458.205 Basic Computer Methods in Chemical and Biological Engineering
Chapter 1: Converting the Earth's Resources into Useful Products

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Syllabus - Read Carefully

- This course uses etl
    - etl.snu.ac.kr

Why do we need chemical processes?

- Make a material with desired properties.
- Convert waste material into useful products.
- Increase availability of desired products.
- Obtain energy from materials.

Chemical processes by the numbers

Type of Chemical Process	Typical Plant Capacity [lb/yr]	Typical Product Value [$/lb]	Typical Waste Generation [lb waste/lb product]
Petroleum	1-100 billion	0.1	0.1
Bulk commodity	10-1000 million	0.1-2	0.1-5
Fine specialty	0.1-10 million	2-10	2-50
Pharmaceutical	1-100 thousand	10-priceless	10-100

The first step in process synthesis

- For the product we want, choose
  - the best raw materials
  - and the best reaction pathways
    - Generation-consumption analysis is useful.
- For the scale-up, how do we compare different options?
  - Quantitative measures of efficiency
    - atom economy
    - process economy

Balancing chemical reactions

$$C_6H_{12}O_6 + O_2 \longrightarrow CO_2 + H_2O$$

$$C_6H_{12}O_6 + O_2 \longrightarrow 6CO_2 + 6H_2O$$

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$$

Stoichiometric coefficients ν :

- negative if reactant, positive if product
- relative ratio (not absolute quantity)

$$\nu_{\mathrm{glucose}} = -1, \quad \nu_{\mathrm{O_2}} = -6, \quad \nu_{\mathrm{CO_2}} = 6, \quad \nu_{\mathrm{H_2O}} = 6$$

$$\frac{1}{3}C_6H_{12}O_6 + 2O_2 \longrightarrow 2CO_2 + 2H_2O$$

$$\nu_{\mathrm{glucose}} = -1/3, \quad \nu_{\mathrm{O_2}} = -2, \quad \nu_{\mathrm{CO_2}} = 2, \quad \nu_{\mathrm{H_2O}} = 2$$

Formal procedure for balancing chemical rxns

$$\mathrm{C_6H_{12}O_6} + 6\mathrm{O_2} \longrightarrow 6\mathrm{CO_2} + 6\mathrm{H_2O}$$

i = counter for compound

h = counter for element

ν_i = stoichiometric coeff. for compound *i*

ε_{hi} = number of atoms of element h in compound *i*

$$\sum \varepsilon_{hi}\nu_i = 0$$

$$\sum \varepsilon_{\mathrm{C}i}\nu_i = [6 \times (-1)] + [0 \times (-6)] + [1 \times 6] + [0 \times 6]$$

$$\sum \varepsilon_{\mathrm{H}i}\nu_i = [12 \times (-1)] + [0 \times (-6)] + [0 \times 6] + [2 \times 6]$$

$$\sum \varepsilon_{\mathrm{O}i}\nu_i = [6 \times (-1)] + [2 \times (-6)] + [2 \times 6] + [1 \times 6]$$

Element balance for stoichiometric coeff.

$$\mathrm{NH_3} + \mathrm{O_2} \longrightarrow \mathrm{NO} + \mathrm{H_2O}$$

$$\sum \varepsilon_{\mathrm{N}i}\nu_i = [1 \times \nu_{\mathrm{NH_3}}] + [0 \times \nu_{\mathrm{O_2}}] + [1 \times \nu_{\mathrm{NO}}] + [0 \times \nu_{\mathrm{H_2O}}]$$
$$\sum \varepsilon_{\mathrm{H}i}\nu_i = [3 \times \nu_{\mathrm{NH_3}}] + [0 \times \nu_{\mathrm{O_2}}] + [0 \times \nu_{\mathrm{NO}}] + [2 \times \nu_{\mathrm{H_2O}}]$$
$$\sum \varepsilon_{\mathrm{O}i}\nu_i = [0 \times \nu_{\mathrm{NH_3}}] + [2 \times \nu_{\mathrm{O_2}}] + [1 \times \nu_{\mathrm{NO}}] + [1 \times \nu_{\mathrm{H_2O}}]$$

Set $\nu_{\mathrm{NH_3}}$ **=-4**

$$\nu_{\mathrm{NO}} = +4,\ \nu_{\mathrm{H_2O}} = +6,\ \nu_{\mathrm{O_2}} = -5$$

$$4\mathrm{NH_3} + 5\mathrm{O_2} \longrightarrow 4\mathrm{NO} + 6\mathrm{H_2O}$$

Combining chemical rxns into a rxn pathway

$$4\mathrm{NH_3} + 5\mathrm{O_2} \longrightarrow 4\mathrm{NO} + 6\mathrm{H_2O}$$

$$\mathrm{NO} + \frac{1}{2}\mathrm{O_2} \longrightarrow \mathrm{NO_2}$$

$$3\mathrm{NO_2} + \mathrm{H_2O} \longrightarrow 2\mathrm{HNO_3} + \mathrm{NO}$$

What we want:

- Net generation of HNO_3
- Net consumption of NH_3, O_2
- Zero net generation or consumption of NO, NO_2
- Acceptable generation or consumption of H_2O

Generation-consumption
Step 4: Find Calculate

$$(\mathrm{R1})\ 4\mathrm{NH_3} + 5\mathrm{O_2} \rightarrow 4\mathrm{NO} + 6\mathrm{H_2O}$$

$$(\mathrm{R2})\ \mathrm{NO} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{NO_2}$$

$$(\mathrm{R3})\ 3\mathrm{NO_2} + \mathrm{H_2O} \rightarrow 2\mathrm{HNO_3} + \mathrm{NO}$$

Compound	ν_{i1}	ν_{i2}	ν_{i3}	$\nu_{i,net}$
NH_3	(-4)			-2
O_2	(-5)	(-0.5)		-4
NO	(+4)	(-1)	+1	0
NO_2		(+1)	-3	0
HNO_3			+2	+2
H_2O	(+6)		-1	+2

The bottom-line: Process economy

Value of products generated divided by cost of reactants consumed.

Basis: 63 million lb/yr nitric acid
Scale-up factor: 63 million/126 = 0.5 million

Compound	$\nu_{i,net}\, M_i$	Flow Rate (million lb/yr)	Value ($/lb)	Value ($million/yr)
NH_3	-34	-17	0.23	-3.91
O_2	-128	-64	0.03	-1.92
HNO_3	+126	+63	0.11	+6.93
H_2O	+36	+18	0	0

Net Profit: 6.93-3.91-1.92 = 1.10 million $/yr

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Chapter 2: Process Flow: Variables, Diagrams, Balances

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2.1 Introduction

- Chemical process plant
  - A physical facility in which the raw materials undergo chemical and physical changes to make desired products
  - Common features:
    - Feed preparation facilities
    - Reactors
    - Separators
    - Environmental control facilities
    - Material transfer equipment
    - Energy transfer equipment

2.2 Process Variables

- moles, mass, composition, concentration, pressure, temperature, volume, density, and flowrate
- Dimensions
  - M: mass
  - L: length
  - t: time
  - T: thermodynamic temperature
  - N: amount of substance

2.3 Process Flow Sheets

Visual representations of chemical and physical changes that occur as the raw materials are transformed into the desired products

A new route to styrene?

$$C_2H_4 + C_6H_6 \rightarrow C_8H_8 + H_2$$

$$CH_3OH + C_7H_8 \rightarrow C_8H_8 + H_2O + H_2$$

Compound	ν_i	M_i	$\nu_i\ M_i$	Flow Rate (tons/yr)	\$/ton	\$M/yr
CH_3OH	-1	32	-32	-76,900	450	-35
C_7H_8	-1	92	-92	-221,200	1010	-223
C_8H_8	+1	104	+104	+250,000	1380	+345
H_2O	+1	18	+18	+43,300	0	
H_2	+1	2	+2	+4,800	0	

Atom economy: 84%, Profit: $87M/yr

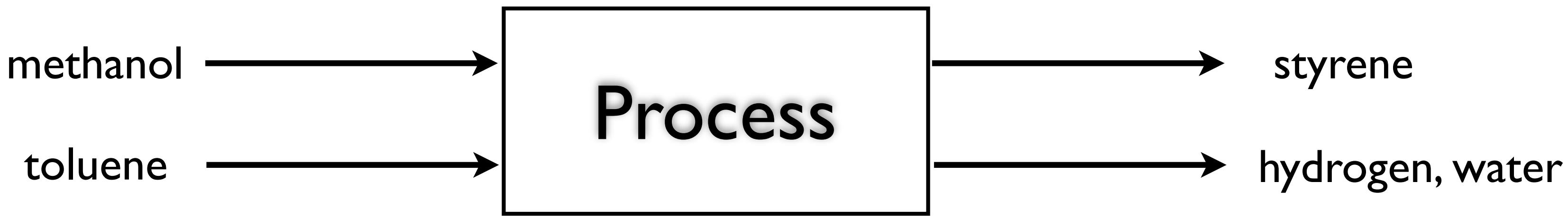
Types of process flowsheets

- Input-Output Diagram
- Block Flow Diagram
- Process Flow Diagram (PFD)

Increasing Complexity

Input-Output Diagram

$$CH_3OH + C_7H_8 \rightarrow C_8H_8 + H_2O + H_2$$



- A box represents the entire process.
- Lines with arrows show flow of reactants into process, and flow of products and byproducts out of process.

Input-Output Diagram

Compound	ν_i	M_i	ν_i M_i	Flow Rate (tons/yr)	$/ton	$M/yr
CH_3OH	-1	32	-32	-76,900	450	-35
C_7H_8	-1	92	-92	-221,200	1010	-223
C_8H_8	+1	104	+104	+250,000	1380	+345
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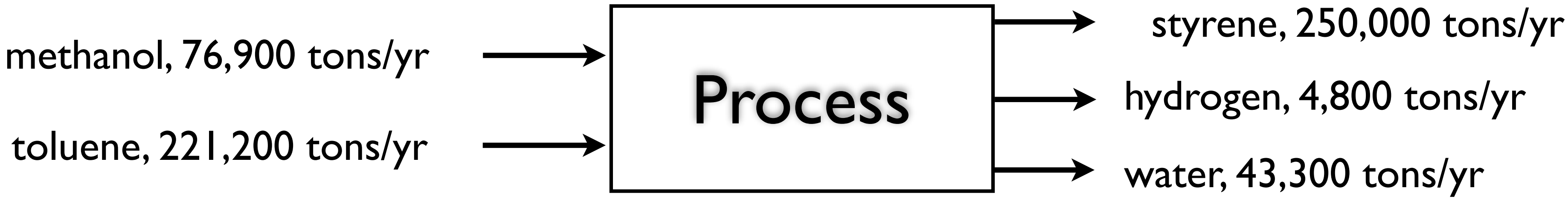


methanol, 76,900 tons/yr

toluene, 221,200 tons/yr

Process

styrene, 250,000 tons/yr

hydrogen, 4,800 tons/yr

water, 43,300 tons/yr

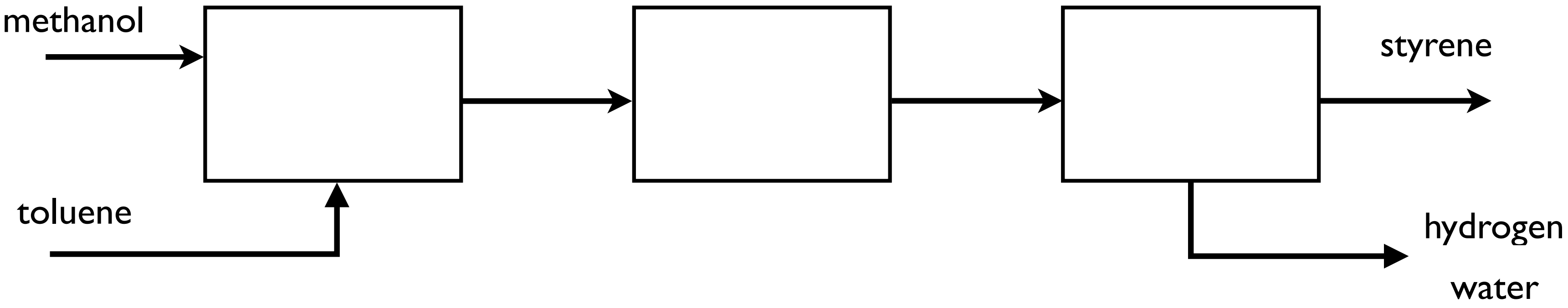
Block Flow Diagram

- Boxes represent process units.
- Each process unit represents a specific process function:

  mixer, splitter, reactor, separator.
- Lines with arrows show flow of materials into and out of

  process units.

Block Flow Diagram



Stream / Flow rate ton/yr	Methanol feed to mixer	Toluene feed to mixer	Reactor input	Reactor output	Product from separator	Byproduct from separator
Methanol	76,900		76,900			
Toluene		221,200	221,200			
Styrene				250,000	250,000	
Hydrogen				4,800		4,800
Water				43,300		43,300
Total	76,900		298,100	298,100	250,000	48,100

Process Flow Diagram (PFD)

- Process equipment is shown representatively, with icons. Decisions have been made about reactor type and separation methods.
- Equipment for moving materials or for heat exchange may be shown.
- Information about utilities may be shown.
- Lines with arrows show flow of materials into and out of process units.

Mixer

- Mixer 아이콘을 사용하지 않고 두 개의 선이 만나는 모양.
- 이는 혼합이 파이프 라인에서 이루어짐을 의미함.

Fired Heater

- Furnace라고도 함.
- “Off gas”: 공정에서 발생하는 배가스 중 연료로 사용가능한 것
- 혼합된 반응물을 일정 온도까지 올리는 역할
- 연소시 발생하는 열을 이용해 BFW(Boiler Feed Water)로부터 스팀 생산

Reactor

- 부산물: 수소 및 물
- 부반응으로 인해 에틸벤젠과 타르 생성
- Pellet형태로 촉매가 채워져 있는 “packed bed reactor”
- 반응물은 밑으로 들어가고 생성물은 위에서 나옴

Heat exchanger

- 반응기에서 나오는 뜨거운 가스가 열교환기를 통해 냉각됨
- 주로 Shell-and-Tube 형태
- 뜨거운 생성가스가 튜브를 통과함
- 재순환되는 차가운 톨루엔 스트림을 반응기에 넣기전에 가열필요

Condenser

- 열교환기와 분리기가 결합된 형태
- CW(cooling water)와 열교환을 하여 추가로 생성가스 추가 냉각
- 냉각수는 상온이므로 섭씨 25-30도 정도로 냉각 가능
- 톨루엔, 스타이렌, 에틸벤진, 타르, 물 모두 액화
- 수소는 상온에서 아직 기체임. 따라서 수소 가스 분리가 용이

Phase separator

- 유입 스트림이 유성의 유기물과 물을 포함하므로 자연스레 two-phase형성
- 스트림을 horizontal vessel내에 놔두면 상분리가 됨
- 상부에서 유기물, 하부에서 물을 분리할 수 있음 (밀도 차)

Toluene recovery column

- 증류탑을 이용해 반응하지 않은 톨루엔을 스타이렌과 기타 부산물로부터 분리 - 휘발도(volatility) 차이
- 증류탑의 두 개 product 스트림: distillate and bottoms
- 상부에서 끓는점이 가장 낮은 톨루엔 분리, 하부에서 나머지 회수
- 증류탑 내부에는 “tray”가 있고 기액평형이 일어남

Reflux

- 증류탑 상단으로 vapor가 빠져나가고 이는 다시 냉각되어 일부 증류탑으로 되돌려진다. 이를 reflux라 부름
- 나머지는 distillate

Recycle

- 펌프를 나타내는 아이콘 사용
- 액체 수송은 펌프, 기체 수송은 컴프레서가 담당.
- 반응하지 않은 톨루엔을 재순환 시켜 톨루엔을 늘 excess로 유지시킴 (부반응을 줄이기 위한 방법)

Reboiler

- 증류탑 하부 근처에는 reboiler(재비기)가 있음
- 재비기는 하부로 유출되는 액체 일부를 끓여 기화시켜 증류탑 안으로 보냄

Ethylbenzene/styrene column

- 증류탑. 부산물인 EB를 스티렌으로 부터 분리 (EB가 끓는점이 낮음)
- 탑 하부로 스티렌과 타르 혼합물이 나옴
- 주의: PFD상에 splitter로 명명됐으나 엄밀한 의미의 splitter가 아님 (교과서 정의)

Styrene purification column

- 스티렌 모노머를 타르로부터 분리 (스티렌이 끓는점이 낮음)
- 타르는 공정 내의 다른 곳에서 에너지원료로 사용가능
- 세 개의 증류탑으로 4성분을 분리해냈음

Modes of process operation

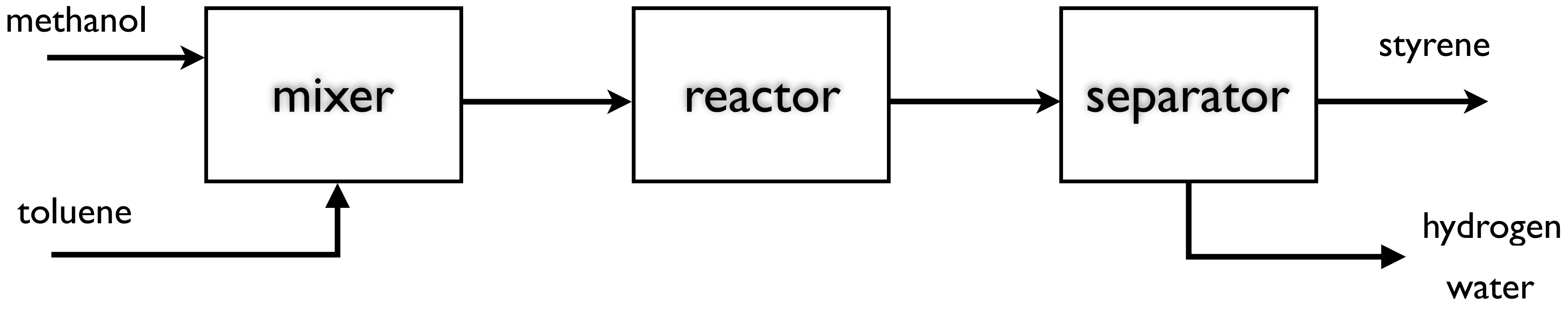
- Batch: Raw materials enter all at once, physical and/or chemical changes occur, and later products are removed all at once.
- Continuous-flow: Raw materials enter a process continuously, and products leave continuously.
- Semi-batch: Some combination of batch and continuous-flow.

- Steady-state: Process variables do not change with time.
- Unsteady-state: Process variables change with time.

Process flowsheet definitions

System: A specified volume with a well-defined boundary.

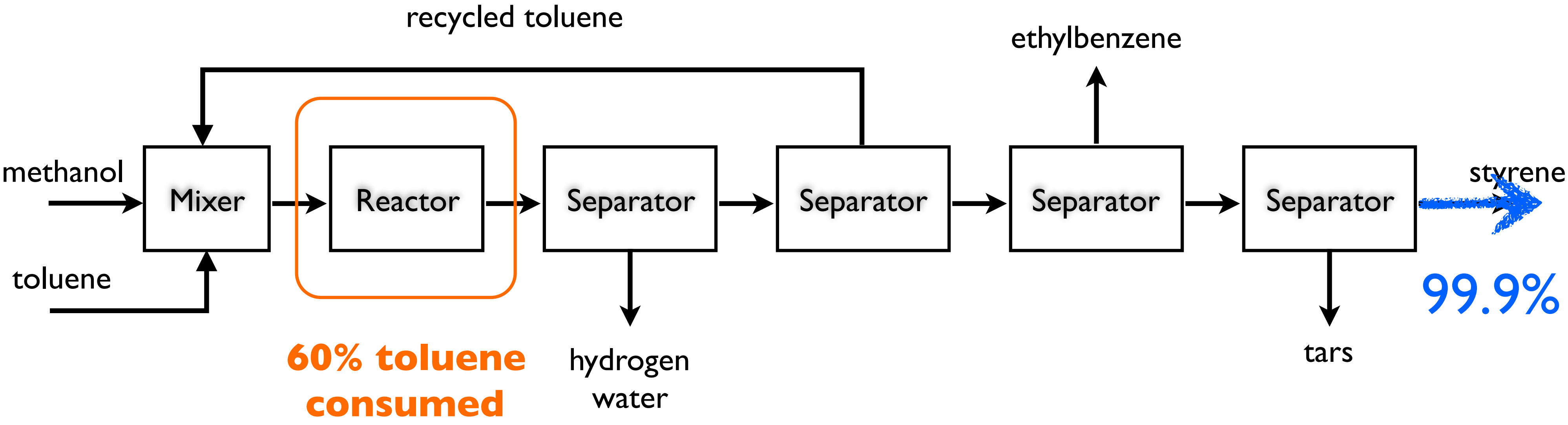
Stream: Material moving into or out of a system.



Process flowsheet specifications

System performance specification: Quantitative description of the extent to which chemical and/or physical changes happen inside a system.

Stream composition specification: Quantitative description of the composition of a stream.



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Chapter 3: Mathematical Analysis of Material Balance Equations and Process Flow Sheets

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Extent of reaction

$\dot{r}_{ik}$ molar rate of reaction of component i by reaction k (negative if consumed, positive if generated)

$$\mathrm{A} + 2\mathrm{B} \longrightarrow 3\mathrm{C} \qquad \text{(R1)}$$

$$\dot{r}_{B1} = 2 \times \dot{r}_{A1}$$

$$\dot{r}_{C1} = -3 \times \dot{r}_{A1}$$

$$\dot{r}_{C1}/3 = \dot{r}_{B1}/-2 = \dot{r}_{A1}/-1 = \dot{r}_{i1}/\nu_{i1} = \dot{\xi}_1$$

$$\dot{r}_{ik} = \nu_{ik} \times \dot{\xi}_k$$

The material balance equation

$$\mathrm{A} + 2\mathrm{B} \longrightarrow 3\mathrm{C} \qquad \text{(R1)}$$

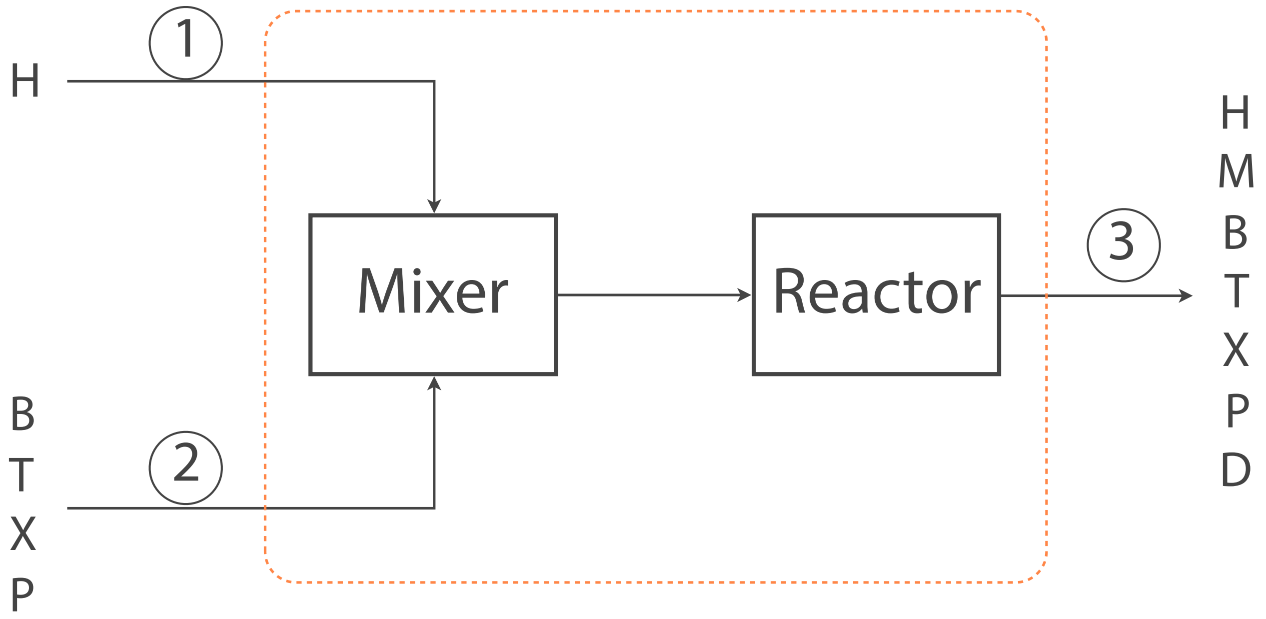
In - Out + Generation - Consumption = Accumulation

$$\dot{n}_{Ain} - \dot{n}_{Aout} + \nu_{A1}\dot{\xi}_1 = \frac{dn_{A,sys}}{dt}$$

<u>Differential mole balance equation for component *i*</u>

$$\underbrace{\sum \dot{n}_{ij}}_{\text{summed over all J input streams}} - \underbrace{\sum \dot{n}_{ij}}_{\text{summed over all J output streams}} + \underbrace{\sum \nu_{ik}\dot{\xi}_k}_{\text{summed over all K reactions}} = \frac{dn_{i,sys}}{dt}$$

Flow diagram and DOF analysis



Stream variables	
System variables	
Specified flows	
Specified compositions	
Performance specifications	
Material balances	
DOF	

Specifications

Specified flows and compositions

$$\dot{n}_{H1} = 500$$

$$\dot{n}_{B2} = 0.05 \times 100 = 5$$

$$\dot{n}_{T2} = 0.20 \times 100 = 20$$

$$\dot{n}_{X2} = 0.25 \times 100 = 25$$

$$\dot{n}_{P2} = 0.50 \times 100 = 50$$

System performance specifications

$$f_{Ci} = -\sum \nu_{ik}\dot{\xi}_k / \dot{n}_{i,in}$$

$$f_{CH} = -\left(-\dot{\xi}_1 - \dot{\xi}_2 - \dot{\xi}_3 + \dot{\xi}_4\right) / \dot{n}_{H1} = 0.24$$

$$f_{CT} = -\left(-\dot{\xi}_1 + \dot{\xi}_2\right) / \dot{n}_{T2} = 0.50$$

$$f_{CX} = -\left(-\dot{\xi}_2 + \dot{\xi}_3\right) / \dot{n}_{X2} = 0.20$$

$$f_{CP} = -\left(-\dot{\xi}_3\right) / \dot{n}_{P2} = 0.70$$

$$\dot{\xi}_3 = 0.70 \times 50 = 35$$

$$\dot{\xi}_2 = (0.20 \times 25) + 35 = 40$$

$$\dot{\xi}_1 = (0.50 \times 20) + 40 = 50$$

$$\dot{\xi}_4 = -(0.24 \times 500) + 50 + 40 + 35 = 5$$

Material balances

$$\sum \dot{n}_{ij} - \sum \dot{n}_{ij} + \sum \nu_{ik}\dot{\xi}_k = \frac{dn_{i,sys}}{dt}$$

summed over all J
input streams

summed over all J
output streams

summed over all K
reactions

$$\sum_{out} \dot{n}_{ij} = \sum_{in} \dot{n}_{ij} + \sum \nu_{ik}\dot{\xi}_k$$

$$\dot{n}_{i3} = \dot{n}_{i,in} + \nu_{i1}\dot{\xi}_1 + \nu_{i2}\dot{\xi}_2 + \nu_{i3}\dot{\xi}_3 + \nu_{i4}\dot{\xi}_4$$

The material balance equation (integral version)

Differential material balance equation on mass of i

(one input, one output, one reaction)

$$\frac{dm_{i,sys}}{dt} = \dot{m}_{i,in} - \dot{m}_{i,out} + \nu_i M_i \dot{\xi}$$

$$\int_{t_0}^{t_f} \frac{dm_{i,sys}}{dt} dt = \int_{t_0}^{t_f} \dot{m}_{i,in} dt - \int_{t_0}^{t_f} \dot{m}_{i,out} dt + \int_{t_0}^{t_f} \nu_i M_i \dot{\xi} dt$$

Integral material balance equation on mass of i

(one input, one output, one reaction)

$$m_{i,sys,f} - m_{i,sys,o} = \int_{t_0}^{t_f} \dot{m}_{i,in} dt - \int_{t_0}^{t_f} \dot{m}_{i,out} dt + \int_{t_0}^{t_f} \nu_i M_i \dot{\xi} dt$$

Summary

In - Out + Generation - Consumption = Accumulation

$$\underbrace{\sum}_{\text{summed over all J input streams}} \dot{n}_{ij} - \underbrace{\sum}_{\text{summed over all J output streams}} \dot{n}_{ij} + \underbrace{\sum}_{\text{summed over all K reactions}} \nu_{ik}\dot{\xi}_k = \frac{dn_{i,sys}}{dt}$$

$$m_{i,sys,f} - m_{i,sys,o} = \int_{t_0}^{t_f} \dot{m}_{i,in} dt - \int_{t_0}^{t_f} \dot{m}_{i,out} dt + \int_{t_0}^{t_f} \nu_i M_i \dot{\xi} dt$$

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Chapter 4: Synthesis of Reactor Flow Sheets and Selection of Reactor Process Conditions

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Reactor design variables

- Temperature and pressure (kinetics, equilibrium)
- Volume and residence time (conversion)
- Reactant feed ratio and order of addition
- Use of catalysts
  - solution
  - solid
- Mixing patterns
  - stirred batch tank
  - continuous-flow stirred tank
  - plug flow (packed bed)

“Perfect” chemical reactors

- one and only one reactions
- reactants fed at stoichiometric ratio
- 100% conversion

$$2A + B \longrightarrow C + D$$

$$\dot{n}_{Ain}/\dot{n}_{Bin} = \nu_A/\nu_B = 2/1$$

$$f_{CA} = f_{CB} = 1.0$$

“Real” chemical reactors

- multiple reactions
- reactants not at stoichiometric ratio
- less than 100% conversion

$$2A + B \longrightarrow C + D$$

$$A + B \longrightarrow E \quad \text{(parallel)}$$

$$C + 2D \longrightarrow F \quad \text{(series)}$$

$$\dot{n}_{Ain}/\dot{n}_{Bin} \neq \nu_A/\nu_B \qquad \Longrightarrow \qquad f_{CA} \neq f_{CB} \neq 1.0$$

Reactor performance specifications

Conversion

Fractional conversion of A

f_{CA} = net moles of A consumed by reaction/moles of A fed

$$f_{CA} = -\sum \nu_{Ak}\dot{\xi}_k/\dot{n}_{A,in}$$

Yield

Fractional yield of product P from reactant A

$y_{A\to P}$ = net moles of A consumed to make P/moles of A fed

$$y_{A\to P} = -(\nu_{A1}/\nu_{P1})\sum \nu_{Pk}\dot{\xi}_k/\dot{n}_{A,in}$$

Selectivity

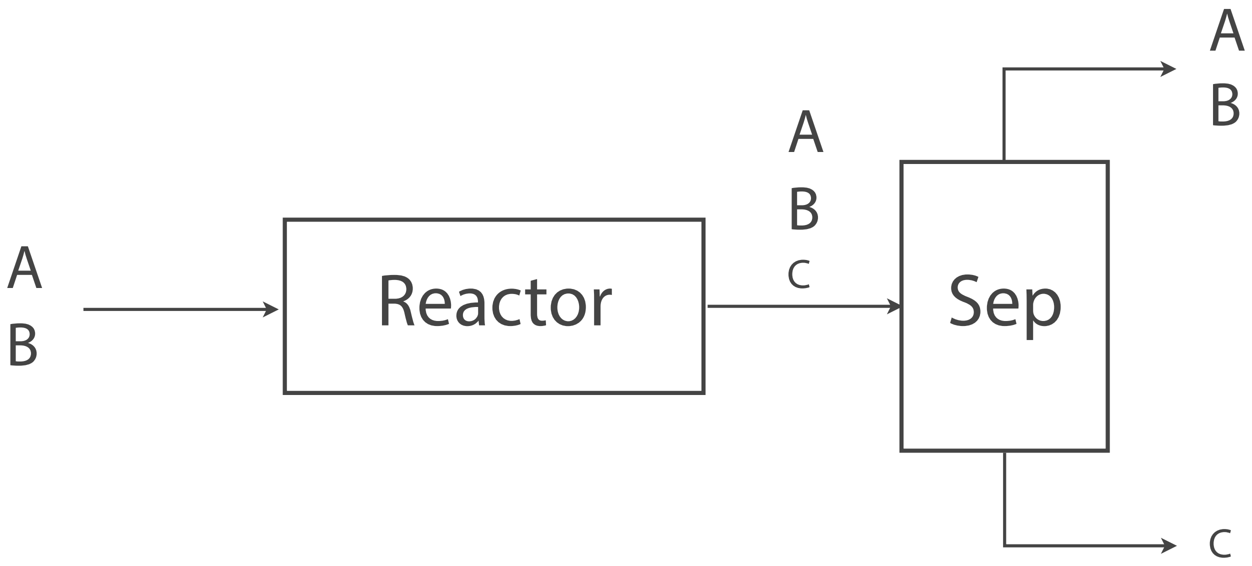
Yield = conversion x selectivity

Fractional selectivity of product P from reactant A

$S_{A\to P}$ = net moles of A consumed to make P/moles of A consumed

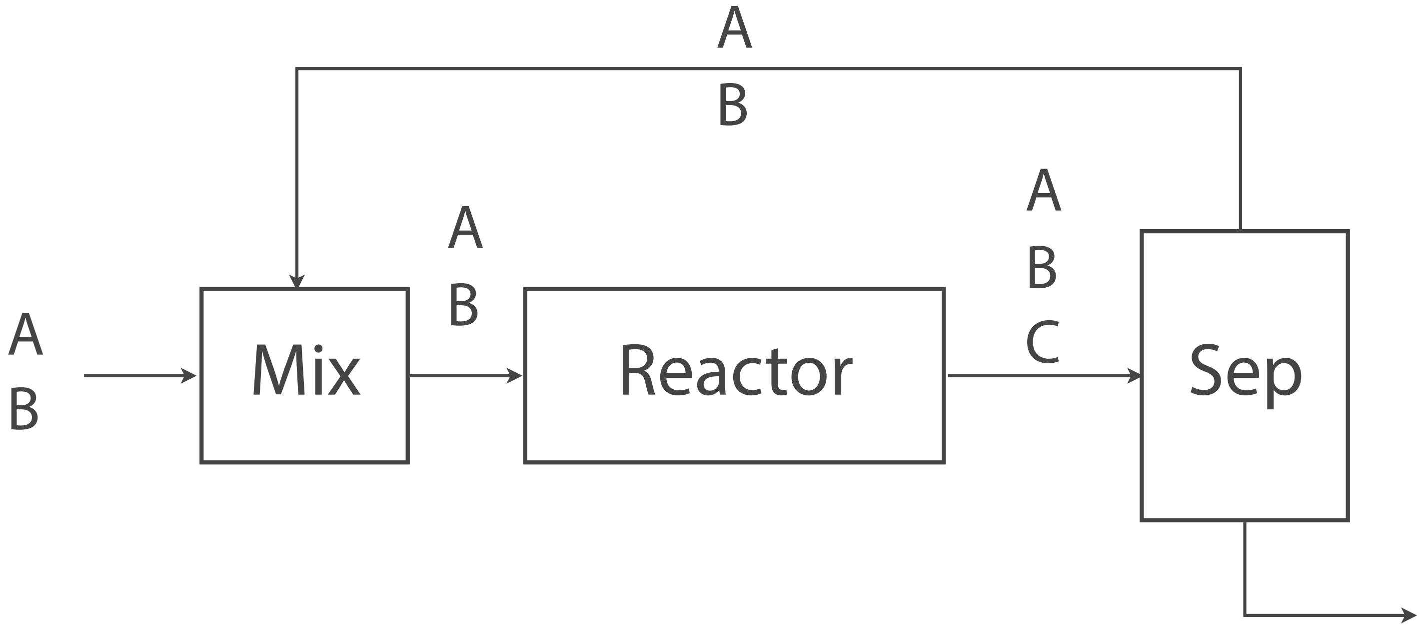
$$S_{A\to P} = (\nu_{A1}/\nu_{P1})\sum \nu_{Pk}\dot{\xi}_k/\sum \nu_{Ak}\dot{\xi}_k$$

Low conversion: recycle


A
B
Reactor
A
B
C
Sep
A
B
C

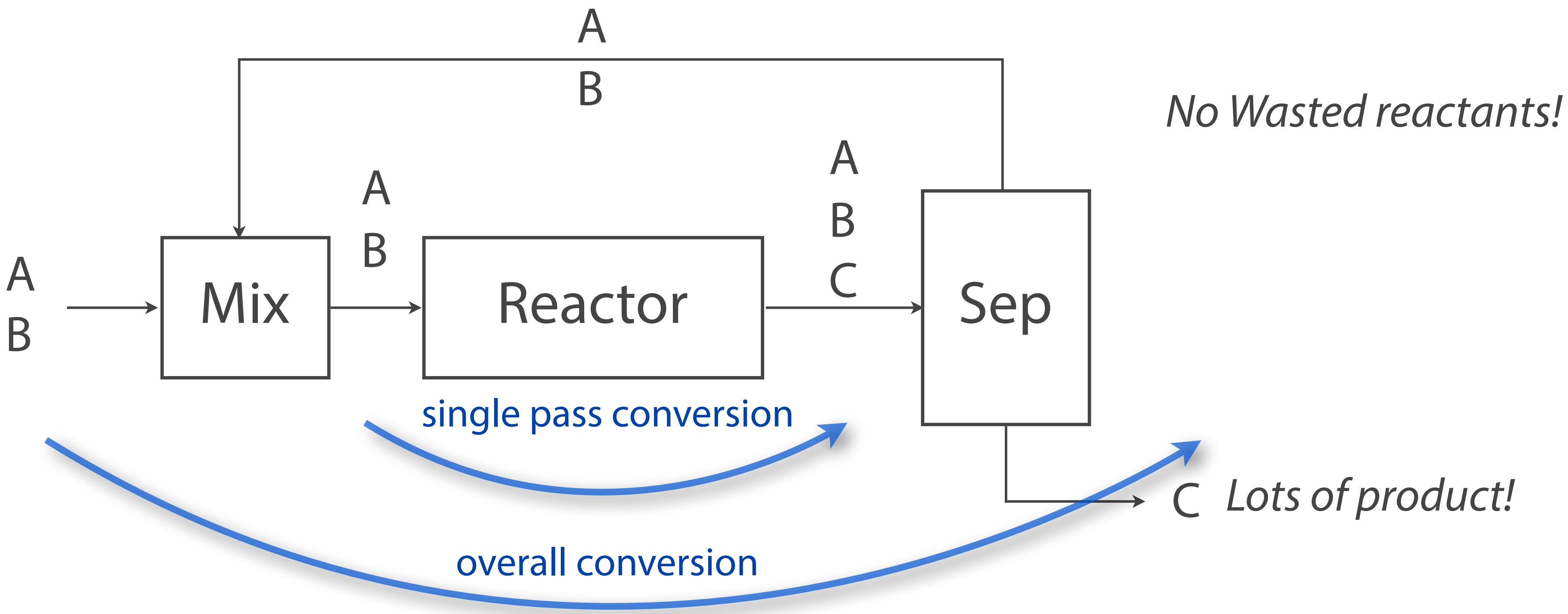
Wasted reactants!

Not much product!


A
B
Mix
A
B
Reactor
A
B
C
Sep
A
B
C

No Wasted reactants!

Lots of product!



No Wasted reactants!

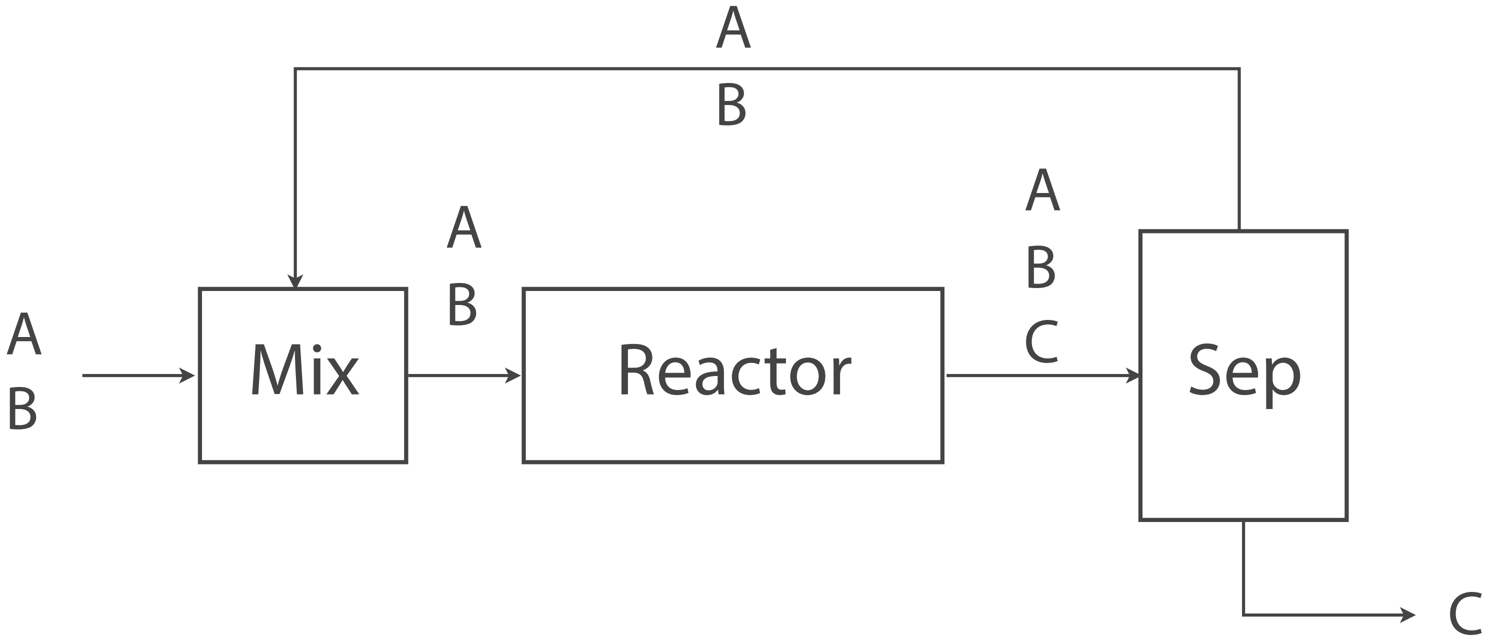
Lots of product!

single pass conversion

overall conversion

$$f_C = \frac{-\sum \nu_{ik}\dot{\xi}_k}{\dot{n}_{i,in}}$$

Recycle and purge



Some important chemical reactions

- Oxidation: complete or partial
  - $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
- Hydrogenation/dehydrogenation
  - $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH + H_2 \rightarrow CH_3(CH_2)_{16}COOH$
- Alkylation/de-alkylation
  - $C_4H_{10} + C_4H_8 \rightarrow C_8H_{18}$
- Hydrolysis/de-hydration
  - $NH_2R^1COOH + NH_2R^2COOH \rightarrow NH_2R^1CONHR^2COOH + H_2O$
- Halogenation
  - $C_2H_4 + Cl_2 \rightarrow C_2H_3Cl + HCl$
- Isomerization
  - Glucose ($C_6H_{12}O_6$) → Fructose ($C_6H_{12}O_6$)

Combustion

Complete combustion is defined by

All C → CO_2
All H → H_2O
All S → SO_2
All N → N_2

Examples: $2CH_3CN + 5.5O_2 \rightarrow 4CO_2 + 3H_2O + N2$

$CH_3SH + 3O_2 \rightarrow CO_2 + 2H_2O + SO_2$

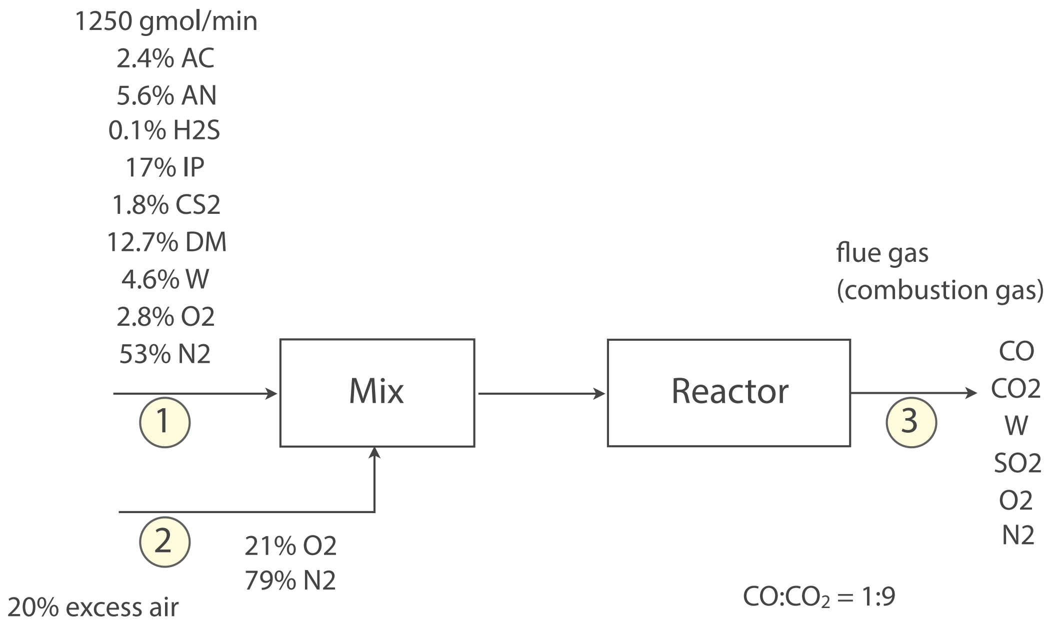
Excess oxygen: oxygen fed in excess of the stoichiometric requirement for complete combustion

Examples:

3.6 gmol/min O_2 mixed with 1 gmol/min CH_3SH = 20% excess oxygen

17.1 gmol/min air mixed with 1 gmol/min CH_3SH = 20% excess air

Excess air calculations



1250 gmol/min
2.4% AC
5.6% AN
0.1% H2S
17% IP
1.8% CS2
12.7% DM
4.6% W
2.8% O2
53% N2

① Mix Reactor ③

flue gas
(combustion gas)

CO
CO2
W
SO2
O2
N2

②
21% O2
79% N2

20% excess air

$CO:CO_2 = 1:9$

Q1: 20% excess air: how do we convert to a flow rate?

Q2: 7 reactions: what are they?

$C_3H_6O + 16/4\ O_2 \rightarrow 3CO_2 + 6/2\ H_2O$ (R1)
$C_2H_3N + 11/4\ O_2 \rightarrow 2CO_2 + 3/2\ H_2O + 1/2\ N_2$ (R2)
$H_2S + 6/4\ O_2 \rightarrow H_2O + SO_2$ (R3)
$C_3H_8O + 18/4\ O_2 \rightarrow 3CO_2 + 8/2\ H_2O$ (R4)
$CS_2 + 12/4\ O_2 \rightarrow CO_2 + 2\ SO_2$ (R5)
$C_2H_7N + 15/4\ O_2 \rightarrow 2CO_2 + 7/2\ H_2O + 1/2\ N_2$ (R6)

Compound	gmol/min (compound)	Moles O_2 per mole compound	gmol/min (O_2)
C_3H_6O	30	4	120
C_2H_3N	70	2.75	192.5
H_2S	1.25	1.5	1.88
C_3H_8O	212.5	4.5	956
CS_2	22.5	3	67.5
C_2H_7N	158.8	3.75	595.5
H_2O	57.5	--	--
O_2	35		-35
N_2	662.5		--

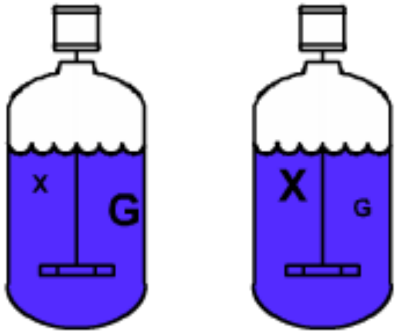
Sum: 1898

In general:

$$C_xH_yO_zN_wS_v + (x + y/4 + v - z)O_2 \rightarrow x\ CO_2 + y/2\ H_2O + w/2\ N_2 + v\ SO_2$$

20% excess oxygen = 1.2 x 1898 = 2278 gmol/min
20% excess air = 2278/0.21 = 10,850 gmol/min

Mass rates of reaction



$t = 0$

$m_{X,sys,0} = 0.1\ g$

$m_{G,sys,0} = 1500\ g$

t

$m_{X,sys}$

$m_{G,sys}$

Acc = In - Out + Gen - Cons

458.205 Basic Computer Methods in Chemical and Biological Engineering

Chapter 5: Selection of Separation Technologies and Synthesis of Separation Flow Sheets

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Separation Processes

- Definitions and terminology
- Separation technologies
- Separator performance
- Entrainment

Separations

Physical Property Differences

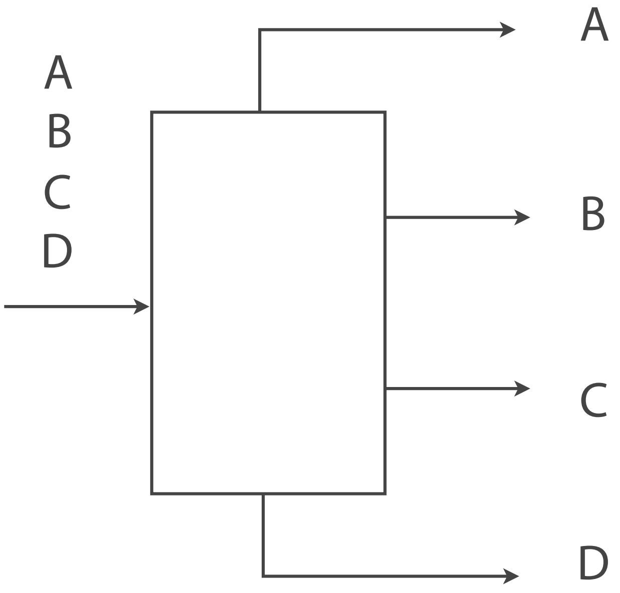
- Size
- Density
- Volatility
- Solubility

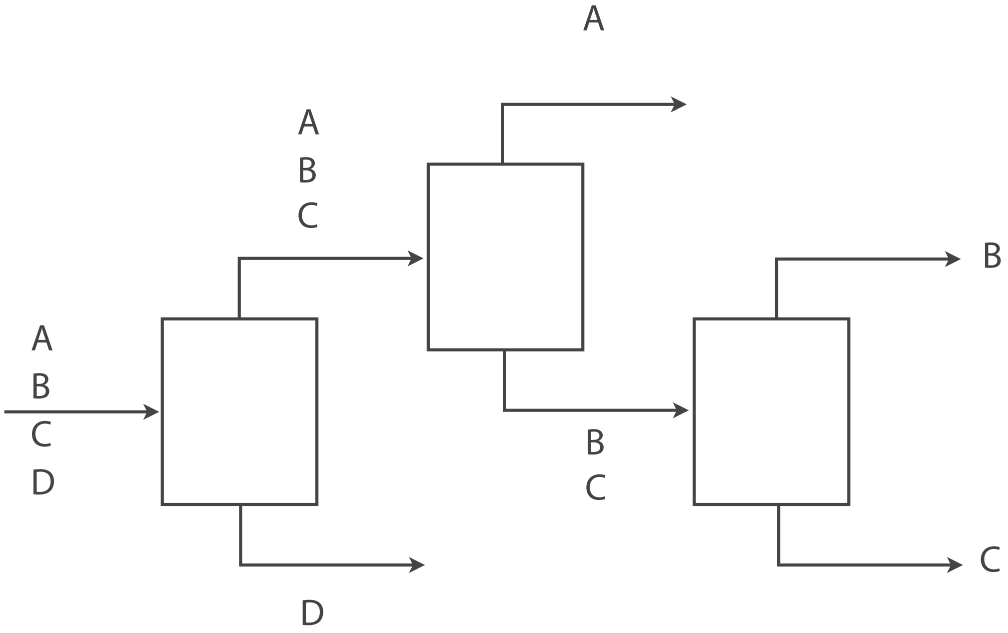
Classification of separation technologies

Classification	Feed	Output	Basis for separation
Mechanical	Two phases	Two phases	Differences in size or density
Rate-based	One phase	One phase	Differences in rate of transport through a medium
Equilibrium-based	One phase	Two phases	Differences in composition of two phases at equilibrium

Classification	Examples
Mechanical	Filtration, Sedimentation, Flotation, Centrifugation
Rate-based	Gel Electrophoresis, Paper Chromatography, Reverse Osmosis
Equilibrium-based	Distillation, Extraction, Crystallization, Absorption, Adsorption

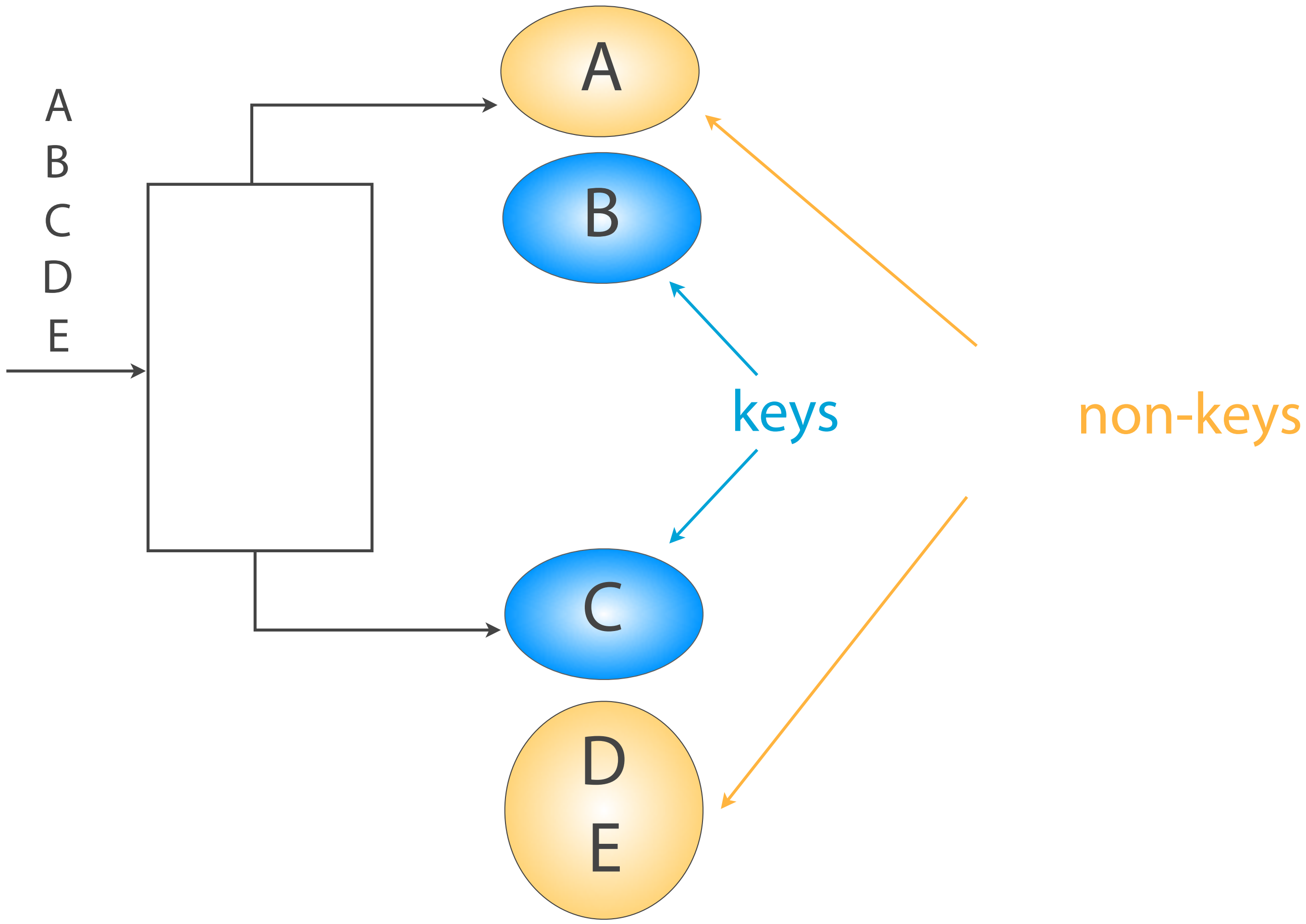
Heuristics for sequencing separation technologies





1. Remove hazardous, toxic, or corrosive materials first.
2. Separate out the components present in largest quantities first.
3. Save the most difficult separations for last.
4. Divide streams into equal parts.
5. Avoid mixing after separating.
6. Meet all product specifications, but don’t overpurify.

Separator DOF analysis



Separator performance specifications

Purity of product stream:

moles of component *i* in stream *j*/total moles in stream *j*

$x_{ij} = n_{ij}/n_j$

Recovery of component:

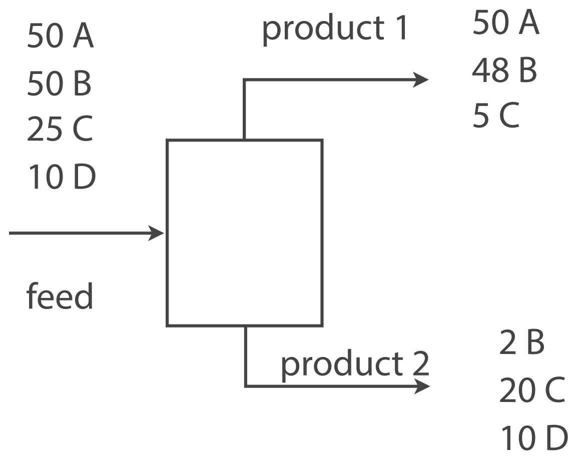
moles of component *i* in stream *j*/moles of *i* fed

$f_{Rij} = n_{ij}/n_{jF}$

Separation factor:

$\alpha_{BC} = (x_{B1}/x_{C1})^*(x_{C2}/x_{B2})$

$\alpha_{BC} = (f_{RB1}/f_{RC1})^*(f_{RC2}/f_{RB2})$



50 A
50 B
25 C
10 D

feed

product 1

50 A
48 B
5 C

product 2

2 B
20 C
10 D

Example

Keys: B and C

Purity: $x_{B1} = 0.466$, $x_{C2} = 0.625$

Recovery: $f_{RB1} = 0.96$, $f_{RC2} = 0.80$

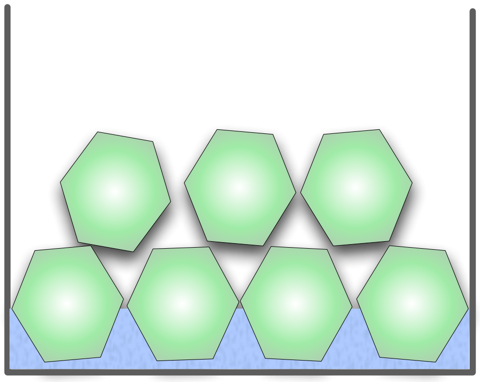
Separation factor:

$\alpha_{BC} = (0.466/0.0485)(0.625/0.0625) = 96$

$\alpha_{BC} = (0.96/0.20)(0.80/0.04) = 96$

Entrainment: Incomplete phase separation

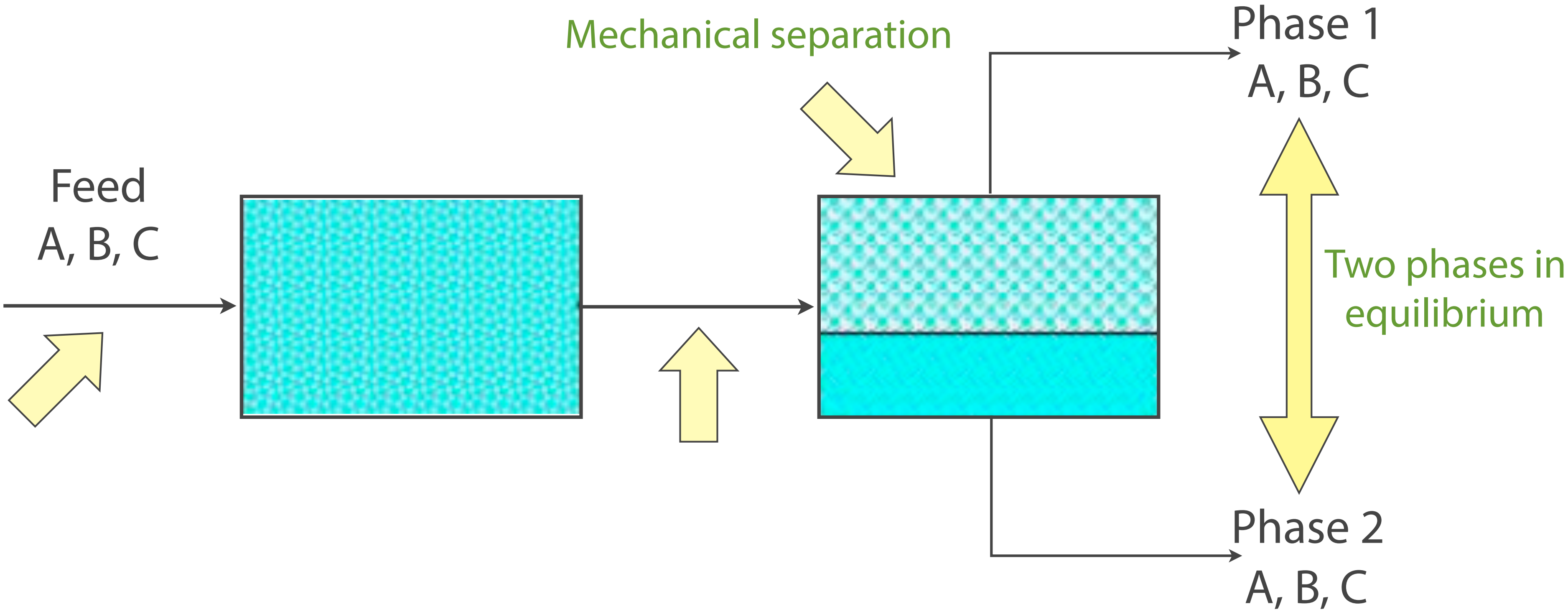
- liquid that coats solid particles
- liquid droplets that are carried along in a gas stream
- gas bubbles that are trapped in a viscous liquid



Phase Equilibrium

- Equilibrium Stage Concept
- Phase Equilibrium Diagrams

The Equilibrium Stage



Mechanical separation

Phase 1
A, B, C

Feed
A, B, C

Two phases in
equilibrium

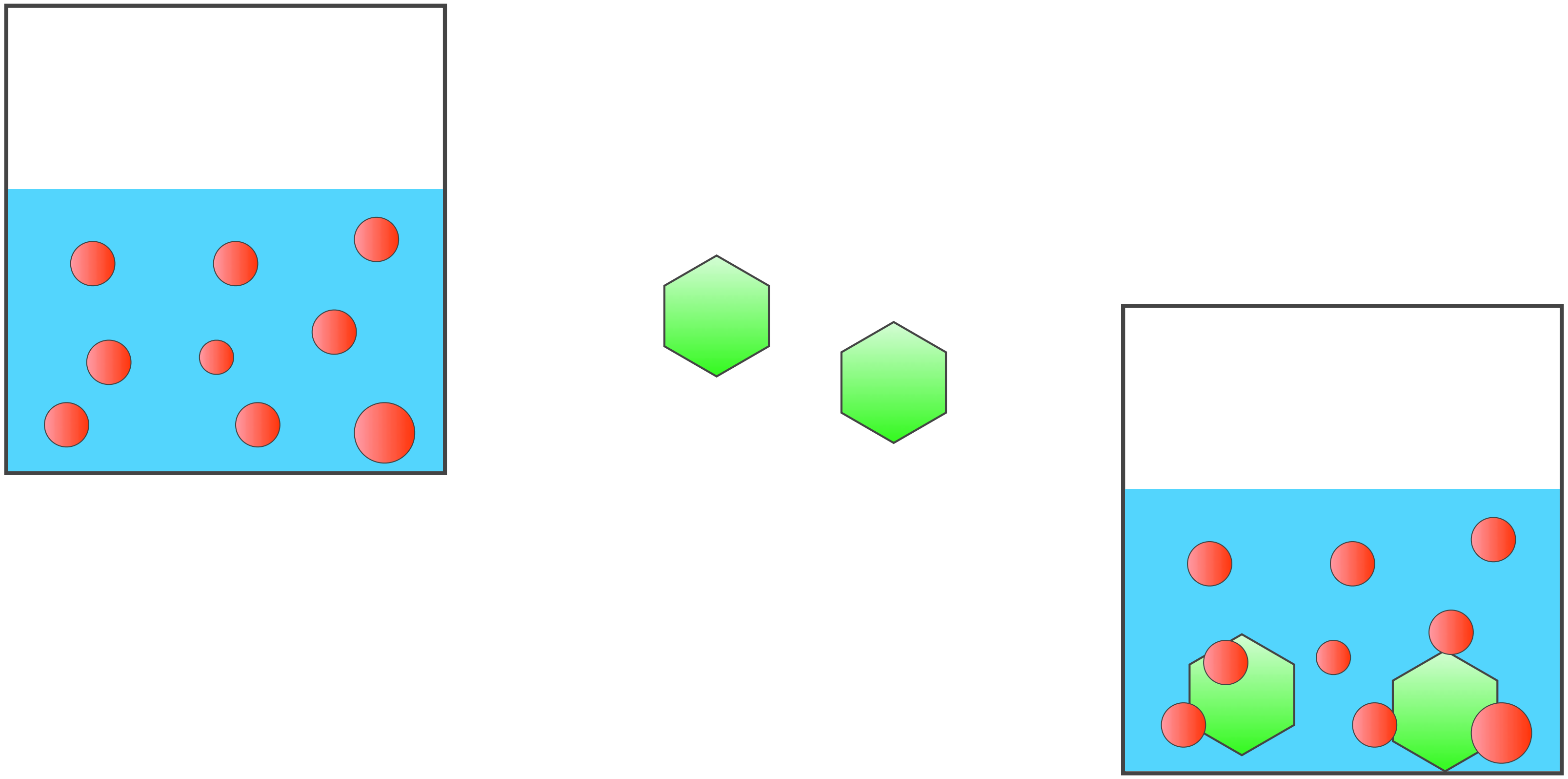
Phase 2
A, B, C

If phases are at equilibrium

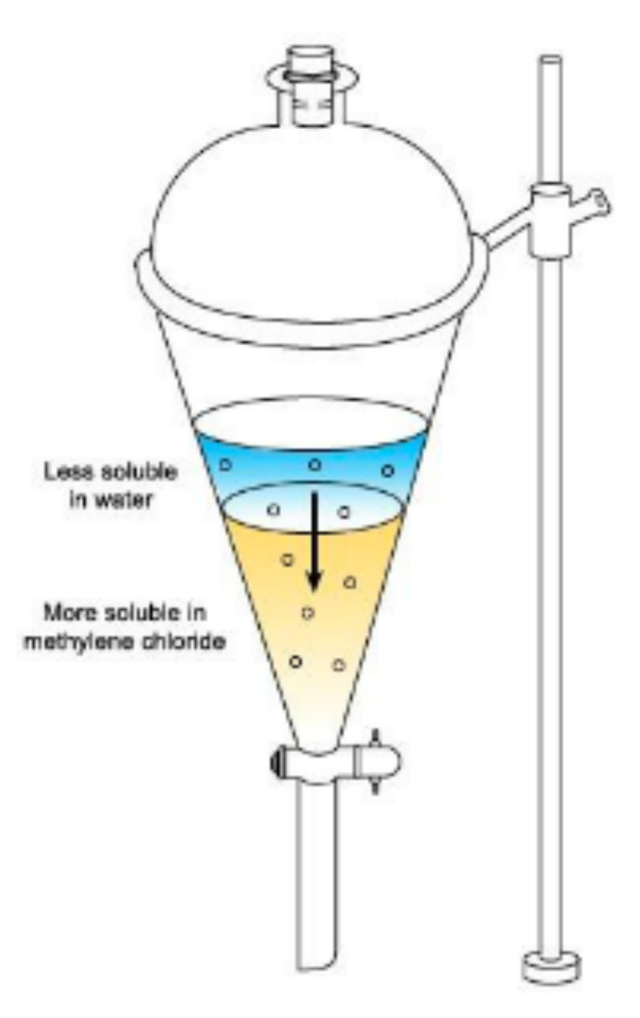
$$T_1 = T_2$$
$$P_1 = P_2$$
$$x_{A1} \neq x_{A2}$$

$$x_{A1} = f(T, P, x_{A2}, x_{B2}, x_{C2})$$
$$x_{B1} = f(T, P, x_{A2}, x_{B2}, x_{C2})$$
$$x_{C1} = f(T, P, x_{A2}, x_{B2}, x_{C2})$$

Fluid-solid equilibrium



Liquid-liquid equilibrium



Phase Equilibrium Models

- Raoult’s Law
- Henry’s Law

Saturation pressure

Single Component

Liquid + Vapor

$F = 1 + 2 - 2 = 1$

Solid + Vapor

$F = 1 + 2 - 2 = 1$

At saturation:

$P^{sat} = P$

Antoine's equation:

$\log_{10} P^{sat} = A - B/(T+C)$

A, B, C are constants

T is temperature

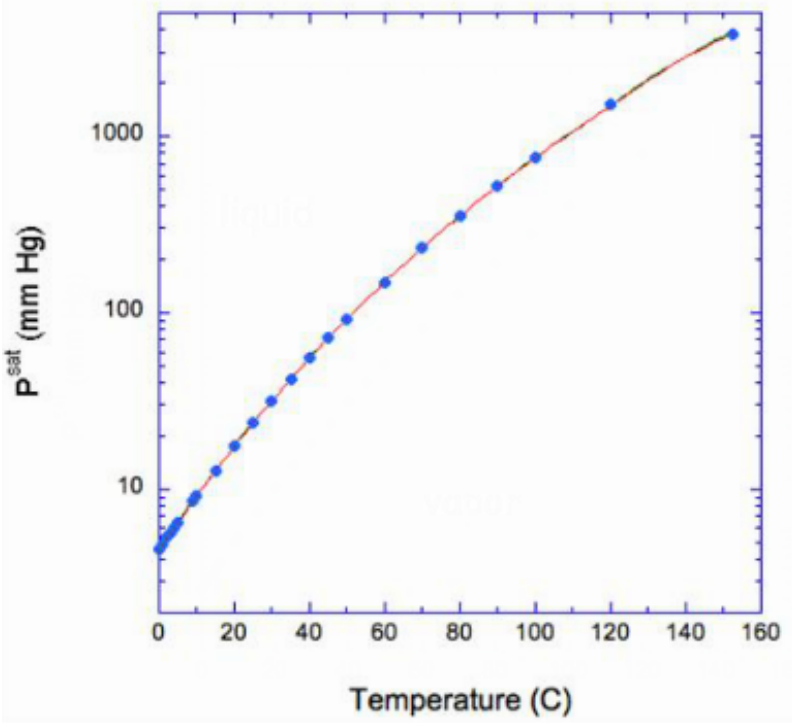
Antoine’s equation

Antoine’s equation:

$\log_{10}P^{sat} = A - B/(T+C)$

A, B, C are constants

T is temperature



For water:

with P^{sat} in mm Hg

T in °C

From 0 - 60 °C

A = 8.10765

B = 1750.286

C = 235.0

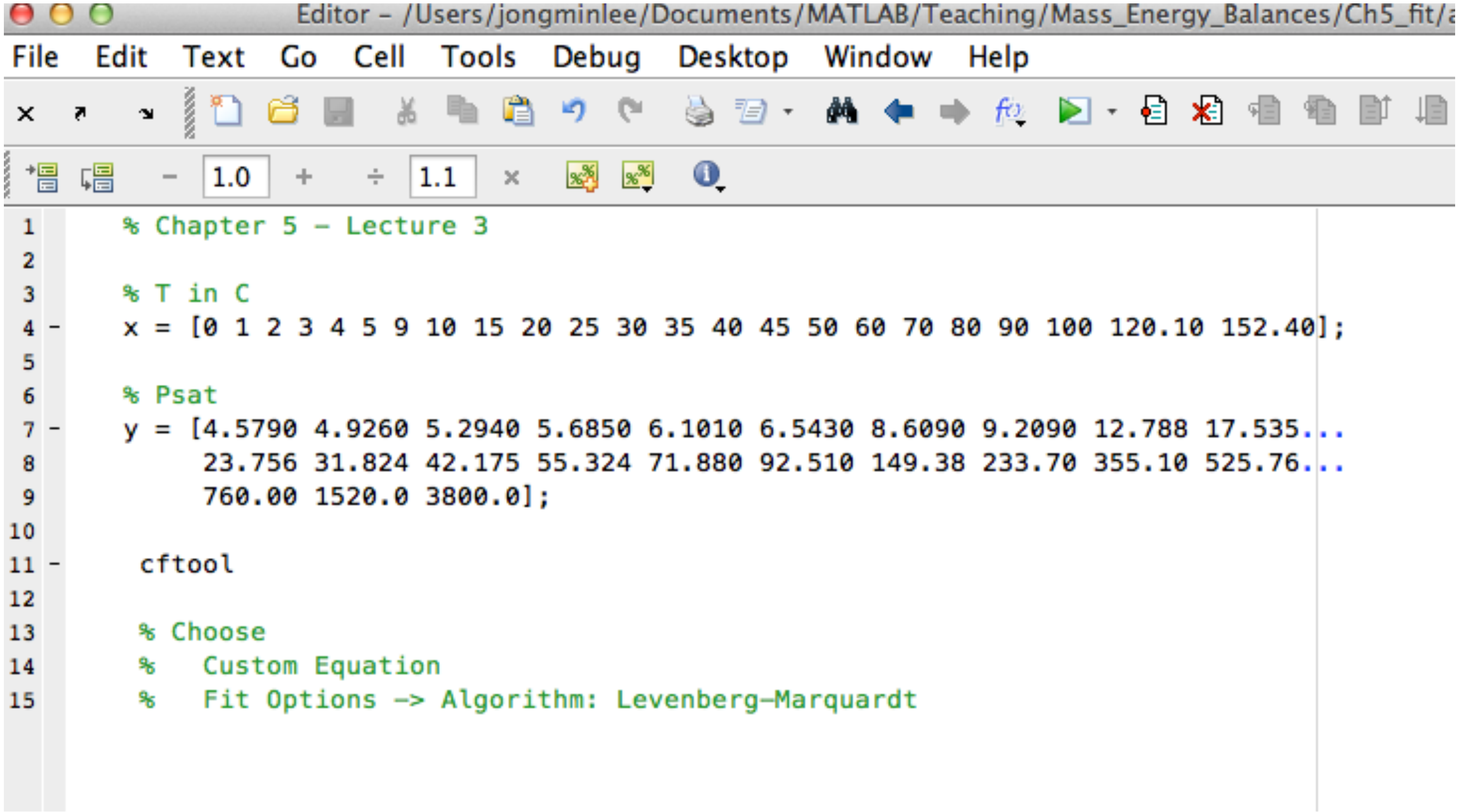
From 60 - 150 °C

A = 7.96681

B = 1668.21

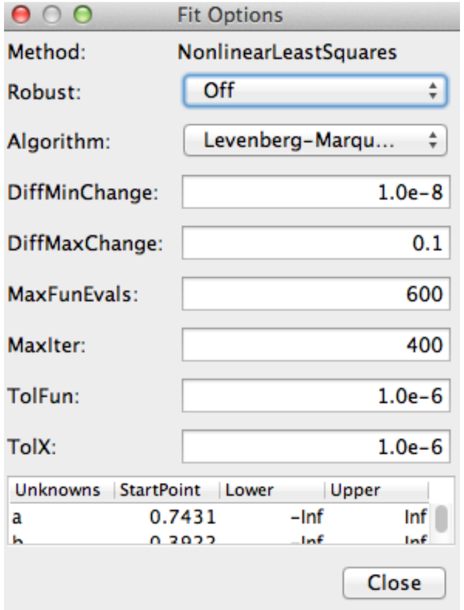
C = 228.0

Parameter estimation with Matlab



```
% Chapter 5 - Lecture 3

% T in C
x = [0 1 2 3 4 5 9 10 15 20 25 30 35 40 45 50 60 70 80 90 100 120.10 152.40];

% Psat
y = [4.5790 4.9260 5.2940 5.6850 6.1010 6.5430 8.6090 9.2090 12.788 17.535...
     23.756 31.824 42.175 55.324 71.880 92.510 149.38 233.70 355.10 525.76...
     760.00 1520.0 3800.0];

 cftool

 % Choose
 %   Custom Equation
 %   Fit Options -> Algorithm: Levenberg-Marquardt
```

Parameter estimation with Matlab



Method: NonlinearLeastSquares

Robust: Off

Algorithm: Levenberg-Marqu...

DiffMinChange: 1.0e-8

DiffMaxChange: 0.1

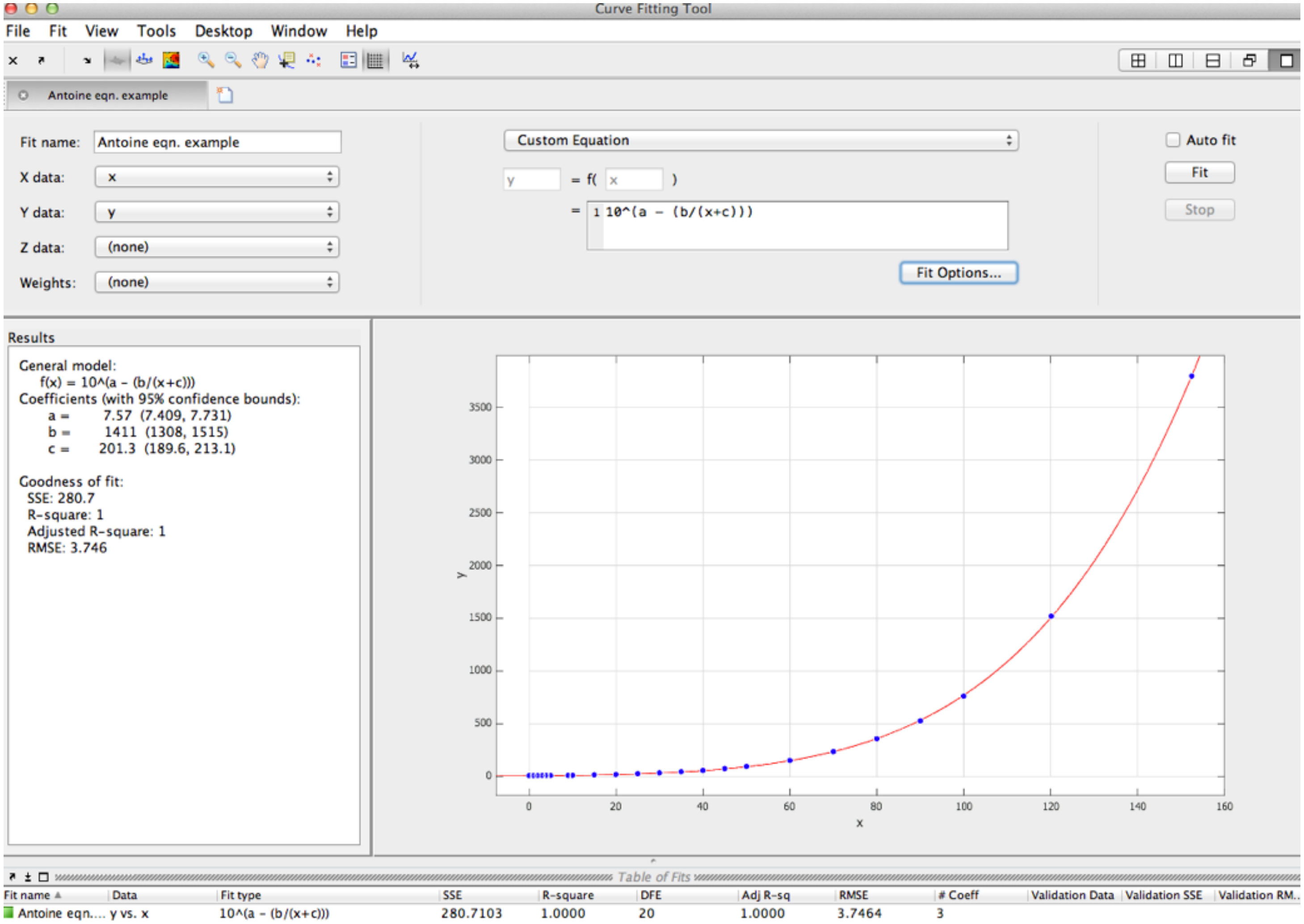
MaxFunEvals: 600

MaxIter: 400

TolFun: 1.0e-6

TolX: 1.0e-6

Unknowns	StartPoint	Lower	Upper
a	0.7431	-Inf	Inf
b	0.3922	-Inf	Inf



Fit name: Antoine eqn. example

X data: x

Y data: y

Z data: (none)

Weights: (none)

Custom Equation

y = f(x)

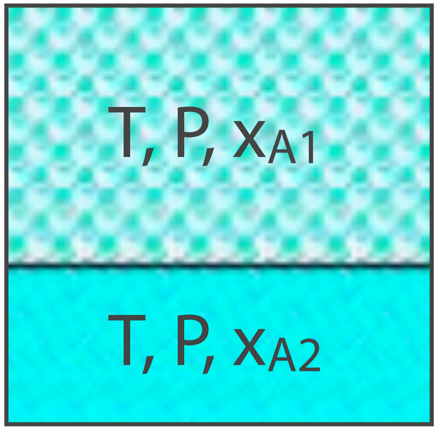
= 10^(a - (b/(x+c)))

Results

```
General model:
    f(x) = 10^(a - (b/(x+c)))
Coefficients (with 95% confidence bounds):
      a =       7.57  (7.409, 7.731)
      b =       1411  (1308, 1515)
      c =      201.3  (189.6, 213.1)

Goodness of fit:
  SSE: 280.7
  R-square: 1
  Adjusted R-square: 1
  RMSE: 3.746
```

Fit name ▲	Data	Fit type	SSE	R-square	DFE	Adj R-sq	RMSE	# Coeff	Validation Data	Validation SSE	Validation RM..
🟩 Antoine eqn....	y vs. x	10^(a - (b/(x+c)))	280.7103	1.0000	20	1.0000	3.7464	3			

Multicomponent vapor-liquid equilibrium



Two Components

Two phases

$F = 2 + 2 - 2 = 2$

By convention -

vapor - y_A

liquid - x_A

Variables

T, P, x_A, y_A

Raoult's Law

$$y_A = (P_A^{sat}/P)x_A$$

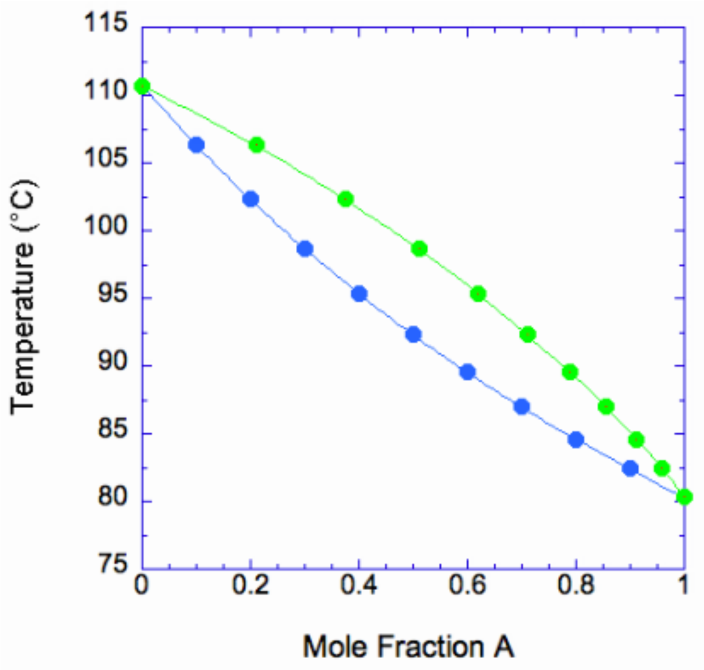
(single component: $y_A = 1$, $x_A = 1$, $P^{sat} = P$)

$$y_B = (P_B^{sat}/P)x_B$$

$$y_A + y_B = 1$$

$$x_A + x_B = 1$$

$$y_A + x_A \neq 1$$



$\log_{10} P_A^{sat} = 6.90 - 1211/(T + 221)$

$\log_{10} P_B^{sat} = 6.96 - 1345/(T + 219)$

Set P = 760 mm Hg
Set $x_A = 0.1$

Solve: T = 106.3 °C
$x_B = 0.9$, $y_A = 0.21$, $y_B = 0.79$

Gas-liquid equilibrium

Gas: a component that will not condense at ‘normal’ T and P.

Partial pressure: pressure that one gas in a mixture would exert if it were alone in the same volume. $p_i = y_i P$

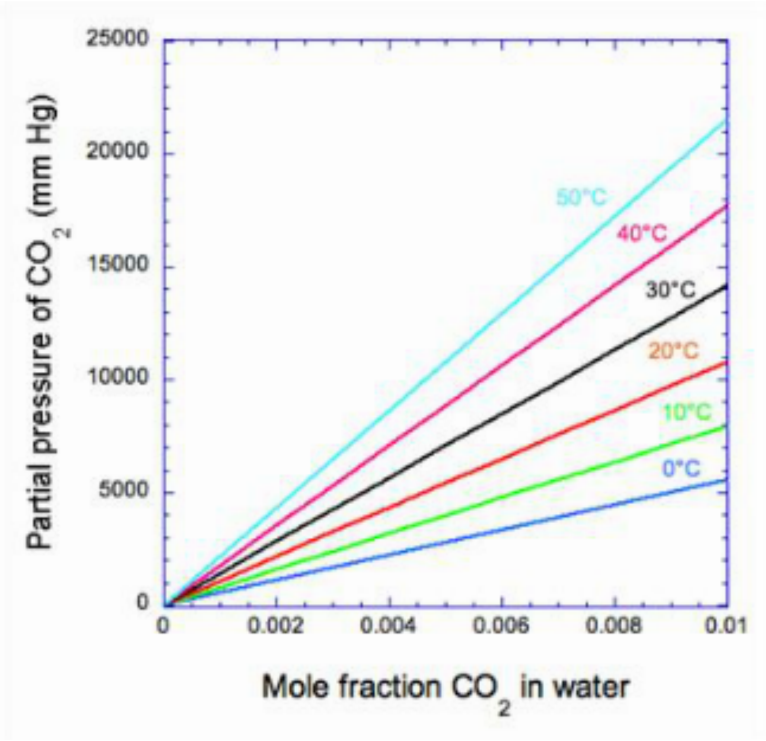
Henry’s Law

$$y_A = (H_A/P)x_A \qquad H_A = f(T, \text{solute}, \text{solvent})$$

$$y_A P = p_A = H_A x_A$$

Example: CO_2 in H_2O

T (0 ^{o}C)	H_A(mmHg)
0	553,280
10	790,400
20	1,079,200
30	1,413,600
40	1,770,800
50	2,150,800

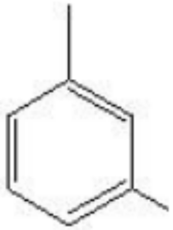


Equilibrium-based Separations: Energy separating agents

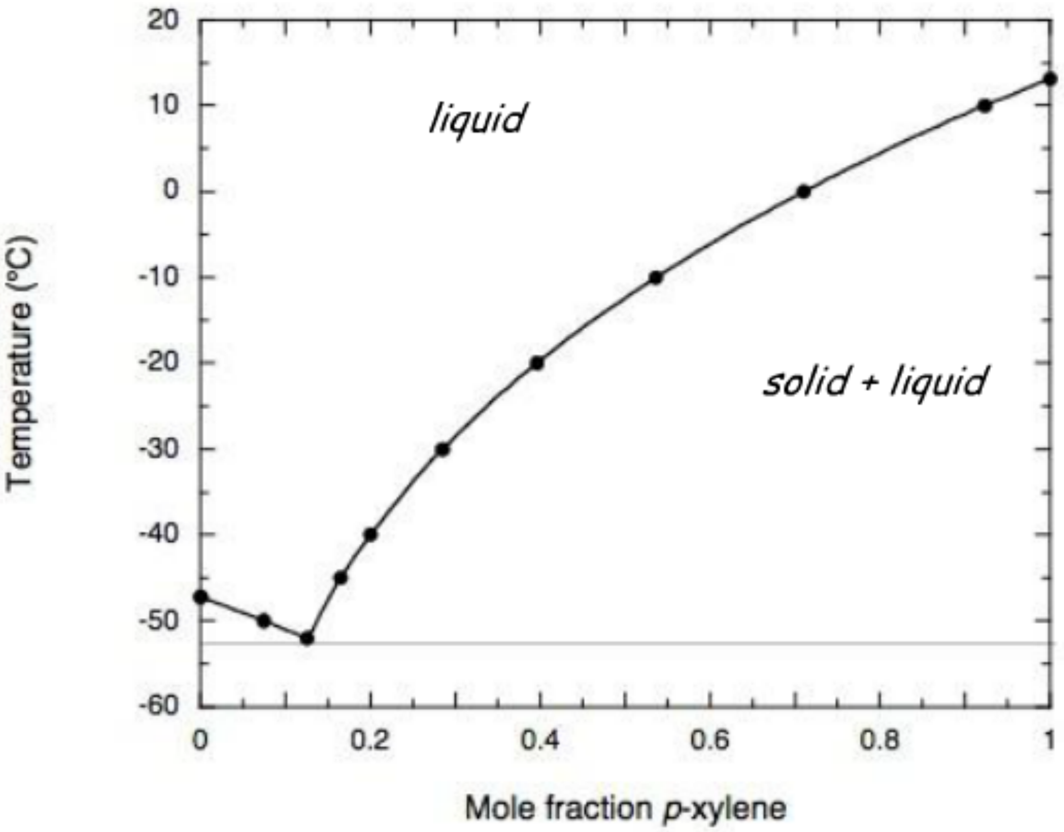
- Crystallization
- Evaporation / Condensation
- Equilibrium Flash
- Distillation

Xylene isomer phase equilibrium

p-xylene

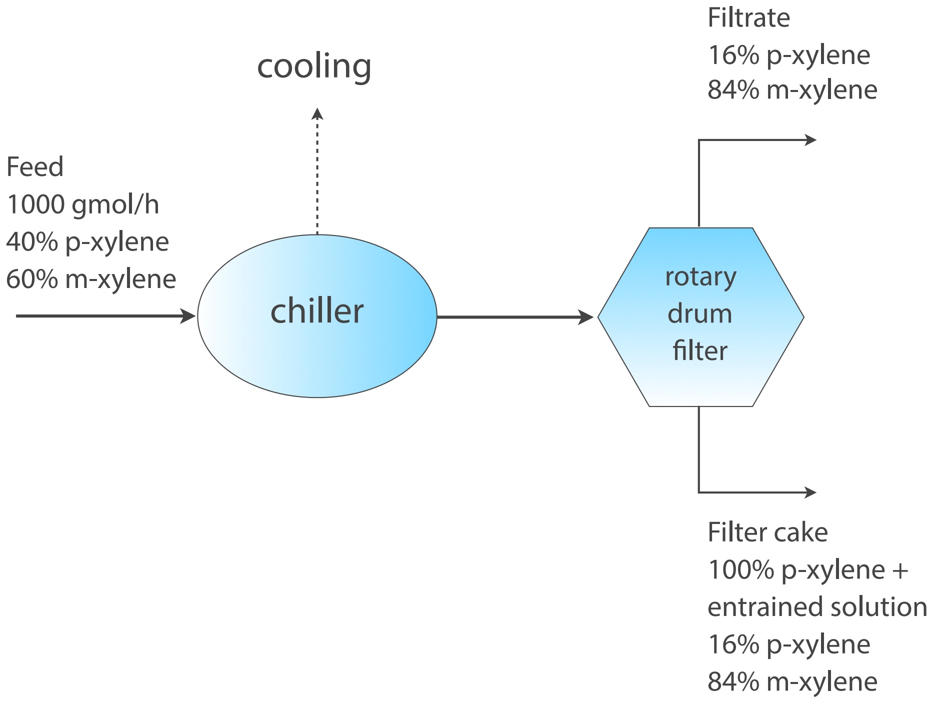


m-xylene



Xylene isomer separation by crystallization

F: feed
L: filtrate
C: cake
ES: entrained solution



Feed
1000 gmol/h
40% p-xylene
60% m-xylene

cooling

chiller

rotary
drum
filter

Filtrate
16% p-xylene
84% m-xylene

Filter cake
100% p-xylene +
entrained solution
16% p-xylene
84% m-xylene

MB on p-xylene

MB on m-xylene

Specification on filter drum performance:

p-xylene purity:
$[286+0.16(32)]/[286+32] = 0.915$

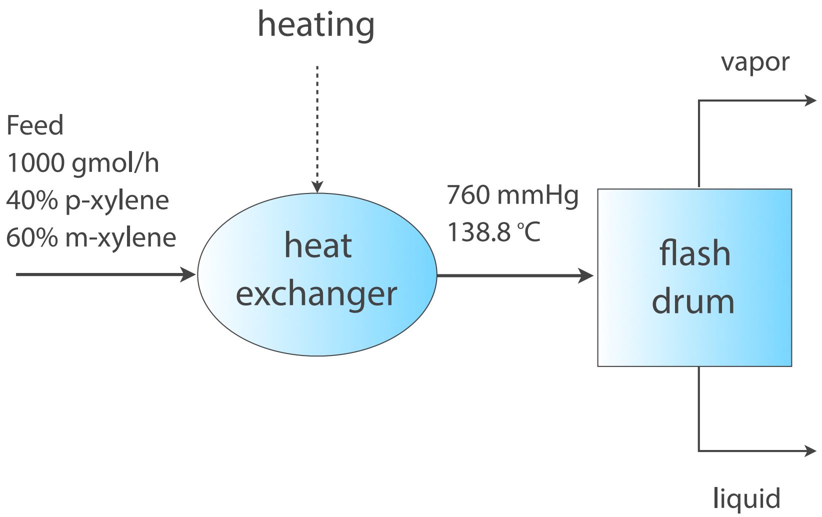
p-xylene recovery:
$[286+0.16(32)]/[400] = 0.73$

Separation factor:
$[0.915/0.085]*[0.84/0.16] = 56$

Solving...
Filtrate: 682 gmol/h, 16% p-xylene
Retentate: 286 gmol/h solids +
32 gmol/h entrained soln

Xylene isomer separation by equilibrium flash

MB on p-xylene



heating

Feed
1000 gmol/h
40% p-xylene
60% m-xylene

heat exchanger

760 mmHg
138.8 °C

flash drum

vapor

liquid

MB on m-xylene

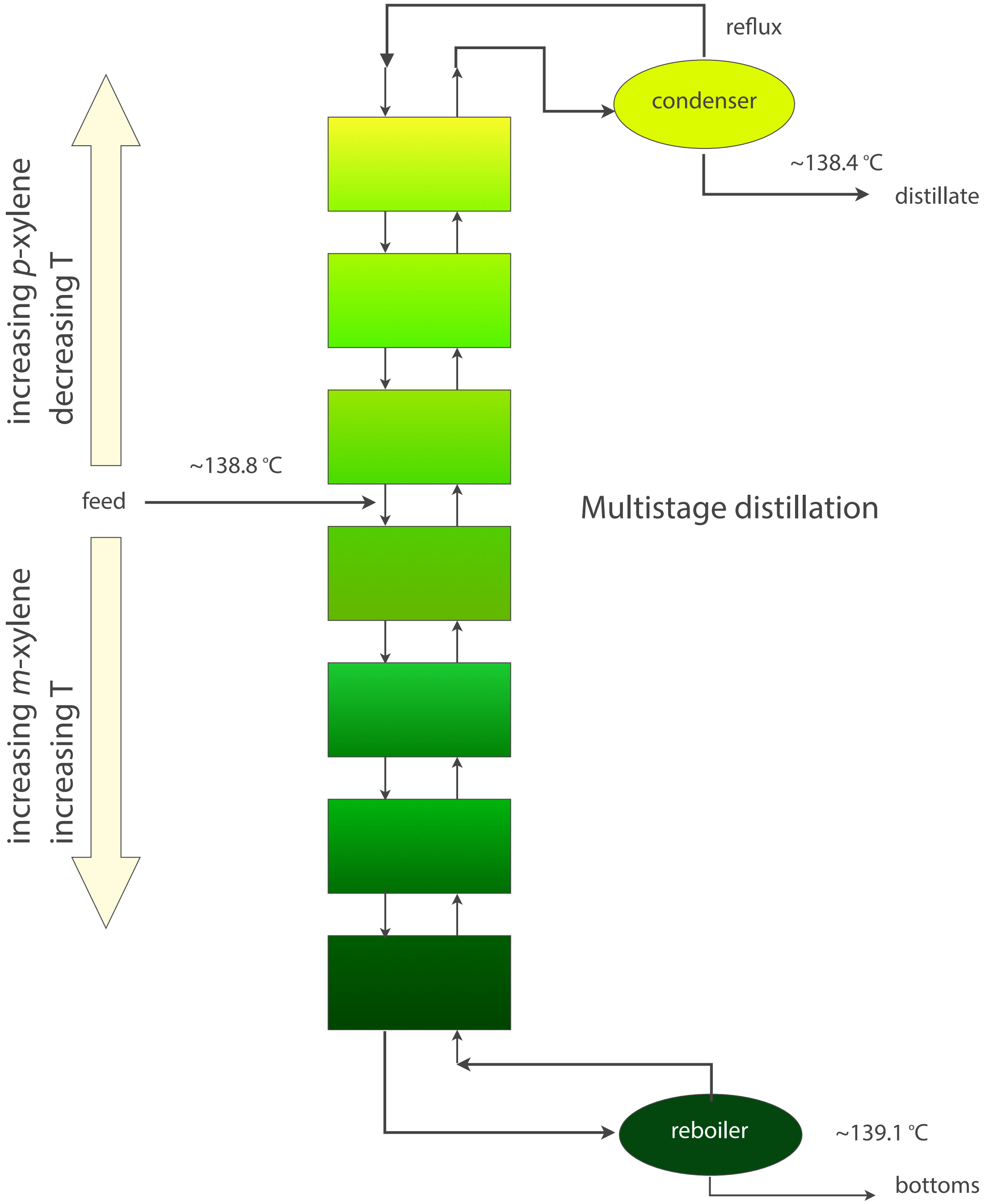
Phase equilibrium relationships

$$y_p = (P_p^{sat}/P)x_p \quad \log_{10} P_p^{sat} = 6.99052 - 1453.43/(T+215.31)$$

$$y_m = (P_p^{sat}/P)x_m \quad \log_{10} P_m^{sat} = 7.00908 - 1462.266/(T+215.11) \quad (T \text{ in C}, P \text{ in mmHg})$$

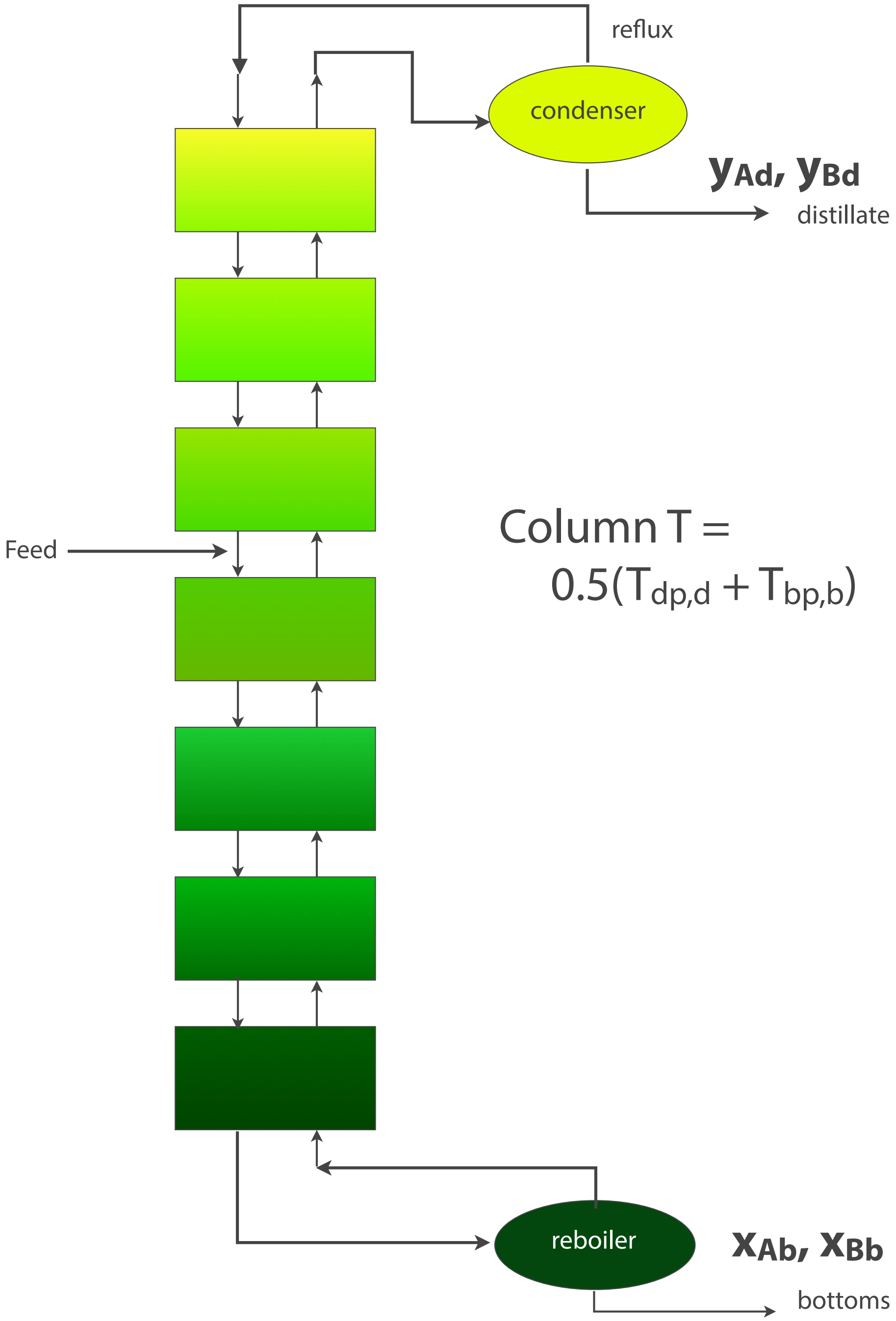
Vapor: 764.4 gmol/h, 40.11 mol% p-xylene, 59.89 mol% m-xylene
Liquid: 235.6 gmol/h, 39.63 mol% p-xylene, 60.37 mol% m-xylene

Recoveries: 76.6% p-xylene in vapor, 23.7% m-xylene in liquid
Separation factor: 1.02 (compare to 56 with crystallization!)

reflux
condenser
~138.4 °C
distillate
increasing *p*-xylene
decreasing T
~138.8 °C
feed
Multistage distillation
increasing *m*-xylene
increasing T
reboiler
~139.1 °C
bottoms

The Fenske equation

$$N_{\min} = \frac{\log\left[\left(\frac{y_{Ad}}{y_{Bd}}\right)\left(\frac{x_{Bb}}{x_{Ab}}\right)\right]}{\log\left[\frac{P_A^{sat}}{P_B^{sat}}\right]}$$



Column T =
$0.5(T_{dp,d} + T_{bp,b})$

Xylene isomer distillation

Equivalent separation to crystallization process:

Distillate: 318 gmol/h, 91.5% p-xylene, 8.5% m-xylene

Bottomes: 682 gmol/h, 16% p-xylene, 84% m-xylene

$$\left[\left(\frac{y_{Ad}}{y_{Bd}}\right)\left(\frac{x_{Bb}}{x_{Ab}}\right)\right] = \left[\left(\frac{0.915}{0.085}\right)\left(\frac{0.84}{0.16}\right)\right] = 56$$

$\alpha_{\text{mx-px}}$ for process

Column temperature calculation (assume column P = 760 mm Hg):

Dewpoint of 91.5% p-xylene, 8.5% m-xylene: 138.4°

Bubblepoint of 16% p-xylene, 84% m-xylene: 138.8°

$$\left[\frac{P_P^{sat}}{P_{in}^{sat}}\right] = \frac{765}{754} = 1.015$$

$\alpha_{\text{mx-px}}$ for single stage

$$N_{\min} = \frac{\log 56}{\log 1.015} = 270$$

458.205 Basic Computer Methods in Chemical and Biological Engineering

Chapter 6: Process Energy Calculations and Synthesis of Safe and Efficient Energy Flow Sheets

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Process Energy Calculations

- Energy balance equation
- Types of energy
- Heat and work

Energy balance equation

Accumulation = In - Out

Differential (overall) mass balance equation

$$\frac{dm_{sys}}{dt} = \sum \dot{m}_{j,in} - \sum \dot{m}_{j,out}$$

Differential energy balance equation

$$\frac{dE_{sys}}{dt} = \sum \dot{E}_{j,in} - \sum \dot{E}_{j,out}$$

Energy flows in the absence of material flow: heat and work

Heat (Q): Energy flow across system boundary due to difference in temperature

$Q > 0$ $T_{surr} > T_{sys}$

$Q < 0$ $T_{surr} < T_{sys}$

If $T_{surr} = T_{sys}$, $Q = 0$ (isothermal)

If system boundary is insulated, $Q = 0$ (adiabatic)

Work (W): Flow of mechanical energy across system boundary due to driving forces other than temperature difference

$W > 0$ If surroundings do work on system

$W < 0$ If system does work on surroundings

W_s: shaft work (pump, compressor, turbine, mixer)

W_{fl}: flow work (fluid pushing on system, or system pushing on fluid.)

$$W_{fl} = PV_{in} - PV_{out}$$

Kinetic and potential energy

$$E_k = mv^2/2$$

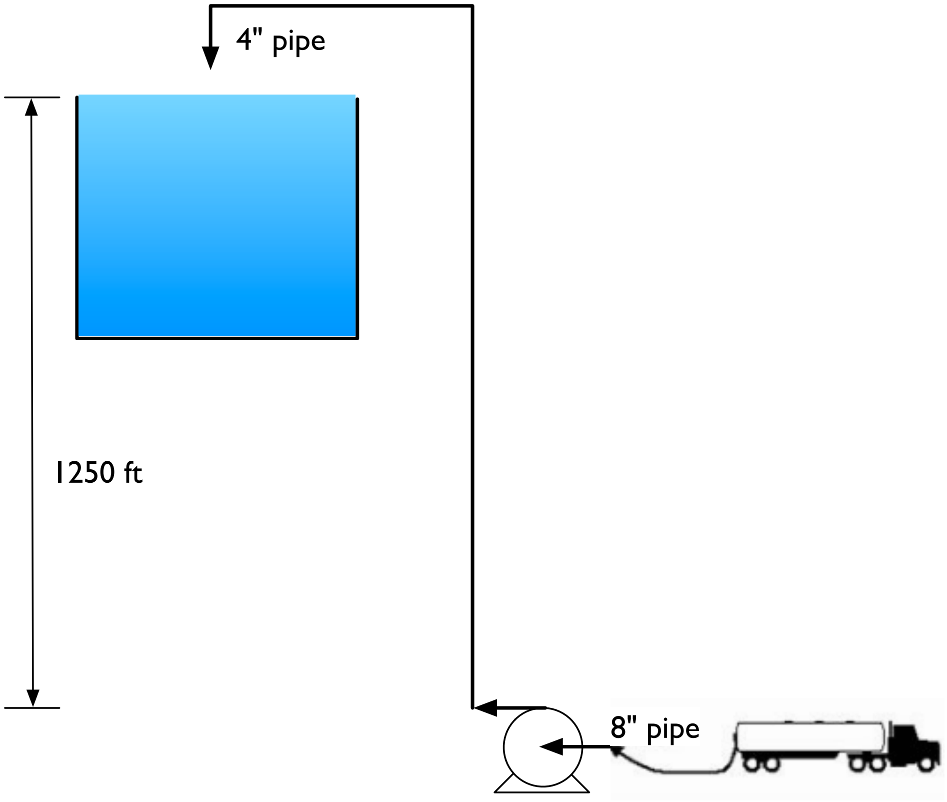
$$E_p = mgh$$

$$\begin{aligned}\dot{E}_{k,out} &= \dot{m}v^2/2 = (72\ \mathrm{lb/s})(13.2\ \mathrm{ft/s})^2/2\\ &= 6270\ \mathrm{lb\ f^2/s^3} = 0.26\ \mathrm{kJ/s}\end{aligned}$$

$$\begin{aligned}\dot{E}_{p,out} &= \dot{m}gh = (72\ \mathrm{lb/s})(32.174\ \mathrm{ft/s^2})(1250\ \mathrm{ft})\\ &= 2.9 \times 10^6\ \mathrm{lb\text{-}f^2/s^3} \times (1\ \mathrm{lbf}/32.174\ \mathrm{lb\text{-}ft/s^2})\\ &= 90,000\ \mathrm{ft\text{-}lb_f/s} \times (1\ \mathrm{kJ}/737.6\ \mathrm{ft\text{-}lb_f})\\ &= 122\ \mathrm{kJ/s}\end{aligned}$$

$$\begin{aligned}\dot{E}_{k,in} &= \dot{m}v^2/2 = (72\ \mathrm{lb/s})(3.4\ \mathrm{ft/s})^2/2\\ &= 410\ \mathrm{lb\ f^2/s^3} = 0.017\ \mathrm{kJ/s}\end{aligned}$$

$$\dot{E}_{p,in} = \dot{m}gh = (72\ \mathrm{lb/s})(32.2\ \mathrm{ft/s^2})(0\ \mathrm{ft}) = 0$$



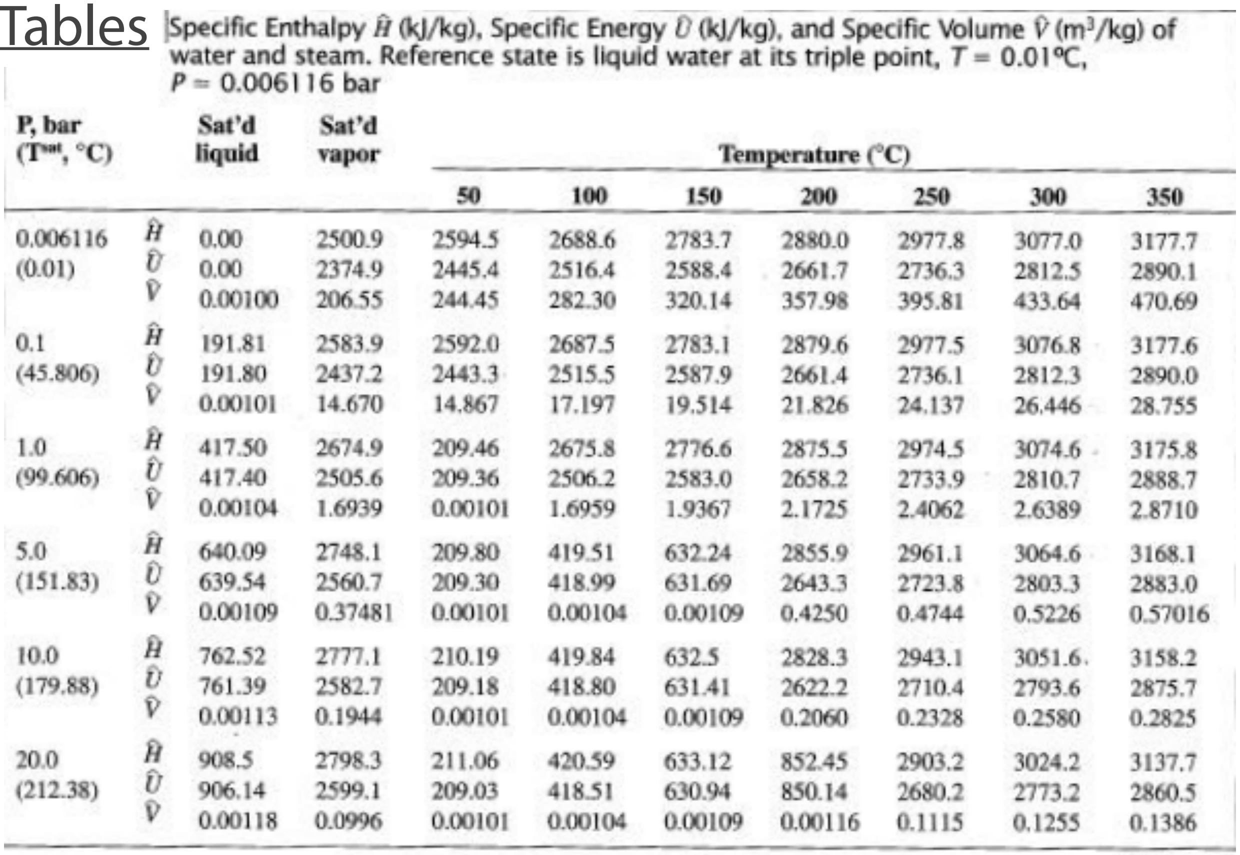
flow rate = 72 lb/s

v = (72 lb/s)(ft^3/62.4 lb)/(π(0.33)^2) = 3.4 ft/s

Internal energy and enthalpy

$H = U + PV,\ \hat{H} = \hat{U} + P\hat{V}$ ... function of T, P, φ, xi

Steam Tables



Specific Enthalpy $\hat{H}$ (kJ/kg), Specific Energy $\hat{U}$ (kJ/kg), and Specific Volume $\hat{V}$ (m^3/kg) of water and steam. Reference state is liquid water at its triple point, $T = 0.01$°C, $P = 0.006116$ bar

P, bar (T^{sat}, °C)		Sat'd liquid	Sat'd vapor	Temperature (°C)						
				50	100	150	200	250	300	350
0.006116 (0.01)	$\hat{H}$	0.00	2500.9	2594.5	2688.6	2783.7	2880.0	2977.8	3077.0	3177.7
	$\hat{U}$	0.00	2374.9	2445.4	2516.4	2588.4	2661.7	2736.3	2812.5	2890.1
	$\hat{V}$	0.00100	206.55	244.45	282.30	320.14	357.98	395.81	433.64	470.69
0.1 (45.806)	$\hat{H}$	191.81	2583.9	2592.0	2687.5	2783.1	2879.6	2977.5	3076.8	3177.6
	$\hat{U}$	191.80	2437.2	2443.3	2515.5	2587.9	2661.4	2736.1	2812.3	2890.0
	$\hat{V}$	0.00101	14.670	14.867	17.197	19.514	21.826	24.137	26.446	28.755
1.0 (99.606)	$\hat{H}$	417.50	2674.9	209.46	2675.8	2776.6	2875.5	2974.5	3074.6	3175.8
	$\hat{U}$	417.40	2505.6	209.36	2506.2	2583.0	2658.2	2733.9	2810.7	2888.7
	$\hat{V}$	0.00104	1.6939	0.00101	1.6959	1.9367	2.1725	2.4062	2.6389	2.8710
5.0 (151.83)	$\hat{H}$	640.09	2748.1	209.80	419.51	632.24	2855.9	2961.1	3064.6	3168.1
	$\hat{U}$	639.54	2560.7	209.30	418.99	631.69	2643.3	2723.8	2803.3	2883.0
	$\hat{V}$	0.00109	0.37481	0.00101	0.00104	0.00109	0.4250	0.4744	0.5226	0.57016
10.0 (179.88)	$\hat{H}$	762.52	2777.1	210.19	419.84	632.5	2828.3	2943.1	3051.6	3158.2
	$\hat{U}$	761.39	2582.7	209.18	418.80	631.41	2622.2	2710.4	2793.6	2875.7
	$\hat{V}$	0.00113	0.1944	0.00101	0.00104	0.00109	0.2060	0.2328	0.2580	0.2825
20.0 (212.38)	$\hat{H}$	908.5	2798.3	211.06	420.59	633.12	852.45	2903.2	3024.2	3137.7
	$\hat{U}$	906.14	2599.1	209.03	418.51	630.94	850.14	2680.2	2773.2	2860.5
	$\hat{V}$	0.00118	0.0996	0.00101	0.00104	0.00109	0.00116	0.1115	0.1255	0.1386

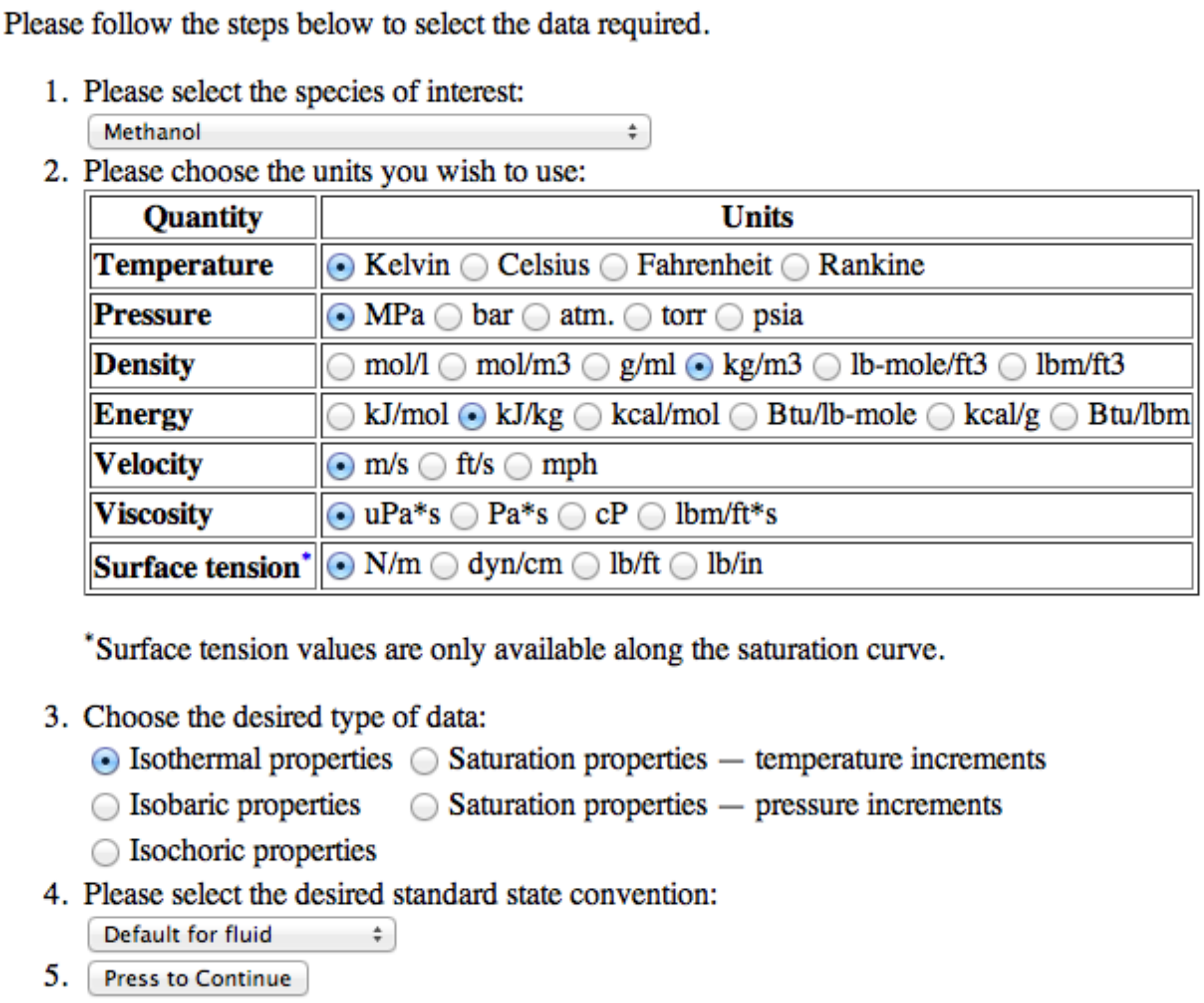
Saturation conditions

- Two or more phases of a pure substance can exist together in equilibrium
- A second phase need not actually be present
- A phase is considered saturated so long as it is at conditions where another phase *could* exist in equilibrium
- In the case where a single phase is found, it is in a condition where any system changes (temperature, pressure, enthalpy) will cause some material to change phase.

- Another way of looking at saturation conditions is that a change of phase can occur without a change in pressure or temperature (what occurs is a change in enthalpy).
- Yet another approach is to consider a saturation state to be the conditions at which a phase change begins, takes place, or ends

Sources of U and H data

NIST Thermophysical Properties   http://webbook.nist.gov/chemistry/fluid/



Please follow the steps below to select the data required.

1. Please select the species of interest:
   Methanol
2. Please choose the units you wish to use:

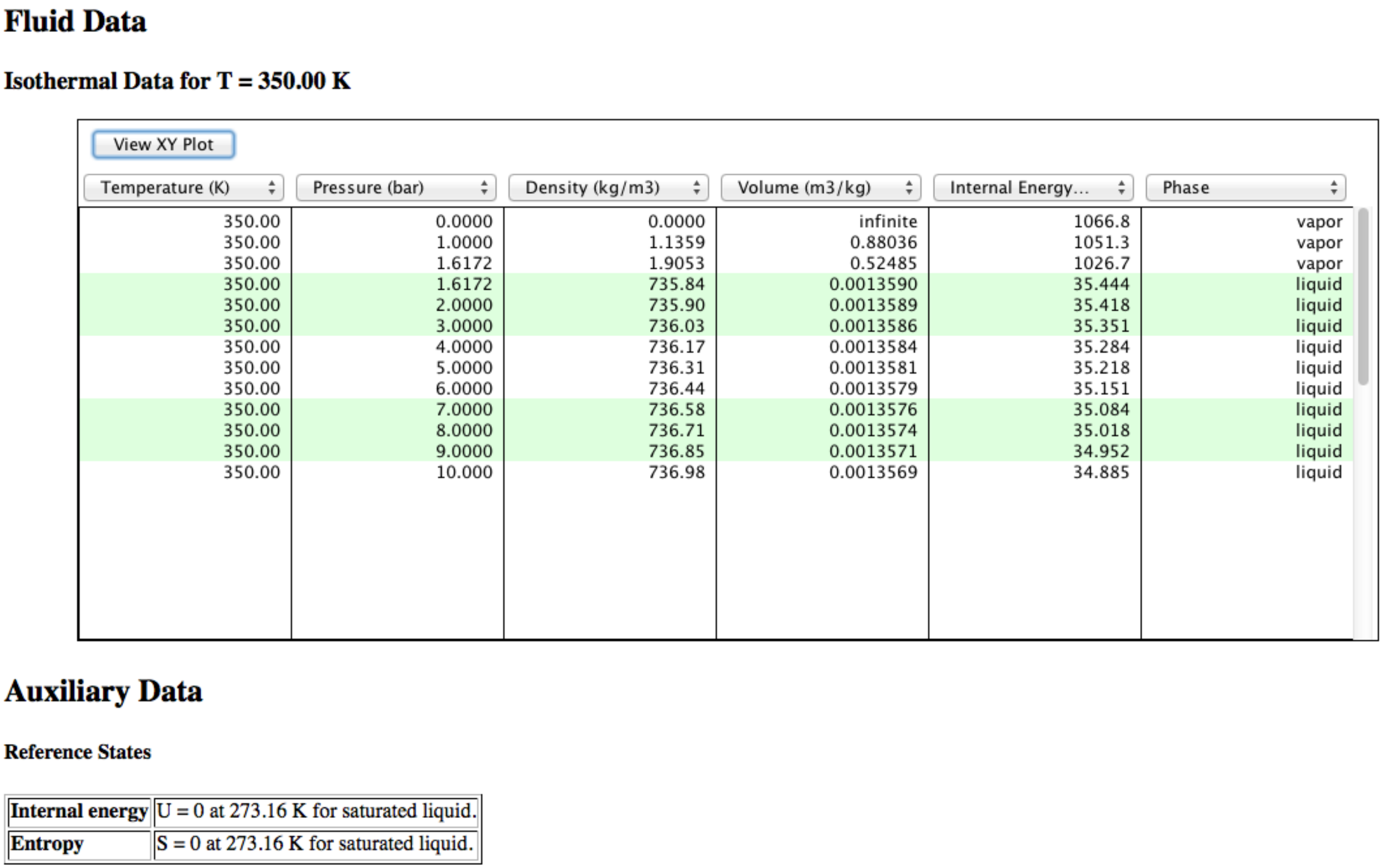
Quantity	**Units**
Temperature	● Kelvin ○ Celsius ○ Fahrenheit ○ Rankine
Pressure	● MPa ○ bar ○ atm. ○ torr ○ psia
Density	○ mol/l ○ mol/m3 ○ g/ml ● kg/m3 ○ lb-mole/ft3 ○ lbm/ft3
Energy	○ kJ/mol ● kJ/kg ○ kcal/mol ○ Btu/lb-mole ○ kcal/g ○ Btu/lbm
Velocity	● m/s ○ ft/s ○ mph
Viscosity	● uPa*s ○ Pa*s ○ cP ○ lbm/ft*s
Surface tension*	● N/m ○ dyn/cm ○ lb/ft ○ lb/in

*Surface tension values are only available along the saturation curve.

3. Choose the desired type of data:
   ● Isothermal properties ○ Saturation properties — temperature increments
   ○ Isobaric properties ○ Saturation properties — pressure increments
   ○ Isochoric properties
4. Please select the desired standard state convention:
   Default for fluid
5. Press to Continue

Sources of U and H data

NIST Thermophysical Properties http://webbook.nist.gov/chemistry/fluid/



Fluid Data

Isothermal Data for T = 350.00 K

Temperature (K)	Pressure (bar)	Density (kg/m3)	Volume (m3/kg)	Internal Energy...	Phase
350.00	0.0000	0.0000	infinite	1066.8	vapor
350.00	1.0000	1.1359	0.88036	1051.3	vapor
350.00	1.6172	1.9053	0.52485	1026.7	vapor
350.00	1.6172	735.84	0.0013590	35.444	liquid
350.00	2.0000	735.90	0.0013589	35.418	liquid
350.00	3.0000	736.03	0.0013586	35.351	liquid
350.00	4.0000	736.17	0.0013584	35.284	liquid
350.00	5.0000	736.31	0.0013581	35.218	liquid
350.00	6.0000	736.44	0.0013579	35.151	liquid
350.00	7.0000	736.58	0.0013576	35.084	liquid
350.00	8.0000	736.71	0.0013574	35.018	liquid
350.00	9.0000	736.85	0.0013571	34.952	liquid
350.00	10.000	736.98	0.0013569	34.885	liquid

Auxiliary Data

Reference States

Internal energy	U = 0 at 273.16 K for saturated liquid.
Entropy	S = 0 at 273.16 K for saturated liquid.

Change in P (constant T, φ, x_i)

State 1: P_1, T_1, φ_1, x_{i1} $\longrightarrow$ State 2: P_2, T_1, φ_1, x_{i1}

$$\hat{U}_1,\ \hat{H}_1 \qquad\qquad \hat{U}_2,\ \hat{H}_2$$

Ideal gas:

$$\hat{U}_2 = \hat{U}_1$$

$$\hat{H}_2 = \hat{H}_1$$

Solids/liquids:

$$\hat{U}_2 = \hat{U}_1$$

$$\hat{H}_2 = \hat{H}_1 + \hat{V}(P_2 - P_1)$$

Change in T (constant P, φ, x_i)

State 1: P_1, T_1, φ_1, x_{i1} → State 2: P_1, T_2, φ_1, x_{i1}

$$\hat{U}_1,\ \hat{H}_1 \qquad\qquad \hat{U}_2,\ \hat{H}_2$$

C_v: "constant-volume heat capacity"

C_p: "constant-pressure heat capacity"

$C_p = a + bT + cT^2 + dT^3$

$$\hat{U}_2 - \hat{U}_1 = \int_{T_1}^{T_2} C_V dT \ \sim\ C_v(T_2 - T_1)$$

$$\hat{H}_2 - \hat{H}_1 = \int_{T_1}^{T_2} C_p dT \ \sim\ C_p(T_2 - T_1)$$

Ideal gases: $C_p = C_v + R$

Solids/liquids: $C_p \sim C_v$

Water (liquid): $C_p \sim 4\ \mathrm{J/g^\circ C} \sim 1\ \mathrm{cal/g^\circ C} \sim 1\ \mathrm{BTU/lb^\circ F}$

Organic liquids: $C_p \sim 2\ \mathrm{J/g^\circ C}$

Gases: $C_p \sim 1\ \mathrm{J/g^\circ C}$

Change in φ (constant P, T, x_i)

State 1: $P_1, T_1, \varphi_1, x_{i1}$ → State 2: $P_1, T_1, \varphi_2, x_{i1}$

$$\hat{U}_1,\ \hat{H}_1 \qquad\qquad \hat{U}_2,\ \hat{H}_2$$

$\Delta\hat{H}_V$: enthalpy of vaporization (liquid to vapor) $\hat{H}_2 - \hat{H}_1 = \Delta\hat{H}_v$

$\Delta\hat{H}_m$: enthalpy of melting (solid to liquid) $\hat{H}_2 - \hat{H}_1 = \Delta\hat{H}_m$

$$\Delta\hat{U}_v \sim \Delta\hat{H}_v - RT_b$$

$$\Delta\hat{U}_m \sim \Delta\hat{H}_m$$

Water (liquid): $\Delta\hat{H}_v \sim 2000\ \mathrm{J/g} \sim 1000\ \mathrm{BTU/lb}$

Organic liquids: $\Delta\hat{H}_v \sim 500\ \mathrm{J/g} \sim 250\ \mathrm{BTU/lb}$

Change in x_i (constant P, T, φ)

State 1: $P_1, T_1, \varphi_1, x_{i1}$ → State 2: $P_1, T_2, \varphi_1, x_{i2}$

$$\hat{U}_1,\ \hat{H}_1 \qquad\qquad \hat{U}_2,\ \hat{H}_2$$

$\Delta\hat{H}_{\mathrm{mix}}$: enthalpy of mixing (liquids)

$$\hat{H}_{\mathrm{mix}} - \sum x_i \hat{H}_i = \Delta\hat{H}_{\mathrm{mix}}$$

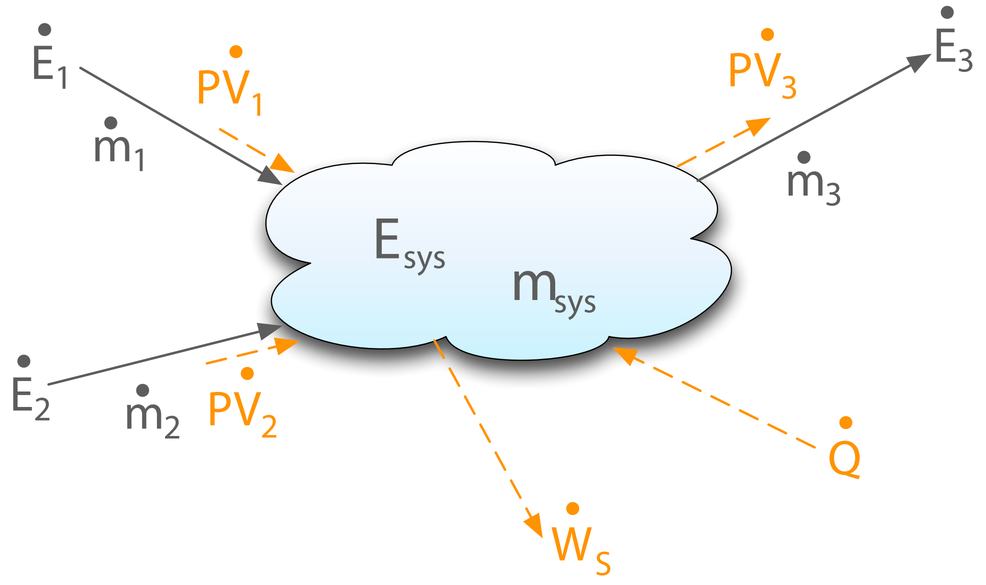
$\Delta\hat{H}_{\mathrm{soln}}$: enthalpy of solution (solid into liquid)

$$\hat{H}_{\mathrm{soln}} - \left(x_{iL}\hat{H}_{iL} + x_{iS}\hat{H}_{iS}\right) = \Delta\hat{H}_{\mathrm{soln}}$$

$\Delta\hat{H}_{\mathrm{r}}$: enthalpy of reaction

$$\sum \nu_i \Delta\hat{H}_{f,i} = \Delta\hat{H}_r$$

System energy and energy flows



$$E_{sys} = m_{sys}\hat{E}_{sys} = E_{k,sys} + E_{p,sys} + U_{sys}$$

system energy

$$\left.\begin{aligned} \dot{E}_1 &= \dot{m}_1\hat{E}_1 = \dot{E}_{k,1} + \dot{E}_{p,1} + \dot{U}_1 \\ \dot{E}_2 &= \dot{m}_2\hat{E}_2 = \dot{E}_{k,2} + \dot{E}_{p,2} + \dot{U}_2 \\ \dot{E}_3 &= \dot{m}_3\hat{E}_3 = \dot{E}_{k,3} + \dot{E}_{p,3} + \dot{U}_3 \end{aligned}\right\}$$

energy flow due to mass flow

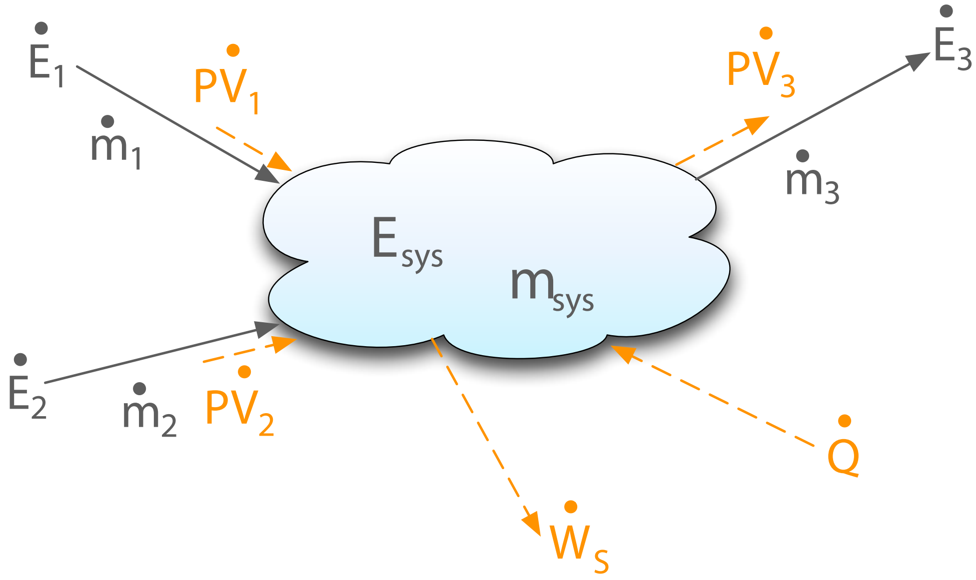
$$\frac{dE_{sys}}{dt} = \sum_{\text{all } j \text{ in}} \dot{E}_j - \sum_{\text{all } j \text{ out}} \dot{E}_j$$

$\dot{Q}$ energy flow due to heat transfer

$$\dot{W}_s + \sum W_{fl} = \dot{W}_s + P\dot{V}_1 + P\dot{V}_2 - P\dot{V}_3$$

energy flow due to shaft and flow work

The differential energy balance equation



$$\frac{dE_{sys}}{dt} = \sum_{\text{all } j \text{ in}} \dot{E}_j - \sum_{\text{all } j \text{ out}} \dot{E}_j$$

$$\frac{d\left(E_{k,sys} + E_{p,sys} + U_{sys}\right)}{dt} = \left(\dot{E}_{k,1} + \dot{E}_{p,1} + \dot{U}_1\right) + \left(\dot{E}_{k,2} + \dot{E}_{p,2} + \dot{U}_2\right) - \left(\dot{E}_{k,3} + \dot{E}_{p,3} + \dot{U}_3\right) + \dot{Q} + \dot{W}_s + P_1\dot{V}_1 + P_2\dot{V}_2 - P_3\dot{V}_3$$

$$\frac{d\left(E_{k,sys} + E_{p,sys} + U_{sys}\right)}{dt} = \left(\dot{E}_{k,1} + \dot{E}_{p,1} + \dot{H}_1\right) + \left(\dot{E}_{k,2} + \dot{E}_{p,2} + \dot{H}_2\right) - \left(\dot{E}_{k,3} + \dot{E}_{p,3} + \dot{H}_3\right) + \dot{Q} + \dot{W}_s$$

Simplifying the energy balance equation

$$\frac{d\left(E_{k,sys}+E_{p,sys}+U_{sys}\right)}{dt}=\left(\dot{E}_{k,1}+\dot{E}_{p,1}+\dot{H}_1\right)+\left(\dot{E}_{k,2}+\dot{E}_{p,2}+\dot{H}_2\right)-\left(\dot{E}_{k,3}+\dot{E}_{p,3}+\dot{H}_3\right)+\dot{Q}+\dot{W}_s$$

Mechanical equipment and fluid flow problems at steady state:
velocity, position change; no significant change in T, P, φ, x_i

$$\left(\dot{E}_{k,3}+\dot{E}_{p,3}\right)-\left[\left(\dot{E}_{k,1}+\dot{E}_{p,1}\right)+\left(\dot{E}_{k,2}+\dot{E}_{p,2}\right)\right]=\dot{Q}+\dot{W}_s$$

Reactors, separators, and/or heat exchangers at steady state:
T, P, φ, x_i change; no significant change in velocity or position, no mechanical equipment

$$\dot{H}_3-\left(\dot{H}_1+\dot{H}_2\right)=\dot{Q}$$

Batch process, no material flow in or out:

$$\frac{dU_{sys}}{dt}=\dot{Q}+\dot{W}_s$$

See Section 6.6.3 for example problems!