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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 H₂O 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 H₂O. Pump circulates at 10 gpm. How long does it take for all the H₂O 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**.

$$3 \text{ cm} + 43 \text{ mm} = 30 \text{ mm} + 43 \text{ mm} = 73 \text{ mm}$$

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

$$44 \text{ m}/11 \text{ s} = 4 \text{ m/s}$$

- 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 H₂O 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 $^{\circ}$ 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

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

- Conversion factors can be ganged. Example: show that

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

3.5 Dimensional homogeneity

As you will learn in Thermodynamics, the internal energy U is related to other thermodynamic quantities by the relation

$$U = TS - PV + \mu N \quad (1)$$

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:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi = E\psi \quad (2)$$

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

$$F = ma$$

- English force units messy

$$1 \text{ lbf} = 32.174 \text{ lb}_m \text{ ft/s}^2$$

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

$$w = mg$$

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

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

Water has a density of $62.4 \text{ lb}_m/\text{ft}^3$. How much does 2 ft^3 of water weigh on the earth? On the moon ($g = 1.62519 \text{ m s}^{-2}$)?

```
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.

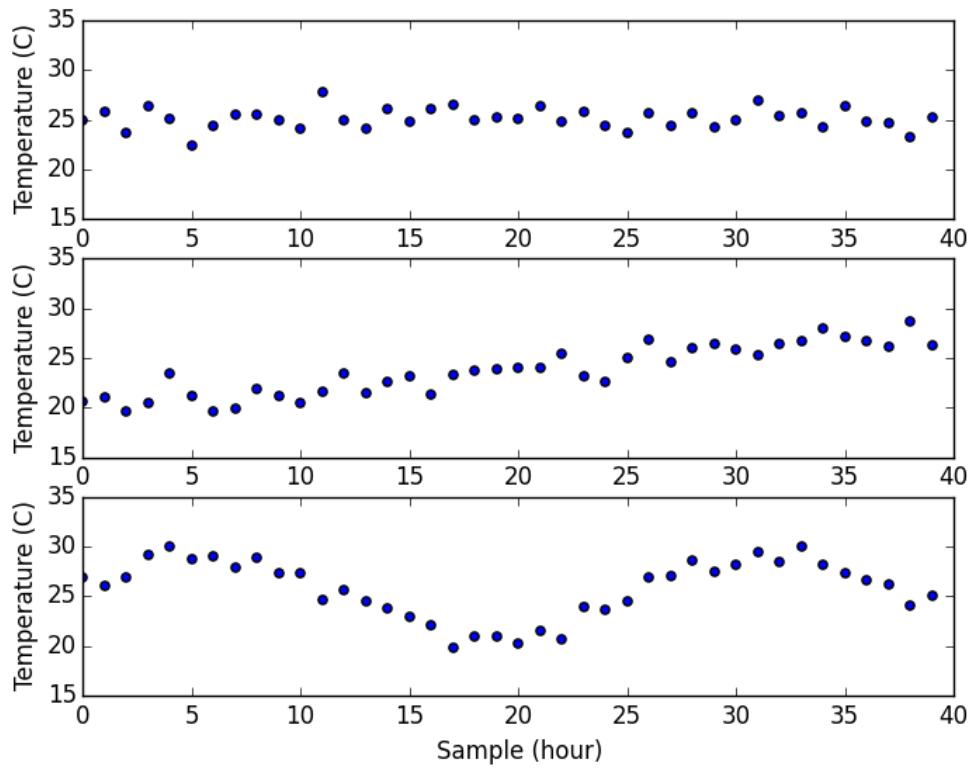
3.7.2 Validating results

- 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

```
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?

```

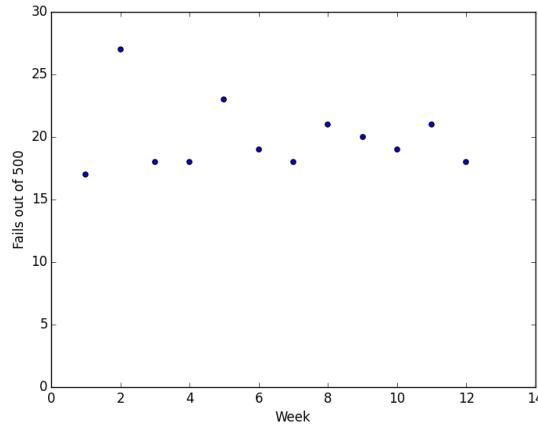
1 import numpy as np
2 import matplotlib.pyplot as plt
3
4 Week = np.array([1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12])
5 Y = np.array([17, 27, 18, 18, 23, 19, 18, 21, 20, 19, 21, 18 ])
6 plt.scatter(Week,Y)
7 plt.ylim(0,30)
8 plt.xlabel('Week')
9 plt.ylabel('Fails out of 500')
10 plt.savefig('../figs/QA.png')
11
12 N = Y.size
13 Sum = np.sum(Y)
14 Average = Sum/N
15
16 Variance = np.sum((Y - Average)**2)/(N-1)
17 StdDev = Variance**0.5
18
19 print('N   Sum   Average   Variance   Std. Dev')
20 print("{0:3d} {1:4d} {2:5.2f} {3:5.2f} {4:5.2f}".format(N,Sum,Average,Variance,StdDev))
21
22 Shutdown = Average + 3 * StdDev
23 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

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

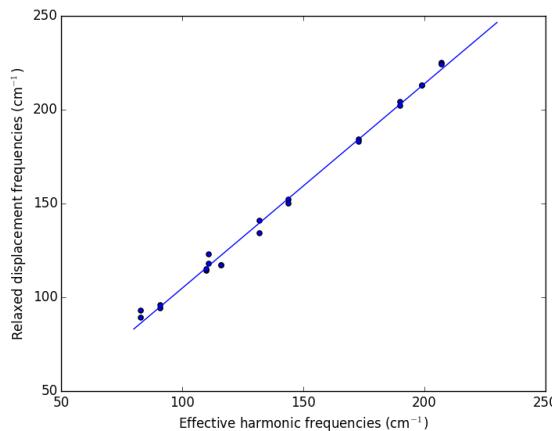
- Linearizing data (e.g. Arrhenius plot). (*Danger:* Error can be skewed by linearizing. Non-linear regression a good alternative.)

```

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 H₂O at 4°C

$$\rho_{\text{H}_2\text{O}}(4\text{ }^{\circ}\text{C}) = 1.00 \text{ g cm}^{-3} = 62.43 \text{ lb}_m/\text{ft}^3 \quad (3)$$

- 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*

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

- **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**

- What is volume of 215 kg Hg at 100°C?
- What is change in height between 20 and 100°C of a 0.25 in diameter Hg cylinder?

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

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

$$h = V/A$$

```

1 import numpy as np
2
3 def V(T):
4     # Volume relative to volume at 0 C
5     a = 0.18182e-3
6     b = 0.0078e-6
7     return 1. + T * (a + b*T)
8 def h(V):
9     area = np.pi * (0.25/12./2.)**2
10    return V/area
11
12 V20 = 0.560
13 h20 = h(V20)
14 V100 = V20 * V(100.)/V(20.)
15 h100 = h(V100)
16 print('Temperature      Volume (ft3)      Height (ft)')
17 print("{0:8.1f}          {1:6.3f}          {2:6.2f}".format(20,V20,h20))
18 print("{0:8.1f}          {1:6.3f}          {2:6.2f}".format(100,V100,h100))
19
20 deltah = h100-h20
21 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 $\{^{12}\text{C}\}$, defined to have a mass of 12
- Avogadro’s number $N_A = 6.022 \times 10^{23}$ number of $\{^{12}\text{C}\}$ 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

The table is a standard periodic table where each element is represented by a box containing its atomic number, symbol, name, and atomic mass. The elements are organized into groups based on their chemical properties. The groups are color-coded: Alkali Metals (pink), Alkaline Earth (orange), Transition Metals (yellow), Basic Metals (green), Semimetal (blue), Nonmetals (light blue), Halogens (purple), Noble Gases (brown), Lanthanides (tan), and Actinides (red). The Lanthanide and Actinide series are also highlighted with their respective colors.

- $\text{CO}_2 = 44 \text{ g/g-mol} = 44 \text{ kg/kg-mol} = 44 \text{ lbm/lb-mol} = 44 \text{ ton/ton-mol}$
- 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 /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 \rightarrow intensive); or use in conversions of extensive \rightarrow 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) H₂SO₄ has a specific gravity of 1.2563. What volume of solution is needed to obtain 500 g-mol H₂SO₄? (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 H₂SO₄ in 35.0%(w/w) solution? (intensive to intensive)

```

1 MWH2S04 = 2*1.008 + 32.0 + 4 * 16.00
2 MWH2O  = 2 *1.008 + 16.00
3
4 molH2S04 = 35.0 / MWH2S04      # mol H2S04
5 molH2O   = (100.-35.0)/ MWH2O # mol H2O
6
7 fracH2S04 = molH2S04/(molH2S04+molH2O)
8
9 print("{0:6.3f}%(mol/mol) H2S04".format(fracH2S04*100))

```

9.006%(mol/mol) H₂S04

- 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% N₂ and 23.3% O₂ by mass?

```

1 # 100 g basis
2 MWN2 = 28.0
3 MW02 = 32.0
4 molN2 = 76.7 / MWN2
5 molO2 = 23.3 / MW02
6 moltot= molN2 + molO2
7 fracN2 = molN2/moltot
8 fracO2 = molO2/moltot
9 MWbar = fracN2*MWN2 + fracO2*MW02
10
11 print("100 g basis")
12 print("      N2      O2")
13 print("MW:      {0:4.2f} {1:4.2f}".format(MWN2,MW02))
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 H₂SO₄ flows into a process unit at 1.25 m³ min⁻¹. S.G. = 1.03.

(a) Mass concentration? (b) mass flow rate of H₂SO₄? (c) mass fraction H₂SO₄?

```

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))

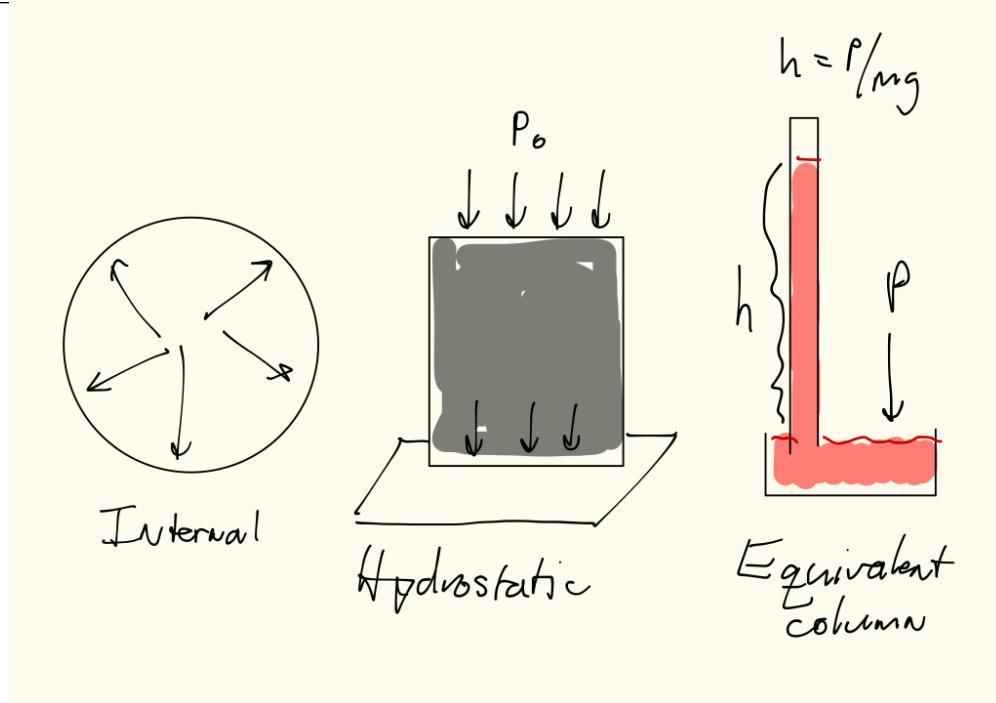
```

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, $\rho_{\text{Hg}} = 13.6 \text{ g cm}^{-3} = 13.594 \text{ kg m}^{-3}(0^\circ\text{C})$

$$h = P/\rho g$$

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

$$P = P_0 + \rho gh$$

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

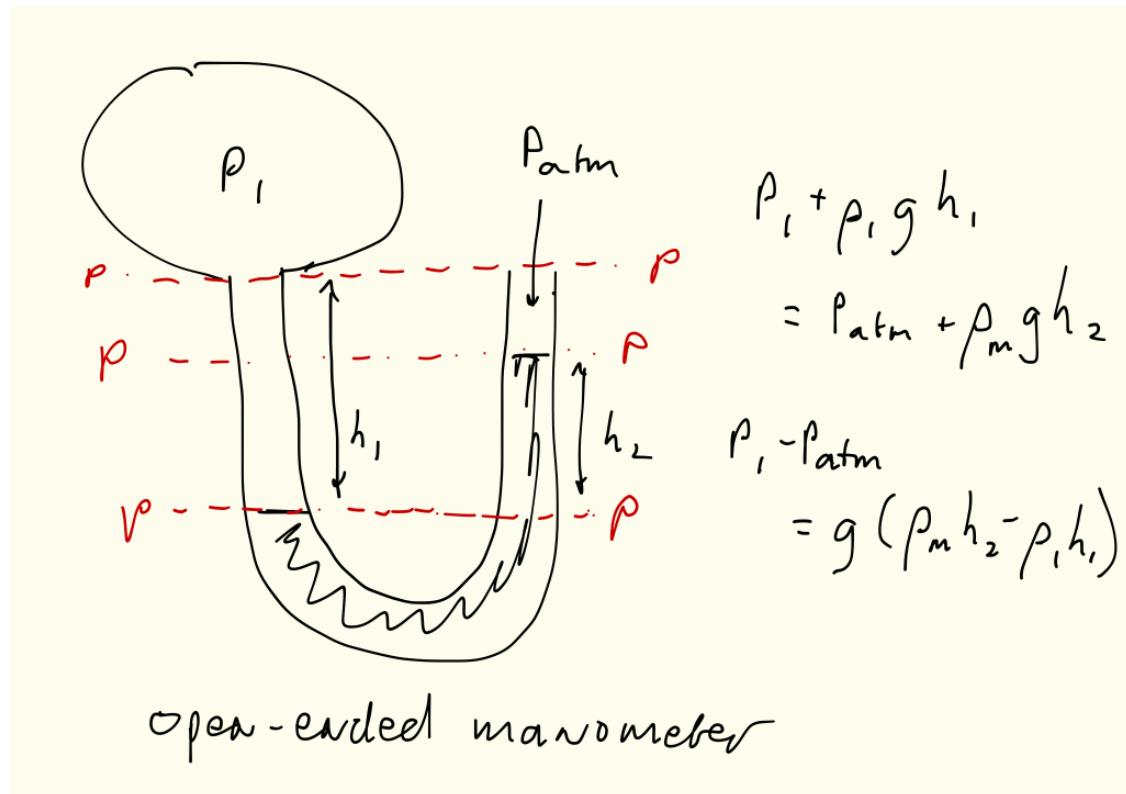
- absolute pressure = pressure relative to a vacuum, always > 0
- gauge pressure difference from atmosphere, can be positive or negative

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

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.

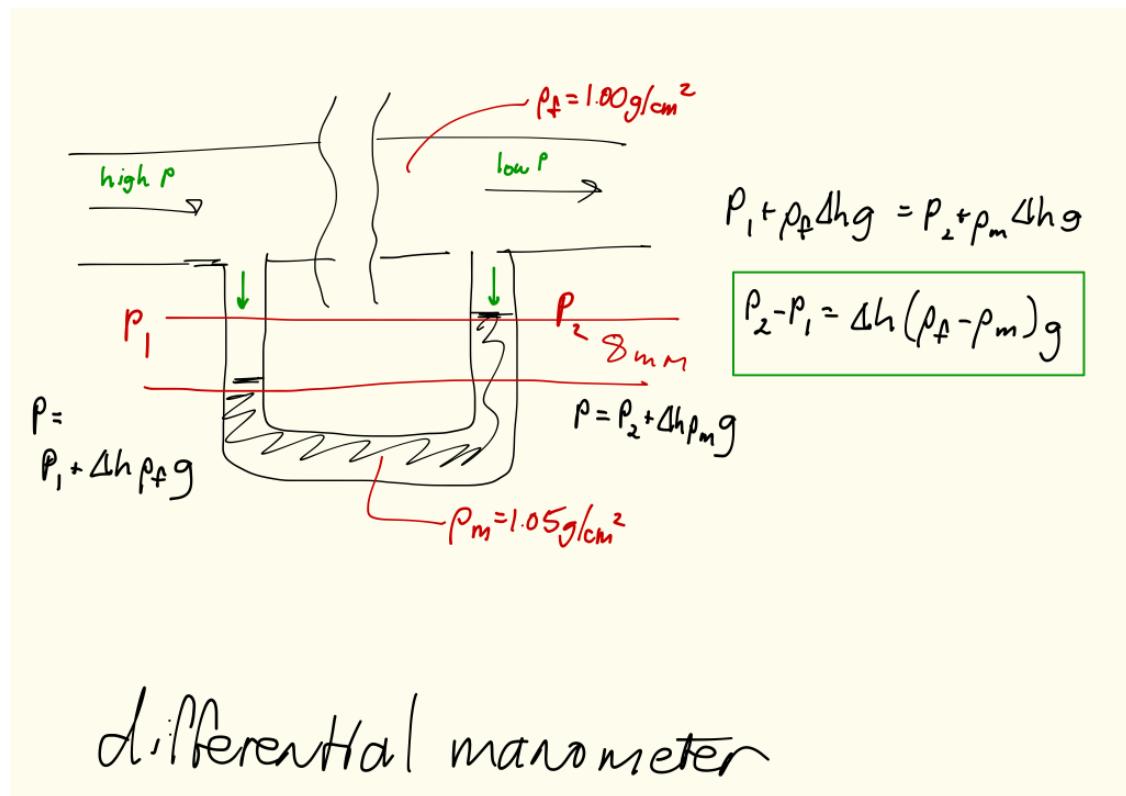
```

1 hatm = 760
2 hgauge = -25    # mmHg
3 habsolute = hgauge + hatm
4 print('Gauge = {0:5.1f}  Abs = {1:5.1f} mmHg'.format(hgauge,habsolute))
5
6 g = 9.807      # m/s2
7 rhoHg = 13600  # kg/m3
8 pgauge = rhoHg * g * hgauge/1000.    # Pa
9 pabsolute = rhoHg * g * habsolute/1000. # Pa
10 print('Gauge = {0:5.0f}  Abs = {1:5.0f} Pa'.format(pgauge,pabsolute))
11
12 pgauge = pgauge * (14.696/ 1.01325e5)  # lbf/in2
13 pabsolute = pabsolute * (14.696/ 1.01325e5) # lbf/in2
14 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



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

```

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/cm^2
7
8 print("\Delta P = {0:5.1f} dyne/cm^2".format(dP))

```

$\Delta P = -39.2 \text{ dyne/cm}^2$

4.6.6 Closed manometer

4.7 Temperature

4.7.1 Scales

- Kelvin: absolute scale, $0 \rightarrow \infty$
- Celsius: $T(^{\circ}\text{C}) = T(K) - 273.15$
- Fahrenheit: $T(^{\circ}\text{F}) = 1.8T(^{\circ}\text{C}) + 32$
- Rankine: absolute scale, $T(^{\circ}\text{R}) = T(^{\circ}\text{F}) + 459.67$
- Use care in using 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

$$\text{output} = \text{input} + \text{generation} - \text{consumption} - \text{accumulation}$$

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?

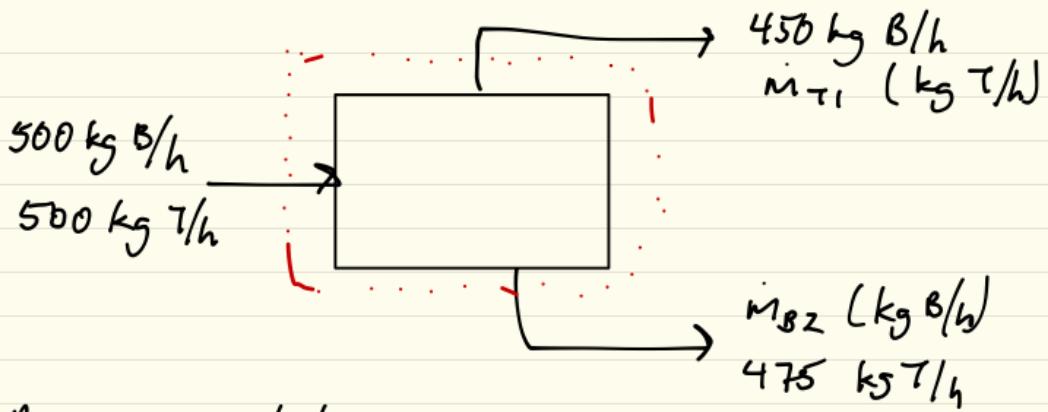
```
1 input = 50000; output=75000; generation=22000; consumption=19000;
2 accumulation =input + generation - output - consumption
3 print('accumulation = {0} people/year'.format(accumulation))
```

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 kg h⁻¹ mixture of 50%(w/w) benzene and toluene is distilled into two streams, one containing 450 kg h⁻¹ benzene and other containing 475 kg h⁻¹ toluene. Solve for unknown flow rates.



Benzene mass balance:

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

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

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

Toluene mass balance

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

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

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

Total mass balance

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

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

5.3 Mass balance procedure

- Illustrates general procedure:

1. Create a flow chart
2. Label all known quantities along each stream

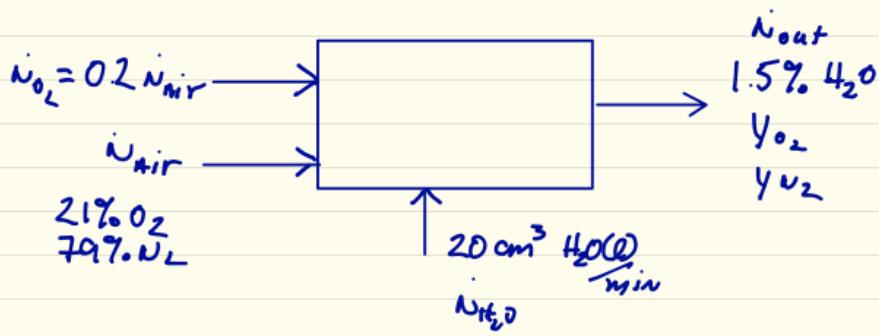
-
- (a) molar or mass flow rates
 - (b) concentrations
3. Label all *unknown* quantities with symbols
 4. Work in only mass or molar quantities
-

- 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

$$n_{H_2O} = 20 \frac{cm^3}{min} \cdot \frac{1g}{cm^3} \cdot \frac{1mol}{18g} = 1.11 mol H_2O/min$$

output = input

$$n_{H_2O} = 0.015 \cdot n_{out}$$

$$n_{out} = 74.1 \text{ mol/min}$$

N₂ balance output = input

$$y_{N_2} \cdot n_{out} = 0.79 n_{air}$$

$$\begin{aligned} \underline{\text{O}_2 \text{ balance}} \quad y_{O_2} \cdot n_{out} &= 0.21 n_{air} + 0.2 n_{air} \\ &= 0.41 n_{air} \end{aligned}$$

unknowns:

$$y_{N_2}, y_{O_2}, n_{air} \quad \text{But} \quad y_{N_2} + y_{O_2} = 0.985$$

3 eqs., 3 unknowns \rightarrow 1 sol/n

Shortcut: total mole balance

output = input

$$n_{out} = n_{H_2O} + n_{air} + 0.2 n_{air}$$

$$74.1 \frac{\text{mol}}{\text{min}} = 1.1 \frac{\text{mol}}{\text{min}} + 12 n_{air}$$

$$n_{air} = 60.8 \text{ mol/min} \quad n_{O_2} = 12.1 \text{ mol/min}$$

$$y_{N_2} = 0.79 \frac{n_{air}}{n_{out}} = 0.65 \quad y_{O_2} = 0.34$$

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 H₂O. Condensate removed at 225 L/min. Calculate flow rate and composition of gas stream leaving condenser.

$$\begin{aligned} n_{\text{Air}} \\ y_{N_2} = 0.79 \\ y_{O_2} = 0.21 \end{aligned}$$

$$n_{H_2O}$$



$$\begin{aligned} z_{H_2O} \\ z_{N_2} \\ z_{O_2} \end{aligned}$$

Unknowns

$$n_{\text{Air}}$$

$$n_{H_2O}$$

$$n_{\text{out}}$$

$$z_{H_2O}$$

$$\begin{matrix} z_{N_2} \\ z_{O_2} \end{matrix}$$

equations²

$$\sum z = 1$$

H_2O balance

N_2 balance

O_2 balance

$$z_{H_2O}$$

Unknowns - equations = 6 - 5 = 1 DOF

Need another piece of info to balance

Range of solutions - potl 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.

```

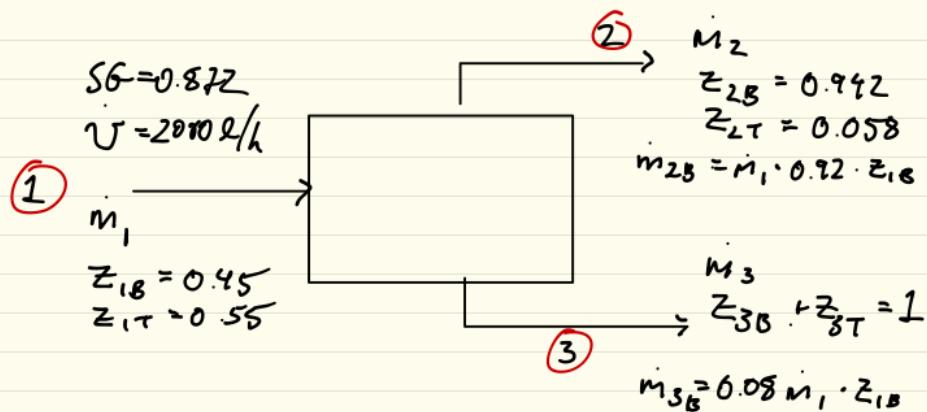
1 # Convert stream 2 to mass basis
2 MWb = 6 * 12.0 + 6 * 1.008
3 Mwt = 7 * 12.0 + 8 * 1.008
  
```

```

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



1. Decision 1: mass or moles? Mass

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

$$5\% \rightarrow 0.058$$

2. Label flowchart.

number inputs + outputs

3. DOF

unknowns: m_1, m_2, m_3, Z_{3B}

equations: 2 mass balances, flow rate, benzene split
Good to go!

4. Do all simple calculations

$$m_1 = V \cdot \rho = 1744 \text{ kg/hr}$$

$$m_{2B} = 0.08 m_1 \cdot Z_{1B} = 722 \text{ kg/hr}$$

$$m_{3B} = 63 \text{ "}$$

$$Z_{2B} = \frac{m_{2B}}{m_2} \rightarrow m_2 = \frac{m_{2B}}{Z_{2B}} = 767 \text{ kg/hr}$$

5. use balances

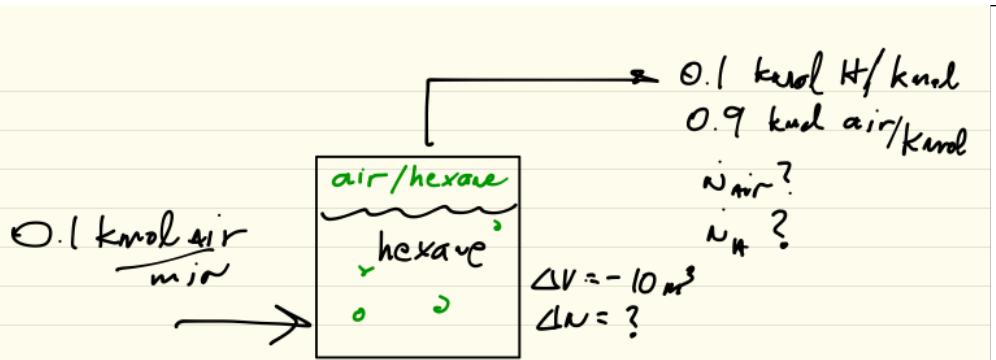
$$m_1 = m_2 + m_3 \rightarrow m_3 = m_1 - m_2 = 977 \text{ kg/hr}$$

6. clean up

$$Z_{3B} = \frac{m_{3B}}{m_3} = 0.064$$

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

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 m³ of the liquid.



air contains hexane, carries some out
time to vaporize 10.0 m^3 hexane?

hexane balance

$$\text{output} = \text{input} + \text{gen} - \text{con} - \text{accum}$$

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

$$\begin{aligned} \text{accum} &= -10 \text{ m}^3 \cdot \rho_{\text{H}_2} \cdot \frac{1}{M_{\text{H}_2}} \cdot \frac{\text{kg}}{\text{m}^3} \\ &= -10 \text{ m}^3 \cdot \left(\frac{659 \text{ kg}}{\text{m}^3} \right) \left(\frac{1 \text{ kmol}}{82.6 \text{ kg}} \right) = -76.45 \text{ kmol H}_2 \end{aligned}$$

$$\text{output} = 76.45 \text{ kmol H}_2 = t \cdot \text{rate}$$

$$(\text{mol}) \quad \left(\frac{\text{mol}}{\text{s}} \right)$$

$$t = \frac{\text{Output}}{n_{\text{H}_2}}$$

Air balance

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

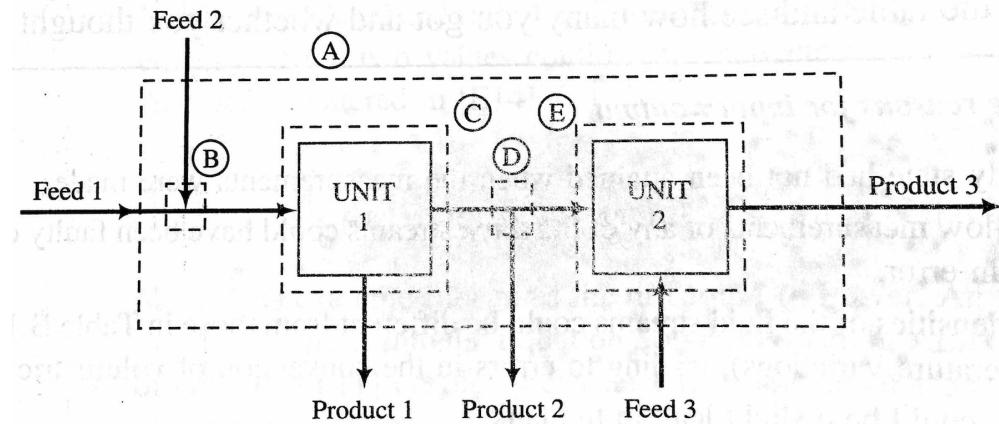
$$n_{\text{H}_2} = n_{\text{air}} \cdot \left(\frac{x_{\text{H}_2}}{x_{\text{air}}} \right) = 0.1 \left(\frac{0.1}{0.9} \right) = 0.111 \frac{\text{kmol H}_2}{\text{min}}$$

$$t = \frac{76.45 \text{ kmol H}_2}{0.111 \frac{\text{kmol H}_2}{\text{min}}} = \underline{\underline{6880 \text{ min}}}$$

-
- Does life always balance? No!

5.4 Multi-unit processes

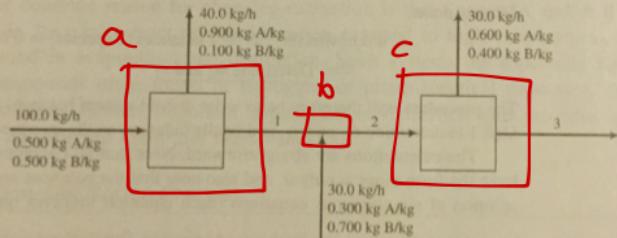
- Real processes will contain multiple sub-processes
- Can write a balance on any portion we can draw a box around



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

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

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

Balance on b

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

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

Balance on c

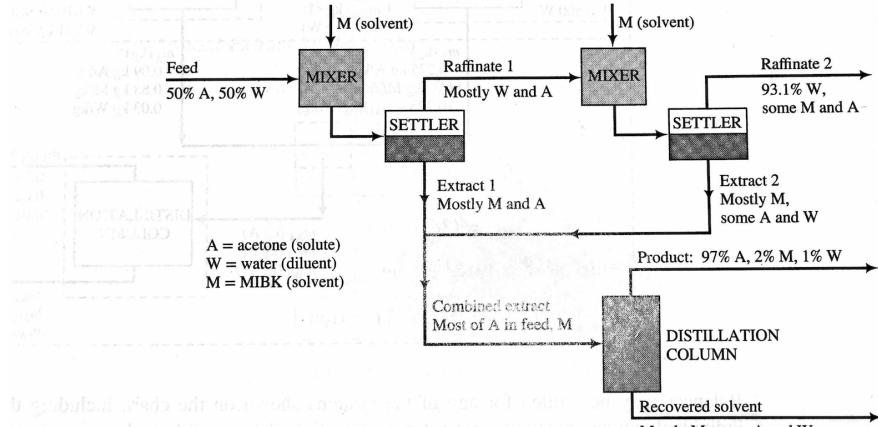
$$m_{3A} = 23 \text{ kg/hr} - 0.6(30) = 5 \text{ kg/hr}$$

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

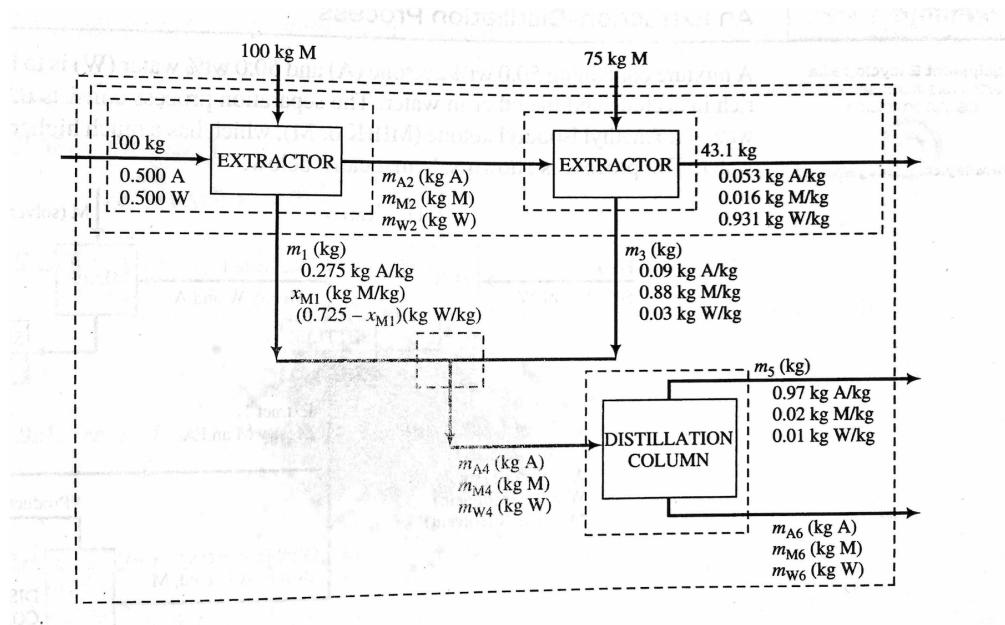
EXAMPLE Multi-stage extraction-distillation.

An Extraction-Distillation Process

- 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.



- ⁷For 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*, Canda 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

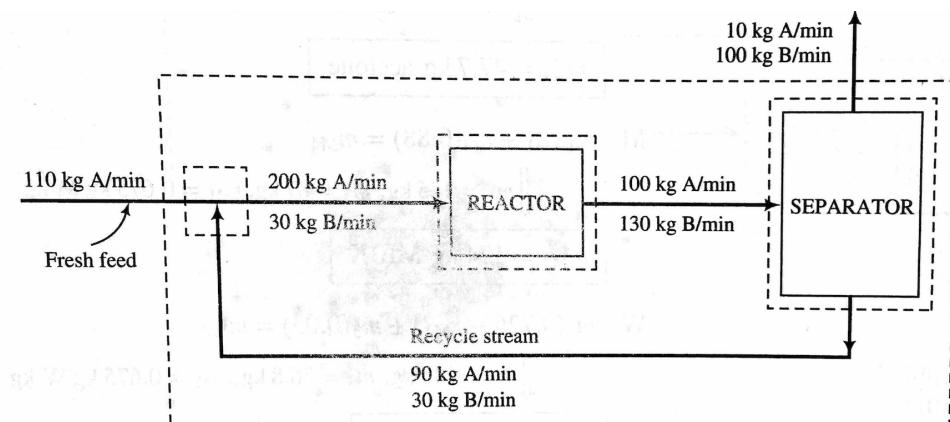
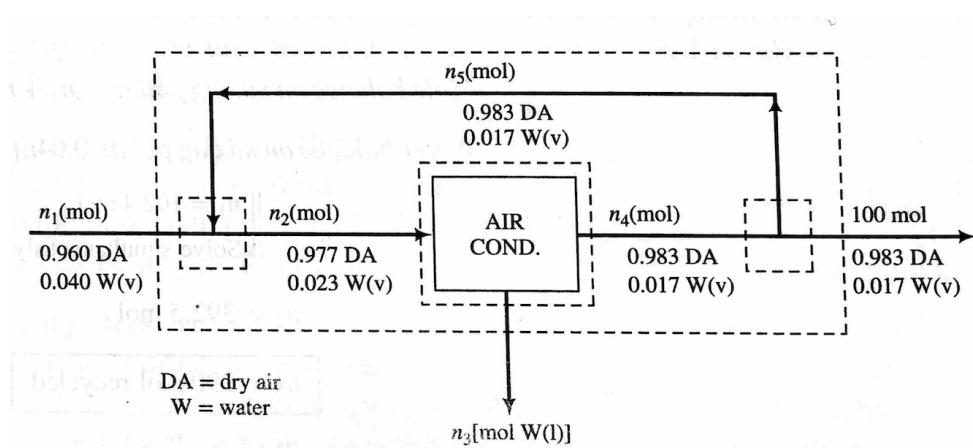


FIGURE 4.5-1 Flowchart of a reactor with separation and recycle of unconsumed reactant.

EXAMPLE Fresh, humid air, 4% H₂O, 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% H₂O. Water leaves as pure water. Find all flow rates.



-
- Mass or moles?
 - Basis? 100 mol/s outlet.
 - Overall balance
 - $\dot{n}_1 = 102.4$, $\dot{n}_3 = 2.4$
 - Mixing point balance
 - $\dot{n}_2 = 392.5$, $\dot{n}_5 = 290$
 - Split point balance
 - $\dot{n}_4 = 100 + \dot{n}_5 = 390$

6 Material balances on reactive systems

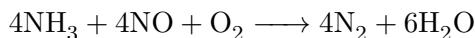
6.1 Revision idea

- First introduce balance using single reaction and molecular balance
- Then introduce extent
- Then multiple reactions...

6.2 Stoichiometry

- Chemical reaction: a transformation between 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?



- 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:

$$n_{tot} = n_{A0} + n_{B0} = n_A + n_B$$
$$n_B = n_{tot} - n_A$$

Plot n_B vs. n_A .

- Illustrate “ICE” procedure for SCR reaction

-
- Reaction advancement/extent ξ :

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

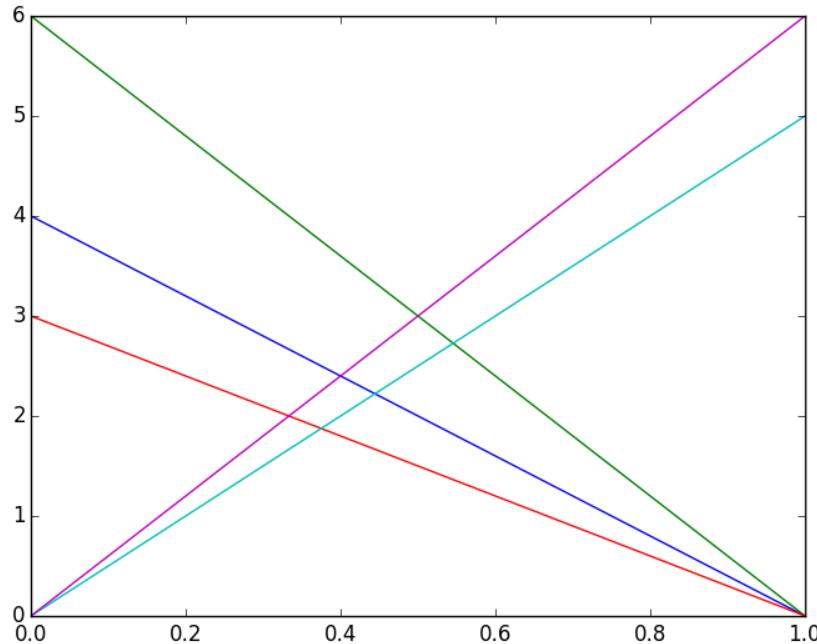
- we define ξ to be extensive, units of “moles” or “moles/time”

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

```

1 import matplotlib.pyplot as plt
2 import numpy as np
3
4 nu = np.array([[-4, -6, -3, 5, 6]])
5 n0 = np.array([[4, 6, 3, 0, 0]])
6
7 xi = np.linspace(0,1)
8
9 n = np.transpose(n0) + np.dot(np.transpose(nu),xi)
10
11 for i in range(5):
12     plt.plot(xi[0],n[i])
13
14 plt.savefig('../figs/advancement1.png')

```



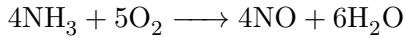
- Must have $n_j \geq 0$ for all j , or $\xi \leq -\frac{n_{j0}}{\nu_j}$:

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

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

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

Air oxidation of NH₃.



0.1 g/s NH₃ and 0.95 g/s air flow into a reactor. What is limiting reagent? How much NH₃ at completion?

```

1 MWNH3 = 17; MW02 = 32; MWN2 = 28;
2 MWair = 0.79 * MWN2 + 0.21 * MW02
3
4 mNH30 = 0.1; mair0 = 0.95
5 nNH30 = mNH30 / MWNH3
6 n020 = (mair0 / MWair) * 0.21
7
8 print('ndot NH3 = {0:6.4f}  ndot 02= {1:6.4f} mol/s\n'.format(nNH30,n020))
9
10 nuNH3 = -4.0; nu02 = -5.0;
11
12 xiNH3 = -nNH30/nuNH3; xi02 = -n020/nu02
13
14 print('ndot/nu NH3 = {0:7.5f}  ndot/nu 02 = {1:7.5f}\n'.format(xiNH3,xi02))
15
16 print('02 limiting\n')
17
18 xilim = xi02
19
20 nNH3 = nNH30 + nuNH3 * xilim; n02 = n020 + nu02 * xilim
21
22 print('ndot NH3 = {0:7.5f}  ndot02 = {1:7.5f}\n'.format(nNH3,n02))
23
24 fNH3 = 100*(nNH30 - nNH3)/nNH30
25 print('Fraction NH3 consumed = {0:4.2f}%'.format(fNH3))
```

ndot NH3 = 0.0059 ndot 02= 0.0069 mol/s

ndot/nu NH3 = 0.00147 ndot/nu 02 = 0.00138

02 limiting

ndot NH3 = 0.00035 ndot02 = 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:

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

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

-
- X is unitless and (for forward reaction) $0 \leq X \leq 1$
 - all n_j can be written in terms of X :

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

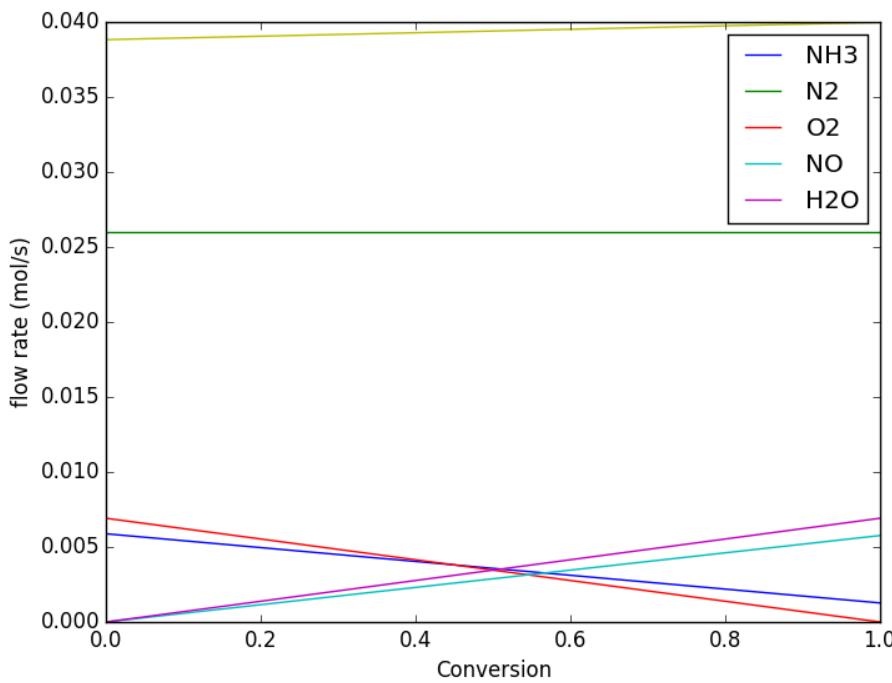
EXAMPLE NH₃ oxidation goes to 50% completion. What is composition of exit stream?

```

1 import numpy as np
2 import matplotlib.pyplot as plt
3
4 species = ('NH3', 'N2', 'O2', 'NO', 'H2O')
5 nu = np.array([-4, 0, -6, 5, 6])
6
7 MWNH3 = 17; MWO2 = 32; MWN2 = 28;
8 MWair = 0.79 * MWN2 + 0.21 * MWO2
9
10 mNH30 = 0.1; mair0 = 0.95
11 nNH30 = mNH30 / MWNH3
12 nO20 = (mair0 / MWair) * 0.21
13 nN20 = (mair0 / MWair) * 0.79
14
15 n0 = np.array([[nNH30, nN20, nO20, 0, 0]])
16
17 X = 0.5
18
19 n = n0 - (nu/nu[0,2]) * n0[0,2] * X
20
21 print(species)
22 print(n, ' mol/s')
23
24 X = np.array([np.linspace(0,1)])
25
26 n = np.transpose(n0) - np.dot(n0[0,2]*np.transpose(nu/nu[0,2]),X)
27
28 ntot= 0
29
30 for i in range(5):
31     plt.plot(X[0],n[i],label=species[i])
32     ntot = ntot + n[i]
33 legend = plt.legend()
34
35 plt.plot(X[0],ntot)
36 plt.xlabel('Conversion')
37 plt.ylabel('flow rate (mol/s)')
38
39 plt.savefig('../figs/conversion1.png')

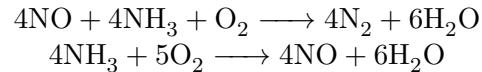
```

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



6.4 Multiple reactions

- NH₃ oxidation and SCR together, for example, are parallel reactions
- competition between the two
- each species has a stoichiometric coefficient in each parallel reaction



$$\begin{aligned} -4\text{NO} - 4\text{NH}_3 - 1\text{O}_2 + 4\text{N}_2 + 6\text{H}_2\text{O} &= 0 \\ 4\text{NO} - 4\text{NH}_3 - 5\text{O}_2 + 0\text{N}_2 + 6\text{H}_2\text{O} &= 0 \end{aligned}$$

- reaction expression:

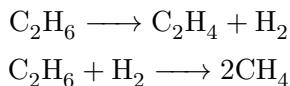
$$\begin{pmatrix} & & & & \\ -4 & -4 & -1 & 4 & 6 \\ 4 & -4 & -5 & 0 & 6 \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \\ A_3 \\ A_4 \\ A_5 \end{pmatrix} = 0 \quad (5)$$

- In general $\sum_j \nu_{ij} A_j = 0$
- each parallel reaction has its own advancement ξ_i (i for reactions, j for species)

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

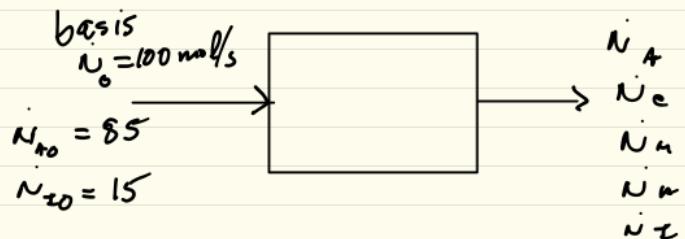
- *yield* defined as amount (molar) of desired product over maximum possible amount of desired product
- *selectivity* (often) defined as amount of desired product over amount of undesired. Be careful with this one.

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



Solve to work in molar flows

$$\text{C}_2\text{H}_6 : \alpha \quad \text{C}_2\text{H}_4 : e \quad \text{CH}_4 : m \quad \text{H}_2 : h \quad \text{Inert} : I$$



inert: $N_2 = N_h = 15 \text{ mol/s}$ ✓

ethane: $N_4 = N_{40} - \xi_1 - \xi_2$

ethylene: $N_e = \xi_1$

ethylene yield: $N_e = 0.471(85.0)$ ← max possible ethylene
 $= 40.0$ ✓
 $\approx \xi_1$

ethane conversion: $N_a = (1 - 0.501)N_{40}$ ✓
 $= 42.4 \text{ mol/s}$

$\xi_2 = 2.6$ ↩ $= N_{40} - \xi_1 - \xi_2$

methane: $N_m = 2\xi_2 = 5.2 \text{ mol/s}$

hydrogen: $N_h = \xi_1 - \xi_2 = 37.4 \text{ mol/s}$

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

$$= n_{z0} n_{h0} + \xi_1 \\ = 140 \text{ mol/s}$$

$$y_j = \frac{n_j}{n_{tot}} \quad y_e = \frac{40}{140} = 0.286 \quad y_z = 10.7\% \\ y_m = \frac{5.2}{140} = 0.037 \quad y_H = 0.303 \\ y_{H_2} = 0.267$$

Selectivity: $\frac{y_e}{y_m} = \frac{40.0}{5.2} = 7.7$

- 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:

$$\text{output} = \text{input} + \text{generation} - \text{consumption} - \text{accumulation}$$

- 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*

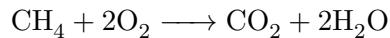
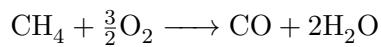
-
- No generation or consumption; $input = output$

C balance: $2\dot{n}_{A0} = 2\dot{n}_A 2\dot{n}_e + \dot{n}_m$

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 CO₂:



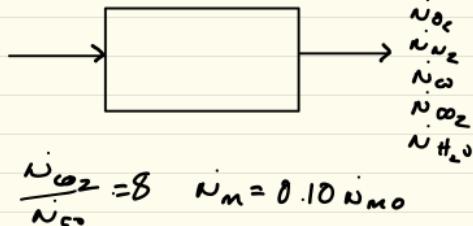
Feed contains 7.8%(mol/mol) CH₄ and balance air (19.4% O₂, 72.8% N₂). Methane conversion is 90.0% and exit contains 8 mol CO₂/CO. Calculate composition of exit stream.

100 mol/s basis

$$N_{MO} = 7.8$$

$$N_{N_2O} = 72.8$$

$$N_{O_2} = 19.4$$



non-reactive: $IN = OUT$

$$N_{N_2} = N_{N_2O} = 72.8 \text{ mol/s}$$

Atomic: $IN = OUT$

$$C: \quad N_{MO} = N_m + N_{CO} + N_{CO_2}$$

$$H: \quad 4N_m = 4N_m + 2N_{H_2O}$$

$$O: \quad 2N_{O_2} = 2N_{O_2} + N_{CO} + 2N_{CO_2} + N_{H_2O}$$

$$C + Z \text{ knowns} \rightarrow N_{CO} = 0.78 \quad N_{CO_2} = 6.24$$

$$H \rightarrow N_{H_2O} = 2(0.9) \cdot N_{MO} = 14.0$$

$$O \rightarrow N_{O_2} = 5.75$$

Advancement $OUT = IN + gen - consump$

$$N_m = N_{MO} - \xi_1 - \xi_2$$

$$N_{CO} = \xi_1, \quad N_{CO_2} = \xi_2 \rightarrow \frac{\xi_2}{\xi_1} = 8$$

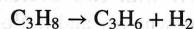
$$\xi_1 = \frac{N_{CO} - N_m}{9} = 0.087 \quad \xi_2 = 0.693$$

6.6 Reactive balances on multi-unit processes

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

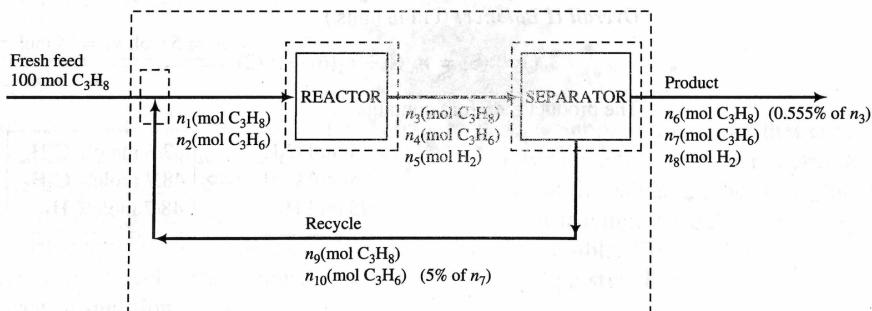
Dehydrogenation of Propane

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



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



Overall

3 unknowns - 2 atomic - 95% conv. ✓

$$N_6 = 0.05(100 \text{ mol/s}) = 5 \text{ mol/s}$$

$$C: 3(100) = 3N_6 + 3N_7 \quad N_7 = 95 \text{ mol/s}$$

$$H: 8(100) = 8N_6 + 6N_7 + 2N_8 \quad N_8 = 95 \text{ mol/s}$$

$$\gamma_i = \frac{N_i}{N_{\text{tot}}} \quad \begin{matrix} 2.6 \\ \diagdown \\ \approx \end{matrix} \quad \begin{matrix} 48.7 \\ \diagup \\ H_2 \end{matrix} \quad \begin{matrix} 48.7 \\ \diagup \\ H_2 \end{matrix}$$

Separator (not reactive)

5 unknowns - 3 species - 2 constraints ✓

$$N_5 = N_8 = 95 \text{ mol/s}$$

$$N_6 = (0.555 \times 10^{-2}) u_s \quad N_8 = 901 \text{ mol/s}$$

$$N_{10} = 0.05 N_7 \quad N_{10} = 4.75 \text{ mol/s}$$

$$\wedge: u_3 = u_6 + u_9 \quad N_9 = 896 \text{ mol/s}$$

$$\wedge: N_4 = u_7 + N_{10} \quad N_4 = 100 \text{ mol/s}$$

Mixing point: (not reactive)

2 unknowns - 2 species

$$N_2 = N_{10} = 4.75 \text{ mol/s}$$

$$N_1 = N_5 + 100 = 996 \text{ mol/s}$$

$$\text{Recycle ratio: } \frac{N_7 + N_{10}}{100} = 9.00$$

$$\boxed{\text{1 pass conversion: } \frac{N_1 - N_3}{N_1} = 9.6\%}$$

- 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

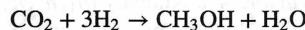
- Recycle example above works because system is continuously fed pure reactant
- If system fed unreactive species, unless it is removed at same rate it enters, it will build up and eventually kill the process
- Purge stream used to bleed off that species

Purge Example CO₂ to methanol. Single pass 60.0% H₂ conversion.

4.7 Balances on Reactive Processes 155

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:

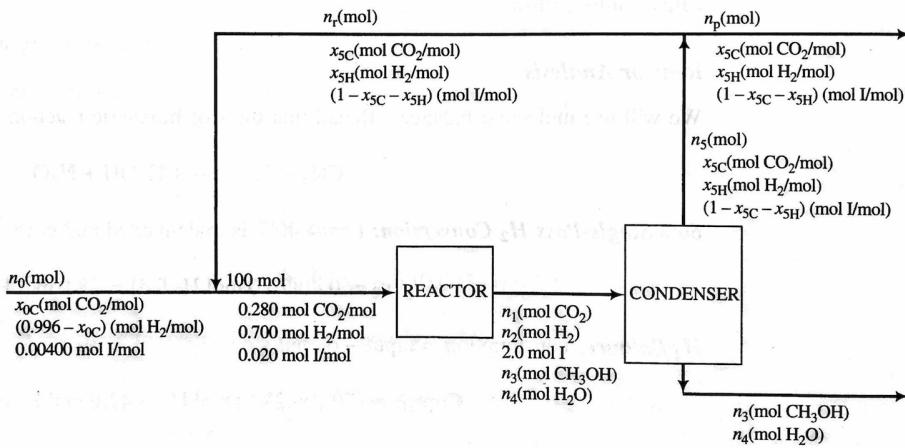


The fresh feed to a methanol synthesis process contains hydrogen, carbon dioxide, and 0.400 mole% inert (I). The reactor effluent passes to a condenser that removes essentially all of the methanol and water formed and none of the reactants or inert. The latter substances are recycled to the reactor. To avoid buildup of the inert 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% CO₂, 70.0 mole% H₂, and 2.00 mole% inert. 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 CH₃OH/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 ₃ OH	H ₂ O
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 H₂O) 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

$$R = 8.314472 \text{ J / (K mol)} \quad 0.082057 \text{ atm l / (K mol)} \quad 1.3806504e-23 \text{ J / K}$$

- 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 ft³ of air at 70 F and 1.00 atm is heated to 610 F and compressed to 2.50 atm. Final volume?

```

1 VO = 10.
2 TO = 70 + 459.67 # R
3 T = 610 + 459.67
4 P0 = 1. # atm
5 P = 2.50 # atm
6
7 V = VO*(P0/P)*(T/TO)
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 ft³/hr

7.3 Ideal gas mixture

- ideal mixture → 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 → 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 L min^{-1} and exits at a partial pressure (gauge) of 501 mm Hg at 325°C . Total pressure of exit is 6.2 atm (gauge). What is flow rate and composition of exit? Atmospheric pressure is 763 mm Hg .

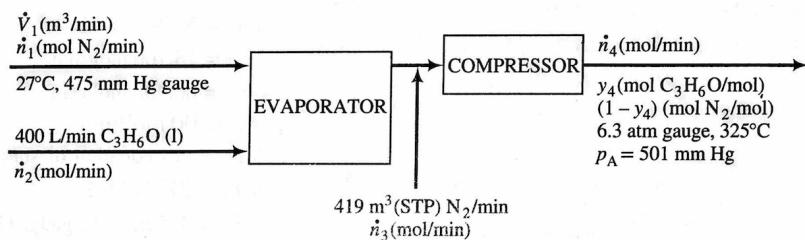
Material Balances on an Evaporator-Compressor

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?

1 Basis: Given Feed Rates

Assume ideal-gas behavior. Let $\dot{n}_1, \dot{n}_2, \dots$ (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 unknowns ($\dot{V}_1, \dot{n}_1, \dot{n}_2, \dot{n}_3, \dot{n}_4, y_4$)
-1 specific gravity relationship (\dot{n}_2)
-2 molecular balances (overall, C_3H_6O)
-1 ideal-gas equation of state (\dot{V}_1)
-1 partial pressure relationship (y_4)
-1 ideal-gas equation of state (\dot{n}_3)
0 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

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

```

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

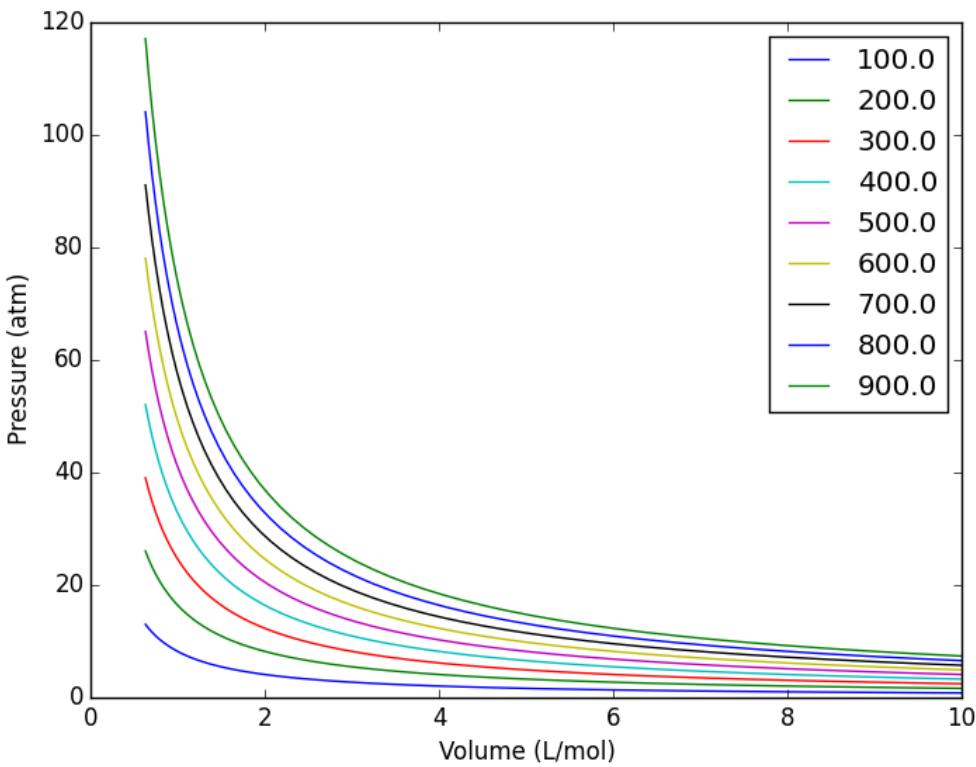
7.4.1 Ideal gas

- 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:

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

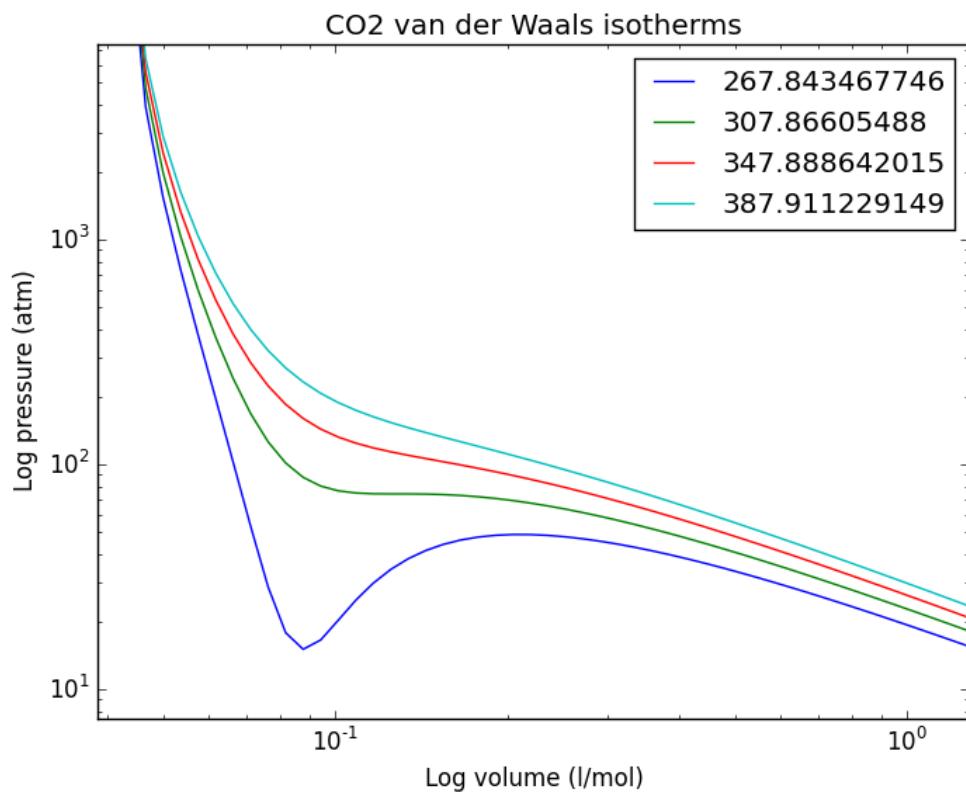
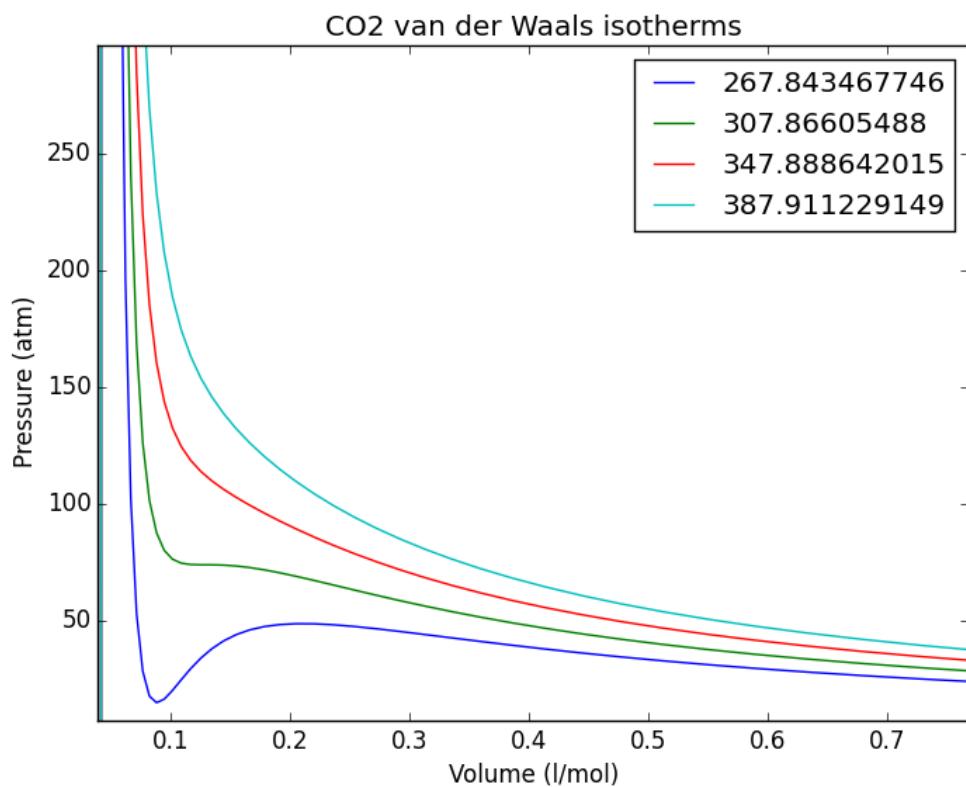
- b has units of volume/mole
- a has units of pressure * (volume/mol)² = energy * volume/mol

	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

```

1 import numpy as np
2 import matplotlib.pyplot as plt
3
4 R = 0.0821 # l atm/mol K
5
6 a = 3.640; b = 0.04267;
7
8 vc = 3 * b; Tc = (8./9.)*a / (R * vc); Pc = (R * Tc)/(vc-b) - a/(vc*vc);
9
10 vr = np.logspace(-0.5,1.)
11
12 plt.figure(1)
13 for Tr in np.arange(0.87,1.3,0.13):
14     Pr = 8 * Tr/(3 * vr -1) - 3 *(1/vr) *(1/vr)
15     plt.plot(vr*vc,Pr*Pc,label=Tr*Tc)
16
17 plt.title('CO2 van der Waals isotherms')
18 plt.ylim([.1*Pc,4*Pc])
19 plt.xlim([.3*vc,6*vc])
20 plt.xlabel('Volume (l/mol)')
21 plt.ylabel('Pressure (atm)')
22 legend=plt.legend()
23
24 plt.savefig('../figs/vdWgas.png')
25
26 plt.figure(2)
27 for Tr in np.arange(0.87,1.3,0.13):
28     Pr = 8 * Tr/(3 * vr -1) - 3 *(1/vr) *(1/vr)
29     plt.loglog(vr*vc,Pr*Pc,label=Tr*Tc,basex=10)
30
31 legend = plt.legend()
32
33 plt.ylim([.1*Pc,100*Pc])
34 plt.xlim([.3*vc,10*vc])
35 plt.xlabel('Log volume (l/mol)')
36 plt.ylabel('Log pressure (atm)')
37 plt.title('CO2 van der Waals isotherms')
38
39 plt.savefig('../figs/logvdWgas.png')

```



-
- 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 :

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

- 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)

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

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

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

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

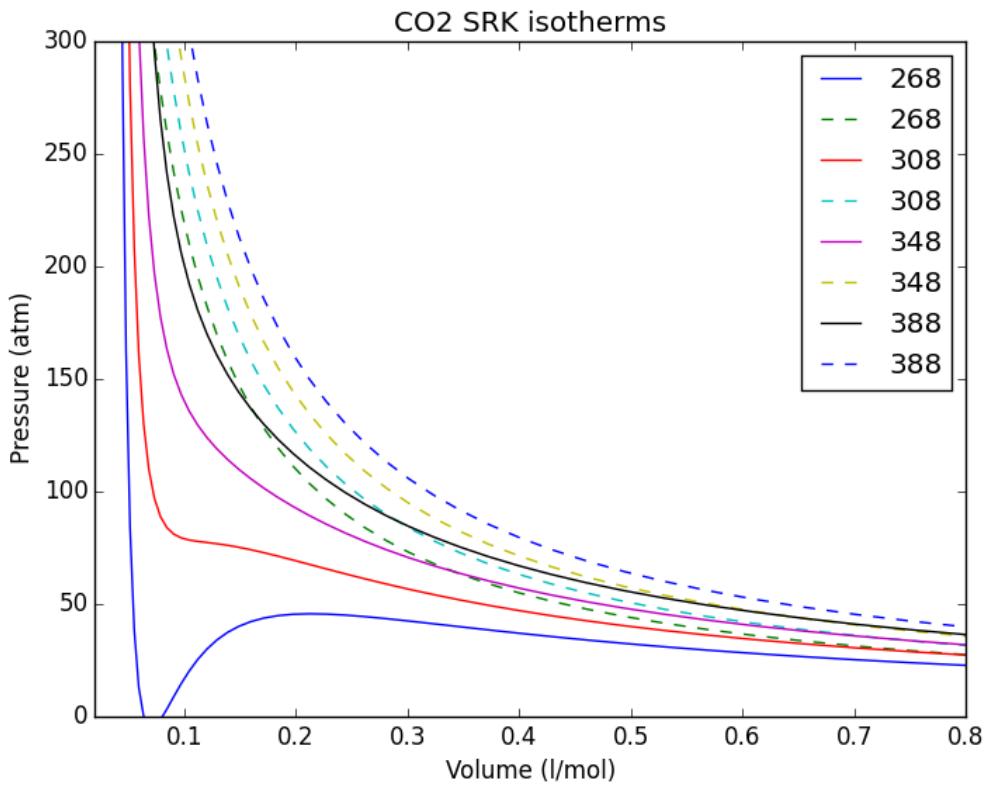
$$\omega = -\log \left(\frac{P_{sat}}{P_c} \right) \Big|_{T_r=0.7} - 1$$

	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,base10=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')

```



- 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

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

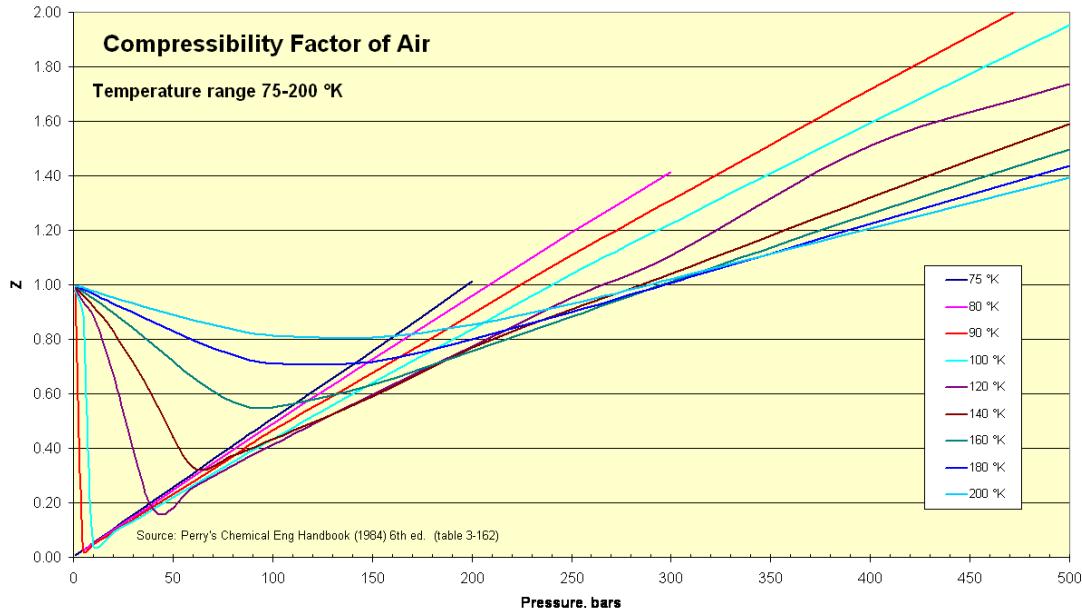
7.4.5 Law of corresponding states

- 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

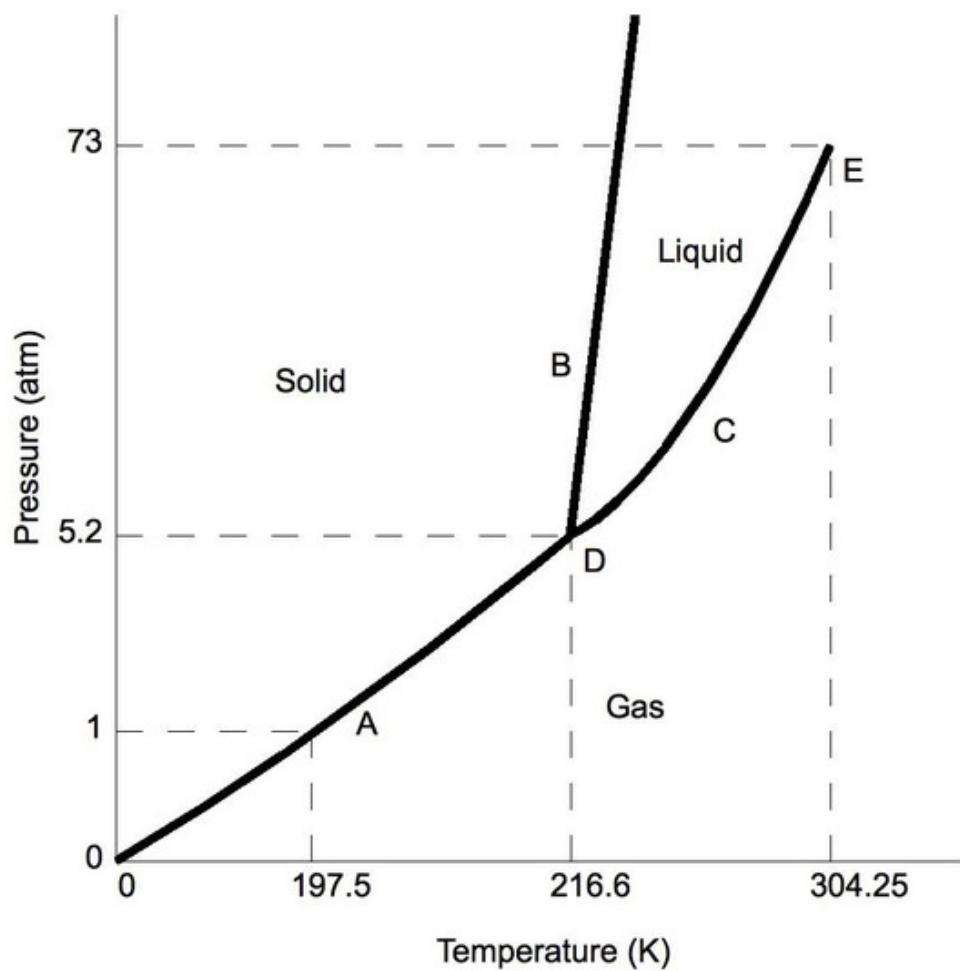
- Even messier problem
- Mixing rules to combine parameters from individual components

8 Two-phase systems

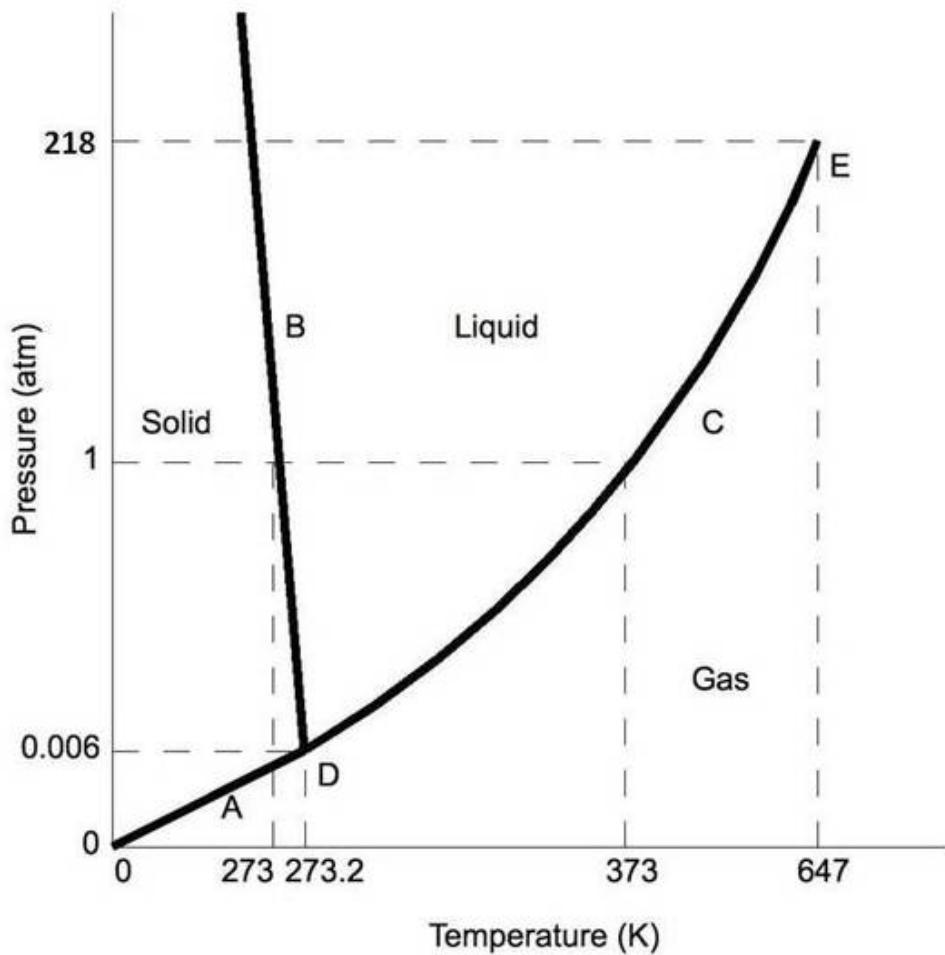
Very often interested in systems in which two distinct phases are present, e.g. l/g . Common in separations problems, including my favorite, extracting tasty coffee from coffee beans, and second favorite, CO_2 from flue gas.

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
- H₂O 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 \rightarrow vapor transition, ignoring liquid volume, and treating vapor as ideal gives the Clausius-Clapeyron equation:

$$\begin{aligned}
 \frac{dP^*}{dT} &= \frac{\Delta H_{\text{vap}}}{T(v_g - v_l)} \\
 &\approx \frac{\Delta H_{\text{vap}}}{Tv_g} \\
 &\approx \frac{P\Delta H_{\text{vap}}}{RT^2} \\
 \frac{d \ln P}{d 1/T} &= -\frac{\Delta H_{\text{vap}}}{R}
 \end{aligned}$$

-
- 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 kJ 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. H₂O) 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 H₂O 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 = {:.3.0f}% N2 = {:.3.0f}% O2 = {:.3.0f}%'.format(yH2O*100,yN2*100,yO2*100))
```

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

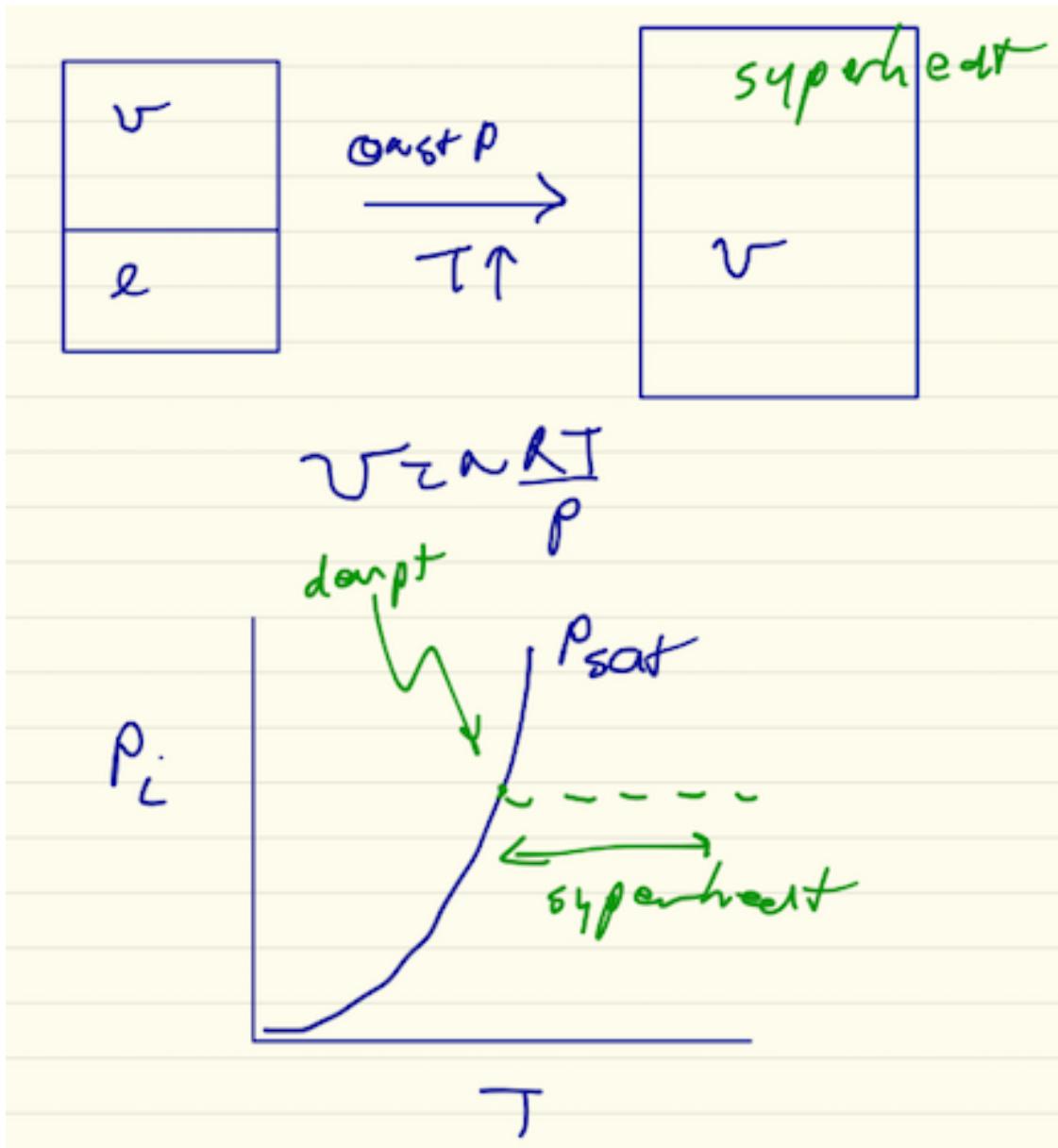
- Raoult’s Law applies to equilibrium. Change any constraint, other variables must adjust to restore equilibrium
- Often two-phase systems are **not** at equilibrium
- Uncommon for vapor composition to be greater than equilibrium—vapor would just condense
- Opposite is possible, if there isn’t enough 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  yH200 = 0.10
6  Psat = 760.      # duh!  Psat = Patm at 100 C!  We all know that.
7
8  PH20 = P0 * yH200
9
10 print('Partial pressure of H2O = {0:4.0f} mmHg'.format(PH20))
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 yH2080 = 355.1/5250
19
20 # draw a condenser feed and do mass balance on both streams
21 n0H20 = 0.1*100; n0air = 0.9*100;
22
23 # air balance
24 ndotv = 100 * 0.9 / (1 - yH2080)
25
26 # H2O balance
27
28 ndotH20 = 100* 0.1 - ndotv * yH2080
29
30 deltaH20 = (ndotH20)/n0H20
31
32 print('80 C composition ={0:6.4f}'.format(yH2080))
33
34 print('Fraction of water condensed ={0:3.0f}%\n'.format(deltaH20*100))
35
36 # Compress isothermally to 8500 mmHg at 100 C
37 Pcomp = 8500
38 PH20 = yH200 * 8500
39
40 print('Partial pressure of H2O = {0:4.0f} mmHg'.format(PH20))
41
42 yH20comp = Psat/Pcomp
43
44 # air balance
45 ndotv = 100 * 0.9 / (1 - yH20comp)
46
47 # H2O balance
48
49 ndotH20 = 100* 0.1 - ndotv * yH20comp
50
51 deltaH20 = (ndotH20)/n0H20
52
53 print('8500 mmHg composition ={0:6.4f}'.format(yH20comp))
54
55 print('Fraction of water condensed ={0:3.0f}%\n'.format(deltaH20*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 H₂O, in which we refer to H₂O vapor as *humidity*
- Common to define *relative humidity*, fraction of maximum H₂O 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 h⁻¹. Determine molar flow rate of all components.

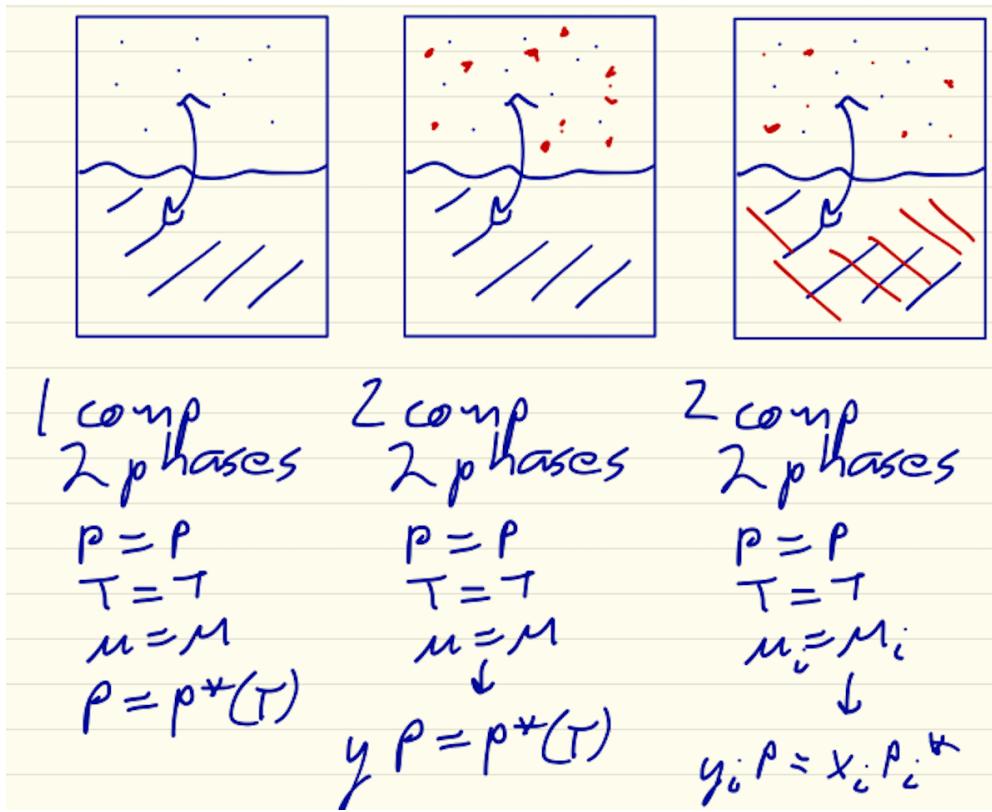
```

1 Psat75 = 289. # mmHg
2 RH = 0.30
3 P = 1.1 * 760 / 1.01325 # torr
4
5 PH2O = RH*Psat75
6
7 print('PH2O = {0} torr'.format(PH2O))
8
9 yH2O = PH2O/P
10 yN2 = (1-yH2O)*0.79
11 yO2 = (1-yH2O)*0.21
12
13 print('H2O = {0} N2 = {1} O2 = {2} mol/mol'.format(yH2O,yN2,yO2))
14
15 # MWavg = (18. * yH2O + 28 * yN2 + 32 * yO2)/1000. # kg/mol
16
17 R = 8.314
18 T = 75 + 273
19 P = 1.1e5 # Pa
20 vdot = 1000. # m3/hr
21 ndot = P * vdot / ( R * T)
22
23 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



- Combine two liquids, both of which have finite (but different) P_{sat} 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 :

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

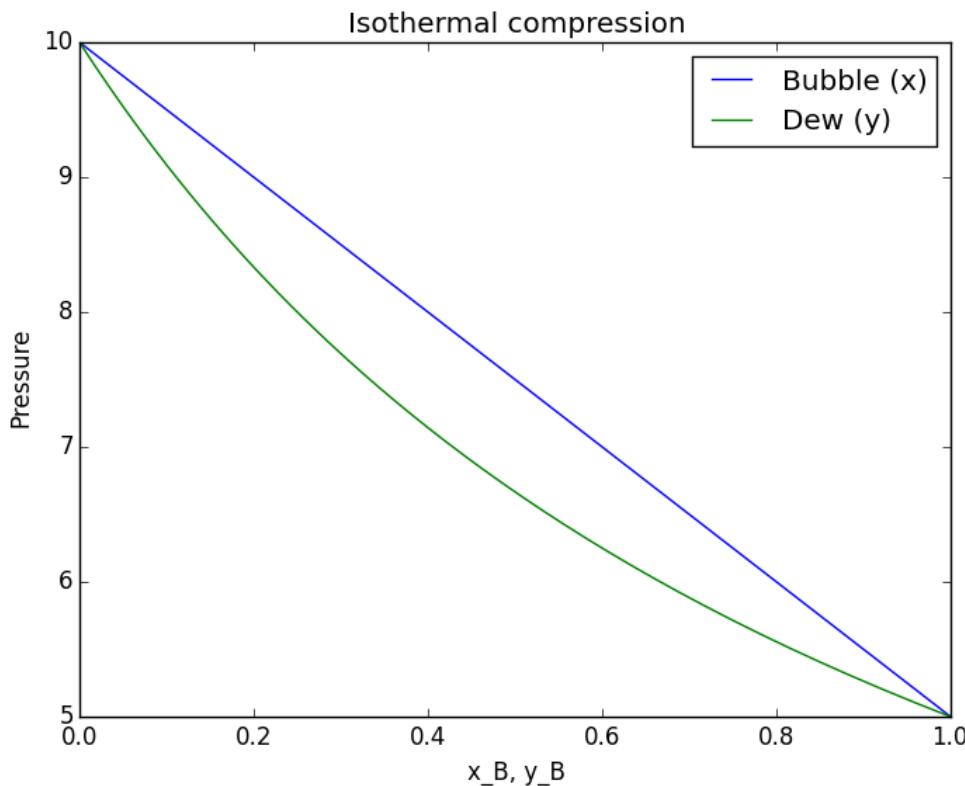
- If we know the vapor composition y_i , can determine the dew point by substitution from

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

```

1 import numpy as np
2 import matplotlib.pyplot as plt
3
4 xB = np.linspace(0,1)
5 PAs = 10
6 PBs = 5
7
8 PB = xB * PBs
9 PA = (1-xB) * PAs
10 P = PA + PB
11
12 yB = PB/P
13
14 plt.plot(xB,P,yB,P)
15 # plt.plot(xB,PB,xB,PA,xB,P)
16 plt.ylabel('Pressure')
17 plt.xlabel('x_B, y_B')
18 plt.title('Isothermal compression')
19 plt.legend(['Bubble (x)', 'Dew (y)'])
20
21 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 P_x 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.

```

1 PBs = 756 # torr
2 PTs = 291 # torr
3 yB = 0.15
4 yT = 0.10
5
6 # eliminate xB
7 P = 1/((yB/PBs) + (yT/PTs))
8
9 xB = yB * P /PBs
10
11 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 T_x diagram at constant P
- Need model for how saturation pressure varies with T

```

1 import numpy as np
2 import matplotlib.pyplot as plt
3 from scipy.optimize import fsolve
4
5 def PAo(T):
6     A = 6.89272; B= 1203.531; C=219.888 # benzene Antoine
7     logP = A - B/(T+C)
8     return 10**logP
9 # PAO = 10
10 # H = 800
11 # return PAO * np.exp(-H/T)
12
13 def PBs(T):
14     A = 6.95805; B= 1346.773; C=219.693 # toluene Antoine
15     logP = A - B/(T+C)
16     return 10**logP
17
18 Pressure = 760.0
19
20 def PAsopt(T):
21     return PAo(T) - Pressure
22
23 def PBsopt(T):
24     return PBs(T) - Pressure
25
26 TA = fsolve(PAsopt,100)

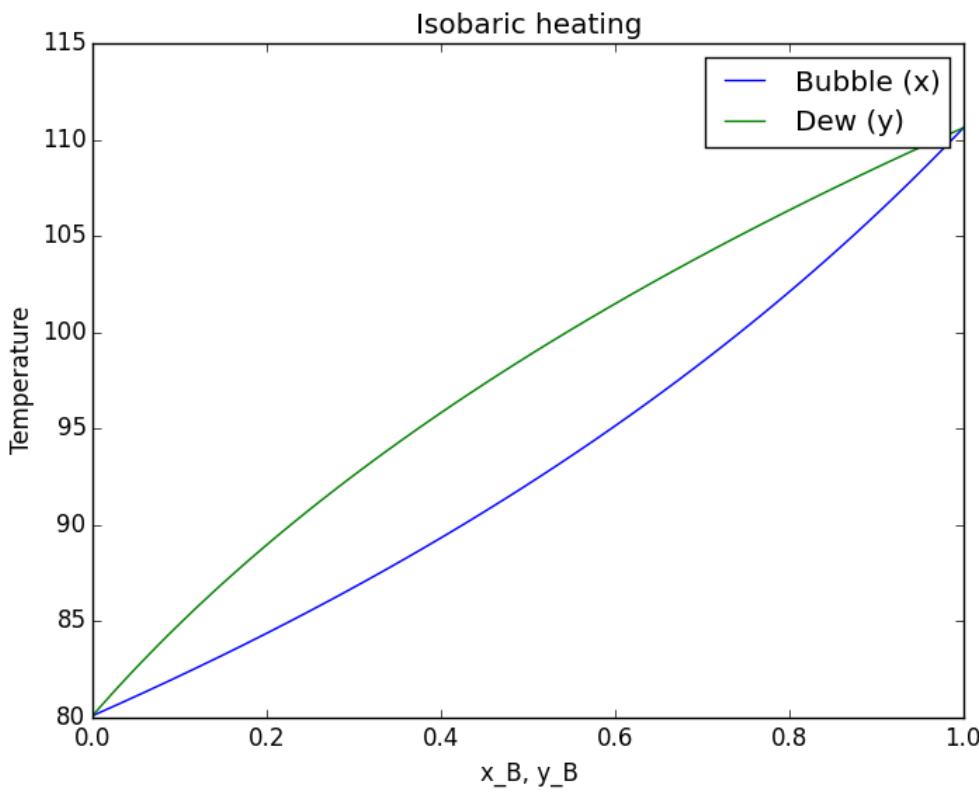
```

```

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

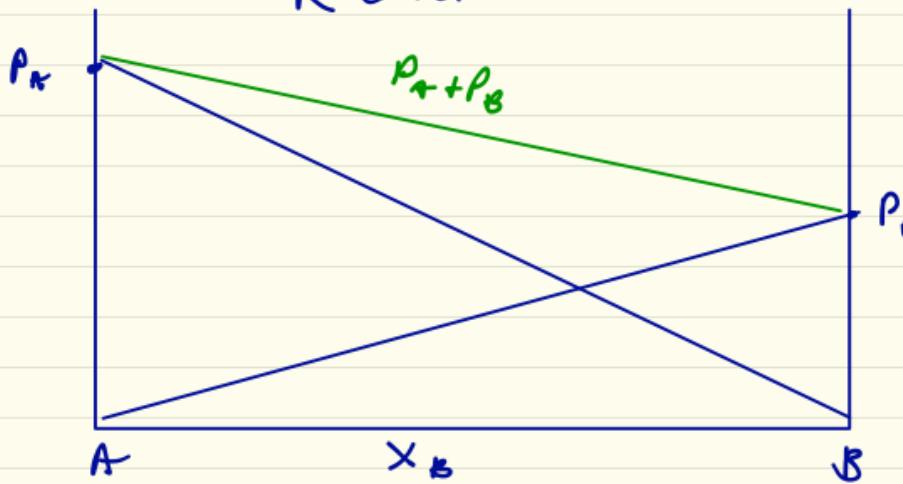


8.4.2 Henry's Law

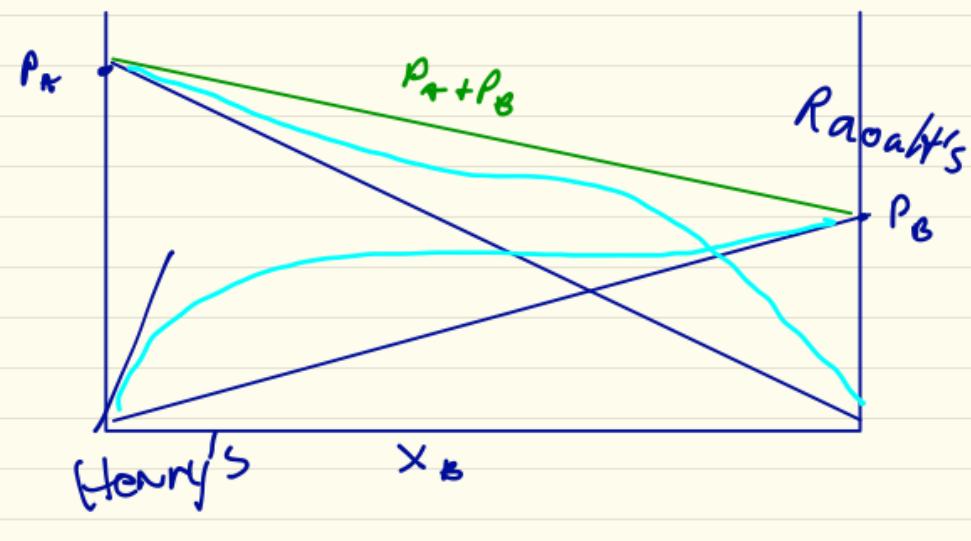
- Model appropriate for a dilute solute

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

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.

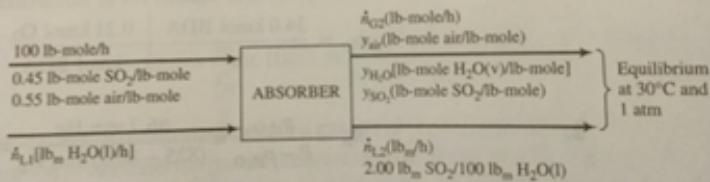
The best way to evaluate equilibrium compositions is from *Engineers' Handbook* (see Footnote 1), pp. 2-80 through 2-94, gives partial pressures over various liquid solutions. Example 6.4-1 illustrates the use of such data.

1 Absorption of SO₂

Sulfur dioxide (SO₂) is produced when coal is burned in power plants. Prior to implementation of clean-air standards, SO₂ emissions were responsible for acid rain, but utilization of absorbers (sometimes referred to as *scrubbers*) to remove SO₂ from combustion products has significantly reduced the problem.

In a simple implementation of that emission-control strategy, a gas mixture containing 45 mole% SO₂ and the balance air (an SO₂ 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 SO₂ per 100 g of H₂O. 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 SO₂ absorbed in the water and the required water feed rate.

Basis: Given Feed Rate of Gas



exit liquid: $2 \text{ lb}_m \text{ SO}_2 / 100 \text{ lb}_m \text{ H}_2\text{O}$ @ 30°C

$$\Rightarrow P_{\text{SO}_2} = 176 \text{ mmHg} \quad P_{\text{H}_2\text{O}} = 31.6 \text{ mmHg}$$

$$P_{\text{atm}} = 760 - 176 - 31.6 =$$

$$y_{\text{SO}_2} = 0.232 \quad y_{\text{H}_2\text{O}} = 0.0416 \quad y_{\text{air}} = 0.727$$

Unknowns: n_{L1}, n_{L2}, n_{G2}

3 balances

air: $\text{out} = \text{in}$

$$n_{G2} \cdot y_{\text{air}} = 100 \cdot 0.55 \Rightarrow n_{G2} = 55 \text{ mol/hr}$$

$$\text{in} = \text{out} + \text{out}$$

SO₂: $100 \cdot 0.45 = n_{L2} \cdot y_{SO_2} + m_{L2} \cdot \omega_{SO_2} \cdot 64$

($\omega_{SO_2} = 0.0196 \frac{\text{mole}}{\text{mole SO}_2}$)

$\rightarrow m_{L2} = 89600 \text{ lb}_m$

H₂O: $\text{in} = \text{out}$

$$m_{1L} = n_{L2} \cdot y_{H_2O} \cdot 18 + m_{L2} \cdot \omega_{H_2O}$$

$\rightarrow m_{1L} = 87,900 \text{ lb}_m / \text{hr}$

SO₂ fraction absorbed

$$\frac{m_{L2} \cdot \omega_{SO_2} \cdot 64}{100 \cdot 0.45} = 0.61 \frac{\text{mol}}{\text{mol}} SO_2$$

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?

```

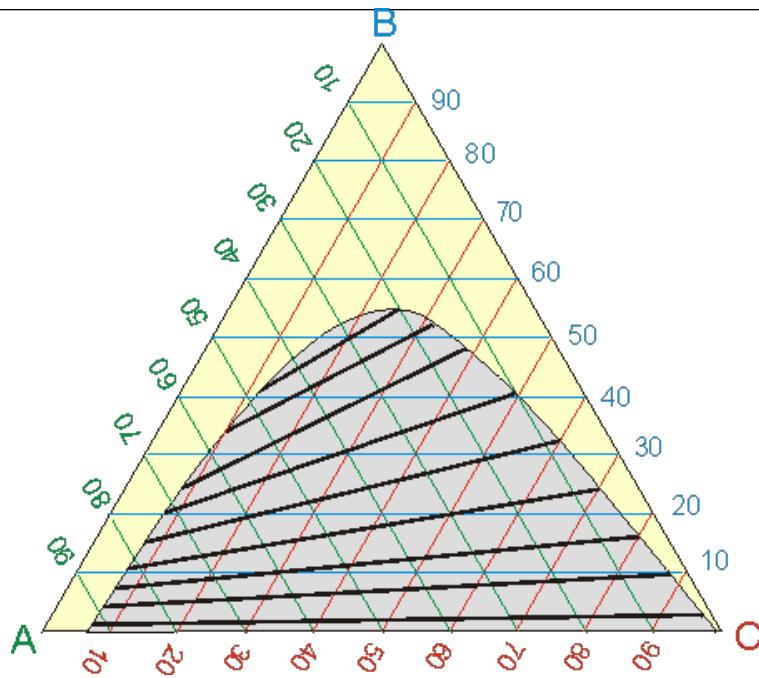
1 R = 8.31441
2 Hb = 40656. # J/mol
3 Tb = 273.16 + 100. # K
4 dT = 100.421 - 100.
5
6 x = dT * Hb / (R * Tb * Tb) # mol fraction solute
7
8 nH2O = 100.0 / 18.011 # mol
9
10 nSol = nH2O * x /(1-x)
11
12 MW = 5.000/nSol
13
14 print('Moles solute = {0:5.3f} MW = {1:5.3f} g/mol'.format(nSol,MW))

```

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 = 3-2 + 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, $\Delta E_{universe} = 0$
 - 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

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

- 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?

```

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

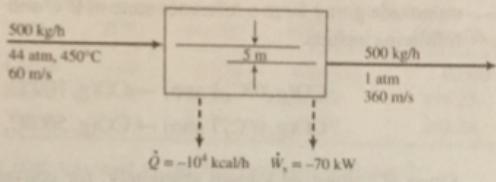
$$\dot{E}_V = \dot{m} g z$$

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

2 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 10⁴ kcal/h. Calculate the specific enthalpy change associated with the process.

tion



$$\Delta H + \Delta E_k + \Delta E_v = \dot{Q} + \dot{W}_s$$

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

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

mass conserved:

$$m_{in} = m_{out} = 500 \text{ kg/s}$$

$$\Delta E_k = \frac{1}{2} m (u_{out}^2 - u_{in}^2) = 8.75 \text{ kW}$$

$$\Delta E_v = m g (z_{out} - z_{in}) = m g (-5 \text{ m}) = -6.8 \times 10^{-3} \text{ kW}$$

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

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

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 than 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 $133.5\text{ }^{\circ}\text{C}$?
(Table B.6): 3.0 bar, 2543.0 kJ/kg, 2724.7 kJ/kg

EXAMPLE Specific volume, internal energy, and enthalpy of steam at $400\text{ }^{\circ}\text{C}$ and 10 bar, relative to triple point.

At 10 bar, saturation temperature is $179.9\text{ }^{\circ}\text{C}$ (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) ($T_{\text{sat}}, ^\circ\text{C}$)	Sat'd Water		Sat'd Steam		Temperature ($^\circ\text{C}$) →							
	\hat{H}	\dot{U}	\hat{H}	\dot{U}	50	75	100	150	200	250	300	350
0.0	—	—	—	—	2595	2642	2689	2784	2880	2978	3077	3177
(—)	—	—	—	—	2446	2481	2517	2589	2662	2736	2812	2890
0.1	—	—	—	—	—	—	—	—	—	—	—	—
(45.8)	\hat{H}	191.8	2584.8	2593	2640	2688	2783	2880	2977	3077	3177	3177
	\dot{U}	191.8	2438.0	2444	2480	2516	2588	2661	2736	2812	2890	2890
	\hat{V}	0.00101	14.7	14.8	16.0	17.2	19.5	21.8	24.2	26.5	28.7	28.7
0.5	\hat{H}	340.6	2646.0	209.3	313.9	2683	2780	2878	2979	3076	3177	3177
(81.3)	\dot{U}	340.6	2484.0	209.2	313.9	2512	2586	2660	2735	2811	2889	2889
	\hat{V}	0.00103	3.24	0.00101	0.00103	3.41	3.89	4.35	4.83	5.29	5.75	5.75
1.0	\hat{H}	417.5	2675.4	209.3	314.0	2676	2776	2875	2975	3074	3176	3176
(99.6)	\dot{U}	417.5	2506.1	209.2	313.9	2507	2583	2658	2734	2811	2889	2889
	\hat{V}	0.00104	1.69	0.00101	0.00103	1.69	1.94	2.17	2.40	2.64	2.87	2.87
5.0	\hat{H}	640.1	2747.5	209.7	314.3	419.4	632.2	2855	2961	3065	3168	3168
(151.8)	\dot{U}	639.6	2560.2	209.2	313.8	418.8	631.6	2643	2724	2803	2883	2883
	\hat{V}	0.00109	0.375	0.00101	0.00103	0.00104	0.00109	0.425	0.474	0.522	0.571	0.571
10	\hat{H}	762.6	2776.2	210.1	314.7	419.7	632.5	2827	2943	3052	3159	3159
(179.9)	\dot{U}	761.5	2582	209.1	313.7	418.7	631.4	2621	2710	2794	2876	2876
	\hat{V}	0.00113	0.194	0.00101	0.00103	0.00104	0.00109	0.206	0.233	0.258	0.282	0.282
20	\hat{H}	908.6	2797.2	211.0	315.5	420.5	633.1	852.6	2902	3025	3139	3139
(212.4)	\dot{U}	906.2	2598.2	209.0	313.5	418.4	603.9	850.2	2679	2774	2862	2862
	\hat{V}	0.00118	0.09950	0.00101	0.00102	0.00104	0.00109	0.00116	0.111	0.125	0.139	0.139
40	\hat{H}	1087.4	2800.3	212.7	317.1	422.0	634.3	853.4	1085.8	2962	3095	3095
(250.3)	\dot{U}	1082.4	2601.3	208.6	313.0	417.8	630.0	848.8	1080.8	2127	2829	2829
	\hat{V}	0.00125	0.04975	0.00101	0.00102	0.00104	0.00109	0.00115	0.00125	0.0588	0.0665	0.0665
60	\hat{H}	1213.7	2785.0	214.4	318.7	423.5	635.6	854.2	1085.8	2885	3046	3046
(275.6)	\dot{U}	1205.8	2590.4	208.3	312.6	417.3	629.1	847.3	1078.3	2668	2792	2792
	\hat{V}	0.00132	0.0325	0.00101	0.00103	0.00104	0.00109	0.00115	0.00125	0.0361	0.0422	0.0422
80	\hat{H}	1317.1	2759.9	216.1	320.3	425.0	636.8	855.1	1085.8	2787	2990	2990
(295.0)	\dot{U}	1306.0	2571.7	208.1	312.3	416.7	628.2	845.9	1075.8	2593	2750	2750
	\hat{V}	0.00139	0.0235	0.00101	0.00102	0.00104	0.00109	0.00115	0.00124	0.0243	0.0299	0.0299
100	\hat{H}	1408.0	2727.7	217.8	322.9	426.5	638.1	855.9	1085.8	1343.4	2926	2926
(311.0)	\dot{U}	1393.5	2547.3	207.8	311.7	416.1	627.3	844.4	1073.4	1329.4	2702	2702
	\hat{V}	0.00145	0.0181	0.00101	0.00102	0.00104	0.00109	0.00115	0.00124	0.00140	0.0224	0.0224
150	\hat{H}	1611.0	2615.0	222.1	326.0	430.3	641.3	858.1	1086.2	1338.2	2695	2695
(342.1)	\dot{U}	1586.1	2459.9	207.0	310.7	414.7	625.0	841.0	1067.7	1317.6	2523	2523
	\hat{V}	0.00166	0.0103	0.00101	0.00102	0.00104	0.00108	0.00114	0.00123	0.00138	0.0115	0.0115
200	\hat{H}	1826.5	2418.4	226.4	330.0	434.0	644.5	860.4	1086.7	1334.3	1647.1	1647.1
(365.7)	\dot{U}	1785.7	2300.8	206.3	309.7	413.2	622.9	837.7	1062.2	1307.1	1613.7	1613.7
	\hat{V}	0.00204	0.005875	0.00100	0.00102	0.00103	0.00108	0.00114	0.00122	0.00136	0.00167	0.00167
221.2(P_c)	\hat{H}	2108	2108	228.2	331.7	435.7	645.8	861.4	1087.0	1332.8	1635.5	1635.5
(374.15)(T_c)	\dot{U}	2037.8	2037.8	206.0	309.2	412.8	622.0	836.3	1060.0	1302.9	1600.3	1600.3
	\hat{V}	0.00317	0.00317	0.00100	0.00102	0.00103	0.00108	0.00114	0.00122	0.00135	0.00163	0.00163
250	\hat{H}	—	—	230.7	334.0	437.8	647.7	862.8	1087.5	1331.1	1625.0	1625.0
(—)	\dot{U}	—	—	205.7	308.7	412.1	620.8	834.4	1057.0	1297.5	1585.0	1585.0
300	\hat{H}	—	—	235.0	338.1	441.6	650.9	865.2	1088.4	1328.7	1609.9	1609.9
(—)	\dot{U}	—	—	205.0	307.7	410.8	618.7	831.3	1052.1	1288.7	1563.3	1563.3
500	\hat{H}	—	—	251.9	354.2	456.8	664.1	875.4	1093.6	1323.7	1576.3	1576.3
(—)	\dot{U}	—	—	202.4	304.0	405.8	611.0	819.7	1034.3	1259.3	1504.1	1504.1
1000	\hat{H}	—	—	293.9	394.3	495.1	698.0	903.5	1113.0	1328.7	1550.5	1550.5
(—)	\dot{U}	—	—	196.5	295.7	395.1	594.4	795.3	999.0	1207.1	1419.0	1419.0
	\hat{V}	—	—	0.0009737	0.0009852	0.001000	0.00104	0.00108	0.00114	0.00122	0.00131	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), \dot{U} = specific internal energy (kJ/kg), \hat{V} = specific volume (m^3/kg). Note: kJ/kg × 0.4303 = Btu/lb_m.

(continued)

EXAMPLE Steam at 10 bar absolute and 190 °C superheat enters turbine at $\dot{m} = 2000 \text{ kg/hr}$. 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

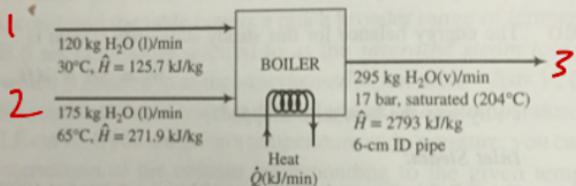
- Example 7.6-1

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

$$\Delta H + \Delta E_k + \cancel{\Delta E_p} < \dot{q}_e + \dot{w}_s$$

mass balance $m_1 = 120 \text{ kg/min}$

$$m_2 = 175 \text{ kg/min}$$

$$\Rightarrow m_3 = 295 \text{ kg/min}$$

$$\hat{H}_1: \text{H}_2\text{O}(l) \text{ } 30^\circ\text{C} \sim 125.7 \text{ kJ/kg (Table B5)}$$

$$\hat{H}_2: \text{H}_2\text{O}(l) \text{ } 65^\circ\text{C} \text{ interpolate on Table B5} \\ \sim 272 \text{ kJ/kg}$$

$$\hat{H}_3: 17 \text{ bar sat} \rightarrow 204.3^\circ\text{C}$$

$$\Delta \hat{H}_3 = 2793.4 \text{ kJ/kg}$$

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

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

$$\begin{aligned} \dot{m} &= 295 \text{ kg/min} \\ \hat{v} &= 0.1166 \text{ m}^3/\text{kg} \end{aligned} \quad \left. \begin{array}{l} \dot{m} \\ \hat{v} \end{array} \right\} \rightarrow 34.40 \text{ m}^3/\text{min} = \dot{V}$$

$$\begin{aligned} \dot{v} &= \dot{V}/\text{Area}_A \quad d = 6 \text{ cm} \rightarrow A = \pi(3 \text{ cm})^2 = 28.3 \text{ cm}^2 \\ &= 203 \text{ m/s} \end{aligned}$$

$$\dot{E}_{k,out} = \frac{1}{2} (295 \text{ kg/min}) (203 \frac{\text{m}}{\text{s}})^2 = 6060 \text{ kJ/min}$$

$$\begin{aligned} \dot{Q} &= \Delta H + \Delta E_k \\ &= 7.61 \times 10^5 + 0.061 \times 10^5 \\ &= 7.67 \times 10^5 \text{ kJ/min} \end{aligned}$$

- Example 7.6-3

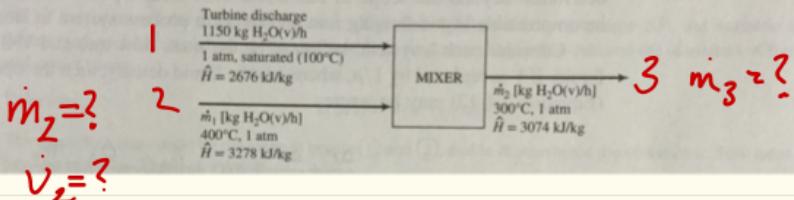
6-3

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.)



All @ 1 atm, no height change $\rightarrow \Delta E_k = \Delta E_p = 0$

mass balance: $m̄₁ + m̄₂ = m̄₃$
150 kg/hr

energy balance: $\Delta H = 0$ adiabatic

$$\cancel{m̄₃ \cdot \hat{H}_3} - \cancel{m̄₂ \cdot \hat{H}_2} - \cancel{m̄₁ \cdot \hat{H}_1} = 0$$

$$3674 - 3278 - 2676 = 0$$

2 equations, 2 unknowns \Rightarrow

$$m̄₂ = 2240 \text{ kg/hr} \quad m̄₃ = 3390 \text{ kg/hr}$$

$$v̄₂ = m̄₂ \cdot \frac{1}{\rho} = \frac{2240}{311 \text{ kg/m}^3} = 6980 \text{ m}^3/\text{hr}$$

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:

$$\frac{1}{2}\dot{m}\Delta u^2 + \dot{m}g\Delta z + (\Delta\dot{U} - \dot{q}) - \dot{W}_s + \dot{V}\Delta P = 0$$

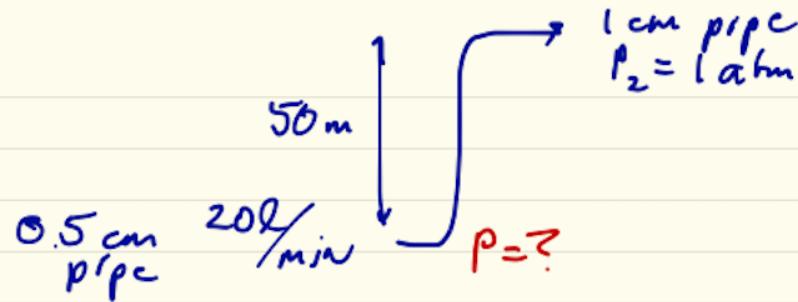
- Third term always has a positive friction component:

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

- 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 L min^{-1} water 50 m uphill from a 0.5 cm pipe into a 1 cm pipe.



Required P_2 . Neglect friction.

$$u_{in} = \frac{V}{\text{Area}} = 17.0 \text{ m/s} \quad u_{out} = 4.24 \text{ m/s}$$

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

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

$$\Delta P/\rho = -\left(\frac{\Delta u^2}{2} + g\Delta Z\right) = -358 \text{ m}^2/\text{s}^2$$

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

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

- 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

$\frac{1}{4}$ " id tube

$$\rho = 50.0 \text{ lb}_m/\text{ft}^3$$

$$\text{Friction} = 0.80 \text{ ft} \cdot \left(\frac{\text{lb}_f}{\text{lb}_m} \right)$$

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

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

$$g = 32.1 \text{ ft/s}^2 \quad g \Delta z = -80.4 \text{ ft/s}^2$$

$$\hat{F} = 0.8 \text{ ft} \left(\frac{\text{lb}_a}{\text{lb}_m} \right) = 0.8 \cdot (32.174 \text{ lb}_m \cdot \text{ft/s}^2) \cdot \text{ft}$$
$$= 25.7 \text{ ft}^2/\text{s}^2$$

$$u_{in} \approx 0$$

$$\frac{1}{2} u_f^2 = (80.4 - 25.7) \text{ ft/s}^2$$

$$u_f = 10.5 \text{ ft/s}$$

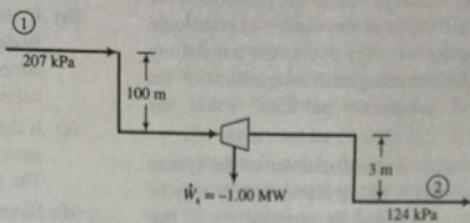
$$V = u_f \cdot A = 10.5 \cdot (0.050 \text{ in}^2) = 3.56 \times 10^{-3} \text{ ft}^3/\text{s}$$
$$= 0.026 \text{ gal/s}$$

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

- Water turbine

3 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?



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

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

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

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

$$\begin{aligned} m &= -1 \text{ MW} / 1092 \text{ m}^2/\text{s}^2 = 915 \text{ kg/s} \\ &= 0.9 \text{ m}^3/\text{s} \end{aligned}$$

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 condensable
 - two component, single phase
 - two component, two phase

10.2 Isothermal pressure dependence

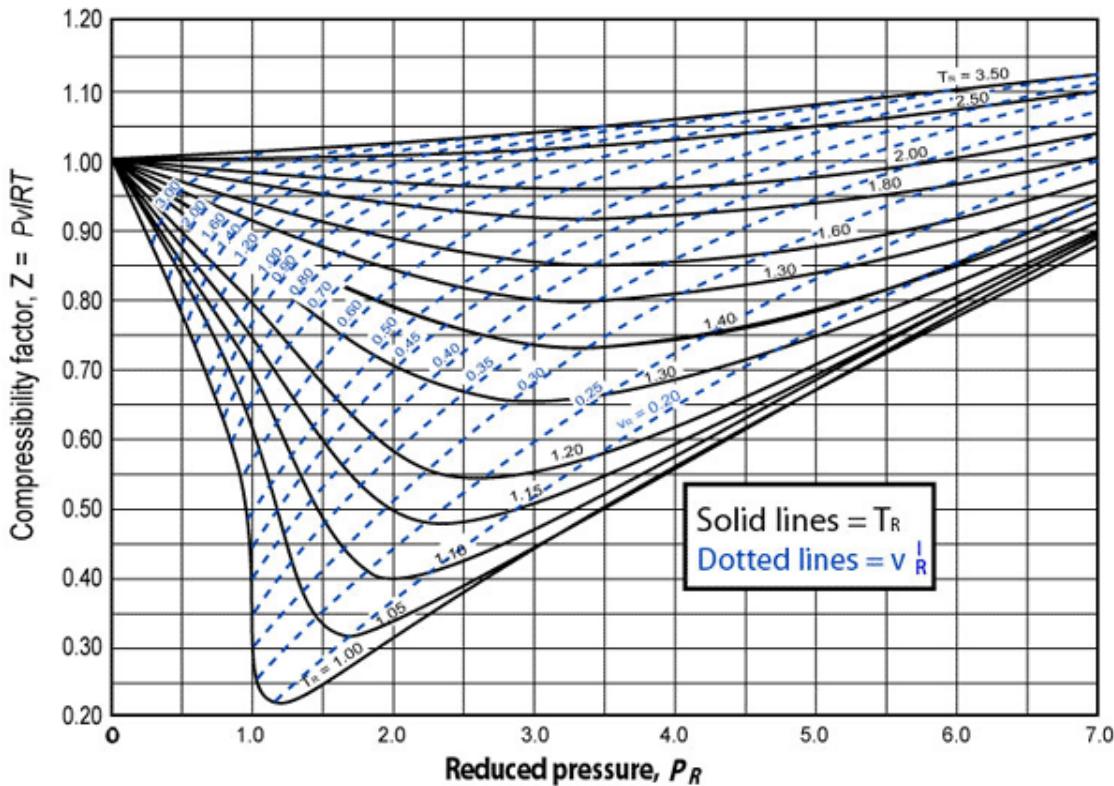
- Ideal gas energy/enthalpy *only* a function of T
- Real gas has weak dependence, use tabulation or EOS
- The volumes of solids and liquids are roughly independent of P
 - $U(T, P_2) - U(T, P_1) \approx 0$
 - $H(T, P_2) - H(T, P_1) \approx \hat{V}\Delta P$

Is it safe to ignore pressure effect in C₂H₆ (g, 25C, 1 atm) → C₂H₆ (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



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 N₂O 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! $q = \Delta U = 24200 \text{ kJ}$

- 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

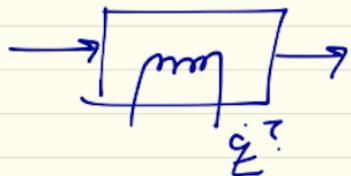
10.4 No data?

- 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% C_1H_4 in air, 2000 l(STP)/min
heat $20 \rightarrow 300^\circ\text{C}$



$$\text{mass balance? } n_{in} = n_{out} = \frac{(1 \text{ atm})(2000)}{R (273 \text{ K})} = 89.3 \frac{\text{mol}}{\text{min}}$$

energy balance?

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

$$\Delta H = n \Delta \hat{H} = n (\hat{H}_{out}(300, P_{out}) - \hat{H}_{in}(20, P_{in}))$$

1) Assume $\hat{H} \sim \text{ind. of } P$

2) Assume $\hat{H}_{mix} = \sum y_i \hat{H}_i$

$$\Delta H = n \sum_i y_i (\hat{H}_i(300) - \hat{H}_i(20))$$

$$\text{CA}_q: \Delta \hat{H} = \int_{20}^{300} C_p(T) dT = 12.07 \text{ kJ/mol}$$

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

air: interpolate on Table B8

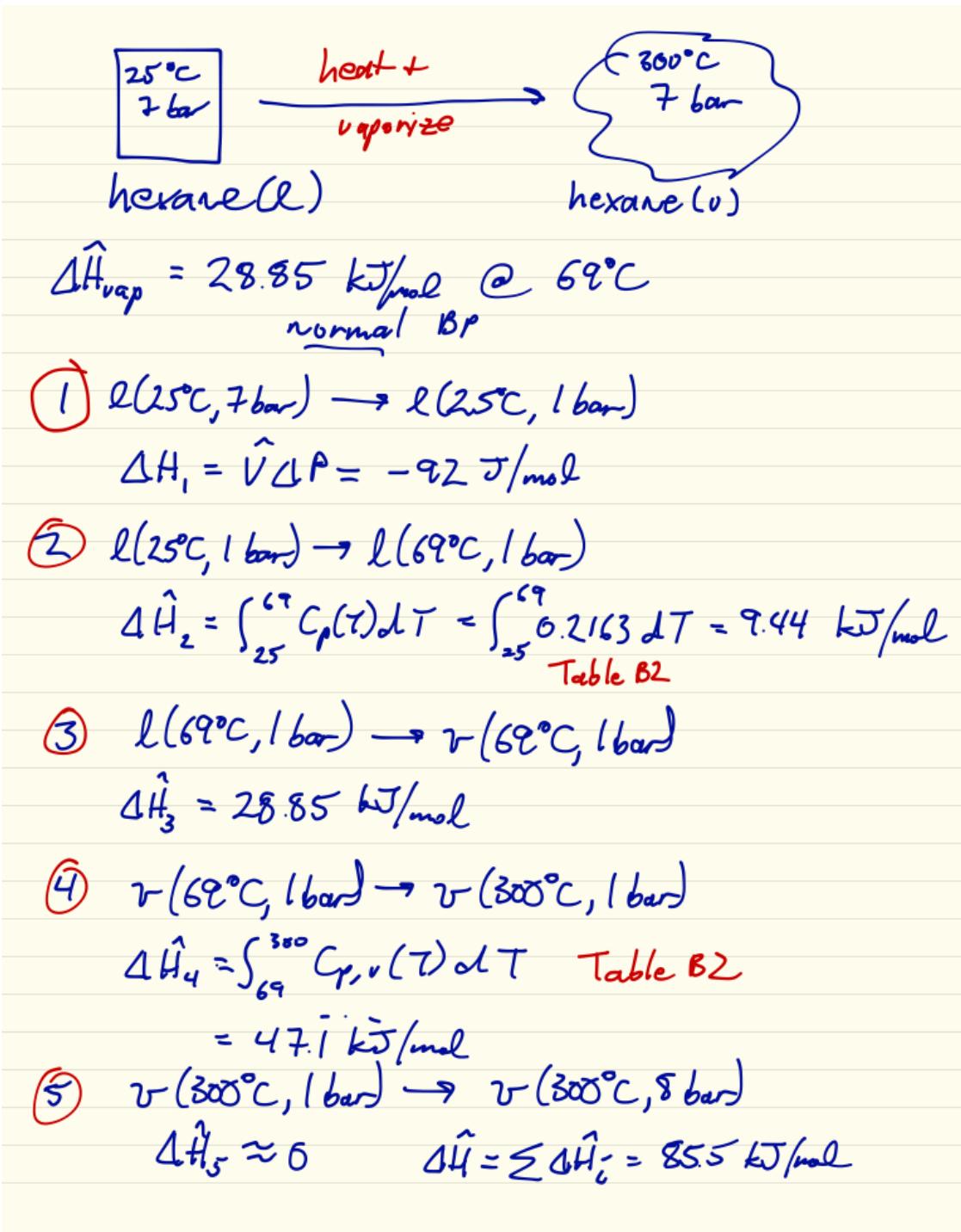
$$\Delta \hat{H}_{air} = 8.37 \text{ kJ/mol}$$

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

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



- 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

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

- many other correlations can be found
- how might you make such a correlation???

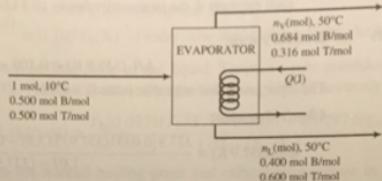
10.6 Phase change + mass balance

4 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

Media
Heater



mass balance: 2 unknowns, 2 mass balances

$$\begin{aligned} n_v + n_L &= 1 \text{ mol} \\ B: 0.5 \cdot 1 &= 0.684 n_v + 0.4 n_L \end{aligned} \quad \left\{ \begin{array}{l} n_v = 0.352 \\ n_L = 0.648 \end{array} \right.$$

energy balance 1 unknown, 1 energy balance

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

<u>in</u>	<u>out</u>	$\sum C_p dT =$
B(l) 10°C	B(l) 50°C	$\int C_p dT = 5.3$
T(l) 10°C	T(l) 50°C	" " = 6.3
	B(v) 50°C	
	T(v) 50°C	

How could we get P ?

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

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

Toluene 110.62°C 33.47

```

1 import numpy as np
2 import matplotlib.pyplot as plt
3 from scipy.optimize import fsolve
4
5 def PBs(T):
6     A = 6.89272; B= 1203.531; C=219.888 # benzene Antoine, C and mmHg
7     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 = {:.6f} mmHg'.format(P))
24    print('Vapor yB,yT)
```

Pressure = 163.8 mmHg
0.6625107083992408 0.33748929160075913

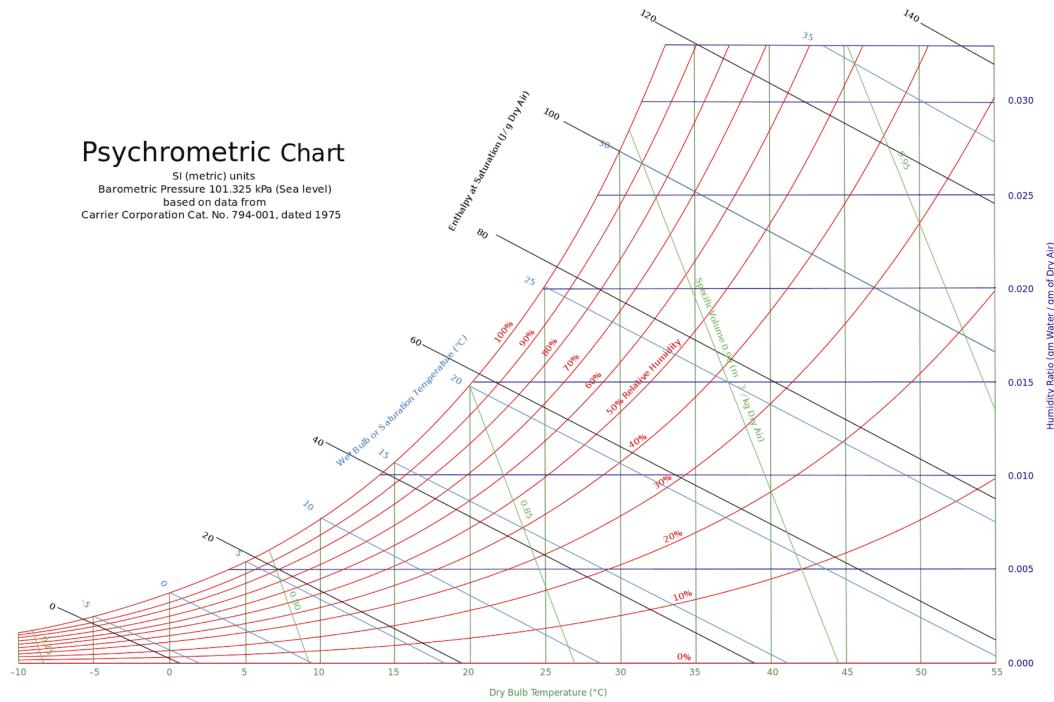
$$\delta C_v, 50^\circ \text{C} = \int_{16}^{80} C_{p,v} dT + \Delta H_v + \int_{80}^{50} C_{p,u} dT \\ = 37.53 \text{ kJ/mol}$$

$$\text{ditto } T \rightarrow 42.94 \text{ kJ/mol}$$

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

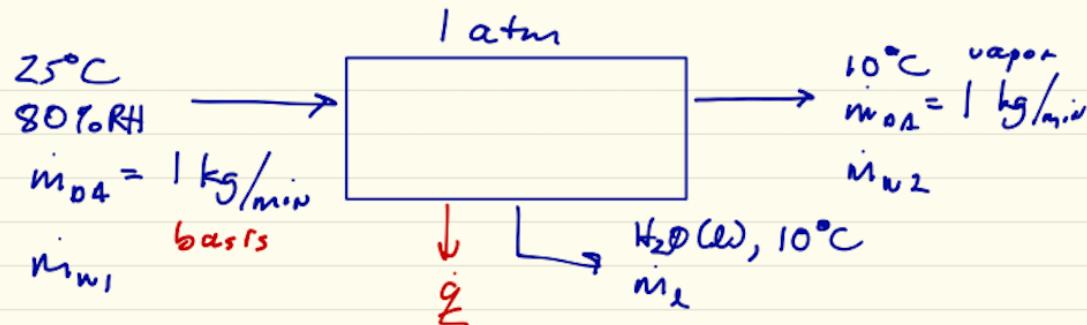
10.7 Psychrometric charts

- 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



- 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 $1 \text{ m}^3 \text{ min}^{-1}$ of humid air.



mass balance

$$\text{inlet: } \left. \begin{array}{l} 80\% \text{ RH} \\ 25^\circ \text{C} \end{array} \right\} \rightarrow 0.016 \frac{\text{kg H}_2\text{O}}{\text{kg OA}} \quad \text{psychrometric}$$

$$m_{w1} = 1 \frac{\text{kg}}{\text{min}} \cdot 0.016 = 0.016 \frac{\text{kg H}_2\text{O}}{\text{min}}$$

$$\text{outlet: } \left. \begin{array}{l} 100\% \text{ RH} \\ 10^\circ \text{C} \end{array} \right\} \rightarrow 0.007 \frac{\text{kg H}_2\text{O}}{\text{kg OA}}$$

$$m_{w2} = 1 \frac{\text{kg}}{\text{min}} \cdot 0.007 \frac{\text{kg H}_2\text{O}}{\text{kg OA}} = 0.007 \frac{\text{kg H}_2\text{O}}{\text{min}}$$

$$m_e = m_{w1} - m_{w2} = 0.009 \frac{\text{kg H}_2\text{O}}{\text{min}}$$

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

energy balance

$$\text{inlet: } \hat{H} \sim 65 \frac{\text{kJ}}{\text{kg OA}} \quad \text{psychrometric}$$

$$\text{outlet vapor: } \hat{H} \sim 30 \frac{\text{kJ}}{\text{kg OA}}$$

$$\text{water: } \hat{H} = \int_0^{10} C_p dT = 42 \frac{\text{kJ}}{\text{kg H}_2\text{O}}$$

$$\begin{aligned} \dot{Q} &= \sum_{\text{out}} n_i \hat{H} - \sum_{\text{in}} n_i \hat{H} \\ &= 30 \frac{\text{kJ}}{\text{kg}} \cdot 1 \frac{\text{kg}}{\text{min}} + 42 \frac{\text{kJ}}{\text{kg}} \cdot 0.009 \frac{\text{kg}}{\text{min}} \\ &\quad - 65 \frac{\text{kJ}}{\text{kg}} \cdot 1 \frac{\text{kg}}{\text{min}} \\ &= -34.6 \frac{\text{kJ}}{\text{min}} / \text{kg} \text{ DA} \end{aligned}$$

$$\text{Final air} \sim 0.81 \frac{\text{m}^3}{\text{kg}} \text{ DA}$$

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

10.8 Non-ideal mixtures

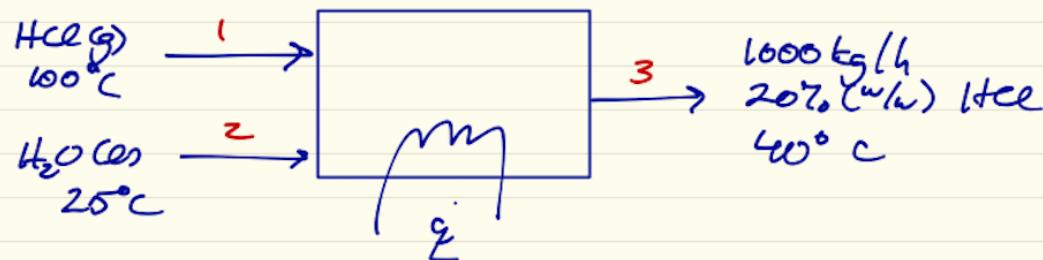
- Enthalpies additive in ideal mixture
- Real mixture, $\hat{H}_{soln} \neq \sum \hat{H}_i$
- Differential interactions, $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$, or $\text{NaOH} + \text{H}_2\text{O}$
- Can be tabulated as *integral heat of solution*
 - enthalpy to dissolve 1 mole solute in r moles 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 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 H₂O (l). HCl(g) at 100 °C and H₂O at 25 °C fed to produce 1000 kg h⁻¹ 20.0%(w/w) HCl at 40 °C.



mass balance

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

$$800 \frac{\text{kg}}{\text{hr}} \text{ HCl} \times \frac{1000 \text{ mol}}{18.0 \text{ kg}} = 44,400 \frac{\text{mol H}_2\text{O}}{\text{hr}}$$

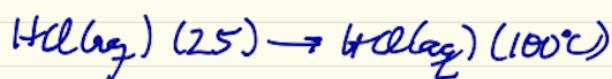
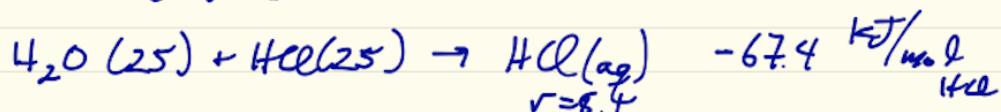
energy balance

enthalpy rels: HCl(g) + H₂O @ 25°C

$$\hat{H}_1 = \int_{25}^{100} C_p, \text{HCl}(T) dT = 21.78 \frac{\text{kJ}}{\text{mol HCl}}$$

$$\hat{H}_2 = 0$$

$$\hat{H}_3 : \frac{44,000 \text{ mol H}_2\text{O}}{5480 \text{ mol HCl}} = 8.10 \frac{\text{mol H}_2\text{O}}{\text{mol HCl}}$$



C_p tabulate per mass sol'n vs mol fraction

$$X_{\text{HCl}} = \frac{5480}{5480 + 44,000} = 0.110 \frac{\text{mol HCl}}{\text{mol soln}}$$

$$\Rightarrow C_p = 0.73 \frac{\text{kcal}}{\text{kg} \cdot ^\circ\text{C}}$$

would like this per mole HCl

$$0.73 \frac{\text{kcal}}{\text{kg} \cdot ^\circ\text{C}} \times \frac{100 \text{ kg}}{20 \text{ kg HCl}} \times \frac{36.5 \text{ kg}}{1000 \text{ mol}} + 4.184 = 0.557 \frac{\text{kJ}}{\text{mol HCl} \cdot ^\circ\text{C}}$$

$$\hat{U}(40) - \hat{U}(20) = \int_{20}^{40} 0.557 dT = 8.36 \frac{\text{kJ}}{\text{mol HCl}}$$

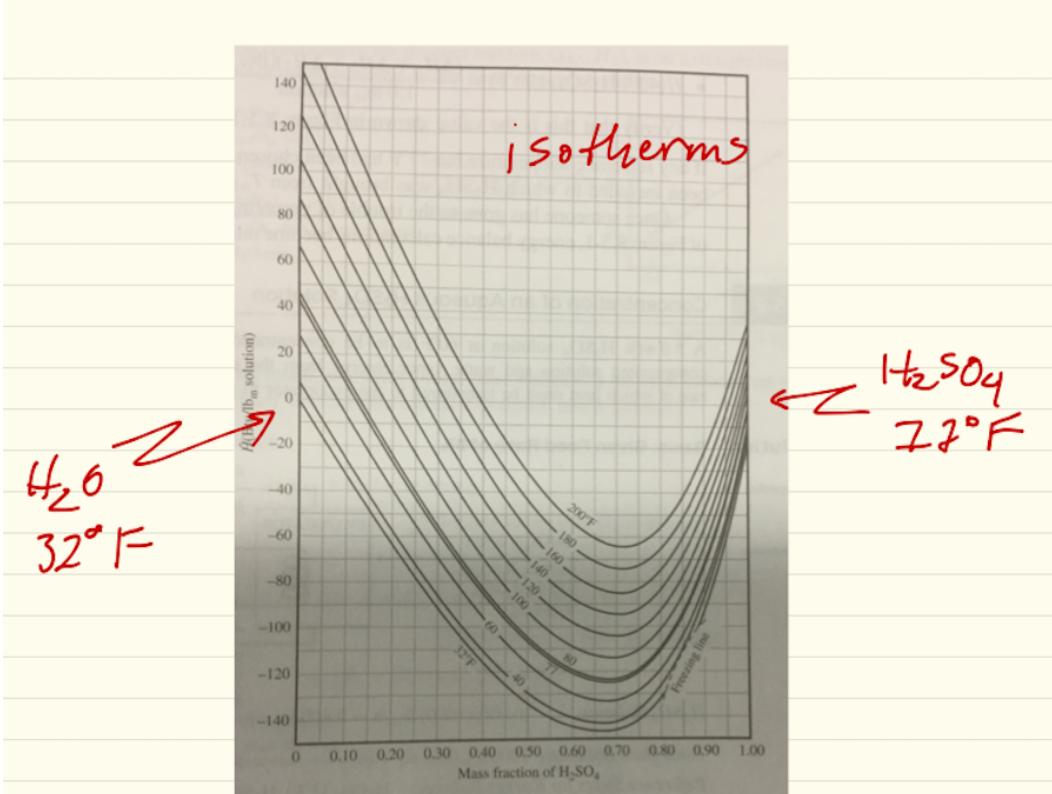
$$\hat{H}_3 = 8.36 - 67.4 = -59.0 \frac{\text{kJ}}{\text{mol HCl}}$$

$$\Delta H = \text{out} - \text{in}$$

$$= -59.0 \left(5480 \frac{\text{mol HCl}}{\text{hr}} \right) - [0 + 21.78 \cdot 5480]$$

$$= -3.35 \times 10^5 \frac{\text{kJ}}{\text{hr}} = \underline{\underline{E}}$$

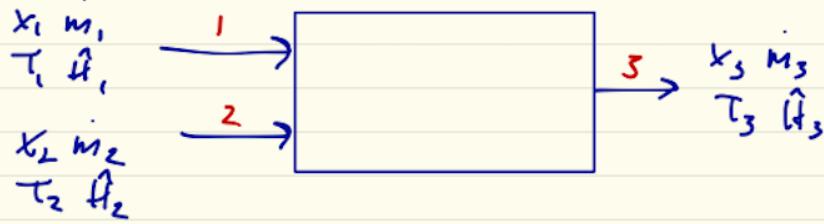
- Enthalpy-concentration chart, normalized to total amount of solution rather than amount of solute



$\text{H}_2\text{SO}_4 / \text{H}_2\text{O}$ 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



$$\text{total mass} \quad m_3 = m_1 + m_2$$

$$\text{At mass} \quad x_1 m_1 + x_2 m_2 = x_3 m_3 \\ = x_3 (m_1 + m_2)$$

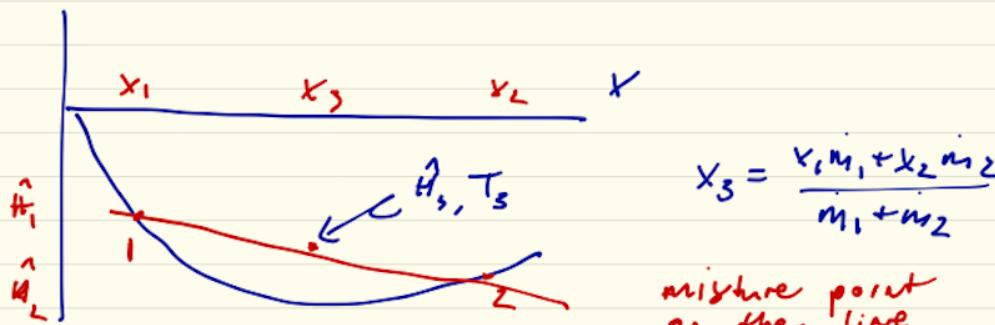
$$m_1(x_3 - x_1) = m_2(x_2 - x_3) \quad (1)$$

$$\text{H adiabatic} \quad H_{\text{out}} - H_{\text{in}} = 0$$

$$m_1 \hat{H}_1 + m_2 \hat{H}_2 = m_3 \hat{H}_3 \\ = (m_1 + m_2) \hat{H}_3$$

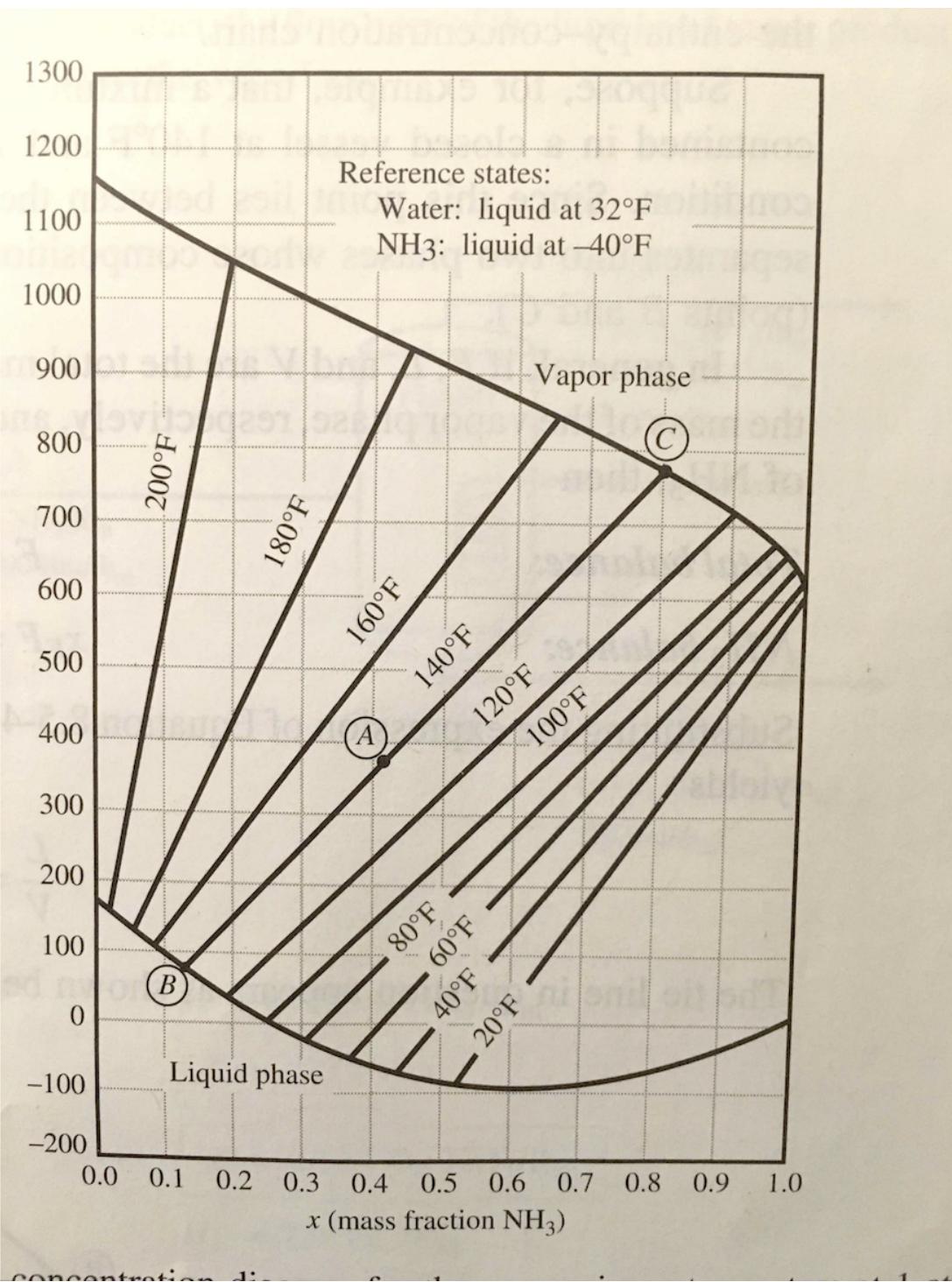
$$m_1(\hat{H}_3 - \hat{H}_1) = m_2(\hat{H}_2 - \hat{H}_3) \quad (2)$$

$$\frac{(2)}{(1)} : \quad \frac{\hat{H}_3 - \hat{H}_1}{x_3 - x_1} = \frac{\hat{H}_2 - \hat{H}_3}{x_2 - x_3} \quad \text{same slope!}$$



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”



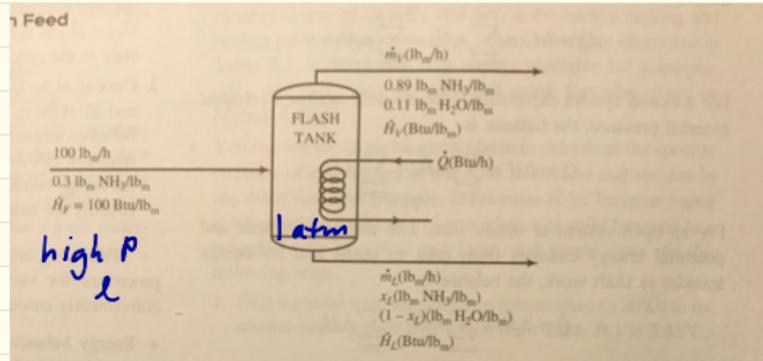
EXAMPLE: Two-phase H₂O/NH₃ system at 160 F. What are compositions of two phases? Enthalpies? Total enthalpy if 95% of mass is liquid?

- 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 NH₃ stream "flashed" to lower pressure. Very simple unit op to lower T and enrich liquid/vapor phases.

NH₃/H₂O "flash"



vapor: 1 atm, 89% (w/w) NH₃ $\rightarrow T = 120^\circ F$

liquid: tie line \rightarrow 18.5% NH₃

inlet 30% (w/w) NH₃: lever rule

$$\frac{m_L}{m_V} = \frac{89 - 30}{30 - 18.5} = 5.13$$

$$m_V = 100 \text{ lb}/\text{h} \rightarrow m_L = 84 \text{ lb}/\text{h} \quad m_V = 16 \text{ lb}/\text{h}$$

$$\hat{H}_{in} = 100 \text{ Btu/lb} \quad \hat{H}_L = \sim 45 \quad \hat{H}_V \sim 728 \text{ BTU/lb}$$

same ret

$$\begin{aligned} \Delta H &= (45)(84) + 728(16) - 100 \cdot 100 \\ &= 5400 \text{ Btu/hr} = \dot{Q} \end{aligned}$$

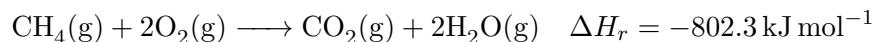
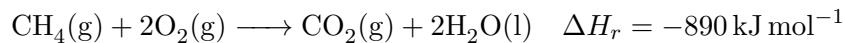
11 Energy balances on reactive systems

11.1 Heats of reaction

- Rearrangements of bonds → change in enthalpy
- “heat of reaction” defined for specific reaction stoichiometry and (generally) for pure species in specified states



- Define *endo* and *exothermic*
- ΔH_r function of state and conditions
 - Weak function of P , strong function of T and state



- *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

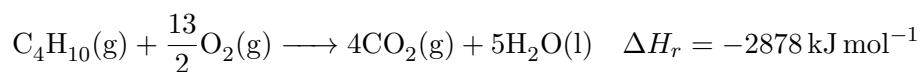
$$\Delta H = \Delta H_r \frac{n_j - n_{j0}}{\nu_j} = \Delta H_r \xi$$

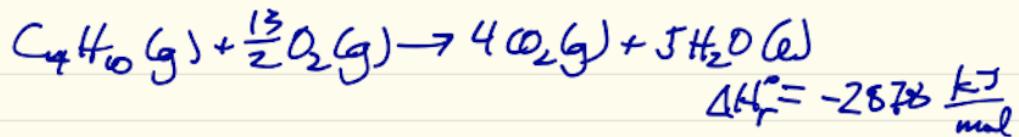
- Flow context, same idea

$$\dot{n}_j = \dot{n}_{j0} + \nu_j \xi$$

$$\Delta \dot{H} = \Delta H_r \frac{\dot{n}_j - \dot{n}_{j0}}{\nu_j} = \Delta H_r \xi$$

EXAMPLE: Enthalpy of reaction. Butane combustion:





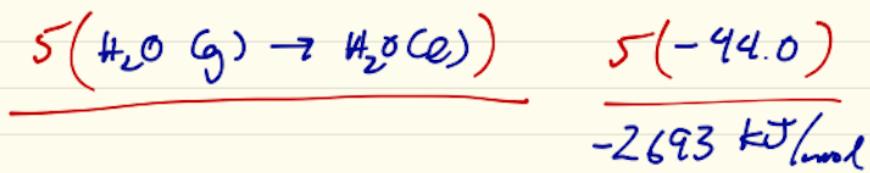
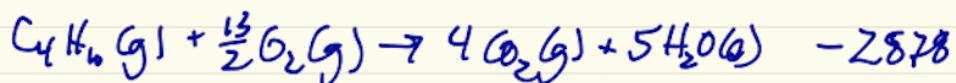
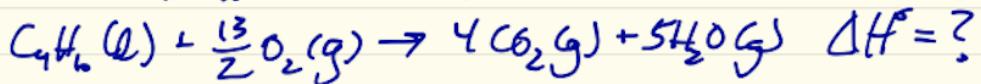
1) 2400 mol/s CO_2 produced $\Delta H = ?$

$$\frac{N_{CO_2} - N_{CO_2,0}}{v_{CO_2}} = \frac{2400 \text{ mol/s}}{4} = 600 \text{ mol/s} = \xi$$

$$\Delta H = -2878(600) = -1.73 \times 10^6 \text{ kJ}$$

2) $\Delta H_{\text{vap}, H_2O} = 44.0 \frac{\text{kJ}}{\text{mol}}$

$$C_4H_{10} = 19.2 \text{ kJ/mol}$$



- 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,” $\Delta \hat{H}_f$

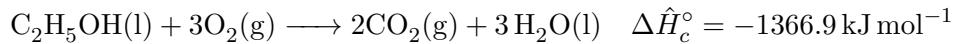


- By this convention, the enthalpy of formation of the elements is zero
- Heats of formation measured indirectly, widely tabulated (Table B.1)

-
- 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



- 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

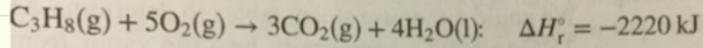
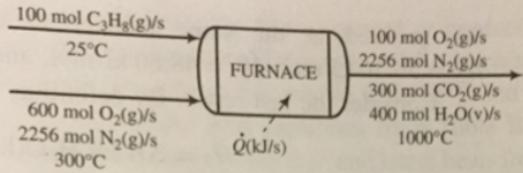
- “Heat of reaction” method
 - Choose a convenient reference state for each reactant and product, typically ones for which the heat of reaction is known
 - Construct path reactant state \rightarrow standard reactants \rightarrow standard products \rightarrow product state
 - Easy for single reaction

$$\Delta \dot{H} = \xi \Delta \hat{H}_r^\circ + \sum_{out} \dot{n}_{out} \hat{H}_{out} - \sum_{in} \dot{n}_{in} \hat{H}_{in}$$

- 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



$$\dot{G} = \frac{\dot{n}_{out} - \dot{n}_{in}}{2} = \frac{0 - 100}{-1} = 100 \text{ mol/s}$$

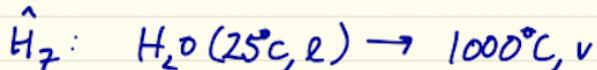
References: $\text{C}_3\text{H}_8(\text{g})$, $\text{O}_2(\text{g})$, $\text{N}_2(\text{g})$, $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$
at 25°C and 1 atm

Substance	\dot{n}_{in} (mol/s)	\dot{H}_{in} (kJ/mol)	\dot{n}_{out} (mol/s)	\dot{H}_{out} (kJ/mol)
C_3H_8	100	0	—	—
O_2	600	\dot{H}_2	100	\dot{H}_4
N_2	2256	\dot{H}_3	2256	\dot{H}_5
CO_2	—	—	300	\dot{H}_6
H_2O	—	—	400	\dot{H}_7

$$\hat{H}_2 = \int_{25}^{300} C_{p, \text{O}_2} dT = 8.47 \text{ kJ/mol}$$

or tabulation

$$\hat{H}_3 = 8.12 \quad \hat{H}_4 = 32.47 \quad \hat{H}_5 = 30.56 \quad \hat{H}_6 = 48.60$$



steam tables - or

$$\int_{25}^{100} C_p dT + \Delta H_{vap} \leftarrow \int_{25}^{1000} C_p dT$$

$$\Delta \dot{H} = 100 \text{ mol/s} \cdot (-2220 \text{ kJ/mol}) + \sum - \sum = -1.26 \times 10^5 \text{ kJ/s}$$

- “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), H₂(g), O₂(g), N₂(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

$$\hat{H}_1 = \Delta H_{f,C_3H_8}^\circ = \sim 103.8 \text{ kJ/mol}$$

$$\begin{cases} \hat{H}_2 = 0 + (\hat{H}(300) - \hat{H}(25)) = 8.47 \text{ kJ/mol} \\ \hat{H}_4 = 0 + (\hat{H}(1000) - \hat{H}(25)) = 32.47 \end{cases}$$

$$\text{Diss } N_2 \quad \hat{H}_3 = 8.12 \quad \hat{H}_5 = 30.56$$

$$\begin{aligned} \hat{H}_6 &= \Delta H_{f,CO_2}^\circ + (\hat{H}(1000) - \hat{H}(25)) = -344.9 \text{ kJ/mol} \\ &- 393.5 + (48.60 - 0) = \\ &\text{B.1} \qquad \qquad \text{B.8} \end{aligned}$$

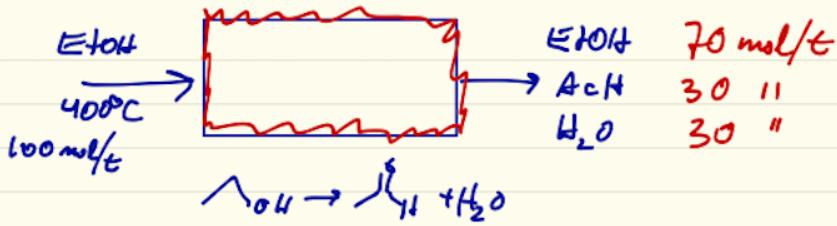
$$\hat{H}_7 = \dots = -204.1 \text{ kJ/mol}$$

$$\begin{aligned} \Delta H &= \sum_{\text{out}} n_i \hat{H}_i - \sum_{\text{in}} n_i \hat{H}_i \\ &= -1.26 \times 10^5 \text{ kJ/mol} \end{aligned}$$

- “Heat of formation” method nice for multiple reactions

11.4 Adiabatic reactors

- Sometimes faced with unknown final T



① conversion = 30%

$$EtOH_{out} = (1 \rightarrow) EtOH_{in} = 70 \text{ mol/t}$$

$$AcH = H_2O = 30 \text{ mol/t}$$

$$\xi = \frac{n_j - n_{j^\circ}}{\gamma_j} = 30 \text{ mol/t}$$

② Outer T? If adiabatic? rxn method

$$\Delta H_r = \Delta H_f^{\circ}_{AcH} - \Delta H_f^{\circ}_{EtOH} - \Delta H_f^{\circ}_{H_2O} = 69.11 \text{ kJ/mol}$$

$$\text{IN: } \hat{H}_{EtOH}(400^\circ\text{C}) = \int_{25}^{400} C_p, EtOH(T) dT = 33.79 \frac{\text{kJ}}{\text{mol}}$$

out: Don't know T!!

$$\hat{H}_{EtOH} = \int_{25}^T C_p(T) dT = \hat{H}_{EtOH}(T) \dots$$

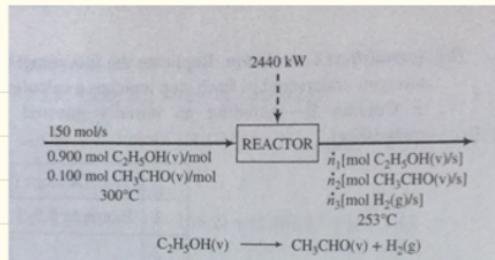
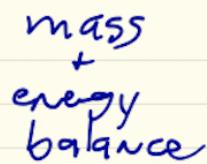
$$\Delta H + \cancel{\Delta E_k} + \cancel{\Delta E_v} = \cancel{\epsilon} + \cancel{\epsilon} \quad \Delta H = 0$$

$$\Rightarrow 3\Delta H_r + 70\hat{H}_{EtOH}(T) + 30\hat{H}_{AcH}(T) + 30\hat{H}_{H_2O}(T) - 100(33.79) = 0$$

In general non-linear eq. Guess & check.

... $T = 185^\circ\text{C}$ (should put in spreadsheet or python)

- Or combined mass and energy



unknowns: 3 equations: 2 mass balances
 1 energy balance

mass balance

$$C: 2i_1 + 2i_2 = 150(0.8)2 + 150(0.1) \cdot 2 = 300 \text{ mol/s}$$

$$H: 6n_1 + 4n_2 + 2n_3 = 150(0.9) \cdot 6 + 150(0.1) \cdot 4 = 870 \text{ mol/s}$$

energy balance

$$\text{KetoOH} \quad \frac{\text{in}}{\Delta H_f^\circ + \int_{25}^{300} C_p} = -212.19 \quad \frac{\text{out}}{\Delta H_f^\circ + \int_{25}^{253} C_p} = -216.81$$

Acht -147.07 -156.90

H₂ - 6.595

$$\begin{aligned} \Delta H &= 2 \\ &= n_1(-216.8) + n_2(-150.9) + n_3(6.595) \\ &\quad - 0.9(150)(-212.19) - 0.1(150)(-147.08) \\ &= 2440 \text{ kJ} \end{aligned}$$

3 linear eq, 3 unknowns

$$\begin{pmatrix} 2 & 2 & 0 \\ 6 & 4 & 2 \\ -216.8 & -158.9 & 6.595 \end{pmatrix} \begin{pmatrix} n_1 \\ n_2 \\ n_3 \end{pmatrix} = \begin{pmatrix} 300 \\ 800 \\ -28412 \end{pmatrix}$$

$$n_1 = 92 \text{ m} \quad n_2 = 58 \quad n_3 = 43.0 \quad X_{EloH} = \frac{135 - 92}{135} = 0.3$$

11.5 Other applications

- Heats of solution
 - Combustion

12 Transient processes

- General balance around any system or element of a system

$$\text{output} = \text{input} + (\text{generation} - \text{consumption}) - \text{accumulation}$$

- 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.

Balance on a filling tank

- For chemical reaction, rate related to chemical reaction rate.