Contents

1   Revised order

- variables

- mass balances, single phase, mixtures, . . .

    - systems of linear equations

- energy balances, single phase, mechanical, . . .

- single component, two-phase

- two-component, two-phase, ideal

- reactions

- two-component, two-phase, non-ideal

2   Intro to Chemical Engineering

1. Pop quiz

    (a) Which weighs more, the Earth or the moon?

    (b) Mix together 100 mL H_2O and 50 mL alcohol. What's the final volume?

    (c) Add 10 g Fe ball at 100 C to 10 g H2O at 20 C. What's the final temperature?

(d) My pool holds 20,000 gal of H_2O. Pump circulates at 10 gpm. How long does it take for all the H_2O to pass through the filter? (Depends on whether it recirculates!)

2. Instructor

3. Students

4. Syllabus

5. Assignment: Read Chapter 1

3   Introduction to Engineering Calculation

3.1   Objectives

1. unit conversions

2. SI, cgs, English systems

3. sig figs

4. Is my answer reasonable?

5. Basic stats

6. Data fitting

3.2   Units and dimensions

- Engineering always deal with quantifiable, computable things.

- Anything we can quantify has a **value** (number) and a **unit** (number of what? meters, bananas, bits, seconds)

- A **dimension** is a property of a quantity, like *length, time, speed = length / time, density = mass / volume.* Most physical quantities have a dimension (other than pesky dimensionless quantities!).

- Quantities of the **same dimension** can be added or subtracted. First they have to be put into the **same units**.

$$\boxed{3\,\mathrm{cm} + 43\,\mathrm{mm} = 30\,\mathrm{mm} + 43\,\mathrm{mm} = 73\,\mathrm{mm}}$$

- Quantities of different dimension can be multiplied or divided and carry the combined dimension

$$\boxed{44\,\mathrm{m}/11\,\mathrm{s} = 4\,\mathrm{m/s}}$$

- Units *not welcome* inside transcendental functions, sin, cos, ln, . . .

- Equations must be *dimensionally homogeneous*: all additive terms on either side of an equality must have the same units

- **ALWAYS** carry units in engineering computations

3.3 Systems of units

- Base units

Dimension	SI	cgs	English
Length	m	cm	in, ft, mi
Mass	kg	g	lb_m
Time	s	s	s
Temperature	K	K	F
Current	A	A	
Light intensity	cd	cd	

- Multiplicative factors: T, G, M, k, c, d, m, μ, n, f

- Important chemical eng. derived units

Volume	liter	L	1000 cm^3
Force	Newton	N	1 kg m/s^2
	dyne		1 g cm/s^2
Energy/Work	Joule	J	1 N m = 1 kg m^2/s^2
	erg		1 dyne cm = 1 g cm^2/s^2
	calorie	cal	4.184 J
	Btu		1 Btu = 1055.05585 J
Power	Watt	W	1 J/s
	Horsepower	hp	1 hp = 745.7 W
Pressure	Pascal	Pa	1 N/m^2 = 1 J/m^3
	bar		10^5 Pa
	atmosphere	atm	1 atm = 1.01325 bar
	torr	torr	1/760 atm

- Inside book cover has many useful conversions

- Fun facts: 1 L of H_2O has a mass of 1 kg or about 2.2 lb_m. What about a liter of gasoline?

- Fun facts: 1 Btu is amount of heat released in burning 1 4 in wood match, or heat needed to raise the temperature of 1 lb_m water by 1°F. "Horsepower" used by Watt to compare the power output of a draft horse to his steam engine. Definitions abound!

- Pain in the neck to go between systems of units. Need conversion factors. E.g,. 1 lb_m = 453.5932 g. 1 in = 2.54 cm. Unless *forced* otherwise, use SI!

3.4 Unit conversions

- Conversion factors are ratios

$$4\,\frac{\mathrm{m}}{\mathrm{s}} * 100\,\frac{\mathrm{cm}}{\mathrm{m}} = 400\,\frac{\mathrm{cm}}{\mathrm{s}}$$

- Conversion factors can be ganged. Example: show that

$$1.00\,\mathrm{cm\,s^{-2}} = 9.95 \times 10^9\,\mathrm{km/year^2}$$

3.5 Dimensional homogeneity

> As you will learn in Thermodynamics, the internal energy U is related to other thermodynamic quantities by the relation
> $$U = TS - PV + \mu N \qquad (1)$$
> What are units on the entropy, S? Chemical potential, μ? What does this say about the dimensionality of pressure?

> The Schrödinger equation is the fundamental equation of quantum mechanics:
> $$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + V(x)\psi = E\psi \qquad (2)$$
> E has units of energy and m units of mass. What are the units on $V(x)$? $\hbar$? $\psi(x)$?

3.6 Mass, force, weight

- *mass* of an object is an intrinsic property, resistance to an applied force

- Newton's 3rd Law

$$\boxed{F = ma}$$

- English force units messy

$$\boxed{1\,\text{lb}_\text{f} = 32.174\,\text{lb}_\text{m}\text{ft/s}^2}$$

- *weight* is force exerted by a gravitational field on a mass

$$\boxed{w = mg}$$

- g depends on the planet you are standing on, as well as where you are standing

$$
\begin{aligned}
g &= 9.8066\,\text{m}\,\text{s}^{-2}\\
&= 32.174\,\text{ft/s}^2
\end{aligned}
$$

> Water has a density of $62.4\,\text{lb}_\text{m}/\text{ft}^3$. How much does $2\,\text{ft}^3$ of water weigh on the earth? On the moon ($g = 1.625\,19\,\text{m}\,\text{s}^{-2}$)?

```
1  earth = 2 * 62.4 * 32.174 * (1./32.174)
2  moon = earth * 1.62519/9.8066
3  print('earth:',earth,'lbf')
4  print('moon:',moon,'lbf')
```

```
earth: 124.80000000000001 lbf
moon: 20.682368201007485 lbf
```

3.7 Numerical calculations

3.7.1 Scientific notation, significant figures, precision

- Significant figures imply a precision

- *Always* report numbers with reasonable significant figures.

- Examples of adding and multiplying with sig figs.

- Round to even number: 1.35 to 1.45 all round to 1.4.

3.7.2 Validating results

- Does the result make physical sense?

- Do a ballpark estimate.

- Back-substitute

3.7.3 Sources of error

- Few, if anything, can be measured exactly. Processes have intrinsic variability

- CSTR example: flow rate may fluctuate, temperature fluctuate, slightly inhomogeneous. So do measurements (thermocouple). Best we can do is estimate the "truth."

  - random error
  - systematic error
  - Show random scatter, systematic drift, oscillation

```python
1   import numpy as np
2   import matplotlib.pyplot as plt
3   x = np.arange(40.)
4   sigma = 1.
5   T = 25. + sigma*np.random.randn(40)
6   T1 = 20. + .2 * x + sigma*np.random.randn(40)
7   T2 = 25. + 4. * np.sin(x/4.) + sigma*np.random.randn(40)
8
9   plt.subplot(311)
10  plt.scatter(x,T)
11  plt.ylim(15,35)
12  plt.xlim(0,40)
13  plt.ylabel('Temperature (C)')
14
15  plt.subplot(312)
16  plt.scatter(x,T1)
17  plt.ylim(15,35)
18  plt.xlim(0,40)
19  plt.ylabel('Temperature (C)')
20
21  plt.subplot(313)
22  plt.scatter(x,T2)
23  plt.ylim(15,35)
24  plt.xlim(0,40)
25  plt.xlabel('Sample (hour)')
26  plt.ylabel('Temperature (C)')
27  plt.savefig('./figs/random.png')
```
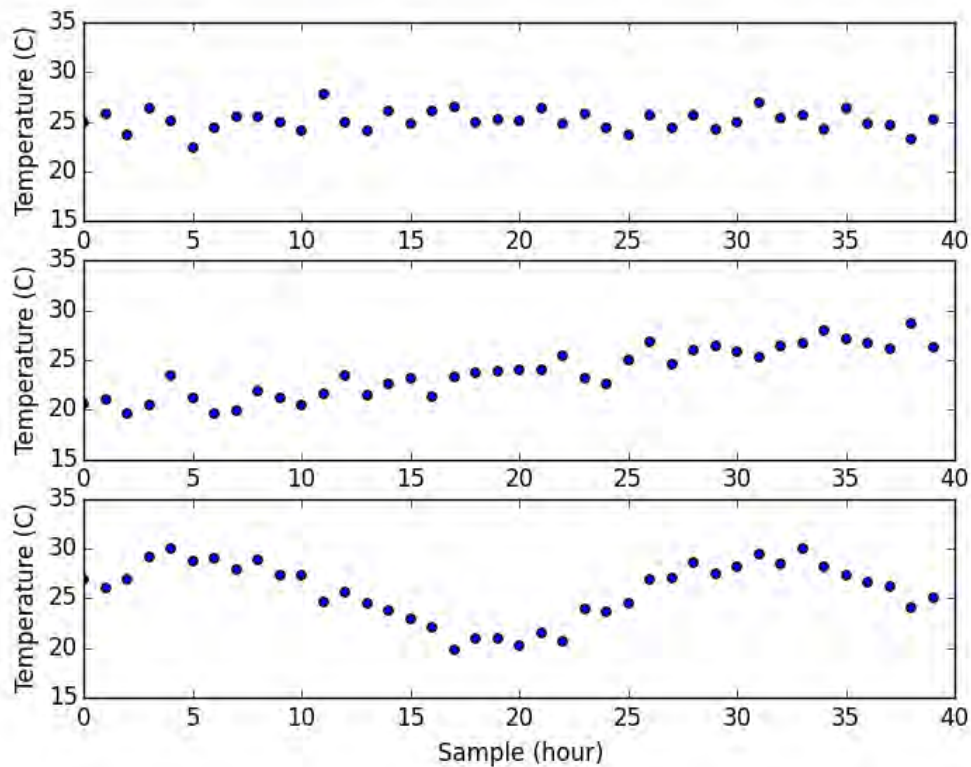
3.7.4 Sample mean

- *sample mean* to estimate truth

$$\bar{X} = \sum_{1}^{n} X_i$$

3.7.5 Measures of scatter

- *Range*

- *Sample variance*

$$s_X^2 = \frac{1}{N-1} \sum_{1}^{n} (X_i - \bar{X})^2$$

- *Standard deviation* has same units as X

$$s_x = \sqrt{s_X^2}$$

- If a random variable is Gaussian, about $2/3$ of measurements are within s_x of the mean, 95% within $2s_x$, 99% within $3s_x$.

- Example 2.5.2

QA on pigment. Let Y be the number of batches that fail QA out of 500 in a week. If process is shutdown for maintenance if $Y > \bar{Y} + 3S_Y$, how many bad batches are required for a shutdown?

```python
import numpy as np
import matplotlib.pyplot as plt

Week = np.array([1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12])
Y = np.array([17,  27,  18,  18,  23,  19,  18,  21,  20,  19,  21,  18 ])
plt.scatter(Week,Y)
plt.ylim(0,30)
plt.xlabel('Week')
plt.ylabel('Fails out of 500')
plt.savefig('./figs/QA.png')

N = Y.size
Sum = np.sum(Y)
Average = Sum/N

Variance = np.sum((Y - Average)**2)/(N-1)
StdDev = Variance**0.5

print('N   Sum   Average  Variance  Std. Dev')
print("{0:3d} {1:4d} {2:5.2f}   {3:5.2f}   {4:5.2f}".format(N,Sum,Average,Variance,StdDev))

Shutdown = Average + 3 * StdDev
print('Shutdown if Y > {0:5.2f}'.format(Shutdown))
```

```
N   Sum   Average  Variance  Std. Dev
 12   239 19.92     7.90      2.81
Shutdown if Y > 28.35
```
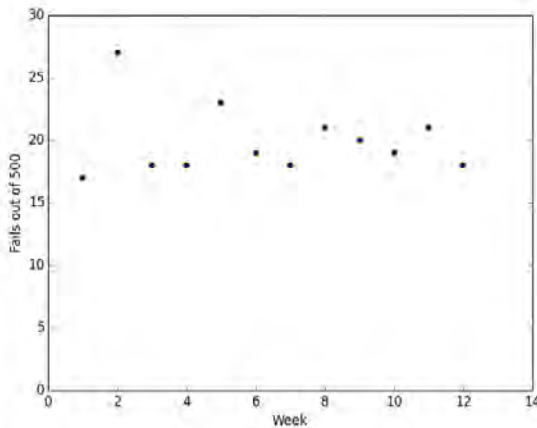

3.8   Process data modeling

- Often interested in the relationship between two correlated variables. E.g. a correlation curve between a thermocouple resistance and a temperature. An optical density and a concentration.

- *Linear regression* to fit linear data (Appendix A); minimizes *residuals* between data and a fit line

- r^2 measures fraction of variance in y "explained" by variance in x; 1 is best, 0 is worst

$$r^2 = 1. - \frac{\sum \text{res}_{\text{lg}}^2}{\sum \text{res}_{\text{null}}^2}$$

- Linearizing data (e.g. Arrhenius plot). (*Danger*: Error can be scewed by linearizing. Non-linear regression a good alternative.)

```
1  import numpy as np
2  import matplotlib.pyplot as plt
3  from scipy import stats
4
5  EHxy = [ 144,144, 132, 132, 116, 116, 190, 190, 173, 173, 111, 111, 91, 91, 207, 207, 199, 199, 110, 110, 83, 83]
6  RDxy = [152, 150, 141, 134, 117, 117, 204, 202, 184, 183, 123, 118, 94, 96, 225, 224, 213, 213, 114, 115, 89, 93]
7
8  m, b, r, p, e = stats.linregress(EHxy,RDxy)
9  print("Slope       Intercept          r**2")
10 print(m,b,r**2)
11
12 nu = np.linspace(80,230)
13 fit = m * nu + b
14
15 plt.scatter(EHxy,RDxy)
16 plt.plot(nu,fit)
17 plt.xlim((50,250))
18 plt.ylim((50,250))
19 plt.xlabel('Effective harmonic frequencies (cm$^{{-1}}$)')
20 plt.ylabel('Relaxed displacement frequencies (cm$^{{-1}}$)')
21 plt.savefig('./figs/freq.png')
```

```
Slope         Intercept         r**2
1.08962211596 -4.08654658558 0.995318037198
```
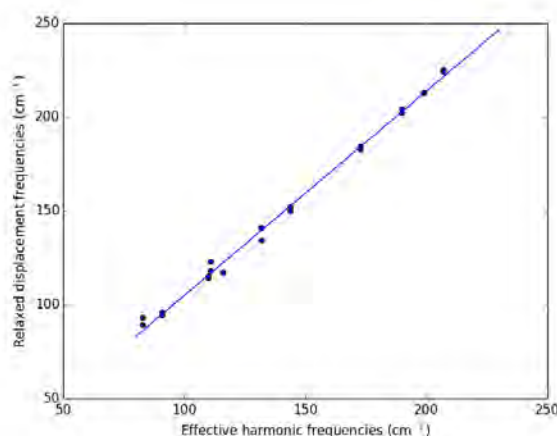
4 Processes and process variables

4.1 Learning objectives

- density

- flow rates

- composition

- pressure

4.2 Mass, volume, density

- mass, volume are *extensive* quantities

- *density* (ρ) = mass / volume is *intensive*, characteristic of a substance at some T and P

- tabulated in common handbooks, allows us to convert between m and V

- *specific gravity* is density relative to some reference, commonly H_2O at $4\,°C$

$$\rho_{H_2O}(4\,°C) = 1.00\,\text{g cm}^{-3} = 62.43\,\text{lb}_m/\text{ft}^3 \tag{3}$$

- mass is independent of T, volume changes with T, therefore so does ρ

- can find tabulations of $\rho(T)$, $V(T)$, or *coefficient of thermal expansion*

$$\alpha(T) = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{4}$$

- **Example 3.1.1**

  Specific gravity of Hg at $20\,°C$ is 13.456. Density? Volume of 215 kg?

```
1  rho = 13.546 * 62.43
2  print('Density = ',rho,' lbm/ft^3')
3  print('Volume = mass/density')
4  volume = 215 * (1./0.454) / rho
5  print('Volume =',volume,'ft3')
```

```
Density =  845.67678  lbm/ft^3
Volume = mass/density
Volume = 0.5599873298381516 ft3
```

- **Example 3.1.2**

  (a) What is volume of 215 kg Hg at $100\,°C$?

  (b) What is change in height between 20 and $100\,°C$ of a 0.25 in diameter Hg cylinder?

$$V_{Hg}(T) = V(0)[1 + 0.18182 \times 10^{-3}T + 0.0078 \times 10^{-6}T^2]$$

$$V(100) = V(20) * \frac{V(100)}{V(20)}$$

$$h = V/A$$

```python
import numpy as np

def V(T):
# Volume relative to volume at 0 C
    a = 0.18182e-3
    b = 0.0078e-6
    return 1. + T * (a + b*T)
def h(V):
    area = np.pi * (0.25/12./2.)**2
    return V/area

V20 = 0.560
h20 = h(V20)
V100 = V20 * V(100.)/V(20.)
h100 = h(V100)
print('Temperature    Volume (ft3)   Height (ft)')
print("{0:8.1f}       {1:6.3f}        {2:6.2f}".format(20,V20,h20))
print("{0:8.1f}       {1:6.3f}        {2:6.2f}".format(100,V100,h100))

deltah = h100-h20
print("Delta h = {0:6.2f} ft".format(deltah))
```

```
Temperature    Volume (ft3)   Height (ft)
    20.0          0.560          1642.78
   100.0          0.568          1666.72
Delta h =  23.93 ft
```

4.3   Flow rate

- mass flow rate $\dot{m}$: mass passing an area in a time

- volume flow rate $\dot{V}$: volume passing an area in a time

$$\rho = \frac{m}{V} = \frac{\dot{m}}{\dot{V}}$$

- Gas flows down a tapered cone. How does mass flow rate compare at entrance and exit?

  – Same

- If density is constant, how does volumetric flow rate compare?

  – Same

- How does linear velocity compare

  – Goes up!

- Molar flow rate, $\dot{F}$? Need to know MW!

4.4   Chemical composition

4.4.1   Moles and molecular weights

- atomic theory, we can count atoms and molecules. They are tiny, so need a big unit to count with!

- molecular "weight" (MW) is mass relative to $\{^{12}C\}$, defined to have a mass of 12

- Avogadro's number $N_A = 6.022 \times 10^{23}$ number of $\{^{12}C\}$ to make 12 grams, called a `mole` or `gram-mole` (yech!)

- `kmol` makes 12 kg, `lb-mole` makes 12 lbm

- periodic table records masses of all elements relative to $12\,C$

Periodic Table of the Elements

- $CO_2 = 44$ g/g-mol $= 44$ kg/kg-mol $= 44$ lbm/lb-mol $= 44$ ton/ton-mol

- calculate molar flow rate from mass flow rate

  EXAMPLE What is molar flow rate of O in a stream of 4400 kg/hr CO_2?

```
1   F = 4400 * (1./44.) * 2
2   print("{0:6.2f} kmol O/hr".format(F))
```

```
200.00 kmol/hr
```

4.5   Mixtures

- Always expressed as something/something

- Generally faced with two types of problems: turn one concentration measure into another (intensive → intensive); or use in conversions of extensive → extensive

4.5.1   Mass and mole fractions

- mass fraction A = mass A/total mass

- mole fraction A = mol A/total mol

- vol fraction A = vol A/total vol

EXAMPLE 35.0 %(w/w) H_2SO_4 has a specific gravity of 1.2563. What volume of solution is needed to obtain 500 g-mol H_2SO_4? (Extensive to extensive)

```
1  MW = 2.*(1.008) + 32.0 + 4 * 16.0    # g/g-mol
2  mass = 500 * MW                       # g
3  mass_soln = mass * (100./35.0)        # g
4  rho = 1.2563                          # g/mL
5  volume = mass_soln/rho/1000           # L
6  print("Volume={0:6.3f} L".format(volume))
```

```
Volume=111.457 L
```

EXAMPLE What is mole fraction H_2SO_4 in 35.0%(w/w) solution? (intensive to intensive)

```
1  MWH2SO4 = 2*1.008 + 32.0 + 4 * 16.00
2  MWH2O = 2 *1.008 + 16.00
3
4  molH2SO4 = 35.0 / MWH2SO4      # mol H2SO4
5  molH2O   = (100.-35.0)/ MWH2O  # mol H2O
6
7  fracH2SO4 = molH2SO4/(molH2SO4+molH2O)
8
9  print("{0:6.3f}%(mol/mol) H2SO4".format(fracH2SO4*100))
```

```
9.006%(mol/mol) H2SO4
```

- trace species in a gas often expressed as ppm or ppb rather than %

- EPA ozone standard is 70 ppb, 70 ozone molecules/billion molecules of air

- less frequently mass rather than mole basis

4.5.2 Average molecular weight

$$\bar{MW} = \sum_i y_i MW_i$$

EXAMPLE What is average molecular weight of air, which is 76.7% N_2 and 23.3% O_2 by mass?

```
1  # 100 g basis
2  MWN2 = 28.0
3  MWO2 = 32.0
4  molN2 = 76.7 / MWN2
5  molO2 = 23.3 / MWO2
6  moltot= molN2 + molO2
7  fracN2 = molN2/moltot
8  fracO2 = molO2/moltot
9  MWbar = fracN2*MWN2 + fracO2*MWO2
10
11 print("100 g basis")
12 print("             N2        O2")
13 print("MW:         {0:4.2f}    {1:4.2f}".format(MWN2,MWO2))
14 print("moles:      {0:4.2f}    {1:4.2f}".format(molN2,molO2))
15 print("mole frac:  {0:4.2f}    {1:4.2f}".format(fracN2,fracO2))
16 print("\nMWbar = {0:6.2f} g/mol".format(MWbar))
```

```
100 g basis
            N2      O2
MW:         28.00   32.00
moles:      2.74    0.73
mole frac:  0.79    0.21

MWbar =  28.84 g/mol
```

4.5.3 Concentrations

- "concentration" sometimes reserved for amount/volume

- `molarity` = mol/volume; mass/volume less common

  EXAMPLE 0.50 M H_2SO_4 flows into a process unit at $1.25 \, \mathrm{m^3 \, min^{-1}}$. S.G. = 1.03.
  (a) Mass concentration? (b) mass flow rate of H_2SO_4? (c) mass fraction H_2SO_4?

```python
1   Molarity = 0.50                    # mol/L
2   MW  = 2*1.0 + 32.0 + 4 * 16.0      # g/mol
3   flow = 1.25                        # m3/min
4   density = 1.03                     # kg/L
5
6   mass_conc = Molarity * (MW) * (1/1000) * (1000/1)   # kg H2SO4/m3
7
8   H2SO4_mass_flow = mass_conc * flow * (1/60)          # kg H2SO4/s
9
10  total_mass_flow = flow * (1/60) * (1000/1) * density  # kg/s
11
12  mass_frac = H2SO4_mass_flow/total_mass_flow
13
14  print("{0:5.2f} kg H2SO3/m3   {1:5.2f} kg/s   {2:5.4f} kg H2SO4/kg".format(mass_conc,H2SO4_mass_flow,mass_frac))
```

```
49.00 kg H2SO3/m3    1.02 kg/s    0.0476 kg H2SO4/kg
```

4.6 Pressure

4.6.1 Measures of pressure

- Pressure = Force/area required to resist motion of a frictional piston against a fluid

- Internal fluid pressure arises from molecular motions and is present in any confined fluid

- *hydrostatic pressure* arises from gravitational force
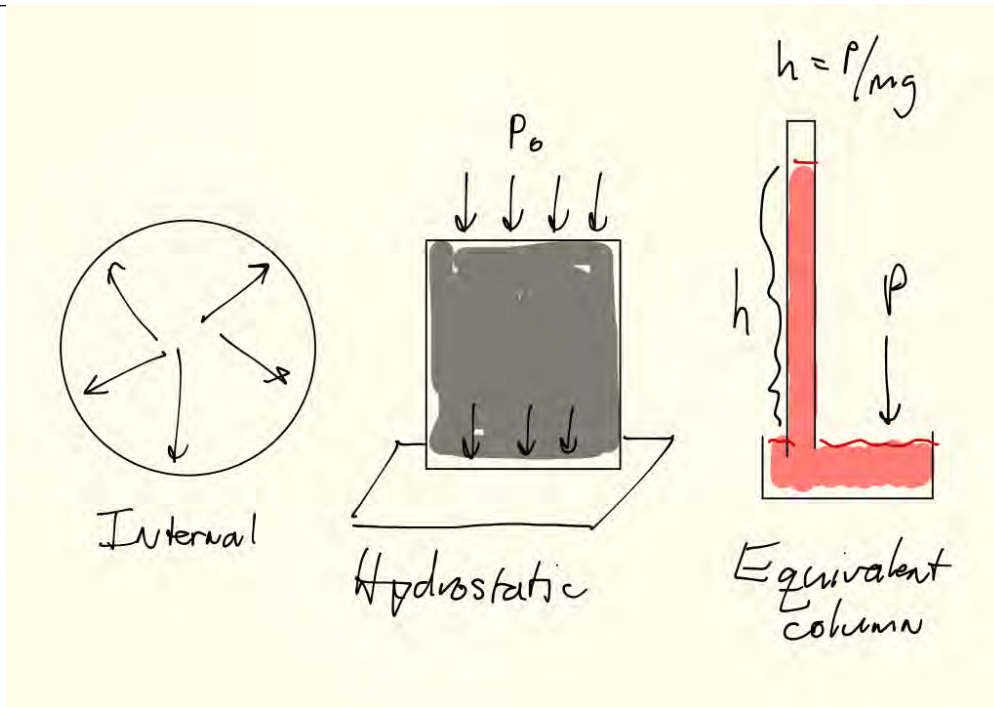
- *air pressure* is hydrostatic pressure of the atmosphere (1 atm)

- measured in standard pressure units (Pa, bar, atm)

- *or* measured in equivalent height of a fluid column in vacuum, most commonly mmHg, $\rho_{Hg} = 13.6\,\mathrm{g\,cm^{-3}} = 13\,594\,\mathrm{kg\,m^{-3}}(0\,°\mathrm{C})$

$$h = P/\rho g$$

EXAMPLE Express 1 atm in mmHg and mmH2O.

```
1  pressure = 1.01325e5 # Pa
2  density = 13594.  # kg/m3
3  g = 9.807  #  m/s2
4
5  heightHg = pressure /(density * g) # m
6  heightH2O = 13.6 * heightHg
7  print('{0:6.1f} mmHg   {1:8.2f} mH2O'.format(heightHg*1000,heightH2O))
```

```
760.0 mmHg      10.34 mH2O
```

- open column of fluid (or solid) will have a total hydrostatic pressure at the base of atmospheric pressure plus column pressure

$$P = P_0 + \rho g h$$

EXAMPLE Hydrostatic pressure 30.0 m below the surface of a lake?

```
1    print('Easy way...40.3 m H2O!')
2
3    rho = 1000.    # kg/m3
4    g = 9.807    # m/s2
5    h = 30.0    # m
6    P0 = 1.01325e5 # Pa
7
8    pressure = P0 + rho*g*h   # Pa
9    pressureatm = pressure *( 1/P0)
10   pressurepsi = pressureatm * 14.696
11   print('Hard way...')
12   print('{0:5.2f} bar    {1:5.2f} atm     {2:5.2f} psi'.format(pressure/1e5,pressureatm,pressurepsi))
```

```
Easy way...40.3 m H2O!
Hard way...
 3.96 bar    3.90 atm     57.37 psi
```

4.6.2   Absolute vs. gauge

- absolute pressure = pressure relative to a vacuum, always > 0

- gauge pressure difference from atmosphere, can be positive or negative

$$P_{gauge} = P_{abs} - P_{atm}$$

4.6.3   Pressure gauges

- electronic devices (e.g. piezoelectric)

- mechanical, based on a diaphragm or other deformable object

- manometers: two-armed device. Pressures at equivalent heights within fluid must be the same.

4.6.4 open-end manometer:
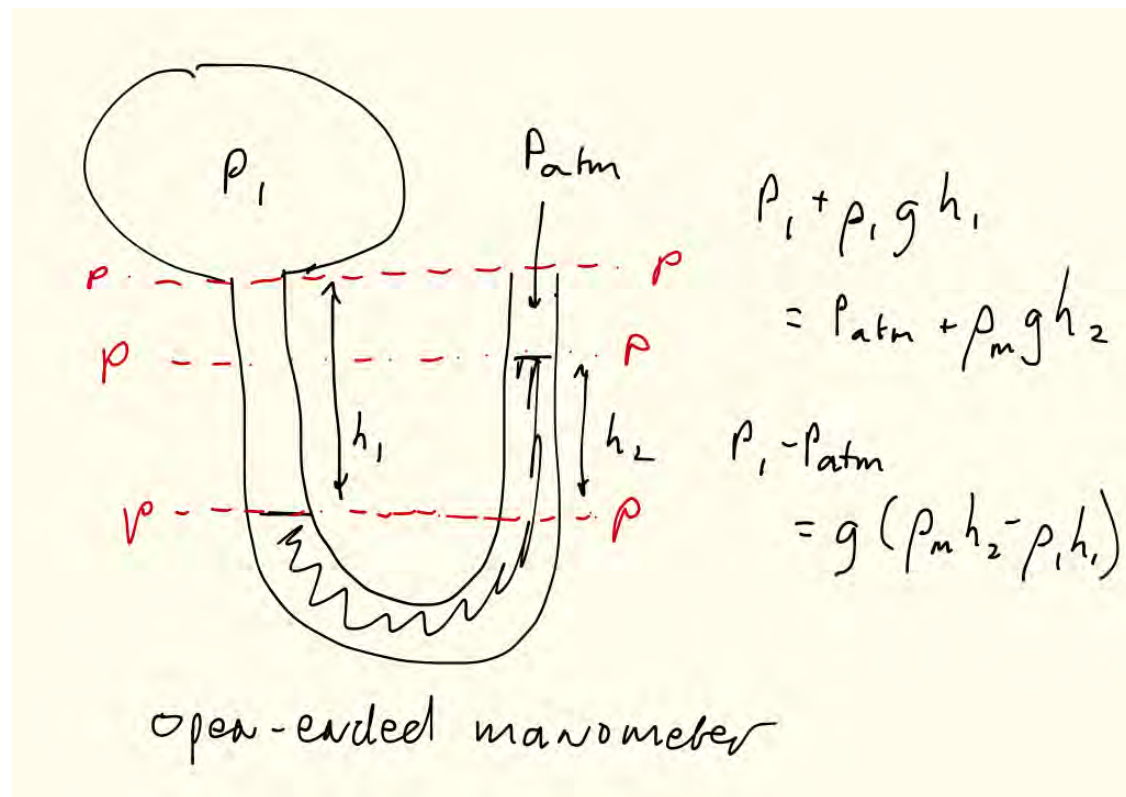
EXAMPLE Manometer fluid is Hg and $h_2 = -25$ mm. What is gauge pressure? What is absolute pressure? In mmHg and in psi.

```
hatm = 760
hgauge = -25    # mmHg
habsolute = hgauge + hatm
print('Gauge = {0:5.1f}  Abs = {1:5.1f} mmHg'.format(hgauge,habsolute))

g = 9.807       # m/s2
rhoHg = 13600   # kg/m3
pgauge = rhoHg * g * hgauge/1000.    # Pa
pabsolute = rhoHg * g * habsolute/1000.    # Pa
print('Gauge = {0:5.0f}  Abs = {1:5.0f} Pa'.format(pgauge,pabsolute))

pgauge = pgauge * (14.696/ 1.01325e5)  # lbf/in2
pabsolute = pabsolute * (14.696/ 1.01325e5)   # lbf/in2
print('Gauge = {0:5.3}  Abs = {1:5.3f} psi'.format(pgauge,pabsolute))
```

```
Gauge = -25.0   Abs = 735.0 mmHg
Gauge = -3334   Abs = 98031 Pa
Gauge = -0.484   Abs = 14.218 psi
```

4.6.5 differential manometer

differential manometer
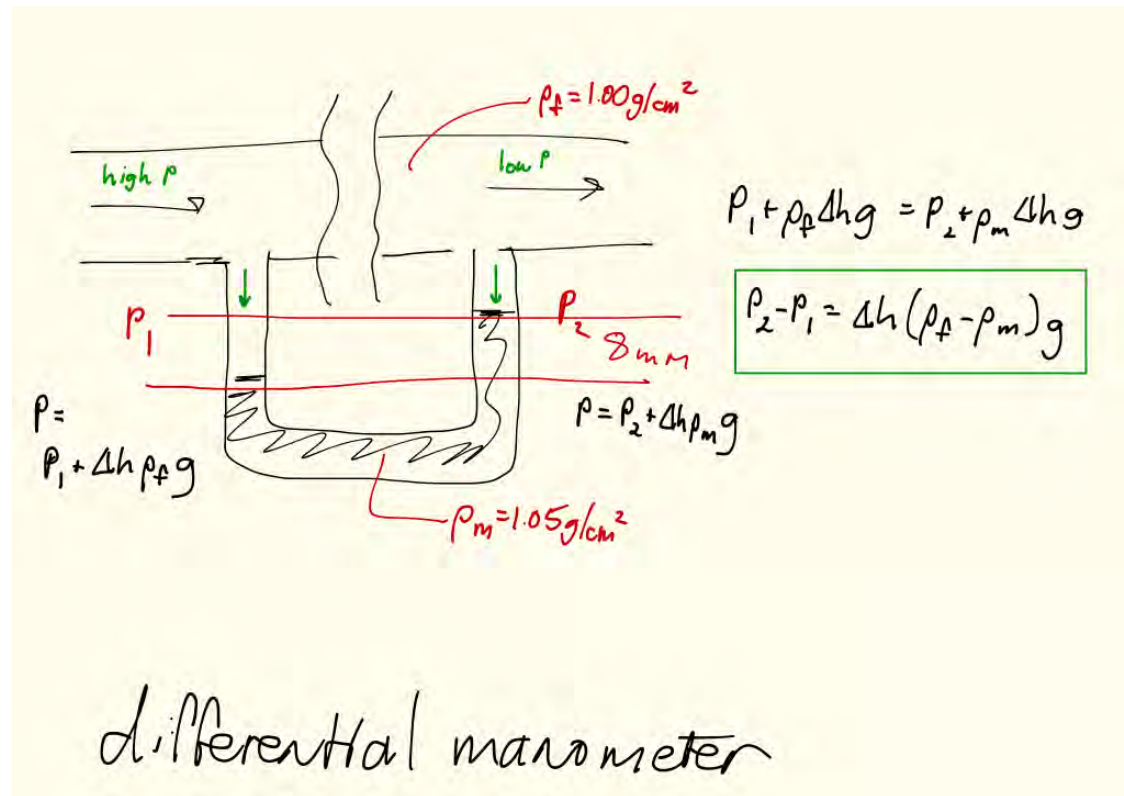
$$P_2 - P_1 = g(\rho_f - \rho_m)\Delta h$$

```
1  g  =   980.7   # cm/s^2
2  Dh = 0.8       # cm
3  rhom = 1.05 # g/cm^3
4  rhof = 1.00 # g/cm^3
5
6  dP = g * Dh * (rhof - rhom) # dyne/cm2
7
8  print("\Delta P = {0:5.1f} dyne/cm2".format(dP))
```

```
\Delta P = -39.2 dyne/cm2
```

4.6.6 Closed manometer

4.7 Temperature

4.7.1 Scales

- Kelvin: absolute scale, $0 \rightarrow \infty$

- Celsius: $T(°C) = T(K) - 273.15)$

- Fahrenheit: $T(°F) = 1.8T(°C) + 32)$

- Rankine: absolute scale, $T(°R) = T(°F) + 459.67$

- **Use care** in using in unit conversion calculations. Ratios work for converting temperature *differences*, but not for converting absolute temperatures

4.7.2   Measurement devices

- volume-based (thermometer)

- radiation-based (pyrometer)

- voltage-based (thermocouple) - change in potential between two dissimilar metals

- resistance-based (thermistor)

5 Material balances on non-reactive systems

5.1 Process types

- batch

- continuous

- semi-batch (filling a balloon)

- steady-state vs. transient

5.2 General balance equation

> output = input + generation - consumption - accumulation

EXAMPLE Every year 50,000 Leute move into a city, 75,000 move out, 22,000 are born, and 19,000 die. Write a differential balance on the population, i.e., what is change in population with time?

```
1  input = 50000; output=75000; generation=22000; consumption=19000;
2  accumulation =input + generation - output - consumption
3  print('accumulation = {0} people/year'.format(accumulation))
```

```
accumulation = -22000 people/year
```

- example of *differential* balance, a change over time (or space)

- *integral* balance is sum of differential balance over some unit of time or space

- batch: input = output = 0

- continuous, steady-state, non-reactive: accumulation = generation = consumption = 0

- Can balance *total mass*: generation = consumption = 0

- Can balance *mass* or *moles* of an element or molecular species

  EXAMPLE Differential balance on a continuous, steady-state process

  $1000 \, \mathrm{kg \, h^{-1}}$ mixture of 50%(w/w) benzene and toluene is distilled into two streams, one containing $450 \, \mathrm{kg \, h^{-1}}$ benzene and other containing $475 \, \mathrm{kg \, h^{-1}}$ toluene. Solve for unknown flow rates.

450 kg B/h
m_{T1} (kg T/h)

500 kg B/h
500 kg T/h

m_{B2} (kg B/h)
475 kg T/h
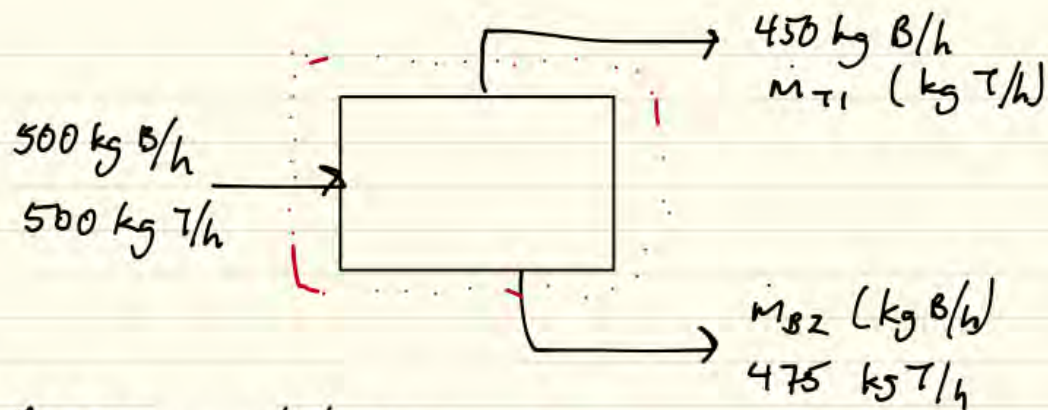
Benzene mass balance:

output = input + gen - con - accum

$$450 \text{ kg/h} + m_{B2} = 500 \text{ kg/h}$$

$$m_{B2} = 50 \text{ kg/h}$$

Toluene mass balance

output = input

$$m_{T1} + 475 \text{ kg/h} = 500 \text{ kg/h}$$

$$m_{T1} = 25 \text{ kg/h}$$

Total mass balance

output = input

$$450 + 50 + 475 + 25 = 500 + 500 \quad \checkmark$$

5.3   Mass balance procedure

- Illustrates general procedure:

1. Create a flow chart

2. Label all known quantities along each stream

(a) molar or mass flow rates

(b) concentrations

3. Label all *unknown* quantities with symbols

4. Work in only mass or molar quantities

- A flow sheet is *balanced* if all material balances are closed

- A balanced flow sheet can be *scaled*; all flows multiplied by a constant value

- Allows one to choose arbitrarily a *basis*

  EXAMPLE Air humidification example. Three inputs are fed into an evaporation chamber:

  - Liquid H_2O, $20\,min^{-1}$
  - Air
  - O_2, at a rate 1/5 of the air

  The output contains 1.5% H_{20}. What are the output compositions and other flow rates?
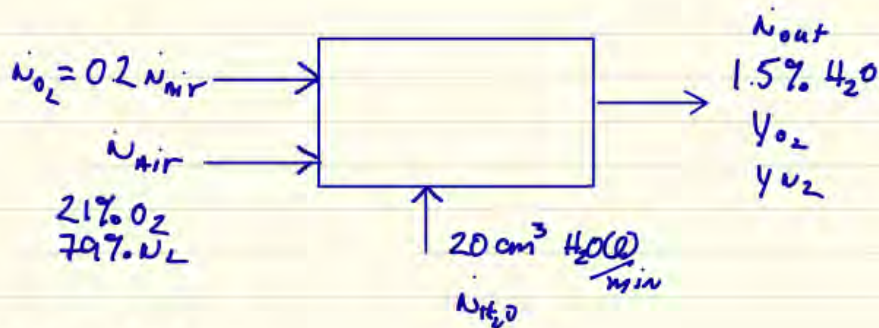
Water balance

$$\dot{N}_{H_2O} = 20 \frac{cm^3}{min} \cdot \frac{1 g}{cm^3} \cdot \frac{1 mol}{18 g} = 1.11 \; mol_{H_2O}/min$$

output = input

$$\dot{N}_{H_2O} = 0.015 \cdot \dot{N}_{out}$$

$$\dot{N}_{out} = 74.1 \; mol/min$$

N_2 balance   output = input

$$y_{N_2} \cdot \dot{N}_{out} = 0.79 \; \dot{N}_{Air}$$

O_2 balance

$$y_{O_2} \dot{N}_{out} = 0.21 \; \dot{N}_{Air} + 0.2 \; \dot{N}_{Air}$$
$$= 0.41 \; \dot{N}_{Air}$$

unknowns:

$y_{N_2}, y_{O_2}, \dot{N}_{Air}$ But $y_{N_2} + y_{O_2} = 0.985$

3 eqs., 3 unknowns → 1 sol'n

Shortcut: total mole balance

$$\text{output} = \text{input}$$

$$\dot{N}_{out} = \dot{N}_{H_2O} + \dot{N}_{Air} + 0.2\,\dot{N}_{Air}$$

$$74.1\ \frac{mol}{min} = 1.11\ \frac{mol}{min} + 1.2\ \dot{N}_{Air}$$

$$\dot{N}_{Air} = 60.8\ mol/min \qquad \dot{N}_{O_2} = 12.1\ mol/min$$

$$y_{N_2} = 0.79\ \frac{\dot{N}_{Air}}{\dot{N}_{out}} = 0.65 \qquad y_{O_2} = 0.34$$

Math is simple. Challenge
is to set up correctly
and to choose order of
solution wisely.

- Number of equations = number of unknowns. Say *degrees of freedom* = 0.

  EXAMPLE DOF analysis. Humid air passes through a condenser that removes 95% of H_2O. Condensate removed at 225 L/min. Calculate flow rate and composition of gas stream leaving condenser.
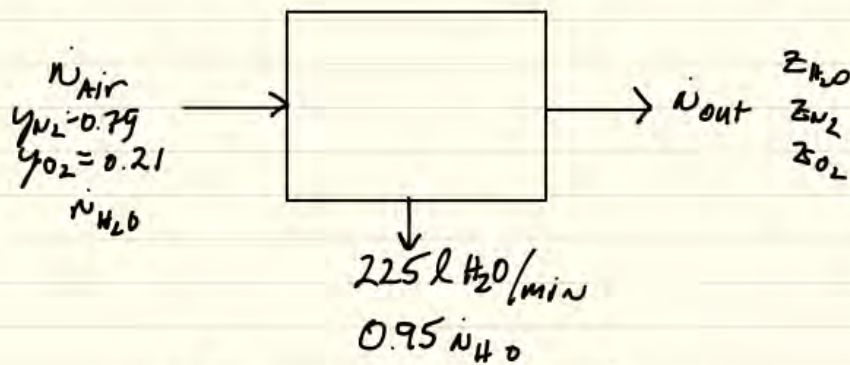
$$\dot{N}_{Air}$$
$$y_{N_2} = 0.79$$
$$y_{O_2} = 0.21$$
$$\dot{N}_{H_2O}$$

$$\dot{N}_{out} \quad z_{H_2O} \quad z_{N_2} \quad z_{O_2}$$

$$225\ \ell\ H_2O/min$$
$$0.95\ \dot{N}_{H_2O}$$

unknowns

$\dot{N}_{Air}$
$\dot{N}_{H_2O}$
$\dot{N}_{out}$
z_{H_2O}
z_{N_2}
z_{O_2}

equations

$\sum z = 1$
H_2O balance
N_2 balance
O_2 balance
$\dot{v}_{H_2O}$

Unknowns − equations = 6 − 5 = 1 DoF

Need another piece of info to balance

Range of solutions — pot'l to optimize

EXAMPLE 45.0%(w/w) benzene and balance toluene are fed to a distillation column. The overhead product contains 95.0%(mol/mol) benzene and accounts for 92% of total fed benzene. The fed enters at 2000 L/h and has specific gravity 0.872. Determine mass flow rates of overhead and bottom streams and bottom composition.

```
1   # Convert stream 2 to mass basis
2   MWb = 6 * 12.0 + 6 * 1.008
3   MWt = 7 * 12.0 +8 * 1.008
```

```
 4   x2B = 0.95
 5   x2T = 0.05
 6
 7   basis = 100.
 8   m2B = basis * x2B * MWb
 9   m2T = basis * x2T * MWt
10   m2tot = m2B + m2T
11
12   z2B = m2B/m2tot
13   z2T = m2T/m2tot
14   print('Z2Benzene = {0:5.3f} Z2Toluene = {1:5.3f} kg/kg'.format(z2B,z2T))
15
16   # total mass flow rate
17   SG = 0.872
18   v1 = 2000   # l/h
19   m1 = v1 * SG
20
21   # benzene flow rates
22   z1B = 0.45
23   m3B = 0.08 * m1 * z1B
24   m2B = 0.92 * m1 * z1B
25
26   print('Mdot1 = {0:6.1f}  Mdot2B = {1:6.1f}   Mdot3B = {2:6.1f} kg/hr'.format(m1,m2B,m3B))
27
28   # mass balances
29   m2 = m2B/z2B
30   m3 = m1 - m2
31   print('Mdot2 = {0:6.1f}  Mdot3 = {1:6.1f} kg/hr'.format(m2,m3))
32
33   # last gasp
34   z3B = m3B/m3
35   print('Z3Benzene = {0:5.3f}  Z3Toluene = {1:5.3f} kg/kg'.format(z3B,1-z3B))
```

```
Z2Benzene = 0.942 Z2Toluene = 0.058 kg/kg
Mdot1 = 1744.0  Mdot2B =  722.0   Mdot3B =   62.8 kg/hr
Mdot2 =  766.8  Mdot3 =  977.2 kg/hr
Z3Benzene = 0.064  Z3Toluene = 0.936 kg/kg
```

$SG = 0.872$

$\dot{U} = 2000 \, \ell/h$

(1) $\dot{m}_1$

$z_{1B} = 0.45$
$z_{1T} = 0.55$

(2) $\dot{m}_2$
$z_{2B} = 0.942$
$z_{2T} = 0.058$
$m_{2B} = \dot{m}_1 \cdot 0.92 \cdot z_{1B}$

$\dot{m}_3$
$z_{3B} + z_{3T} = 1$
(3)
$m_{3B} = 0.08 \, \dot{m}_1 \cdot z_{1B}$
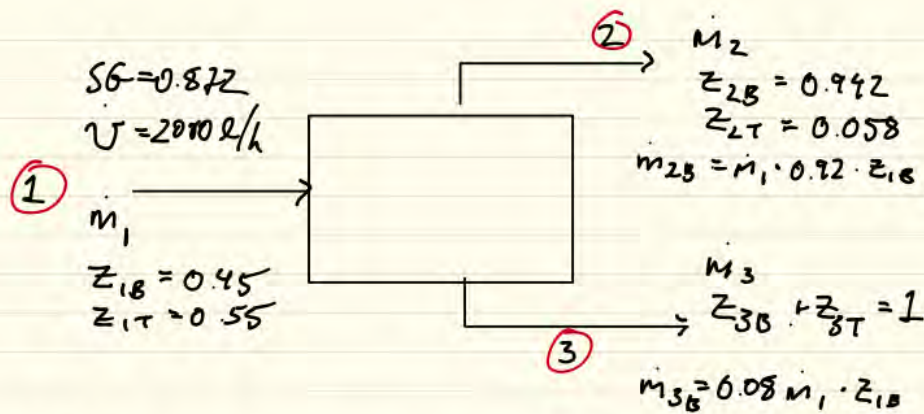
1. Decision 1: mass or moles? Mass

$\quad 95\% \, (\text{mol}/\text{mol}) \rightarrow 0.942 \, (\text{kg}/\text{kg})$

$\quad\quad 5\% \rightarrow 0.058$

2. Label flowchart.

$\quad$ Number inputs + outputs

3. DOF

$\quad$ unknowns: $\dot{m}_1, \dot{m}_2, \dot{m}_3, z_{5B}$

$\quad$ equations: 2 mass balances, flow rate, benzene split

$\quad\quad$ Good to go!

4. Do all simple calculations

$\quad \dot{m}_1 = \dot{v}_1 \cdot \rho \quad = \boxed{1744 \, kg/hr}$

$\quad\quad (\ell/h) \, (kg/\ell)$

$\quad \dot{m}_{2B} = 0.08 \, \dot{m}_1 \cdot z_{1B} = 722 \, kg/hr$

$\quad m_{3B} = \quad\quad\quad = \quad 63 \, "$

$$Z_{2B} = \dot{M}_{2B} / \dot{M}_2 \implies \boxed{\dot{M}_2 = \frac{\dot{M}_{2B}}{Z_{2B}} = 767 \, ^{kg}/_{hr}}$$

5. use balances

$$\dot{M}_1 = \dot{M}_2 + \dot{M}_3 \implies \boxed{\dot{M}_3 = \dot{M}_1 - \dot{M}_2 \approx 977 \, kg/hr}$$

6. clean up

$$Z_{3B} = \frac{\dot{M}_{3B}}{\dot{M}_3} = 0.064$$

$$Z_{3T} = 1 - Z_{3B} = 0.936$$

EXAMPLE Integral balance on semi-batch, non-steady state process. Air is bubbled through a tank of liquid hexane at a rate of 0.100 kmol/min. The gas stream leaving the tank contains 10.0%(mol/mol) hexane vapor. The air is essentially insoluble in hexane. Estimate the time required to vaporize $10 \, \text{m}^3$ of the liquid.

$\Rightarrow$ 0.1 kmol H/kmol

0.9 kmol air/kmol

$\dot{N}_{air}$?

$\dot{N}_H$?

air/hexane

hexane

0.1 kmol air / min

$\Delta V = -10 \, m^3$

$\Delta N = ?$
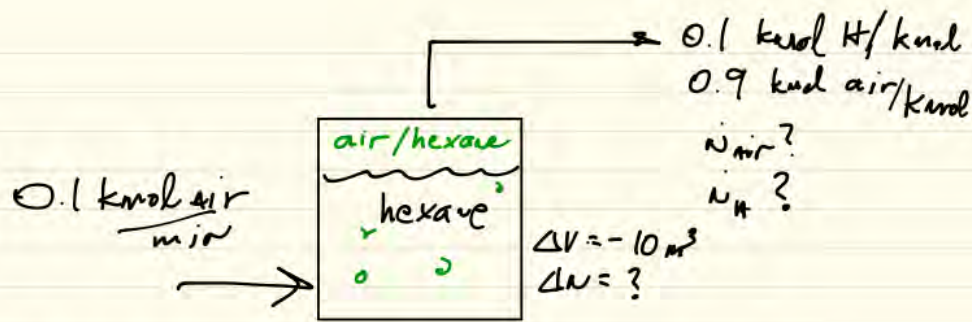
air entrains hexane, carries some out

time to vaporize $10.0 \, m^3$ / hexane?

hexane balance

$$\text{output} = \cancel{\text{input}}^0 + \cancel{\text{gen}}^0 - \cancel{\text{con}}^0 - \text{accum}^{<0}$$

$$\text{output} = -\text{accum}$$

$$\text{accum} = -10 \, m^3 \cdot \rho_H \cdot \frac{1}{MW_H}$$
$$\left(\frac{kg}{m^3}\right) \quad \left(\frac{kmol}{kg}\right)$$

$$= -10 \, m^3 \cdot \left(\frac{659 \, kg}{m^3}\right)\left(\frac{1 \, kmol}{82.6 \, kg}\right) = -76.45 \, kmol_H$$

$$\text{output} = 76.45 \, kmol_H = t \cdot \text{rate}$$
$$(mol) \qquad\qquad \left(\frac{mol}{t}\right)$$

$$\boxed{t = \frac{\text{output}}{\dot{N}_H}}$$

Air balance

$$\text{output} = \text{input} = 0.1 \, kmol/min$$

$$\dot{N}_H = \dot{N}_{air} \cdot \left(\frac{x_H}{x_{air}}\right) = 0.1\left(\frac{0.1}{0.9}\right) = 0.111 \, \frac{kmol_H}{min}$$

$$t = \frac{76.45 \, kmol_H}{0.111 \, kmol_H/min} = \underline{6880 \, min}$$

June 1, 2016

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- Does life always balance? No!

5.4 Multi-unit processes

- Real processes will contain multiple sub-processes

- Can write a balance on any portion we can draw a box around
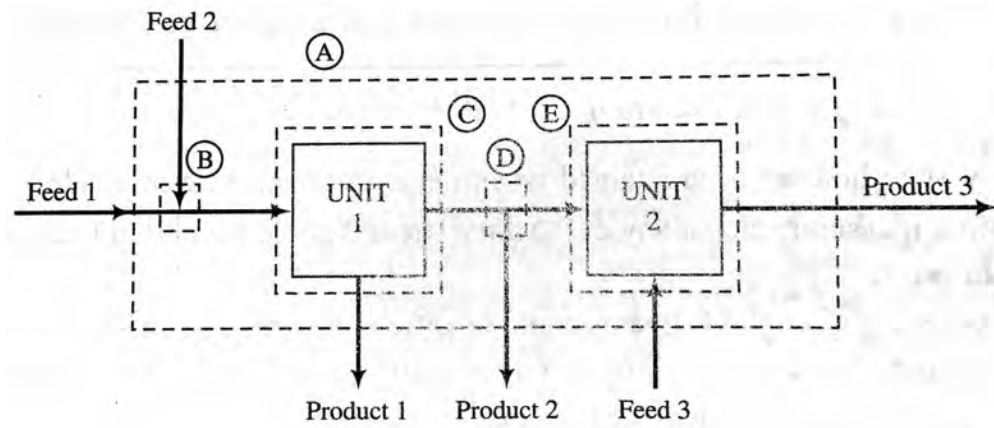
EXAMPLE The flow chart below is for a two step, steady-state process involving components A and B. Find the unknown flow rates.

Two-Unit Process

A labeled flowchart of a continuous steady-state two-unit process is shown below. Each stream contains two components, A and B, in different proportions. Three streams whose flow rates and/or compositions are not known are labeled 1, 2, and 3.
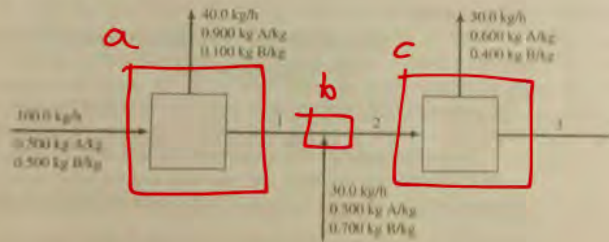
Calculate the unknown flow rates and compositions of streams 1, 2, and 3.

Balance on a

$$\dot{m}_{1A} = 0.5(100) - 0.9(40) = 14 \text{ kg/h}$$

$$\dot{m}_{1B} = 0.5(100) - 0.1(40) = 46 \text{ kg/h}$$

Balance on b

$$\dot{m}_{2A} = 14 \text{ kg/hr} + 0.3(30) = 23 \text{ kg/hr}$$

$$\dot{m}_{2B} = 46 \text{ kg/hr} + 0.7(30) = 67 \text{ kg/hr}$$

Balance on c

$$\dot{m}_{3A} = 23 \text{ kg/hr} - 0.6(30) = 5 \text{ kg/hr}$$

$$\dot{m}_{3B} = 67 \text{ kg/hr} - 0.4(30) = 55 \text{ kg/hr}$$

EXAMPLE Multi-stage extraction-distillation.

A mixture containing 50.0 wt% acetone (A) and 50.0 wt% water (W) is to be separated into two streams—one rich in acetone and the other in water. The separation process consists of extraction of the acetone from the water into methyl isobutyl ketone (MIBK or M), which has a much higher affinity for acetone than it does for water. The process is shown schematically below.
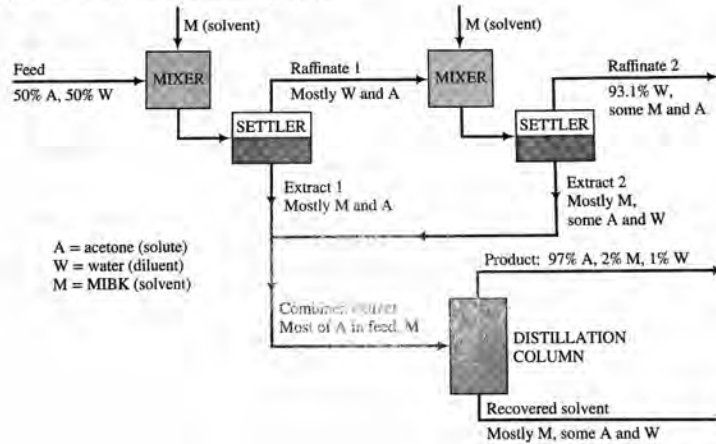
[7] For example, a solvent extraction process was a key development in the large-scale production of penicillin in the 1940s. (R. I. Mateles, Ed., *Penicillin: A Paradigm for Biotechnology*, Candida Corporation, Chicago, IL, 1998.)
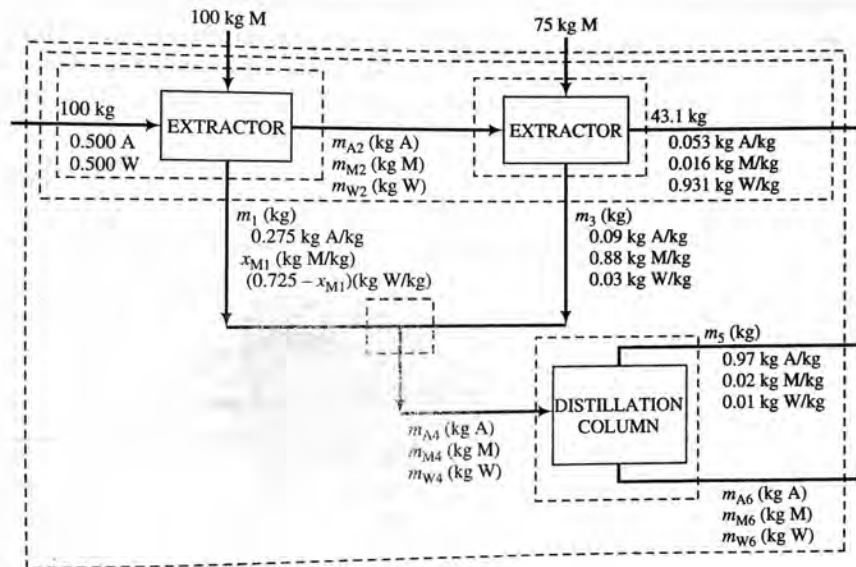
- Balance extractor pair

  - Three unknowns

  - Total mass + A balance: $\dot{m}_1 = 145, \dot{m}_2 = 86.8$

       – M balance: $x_{M1} = 0.675$

- Balance extractors individually

- Balance mixing point

       – $\dot{m}_{A4} = 86.8, \dot{m}_{M4} = 174, \dot{m}_{W4} = 9.9$

- Balance column: 4 unknowns, 3 balances $\rightarrow$ under-determined

5.5 Recycle and bypass

- *Recycle* and *bypass* are ways to control the composition in a process

- *Recycle* a way to recover and re-feed unused reactants

- Changes effective residence time in the process
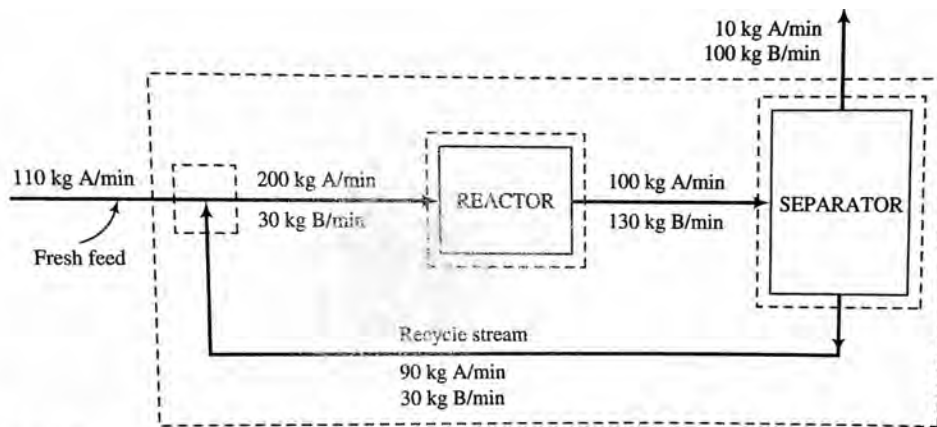
FIGURE 4.5-1 Flowchart of a reactor with separation and recycle of unconsumed reactant.

EXAMPLE Fresh, humid air, 4% H_2O, is to be cooled and dehumidified to 1.7%. Some of the dehumidified air leaving the air conditioner is recycled into the inlet air. The blended stream is 2.30% H_2O. Water leaves as pure water. Find all flow rates.
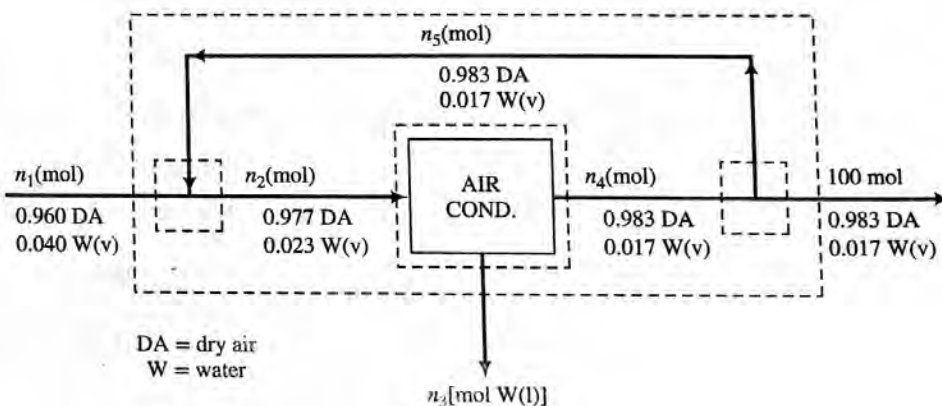
- Mass or moles?

- Basis? 100 mol/s outlet.

- Overall balance

    - $\dot{n}_1 = 102.4, \quad \dot{n}_3 = 2.4$

- Mixing point balance

    - $\dot{n}_2 = 392.5, \quad \dot{n}_5 = 290$

- Split point balance

    - $\dot{n}_4 = 100 + \dot{n}_5 = 390$

6 Material balances on reactive systems

6.1 Revision idea

- First introduce balance using single reaction and molecular balance

- Then introduce extent

- Then multiple reactions...

6.2 Stoichiometry

- Chemical reaction: a transformation between between chemical species

    - Conserves *mass* and *atom numbers*
    - Isomerization (e.g. *cis- trans*) A $\rightleftharpoons$ B,
    - Condensation (e.g. add H_2O to double bond) $A^+B \rightleftharpoons C$
    - Combustion (e.g. methane) $A + 2B \longrightarrow C + 2D$

- Each has a distinct *stoichiometry* that guarantees atom and mass conservation

- Tells us *ratio* consumption/generation

EXAMPLE Balance SCR reaction. Engine emits 0.02 mol NO/mile. How many grams NH_3 needed/mile?

$4NH_3 + 4NO + O_2 \longrightarrow 4N_2 + 6H_2O$
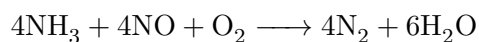
- Reaction short-hand: species $j \rightarrow A_j$

- Stoichiometric coefficient:

$$\nu_j = \begin{cases} < 0 & \text{reactant} \\ > 0 & \text{product} \end{cases}$$

$$\sum_j \nu_j A_j = 0$$

- Can scale by arbitrary constant c

6.3 Reaction progress

- Stoichiometry tells us how moles of reactants/products vary along course of reaction

EXAMPLE A $\longrightarrow$ B. Total moles conserved:

$$\begin{aligned} n_{tot} &= n_{A0} + n_{B0} = n_A + n_B \\ n_B &= n_{tot} - n_A \end{aligned}$$

Plot n_B vs. n_A.

- Illustrate "ICE" procedure for SCR reaction

- Reaction advancement/extent ξ:

$$n_j = n_{j0} + \nu_j \xi$$

- we define ξ to be extensive, units of "moles" or "moles/time"

EXAMPLE Stoichiometric SCR mixture. Plot moles of each species as a function of advancement.

```python
import matplotlib.pyplot as plt
import numpy as np

nu = np.array([[-4, -6, -3, 5, 6]])
n0 = np.array([[4, 6, 3, 0, 0]])

xi = np.array([np.linspace(0,1)])

n = np.transpose(n0) + np.dot(np.transpose(nu),xi)

for i in range(5):
    plt.plot(xi[0],n[i])

plt.savefig('./figs/advancement1.png')
```
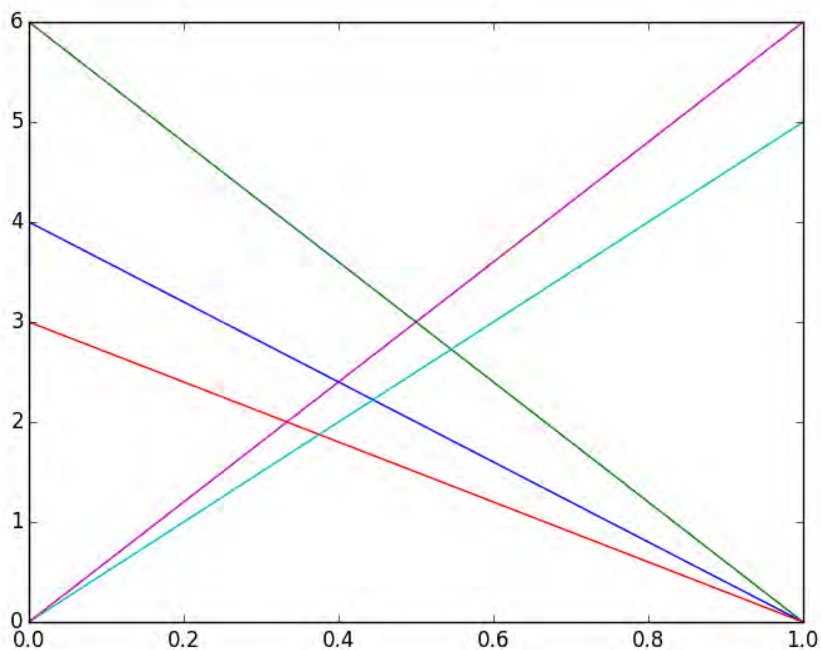

- Must have $n_j \geq 0$ for all j, or $\xi \leq -\frac{n_{j0}}{\nu_j}$:

$$\text{Forward: } \xi_{max} = \min_{\text{reactants}} \left(-\frac{n_{j0}}{\nu_j} \right)$$

$$\text{Reverse: } \xi_{min} = \max_{\text{products}} \left(-\frac{n_{j0}}{\nu_j} \right)$$

$$\xi_{min} \leq \xi \leq \xi_{max}$$

Air oxidation of NH_3.

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$
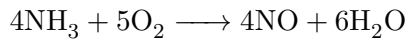
0.1 g/s NH_3 and 0.95 g/s air flow into a reactor. What is limiting reagent? How much NH_3 at completion?

```
1   MWNH3 = 17; MWO2 = 32; MWN2 = 28;
2   MWair = 0.79 * MWN2 + 0.21 * MWO2
3
4   mNH30 = 0.1; mair0 = 0.95
5   nNH30 = mNH30 / MWNH3
6   nO20 = (mair0 / MWair) * 0.21
7
8   print('ndot NH3 = {0:6.4f}  ndot O2= {1:6.4f} mol/s\n'.format(nNH30,nO20))
9
10  nuNH3 = -4.0; nuO2 = -5.0;
11
12  xiNH3 = -nNH30/nuNH3; xiO2 = -nO20/nuO2
13
14  print('ndot/nu NH3 = {0:7.5f}  ndot/nu O2 = {1:7.5f}\n'.format(xiNH3,xiO2))
15
16  print('O2 limiting\n')
17
18  xilim = xiO2
19
20  nNH3 = nNH30 + nuNH3 * xilim; nO2 = nO20 + nuO2 *xilim
21
22  print('ndot NH3 = {0:7.5f}  ndotO2 = {1:7.5f}\n'.format(nNH3,nO2))
23
24  fNH3 = 100*(nNH30 - nNH3)/nNH30
25  print('Fraction NH3 consumed = {0:4.2f}%'.format(fNH3))
```

```
ndot NH3 = 0.0059  ndot O2= 0.0069 mol/s

ndot/nu NH3 = 0.00147  ndot/nu O2 = 0.00138

O2 limiting

ndot NH3 = 0.00035  ndotO2 = 0.00000

Fraction NH3 consumed = 94.08%
```

- *conversion* often used to measure consumption of a species:

$$X_j = \frac{n_{j0} - n_j}{n_{j0}} = -\frac{\nu_j \xi}{n_{j0}}$$

- conventional to define "the" conversion in terms of limiting reagent:

$$X = 1 - \frac{n_{\lim}}{n_{\lim,0}} = -\frac{\nu_j \xi}{n_{j0}}$$

$$\xi = -X\frac{n_{\lim,0}}{\nu_{\lim}}$$

- X is unitless and (for forward reaction) $0 \leq X \leq 1$

- all n_j can be written in terms of X:

$$n_j = n_{j0} - X n_{\text{lim},0} * \frac{\nu_j}{\nu_{\text{lim}}}$$

EXAMPLE NH_3 oxidation goes to 50% completion. What is composition of exit stream?

```python
import numpy as np
import matplotlib.pyplot as plt

species = ('NH3', 'N2', 'O2', 'NO', 'H2O')
nu = np.array([[-4, 0, -6, 5, 6]])

MWNH3 = 17; MWO2 = 32; MWN2 = 28;
MWair = 0.79 * MWN2 + 0.21 * MWO2

mNH30 = 0.1; mair0 = 0.95
nNH30 = mNH30 / MWNH3
nO20 = (mair0 / MWair) * 0.21
nN20 = (mair0 / MWair) * 0.79

n0 = np.array([[nNH30, nN20, nO20, 0, 0]])

X = 0.5

n = n0 - (nu/nu[0,2]) * n0[0,2] * X

print(species)
print(n,' mol/s')

X = np.array([np.linspace(0,1)])

n = np.transpose(n0) - np.dot(n0[0,2]*np.transpose(nu/nu[0,2]),X)

ntot= 0

for i in range(5):
    plt.plot(X[0],n[i],label=species[i])
    ntot =ntot + n[i]
legend = plt.legend()

plt.plot(X[0],ntot)
plt.xlabel('Conversion')
plt.ylabel('flow rate (mol/s)')

plt.savefig('./figs/conversion1.png')
```

```
('NH3', 'N2', 'O2', 'NO', 'H2O')
[[ 0.00357653  0.02602288  0.00345874  0.00288228  0.00345874]]  mol/s
```
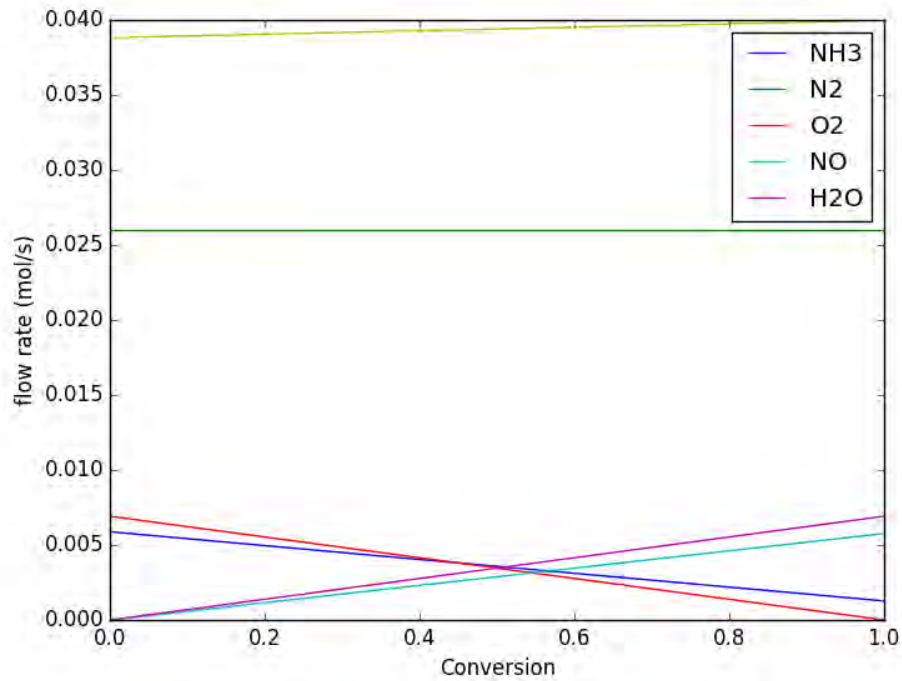
6.4 Multiple reactions

- NH_3 oxidation and SCR together, for example, are parallel reactions

- competition between the two

- each species has a stoichiometric coefficient in each parallel reaction

$$4NO + 4NH_3 + O_2 \longrightarrow 4N_2 + 6H_2O$$
$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$
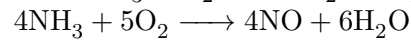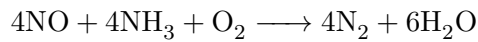
$$-4NO - 4NH_3 - 1O_2 + 4N_2 + 6H_2O = 0$$
$$4NO - 4NH_3 - 5O_2 + 0N_2 + 6H_2O = 0$$

- reaction expression:

$$\begin{pmatrix} -4 & -4 & -1 & 4 & 6 \\ 4 & -4 & -5 & 0 & 6 \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \\ A_3 \\ A_4 \\ A_5 \end{pmatrix} = 0 \tag{5}$$

- In general $\sum_j \nu_{ij} A_j = 0$

- each parallel reaction has its own advancement ξ_i (i for reactions, j for species)

$$n_j = n_{j0} + \sum_i \nu_{ij} \xi_i$$

- *yield* defined as amount (molar) of desired product over maximum possible amount of desired product

- *selectivity* (often) defined as amount of desired product over amount of undesired. Be careful with this one.

Selectivity and yield Ethane cracking. Feed contains 85.0% (mol/mol) ethane, balance inerts. 50.1% of ethane is converted, and ethylene yield is 47.1%. Molar composition of gases and selectivity to ethylene?

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$
$$C_2H_6 + H_2 \longrightarrow 2CH_4$$
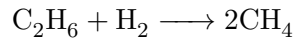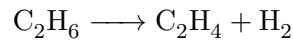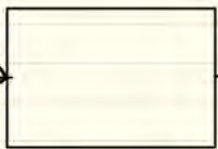
Safer to work in molar flows

$C_2H_6 : a \quad C_2H_4 : e \quad CH_4 : m \quad H_2 : H \quad Inert : I$

basis
$\dot{N}_0 = 100 \text{ mol/s}$

$\dot{N}_{A0} = 85$

$\dot{N}_{I0} = 15$

$\dot{N}_A$
$\dot{N}_e$
$\dot{N}_m$
$\dot{N}_m$
$\dot{N}_I$

inert: $\dot{N}_I = \dot{N}_{0I} = 15 \text{ mol/s}$ ✓

ethane: $\dot{N}_A = \dot{N}_{0A} - \xi_1 - \xi_2$

ethylene: $\dot{N}_e = \xi_1$

ethylene yield: $\dot{N}_e = 0.471 \,(85.0)$ ← max possible ethylene
$= 40.0$ ✓
$= \xi_1$

ethane conversion:
$\dot{N}_a = (1 - 0.501)\dot{N}_{a0}$ ✓
$= 42.4 \text{ mol/s}$

$\xi_2 \doteq 2.6$ $\quad = \dot{N}_{A0} - \xi_1 - \xi_2$

methane: $\dot{N}_m = 2\xi_2 = 5.2 \text{ mol/s}$

hydrogen: $\dot{N}_H = \xi_1 - \xi_2 = 37.4 \text{ mol/s}$

$$N_{tot} = \sum_j \nu_j = \sum_\upsilon \omega_{j0} + \sum_{ij} \nu_{ij} \xi_i$$

$$= N_{I0} + N_{A0} + \xi_1$$

$$= 140 \, mol/s$$

$$y_j = {}^{N_j}\!/_{N_{tot}} \qquad y_e = \frac{40}{140} = 0.286 \qquad y_I = 10.7\%$$

$$y_m = \frac{5.2}{140} = 0.037 \qquad \begin{array}{l} y_A = 0.303 \\ y_H = 0.267 \end{array}$$

$$\underline{selectivity}: \quad \frac{\dot{N}_e}{\dot{N}_m} = \frac{40.0}{5.2} = 7.7$$

- DOF analysis: 5 flow rates + 2 reactions - 5 species - 2 constraints = 0 DOFs

- Example of a balance on a reactive system

6.5 Reactive balances

- General balance expression:

> output = input + generation - consumption - accumulation

- can write balances on *molecular species*:

$$\dot{n}_A = \dot{n}_{A0} - \dot{n}_e - \frac{1}{2}\dot{n}_m$$

- for more than one reaction, this gets messy

- extent of reaction

  - each *independent* extent becomes an additional unknown (linearly independent extents)
  - each species balance becomes an equation
  - species balances must include *generation* and *consumption*

$$\dot{n}_A = \dot{n}_{A0} + \sum_i \nu_{iA}\xi_i$$

- atomic species

  - one equation for each reactive *atomic species*

- No generation or consumption; *input = output*

C balance: $2n_{A0}^{\cdot} = 2n_A^{\cdot} 2n_e^{\cdot} + n_m^{\cdot}$
H balance: $4\dot{n}_{A0} = 6\dot{n}_A + 4\dot{n}_e + 4\dot{n}_m + 2\dot{n}_H$

- one equation for each non-reactive species

Reactive balances Methane is burned in air to make CO and CO_2:

$$CH_4 + \tfrac{3}{2}O_2 \longrightarrow CO + 2H_2O$$
$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$
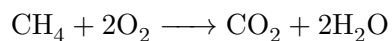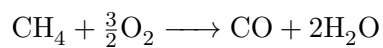
Feed contains 7.8%(mol/mol) CH_4 and balance air (19.4% O_2, 72.8% N_2). Methane conversion is 90.0% and exit contains 8 mol CO_2/CO. Calculate composition of exit stream.

100 mol/s basis

$\dot{N}_{MO} = 7.8$
$\dot{N}_{N_2O} = 72.8$
$\dot{N}_{O_2O} = 19.4$
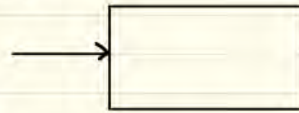
output: $\dot{N}_M$, $\dot{N}_{O_2}$, $\dot{N}_{N_2}$, $\dot{N}_{CO}$, $\dot{N}_{CO_2}$, $\dot{N}_{H_2O}$

$\dfrac{\dot{N}_{CO_2}}{\dot{N}_{CO}} = 8$ $\dot{N}_M = 0.10\,\dot{N}_{MO}$

Non-reactive: in = out

$$\dot{N}_{N_2} = \dot{N}_{N_2O} = 72.8 \text{ mol/s}$$

Atomic: in = out

C: $\quad \dot{N}_{MO} = \dot{N}_M + \dot{N}_{CO} + \dot{N}_{CO_2}$

H: $\quad 4\dot{N}_{MO} = 4\dot{N}_M + 2\dot{N}_{H_2O}$

O: $\quad 2\dot{N}_{O_2O} = 2\dot{N}_{O_2} + \dot{N}_{CO} + 2\dot{N}_{CO_2} + \dot{N}_{H_2O}$

C + 2 knowns $\rightarrow$ $\dot{N}_{CO} = 0.78$ $\dot{N}_{CO_2} = 6.24$

H $\rightarrow$ $\dot{N}_{H_2O} = 2(0.9)\cdot\dot{N}_{MO} = 14.0$

O $\rightarrow$ $\dot{N}_{O_2} = 5.75$

Advancement out = in + gen − consump

$\dot{N}_M = \dot{N}_{MO} - \xi_1 - \xi_2$

$\dot{N}_{CO} = \xi_1$ $\dot{N}_{CO_2} = \xi_2$ $\longrightarrow$ $\dfrac{\xi_2}{\xi_1} = 8$

$\xi_1 = \dfrac{\dot{N}_{MO} - \dot{N}_M}{9} = 0.087$ $\xi_2 = 0.693$

6.6   Reactive balances on multi-unit processes

- Can do extent or atomic balances on any part of a process

Dehydrogenation of Propane

Propane can be dehydrogenated to form propylene in a catalytic reactor:

$$C_3H_8 \rightarrow C_3H_6 + H_2$$
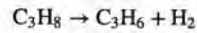
A process is to be designed for a 95% overall conversion of propane. The reaction products are separated into two streams: the first, which contains H_2, C_3H_6, and 0.555% of the propane that leaves the reactor, is taken off as product; the second stream, which contains the balance of the unreacted propane and propylene in an amount equal to 5% of that in the first stream, is recycled to the reactor. Calculate the composition of the product, the ratio (moles recycled)/(mole fresh feed), and the single-pass conversion.

Basis: 100 mol Fresh Feed

Fresh feed
100 mol C_3H_8

REACTOR

n_1(mol C_3H_8)
n_2(mol C_3H_6)

n_3(mol C_3H_8)
n_4(mol C_3H_6)
n_5(mol H_2)

SEPARATOR

Product
n_6(mol C_3H_8) (0.555% of n_3)
n_7(mol C_3H_6)
n_8(mol H_2)

Recycle
n_9(mol C_3H_8)
n_{10}(mol C_3H_6) (5% of n_7)
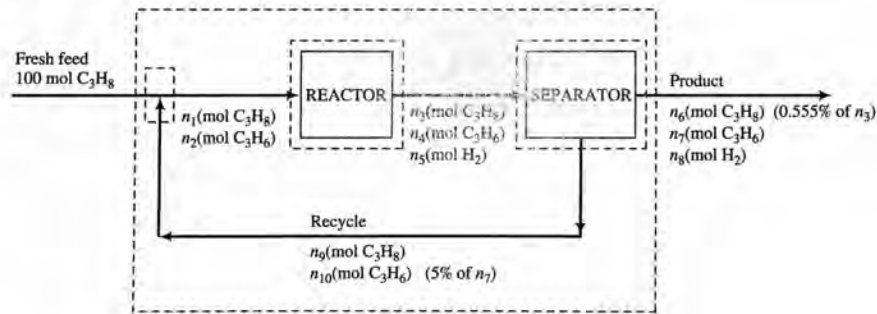
Overall

3 unknowns − 2 atomic − [95% conv.] ✓

$\dot{N}_6 = 0.05 \, (100 \, mol/s) = 5 \, mol/s$

C: $3(100) = 3\dot{N}_6 + 3\dot{N}_7$ $\dot{N}_7 = 95 \, mol/s$

H: $8(100) = 8\dot{N}_6 + 6\dot{N}_7 + 2\dot{N}_8$ $\dot{N}_8 = 95 \, mol/s$

$y_i = \dfrac{\dot{N}_c}{\dot{N}_{tot}}$ 2.6   48.7   48.7
                          ∧   ∧ H_2

Separator (not reactive)

5 unknowns − 3 species − 2 constraints ✓

$\dot{N}_5 = \dot{N}_8 = 95 \, mol/s$

$\dot{N}_6 = (0.555 \times 10^{-2}) \, \dot{N}_5$ $\dot{N}_3 = 901 \, mol/s$

$\dot{N}_{10} = 0.05 \, \dot{N}_7$ $\dot{N}_{10} = 4.75 \, mol/s$

∧: $\dot{N}_3 = \dot{N}_6 + \dot{N}_9$ $\dot{N}_9 = 896 \, mol/s$

⋀: $\dot{N}_4 = \dot{N}_7 + \dot{N}_{10}$ $\dot{N}_4 = 100 \, mol/s$

Mixing point: (not reactive)

2 unknowns − 2 species

$\dot{N}_2 = \dot{N}_{10} = 4.75 \, mol/s$

$\dot{N}_1 = \dot{N}_9 + 100 = 996 \, mol/s$

Recycle ratio: $\dfrac{\dot{N}_9 + \dot{N}_{10}}{100} = 9.00$ [1 pass conversion: $\dfrac{\dot{N}_1 - \dot{N}_3}{\dot{N}_1} = 9.6\%$]

- Compare single-pass and overall conversion

- Separation and recycle allows reactor to run at lower conversion at cost of separation unit and larger flows through reactor

6.7   Purge

- Recycle example above works because system is continuously fed pure reactant

- If system fed unreactive species, unless it is removed at same rate it enters, it will build up and eventually kill the process

- Purge stream used to bleed off that species

Purge Example CO_2 to methanol. Single pass 60.0% H_2 conversion.

Recycle and Purge in the Synthesis of Methanol

Methanol (also known as methyl alcohol and wood alcohol) is used as a raw material in the manufacture of formaldehyde, acetic acid, methyl tertiary-butyl ether (MTBE), and a number of other important chemicals. It also has many other uses, including as a solvent, a disinfectant, and a clean-burning fuel. One of the ways it can be synthesized is by reacting carbon dioxide and hydrogen:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$
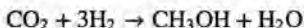
The fresh feed to a methanol synthesis process contains hydrogen, carbon dioxide, and 0.400 mole% inerts (I). The reactor effluent passes to a condenser that removes essentially all of the methanol and water formed and none of the reactants or inerts. The latter substances are recycled to the reactor. To avoid buildup of the inerts in the system, a purge stream is withdrawn from the recycle.

The feed to the *reactor* (not the fresh feed to the process) contains 28.0 mole% CO_2, 70.0 mole% H_2, and 2.00 mole% inerts. The single-pass conversion of hydrogen is 60.0%. Calculate the molar flow rates and molar compositions of the fresh feed, the total feed to the reactor, the recycle stream, and the purge stream for a methanol production rate of 155 kmol CH_3OH/h.

(a) Choose a basis of calculation of 100 mol of the feed to the reactor (a convenient basis since you know the composition of this stream), and draw and label a flowchart.

(b) Perform a degree-of-freedom analysis for the system. As a suggested sequence, determine the difference between the number of equations and number of variables for each of the following: overall system, recycle-fresh feed mixing point, reactor, condenser, and recycle-purge splitting point. Verify that there are zero degrees of freedom for the entire process and identify an efficient procedure for carrying out the calculations (including scaling up the calculated process variables to the desired methanol production rate).

(c) Write the system equations and use Excel's Solver to solve them for all of the variables.

(a) Basis: 100 mol Combined Feed to the Reactor
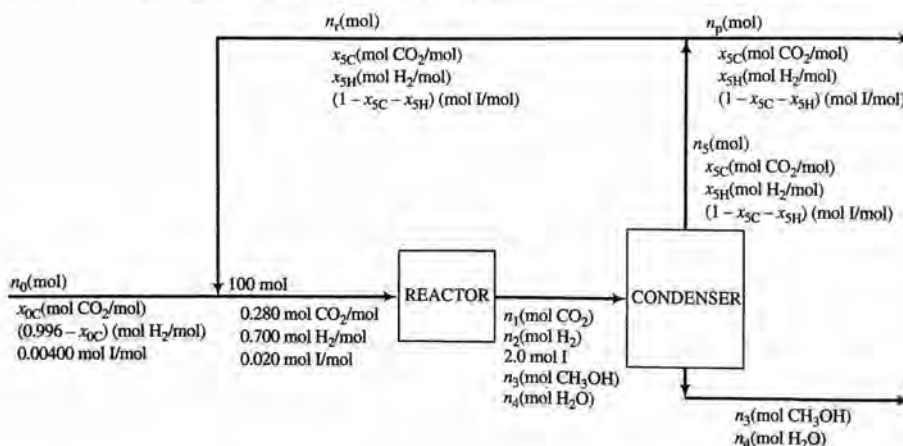
- Reactor balance, 4 DOFs - 3 balances - 1 conversion:

CO_2	H_2	CH_3OH	H_2O
14.0	28.0	14.0	14.0

- Condenser balance, simple split, BUT, inert concentration goes up!!!!

	CO$_2$	H$_2$	Inert
14.0	28.0	2	

- mixing point, non-reactive, 4 DOFs - 3 balances - 1 total

n$_0$	n$_r$
61.4	38.6

- purge split $n_5 = n_r + n_p$

n$_p$
5.4

6.8 Combustion in air

7 Properties of single-phase systems

- Can't design a reactor around masses and moles; have to know sizes, volumes

- $\rho = \rho(T, P, x_i)$, example of what is called an equation of state

- Material balances often require we know the physical properties (e.g, densities, thermal expansion coefficient, . . .) of pure substance and of mixtures

- Where to get this information?

  - Look it up (Perry's handbook, literature)
  - Measure it (laboratory)
  - Estimate from physical property models
  - Compute from molecular models

7.1 Liquid and solid densities

- Liquids and solids generally incompressible and small coefficients of thermal expansion

- Pure densities from measurement or estimate

- Mixture densities depend. . .

- Ideal solution (MeOH and H_2O) has additive molar volumes:

$$v \text{ (l/mol)} = \sum_i x_i v_i$$

- or equivalently additive inverse densities (ω_i are mass fractions):

$$\frac{1}{\bar{\rho}} = \sum_i^n \frac{\omega_i}{\rho_i}$$

- Many solutions **not** ideal, e.g., ethanol/methyl formate positive deviation; methanol/methyl formate negative deviation

- Sometimes other empirical relations are observed

$$\bar{\rho} = \sum_i^n x_i \rho_i$$

- See Perry's Handbook for data

7.2 Ideal gas

es

- Gas volumes are much more sensitive to temperature and pressure

- Relationship captured in an "equation of state"

- Ideal gas equation of state very familiar

$$PV = nRT \text{ or } Pv = RT \text{ or } v = \frac{RT}{P}$$

- R = gas constant is a fundamental physical constant of nature, closely related to concept of temperature

  R   8.314472 J / (K mol)   0.082057 atm l / (K mol)   1.3806504e-23 J / K

- v replaced by $\dot{v}$ in flow context

Ideal gas Flow Butane at $360\,°C$ and 3.0 atm absolute pressure flows into a reactor at $1100\,kg\,h^{-1}$. Volumetric flow rate?

```
1   R = 0.082057 # l atm/mol K
2   MW = (4*12.00 + 10 * 1.008)/1000 # kg/mol
3
4   T = 360 + 273.15 # K
5   P = 3.00 # atm
6   mdot = 1100 # kg/hr
7
8   vdot = (mdot/MW) * (R * T / P)
9   print('{0:6.2f} l/hr'.format(vdot))
```

327994.88 l/hr

Ideal gas ratios $10\,ft^3$ of air at 70 F and 1.00 atm is heated to 610 F and compressed to 2.50 atm. Final volume?

```
1   V0 = 10.
2   T0 = 70 + 459.67 # R
3   T = 610 + 459.67
4   P0 = 1. # atm
5   P = 2.50 # atm
6
7   V = V0*(P0/P)*(T/T0)
8   print('{0:6.2f} ft3'.format(V))
```

8.08 ft3

- v is only a function of T and P, suggests "standard" volume at "standard" conditions, typically 273 K and 1 atm for SI/cgs, 32 F and 1 atm for English.

$$v_s = 22.415 \text{ L/mol} = 0.022415 \text{ m}^3/\text{mol} = 359.05 \text{ ft}^3/\text{lb-mol}$$

Standard gas The flow rate of methane at 285 F and 1.30 atm absolute is reported to be 3.95×10^5 SCFH. Molar flow rate? Volumetric flow rate?

```
1    VSCFH = 3.95e5 # std ft3/hr
2    PS = 1.0 #
3    P = 1.30 #
4    TS = 459.67 + 32 # R
5    T = TS + 285.
6
7    Vs = 359.05 # std ft3/lb-mol
8
9    ndot = VSCFH /Vs  # lb-mol/hr
10
11   V = VSCFH * ( PS/P) * (T/TS)
12
13   print('{0:6.2e} mol/hr   {1:6.2e} ft^3/hr'.format(ndot,V))
```

1.10e+03 mol/hr   4.80e+05 ft^3/hr

7.3   Ideal gas mixture

- ideal mixture $\rightarrow$ volumes are additive:

$$V(N, T, P) = V_1(N_1, T, P) + V_2(N_2, T, P)$$

- Called "Amagat's Law," applies $\approx$ both ideal and non-ideal gases

- individual components ideal gas $\rightarrow$ mixture is ideal gas:

$$
\begin{aligned}
V(N, T, P) &= \frac{N_1 RT}{P} + \frac{N_2 RT}{P} \\
&= \frac{(N_1 + N_2)RT}{P} \\
&= \frac{NRT}{P}
\end{aligned}
$$

- "Partial pressures" additive:

$$
\begin{aligned}
P &= \frac{N_1 RT}{V} + \frac{N_2 RT}{V} \\
&= P_1 + P_2
\end{aligned}
$$

- Partial pressure proportional to mole fraction:

$$\frac{P_1}{P} = \frac{N_1 RT/V}{NRT/V} = y_1$$

- Volume fraction proportional to mole fraction:

$$\frac{V_1}{V} = \frac{N_1}{N} = y_1$$

- Use mole fraction and volume fraction and partial pressure interchangeably for ideal gas mixture

---

Partial Pressures Acetone and nitrogen mixed in an evaporator and flowed through a compressor. Liquid acetone enters system at a flow rate of $400\,\mathrm{L\,min^{-1}}$ and exits at a partial pressure (gauge) of 501 mm Hg at $325\,°\mathrm{C}$. Total pressure of exit is 6.2 atm (gauge). What is flow rate and composition of exit? Atmospheric pressure is 763 mm Hg.

Material Balances on an Evaporator-Compressor

Liquid acetone (C_3H_6O) is fed at a rate of 400 L/min into a heated chamber, where it evaporates into a nitrogen stream. The gas leaving the heater is diluted by another nitrogen stream flowing at a measured rate of 419 m³(STP)/min. The combined gases are then compressed to a total pressure $P = 6.3$ atm (gauge) at a temperature of 325°C. The partial pressure of acetone in this stream is $p_A = 501$ mm Hg. Atmospheric pressure is 763 mm Hg.

1. What is the molar composition of the stream leaving the compressor?
2. What is the volumetric flow rate of the nitrogen entering the evaporator if the temperature and pressure of this stream are 27°C and 475 mm Hg gauge?

Basis: Given Feed Rates

Assume ideal-gas behavior. Let $\dot{n}_1, \dot{n}_2, \ldots$ (mol/min) be the molar flow rates of each stream.
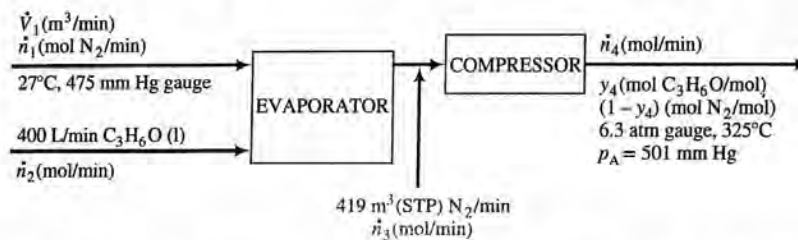
You should be able to examine the flowchart and see exactly how the solution will proceed.

1. Perform a degree-of-freedom analysis for the system and verify that the problem can be solved.
2. Calculate $\dot{n}_2$ (from the given volumetric flow rate and a tabulated density of liquid acetone), $\dot{n}_3$ (from the ideal-gas equation of state), and y_4 ($= p_A/P$).
3. Calculate $\dot{n}_4$ (overall acetone balance), $\dot{n}_1$ (overall mass balance), and $\dot{V}_1$ (ideal-gas equation of state).

Degree-of-Freedom Analysis

$$6 \text{ unknowns } (\dot{V}_1, \dot{n}_1, \dot{n}_2, \dot{n}_3, \dot{n}_4, y_4)$$
$$-1 \text{ specific gravity relationship } (\dot{n}_2)$$
$$-2 \text{ molecular balances (overall, } C_3H_6)$$
$$-1 \text{ ideal-gas equation of state } (\dot{V}_1)$$
$$-1 \text{ partial pressure relationship } (y_4)$$
$$-1 \text{ ideal-gas equation of state } (\dot{n}_3)$$
_____
$$0 \text{ degrees of freedom}$$

Calculate Molar Flow Rate of Acetone

From Table B.1 in Appendix B, the density of liquid acetone is 0.791 g/cm³ (791 g/L), so that

$$\dot{n}_2 = \frac{400 \text{ L}}{\text{min}} \left| \frac{791 \text{ g}}{\text{L}} \right| \frac{1 \text{ mol}}{58.08 \text{ g}} = 5450 \frac{\text{mol } C_3H_6O}{\text{min}}$$

```
1   rho_acetone = 0.791 # g/cm3
2   vdot_acetone = 400. # l/min
3   MW_acetone = 58.08 # g/mol
4
5   ndot_acetone = vdot_acetone * 1000. * rho_acetone / MW_acetone
6
```

```
7   print('acetone = {0:6.0f} mol/min'.format(ndot_acetone))
8
9   P_atm = 763.
10  P_exit = 6.2 * 760. + P_atm   # mm Hg
11  P_acetone = 501. + P_atm # mm Hg
12  P_N2 = P_exit - P_acetone
13  y_N2 = P_N2/P_exit; y_acetone = P_acetone/P_exit
14
15  print('acetone = {0:5.3f}  N2 = {1:5.3f} mol/mol'.format(y_acetone,y_N2))
16
17  n_exit = ndot_acetone * (1 + y_N2/y_acetone) # mol/min
18
19  T_exit = 325 + 273.15   # K
20
21  R = 62.36 # L mm Hg/mol K
22
23  V_exit = n_exit * R * T_exit /P_exit
24
25  print('exit {0:6.1f} mol/min  {1:6.1f} l/min'.format(n_exit,V_exit))
```

```
acetone =    5448 mol/min
acetone = 0.231  N2 = 0.769 mol/mol
exit 23596.5 mol/min  160760.4 l/min
```

7.4   Real equations of state

7.4.1   Ideal gas

- No condensation

```
1   import numpy as np
2   import matplotlib.pyplot as plt
3
4   import numpy as np
5   import matplotlib.pyplot as plt
6
7   R = 0.0821 # l atm/mol K
8   v = np.logspace(-0.2,1)
9
10  for T in np.arange(100.,1000,100):
11      P = R * T *(1/v)
12      plt.plot(v,P,label=T)
13
14  legend = plt.legend()
15
16  plt.xlabel('Volume (L/mol)')
17  plt.ylabel('Pressure (atm)')
18
19  plt.savefig('./figs/idealgas.png')
```
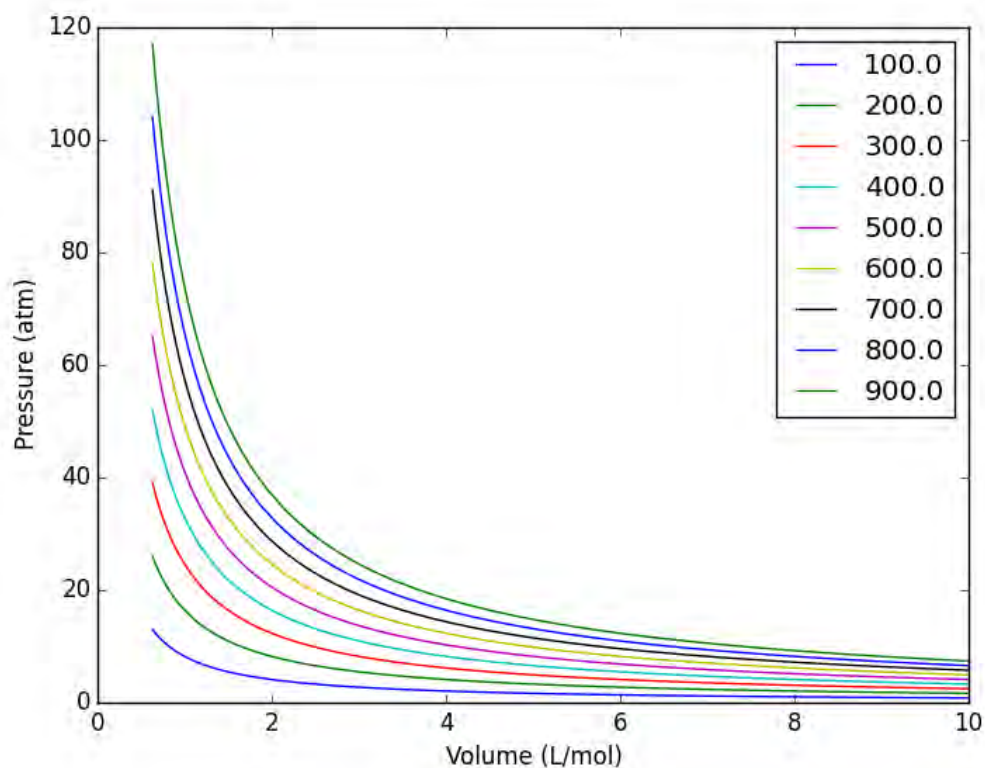
7.4.2 van der Waals model

- molecules have volume: $v \rightarrow v - b$

- molecules attract: $P \rightarrow P - a/v^2$

$$P_{\text{vdW}} = \frac{RT}{v - b} - \frac{a}{v^2}$$

- "cubic" equation of state:

$$v^3 - \left(b + \frac{RT}{P}\right)v^2 + \frac{a}{P}v - \frac{ab}{P}$$

- b has units of volume/mole

- a has units of pressure * (volume/mol)^2 = energy * volume/mol

	a ((L/mol)2 bar	b (L/mol)
H_2	0.2476	0.02661
N_2	1.370	0.0387
CH_4	2.283	0.04278
CO_2	3.640	0.04267

```python
import numpy as np
import matplotlib.pyplot as plt

R = 0.0821 # l atm/mol K

a = 3.640; b = 0.04267;

vc = 3 * b; Tc = (8./9.)*a /(R * vc); Pc = (R * Tc)/(vc-b) - a/(vc*vc);

vr = np.logspace(-0.5,1.)

plt.figure(1)
for Tr in np.arange(0.87,1.3,0.13):
    Pr = 8 * Tr/(3 * vr -1) - 3 *(1/vr) *(1/vr)
    plt.plot(vr*vc,Pr*Pc,label=Tr*Tc)

plt.title('CO2 van der Waals isotherms')
plt.ylim([.1*Pc,4*Pc])
plt.xlim([.3*vc,6*vc])
plt.xlabel('Volume (l/mol)')
plt.ylabel('Pressure (atm)')
legend=plt.legend()

plt.savefig('./figs/vdWgas.png')

plt.figure(2)
for Tr in np.arange(0.87,1.3,0.13):
    Pr = 8 * Tr/(3 * vr -1) - 3 *(1/vr) *(1/vr)
    plt.loglog(vr*vc,Pr*Pc,label=Tr*Tc,basex=10)

legend = plt.legend()

plt.ylim([.1*Pc,100*Pc])
plt.xlim([.3*vc,10*vc])
plt.xlabel('Log volume (l/mol)')
plt.ylabel('Log pressure (atm)')
plt.title('CO2 van der Waals isotherms')

plt.savefig('./figs/logvdWgas.png')
```

CO2 van der Waals isotherms

CO2 van der Waals isotherms
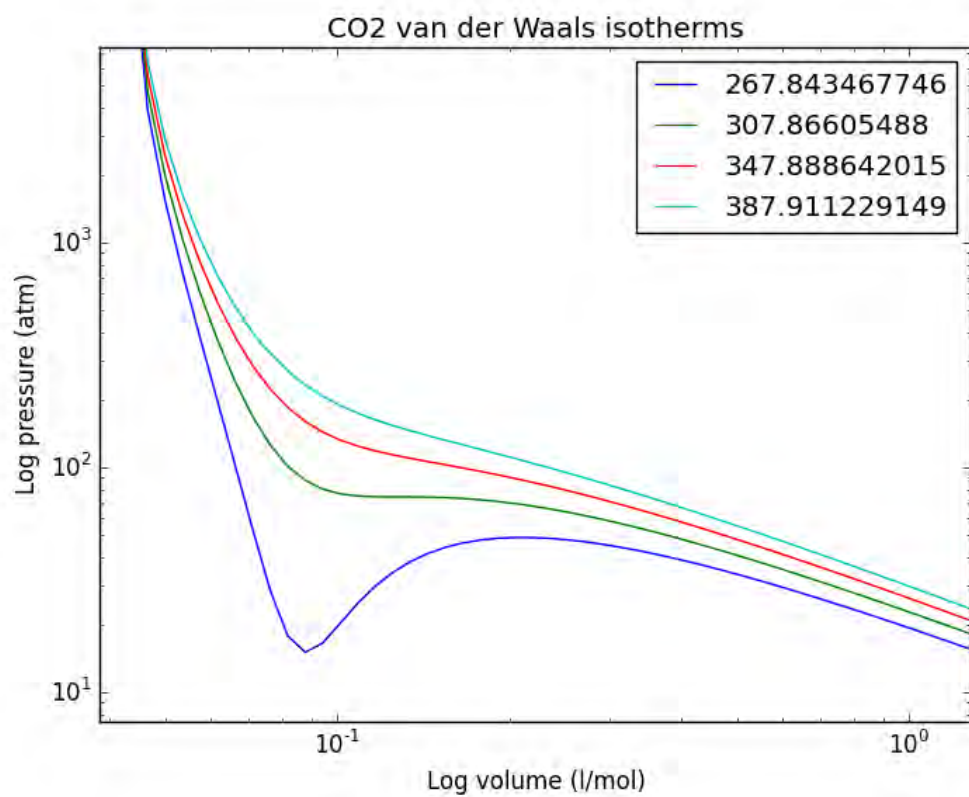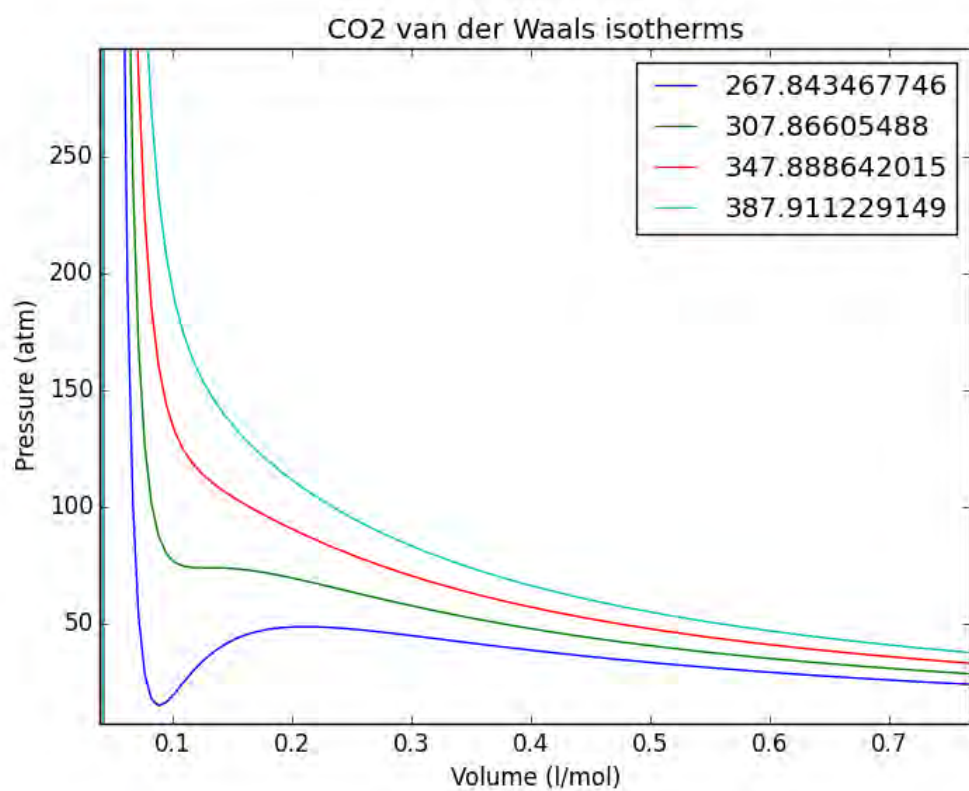
- At higher temperature, pressure and volume vary approximately inversely (gas)

- At lower temperature, follow isotherm, reach region where compressing causes P to go *down*, unphysical,

  - form two phases, dense (liquid) and dilute (vapor)
  - middle intersection point unphysical
  - One pressure and temperature at which two phases coexist (same chemical potential)
  - Called "saturation pressure," $P_{sat}(T)$
  - Given volumes, easy to solve for P_{sat}, other way not so easy ($\mu_v = \mu_l$)

- Transition point between the two regions, called the "critical point"

- $T > T_c$, $P > P_c$ called "supercritical"

- At critical point, density of liquid and vapor are the same

- As move below the critical point, the densities/volumes move apart

- Critical constants related to a and b:

$$b = v_c/3 \qquad a = \frac{9}{8}RT_c v_c$$

- common to refer to the "reduced" temperature, pressure, volume, unitless, scaled to the critical values. As we see below, many species behave the same in reduced variables

$$T_r = T/T_c \quad P_r = P/P_c \quad v_r = v/v_c$$

7.4.3   Other cubic equations of state

- vdW model qualitatively and theoretically important, practically not so accurate

- more elaborate equations necessary to model real fluids more reliably

- *all* are approximations to reality

- Soave-Redlich-Kwong (SRK) one common example (Peng-Robinson another)

$$P_{\text{SRK}} = \frac{RT}{v - b} - \frac{\alpha(T)a}{v(v + b)}$$

- still cubic in v, so same qualitative form, but more parameters to fit

$$
\begin{aligned}
a &= 0.42747\frac{(RT_c)^2}{P_c} \\
b &= 0.08664\frac{RT_c}{P_c} \\
m &= 0.48508 + 1.55171\omega - 0.1561\omega^2 \\
\alpha &= 1 + m(1 - \sqrt{T_r})
\end{aligned}
$$

2

- ω is so-called Pitzer "acentric" factor, compiled along with critical constants

$$\omega = -\log\left(\frac{P_{sat}}{P_c}\right)\Big|_{T_r=0.7} - 1$$

	Pitzer factor	Tc (K)	Pc (atm)
N_2	0.037	126.20	33.5
CH_4	0.011	190.7	45.8
CO_2	0.225	304.2	72.9

```
1   import numpy as np
2   import matplotlib.pyplot as plt
3
4   Tc =304.2; Pc = 72.9; omega = 0.225;
5   R = 0.0821 # l atm/mol K
6
7   a = 0.42747 * (R * Tc)**2 / Pc
8
9   b = 0.08664 * (R * Tc) /Pc
10
11  m = 0.48508 + (1.55171 - 0.1561 * omega )* omega
12
13  v = np.logspace(-1.5,0.)
14
15  plt.figure(1)
16  for T in np.arange(268,390,40):
17      alpha = 1 + m * (1 - (T / Tc)**0.5)
18      Psrk = R * T /(v-b) - alpha * a / (v* (v+b))
19      Pig = R * T /v
20      plt.plot(v,Psrk,label=T)
21      plt.plot(v,Pig,label=T,ls='--')
22
23  plt.title('CO2 SRK isotherms')
24  plt.ylim([0,300])
25  plt.xlim([0.02,0.8])
26  plt.xlabel('Volume (l/mol)')
27  plt.ylabel('Pressure (atm)')
28  legend=plt.legend()
29
30  plt.savefig('./figs/SRKgas.png')
31
32  # plt.figure(2)
33  # for T in np.arange(268,390,40):
34  #     alpha = 1 + m * (1 - (T / Tc)**0.5)
35  #     Psrk = R * T /(v-b) - alpha * a / (v* (v+b))
36  #     plt.loglog(v,Psrk,label=T,basex=10)
37
38  # legend = plt.legend()
39
40  # plt.ylim([1e1,1e4])
41  # plt.xlim([0.01,1.1])
42  # plt.xlabel('Log volume (l/mol)')
43  # plt.ylabel('Log pressure (atm)')
44  # plt.title('CO2 SRK vs. Ideal Gas isotherms')
45
46  # plt.savefig('./figs/logSRKgas.png')
```

CO2 SRK isotherms
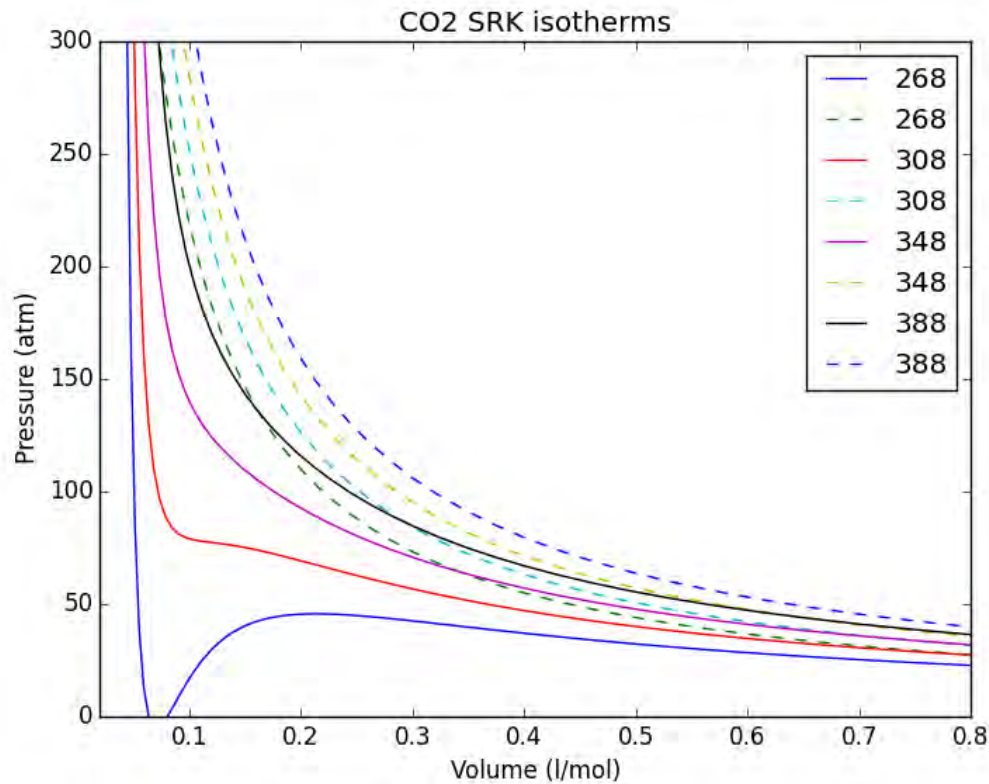
- errors largest at low v, low T

- given T and v, easy to find P

- given T and P, harder to find v; solve numerically

7.4.4   Virial expansion

$$P = \frac{RT}{v} \left(1 + \frac{B_2(T)}{v} + \frac{B_3(T)}{v^2} + \cdots\right)$$

7.4.5   Law of corresponding states

- Observed empirically that PvT properties of many fluids behave similarly when expressed in terms of reduced variables

- Reflects common competition between size/entropy and interaction/energy

- Define unitless *compressibility*:

$$Z = \frac{P(v,T)v}{RT}$$

- $Z_{ig} = 1$

- $Z_c = 0.27$ for many common fluids

- Plot of Z vs. P_r for various T_r

    - Negative deviations at low P, attractions reduce pressure relative to ideal gas
    - Positive deviations at high P, repulsive regime due to short-range repulsion
    - Deviations increase with decreasing T_r
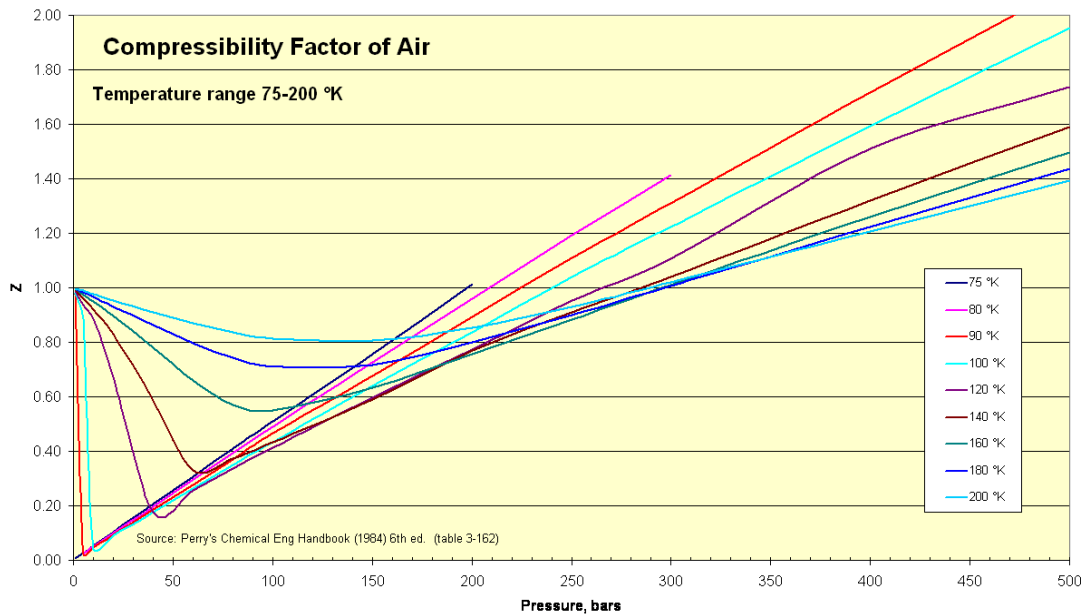
- Algorithm: given two of PvT and corresponding critical constants, convert to reduced values, read unknown value off of compressibility chart, and back-convert to real value.

- Rather arcane, not-computer-friendly way of getting PvT information

7.5   Real gas mixtures

- Even messier problem

- Mixing rules to combine parameters from individual components

8 Two-phase systems

Very often interested in systems in which two distinct phases are present, e.g. *l*-/g/. Common in separations problems, including my favorite, extracting tasty coffee from coffee beans, and second favorite, CO_2 from flue gas.

8.1 One-component phase diagrams

- Pure substances can exist in multiple "phases." *s*, *l*, *v* familiar, but can have e.g. multiple solid phases, example C

- Stable phase at any given condition is a function of *T* and *P*

- Captured in a "phase diagram," which shows which phase is stable at a give condition

- Have already talked about properties of single phases

- Often interested in *phase transitions*, boundaries between two phases

- Give example from vdW isotherm; for given *T*, only one *P* at which both phases

- Mention heat flow

- In two-phase region, temperature sets one and only one saturation pressure

- Mention *latent heat*

- Change the temperature, change the saturation pressure

- CO_2 phase diagram representative:
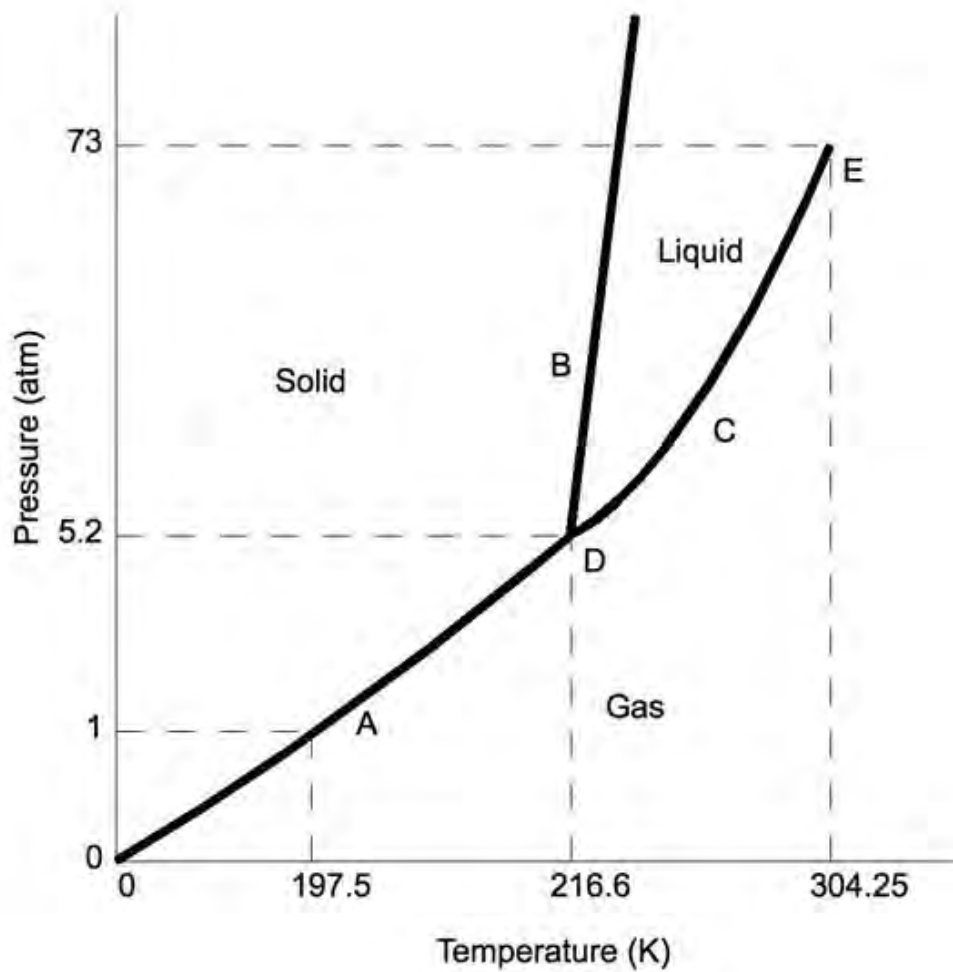
- Key features:

  - boiling point
  - "normal" boiling point
  - critical point and supercritical region
  - melting/freezing point
  - sublimation point
  - "triple" point

- H_2O diagram somewhat anomalous:
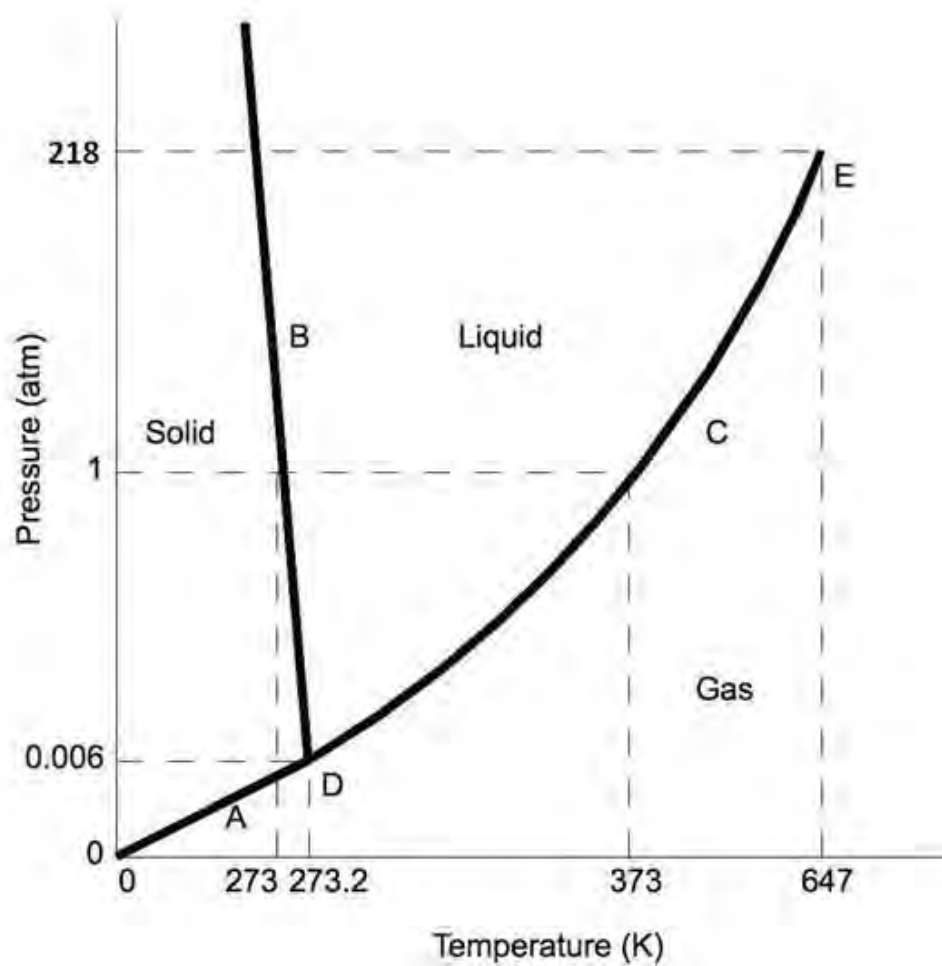
- Will find tabulations of boiling/freezing points, critical points, triple points in Perry's Handbook, CRC, http://webbook.nist.gov

8.1.1 Clapeyron equation

- Thermodynamics gives us a relationship for the slope of a coexistence line:

$$\frac{dP^*}{dT} = \frac{\Delta H_{\text{latent}}}{T(v_b - v_a)}$$

- Applied to liquid → vapor transition, ignoring liquid volume, and treating vapor as ideal gives the Clausius-Clapeyron equation:

$$
\begin{aligned}
\frac{dP^*}{dT} &= \frac{\Delta H_{\text{vap}}}{T(v_g - v_l)} \\
&\approx \frac{\Delta H_{\text{vap}}}{T v_g} \\
&\approx \frac{P \Delta H_{\text{vap}}}{R T^2}
\end{aligned}
$$

$$\frac{d \ln P}{d 1/T} = -\frac{\Delta H_{\text{vap}}}{R}$$

- Assuming ΔH_vap is not a function of T, integrates to

$$\ln \frac{P_2^*}{P_1^*} = -\frac{\Delta H_\text{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

- Plot of $\ln P$ vs. $1/T$ is approximately linear with slope related to latent enthalpy

Clausius-Clapeyron example Benzene normal boiling point is 353.2 K at 760 Torr. Heat of vaporization is $30.8\,\text{kJ}\,\text{mol}^{-1}$. What is saturation pressure at 373.2 K?

```
1   import numpy as np
2
3   R = 8.314
4   T1 = 353.2
5   T2 = 373.2
6   deltaH = 30800.
7
8   lnP = -(deltaH/R)*(1/T2 - 1/T1) + np.log(760)
9
10  P = np.exp(lnP)
11
12  print('ln P = {0:6.2f}  P = {1:6.0f} torr'.format(lnP,P))
13  print('Experiment = 1360 torr')
```

```
ln P =   7.20  P =   1333 torr
Experiment = 1360 torr
```

8.1.2 Antoine equation

- Approximations underlying Clausius-Clapeyron are too severe for engineering work

- Antoine equation is a modification empirically observed to fit saturation pressure/temperature data better:

$$\log_{10} P^* = A - \frac{B}{T + C}$$

- Values of A, B, and C are tabulated in standard references

- Pay attention to units!

- Because this is empirical, only apply within range of fit

8.2 Gibbs phase rule

- In single-phase region, can specify both T and P—2 DOFs

- At phase-boundary, only T or P is independent—1 DOF

- Reflects Gibbs phase rule:

$$DOF = c - \Pi - r + 2$$

- DOF are number of *intensive* variables that can be freely set and still satisfy the composition conditions

- Applies more generally to mixtures, including ones in which chemical reactions can occur

8.3 Single-component VLE

- Common situation to have a liquid A (e.g. H_2O) in equilibrium with a vapor mixture (e.g. moist air)

- Important in humidification, dehumidification, drying, evaporation, . . .

- At equilibrium, vapor is said to be "saturated"

- DOF = 2 - 2 + 2 = 2; any two of T, P, y_1

8.3.1 Raoult's Law

- Pretty reliable relationship between variables is that partial pressure of volatile component is equal to saturation pressure:

$$P_i = y_i P = P_i^*(T)$$

Raoult's Law Example Saturation pressure of H_2O is 289 mmHg at 75 °C (See Appendix of book). What is equilibrium composition of air at this temperature? (This would correspond to 100% relative humidity. Wet!)

```
1  psat = 289.
2  yH2O = psat/760.
3  yair = 1. - yH2O
4  yN2 = 0.79*yair
5  yO2 = 0.21*yair
6
7  print('H2O = {0:3.0f}%  N2 = {1:3.0f}%  O2 = {2:3.0f}%'.format(yH2O*100,yN2*100,yO2*100))
```

```
H2O =  38%  N2 =  49%  O2 =  13%
```

- Raoult's Law applies to equilibrium. Change any constraint, other variables must adjust to restore equilibrium

- Often two-phase systems are **not** at equilibrium

- Uncommon for vapor composition to be greater than equilibrium—vapor would just condense

- Opposite is possible, if there isn't enough liquid phase to saturate the vapor

- A "superheated" vapor is one that is below its saturation pressure

$$y_i P < P_i^*(T)$$

- Called superheated because vapor would have to be cooled at constant pressure and composition to reach equilibrium

- Or compressed at constant T; at least one of three variables has to change

- (Lower) temperature at which a superheated vapor would start to condense at constant P is called "dew point temperature"

$$y_i P = P_i^*(T_{\text{dewpt}})$$

- $T - T_{\text{dewpt}} = $ degrees of superheat
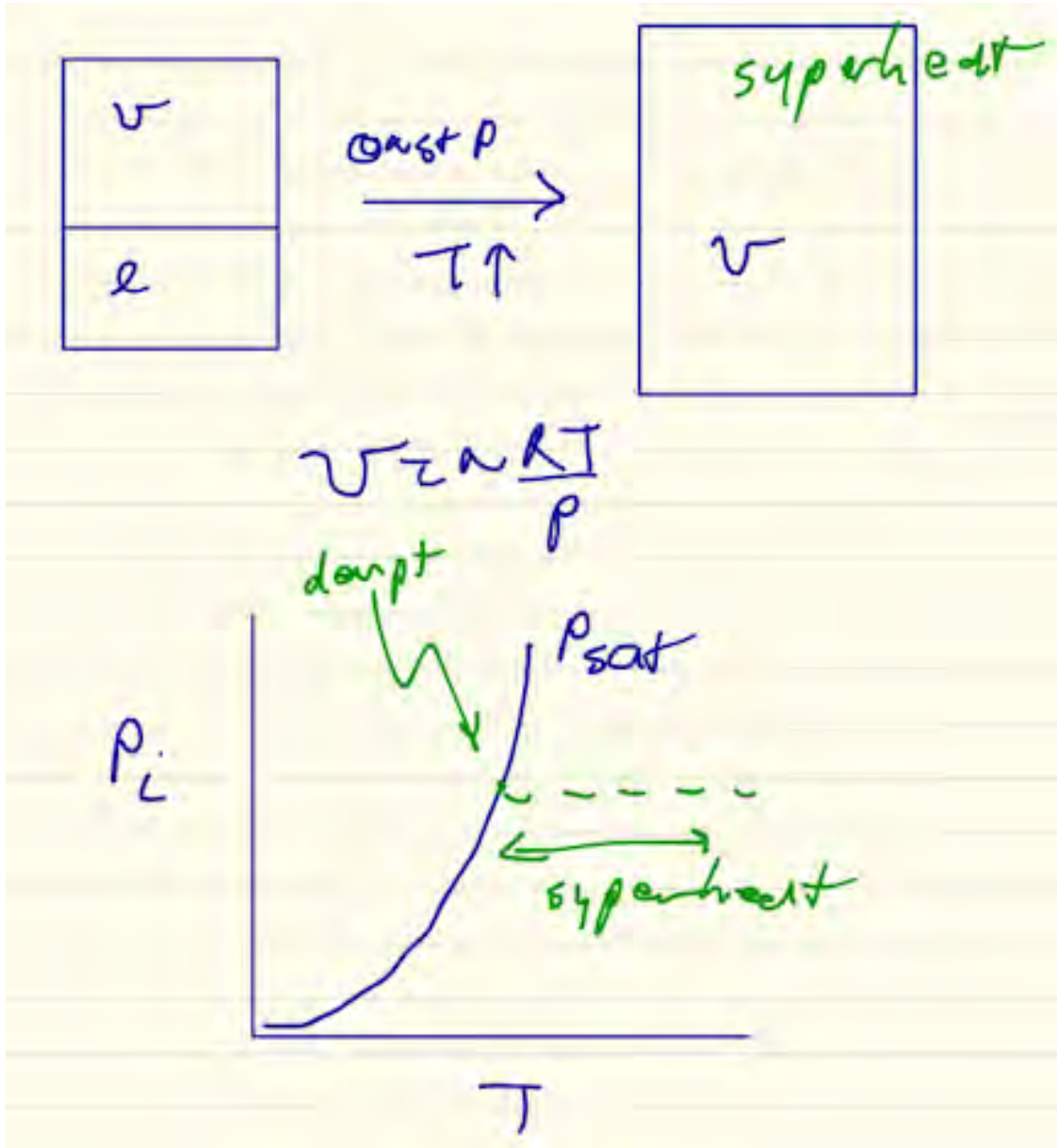
Superheat example A stream of air is at $100\,°C$, 5260 mmHg, and contains 10.0% H_2O. (1) Dewpoint? (2) Degrees of superheat? (3) Fraction of vapor that condenses and final gas phase composition if cooled to $80\,°C$ at constant P? (4) Ditto if air is isothermally compressed to 8500 mmHg.

```
1   import scipy.optimize as opt
2
3   T0 = 100.        # C
4   P0 = 5260.       # mmHg
```

```
5   yH2O0 = 0.10
6   Psat = 760.        # duh!  Psat = Patm at 100 C!  We all know that.
7
8   PH2O = P0 * yH2O0
9
10  print('Partial pressure of H2O = {0:4.0f} mmHg'.format(PH2O))
11
12  dewpoint = 90.0    # from table
13  superheat = T0 - dewpoint
14  print('Dew point = {0:4.0f} degC    Superheat = {1:4.0f} degC'.format(dewpoint,superheat))
15
16  # Cool isobarically to 80 C
17  Psat80 = 355.1   # mmHg
18  yH2O80 = 355.1/5250
19
20  # draw a condenser feed and do mass balance on both streams
21  n0H2O = 0.1*100; n0air = 0.9*100;
22
23  # air balance
24  ndotv = 100 * 0.9 / (1 - yH2O80)
25
26  # H2O balance
27
28  ndotH2O = 100* 0.1 - ndotv * yH2O80
29
30  deltaH2O = (ndotH2O)/n0H2O
31
32  print('80 C composition ={0:6.4f}'.format(yH2O80))
33
34  print('Fraction of water condensed ={0:3.0f}%\n'.format(deltaH2O*100))
35
36  # Compress isothermally to 8500 mmHg at 100 C
37  Pcomp = 8500
38  PH2O = yH2O0 * 8500
39
40  print('Partial pressure of H2O = {0:4.0f} mmHg'.format(PH2O))
41
42  yH2Ocomp = Psat/Pcomp
43
44  # air balance
45  ndotv = 100 * 0.9 / (1 - yH2Ocomp)
46
47  # H2O balance
48
49  ndotH2O = 100* 0.1 - ndotv * yH2Ocomp
50
51  deltaH2O = (ndotH2O)/n0H2O
52
53  print('8500 mmHg composition ={0:6.4f}'.format(yH2Ocomp))
54
55  print('Fraction of water condensed ={0:3.0f}%\n'.format(deltaH2O*100))
```

```
Partial pressure of H2O =  526 mmHg
Dew point =   90 degC    Superheat =   10 degC
80 C composition =0.0676
Fraction of water condensed = 35%


Partial pressure of H2O =  850 mmHg
8500 mmHg composition =0.0894
Fraction of water condensed = 12%
```

- If $P^* < P$, liquid *evaporates* from surface

- If $P^* \geq P$, liquid *boils* throughout

8.3.2 Humidity

- These concepts very often applied to H_2O, in which we refer to H_2O vapor as *humidity*

- Common to define *relative humidity*, fraction of maximum H_2O in air at given T

$$RH(T) = P_{H_2O}/P^*_{H_2O}(T)$$

Relative humidity example Humid air at $75\,°C$, 1.1 bar, and 30% RH is fed into a process unit at $1000\,\mathrm{h}^{-1}$. Determine molar flow rate of all components.

```python
Psat75 = 289.   # mmHg
RH = 0.30
P = 1.1 * 760 / 1.01325 # torr

PH2O = RH*Psat75

print('PH2O = {0} torr'.format(PH2O))

yH2O = PH2O/P
yN2  = (1-yH2O)*0.79
yO2  = (1-yH2O)*0.21

print('H2O = {0}  N2 = {1}  O2 = {2} mol/mol'.format(yH2O,yN2,yO2))

# MWavg = (18. * yH2O + 28 * yN2 + 32 * yO2)/1000.   # kg/mol

R = 8.314
T = 75 + 273
P = 1.1e5        # Pa
vdot = 1000.     # m3/hr
ndot = P * vdot / ( R * T)

print('H2O = {0}  N2 = {1}  O2 = {2} mol/hr'.format(yH2O*ndot,yN2*ndot,yO2*ndot))
```

```
PH2O = 86.7 torr
H2O = 0.10508226674641148  N2 = 0.7069850092703349  O2 = 0.18793272398325359 mol/mol
H2O = 3995.147826441919  N2 = 26879.03211994477  O2 = 7145.05917112456 mol/hr
```

8.4 Multi-component VLE

$$1 \text{ comp} \qquad 2 \text{ comp} \qquad 2 \text{ comp}$$
$$2 \text{ phases} \qquad 2 \text{ phases} \qquad 2 \text{ phases}$$

$$P = P \qquad\qquad P = P \qquad\qquad P = P$$
$$T = T \qquad\qquad T = T \qquad\qquad T = T$$
$$\mu = \mu \qquad\qquad \mu = \mu \qquad\qquad \mu_i = \mu_i$$
$$P = P^*(T) \qquad \downarrow \qquad\qquad \downarrow$$
$$\qquad\qquad y\, P = P^*(T) \qquad y_i\, P = x_i\, P_i^*$$
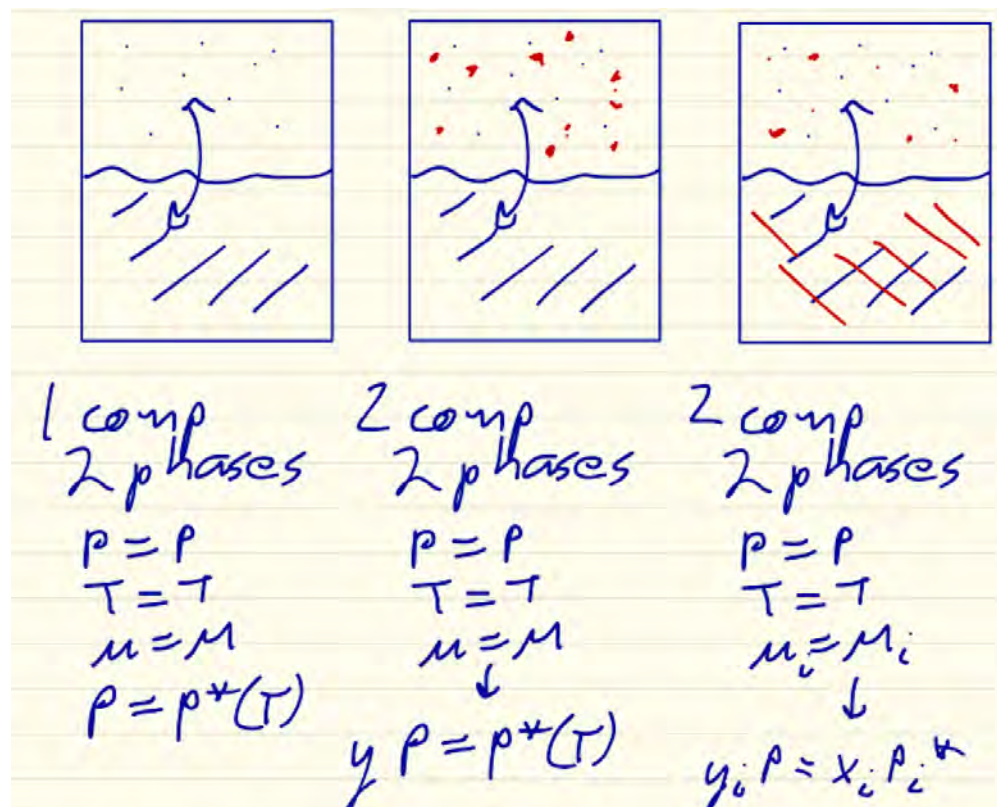
- Combine two liquids, both of which have finite (but different) Psat at given T, in a closed container

- Vapor composition will in general be different from liquid.

- Given a liquid composition (x), "bubble point" is P or T at which first bit of vapor appears

- Given a vapor composition (y), "dew point" is P or T at which first bit of condensate appears

8.4.1 Raoult's Law

- One model for VLE, most appropriate for majority material $\rightarrow 100\%$

- Partial pressure is saturation pressure scaled by fraction of molecules at surface:

$$x_A P_A^*(T) = P_A = y_A P$$

- Assumes ideal liquid mixture and ideal gas mixture

- If liquid only contains condensable components ($\sum_i x_i = 1$)

$$P_{\text{bubble}} = \sum x_i P_i^*$$

- Given x_i, P, can find y_i:

$$y_i = x_i P_i^* / P$$

- If we know the vapor composition y_i, can determine the dew point by substitution from

$$\sum_i x_i = 1 \rightarrow P_{\text{dew}} = \left(\sum_i \frac{y_i}{P_i^*} \right)^{-1}$$

```python
import numpy as np
import matplotlib.pyplot as plt

xB = np.linspace(0,1)
PAs = 10
PBs = 5

PB = xB * PBs
PA = (1-xB) * PAs
P = PA + PB

yB = PB/P

plt.plot(xB,P,yB,P)
# plt.plot(xB,PB,xB,PA,xB,P)
plt.ylabel('Pressure')
plt.xlabel('x_B, y_B')
plt.title('Isothermal compression')
plt.legend(['Bubble (x)','Dew (y)'])

plt.savefig('./figs/PressureVLE.png')
```
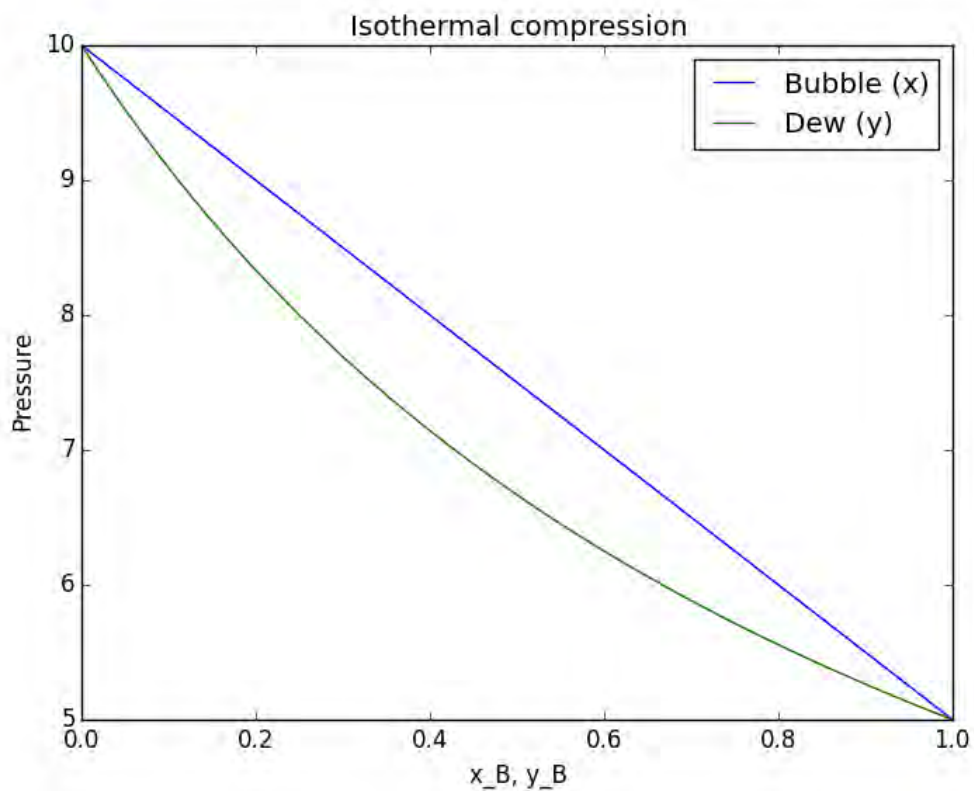
- Go up in pressure starting from 50:50 mix, hit dew line, first drop of liquid forms

- Called dew pressure

- Has composition of bubble line

- Keep going up, vapor gradually condenses, composition follows dew line, liquid follows bubble line

- Finally at bubble pressure last bit of vapor disappears

- Call Px diagram

Bubble pressure example 15% benzene and 10% toluene in N_2 at $80\,°C$. At what pressure does vapor condense, and what is its composition? Answer: condenses when partial pressure matches dew point.

```python
PBs = 756   # torr
PTs = 291   # torr
yB  = 0.15
yT  = 0.10

# eliminate xB
P = 1/((yB/PBs) + (yT/PTs))

xB = yB * P /PBs

print('Dew point pressure = {0:5.0f}  Benzene fraction = {1:5.3f}'.format(P,xB))
```

Dew point pressure = 1845 Benzene fraction = 0.366

- Can similarly create Tx diagram at constant P

- Need model for how saturation pressure varies with T

```python
import numpy as np
import matplotlib.pyplot as plt
from scipy.optimize import fsolve

def PAs(T):
    A = 6.89272; B= 1203.531; C=219.888 # benzene Antoine
    logP = A - B/(T+C)
    return 10**logP
#    PA0 = 10
#    H = 800
#    return PA0 * np.exp(-H/T)

def PBs(T):
    A = 6.95805; B= 1346.773; C=219.693 # toluene Antoine
    logP = A - B/(T+C)
    return 10**logP

Pressure = 760.0

def PAsopt(T):
    return PAs(T) - Pressure

def PBsopt(T):
    return PBs(T) - Pressure

TA = fsolve(PAsopt,100)
```

```
27    TB = fsolve(PBsopt,100)
28
29    print(TA,TB)
30
31    T = np.linspace(TA,TB)
32
33    xB = (Pressure - PAs(T))/(PBs(T) - PAs(T))
34
35    yB = xB * PBs(T)/Pressure
36
37    plt.plot(xB,T,yB,T)
38    plt.xlim(0,1)
39    plt.ylabel('Temperature')
40    plt.xlabel('x_B, y_B')
41    plt.title('Isobaric heating')
42    plt.legend(['Bubble (x)','Dew (y)'])
43
44    plt.savefig('./figs/TemperatureVLE.png')
45
46
47    print(PAs(90)/760,PBs(90)/760)
```

[80.10179978] [110.62216089]
1.343213901504202 0.5351810463458321
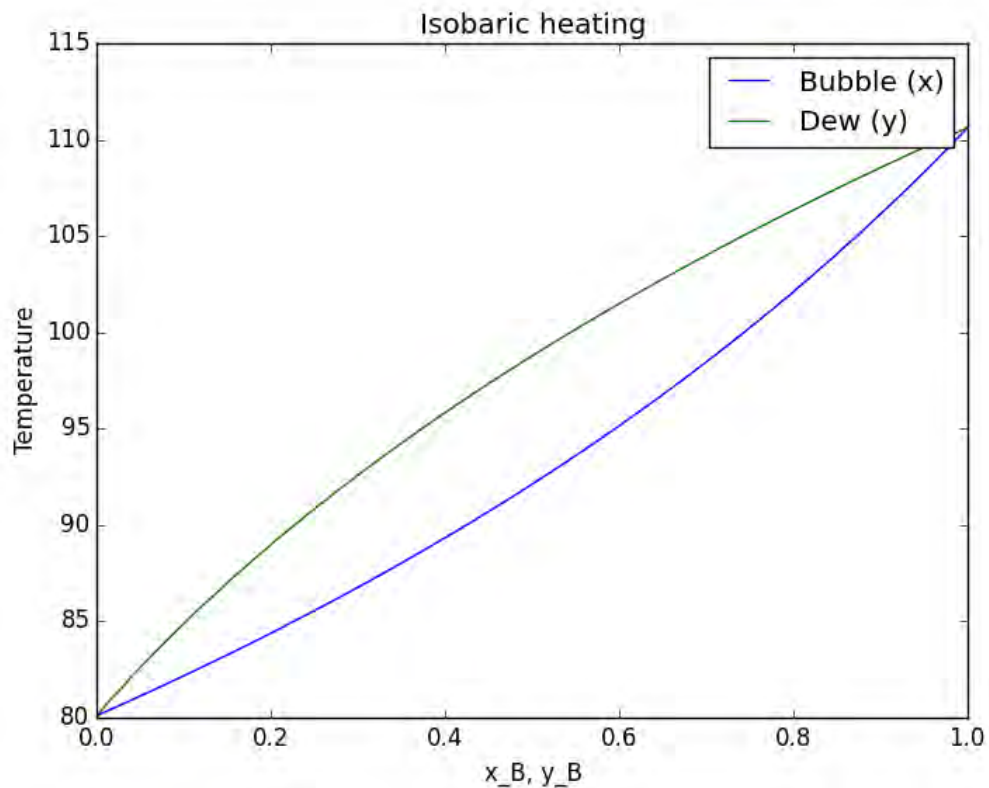
8.4.2   Henry's Law

- Model appropriate for a dilute solute

$$x_A H_A(T) = P_A = y_A P$$

Raoult's Law

Henry's Law
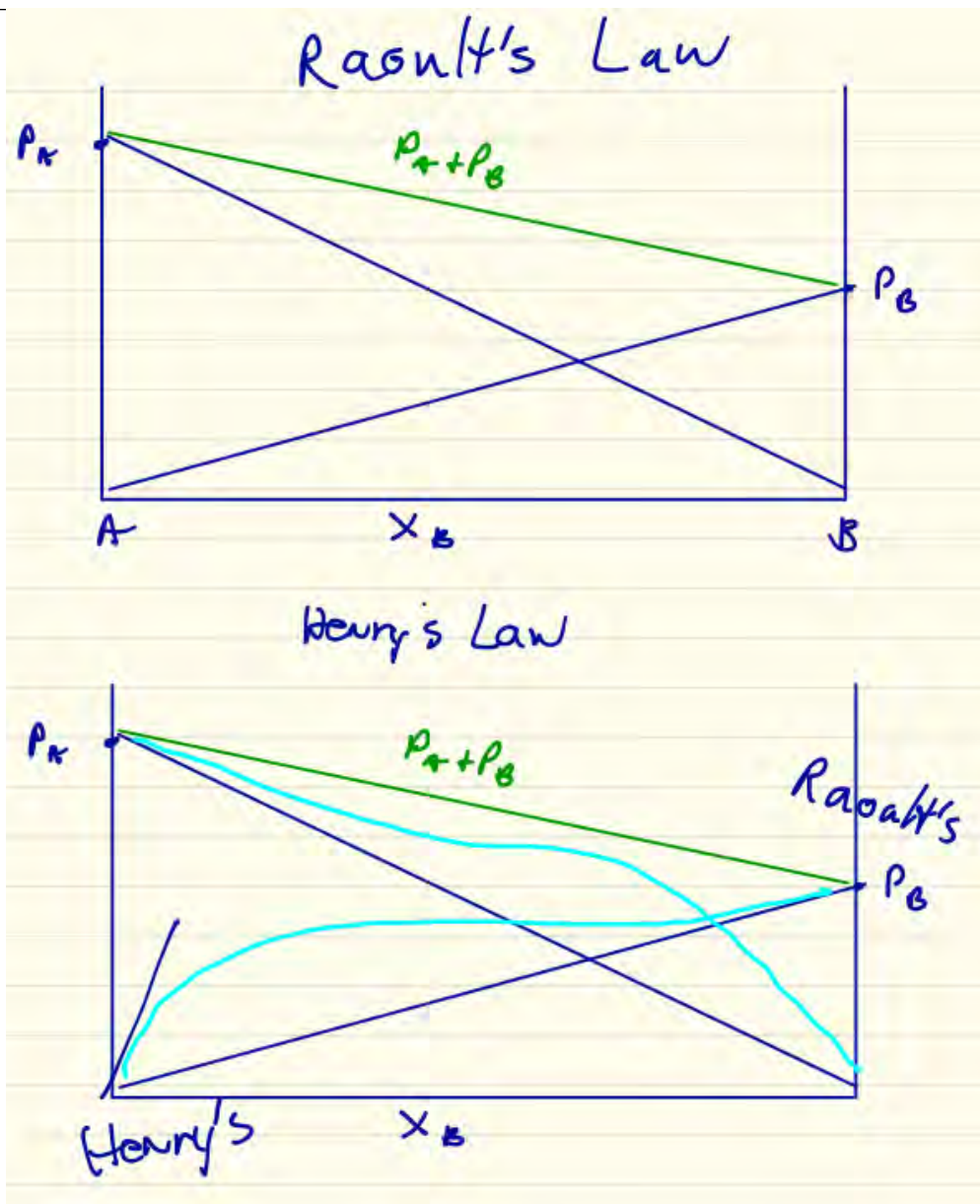
- Henry's constants are measured and tabulated

8.4.3 Tabulations

VLE example from tabulation In this example, partial pressures of H_2O and SO_2 over a solution of a given composition and temperature are read from a compilation.

The best way to evaluate equilibrium compositions is from ~~~~ Engineers' Handbook (see Footnote 1), pp. 2-80 through 2-94, gives partial pressure~~ over various liquid solutions. Example 6.4-1 illustrates the use of such data.

Absorption of SO_2

Sulfur dioxide (SO_2) is produced when coal is burned in power plants. Prior to implementation of clean-air standards, SO_2 emissions were responsible for acid rain, but utilization of absorbers (sometimes referred to as *scrubbers*) to remove SO_2 from combustion products has significantly reduced the problem.

In a simple implementation of that emission-control strategy, a gas mixture containing 45 mole% SO_2 and the balance air (an SO_2 concentration much higher than values normally encountered in power-plant emissions) flowing at a rate of 100 lb-mole/h is contacted with liquid water in a continuous absorber. The liquid leaving the absorber is analyzed and found to contain 2.00 g of SO_2 per 100 g of H_2O. Assuming that the gas and liquid streams leaving the absorber are in equilibrium at 30°C and 1 atm, calculate the fraction of the entering SO_2 absorbed in the water and the required water feed rate.

Basis: Given Feed Rate of Gas
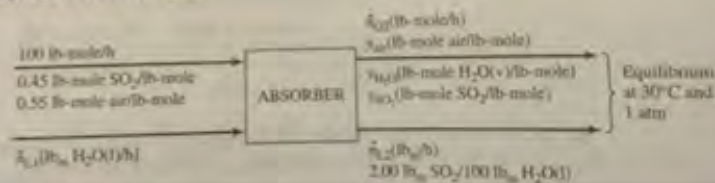
exit liquid: $2 \, lb_m \, SO_2/100 \, lb_m \, H_2O$ @ 30°C

$\rightarrow \quad P_{SO_2} = 176 \, mmHg \quad P_{H_2O} = 31.6 \, mmHg$

$P_{air} = 760 - 176 - 31.6 =$

$y_{SO_2} = 0.232 \quad y_{H_2O} = 0.0416 \quad y_{air} = 0.727$

Unknowns: $\dot{N}_{L1}, \dot{N}_{L2}, \dot{N}_{G2}$

3 balances

air: $\quad out = in$

$\dot{N}_{G2} \cdot y_{air} = 100 \cdot 0.55 \rightarrow \dot{N}_{G2} = 75.7 \, mol/hr$

$$SO_2: \quad \underset{IN}{100 \cdot 0.45} = \underset{out}{\dot{N}_{G2} \cdot y_{SO_2}} + \underset{out}{\dot{M}_{L2} \cdot \omega_{SO_2} \cdot 64}$$

$$\left(\omega_{SO_2} = 0.0196 \; \frac{mass}{mass} \; SO_2\right)$$

$$\searrow \dot{M}_{L2} = 89600 \; lb_m$$

$H_2O:$
$$in = out$$

$$\dot{M}_{1L} = \dot{N}_{G2} \cdot y_{H_2O} \cdot 18 + \dot{M}_{L2} \cdot \omega_{H_2O}$$

$$\searrow \boxed{\dot{M}_{1L} = 87{,}900 \; lb_m/hr}$$

SO_2 fraction absorbed

$$\frac{\dot{M}_{L2} \cdot \omega_{SO_2} \cdot 64}{100 \cdot 0.45} = 0.61 \; \frac{mol}{mol} \; SO_2$$

$$61\%$$

8.5 Solid-liquid

8.5.1 Solubility

- Solids have limited solubility in liquids, called solubility limit. Strong function of T and of what exactly precipitates (anhydrous, hydrate, ...)

8.5.2 Colligative properties

- influence of solute on properties of solvent, depends on number but not type of solute

- vapor pressure lowering $\rightarrow$ boiling point elevation

- vapor pressure lowering $\rightarrow$ melting point lowering

- combine Raoult's Law and Clausius-Clapeyron equation:

$$\Delta T_b = \frac{RT_b^2}{\Delta H_{vap}^*} x$$

$$\Delta T_m = \frac{RT_m^2}{\Delta H_m^*} x$$

- Can run in both directions, know composition, predict T change, know T change, compute x

EXAMPLE 5.000 g solute in 100.0 g H_2O at 1 atm boils at 100.421 °C. Molecular weight of solute?

```
1   R = 8.31441
2   Hb = 40656.    # J/mol
3   Tb = 273.16 + 100.    # K
4   dT = 100.421 - 100.
5
6   x = dT * Hb / (R * Tb * Tb ) # mol fraction solute
7
8   nH2O = 100.0 / 18.011    # mol
9
10  nSol = nH2O * x /(1-x)
11
12  MW = 5.000/nSol
13
14  print('Moles solute = {0:5.3f}   MW = {1:5.3f} g/mol'.format(nSol,MW))
```

```
Moles solute = 0.083    MW = 60.014 g/mol
```

8.6 Liquid-liquid

- Two liquids that can be mixed in any proportions (ethanol and H_2O) are called *miscible*

- Two that do not mix (hexane and H_2O) are called *immiscible*

- Two that mix in only some proportions are called *partially miscible*

- Often expressed in terms of a *partition coefficient* of a solute between two solvents

- Or on a ternary phase diagram

- Gibbs phase rule: dof $= 3\text{-}2 + 2 = 3$

    − T, P, one composition variable fixes all the others

- Basis of liquid-liquid extraction

    − A = H_2O, B = acetone, C = MIBK
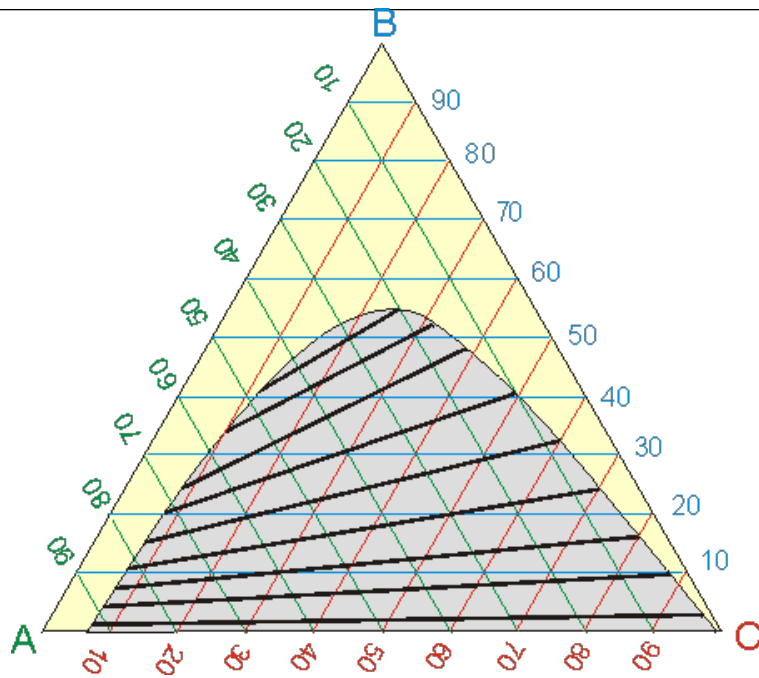
8.7 Solid-gas

- isotherms

9 Energy balances

9.1 What's energy?

- kinetic (E_K), translational or rotational energy

$$E_K = \frac{1}{2}mv^2$$

- potential (E_V), due to position with respect to an external field (gravitational, electric, magnetic)

$$E_{grav} = mgh$$

- internal energy (U), stored in bonds, in motion of molecules relative to one another, ...

  - *thermal* energy is one subset of internal
  - strong function of chemical composition, of phase, of T, usually weak function of P

- energy is *additive*, so $E_{tot} = E_K + E_V + U$

- energy is *conserved*, so for all processes, $\Delta E_{\text{universe}} = 0$

  - First Law of Thermodynamics!

9.2 Closed system (little different from thermo definition)

- distinguish *system* from *surroundings*

- no *material* crosses boundary

- *energy* can be transferred as heat (q) - positive when added to a system

- *energy* can be transferred by doing work (w) - positive when done on a system

- basic balance for a closed system:

$$\Delta E_{sys} + \Delta E_{sur} = 0$$

$$\Delta U + \Delta E_K + \Delta E_V - q - w = 0$$

- If system is not accelerating, $\Delta E_K = 0$

- If system is not rising or falling, $\Delta E_V = 0$

- *adiabatic* process has $q = 0$

- If no mechanical interactions with surroundings (shaft, piston, magnetic rotor) $w = 0$

EXAMPLE Gas in a cylinder. (a) Add 2 kcal of heat and temperature rises from 25 to 100 °C while piston is fixed. (b) Piston is released, does 100 J of work, temperature of gas is constant.
  (a) $\Delta E_K = \Delta E_V = w = 0$. $q = 2 * 1000 * 4.184 = 8368$ J. $\Delta U = 8368$ J.
  (b) $\Delta E_K = \Delta E_V = 0$. $\Delta U = 0$ if gas is ideal. $w = -100$ J $\rightarrow q = 100$ J.

9.3 Open system, steady state

- In open system at steady-state, energy balance changes to a power balance:

$$\Delta \dot{U} + \Delta \dot{E}_K + \Delta \dot{E}_V - \dot{q} - \dot{w} = 0$$

- Each delta is a sum over all the output less all the input streams. Let's take these pieces apart.

9.3.1 Flow and shaft work

When material flows through a system, work is done *on* the system as material is pushed in and done *by* the system as material is pushed back out. Helpful to define some terms.

- *shaft work* ($\dot{W}_s$)is work done by a moving part on a system (like a turbine or rotor)

- *flow work* ($\dot{W}_f$) is difference between work done by fluid moving in and out of system

$$\dot{W}_f = P_{\text{in}}\dot{V}_{\text{in}} - P_{\text{out}}\dot{V}_{\text{out}}$$

- If fluid is incompressible and there are frictional losses, what must be true about $\dot{V}$? What is true about $P_{in} - P_{out}$?

- Conventional to define a new thermodynamic function, *enthalpy*, to include the flow work:

$$H = U + PV$$

- energy balance becomes

$$\Delta \dot{H} + \Delta \dot{E}_K + \Delta E_P = \dot{q} + \dot{W}_s$$

9.3.2 Specific properties

- *specific* property is (extensive) property per unit mass or per unit moles. Book uses both, so watch!

- specific volume $\hat{V} = 1/\rho$ l/g

- related to flow rate via mass flow rate

$$\dot{V} = \dot{m}\hat{V}$$

- U and H are properties of the chemical species but not time, tabulated on a per mole or per mass basis

- If on a per mole basis, related to molar flow rate

$$\dot{U} = \hat{U}\dot{n} \quad \dot{H} = \hat{H}\dot{n}$$

EXAMPLE Specific internal energy and volume of He at 300 K and 1 atm are 3800 J/mol and 24.63 L/mol, respectively. What are specific enthalpy and enthalpy rate when flowed at 250 kmol/h?

```python
1   Uhat = 3800  # J/mol
2
3   P = 1          # atm
4   Vhat = 24.63   # L/mol
5
6   Ratm = 0.0821   # L atm /mol K
7   RJ = 8.314      # J/mol K
8
9   Hhat = Uhat + P * Vhat * (RJ/Ratm)
10
11  Vdot = 250000   # mol/h
12
13  Hdot = Hhat * Vdot
14
15  print('Hhat = {0:6.1f} J/mol    Hdot = {1:6.3e} J/h'.format(Hhat,Hdot))
```

```
Hhat = 6294.2 J/mol    Hdot = 1.574e+09 J/h
```

9.3.3 Kinetic energy

- related to mass flow rates, where u is linear velocity

$$\dot{E}_K = \frac{1}{2}\dot{m}u^2$$

9.3.4 Potential energy

- If we consider only gravitational PE, then related to height z relative to some reference

$$\dot{E}_V = \dot{m}gz$$

EXAMPLE 500 kg/hr steam drive a turbine. Steam enters at 44 atm, 450 °C, and $60\,\mathrm{m\,s^{-1}}$, leaves at a point 5 m lower, at 1 atm and at $360\,\mathrm{m\,s^{-1}}$. Shaft work delivered is 70 kW and heat loss is 10^4 kcal/hr. Change in enthalpy of steam?

Energy Balance on a Turbine

Five hundred kilograms per hour of steam drives a turbine. The steam enters the turbine at 44 atm and 450°C at a linear velocity of 60 m/s and leaves at a point 5 m below the turbine inlet at atmospheric pressure and a velocity of 360 m/s. The turbine delivers shaft work at a rate of 70 kW, and the heat loss from the turbine is estimated to be 10^4 kcal/h. Calculate the specific enthalpy change associated with the process.

tion

$$\Delta \dot{H} + \Delta \dot{E}_k + \Delta \dot{E}_v = \dot{Q} + \dot{W}_s$$

$$\dot{W}_s = -70 \text{ kW}$$

$$\dot{Q} = -10{,}000 \text{ kcal/h} = -11.6 \text{ kW}$$

mass conserved:

$$\dot{m}_{in} = \dot{m}_{out} = 500 \text{ kg/s}$$

$$\Delta \dot{E}_k = \tfrac{1}{2}\dot{m}\left(u_{out}^2 - u_{in}^2\right) = 8.75 \text{ kW}$$

$$\Delta \dot{E}_v = \dot{m}g\left(z_{out} - z_{in}\right) = \dot{m}g(-5m) = -6.8 \times 10^{-3} \text{ kW}$$

$$\Delta \dot{H} = -90.5 \text{ kW}$$

$$\Delta \hat{H} = \Delta \dot{H}/\dot{m} = -650 \text{ kJ/kg}$$

9.4 Thermodynamic data

- Internal energy and enthalpy are *state functions*: they depend only on the intensive properties (T, P), composition, and state of a material

- Because they are *energies*, they have no absolute value. Rather, can only measure/know *changes* in these properties between two states

- *Measured* by contriving an experiment in which all energy changes other then ΔU or ΔH are known.

- Generally tabulated relative to some (stated or unstated) *reference state*, which is defined to have a value of zero

- Tabulated in *Perry's*, on line, see Table B.8

- Or NIST, http://webbook.nist.gov/chemistry/fluid/

- Because H_2O is so important to power generation and other chemical engineering processes, thermodynamic properties of water are tabulated in *steam tables*

- Table B.5: saturated steam (on phase equilibrium line), in increments of T

- Table B.6: saturated steam (on phase equilibrium line), in increments of P

- Table B.7: superheated steam (beyond phase equilibrium)

EXAMPLE Pressure, specific internal energy, and enthalpy of saturated steam at 133.5 °C? (Table B.6): 3.0 bar, 2543.0 kJ/kg, 2724.7 kJ/kg

---

EXAMPLE Specific volume, internal energy, and enthalpy of steam at 400 °C and 10 bar, relative to triple point.
At 10 bar, saturation temperature is 179.9 °C (dew point, Table B.6). Thus, this must be superheated steam.

   (Table B.7): 0.307 m3/kg, 2958 kJ/kg, 3264 kJ/kg

- Note that energies are stronger function of T than P.

TABLE B.7 Properties of Superheated Steam[a]

P(bar) (T_{sat},°C)		Sat'd Water	Sat'd Steam	Temperature (°C)→ 50	75	100	150	200	250	300	350
0.0 (—)	$\hat{H}$	—	—	2595	2642	2689	2784	2880	2978	3077	3177
	$\hat{U}$	—	—	2446	2481	2517	2589	2662	2736	2812	2890
	$\hat{V}$	—	—	—	—	—	—	—	—	—	—
0.1 (45.8)	$\hat{H}$	191.8	2584.8	2593	2640	2688	2783	2880	2977	3077	3177
	$\hat{U}$	191.8	2438.0	2444	2480	2516	2588	2661	2736	2812	2890
	$\hat{V}$	0.00101	14.7	14.8	16.0	17.2	19.5	21.8	24.2	26.5	28.7
0.5 (81.3)	$\hat{H}$	340.6	2646.0	209.3	313.9	2683	2780	2878	2979	3076	3177
	$\hat{U}$	340.6	2484.0	209.2	313.9	2512	2586	2660	2735	2811	2889
	$\hat{V}$	0.00103	3.24	0.00101	0.00103	3.41	3.89	4.35	4.83	5.29	5.75
1.0 (99.6)	$\hat{H}$	417.5	2675.4	209.3	314.0	2676	2776	2875	2975	3074	3176
	$\hat{U}$	417.5	2506.1	209.2	313.9	2507	2583	2658	2734	2811	2889
	$\hat{V}$	0.00104	1.69	0.00101	0.00103	1.69	1.94	2.17	2.40	2.64	2.87
5.0 (151.8)	$\hat{H}$	640.1	2747.5	209.7	314.3	419.4	632.2	2855	2961	3065	3168
	$\hat{U}$	639.6	2560.2	209.2	313.8	418.8	631.6	2643	2724	2803	2883
	$\hat{V}$	0.00109	0.375	0.00101	0.00103	0.00104	0.00109	0.425	0.474	0.522	0.571
10 (179.9)	$\hat{H}$	762.6	2776.2	210.1	314.7	419.7	632.5	2827	2943	3052	3159
	$\hat{U}$	761.5	2582	209.1	313.7	418.7	631.4	2621	2710	2794	2876
	$\hat{V}$	0.00113	0.194	0.00101	0.00103	0.00104	0.00109	0.206	0.233	0.258	0.282
20 (212.4)	$\hat{H}$	908.6	2797.2	211.0	315.5	420.5	633.1	852.6	2902	3024	3139
	$\hat{U}$	906.2	2598.2	209.0	313.5	418.4	603.9	850.2	2679	2774	2862
	$\hat{V}$	0.00118	0.09950	0.00101	0.00102	0.00104	0.00109	0.00116	0.111	0.125	0.139
40 (250.3)	$\hat{H}$	1087.4	2800.3	212.7	317.1	422.0	634.3	853.4	1085.8	2962	3095
	$\hat{U}$	1082.4	2601.3	208.6	313.0	417.8	630.0	848.8	1080.8	2727	2829
	$\hat{V}$	0.00125	0.04975	0.00101	0.00102	0.00104	0.00109	0.00115	0.00125	0.0588	0.0665
60 (275.6)	$\hat{H}$	1213.7	2785.0	214.4	318.7	423.5	635.6	854.2	1085.8	2885	3046
	$\hat{U}$	1205.8	2590.4	208.3	312.6	417.3	629.1	847.3	1078.3	2668	2792
	$\hat{V}$	0.00132	0.0325	0.00101	0.00103	0.00104	0.00109	0.00115	0.00125	0.0361	0.0422
80 (295.0)	$\hat{H}$	1317.1	2759.9	216.1	320.3	425.0	636.8	855.1	1085.8	2787	2990
	$\hat{U}$	1306.0	2571.7	208.1	312.3	416.7	628.2	845.9	1075.8	2593	2750
	$\hat{V}$	0.00139	0.0235	0.00101	0.00102	0.00104	0.00109	0.00115	0.00124	0.0243	0.0299
100 (311.0)	$\hat{H}$	1408.0	2727.7	217.8	322.9	426.5	638.1	855.9	1085.8	1343.4	2926
	$\hat{U}$	1393.5	2547.3	207.8	311.7	416.1	627.3	844.4	1073.4	1329.4	2702
	$\hat{V}$	0.00145	0.0181	0.00101	0.00102	0.00104	0.00109	0.00115	0.00124	0.00140	0.0224
150 (342.1)	$\hat{H}$	1611.0	2615.0	222.1	326.0	430.3	641.3	858.1	1086.2	1338.2	2695
	$\hat{U}$	1586.1	2459.9	207.0	310.7	414.7	625.0	841.0	1067.7	1317.6	2523
	$\hat{V}$	0.00166	0.0103	0.00101	0.00102	0.00104	0.00108	0.00114	0.00123	0.00138	0.0115
200 (365.7)	$\hat{H}$	1826.5	2418.4	226.4	330.0	434.0	644.5	860.4	1086.7	1334.3	1647.1
	$\hat{U}$	1785.7	2300.8	206.3	309.7	413.2	622.9	837.7	1062.2	1307.1	1613.7
	$\hat{V}$	0.00204	0.005875	0.00100	0.00102	0.00103	0.00108	0.00114	0.00122	0.00136	0.00167
221.2(P_c) (374.15)(T_c)	$\hat{H}$	2108	2108	228.2	331.7	435.7	645.8	861.4	1087.0	1332.8	1635.5
	$\hat{U}$	2037.8	2037.8	206.0	309.2	412.8	622.0	836.3	1060.0	1302.9	1600.3
	$\hat{V}$	0.00317	0.00317	0.00100	0.00102	0.00103	0.00108	0.00114	0.00122	0.00135	0.00163
250 (—)	$\hat{H}$	—	—	230.7	334.0	437.8	647.7	862.8	1087.5	1331.1	1625.0
	$\hat{U}$	—	—	205.7	308.7	412.1	620.8	834.4	1057.0	1297.5	1585.0
	$\hat{V}$	—	—	0.00100	0.00101	0.00103	0.00108	0.00113	0.00122	0.00135	0.00160
300 (—)	$\hat{H}$	—	—	235.0	338.1	441.6	650.9	865.2	1088.4	1328.7	1609.9
	$\hat{U}$	—	—	205.0	307.7	410.8	618.7	831.3	1052.1	1288.7	1563.3
	$\hat{V}$	—	—	0.0009990	0.00101	0.00103	0.00107	0.00113	0.00121	0.00133	0.00155
500 (—)	$\hat{H}$	—	—	251.9	354.2	456.8	664.1	875.4	1093.6	1323.7	1576.3
	$\hat{U}$	—	—	202.4	304.0	405.8	611.0	819.7	1034.3	1259.3	1504.1
	$\hat{V}$	—	—	0.0009911	0.00100	0.00102	0.00106	0.00111	0.00119	0.00129	0.00144
1000 (—)	$\hat{H}$	—	—	293.9	394.3	495.1	698.0	903.5	1113.0	1328.7	1550.5
	$\hat{U}$	—	—	196.5	295.7	395.1	594.4	795.3	999.0	1207.1	1419.0
	$\hat{V}$	—	—	0.0009737	0.0009852	0.001000	0.00104	0.00108	0.00114	0.00122	0.00131

[a] Adapted from R. W. Haywood, *Thermodynamic Tables in SI (Metric) Units*, Cambridge University Press. London. 1968. Water is a liquid in the enclosed region between 50°C and 350°C. $\hat{H}$ = specific enthalpy (kJ/kg), $\hat{U}$ = specific internal energy (kJ/kg), $\hat{V}$ = specific volume (m³/kg). Note: kJ/kg × 0.4303 = Btu/lb_m.

(continued)

EXAMPLE Steam at 10 bar absolute and 190 °C superheat enters turbine at $\dot{m} = 2000$ kg/hr. Turbine is adiabatic, and effluent is saturated steam at 1 bar. Work output of turbine? Found above that kinetic and potential energy changes are small, so neglect here.

$$\dot{W}_s = \Delta\dot{H} = \dot{m}\Delta\hat{H}$$

```
1   Pin = 10.  # bar
2   Tdew = 180. # celsius
3   Tin = 190. + Tdew
4
5   H350= 3159.  # kJ/kg
6   H400= 3264.  # kJ/kg
7
8   Hin = H350 + 20. * (H400 - H350)/(400. - 350.)
9
10  print('Interpolated Hin = {0:5.1f} kJ/kg'.format(Hin))
11
12  Hout = 2675.
13  mdot = 2000. # kg/hr
14
15  Work = mdot * (Hout - Hin)/3600     # kW
16
17  print('Shaft work = {0:5.1f} kW'.format(Work))
```

```
Interpolated Hin = 3201.0 kJ/kg
Shaft work = -292.2 kW
```

9.5   Combined mass and energy balances

- Example 7.6-1

Energy Balance on a One-Component Process

Two streams of water are mixed to form the feed to a boiler. Process data are as follows:

Feed stream 1	120 kg/min @ 30°C
Feed stream 2	175 kg/min @ 65°C
Boiler pressure	17 bar (absolute)

Steam emerges from the boiler through a 6-cm ID pipe. Calculate the required heat input to the boiler in kilojoules per minute if the emerging steam is saturated at the boiler pressure. Neglect the kinetic energies of the liquid inlet streams.
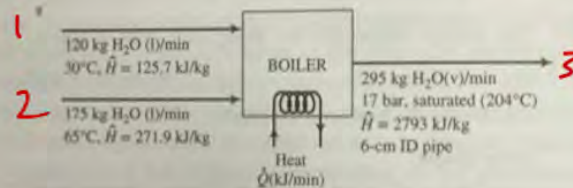
energy balance

$$\Delta \dot{H} + \Delta \dot{E}_k + \cancel{\Delta \dot{E}_p}^{0} = \dot{q} + \cancel{\dot{w}_s}^{0}$$

mass balance $\dot{m}_1 = 120 \ kg/min$

$\dot{m}_2 = \underline{175 \ kg/min}$

$\dot{m}_3 = 295 \ kg/min$

$\hat{H}_1$: $H_2O(\ell)$ 30°C   ~125.7 kJ/kg   (Table B5)

$\hat{H}_2$: $H_2O(\ell)$ 65°C   interpolate on Table B5
~272 kJ/kg

$\hat{H}_3$: 17 bar sat → 204.3°C
$\Delta \hat{H}_3 = 2793.4 \ kJ/kg$

$$\Delta \dot{H} = \sum_{in} \dot{m}\hat{H} - \sum_{out} \dot{m}\hat{H} = 7.61 \times 10^5 \text{ kJ/min}$$

$\dot{E}_{k,out}$: need linear velocity

$$\dot{m} = 295 \text{ kg/min} \atop \hat{U} = 0.1166 \text{ m}^3/\text{kg} \Biggr\} \to 34.40 \text{ m}^3/\text{min} = \dot{U}$$

$$\dot{u} = \dot{U}/\text{Area} \qquad d = 6 \text{ cm} \to A = \pi(3 \text{ cm})^2 = 28.3 \text{ cm}^2$$

$$= 205 \text{ m/s}$$

$$\dot{E}_{k,out} = \frac{1}{2}\left(295 \text{ kg/min}\right)\left(205 \text{ m/s}\right)^2 = 6060 \text{ kJ/min}$$

$$\dot{Q} = \Delta\dot{H} + \Delta\dot{E}_k$$
$$= 7.61 \times 10^5 + 0.061 \times 10^5$$
$$\boxed{= 7.67 \times 10^5 \text{ kJ/min}}$$

- Example 7.6-3

6-3 Simultaneous Material and Energy Balances

Superheated steam at 300°C and 1 atm (absolute) is to be fed to a heat exchanger. It is produced by mixing an available stream of saturated steam at 1 atm discharged from a turbine at a rate of 1150 kg/h with a second stream of superheated steam at 400°C and 1 atm. The mixing may be considered adiabatic. Calculate the amount of superheated steam at 300°C produced and the required volumetric flow rate of the 400°C steam.

Solution Specific enthalpies of the two feed streams and the product stream are obtained from the steam tables and are shown below on the flowchart. (*Note:* We have neglected the small difference between 1 atm and 1 bar.)

$\dot{m}_2 = ?$
$\dot{V}_2 = ?$

$3 \quad \dot{m}_3 = ?$
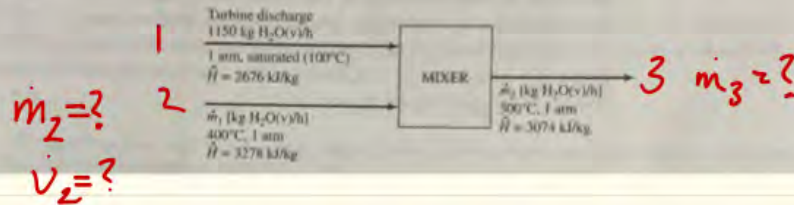
All @ 1 atm, no height change $\rightarrow \Delta E_k = \Delta E_p \approx 0$

mass balance: $\dot{m}_1 + \dot{m}_2 = \dot{m}_3$
$\qquad\qquad 1150 \, kg/hr$

energy balance: $\Delta H = 0 \qquad$ adiabatic

$$\dot{m}_3 \hat{H}_3 - \dot{m}_2 \hat{H}_2 - \dot{m}_1 \hat{H}_1 = 0$$
$\qquad 3074 \qquad 3278 \qquad 2676$

2 equations, 2 unknowns $2\rightarrow$

$\qquad \dot{m}_2 = 2240 \, kg/hr \qquad \dot{m}_3 = 3390 \, kg/hr$

$$\dot{V}_2 = \dot{m}_2 \cdot \tilde{V} \qquad = 6980 \, m^3/h$$
$\qquad\qquad 3.11 \, m^3/kg$

9.6 Mechanical balances

- Examples to this point emphasize changes involving either change in T or chemical composition. Such processes are often dominated by ΔH; work, kinetic, and potential terms are generally small

- Opposite extreme is isothermal, no chemical reaction, e.g. when pumping/moving fluids around

- General energy balance

$$\Delta \dot{U} + \Delta \dot{E}_K + \Delta \dot{E}_V - \dot{q} - \dot{W}_s - \dot{W}_f = 0$$

- If we have a single, incompressible fluid ($\rho = \dot{m}/\dot{V}$ is constant), can simplify energy balance:

$$\frac{1}{2}\dot{m}\Delta u^2 + \dot{m}g\Delta z + \left(\Delta \dot{U} - \dot{q}\right) - \dot{W}_s + \dot{V}\Delta P = 0$$
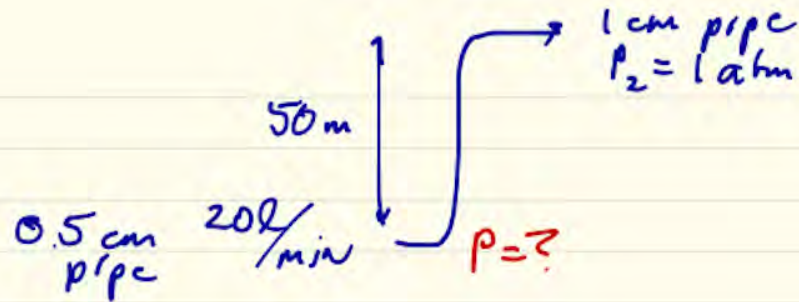
- Third term always has a positive friction component:

$$\frac{1}{2}\dot{m}\Delta u^2 + \dot{m}g\Delta z + \dot{m}\hat{F} - \dot{W}_s + \frac{\dot{m}}{\rho}\Delta P = 0$$

- Neglecting friction and shaft work gives *Bernoulli equation*:

$$\frac{1}{2}\Delta u^2 + g\Delta z + \frac{1}{\rho}\Delta P = 0$$

Example 7.7-1 Pressure required to push $20\,\mathrm{L\,min^{-1}}$ water 50 m uphill from a 0.5 cm pipe into a 1 cm pipe.

$$50\text{m}$$

$$0.5\text{cm pipe} \quad 20\,\ell/\text{min}$$

1 cm pipe
$P_2 = 1\,\text{atm}$

$P = ?$

Required P? Neglect friction.

$$u_{in} = \dot{V}/\text{Area} = 17.0\,\text{m/s} \qquad u_{out} = 4.24\,\text{m/s}$$

$$\Delta u^2 = -270\,\text{m}^2/\text{s}^2$$

$$g\Delta Z = 9.8 \times 50 = 490\,\text{m}^2/\text{s}^2$$

$$\Delta P/\rho = -\left(\frac{\Delta u^2}{2} + g\Delta z\right) = -355\,\text{m}^2/\text{s}^2$$

$$\rho = 1\,\text{g/cm}^3 \qquad \leadsto \Delta P = 3.54\,\text{bar}$$

$$P_{in} = 1\,\text{atm} + 3.54\,\text{bar} = \boxed{4.56\,\text{bar}}$$

- Siphon

Example 7.7-2 Estimate time to siphon 5 gallons out of a gas tank through a 1/4 in i.d. plastic tube. Assume top tank is large, so its surface doesn't move, and hose end is 2.5 ft below upper fluid level.

Example 7.7-2

¼" id tube

$\rho = 50.0 \, lb_m/ft^3$

Friction $= 0.80 \, ft \cdot \left(\frac{lb_f}{lb_m}\right)$

$$\frac{1}{2}\Delta u^2 + g\Delta z + \frac{1}{\rho}\Delta P^{\nearrow 0} + \hat{F} = 0$$

$P_{in} \approx P_{out}$

$g = 32.1 \, ft/s^2$ $g\Delta z = -80.4 \, ft^2/s^2$

$\hat{F} = 0.8 \, ft\left(\frac{lb_f}{lb_m}\right) = 0.8 \cdot (32.174 \, lb_m \cdot ft/s^2) \cdot ft$
$= 25.7 \, ft^2/s^2$

$U_{in} \approx 0$
$\frac{1}{2}u_f^2 = (80.4 - 25.7) \, ft^2/s^2$

$u_f = 10.5 \, ft/s$

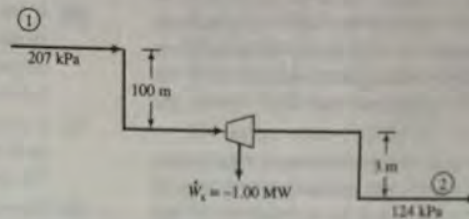$\dot{V} = u_f \cdot A = 10.5 \cdot (0.050 \, in^2) = 3.56 \times 10^{-3} \, ft^3/s$
$= 0.026 \, gal/s$

$5 \, gal/0.026 = \boxed{188 \, s}$

- Water turbine

Hydraulic Power Generation

Water flows from an elevated reservoir through a conduit to a turbine at a lower level and out of the turbine through a similar conduit. At a point 100 m above the turbine the pressure is 207 kPa, and at a point 3 m below the turbine the pressure is 124 kPa. What must the water flow rate be if the turbine output is 1.00 MW?

$$\frac{1}{2}\cancel{\Delta \dot{u}^2}^{\nearrow 0} + g\Delta z + \cancel{\hat{F}}^{\nearrow 0} - \frac{\dot{W}_s}{\dot{m}} + \frac{1}{\rho}\Delta P = 0$$

$$\frac{\dot{W}_s}{\dot{m}} = g\Delta z + \frac{1}{\rho}\Delta P$$

$$g\Delta z = 9.8\,m/s^2 \cdot (-103\,m) = -1009\,m^2/s^2$$

$$\frac{\Delta P}{\rho} = \frac{124 - 207\,kPa}{1\,g/cm^3} = -83\,m^2/s^2$$

$$\dot{m} = -1\,MW/1092\,m^2/s^2 = 915\,kg/s$$
$$= 0.9\,m^3/s$$

10 Energy balances on non-reactive systems

10.1 State function

- Can use any path we want to compute the energy/enthalpy difference between any two well defined points

- $A(T_2, P_2) = A(T_1, P_1) + (A(T_1, P_2) - A(T_1, P_1)) + (A(T_2, P_2) - A(T_1, P_2))$

    - single component, single phase
    - single component, two phase
    - two component, two phase, only one condensible
    - two component, single phase
    - two component, two phase
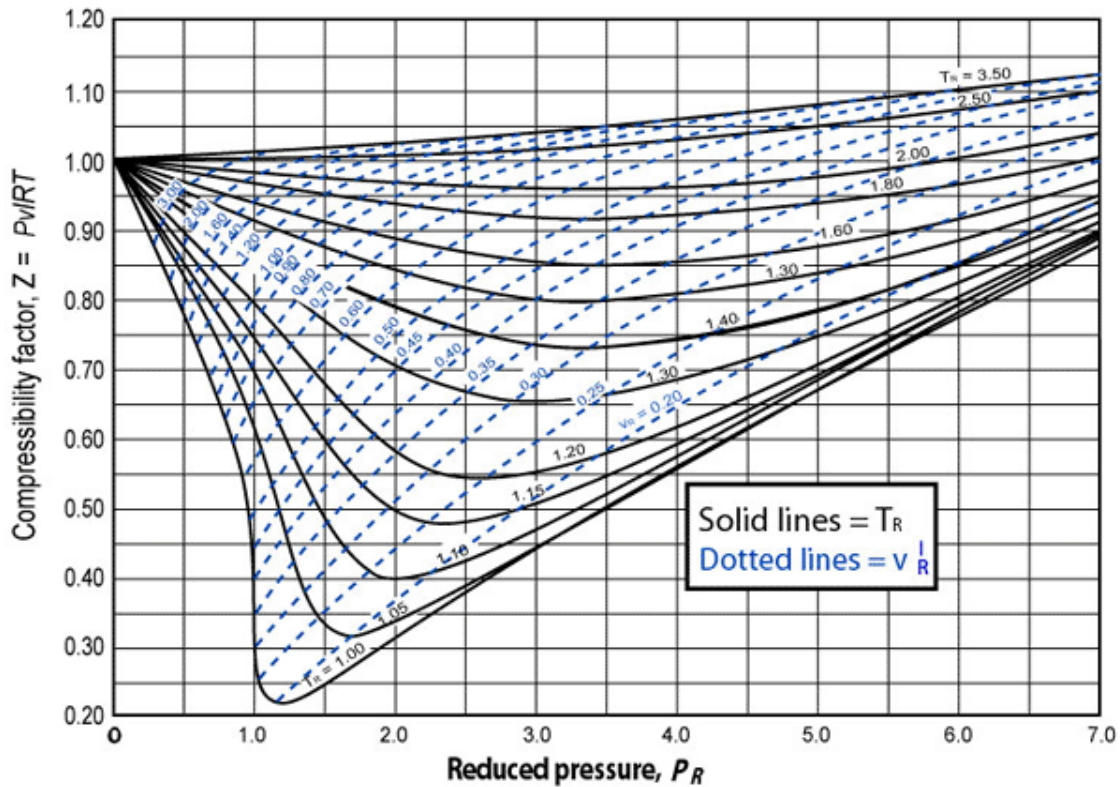
10.2 Isothermal pressure dependence

- Ideal gas energy/enthalpy *only* a function of T

- Real gas has weak dependence, use tabulation or EOS

- The volumes of solids and liquids are roughly independent of P

    - $U(T, P_2) - U(T, P_1) \approx 0$
    - $H(T, P_2) - H(T, P_1) \approx \hat{V} \Delta P$

Is it safe to ignore pressure effect in C_2H_6 (g, 25C, 1 atm) $\longrightarrow$ C_2H_6 (g, 25C, 30 atm)? Consider reduced /T/, /P/.

```
1   Tc = 305.4 # K
2   Pc = 48.2  # atm
3
4   T = 25 + 273 # K
5   P = 30        # atm
6
7   Tr = T/Tc
8   Pr = P/Pc
9
10  print('Tr = {0:5.2f}  Pr = {1:5.2f}'.format(Tr,Pr))
```

```
Tr =  0.98  Pr =  0.62
```

- Generalized compressibility chart

Compressibility factor chart: Compressibility factor, $Z = Pv/RT$ versus Reduced pressure, P_R. Legend: Solid lines = T_R; Dotted lines = v_R^I.

10.3 Isochoric temperature dependence

- Energy stronger function of temperature

- Dependence defined as *heat capacity*, heat flow is *sensible heat*

- Constant volume heat capacity often tabulated as a polynomial

$$C_v(T) = \left(\frac{\partial \hat{U}}{\partial T}\right)_v$$

$$\hat{U}(T_2) - \hat{U}(T_1) = \int_{T_1}^{T_2} C_v(T)dT$$

Heat capacity example. Heat necessary to warm 200 kg N_2O from 20 to 150 °C in constant volume vessel?

$$C_v = a + bT, \quad a = 0.855 \text{kJ/kg C}, \quad b = 9.42 \times 10^{-4} \text{kJ/kg C}^2$$

Integrate! $q = \Delta U = 24200$ kJ

- Heat flow at constant *pressure* similarly related to enthalpy:

$$C_p(T) = \left(\frac{\partial \hat{H}}{\partial T} \right)_p$$

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

- For liquids and solids, $C_p \approx C_v$

- For ideal gas, $C_p = C_v + R$

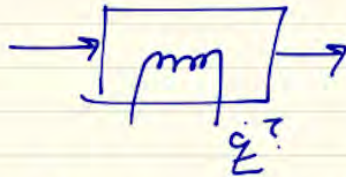- For real gas, need an equation, tabulation, or computer program to evaluate

10.4 No data?

- Correlations, e.g. "Kopp's rule"

- For mixtures, assume additive

$$C_p(T) \approx \sum_i y_i C_{p,i}(T)$$

- Or if dilute, treat as pure

10% CH_4 in air, 2000 ℓ(STP)/min
heat 20 → 300°C

mass balance? $\dot{v}_{in} = \dot{N}_{out} = \dfrac{(1\,atm)(2000)}{R\,(273\,K)} = 89.3\ \dfrac{mol}{min}$

energy balance?

$$\Delta \dot{H} = \dot{q}$$

$$\Delta \dot{H} = \dot{N}\,\Delta \hat{H} = \dot{N}\left(\hat{H}_{out}(300, P_{out}) - \hat{H}_{in}(20, P_{in})\right)$$

1) Assume $\hat{H}$ ~ ind. of P
2) Assume $\hat{H}_{mix} = \sum_i y_i \hat{H}_i$

$$\Delta \dot{H} = \dot{N} \sum_i y_i \left(\hat{H}_i(300) - \hat{H}_i(20)\right)$$

CH_4: $\Delta \hat{H} = \displaystyle\int_{20}^{300} C_p(T)\,dT = 12.07\ kJ/mol$

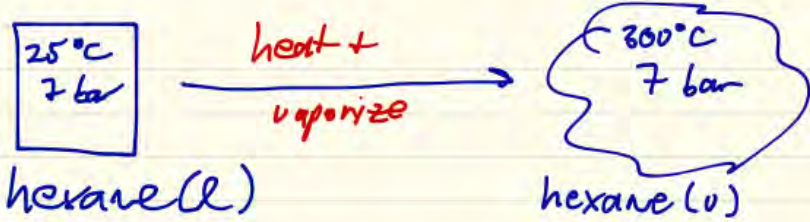$\qquad\qquad C_p = a + bT + \dots$

air: interpolate on Table B8
$\Delta \hat{H}_{air} = 8.37\ kJ/mol$

··· $\boxed{\Delta \dot{H} = \dot{q} = 12.9\ kW}$

10.5 Phase change

- phase change involves change in enthalpy at constant T and P

- termed "latent" heat of transition

  - melting/fusion
  - vaporization/condensation

- tend to be large relative to heat capacity

- like heat capacity, strong function of T, weak function of P

  - recall steam tables

$$\Delta \hat{H}_{vap} = 28.85 \text{ kJ/mol} @ 69°C$$

normal BP

① $\ell(25°C, 7 \text{ bar}) \longrightarrow \ell(25°C, 1 \text{ bar})$

$$\Delta H_1 = \hat{V} \Delta P = -92 \text{ J/mol}$$

② $\ell(25°C, 1 \text{ bar}) \longrightarrow \ell(69°C, 1 \text{ bar})$

$$\Delta \hat{H}_2 = \int_{25}^{69} C_p(T) \, dT = \int_{25}^{69} 0.2163 \, dT = 9.44 \text{ kJ/mol}$$

Table B2

③ $\ell(69°C, 1 \text{ bar}) \longrightarrow v(69°C, 1 \text{ bar})$

$$\Delta \hat{H}_3 = 28.85 \text{ kJ/mol}$$

④ $v(69°C, 1 \text{ bar}) \longrightarrow v(300°C, 1 \text{ bar})$

$$\Delta \hat{H}_4 = \int_{69}^{300} C_{p,v}(T) \, dT \quad \text{Table B2}$$

$$= 47.1 \text{ kJ/mol}$$

⑤ $v(300°C, 1 \text{ bar}) \longrightarrow v(300°C, 8 \text{ bar})$

$$\Delta \hat{H}_5 \approx 0 \qquad \Delta \hat{H} = \sum \Delta \hat{H}_i = 85.5 \text{ kJ/mol}$$

- Recall latent heats can be gotten rigorously from the Clapeyron equation and approximately from Clausius-Clapeyron

- Trouton's rule an example of a *correlation.* Note positive correlation between boiling point and enthalpy

$$\Delta H_v(\text{kJ/mol}) \approx \begin{cases} 0.088 T_b & \text{(K)} & \text{(non-polar liquids)} \\ 0.109 T_b & \text{(K)} & \text{(water and small alcohols)} \end{cases}$$

- many other correlations can be found

- how might you make such a correlation???

10.6 Phase change + mass balance

Partial Vaporization of a Mixture

An equimolar liquid mixture of benzene (B) and toluene (T) at 10°C is fed continuously to a vessel in which the mixture is heated to 50°C. The liquid product is 40.0 mole% B, and the vapor product is 68.4 mole% B. How much heat must be transferred to the mixture per g-mole of feed?

Solution Basis: 1 mol Feed
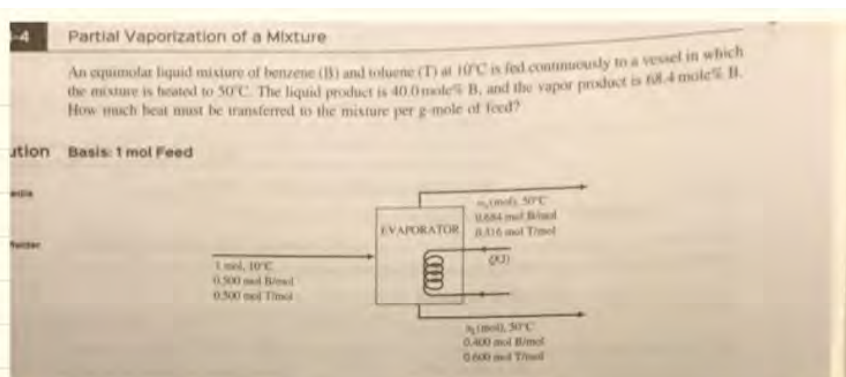
mass balance: 2 unknowns, 2 mass balances

$$\dot{n}_v + \dot{n}_\ell = 1 \text{ mol/t}$$

$$B: \quad 0.5 \cdot 1 = 0.684 \dot{n}_v + 0.4 \dot{n}_\ell \Bigg\} \longrightarrow \quad \dot{N}_v = 0.352$$
$$\dot{N}_\ell = 0.648$$

energy balance 1 unknown, 1 energy balance

$$\Delta \dot{H} = \dot{Q} = \sum_{out} \dot{N}_i \hat{H}_i - \sum_{in} \hat{H}_i$$

in	$\hat{H}$	out	$\hat{H}$
B(ℓ) 10°C	0	B(ℓ) 56°C	$\int C_p dT = 5.3$
T(ℓ) 10°C	0	T(ℓ) 50°C	" = 6.3
	$\longrightarrow$	B(v) 50°C	
		T(v) 50°C	

How could we get p?

$$X_B P_B^{sat}(50) + X_T P_T^{sat}(50) = 164 \text{ mmHg}$$

Benzene normal BP = 80.10°C $\Delta H_v = 30.765 \text{ kJ/mol}$
Toluene   110.62°C   33.47

```python
import numpy as np
import matplotlib.pyplot as plt
from scipy.optimize import fsolve

def PBs(T):
    A = 6.89272; B= 1203.531; C=219.888 # benzene Antoine, C and mmHg
    logP = A - B/(T+C)
```

```
 8          return 10**logP
 9
10  def PTs(T):
11          A = 6.95805; B= 1346.773; C=219.693  # toluene Antoine, C and mmHg
12          logP = A - B/(T+C)
13          return 10**logP
14
15  T = 50.
16
17  xB = 0.4; xT=1-xB
18
19  P = xB*PBs(T) + xT*PTs(T)
20
21  yB = xB*PBs(T)/P; yT = xT*PTs(T)/P
22
23  print('Raoult's Law Pressure = {0:6.1f} mmHg'.format(P))
24  print('Vapor yB,yT)
```

```
Pressure =   163.8 mmHg
0.6625107083992408 0.33748929160075913
```


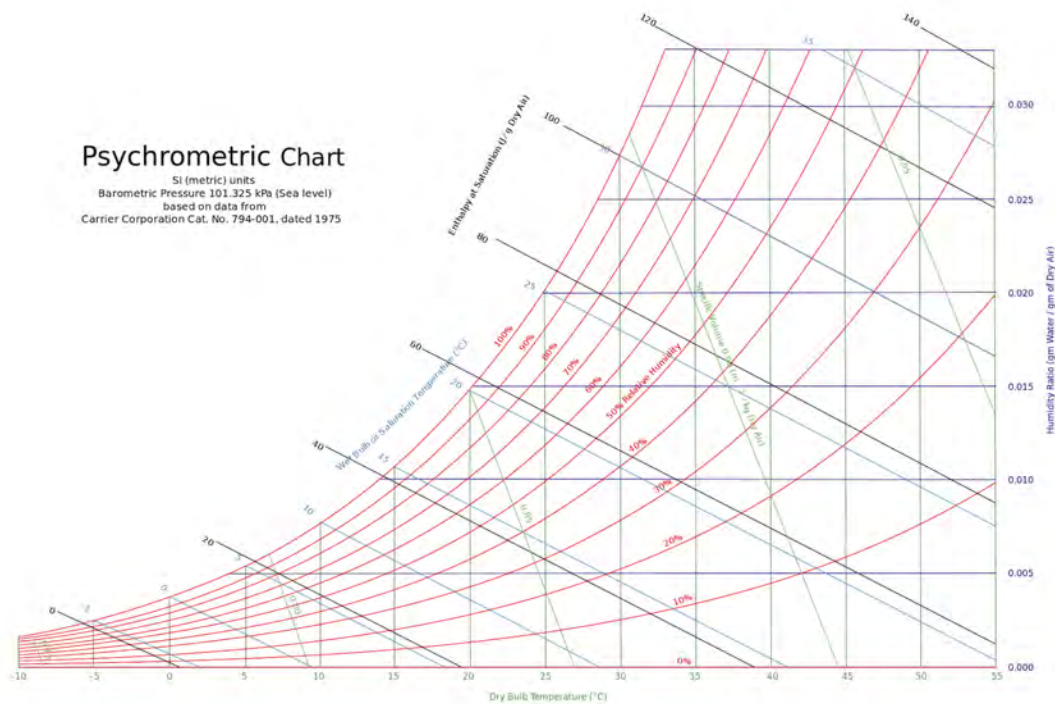$$B(v, 50°C) = \int_{16}^{80} C_{p,\ell} \, dT + \Delta H_v + \int_{80}^{50} C_{p,v} \, dT$$

$$= 37.53 \text{ kJ/mol}$$

ditto T $\Rightarrow$ 42.94 kJ/mol

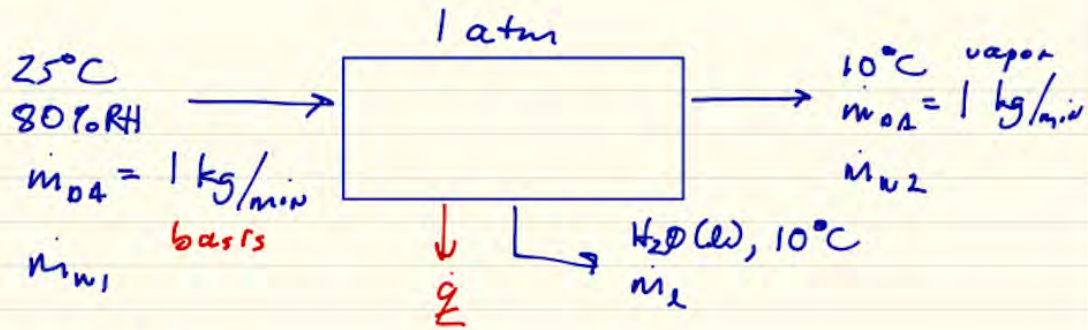$\Rightarrow$ $\Delta H = \sum = 17.7 \text{ kJ/t}$

10.7   Psychrometric charts

- Alternative way of representing VLE data

- Recall phase rule: an air-water vapor mixture has $2 - 1 + 2 = 3$ DOFs, commonly T, P, y

- Hard to measure y, easier to measure "wet bulb temperature," T_{wb}

    - Temperature of a thermometer with its bulb swathed in wet gauze. T differences measures distance of air from saturation.

    - At dew point, $T_{wb} = T$

    - At less than saturation, $T_{wb} < T$

- Psychrometric chart summarizes these relationships and other properties of air-water vapor at fixed total P

Psychrometric Chart
SI (metric) units
Barometric Pressure 101.325 kPa (Sea level)
based on data from
Carrier Corporation Cat. No. 794-001, dated 1975

- Choose T and T_{wb}

    - Find RH

    - Find density

    - Find mixture composition/absolute humidity (all the way to the right)

    - Find dew point (all the way to the left)

    - Find enthalpy of saturated air

    - Find enthalpy at point: follow enthalpy at saturation line; accurate calculations include a small deviation term that we won't worry about

- Paths left and right correspond to cooling and heating air at fixed composition

---

Example: air conditioning. Air at $25\,°C$, 80% RH, and 1 atm is isobarically cooled to $10\,°C$. Calculate the fraction of H_2O vapor that condenses and the heat removal rate to deliver $1\,m^3\,min^{-1}$ of humid air.

---

1 atm

25°C
80% RH
$\dot{m}_{DA} = 1$ kg/min
basis
$\dot{m}_{W1}$

$\downarrow$ $\dot{Q}$ $\rightarrow$ H_2O (l), 10°C $\dot{m}_\ell$

10°C vapor
$\dot{m}_{DA} = 1$ kg/min
$\dot{m}_{W2}$

mass balance

inlet: 80% RH $\Big\}$ $\rightarrow$ $0.016 \frac{g\, H_2O}{g\, DA}$ psychrometric
25°C

$\dot{m}_{V1} = 1 \frac{kg}{min} \cdot 0.016 = 0.016 \frac{kg\, H_2O}{min}$

outlet: 100% RH $\Big\}$ $\rightarrow$ $0.007 \frac{g\, H_2O}{g\, DA}$
10°C

$\dot{m}_{W2} = 1 \frac{kg}{min} \cdot 0.007 \frac{g\, H_2O}{g\, DA} = 0.007 \frac{kg\, H_2O}{min}$

$\dot{m}_\ell = \dot{m}_{W1} - \dot{m}_{W2} = 0.009$ kg H_2O/min

fraction cond $= \frac{0.009}{0.016} = 56\%$

energy balance

inlet: $\hat{H} \sim 65$ kJ/kg DA   psychrometric

outlet vapor: $\hat{H} \sim 30$ kJ/kg DA

water: $\hat{H} = \int_0^{10} C_p\, dT = 42$ kJ/kg H_2O

$$q = \sum_{out} m_i \hat{H} - \sum_{in} m_i \hat{H}$$

$$= 30 \frac{kJ}{kg} \cdot 1 \frac{kg}{min} + 42 \frac{kJ}{kg} \cdot 0.009 \frac{kg}{min}$$

$$- 65 \, kJ/kg \cdot 1 \, kg/min$$

$$= -34.6 \, kJ/min / 1 \, kg \, DA$$

Final air $\sim 0.81 \, m^3/kg \, DA$

$$-34.6/0.81 = \sim 46 \, kJ/m^3 \text{ moist air}$$

10.8 Non-ideal mixtures

- Enthalpies additive in ideal mixture

- Real mixture, $\hat{H}_{soln} \neq \sum \hat{H}_i$

- Differential interactions, $H_2SO_4 + H_2O$, or $NaOH + H_2O$

- Can be tabulated as *integral heat of solution*

  − enthalpy to dissolve 1 mole solute in r moles solvent (draw picture)

Table 1: integral heat of solution of HCl(g) in H_2O (l)

H_2O (mol)	$\Delta\hat{H}(r)_{soln}(298 \text{ K})$
1	-26.22
10	-69.49
100	-73.85
1000	-74.68
10000	-74.99
100,000	-75.10
∞	-75.14

- Table reports $\hat{H}_{soln}$ relative to pure components

- Alternative reference possible, e.g. $\hat{H} = \hat{H}(r) - \hat{H}(\infty)$ references infinite dilution

EXAMPLE solution. Adsorb HCl (g) in H_2O (l). HCl(g) at $100\,°C$ and H_2O at $25\,°C$ fed to produce $1000\,kg\,h^{-1}$ $20.0\%(w/w)$ HCl at $40\,°C$.
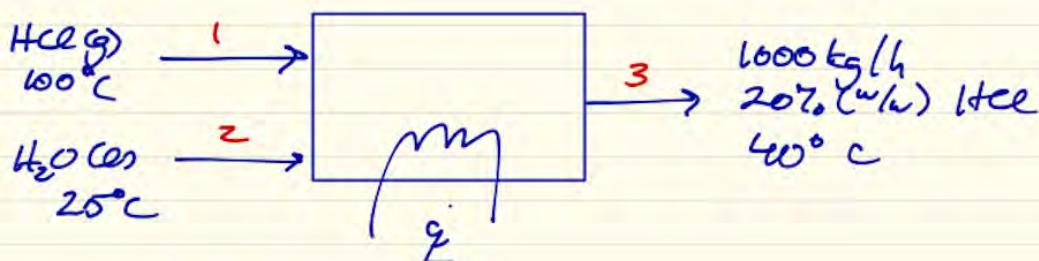
mass balance

exit: $200\ \dfrac{kg}{hr}$ HCl $\times \dfrac{1000\ mol}{36.5\ kg} = 5480\ \dfrac{mol\ HCl}{hr}$

$800\ \dfrac{kg}{hr}$ HCl $\times \dfrac{1000\ mol}{18.0\ kg} = 44{,}400\ \dfrac{mol\ H_2O}{hr}$

energy balance

enthalpy refs : HCl(g) + H_2O @ $25°C$

$\hat{H}_1 = \displaystyle\int_{25}^{100} C_{p,HCl(g)}\,dT = 21.78\ kJ/mol\ HCl$

$\hat{H}_2 = 0$

$\hat{H}_3 : \dfrac{44{,}000\ mol\ H_2O}{5486\ mol\ HCl} = 8.10\ \dfrac{mol\ H_2O}{mol\ HCl}$

$H_2O\ (25) + HCl(25) \longrightarrow HCl(aq)\quad -67.4\ \dfrac{kJ}{mol\ HCl}$
$\qquad\qquad\qquad\qquad r=8.4$

$HCl(aq)\ (25) \longrightarrow HCl(aq)\ (100°C)$
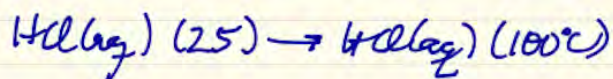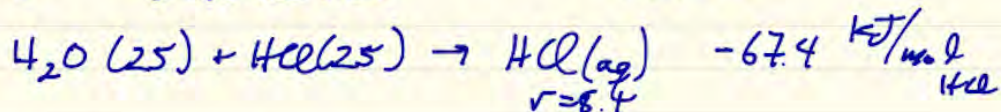
C_p tabulate per mass sol'n $\underline{vs}$ mol fraction

$$X_{HCl} = \frac{5480}{5480 + 44,000} = 0.110 \frac{mol\ HCl}{mol\ soln}$$

$$\Longrightarrow C_p = 0.73\ kcal/_{kg\ °C}$$

Would like this per mole HCl

$$\frac{0.73\ kcal}{kg\ °C} \times \frac{100\ kg}{20\ kg\ HCl} \times \frac{36.5\ kg}{1000\ mol} \times 4.184 = \underset{mol_{HCl}\ °C}{\underset{kJ/}{0.557}}$$

$$\hat{H}(40) - \hat{H}(20) = \int_{20}^{40} 0.557\ dT = 8.36\ kJ/_{mol\ HCl}$$

$$\hat{H}_3 = 8.36 - 67.4 = -59.0\ kJ/_{mol\ HCl}$$

$$\Delta \dot{H} = out - in$$

$$= -59.0 \left(5480\ \frac{mol\ HCl}{hr} \right) - \left[0 + 21.78 \cdot 5480 \right]$$

$$= -3.35 \times 10^5\ kJ/_h = \dot{Q}$$

- Enthalpy-concentration chart, normalized to total amount of solution rather than amount of solute

isotherms

H_2SO_4
77°F

H_2O
32°F

Mass fraction of H_2SO_4
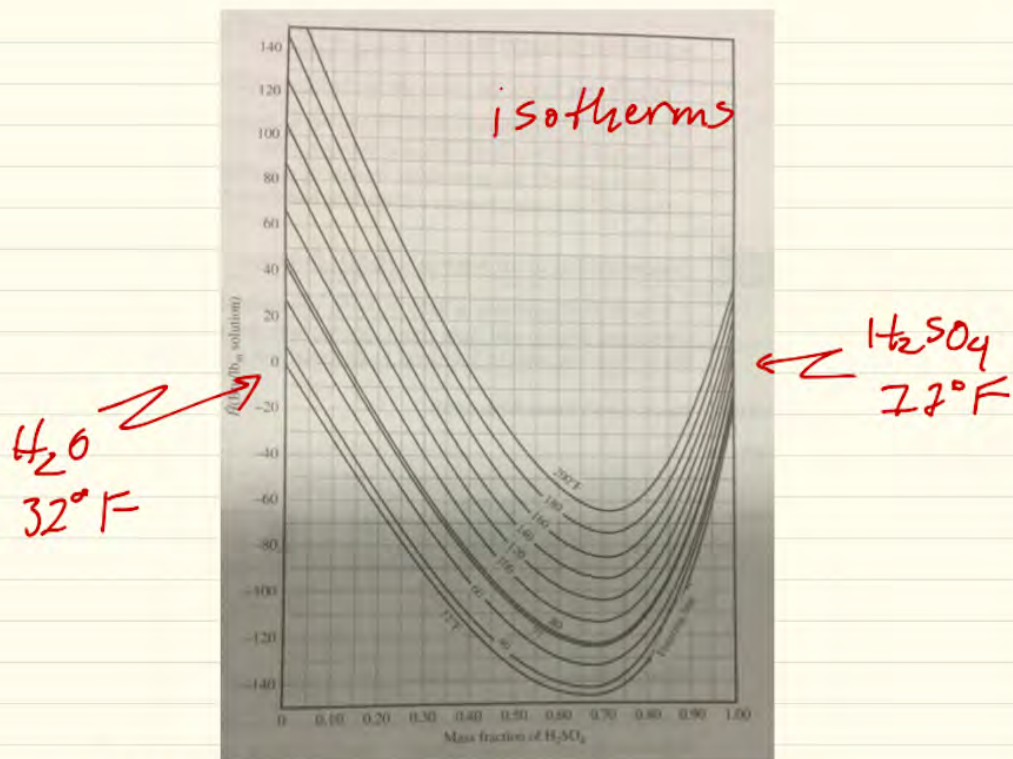
H_2SO_4/H_2O enthalpy/composition

① T change when some amt of water
   mixed w/ given conc H_2SO_4?
      — find comp, draw line

② max T?
      — comp that intersects @ max T
                              isotherm

x_1 $\dot{m}_1$
T_1 $\hat{H}_1$

x_2 $\dot{m}_2$
T_2 $\hat{H}_2$

$\xrightarrow{\;1\;}$
$\xrightarrow{\;2\;}$
$\xrightarrow{\;3\;}$ x_3 $\dot{m}_3$
T_3 $\hat{H}_3$
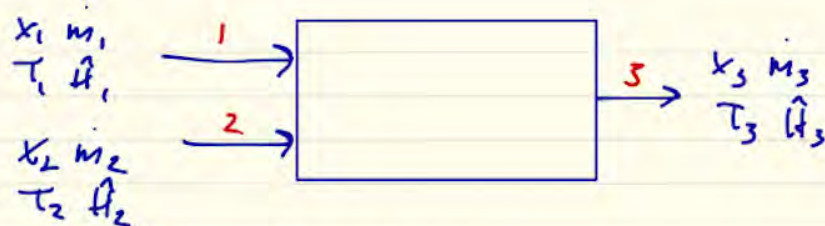
$\underline{\text{total mass}}$ $\quad \dot{m}_3 = \dot{m}_1 + \dot{m}_2$

$\underline{A \text{ mass}}$ $\quad x_1 \dot{m}_1 + x_2 \dot{m}_2 = x_3 \dot{m}_3$
$$= x_3 (\dot{m}_1 + \dot{m}_2)$$
$$\dot{m}_1 (x_3 - x_1) = \dot{m}_2 (x_2 - x_3) \qquad ①$$

$\underline{H \text{ adiabatic}} \qquad \dot{H}_{out} - \dot{H}_{in} = 0$
$$\dot{m}_1 \hat{H}_1 + \dot{m}_2 \hat{H}_2 = \dot{m}_3 \hat{H}_3$$
$$= (\dot{m}_1 + \dot{m}_2) \hat{H}_3$$
$$\dot{m}_1 (\hat{H}_3 - \hat{H}_1) = \dot{m}_2 (\hat{H}_2 - \hat{H}_3) \qquad ②$$

$\dfrac{②}{①}:\quad \dfrac{\hat{H}_3 - \hat{H}_1}{x_3 - x_1} = \dfrac{\hat{H}_2 - \hat{H}_3}{x_2 - x_3} \qquad \begin{array}{l}\text{same}\\ \text{slope!}\end{array}$

$x_1 \qquad x_3 \qquad x_2 \qquad x$

$\hat{H}_1$

$\hat{H}_2$

$\hat{H}_3, T_3$
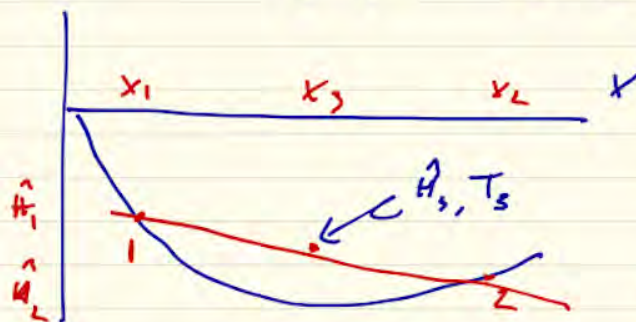
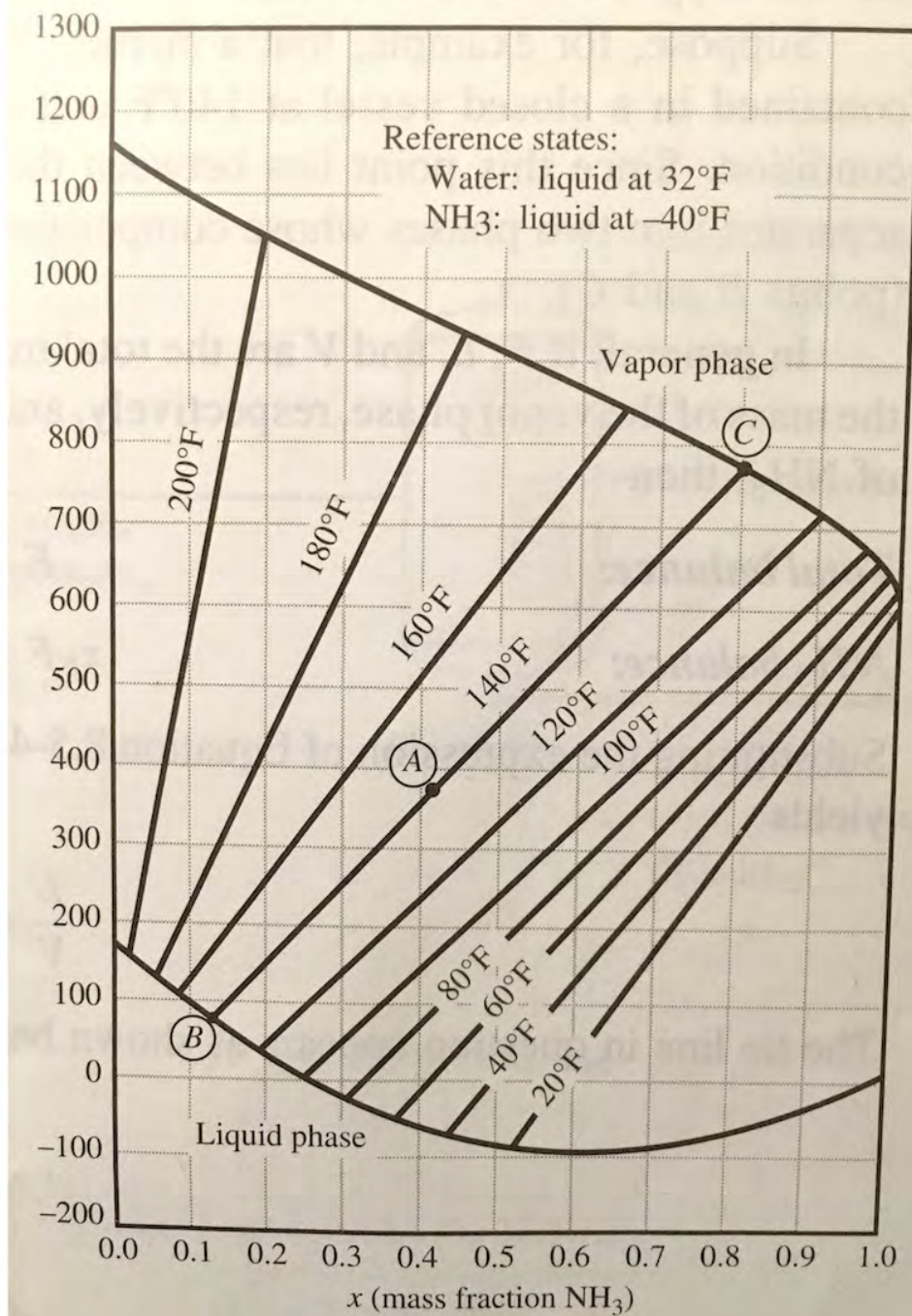$x_3 = \dfrac{x_1 \dot{m}_1 + x_2 \dot{m}_2}{\dot{m}_1 + \dot{m}_2}$

mixture point on the line

10.9 Two-phase, non-ideal mixtures

- Two two-component phases in equilibrium have $2 - 2 + 2 = 2$ DOF, e.g. P and T or some x

  – Determines all other properties, e.g. enthalpies
  – Summarized in enthalpy chart like that above, but now lines for liquid and vapor, connected by "tie lines"

The chart plots enthalpy (y-axis, from -200 to 1300) versus x (mass fraction NH₃) (x-axis, from 0.0 to 1.0). Constant-temperature lines are labeled: 200°F, 180°F, 160°F, 140°F, 120°F, 100°F, 80°F, 60°F, 40°F, 20°F. Regions labeled "Vapor phase" and "Liquid phase". Points labeled A, B, C.

Reference states:
Water: liquid at 32°F
NH3: liquid at –40°F

Vapor phase

Liquid phase

x (mass fraction NH$_3$)

EXAMPLE: Two-phase H$_2$O/NH$_3$ system at 160 F. What are compositions of two phases? Enthalpies? Total enthalpy if 95% of mass is liquid?

- Given total composition of system, "lever rule" tells us relative fractions of two phases (short segment → lots of that fraction)

$$\frac{l}{v} = \frac{x_v - x_T}{x_T - x_l}$$

EXAMPLE: Flash Aqueous NH_3 stream "flashed" to lower pressure. Very simple unit op to lower T and enrich liquid/vapor phases.

NH_3 / H_2O "flash"
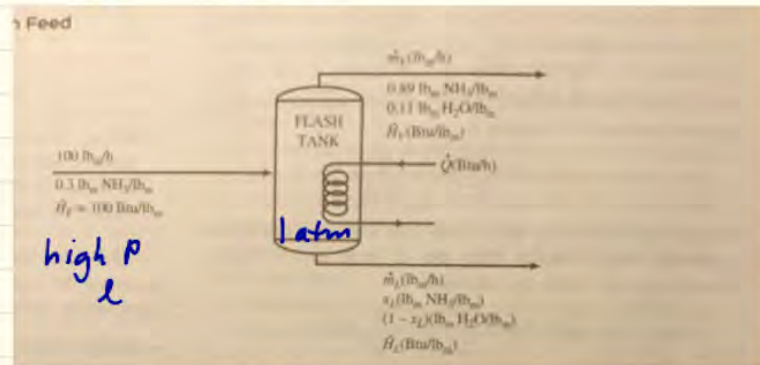
vapor: 1 atm, $89\% (^w/_w)$ NH_3 $\rightarrow$ $T = 120°F$

liquid: tie line $\rightarrow$ 18.5% NH_3

inlet $30\% (^w/w)$ NH_3: __lever rule__

$$\frac{m_l}{m_v} = \frac{89-30}{30-18.5} = 5.13$$

$\dot{m} = 100 \, lb/h \rightarrow \dot{m}_l = 84 \, lb/h \quad \dot{m}_v = 16 \, lb/h$

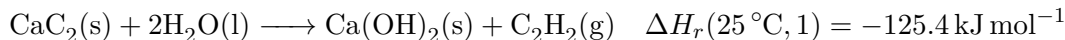$\hat{H}_{in} = 100 \, Btu/lb \quad \hat{H}_L = \sim 45 \quad \hat{H}_v \sim 728 \, BTU/lb$

same ref

$\Delta H = (45)(84) + 728(16) - 100 \cdot 100$
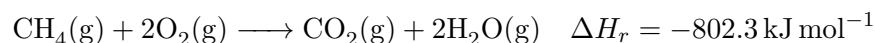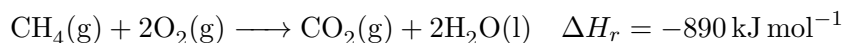
$\quad = 5400 \, Btu/hr = \dot{q}$

11 Energy balances on reactive systems

11.1 Heats of reaction

- Rearrangements of bonds $\rightarrow$ change in enthalpy

- "heat of reaction" defined for specific reaction stoichiometry and (generally) for pure species in specified states

$$CaC_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(s) + C_2H_2(g) \quad \Delta H_r(25\,°C, 1) = -125.4\,\text{kJ mol}^{-1}$$

- Define *endo* and *exothermic*

- ΔH_r function of state and conditions

  − Weak function of P, strong function of T and state

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \quad \Delta H_r = -890\,\text{kJ mol}^{-1}$$

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) \quad \Delta H_r = -802.3\,\text{kJ mol}^{-1}$$

- *Standard* heat of reaction defined as everything in their most stable states at 25 °C and 1 atm

- Enthalpy algebra

$$\sum_j \nu_j A_j = 0 \quad \Delta H_r(T_0, P_0)$$

$$n_j = n_{j0} + \nu_j \xi$$

- For specific amount of reaction

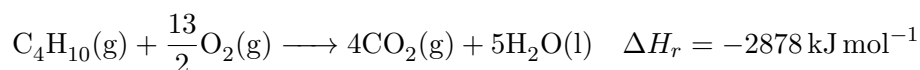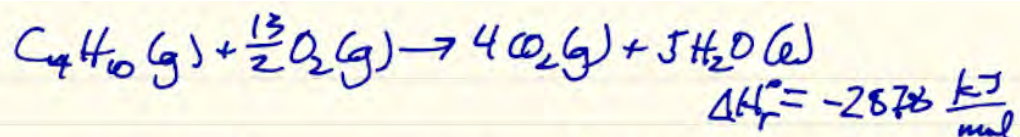$$\Delta H = \Delta H_r \frac{n_j - n_{j0}}{\nu_j} = \Delta H_r \xi$$

- Flow context, same idea

$$\dot{n}_j = \dot{n}_{j0} + \nu_j \xi$$

$$\Delta \dot{H} = \Delta H_r \frac{\dot{n}_j - \dot{n}_{j0}}{\nu_j} = \Delta H_r \xi$$
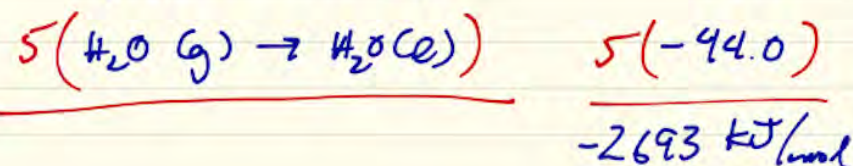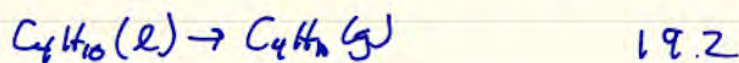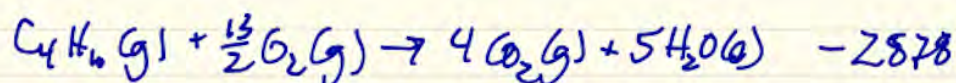

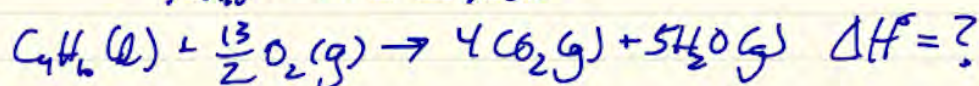**EXAMPLE: Enthalpy of reaction**. Butane combustion:

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l) \quad \Delta H_r = -2878\,\text{kJ mol}^{-1}$$

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(\ell)$$
$$\Delta H_f^\circ = -2878 \frac{kJ}{mol}$$

1) 2400 mol/s CO_2 produced $\Delta \dot{H} = ?$

$$\frac{\dot{N}_{CO_2} - \dot{N}_{CO_2,6}}{\nu_{O_2}} = \frac{2400\ mol/s}{4} = 600\ mol/s = \dot{\xi}$$

$$\Delta \dot{H} = -2878(600) = -1.73 \times 10^6\ kJ$$

2) $\Delta H_{vap, H_2O} = 44.0\ kJ/mol$

   , $C_4H_{10} = 19.2\ kJ/mol$

$$C_4H_{10}(\ell) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g)\quad \Delta H^\circ = ?$$

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(\ell)\qquad -2878$$

$$C_4H_{10}(\ell) \rightarrow C_4H_{10}(g)\qquad\qquad\qquad 19.2$$

$$5(H_2O(g) \rightarrow H_2O(\ell))\qquad\qquad 5(-44.0)$$

$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad\qquad -2693\ kJ/mol}$$

- Example of *Hess's Law* - reaction enthalpies are additive

11.2   Formation and combustion reactions

- In the context of chemical energies, everyone has agreed on a reference state convention

- Define a "formation reaction" to be the (hypothetical) formation of a compound from the constituent elements at 25 °C and 1 atm

- Enthalpy of this reaction defined to the "heat of formation," $\Delta \hat{H}_f$

$$N_2(g) + 2H_2(g) + \frac{3}{2}O_2(g) \longrightarrow NH_4NO_3(s)\quad \Delta \hat{H}_f^\circ = -365.14\,\mathrm{kJ\,mol^{-1}}$$

- By this convention, the enthalpy of formation of the elements is zero

- Heats of formation measured indirectly, widely tabulated (Table B.1)

- Easy to show

$$\Delta H_r^\circ = \sum_j \nu_j \Delta \hat{H}_{f,j}^\circ$$

- Various methods exist to estimate ΔH_f

    - bond additivity, quantum mechanics

- Similar concept applies to combustion reaction, defined as enthalpy of complete combustion with all species at standard conditions

$$\mathrm{C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3\,H_2O(l)} \quad \Delta \hat{H}_c^\circ = -1366.9\,\mathrm{kJ\,mol^{-1}}$$
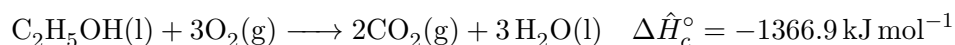
- Similarly tabulated, follows similar additive rule to find enthalpy of any reaction (note sign change):

$$\Delta H_r^\circ = -\sum_j \nu_j \Delta \hat{H}_{c,j}^\circ$$

11.3   Energy balances

- "Heat of reaction" method

    - Choose a convenient reference state for each reactant and product, typically ones for with the heat of reaction is known

    - Construct path reactant state $\rightarrow$ standard reactants $\rightarrow$ standard products $\rightarrow$ product state

    - Easy for single reaction

$$\Delta \dot{H} = \xi \Delta \hat{H}_r^\circ + \sum_{out} \dot{n}_{out} \hat{H}_{out} - \sum_{in} \dot{n}_{in} \hat{H}_{in}$$

- Requires solving for multiple advancements for parallel reactions

$$\Delta \dot{H} = \sum_i \xi_i \Delta \hat{H}_r^\circ + \sum_{out} \dot{n}_{out} \hat{H}_{out} - \sum_{in} \dot{n}_{in} \hat{H}_{in}$$

9.5 Energy Balances on Reactive Processes

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l): \quad \Delta H_r^\circ = -2220 \text{ kJ}$$
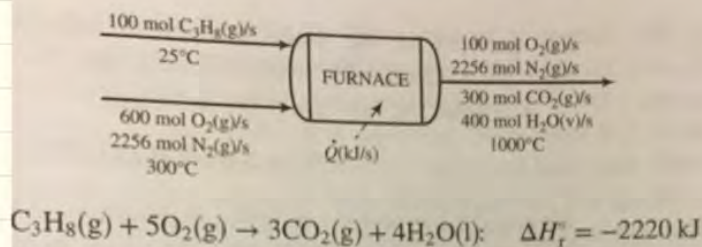
$$\xi = \frac{\dot{N}_{out} - \dot{N}_{in}}{\nu} = \frac{0 - 100}{-1} = 100 \text{ mol/s}$$

References: $C_3H_8(g)$, $O_2(g)$, $N_2(g)$, $CO_2(g)$, $H_2O(l)$
at 25°C and 1 atm

Substance	$\dot{n}_{in}$ (mol/s)	$\hat{H}_{in}$ (kJ/mol)	$\dot{n}_{out}$ (mol/s)	$\hat{H}_{out}$ (kJ/mol)
C_3H_8	100	0	—	—
O_2	600	$\hat{H}_7$	100	$\hat{H}_4$
N_2	2256	$\hat{H}_1$	2256	$\hat{H}_5$
CO_2	—	—	300	$\hat{H}_6$
H_2O	—	—	400	$\hat{H}_7$

$$\hat{H}_2 = \int_{25}^{300} C_{p,O_2} dT = 8.47 \text{ kJ/mol}$$
or tabulation

$$\hat{H}_3 = 8.12 \quad \hat{H}_4 = 32.47 \quad \hat{H}_5 = 30.56 \quad \hat{H}_6 = 48.60$$

$\hat{H}_7$: $H_2O (25°C, \ell) \rightarrow 1000°C, v$
  steam tables — or

$$\int_{?}^{100} C_p \, dT + \Delta H_{vap} + \int_{100}^{1000} C_p \, dT$$

$$\Delta \dot{H} = 100 \text{ mol/s} \cdot (-2220 \text{ kJ/mol}) + \Sigma \cdot \Sigma = -1.26 \times 10^5 \text{ kJ/s}$$

- "Heat of formation" method
    - Choose elements in their standard states as reference

$$\Delta \dot{H} = \sum_{out} \dot{n}_{out} \hat{H}_{out} - \sum_{in} \dot{n}_{in} \hat{H}_{in}$$

References: C(s), H$_2$(g), O$_2$(g), N$_2$(g) at 25°C and 1 atm

Substance	$\dot{n}_{in}$ (mol/s)	$\hat{H}_{in}$ (kJ/mol)	$\dot{n}_{out}$ (mol/s)	$\hat{H}_{out}$ (kJ/mol)
C$_3$H$_8$	100	$\hat{H}_1$	—	—
O$_2$	600	$\hat{H}_2$	100	$\hat{H}_4$
N$_2$	2256	$\hat{H}_3$	2256	$\hat{H}_5$
CO$_2$	—	—	300	$\hat{H}_6$
H$_2$O	—	—	400	$\hat{H}_7$

$$\hat{H}_1 = \Delta \hat{H}^\circ_{f,C_3H_8} = -103.8 \text{ kJ/mol}$$

$$O_2 \begin{cases} \hat{H}_2 = 0 + (\hat{H}(300) - \hat{H}(25)) = 8.47 \text{ kJ/mol} \\ \hat{H}_4 = 0 + (\hat{H}(1000) - \hat{H}(25)) = 32.47 \end{cases}$$

Ditto N$_2$ $\hat{H}_3 = 8.12$ $\hat{H}_5 = 30.56$

$$\hat{H}_6 = \Delta \hat{H}^\circ_{f,CO_2} + (\hat{H}(1000) - \hat{H}(25)) = -344.9 \text{ kJ/mol}$$
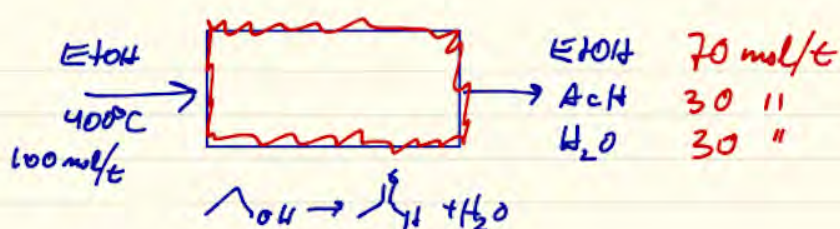$$-393.5 + (48.60 - 0) =$$
$$\quad\text{B.1} \qquad\qquad \text{B.8}$$

$$\hat{H}_7 = \dots \qquad = -204.1 \text{ kJ/mol}$$

$$\Delta \dot{H} = \sum_{out} \dot{n} \hat{H} - \sum_{in} \dot{n} \hat{H}$$
$$= -1.26 \times 10^5 \text{ kJ/mol}$$

- "Heat of formation" method nice for multiple reactions

11.4   Adiabatic reactors

- Sometimes faced with unknown final T

EtOH →[400°C][100 mol/t] [box] → EtOH 70 mol/t
                                    AcH   30 ''
                                    H_2O 30 ''

$\wedge_{OH} \rightarrow \downarrow^{\S}_{H} + H_2O$

① conversion = 30%

$EtOH_{out} = (1-x) EtOH_{in} = 70 \text{ mol/}t$

$AcH = H_2O = 30 \text{ mol/}t$

$\xi = \dfrac{N_j - N_{j°}}{\nu_j} = 30 \text{ mol/}t$

② Outlet T? If adiabatic? rxn method

$\Delta H_r = \Delta H^°_{f, AcH} - \Delta H^°_{f, EtOH} - \Delta H^°_{f, H_2O} = 69.11 \text{ kJ/mol}$

IN: $\hat{H}_{EtOH}(400°C) = \int_{25}^{400} C_{P, EtOH}(\tau)\, d\tau = 33.79 \dfrac{kJ}{mol}$

out: Don't know T!!

$\hat{H}_{EtOH} = \int_{25}^{T} C_p(\tau)\, dT = \hat{H}_{EtOH}(\tau)$ ...

$\Delta \dot{H} + \cancel{\Delta \dot{E}_k}^{°} + \cancel{\Delta \dot{E}_v}^{°} = \cancel{\dot{Q}}^{°} + \cancel{\dot{W}_s}^{°}$ $\Delta \dot{H} = 0$

$\Rightarrow \xi \Delta H_r + 70 \hat{H}_{EtOH}(\tau) + 30 \hat{H}_{H_2}(\tau) + 30 \hat{H}_{AcH}(\tau) - 100(33.79) = 0$

In general non-linear eq. Guess + check.

... T = 185°C   (should put in spreadsheet
                  or python)

- Or combined mass and energy

mass
+
energy
balance

2440 kW

150 mol/s
0.900 mol $C_2H_5OH(v)$/mol
0.100 mol $CH_3CHO(v)$/mol
300°C

REACTOR

$\dot{n}_1$[mol $C_2H_5OH(v)$/s]
$\dot{n}_2$[mol $CH_3CHO(v)$/s]
$\dot{n}_3$[mol $H_2(g)$/s]
253°C

$C_2H_5OH(v) \longrightarrow CH_3CHO(v) + H_2(g)$
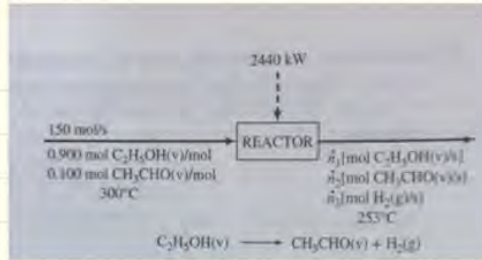
unknowns: 3   equations: 2 mass balances
                                        1 energy balance

__mass balances__   out = in

C: $2\dot{n}_1 + 2\dot{n}_2 = 150(0.9)\cdot2 + 150(0.1)\cdot2 = 300$ mol/s

H: $6\dot{n}_1 + 4\dot{n}_2 + 2\dot{n}_3 = 150(0.9)\cdot6 + 150(0.1)\cdot4 = 870$ mol/s

__energy balance__   in   out

EtOH $\quad \Delta H_f^\circ + \int_{28}^{300} C_p = -212.19 \quad \Delta H_f^\circ + \int_{28}^{253} C_p = -216.81$

AcH $\quad\quad -147.07 \quad\quad\quad\quad\quad\quad\quad\quad -156.90$

$H_2 \quad\quad\quad - \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad 6.595$

$\underline{\Delta\dot{H} = \dot{q}}$ $\quad \dot{n}_1(-216.8) + \dot{n}_2(-156.9) + \dot{n}_3(6.595)$

$\quad\quad\quad -0.9(150)(-212.19) - 0.1(150)(-147.07)$

$\quad\quad\quad = 2440$ kW

3 linear eq, 3 unknowns

$$\begin{pmatrix} 2 & 2 & 0 \\ 6 & 4 & 2 \\ -216.8 & -156.9 & 6.595 \end{pmatrix} \begin{pmatrix} \dot{n}_1 \\ \dot{n}_2 \\ \dot{n}_3 \end{pmatrix} = \begin{pmatrix} 300 \\ 800 \\ -28412 \end{pmatrix}$$

$\dot{n}_1 = 92$ mol/s $\quad \dot{n}_2 = 58 \quad \dot{n}_3 = 43.0 \quad X_{EtOH} = \frac{135-92}{135} = 0.3$

11.5   Other applications

- Heats of solution

- Combustion

12 Transient processes

- General balance around any system or element of a system

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output = input + (generation - consumption) - accumulation

</div>

- In general can vary with time. Each term has units amount/time

$$\dot{F}_{out}(t) = \dot{F}_{in}(t) + r_F(t) - \frac{dF}{dt}$$

- For total mass, simplifies because mass cannot be created or destroyed

$$\dot{m}_{out}(t) = \dot{m}_{in}(t) - \frac{dm}{dt}$$

- Differential equation. Needs a boundary condition to be solvable.

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Balance on a filling tank

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- For chemical reaction, rate related to chemical reaction rate.