure of pure water on the other side is zero. The equation given for osmotic pressure is $\pi = RTc/M$.

R = 8.314 kPa-m^3/kmol-K
T = 298 K
c = 0.035 g/cm^3 = 35 kg/m^3
M = 31.5 kg/kmol

Minimum pressure difference across a membrane =

$$\pi = \frac{(8.314)(298)(35)}{31.5} = 2,750 \text{ kPa}$$

Exercise 1.7

Subject: Basic separation techniques.

Given: A list of 10 separation operations.

Find: The basic separation technique for each of the 10.

Analysis:

1. Phase creation: distillation, flash vaporization

2. Phase addition: absorption, adsorption, extraction, stripping

3. Barrier: dialysis, gas permeation, pervaporation, reverse osmosis

Exercise 1.8

Subject: Methods for removing organic pollutants from wastewater.

Given: Available industrial processes:

(1) adsorption
(2) distillation
(3) liquid-liquid extraction
(4) membrane separation
(5) stripping with air
(6) stripping with steam

Find: Advantages and disadvantages of each process.

Analysis:

Some advantages and disadvantages are given in the following table:

Method	**Advantages**	**Disadvantages**
Adsorption	Adsorbents are available.	Difficult to recover pollutant. Best to incinerate it.
Distillation	May be practical if pollutant is more volatile.	Impractical is water is more volatile.
L-L extraction	Solvent are available.	Water will be contaminated with solvent.
Membrane	May be practical if a membrane can be found that is highly selective for pollutant.	May need a large membrane area if water is the permeate.
Air stripping	May be practical if pollutant is more volatile.	Danger of producing a flammable gas mixture.
Steam stripping	May be practical if pollutant is more volatile.	Must be able to selectively condense pollutant from overhead.

With adsorption, can incinerate pollutant, but with a loss of adsorbent.
With distillation, may be able to obtain a pollutant product.
With L-L extraction, will have to separate pollutant from solvent.
With a membrane, may be able to obtain a pollutant product.
With air stripping, may be able to incinerate pollutant.
With steam stripping may be able to obtain a pollutant product.

Exercise 1.9

Subject: Removal of VOCs from a waste gas stream.

Given: Waste gas containing VOCs that must be removed by any of the following methods:

(1) absorption
(2) adsorption
(3) condensation
(4) freezing
(5) membrane separation

Find: Advantages and disadvantages of each method.

Analysis:

Some advantages and disadvantages are given in the following table:

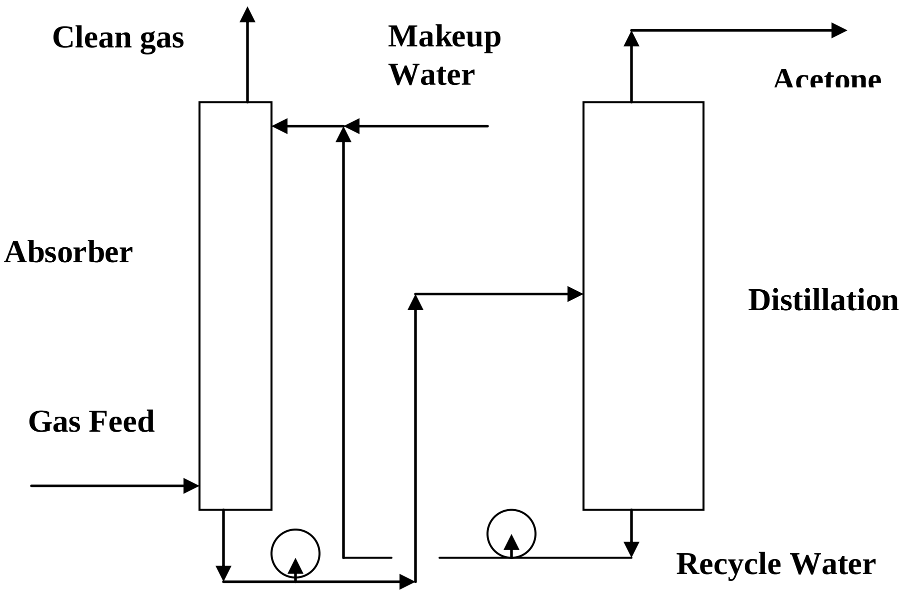
Method	**Advantages**	**Disadvantages**
Absorption	Good absorbents probably exist.	Absorbent may stripped into the waste gas.
Adsorption	Good adsorbents probably exist.	May have to incinerate the spent adsorbent.
Condensation	May be able to recover the VOC as a product.	May require high pressure and/or low temperature.
Freezing	May be able to recover the VOC as a product.	May require a low temperature.
Membrane	May be able to recover the VOC as a product.	May be difficult to obtain high selectivity. May require a very high pressure.

With absorption, may be able to distil the VOC from the absorbent.
With adsorption, may be able to incinerate the VOC or recover it.
With condensation, can recover the VOC as a product.
With freezing, can recover the VOC as a product.
With a membrane, can recover the VOC as a product.

The process shown on the following page shows a process for recovering acetone from air. In the first step, the acetone is absorbed with water. Although water is far from being the most ideal solvent because of the high volatility of acetone in water, the air will not be contaminated with an organic solvent. The acetone-water mixture is then easily separated by distillation, with recycle of the water.

Exercise 1.9 (continued)

One possible process-flow diagram:



Exercise 1.10

Subject: Separation of air into nitrogen and oxygen.

Given: Air to be separated.

Find: Three methods for achieving the separation.

Analysis: Three methods are used commercially for separating air into oxygen and nitrogen:

1. Gas permeation mainly for low capacities
2. Pressure-swing gas adsorption for moderate capacities.
3. Low-temperature distillation for high capacities.

Exercise 1.11

Subject: Sequence of three distillation columns in Fig. 1.10 for separating light hydrocarbons.

Given: Feed to column C3 is stream 5 in Table 1.5. Alter the separation to produce a distillate containing 95 mol% iC_4 at a recovery of 96%.

Find: (a) Component flow rates in the distillate and bottoms from column C3.
(b) Percent purity of nC_4 in the bottoms.
(c) Percent recovery of iC_4, for 95 mol% iC_4 in the distillate, that will maximize the percent purity of nC_4 in the bottoms.

Assumptions: Because of the relatively sharp separation in column C3 between iC_4 and nC_4, assume that all propane in the feed appears in the distillate and all C_5s appear in the bottoms.

Analysis: (a) Isobutane to the distillate = (0.96)(171.1) = 164.3 lbmol/h
Total distillate rate = 164.3/0.95 = 172.9 lbmol/h
Normal butane to the distillate = 172.9 - 2.2 - 164.3 = 6.4

Material balance around column C3, in lbmol/h:

Component	Feed	Distillate	Bottoms
Propane	2.2	2.2	0.0
Isobutane	171.1	164.3	6.8
Normal butane	226.6	6.4	220.2
Isopentane	28.1	0.0	28.1
Normal pentane	17.5	0.0	17.5
Total	445.5	172.9	272.6

(b) % Purity of nC_4 in bottoms = (220.2/272.6) x 100% = 80.8%

(c) Let x = lbmol/h of nC_4 in the distillate
y = lbmol/h of iC_4 in the distillate
P = mole fraction purity of nC_4 in the bottoms

$$P = \frac{226.6 - x}{(171.1 - y) + (226.6 - x) + 28.1 + 17.5} = \frac{226.6 - x}{443.3 - y - x} \qquad (1)$$

$$\text{Fractional purity of } iC_4 \text{ in the distillate } = \frac{y}{2.2 + y + x} = 0.95 \qquad (2)$$

Combining (1) and (2) to eliminate x, and optimization of P with respect to y gives:
P = 0.828 or 82.8 mol% nC_4 in the bottoms, x = 6.8 lbmol/h, y = 171.1 lbmol/h
Therefore, 100% recovery of iC_4 in the distillate maximizes the purity of nC_4 in the bottoms.

Exercise 1.12

Subject: Sequence of two distillation columns, C1- C2, for the separation of alcohols.

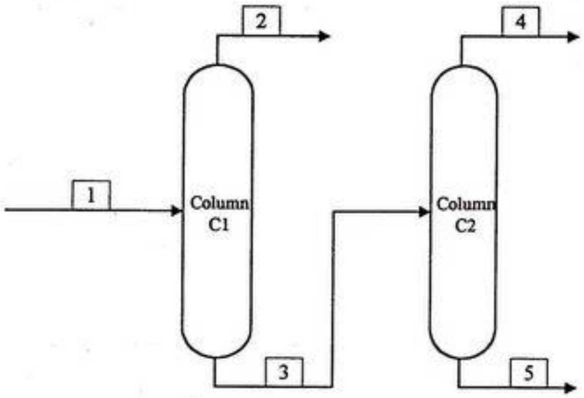
Given: 500 kmol/h feed of 40% methanol (M), 35% ethanol (E), 15% isopropanol (IP), and 10% normal propanol (NP), all in mol%. Distillate from column C1 is 98 mol% M, with a 96% recovery. Distillate from column C2 is 92 mol% E, with a recovery of 95% based on the feed to column C1.

Find: (a) Component flow rates in the feed, distillates and bottoms.
(b) Mol% purity of combined IP and NP in the bottoms from column C2.
(c) Maximum achievable purity of E in the distillate from column C2 for 95% recovery of E from the feed to column C1.
(d) Maximum recovery of E from the feed to column C1 for a 92 mol% purity of E in the distillate from column C2.

Assumptions: Because of the sharp separation in column C1, neglect the presence of propanols in the distillate from column C1. Neglect the presence of M in the bottoms from column C2. The distillate from C2 does not contain normal propanol.

Analysis: (a) M in distillate from C1 = (0.96)(500)(0.40) = 192 kmol/h
Total distillate from C1 = 192/0.98 = 195.92 kmol/h
E in distillate from C1 = 195.92 - 192 = 3.92 kmol/h
E in feed to C2 = (500)(0.35) - 3.92 = 171.08 kmol/h
M in feed to C2 = M in distillate from C2 = (500)(0.40) - 192 = 8 kmol/h
E in distillate from C2 = (500)(0.35)(0.95) = 166.25 kmol/h
Total distillate from C2 = 166.25/0.92 = 180.71 kmol/h
IP in distillate from C2 = 180.71 - 166.25 - 8 = 6.46 kmol/h

Block flow diagram:



Exercise 1.12 (Continued)

Analysis: (a) continued

Material balance table (all flow rates in kmol/h):

Component	Stream 1	2	3	4	5
M	200	192.00	8.00	8.00	0.00
E	175	3.92	171.08	166.25	4.83
IP	75	0.00	75.00	6.46	68.54
NP	50	0.00	50.00	0.00	50.00
Total	500	195.92	304.08	180.71	123.37

The assumption of negligible NP in stream 4 is questionable and should be corrected when designing the column.

(b) Mol% purity of (IP + NP) in bottoms of C2 = (68.54 + 50.00)/123.37 or 96.08%

(c) If the overall recovery of E in the distillate from C2 is fixed at 95%, the maximum purity of E in that distillate occurs when no propanols appear in that distillate. Then,

mol% purity of E = 100% x 166.25/(166.25 + 8.0) = 95.41%

(d) The maximum recovery of E in the distillate from C2 occurs when E does not appear in the bottoms from C2. Thus, that maximum is 100% x (171.08/175) = 97.76%

Exercise 1.13

Subject: Pervaporation for the partial separation of ethanol and benzene

Given: 8,000 kg/h of 23 wt% ethanol and 77 wt% benzene. Polymer membrane is selective for ethanol. Permeate is 60 wt% ethanol. Retentate is 90 wt% benzene.

Find: (a) and (b) Component flow rates in feed, permeate, and retentate on a diagram.
(c) Method to further separate the permeate.

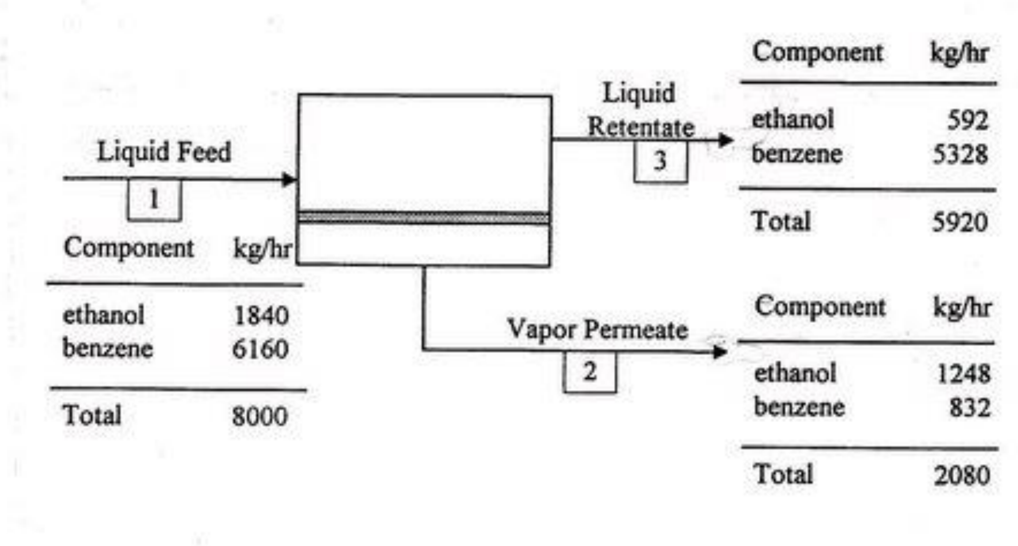
Analysis: (a) and (b) Let: P = permeate flow rate
R = retentate flow rate

Total material balance: $8{,}000 = P + R$ (1)

Ethanol material balance: $8{,}000(0.23) = (0.60)\,P + (0.10)\,R$ (2)

Solving (1) and (2) simultaneously, P = 2,080 kg/h and R = 5,920 kg/h

The resulting material balance and flow diagram is:



(c) Gas adsorption, gas permeation, or distillation to obtain ethanol and the azeotrope, which can be recycled.

Exercise 1.14

Subject: Creation of a flow sheet and material balance for the separation of acetone from nitrogen.

Given: Feed compositions and column splits.

Find: Material balance

Assumptions: Nitrogen is not soluble in MIBK.

Analysis: A typical flow diagram for an absorber followed by distillation to separate the absorbent from the acetone is shown in Figure 6.16c. However, in this exercise, the absorbent is not recycled. In practice it would be.

The material balance in kmol/h for the process is as follows where the stream numbers correspond to the following streams:
1 – gas feed to absorber
2 – absorbent feed to absorber
3 – gas leaving absorber
4 – liquid bottoms from absorber to distillation
5 – distillate from distillation
6 – bottoms from distillation

Steam	**2**	**3**	**1**	**4**	**5**	**6**
Nitrogen	0	100	100	0	0	0
MIBK	500	10	0	490	17.3	472.7
Acetone	0	45	900	855	850.2	4.8
Total	500	155	1000	1345	867.5	477.5

Exercise 1.15

Subject: Separation of hydrogen from light gases by gas permeation with hollow fibers.

Given: Feed gas of 42.4 kmol/h of H_2, 7.0 kmol/h of CH_4, and 0.5 kmol/h of N_2 at 40°C and 16.7 MPa. Retentate exits at 16.2 kPa and permeate exits at 4.56 kPa. Gas heat capacity ratio = $\gamma = 1.4$.

Assumptions: Membrane is not permeable to nitrogen. Reversible gas expansion with no heat transfer between the retentate and permeate. Separation index is based on mole fractions.

Find: (a) Component flows in the retentate and permeate if the mole ratio of methane to hydrogen in the permeate is 0.0117 and the split fraction (recovery), SF, for hydrogen from the feed to the permeate is 0.6038.

(b) Percent purity of hydrogen in the permeate..

(c) Process flow diagram with complete material balance

Analysis: (a) and (c)

Hydrogen in permeate = (0.6038)(42.4) = 25.6 kmol/h

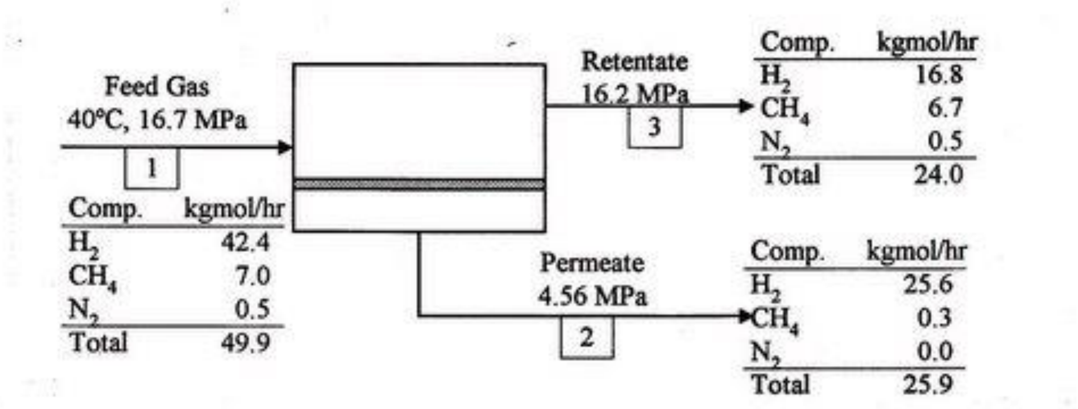
Hydrogen in retentate = 42.4 - 25.6 = 16.8 kmol/h

Let: x = kmol/h of methane in permeate

Solving, $x = 0.0117(25.6) = 0.3$ kmol/h

Methane in the retentate = 7.0 - 0.3 = 6.7 kmol/h

The resulting material balance and flow diagram is:



Comp.	kgmol/hr
H_2	42.4
CH_4	7.0
N_2	0.5
Total	49.9

Comp.	kgmol/hr
H_2	16.8
CH_4	6.7
N_2	0.5
Total	24.0

Comp.	kgmol/hr
H_2	25.6
CH_4	0.3
N_2	0.0
Total	25.9

(b) Percent purity of hydrogen in permeate = 100% x 25.6/25.9 = 98.8%

Exercise 1.16

Subject: Natural gas is produced when injecting nitrogen into oil wells. The nitrogen is then recovered from the gas for recycle.

Given: 170,000 SCFH (60^{o}F and 14.7 psia) of gas containing, in mol%, 18% N_2, 75% CH_4, and 7% C_2H_6 at 100_{o}F and 800 psia. Recover the N_2 by gas permeation followed by adsorption.
The membrane is selective for nitrogen. The adsorbent is selective for methane. The adsorber operates at 100^{o}F, and 275 psia during adsorption and 15 psia during regeneration. Permeate exits the membrane unit at 20^{o}F and a low pressure. Two stages of compression with cooling are needed to deliver the permeate gas to the adsorber. The regenerated gas from the adsorber is compressed in three stages with cooling, and is combined with the retentate to give the natural gas product.

Assumptions: The membrane is not permeable to ethane. The separation index, SP, defined by Eq. (1-4), is applied to the exiting retentate and permeate.

Find: (a) Draw a labeled process flow diagram.
(b) Compute the component material balance, based on the following data:
Nitrogen in permeate = 90.83% of nitrogen in the feed. Mole ratio of methane to nitrogen in the permeate = 1.756. The adsorption step gives 97 mol% methane in the adsorbate with an 85% recovery based on the feed to the adsorber. The pressure drop across the membrane is 760 psi. The retentate exits at 800 psia.
The combined natural gas product contains 3 mol% nitrogen. Place the results of the material balance in a table.

Analysis: (b) Refer to the process flow diagram on next page for stream numbers.
Let: ai = molar flow rate of N_2 in lbmol/h in stream i.
bi = molar flow rate of CH_4 in lbmol/h in stream i
ci = molar flow rate of ethane in lbmol/h in stream i

Feed flow rate = 170,000 SCFM / 379 SCF/lbmol at SC = 448.5 lbmol/h
a1 = 0.18(448.5) = 80.7, b1 = 0.75(448.5) = 336.4, c1 = 0.07(448.5) = 31.4
Because ethane does not permeate through the membrane, c3 = c6 = 31.4
and c2 = c4 = c5 = 0
Solve for a2, a3, a4, a5, a6, and b2, b3, b4, b5, b6 from 10 equations in 10 unknowns.
Nitrogen in permeate = 0.9083(80.7) = 73.3
For the permeate: a2/b2 = 1/732
Component balances around the membrane unit:
a2 + a3 = 80.7 b2 + b3 = 336.4
Component balances around the adsorber:
a2 = a4 + a5 b2 = b4 + b5

Exercise 1.16 (continued)

Component balances around the line mixer that mixes retentate with adsorbate gas:

$a6 = a3 + a5$ $\qquad$ $b6 = b3 + b5$

Methane purity in the adsorbate:

$b5 = 0.97(b5 + a5)$

Find: (b) (continued)

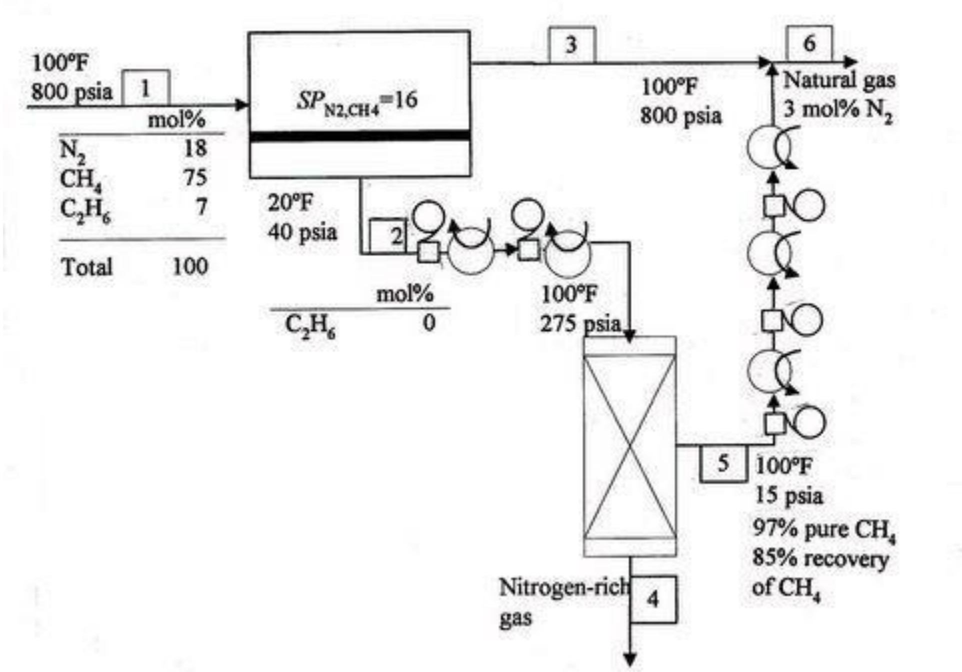
Methane recovery: $b5 = 0.85\ b2$

Mol% nitrogen in the final natural gas: $a6 = 0.03(a6 + b6 + 31.4)$

All equations are linear. Solving these 10 equations with linear equation solver, such as in the Polymath program, results in the following material balance table:

			Flow rate,	lbmol/h		
Component	Stream 1	2	3	4	5	6
Nitrogen	80.7	73.3	7.4	69.9	3.4	10.8
Methane	336.4	128.7	207.7	19.3	109.4	317.1
Ethane	31.4	0.0	31.4	0.0	0.0	31.4
Total	448.5	202.0	246.5	89.2	112.8	359.3

(a) Labeled process flow diagram



The SP in the membrane block refers to a separation power = a2 b3/a3 b2 computed from the material balance.

Exercise 1.17

Subject: Partial condensation of a reactor effluent.

Given: The effluent from the partial condensation of the reactor effluent of a toluene hydrodealkylation process is cooledand partially condensed. The resulting liquid phase is distilled in a sequence of three distillation columns to give the following four products.

Component	Off-gas, kmol/h	Benzene Product, kmol/h	Toluene Recycle, kmol/h	Biphenyl Byproduct, kmol/h
Hydrogen	1.48	0.00	0.00	0.00
Methane	11.07	0.06	0.00	0.00
Benzene	0.80	264.72	1.33	0.00
Toluene	0.00	0.09	88.79	0.45
Biphenyl	0.00	0.00	0.02	4.59
Total	13.35	264.87	90.14	5.04

Assumptions: Continuous, steady-state operation.

Find:
(a) The % recoveries for benzene and biphenyl.
(b) The mol% purities for benzene and biphenyl.
(c) Why is there a toluene recycle stream?
(d) What would happen if the biphenyl was not separated from the toluene, but was recycled back to the reactor with the toluene?

Analysis:
(a) Percent recovery of benzene = 264.72/(264.72 + 0.80 + 1.33) = 0.992 or 99.2%
Perceent recovery of biphenyl = 4.59/(4.59 + 0.02) = 0.9957 or 99.57%
(b) Mol% purity of benzene in the benzene product = 264.72/264.87 = 0.9994 or 99.94%
Mol% purity of biphenyl in the biphenyl product = 4.59/5.04 = 0.9107 = 91.07%
(c) The reaction must be quite incomplete.
(d) The biphenyl would build up until the side reaction reached equilibrium.

Exercise 1.18

Subject: Separation by Gas Permeation

Given: A hydrodealkylation process of the type stated in Exercises 1.17 and 1.22, in which a gas rich in hydrogen and methane is separated from the reactor effluent by partial condensation. The gas is then sent to a gas permeation membrane separator (Operation 3 in table 1.3) to separate the hydrogen from the methane. The hydrogen is recycled to the reactor and the methane is used for fuel. The component flow rates for the membrane feed, membrane retentate, and recycled membrane permeate are as follows:

Component	**Feed, kmol/h**	**Retentate, kmol/h**	**Permeate, kmol/h**
Hydrogen	1575.7	157.6	1418.1
Methane	2388.1	2313.5	74.6
Benzene	29.8	29.8	0.0
Toluene	3.5	3.5	0.0
Biphenyl	0.0	0.0	0.0
Total	3997.1	2504.4	1492.7

Assumptions: Continuous, steady-state operation.

Find:

(a) Percent recovery of hydrogen in permeate; methane in retentate.
Mol% purity of hydrogen in permeate and methane in retentate.
(b) Could hydrogen be separated from methane by distillation or absorption.

Analysis:

(a) Percent recovery of hydrogen in permeate = 1418.1/1575.7 = 0.900 or 90.0%
Percent recovery of methane in retentate = 2313.5/2388.1 = 0.969 or 96.9%

Mol% purity of hydrogen in permeate = 1418.1/1492.7 = 0.950 or 95.0%
Mol% purity of methane in retentate = 2323.5/2504.4 = 0.928 or 92.8%

(b) They could be separated by distillation or absorption with a hydrocarbon absorbent such as propane. Both would probably require low temperature and high pressure. Therefore they may be expensive.

Exercise 1.19

Subject: Suitable distillation sequence and all alternative distillation sequences

Given: The following feed to a distillation sequence:

Component	Feed rate, kmol/h	Normal boiling point, K
Methane	19	112
Benzene	263	353
Toluene	85	384
Ethylbenzene	23	409

Assumptions: Applicability of distillation heuristics in Section 1.8.2.

Find: (a) A suitable distillation sequence of 3 columns. (b) All possible sequences of 4 columns for the separation of a 5-component feed.

Analysis: **(a)** The feed components are already ordered by volatility. The most applicable heuristic of Section 1.8.2 is: Remove, early in the sequence, those components of greatest molar percentage in the feed. This is because the amount of benzene in the feed greatly exceeds that of the other three components. Applying this heuristic to the first column, separate between benzene and toluene. Then, in the remaining two columns in parallel, separate the two resulting binary mixtures. Thus, a reasonable sequence is: