



Principles 1

First semester 2025-2026

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TABLE 2.3-1 SI and CGS Units

Base Units		
Quantity	Unit	Symbol
Length	meter (SI)	m
	centimeter (CGS)	cm
Mass	kilogram (SI)	kg
	gram (CGS)	g
Moles	gram-mole	mol or g-mole
Time	second	s
Temperature	kelvin	K
Electric current	ampere	A
Light intensity	candela	cd

FACTORS FOR UNIT CONVERSIONS

Quantity	Equivalent Values
Mass	1 kg = 1000 g = 0.001 metric ton (tonne) = 2.20462 lb _m = 35.27392 oz 1 lb _m = 16 oz = 5 × 10 ⁻⁴ ton = 453.593 g = 0.453593 kg
Length	1 m = 100 cm = 1000 mm = 10 ⁶ microns (μm) = 10 ¹⁰ angstroms (Å) = 39.37 in = 3.2808 ft = 1.0936 yd = 0.0006214 mile 1 ft = 12 in = 1/3 yd = 0.3048 m = 30.48 cm
Volume	1 m ³ = 1000 L = 10 ⁶ cm ³ = 10 ⁶ mL = 35.3145 ft ³ = 219.97 imperial gallons = 264.17 gal = 1056.68 qt 1 ft ³ = 1728 in ³ = 7.4805 gal = 29.922 qt = 0.028317 m ³ = 28.317 L
Density	1 g/cm ³ = 1000 kg/m ³ = 62.43 lb _m /ft ³ = density of liquid water at 4°C (reference for specific gravities)
Force	1 N = 1 kg·m/s ² = 10 ⁵ dynes = 10 ⁵ g·cm/s ² = 0.22481 lb _f 1 lb _f = 32.174 lb _m ·ft/s ² = 4.4482 N = 4.4482 × 10 ⁵ dynes
Pressure	1 atm = 1.01325 × 10 ⁵ N/m ² (Pa) = 101.325 kPa = 1.01325 bar = 1.01325 × 10 ⁶ dynes/cm ² = 14.696 lb _f /in ² (psi) = 760 mm Hg at 0°C (torr) = 10.333 m H ₂ O(l) at 4°C = 29.921 inches Hg at 0°C = 406.8 inches H ₂ O(l) at 4°C
Energy	1 J = 1 N·m = 10 ⁷ ergs = 10 ⁷ dyne·cm = 1 kg·m ² /s ² = 2.778 × 10 ⁻⁷ kW·h = 0.23901 cal = 0.23901 × 10 ⁻³ kcal (food calorie) = 0.7376 ft·lb _f = 9.486 × 10 ⁻⁴ Btu
Power	1 W = 1 J/s = 1 N·m/s = 0.23901 cal/s = 0.7376 ft·lb _f /s = 9.486 × 10 ⁻⁴ Btu/s = 1.341 × 10 ⁻³ hp

Derived Units

Quantity	Unit	Symbol	Equivalent in Terms of Base Units
Volume	liter	L	0.001 m ³ 1000 cm ³
Force	newton (SI) dyne (CGS)	N	1 kg·m/s ² 1 g·cm/s ²
Pressure	pascal (SI)	Pa	1 N/m ²
Energy, work	joule (SI) erg (CGS)	J	1 N·m = 1 kg·m ² /s ² 1 dyne·cm = 1 g·cm ² /s ²
	gram-calorie	cal	4.184 J = 4.184 kg·m ² /s ²
Power	watt	W	1 J/s = 1 kg·m ² /s ³

newton → dyne

joule → erg



2.1 UNITS AND DIMENSIONS.

- Dimension is a property that can be measured, such as length, time, mass or temperature, or calculated by multiplying or dividing other dimensions.

Note: Numerical Values of 2 quantities may be added, subtracted or equated only if the dimensions and units are the same for multiplication and division even if units are unlike

2.2 CONVERSION OF UNITS

- Conversion Factor shows the relationship between 2 different units of the same quantity.

Example 2.2-1

✓ Convert an acceleration of 1 cm/s^2 to its equivalent km/yr^2

$$\frac{1 \text{ cm}}{\text{s}^2} \cdot \frac{(60)^2 \text{ s}^2}{1 \text{ min}^2} \cdot \frac{60^2 \text{ min}^2}{1^2 \text{ hr}^2} \cdot \frac{24^2 \text{ hr}^2}{1^2 \text{ day}^2} \cdot \frac{365^2 \text{ days}^2}{1^2 \text{ yr}^2} \cdot \frac{1 \text{ m}}{100 \text{ cm}} \cdot \frac{1 \text{ km}}{1000 \text{ m}}$$

$$= 9.95 \times 10^9 \text{ km/yr}^2$$

Dimension analysis → is a method that uses a conversion factor to convert a quantity expressed in one unit to an equivalent quantity in a different unit.

$$1 \text{ mL} = 1 \text{ cm}^3$$

2.3 SYSTEM OF UNITS.

↳ A system of units has the following components:

1. Base Units for mass, length, time, temperature, electrical current and light intensity

2. Multiple units which are defined as multiples or fractions of base units

3. Derived units, obtained in one of 2 ways:

(a) by multiplying and dividing base or multiples units (cm^2 , ft/min , $\text{kg} \cdot \text{m/s}^2$, etc). Derived units of this type are compound units.

(b) As defined equivalents of compound units (eg, $1 \text{ erg} = 1 \text{ g} \cdot \text{cm}^2/\text{s}^2$, $1 \text{ lbf} = 32.174 \text{ lbm} \cdot \text{ft/s}^2$)

↳ The CGS System is almost identical to SI, the principle difference being that grams (g) and centimeters (cm) are used instead of kilograms (kg) and meters (m) as the base units of mass and L.

↳ Multiple unit preferences.

Tera (T) = 10^{12}	centi (c) = 10^{-2}
Giga (G) = 10^9	mili (m) = 10^{-3}
Mega (M) = 10^6	micro (μ) = 10^{-6}
Kilo (K) = 10^3	nano (n) = 10^{-9}

note: if the decimal moves to the right (the power decreases)
if the decimal moves to the left (the power increases)

↳ Example 2-3-1

Convert $23 \text{ lbf} \cdot \text{ft/min}^2$ to its equivalent in $\text{kg} \cdot \text{cm/s}^2$

$$\frac{23 \text{ lbf} \cdot \text{ft}}{\text{min}^2} \cdot \frac{0.453593 \text{ kg}}{1 \text{ lbf}} \cdot \frac{100 \text{ cm}}{3.281 \text{ ft}} \cdot \frac{1^2 \text{ min}^2}{(60)^2 \text{ s}^2}$$

$$= 0.088 \frac{\text{kg} \cdot \text{cm}}{\text{s}^2}$$

Q convert 800 mmHg into bars

$$800 \text{ mmHg} \cdot \frac{1.013 \text{ bar}}{760 \text{ mmHg}} = 1.07 \text{ bar}$$

Q 36 mg to g

$$36 \text{ mg} \cdot \frac{1 \text{ g}}{1000 \text{ mg}} = 0.036 \text{ g}$$

Q how many km in 15,000 decimeters

$$15,000 \text{ dm} \cdot \frac{1 \text{ m}}{10 \text{ dm}} \cdot \frac{1 \text{ km}}{1000 \text{ m}} = 1.5 \text{ km}$$

2.4 FORCE AND WEIGHT

$$1 \text{ N} = 1 \text{ kg} \cdot \text{m/s}^2 \text{ (SI)}$$

$$1 \text{ dyne} = 1 \text{ g} \cdot \text{cm/s}^2 \text{ (CGS)}$$

$$1 \text{ lbf} = 32.174 \text{ lbf} \cdot \text{ft/s}^2 \text{ (American)}$$

$$g = 9.8066 \text{ m/s}^2$$

$$= 980.66 \text{ cm/s}^2$$

$$= 32.174 \text{ ft/s}^2$$

Q The force in lbf required to accelerate a mass of 4 lbf at rate 9 ft/s^2

$$4 \text{ lbf} \cdot 9 \text{ ft/s}^2 \cdot \frac{1 \text{ lbf}}{32.174 \text{ lbf} \cdot \text{ft/s}^2} = 1.12 \text{ lbf}$$

↳ The weight of an object is the force exerted on the object by gravitational attraction

$$W = mg$$



★ TEST YOURSELF (page 11)

1. $2 \text{ Kg} \cdot \text{m/s}^2$ in N? what is $2 \text{ lbm} \cdot \text{ft/s}^2$ equivalent in lbf?

$$2 \text{ N and } 2 \text{ lbm} \cdot \text{ft/s}^2 \cdot \frac{1 \text{ lbf}}{32.174 \text{ lbm} \cdot \text{ft/s}^2} = 0.062 \text{ lbf}$$

Test Yourself
(Answers, p. 654)

1. What is a force of $2 \text{ kg} \cdot \text{m/s}^2$ equivalent to in newtons? What is a force of $2 \text{ lbm} \cdot \text{ft/s}^2$ equivalent to in lbf?
2. If the acceleration of gravity at a point is $g = 9.8 \text{ m/s}^2$ and an object is resting on the ground at this point, is this object accelerating at a rate of 9.8 m/s^2 ? **NO**
3. Suppose an object weighs 9.8 N at sea level. What is its mass? Would its mass be greater, less, or the same on the moon? How about its weight? **less 0.999**
4. Suppose an object weighs 2 lb at sea level. What is its mass? Would its mass be greater, less, or the same at the center of the earth? How about its weight? (Careful!) **same less**

2.5 NUMERICAL CALCULATION AND ESTIMATION

↳ Scientific Notation in which a number is expressed as the product of another number

2.6 DIMENSIONAL HOMOGENEITY

↳ Every valid equation must be dimensionally homogeneous: that is all additive terms on both sides of the equation must have the same dimensions. (or units)

↳ Example 2-6-1

$$D(\text{ft}) = 3t(\text{s}) - 4$$

$$- 4: \text{ft and } 3t: \text{ft/s}$$

- Derive an equation for distance in m and time in minutes

$$D(\text{ft}) = 3t(\text{s}) - 4$$

$$D(\text{ft}) = D'(\text{m}) \cdot \frac{3.28 \text{ ft}}{1 \text{ m}} = 3.28 D'(\text{m})$$

$$t(\text{s}) = t'(\text{min}) \cdot \frac{60 \text{ s}}{1 \text{ min}} = 60 t'(\text{min})$$

$$\frac{3.28 D'(\text{m})}{3.28} = \frac{3.60 t'(\text{min}) - 4}{3.28}$$

$$D'(\text{m}) = 55 t'(\text{min}) + 1.22 \text{ m}$$

↳ Example 2-6-2 Dimensional Homogeneity Dimensionless Groups

Q a quantity K depends on the temperature T in the following manner:

$$K \left(\frac{\text{mol}}{\text{cm}^3 \cdot \text{s}} \right) = 1.2 \times 10^5 e^{-\left(\frac{20,000}{1.997 T} \right)}$$

T is in Kelvin the units of the quantity $20,000$ are cal/mol , what are the units of 1.2×10^5 and 1.997 ?

$$\frac{20,000 \text{ cal}}{\text{mol}} \cdot \frac{1}{T(\text{K})} \cdot \frac{\text{mol} \cdot \text{K}}{1.997 \text{ cal}}$$

$$= 1.2 \times 10^5 \text{ mol/cm}^3 \cdot \text{s} \text{ and } 1.997 \text{ cal/mol} \cdot \text{K}$$

↳ Dimensionless Quantity can be a pure number or a multiplicative combination of variables with no net dimensions

- a quantity such as M/M_0 or Du/ν is called dimensionless group.

- Exponents (such as the 2 in x^2)

- Transcendental functions (such as \log , \exp , \sin)

- Arguments of transcendental functions (such as the x in $\sin x$)

↳ Example Questions

$$Q \ 23 \text{ lbm} \cdot \text{ft/min}^2 \rightarrow \text{kg} \cdot \text{cm/s}^2$$

$$\frac{23 \text{ lbm} \cdot \text{ft}}{\text{min}^2} \cdot \frac{1 \text{ kg}}{2.20462 \text{ lbm}} \cdot \frac{20.48 \text{ cm}}{1 \text{ ft}} \cdot \frac{1 \text{ min}^2}{(60)^2 \text{ sec}^2} = 0.0885 \text{ kg} \cdot \text{cm/s}^2$$

$$Q \ 400 \text{ in}^3/\text{day} \text{ to } \text{cm}^3/\text{min}$$

$$\frac{400 \text{ in}^3}{\text{day}} \cdot \frac{100^3 \text{ cm}^3}{(39.37)^3 \text{ in}^3} \cdot \frac{1 \text{ day}}{1440} = 4.55 \text{ cm}^3/\text{min}$$

$$Q \ 16 \text{ L}/1000 \text{ km} \rightarrow \text{gal}/\text{mile}$$

$$\frac{16 \text{ L}}{1000 \text{ km}} \cdot \frac{2.6417 \text{ gal}}{1000 \text{ L}} \cdot \frac{1 \text{ mi}}{0.0006214 \text{ km}} \cdot \frac{1 \text{ km}}{1000 \text{ m}} = 0.068 \text{ gal}/\text{mile}$$

$$Q \ (p + \frac{a}{v^2}) \times (v - b) = RXT \text{ What are the dimensions of } a \text{ \& } b?$$

$$a \rightarrow \text{Pressure} \times (\text{vol}/\text{time})^2$$

$$b \rightarrow (\text{volume}/\text{time})$$

↳ Example 2-4-1

Q water has a density of 62.4 lbm/ft^3 . How much does 2.000 ft^3 of water weigh (1) at sea level and 45° latitude and (2) denver 5374 ft and g is 32.139 ft/s^2 .

$$\text{mass} = D \cdot V = \frac{62.4 \text{ lbm}}{\text{ft}^3} \cdot \frac{2 \text{ ft}^3}{1} = 124.8 \text{ lbm}$$

$$W = m \cdot g = 124.8 \text{ lbm} \cdot \frac{g}{32.174}$$

$$124.8 \cdot \frac{32.174}{32.174} = 124.8$$

$$124.8 \cdot \frac{32.139}{32.174} = 124.7 \text{ lbf}$$



Test Yourself

(Answers, p. 654)

- What are the factors (numerical values and units) needed to convert
 - meters to millimeters? $\frac{1m}{1000mm}$
 - nanoseconds to seconds? $\frac{1sec}{1 \times 10^9 ns}$
 - square centimeters to square meters? $\frac{(100)^2 cm^2}{1 m^2}$
 - cubic feet to cubic meters (use the conversion factor table on the inside front cover)? $1m^3 / 35.3145 ft^3$
 - horsepower to British thermal units per second?
- What is the derived SI unit for velocity? The velocity unit in the CGS system? In U.S. customary units?

ft/s
m/s
cm/s

all additive terms have the same dimensions

Test Yourself

(Answers, p. 654)

- What is a dimensionally homogeneous equation? If an equation is dimensionally homogeneous, is it necessarily valid? If an equation is valid, is it necessarily dimensionally homogeneous?

NO
yes
- If $y(m/s^2) = az(m^3)$, what are the units of a ? $\frac{1}{m^2 s^2}$
- What is a dimensionless group? What multiplicative combination of $r(m)$, $s(m/s^2)$, and $t(s)$ would constitute a dimensionless group?
- If $z(lbf) = a \sin(Q)$, what are the units of Q and Q ?

$a (lbf)$
 Q no unit

$$3) \frac{r}{st^2}$$

Q $r (\text{crystal/min}) = 200 D - 10D^2$ (D in mm)

1. $200 \rightarrow \frac{\text{crystal}}{\text{min} \cdot \text{mm}}$ 2. $10 \rightarrow \frac{\text{crystal}}{\text{min} \cdot \text{mm}^2}$

2. Calculate crystal nucleation rate (crystal /s) corresponding to

0.0050 inch

$0.050 \text{ inch} \cdot \frac{1000 \text{ mm}}{25.4 \text{ inch}} = 1.27 \text{ mm}$

$r = 200 (1.27) - 10 (1.27)^2 = 237.871 \text{ crystal/min}$

$\frac{237.871 \text{ cry.}}{\text{min}} \cdot \frac{1 \text{ min}}{60 \text{ SEC}} = 3.96 \text{ crystal /Sec}$

3. Derive a formula for r (crystal/s) in terms of D (inches)

$$r \left(\frac{\text{crystal}}{s} \right) = \frac{1}{60} [200 (25.4 D \text{ in}) - 10 (25.4 D \text{ in})^2]$$



CHAPTER 3 : PROCESS AND PROCESS VARIABLE

3-1 MASS AND VOLUME

(Temperature and pressure only)

↳ Density (ρ :row) is the mass per unit volume of a material (Pure compound, solution, mixture) · SI unit (kg/m^3)

- Specific Property : is the amount of property per unit mass of the substance (xx/kg)

- Specific Volume (\hat{V}) : is the volume occupied by unit mass of the substance (m^3/kg)

↳ Something per unit mass

$$\text{Density} \xrightarrow{\text{inverse}} \text{Specific volume}$$

$$\left(\frac{\text{kg}}{\text{m}^3} \right) \quad \left(\frac{\text{m}^3}{\text{kg}} \right)$$

↳ Densities of pure solids are essentially independent of pressure and vary relatively slightly with temperature.

→ the density of a substance can be used as a conversion factor to relate the mass and volume of quantity of the substance

- Specific gravity of a substance is the ratio of the density ρ of the substance to the density ρ_{ref} of a reference substance at a specific condition

$$\text{SG} = \rho / \rho_{\text{ref}}$$

→ The reference most commonly used for solids and liquids is water at 4.0°C which has the following density.

$$\begin{aligned} \rho_{\text{H}_2\text{O}} (\text{liq}) \text{ } 4^\circ\text{C} \\ &= 1.000 \text{ g/cm}^3 \\ &= 1000 \text{ kg/m}^3 \\ &= 62.43 \text{ lbm/ft}^3 \end{aligned}$$

↳ Note that the density of a liquid or solid in g/cm^3 is numerically equal to the specific gravity of that substance.

- if you are given the specific gravity of a substance, multiply it by the reference density in any units to get the density of the substance in the same unit

Example : suppose a liquid has specific gravity = 0.80

The density of water 1 g/cm^3 or 1000 kg/m^3

multiply SG x (Density of water) → gives you the actual density

Test Yourself

(Answers, p. 654)

- What are the units of specific gravity? **dimensionless**
- A liquid has a specific gravity of 0.50. What is its density in g/cm^3 ? What is its specific volume in cm^3/g ? What is its density in lbm/ft^3 ? What is the mass of 3.0 cm^3 of this liquid? What volume is occupied by 18 g? **0.5 g/cm^3 , $2 \text{ cm}^3/\text{g}$**
- If substance A and substance B each have a density of 1.34 g/cm^3 , must 3 cm^3 of A have the same mass as 3 cm^3 of B? **YES, if 2 substances have the same density and you take equal volumes, they must have equal masses.**
- If substance A and substance B each have a specific gravity of 1.34, must 3 cm^3 of A have the same mass as 3 cm^3 of B? Why not? **NO**
- Freezing a sealed full bottle of water leads to a broken bottle, and freezing a sealed full flexible-walled container of *n*-butyl alcohol leads to a container with concave walls. What can you conclude about the densities of the solid and liquid forms of these two substances?
- Does the density of liquid mercury increase or decrease with increasing temperature? Justify your answer using a thermometer as an illustration.
- Density **decreases because** the mass occupies a greater volume.
- $\rho_{\text{H}_2\text{O}} (\text{cs}) < \rho_{\text{H}_2\text{O}} (\text{li})$; $\rho_{\text{NBA}} (\text{cs}) > \rho_{\text{NBA}} (\text{li})$

$$2. \frac{1 \text{ g}}{\text{cm}^3} \cdot \frac{1 \text{ lbm}}{453.593 \text{ g}} \cdot \frac{10^6 \text{ cm}^3}{35.2335 \text{ ft}^3} = 62.43 \text{ lbm/ft}^3$$

$$0.50 \times 62.43 = 31.2 \text{ lbm/ft}^3$$

$$m = D \cdot V = \frac{0.50 \text{ g}}{\text{cm}^3} \cdot 3 \text{ cm}^3 = 1.5 \text{ g}$$

$$V = \frac{m}{D} = \frac{19 \text{ g}}{0.50} = 38 \text{ cm}^3$$

↳ Example 3-1-1

Calculate the density of mercury in lbm/ft^3 from a tabulated specific gravity, and calculate the volume in ft^3 occupied by 215 kg of mercury

- Specific gravity of Mercury at 20°C is 13.546. Therefore.

$$\frac{1 \text{ g}}{\text{cm}^3} \cdot \frac{1 \text{ lbm}}{453.593 \text{ g}} \cdot \frac{10^6 \text{ cm}^3}{35.2335 \text{ ft}^3} = 62.43 \text{ lbm/ft}^3$$

$$62.43 \times 13.546 = 845.7 \text{ lbm/ft}^3$$

$$215 \text{ kg} \cdot \frac{1 \text{ lbm}}{0.454 \text{ kg}} \cdot \frac{1 \text{ ft}^3}{845.7 \text{ lbm}} = 0.560 \text{ ft}^3$$

↳ Example 3-1-2

Example 3-1-2 Effect of Temperature on Liquid Density

In Example 3-1-1, 215 kg of mercury was found to occupy 0.560 ft^3 at 20°C. (1) What volume would the mercury occupy at 100°C? (2) Suppose the mercury is contained in a cylinder having a diameter of 0.25 in. What change in height would be observed as the mercury is heated from 20°C to 100°C?

$$\begin{aligned} 1) V(t) &= V_0 [1 + 0.18192 \times 10^{-4} t + 0.0078 \times 10^{-6} t^2] \\ 0.560 &= 2 [1 + 0.18192 \times 10^{-4} (20) + 0.0078 \times 10^{-6} (20)^2] \\ V_0 &= 0.558 \\ V(100^\circ\text{C}) &= 0.568 \text{ ft}^3 \end{aligned}$$

$$\begin{aligned} H(100^\circ\text{C}) - H(20^\circ\text{C}) \\ \frac{V(100^\circ\text{C}) - V(20^\circ\text{C})}{\frac{\pi D^2}{4}} \\ = 23.5 \text{ ft} \end{aligned}$$



3.2 MASS AND VOLUMETRIC FLOW RATE

↳ **Flowmeter**: is a device mounted in a process line that provides a continuous reading of the flow rate in the line

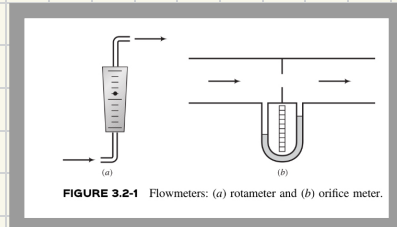
1. The **rotameter** is a tapered vertical tube containing a float; the larger the flow rate, the higher the float rises in the tube.
2. **Orifice meter** measures the pressure drop across an orifice (a small opening) in a thin plate restricting the flow in a conduit

↳ **flow rate**: the rate at which a material is transported through a process line is the flow rate of that material.

- The flow rate of a process stream may be expressed as **mass flow rate** (mass/time)
- or as a **volumetric flow rate** (volume/time)

- The density of a fluid can be used to convert a known volumetric flow rate of a process stream to the mass flow rate of that stream or vice versa.

→ Variables whose symbol include a dot (·) are rates; for example \dot{m} is flow rate and \dot{V} is volumetric flow rate



$$\begin{aligned} \dot{m} &= \rho \dot{Q} \\ \dot{Q} &= \frac{\dot{m}}{\rho} \end{aligned}$$

↳ mass flow rate
↳ volumetric flow rate

↳ Test yourself page 49.

Q1. The mass flow rate of n-hexane ($\rho = 0.659 \text{ g/cm}^3$) in a pipe is 6.59 g/s . What is the volumetric flow rate of the hexane.

$$\dot{Q} = \frac{\dot{m}}{\rho} = \frac{6.59}{0.659} = 10 \text{ cm}^3/\text{s}$$

Q2. The Volumetric flow rate of CCl_4 ($\rho = 1.595 \text{ g/cm}^3$) in a pipe is $100 \text{ cm}^3/\text{min}$. what is the mass flow rate of the CCl_4 ?

$$\dot{m} = \dot{Q} \rho = 1.595 \text{ g} \cdot \frac{100 \text{ cm}^3}{\text{cm}^3} = 159.5 \text{ g/min}$$

Q3. Same, Same, greater outlet.

Test Yourself

(Answers, p. 654)

1. A steadily flowing stream of water is funneled into a graduated cylinder for exactly 30 s, during which time 50 mL is collected. What is the volumetric flow rate of the stream? The mass flow rate? 100 mL/min ; 100 g/min
2. What is a rotameter? An orifice meter?
3. A rotameter calibration curve (flow rate versus float position) obtained using a liquid is mistakenly used to measure a gas flow rate. Would you expect the gas flow rate determined in this manner to be too high or too low? too low, the gas is much less dense

- ② 1. The **rotameter** is a tapered vertical tube containing a float; the larger the flow rate, the higher the float rises in the tube.
2. **Orifice meter** measures the pressure drop across an orifice (a small opening) in a thin plate restricting the flow in a conduit

3.3 MOLES AND MOLECULAR WEIGHT

Mole (n)

- The amount of substance that contains 6.022×10^{23} entities
- SI and CGS unit is **(g-mole = mol)**. British Unit is **(lb-mole)**

↳ Molecular Weight (M)

- The sum of the atomic weights of the atoms that constitute a molecule of the compound

↳ atomic weight

it tells you how heavy one atom of an element is relative to 1/12 the mass of a carbon-12 atom.

↳ Example 3.3-1

How many of each of the following are contained in 100g of CO_2 ($M = 44.01$)? (1) mol CO_2 ; (2) lb-moles CO_2 ;

(3) mol C; (4) mol O; (5) mol O_2 ; (6) g O; (7) g O_2 ; (8) molecules CO_2

$$1) \quad 100 \text{ g of } \text{CO}_2 \cdot \frac{1 \text{ mol } \text{CO}_2}{44.01 \text{ g } \text{CO}_2} = 2.27 \text{ mol } \text{CO}_2$$

$$4) \quad 100 \text{ g of } \text{CO}_2 \cdot \frac{1 \text{ mol } \text{CO}_2}{44.01 \text{ g } \text{CO}_2} \cdot \frac{2 \text{ mol O}}{1 \text{ mol } \text{CO}_2} = 4.54 \text{ mol O}$$

$$2) \quad 2.273 \text{ mol } \text{CO}_2 \cdot \frac{1 \text{ lb-mol}}{453.6 \text{ mol}} = 5 \times 10^{-3} \text{ lb-mole}$$

$$5) \quad 100 \text{ g of } \text{CO}_2 \cdot \frac{1 \text{ mol } \text{CO}_2}{44.01 \text{ g } \text{CO}_2} \cdot \frac{1 \text{ mol } \text{O}_2}{1 \text{ mol O}} = 2.273 \text{ mol } \text{O}_2$$

$$3) \quad 100 \text{ g of } \text{CO}_2 \cdot \frac{1 \text{ mol } \text{CO}_2}{44.01 \text{ g } \text{CO}_2} \cdot \frac{1 \text{ mol C}}{1 \text{ mol } \text{CO}_2} = 2.273 \text{ mol C}$$

$$6) \quad 100 \text{ g of } \text{CO}_2 \cdot \frac{1 \text{ mol } \text{CO}_2}{44.01 \text{ g } \text{CO}_2} \cdot \frac{2 \text{ mol O}}{1 \text{ mol } \text{CO}_2} \cdot \frac{16 \text{ g O}}{1 \text{ mol O}} = 72.7 \text{ g O}$$

$$6) \quad 100 \text{ g of } \text{CO}_2 \cdot \frac{1 \text{ mol } \text{CO}_2}{44.01 \text{ g } \text{CO}_2} \cdot \frac{2 \text{ mol O}}{1 \text{ mol } \text{CO}_2} \cdot \frac{16 \text{ g}}{1 \text{ mol O}} = 72.7 \text{ g}$$

$$8) \quad 100 \text{ g of } \text{CO}_2 \cdot \frac{1 \text{ mol } \text{CO}_2}{44.01 \text{ g } \text{CO}_2} \cdot \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol } \text{CO}_2} = 1.368 \times 10^{24} \text{ molecules}$$

- The **molecular weight** of a species can be used to relate the mass flow rate of a continuous stream of this species to the corresponding **molar flow rate**.

↳ The **dalton** is often used in discussions involving molecular weight and the size of molecules

Test Yourself

(Answers, p. 654)

- What is a mol of a species of molecular weight M , in terms of (a) a number of molecules?
(b) a mass? **1 gram**
- What is a ton-mole of a species? **The molecular weight of the species expressed in tons**
- How many **lb-moles and lb** of (a) H_2 and (b) H are contained in **1 lb-mole of H_2O** ?
- How many **gram-moles of C_2H_6** are contained in 2 kmol of this substance?

$$6.02 \times 10^{23} \text{ molecules}$$

$$3(a) \cdot 1 \text{ lb-mole } H_2, 2 \text{ lbm} \quad (b) 2 \text{ lbmol}, 2 \text{ lbm}$$

$$4 \cdot 2 \text{ kmol} \cdot \frac{1000 \text{ g mol}}{1 \text{ kmol}} = 2000$$

5. One hundred kilograms of molecular hydrogen (H_2) is fed into a reactor each hour the molar flow rate of this stream in gram-moles/hour?

6. How many g-moles are in 2.0 g of **chicken-egg white lysozyme**?

$$5) \frac{100 \text{ Kg}}{1 \text{ hr}} \cdot \frac{1000 \text{ g}}{1 \text{ Kg}} \cdot \frac{1 \text{ gram-mole } H_2}{2 \text{ gram } H_2} = 50 \times 10^3 \text{ gram-mole } H_2$$

$$6) 2 \text{ g} \cdot \frac{1 \text{ mol}}{14,300} = 1.4 \times 10^{-4} \text{ g-mole}$$

3.3 MASS AND MOLE FRACTIONS AND AVERAGE MOLECULAR WEIGHT

- process streams occasionally contain one substance, but more often they consist of **mixtures** of more than one substance
- physical properties of a mixture depend strongly on the composition of mixture
- To express the **composition** of a mixture we use the **fraction** of a species (eg. for substance A):

↳ mass fraction

$$x_A = \frac{\text{mass of A}}{\text{total mass}} \left(\frac{\text{Kg A}}{\text{Kg total}} \text{ or } \frac{\text{g A}}{\text{g total}} \text{ or } \frac{\text{lbm A}}{\text{lbm total}} \right)$$

(the mass percent of A is 100 x_A %)

↳ mole fraction

$$y_A = \frac{\text{moles of A}}{\text{total moles}} \left(\frac{\text{kmol A}}{\text{kmol total}} \text{ or } \frac{\text{mol A}}{\text{mol total}} \text{ or } \frac{\text{lb-moles A}}{\text{lb-mole total}} \right)$$

*NOTE: fraction is always less than 1

the summation of all is 1 and its unitless

↳ Example 3.3-2

- a solution contains 15% by mass ($x_A = 0.15$) and 20 mole % B ($y_B = 0.20$)

1. Calculate the mass A in 175 Kg of the solution:

$$175 \text{ Kg} \cdot 0.15 = 26.25 \text{ Kg A}$$

2. Calculate the mass flow rate of A in a stream of solution flowing at a rate of **53 lbm/h**

$$\dot{m} = \dot{Q}$$

$$\frac{53 \text{ lbm}}{\text{h}} \cdot \frac{0.15 \text{ lbm A}}{1 \text{ lbm}} = \frac{7.95 \text{ lbm A}}{\text{h}}$$

3. Calculate the molar flow rate of B in a stream flowing at a rate of 1000 mol/min

$$\frac{1000 \text{ mol}}{\text{min}} \cdot \frac{0.20 \text{ mol B}}{1 \text{ mol}} = \frac{200 \text{ mol B}}{\text{min}}$$

4. Calculate the total solution flow rate that corresponds to a molar flow rate of 28 kmol B/s

$$\frac{28 \text{ kmol B}}{\text{s}} \cdot \frac{1 \text{ kmol solution}}{0.20 \text{ kmol B}} = \frac{140 \text{ kmol solution}}{\text{s}}$$

5. Calculate the mass of the solution that contains 300 lbm of A.

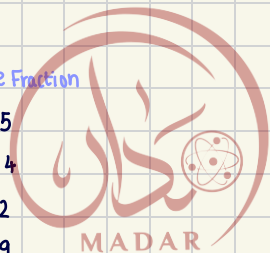
$$300 \text{ lbm A} \cdot \frac{1 \text{ lbm solution}}{0.15 \text{ lbm A}} = 2000 \text{ lbm solution}$$

↳ Example 3.3-3

a mixture of gases has the following composition by mass

O_2	16%
CO	4%
CO_2	17%
N_2	63%

Component	mass fraction	mass (g)	molecular weight	Moles	Mole Fraction
O_2	0.16	16	32	0.5	0.15
CO	0.04	4	28	0.14	0.04
CO_2	0.17	17	44	0.39	0.12
N_2	0.63	63	28	2.25	0.69
total	1	100		3.28	1.00



- the **average molecular weight** \bar{M} (Kg/Mol, lbm/lb-mole, etc.) is the ratio of the mass of a sample of the mixture (m_t) to the number of moles of all species (n_t) in the sample. If y_i is the mole fraction of the i th component of the mixture and M_i is the molecular weight of this component

$$\bar{M} = y_1 M_1 + y_2 M_2 + \dots = \sum_{\text{all comp.}} y_i M_i \quad \text{mole fraction}$$

$$\frac{1}{\bar{M}} = \frac{n}{M_t} \quad \text{mass fraction}$$

↳ Example 33-4

1) average molecular weight of air (a) from its approx. molar composition of 79% N_2 , 21% O_2 and (2) from its approx. composition by mass 76.7% N_2 , 23.3% O_2

average M.W. $\bar{M} = y_1 M_1 + y_2 M_2 + \dots = \sum y_i M_i$

b) $\frac{1}{\bar{M}} = \frac{n}{M_t} = 0.035 \text{ mol/g}$

$y_1 = 0.79, y_2 = 0.21$

$\bar{M} = 0.79 \times 28 + 0.21 \times 32 = 29 \frac{\text{g}}{\text{mol}}$

↳ Example

A gas mixture contains 40 g O_2 , 25 g SO_2 , and 30 g SO_3 . Calculate the composition of the mixture in

(a) mass fraction

(b) mole fraction

component	mass (g)	% mass frac [-]	M_i [g/mol]	mol	mol fraction = mol/total mol
O_2	40	$40/95 = 0.421$	32	$40/32 = 1.25$	$1.25/2.01 = 0.62$
SO_2	25	$25/95 = 0.263$	64.07	$25/64 = 0.39$	$0.39/2.01 = 0.19$
SO_3	30	$30/95 = 0.315$	80.07	$30/80 = 0.37$	0.19
	95	1		2.01 mol	

mass Fraction $\frac{1}{\bar{M}} = \sum \frac{z_i}{M_i}$

Test Yourself

(Answers, p. 655)

- The molecular weight of atomic hydrogen is approximately 1, and that of atomic bromine is 80. What are (a) the mass fraction and (b) the mole fraction of bromine in pure HBr?
- If $100 \text{ lb}_m/\text{min}$ of A ($M_A = 2$) and $300 \text{ lb}_m/\text{min}$ of B ($M_B = 3$) flow through a pipe, what are the mass fractions and mole fractions of A and B, the mass flow rate of A, the molar flow rate of B, the total mass flow rate, and the total molar flow rate of the mixture?

1 a. $\text{Br} = \frac{80}{81} = 0.988$

2. $\frac{1}{1+1} = 0.5$

2 a. the mass fraction

$A = \frac{100}{400} = 0.25$ $B = \frac{300}{400} = 0.75$

b. $100 \text{ lb}_m A \cdot \frac{1 \text{ mol } A}{2 \text{ lb}_m A} = 50 \text{ mol } A$

$200 \text{ lb}_m B \cdot \frac{1 \text{ mol } B}{3 \text{ lb}_m B} = 100 \text{ mol } B$

$A = \frac{50}{150} = 0.33$ $B = \frac{100}{150} = 0.66$

c) $\frac{100 \text{ lb}_m}{\text{min}}$

d) $\frac{300 \text{ lb}_m}{\text{min}} \cdot \frac{1 \text{ mol } B}{3 \text{ lb}_m B} = \frac{100 \text{ lb}_m \text{ mol}}{\text{min}}$

e) $400 \text{ lb}_m/\text{min}$
 150 mol/min



3.3 CONCENTRATION → density

- The **mass concentration** of a component of a mixture or solution is the mass of this component per unit volume of this mixture (g/cm^3 , lbm/ft^3 , kg/in^3 ...)
- The **molar concentration** of a component is the number of moles of the component per unit volume (kmol/m^3 , lb-moles/ft^3 , ...).
- The **molarity** of a solution is the value of the molar concentration of the solute expressed in gram-moles solute / liter solution

Test Yourself

A solution with volume $V(\text{L})$ contains $n(\text{mol})$ of a solute A with a molecular weight of $M_A(\text{g A/mol})$. In terms of V , n , and M_A :

1. What is the **molar concentration** of A? $\text{mol A/L} = n/V$
2. What is the **mass concentration** of A? $\text{g A/L} = nM/V$

$$V = \frac{\text{mol}}{M} = \frac{\text{mol A}}{M_A} \cdot \frac{\text{L}}{\text{mol A}} = 20 \text{ L}$$
3. What volume of the solution contains 20 mol of A?
4. What is the mass flow rate of A in a stream whose **volumetric flow rate** is 120 L/h ?

$$\dot{m} = C_A \times 120 = 120 C_A$$

$$C_A = \frac{n_A}{V}$$

- **concentration quantity of a component per unit volume of a mixture.**

Example 3-3-5

A 0.50 -molar aqueous solution of sulfuric acid flows into a process unit at a rate of $1.25 \text{ m}^3/\text{min}$. The specific gravity of the solution is 1.03 .

1) the **mass concentration** of H_2SO_4 in kg/m^3

$$\frac{0.50 \text{ mol H}_2\text{SO}_4}{\text{L}} \cdot \frac{98 \text{ g}}{1 \text{ mol H}_2\text{SO}_4} \cdot \frac{1 \text{ kg}}{1000 \text{ g}} \cdot \frac{1000 \text{ L}}{1 \text{ m}^3} = 49 \text{ kg/m}^3 \text{ H}_2\text{SO}_4$$

2) the **mass flow rate** of H_2SO_4 in kg/s

$$\dot{m} = \frac{1.25 \text{ m}^3}{\text{min}} \cdot \frac{49 \text{ kg}}{\text{m}^3} \cdot \frac{1 \text{ min}}{60 \text{ s}} = 1.04 \text{ kg H}_2\text{SO}_4/\text{s}$$

3) the **mass fraction** of H_2SO_4

$$\rho_{\text{solution}} = (1.03)(1000 \text{ kg/m}^3) = 1030 \text{ kg/m}^3$$

$$\dot{m} = \frac{1030 \text{ kg}}{\text{m}^3} \cdot \frac{1.25 \text{ m}^3}{\text{min}} \cdot \frac{1 \text{ min}}{60 \text{ s}} = 21.46 \text{ kg/s}$$

$$\% \text{H}_2\text{SO}_4 = \frac{\dot{m}_{\text{H}_2\text{SO}_4}}{\dot{m}_{\text{solution}}} \cdot \frac{1 \text{ kg H}_2\text{SO}_4/\text{s}}{21.46 \text{ kg/s}} = 0.048 \text{ kg H}_2\text{SO}_4 / \text{kg solution}$$

3.3d Parts Per Million and Parts Per Billion

$$\text{ppm} = \text{mg/L} \times 10^6$$

$$\text{ppb} = \text{mg/L} \times 10^3$$

Test Yourself

(Answers, p. 655)

BIOENGINEERING

A blood sample is reported to contain **68 ppm** creatinine (mass basis).

1. What is the mass fraction of creatinine in the blood? $68 \times 10^{-6} \text{ per g}$
2. How many milligrams of creatinine are contained in one kilogram of the blood? 68 mg
3. What is the approximate concentration of creatinine in the blood in g/L ? $1060 \times 68 \times 10^{-3} \times \frac{1}{1000} = 0.0721 \text{ g/L}$

3.4 PRESSURE

- Pressure ratio of **Normal Force** to the area on which the force acts

$$p = \frac{\text{Force}}{\text{Area}} = \frac{F}{A}$$

SI Unit $\rightarrow \frac{\text{N}}{\text{m}^2} = \text{Pa (Pascal)}$

$$\text{CGI} \rightarrow \frac{\text{dynes}}{\text{cm}^2}$$

American: lb_f/in^2 or psi

- **fluid pressure** may be defined as the ratio $\frac{F}{A}$, where F is the minimum force that would have to be exerted on a frictionless plug in the hole to keep the fluid from emerging

3.4a

- **hydrostatic pressure**: pressure of the fluid at the base of a column. it is the force (F) exerted on the base divided by the base Area (A)

$$P = P_a + \rho \cdot g \cdot h$$

usually atm pressure

density \uparrow gravity \uparrow height \rightarrow

$\frac{\text{kg}}{\text{m}^3} \cdot \frac{\text{m}}{\text{s}^2} \cdot \text{m} = \frac{\text{kg}}{\text{m} \cdot \text{s}^2} = \text{Pa}$

$$P (\text{force/area}) = \rho_{\text{fluid}} \cdot g \cdot h (\text{head of fluid})$$

Example 3-4-1 Calculation of a pressure as a head of fluid

- Express a pressure of $2 \times 10^5 \text{ Pa}$ in terms of mmHg .

$$P_h = \frac{P}{\rho_H g} = \frac{2 \times 10^5 \text{ Pa}}{13,600 \cdot 9.807} = 1.50 \times 10^3 \text{ mmHg}$$

$$\frac{2 \times 10^5 \text{ N}}{\text{m}^2} \cdot \frac{\text{m}^2}{13,600 \text{ kg}} \cdot \frac{\text{s}^2}{9.807 \text{ m/s}^2} \cdot \frac{1 \text{ kg} \cdot \text{m/s}^2}{1 \text{ N}} \cdot \frac{10^3 \text{ mm}}{1 \text{ m}} = 1.50 \times 10^3 \text{ mmHg}$$

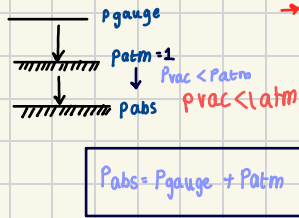


↳ Example 3-4-2

What is the pressure 30m below the surface of a lake? Atmospheric pressure is 10.4m H₂O and the density of water 1000 kg/m³ assume $g = 9.807 \text{ m/s}^2$

$$P_h = 10.4 + 30 \text{ m} = 40.4 \text{ m H}_2\text{O}$$

- Atmospheric pressure (P_{atm}) is the pressure caused by the weight of atmosphere on surface of earth



→ a vacuum reading is normally a gauge pressure below atmospheric pressure not an abs pressure

$$P_{gauge} = -P_{vac}$$

gauge → gauge	only units
abs → gauge	-760 mmHg
gauge → abs	$+760 \text{ mmHg}$

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

- The Pressure of the atmosphere can be thought of as the pressure at the base of a column of fluid (air) located at the point of measurement

- The fluid pressures referred to so far are all absolute pressures, in that a pressure of zero corresponds to a perfect vacuum. (abs pressure is total pressure and relative to a perfect vacuum)

- Gauge pressure of zero indicates that the absolute pressure of the fluid is equal to atmospheric pressure
is the pressure of the fluid relative to atmospheric pressure; it equals to P_{abs} minus P_{atm}

Test Yourself

(Answers, p. 655)

1. Is atmospheric pressure always equal to 1 atm? NO
2. What is absolute pressure? Gauge pressure pressure relative to atmospheric pressure
pressure of 0 corresponds to perfect vacuum
3. The gauge pressure of a gas is -20 mm Hg at a point where atmospheric pressure is 755 mm Hg . How else can the gas pressure be expressed in terms of mm Hg ? (Give two values.)
4. A mercury column is open to the atmosphere on a day when atmospheric pressure is 29.9 inches Hg . What is the gauge pressure 4 inches below the surface? The absolute pressure? (Give the answers in inches Hg.)

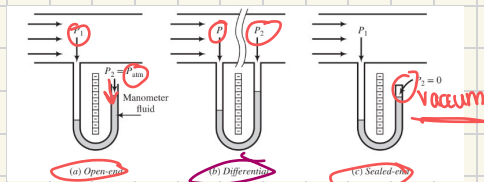
$$755 - 20 = 735$$

$$3 \cdot 735 \text{ mmHg} ; 20 \text{ mmHg of vacuum}$$

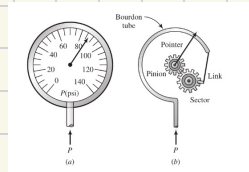
$$4 \cdot 4 \text{ inches Hg} ; 33.9 \text{ inches Hg}$$

3.4c FLUID PRESSURE MEASUREMENT

1. Elastic-element Bourdon tubes, bellows, diaphragms
2. liquid-column methods - manometers.
3. electrical methods - strain gauges, piezoresistors and piezoelectric transducers.



manometers



Bourdon gauge.

- Bourdon gauge the most common mechanical device used for pressure measurement.

Bourdon gauge are used to measure fluid pressures from nearly perfect vacuums to about 700 atm

More accurate measurements of pressures below about 3 atm are provided by manometer

- Manometer is a u-shaped tube partially filled with a fluid of known density (the manometer fluid). When the ends of the tube are exposed to diff pressures:

- if the open end of a sealed-end manometer is exposed to atmosphere ($P_i = P_{atm}$) the device functions as a barometer

1. General Manometer Equation:

$$P_1 + \rho_1 g d_1 = P_2 + \rho_2 g d_2 + \rho_f g h$$

2. Differential Manometer Equation

$$P_1 - P_2 = (\rho_f - \rho) g h \quad \text{if both fluids are gases} \quad P_1 - P_2 = \rho_f g h$$

3. Manometer formula for gases:

$$P_1 - P_2 = h$$

$$P_1 - P_{atm} = P_{gauge}$$

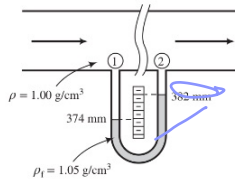


$$P_1 - P_2 = (\rho_f - \rho)gh$$

Example 3.4-3

Pressure Measurement with Manometers

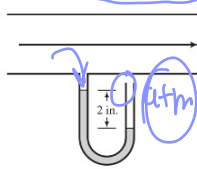
1. A differential manometer is used to measure the drop in pressure between two points in a process line containing water. The specific gravity of the manometer fluid is 1.05. The measured levels in each arm are shown below. Calculate the pressure drop between points 1 and 2 in dynes/cm^2 .



$$P_1 - P_2 = (\rho_f - \rho)gh$$

$$\frac{1.05 - 1.0}{\text{cm}^3/\text{cm}^3} \cdot \frac{980 \text{ cm}}{\text{s}^2} \cdot \frac{1 \text{ dyne}}{1 \text{ g} \cdot \text{cm/s}^2} \cdot \frac{8 \text{ mm}}{10 \text{ mm}} \cdot \frac{1 \text{ cm}}{10 \text{ mm}} = \frac{40 \text{ dynes}}{\text{cm}^2}$$

2. The pressure of gas being pulled through a line by a vacuum pump is measured with an open-end mercury manometer. A reading of 2 inches is obtained. What is the gauge pressure of the gas in inches of mercury? What is the absolute pressure if $P_{\text{atm}} = 30$ inches Hg?



$$P_1 - P_{\text{atm}} = P_{\text{gauge}} = -2 \text{ in}$$

$$P_1 = P_{\text{atm}} + P_{\text{gauge}} = (30 - 2) \text{ in Hg} = 28 \text{ in Hg}$$

3.5 TEMPERATURE

$$T(\text{K}) = T(^{\circ}\text{C}) + 273.15$$

$$T(^{\circ}\text{R}) = T(^{\circ}\text{F}) + 459.67$$

$$T(^{\circ}\text{R}) = 1.8 T(\text{K})$$

$$T(^{\circ}\text{F}) = 1.8 T(^{\circ}\text{C}) + 32$$

- Temperature is a measure of the average KE of the molecules of a substance.

- it is measured indirectly using scale relative to a measurable physical property that depend on temperature

Example 3.5-1

Derive equation $T(^{\circ}\text{F}) = 1.8 T(^{\circ}\text{C}) + 32$ in terms of $T(^{\circ}\text{C})$. Use $T_1 = 0^{\circ}\text{C}$ (32°F) and $T_2 = 100^{\circ}\text{C}$ (212°F)

$$T(^{\circ}\text{F}) = a T(^{\circ}\text{C}) + b$$

$$32 = (a)(0) + b \rightarrow b = 32$$

$$212 = (a)(100) + 32 \rightarrow a = 1.8$$

$$T(^{\circ}\text{F}) = 1.8 T(^{\circ}\text{C}) + 32$$

conversion factors (Temp interval)

$$\frac{1.8^{\circ}\text{F}}{1^{\circ}\text{C}}, \frac{1.8^{\circ}\text{R}}{1\text{K}}, \frac{1^{\circ}\text{F}}{1^{\circ}\text{R}}, \frac{1^{\circ}\text{C}}{1\text{K}}$$

Test Yourself

(Answers, p. 655)

- Suppose you were given a glass tube with mercury in it but no scale markings, and you were given only a beaker of water, a freezer, and a bunsen burner with which to work. How would you calibrate the thermometer to provide readings in $^{\circ}\text{C}$? $0^{\circ}\text{C} \rightarrow \text{water freezes}$, $100^{\circ}\text{C} \rightarrow \text{water boils}$.
- Which is warmer, a temperature of 1°C or 1°F ? $1^{\circ}\text{C} = 33^{\circ}\text{F}$
- Which reflects a greater change in temperature, an increase of 1°C or 1°F ?

Example 3.5-2

consider the interval from $20^{\circ}\text{F} \rightarrow 80^{\circ}\text{F}$

- Calculate the equivalent temps in $^{\circ}\text{C}$ and the interval between them.
- Calculate directly the interval in $^{\circ}\text{C}$ between the temps

$$1. \quad 20^{\circ}\text{F} = 1.8 T(^{\circ}\text{C}) + 32 = -6.67^{\circ}\text{C}$$

$$80^{\circ}\text{F} = 1.8 T(^{\circ}\text{C}) + 32 = 26.66^{\circ}\text{C}$$

$$26.66 - (-6.67) = 33.33^{\circ}\text{C}$$

$$2. \quad (80 - 20)^{\circ}\text{F} \cdot \frac{1^{\circ}\text{C}}{1.8^{\circ}\text{F}} = 33.33^{\circ}\text{C}$$



↳ Example 3.5-3

The heat capacity of ammonia defined as the amount of heat required to raise the temp of a unit mass of ammonia by precisely 1°C at a constant pressure is, over a limited temprange, given by the expression:

$$C_p \left(\frac{\text{Btu}}{\text{lbm} \cdot ^\circ\text{F}} \right) = 0.487 + 2.29 \times 10^{-4} T(^{\circ}\text{F})$$

Determine the expression for C_p in $\text{J}/(\text{g} \cdot ^\circ\text{C})$ in terms $T(^{\circ}\text{C})$

$$C_p \left(\frac{\text{Btu}}{\text{lbm} \cdot ^\circ\text{F}} \right) = 0.487 + 2.29 \times 10^{-4} [1.8 T(^{\circ}\text{C}) + 32]$$

$$C_p \left(\frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \right) = [0.494 + 4.12 \times 10^{-4} T(^{\circ}\text{C})] \frac{\text{Btu}}{\text{lbm} \cdot ^\circ\text{F}} \cdot \frac{1.8^{\circ}\text{F}}{1^{\circ}\text{C}} \cdot \frac{1\text{J}}{9.486 \times 10^{-4} \text{Btu}} \cdot \frac{1\text{lbm}}{454\text{g}}$$

$$C_p \left(\frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \right) = 2.06 + 1.72 \times 10^{-3} T(^{\circ}\text{C})$$

*note: the abs. pressure of a fluid is the pressure relative to a perfect vacuum ($P=0$)

the gauge pressure is the pressure relative to atmospheric. $P_{\text{gauge}} = P_{\text{abs}} - P_{\text{atm}}$. Common pressure gauges like a Bourdon gauge and an open-end manometer provide a direct reading of gauge pressure.

0-7000atm

Test Yourself

(Answers, p. 655)

1. What is a Bourdon gauge? What range of pressures can it be used to measure? As it is normally calibrated, does it measure gauge or absolute pressure?
2. What is an open-end manometer? A differential manometer? A sealed-end manometer?
3. True or false?
 - 1 end atm | end open 2 ends open 1 end is sealed vacuum
- (a) An open-end manometer provides a direct reading of the gauge pressure of a gas. T
- (b) A sealed-end manometer provides a direct reading of the absolute pressure of a gas, provided that the gas pressure in the sealed end may be neglected. T
- (c) The reading of a differential manometer does not depend on the density of the fluid in the pipeline but only on that of the manometer fluid. F
4. The pressure of a gas in a pipeline is measured with an open-end mercury manometer. The mercury level in the arm connected to the line is 14 mm *higher* than the level in the open arm. What is the gauge pressure of the gas in the line? -14 mm Hg

Test Yourself

(Answers, p. 655)

1. Define (a) the pressure of a fluid flowing in a pipe, (b) hydrostatic pressure, and (c) a head of a fluid corresponding to a given pressure.
2. Consider the tank in Figure 3.4-1. Does the pressure at the plug depend on the height of the opening in the tank? (*Hint: Yes.*) Why? Would you expect the difference between the pressure at the top and that at the bottom to be very large if the fluid were air? How about water? Mercury?
3. Suppose the pressure in the tank of Figure 3.4-1 is given as 1300 mm Hg. Does this tell you anything about the height of the tank? If you were given the area of the hole (say, 4 cm^2), how would you calculate the force needed to hold the plug in the hole?
4. Suppose the pressure at a point within a column of mercury in a tube is 74 mm Hg. What is the pressure 5 mm below this point? (If this takes you more than one second, you are probably doing it wrong.)



CHAPTER 4 : Fundamentals Of Material Balances -

-The basis to this is the law of conservation of mass, which states that mass can neither be created nor destroyed.

4.1 PROCESS CLASSIFICATION

a) Types of systems

open system

Material flow across the system boundary during the interval of time being studied

closed system

No flows cross the system boundary, in or out

no input or output during the operation time
 $\Delta t = t_f - t_0$

b) Values of the variables

1: **Steady state** if the values of all variables in a process don't change with time, except possibly for minor fluctuations

2: **unsteady state** if any of the process variables change with time.
or transient

c) classification based on how materials are added/removed.

1: **Batch process** closed system, usually unsteady state, amount unit (kg, mol, etc) no material enters or leaves while the process is happening

2: **continuous process** open system, steady state, (kg/s, mol/h), the inputs and outputs flow continuously throughout the duration of the process.

3: **Semibatch process** unsteady state, open state, neither batch nor continuous either leaves or enters continuously

→ Batch processing is commonly used when relatively small quantities of a product are to be produced, while continuous processing is generally better suited to large production rates.

Test Yourself

Classify the following processes as batch, continuous, or semibatch, and transient or steady-state.

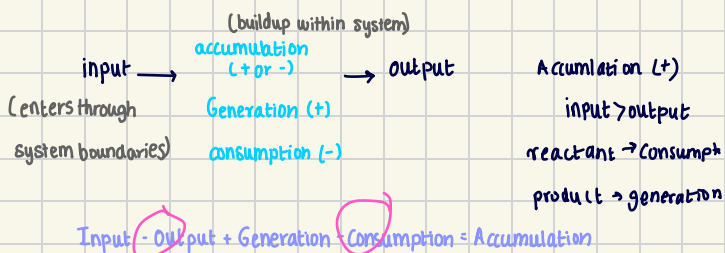
Answers, p. 655)

1. A balloon is filled with air at a steady rate of 2 g/min. **transient, semibatch**
2. A bottle of milk is taken from the refrigerator and left on the kitchen table. **Batch, Transient**
3. Water is boiled in an open flask. **Semibatch, transient**
4. Carbon monoxide and steam are fed into a tubular reactor at a steady rate and react to form carbon dioxide and hydrogen. Products and unused reactants are withdrawn at the other end. The reactor contains air when the process is started up. The temperature of the reactor is constant, and the composition and flow rate of the entering reactant stream are also independent of time. Classify the process (a) initially and (b) after a long period of time has elapsed.

Equipment Encyclopedia
reactors-PFR
www.wiley.com/college/feider

4.2 General Balance Equation

it is based on Law of conservation of mass



→ $\text{accu} = 0$ (material balance)

1: continuous Steady-state processes

$\text{input} + \text{generation} = \text{Output} + \text{Consumption}$
non-reactive
 $\text{input} = \text{output}$

2: integral Balances on batch processes

$\text{initial input} + \text{generation} = \text{Final Output} + \text{Consumption}$

- **Accumulation** is the rate of change of material within the system

- 1: **positive** : material increasing (unsteady state)
- 2: **negative** material decreasing (unsteady state)
- 3: **Zero** steady state

Types of Balances

1. **Differential Balances**: indicates what is happening with a system at an instant in time. Each term of the balanced equation is a rate and has units of the balanced quantity unit divided by time unit. This is the type of balance usually applied to a continuous process.
2. **Integral Balances** describe what happens between 2 instants of time. Each term of the equation is an amount of the balanced quantity and has the corresponding unit.



- if the balanced quantity is total mass, set generation = 0 and consumption = 0

- if the balance substance is a non-reactive species set $gen = 0$ $cons = 0$

- if the system is at steady state $acc = 0$. $input + generation = output + consumption$

if the balance is on a nonreactive species or on total mass, the generation and consumption terms equal zero and the eq. is $input = output$.

- integral Balances on batch processes:

initial input + gen = final output + consumption

4.3 MATERIAL BALANCE CALCULATIONS

★ **Flow chart**: drawing a process, using boxes or other symbols to represent process units and lines with arrows to represent inputs and outputs.

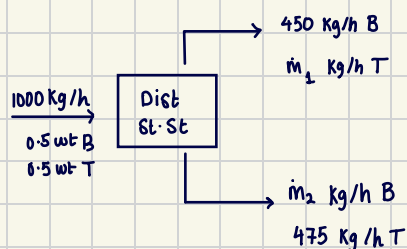
[can help get material balance calculations started and keep them moving, but must be fully labeled

↳ Rules for labelling flowcharts

1- label either a total flow rate (or amount) and component mass or mole fractions

2- assign algebraic symbols to unknown stream variables and write these variable names and their associated units on the chart.

3- if volumes (or volumetric flow rates) of streams are either given or required, include labels both for them and for mass or molar quantities.



Sources of eqns:

Mass Balance

$$input + gen = output + con$$

{ B balance
T balance

$$input_B = output_B$$

$$0.5(1000) = 450 + m_1$$

$$0.5(1000) = m_2 + 475$$

$$total\ in = total\ out$$

$$1000 = (450 + m_1) + (m_2 + 475)$$

- The masses (but not the mass fractions) all streams could be multiplied by a common factor and the process would remain balanced

moreover the stream masses could be changed to mass flow rates

★ **Scaling**: The procedure of changing the value of all stream amounts or flow rates by proportional amount while leaving the stream compositions unchanged

★ **Balanced**: $(atoms)_{in} = (atoms)_{out}$ for each atomic species

★ **Basis of calculation**: an assumed amount of an input or output stream

- The maximum number of independent eqns. you can write (single units)

it is equal to the number of chemical species in the input and output stream.

you can also write a total Mass Balance ($m_{in} = m_{out}$)

4.3 Degree of freedom

it determines whether you have enough information to solve the given problem

↳ procedure

1- draw & label flowchart

2- count the number of unknown variables (n unknown)

3- count the number of independent equations relating to them (n indep eqns)

4- degrees of freedom of the process is (n df) where

$$n_{df} = (n \text{ unknowns} - n \text{ indep eqns}) \rightarrow \text{DOF}$$

There are 3 possibilities for (n df)

$n_{df} = 0$ completely defined (unique sol)

$n_{df} > 0$ under defined (infinite no. of sol)

$n_{df} < 0$ over defined (Many Boundaries)

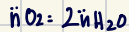
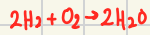


→ the sources of equations:

- 1- material balance
- 2- Energy Balance
- 3- process specifications
- 4- physical properties & laws ($R = nR$, densities etc)
- 5- physical constraint

$$\sum x_i = 1 \quad \sum y_i = 1$$

6- stoichiometric relations



→ flow rates have to be +ve
and abs pressure > 0

purging → splitting

it is a small stream bled off

Make up: required to replace losses to leaks, carryover etc. within the recycle loop

Purge: small stream bled off from recycle loop to prevent

building of inerts or impurities in the system can be neglected because of size
(bled off and directed out the system)

System: any portion of a process that can be
enclosed within or defined

Bypass: is a fraction of the feed to a process unit that is diverted around the unit & combined
with the output stream
- it introduces a splitting and mixing point

4.5 RECYCLE AND BYPASS

- Recovering and reusing unconsumed Reactants

- 1- Recovery of catalyst
- 2- Dilution of a process stream
- 3- control of a process variable
- 4- Circulation of a working fluid

4.6 CHEMICAL REACTION STOICHIOMETRY

★ **Stoichiometric equation** is a statement of the relative number of molecules

A reactant is limiting if it is present in less than its stoichiometric proportion relative to every other reactant.

$$\text{Fractional Excess of A} = \frac{(n_A)_{\text{feed}} - (n_A)_{\text{stoich}}}{(n_A)_{\text{stoich}}}$$

$$\text{fractional Conversion} \leftarrow f = \frac{\text{moles reacted}}{\text{moles fed}}$$

★ **Extent of reaction** measure of how far a reaction has proceeded from its initial state

using the extent of reaction makes it easy to keep track of the molar quantities or flow rates of reactants and products in feed and outlet streams

→ ν_i stoichiometric coefficient of the i th species in a chemical reaction

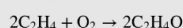
★ negative for reactants and +ve for products

$$\xi = \frac{(n_i - n_{i0})}{\nu_i} \quad (\text{dimensionless})$$

Test Yourself

(Answers, p. 655)

The oxidation of ethylene to produce ethylene oxide proceeds according to the equation



The feed to a reactor contains 100 kmol C_2H_4 and 100 kmol O_2 .

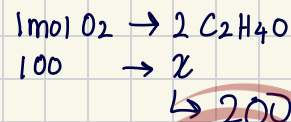
1. Which reactant is limiting? C_2H_4
2. What is the percentage excess of the other reactant? 100% 50 mol O_2
3. If the reaction proceeds to completion, how much of the excess reactant will be left; how much C_2H_4O will be formed; and what is the extent of reaction? 100 mol will be formed
4. If the reaction proceeds to a point where the fractional conversion of the limiting reactant is 50%, how much of each reactant and product is present at the end, and what is the extent of reaction?
5. If the reaction proceeds to a point where 60 kmol of O_2 is left, what is the fractional conversion of C_2H_4 ? The fractional conversion of O_2 ? The extent of reaction?

$$4. C_2H_4 \text{ conv} = 0.50 \times 100 = 50 \text{ kmol}$$

$$\xi = \frac{50}{2} = 25 \text{ kmol}$$

$$n_i = n_{i0} + \nu_i \xi$$

$$C_2H_4 \Rightarrow 100 + (-2)(25) = 50$$



$$3. C_2H_4$$

$$0 - 100 = -100$$

$$\nu = -2$$

$$\xi = \frac{-100}{-2} = 50 \text{ kmol}$$

$$n_{C_2H_4O} = 0 + (2)(25) = 50$$

$$n_{O_2} = 100 + (-1)(25) = 75 \text{ kmol}$$

4.7 Balances on reactive processes

In a reactive system we have:

1. Atomic Species (atoms)

2. Chemical Reaction(s)

- Balances on atomic species can be written $\text{input} = \text{Output}$, since atoms can neither be created ($\text{gen} = 0$) nor destroyed ($\text{cons} = 0$) in a chemical reaction

- Chemical Reactions are **independent** if the stoichiometric equation of any one of them can't be obtained by adding and subtracting multiples of the stoichiometric equations of the others.

dependent Reactions if we can get one in terms of the other by $+$, $-$, \times



4.7e Extent of Reaction

+ No. unknown labeled variables

+ No. **independent reactions** (one unknown ξ for each reaction) number of reactions in process

- No. **independent reactive species** (one eqn for each species in term of ξ)

- No. **independent non reactive species** (one balance eqn for each)

- No. other eqns relating unknown variables

= Number of DOF (N_{DF})

4.7 PRODUCT SEPARATION AND RECYCLE

- overall Conversion: $\frac{\text{reactant input to process} - \text{reactant output from process}}{\text{reactant input to process}}$

- Single-Pass Conversion: $\frac{\text{reactant input to reactor} - \text{reactant output from reactor}}{\text{reactant input to reactor}}$

PURGING.

note: for split stream 1 inap material balance

- Why purging is needed?

- 1- inert gases (N_2 , Ar , etc.) are used in processes because they don't undergo chemical reactions under given conditions
- 2- Using inert gas prevents undesirable chemical reactions from occurring (eg oxidation, hydrolysis, combustion)
- 3- purging with (N_2) minimizes hazards of residual solvents or process fluids
- 4- if an inert gas is introduced to the system and it doesn't react, it has to exit the system somewhere, builds up & Shutdown.

- Atomic Balance

Balances on atomic species can be written $\text{input} = \text{output}$ since atoms can neither be created ($\text{gen} = 0$) nor destroyed ($\text{cons} = 0$) in a chemical reaction.

4.7 b Independent Equations, Independent Species, and Independent Reactions:

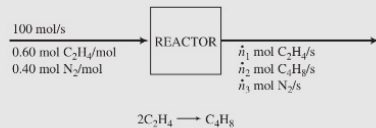
- if 2 atomic species occur in the same ratio wherever they appear in a process, Balances on those species will not be independent equations.
- Chemical reactions are independent if the stoichiometric equation of any one of them cannot be obtained by adding and subtracting multiples of the stoichiometric equations of the others



Test Yourself

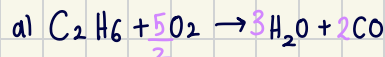
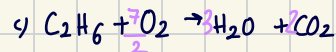
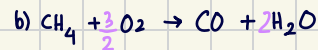
(Answers, p. 655)

1. A mixture of ethylene and nitrogen is fed to a reactor in which some of the ethylene is dimerized to butene.



How many independent molecular species are involved in the process? How many independent atomic species are involved? Prove the latter claim by writing balances on C, H, and N.

2. Write the stoichiometric equations for the combustion of methane with oxygen to form (a) CO₂ and H₂O and (b) CO and H₂O; and for the combustion of ethane with oxygen to form (c) CO₂ and H₂O and (d) CO and H₂O. Then prove that only three of these four reactions are independent.



4.7d Atomic Species Balances

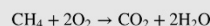
NO. unknown labeled variables

- NO. independent atomic species balance
 - NO. independent species balances on non-reactive species
 - NO. other eqns. relating unknown variables
- = NO. degrees of freedom.

Test Yourself

(Answers, p. 656)

Methane is burned to form carbon dioxide and water in a batch reactor:



The feed to the reactor and the products obtained are shown in the following flowchart:



- How much methane was consumed? What is the fractional conversion of methane?
 $100 - 40 = 60 \text{ mol CH}_4$
- How much oxygen was consumed? What is the fractional conversion of oxygen?
 $250 - 130 = 120 \text{ mol O}_2$
- Write the extent of reaction equation (4.6-4) for methane, oxygen, and CO₂. Use each equation to determine the extent of reaction, ξ , substituting inlet and outlet values from the flowchart.
 $\xi = 60$
- How many independent molecular species balances can be written? How many independent atomic species balances can be written?
X
- Write the following balances and verify that they are all satisfied. The solution of the first one is given as an example.
(a) Methane. $(I = O + C) \Rightarrow 100 \text{ mol CH}_4 \text{ in} = 40 \text{ mol CH}_4 \text{ out} + 60 \text{ mol CH}_4 \text{ consumed}$
(b) Atomic oxygen (O).
(c) Molecular oxygen (O₂).
(d) Water.
(e) Atomic hydrogen.

$$d) 120 = 120$$

e. atomic hydrogen:

$$4(100) = 4(40) + 120(2)$$

1) 2 independent atomic species (N & C or H)

a) C Balance:

$$120 = 2n_1 + 4n_2$$

b) H Balance: $240 = 4n_1 + 8n_2 \div 2$

$$120 = 2n_1 + 4n_2 \rightarrow \text{dependent}$$

c) N Balance:

$$(0.40)(2) = (2)(0.3) \rightarrow \text{independent}$$

3. a) CH₄:

$$40 = 100 - \xi$$

$$\xi = 60$$

$$d) H_2O \rightarrow 120 = 0 + 2\xi$$

b) O₂

$$130 = 250 - 2\xi$$

c) CO₂

$$60 = 0 + \xi$$

4) 3 atomic species (C, H, O)

$$C \text{ Balance } 100 = 40 + 60$$

$$H \text{ Balance } 4(100) = 4(40) + 2(120)$$

$$O \text{ Balance } 2(250) = 2(130) + 60(2) + 120$$

5) b. O Balance

$$2(250) = 2(130) + 2(60) + 120$$

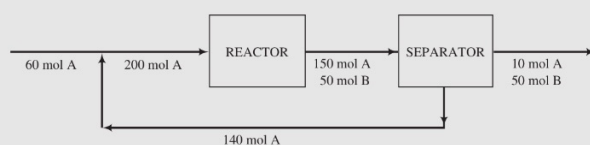
c. molecular (O₂)

$$250 = 130 + 60(2)$$

Test Yourself

(Answers, p. 656)

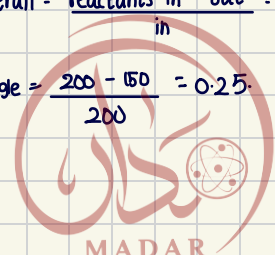
A reaction with stoichiometry $A \rightarrow B$ takes place in a process with the following flowchart:



1. What is the overall conversion of A for this process? What is the single-pass conversion?

$$1. \text{ overall} = \frac{\text{reactants in} - \text{out}}{\text{in}} = \frac{60 - 10}{60} = 0.83$$

$$\text{single} = \frac{200 - 150}{200} = 0.25$$



4.8 Combustion Reaction is the rapid reaction of a substance with oxygen

- is the rapid reaction of a fuel with oxygen that produces tremendous quantities of energy

Types of fuels: 1. Solid fuels: Coal, oil shale, biomass

2. Liquid fuels: fuel oil

3. Gaseous fuel: Natural gas, primarily methane or liquefied petroleum gas [usually propane / Butane]

when a fuel is burned: $\xrightarrow{\text{complete comb.}} \text{C} \rightarrow \text{CO}_2 \text{ or } \text{CO}$ $\xrightarrow{\text{partial even if CO}_2 \text{ is present comb.}} \text{N} \rightarrow \text{NO and NO}_2$

$\text{H} \rightarrow \text{H}_2\text{O}$

$\text{S} \rightarrow \text{SO}_x$

- Average MW of air 29.

- Air is the source of oxygen in most combustion reactors.

Wet basis: component mole fractions of a gas that contains water.

Dry basis: " without the water.

Stack gas: product gas that leaves a combustion furnace.

Test Yourself

(Answers, p. 656)

1. What is the approximate molar composition of air? What is the approximate molar ratio of N_2 to O_2 in air? (Committing these quantities to memory will save you lots of effort.)
2. A gas contains 1 mol H_2 , 1 mol O_2 , and 2 mol H_2O . What is the molar composition of this gas on a wet basis? On a dry basis?
3. A flue gas contains 5 mole% H_2O . Calculate the ratios
 - (a) kmol flue gas/kmol H_2O .
 - (b) kmol dry flue gas/kmol flue gas.
 - (c) kmol H_2O /kmol dry flue gas.

$$1. 79\% \text{ N}_2 \text{ and } 21\% \text{ O}_2 \quad \frac{0.79}{0.21} = \frac{3.76 \text{ mol N}_2}{\text{mol O}_2}$$

$$2) \text{ dry } 50\% \text{ H}_2, 50\% \text{ O}_2, \text{ wet: } 25\% \text{ H}_2, 25\% \text{ O}_2$$

$$3) 20$$

$$b) \frac{95}{100} = 0.95$$

$$c) \frac{5}{95} = 0.0526$$

- Theoretical and Excess Oxygen and Air

Stoic \leftarrow *Theoretical Oxygen: amount of (O_2 or air) needed for complete combustion of the full amount of fuel fed to the reactor.
*Theoretical Air: the quantity of air that contains the theoretical oxygen.

$n^* \text{ O}_2 = \text{Theoretical amount O}_2$

$$n^* n_2 = n^* \text{ O}_2 \quad \begin{array}{l} 0.78 \text{ mol N}_2 \\ 0.21 \text{ mol O}_2 \end{array}$$

$$n^* \text{ Air} = n^* \text{ O}_2 \quad \begin{array}{l} 1 \text{ mol air} \\ 0.21 \text{ mol O}_2 \end{array}$$

- Excess Air: The amount by which the air fed to the reactor exceeds the theoretical air.

$$\text{Percent Excess Air} = \frac{(\text{moles air})_{\text{fed}} - (\text{moles air})_{\text{theoretical}}}{(\text{moles air})_{\text{theoretical}}} \times 100\%$$

$$n_{\text{stoic}} \cdot n_{\text{theo}} = n^*$$

$$Ex = \frac{n_f - n^*}{n^*} \quad Ex = \frac{n_f}{n^*} - 1 \rightarrow Ex = \frac{n_f}{n^*} - 1 \quad 1 + Ex = \frac{n_f}{n^*}$$

- we use excess air to ensure all the fuel combusts [Complete combustion] $\rightarrow \text{CO}_2$ incomplete combustion $\rightarrow \text{CO}$

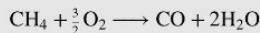
yield Selectivity $\left\{ \begin{array}{l} \text{multiple reactions} \\ A \rightarrow B \text{ (desired)} \\ A \rightarrow C \text{ (not desired)} \end{array} \right.$

$$\text{Selectivity} = \frac{\text{amount desired}}{\text{amount not desired}} \quad (\text{has to be a large number})$$

$$\text{fractional yield} = \frac{\text{moles of desired product formed}}{\text{moles that will be formed w/o side reactions}} \quad (\text{max yield} = 1) \quad \text{it is a fraction}$$

Test Yourself

Methane burns in the reactions



(Answers, p. 656)

One hundred mol/h of methane is fed to a reactor.

1. What is the theoretical O_2 flow rate if complete combustion occurs in the reactor?
2. What is the theoretical O_2 flow rate assuming that only 70% of the methane reacts? (Careful!)
3. What is the theoretical air flow rate?
4. If 100% excess air is supplied, what is the flow rate of air entering the reactor?
5. If the actual flow rate of air is such that 300 mol O_2/h enters the reactor, what is the percent excess air?

100 mol of $\text{CH}_4 \longrightarrow$

1. 200 mol

2. 200 mol

$$3. 4.76 \times 200 = 200 \times \frac{100}{21} = 952 \text{ mol/hr}$$

$$4. 2 \times 4.76 \times 200 = 2 \times 952 = 1904 \text{ mol/hr}$$

$$\% \text{ Excess Air} = \frac{\text{Actual Air} - \text{Theoretical Air}}{\text{Theoretical Air}} \times 100\%$$

5. Actual air = 300 mol/hr

$$\% \text{ E.A.} = \frac{300 - 952}{952} \times 100\% = -68.5\%$$

Example 4.8-1

Composition on Wet and Dry Bases

1. Wet Basis \Rightarrow Dry Basis.

A stack gas contains 60.0 mole% N_2 , 15.0% CO_2 , 10.0% O_2 , and the balance H_2O . Calculate the molar composition of the gas on a dry basis.

$$60 + 15 + 10 = 85 \text{ mol dry gas}$$

$$\frac{60}{85} = 0.706 \frac{\text{mol N}_2}{\text{mol dry gas}}$$

$$\frac{15}{85} = 0.176 \frac{\text{mol CO}_2}{\text{mol dry gas}}$$

$$\frac{10}{85} = 0.118 \frac{\text{mol O}_2}{\text{mol dry gas}}$$

Wet Basis \rightarrow dry Basis

assume 100 mol of wet gas

dry basis \rightarrow wet basis

assume 100 mol of dry gas

$$0.07 \frac{\text{mol of H}_2\text{O}}{\text{mol of dry gas}} = 0.930 \frac{\text{lb-mol dry gas}}{\text{lb-mol wet gas}}$$

$$\frac{0.0700 \text{ lb-mole H}_2\text{O} / \text{lb-mole wet gas}}{0.930 \text{ lb-mole dry gas} / \text{lb-mole wet gas}} = 0.0753 \frac{\text{lb-mole H}_2\text{O}}{\text{lb-mole dry gas}}$$

$$100 \text{ lb-mole dry gas} \times 0.0753 \frac{\text{lb-mole H}_2\text{O}}{\text{lb-mole dry gas}} = 7.53 \text{ lb-moles H}_2\text{O}$$

$$100 \text{ lb-moles dry gas} \times 0.65 \frac{\text{lb-mole N}_2}{\text{lb-mole dry gas}} = 65 \text{ lb moles N}_2$$

$$(100)(0.140) \text{ CO}_2 = 14 \text{ lb-mole CO}_2$$

$$(100)(0.110) = 11 \text{ lb-mole CO}$$

$$(100)(0.100) = 10 \text{ lb-mole O}_2$$

$$107.53 \text{ lb-mole of wet gas}$$

$$y_{\text{H}_2\text{O}} = \frac{7.53}{107.5} = 0.070 \frac{\text{lb-mole H}_2\text{O}}{\text{lb-mole wet gas}}$$

$$y_{\text{N}_2} = \frac{65}{107.5} = 0.6$$

$$y_{\text{CO}_2} = \frac{14}{107.5} = 0.130$$

$$y_{\text{CO}} = \frac{11}{107.5} = 0.102$$

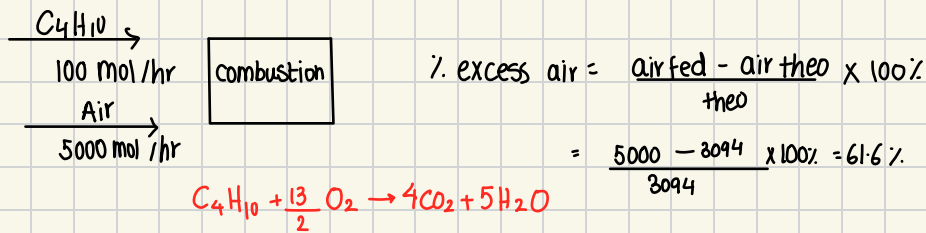
$$y_{\text{O}_2} = \frac{10}{107.5} = 0.093$$



Example 4.8-2

Theoretical and Excess Air

One hundred mol/h of butane (C_4H_{10}) and 5000 mol/h of air are fed to a combustion reactor. Calculate the percent excess air.



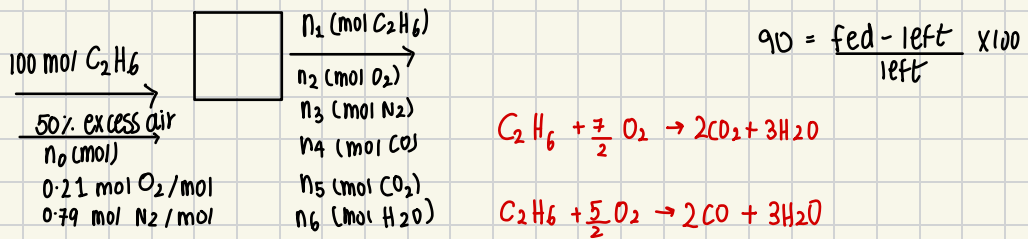
$$(n_{O_2})_{\text{theo}} = \frac{100 \text{ mol } C_4H_{10}}{\text{hr}} \times \frac{6.5 \text{ mol}}{1 \text{ mol}} = 650 \text{ mol } \frac{O_2}{h}$$

$$(n_{\text{air}}) = 650 \cdot \frac{4.76 \text{ mol air}}{1 \text{ mol } O_2} = 3094 \text{ mol air/h} \quad 4.76 = \frac{1}{0.21}$$

Example 4.8-3

Combustion of Ethane

Ethane is burned with 50% excess air. The percentage conversion of the ethane is 90%; of the ethane burned, 25% reacts to form CO and the balance reacts to form CO_2 . Calculate the molar composition of the stack gas on a dry basis and the mole ratio of water to dry stack gas.



7 unknown + 2 Reactions - 3 extra info - 6 components = 0

- 50% Excess Air

$$(n_{O_2})_{\text{Theoretical}} = 100 \text{ mol } C_2H_6 \times \frac{3.5 \text{ mol } O_2}{1 \text{ mol } C_2H_6} = 350 \text{ mol } O_2$$

$$0.21 n_0 = 1.50 (350 \text{ mol } O_2) = n_{O_2} = 2500 \text{ mol air fed}$$

- 90% ethane conversion (10% unreacted) \rightarrow Total Air = Theoretical Air + Excess Air

$$n_1 = 0.1(100) = 10 \text{ mol } C_2H_6$$

$$90 \text{ mol } C_2H_6 \text{ react}$$

- 25% conversion to CO

$$n_4 = (0.25 \times 90) \cdot \frac{2 \text{ mol CO}}{1 \text{ mol } C_2H_6} = 45 \text{ mol CO}$$

$$n_3 = 0.79 (2500) = 1975 \text{ mol } N_2$$

- Atomic Carbon Balance

$$100 \text{ mol } C_2H_6 \times \frac{2 \text{ mol C}}{1 \text{ mol } C_2H_6} = n_1 (\text{mol } C_2H_6) \times \frac{2 \text{ mol C}}{1 \text{ mol}} + n_4 (\text{mol CO}) \cdot \frac{1 \text{ mol C}}{1 \text{ mol CO}} + n_5 (\text{mol } CO_2) \cdot \frac{1 \text{ mol C}}{1 \text{ mol } CO_2}$$

$$n_5 = 135 \text{ mol } CO_2$$

- Atomic Hydrogen Balance

$$100 \text{ mol } C_2H_6 \times \frac{6 \text{ mol H}}{1 \text{ mol } C_2H_6} = 10 \text{ mol } C_2H_6 \times \frac{6 \text{ mol H}}{1 \text{ mol } C_2H_6} + n_6 \text{ mol } H_2O \cdot 2 = n_6 = 270 \text{ mol } H_2O$$

$$525 \cdot 2 = n_2 \cdot 2 + 45 + 135(2) + 270$$

$$n_2 = 232 \text{ mol } O_2$$

The analysis of the stack gas is now complete. Summarizing:

$n_1 = 10 \text{ mol } C_2H_6$
$n_2 = 232 \text{ mol } O_2$
$n_3 = 1974 \text{ mol } N_2$
$n_4 = 45 \text{ mol CO}$
$n_5 = 135 \text{ mol } CO_2$
Total dry stack gas = 2396 mol dry gas
+ $n_6 = 270 \text{ mol } H_2O$
Total stack gas = 2666 mol

Hence the stack gas composition on a dry basis is

$y_1 = \frac{10 \text{ mol } C_2H_6}{2396 \text{ mol dry gas}} = 0.00417 \frac{\text{mol } C_2H_6}{\text{mol}}$
$y_2 = \frac{232 \text{ mol } O_2}{2396 \text{ mol dry gas}} = 0.0970 \frac{\text{mol } O_2}{\text{mol}}$
$y_3 = \frac{1974 \text{ mol } N_2}{2396 \text{ mol dry gas}} = 0.824 \frac{\text{mol } N_2}{\text{mol}}$
$y_4 = \frac{45 \text{ mol CO}}{2396 \text{ mol dry gas}} = 0.019 \frac{\text{mol CO}}{\text{mol}}$
$y_5 = \frac{135 \text{ mol } CO_2}{2396 \text{ mol dry gas}} = 0.0563 \frac{\text{mol } CO_2}{\text{mol}}$

and the mole ratio of water to dry stack gas is

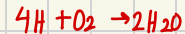
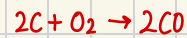
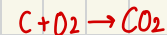
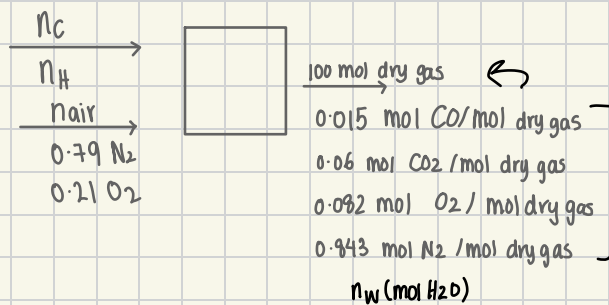
$$\frac{270 \text{ mol } H_2O}{2396 \text{ mol dry stack gas}} = 0.113 \frac{\text{mol } H_2O}{\text{mol dry stack gas}}$$



Example 4.8-4

Combustion of a Hydrocarbon Fuel of Unknown Composition

A hydrocarbon gas is burned with air. The dry-basis product gas composition is 1.5 mole% CO, 6.0% CO₂, 8.2% O₂, and 84.3% N₂. There is no atomic oxygen in the fuel. Calculate the ratio of hydrogen to carbon in the fuel gas and speculate on what the fuel might be. Then calculate the percent excess air fed to the reactor.



4 unknown + 3 reactions - 7 components = 0

$$100(0.843) = n_{air}(0.79)$$

$$n_{air} = 106.71 \text{ mol air}$$

- atomic O Balance

$$0.21 n_a (2) = n_w (1) + 100 [(0.015) + (0.060)(2) + (0.082)(2)]$$

- atomic H Balance

$$n_w = 14.9 \text{ mol H}_2O$$

$$n_H = n_w (2)$$

$$n_H = 29.8 \text{ mol H}$$

- $\frac{C}{H}$ ratio in the fuel

$$\frac{n_H}{n_C} = \frac{29.8}{7.5} = 3.97 \frac{\text{mol H}}{\text{mol C}}$$

- % Excess air

$n_{O_2} + n_{H_2O}$

$$= 7.5 \text{ mol C} \cdot \frac{1 O_2}{1 C} + 29.8 \text{ mol H} \cdot \frac{1}{4} \frac{O_2}{H} = 14.95 \text{ mol } O_2$$

$$(n_{O_2})_{fed} = 0.21 (106.7 \text{ mol air}) = 22.4 \text{ mol } O_2$$

$$\% = \frac{22.4 - 14.95}{14.95} \times 100 = 49.8\%$$



CHAPTER (5) SINGLE-PHASE SYSTEMS

- Equation of state (EOS) relationship between P, V, n and temperature (T) of gas

- Solid and liquid densities are independent of temp: changes in pressure don't cause significant changes in lig & solids (incompressible)

- Assuming volume additivity

$$\frac{1}{\rho} = \sum \frac{x_i}{\rho_i} = \frac{x_1}{\rho_1} + \frac{x_2}{\rho_2}$$

- Assuming average of the pure components

$$\bar{\rho} = \sum x_i \cdot \rho_i = x_1 \cdot \rho_1 + x_2 \cdot \rho_2 + \dots$$

Test Yourself

(Answers, p. 656)

- The specific gravity of water is 1.0000 at 4.0°C. A stream of water at 4°C has a mass flow rate of 255 g/s. What is its volumetric flow rate? If the stream temperature is raised to 75°C, does the mass flow rate change? How would you expect the volumetric flow rate to change? How would you calculate the volumetric flow rate at 75°C without actually measuring it?
- The pressure equivalence 14.696 lb_f/in² \Leftrightarrow 760 mm Hg is not complete—it should be stated as

$$14.696 \text{ lb}_f/\text{in}^2 \Leftrightarrow 760 \text{ mm Hg at } 0^\circ\text{C}$$

Why is it technically necessary to state a temperature? Why is omitting the temperature not a serious mistake?

P varies with temperature

- Suppose you mix m_1 (g) of liquid A₁ with density ρ_1 (g/cm³) (m_2 (g) of liquid A₂ with density ρ_2 , ..., and m_n (g) of liquid A_n with density ρ_n . Assuming that the volumes are additive, show that the density of the mixture is given by Equation 5.1-1.

- mass flow rate stays the same \dot{V} increases a bit

$$\dot{V} = \frac{\dot{m}}{\rho} \rightarrow \frac{255 \text{ g}}{\text{s}} \cdot \frac{\text{cm}^3}{1 \text{ g}} = 255 \frac{\text{cm}^3}{\text{s}}$$

$$3. V = \frac{m_1}{\rho_1} + \frac{m_2}{\rho_2} + \dots + \frac{m_n}{\rho_n}$$

$$\frac{1}{\rho} = \frac{V_{\text{tot}}}{m_{\text{tot}}} = \frac{m_1}{m_{\text{tot}} \rho_1} + \frac{m_2}{m_{\text{tot}} \rho_2} + \dots = \frac{x_1}{\rho_1} + \frac{x_2}{\rho_2}$$

$$P\hat{V} = RT$$

$$P\hat{V} = nRT \quad (\text{no need to know the type of gas})$$

abs pressure \downarrow \rightarrow abs Temp (K, R)

validity = at high temp ($> 0^\circ\text{C}$) and low pressure ($= 1 \text{ atm}$)

$$1 \text{ m}^3 \cdot \text{Pa} = 1 \text{ J}$$

The Kinetic Theory of gases

- gas molecules have negligible volume, exert no forces on one another, collide elastically with walls

- Specific molar volume:

\hat{V} = The specific molar volume = volume per mol

$$\hat{V} = \frac{V}{n} = \frac{\dot{V}}{\dot{n}}$$

- Relative Error (E) of ideal gas law

$$E = \frac{X_{\text{ideal}} - X_{\text{true}}}{X_{\text{true}}} \times 100\%$$

\hat{V}_{ideal} = the ideal specific molar volume $P \cdot \hat{V} = RT$

- standard Temp and pressure

	Ts	Ps	Vs	ns
SI	273K	1atm	0.022415 m ³	1mol
CGS	273K	1atm	22.415L	1mol
American	492°R	1atm	359.05 ft ³	1 lb-mol

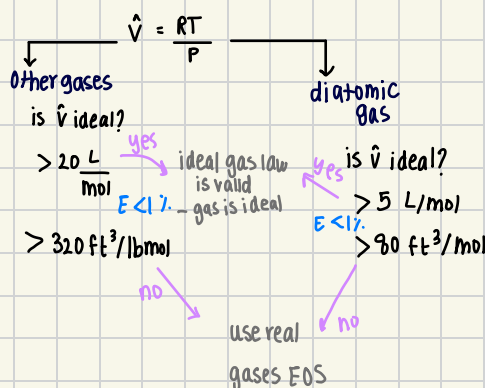
- Standard Cubic Meters (SCM) denotes m³ (STP)

- Standard Cubic Feet (SCF) denotes ft³ (STP)

SCMH means Standard Cubic Meters per Hour

$$\frac{PV = nRT}{P_0 \hat{V}_0 = R T_0} = \frac{PV}{P_0 \hat{V}_0} = \frac{n T}{T_0} \quad (\text{you don't need value for } R)$$

$$V_0 = 22.4 \frac{\text{m}^3}{\text{kmol}} \text{ or } 22.4 \frac{\text{L}}{\text{mol}} \text{ or } 359 \frac{\text{ft}^3}{\text{lb-mole}} \text{ (STP)}$$



1) using gas constant $PV = nRT$

2) using relative method . Transfer from conditions (1) to conditions (2)

- gas at conditions (2) relative to standard conditions

$$\frac{P_2 V_2}{P_1 V_1} = \frac{n_2 T_2}{n_1 T_1}$$

$$\frac{P_2 V_2}{P_2 V_2} = \frac{n_2 T_2}{n_2 T_2}$$

3) Density calculations

Density of pure gas

for ideal gas mixture

$$\bar{M} = \sum y_i M_i$$

$$T(K) = T(^{\circ}\text{C}) + 273.15$$

$$T(^{\circ}\text{R}) = T(^{\circ}\text{F}) + 459.67$$

$$T(^{\circ}\text{R}) = 1.8 T(K)$$

$$T(^{\circ}\text{F}) = 1.8 T(^{\circ}\text{C}) + 32$$

$$1 \text{ atm} = 14.7 \frac{\text{lb}_f}{\text{in}^2} = 101325 \text{ Pa} = 760 \text{ mm Hg}$$

Example 5.2-2 Conversion from Standard Conditions

Butane (C_4H_{10}) at $360^\circ C$ and 3.00 atm absolute flows into a reactor at a rate of 1100 kg/h . Calculate the volumetric flow rate of this stream using conversion from standard conditions.

$$\text{answer: } \frac{3}{1(22.4)} = \frac{1100}{(12 \times 4) + (10 \times 2)} \frac{360 + 273}{273} = 19(22.4) \left(\frac{633 \text{ K}}{273 \text{ K}} \right) \left(\frac{1}{3} \right) = 329 \frac{\text{m}^3}{\text{h}}$$

Example 5.2-1 The Ideal-Gas Equation of State

One hundred grams of nitrogen is stored in a container at $23.0^\circ C$ and 3.00 psig .

- Assuming ideal-gas behavior, calculate the container volume in liters.
- Verify that the ideal-gas equation of state is a good approximation for the given conditions.

$$V = \frac{nRT}{P} = \frac{100(8.314)(23 + 273.15)}{29 \cdot (122.037 \times 10^3)} = 0.072 \text{ m}^3 \cdot \frac{1000 \text{ L}}{1 \text{ m}^3} = 72 \text{ L}$$

$$3 \text{ psig} \rightarrow P_a$$

$$2. \hat{V} > 5 \text{ L/mol} \text{ ideal gas Law is valid } \checkmark$$

$$\hat{V} = \frac{V}{n} = \frac{72 \text{ L}}{3.57} = 20.2 \text{ L/mol} > 5 \text{ L/mol}$$

Test Yourself

(Answers, p. 656)

- What is an equation of state? What is the ideal-gas equation of state? At what conditions (high or low temperature, high or low pressure) does the ideal-gas equation provide the most accurate estimates? **no**
- Two gas cylinders have identical volumes and contain gases at identical temperatures and pressures. Cylinder A contains hydrogen and cylinder B contains carbon dioxide. Assuming ideal-gas behavior, which of the following variables differ for the two gases: (a) number of gram-moles, (b) number of molecules, (c) masses, (d) specific molar volumes (L/mol), (e) mass densities (g/L)? For each of the quantities that differ, which one is bigger and by how much? (Assume ideal-gas behavior.)
- One hundred grams per hour of ethylene (C_2H_4) flows through a pipe at 1.2 atm and $70^\circ C$ and 100 g/h of butene (C_4H_8) flows through a second pipe at the same temperature and pressure. Which of the following quantities differ for the two gases: (a) volumetric flow rate, (b) specific molar volume (L/mol), (c) mass density (g/L)? For each of the quantities that differ, which one is bigger and by how much? (Assume ideal-gas behavior.)
- A gas is stored at $T = 200 \text{ K}$ and $P = 20 \text{ atm}$. Show whether or not the ideal-gas equation of state would provide an estimate of the specific volume of the gas, \hat{V} (L/mol), within 1% of the true value.

The relationship between the density ρ (mass/volume), temperature, and pressure of an ideal gas can be obtained by first relating the specific molar volume, \hat{V} (volume/mole), to the density. Using a specific set of units for illustration,

$$\hat{V} \left(\frac{\text{L}}{\text{mol}} \right) = \frac{\bar{M} (\text{g/mol})}{\rho (\text{g/L})}$$

where \bar{M} is the average molecular weight of the gas (the molecular weight if the gas is a single species or Equation 3.3-7 for a mixture). Substituting $\hat{V} = \bar{M}/\rho$ into Equation 5.2-2 and solving for ρ yields

$$\rho = \frac{P\bar{M}}{RT} \quad (5.2-4)$$

a. Relationship between P, V, n, T of gas, $0 < P < 1 \text{ atm}$, $\downarrow \text{ pressure } \uparrow \text{ temp, } PV=nRT$

2. (c), (e). The mass and mass density of CO_2 are

$$\text{each greater by } \frac{M_{wCO_2}}{M_{wH_2}} = 22$$

$$(a) \text{ no, } n = \frac{PV}{RT} \text{ all const}$$

$$(b) \text{ no, } N = n \times N_A \text{ both const.}$$

$$(c) \text{ yes, } M = n \times M$$

cylinder B 2 x heavier.

$$(d) \text{ no, } v = \frac{RT}{P} \text{ all const.}$$

$$(e) \text{ yes } = PM/RT \sim \text{cylinder B} \sim 22 \times \text{denser}$$

3. (a) and (c)

E \rightarrow ethylene B \rightarrow Butane

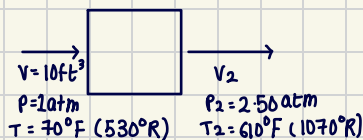
$$M_{wB} = 2M_{wE} \rightarrow V_E = 2 \hat{V}_B$$

$$\rho_B = 2\rho_E$$

Example 5.2-3 Effect of T and P on Volumetric Flow Rates

Ten cubic feet of air at $70^\circ F$ and 1.00 atm is heated to $610^\circ F$ and compressed to 2.50 atm . What volume does the gas occupy in its final state?

10 ft³



$$\frac{P_2 V_2}{P_1 V_1} = \frac{T_2}{T_1} \quad \frac{2.50(V_2)}{(1)(10)} = \frac{1070}{530} = 8.08 \text{ ft}^3$$



- ideal gas mixture

$$P_A V = n_A R T$$

$$P_A = y_A P$$

↳ mole fraction

$$V_A = y_A V$$

$$P_A + P_B + \dots = (y_A + y_B + \dots) P = P$$

$$V = V_A + V_B + V_C \quad \text{Amagat's Law}$$

- Partial Pressure depends on the mole fraction not the weight fraction.

Example 5.2-4

Standard and True Volumetric Flow Rates

Equipment Encyclopedia
flowmeter



www.wiley.com/college/felder

The flow rate of a methane stream at 285°F and 1.30 atm is measured with an orifice meter. The calibration chart for the meter indicates that the flow rate is 3.95×10^5 SCFH. Calculate the molar flow rate and the true volumetric flow rate of the stream.

$$\begin{aligned} 285^\circ\text{F} \\ 1.30 \text{ atm} \\ 3.95 \times 10^5 \text{ SCFH} \\ \dot{V} = ? \\ \dot{n} = ? \end{aligned}$$

$$\dot{n} = 3.95 \times 10^5 \frac{\text{ft}^3}{\text{hr}} \cdot \frac{1 \text{ lb-mole}}{359 \text{ ft}^3} = 1.10 \times 10^3 \text{ lb-moles/hr}$$

$$\frac{P_2 V_2}{P_1 V_1} = \frac{P_2 T_2}{P_1 T_1}$$

$$\frac{1.30 (V_2)}{1 (3.95 \times 10^5)} = \frac{745^\circ}{492^\circ} \Rightarrow 4.6 \times 10^5 \frac{\text{ft}^3}{\text{hr}}$$

Test Yourself

(Answers, p. 656)

↓

- What are standard temperature and pressure? What are the values of \dot{V}_s in SI, CGS, and U.S. customary units? $0.0224 \text{ m}^3/\text{hr}$ 22.4 L/hr $359 \text{ ft}^3/\text{hr}$
- What happens to the volume of an ideal gas when you double the pressure at a fixed temperature? When you double the temperature at a fixed pressure? $2V$
- What happens to the density of a fixed quantity of an ideal gas when you raise the temperature at a fixed pressure? When you raise the temperature at a fixed volume? nothing
- The volumetric flow rate of an ideal gas is given as 35.8 SCMH. The temperature and pressure of the gas are -15°C and 1.5 atm. Is the actual volumetric flow rate of the gas (a) $< 35.8 \text{ m}^3/\text{h}$, (b) $35.8 \text{ m}^3/\text{h}$, (c) $> 35.8 \text{ m}^3/\text{h}$, or (d) indeterminate without additional information?

$$4. \dot{V} = 35.8 \frac{\text{m}^3}{\text{hr}}$$

$$T = -15^\circ\text{C} + 273.15$$

$$P = 1.5 \text{ atm}$$

$$\frac{(15)(x)}{288.15} = \frac{(1)(35.8)}{273.15} = 25.17 \text{ m}^3/\text{hr} \quad (a) \checkmark$$

Test Yourself

(Answers, p. 656)

- A cylinder containing a mixture of N_2 and O_2 is taken from the basement to the top of a 50-story building. Assuming that the temperature remains constant, which of the following properties of the gas change during the ascent? (a) mass, (b) weight, (c) absolute pressure, (d) gauge pressure, (e) partial pressure of N_2 , (f) pure-component volume of O_2 , (g) density, (h) specific molar volume. b, d
- An ideal-gas mixture at 10 bar absolute and 200°C in a 100-m^3 tank contains 50 mole% H_2 and 50 mole% N_2 . What is the partial pressure of H_2 ? What is the pure-component volume of H_2 ? What would happen to p_{H_2} and V_{H_2} if the temperature were raised?
- An ideal-gas mixture at 10 atm absolute contains 50 wt% H_2 and 50 wt% N_2 . Is the partial pressure of H_2 less than, equal to, or greater than 5 atm? greater than

$$\begin{aligned} p &= 10 \text{ bar} \\ T &= 200^\circ\text{C} \\ V &= 100 \text{ m}^3 \end{aligned}$$

(2)

$$0.5(10) = 5 \text{ bar}$$

$$0.5(100) = 50 \text{ m}^3$$

$$P_{\text{H}_2} \uparrow$$

V unchanged

(3)

50g of H_2 contains many more moles than 50g of N_2 $\uparrow y_{\text{H}_2} > 5 \text{ atm}$

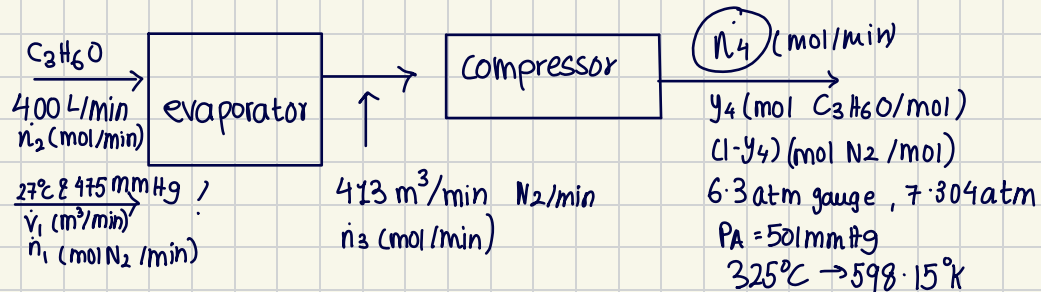


Example 5.2-5

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?



$$\dot{n}_2 = 400 \frac{\text{L}}{\text{min}} \cdot \frac{761.9}{\text{L}} \cdot \frac{1 \text{ mol}}{58.08 \text{ g}} = 5450 \frac{\text{mol } C_3H_6O}{\text{min}}$$

$$P_A = P y_4$$

$$P = P_{\text{gauge}} + P_{\text{atm}} = 6.3 \text{ atm} \quad \left| \begin{array}{l} 760 \text{ mmHg} \\ 1 \text{ atm} \end{array} \right. + 763 \text{ mmHg} = 5550 \text{ mmHg}$$

$$y_4 = \frac{501}{5550} = 0.0903 \frac{\text{mol } C_3H_6O}{\text{mol}}$$

$$1 - y = 0.9097 \frac{\text{mol } N_2}{\text{mol}}$$

$$\dot{n}_3 =$$

$$\frac{419 \text{ m}^3}{\text{min}} \cdot \frac{1 \text{ mol}}{0.0224 \text{ m}^3} = 18,700 \frac{\text{mol}}{\text{min}}$$

$$\dot{n}_1 + \dot{n}_2 + \dot{n}_3 = \dot{n}_4$$

$$5450 + 18,700 + 60,400 = \dot{n}_4$$

$$\dot{n}_1 = 36,200 \text{ mol/min}$$

$$\dot{V}_1 = \dot{n}_1 \frac{V_S}{n_S} \frac{T_1}{T_S} \frac{P_S}{P_1}$$

$$= 36,200 \frac{\text{mol}}{\text{min}} \cdot \frac{0.0224 \text{ m}^3}{1 \text{ mol}} \cdot \frac{300 \text{ K}}{273 \text{ K}} \cdot \frac{760 \text{ mmHg}}{1238 \text{ mmHg}}$$

$$\dot{V}_1 = 550 \text{ m}^3 \text{ N}_2/\text{min}$$



5.3 EQUATION OF STATE FOR NON-IDEAL GASES

- Critical Temperature and Pressure

- how well or poorly the ideal-gas equation depends on T_c and P_c
- a vapor is a gaseous species below its critical temp, and a gas is a species above its critical temp at a pressure low enough for the species to be more like a vapor than a liquid
- Substances at temperatures above T_c and pressures above P_c are referred to as supercritical fluids.

- Real gases

- The critical temperature of a species (T_c) is the highest temperature at which the species can coexist in 2 phases (liquid vapor)
- The critical pressure (P_c) is the corresponding pressure at T_c
- a substance at T_c and P_c is said to be at its critical state

Virial Equations of state

$$\frac{P\hat{V}}{RT} = 1 + \frac{B}{\hat{V}} + \frac{C}{\hat{V}^2} + \frac{D}{\hat{V}^3} + \dots$$

Test Yourself

(Answers, p. 656)

The critical temperature and pressure of isopropanol (isopropyl alcohol) are $T_c = 508.8 \text{ K}$ and $P_c = 53.0 \text{ atm}$.

1. Isopropanol is in a gaseous state at $T = 400 \text{ K}$ and $P = 1 \text{ atm}$. Would it be classified as a vapor or a gas? **vapor**
2. Isopropanol is compressed isothermally at 400 K until at pressure P_a a liquid phase forms. The vapor and liquid densities at that point are, respectively, ρ_{va} and ρ_{la} . In a second experiment, isopropanol is compressed at 450 K until condensation occurs, at which point the pressure and vapor and liquid densities are P_b , ρ_{vb} , and ρ_{lb} . What are the relationships ($>$, $=$, $<$, or $?$) between (a) P_a and P_b , (b) ρ_{va} and ρ_{vb} , and (c) ρ_{la} and ρ_{lb} ?
3. If isopropanol at 550 K and 1 atm is compressed isothermally to 100 atm , will a condensate form? What term might you use to refer to the fluid at its initial condition? At its final condition?

$$P_a < P_b \quad (b) \rho_{va} ? \rho_{vb} \quad (c) \rho_{la} > \rho_{lb}$$

1. Vapor pressure \uparrow as temp

3. liquid expand and becomes less dense as they get hotter.

gas

Supercritical: if both temp & pressure exceed their values

- Compressibility Factor Equation.

$Z = \frac{P\hat{V}}{RT}$ for ideal gas $Z = 1$ to which Z differs from 1 is a measure of the extent to which the gas is behaving non ideally

- The compressibility factor is a function of temp and pressure [of a gaseous species is defined as the ratio]

$$Z = f(T, P)$$

$$PV = ZnRT \quad Z = \frac{PV}{RT}$$

- an alternative method uses Law of corresponding states to estimate Z , and sub is C-F EOS

The Law states that the compressibility factor of any gas at a specific value of reduced Temp ($\frac{T}{T_c}$) & reduced pressure ($\frac{P}{P_c}$) has approx the same value for all species

Reduced Temp: $T_r = \frac{T}{T_c}$ $P_r = \frac{P}{P_c}$ reduced Pressure.

T_r
 P_r
 \hat{V}_{ideal} } Z needs 2 values

$$\hat{V}_{ideal} = \frac{\hat{V}}{\hat{V}_c} = \frac{\hat{V}}{RT_c/P_c} = \frac{P_c \hat{V}}{RT_c}$$



- The procedure for using generalized comp. chart

1. T_c and P_c

2. if the gas is He or H_2 adjusted critical constants from the empirical formulas

$$\begin{aligned} T_c^a &= T_c + 8K \\ P_c^a &= P_c + 8 \text{ atm} \end{aligned} \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{Newton's corrections}$$

3. Calculate reduced values of 2 known variables

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

$$P_r = \frac{P}{P_c}$$

$$V_r^{\text{ideal}} = \frac{P_c \hat{V}}{R T_c}$$

- reduced variables are dimensionless

- all temps & pressures must be abs.

4. use the compressibility chart to determine Z and then $PV = ZnRT$

Test Yourself

(Answers, p. 656)

- Suppose you need to know the volume that would be occupied by 10 kmol of H_2 at -190°C and 300 atm. Would you consider it reasonable to use a value calculated from the ideal-gas equation of state? How would you use the generalized compressibility chart for this calculation?
- Why would a chart such as that in Figure 5.4-1 be useless if T and P were the chart parameters? need a diff chart for diff species
- What is the law of corresponding states, and how does it provide a basis for the generalized compressibility chart?

NO

3. The Law states that the compressibility factor of any gas at a specific value of reduced Temp ($\frac{T}{T_c}$)

& reduced pressure ($\frac{P}{P_c}$) has approx the same value for all species

Kay's rule estimates pseudocritical properties of mixtures as simple averages of pure-component critical constant (non-polar compounds)

Pseudocritical Temp: $T'_c = y_A T_{cA} + y_B T_{cB} + y_C T_{cC} + \dots$ y_A, y_B, \dots are mole fractions

Pseudocritical Pressure: $P'_c = y_A P_{cA} + y_B P_{cB} + y_C P_{cC} + \dots$

Pseudoreduced Temp: $T'_r = T/T'_c$

Pseudoreduced Pressure: $P'_r = P/P'_c$

Test Yourself

(Answers, p. 656)

What is Kay's rule? How would you use it to calculate the specific molar volume of an equimolar mixture of gases at a given temperature and pressure? For what types of gases would you have the greatest confidence in the answer? non-polar compounds with similar critical properties

Example 5.4-2

Kay's Rule

A mixture of 75% H_2 and 25% N_2 (molar basis) is contained in a tank at 800 atm and -70°C . Estimate the specific volume of the mixture in L/mol using Kay's rule.

$$\begin{aligned} H_2 \rightarrow T_c &= 33.3K + 8 = 41.3K \\ P_c &= 12.8 \text{ atm} + 8 = 20.8 \text{ atm} \end{aligned}$$

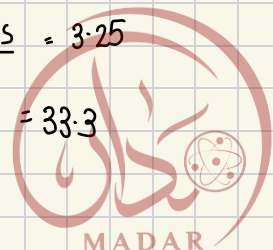
$$\begin{aligned} N_2 \rightarrow T_c &= 126.20K \\ P_c &= 33.5 \text{ atm} \end{aligned}$$

$$\hat{V} = \frac{RT'_c}{P} = \frac{(10.0921)(1.96)(203)}{800} = 0.0397 \frac{\text{L}}{\text{mol}}$$

$$\begin{aligned} T'_c &= 0.75(41.3) + 0.25(126.2K) = 62.53K \\ P'_c &= (0.75)(20.8) + 0.25(33.5) = 24 \text{ atm} \end{aligned}$$

$$T'_r = \frac{T}{T'_c} = \frac{-70 + 273.15}{62.53} = 3.25$$

$$P'_r = \frac{P}{P'_c} = \frac{800}{24} = 33.3$$



CHAPTER (6) Multiphase Systems

- **Phase diagram** of a pure substance is a plot of one system variable against another that shows the conditions at which the substance exists as a solid, liquid, gas.
- if T and P correspond to a point on the Vapor-liquid equil. Curve P is the vapor pressure P^* of the substance at temp T , T is the boiling point
- The boiling point of a substance $P=1$ atm the normal Boiling point
- if (T, P) on solid-liquid equil. curve T is the melting or freezing point at pressure P
- if (T, P) on the solid-vapor equil. curve P is the vapor pressure of the solid at temp T , T is the sublimation point
- The point (T, P) at which S, L, V coexist Triple point
- The Vapor-liquid equilibrium curve terminates at the critical temp & pressure

Test Yourself

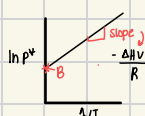
(Referring to Figure 6.1-1)

(Answers, p. 657)

1. What is the sublimation point of H_2O at 3 mm Hg? What is the vapor pressure of ice at $-5^\circ C$? 3 mm Hg
2. What is the triple point of CO_2 ? $-56.6^\circ C, 5.112 \text{ atm}$
3. Describe what happens when the pressure of pure CO_2 is raised from 1 atm to 9.9 atm at $-78.5^\circ C$, and then the temperature is raised from $-78.5^\circ C$ to $0^\circ C$ at 9.9 atm. id
4. What is the vapor pressure of CO_2 at $-78.5^\circ C$? At $-40^\circ C$? 9.9
5. What is the sublimation point of CO_2 at 1 atm? The melting point at 9.9 atm? The boiling point at the latter pressure? $-78.5^\circ C$ $-56.6^\circ C$
6. Does the state of water at point E in Figure 6.1-1a depend on the path followed in changing the temperature and pressure at point A to the values at point E? no

3. all CO_2 solidifies at 1 atm, solid melts at 9.9 atm & $-56^\circ C$, liquid boils at 9.9 atm $-40^\circ C$

- **The Volatility** of a species is the tendency of the species to transfer from the liquid (or solid) state to the vapor state
- The higher the vapor pressure at a given temp the greater the volatility
- a relationship between P^* the vapor pressure of a pure substance and T and $\ln P^*$ Clapeyron Equation:



$$\ln P^* = -\frac{\Delta H_v}{RT} + B$$

ΔH_v → latent heat of vap
 R → const, varies from 1 substance to another

- a relatively simple empirical equation that correlates vapor-pressure temp data extremely well Antoine Equation

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

P^* (mm Hg)
 T (°C) ← tabulated

Test Yourself

(Answers, p. 657)

1. Determine the vapor pressure of n -hexane at $87^\circ C$ using (a) Table B.4, (b) APEX.
2. Name three ways you could determine the normal boiling point of benzene from data in this book—one that involves looking it up, one that requires a hand calculation, and one that uses APEX.
3. Suppose you are given the vapor pressure p^* of a substance at three closely spaced temperatures T_1 , T_2 , and T_3 , and you wish to determine p^* at a fourth temperature T_4 far removed from the other three. If you use the Clausius-Clapeyron equation to correlate p^* and T , how would you plot the data and extrapolate it to T_4 ?

$$\log_{10} P^* = 6.8856 - \frac{1175.817}{87 - 224.96}$$

$$P^* = 1303.96 \text{ mmHg}$$

The Gibbs Phase Rule

- **Extensive Variables** : which depend on the size of the system Example: mass & volume
- **intensive Variables** : which don't depend on the size of the system Example: Temperature, pressure, density, specific vol. → intensive
Extensive
mass

$$DF = 2 + C - \pi - r$$

- The relationship among DF, π, C, r is called The Gibbs phase Rule

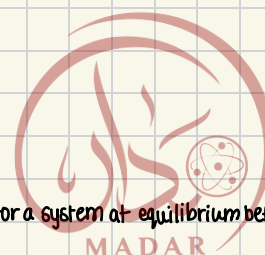
C = number of independent chemical species

π = number of phases in a system at equilibrium

r = number of independent equilibrated chemical reactions among the species

DF = DoF

- in the Gibbs phase rule, the DoF equals the number of intensive variable that must be specified for a system at equilibrium before the remaining intensive variables can be calculated



- Gas-liquid systems: one condensable component

- Raoult's Law, single condensable species

composition of condensable species \rightarrow system total pressure

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

Partial P
of condensable
species

vapor pressure of cond. species

$\rightarrow P^*$ is the equilibrium value.

$$P_A^*(T)$$

P_A Partial pressures

vapor pressure at Temp \rightarrow usually tabulated

- if evaporation takes place at a temp such that $P^* < P$ transfer of molecules from the surface of the liquid to the gas above the surface
- while $P^* = P$ the temp is the boiling point

1. a gas in equilibrium with a liquid must be saturated with the volatile component of that liquid.

2. $P_i = P_i^*$ the vapor is saturated P_i^* can't exceed P_i to increase P_i either by adding more vapor to the gas phase or by increasing the total pressure at const temp - must lead to condensation or \downarrow Temp at const P.

3. a vapor present in a gas in less than its saturation amount is referred to as superheated vapor

$$P_i = y_i P < P_i^*(T) \quad \text{only a saturated vapor can condense}$$

4. if a gas containing a single superheated vapor is cooled at const pressure. The temp at which the vapor becomes saturated is dew point

$$P_i = y_i P = P_i^*(T_{dp})$$

- The difference between the temperature & the dew point of a gas is called degrees of superheat

Example 6.3-2 Material Balances Around a Condenser

A stream of air at 100°C and 5260 mm Hg contains 10.0% water by volume.

1. Calculate the dew point and degrees of superheat of the air.
2. Calculate the percentage of the vapor that condenses and the final composition of the gas phase if the air is cooled to 80°C at constant pressure.
3. Calculate the percentage condensation and the final gas-phase composition if, instead of being cooled, the air is compressed isothermally to 8500 mm Hg .

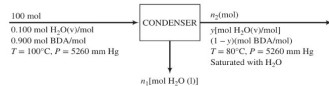
4. Suppose the process of Part 2 is run, the product gas is analyzed, and the mole fraction of water differs considerably from the calculated value. What could be responsible for the disparity between calculated and measured values? (List several possibilities.)

$$P_{H_2O} = y_{H_2O} P = (0.1)(5260) = 526 \text{ mmHg}$$

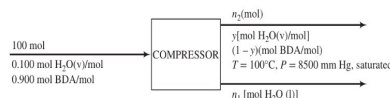
$$T_{dp} = 90^\circ\text{C}$$

$$100^\circ - 90^\circ = 10^\circ\text{C of superheat}$$

2. Basis: 100 mol Feed Gas



Basis: 100 mol Feed Gas



$$DOF = 2 + 1 - 3$$

$$y = \frac{P_{H_2O}^*}{P} = \frac{355 \text{ mmHg}}{5260 \text{ mmHg}} = 0.0675 \frac{\text{mol H}_2\text{O}}{\text{mol}}$$

dry air Balance

$$100 \cdot 0.900 \text{ mol BDA} = n_2(1-y)$$

$$\downarrow y = 0.0675$$

$$n_2 = 96.5 \text{ mol}$$

$$\text{Total mole Balance } 100 = n_1 + n_2$$

$$\downarrow n_2 = 96.5 \text{ mol}$$

$$n_1 = 3.5 \text{ mol H}_2\text{O condensed}$$

$$\text{Percentage condensed } \frac{3.5 \text{ mol H}_2\text{O condensed}}{(0.1 \times 100)} \times 100\% = 35\%$$

$$y = \frac{P_{H_2O}^*}{P} = \frac{760 \text{ mmHg}}{8500 \text{ mmHg}} = 0.0894 \frac{\text{mol H}_2\text{O}}{\text{mol}}$$

Balance BD

$$(100)(0.9) = n_2(0.9106)$$

$$n_2 = 98.84 \text{ mol}$$

$$n_1 + n_2 = 100$$

$$n_1 + 98.84 = 100$$

$$n_1 = 1.2 \text{ mol H}_2\text{O condensed}$$

$$\% = \frac{1.2 \text{ mol}}{(0.1 \times 100)} \times 100 = 12\%$$

Test Yourself

(Answers, p. 657)

1. If water vapor is in equilibrium with liquid water, must the vapor be saturated? Can a vapor be saturated if there is no liquid present in the system? **Yes**

2. The vapor pressure of acetone is 200 mm Hg at 22.7°C. Liquid acetone is kept in a sealed flask at 22.7°C, and the gas above the liquid contains air and acetone vapor at a pressure of 960 mm Hg. What is (a) the partial pressure of acetone in the gas, (b) the partial pressure of

N₂, and (c) the mole fraction of acetone in the gas? What assumption have you made in answering the preceding question? How would you determine the boiling point of the acetone, assuming a constant total pressure of 960 mm Hg?

3. Suppose you have a curve of $p_{H_2O}^*$ versus T , and you are given the temperature and pressure (T_0 and P_0) of a mixture of water and noncondensable gases.

(a) Define the dew point of the gas. Would the vapor be saturated or superheated if

$T_0 > T_{dp}$? If $T_0 = T_{dp}$? **saturated** $p_{H_2O}^* = P_{H_2O}$

(b) If you are told that the gas is saturated, how would you calculate the mole fraction of water in it? What would happen to the vapor if you (i) heated the gas isobarically (at constant pressure), (ii) cooled the gas isobarically, (iii) compressed the gas isothermally (at constant temperature), and (iv) expanded the gas isothermally?

(c) If you are given the mole fraction of water in the gas, how would you calculate the dew point of the gas?

(d) If you are given the degrees of superheat of the gas, how would you calculate the mole fraction of water in the gas?

(b) $p_i = y_i P = p_i^* (T_{dp}) = y_{H_2O} \frac{p^*}{P}$

1. nothing

2. The gas stays saturated, condenses into liquid y_i gas \uparrow

3. The gas stays saturated, water condenses $P_0 \uparrow$ forces P_{H_2O} to exceed $P_{H_2O}^*$ causing condensation

4. nothing

(c) $P_{H_2O} = P_0 y_{H_2O}$

$T_{dp} \rightarrow P_{H_2O}^* = P_{H_2O}$

then use Antoine Equation to find the T

(d) $T_{superheat} = T_0 - T_{dp} \leftarrow$

$P_{H_2O}^* (T_{dp})$ [table]

since $P_{H_2O} = P_{H_2O}^* (T_{dp})$

$\rightarrow y_{H_2O} = \frac{P_{H_2O}^* (T_{dp})}{P_0}$

- The term "saturation" refers to any gas-vapor combination, while "humidity" refers specifically to an air-water system.

- Relative Saturation $S_r(h_r) = \frac{p_i}{p_i^*(T)} \times 100\%$
(humidity)

- molal solution $S_m(h_m) = \frac{p_i}{P - p_i} = \frac{\text{moles of vapor}}{\text{moles of vapor-free (dry) gas}}$

- Abs saturation: $S_a(h_a) = \frac{p_i M_i}{(P - p_i) M_{dry}} = \frac{\text{mass of vapor}}{\text{mass of dry gas}}$

- % saturation = $S_p(h_p) = \frac{S_m}{S_m^*} \times 100\% = \frac{p_i / (P - p_i)}{p_i^* / (P - p_i^*)} \times 100\%$

Test Yourself

(Answers, p. 657)

The vapor pressure of styrene is 100 mm Hg at 82°C and 200 mm Hg at 100°C. A gas that consists of 10 mole% styrene and 90 mole% noncondensables is contained in a tank at 100°C and 1000 mm Hg. Calculate:

1. The dew point of the gas.

2. The relative saturation.

3. The molal saturation and percentage saturation.

1. $y_i P = p_i^*$
 $(0.1)(1000) = 100$ [82°C]

2. $S_r = \frac{p_i}{p_i^*(T)} \times 100 = \frac{(1000)}{(200)} = 50\%$ ✓

3. $S_m = \frac{p_i}{P - p_i} = \frac{100}{1000 - 100} = 0.111$

4. $\frac{200}{1000 - 200} = 0.25 \rightarrow \frac{0.11}{0.25} \times 100 = 44.4\%$

Example 6.3-3

Humid air at 75°C , 1.1 bar, and 30% relative humidity is fed into a process unit at a rate of $1000\text{ m}^3/\text{h}$. Determine (1) the molar flow rates of water, dry air, and oxygen entering the process unit, (2) the molal humidity, absolute humidity, and percentage humidity of the air, and (3) the dew point.

$$\dot{n} = \frac{PV}{RT} = \frac{1000 \cdot 1.1}{348 \cdot 0.0831 \frac{\text{m}^3}{\text{bar}}} = 38 \frac{\text{kmol}}{\text{hr}} \rightarrow 38(0.105) = 3.99 \frac{\text{kmol H}_2\text{O}}{\text{h}}$$

$$(2) \text{ hm} = \frac{P}{P-P} = \frac{86.7}{925-86.7} = 0.117 \frac{\text{mol H}_2\text{O}}{\text{mol BDA}}$$

$$\text{hr\%} = \frac{100 P_{\text{H}_2\text{O}}}{P^*_{\text{H}_2\text{O}}(75^\circ\text{C})}$$

$$P^*_{\text{H}_2\text{O}}(75^\circ\text{C}) = 289 \text{ mmHg}$$

$$P_{\text{H}_2\text{O}}(0.3)(289 \text{ mmHg}) = 86.7 \text{ mmHg}$$

$$P = 1.1 \text{ bar} = 825 \text{ mmHg}$$

$$y_{\text{H}_2\text{O}} = \frac{86.7 \text{ mmHg}}{825 \text{ mmHg}} = 0.105 \text{ mol H}_2\text{O/mol}$$

$$\dot{n}_{\text{O}_2} = 34(0.21) = 7.14 \frac{\text{kmol O}_2}{\text{h}}$$

$$(2) \text{ Abs saturation: } S_a(h_a) = \frac{P_i M_i}{(P-P_i) M_{\text{dry}}}$$

$$= \frac{0.117 \times 18}{29} = 0.0726 \frac{\text{kg H}_2\text{O}}{\text{kg BDA}}$$

$$(3) h^*_{\text{m}} = \frac{P^*_{\text{H}_2\text{O}}}{P - P^*_{\text{H}_2\text{O}}} = \frac{289}{825-289} = 0.539 \frac{\text{kmol H}_2\text{O}}{\text{kmol BDA}}$$

$$h_p = \frac{100 \text{ hm}}{h^*_{\text{m}}} = \frac{0.117}{0.539} \times 100 = 21.7\%$$

$$3. P_{\text{H}_2\text{O}} = 86.7 \text{ mmHg} = P^*_{\text{H}_2\text{O}}(T_{\text{dp}}) \rightarrow 48.7^\circ\text{C}$$

- Multicomponent gas-liquid systems

Example 6.4-1

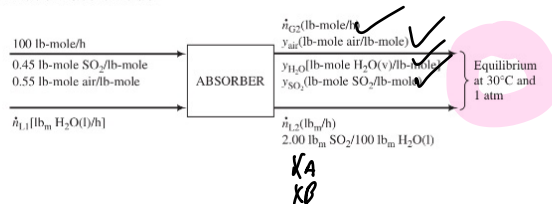
Absorption of SO_2

ENVIRONMENTAL
Equipment Encyclopedia
absorber
wiley.com/college/feider

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

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

Solution Basis: Given Feed Rate of Gas



1. Air balance

$$100(0.55) = \dot{n}_2(0.727) \rightarrow \dot{n}_2 = 75.7 \text{ mol/hr}$$

$$P_{\text{H}_2\text{O}} = 31.6 \text{ mmHg}$$

$$P_{\text{SO}_2} = 176 \text{ mmHg}$$

$$y_{\text{H}_2\text{O}} = \frac{31.6}{760} = 0.0416$$

$$y_{\text{SO}_2} = \frac{176}{760} = 0.232$$

$$y_{\text{air}} = 0.727$$

$$\frac{2}{102} = x_{\text{SO}_2} = 0.0196 \frac{\text{lbm SO}_2}{\text{lbm}}$$

$$x_{\text{H}_2\text{O}} = 0.9804$$

SO_2 Balance

$$(100 \times 0.45) = (75.7)(0.232) + \frac{64}{64}$$

$$\dot{n}_{\text{SO}_2} = 89,600 \text{ lbm/hr}$$

H_2O Balance

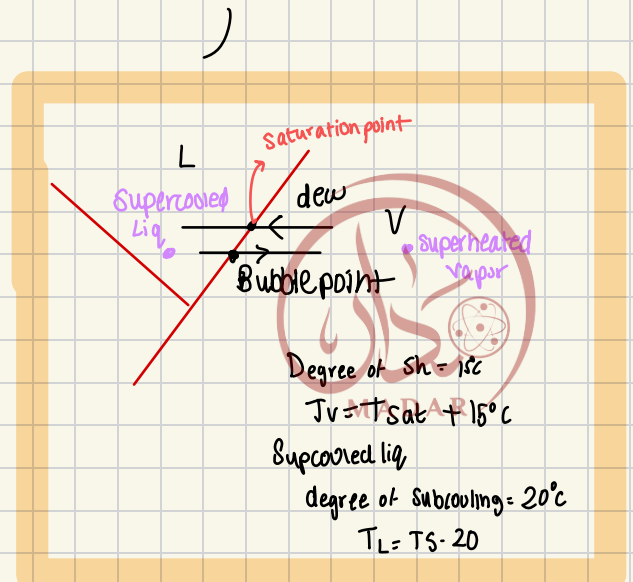
$$\dot{n}_{\text{H}_2\text{O}} = 75.7(0.0416)(18) + (89,600)(0.9804)$$

$$\dot{n}_{\text{H}_2\text{O}} = 87,900 \text{ lbm H}_2\text{O/h}$$

SO_2 Absorbed

$$89,600(0.0196) = 1756 \frac{\text{lbm SO}_2}{\text{hr}}$$

$$\text{SO}_2 \text{ fed} = 100(0.45)(64) = 2880 \frac{\text{lbm SO}_2 \text{ fed}}{\text{hr}} = \frac{1756}{2880} = 0.610 \frac{\text{absorbed}}{\text{fed}}$$



Raoult's Law and Henry's Law

Raoult's Law

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

↑ vapor pressure

↓ mole fraction in gas phase

Raoult usually valid when x_A is close

to 1 - that is when the liquid is almost pure A (liquid)

Henry's Law:

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

↳ Henry's Law const for A in a specific solvent

Henry's Law is generally valid $x_A \sim 0$ [dilute sol of A]

$$P_A = x_A P_A^*$$

$$x_A \sim 1$$

Test Yourself

(Answers, p. 657)

1. What is Raoult's law, and when is it most likely to be valid?
2. What is Henry's law, and when is it most likely to be valid?
3. What is an ideal solution? $P_A = x_A P_A^*$ is obeyed for all species at all sol. composition.
4. A gas containing CO_2 is in equilibrium with liquid water containing a small amount of dissolved CO_2 at 30°C and 3 atm. Would you use Raoult's law or Henry's law to estimate the relationship between (a) x_{CO_2} and p_{CO_2} , and (b) $x_{\text{H}_2\text{O}}$ and $p_{\text{H}_2\text{O}}$, where x denotes mole fraction in the liquid and p denotes partial pressure in the gas? In each case, what would you look up and where would you look for it? Would you expect to observe ideal-solution behavior for this system?
5. After a cold bottle of soda (CO_2 dissolved in water and nonvolatile additives) is opened, bubbles slowly form and emerge. Explain why, using Henry's law in your explanation.

Example 6.4-2

Raoult's Law and Henry's Law

Use either Raoult's law or Henry's law (whichever is most appropriate) to solve the following problems.

1. A gas containing 1.00 mole% ethane is in contact with water at 25.0°C and 20.0 atm. Estimate the mole fraction of dissolved ethane.
2. An equimolar liquid mixture of benzene (B) and toluene (T) is in equilibrium with its vapor at 30.0°C . What is the system pressure and the composition of the vapor?

$$1. \text{ Henry } \chi = \frac{yP}{H} = \frac{(0.01)(20)}{2.67 \times 10^4} = 7.49 \times 10^{-6} \frac{\text{mol C}_2\text{H}_6}{\text{mol}}$$

2. Raoult's

$$\log_{10} P_B^* = 6.909 - \frac{1211}{T + 220.8} \xrightarrow{T=30^\circ\text{C}} 119 \text{ mmHg}$$

$$\log_{10} P_T^* = 6.9533 - \frac{1343.9}{T + 219.38} \xrightarrow{T=30^\circ\text{C}} 36.7 \text{ mmHg}$$

$$P_B = \chi_B P_B^* = (0.5)(119) = 59.5 \text{ mmHg}$$

$$P_T = \chi_T P_T^* = (0.5)(36.7) = 18.35 \text{ mmHg}$$

$$P = P_B + P_T = 77.9 \text{ mmHg}$$

$$y_B = \frac{P_B}{P} = 0.764 \text{ mol Benzene/mol}$$

$$y_T = \frac{P_T}{P} = 0.236 \text{ mole toluene / mole}$$

- The temp at which the first vapor bubble form is the **bubble-point temperature** of liquid at the given pressure

- When a gas (Vapor) is cooled slowly at const pressure the temp first Liquid droplet **dew-point temp**

$$P_i = x_i P_i^*(T_{bp})$$

↳ vapor pressure

$$P = x_A P_A^*(T_{bp}) + x_B P_B^*(T_{bp}) + \dots$$

- The pressure at which the first vapor forms when a liquid is decompressed at a const temp is the **bubble-Point Pressure** of the liquid at given temp

$$y_i = \frac{P_i}{P_{bb}} = \frac{x_i P_i^*(T)}{P_{bp}}$$

$$x_i = \frac{y_i P}{P_i^*(T_{do})} \quad \text{excluding G (noncondensable component)}$$

- at dew point of the gas mixture, the mole fractions of the liquid components (those that are condensable) must sum to 1

$$x_A + x_B + x_C + \dots = 1$$

$$\frac{y_A P}{P_A^*(T_{dp})} + \frac{y_B P}{P_B^*(T_{dp})} + \dots = 1$$

$$P_{dp} = \frac{y_A P_A^*(T) + y_B P_B^*(T) + y_C P_C^*(T)}{1}$$

Example 6.4-3

Bubble- and Dew-Point Calculations

1. Calculate the temperature and composition of a vapor in equilibrium with a liquid that is 40.0 mole% benzene–60.0 mole% toluene at 1 atm. Is the calculated temperature a bubble-point or dew-point temperature?
2. Calculate the temperature and composition of a liquid in equilibrium with a gas mixture containing 10.0 mole% benzene, 10.0% toluene, and the balance nitrogen (which may be considered non-condensable) at 1 atm. Is the calculated temperature a bubble-point or dew-point temperature?
3. A gas mixture consisting of 15.0 mole% benzene, 10.0% toluene, and 75.0% nitrogen is compressed isothermally at 80°C until condensation occurs. At what pressure will condensation begin? What will be the composition of the initial condensate?

liquid x_A
gas/vapor y_A

$$P_{\text{total}} = P_A + P_B = x_A P_A^*(T) + x_B P_B^*(T)$$

$$760 = 0.4 P_A^*(T) + 0.6 P_B^*(T) \quad (T)$$

$$\log_{10}(P^*) = A - \frac{B}{T+C} \quad T = 95.1^\circ\text{C} \rightarrow \log_{10}(P^*) = 6.95905 - \frac{1346.773}{95.1 + 219.693} = 4.79 \text{ mmHg } (0.6) = 287.4 \text{ mmHg}$$

$$y_A = \frac{472.5}{760} = 0.622 \frac{\text{mol B}}{\text{mol}}$$

$$\log_{10}(P^*) = 6.89272 - \frac{1203.531}{95.1 + 219.988} = 1.81 \text{ mmHg } (0.4) = 472.4 \text{ mmHg}$$

$$y_B = 1 - y_A = 0.378 \frac{\text{mol T}}{\text{mol}} = 760$$

- Since the composition of the liquid was given, this was bubble-point calculation

(2) gas \rightarrow so dew point
 $y_i = 10 \text{ mol } \% \text{ Benzene}$
 $10\% \text{ Toluene}$
 $80\% \text{ N}_2$

$$x_A = \frac{y_i P}{P^*} = \frac{(0.1)(760)}{297.4} = 0.256 \quad T_{dp} = 52.4^\circ\text{C}$$

$$\log_{10}(P^*) = 6.95905 - \frac{1346.773}{52.4 + 219.693} = 1.021 \text{ mmHg}$$

$$x_B = 1 - x_A = 0.744 \frac{\text{mol T}}{\text{mol}}$$

$$\log_{10}(P^*) = 6.89272 - \frac{1203.531}{52.4 + 219.988} = 2.974 \text{ mmHg}$$

(3) $T = 80^\circ\text{C}$
 $P_{\text{benzene}}^* = 757.7 \text{ mmHg}$
 $P_{\text{KT}} = 291.2 \text{ mmHg}$

$$P = \frac{1}{\left(\frac{0.150}{757.7 \text{ mmHg}}\right) + \left(\frac{0.1}{291.2 \text{ mmHg}}\right)} = 1847 \text{ mmHg}$$

$$x_A = \frac{y_A P}{P_A^*} = \frac{0.150 (1847 \text{ mmHg})}{757.7 \text{ mmHg}} = 0.366 \frac{\text{mol B}}{\text{mol}}$$

$$x_B = 1 - x_A = 0.634 \frac{\text{mol T}}{\text{mol}}$$

Test Yourself

(Answers, p. 657)

1. What is the bubble point of a liquid mixture at a given pressure? What is the dew point of a vapor mixture at a given pressure?
2. At what temperature will an equimolar liquid mixture of benzene and toluene begin to boil at 1 atm? What is the mole fraction of benzene in the first bubble?
3. At what temperature will an equimolar vapor mixture of benzene and toluene at 1 atm begin to condense? What is the mole fraction of benzene in the first drop? What happens to the system temperature as the condensation proceeds?
4. Would you expect the bubble-point temperature of a liquid mixture to increase, decrease, or remain the same as the pressure increases? What about the dew-point temperature of a vapor mixture? increase, increase
5. When you raise a liquid to its boiling point, the pressure beneath the liquid surface where the bubbles form is different from the gas-phase pressure (why?), so that the boiling does not take place at precisely the calculated temperature. Explain. If the bottom of a vat of water is heated on a day when atmospheric pressure is 1 atm and the height of the water is 5 ft, how would you estimate the boiling temperature?
6. Why does determination of T_{bp} from Equation 6.4-4 or T_{dp} from Equation 6.4-8 involve a trial-and-error calculation?

- 1- The temperature at which the first bubble of vapor forms if the liquid is heated at given pressure.
- The Temp at which the first drop of liquid forms if the vapor mixture is cooled at the given pressure



Solutions of solids in liquids

- solubility of a solid in a liquid is the maximum amount of that substance that can be dissolved in a specific amount of liq. at equil.
- a solution that contains as much of a dissolved species as it can at equilibrium is said to be saturated (has to be if they are at equil.)
- if saturated solution is cooled, the solubility ↓
- conc. of the solute is higher than equil. value **Supersaturated**

Example 6.5-1

Crystallization and Filtration

Equipment Encyclopedia
crystallizer, filter, dryer

www.wiley.com/college/feider

One hundred fifty kilograms of a saturated aqueous solution of AgNO_3 at 100°C is cooled to 20°C , thereby forming AgNO_3 crystals, which are filtered from the remaining solution. The wet filter cake, which contains 80.0% solid crystals and 20.0% saturated solution by mass, is sent to a dryer in which the remaining water is vaporized. Calculate the fraction of the AgNO_3 in the feed stream eventually recovered as dry crystals and the amount of water that must be removed in the drying stage.

-solid solubilities and hydrated salts

a single plot of solubility (an intensive variable) versus temp may be applicable over a wide pressure range

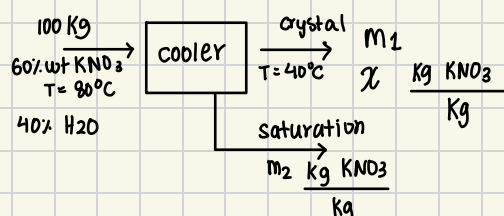
Example 6.5-2

Material Balances on a Crystallizer

Equipment Encyclopedia
crystallizer

www.wiley.com/college/feider

An aqueous potassium nitrate solution containing 60.0 wt% KNO_3 at 80°C is fed to a cooling crystallizer in which the temperature is reduced to 40°C . Determine the temperature at which the solution reaches saturation and the percentage of the potassium nitrate in the feed that forms crystals.



allegedly from graph.

$$X = \frac{63}{63 + 100} = 0.386 \text{ kg KNO}_3 / \text{kg}$$

$$\frac{34.9 \text{ kg}}{60} \times 100\% = 58.2\%$$

H₂O Balance $(100)(0.4) = m_1 \cdot (1 - 0.386) = 65.1 \text{ kg}$

$$100 \text{ kg} - 65.1 + m_2 \quad m_2 = 34.9 \text{ kg KNO}_3(\text{s})$$

(note*)

- when certain solutes crystallize from aqueous solutions, the crystals hydrated salts

Example 6.5-3

Production of a Hydrated Salt

Equipment Encyclopedia
crystallizer

www.wiley.com/college/feider

An aqueous solution of magnesium sulfate at 104°C containing 30.1 wt% MgSO_4 is fed to a cooling crystallizer that operates at 10°C . The stream leaving the crystallizer is a slurry of solid magnesium sulfate heptahydrate particles $[\text{MgSO}_4 \cdot 7\text{H}_2\text{O}(\text{s})]$ suspended in a liquid solution. Solubility data for magnesium sulfate [Perry's Chemical Engineers' Handbook (see Footnote 1), p. 18-40] show that a saturated solution at 10°C contains 23.2 wt% MgSO_4 . Determine the rate at which solution must be fed to the crystallizer to produce 1 metric ton (1 tonne, 1000 kg) of magnesium sulfate heptahydrate per hour.



Test Yourself

(Answers, p. 657)

1. Solid crystals of sodium chloride are slowly added to 1000 kg of water at 60°C. After each small addition, the mixture is stirred until the salt dissolves, and then more salt is added. How much salt can be dissolved if the temperature is maintained at 60°C? What will happen if more than this quantity of salt is added? (Refer to Figure 6.5-1.)

undissolved

2. An aqueous solution contains 50.0 wt% KNO_3 at 80°C. To what temperature would this solution have to be cooled before solid crystals begin to form? What happens as the solution is cooled to progressively lower temperatures?
3. What do the terms *hydrated salt*, *water of hydration*, and *anhydrous salt* mean? What would $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}(\text{s})$ probably be called if this species were found in nature? (Hint: Think about CCl_4 .) **magnesium sulfate tetrahydrate**
4. Given that the molecular weight of MgSO_4 is 120.4, what is the mass fraction of MgSO_4 in **magnesium sulfate monohydrate**?
5. Why is there a slope discontinuity at 40°C in the Na_2SO_4 solubility curve of Figure 6.5-1?

$$1) \frac{39}{100} = \frac{x}{1000} = 390 \text{ g}$$

- the solution is already saturated, any additional won't dissolve

2) 50g of salt, 50g of water
50% is saturated if you cool
solid crystals form

(5) Above 40°C the crystals that precipitate are hydrated salts

- (3) **hydrated salt**: a solid crystalline compound that has water molecules trapped within its crystal lattice.
water of hydration: The specific water molecules found inside the hydrated crystal structure
Anhydrous salt: The compound that remains after all the water has been removed.

$$(4) 120.4 / 139.24 = 0.87$$

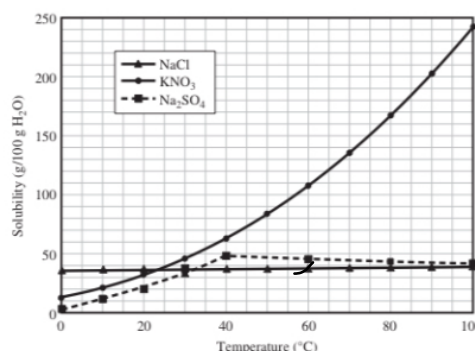


FIGURE 6.5-1 Solubilities of inorganic solutes.

