Lecture 3.
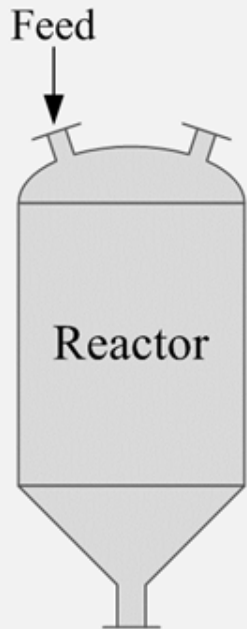# Fundamental Process Variables

What is a process?

General:

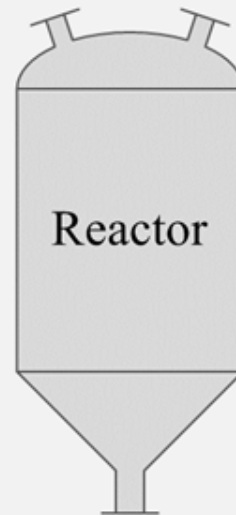"An action or event which causes changes."

Chemical Engineering:

"A process is a series of operations involving the physical, chemical, or biological transformation of an input material for the purpose of achieving a desired product material."

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Types of Chemical Processes – Batch Process

Feed → Reactor

All materials are
added at the start
of the process

Reactor

The process is
allowed to proceed

Products ← Reactor

Products are withdrawn
after completion of
the process

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Types of Chemical Processes – Continuous Process

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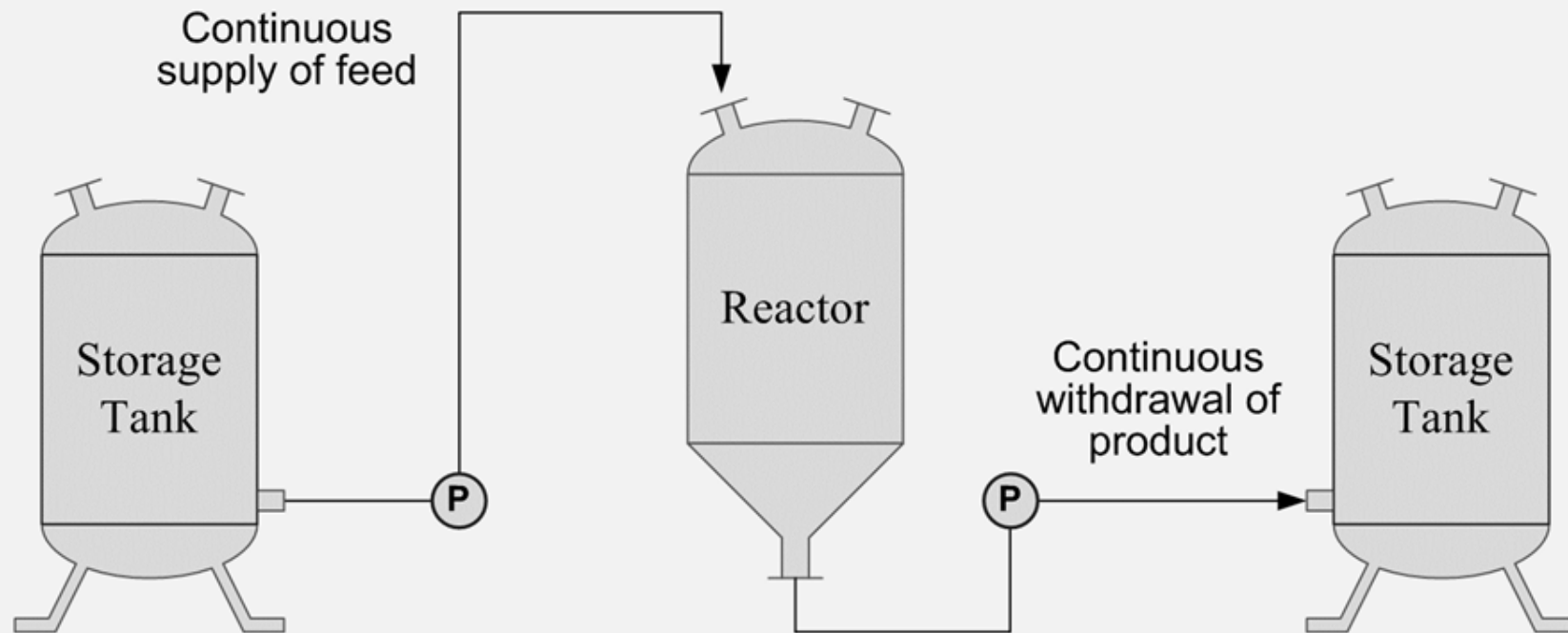
Types of Chemical Processes – Semicontinuous (Semibatch) Process

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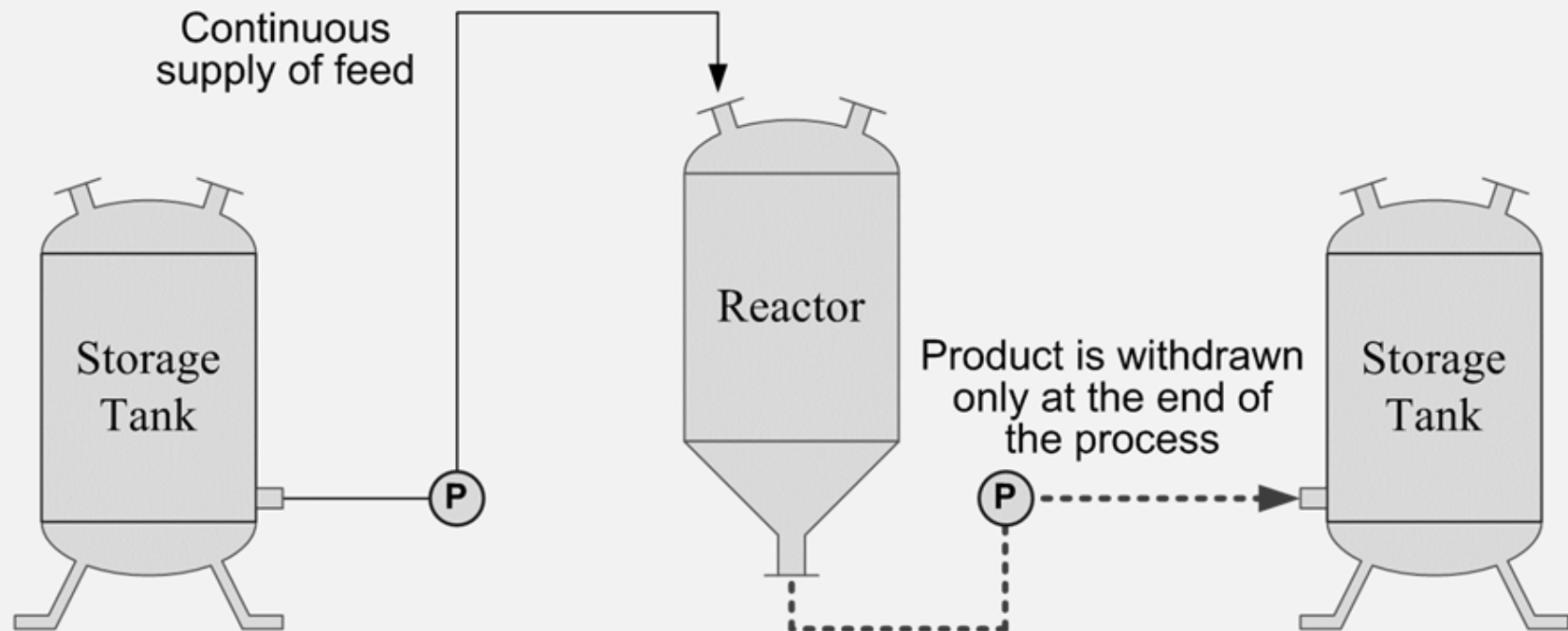
What is a (chemical) process variable?

Any measurement used to characterize or describe a chemical process.

The fundamental process variables

1. Measurements to quantify a material or specify a chemical composition.

Mass, Volume, and Mole

2. Measurements used to specify process conditions.

Pressure and Temperature

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Mass and Volume: Conservation Principles

Conservation Law for Mass:

"Matter is neither created nor destroyed"

$$m_A + m_B = m_T \text{ or } m_A + m_B = m_C + m_D$$

For volume, there is no generalized conservation law.

1. For gases, $V_A + V_B \neq V_T$

2. For liquids, $V_A + V_B = V_T$
   (if volume change is negligible)

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Mass and Volume: Density and Specific Gravity

Density (ρ)
Ratio of mass per unit volume. Used as a factor for inter-conversion of mass and volume.

$$\rho = \frac{\text{mass}}{\text{volume}} \left(\frac{m}{L^3}, \frac{g}{ml}, \frac{kg}{m^3}, \frac{lbm}{ft^3} \right)$$

1. Densities of gases depend on pressure and temperature.

2. Densities of solids and liquids do not change significantly with pressure at ordinary conditions with pressure but change with temperature.

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Mass and Volume: Density and Specific Gravity

Specific Gravity (sp gr)
Ratio of two densities – that of the substance of interest to that of a reference substance.

$$\text{sp gr} = \frac{\rho_A}{\rho_{ref}} = \frac{(g/ml)_A}{(g/ml)_{ref}} = \frac{\left(kg/m^3\right)_A}{\left(kg/m^3\right)_{ref}} = \frac{\left(lbm/ft^3\right)_A}{\left(lbm/ft^3\right)_{ref}}$$

The specific gravity of gases frequently is referred to air, but may be referred to other gases. The reference substance for liquids and solids is normally water at 4^0C:

$$\rho_{H_2O} \text{ at } 4^0C = 1.000 \ \frac{g}{ml} = 1000 \ \frac{kg}{m^3} = 62.43 \ \frac{lbm}{ft^3}$$

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Mass and Volume: Density and Specific Gravity

Specific Gravity (sp gr)

When referring to specific gravity, the temperature at which each density is measured. Thus,

$$\textbf{sp gr} = \textbf{0.73} \left| \frac{\textbf{20}^{\textbf{0}}}{\textbf{4}^{\textbf{0}}} \right|$$

This can be interpreted as the specific gravity when the substance of interest is at 20^{0}C and the reference substance (water) is at 4^{0}C.

If temperatures are not stated, assume ambient temperature and 4^{0}C, respectively.

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The Mole Unit

☐ Refers to a certain number of molecules, atoms, or sub-atomic particles.

☐ "The amount of substance that contains as many elementary entities as there are atoms in 0.012 kg of carbon 12" – *1969 International Committee on Weights and Measures*

☐ Contains Avogadro's number of entities (molecule, atom, or any particles) – 6.02 x 10^{23}

☐ Amount of a chemical species whose mass is equal to its molecular weight.

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The Mole Unit

A **gmol** is the standard unit for mole and contains <u>6.02 x 10^{23}</u> molecules or atoms. But the following units can also be used for mole:

$$1 \text{ kmol} = 1000 \text{ gmol}$$
$$1 \text{ lbmol} = 454.54 \text{ gmol}$$

In fact, any equivalent unit for mole can be used by defining an analogous unit to mass and using the same conversion used for mass.

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The Mole Unit

To convert the number of moles to mass, we make use of the molecular weight (MW):

$$\textbf{Molecular Weight} = \frac{\textbf{mass}}{\textbf{mole}} \left(\frac{\textbf{m}}{\textbf{n}}, \frac{\textbf{g}}{\textbf{gmol}}, \frac{\textbf{kg}}{\textbf{kmol}}, \frac{\textbf{lbm}}{\textbf{lbmol}} \right)$$

If the molecular weight of H_2O is 18, then:

1 gmol contains 18 g of H_2O (MW = 18 g/gmol)
1 kmol contains 18 kg of H_2O (MW = 18 kg/kmol)
1 lbmol contains 18 lbm of H_2O (MW = 18 lbm/lbmol)

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Quantifying Materials in a Continuous Chemical Process

For continuous process, it is best to use flow rates to measure the amount of materials flowing through the process:

1. **Mass Flowrate** $\left(\dot{\mathbf{m}}, \vec{\mathbf{m}} \right)$ $\vec{\mathbf{m}}$ = **mass/time (m/θ)**

2. **Volume Flowrate** $\left(\dot{\mathbf{V}}, \vec{\mathbf{V}} \right)$ $\vec{\mathbf{V}}$ = **volume/time** $\left(\mathbf{L}^3/\boldsymbol{\theta} \right)$

3. **Molar Flowrate** $\left(\dot{\mathbf{n}}, \vec{\mathbf{n}} \right)$ $\vec{\mathbf{n}}$ = **moles/time (n/θ)**

Chemical Composition

In a mixture of two or more components, the composition may be expressed as:

1. Mass Fraction $\quad x_i = \dfrac{\text{mass of component i}}{\text{total mass of mixture}}\left(\dfrac{m_i}{m_T}\right)$

2. Mole Fraction $\quad y_i = \dfrac{\text{moles of component i}}{\text{total moles of mixture}}\left(\dfrac{n_i}{n_T}\right)$

For liquids and solids, it will always be assumed that the composition is on a weight basis unless otherwise stated.

For gases, it will be assumed to be in molar basis.

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Chemical Composition

Other methods of expressing concentration include:

1. **Molarity** (mol/L) and **normality** (equivalents/L).

2. **Parts per million (ppm) and parts per billion (ppb)** – normally used for expressing concentration of extremely dilute solutions.

3. **Partial pressure** – a method to express the concentration of a gas mixture.

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Example 3.1 – Mass and Volume Calculations

The specific gravity of gasoline is approximately 0.70.

a. Determine the mass (kg) of 50.0 liters of gasoline.

b. If the mass flow rate of gasoline delivered by a gasoline pump is 1150 kg/min, what is the corresponding volumetric flow rate in liters/s.

c. Gasoline and kerosene (specific gravity = 0.82) are blended to obtain a mixture with a specific gravity of 0.78. Calculate the volumetric ratio (volume of gasoline/volume of kerosene) of the two compounds in the mixture, assuming the law of additive volume is applicable.

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Example 3.1 – Mass and Volume Calculations

Solution for (a):

$$m_G = \rho_G V_G = (sp\ gr_G)\rho_{ref} V_G$$

$$m_G = (0.70)\left(1000\ \frac{kg}{m^3}\right)(50.0\ L)\left(\frac{1\ m^3}{1000\ L}\right) = 35.0\ kg$$

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Example 3.1 – Mass and Volume Calculations

Solution for (b):

$$\vec{V}_G = \frac{\vec{m}_G}{\rho_G} = \frac{\vec{m}_G}{(sp\ gr_G)\rho_{ref}}$$

$$\vec{V}_G = 1150\frac{kg}{min}\left(\frac{m^3}{0.70\times 1000kg}\right) = 1.643\frac{m^3}{min}$$

$$\vec{V}_G = 1.643\frac{m^3}{min}\left(\frac{1\,min}{60s}\right)\left(\frac{1000L}{m^3}\right) = 27.38\frac{L}{s}$$

Example 3.1 – Mass and Volume Calculations

Solution for (c):

$$\rho_{mix} = \left(sp\ gr_{mix} \right)\left(\rho_{ref} \right) = \frac{m_{mix}}{V_{mix}}$$

$$\left(sp\ gr_{mix} \right)\left(\rho_{ref} \right) = \frac{\left(m_G + m_K \right)}{\left(V_G + V_K \right)} = \frac{\left(V_G \rho_G + V_K \rho_K \right)}{\left(V_G + V_K \right)}$$

$$\left(sp\ gr_{mix} \right)\left(\rho_{ref} \right) = \frac{\left(V_G \left(sp\ gr_G \right) \rho_{ref} + V_K \left(sp\ gr_K \right) \rho_{ref} \right)}{\left(V_G + V_K \right)}$$

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Example 3.1 – Mass and Volume Calculations

Eliminating ρ_{ref} in the equation,

$$\left(sp\ gr_{mix} \right)\left(\rho_{ref} \right) = \frac{\rho_{ref}\left[V_G \left(sp\ gr_G \right) + V_K \left(sp\ gr_K \right) \right]}{\left(V_G + V_K \right)}$$

$$\left(sp\ gr_{mix} \right) = \frac{V_G \left(sp\ gr_G \right) + V_K \left(sp\ gr_K \right)}{\left(V_G + V_K \right)}$$

$$0.78 = \frac{V_G \left(0.70 \right) + V_K \left(0.82 \right)}{V_G + V_K}$$

Example 3.1 – Mass and Volume Calculations

Rearranging the equation,

$$0.78V_G + 0.78V_K = 0.70V_G + 0.82V_K$$
$$(0.78 - 0.70)V_G = (0.82 - 0.78)V_K$$

Solving for the volume ratio,

$$\frac{V_G}{V_K} = \frac{0.82 - 0.78}{0.78 - 0.70} = \frac{0.04}{0.08} = 0.50 \frac{\text{L gasoline}}{\text{L kerosene}}$$

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Example 3.2 – Mass and Volume Calculations

At 25^0C, an aqueous solution containing 35% H_2SO_4 has a specific gravity of 1.2563.

a. Calculate the volume of the solution that will contain 195.5 kg of H_2SO_4.

b. Re-calculate the volume of the solution if pure-component specific gravities of H_2SO_4 (SG = 1.8255) and water had been used for the calculation. Assume additive volume is applicable.

c. Estimate the percent error in volume calculation.

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Example 3.2 – Mass and Volume Calculations

Solution for (a):

Solve for m_{sol} using the weight fraction of H_2SO_4:

$$m_{sol} = 195.5 \, \text{kg} \, H_2SO_4 \left(\frac{1 \, \text{kg solution}}{0.35 \, \text{kg} \, H_2SO_4} \right) = 558.57 \, \text{kg}$$

Solve for V_{sol} using the specific gravity of mixture:

$$V_{sol} = 558.57 \, \text{kg sol} \left(\frac{m^3}{1.2563 \times 1000 \, \text{kg}} \right) \left(\frac{1000 \, \text{L}}{1 \, m^3} \right) = 444.6 \, \text{L}$$

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Example 3.2 – Mass and Volume Calculations

Solution for (b):

If additive volume is applicable:

$$V_{sol} = V_{water} + V_{acid}$$

Solve for the volume of acid:

$$V_{acid} = 195.5 \, kg \, H_2SO_4 \left(\frac{m^3}{1.8255 \times 1000 \ kg} \right) \left(\frac{1000 \ L}{1 \ m^3} \right) = 107.09 \ L$$

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Example 3.2 – Mass and Volume Calculations

Solve for the volume of water:

$$V_{water} = 195.5 \, kg \, H_2SO_4 \left(\frac{0.65 \, kg \, H_2O}{0.35 \, kg \, H_2SO_4} \right) \left(\frac{1 \, m^3}{1000 \, kg} \right) \left(\frac{1000 \, L}{1 \, m^3} \right)$$

$$V_{water} = 363.07 \, L$$

Solving for the total volume of solution:

$$V_{sol} = 363.07 \, L + 107.09 \, L$$
$$V_{sol} = 470.16 \, L$$

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Example 3.2 – Mass and Volume Calculations

Solution for (c):

$$\% \, error = \frac{\left|measured \, value - true \, value\right|}{true \, value} \times 100$$

$$\% \, error = \frac{\left|470.16 \, L - 444.6 \, L\right|}{444.6 \, L} \times 100$$

$$\% \, error = 5.5 \, \%$$

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Example 3.3 – Calculations Involving the Mole Unit

A mixture contains:

> 10.0 mole% ethyl alcohol (C_2H_5OH)
> 75.0 mole % ethyl acetate ($C_4H_8O_2$)
> 15.0 mole% acetic acid (CH_3COOH)

a. Calculate the mass fractions of each component in the mixture.

b. What is the average molecular weight of the mixture?

c. What would be the mass (kg) of a sample containing 25.0 kmol of ethyl acetate?

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Example 3.3 – Calculations Involving the Mole Unit

Solution for (a):

Consider 100.0 gmol of mixture.

Component i	Moles (gmol)	MW (g/gmol)	Mass (g)	Mass Fraction
C_2H_5OH	10.0	46	460	0.0578
$C_4H_8O_2$	75.0	88	6600	0.8291
CH_3COOH	15.0	60	900	0.1131
Total	100.0	- - -	7960	1.0000

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Example 3.3 – Calculations Involving the Mole Unit

Solution for (b):

$$\text{Ave.MW} = \frac{\text{total mass}}{\text{total moles}} = \frac{7960\,\text{g}}{100.0\,\text{gmol}} = 79.6\,\frac{\text{g}}{\text{gmol}}$$

Solution for (c):

$$m_{\text{sample}} = 25\,\text{kmol}\,C_4H_8O_2\left(\frac{1\,\text{kmol mixt.}}{0.75\,\text{kmol}\,C_4H_8O_2}\right)\left(\frac{79.6\,\text{kg mixt.}}{\text{kmol mixt.}}\right)$$

$$m_{\text{sample}} = 2{,}653.3\,\text{kg mixture}$$

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Relative and Absolute Temperature Scales

Temperature: The average kinetic energy possessed by the substance.

Relative Temperature Scale – Celsius and Fahrenheit
The zero value is preset at some arbitrarily defined level.

$$T(^0F) = 1.8T(^0C) + 32$$
$$T(^0C) = (1/1.8)[T(^0F) - 32]$$

Absolute Temperature Scale – Kelvin and Rankine
A temperature scale on which a reading of zero coincides with the theoretical absolute zero (zero entropy configuration)

$$T(K) = T(^0C) + 273.15$$
$$T(^0R) = T(^0F) + 459.67$$

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Unit Temperature Difference

When temperature is used as a unit difference, then the following relationship is used:

$$\Delta\ ^0C = \Delta K$$
$$\Delta\ ^0F = \Delta\ ^0R$$

$$\Delta\ ^0C = 1.8 \times \Delta\ ^0F$$
$$\Delta K = 1.8 \times \Delta\ ^0R$$

Whether temperature is used as a unit temperature difference must be interpreted from the context of the equation or sentence being examined.

Example 3.4 – Temperature and Unit Temperature Difference

The thermal conductivity (k) of aluminum at $32\,^0F$ is:

$$k = 117 \text{ Btu/(hr)(ft}^2\text{)(}^0\text{F/ft)}$$

Find the equivalent value in terms of Btu/(hr)(ft²)(K/ft).

$$117\,\frac{\text{Btu}}{(\text{hr})(\text{ft}^2)(\Delta\,^0\text{F/ft})}\times\left(\frac{1.8\,\Delta\,^0\text{F}}{1\Delta\,^0\text{C}}\right)\times\left(\frac{1\Delta\,^0\text{C}}{1\Delta\text{K}}\right)=221\,\frac{\text{Btu}}{(\text{hr})(\text{ft}^2)(\Delta\text{K/ft})}$$

It is not correct to do the following conversion:

$$117\,\frac{\text{Btu}}{(\text{hr})(\text{ft}^2)\left(\dfrac{1.8\,^0\text{C}+32}{\text{ft}}\right)}$$

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Example – Temperature and Unit Temperature Difference

The heat capacity of sulfuric acid has the units of J/(gmol)(^{0}C) and is given by the relation

$$C_P = 139.1 + (1.56 \times 10^{-1})T(^0C)$$

where T is expressed in ^{0}C. Modify the formula so that the heat capacity has a unit of Btu/(lbmol)(^{0}R) and T is in ^{0}R.

In the given relation, the T is used as a specific temperature value and not a unit temperature difference.

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Example 3.4 – Temperature and Unit Temperature Difference

Establish the relation between T(^{0}R) and T(^{0}C).

$$\textbf{T(}^\textbf{0}\textbf{C) = (1/1.8)} \times \textbf{[T(}^\textbf{0}\textbf{R)} - \textbf{460} - \textbf{32]}$$

Using this equivalence in the given relation.

$$C_P = \left(139.1 + 1.56 \times 10^{-1}\left[\frac{1}{1.8}\left(T(^0R) - 460 - 32\right)\right]\right)\frac{J}{gmol \cdot \,^0C}$$

$$C_P = 215.852 + 8.67 \times 10^{-2}\,T(^0R)\frac{J}{gmol \cdot \,^0C}$$

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Example 3.5 – Temperature and Unit Temperature Difference

Converting the resulting unit for heat capacity:

$$C_P = \left[215.852 + 8.67 \times 10^{-2}\, T(^0R) \frac{J}{gmol \cdot {}^0C} \right]$$

$$\times \left(\frac{1\,Btu}{1055\,J} \right) \left(\frac{454\,gmol}{1\,lbmol} \right) \left(\frac{1\,\Delta^0 C}{1.8\,\Delta^0 R} \right)$$

$$C_P = 23.06 + 2.07 \times 10^{-2}\, T(^0R) \frac{Btu}{lbmol \cdot {}^0R}$$

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Pressure – General Definition

Pressure is defined as normal force per unit area.

Force (F)

Area (A)

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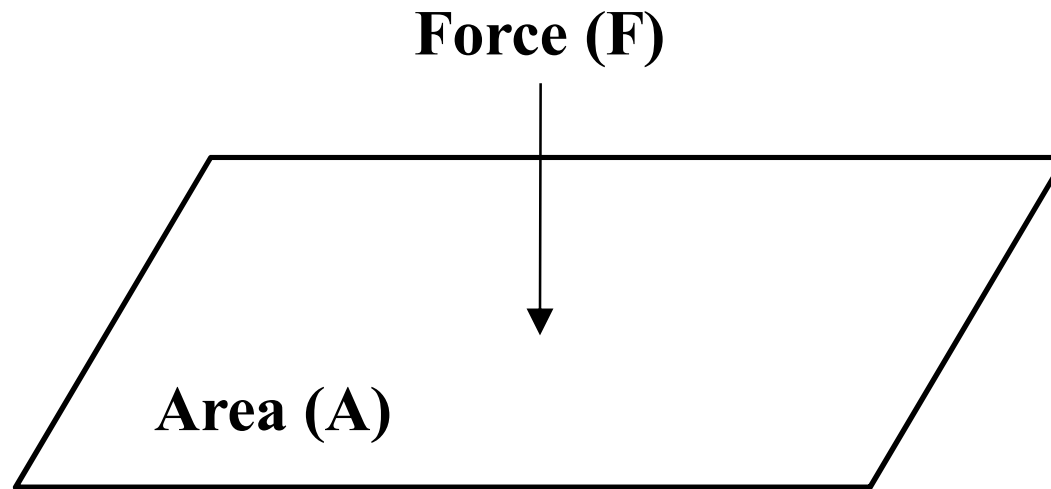
Absolute and Relative Pressures

Absolute Pressure (P_A)
Pressure measured relative to a fixed reference point of zero pressure (vacuum).

Gauge Pressure (P_G)
Pressure measured relative to the atmosphere pressure (relative pressure). Many pressure measurement devices measure only gauge pressure.

$$\mathbf{P_{abs} = P_G + P_{atmospheric}}$$

Note:
When using English units, absolute pressure and gauge pressure are designated as psia and psig, respectively.

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The Atmospheric (Barometric) Pressure

Can vary with location, weather conditions and other factors. Usually determined from a barometer (barometric pressure).
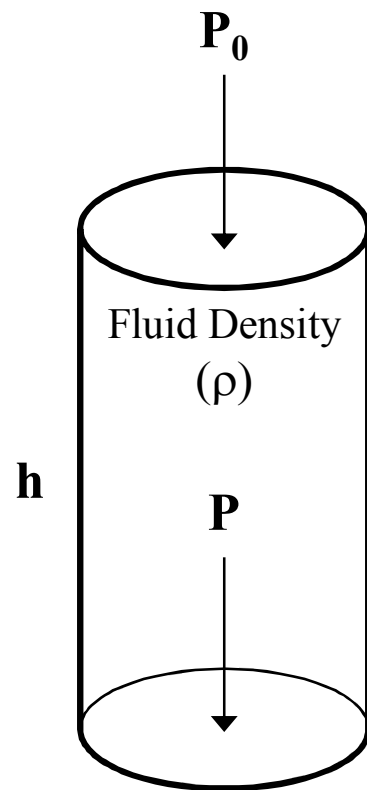
The Standard Atmospheric Pressure:

$$P_{atm} = \textbf{1.000 atm}$$
$$= \textbf{760.0 mmHg}$$
$$= \textbf{101.3 kPa}$$
$$= \textbf{29.92 in Hg}$$
$$= \textbf{33.91 ft } H_2O$$
$$= \textbf{14.7 psi (lbf/in}^2\textbf{)}$$

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Hydrostatic Pressure

Hydrostatic pressure is the pressure at the bottom of a static (non-moving) column of water.

P_0

Fluid Density (ρ)

h

P

Relationship between pressure on top (P_0) and pressure at the bottom (P)

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

where

P   = pressure at the bottom of the fluid
P_0 = pressure at the top of the column
ρ = density of the fluid
h   = height of the fluid
g   = acceleration due to gravity

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Example 3.7 – Hydrostatic Pressure Calculation

The great Boston molasses flood occurred on January 15, 1919. In it, 2.3 million gallons of crude molasses flowed from a 30-foot high storage tank that ruptured, killing 21 people and injuring 150.

The estimated specific gravity of crude molasses is 1.4. What were the mass of molasses in the tank in lb_m and the pressure at the bottom of the tank in $lbf/in.^2$?

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Example 3.7 – Hydrostatic Pressure Calculation

Calculation for mass (in lbm):

$$m_M = \rho_M V_M = SG_M \rho_{ref} V_M$$

$$m_M = 1.4 \left(62.43 \frac{lbm}{ft^3} \right) \left(2.3 \times 10^6 \, gal \right) \left(\frac{1 ft^3}{7.481 \, gal} \right)$$

$$m_M = 2.69 \times 10^7 \, lbm$$

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Example 3.7 – Hydrostatic Pressure Calculation

Calculation for pressure at the tank bottom (in $lbf/in.^2$):

Applying the formula for hydrostatic pressure:

$$P = P_0 + \rho_M gh = P_0 + SG_M \rho_{ref} gh$$

What is the pressure at the top (P_0)?

$$P_0 = P_{atm}$$

In the absence of any information, assume standard atmospheric pressure:

$$P_0 = P_{atm} = 14.7 \; lbf/in.^2$$

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Example 3.7 – Hydrostatic Pressure Calculation

Substituting actual values in the formula:

$$P = \left(14.7\,\frac{lb_f}{in.^2}\right) + 1.4\left(62.43\,\frac{lbm}{ft^3}\right)\left(32.174\,\frac{ft}{s^2}\right)(30\,ft)$$

$$P = 14.7\,\frac{lb_f}{in.^2} + 84{,}362.16\,\frac{lbm \cdot ft}{ft^2 \cdot s^2}\left(\frac{1\,lb_f}{32.174\,lbm \cdot ft/s^2}\right)$$

$$P = 14.7\,\frac{lb_f}{in.^2} + 2{,}622.06\,\frac{lb_f}{ft^2}\left(\frac{1\,ft^2}{144\,in.^2}\right) = (14.7 + 18.1)\frac{lb_f}{in.^2}$$

$$P = 32.91\,\frac{lb_f}{in.^2}\,(or\,psia)$$

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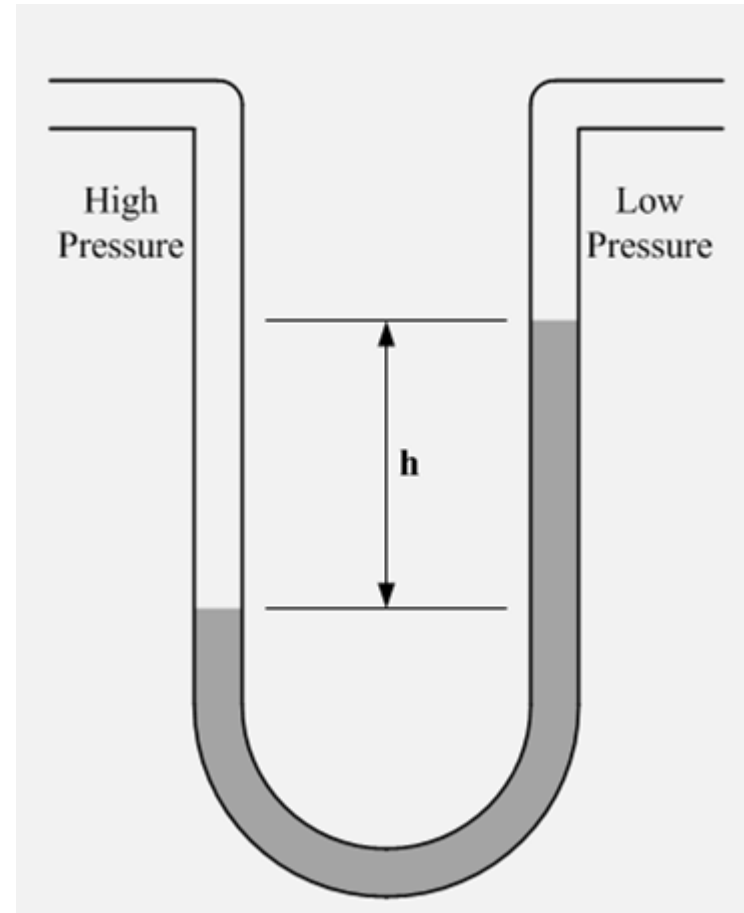
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Pressure Measure Device – The Manometer

Used for measurement of pressures below 3 atm.

U-shaped tube partially filled with a fluid of known density (manometer fluid).

Both ends of the tube are exposed to different pressures causing differences in the level of the manometer fluid in both arms.
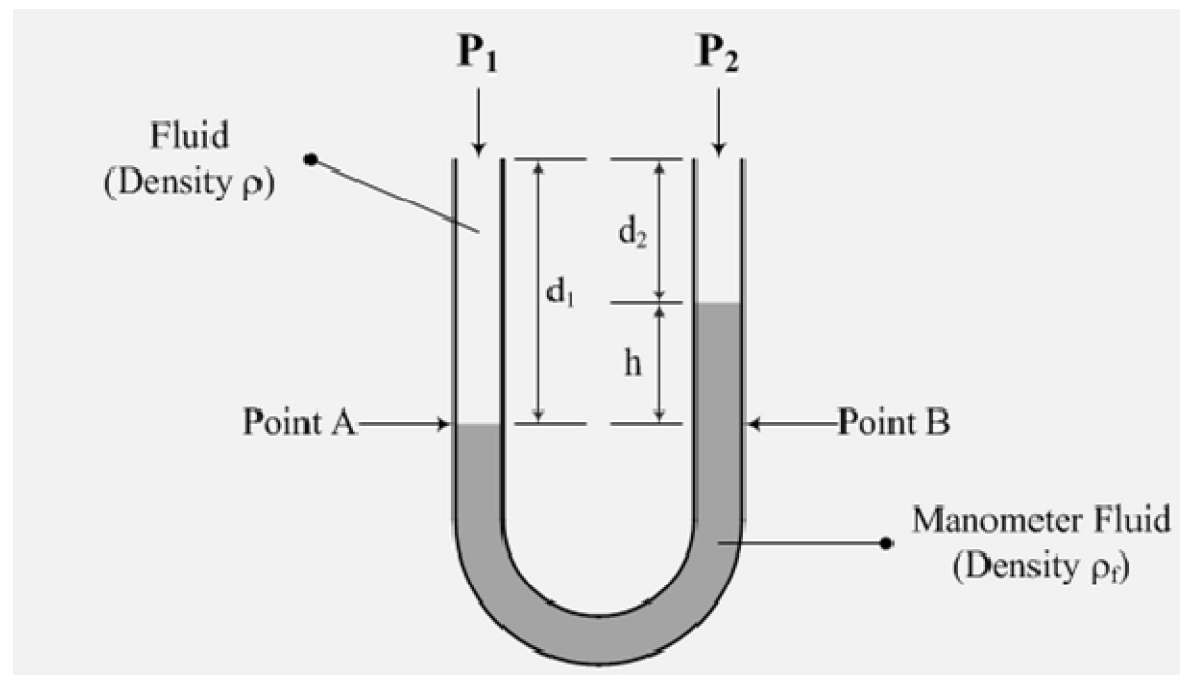
The differences between pressures can be calculated from the measured difference between the liquid levels of each arm.
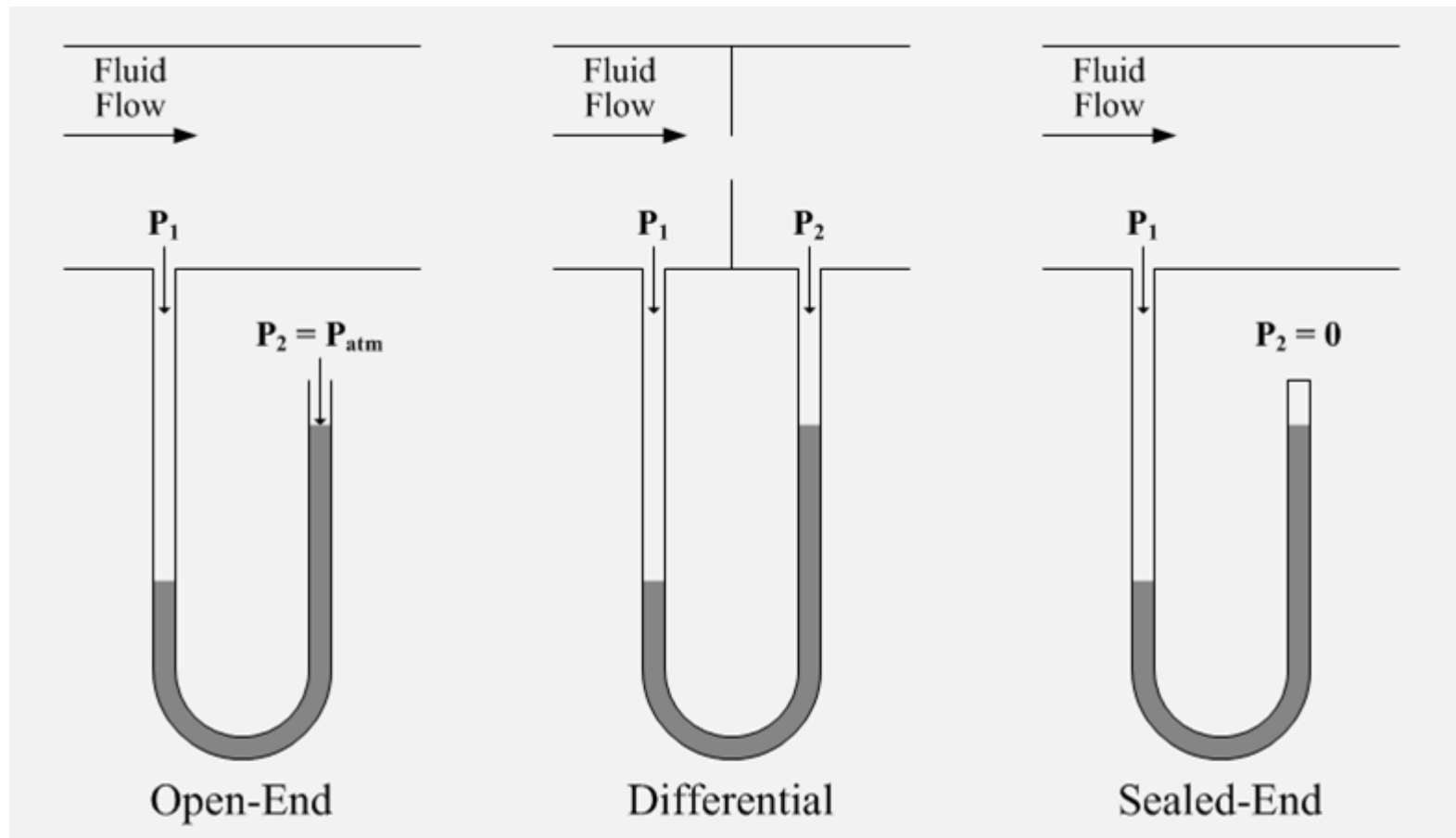
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Manometer Pressure Calculations

Based on the principle that the fluid pressure must be the same at any two points at the same height in a continuous fluid.
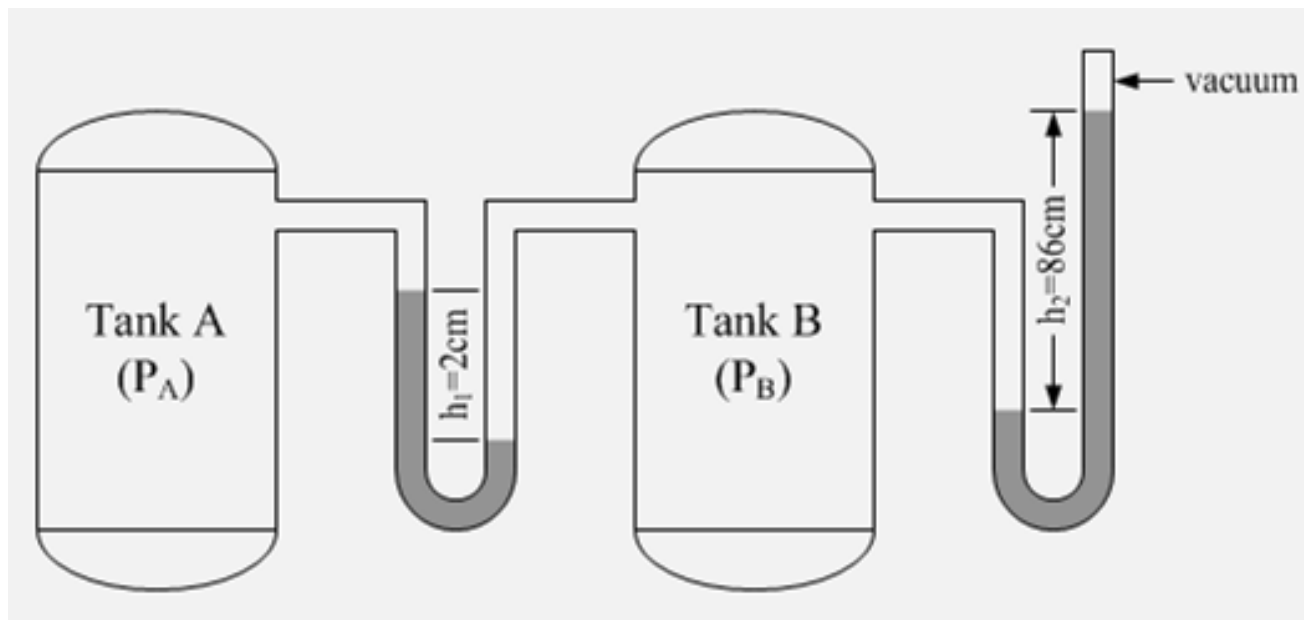
$$\Delta P = P_1 - P_2 = (\rho_f - \rho)gh$$

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Types of Manometer

Open-End — Differential — Sealed-End

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Example 3.8 – Manometer Pressure Calculation

The pressure difference between two gas tanks A and B is measured by a U-tube manometer, with mercury as the manometer liquid. The barometric pressure is 700 mmHg. What are the gauge and absolute pressures in tank A in mmHg?

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Example 3.8 – Manometer Pressure Calculation

Using the pressure difference formula for a manometer:

$$\Delta P = P_A - P_B = (\rho_{Hg} - \rho)gh_1$$

Since the tanks contain gases, the density of the gas (ρ) can be neglected in the calculation:

$$P_A - P_B = \rho_{Hg}gh_1$$

Solving for P_A:

$$P_A = P_B + \rho_{Hg}gh_1$$

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Example 3.8 – Manometer Pressure Calculation

First, calculate for P_B:

$$P_B - (0) = \rho_{Hg}gh_2$$

Substituting the equivalent expression for P_B in the last equation for P_A:

$$P_A = \rho_{Hg}gh_2 + \rho_{Hg}gh_1$$

$$P_A = \rho_{Hg}g(h_2 - h_1)$$

How do we get the density of mercury (ρ_{Hg})?

Example 3.8 – Manometer Pressure Calculation

Knowing the density of mercury is not necessary if mmHg is used as unit for pressure, such that:

$$\mathbf{P_A = h_2 - h_1}$$
$$\mathbf{P_A = (860 - 20) \ mm \ Hg}$$
$$\mathbf{P_A = 840 \ mm \ Hg}$$

Is this pressure in tank A absolute or gauge?

The calculated P_A is an absolute pressure since it was measured relative to a vacuum. To determine the gauge pressure:

$$\mathbf{P_A \ (gauge) = (840 - 700) \ mm \ Hg = 140 \ mm \ Hg}$$

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