Chapters 5-6
(where we are going)

- Ideal gases and liquids (today)
  - Densities
  - Partial pressures
- Non-ideal gases (next time)
  - Eqns. of state
  - Reduced pressures and temperatures
  - Compressibility charts (z)
- Vapor-liquid systems (Ch. 6)
  - Vapor pressure
  - Humidity
  - Raoult's law
  - Bubble and dew points
  - Solid-solid & liquid-liquid systems

1

Class 15

- Properties of Single-Phase Materials
  - Connection to Material Balances
  - Ideal Assumptions
  - Liquids- density of mixtures
  - Ideal Gases
  - Standard conditions

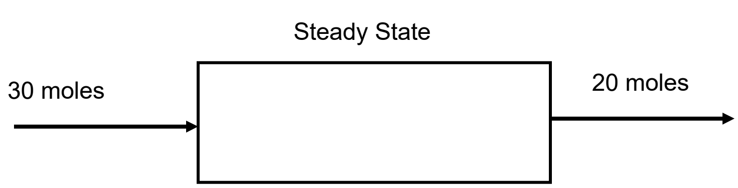
2

Is the following possible?

Not at Steady State!

3

Is the following possible?

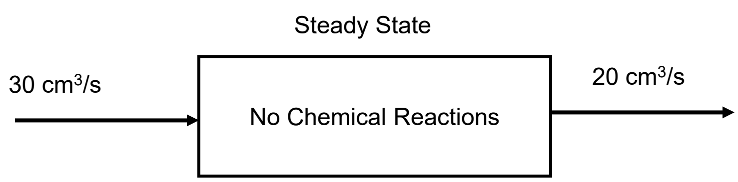


Yes!

Only if reactions occur!

4

Is the following possible?

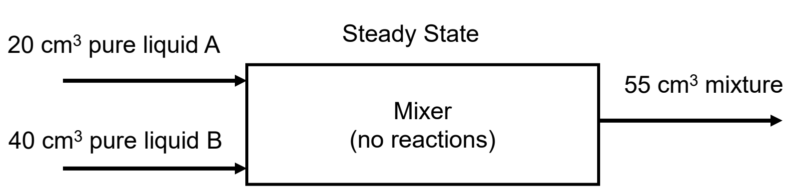


Yes!

Ideal Gas, change in temperature or pressure

5

Is the following possible?



Yes!

Even for liquid systems!

6

Need Relationships Between Variables

- Not easy to measure molar flow rates
- What can we easily measure?
  - Mass flow rate
  - Volumetric flow rate
  - Composition
  - Pressure
  - Temperature
- Relate measured variables to desired quantities

7

Liquid Mixtures

- In general, liquid volume is not conserved

$$V = V_1 + V_2 + V^E$$

- Contraction or expansion occurs because of the difference in interactions between like and unlike molecules
- V^E typically small. Assume $V^E = 0$ for this course.
- This implies that liquid volumes are additive

$$\frac{1}{\bar{\rho}} = \sum_{i=1}^{n} \frac{x_i}{\rho_i}$$

x_i = mass fraction of species i

8

Mass and Mole Fractions Have Units!

- $x_i = \frac{mass\ of\ species\ i}{mass\ of\ mixture}$ (same with moles)

- Look at units of density equation

$$\frac{1}{\bar{\rho}} = \sum_{i=1}^{n} \frac{x_i}{\rho_i}$$

- $\frac{1}{kg/m^3} = \frac{\frac{kg\ of\ i}{kg\ of\ mix}}{\frac{kg\ of\ i}{m^3}}$

9

Example

- What is the density of a mixture containing 20 wt% A (ρ_A = 1 g/cm^3) and the balance B (ρ_B = 2 g/cm^3)?

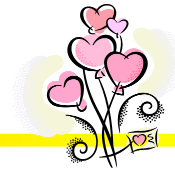
$$\frac{1}{\rho} = \frac{0.2}{\rho_A} + \frac{0.8}{\rho_B} = \frac{0.2}{1} + \frac{0.8}{2}$$

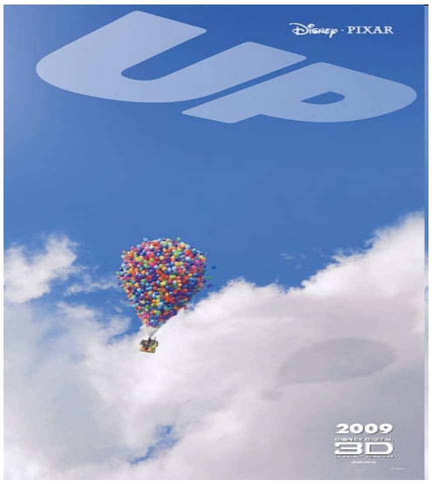
Therefore, ρ = 1.67 g/cm^3

If you used $\rho = \Sigma x_i \rho_i$, you would have calculated
ρ = 0.2*1 + 0.8*2 = 1.8 g/cm^3 …. Oops!

10

Gases





- **Equation of State** (EOS)
  - relates amount (moles) to V, T, P
- Many different equations of state
  - represent behavior of real systems
- **Ideal Gas Law**
  - Simplest equation of state
  - Most widely used

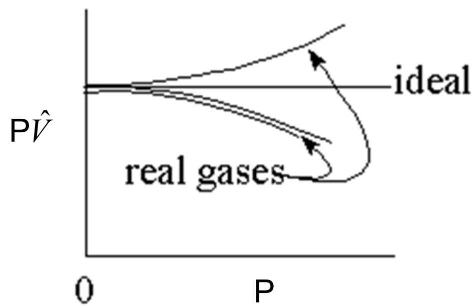
Ideal Gas

- Equation of State: **PV = nRT**
- Also $P\hat{V} = RT$ (i.e., $\hat{V}$ = V/n)

$\hat{V}$ = specific volume

- Assumptions
  - No interaction between molecules
  - Molecules have zero volume
- Valid at low concentration (n/V is small)
  - Best at high or low pressures?
  - Best at high or low temperatures?

Ideal vs. Real Gases



From p. 221, ideal when:

$\hat{V}_{ideal} > 5L/mol \quad (diatomic \;\; gases)$

$\hat{V}_{ideal} > 20L/mol \quad (other \;\; gases)$

$\hat{V}_{ideal} = \frac{RT}{P}$

Does this make sense?

13

Ideal Gas Constant

- In Chemistry and Chemical Engineering, ***R*** is universal (independent of species)
  - Nice table in the back cover of the book for different units
- In Mechanical Engineering, the MW of the species is included in **R**, so there is a different value of ***R*** for each species

14

Ideal Gas Constant

THE GAS CONSTANT

8.314 $m^3 \cdot Pa/(mol \cdot K)$	For ideal gas eqn
0.08314 $L \cdot bar/(mol \cdot K)$	
0.08206 $L \cdot atm/(mol \cdot K)$	
62.36 $L \cdot mm\ Hg/(mol \cdot K)$	
0.7302 $ft^3 \cdot atm/(lb\text{-}mole \cdot °R)$	
10.73 $ft^3 \cdot psia/(lb\text{-}mole \cdot °R)$	
8.314 $J/(mol \cdot K)$	For Energy
1.987 $cal/(mol \cdot K)$	
1.987 $Btu/(lb\text{-}mole \cdot °R)$	

15

from CRC Handbook

Values of Gas Constant, $R = \frac{PV}{nT}$

Absolute Pressure

Volume	Temp.	moles	Atm	psia	mm Hg	cm Hg	in Hg	in H_2O	ft H_2O
ft^3	°K	gm	0.00290	0.0426	2.20	0.220	0.0867	1.18	0.0982
		lb	1.31	19.31	999	99.9	39.3	535	44.6
	°R	gm	0.00161	0.02366	1.22	0.122	0.0482	0.655	0.0546
		lb	0.730	10.73	555	55.5	21.8	297	24.8
cm^3	°K	gm	82.05	1206	62,400	6240	2450	33,400	2780
		lb	37,200	547,000	2.83×10^7	2.83×10^6	1.11×10^6	1.51×10^7	1.26×10^6
	°R	gm	45.6	670	34,600	3460	1360	18,500	1550
		lb	20,700	304,000	1.57×10^7	1.57×10^6	619,000	8.41×10^6	701,000
liters	°K	gm	0.08205	1.206	62.4	6.24	2.45	33.4	2.78
		lb	37.2	547	28,300	2830	1113	15,140	1262
	°R	gm	0.0456	0.670	34.6	3.46	1.36	18.5	1.55
		lb	20.7	304	15,700	1570	619	8410	701

Conversion Factors and Constants

1 lb. = 453.59 gm
1 atm = 14.696 psia
1 atm = 760 mm Hg
1 atm = 76 cm Hg
1 atm = 29.921 in Hg
1 atm = 406.79 in H_2O
1 atm = 33.90 ft H_2O

359.0 ft^3/lb mole
22,414 cm^3/gm mole
1 inch = 2.54 cm
Std. temp. = 273.16°K or 491.69°R
28.31605 liters = 1 ft^3
$R = 8.31432 \pm 0.00034 \times 10^7$ erg $°K^{-1}$ mol^{-1}

$8314.3 \frac{N \cdot m}{kgmol \cdot K}$ or $\frac{J}{kgmol \cdot K}$ $8.3143 \frac{N \cdot m}{gmol \cdot K}$ or $\frac{J}{gmol \cdot K}$

16

Gas Concentration & Density

- Concentration = moles/volume = n/V

$$C = \frac{n}{V} = \frac{P}{RT} \qquad or \qquad C_i = \frac{y_i P}{RT}$$

- Density = mass/volume = n·MW/V = C·MW

$$\rho = \frac{n \cdot MW}{V} = \frac{P \cdot MW}{RT} \qquad or \qquad \rho_i = \frac{y_i P \cdot MW_i}{RT}$$

Sometimes ρ_i is called the mass concentration

17

Application Example

- Suppose the tires on your car are inflated to 32 psig at 25°C (77°F). What is the tire pressure at -10°C (14°F)? Assume that you are at sea level. Would this make a difference in your answer?

Time Saver!

Concept: # moles do not change!

$$n = \frac{P_1 V}{RT_1} = \frac{P_2 V}{RT_2} \Rightarrow P_2/T_2 = P_1/T_1$$

Must use absolute P and T

P_1 = 32 psig + 14.7 psia =46.7 psia
$P_2 = P_1(T_2/T_1)$ = 46.7 psia * (263 K/298 K) = 41.2 psia
41.2 – 14.7 = 26.5 psig

If P_{atm} = 12.5, P_2 = 39.3 psia = 26.8 psig

18

Tom Brady & Deflate-Gate

- T = 72°F indoors (532°R)
- T = 10°F Outdoors (470°R)
- V_{gas} = constant
- Regulation: 12.5 to 13.5 psig
- $\frac{n}{V_{gas}} = constant = \frac{P_1}{RT_1} = \frac{P_2}{RT_2}$
- $P_{out} = P_{indoor}\left(\frac{T_{out}}{T_{indoors}}\right)$

$$12.5\ psig = 27.2\ psia \left(\frac{470°R}{532°R}\right) = 24.0\ psia = 9.3\ psig$$

- 11.9 psig if starting pressure was 13.5 psig

Concepts: # moles do not change!
V_{gas} constant

19

Caution

- Only take ratios of values in <u>absolute</u> units
- **NEVER** take ratios of:
  - Temperatures in °C or °F (instead use K or °R)
  - Gauge pressures (instead use absolute pressures)

20

Standard Conditions

- Provide a reference point for reporting gas flows
- Convenient for use in calculations with ideal gas law
- Units generally reported by flow meters

SI
T_s = 0°C = 273K
P_s = 1 atm
V_s = 0.022415 m^3 (22.415 L/mol)
n_s = 1 gmol

American Engineering
T_s = 492°R (i.e., 32°F)
P_s = 1 atm
$\hat{V}_s$ = 359 ft^3/lb-mol
n_s = 1 lb-mol

Used frequently by author

Society of Petroleum Engineers (common industrial standard)
T_s = 60°F
P_s = 14.7 psia

21

Gas Flows under Standard Conditions

- **SCM**: standard cubic meters (m^3 STP)
- **SCF**: standard cubic feet (ft^3 STP)
- **SCFM**: standard cubic feet per minute (ft^3/min STP)
- **SCMH**: standard cubic meters per hour (m^3/hr STP)
- **SCFH**: standard cubic feet per hour (ft^3/hr STP)
- **SCCM**: standard cubic centimeters per minute (cm^3/min STP)
- **SLPM:** standard liters per minute (lit/min STP)

22

Gas Flows under Standard Conditions

- **SCM**: standard cubic meters (m^3 STP)
- **SCF**: standard cubic feet (ft^3 STP)
- **SCFM**: standard cubic feet per minute (ft^3/min STP)
- **SCMH**: standard cubic meters per hour (m^3/hr STP)
- **SCFH**: standard cubic feet per hour (ft^3/hr STP)
- **SCCM**: standard cubic centimeters per minute (cm^3/min STP)
- **SLPM:** standard liters per minute (lit/min STP)

Frequently used in Dr. Fletcher's experience

23

Standard Conditions and Ideal Gas Calculations

$$PV = nRT$$

Concepts: *n* does not change!
$\dot{n}$ does not change!

$$P_s\hat{V}_s = RT_s$$

(s = standard state)

$$\frac{P\hat{V}}{RT} = \frac{P_s\hat{V}_s}{RT_s}$$

so

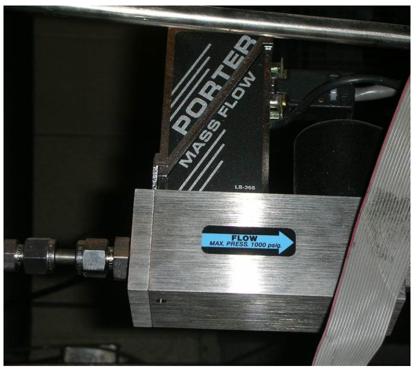
$$\frac{P\hat{V}}{T} = \frac{P_s\hat{V}_s}{T_s} \qquad \frac{P\dot{V}}{T} = \frac{P_s\dot{V}_s}{T_s}$$

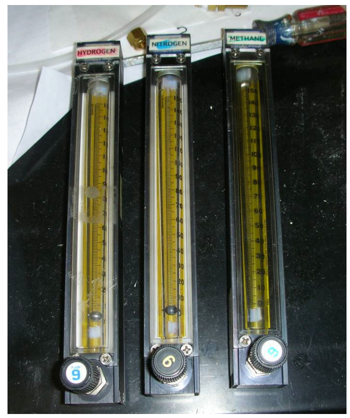
Given standard volume or volumetric flow rate, use ratios to convert to actual volume or volumetric flow rate

24

Flow Meters Often Report Standard Conditions

- Examples from my labs





Mass flow controller
(slpm)

Rotameters
(slpm or sccm)

25

Example

- The flow rate of a stream at 285°F and 1.3 atm is measured with an orifice meter. The calibration chart for the meter indicates that the flow is 3.95 x 10^3 SCFM. Calculate the molar flow rate and the true volumetric flow rate of the stream.

$$\dot{n} = \frac{P\dot{V}}{RT} = \frac{P_s\dot{V}_s}{RT_s}$$

Absolute T's

so

$$\dot{V} = \dot{V}_s\left(\frac{P_s}{P}\right)\left(\frac{T}{T_s}\right) = 3.95 \times 10^3 SCFM\left(\frac{1atm}{1.3atm}\right)\left(\frac{745°R}{492°R}\right)$$
$$= 4.60 \times 10^3 ft^3/\text{min}$$

26

Gas Mixtures

- **Partial pressure** of component A

$$P_A = y_A P_{tot}$$

- Dalton's Law

total P = sum of partial pressures

Example: At sea level, what is the partial pressure of O_2?

$$P_{O2} = y_{O2}\, P_{tot} = 0.21*1.0 \text{ atm} = 0.21 \text{ atm}$$

- Good for both ideal and non-ideal gases!

27

Gas Mixtures (cont.)

- In LaBarge, Wyoming, there is a natural gas well for ExxonMobil
- Gas composition coming from the well is:
  - $y_{CO2} = 0.70$
  - $y_{CH4} = 0.25$
  - $y_{H2S} = 0.05$
- If the total pressure in the well is 20 atm, what is the partial pressure of CH_4?

$$P_{CH4} = y_{CH4}\, P_{tot} = (0.25)(20 \text{ atm}) = 5 \text{ atm}$$

28

Ideal Gas Mixtures

- Amagat's Law

  partial volumes add up to total volume

  $v_A + v_B + \ldots = V_{tot}$

- Volume fraction = mole fraction

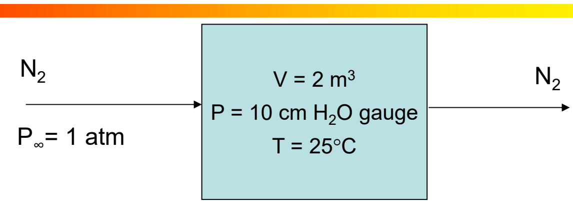
  percent by volume = mole percent

  $v_A = y_A V_{tot}$

Good only for ideal gases!

29

Problem 5.13 (purging a box)



Replace volume every 5 minutes

Find $\dot{m}_{N2}$

$$P_{gauge} = (0.1\ m\ H_2O)\left(\frac{1\ atm}{10.333\ m\ H_2O}\right) = 0.0097\ \text{atm}$$

$$P_{abs} = P_{gauge} + P_{atm} = 1.0097\ atm$$

(a) Calculate $\dot{m}_{N2}$ using the ideal gas equation (easy)

(b) Calculate $\dot{m}_{N2}$ using 22.4 L/mol at standard conditions (this way is confusing)

$$\dot{V} = \frac{V}{time} = \frac{2\ m^3}{5\ min} = 0.4\frac{m^3}{min} = 400\ L/min$$

$$\dot{m} = \rho\dot{V} \qquad \rho = \frac{P \cdot MW}{RT} = \frac{1.0097 atm \cdot 28\frac{g}{mol}}{\frac{0.08205\ L \cdot atm}{K \cdot mol}\ 298\ K} = 1.156\ g/L$$

$$\dot{m} = (400\ L/min)(1.156\ g/L) = 462.5\ g/min$$

30

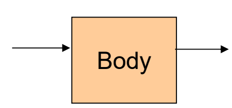
Review

- Ideal liquid mixtures (volume is additive)
  - How to get an average liquid density
- Ideal Gas Law
  - Gas constant in different units
  - Use absolute units of T & P
- Standard Conditions
- Definition of Partial Pressure

31

HW Hints

- 14.1 – Ideal gas & MW
- 14.2 – Ideal gas & safety
- 14.3 – Avg MW, mass fraction
- 14.4 – breathing
  - Find $\dot{V}_{in}$, convert to $\dot{m}_{in}$
  - N_2 balance, find $\dot{m}_{out}$ and $\dot{V}_{out}$



32