



CHE 654

Computer Application for Chemical Engineering Practice

Process Simulation with ASPEN Plus
&
Solving Chemical Engineering Problems Using MATLAB

Exercise Problems

Version 2026



Prepared by

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Section 1

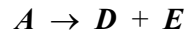
Elementary Modules, Mass Balances, and Degree of Freedom Analysis

1. Degree of Freedom Analysis

Consider the following flowsheet which consists of one mixer, two reactors in series, two separators, and a splitter, all elementary modules. Feed stream S1 contains pure component A, while feed stream S2 contains pure component B which react in the first reactor according to the following two parallel reactions.



Reaction 1

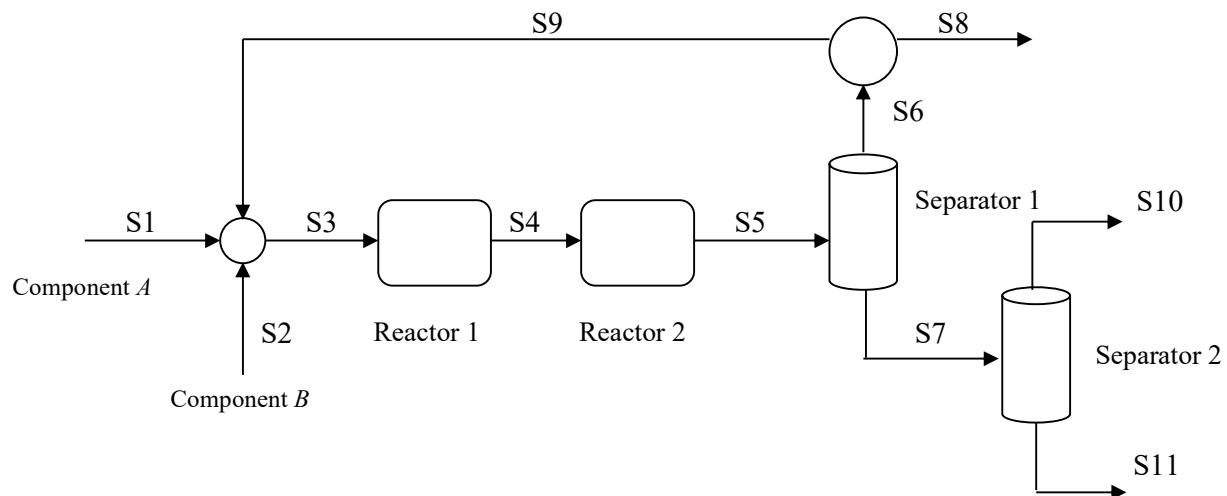


Reaction 2

The following reaction takes place in the second reactor:



Reaction 3



The overall conversion of the two parallel reactions in Reactor 1 based on component A is 80%, while the conversion of Reaction 3 based on component C is 70%. The first separator removes 100% of component A in the Reactor 2 outlet as overhead and removes 100% of component E in Reactor 2 outlet as the bottom. In the second separator, 95% of component B in S7 is recovered as overhead while 99% of component E in S7 is recovered as the bottom.

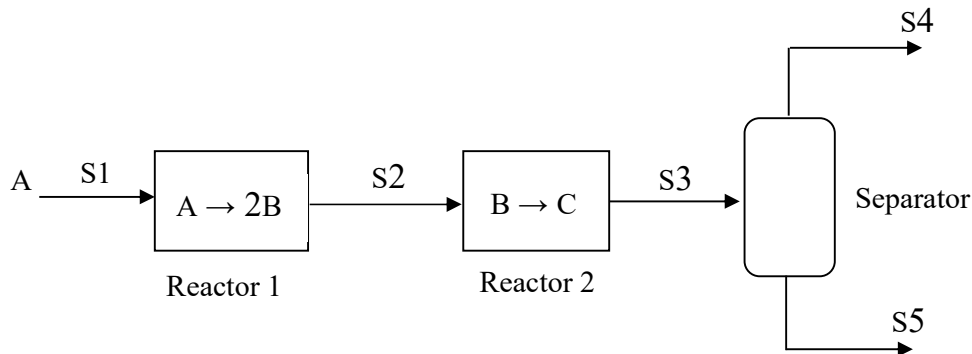
The following additional information is available about the process.

1. The ratio of molar flow rate between component A in S1 and component B in S2 is 2 to 1.
2. The flow rate of S2 is 100 lbmol/hr.
3. The flow rate of component C in stream S4 is 60 lbmol/hr.
4. The total flow rate of S8 is 10 lbmol/hr.
5. The product purity of component E in S11 is 99.9 mole%.
6. S7 contains 50 mole% C and 20 mole% D

Perform a degree of freedom analysis on this process. Is the problem fully specified, under-specified, or over-specified? If the problem is over-specified, how many pieces of data are redundant? If the problem is under-specified, how many more pieces of data are needed to make the problem fully-specified? In any case, write down a list of standard input that are missing or not given in the problem. Do not perform a mass balance on this problem.

2. Mass Balances Involving Constraints with Elementary Modules, I

Consider the following flowsheet which consists of three elementary modules, namely two reactors and a separator. The feed to the flowsheet is pure component A which goes through a series of two reactions as shown. The conversions of the two reactions are not 100%.



(a) The following information is available about the process:

1. Stream S1 has a flow rate of 120 lbmol/hr.
2. The total flow rate of Stream S3 is 223.20 lbmol/hr.
3. The molar ratio of Stream S3 to Stream S4 is 1.9231.
4. The concentration of Component C in Stream S5 is 78.024 mol%.
5. Stream S3 contains 92.88 lbmol/hr of Component C.
6. 80 mol% of Component B in Stream S3 is recovered to Stream S4 in the separator.

Using the degree of freedom analysis, how many standard inputs are missing and how many constraints are there? Is this problem under-specified, fully specified, or over-specified?

(b) Perform a mass balance by hand to determine the flow rates and compositions (in molar flow rates) of every stream in this process. In your calculations, use the symbols A_S , B_S , and C_S to denote the flow rates of components A, B, and C in streams S, respectively. For example, A_{S5} is the flow rate of component A in stream S5. Round off your final answers to 3 decimal places.

Answer the following questions:

Number of missing standard input = _____

Number of constraints = _____

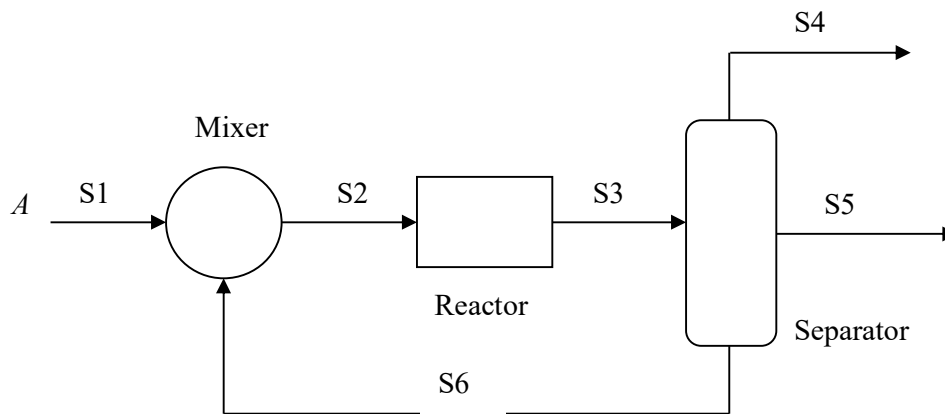
Check one: The problem is: ☐ under-specified ☐ fully specified ☐ over-specified

Complete this table:

Streams	Component Flow Rates (lbmol/hr)			Total Flow
	A	B	C	
S1	120	0	0	120.000
S2				
S3			92.880	223.200
S4				
S5				

3. Mass Balances Involving Constraints with Elementary Modules, II

Consider the following flowsheet which consists of three elementary modules, namely a mixer, a reactor, and a separator. The feed to the flowsheet is pure component *A* which decomposes into component *B* and component *C* according to the reaction: $A \rightarrow B + C$. The conversion of the reaction is not 100%.



(a) The following information is available about the process:

1. The fresh feed contains pure *A* with a flow rate of 82 lbmol/hr.
2. The separator recovers none of *A* in S4 and none of *B* in S6 (see the mass balance table below).
3. The separator recovers 5 mol% of *B* in S5.
4. The ratio of the mole-recovery of *C* in S5 to that of *A* in S6 is exactly 1.
5. The mole fraction of *B* in S4 is 0.9781.
6. The total flow rate of S5 is 84.3 lbmol/hr.
7. S6 contains 18 lbmol/hr of *A*.

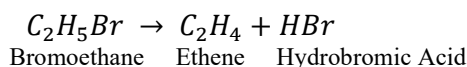
Based on the degree of freedom analysis, this problem is fully specified. List all the missing standard input and the given constraints (whose numbers should be equal).

(b) Perform a mass balance by hand to determine the flow rates and compositions (in molar flow rates) of every stream in this process. In your calculations, use the symbols A_S , B_S , and C_S to denote the flow rates of components *A*, *B*, and *C* in stream *S*, respectively. For example, A_{S5} is the flow rate of component *A* in stream S5.

Complete this table:

Streams	Component Flow Rates (lbmol/hr)			Total Flow
	<i>A</i>	<i>B</i>	<i>C</i>	
S1	82	0	0	82
S2				
S3				
S4	0			
S5				84.3
S6	18	0		

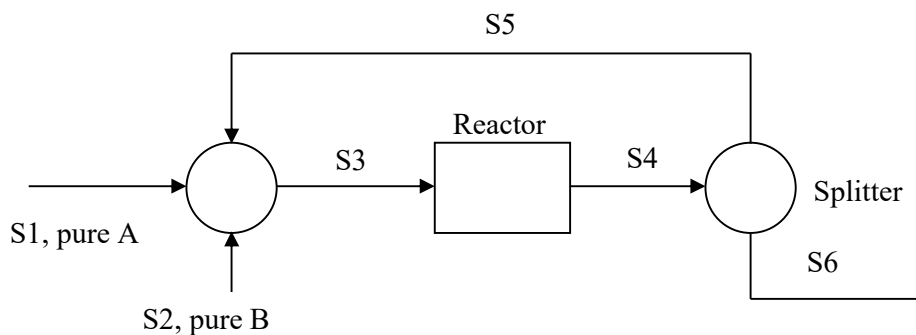
- (c) Perform a mass-balance-only simulation of this problem using A+ and verify your results from hand calculations in Part (b). For the reaction, you may use the following components to represent the elimination reaction of alkyl-halides to produce alkenes:



Note that bromoethane is also known as ethyl-bromide, ethene is also known as ethylene, and hydrobromic acid is also known as hydrogen-bromide.

4. Mass Balances Involving Constraints with Elementary Modules, III

Consider the following flowsheet which consists of a mixer, a reactor and a splitter, all elementary modules. Feed stream S1 contains pure component A while feed stream S2 contains pure component B. The following single reaction occurs in the reactor:



- (a) The following information is available about the process:

1. The mole fraction of B in stream S4 = 0.5.
2. The fractional reaction conversion based on A = 0.6.
3. The total molar flow rate of stream S4 = 160 lbmol/hr.
4. The flow rate of component A in stream S3 = 50 lbmol/hr

This problem is obviously constrained. List all constraints and all standard input that are missing. Using the degree of freedom analysis, is this problem under-specified, fully specified, or over-specified?

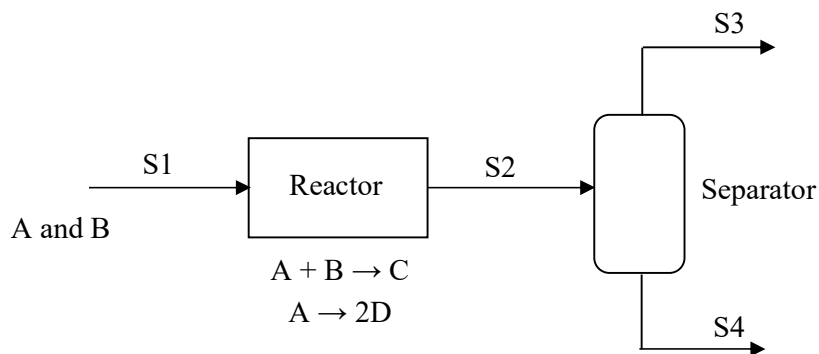
- (b) Perform a mass balance by hand to determine the flow rates and compositions of every stream in this process, including the split fractions of the splitter.

Complete this table:

Streams	Component Flow Rates (lbmol/hr)			Total Flow
	<i>A</i>	<i>B</i>	<i>C</i>	
S1		0	0	
S2	0		0	
S3	50			
S4				160
S5				
S6				

5. Mass Balances Involving Constraints with Elementary Modules, IV

Consider the following flowsheet which consists of two elementary modules, namely a reactor and a separator. The feed to the flowsheet is a mixture of Component A and Component B, which goes through two parallel reactions as shown. The conversions of the two reactions are not 100%.



- (a) The following information is available about the process:

1. The molar ratio of Component B flow rate to that of Component A in Stream S1 is 2.50.
2. The molar ratio of Component D flow rate to that of Component C in Stream S2 is 1.3333.
3. The total flow rate of Stream S3 = 81.68 lbmol/hr.

4. The relative volatility in decreasing order is A, B, C, and D (i.e. A is most volatile and D is least volatile), and we assume Component B is the light key and Component C is the heavy key.
5. 90 mol% of Component B in Stream S2 is recovered in Stream S3 in the separator.
6. The mole fraction of Component B in Stream S3 is 0.8903.
7. The mole fraction of Component C in Stream S4 is 0.3513.

Using the degree of freedom analysis, how many standard inputs are missing and how many constraints are there? Is this problem under-specified, fully specified, or over-specified?

Answer the following questions:

Number of missing standard input = _____

Number of constraints = _____

The missing standard inputs are:

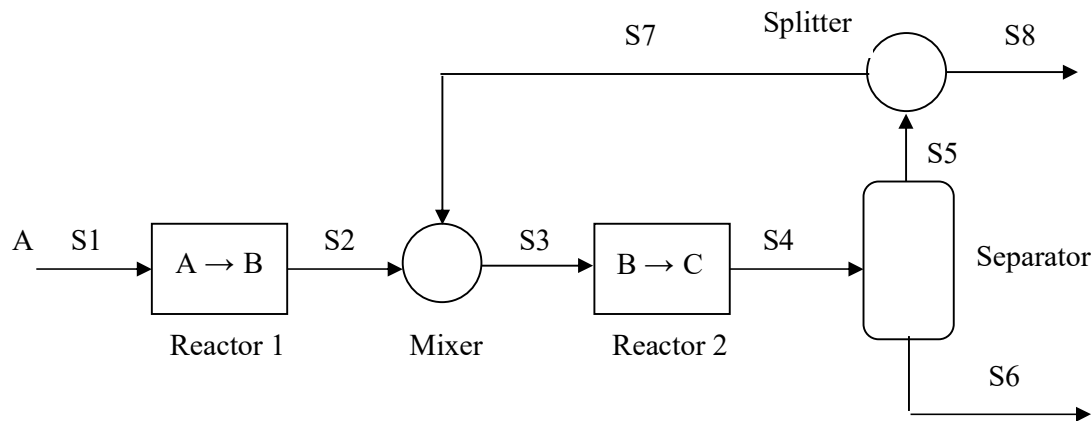
The design targets (constraints) are:

Check one: The problem is: ☐ under-specified ☐ fully specified ☐ over-specified

- (b) Perform a mass balance to determine the flow rates and compositions (in molar flow rates) of every stream in this process, noting that A is the limiting reactant in Reaction 1. In your calculations, use the symbols A_S , B_S , C_S , and D_S to denote the flow rates of components A, B, C, and D in streams S, respectively. For example, A_{S2} is the flow rate of Component A in stream S2. Round off your final answers to 2 decimal places.

6. Solving a Constrained Mass Balance Problem with A+

Consider the following flowsheet which consists of five elementary modules, namely two reactors, a mixer, a separator, and a splitter. The feed to the flowsheet is pure component A which is converted into component B and then into component C according to the reaction: $A \rightarrow B \rightarrow C$. The conversions of the two reactions are not 100%.



(a) The following information is available about the process:

1. The separator recovers 5.0 mole% of A in the overhead stream (S5).
2. The separator recovers 95.0 mole% of B in the overhead stream (S5).
3. The separator recovers 40 mole% of C in the overhead stream (S5).
4. The concentration (mole fraction) of B in S5 is 30.0 mol%.
5. The concentration (mole fraction) of A in S6 is 3.0 mol%.
6. The total flow rate of S6 is 100 lbmol/hr.
7. The splitter fraction of S8 is 1 mol% based on the inlet S5.

This problem is fully specified. Use A+ to perform mass-balance-only calculations and solve for component flow rates of every stream. To simulate the reaction $A \rightarrow B \rightarrow C$, we will assume $A = n$ -pentane, $B = iso$ -pentane, and $C = neo$ -pentane (2,2-dimethylpropane in A+).

Complete this table:

Streams	Component Flow Rates (lbmol/hr)			Total Flow
	A	B	C	
S1				
S2				
S3				
S4				
S5				
S6				100
S7				
S8				

(b) Now, let's add another design target (constraint) to obtain a ratio of B molar flow rate to that of C in S3 with a value of 1.50. The manipulated variable is input data #3 in Part (a), i.e. the mole-recovery of C in Stream S5.

While A+ should converge with the default convergence settings in Part (a), it most likely will not in Part (b). Instead, you must converge the tear stream and all the design-specs simultaneously using either Broyden or Newton. Note that both Broyden and Newton will result in a cryptic Fortran error during simulation but A+ would recover and converge. However, you could get rid of this error by initializing the tear stream chosen by A+ (in my run, the tear stream is S5).

Complete this table:

Streams	Component Flow Rates (lbmol/hr)			Total Flow
	A	B	C	
S1				
S2				
S3				
S4				
S5				
S6				100
S7				
S8				

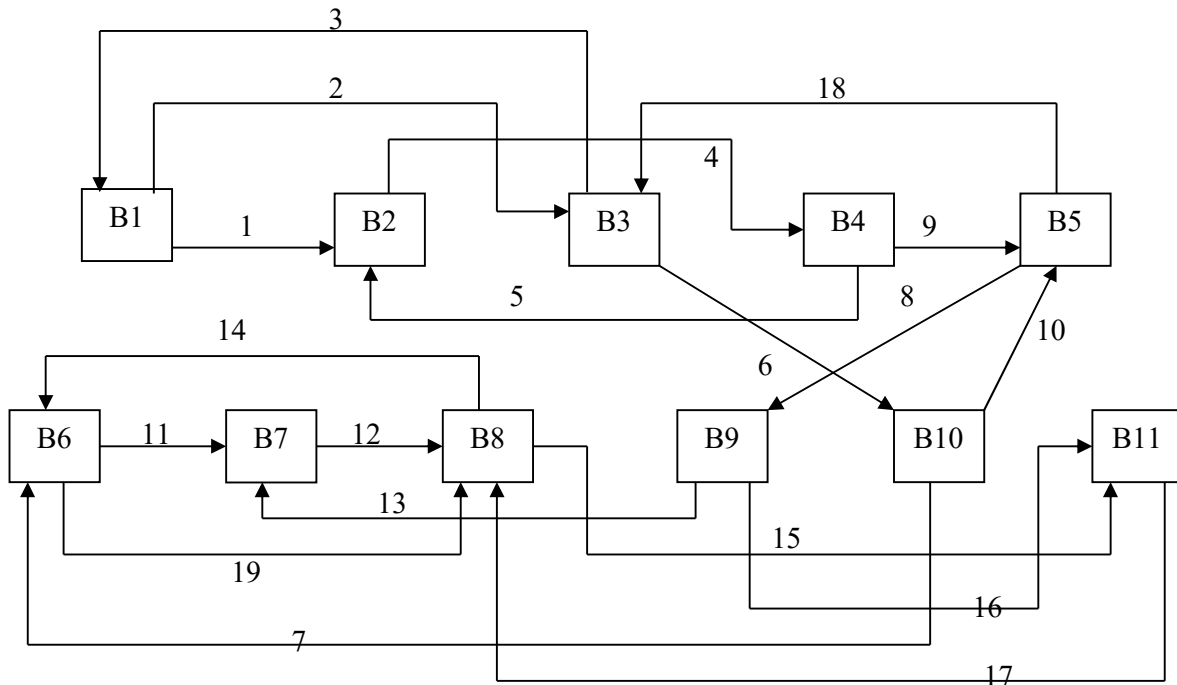
Section 2

Determination of Tear Streams and Computational Order of Flowsheets

7. Determination of Tear Streams and Computation Order, I

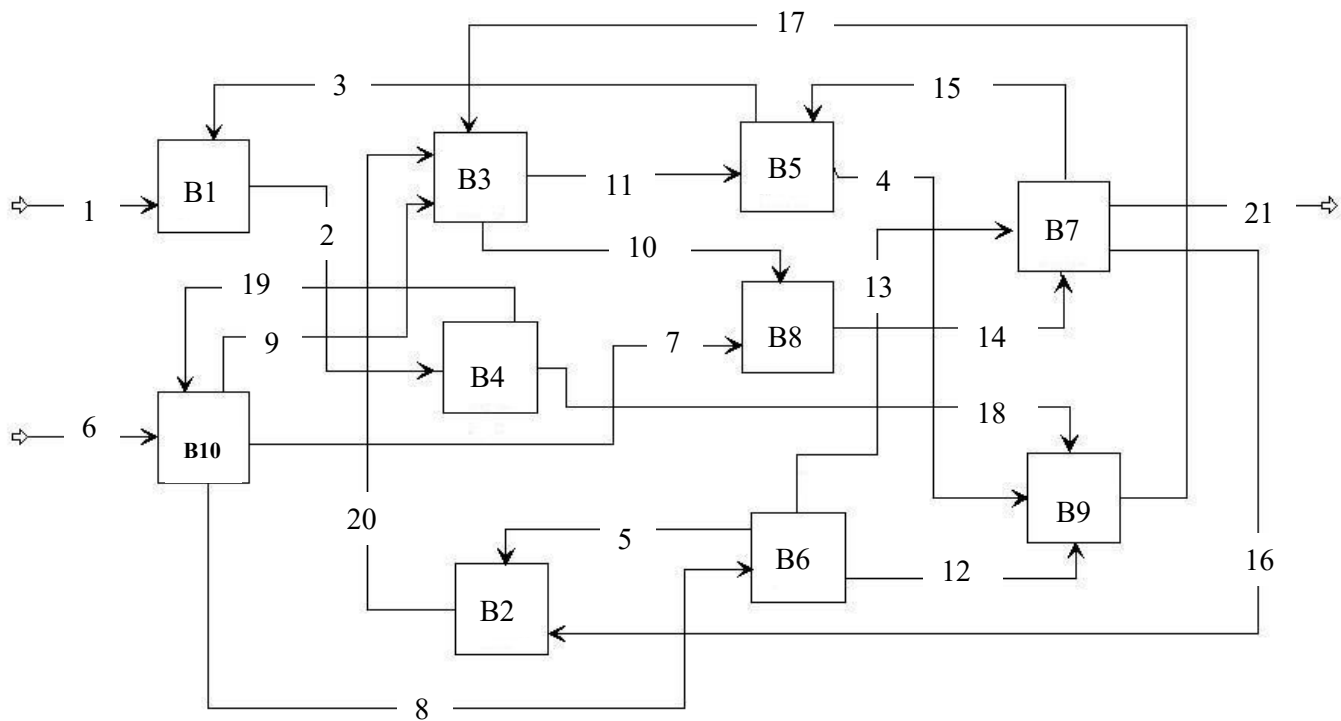
Consider the flowsheet given below.

- (a) Find all irreducible groups in the flowsheet using the method by Sargent and Westerberg. Write down a valid precedence order (calculation sequence) of this flowsheet comprising these irreducible groups.
- (b) For group(s) with more than 1 unit in Part (a), find the minimum number of tear streams and their locations by B & M method. Also, write down a complete calculation sequence for the entire flowsheet.



8. Determination of Tear Streams and Computation Order, II

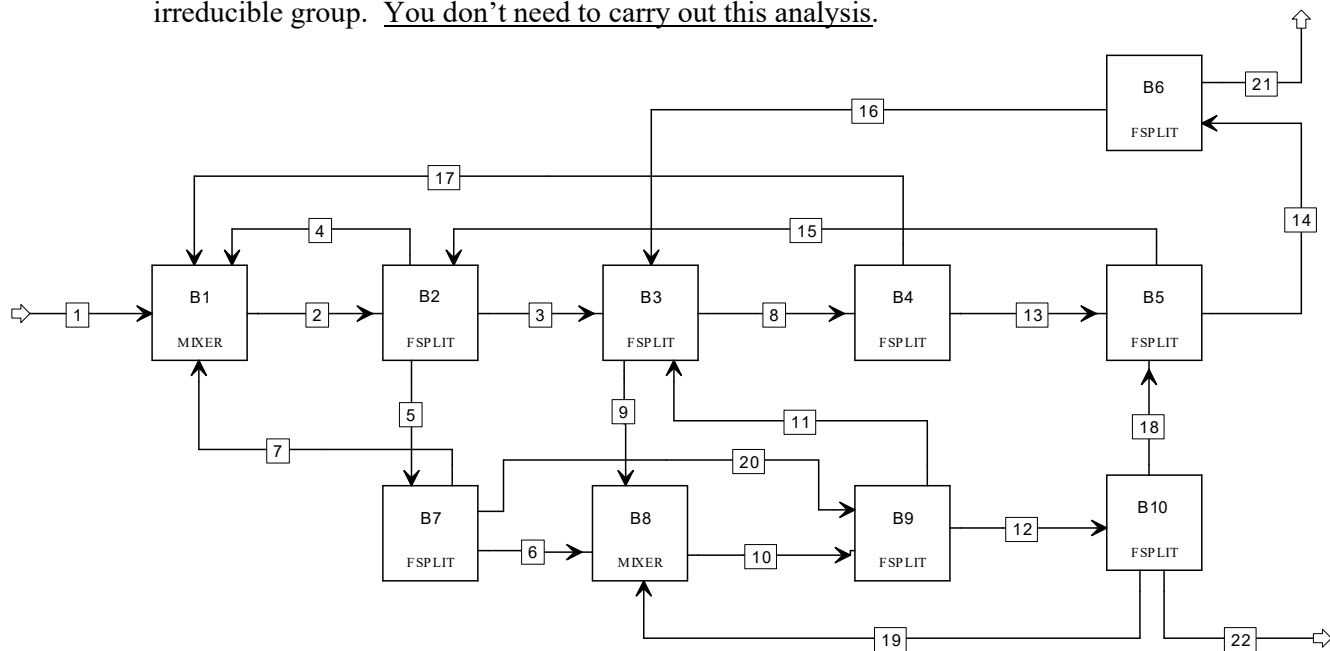
Consider the flowsheet given below. A quick analysis of this flowsheet using the method of Sargent and Westerberg shows that all blocks, B1 through B10, form an irreducible group. You don't need to carry out this analysis.



Find the minimum number of tear streams and their locations in this irreducible group by Barkley & Motard method. Also write down a complete calculation order for this flowsheet. Warning: Some of the streams are crowded so be sure to read the correct stream labels from the flowsheet.

9. Determination of Tear Streams and Computation Order, III

Consider the flowsheet given below (drawn using A+). A quick analysis of this flowsheet using the method of Sargent and Westerberg shows that all blocks, B1 through B10, form an irreducible group. You don't need to carry out this analysis.

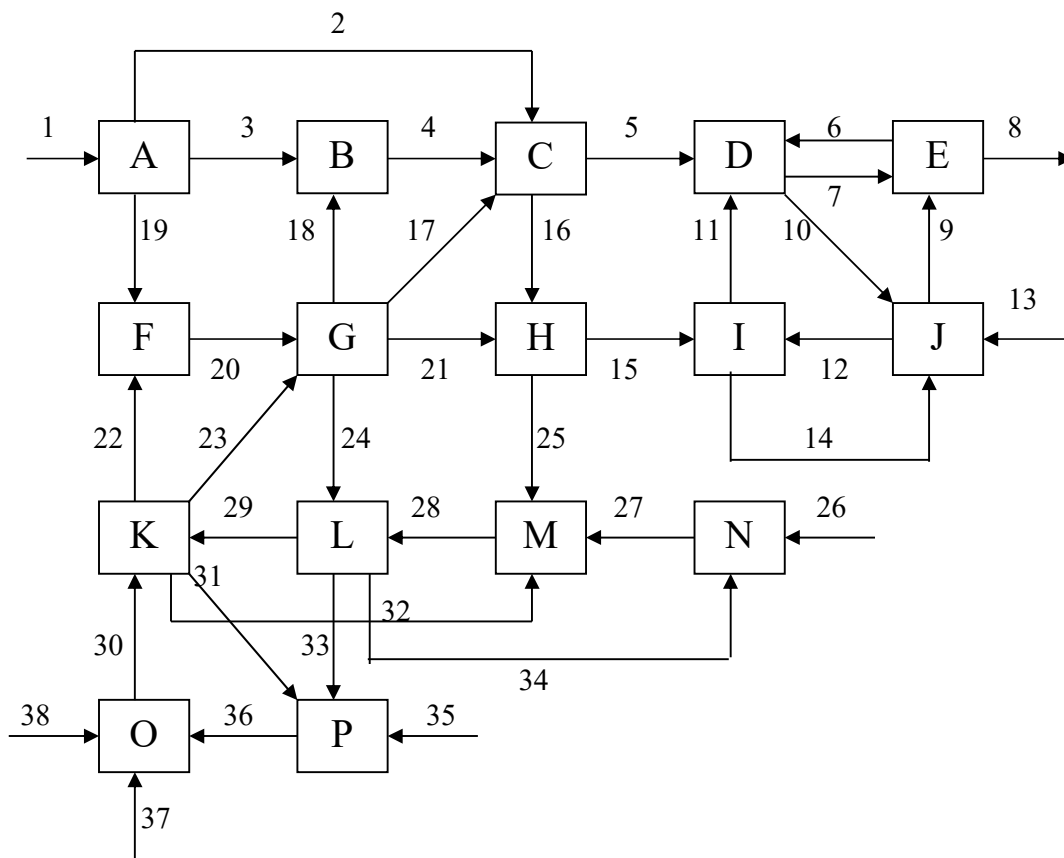


Find the minimum number of tear streams and their locations in this irreducible group by Barkley & Motard method. Also write down a complete calculation order for this flowsheet.

10. Finding Tear Streams and Computational Sequence Using ASPEN Plus

- (a) Consider the flowsheet below. Use ASPEN Plus to find the minimum number of tear streams, their locations, and a computation order for the flowsheet. You must use the same IDs for streams and blocks as given when you draw your flowsheet in ASPEN Plus. Submit a copy of your flowsheet from ASPEN Plus.

Hint: Pick a simple (e.g. requiring the least input) unit operation module or modules to simulate blocks A to P in the flowsheet. Your model needs not converge since we are only interested in the flowsheet analysis, although it is very easy to pick modules that give you convergence.

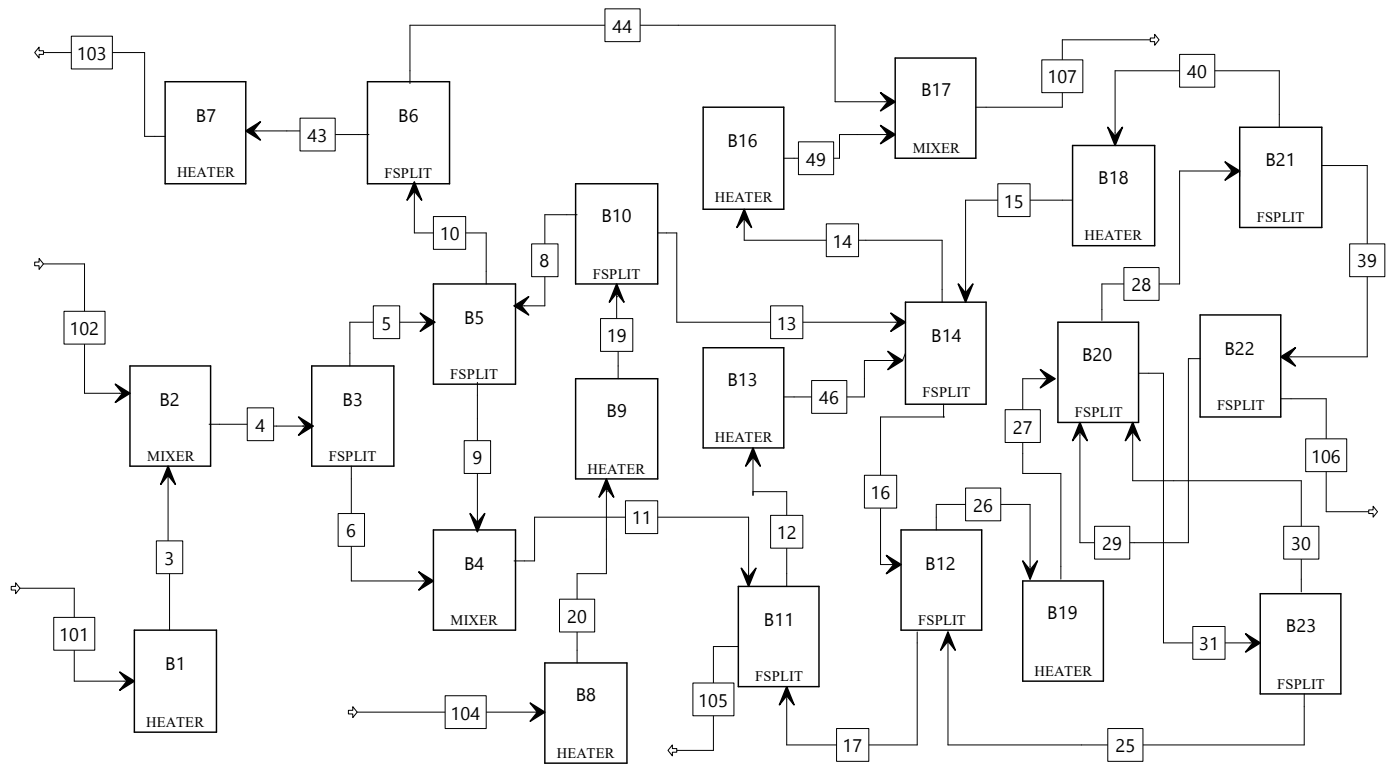


- (b) For the irreducible group that contains the block D, we are interested in knowing if this group contains any exclusive tear sets. Use Forder-Hutchison's loop analysis to determine if there are any exclusive tear sets in this irreducible group? If so, write down 3 such tear sets.

11. Determination of Tear Streams and Computational Order, IV

Consider the flowsheet given below. A quick analysis of this flowsheet using the method of Sargent and Westerberg shows that blocks B11, B12, B13, B14, B18, B19, B20, B21, B22, and B23 form an irreducible group. Find the minimum number of tear streams and

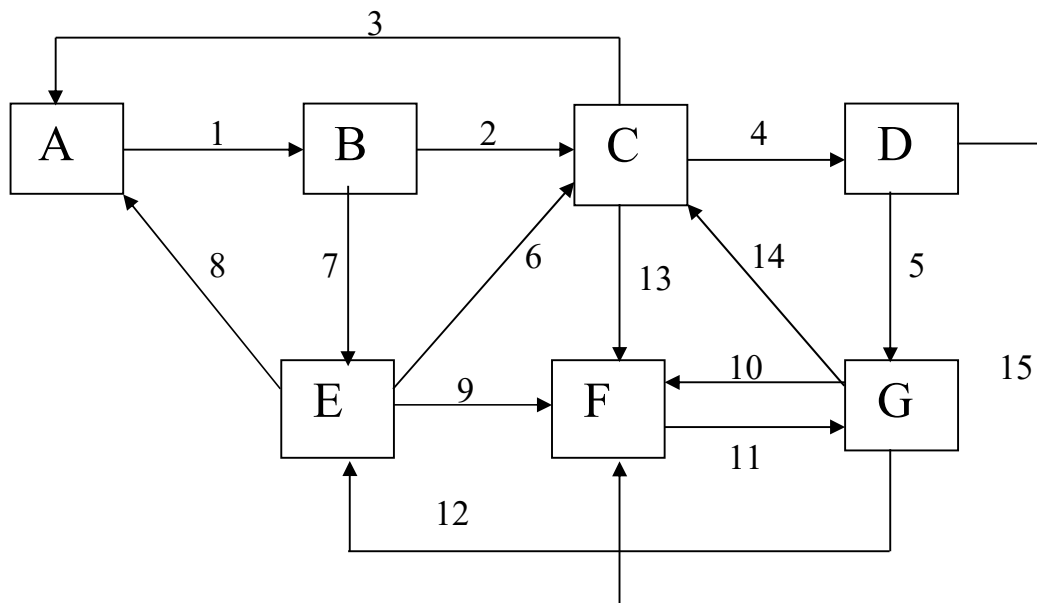
their locations in this irreducible group by B & M method. There is no need to write down a complete calculation sequence.



12. Determination of Tear Streams and Computation Order, V

Consider the flowsheet given below. A quick analysis of this flowsheet using the method of Sargent and Westerberg shows that all blocks, A through G, form an irreducible group. You don't need to carry out this analysis.

Find the minimum number of tear streams and their locations in this irreducible group by B & M method. Also write down a complete calculation sequence.



Section 3

Using A+ to Build Base-Case Simulation Models in Producing Certain Chemical Compounds

13. Simulation of a Butane Isomerization Process

In a petroleum refinery, reforming operations produce a relatively large amount of C₄ paraffin, mostly *n*-butane but some isobutane. However, isobutane is much more useful than *n*-butane in a refinery, and it has other uses as well. Thus, there arises the need to convert *n*-butane to isobutane by isomerization. The isomerization reaction occurs over a supported aluminum chloride catalyst in a fixed bed reactor and in the presence of hydrogen.

A C₄ feed stream of 100 lbmol/hr *n*-butane and 10 lbmol/hr isobutane is available. It is desired to produce at least 100 lbmol/hr of a stream containing at least 98 mol% isobutane. A design for an isomerization process to carry out this task has been proposed and is described in detail below. Your job is to evaluate the design by simulating its performance. For this purpose, you should use the process simulation program ASPEN Plus. The flowsheet for the proposed design is shown in Figure 1. The details are as follows:

C₄ Feed:

Temperature:	560 °R
Pressure:	120 psia
Flowrates:	
<i>n</i> -butane	100 lbmol/hr
isobutane	10 lbmol/hr

H₂ Feed (Make-up):

Temperature:	560 °R
Pressure:	120 psia
Flowrates:	3.5 lbmol/hr

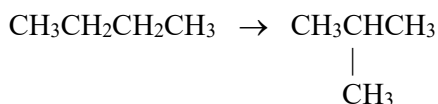
Deisobutanizer Column: This distillation column should provide enough ideal stages to take 97 mole% of the isobutane out with the distillate and 99% of the *n*-butane out with the bottoms. It is proposed that the reflux ratio be 1.4 times the minimum. The pressures at the top and bottom of the column are 160 and 180 psia, respectively. Use the Winn-Underwood-Gilliland short-cut design procedure with feed tray location. A total condenser is used.

Recycle Pump: The deisobutanizer bottoms product is recycled to the reactor. The required output pressure is 250 psia. Assume it is electrically driven.

Heat Exchanger (Preheat): In order to partially preheat the feed to the reactor, a heat exchanger is used in which the reactor effluent provides heat. The minimum approach temperature on the hot-side outlet is 10 °F, and there is a 5 psi pressure drop on both tube side and shell side. The estimated overall heat transfer coefficient is 100 Btu/hr-ft²-R.

Fired Heater (Preheat): A fired heater is used to provide the remaining preheating. The input to the reactor should be at 671 °R. The pressure drop is 5 psi.

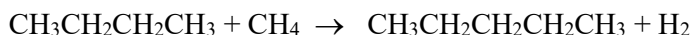
Reactor: The main reaction is the isomerization reaction



The conversion of *n*-butane is 75%. Two side reactions are important. Of the 25% of the *n*-butane not isomerized, 40% is hydrocracked:



Of the *n*-butane neither isomerized nor hydrocracked, 5% is converted to *n*-pentane:



Enough heat should be removed or supplied to the reactor to make the outlet temperature 675 °R. The pressure drop in the reactor is estimated to be 10 psia.

Pentane Treatment: The reactor effluent must first be treated to remove pentane from the stream. Assume a 100% treatment efficiency.

Heat Exchanger (Effluent Cooldown): The effluent must be cooled to 600 °R. This is done partially in the heat exchanger that preheats the feed. A standard water-cooled heat exchanger provides the remaining cooldown. Water at 25 °C is used for cooling, and its flowrate is 1000 lbmol/hr. The estimated overall heat transfer coefficient is 100 Btu/hr-ft²-R. The pressure drop in the effluent is 5 psi.

Flash Drum: A flash drum is used to remove most of the hydrogen from the effluent. Assume the flash is adiabatic and the outlet pressure is 220 psia.

Compressor: The hydrogen feed is compressed by an isentropic compressor. The required compressor outlet is 250 psia.

Stabilizer Column: The liquid outlet from the flash is distilled to remove most of the components lighter than C₄. These are to be combined with the vapor stream from the flash drum and used as fuel gas. The column should provide enough stages that 99 mole% of the propane leaves with the distillate and 99 mole% of the isobutane leaves with the bottoms. It is proposed that the column operate at a reflux ratio 1.3 times the minimum. The pressures at the top and bottom of the column are 160 and 180, respectively. Use the Winn-Underwood-Gilliland short-cut design procedure with feed tray location. A partial condenser is used, which should allow all hydrogen in the overhead to leave as vapor distillate (say 10% of the total distillate).

- (a) Develop a flowsheet simulation model to determine all product and intermediate stream conditions and the performance of each major process unit. Use the PENG-ROB equation of state for property calculations and STEAMNBS for steam/water properties. Export your model to an input summary file and submit this .INP file. What is the flowrate and purity of the isobutane product stream? Does it meet the desired product specifications?
- (b) For the distillation units, what are the numbers of theoretical stages and feed tray locations? What are the utility requirements? What are the heat transfer area requirements for heat exchangers?
- (c) The PENG-ROB method is the Peng-Robinson cubic equation of state (EOS), which is recommended for gas processing, refinery, and other hydrocarbon applications, in which nonpolar or mildly polar mixtures are involved. ASPEN Plus uses this EOS to calculate all thermodynamic properties except one. What is the property in this exception, and what property model is used by ASPEN Plus in this flowsheet to calculate this thermodynamic property?

- (d) For accurate results, the PENG-ROB method requires binary interaction parameters between components in the system. What is the name of this parameter used in ASPEN Plus? Is the parameter symmetric or asymmetric? (i.e. is $k_{ij} = k_{ji}$?)

ASPEN Plus automatically retrieves the binary parameters for the PENG-ROB method from its binary databank. What binary databanks were searched, and what is the data source of these binary parameters? With the 7 components in the system (not counting water because it never co-exists with other components), what is the total number of possible component pairs (e.g. CH₄-H₂, C₂H₆-H₂ etc.) for binary parameters? List all the possible component pairs. List the pairs whose binary parameters were not retrieved by ASPEN Plus.

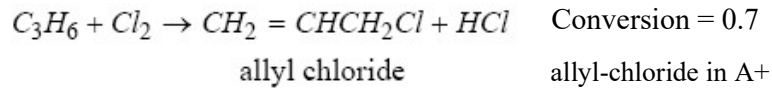
- (e) Are there any tear stream convergence loops in this flowsheet? If so, what is the minimum number of tear streams and the tear stream locations determined by ASPEN Plus? What is the computation order for the flowsheet?
- (f) What is the total number of iterations for the tear stream convergence in your run? What variables in the tear stream were being converged upon by ASPEN Plus? What was the initial guess for the variables in the tear stream(s)? What suggestion do you have to reduce the total number of iterations, hence the simulation time, of this flowsheet?

14. Simulating an Allyl-Chloride Production Process with ASPEN Plus

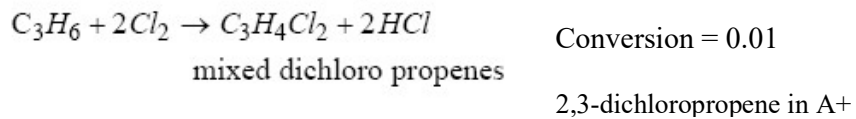
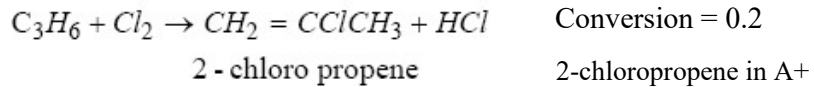
Allyl chloride can be produced from propylene (C_3H_6) and chlorine (Cl_2) in an isothermal stoichiometric reactor.

The following reactions occur:

Main reaction



Side reactions



A process flow diagram of allyl chloride production is given below. Pure high-pressure propylene and chlorine enter the process at 25 °C and 12 bar. The flow rate of both chlorine fresh feed and propylene fresh feed is 100 kmol/hr. Together with recycled unreacted propylene and chlorine, the two feeds enter a preheater ($\Delta P = 0.5$ bar) which increases the combined mixture to 480 °C. The heated stream then enters an isothermal reactor (RSTOIC with $\Delta P = 0.5$ bar) where the three reactions occur. The reactor effluent is then cooled to 80 °C in a cooler ($\Delta P = 1.0$ bar) before being sent to a series of 3 distillation columns. The first column removes most of the HCl in the overhead, while the overhead in the second column contains mostly unreacted propylene and chlorine and is recycled back to the preheater. The last column (rigorous model) separates ally chloride from the propenes as a high-purity product. There is an isentropic compressor used to pressurize the recycle stream back to 12 bar.

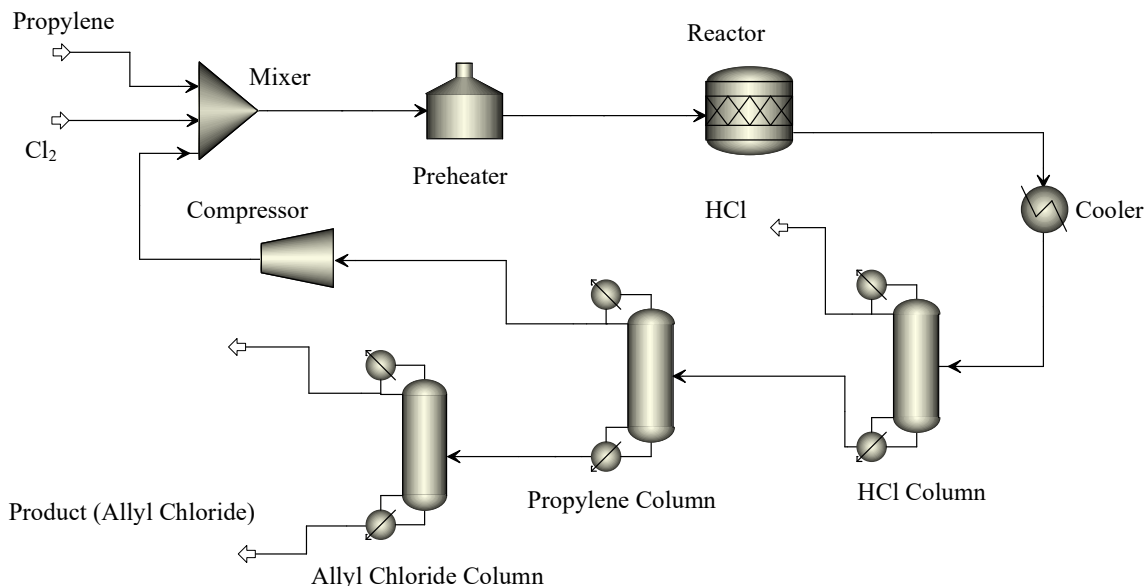


Figure 2: PFD of an Allyl-Chloride Production Process

The three columns have the following operating parameters and conditions:

	<u>HCl Column</u>	<u>Propylene Column</u>	<u>Allyl Column</u>
Reflux ratio	1.2 times RR_{min}	3 times RR_{min}	8.0
Condenser pressure	8.0 bar	4.0 bar	2.0 bar
Condenser type	Partial with all vapor distillate	Partial with all vapor distillate	Total
Reboiler pressure	8.2 bar	4.2 bar	2.1 bar
Light key (LK)	HCl	Cl_2	---
LK Recovery	0.99 (distillate)	0.9995	---
Heavy key (HK)	Propylene	2-chloro-propene	---
HK Recovery	0.05 (distillate)	0.0005	---
Bottom to feed ratio	---	---	0.78
Number of stages (including condenser and reboiler)	---	---	30
Feed tray location	---	---	15

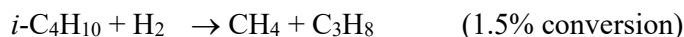
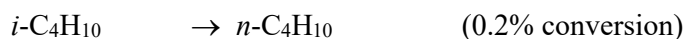
Use ASPEN Plus to simulate this allyl chloride production process. For properties, use the Peng-Robinson equation of state.

15. Simulating Isobutene Production with ASPEN Plus

Isobutene (isobutylene) is an important feedstock for the production of MTBE, an important gasoline anti-knock additive. Isobutane can be converted to isobutene using an isothermal packed bed reactor, in which the following dehydrogenation reaction takes place:



There are 4 important side reactions:



*2- C_4H_8 is 2-butene (assume the *cis* configuration).

Isobutane feed enters a preheater ($\Delta P = 3$ psia) in order to raise the feed stream temperature to 1100 °F before being fed into a reactor. The reactor operates at the same temperature as the preheater with a pressure drop of 2 psia. The reactor effluent is cooled inside a heat exchanger ($\Delta P = 3$ psia) to a temperature of 300 °F. The gas leaving the cooler is at a fairly low pressure, and so an isentropic compressor is used to bring the pressure up to 50 psia. The outlet from the compressor goes into an absorber in which all the hydrogen gas is removed along with 30 mole% of methane, 20% of ethane, and 10% of propane. After that, a series of 2 distillation columns is used to purify the isobutene product. The key components for separation in the first column are propane and isobutane, while those of the second column are isobutane and isobutene. Note that 60% of the bottom stream of the

first column is returned to the absorber to provide the liquid flow to the top of the tower. Unreacted isobutene is sent back to the preheater and the reactor via a recycle stream. A PFD of this process is provided below in Figure 3.

Use ASPEN Plus to simulate this isobutene production process. For properties, use the Peng-Robinson equation of state. Export your model to an input summary file and submit this .INP file. What are the flow rate and purity (mole%) of isobutene product stream?

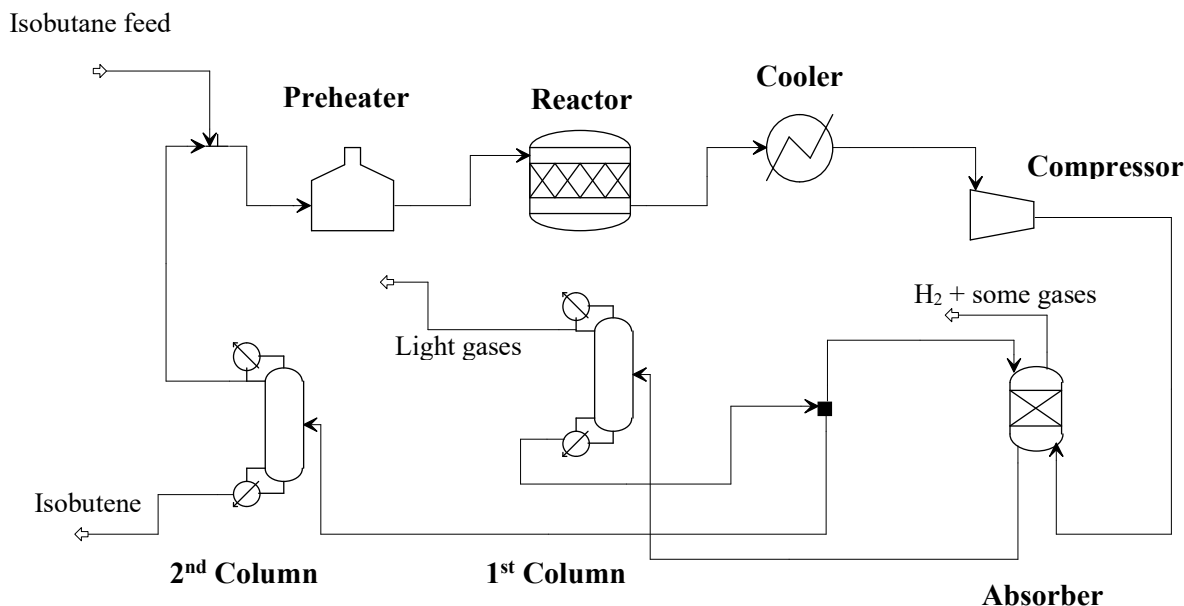


Figure 3: PFD of an Isobutene Production Process

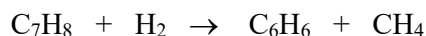
The following additional data are available for the 2 columns:

	<u>1st Column</u>	<u>2nd Column</u>
Operating reflux ratio	1.3 of minimum	1.5 of minimum
Condenser type	Partial (all vapor distillate)	Total
Condenser pressure (psia)	20	20
Reboiler pressure (psia)	22	22
Light key recovery in distillate	99%	99%
Heavy key recovery in bottom	99%	99%

Isobutane feed stream: T = 60 °F, P = 20 psia, Total flow = 300 lbmol/hr, isobutane = 98 mole%, methane = 1 mole%, ethane = 0.5 mole%, and propane = 0.5 mole%

16. Simulation of Benzene Production Using ASPEN Plus

The reactor section of a process shown in Figure 4 to produce benzene (C₆H₆) by hydrodealkylation of toluene (C₇H₈) is to be simulated using ASPEN Plus. This example is typical of a model developed for preliminary flowsheet evaluation. Toluene is to be converted thermally to benzene in a hydrodealkylation reactor. The main reaction is:



An unavoidable side reaction occurs that produces diphenyl as follows:



Conversion of toluene in the reactor is 75%, while 2% of the benzene present after the first reaction occurs is converted to diphenyl. The conditions for the feed and the two recycle streams are:

Component Flow Rates (lbmoles/hr)	Feed	Recycle	Gas Recycle
H ₂	0	0	2045.9
CH ₄	0	0	3020.8
C ₆ H ₆	0	3.4	42.8
C ₇ H ₈	274.2	82.5	5.3
C ₁₂ H ₁₀	0	1.0	0

Develop a flowsheet simulation model to determine all product and intermediate stream conditions and the performance of each major process unit. The important process conditions are given in Figure 4. Use the Redlich-Kwong-Soave equation of state for property calculations.

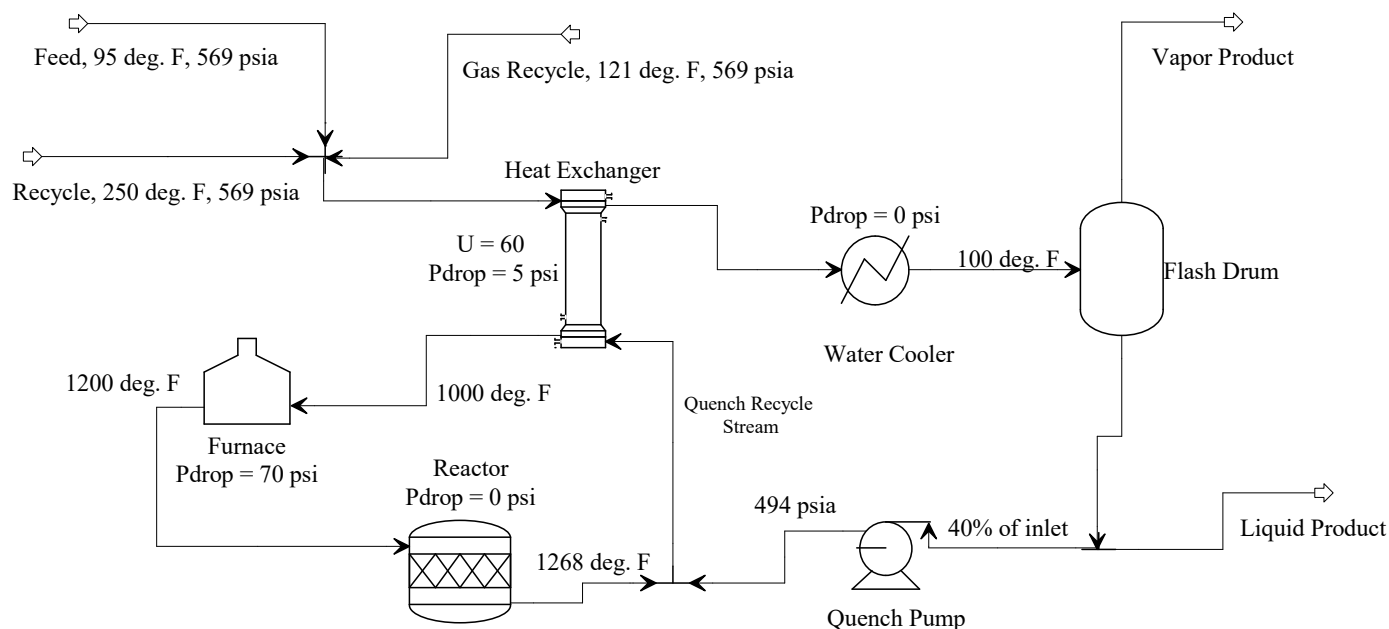


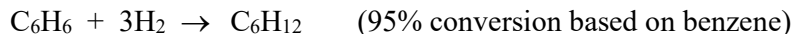
Figure 4: Benzene Production Process by Hydroalkylation of Toluene

Notes: The heat exchanger uses the very hot stream from the reactor to heat up the combined feed to 1000 °F. $U = 60 \text{ Btu/hr-ft}^2\text{-R}$ and $\Delta P = 5 \text{ psia}$ applies to both hot-side and cold-side of the heat exchanger.

17. Producing Cyclohexane from Benzene-Water Waste

A waste stream containing water, benzene and some acetone and methanol go through an adiabatic decanter to remove most of the water. The remaining organics, mixed with hydrogen, are preheated to a temperature of 150 °F fed and then fed to an adiabatic reactor

in which benzene reacts with hydrogen to form cyclohexane according to the following reaction:



The effluent from the reactor is cooled by the water from the decanter and fresh cooling water inside a counter-current heat exchanger ($\Delta P = 5$ psia in both hot side and cold side and $U = 200$ Btu/hr-ft²-R) which vaporizes 80% of the cold stream at the outlet. The cooled organic stream then enters an adiabatic flash in order to recycle the unreacted hydrogen. The bottom of the flash finally enters a treatment unit where cyclohexane is separated to very high purity. The second stream, rich in benzene, acetone, and methanol, from the treatment unit is recycled back to the reactor. The recovery of all components based on the cyclohexane product stream is as follows: 1% for benzene, 0% for acetone and methanol, 99% for water and cyclohexane, and 100% for hydrogen. There is a pressure drop of 5 psia in the treatment unit. A flow diagram of this process is given below in Figure 5, and the following data are available regarding the process feeds (all flowrates are in lbmol/hr):

	Waste	Cooling Water	Hydrogen
Water	500	1000	---
Benzene	300	---	---
Acetone	50	---	---
Methanol	60	---	---
Hydrogen	---	---	900
Temperature (°F)	60.0	60.0	80.0
Pressure (psia)	50.0	14.7	50.0

Note: For the compressor, you must specify Valid Phases = Vapor-Liquid in the Convergence tab instead of using the default. Otherwise, an error in the compressor will occur because liquid is detected during the compressor calculations. Also, for the waste feed, be sure to change the flash calculation from Vapor-Liquid to Vapor-Liquid-Liquid.

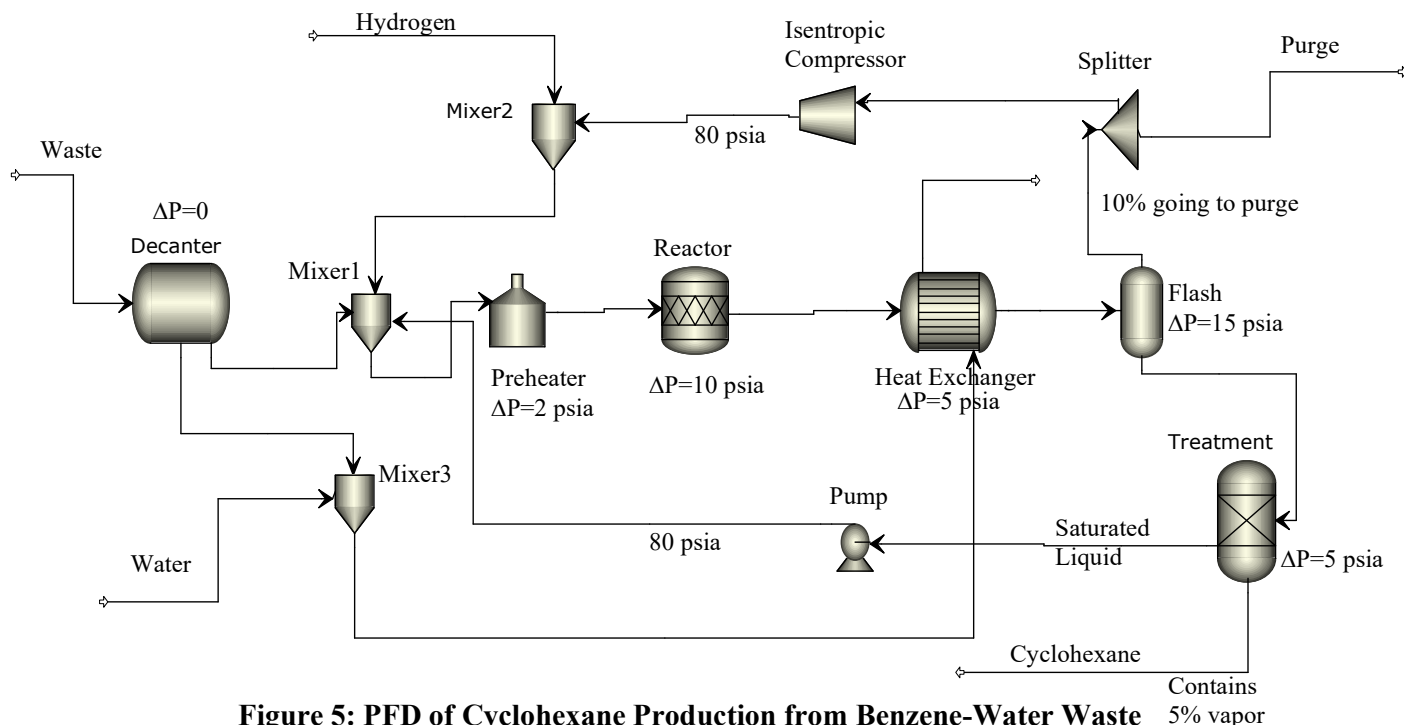


Figure 5: PFD of Cyclohexane Production from Benzene-Water Waste

Use ASPEN Plus to simulate the process. For properties, use NRTL-RK (remember to declare Henry's components if any exists).

18. Simulating an *n*-Octane Production Process with ASPEN Plus

n-octane can be produced from ethylene (C₂H₄) and *i*-butane (C₄H₁₀) in an adiabatic stoichiometric reactor ($\Delta P = 2$ psia) according to the reaction:



A process flow diagram of *n*-octane production is given below in Figure 6. Temperatures and pressures are given for some of the streams. Notice that this process produces two grades of *n*-octane, namely low-grade and high-grade octane. The low-grade is recovered as the bottom of the flash which has a lower purity than the high-grade produced from the bottom of the distillation column.

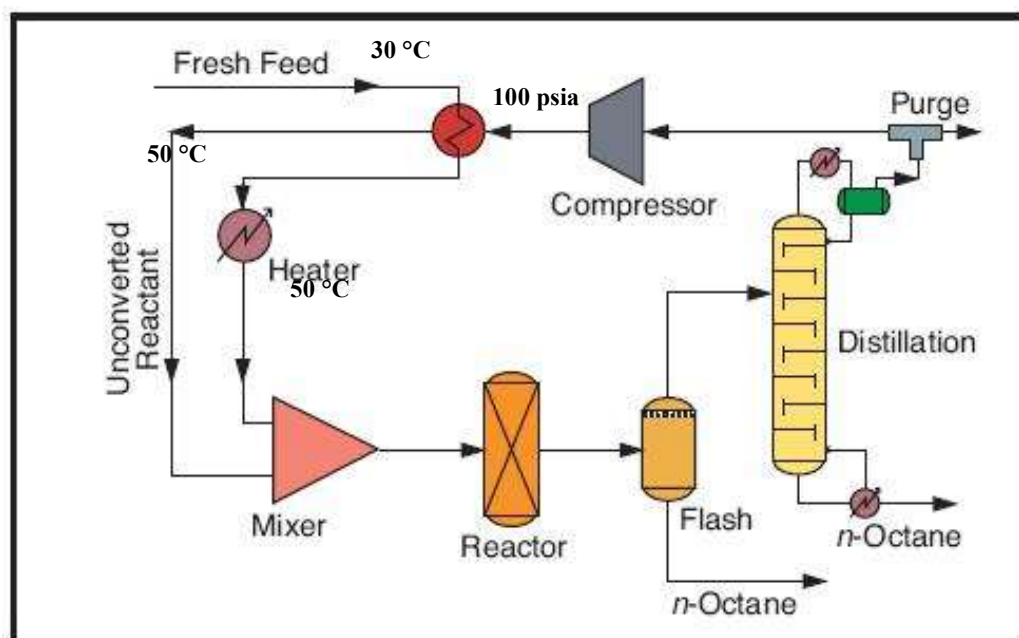


Figure 6: PFD of *n*-Octane Production Process

The fresh feed contains in kmol/hr 1.0 nitrogen (N₂), 100 ethylene (C₂H₄), 3.0 *n*-butane (*n*-C₄H₁₀), and 50 *i*-butane (*i*-C₄H₁₀) at 30 °C and 20 psia.

The following data are also known about the process:

1. The flash vessel is isobaric (i.e. inlet and outlet pressures are equal or $\Delta P = 0$ with cooling to condense enough *n*-octane.)
2. The pressure drops across the heat exchanger, the heater, and the mixer are considered negligible.
3. The compressor is isentropic, and the purge takes out 5% of the column overhead.
4. The column (short-cut model) operates at 1.5 times the minimum reflux ratio and recovers 99.5 mol% *n*-butane in the overhead and 99.9 mol% *n*-octane in the bottom.
5. The condenser of the column is partial with all vapor distillate and its pressure is 15 psia. The pressure in the reboiler is 16 psia.

6. The process must produce 20 kmol/hr of low-grade *n*-octane from the flash vessel.
7. The fractional conversion of the reaction based on ethylene is 90%.

Use ASPEN Plus to simulate this *n*-octane production process. For properties, use the Peng-Robinson equation of state.

Section 4

Using A+ to Perform Basic Engineering Calculations
and Simulate Complex Chemical Processes
Involving Many Design Targets, Sensitivity
Analyses, and Calculator Blocks

19. Using ASPEN Plus to Perform Basic Calculations

Part I:

- (a) A mixture contains 20 mole% water, 30 mole% acetone, and 50 mole% methanol. Use ASPEN PLUS to answer the following questions. In all cases, use NRTL-RK as the property method.
- Determine the bubble point and dew point temperatures of the mixture at 1.01325 bar (or 1 atm).
 - Determine the bubble point and dew point pressures of the mixture at 100°C.
 - Suppose the above mixture with a flow rate of 100 kmol/hr at 100°C and 100 bar is adiabatically flashed. Determine the temperature at which the flash will produce a vapor stream containing exactly 50 mole% ($\pm 0.01\%$) acetone.
- (b) A binary mixture of benzene and toluene with a total flow rate of 100 kg/hr at 100 °C and 100 bar is adiabatically flashed at 1 bar to produce a vapor stream containing exactly 60 mass% ($\pm 0.01\%$) benzene. Use ASPEN PLUS with the Redlich-Kwong-Soave equation of state to determine the composition (mass fractions) of this benzene-toluene feed.

Hint: This problem is deceptively simple to describe but really tests your true knowledge of A+ and requires a combination of features we discussed in the class to solve.

Part II:

- (a) Calculate the bubble-point temperature in °C of a mixture containing 30 mol% benzene, 30 mol% cyclohexane, 20 mol% toluene, and 20 mol% *n*-octane at 1.01325 bar. Use PENG-ROB as the property method.

Answer: $T_{\text{BUBBLE}} = \underline{\hspace{2cm}}$ °C

- (b) Calculate the solubility of 1-pentanol in water in terms of mole% when we mix 1.0 lbmol of 1-pentanol with 1.0 lbmol of water at 14.7 psia and 100 °F. Use UNIQUAC as the property method.

Answer: Solubility (mol%) of 1-pentanol in water = $\underline{\hspace{2cm}}$ mol%

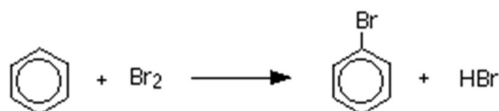
- (c) Determine the solubility in ppm-mole of argon gas in water when we mix 1.0 lbmol of argon with 10.0 lbmol of water at 50 °F and 14.7 psia. Use IDEAL with Henry's Law as the property method.

Answer: Solubility of argon in water = $\underline{\hspace{2cm}}$ ppm (mole)

- (d) Determine the temperature in °C at which a mixture of 20 mol% acetone, 30 mol% ethanol, and 50 mol% water at 1.01325 bar gives rise to a vapor stream with 50 mol% of acetone. Use NRTL-RK as the property method.

Answer: $T = \underline{\hspace{2cm}}$ °C

- (e) The reaction between benzene and bromine in the presence of either aluminium bromide or iron gives bromobenzene as follows.

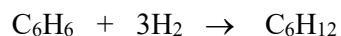


Calculate the heat of reaction ΔH_{rxn} of this gas-phase reaction at 200°C and 1 bar, based on one gmole of each reactant and assuming 100% conversion. Determine if the reaction is endothermic or exothermic. Use PENG-ROB as the property method.

Answer: $\Delta H_{rxn} =$ _____ cal/gmol (Circle one: endothermic or exothermic)

20. Simulation of a Cyclohexane Production Process

The process shown in the figure below (Figure 7) to produce cyclohexane by hydrogenation of benzene is to be simulated using ASPEN Plus (Your A+ flowsheet must use the same stream IDs and block IDs as shown in the figure.) Fresh benzene and make-up hydrogen are mixed with recycle hydrogen from the process and fed to a fixed-bed catalytic reactor, in which the following reaction occurs:



The heat of reaction for this highly exothermic reaction is removed by cooling and maintaining an isothermal temperature inside the reactor. The reactor effluent is cooled inside a feed pre-heater, resulting in a mixed phase which is separated into vapor and liquid inside a flash vessel. Most of the vapor phase which contains light gases and unreacted hydrogen from the flash is recycled, while a small fraction is purged to avoid accumulation of these light gases. The liquid phase is fed to a distillation column to separate cyclohexane as a product in the bottom stream.

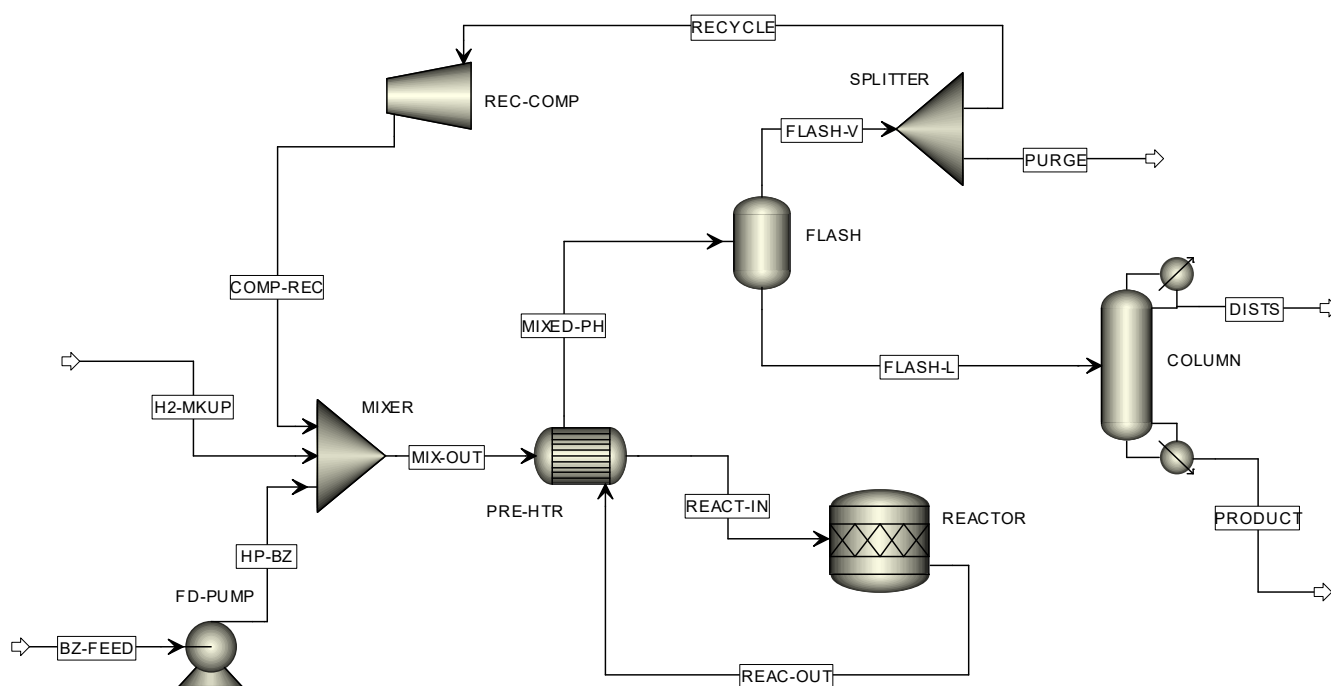


Figure 7: PFD of Cyclohexane Production Process

The following data and operating conditions are available:

Feed streams:

Composition (mole fractions)	Fresh Benzene	Make-up Hydrogen
Hydrogen	0.0	0.975
Nitrogen	0.0	0.005
Methane	0.0	0.02
Benzene	1.0	0.0
Total Flow (lbmol/hr)	100.0	310.0
Temperature (°F)	100.0	120.0
Pressure (psia)	15.0	300.0

Feed Pump:

Outlet pressure (psia) 300

Feed Preheater:

Cold-side outlet temperature (°F) 400
Pressure drop (psi) 10
(both hot and cold sides)

Reactor:

Reaction: $C_6H_6 + 3H_2 \rightarrow C_6H_{12}$
Conversion: 98.0 percent conversion of benzene in inlet
Outlet temperature (°F) 500
Pressure drop (psi) 20

Flash:

Heat loss Negligible
Pressure drop Negligible

Purge:

Purge rate A small fraction of vapor from flash

Recycle Compressor:

Isentropic
Outlet pressure (psia) 300

Stabilizer:

Reflux ratio 1.2 times RR_{min}
Pressure See explanations below
Cyclohexane recovery in bottoms 99.99%
Methane recovery in distillates 99.99%
Condenser Partial with all vapor distillate

Note that the operating pressures in the top and bottom of the column have been empirically correlated to some column feed parameters as follows:

$$P_{TOP} \text{ (in psia)} = 3900 T^{1/2} [Bz][H_2]$$

$$P_{\text{BOT}} (\text{in psia}) = P_{\text{TOP}} - 10$$

where T is the column inlet temperature in °F and $[Bz]$ and $[H_2]$ are the mass concentrations (lbm/ft³) of benzene and hydrogen in the column inlet, respectively.

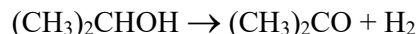
To maintain a high conversion in the reactor, it is also desirable to maintain a molar ratio of 3.5 between hydrogen and benzene that flow into the reactor. This is achieved by varying the purge rate. Use PENG-ROB as the property method in your simulation.

Notes: There are two tear streams in this flowsheet which will not converge if you use the default convergence method of Wegstein. Instead, you must use Broyden by following the steps below:

1. Click the Convergence Folder, and then click the Convergence Subfolder.
2. Click the New button in the Convergence Menu.
3. Select Broyden as the convergence algorithm.
4. Go to Tear Streams Tab and specify COMP-REC and REAC-OUT as the tear streams.
5. Go to Parameters Tab and increase the Maximum Flowsheet Evaluations from 30 iterations to 50 iterations.

21. Simulating an Acetone Production Process

A process to produce acetone by dehydrogenation of isopropyl alcohol (IPA) is to be simulated using ASPEN Plus (Your A+ flowsheet must use the same stream IDs and block IDs as shown in the figure given for the process below.) Fresh IPA with a small amount of water is fed to a preheater and then to a continuous stirred tank reactor in which the following endothermic reaction occurs:



A flash vessel is used to purge the hydrogen product from the reactor effluent, while the liquid goes into a distillation column which separates out acetone as a product in the overhead. A second distillation column is required to separate water from unreacted IPA so that the alcohol can be recycled back to the reactor via a high-pressure pump.

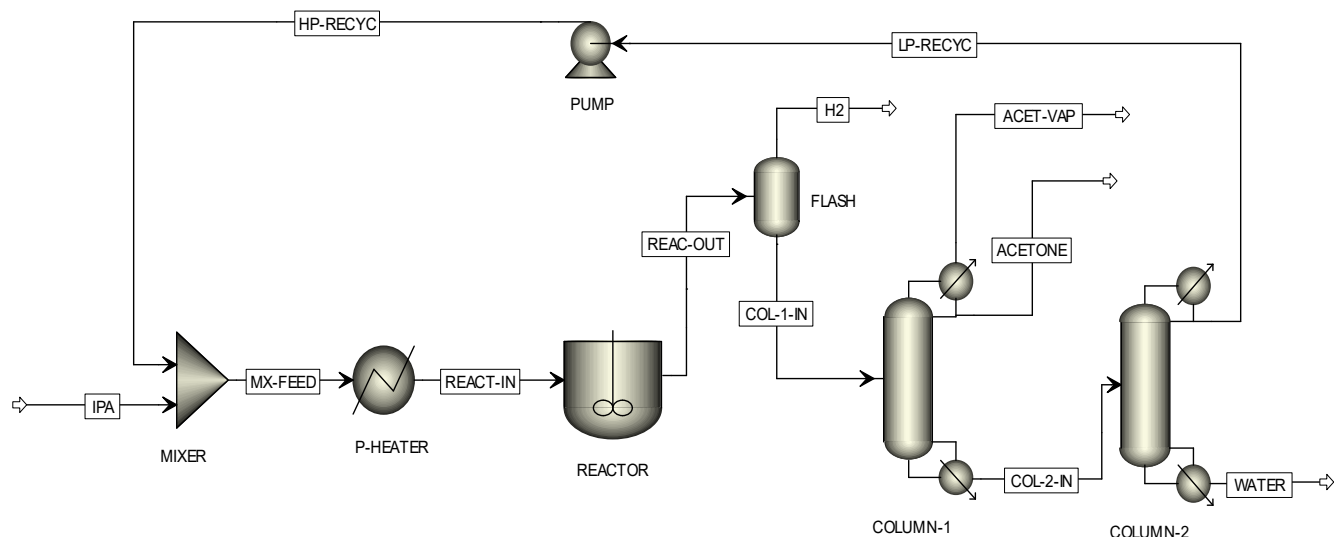


Figure 8: PFD of Acetone Production Process

The following data and operating conditions are available:

Feed stream:

Composition (mole fractions)	
IPA	0.85
Water	0.15

Total Flow (lbmol/hr)	500.0
Temperature (°F)	100.0
Pressure (psia)	30.0

Recycle Pump:

Outlet pressure (psia)	30.0
------------------------	------

Feed Preheater:

Outlet temperature (°F)	550.0
Pressure drop (psi)	3.0

Reactor:

Reactor type	Adiabatic CSTR
Reaction (gas phase)	$(CH_3)_2CHOH \rightarrow (CH_3)_2CO + H_2$
Reactor volume (ft ³)	2500
Phase calculations	Vapor-liquid (because the reaction is endothermic and may result in some condensation)

Kinetics: 1st-order power-law reaction

$$r_{IPA} = 5.25 \times 10^5 e^{-15000/RT} [(CH_3)_2CHOH]$$

where E is in the unit of Btu/lbmol.

Pressure drop (psi), DP

Based on the following empirical correlation

$$DP = \frac{2.85 \times 10^6 \phi^{3/2} x_{ACETONE}^2}{T}$$

Stream REAC-IN { where ϕ = mass-density (lbm/ft³)
 $x_{ACETONE}$ = mole fraction of acetone
 T = temperature

Flash:

Heat loss	Negligible
Pressure drop	Negligible

Column-1 (rigorous model):

Number of stages	50
Feed tray location	25
Reflux ratio (molar basis)	3.0
Distillate to feed ratio (mole basis)	0.60
Pressure in condenser (psia)	15.0

Pressure in reboiler (psia)	16.0
Condenser	Partial with both vapor and liquid distillates
Design target	Loss of acetone from the column as vapor distillate is limited to exactly 10 lbmol/hr.
<u>Column-2</u> (rigorous model):	
Number of stages	30
Feed tray location	15
Reflux ratio (molar basis)	3.0
Pressure in condenser (psia)	12.0
Pressure in reboiler (psia)	13.0
Condenser	Total
Design target	Concentration of IPA in the wastewater stream (Stream WATER) must be limited to 1.0 mole%

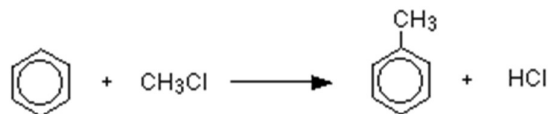
Use NRTL-RK as the property method in your simulation while declaring hydrogen as Henry's Law component. The reason why NRTL-RK must be used is that IPA, water, and acetone form a highly nonideal solution. In fact, IPA and water form an azeotrope at 31.7 mol% IPA, but luckily the water concentration in Stream COL-2-IN with lots of acetone is higher than this number so we are able to separate water to very high purity.

To receive full credit for this problem, you must converge your model with a Reset.

Notes: To converge this flowsheet and obtain a correct solution, correct property parameters must be used. Be sure to visit Methods → Parameters → Binary Interaction → NRTL-1 menu and see that 3 pairs of binary interaction parameters are retrieved from APV140 VLE-IG Databank. More importantly, make sure that you visit HENRY-1 menu too and select all 3 databanks (APV140 BINARY, APV140 ENRTL-RK APV140 HENRY-AP) in the Databanks sheet so that Henry's Law constants between H₂-water and H₂-acetone are retrieved as well.

22. Solving a Highly Constrained Toluene Production Problem

Commercial-grade toluene can be produced by Friedel-Crafts alkylation of benzene, which reacts with methyl-chloride (aka chloromethane) in the presence of aluminum chloride as a catalyst, according to the following gas-phase reaction:



For the purpose of this simulation, we will assume that only monosubstitution occurs and no further methyl groups are substituted around the ring. A basic process flow diagram of the toluene production process is shown below.

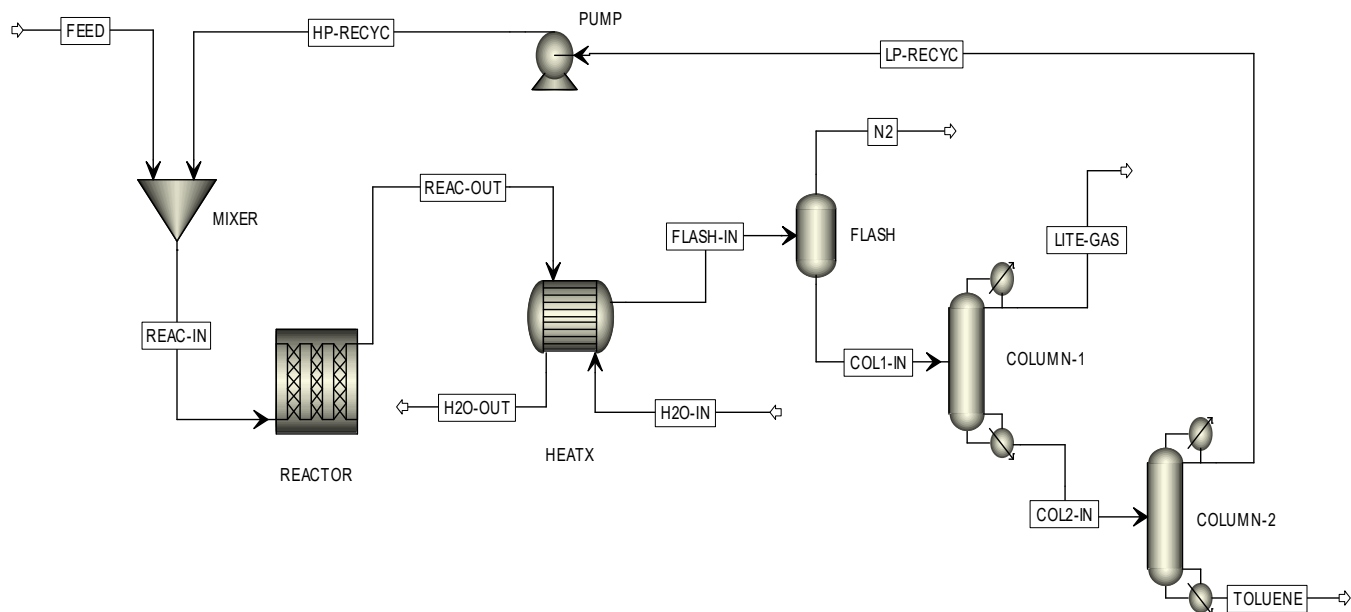


Figure 9: PFD of Toluene Production Process

The following data are known about the process:

1. The temperature of the process feed which contains the two reactants is 100 °F and its pressure is 20 psia. The feed composition is: 48% benzene, 48% methyl-chloride, and 4% nitrogen (all molar basis).
2. The plug flow reactor operates adiabatically and has a diameter of 4 ft and a length-to-diameter ratio that is larger than 5. The kinetics for the toluene reaction follows the power-law expression and is given as:

$$r_{\text{toluene}} = k C_{\text{chloromethane}} C_{\text{benzene}}$$

$$k = 1.25 \times 10^5 \exp\left(\frac{-9000}{RT}\right)$$

where the unit of the activation energy is Btu/lbmol and C_i is molar concentration. The conversion of the toluene reaction is maintained at 75% based on the reactant benzene.

3. The hot effluent from the plug flow reactor is cooled to 80 °F inside a heat exchanger by cooling water. Assume a pressure drop of 1 psia in both hot and cold sides of the heat exchanger.
4. The cooling water used for the heat exchanger has an inlet temperature of 50 °F with a pressure of 14.7 psia. The discharge temperature of this cooling water must be 100 °F because of environmental regulations.
5. An adiabatic flash vessel is used to remove most of the nitrogen in the process stream. Assume negligible pressure drop in this vessel.
6. The first column (COLUMN-1) recovers 99.9 mol% of methyl-chloride in the overhead distillate and 99.9 mol% of benzene in the bottom stream. The column operates at 2 times the minimum reflux ratio and has a partial-vapor-liquid condenser with a very high vapor fraction. The top and bottom pressure of the column are 14.7 psia and 15 psia, respectively. Use a short-cut model for this column.

7. The second column (COLUMN-2) recovers 95 mol% of benzene in the overhead distillate and 95 mol% of toluene in the bottom stream. The column operates at 1.5 times the minimum reflux ratio and has a total condenser. The top and bottom pressure of the column are 10 psia and 11 psia, respectively. Use a short-cut model for this column.
8. The discharge pressure of the recycle pump is 20 psia.
9. The temperature of the overhead distillate (LITE-GAS) from COLUMN-1 is -60°F .
10. The bottom stream from the second column is the product stream whose total flow rate is maintained at 500 lbmol/hr, which is the production capacity of this process.

Use ASPEN Plus to simulate this toluene production process. You must use the same block IDs and stream IDs as given in the figure. For properties, use PENG-ROB except for cooling water in which case you should use STEAMNBS. To receive full credit for this problem, you must converge your model with a reset.

Hint: Try to converge the base-case model without design-specs first. Then, slowly add a design-spec one at a time. Whether you are able to converge this problem depends on the initial guesses and the range of the manipulated variables in the design-specs.

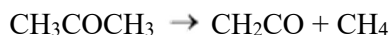
Answer the following questions:

1. Total flow rate of Stream FEED = _____ lbmol/hr
2. Flow rate of cooling water = _____ lbmol/hr
3. Reactor length = _____ feet
4. Vapor fraction in Stream LITE-GAS = _____
5. Purity of toluene in the product stream TOLUENE = _____ mole%

23. Solving a Highly Constrained Acetic-Anhydride Production Problem

Acetic-anhydride is an important chemical in the manufacture of cellulose acetate for films and plastic goods. Acetic-anhydride can be produced by reacting ketene with acetic-acid in a reactor, which cracks acetone into ketene and methane. Acetic-anhydride can in turn be produced by reacting ketene with acetic-acid. The complete process flow diagram is given below in Figure 10.

A flow of 100 gmol/min of pure acetone at 600°C and 1.5 atm is first fed into a plug flow reactor with a 0.5-m diameter which cracks acetone into ketene and methane according to the following reaction.



This reaction is endothermic, so the reactor temperature is maintained at 150°C and there is negligible pressure drop across the reactor. The reaction obeys the power-law expression as given by:

$$r_{\text{ketene}} = 1.0 \times 10^{10} e^{-20 \left[\frac{\text{cal}}{\text{gmol}} \right] / RT} [\text{CH}_3\text{COCH}_3]$$

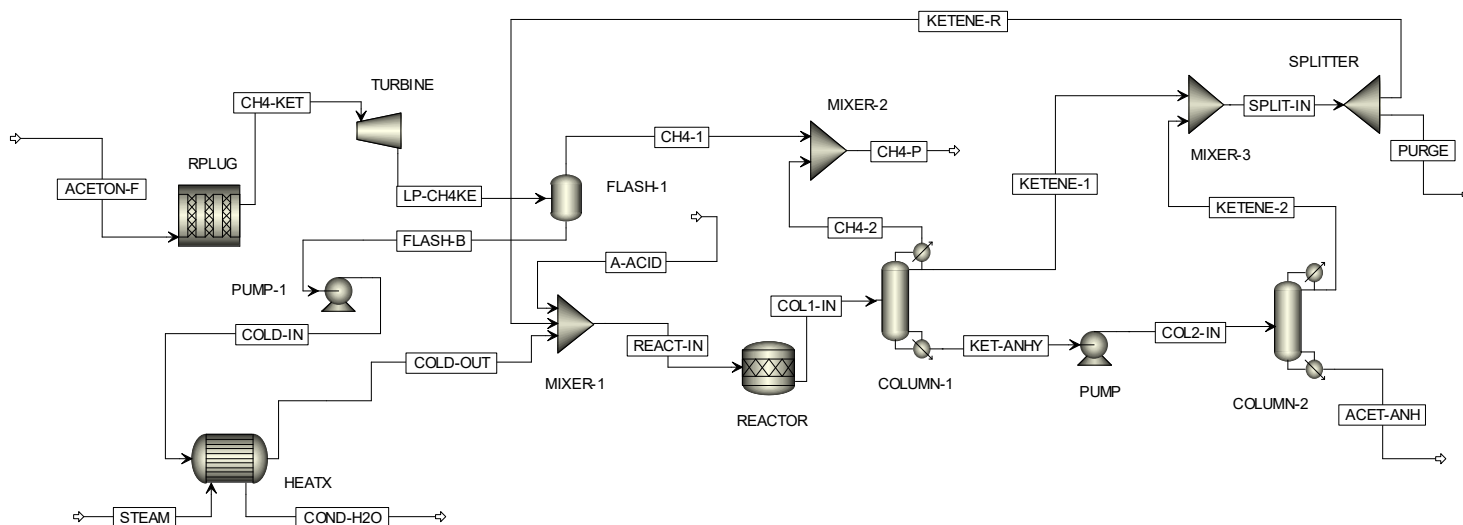
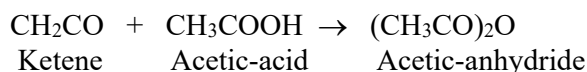


Figure 10: PFD of Acetic-Anhydride Production Process

The reactor effluent then goes through an expander (an isentropic turbine) to drop the pressure to near vacuum of 0.1 atm. The cooled gas mixture of methane and ketene enters a cryogenic flash vessel with negligible pressure drop to separate methane and ketene. The subzero liquid ketene goes through a pump to bring the pressure back up to 1.6 atm and then enters a heat exchanger in which high-pressure saturated steam at 10 atm is used to heat the stream to 100 °C. The resulting ketene vapor stream will then be combined with a fresh acetic-acid feed and a recycle stream before entering another reactor which operates adiabatically at 1.5 atm where the following reaction occurs. This reaction conversion is 95% based on acetic-acid.



On the other hand, pure acetic-acid at 80 °C and 1.5 atm is fed into the process. In the separation process, there are two distillation columns – one at low pressure and one at high pressure. A pump between the two columns is used to boost the pressure from the bottom of the low-pressure column to 6 atm. The first and low-pressure column is used to separate the remaining methane and some ketene from acetone and acetic-anhydride. The high-pressure column is then used to separate out acetic-anhydride as the bottom product. Unreacted ketenes from the two columns are combined and recycled back to the second reactor. To keep the ketene flow in the recycle at a manageable level, a flow splitter is used to purge some ketene and acetone.

The two columns consist of the following operating parameters:

	<u>LP-Column</u>	<u>HP-Column</u>
Number of stages	20	12
Top pressure	0.5 atm	5 atm
Bottom pressure	0.55 atm	5.1 atm
Condenser	Partial (Mole-RDV = 0.02)	Total
Feed tray	10	6
Reflux ratio	3.0 (mole)	3.0 (mole)
Distillate to feed ratio	0.75	> 0.50

The following additional information is also known about the process:

1. The desired flow rate of the product stream (Stream ACET-ANH) is 35.0 gmol/min with a desired purity of 99.5 mol%.
2. The reaction conversion of acetone in the plug flow reactor is 95% on a molar basis.
3. The hot stream in the heat exchanger leaves as saturated water. Assume negligible pressure drop in both the tube and shell side.
4. Methane (Stream CH₄-P) produced in the plug flow reactor can be sold as a by-product, but its purity must be 95.0 mol%.
5. To keep the ketene flow in the recycle stream at a manageable level, the molar ratio of ketene in the KETENE-R recycle stream and acetic-acid in the A-ACID feed stream must be kept at 15.0.

For properties, use NRTL-HOC (because of the presence of acetic-acid). You will notice that not all binary interaction parameters in the NRTL model are available from the A+ databanks. First, select all databanks (don't use default) when looking at the NRTL binary interaction parameter menu. Second, make sure you check "Estimate using UNIFAC" to ask A+ to estimate the NRTL values of the missing pairs.

Answer the following questions:

1. Steam flow rate = _____ gmol/min
2. Acetic-acid feed flow rate = _____ gmol/min
3. Flash temperature = _____ °C
4. Splitter purge fraction = _____
5. Plug flow reactor length = _____ m
6. High-pressure column D/F = _____

Section 5

Physical Properties in A+

24. Quick Property Analysis, I

The following binary systems are known to form homogeneous azeotropes at atmospheric pressure. This means that any solution containing the 2 components can be continuously rectified to give at best mixtures at the azeotropic composition (and not beyond).

<u>Component A</u>	<u>Component B</u>	<u>Mole% A</u>	<u>Temperature</u>
Acetonitrile	Water	69.26	76.5 °C
Ethanol	Butyl-amine	60.40	82.2 °C
Acetic acid	Pyridine	58.50	139.7 °C

You've been asked to study the separation of these binary mixtures. Obviously, the first thing you need to find out is whether ASPEN Plus can predict the azeotrope using one of its property models and binary parameters retrieved from the databanks.

- Use the UNIQ-RK method. What are the values of the retrieved binary parameters in °C for the 3 binary systems? For what range of temperatures are these values applicable?
- Briefly describe a *minimum-boiling* azeotrope and a *maximum-boiling* azeotrope, and classify each binary system.
- In this case, UNIQ-RK is not good for characterizing the properties of the acetic-acid and pyridine mixture. Why (state 2 reasons)? Propose an alternate property method better suited to predict the azeotrope for this system.
- Using the Quick Property Analysis feature in ASPEN Plus, generate a plot of T - xy diagram and x - y for each binary system. From the diagrams, determine the azeotropic temperatures (in °C) and compositions to your best ability, and calculate the relative errors when compared to the given data. Use the following property methods for each system:

<u>Binary System</u>	<u>Property Method</u>
Acetonitrile-Water	UNIQ-RK
Ethanol-Butylamine	UNIQ-RK
Acetic-acid-Pyridine	The method from Part (c)

Can you explain the large errors in the ethanol-butyl-amine mixture?

- We want to find out the relative volatility of all 6 components. Use the Quick Property Analysis to generate a plot of vapor pressure (in psia) as a function of temperature (from 0 °C to 100 °C).

25. Quick Property Analysis, II

The following binary systems are known to form homogeneous azeotropes at atmospheric pressure. This means that any solution containing the 2 components can be continuously rectified to give at best mixtures at the azeotropic composition (and not beyond).

<u>Component A</u>	<u>Component B</u>	<u>Mole% A</u>	<u>Temperature</u>
Chloroform	Ethanol	84.0	59.3°C
Water	Formic acid	43.3	107.1°C
Isobutyl alcohol	α -pinene	96.5	107.9°C

You've been asked to study the separation of these binary mixtures. Obviously, the first thing you need to find out is whether ASPEN Plus can predict the azeotrope using one of its property models and binary parameters retrieved from the databanks.

- Use the UNIQU-RK method. What are the values of the retrieved binary parameters in °C for the 3 binary systems from Databank APV140 VLE-RK? For what range of temperatures are these values applicable?
- Classify each binary system as either maximum-boiling-point or minimum-boiling-point azeotrope.
- In this case, UNIQU-RK is not good for characterizing the properties of the water-acid and alcohol-pinene pairs (why?). Propose 2 alternate property methods better suited to predict the azeotrope for each system.
- Using the Quick Property Analysis feature in ASPEN Plus, generate a plot of T - xy diagram and x - y for each binary system. From the diagrams, determine the azeotropic temperatures (in °C) and compositions to your best ability, and calculate the relative errors when compared to the given data. Use the following property methods for each system:

<u>Binary System</u>	<u>Property Method</u>
Chloroform-Ethanol	UNIQU-RK
Water-Formic acid	1 method from Part (c)
Isobutyl alcohol-pinene	1 method from Part (c)

- We like to find out the relative volatility of all 6 components. Use the Quick Property Analysis to generate a plot of vapor pressure (in psia) as a function of temperature (from 0 °C to 100 °C).

26. Choosing Appropriate Property Methods, I

Consider the following mixtures at some given operating conditions. Choose an appropriate property method in ASPEN PLUS to calculate a desired property using any of the property features we learned such as Quick Property Analysis, Prop-Sets, and unit operation modules. Note that there is more than one choice but you are to pick one that gives high, if not the best, accuracy. There is no need to save your work, except for Problem (h). Just write down the answers in the blank spaces below and tick if your property method uses Henry's Law.

- Activity coefficient γ of ethanol in an equimolar liquid solution of ethanol and cyclohexane at 60 °F and 20 psia.

Property Method: _____ ☐ With ☐ Without Henry's Law

Activity coefficient of ethanol = _____

- (b) Critical temperature of a mixture with a composition of 30 mol% benzene, 30 mol% cyclohexane, 30 mol% *n*-hexane, and 10 mol% N₂.

Property Method: _____ O With O Without Henry's Law

Critical temperature of the mixture = _____ °C

- (c) Vapor fugacity coefficient ϕ^V of formic-acid in an equimolar mixture of formic-acid and water at 20 psia in which 50 mol% of the mixture is vapor.

Property Method: _____ O With O Without Henry's Law

Vapor fugacity coefficient of formic-acid = _____

- (d) Which gas has higher solubility in the liquid solution and by how much: 1 lbmol of helium or 1 lbmol of argon in a liquid solution of 10 lbmol of ethanol at 70 °F and 14.7 psia? (Special note: you are not allowed to pick an equation of state for this problem).

Property Method: _____ O With O Without Henry's Law

Gas with higher solubility is _____ and by more than _____ ppm (mole)

- (e) Energy required to vaporize 1 gmol (i.e. heat of vaporization) of a saturated liquid containing 40 mol% aniline, 40 mol% acetol, and 20 mol% cyclohexene at 1 bar.

Property Method: _____ O With O Without Henry's Law

Energy required = _____ cal/gmol

- (f) Vapor compressibility factor *Z* of a mixture containing 40 mol% formaldehyde, 40 mol% chloroform, and 20 mol% acetylene at 150 °C and 20 bar.

Property Method: _____ O With O Without Henry's Law

Vapor compressibility factor = _____

- (g) Solubility of water in the organic phase in a mixture containing 45 mol% water, 45 mol% 1-methylcyclohexanol, and 10 mol% O₂ at 20 °C and 1 bar.

Property Method: _____ O With O Without Henry's Law

Solubility of water = _____ mol%

- (h) What temperature increase is required to produce a vapor stream containing 30 mol% acetone from a one-lbmole saturated liquid mixture with an overall composition of 40 mol% water, 40 mol% benzene, and 20 mol% acetone at 14.7 psia, assuming there is no pressure change in the vaporization? (You must save this problem and email the file to me at the end of the exam.)

Property Method: _____ O With O Without Henry's Law

Temperature increase = _____ °F

27. Choosing Appropriate Property Methods, II

Consider the following mixtures at some given operating conditions. Choose an appropriate property method in ASPEN Plus to calculate a desired property using any of the property features we learned such as Quick Property Analysis, Prop-Sets, and unit operation modules. Note that there is more than one choice but you are to pick one that gives high, if not best, accuracy. There is no need to save your work. Just write down the answers in the blank spaces below and tick if your property method uses Henry's Law.

- (a) Which of the following 3 components has the lowest volatility at $T = 80^\circ\text{F}$: cyclobutane, 1,2-butadiene, or ethyl-chloride?

Property Method: _____ O With O Without Henry's Law

Component with the lowest volatility = _____

- (b) The K-value of ethanol in a binary mixed-phase (30 mole% vapor) mixture of 50 mole% water and 50 mole% ethanol at 200 psia.

Property Method: _____ O With O Without Henry's Law

K-value of ethanol = _____

- (c) Solubility (mole ppm) of CO_2 in water in a mixture of 20 mole% CO_2 and 80 mole% water at 1 atm and 80°C .

Property Method: _____ O With O Without Henry's Law

Solubility of CO_2 = _____ ppm

- (d) Solubilities (mole%) of acetone in the aqueous phase and alcohol phase of a mixture of 20 mole% *n*-butanol, 20 mole% acetone, and 60 mole% water at 14.7 psia and 50°F .

Property Method: _____ O With O Without Henry's Law

Solubility in aqueous phase = _____ %; Solubility in alcohol phase = _____ %

- (e) Heat of mixing (excess enthalpy) when 1 lbmol of acetol is mixed with 1 lbmol of acetonitrile at 20 psia and 100°F .

Property Method: _____ O With O Without Henry's Law

Heat of mixing = _____ Btu/lbmol

- (f) Vapor fugacity coefficient of acetic-acid in a vapor-liquid mixture (with 30 mole% vapor) containing 30 mole% acetic-acid, 30 mole% acetone, and 40 mole% ethanol at 20 psia.

Property Method: _____ O With O Without Henry's Law

Vapor fugacity coefficient of acid = _____

- (g) Bubble-point pressure of a mixture of 30 mole% *n*-pentane, 30 mole% benzene, and 40 mole% cyclohexane at 30 °C.

Property Method: _____ O With O Without Henry's Law

P_{BUBBLE} = _____ bar

28. Choosing Appropriate Property Methods, III

Consider the following mixtures at some given operating conditions. Choose an appropriate property method in ASPEN Plus to calculate a desired property using any of the property features we learned such as Quick Property Analysis, Prop-Sets, and unit operation modules. Note that there is more than one choice but you are to pick one that gives high, if not best, accuracy. There is no need to save your work. Just write down the answers in the blank spaces below and tick if your property method uses Henry's Law.

- (a) Solubility (mole ppm) of N₂ in a two-phased mixture of 20 mole% N₂, 30 mole% water, 20 mole% methanol, and 30 mole% acetone at 1 atm and 30 °C.

Property Method: _____ O With O Without Henry's Law

Solubility of N₂ = _____ ppm

- (b) Solubility (mass fraction) of water in the organic phase of a two-liquid mixture with 50 mass% isoheptanol and 50 mass% water at 1 atm and 20 °C.

Property Method: _____ O With O Without Henry's Law

Solubility of water = _____

- (c) Heat of mixing of a mixture of 30 mole% benzene, 30 mole% toluene, and 40 mole% para-xylene at 20 atm and 10 °C.

Property Method: _____ O With O Without Henry's Law

Heat of mixing = _____ Btu/lbmol

- (d) Liquid fugacity coefficient of ethanol in a liquid mixture of 50 mole% ethanol and 20 mole% propane, and 30 mole% acetylene at 50 atm and 25 °C.

Property Method: _____ O With O Without Henry's Law

Liquid fugacity coefficient = _____

(e) Heat of vaporization of pure water at 80 °C.

Property Method: _____ O With O Without Henry's Law

Heat of vaporization = _____ Btu/lbmol

(f) Vapor enthalpy of a 2-phase mixture of 20 mole% ammonia, 30 mole% benzoic-acid, and 50 mole% *n*-butane at 1 atm and vapor fraction = 0.3.

Property Method: _____ O With O Without Henry's Law

Vapor enthalpy = _____ Btu/lbmol

(g) Which of the following 5 components has the 3rd highest volatility (i.e. 2 components are more volatile and 2 components are less volatile) at T = 100 °F: 1-hexene, 1,4-hexadiene, methanol, chloroform, and 3-methylcyclopentene?

Property Method: _____ O With O Without Henry's Law

Component with the 3rd highest volatility = _____

(h) Solubility (mole ppm) of O₂ in a two-phased mixture of 10 mole% O₂, 30 mole% ethanol, 30 mole% 1-propanol, and 30 mole% *n*-butanol at 14.7 psia and 100 °F.

Property Method: _____ O With O Without Henry's Law

Solubility of O₂ = _____ ppm

29. Waste Stream Purification Using Multiple Property Methods

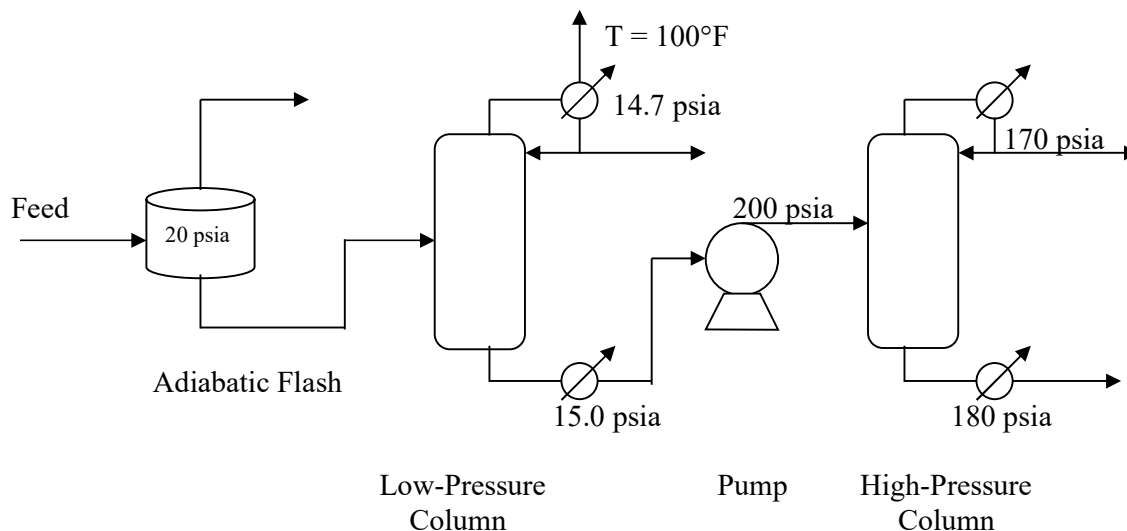
A waste stream contains some light gases, vinyl-chloride, acetone, formic acid, and water with the following composition:

Pressure = 50 psia, Temperature = 150°F

Total flow rate: 1000 lbmol/hr

CO ₂	5.0	mole%	Acetic acid	20.0
H ₂ S	10.0		Water	27.5
Vinyl-chloride	7.5		Acetone	30.0

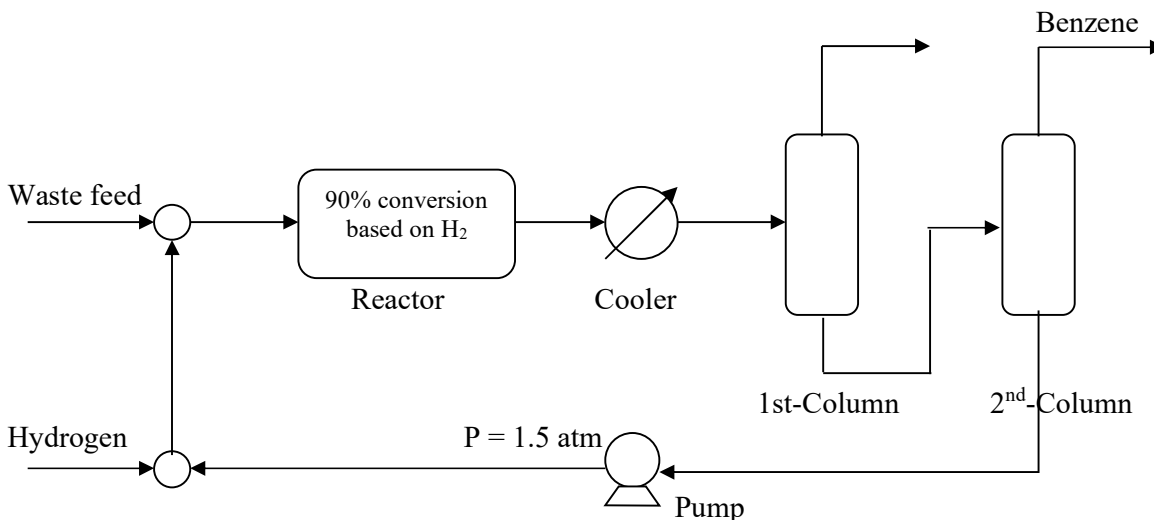
Light gases are first removed in a flash. The remaining heavier components are then separated in the first distillation column. The first column separates acetone from the acid and water. The bottom from the first column is fed to a second column which separates acetic acid from water. A process flow diagram and operating conditions are shown in the following figure:



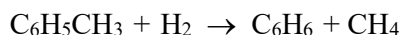
- (a) For the high-pressure section of the process (pump + HP-column), the SR-POLAR property method is appropriate (why?). For the low-pressure section, propose as many suitable property methods in ASPEN Plus as you can.
- (b) Simulate the given process with ASPEN Plus. Use NRTL-HOC for the low-pressure section and SR-POLAR for the high-pressure section. Be sure to estimate all missing parameters in the NRTL model. The LP-column has a partial condenser, and both columns operate at 1.5 times the minimum reflux ratio. The mole-recovery for heavy keys and light keys in both columns are 99%.

30. Toluene-Benzene Recovery Process with Multiple Property Methods

A waste stream containing a mixture of acetone and toluene is to be purified in order to recover benzene as a product from reacting toluene with hydrogen. The recovery process is shown in the figure below.



Hydrogen reacts with toluene at elevated temperature by splitting the methyl group from toluene to form benzene and methane according to the stoichiometry:



The two fresh feeds enter the process at 50°C and 1.5 atm and contain the following compositions:

	<u>Hydrogen Feed</u>	<u>Waste Feed</u>
Hydrogen	50 gmol/min	-----
Acetone	-----	30 gmol/min
Toluene	-----	48 gmol/min

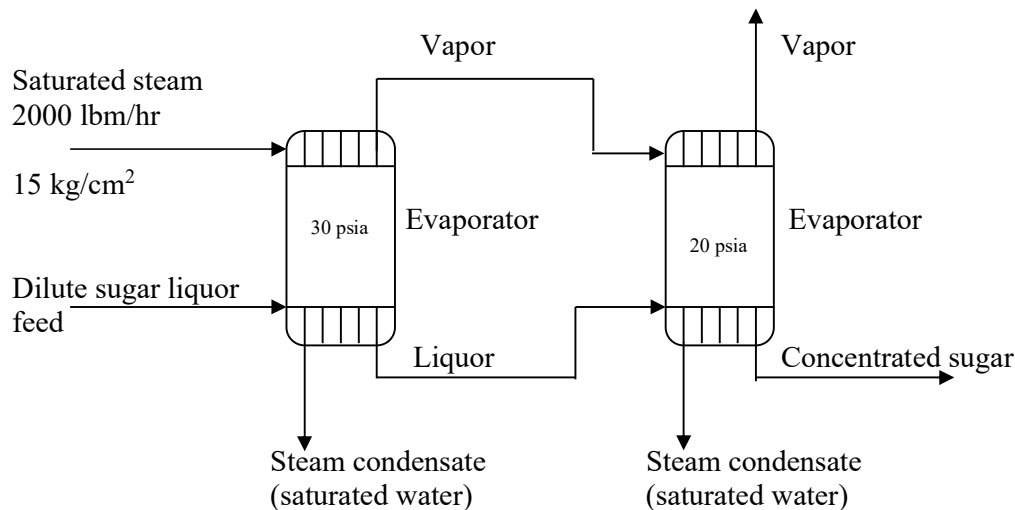
The reactor operates at 300°C with a pressure drop of 0.2 atm. The cooler reduces the reactor outlet stream to 100°C (assume negligible ΔP). The first column separates the light gases and acetone through the overhead, while the second column purifies benzene and toluene. The following data are available on the 2 distillation columns (rigorous):

	<u>1st-Column</u>	<u>2nd-Column</u>
Number of stages	20	30
Top pressure	1.0 atm	0.8 atm
Bottom pressure	1.2 atm	1.0 atm
Condenser	10°C	Total
Feed tray	10	15
Reflux ratio	5.0 (mole)	-----
Distillate to feed ratio	0.55	-----
Reflux rate	-----	200 gmol/min
Bottom flow	-----	20 gmol/min

- Choosing two appropriate property methods, one for the hydrogen mixer, 2nd-Column, and the pump, and the other for the rest of the flowsheet, simulate the above process using ASPEN Plus. If you choose a gamma model, be sure to estimate all missing interaction parameters. **Hints:** There are many combinations of property methods that will converge this flowsheet. Also, methane is not supercritical at the given operating conditions.
- It is desirable to maintain the molar ratio of toluene to hydrogen in the reactor feed at exactly 1.2. Set up a design specification in ASPEN PLUS to vary the fresh feed flow of hydrogen in order to satisfy this ratio constraint.

31. Double-Effect Evaporator

We wish to use ASPEN Plus to simulate a process in which sugar is being concentrated in a double-effect evaporator with forward feed as shown in the figure below.



The process feed data are as follows:

Feed: Temp = 100 °F Pres = 30 psia
 Sugar 300.0 lbm/hr (pounds mass per hour)
 Water 3000.0 lbm/hr

- For simplicity, the IDEAL property method will be used for the entire flowsheet including the hot and cold sides of the evaporators. Treating sugar as a non-databank component, write down all of its required parameters in IDEAL.
- Simulate the double-effect evaporator. Use a countercurrent HEATX block to model each evaporator. The operating pressure in the first evaporator is 30 psia while that of the second evaporator is 20 psia. This pressure difference provides the driving force for evaporation using the vapor from the first evaporator as the heating medium for the second evaporator. Submit a copy of the input summary and process flow diagram from ASPEN Plus for this problem. Hint: Make sure the liquor feed enters each evaporator at the desired operating pressure.

The following data are available for sugar.

Sugar property data:

MW = 342.30	$T_C = 1086 \text{ K}$	$Z_C = 0.227$	$P_C = 2.69 \times 10^6 \text{ N/m}^2$
$T_B = 751 \text{ K}$	$V_C = 0.761 \text{ m}^3$	$\Omega = 0.365256$ (Pitzer acentric factor)	
$DHFORM = -3.6 \times 10^9 \text{ J/kmol}$		$MUP = 8.85459 \times 10^{-25} (\text{J-m}^3)^{1/2}$	
PLXANT coefficients in SI units		Heat of Vaporization (Btu/lbmol)	
<u>Element</u>	<u>Coefficient</u>	<u>Temp (°F)</u>	<u>ΔH^{VAP}</u>
1	67.812	100	38609.6
2	-1.2635×10^4	150	38023.3
3	0.0	200	37436.9
4	0.0	250	36850.6

5	-5.9648	300	36264.2
6	1.9713×10^{-19}	Use Tabpoly to enter the ΔH^{VAP} data	
7	6		

DIPPR ideal gas heat capacity, CPIGDP, coefficients in SI units:

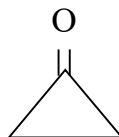
Element	Coefficient
1	1.9847×10^5
2	7.9592×10^5
3	1.2×10^3
4	4.629×10^5
5	5.5677×10^2

Note that you are given more data than needed. If you enter all data or some redundant data, points will be deducted. So enter only the necessary data from Part (a). Watch your mole/mass basis carefully and be sure to use the correct unit sets for all data.

32. Separation of Compound X

Compound X (cyclopropanone), which has the following molecular structure and properties, is to be extracted via a single separation column in a gas processing plant.

Molecular formula: $\text{C}_3\text{H}_4\text{O}$



MW = 56.064 $T_B = 74.12^\circ\text{C}$ $Z_C = 0.214$ $V_B = 77.62 \text{ cc/gmol}$
 $P_C = 58.45 \text{ bar}$ $\text{DHFORM} = -75240.76 \text{ Btu/lbmol}$

Vapor pressure data in ENG units (Use Tabpoly to enter the data):

Temp ($^\circ\text{F}$)	P^{VAP} (psia)	Temp ($^\circ\text{F}$)	P^{VAP} (psia)
0	0.305	105	5.023
30	0.724	120	7.459
60	1.867	135	9.883
75	2.890	150	13.503
90	3.921		

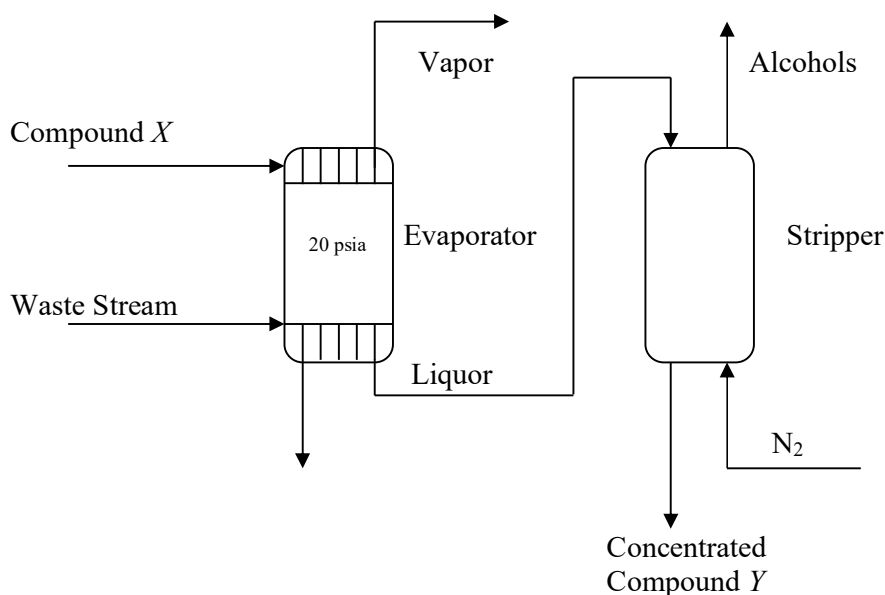
Your job is to simulate this column using RADFRAC and BWR-Lee-Starling equation of state in A+. In particular, we are interested in obtaining certain purity of Compound X in the bottom of the column and its liquid thermal diffusivity.

- Apparently for BWR-LS, not all property data given are required for this equation of state, while some required data are missing and have to be estimated by PCES. Write down the parameters that are redundant and those that are required but are missing.
- You are given the following additional data. Use A+ to simulate the column.

<u>Feed:</u>	Temp = 100 °F	Pres = 20 psia	<u>Column:</u>
H ₂	20	lbmol/hr	Number of stages = 30
H ₂ S	10	lbmol/hr	(including condenser and reboiler)
CH ₄	50	lbmol/hr	Feed tray location = 15
C ₂ H ₆	60	lbmol/hr	Condenser temperature = -50 °F
C ₃ H ₈	100	lbmol/hr	Condenser pressure = 14.7 psia
n-C ₄ H ₁₀	200	lbmol/hr	Reboiler pressure = 15.0 psia
n-C ₅ H ₁₂	100	lbmol/hr	Reflux ratio = 3.0
X	500	lbmol/hr	Purity of X at column bottom = 99 mole%

33. Extracting Compound Y via an Evaporator and a Stripper Using Compound X

A waste stream contains a substantial amount of a valuable organic compound, called Compound Y, which is to be extracted via an evaporator and a stripper as shown in the figure below (Note that the evaporator can be simulated using a combination of HEATX and FLASH2 blocks. The function of the flash block is simply to separate the incoming mixed-phase mixture into a vapor stream and a liquid stream at the same thermodynamic condition as that of the inlet stream.). Instead of hot steam, the evaporator uses a hot stream containing pure Compound X as the heating medium. The liquor from the evaporator is still not sufficiently pure so a stripper is used to strip more alcohols from the liquor using hot nitrogen gas. In this simulation, we will use NRTL-RK except for the hot-side of the evaporator which will use IDEAL.



The following process data are given:

<u>Feed Stream</u>	<u>Composition (lbmol/hr)</u>	<u>Temp (°F)</u>	<u>Pressure (psia)</u>
Compound X	300	350	20
N ₂	10	200	20
Waste Stream	60.0 Y, 20.0 methanol, 15.0 ethanol, and 5.0 N ₂	100	20

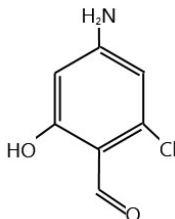
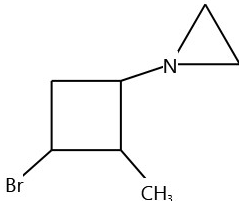
Evaporator:

1. Assume co-current flow when using HEATX.
2. The waste stream is heated to 250 °F.
3. Assume IDEAL property method for the hot-side.
4. Assume negligible pressure drop in both hot and cold sides.
5. Make sure the default constant U value is used.

Stripper:

1. Assume 20 theoretical stages in the column.
2. The top pressure is 15 psia, and the bottom pressure is 16 psia.

Unfortunately, very few property data are known about Compound X and Compound Y . As a result, we will use A+ to estimate all the missing properties of the two compounds before using the software to simulate the purification process. The molecular structures of Compound X and Compound Y and their normal boiling points are shown below.

Compound	Boiling Point (° F)	Structure
Compound X	580	
Compound Y	415	

For Compound X , we will use NIST TDE to estimate its property constants, while those of Compound Y will be estimated using PCES. In addition to their boiling points, the following data are also known about the two compounds, which should be used to enhance the accuracy of NIST TDE and PCES:

Experimental vapor pressure data for Compound X :

Temp (°F)	200	250	300	350	400	450	500	550	600
P^{VAP} (psia)	0.0002	0.0013	0.0066	0.0273	0.0955	0.2910	0.7897	1.9411	4.3832

Experimental heat of vaporization data for Compound Y at 1 atm:

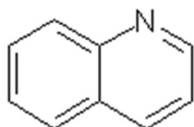
Temp (°F)	200	250	300	320	350	370	400	420	450
ΔH^{VAP} (Btu/lbmol)	19166	17506	15791	15021	13504	12494	10666	9089	5193

Notes: You must follow the following steps when working on this simulation problem:

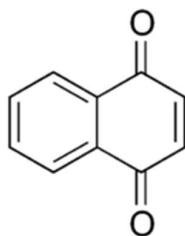
1. Use NIST TDE to estimate the missing properties of Compound *X*, but do not Calculate Bonds of *X* in the Molecular Structure folder since we are not using PCES for this compound.
2. When saving parameters from TDE, notice that TB of *X* was estimated again and stored in TDE-1 under Parameters → Pure Components. This will conflict with the TB you entered and stored under USRDEF. So you should delete the TB value from TDE-1.
3. Use PCES to estimate the missing properties Compound *Y* and do Calculate Bonds. There appears to be a bug in the NIST that prevents TB of Compound *Y* from being input properly when used with PCES. Make sure you check Parameters → Pure Components subfolder and use it to enter this number.
4. Do a property estimation before you add the remaining components and building your flowsheet.
5. After you put together your flowsheet, visit the Estimation → Input form and carry out an “Estimate only the selected parameters” and click “Binary interaction parameters”. The objective here is to estimate the NRTL parameters of the two component pairs, namely *Y*-methanol and *Y*-ethanol, using UNIFAC method in the Binary menu. Do not click “Estimate ...” in the Binary Interaction – NRTL-1 form.
6. Ignore the warnings from PCES and HEATX at the end of the simulation. In this case, it is okay to end your simulation with “Results Available with Warnings”.
7. Finally, to get full credit, you must do a reset before running your model.

34. Separation of Compound *X*, II

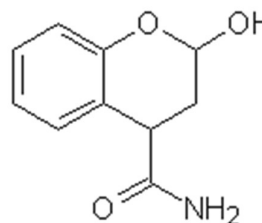
A mixture of hydrogen, quinoline, naphthaquinone, and Compound *X* is to be separated in a single distillation column. Quinoline is found in the A+ databanks, while both naphthaquinone and Compound *X* are not in the A+ databanks. The three chemical components have the following molecular structures:



Quinoline



Naphthaquinone



Compound *X*

We do, however, have the following data on naphthaquinone:

MW = 158.156 T_B = 638.9 °F T_C = 1119.3 °F P_C = 40.14 atm
V_C = 0.4375 m³/kmol Z_C = 0.2440 Ω = 0.570
DHFORM = -37095 kcal/kmol DGFORM = -5436 kcal/kmol
GMSHVL = 2.456 ft³/lbmol
DELTA (solubility parameter at 25 °C) = 126.56 (Btu/ft³)^{1/2}
Heat of vaporization at T_B = 26784.8 Btu/lbmol

CPIG = 31.1 + 0.0635 T - 1.658×10⁻⁵ T² - 6.4708×10⁻¹⁰ T³ in Btu/lbmol-R and T in °F

Vapor pressure data in ENG units (Use Tabpoly to enter the data):

Temp (°F)	P ^{VAP} (psia)	Temp (°F)	P ^{VAP} (psia)
420	0.599	620	11.727
460	1.204	660	18.693
500	2.283	700	28.659
540	4.115	740	42.419
580	7.088	780	60.876

On the other hand, little is known about Compound *X*, except the molecular structure and the following properties. As a result, we will need to use PCES in A+ to estimate all the required and missing parameters.

MW = 193.20

T_B = 821.4 °F

GMSHVL = 1.65 ft³/lbmol

Vapor pressure data in ENG units (Use Data Folder to enter the data):

Temp (°F)	P ^{VAP} (psia)	Temp (°F)	P ^{VAP} (psia)
600	0.478	800	11.116
640	0.982	840	18.550
680	1.921	880	29.772
720	3.588	920	46.105
760	6.434	960	69.145

Your job is to simulate this column using RADFRAC and the GRAYSON property method in A+. In particular, we are interested in obtaining certain purity of Compound *X* in the bottom of the column.

- (a) Apparently for GRAYSON, not all property data given for naphthaquinone are required for this property package. Write down the parameters that are redundant. Note that in Part (b), points will be deducted for entering a redundant parameter into A+.

Redundant parameters for naphthaquinone:

- (b) You are given the following additional data on the column. Use RADFRAC in A+ to simulate the column. The desired product purity of Compound *X* leaving the bottom of the column is 99.5 mole%, while in the partial condenser, we will allow exactly 50 lbmol/hr of quinoline to leave in the vapor distillate. Be sure to enter only the required parameters for naphthaquinone and answer all the questions below.

Feed:

Temp = 500 °F	Pres = 20 psia
H ₂	100 lbmol/hr
Quinoline	300 lbmol/hr
Naphthaquinone	300 lbmol/hr
Compound <i>X</i>	300 lbmol/hr

Column:

Number of stages = 10
(including a partial-V-L condenser
and a kettle-type reboiler)
Feed tray location = 5, above-stage
Condenser pressure = 15.0 psia
Reboiler pressure = 17.0 psia
Reflux ratio = 1.0

35. Property Requirements and PCES, I

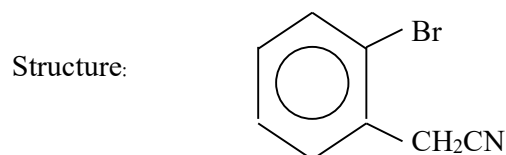
Suppose you want to represent the physical properties of a chemical system consisting of 50 mole% H₂O, 45 mole% 2-bromo phenyl acetonitrile (2-BHA), 3 mole% N₂, and 2 mole% O₂. It was decided that the UNIQUAC activity coefficient model will be used to do all the calculations. Specifically, we will create a new property method (called UNIQ-RKS) which uses the Redlich-Kwong-Soave equation of state for the vapor side (as opposed to just Redlich-Kwong in the built-in UNIQ-RK method) and the UNIQUAC gamma model for the liquid side. ASPEN Plus allows a new property method to be created, but we didn't discuss it because the topic is beyond the scope of the course.

(a) The compound 2-BHA is not in the ASPEN Plus databanks (while the rest of the components are). Determine all the required parameters that are missing from this UNIQ-RKS method whose values need to be estimated or supplied. Be very specific in your answers, i.e. if you list CPIG as required, you must specify for which component. Assume the following:

- (i) No chemical reactions occur in this simulation model.
- (ii) The Free-Water calculation option isn't selected.
- (iii) Prop-sets liquid viscosity and liquid thermal conductivity are requested.

(b) Use the PCES feature to estimate the pure-component properties of 2-BHA that are missing.

From your company laboratory, you obtained the following data for 2-BHA:



Molecular formula: 2-Br-C₆H₄CH₂CN

Molecular weight: 196.05

Normal boiling point: 146.0 °C

Vapor pressure:

T (°C)	Pres(mmHg)
60.0	27.6
80.0	69.0
100.0	156.1
120.0	325.1
140.0	630.7
160.0	1146.7
180.0	1954.5
200.0	3152.8

 (Use TabPoly to enter the data)

T (°C)	Pres(mmHg)
60.0	27.6
80.0	69.0
100.0	156.1
120.0	325.1
140.0	630.7
160.0	1146.7
180.0	1954.5
200.0	3152.8

Export the estimated data to a text file in SI units.

- (c) Using the PCES-estimated values of the CPIG parameter from Part (b) for 2-BHA, compute by hand the value of CPIG (in Btu/lbmol-R) at 500 °F. Repeat the calculation at 32 °F. You may verify your answer with a quick ASPEN Plus run.
- (d) Compute by hand H_v^{IG} (ideal gas enthalpy) of 2-BHA at 500 °F using 25 °C and ideal gas of 2-BHA as the reference state for enthalpy. Also, compute H_L (liquid enthalpy) at 500 °F using the same reference state.
- (e) Is the UNIQU-RKS property method a good choice for representing the properties of this system, assuming low temperature and low pressure of operation? If the answer is yes, please explain why. If the answer is no, please explain why too. In either case, suggest 2 more property methods (system built-in) that can model the properties of this system accurately.

36. *Property Requirements and PCES, II*

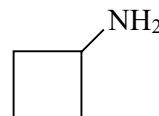
Suppose you want to represent the physical properties of a chemical system consisting of 50 mole% benzene, 45 mole% cyclobutylamine (CBA), 3 mole% N_2 , and 2 mole% O_2 . It was decided that the UNIQUAC activity coefficient model will be used to do all the calculations. Specifically, we will create a new property method (called UNIQU-RKS) which uses the Redlich-Kwong-Soave equation of state for the vapor side (as opposed to just Redlich-Kwong in the built-in UNIQU-RK method) and the UNIQUAC gamma model for the liquid side. ASPEN Plus allows a new property method to be created, but we didn't discuss it because the topic is beyond the scope of the course.

- (a) The compound CBA is not in the ASPEN Plus databanks (while the rest of the components are). Determine all the required parameters that are missing from this UNIQU-RKS method whose values need to be estimated or supplied. Be very specific in your answers, i.e. if you list CPIG as required, you must specify for which component. Assume the following:
 - (i) No chemical reactions occur in this simulation model.
 - (ii) The Free-Water calculation option isn't selected.
 - (iii) Prop-sets liquid viscosity and liquid thermal conductivity are requested.
- (b) Use the PCES feature to estimate the pure-component properties of CBA that are missing.

From your company laboratory, you obtained the following data for CBA:

Cyclobutylamine structure and property data:

Molecular formula: C_4H_9N



$$MW = 71.12 \quad T_B = 81.85 \text{ }^\circ\text{C} \quad V_C = 0.2375 \text{ m}^3/\text{kmol}$$

$$MUP = 5.3569 \times 10^{-25} (\text{J} \cdot \text{m}^3)^{1/2}$$

PLXANT coefficients in ENG units: Heat of Vaporization in J/kmol at 1 atm:

Element	Coefficient	Temp ($^\circ\text{C}$)	ΔH^{VAP}
1	53.30	81.85	3.289×10^7
2	-10701	124.28	2.995×10^7
3	0.0	166.71	2.624×10^7
4	0.0	209.14	2.135×10^7
5	-5.2458	251.58	1.400×10^7
6	3.1307×10^{-19}	Use Tabpoly to enter the ΔH^{VAP} data	
7	6.0		

Watch your mole/mass basis carefully and be sure to use the correct unit sets for all data. Export the estimated data to a text file in SI units.

- (c) Using the PCES-estimated values of the CPIG parameter from Part (b) for CBA, compute by hand H_v^{IG} (ideal gas enthalpy) of CBA at 200 $^\circ\text{F}$ using 25 $^\circ\text{C}$ and ideal gas of CBA as the reference state for enthalpy. Also, compute H_L (liquid enthalpy) at 200 $^\circ\text{F}$ using the same reference state.
- (d) Choose an appropriate property method (built-in) and compute the dew-point temperature of the above mixture at 1 atm. Do the same thing but this time at a pressure of 50 atm.

37. Extractive Distillation, I

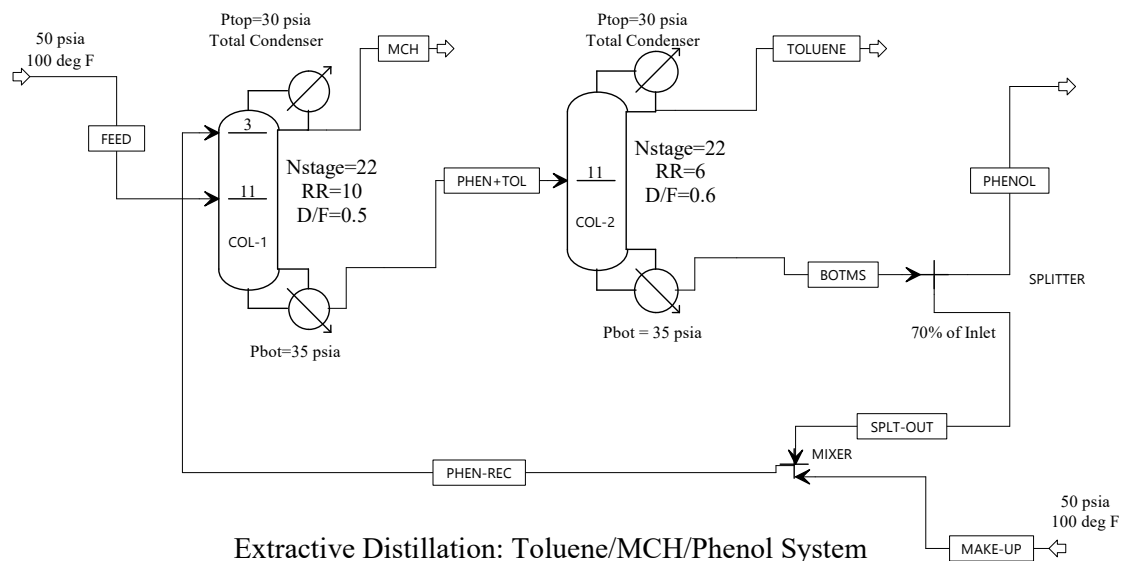
Extractive distillation is a special case of multicomponent distillation used for separation of binary mixtures which are difficult or impossible to separate by ordinary fractionation. A third component, termed a *solvent*, is added which alters the relative volatility of the original constituents, thus permitting the separation. The added solvent is, however, of low volatility and is itself not appreciably vaporized in the fractionator.

A classic example of such an operation is the separation between toluene (bp = 110.6 $^\circ\text{C}$, MW = 92.15) and paraffin hydrocarbons of approximately the same molecular weight, say methylcyclohexane (MCH, bp = 100.9 $^\circ\text{C}$, MW = 98.19). In the presence of phenol (bp = 181.7 $^\circ\text{C}$, MW = 94.11), however, the relative volatility of MCH increases so that its separation from toluene is relatively easy.

- (a) Consider the flowsheet below which consists of 2 distillation columns, a splitter, and a mixer. The FEED stream with a flowrate of 100 lbmol/hr contains 50 mol% toluene and 50 mol% MCH. The MAKE-UP stream contains pure phenol with a flow rate of 10 lbmol/hr. Using the UNIQ-RK property method, simulate this process using ASPEN Plus. Submit a copy of your input summary. What is the purity (in mole%) of MCH and toluene in the two product streams?
- (b) The desired product specification of the second column is 95 mol% toluene, which was not achieved with the given column parameters. Include an internal design-

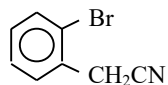
specification in the second column to vary the D/F ratio in order to achieve the desired purity. What is the final value of the D/F ratio?

- (c) We are also interested in the vapor and liquid density profile of the second column. Include a Prop-Set to calculate and report the density profile for all stages. Submit a plot of the densities as a function of tray number.

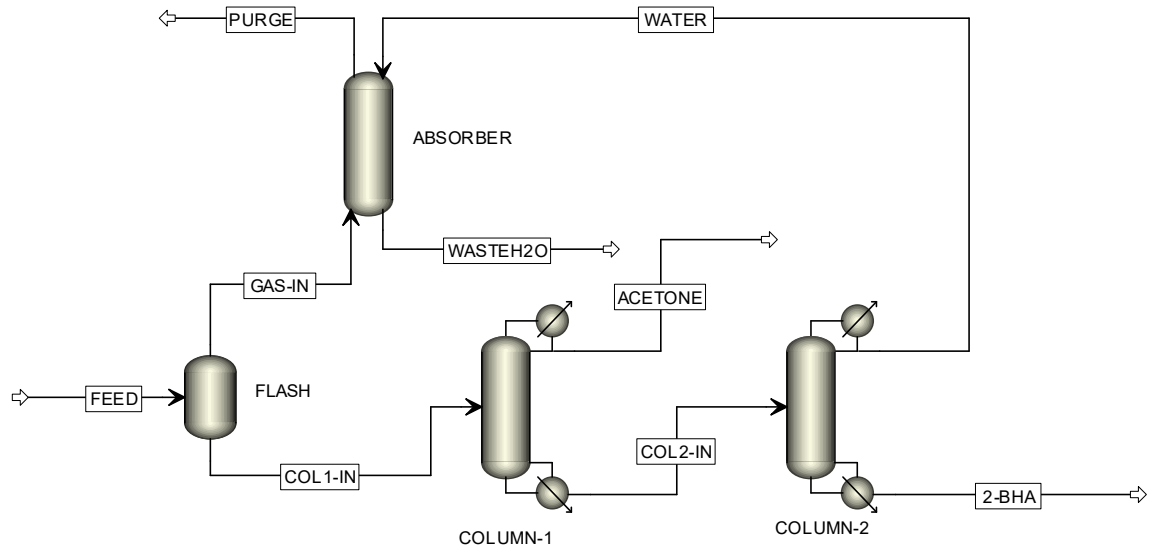


38. Recovering Acetone from a Wastewater Stream

We wish to use ASPEN Plus to simulate a process in which acetone is recovered from wastewater stream (300 lbmol/hr at 100 °F and 25 psia) containing 2 mol% CO₂, 3 mol% O₂, 5% N₂, 15 mol% acetone, 55 mol% water, and 20 mol% 2-bromo phenyl acetonitrile (2-Br-C₆H₄CH₂CN or 2-BHA, to be treated as a non-databank component), which has the following structure:



The process consists of one adiabatic flash drum ($\Delta P = 0$) and three RADFRAC columns (two tray towers and one packed column) as shown. The flash drum takes out most of the light gases. The first tray tower recovers acetone as the overhead product, while the second tray tower separates water from 2-BHA. The water from the second tower is then sent to an absorber which absorbs most of the acetone trapped in the vapor stream from the flash drum.



The non-databank component 2-BHA has the following properties:

MW = 196.05 $V_C = 0.4635 \text{ m}^3/\text{kmol}$ $T_B = 309.2 \text{ }^\circ\text{C}$ $Z_C = 0.254$
 $\Omega = 0.5855$ (Pitzer acentric factor)

CPIG coefficients in ENG units

Element	Coefficient
1	30.754
2	0.0541
3	-2.4316×10^{-5}
4	4.6033×10^{-9}
5	0
6	0

Heat of vaporization:

Temperature ($^\circ\text{F}$)	Heat of Vaporization (Btu/lbmol)
100	29849
140	29754
180	29623
220	29452
260	29239
300	28982
340	28677
380	28320

You are given the following additional data:

	<u>Column 1</u>	<u>Column 2</u>
Condenser	Total	Total
Number of trays (including condenser and reboiler)	40	20
Feed tray location	20	10
Condenser pressure	20 psia	18 psia
Reboiler pressure	23 psia	20 psia
D:F molar ratio	---	0.75
Reflux ratio	5.0	3.0

The absorber contains packing equivalent to 50 equilibrium stages with a top pressure of 15 psia and a bottom pressure of 16 psia. The environmental regulations stipulate that the acetone released in the purge gas released from the absorber should contain no more than

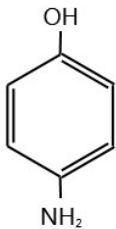
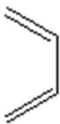
1.5 mol% acetone. For the purpose of this study, we will set this target at exactly 1.5 mol% (± 0.0001).

Use NRTL-RK for property calculations. No two liquid phase split is expected. Note that you need to use PCES to estimate all the missing property data of 2-BHA. Every time you save your run, be careful to click “No to All” when asked about replacing existing data with estimated values from PCES so you don’t overwrite the property data you entered. Finally, be careful with the units of the given data. You may need to change the convergence algorithm or increase the maximum number of iterations in RADFRAC columns to obtain convergence.

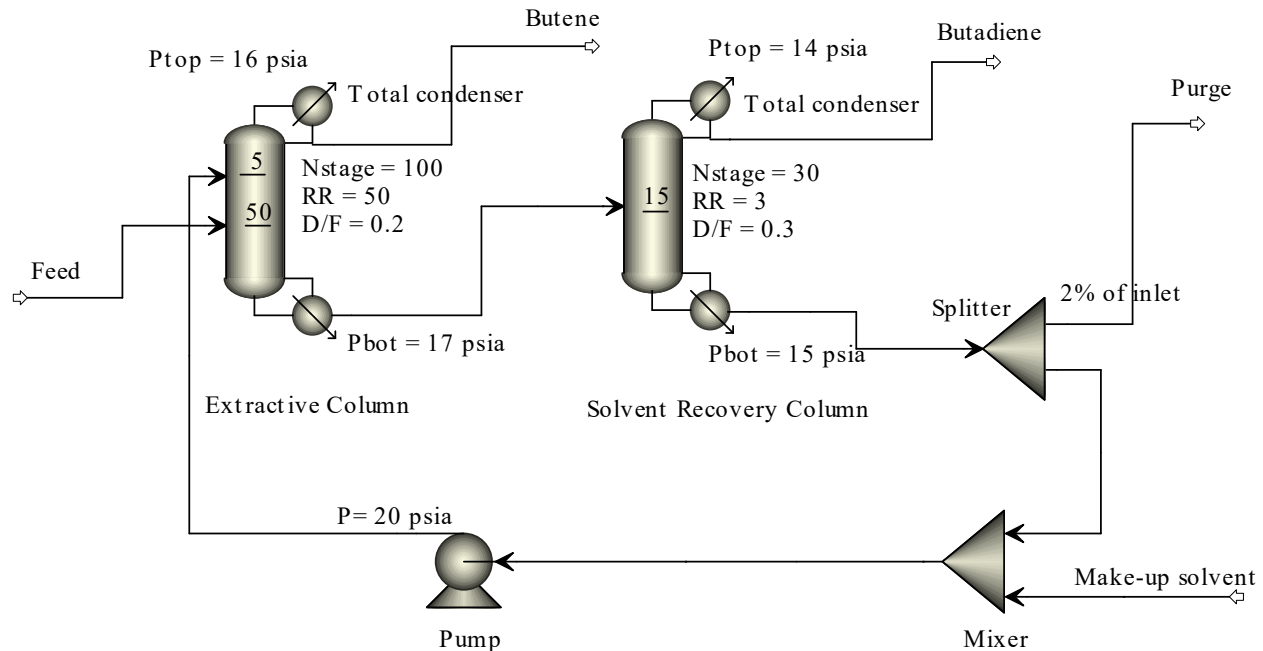
39. Extractive Distillation, II

Extractive distillation is a special case of multicomponent distillation used for separation of binary mixtures which are difficult or impossible to separate by ordinary fractionation. A third component, termed a *solvent*, is added which alters the relative volatility of the original constituents, thus permitting the separation. The added solvent is, however, of low volatility and is itself not appreciably vaporized in the fractionator.

One common industrial use of extractive distillation is in the separation of butadiene from a mixture containing butane and butene. Close boiling points of the feed components, shown in the table below with the boiling point of a solvent, called Compound *X*, make distillation by other means ineffective. Addition of the solvent lowers the activity of butadiene due to their structural similarity. Butadiene, submersed in the higher boiling solvent-rich stream at the bottom of the column, is distilled from the solvent at a higher temperature than in its pure form. Because Compound *X* is chemically more similar to butadiene and differs from the compounds butene and butane, only one component of the feed becomes submersed in the solvent. The structural similarity is shown in the table below.

Compound	Boiling Point (°C)	Structure
Solvent <i>X</i>	240	
1,3-Butadiene	-4.4	
1-Butene	-6.3	
<i>n</i> -Butane	-0.45	

The extractive distillation will be carried out and simulated based on the following process, which consists of 2 distillation columns, a splitter, a mixer, and a pump.



The solvent or Compound *X* is a non-databank component whose properties must be estimated using PCES in ASPEN Plus (do not use NIST TDE). In addition to its boiling point, the following data are also known about Compound *X*, which should be used to enhance the accuracy of PCES:

Watson heat of vaporization model:

$$\Delta H_{VAP}(T) = \Delta H_{VAP}(T_1) \left(\frac{1 - T/T_C}{1 - T_1/T_C} \right)^{a+b(1-T/T_C)}$$

where $\Delta H_{VAP}(T_1) = 24525.3$ Btu/lbmol, $T_1 = 470.05$ °F, $a = 0.422$, and $b = -0.314$

Experimental vapor pressure data:

Temp (°F)	300	320	340	360	380	400	420	440	460	480
P _{VAP} (psia)	0.677	1.042	1.571	2.320	3.364	4.793	6.721	9.284	12.645	16.990

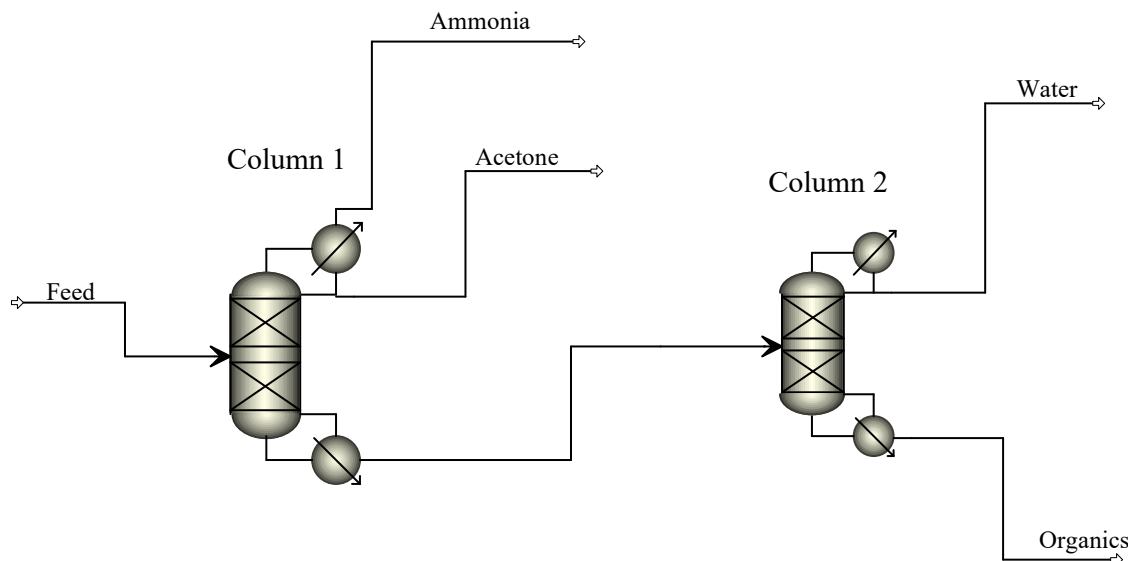
The feed stream with a flow rate of 100 lbmol/hr contains 44 mol% butene, 55 mol% butadiene, and 1 mole% butane at 20 psia and 0 °F. The make-up stream contains pure solvent with a flow rate of 3 lbmol/hr at 20 psia and 100 °F. Using the NRTL-RK (Any missing binary interaction parameters should be estimated from PCES rather than inside the NRTL folder), simulate this process using ASPEN Plus.

Note: Try running PCES first and estimate all missing property parameters including the binary interaction parameters before building your flowsheet. I ran into some bugs where

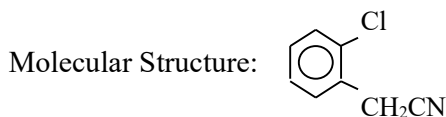
running PCES together with your simulation caused some problems in ASPEN Plus on my laptop. Also, to get full credit, you must converge your flowsheet with reset.

40. Purifying a Wastewater Stream

A 1000-lbmol/hr wastewater stream containing 5 mole% ammonia, 15 mole% acetone, 10 mole% aniline, 20 mole% 2-CHA (2-chloro-phenyl-acetonitrile, see the molecular structure below), and 50 mole% water at 80 °C and 20 psia is to be purified in a series of two distillation columns to remove the organics so that the treated water can be discharged safely into the environment as shown in the figure below. Your task is to simulate the process using ASPEN Plus and determine column operating conditions.



2-CHA is a non-databank component whose properties must be input into the simulator (be careful with the units of all numbers). The following is known about 2-CHA:



$$\text{MW} = 151.595 \quad T_B = 280 \text{ } ^\circ\text{C} \quad P_C = 33.0 \text{ atm} \quad \Omega = 0.516$$

$$\text{CPIG} = 32.32 + 0.0925T - 7.008 \times 10^{-5}T^2 + 2.085 \times 10^{-8}T^3 \quad \text{in cal/gmol-K and } T \text{ in } ^\circ\text{C}$$

$$\ln P^{\text{VAP}} = -9.5745 + 0.0793T - 1.7854 \times 10^{-4}T^2 + 1.8453 \times 10^{-7}T^3 \quad \text{in psia and } T \text{ in } ^\circ\text{C}$$

Heat of vaporization (Use Tabpoly to enter the data):

Temp (°C)	H ^{VAP} (Btu/lbmol)	Temp (°C)	H ^{VAP} (Btu/lbmol)
50	27,200	210	24,900
70	27,036	230	24,423
90	26,840	250	23,893
130	26,350	270	23,305
170	25,711	300	22,304

Use UNIFAC property method in your model since the interaction parameters between 2-CHA and the other components are missing from the databanks.

You are given the following additional data on the two columns. Use RADFRAC in A+ to simulate the columns. Environmental regulations stipulate that the treated water from the second column must contain exactly 1.5 mole% impurities (i.e. the stream must contain 98.5 mole% water). Note that no two liquid phases are expected anywhere inside the columns.

	<u>Column-1</u>	<u>Column-2</u>
Number of stages (including condenser & reboiler)	20	20
Top pressure	14.7 psia	10 psia
Bottom pressure	16.0 psia	12 psia
Condenser	10 mole% vapor	Total
Reboiler	Kettle	Kettle
Feed tray	10	10
Molar reflux ratio	2.0	0.5
Molar distillate to feed ratio	0.30	----

Hints: The two RADFRAC columns are not easy to converge. If you run into convergence problems, try changing the convergence scheme, increase the maximum number of iterations, specifying better bounds and a better initial guess from sensitivity analysis, etc.

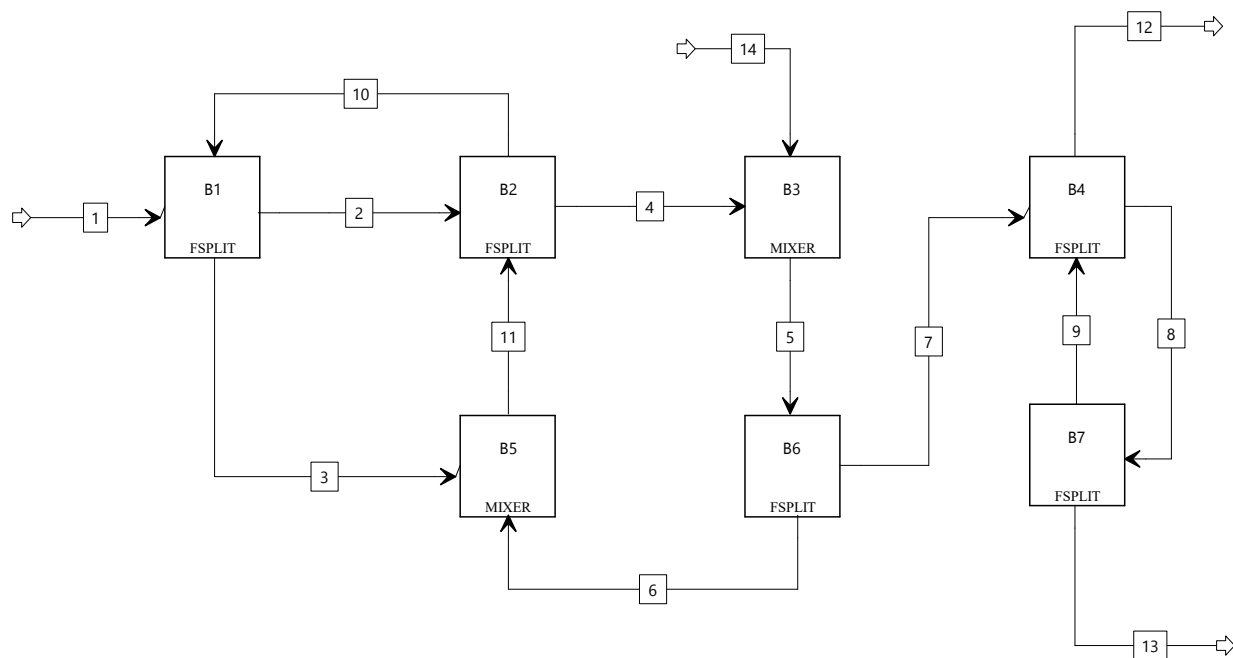
Also, because of a warning in PCES, your run will terminate with “Results Available with Warnings”. As long as your two columns converged, your solution should be correct. Finally, because of PCES, during your session A+ will ask you if you want to replace all property parameters with values estimated from PCES. Always click “No to All” to the question because we want to keep the experimental property data such as T_B , P_C , and Ω that we entered into A+.

Section 6

Flowsheet Convergence in A+

41. Flowsheet Convergence, I

Consider the following flowsheet, which is nothing but a collection of mixer and splitter blocks that process just water. Both fresh feeds contain pure water at 100 °F and 14.7 psia with a flowrate of 100 lbmol/hr each. Note that every splitter block has 2 outlet streams and the split fractions are 0.5 in all cases.



- (a) Using A+, determine the number of irreducible groups in the flowsheet and write down the blocks in each group. Also, for each irreducible group, write down the minimum number of tear streams and their locations.

Number of irreducible groups = _____

The blocks in each group are:

The tear streams in each group are:

- (b) Set up a design-spec to vary the split fraction of Block B1 such that the ratio of molar flows of Stream 3 to Stream 7 is equal to 1.20. Using the default convergence scheme (Level 1), answer the following questions:

Split fraction in Block B1 going to Stream 2 = _____

Is the design-spec loop nested inside or outside one of the tear stream loops? Check one.

O Inside O Outside

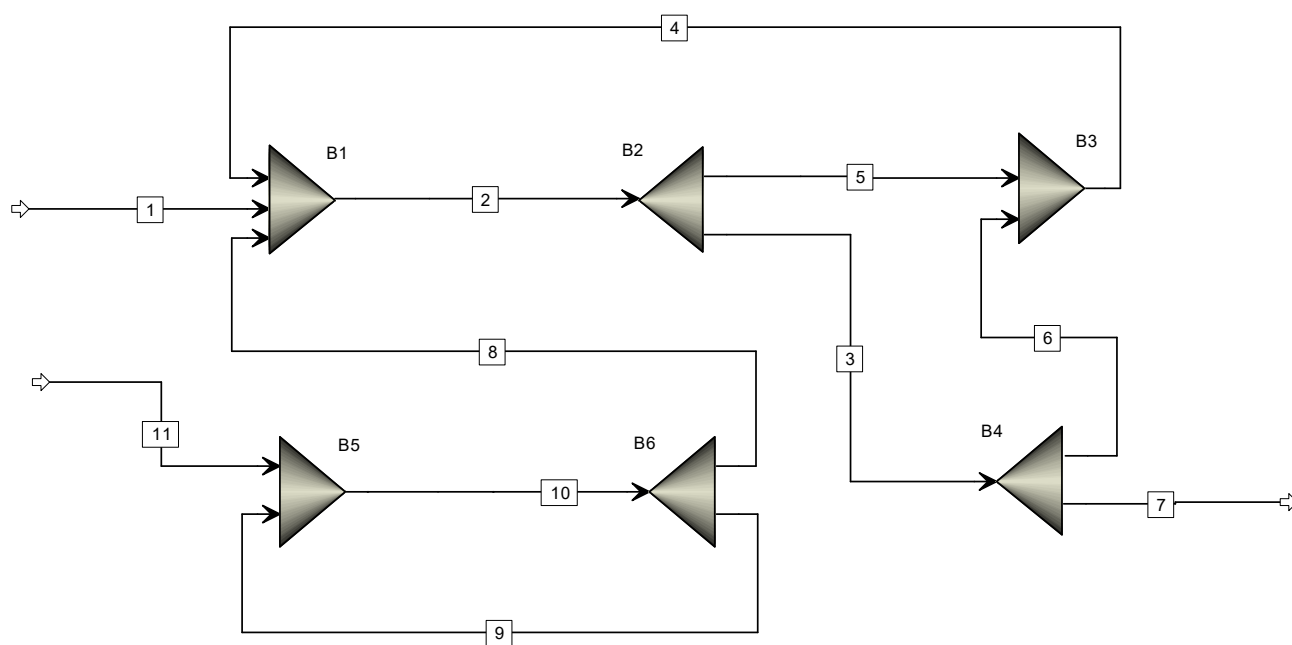
(c) Propose a Level 3 convergence scheme and use it to solve the problem in Part (b) again. For this scheme, you must do the following:

- (i) The design-spec must be converged simultaneously with the tear streams.
- (ii) You must pick the same tear streams as those chosen by A+ in Part (b).
- (iii) You must initialize all tear streams.

42. Flowsheet Convergence, II

Consider the following flowsheet, which is nothing but a collection of mixer and splitter blocks. Stream 1 contains pure ethane feed at 0 °F and 14.7 psia (flowrate is unknown), while Stream 11 contains pure ethylene at 0 °F and 14.7 psia with a flowrate of 100 lbmol/hr. Note that every splitter block has 2 outlet streams and the split fractions are 0.5 in all cases, except for Block B2 whose split fraction is also unknown. The two unknowns can be determined from the following two constraints:

- (1) Total molar flow rate of Stream 4 is equal to 500 lbmol/hr (± 0.01).
- (2) The mole fraction of ethane in Stream 4 is equal to 0.3 (± 0.0001).



(a) Using A+ and automatic convergence and sequencing (Level 1), determine the ethane feed flow in Stream 1 and the split fraction of Stream 5 in Block B2.

Ethane feed flow in Stream 1 = _____ lbmol/hr

Split fraction of Stream 5 in Block B2 = _____

Also, using the flowsheet analysis in A+, write down the number of irreducible groups and the blocks in each group. Also, for each irreducible group, write down the minimum number of tear streams and their locations. Finally, write down the CPU seconds required by your computer to converge this flowsheet.

Number of irreducible groups = _____

The blocks in each group are:

The tear streams in each group are:

Simulation time in CPU seconds: _____

- (b) You undoubtedly noticed that, because of the nesting of various loops, this problem took some time to converge (on my laptop, this CPU time was about 25 seconds). Propose **two** different Level 3 convergence schemes and use them to converge the flowsheet in Part (a) again. Your aim is to cut down the CPU time to less than 10 seconds (if you fail to do so, points will be deducted). In both cases, you are not required to initialize the tear streams and each run must start with a re-initialization, i.e. purge all the results first before running the model.

Briefly write down your two schemes:

Scheme 1: _____

CPU seconds of Scheme 1: _____

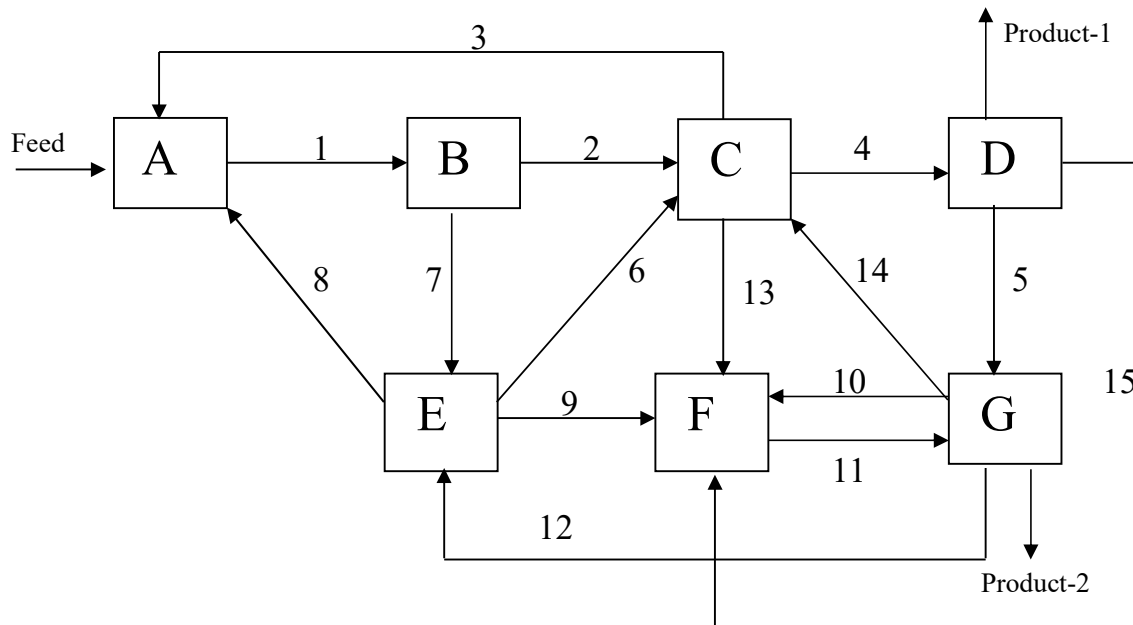
Scheme 2: _____

CPU seconds of Scheme 2: _____

43. Flowsheet Convergence, III

Consider the complex flowsheet from Problem 13 shown below, but this time with a process feed and two process output streams also included. We wish to use ASPEN Plus to study the convergence behavior of this flowsheet by replacing each block with either a mixer or a splitter. For simplicity, we will assume that the process fresh feed contains pure water at 70 °F and 14.7 psia (flowrate is unknown). Except for splitter Block B whose split fraction is unknown, all other splitter blocks split the total inlet feed into outlet streams with equal flow rates. The two unknowns can be determined from the following two constraints:

- (1) The total molar flow rate of the product stream (Product-1) from Block D is equal to 40 lbmol/hr (± 0.01 lbmol/hr).
- (2) The ratio of the molar flow rate of Stream 2 to the molar flow rate of Stream 3 is maintained at 2.0 (± 0.001).



- (a) Using A+ and automatic convergence and sequencing (Level 1), determine the water feed flow in Stream Feed and the split fraction in Block B going to Stream 2.

Water flow rate in Stream Feed = _____ lbmol/hr

Split fraction in Block B going to Stream 2 = _____

Also, write down the CPU seconds required by your computer to converge this flowsheet.

Simulation time in CPU seconds: _____

- (b) You undoubtedly noticed that, because of the nesting of various loops, this problem took some time to converge (on my laptop, this CPU time was nearly 1 second before Report Writer is entered). Propose **two** different Level 3 convergence schemes and use them to converge the flowsheet in Part (a) again. Your aim is to cut down the CPU time. In both cases, you are not allowed to initialize the tear streams and each run must start with a Reset, i.e. purge all the results first before running the model.

Briefly write down your two schemes:

Scheme 1: _____

CPU seconds of Scheme 1: _____

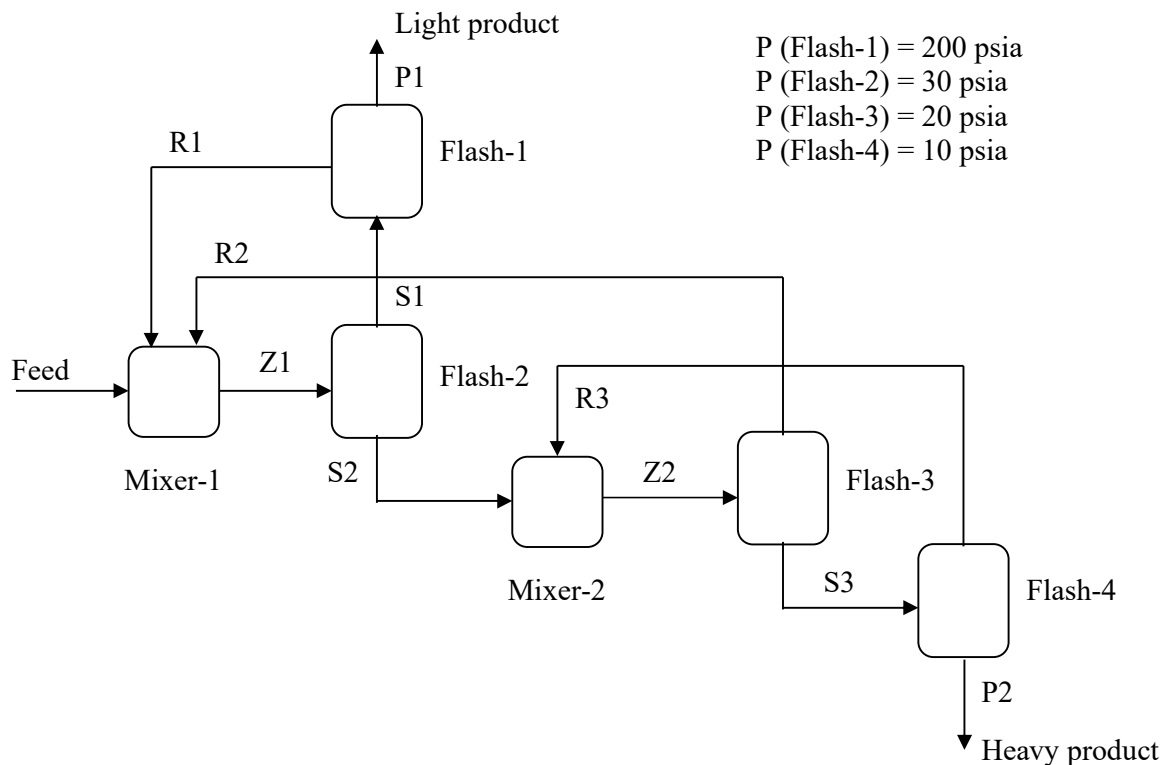
Scheme 2: _____

CPU seconds of Scheme 2: _____

44. Flowsheet Convergence, IV

Consider the following flowsheet by Cavett (1963) which has been used repeatedly in the literature to study tear stream convergence. The flowsheet consists of two mixers and four flashes which are used to separate the feed into light and heavy hydrocarbon products.

The feed is a saturated liquid at 50 psia and has a flowrate of 100 lbmol/hr with the following composition (mole basis): 20% methane, 20% ethane, 20% propane, 20% *n*-butane, and 20% *n*-pentane. All flashes were designed to vaporize 30% of the feed entering the blocks at the pressures given in the flowsheet.



- (a) Converge this flowsheet which contains tear streams with ASPEN Plus using PENG-ROB. Specify exactly how you manage to converge the flowsheet. You may use any convergence scheme, i.e. any user convergence level including the default Level 1. However, in converging the flowsheet, you:
- (i) must reset your run every time.
 - (ii) must not provide any guesses for the tear streams.
 - (iii) must not increase the default maximum number of iterations in the convergence algorithm or change its default settings. If you do, 5 points will be automatically deducted.

i) Your convergence scheme:

Tear streams: _____

Convergence algorithm: _____

ii) Ratio of the total molar flow of stream R2 to that of stream R3 = _____

- (b) Now, we want to add a constraint to the flowsheet such that the ratio of the total molar flow of stream R2 to that of stream R3 is exactly 2.00 (± 0.001). This constraint or design-spec is achieved by varying the vapor fraction in Flash-3. Use ASPEN Plus to converge this constrained problem.

Note that this is an extremely difficult problem to converge. You have to be creative and try many different convergence schemes, including examining the bounds of your manipulated variable. Once again, you must reset each run, may not provide initial guesses for the tear streams, and may not increase the maximum number of iterations or change the default settings of the convergence algorithm. Points will be deducted if you do any of the above (unless you are running out of time and like to see a converged solution).

i) Your convergence scheme:

Tear streams: _____

Convergence algorithm for tear streams: _____

Convergence algorithm for design-spec: _____

Nesting or simultaneous convergence? _____

If nesting, the nesting order: _____

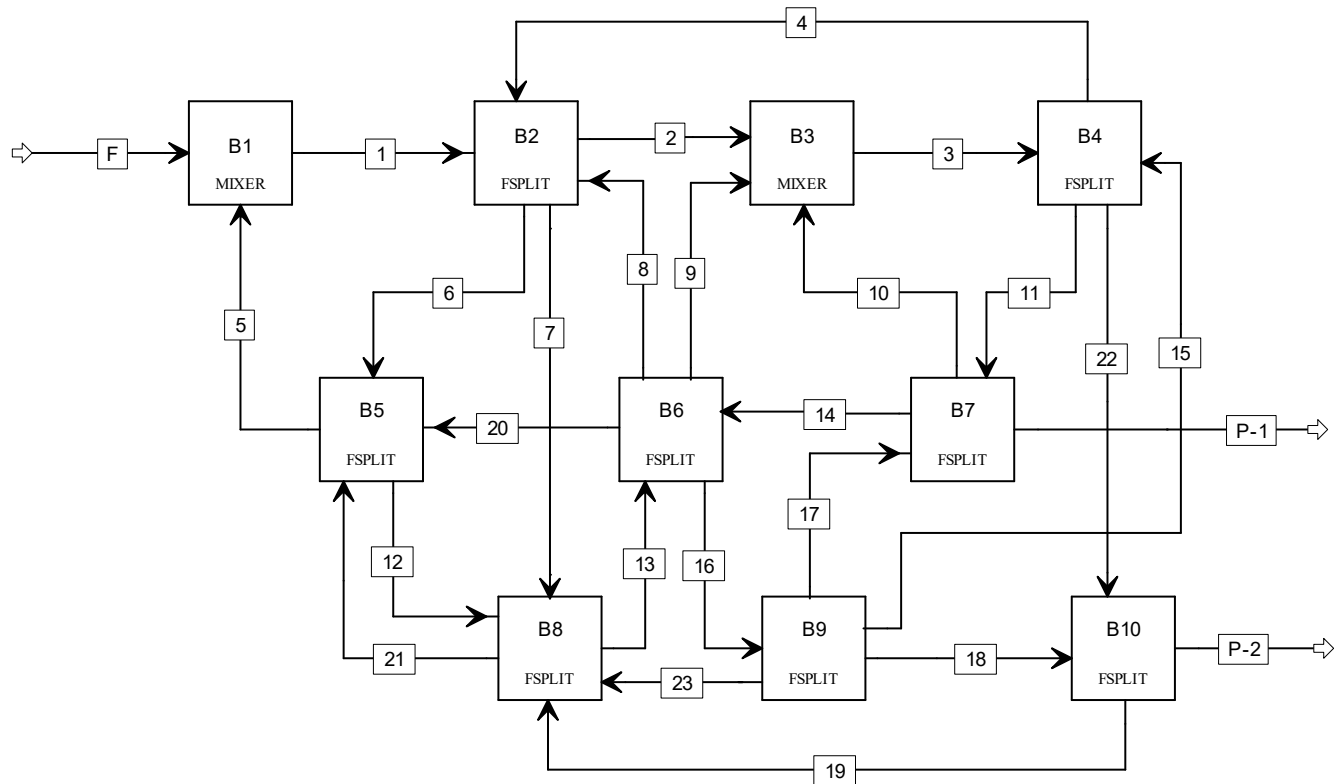
ii) Vapor fraction in Flash-3 = _____

45. Flowsheet Convergence, V

Recall the flowsheet below from Midterm which consists of two mixers and eight splitters. A total flow rate of 100 lbmol/hr of pure water enters the process at 100 °F and 20 psia. Use STEAMNBS as the property method. When you create your flowsheet, you must use the same stream IDs and block IDs as shown in the figure.

The eight splitters have the following split fractions:

Stream 2 = 30%	Stream 6 = 30%	Stream 4 = 30%	Stream 11 = 30%
Stream 12 = 50%	Stream 8 = 25%	Stream 9 = 25%	Stream 16 = 25%
Stream 10 = 30%	Stream 14 = 30%	Stream 21 = 50%	Stream 15 = 25%
Stream 17 = 25%	Stream 18 = 25%	Stream 19 = 50%	



- (a) Converge this flowsheet in A+. In your simulation, you must
- reinitialize your run.
 - use the system-generated tear streams
 - not provide any guesses for the tear streams.
 - not increase the default maximum number of iterations in the algorithm or change its default parameter settings.

Answer the following question:

Flow rate of Stream P-1 = _____ lbmol/hr

- (b) It is desirable to set the total flow rate of Stream P-1 to exactly 50 lbmol/hr (± 0.0001). This is achieved by varying the split fraction in Block B10. Propose a convergence scheme to solve this flowsheet. Be very specific with your answers, e.g. what algorithms are used, what tear streams are used, and whether the convergence is simultaneous or nesting; and if nesting is used, what is the order of nesting.

You may select your own tear streams (or use the A+ default) in Part (b), but in doing so you must:

- reinitialize your run.
- not provide any guesses for the tear streams.

- (iii) not increase the default maximum number of iterations (30) in the algorithm or change its default parameter settings.

Hint: The flowsheet in Part (b) is extremely difficult to converge. To my best knowledge, there is only one way to converge the flowsheet. So you need to be creative as well as being thorough. Good luck!

Answer the following questions:

Your convergence scheme:

Split fraction going to Stream 19 in Block B10 = _____%

Section 7

Using MATLAB to Solve Engineering Problems

46. System of Linear Algebraic Equations, I

Use MATLAB to solve the following system of linear algebraic equations, correct to 4 decimal places:

$$\begin{array}{rcl} x_1 + x_2 - x_3 + 2x_4 - x_6 - 6.5 & = & 0 \\ -2x_1 + x_3 + x_4 - x_5 + 2x_6 - 7 & = & 0 \\ 4x_2 + 3x_3 + 2x_4 + x_5 + x_6 + 4.5 & = & 0 \\ x_1 + x_2 + x_3 + x_4 + x_5 + x_6 - 8.5 & = & 0 \\ -x_1 + x_2 + x_3 - x_4 - x_5 - x_6 + 21.5 & = & 0 \\ 2x_2 + 2x_3 + x_5 + 10 & = & 0 \end{array}$$

47. System of Linear Algebraic Equations, II

Use MATLAB to solve the following system of linear algebraic equations, correct to 4 decimal places:

$$\begin{array}{rcl} x_1 + 3x_2 + 2x_3 - x_5 + 4x_6 & = & -2 \\ 2x_1 - 2x_2 + 4x_3 + x_4 + x_5 & = & 1 \\ -3x_1 - 2x_2 + 4x_3 + 5x_4 + 2x_5 - x_6 & = & 0 \\ -x_2 + 2x_4 + 6x_5 + 4x_6 & = & 3 \\ -2x_1 + 3x_4 + 4x_5 + 5x_6 & = & -6 \\ 6x_1 - 2x_2 - x_3 - 3x_4 + 4x_5 + 2x_6 & = & 5 \end{array}$$

48. System of Nonlinear Algebraic Equations

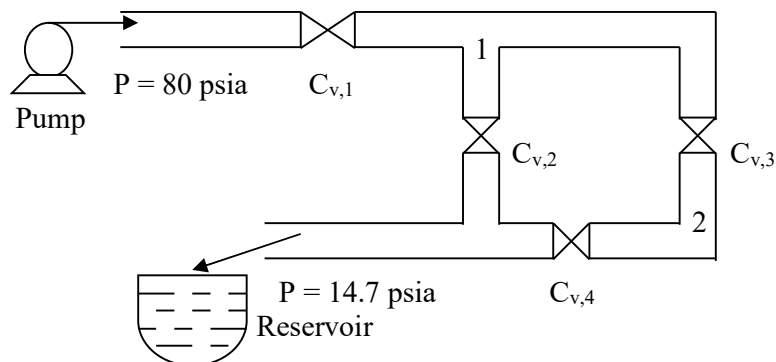
Use MATLAB to solve the following system of nonlinear algebraic equations:

$$\begin{array}{rcl} \exp(-x_1) + x_1x_2 & = & 4 \\ x_1^2 - 2x_2 - \ln(x_3) & = & 0 \\ \sin(x_1x_3) - 0.5\tan(x_2x_3) + x_1x_2x_3 & = & 20 \end{array}$$

49. Pressures in a Pipeline Network

Consider the following interconnected liquid pipeline network which contains 4 valves with the following valve coefficients. Calculate the pressure at each location/node indicated in the network.

$$\begin{array}{ll} C_{v,1} = 0.5 \text{ ft}^3/(\text{psia})^{1/2}\text{-hr} & C_{v,2} = 0.4 \text{ ft}^3/(\text{psia})^{1/2}\text{-hr} \\ C_{v,3} = 0.3 \text{ ft}^3/(\text{psia})^{1/2}\text{-hr} & C_{v,4} = 0.2 \text{ ft}^3/(\text{psia})^{1/2}\text{-hr} \end{array}$$

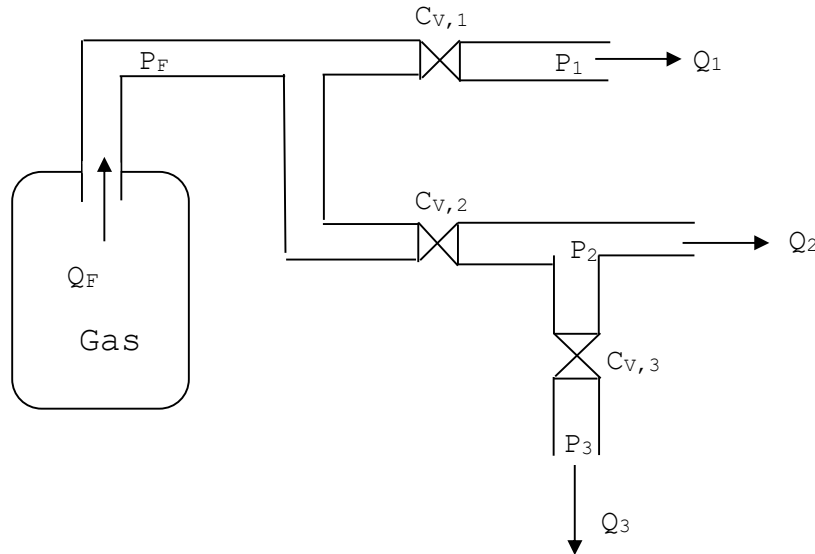


50. Solving for Pressures in a Gas Pipeline Network

A storage vessel contains a gas that is to be distributed via a network of pipeline as shown. You are to use MATLAB to solve for the following unknowns in the system: P_F , Q_1 , Q_2 , and Q_3 . On the other hand, the known parameters in the system are:

$$\begin{array}{llll} Q_F = 50 \text{ ft}^3/\text{min} & P_1 = 20 \text{ psia} & P_2 = 30 \text{ psia} & P_3 = 15 \text{ psia} \\ C_{V,1} = 2.0 \text{ ft}^3/(\text{psia})\text{-min} & C_{V,2} = 1.5 \text{ ft}^3/(\text{psia})\text{-min} & & C_{V,3} = 1.0 \text{ ft}^3/(\text{psia})\text{-min} \end{array}$$

Assume that the gas behaves ideally but is compressible, there is no pressure drop around any bend in the pipeline, and the system is isothermal.



Answer the following questions:

$$\begin{array}{ll} P_F = \text{_____ psia} & Q_1 = \text{_____ ft}^3/\text{min} \\ Q_2 = \text{_____ ft}^3/\text{min} & Q_3 = \text{_____ ft}^3/\text{min} \end{array}$$

51. Simple Calculations and Array Manipulations in MATLAB

Consider the following arrays:

$$\mathbf{A} = \begin{pmatrix} 1 & 3 & 5 \\ 10 & 5 & 30 \\ 6 & 10 & 4 \\ 3 & \pi & 8 \end{pmatrix} \quad \mathbf{B} = \log_{10}(\mathbf{A}) \quad \mathbf{C} = \begin{pmatrix} 2 & 4 & 4 & 8 \\ 8 & 12 & 24 & 7 \\ 0 & -1 & 5 & 6 \end{pmatrix}$$

Write MATLAB expressions in an M-file (script file) to do the following (use “format short” in all calculations unless otherwise told):

- Determine the sum of the second column of $\mathbf{B}$.
- Select the first 3 columns and the first 3 rows of $\mathbf{A}$ and $\mathbf{B}$ and add their determinants.

- (c) Determine the square root of the product (a scalar) between the last row of **C** and the second column of **A**.
- (d) Determine the sum of the second row of **A** divided element-by-element by the third column of **C**.
- (e) Evaluate the hyperbolic secant of $(0.01 * \mathbf{A} * \mathbf{C})$.
- (f) Evaluate the following function: $\tan^{-1}(0.1 * \mathbf{B} * \mathbf{C})$ in 6 decimal places.

52. Inverse and Determinant of 2×2 and 3×3 Matrices

Use MATLAB to write a program that can determine the inverse and determinants of any 2×2 and 3×3 matrices, which can then be used to solve a system of linear algebraic equations in 2 or 3 unknowns.

Recall that the formulae for calculating the determinant of 2×2 and 3×3 matrices are as follows:

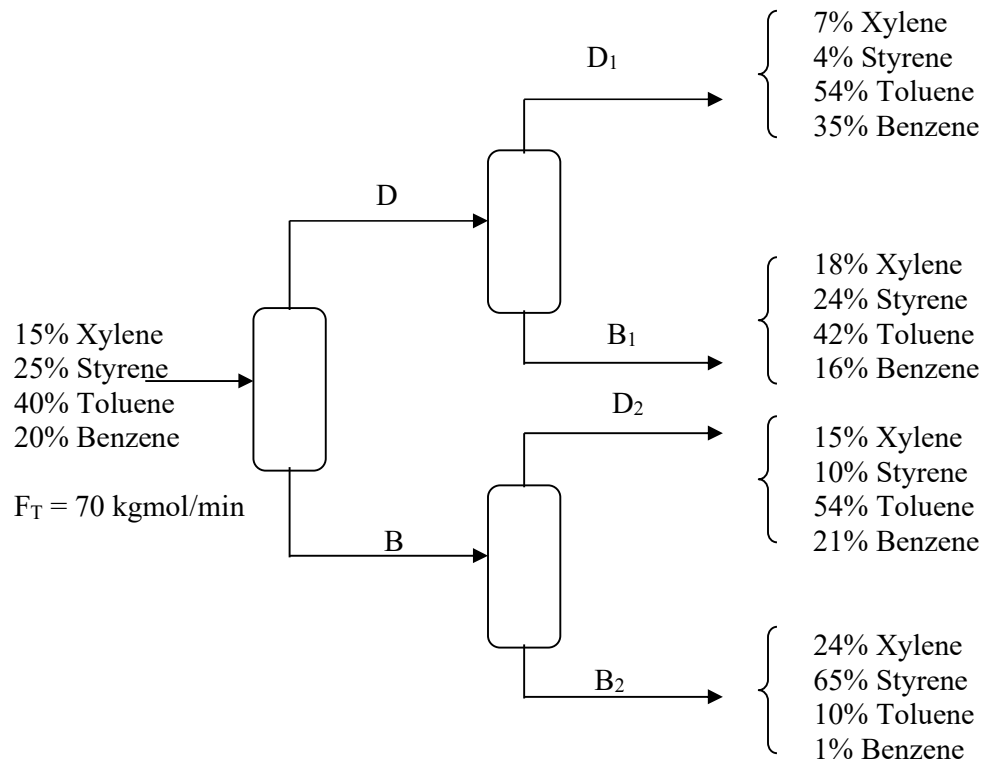
$$\begin{aligned} \text{If } A &= \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} & \text{then } \det(A) &= a_{11}a_{22} - a_{12}a_{21} & A^{-1} &= \frac{1}{\det(A)} \begin{bmatrix} a_{22} & -a_{12} \\ -a_{21} & a_{11} \end{bmatrix} \\ \\ \text{If } A &= \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} & \text{then } \det(A) &= a_{11}(a_{33}a_{22} - a_{32}a_{23}) - a_{21}(a_{33}a_{12} - a_{32}a_{13}) \\ & & & + a_{31}(a_{23}a_{12} - a_{22}a_{13}) \\ & & \text{and } A^{-1} &= \frac{1}{\det(A)} \begin{bmatrix} a_{33}a_{22} - a_{32}a_{23} & a_{32}a_{13} - a_{33}a_{12} & a_{23}a_{12} - a_{22}a_{13} \\ a_{31}a_{23} - a_{33}a_{21} & a_{33}a_{11} - a_{31}a_{13} & a_{21}a_{13} - a_{23}a_{11} \\ a_{32}a_{21} - a_{31}a_{22} & a_{31}a_{12} - a_{32}a_{11} & a_{22}a_{11} - a_{21}a_{12} \end{bmatrix} \end{aligned}$$

Use the above formulae to solve the following two systems of linear algebraic equations:

- (a) $2x_1 - 3x_2 = 6 \quad -x_1 + 2x_2 = -1$
- (b) $x_1 + 2x_2 - 6x_3 = -2 \quad -5x_1 + 3x_2 + x_3 = 0 \quad 4x_1 - x_2 - 2x_3 = 3$

53. Steady-State Material Balances on a Separation Train

Paraxylene, styrene, toluene, and benzene are to be separated with an array of distillation columns shown in the figure below.



Formulate the problem as a system of simultaneous linear equations and solve it using MATLAB.

54. Using MATLAB to Solve the Peng-Robinson Equation of State

The Peng-Robinson equation of state contains 2 empirical parameters a and b , and its conventional form is given by:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2 + 2bV_m - b^2}$$

where

$$a = 0.45724 \left(\frac{\alpha R^2 T_C^2}{P_C} \right)$$

$$b = 0.07780 \left(\frac{RT_C}{P_C} \right)$$

$$\alpha = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5})]^2$$

$$T_r = \frac{T}{T_C}$$

$$\omega = -1.0 - \log_{10} \left[\frac{P^{VAP}(T_r = 0.7)}{P_C} \right]$$

The variables are defined by:

P	= pressure in MPa
V_m	= molar volume in cm ³ /gmole
T	= temperature in K
R	= gas constant (8.314 cm ³ -MPa/gmole-K)
T_C	= the critical temperature (150.86 K for argon)
P_C	= the critical pressure (4.898 MPa for argon)
P^{VAP}	= vapor pressure (0.4946 MPa at $T_r = 0.7$ for argon)

Alternatively, this equation of state can be expressed in polynomial forms as given below:

$$A = \frac{aP}{R^2 T^2}$$

$$B = \frac{bP}{RT}$$

$$Z^3 + (B-1)Z^2 + (A-2B-3B^2)Z + (-AB+B^2+B^3) = 0$$

$$\text{where } Z = \frac{PV_m}{RT}, \text{ the compressibility factor}$$

Use MATLAB to compute the molar volume of argon using both the conventional form and the polynomial form at $T = 105.6$ K and $P = 0.498$ MPa. The two solutions should be the same. Because the two equation forms are both cubic in molar volume, you should obtain 3 different answers in volume. Briefly describe the physical meaning or significance of each answer.

55. Using MATLAB to Component Fugacity Coefficients of Argon Gas

The fugacity coefficient is defined by $\phi = f/P$, where f is the fugacity of the component with units of pressure and P is the pressure. The fugacity coefficients of pure substances can be calculated from a number of equations of state, such as van der Waals and Peng-Robinson which are summarized by Walas (1985).

The van der Waals equation of state is given by:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

where

$$a = \frac{27}{64} \left(\frac{R^2 T_C^2}{P_C} \right)$$

$$b = \frac{RT_C}{8P_C}$$

$$\ln \phi = Z - 1 - \frac{a}{RTV} - \ln \left[Z \left(1 - \frac{b}{V} \right) \right]$$

The Peng-Robinson equation of state contains 2 empirical parameters a and b , and its conventional form is given by:

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + 2bV - b^2}$$

where

$$a = 0.45724 \left(\frac{\alpha R^2 T_C^2}{P_C} \right)$$

$$b = 0.07780 \left(\frac{RT_C}{P_C} \right)$$

$$\alpha = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5})]^2$$

$$T_r = \frac{T}{T_C}$$

$$\omega = -1.0 - \log_{10} \left[\frac{P^{VAP}(T_r = 0.7)}{P_C} \right]$$

The variables are defined by:

P	= pressure in MPa
V	= molar volume in cm ³ /gmole
T	= temperature in K
R	= gas constant (8.314 cm ³ -MPa/gmole-K)
T_C	= the critical temperature
P_C	= the critical pressure
P^{VAP}	= vapor pressure
ϕ	= fugacity coefficient

Alternatively, the Peng-Robinson equation of state can be expressed in polynomial forms as given below:

$$A = \frac{aP}{R^2 T^2}$$

$$B = \frac{bP}{RT}$$

$$Z^3 + (B-1)Z^2 + (A-2B-3B^2)Z + (-AB+B^2+B^3) = 0$$

$$\text{where } Z = \frac{PV}{RT}, \text{ the compressibility factor}$$

$$\ln \phi = Z - 1 - \ln(Z - B) + \left(-\frac{A}{2\sqrt{2}B} \right) \ln \left[\frac{Z + 2.414B}{Z - 0.414B} \right]$$

Write a MATLAB script file to compute the following of argon gas at the temperature $T = 100$ K and the pressure $P = 0.1$ MPa:

- The molar volume of argon gas from van der Waals and Peng-Robinson equations
- The compressibility factor of argon gas from van der Waals and the two forms of Peng-Robinson equations
- The fugacity coefficients of argon gas from van der Waals and Peng-Robinson equation.

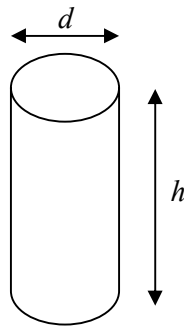
For argon, $T_C = 150.86$ K and $P_C = 4.898$ MPa. $P^{VAP} = 0.4946$ MPa at $T_r = 0.7$.

Answers:

	Gas Molar Volume (cm ³ /gmole)	Z	ϕ
van der Waals			
Traditional Peng-Robinson			
Polynomial Peng-Robinson			

56. Propane Cylinder

A gas cylinder, whose exterior dimensions are a height of $h = 1.35$ m and a diameter of $d = 0.25$ m, is shown below. The cylinder contains $m = 2.9$ kg of propane at $T = 120^\circ\text{C}$.



Suppose that readings from a pressure gauge attached to the cylinder indicate that the pressure of the propane is $P = 30$ bars (absolute). The objective is to determine the interior volume of the cylinder and from that the wall thickness.

Use the Redlich-Kwong equation of state which contains 2 empirical parameters a and b as follows:

$$P = \frac{RT}{\underline{V} - b} - \frac{a}{\underline{V}(\underline{V} + b)\sqrt{T}}$$

where for propane, $a = 182.23 \text{ bar}\cdot\text{m}^6\cdot\text{K}^5/\text{kmol}^2$ and $b = 0.06242 \text{ m}^3/\text{kmol}$

57. Statistical Analyses Using Matrices in MATLAB

You are to use MATLAB to carry out some statistical analyses on a set of data given in the table below.

Undergr. GPA	ChEPS GPA
3.58	3.97
3.33	3.71
3.28	3.57
3.27	3.54
3.15	3.61
3.33	3.75
2.97	3.72
3.09	3.42
3.22	4.00
2.89	3.66
3.05	3.89
2.90	3.28
3.10	3.71
3.01	3.64
3.31	3.64
3.45	3.64
3.22	3.64
3.19	3.61
3.14	3.78
3.16	3.64
3.45	3.85

The data consist of undergraduate GPAs of 21 students from ChEPS Class-11 and their ChEPS GPAs upon graduation. We like to find out if there is a strong correlation between these two set of data. You are asked to carry out a number of statistical analyses using MATLAB's matrix functionality. You must first create a 21×2 matrix that contain the data given in the table. From that matrix, do the following:

1. Compute the maximum, minimum, mean, and median of the students' undergraduate GPAs and ChEPS GPAs.
2. Compute the standard deviations of undergraduate GPAs and ChEPS GPAs using the following formula:

$$s = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (x_i - \mu)^2}$$

where N =total data size and μ =mean of the data. Do not use the built-in function in MATLAB to compute this number.

3. Compute the Pearson's correlation coefficient r , which indicates the correlation between undergraduate GPA and ChEPS GPA, as given by the formula below:

$$r = \frac{N(\sum xy) - (\sum x \sum y)}{\sqrt{[N(\sum x^2) - (\sum x)^2][N(\sum y^2) - (\sum y)^2]}}$$

where x = undergraduate GPA and y = ChEPS GPA.

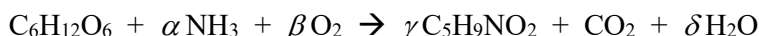
Please note that you are not allowed to use *for* loop or any control statements in your calculations. Use only vectors, matrices, and their manipulations. Finally, use *fprintf* to output your results that look like the table below. The spacing is not important as long as your table looks neat. Note that I want 2 decimal places for the maximum and the minimum and 3 decimal places for the mean, the median, and the standard deviation. For the correlation coefficient, I want an answer in 4 decimal places.

	Maximum	Minimum	Mean	Median	STDEV
Undergr GPA	x.xx	x.xx	x.xxx	x.xxx	x.xxx
ChEPS GPA	x.xx	x.xx	x.xxx	x.xxx	x.xxx

Pearson correlation coefficient $r = 0.xxxx$

58. Using MATLAB to Solve Simple ChE Problems, I

Use MATLAB to determine the stoichiometric ratios of molecular species in the following reaction:



$$\alpha = \underline{\hspace{2cm}} \quad \beta = \underline{\hspace{2cm}} \quad \gamma = \underline{\hspace{2cm}} \quad \delta = \underline{\hspace{2cm}}$$

59. Using MATLAB to Solve Simple ChE Problems, II

It is proposed that a steel tank be used to store carbon dioxide at 300 K. The tank is 2.5 m³ in volume, and the maximum pressure it can safely withstand is 100 atm. Using the Beattie-Bridgeman equation of state given below, determine the maximum number of moles of CO₂ that can be stored in the tank

$$P = \frac{RT}{V} + \frac{\beta}{V^2} + \frac{\gamma}{V^3} + \frac{\delta}{V^4}$$

where

$$R = \text{gas constant} = 0.08206 \text{ L-atm/gmole-K}$$

P, V, T = pressure in atm, molar volume in L/gmole, and temperature in K respectively

$$\beta = RTB_0 - A_0 - \frac{Rc}{T^2}$$

$$\gamma = RTB_0b - A_0a - \frac{RcB_0}{T^2}$$

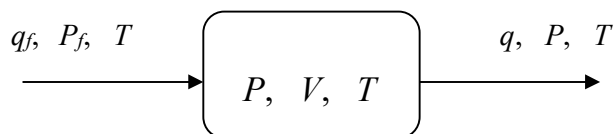
$$\delta = \frac{RTB_0bc}{T^2}$$

For CO₂, $A_0 = 5.0065$, $a = 0.07132$, $B_0 = 0.10476$, $b = 0.07235$, and $c = 66.0 \times 10^4$

Note that 1 m³ = 1000 L and 1 kg-mole = 1000 gmole

60. Dynamics of a Gas Surge Drum

Surge drums are often used as intermediate storage capacity for gas streams that are transferred between chemical process units. Consider a drum in the figure below, where q_f is inlet molar flowrate and q is the outlet molar flowrate.



- (a) Let V , P , and T be the volume, the pressure, and the temperature of the drum, respectively. Write a model (one differential equation) to describe how the pressure in the tank varies with time. Assume ideal gas and isothermal operation.
- (b) Solve for P analytically using the following data:

$$\begin{aligned} q_f &= 2.0 + 0.1t \text{ kmol/min} & q &= 3.0 \text{ kmol/min} \\ V &= 50 \text{ m}^3 & T &= 300 \text{ K} \\ R &= 8314 \text{ m}^3\text{-Pa/kmol-}^\circ\text{K} \end{aligned}$$

if the drum initially contains 10 kmol of methane. Assuming that the vessel was built to withstand a maximum pressure of 50 atm, how long can we run this operation before the inlet gas flow must be shut off?

- (c) The ideal gas law is a poor assumption because of high pressure in the drum. Suppose the methane gas stream obeys the virial equation of state as follows:

$$\frac{PV}{RT} = 1 + \frac{B(T)}{\underline{V}} + \frac{C(T)}{\underline{V}^2} + \frac{D(T)}{\underline{V}^3} + \dots$$

For simplicity, we will truncate all terms after the second virial coefficient $B(T)$. Repeat the calculations in Part (b). For methane, $B(T=300 \text{ K}) = 0.04394 \text{ m}^3/\text{kmol}$.

61. Solving a 2nd-Order Boundary-Value ODE

Consider the following 2nd-order boundary-value ODE over the domain $t = [0, 3]$, where a , b , c , and d are constant coefficients in the equation.

$$a \frac{d^2 y}{dt^2} + b \frac{dy}{dt} + c y = d y \sin(t) \quad \text{s.t. } y(0) = 1, y(3) = 2$$

- (a) Determine the constant coefficients a , b , c , and d in the ODE as follows:

$$\text{Given: } A = \begin{pmatrix} 10 & 3 & 4 & 8 & 12 \\ 20 & 7 & 1 & 14 & 9 \\ 3 & 2 & 5 & 6 & 15 \end{pmatrix} \quad B = \begin{pmatrix} \ln(\pi) & -2 & \sinh(1) \\ -8 & 10 & 3 \\ 11 & e^{\sin(2)} & \log_{10}(\pi) \end{pmatrix}$$

The coefficient a is equal to the inner product between the first row of Matrix B and the third column of Matrix A .

The coefficient b is equal to the sum of a row vector obtained from multiplying element-by-element between the last row of Matrix B and the sub-matrix $\begin{bmatrix} 7 & 1 & 14 \end{bmatrix}$ extracted from Matrix A .

The coefficient c is equal to the largest eigenvalue of Matrix B .

The coefficient d is equal to *inverse hyperbolic cosecant* of the first element (row-1, column-1) in the *inverse* matrix of Matrix B .

Use FORMAT SHORT in all your calculations.

(b) Solve the above 2nd-order ODE using *ode45*. Show answers in FORMAT SHORT.

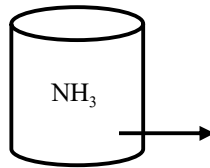
Answers:

(a) $a =$ _____; $b =$ _____; $c =$ _____; $d =$ _____

(b) $y'(0) =$ _____ (accurate to 4 decimal places)

62. Solving a Gas Leak Problem Using an Equation of State

A storage vessel contains ammonia gas that is slowly leaking out. A pressure gauge shows that the tank is losing 0.1 atm every minute. We are to use a very old equation of state first proposed in 1899 called Dieterici equation of state to describe the P - V - T behavior of the ammonia gas inside the vessel.



Dieterici equation of state is given as follows:

$$P = \frac{RT}{\underline{V} - b} \exp\left(-\frac{a}{RT\underline{V}}\right)$$

where $a = \frac{4R^2T_C^2}{P_C e^2}$ $b = \frac{RT_C}{P_C e^2}$ $T_C = 405.5 \text{ K}$ and $P_C = 111.3 \text{ atm}$ for NH₃

$$R = 0.08206 \text{ atm-L/gmole-K}$$

The temperature inside the storage vessel, whose volume is 100 L, is held constant at 320 K. The initial pressure of the vessel (before the leakage starts) is 50.0 atm. Use MATLAB to solve the following problems. You must carry out all calculations inside MATLAB without using a calculator to determine any intermediate or final results.

- (a) First, determine the initial number of moles of NH₃ inside the vessel, i.e. at $t = 0$ minute.
- (b) Solve for the number of moles left in the vessel at $t = 100 \text{ min}$, $t = 300 \text{ min}$, and $t = 460 \text{ min}$ using the *solve* function.
- (c) Derive a 1st-order ODE, dn/dt , i.e. $\frac{dn}{dt} = F(n, t)$, where n is the number of moles of NH₃ inside the vessel at any given time t . Then use MATLAB to solve for the rate of mole leakage at $t = 100 \text{ min}$, $t = 300 \text{ min}$, and $t = 460 \text{ min}$.

- (d) Finally, use *ode45* in MATLAB to solve the ODE in Part (c) which also gives the number of moles left in the vessel at any given time. Note answers from Part (b) and Part (d) should be the same.

Answers: (Show all numbers in 4 decimal places)

The initial number of moles = _____ gmoles

Time (min)	Moles Left in Vessel <i>n</i> in Part (b)	Moles Left in Vessel <i>n</i> in Part (d)	Rate of Leakage (gmoles/min)
100			
300			
460			

63. The Shooting Method to Solve a Linear ODE

Solve the following 2nd-order linear ODEs, which is a boundary-value problem, using MATLAB's *ode45* function with an increment in *x* of 0.05:

$$y'' - xy' + 3y = 11x$$

$$\text{subject to: } y(1) = 1.5 \\ y(2) = 15$$

Make a plot of the equation $y(x)$, and compare your MATLAB solution with the exact solution of $y'(1) = 5.500000$ by reporting the relative % difference. Include 6 decimal places in reporting all your numbers.

64. Solving a 3rd-Order Boundary-Value ODE Using the Shooting Method

Consider the following 3rd-order ODE which is a boundary-value problem:

$$y''' + 2y'' - ty' + y = (2t + 1)e^{-2t} - 4t^2 + 16 \quad 0 \leq t \leq 1$$

$$\text{s.t. } y(0) = 1, y(1) = 5.135335, y''(1) = 8.541341$$

The analytical solution to the above ODE is:

$$y(t) = ae^{-2t} + bt^2 + ct$$

Use *ode23* in MATLAB to solve for numerical solutions of the above ODE between $t = 0$ and $t = 1$ using a step interval of 0.1. Compare the MATLAB solutions with those from the analytical solutions in terms of % relative errors. You will need to solve for the coefficients *a*, *b*, and *c* in the analytical equation either by MATLAB or by hand (or both).

Answers: (Show 6 decimal places in the MATLAB solutions and write them down here)

Time	MATLAB $y(t)$	Exact $y(t)$	% Relative Error
$t = 0.0$		1.000000	
$t = 0.2$			
$t = 0.4$			
$t = 0.6$			
$t = 0.8$			
$t = 1.0$		5.135335	

65. Solving a 2nd-Order Nonlinear ODE Boundary-Value Problem

Consider the following 2nd-order ODE which is a boundary-value problem:

$$y'' + (y')^2 - y = 14t^2 - 7t + 4 \quad 0 \leq t \leq 2, \quad \text{s.t.} \quad y(0) = 1, y(2) = 7$$

Use *ode45* in MATLAB to solve for numerical solutions of the above ODE between $t = 0$ and $t = 2$ using a step interval of 0.1. Start your shooting method with $G1 = -2$ and $G2 = 2$ which will result in $G3$ by linear interpolation. Because the ODE is nonlinear, $G3$ will not produce or match $y(2) = 7$. Use a WHILE loop to keep performing linear interpolation between $G1$ and the newly calculated $G3$ in the WHILE loop until the relative error between $y(2) = 7$ and the MATLAB answer from *ode45* is less than or equal to 10^{-6} . Also, keep track of the number of iterations in the loop needed to produce the accuracy given above.

Answers: (Show 6 decimal places in the MATLAB solutions)

Number of iterations required = _____

Time	$y(t)$	$y'(t)$
$t = 0.0$		
$t = 0.5$		
$t = 1.0$		
$t = 1.5$		
$t = 2.0$		

66. Solving a 3rd-Order ODE Boundary-Value Problem

Consider the following 3rd-order ODE which is a boundary-value problem

$$y''' = ty + (t^3 - 2t^2 - 5t - 3)e^t \quad 0 \leq t \leq 1, \quad \text{s.t.} \quad y(0) = 0, y(1) = 0, y'(1) = -e^1$$

Use *ode45* in MATLAB to solve for numerical solutions of the above ODE between $t = 0$ and $t = 1$, showing a step size of 0.1.

The analytical (exact) solution of the above ODE is: $y(t) = t(a + bt)\exp(ct)$ where a , b , and c are constant coefficients. Also, use MATLAB and the numerical answers from *ode45* to determine the correct values of a , b , and c , without taking any derivatives of $y(t)$

Answers:

$$y(t=0) = \underline{\quad 0 \quad} \quad y'(t=0) = \underline{\hspace{2cm}} \quad y''(t=0) = \underline{\hspace{2cm}}$$

$$y(t=0.5) = \underline{\hspace{2cm}} \quad y'(t=0.5) = \underline{\hspace{2cm}} \quad y''(t=0.5) = \underline{\hspace{2cm}}$$

$$y(t=1) = \underline{\quad 0 \quad} \quad y'(t=1) = \underline{\quad -2.7183 \quad} \quad y''(t=1) = \underline{\hspace{2cm}}$$

The values of coefficients are: $a = \underline{\hspace{1cm}}$ $b = \underline{\hspace{1cm}}$ $c = \underline{\hspace{1cm}}$

67. Solving a 3rd-Order ODE Boundary-Value Problem

Consider the following 3rd-order ODE which is a boundary-value problem:

$$y''' - l^2 y' + a = 0 \quad 0 \leq t \leq 1, \quad \text{s.t.} \quad y(0) = 0.0894, y(0.5) = 0, y'(0.5) = -0.2640$$

The analytical (exact) solution of the above ODE is:

$$y(t) = \frac{a}{l^3} \left[\left(\sinh\left(\frac{l}{2}\right) - \sinh(lt) \right) + l \left(t - \frac{1}{2} \right) + \tanh\left(\frac{l}{2}\right) \left(\cosh(lt) - \cosh\left(\frac{l}{2}\right) \right) \right]$$

Use *ode23* in MATLAB to solve for numerical solutions of the above ODE between $t = 0$ and $t = 1$, when $l = 2$ and $a = -3$, showing a step size of 0.1. Then compare the numerical solutions with the exact solutions by calculating the relative percentage deviation in 6 decimal places at $t = 0, 0.2, 0.4, 0.6, 0.8$, and 1.0 . Note that the percentage deviations must be positive numbers.

Answers: (accurate to 6 decimal places)

$$y(t=0)_{\text{MATLAB}} = \underline{\hspace{2cm}} \quad y(t=0)_{\text{EXACT}} = \underline{\hspace{2cm}} \quad \% \text{ Deviation} = \underline{\hspace{2cm}}$$

$$y(t=1)_{\text{MATLAB}} = \underline{\hspace{2cm}} \quad y(t=1)_{\text{EXACT}} = \underline{\hspace{2cm}} \quad \% \text{ Deviation} = \underline{\hspace{2cm}}$$

68. Solving a 2nd-Order Boundary-Value ODE Using the Shooting Method

The diffusion and simultaneous first-order irreversible chemical reaction in a single phase containing only reactant A and product B results in a second-order ODE given by:

$$\frac{d^2 C_A}{dz^2} = \frac{k}{D_{AB}} C_A$$

where C_A is the concentration of reactant A (kmol/m³), z is the distance variable (m), k is the homogeneous reaction rate constant (s⁻¹), and D_{AB} is the binary diffusion coefficient (m²/s). A typical geometry for the above ODE is that of a one-dimensional layer that has its surface exposed to a known concentration and allows no diffusion across its bottom surface. Thus, the initial and boundary conditions are:

$$C_A(z=0) = C_{A0} \quad \text{and} \quad \frac{dC_A}{dz}(z=L) = 0$$

where C_{A0} is the constant concentration at the surface ($z = 0$) and there is no transport across the bottom surface ($z = L$) so the derivative is zero. This differential equation has an analytical solution given by:

$$C_A = C_{A0} \frac{\cosh\left[L\left(\sqrt{\frac{k}{D_{AB}}}\right)\left(1 - \frac{z}{L}\right)\right]}{\cosh\left[L\left(\sqrt{\frac{k}{D_{AB}}}\right)\right]}$$

- Is the above ODE linear or nonlinear? Write a MATLAB program to implement the shooting method to solve the above ODE (use *ode23*), in which $C_{A0} = 0.2 \text{ kmol/m}^3$, $k = 0.001 \text{ s}^{-1}$, $D_{AB} = 1.2 \times 10^{-9} \text{ m}^2/\text{s}$, and $L = 0.001 \text{ m}$. Use “format short e”.
- Compare the concentration profiles over the thickness as predicted by the numerical solution of (a) with the analytical solution by reporting the relative percentage differences accurate to 6 decimal places with an increment of $\Delta z = 10^{-4}$.
- Obtain a numerical solution for a second-order reaction that requires the C_A term on the right side of the ODE to become squared. The second-order rate constant is given by $k = 0.02 \text{ m}^3/(\text{kmole}\cdot\text{s})$. Use “format short e” and *ode23*. Is this new ODE linear or nonlinear?

69. Solving a Nonlinear 3rd-Order ODE Boundary-Value Problem

Consider the following *nonlinear* 3rd-order ODE which is a boundary-value problem:

$$4y(y''') - t^3 y' + \cos(y) = e^{2t}$$

with the following boundary conditions: $y(0) = 1.0$, $y(2) = 29.3373$, $y''(2) = 5.1807$. Use the shooting method and *ode45* in MATLAB to solve the above equation numerically from $t = 0$ to $t = 2$. Because the ODE is nonlinear, your answer will not be correct after 3 trials. Rather than guessing the answer repeatedly, you are to use the *while* loop in MATLAB to keep interpolating linearly between the two latest guesses until $|\text{answer} - \text{target}| < 0.0001$. Start your shooting method with the following two guesses: $G1 = 10$ and $G2 = 20$. After obtaining $G3$ from linear interpolation, your $G1$ becomes $G2$ and $G2$ becomes $G3$. Keep repeating the process until the tolerance of 0.0001 is achieved.

Answers: (accurate to 4 decimal places)

$y(0) =$	<u>1.0000</u>	$y'(0) =$	_____	$y''(0) =$	_____
$y(1) =$	_____	$y'(1) =$	_____	$y''(1) =$	_____
$y(2) =$	<u>29.3373</u>	$y'(2) =$	_____	$y''(2) =$	<u>5.1807</u>

70. Isothermal Compression of Ethane

Ethane is being compressed isothermally at 50 °C (323.15 Kelvin) to 1/100th (i.e. 1%) of its initial volume in a closed vessel. The initial pressure of the gas is 1.01325 bar.

We wish to calculate the work per gmole required in this compression. For a closed system in a reversible isothermal compression from V_1 to V_2 , the work W done on the system can be calculated from:

$$\frac{dW}{dV} = -P$$

Use MATLAB to do the following:

- Calculate the work W using the ideal gas assumption.
- Calculate the work W using the Redlich-Kwong-Soave equation of state, which is given by:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)}$$

where

$$b = 0.08664 \frac{RT_c}{P_c}$$

$$a = 0.42748 \frac{(RT_c)^2}{P_c} \left[1 + m(1 - \sqrt{T_r}) \right]^2$$

$$T_r = \frac{T}{T_c}$$

and

$$m = 0.480 + 1.574\omega - 0.176\omega^2$$

- P = pressure in bar
- V = molar volume in L/gmole
- T = temperature in K
- R = gas constant (0.08315 bar-L/gmole-K)
- T_c = critical temperature in K (305.556 K for ethane)
- P_c = critical pressure in atm (48.2989 bar for ethane)
- ω = Pitzer acentric factor (0.1064 for ethane)

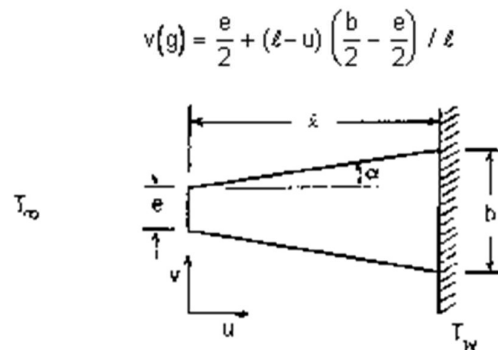
Answers:

(a) Work (ideal gas) = _____ bar-L/gmole

(b) Work (RKS gas) = _____ bar-L/gmole

71. Heat Transfer in a Tapered Fin

Consider a tapered fin of trapezoidal profile:



The governing equation for the temperature distribution in the fin is the dimensionless second-order differential equation

$$\frac{d^2 y}{dx^2} = \frac{2(N_4)y/\cos\alpha + (N_3 - N_2)dy/dx}{N_2 + (N_3 - N_2)(1-x)} - N_1$$

where y = dimensionless temperature = $(T - T_\infty) / (T_w - T_\infty)$

x = dimensionless distance = u / ℓ

$$N_1 = q \ell^2 / k (T_w - T_\infty)$$

where q is the uniform rate of internal heat generation per unit volume (via nuclear fission, electrical dissipation, chemical reaction, etc.) and k is the thermal conductivity.

$$N_2 = e / \ell$$

$$N_3 = b / \ell$$

$$N_4 = \bar{h} \ell / k$$

where $\bar{h}$ is the average convective heat transfer coefficient.

Based upon the known physical conditions for a fin, it is possible to solve for the one dimensional temperature distribution inside the fin if we know the boundary conditions. For this problem, the fin has adiabatic ends, i.e. $T = T_\infty$ at $u = 0$ and $T = T_w$ at $u = \ell$.

The physical conditions of the fin are given as follows:

$$e = 30 \text{ cm}$$

$$b = 60 \text{ cm}$$

$$\ell = 300 \text{ cm}$$

$$T_{\infty} = 20^{\circ}\text{C} \qquad T_w = 100^{\circ}\text{C}$$

Answers: (accurate to 4 decimal places)

$$y'(0) = \quad \quad \quad T(u=150 \text{ cm}) = \quad \quad \quad ^\circ\text{C}$$

$$\sin x = \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)!} x^{2n+1} = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \cdots \text{ for all } x$$

$$\sqrt{1+x} = \sum_{n=0}^{\infty} \frac{(-1)^n (2n)!}{(1-2n)(n!)^2 (4^n)} x^n = 1 + \frac{1}{2}x - \frac{1}{8}x^2 + \frac{1}{16}x^3 - \frac{5}{128}x^4 + \dots \text{ for } |x| < 1$$

$$\frac{\sin(x)}{x} \quad \text{at } x=2, \text{ where } x \text{ is in radians}$$

$$x\sqrt{1+x} \quad \text{at } x=0.5$$
$$|Exact \ Solution - Maclaurin \ Solution| \leq 10^{-14}$$

Answers:

Maclaurin series solution for the sine function =

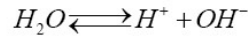
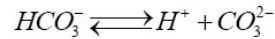
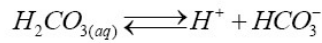
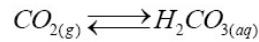
Number of terms required = _____

Maclaurin series solution for the sine function = _____

Number of terms required = _____

73. pH of Natural Rain Water

CO₂ is a trace yet important constituent of the atmosphere that keeps the earth warm enough for life in their current forms. The concentration of CO₂ before the industrial revolution has been relatively constant over a long period. CO₂ is slightly water soluble, which makes the natural rain in a clean atmosphere slightly acidic due to the dissolution of CO₂ into the cloud droplets. The partitioning of CO₂ into a droplet can be described by the following equilibrium relations:



The concentration of hydrogen ion (H⁺) in the water determines its acidity. A higher concentration of H⁺ means higher acidity. The acidity of a rain or cloud droplet is usually quantified by the pH of the droplet, which is related with the concentration of H⁺ ([H⁺]) using the following equation: pH = -log₁₀[H⁺]. Thus, lower pH means higher acidity.

Based on the above equilibrium relationships and the principle of charge balance in an aqueous solution, the [H⁺] in the CO₂/H₂O system (and thus the pH) can be determined using the following equation:

$$\frac{K_w}{[H^+]} + \frac{K_{a1,CO_2} K_{H,CO_2} p_{CO_2}}{[H^+]} + \frac{2K_{a1,CO_2} K_{a2,CO_2} K_{H,CO_2} p_{CO_2}}{[H^+]^2} - [H^+] = 0 \quad (1)$$

where pCO₂ is the partial pressure of CO₂ in the atmosphere (in units of atm); K_{H,CO₂}, K_{a1,CO₂}, K_{a2,CO₂} are Henry's law constant (in units of M/atm), and first and second acid dissociation constants for CO₂, respectively, and K_w is the water dissociation constant (which varies with temperature). For a given value of the partial pressure of CO₂, the concentration of H⁺ and thus the pH can be determined.

(a) Given that K_w = 1.8×10⁻¹⁴ (when T = 30°C) K_{H,CO₂} = 10^{-1.46}, K_{a1,CO₂} = 10^{-6.3}, K_{a2,CO₂} = 10^{-10.3}, and pCO₂ = 280 ppm (atm), use function *solve* in MATLAB to determine the pH of natural rain water. Use *format short* in all your calculations.

(b) Verify the answer in Part (a) by using the function *roots* in MATLAB.

- (c) Equation (1) which is nonlinear can be solved using a root-finding algorithm. One such method discussed in class is *Newton-Raphson* whose iterative formula for one variable is given by:

$$x_{k+1} = x_k - \frac{f(x_k)}{f'(x_k)} \quad k = 1, 2, 3, \dots$$

Write a MATLAB program to generate a plot of CO₂ partial pressure (ppm) vs. pH of natural rain water using Newton-Raphson. Provide a title and label your x -axis and y -axis properly. The pH should be calculated at CO₂ partial pressures between the range of 280 ppm and 420 ppm using an increment of 20 ppm (use a FOR loop). At pCO₂ = 280 ppm, use an initial guess of $[H^+] = 5.0 \times 10^{-6}$ to solve Equation (1). For subsequent pCO₂'s, use the answer from the previous increment as the initial guess, e.g. use the $[H^+]$ solution from the case where pCO₂ = 280 ppm as a starting point for the case where pCO₂ = 300 ppm. You may rearrange Equation (1), $f([H^+]) = 0$, into another form in order to help determine $f'([H^+])$ more easily. The termination criterion for Newton-Raphson is when the absolute relative percent error of the pH (not $[H^+]$) between two successive iterations is less than 10^{-4} .

Answers: pH (pCO₂ = 280 ppm) = _____
 pH (pCO₂ = 360 ppm) = _____ pH (pCO₂ = 420 ppm) = _____

74. Producing a Palindromic Number by Reverse-Then-Add Algorithm

A palindromic number or numeral palindrome is a number that remains the same when its digits are reversed. Examples of numeral palindrome are 22, 16461, and 23232 (notice the symmetry in the numbers). An algorithm called reverse-then-add is known to produce a palindromic number. The algorithm is very simple to state:

Given a positive integer of two digits or more, reverse the digits and add this new number to the original number. Repeat the operation until a palindromic number is obtained.

For example, let's start with a positive integer 19. The reverse-then-add algorithm gives the following sequence of numbers: 19, 91, 110, 11, and 121, the last of which is a palindromic number. Interestingly, this algorithm does not produce palindromes for a few known integers, such as 196, 295, 394, 493, 592, 689, 691, 788, 790, 879, and 887, the smallest of which is 196. As a result, the reverse-then-add algorithm is sometimes known as the 196-algorithm.

On the other hand, some small integers are known to produce very large palindromes. An example is the integer 89 which eventually produces the palindrome 8813200023188.

Write a MATLAB code that implements the 196-algorithm, given a positive integer with two digits or more (no error checking is required except that if the given integer is already palindromic, then your script file should print out this message and exit the program). To implement the algorithm, you will need to know how to reverse an integer. The following compact formula is known to produce the reverse of an integer number x :

$$x10^{\lfloor \log_{10} x \rfloor} - 99 \sum_{k=1}^{\lfloor \log_{10} x \rfloor} \lfloor x10^{-k} \rfloor 10^{\lfloor \log_{10} x \rfloor - k}$$

where $\lfloor \log_{10} x \rfloor$ is the floor of $\log_{10}(x)$. For example, $\lfloor 10.2 \rfloor = 10$ and $\lfloor 10.8 \rfloor = 10$ as well

You must implement this reverse formula as a function in MATLAB. For example, if you call your function *reverse*, then *reverse*(12345) will produce 54321. In your output, store and show the sequence of numbers generated by the 196-algorithm as an $n \times 2$ matrix. For example, given the integer 5208, your MATLAB output should look as follows:

5208	8025
13233	33231
46464	46464

Test your MATLAB program with the following integers: 18, 551, and 8534.

Answer the following questions:

Starting Integer	Palindrome
18	
551	
8534	

75. Programming with MATLAB (Classification of Numbers)

In this problem, you are given a list of positive integers that we like to classify as either prime number, square number, semi-square number, or neither (i.e. the number does not belong to any of the 3 classes). You are to write a MATLAB to do the classification. Here are the definitions of each class of number:

1. *Prime number* – a positive integer larger than 1 that is not divisible by any integer except 1 and the number itself. Examples of prime numbers are 3, 11, 23, and 29.
2. *Square number* – a positive integer n which is the sum of the square of consecutive positive integers starting at 1. For example, 140 is a “square” number because $140 = 1^2 + 2^2 + 3^2 + 4^2 + 5^2 + 6^2 + 7^2$.
3. *Semi-square number* – a positive integer n which is the sum of the square of consecutive positive *odd* or *even* integers starting at 1 or 2, respectively. For example, 84 is a semi-square number because $84 = 1^2 + 3^2 + 5^2 + 7^2$. So is 120 because $120 = 2^2 + 4^2 + 6^2 + 8^2$.

Note that a given positive integer will only belong to one of the four number classes. Finally, you need to know the 4 simple rules of finding a prime number as follows:

- (i) Rule 1: Check if the number is even. If it is, it is not a prime number because it is divisible by 2 (Note that 2 is the exception and is a prime number).
- (ii) Rule 2: Check if the number is divisible by 3 or 5. If it is, it is not a prime number.

- (iii) Rule 3: Find the square root of the number. If the square root results in an integer, the number is not a prime number.
- (iv) Rule 4: Divide the number by all the prime numbers less than the square root (but can skip 2, 3, and 5). If the number is not divisible by any of the prime number less than the square root, the number is a prime. Otherwise, it is a composite. You will also need the following prime numbers up to 100 in Rule (iv):

[7 11 13 17 19 23 29 31 37 41 43 47 53 59 61 67 71 73 79 83 89 97]

You will test your program on a total of 10 positive integers with the following values which you should put into a vector:

[455, 647, 650, 731, 991, 969, 652, 819, 560, 863]

The output from MATLAB should show which class or classes a given number belongs to.

Answers:

Prime numbers are: _____

Square numbers are: _____

Semi-square numbers are: _____

Neither are: _____

76. Implementing a Matrix Processing Algorithm as a MATLAB Function, I

Write a function in MATLAB that processes each element, one by one from left to right and from top to bottom, of a given $n \times m$ matrix called A entered into a main script file. The matrix contains both integers and real numbers (i.e. numbers with decimal places). The processing algorithm is as follows:

1. Separate the elements of A into two row vectors based on whether they are integer numbers or real numbers. But do not sort the numbers from smallest to largest or vice versa.
2. Combine the two vectors by alternatively taking elements from each vector, starting with the first element in each vector, but the first element in the combined vector must be an integer. When you run out of elements to take from either row vector, stop. As a result, your combined row vector will contain equal number of integer numbers and real numbers.
3. Display all elements in your combined row vector in one column as shown in the program output below

Your function must take n , m , and A as input and display the output on the computer screen as shown below. The matrix A is given as:

$$A = \begin{bmatrix} \pi & 1.2340 & 10 & e^2 & 4 \\ 2 & 5.9824 & 6.1832 & 1.1111 & 8 \\ 12 & 5 & 9.9999 & 1 & 5.4321 \\ 7.2467 & 2.1414 & 15 & 3.3333 & 0.3245 \end{bmatrix}$$

The output should look as follows:

The combined column vector:

```
10
3.1416
4
1.2340
2
7.3891
8
5.9824
12
6.1832
5
1.1111
1
9.9999
15
5.4321
```

77. Implementing a Matrix Processing Algorithm as a MATLAB Function, II

Write a function in MATLAB that processes each element, one by one from left to right and from top to bottom, of a given $n \times m$ matrix called **A**, which is to be entered into a main script file. The matrix contains different types of numbers, namely negative numbers (both integer and real), positive integer numbers, positive real numbers, and complex numbers (with both real and imaginary parts). The processing algorithm is as follows:

1. If an element is negative, check to see if the number is an integer. If the number is a negative integer, reverse the sign so that it becomes positive. If the number is a negative real number, take the square root of the number to obtain a complex number.
2. If an element is a positive integer, square the number.
3. If an element is a positive real number, create two numbers from it. One number is the integer part and the second number is the decimal part. For example, if the element has a value of 3.1415, then the first number obtained is an integer 3 while the second number is a real number 0.1415.
4. If an element is a complex number, take the imaginary part of the complex number and make it a real number.

Now write a MATLAB function that takes n , m , and **A** as input. The output from the function which is to be passed back to the script file must contain all the processed numbers sorted by 3 columns. The first column contains all numbers that are integers (can be positive, negative, or zero). The second column contains all numbers that are real (i.e. with decimal places). The third column contains all complex numbers. Note that you need not sort numbers in each column in ascending/descending order. Instead, the numbers in each column appear in the order in which the elements in the matrix **A** is processed. Because the number of elements in each column may not be equal, we will use zeroes as fillers to ensure that each column has the same length of p . Thus, your output from the MATLAB function will be a $p \times 3$ matrix **M**.

Note that you every number in the matrix should be displayed using Format Short (i.e. with 4 decimal places), regardless of whether the number is real, integer, or complex, in the script file.

$$A = \begin{bmatrix} \pi & -1.2340 & 3 & -e^2 & -8 & 2.5 + 1.2i \\ \sqrt{-20} & 5.8934 & -6.1008 & 1.1111 & 8 & -15 \\ 5 & \sqrt[3]{12} & -15.15 & 1 & 5.4321 & -10.25 \\ \sqrt[3]{-30.5} & 0.65^{-2} & -15 & \sqrt[4]{81} & 1.3245 & -3.3333 \end{bmatrix}$$

The output matrix **M** should look as follows:

The output matrix M:

3.0000	0.1416	0 + 1.1109i
9.0000	1.2000	0 + 2.7183i
8.0000	4.4721	0 + 2.4700i
5.0000	0.8934	0 + 3.8923i
1.0000	0.1111	0 + 3.2016i
64.0000	0.2894	0 + 1.7676i
15.0000	0.4321	0 + 1.8257i
25.0000	0.3669	0
2.0000	0.3245	0
1.0000	0	0
5.0000	0	0
2.0000	0	0
15.0000	0	0
9.0000	0	0
1.0000	0	0