THERMAL ENERGY

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Outline

- Definition: Thermal Energy

- Sources

- Propulsion Chain

- Definition: Thermodynamics

- Four Axioms of Thermodynamics

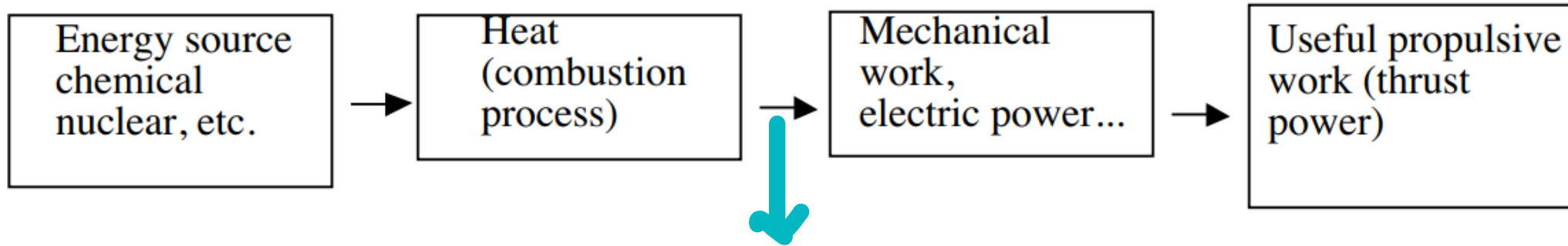- Macroscopic vs. Microscopic

- System Properties

Definition: Thermal Energy

"Thermal energy is the energy possessed by an object/system by virtue of its temperature. When there is a temperature difference between two bodies, thermal energy flows from a higher temperature body to a lower temperature body. In thermodynamics, this flow of thermal energy is referred to as heat."

(Ramachandra Vijjapu & Shaligram Tiwari, 2022)

Sources

- There are two main types of thermal energy sources:
  1. Natural sources
  2. Artificial sources

- Examples of natural thermal energy sources
  - Sun (solar energy)
  - Geothermal energy
  - Biomass energy

- Examples of artificial thermal energy sources
  - Fossil fuels
  - Nuclear energy
  - Waste heat

Propulsion Chain

| Energy source chemical nuclear, etc. | → | Heat (combustion process) | → | Mechanical work, electric power... | → | Useful propulsive work (thrust power) |

Thermodynamics is mainly about ==how to progress from== the second block ==(heat)== ==to== the third (==mechanical work, electric power, etc.==)

Definition: Thermodynamics

- Thermodynamics is the ==science of the regularities== governing processes of energy conversion.

or,

- Thermodynamics is the science that deals with the interaction between energy and material systems.

Four Axioms of Thermodynamics

- Thermodynamics, basically entails four laws or axioms known as Zeroth, First, Second and Third law of thermodynamics.
    1. The Zeroth law deals with thermal equilibrium and establishes a concept of temperature.
    2. The First law throws light on concept of internal energy.
    3. The Second law indicates the limit of converting heat into work and introduces the principle of increase of entropy.
    4. The Third law defines the absolute zero of entropy.

- These laws are based on experimental observations and have no mathematical proof. Like all physical laws, these laws are based on logical reasoning.

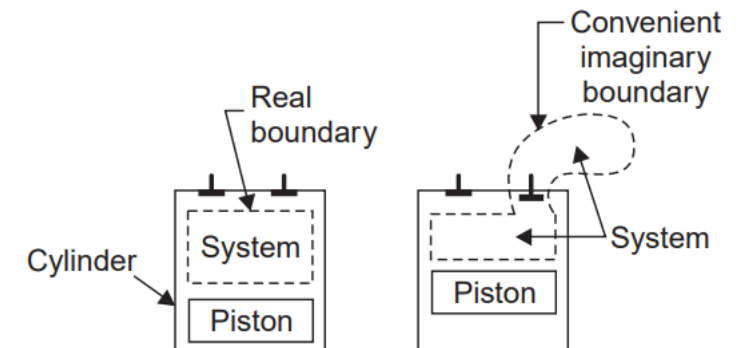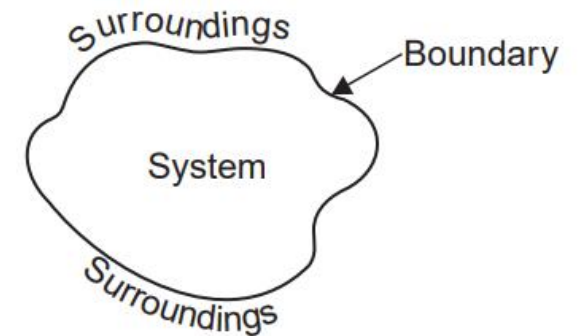# Thermodynamic Systems

- **System.**
  - A system is a finite quantity of matter or a prescribed region of space.

- **Boundary.**
  - The actual or hypothetical envelope enclosing the system is the boundary of the system. The boundary may be fixed or it may move, as and when a system containing a gas is compressed or expanded. The boundary may be real or imaginary.

- Systems can be:
  - ❑ Open: Mass and Energy can transfer between the System and the Surroundings
  - ❑ Closed: Energy can transfer between the System and the Surroundings, but NOT mass
  - ❑ Isolated: Neither Mass nor Energy can transfer between the System and the Surroundings

Macroscopic vs. Microscopic

- Thermodynamic studies are undertaken by the following two different approaches.
    1. **Macroscopic approach**—(Macro mean big or total)
    2. Microscopic approach—(Micro means small)

Characteristics of Macroscopic Approach:

a) In this approach a certain quantity of matter is considered without taking into account the events occurring at molecular level. In other words, this approach to thermodynamics is <mark>concerned with gross or overall behavior</mark>. This is known as classical thermodynamics.

b) The analysis of macroscopic system requires <mark>simple mathematical formulae</mark>.

Macroscopic vs. Microscopic

- Characteristics of Macroscopic Approach:
    c) The <mark>values of the properties</mark> of the system are their <mark>average values</mark>. For example, consider a sample of a gas in a closed container. The pressure of the gas is the average value of the pressure exerted by millions of individual molecules. Similarly, the temperature of this gas is the average value of translational kinetic energies of millions of individual molecules. These properties like pressure and temperature can be measured very easily. The changes in properties can be felt by our senses.

    d) In order to describe a system <mark>only a few properties</mark> are needed.

System Description

- Describing systems requires:
  - ❖ A few macroscopic properties: *p, T, V, n, m,* …
  - ❖ Knowledge if System is Homogeneous or Heterogeneous
  - ❖ Knowledge if System is in Equilibrium State
  - ❖ Knowledge of the number of components. In thermodynamics, a component is one of a collection of chemically independent constituents of a system. A single component system is one which has no composition variable.

Phase

- **Phase:** A phase is a ==quantity of matter which is homogeneous== throughout in chemical composition and physical structure.

- There are two types of system depending on the number of phase in it:

    1. **Homogeneous** System

        A system which consists of a single phase is termed as homogeneous system. Examples : Mixture of air and water vapor, water plus nitric acid and octane plus heptane.

    2. **Heterogeneous** System

        A system which consists of two or more phases is called a heterogeneous system. Examples : Water plus steam, ice plus water and water plus oil.
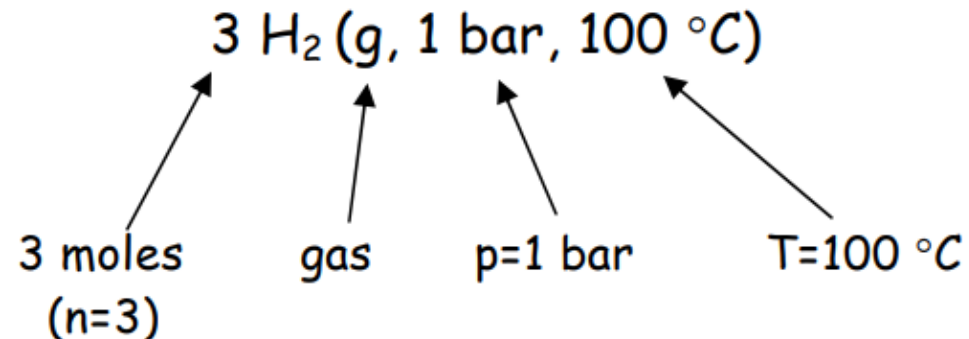
Properties of Systems

- A property of a system is a characteristic of the system which depends upon its state, but not upon how the state is reached.

- There are two sorts of property :
  1. Intensive properties. These properties do not depend on the mass of the system. Examples : Temperature and pressure.
  2. Extensive properties. These properties depend on the mass of the system. Example : Volume. Extensive properties are often divided by mass associated with them to obtain the intensive properties. For example, if the volume of a system of mass m is V, then the specific volume of matter within the system is $v = \dfrac{V}{m}$ which is an intensive property.

State

- State is the condition of the system at an instant of time as described or measured by its properties. Or each unique condition of a system is called a state.

- It follows from the definition of state that each property has a single value at each state. Stated differently, all properties are state or point functions. Therefore, all properties are identical for identical states.

- On the basis of the above discussion, we can determine if a given variable is property or not by applying the following tests :
  - ❖A variable is a property, if and only if, it has a single value at each equilibrium state.
  - ❖A variable is a property, if and only if, the change in its value between any two prescribed equilibrium states is single-valued.

- Therefore, any variable whose change is fixed by the end states is a property.
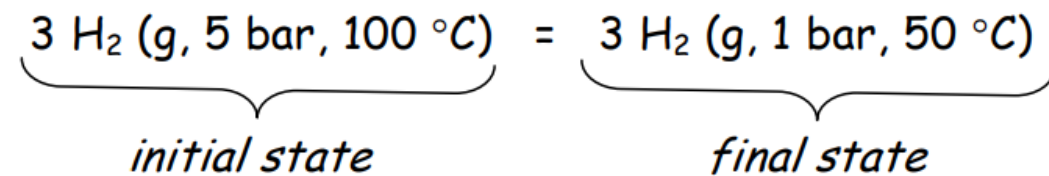
State

- The State of a System at Equilibrium:
  - ❖ Defined by the collection of all macroscopic properties that are described by State variables $(p, n, T, V, \dots)$ [INDEPENDENT of the HISTORY of the SYSTEM]
  - ❖ For a one-component System, all that is required is "n" and 2 variables. All other properties then follow.
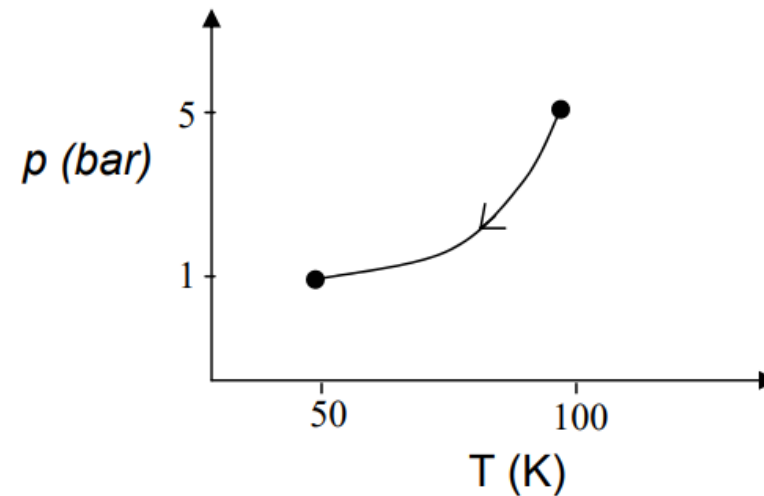
- $V \; = \; f(n, p, T)$ or $p \; = \; g(n, V, T)$

$$3\ H_2\ (g,\ 1\ bar,\ 100\ °C)$$

3 moles   gas   p=1 bar   T=100 °C
(n=3)

(Keith A. Nelson & Moungi Bawendi, n.d.)

State

- Change of state or Transformation
  - ❖ Notation:

$$3\ H_2\ (g,\ 5\ bar,\ 100\ ^\circ C) \underbrace{\qquad}_{\text{initial state}} = \underbrace{3\ H_2\ (g,\ 1\ bar,\ 50\ ^\circ C)}_{\text{final state}}$$

  - ❖ Path: Sequence of intermediate states

Process

- A process occurs when the system undergoes a change in a state or an energy transfer at a steady state.

- A process may be non-flow in which a fixed mass within the defined boundary is undergoing a change of state. Example : A substance which is being heated in a closed cylinder undergoes a non-flow process.

- Closed systems undergo non-flow processes.

- A process may be a flow process in which mass is entering and leaving through the boundary of an open system.

- Quasi-static process.
  - ✓ Quasi means 'almost'. A quasi-static process is also called a reversible process. This process is a succession of equilibrium states and infinite slowness is its characteristic feature.

Process

- Process: Describes the Path
  - ❖ Reversible (always in Equilibrium)
  - ❖ Irreversible (defines direction of time)
  - ❖ Adiabatic (no heat transfer between system and surroundings)
  - ❖ Isobaric (constant pressure)
  - ❖ Isothermal (constant temperature)
  - ❖ Isochoric (constant volume)

Laws of Gas Properties

There are 4 general laws that relate the 4 basic characteristic properties of gases to each other. Each law is titled by its discoverer.

❖**Charles' Law**

Charles' Law- gives the relationship between volume and temperature if the pressure and the amount of gas are held constant:

1. If the Kelvin temperature of a gas is increased, the volume of the gas increases. (p, n Constant)

2. If the Kelvin temperature of a gas is decreased, the volume of the gas decreases. (p, n Constant)

This means that the volume of a gas is directly proportional to its Kelvin temperature. Think of it this way, if you increase the volume of a gas and must keep the pressure constant the only way to achieve this is for the temperature of the gas to increase as well.
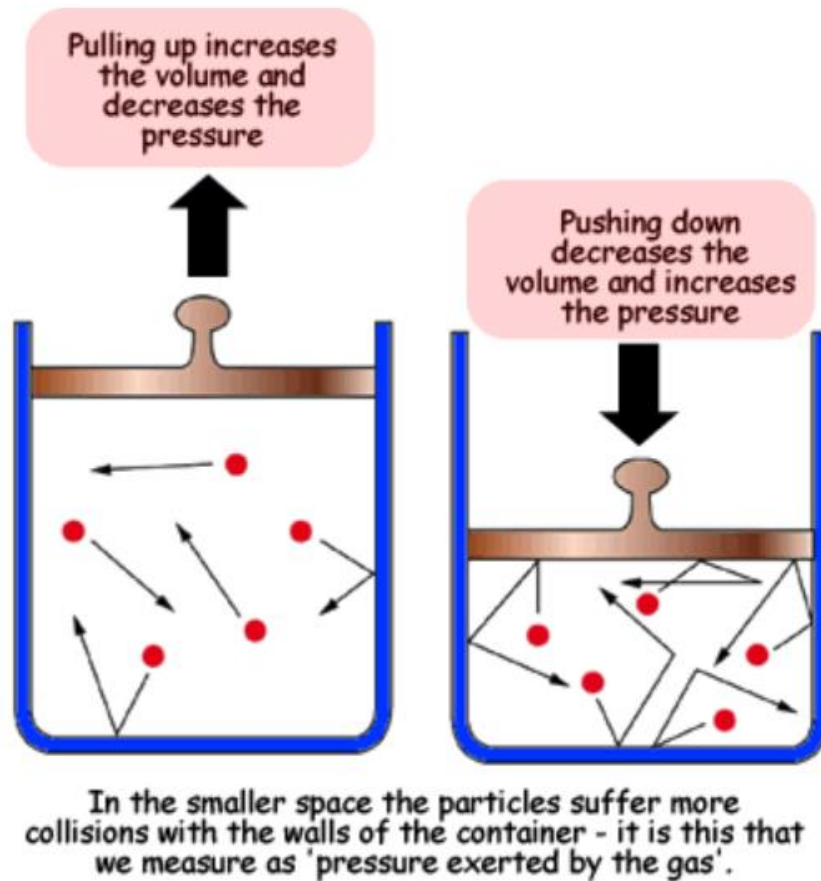
Charles's Law
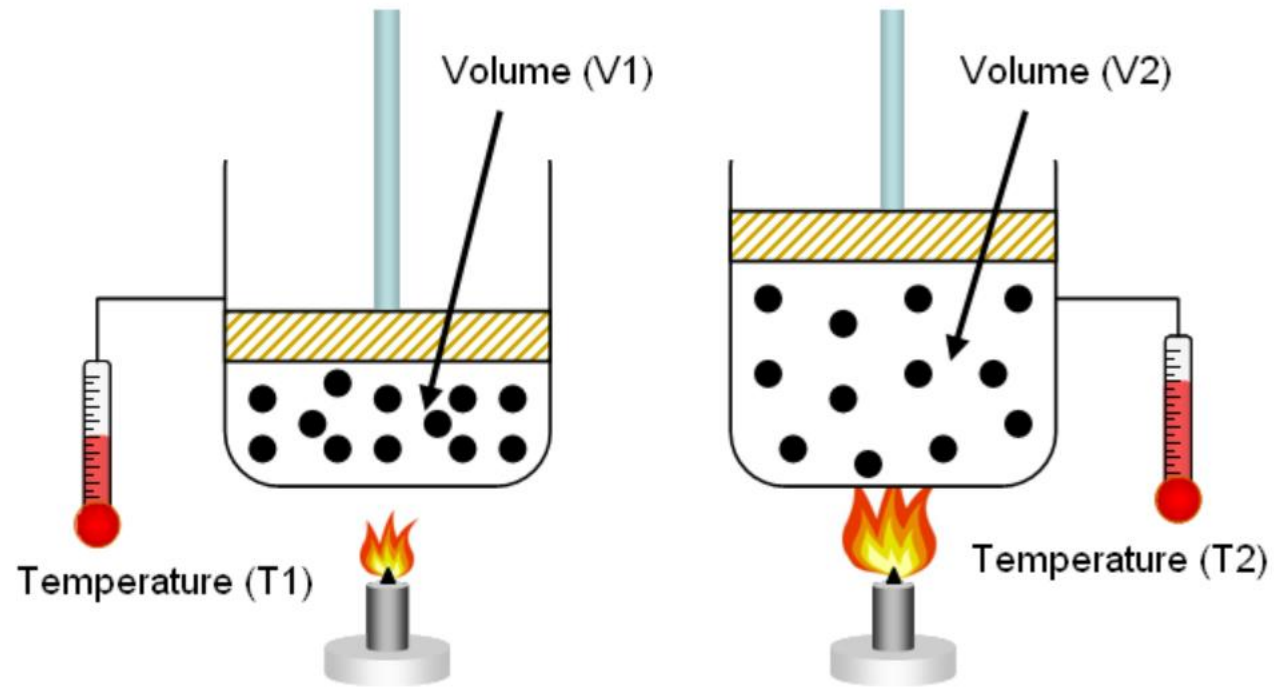
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Laws of Gas Properties

❖**Boyle's Law**

- Boyle's Law **-** states that the volume of a given amount of gas held at constant temperature varies inversely with the applied pressure when the temperature and mass are constant.

- The reduction in the volume of the gas means that the molecules are striking the walls more often increasing the pressure, and conversely if the volume increases the distance the molecules must travel to strike the walls increases and they hit the walls less often thus decreasing the pressure.

Boyle's Law

Pulling up increases the volume and decreases the pressure

Pushing down decreases the volume and increases the pressure

In the smaller space the particles suffer more collisions with the walls of the container - it is this that we measure as 'pressure exerted by the gas'.

$$p_1 V_1 = p_2 V_2$$

Laws of Gas Properties

❖**Avogadro's Law**

Avogadro's Law- Gives the relationship between volume and amount of gas in moles when pressure and temperature are held constant.

If the amount of gas in a container is increased, the volume increases. If the amount of gas in a container is decreased, the volume decreases. This is assuming of course that the container has expandible walls.

The relationship is again directly proportional so the equation for calculations is:

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Laws of Gas Properties

❖**Gay Lussac's Law**

Gay Lussac's Law - states that the pressure of a given amount of gas held at constant volume is directly proportional to the Kelvin temperature.

If you heat a gas, you give the molecules more energy so they move faster. This means more impacts on the walls of the container and an increase in the pressure. Conversely if you cool the molecules down, they will slow and the pressure will be decreased.

Gay Lussac's Law
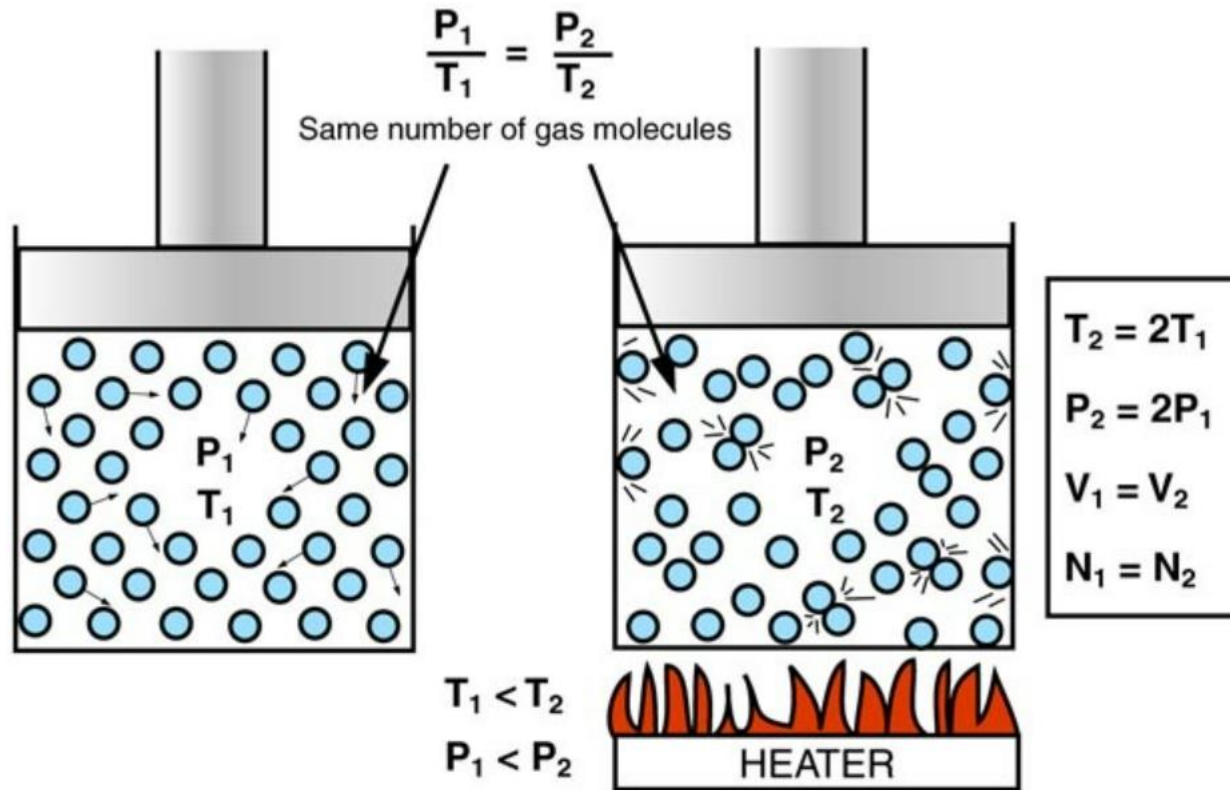
$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Laws of Gas Properties

❖**Ideal Gas Law**

- From experimental observations it has been established that an ideal gas (to a good approximation) behaves according to the simple equation:

$$pV = nRT$$

- where p, V and T are the pressure, volume and temperature of gas having mass n and R is a constant for the gas known as gas constant.

- In a closed system, n is constant.

- The equation can be written as:

$$pv = RT$$

- Where v is specific volume, $v = \dfrac{V}{n}$.

Laws of Gas Properties

❖In reality there is no gas which can be qualified as an ideal or perfect gas. However, all gases tend to ideal or perfect gas behaviour at all temperatures as their pressure approaches zero pressure.

$$p\bar{V} = RT$$ or $$pV = nRT$$

This is an example of an equation of state

$$V = f(n, p, T)$$

Laws of Gas Properties - Summary

Gas Law Formula		
Gas Law	**Formula**	**Description**
Boyle's Law	$P_1V_1 = P_2V_2$	At constant T, as pressure increases, volume decreases.
Charles' Law	$\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$	At constant P, as volume increases, temperature increases.
Gay-Lussac's Law	$\dfrac{P_1}{T_1} = \dfrac{P_2}{T_2}$	At constant V, as pressure increases, temperature increases.
Combined Law	$\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$	Obtained by combining Boyle's Law, Charles' Law and Gay-Lussac's Law.
Ideal Gas Law	$PV = nRT$	
V = volume in dm^3 T = temperature in K	P = pressure in kPa n = number of moles	R = ideal gas constant

Equation of States

- **Ideal Gas Law:**
  - $pV = nRT$ $\qquad\qquad pv = RT$
  - $V = f(n, P, T) \rightarrow n$ and 2 properties

  - Mixture of ideal gases comprising n_i moles of each

$$p_i = \frac{n_i RT}{V} \quad \longleftarrow \quad \text{Partial pressure of i}^{th} \text{ gas}$$

$$p = p_{Total} = \sum_i p_i : \qquad X_i = \frac{n_i}{n} \quad \text{mole fraction of i}^{th} \text{ gas}$$

$$\boxed{p_i = \frac{n_i}{n} p = X_i p} \qquad \text{Dalton's Law}$$

Equation of States

- **Real Gas:**

❖**Compressibility Factor**

$$p\bar{V} = ZRT \qquad Z = \frac{\bar{V}_{real}}{\bar{V}_{ideal}}$$

High T $\Rightarrow$ Repulsions dominate $\qquad Z > 1 \qquad \bar{V}_{real} > \bar{V}_{ideal}$

Low T $\Rightarrow$ Attractions dominate $\qquad Z < 1 \qquad \bar{V}_{real} < \bar{V}_{ideal}$

Example 1

- What is the density of laughing gas, dinitrogen monoxide, N_2O, at a temperature of 325 K and a pressure of 113.0 kPa?

Example 1 - Answer

- What is the density of laughing gas, dinitrogen monoxide, N2O, at a temperature of 325 K and a pressure of 113.0 kPa?

  ➢ $T = 325K$

  ➢ $P = 113000$ Pa

  ➢ Molar mass = $M = \dfrac{m}{n}$, m = mass of a substance, n = number of moles of a substance

  ➢ $M = 44.013 \times 10^{-3}$ kg/mol

  ➢ $pV = nRT$

  ➢ $p = {\rho RT}/{M}$

  ➢ $\rho = {pM}/{RT} = \dfrac{113000\frac{N}{m^2}\times(44.013\times10^{-3})\frac{kg}{mol}}{8.314462\frac{J}{K.mol}\times325K} = 1.84\frac{kg}{m^3}$

$$pV = \frac{m}{M}RT$$

$$p = \frac{m}{V}\frac{RT}{M}$$

$$p = \rho\frac{R}{M}T$$

Example 2

- Calculate the density of Freon 12, CF_2Cl_2, at 30.0°C and 0.954 atm.

Example 2 - Answer

- Calculate the density of Freon 12, CF_2Cl_2, at 30.0°C and 0.954 atm.

  ➤ $T = 303K$

  ➤ $P = 0.954 \text{ atm} = 0.954 \text{ atm} \times 101325 \frac{\text{Pa}}{\text{atm}} = 96664.05 \text{Pa}$

  ➤ $M = 120.9135 \times 10^{-3}$ kg/mol

  ➤ $pV = nRT$

  ➤ $p = \rho RT / M$

  ➤ $\rho = pM / RT = \dfrac{96664.05\frac{N}{m^2} \times (120.9135 \times 10^{-3})\frac{kg}{mol}}{8.314462\frac{J}{K.mol} \times 303K} = 4.64 \frac{kg}{m^3}$

Example 3

- What is the molar mass of a gas if 0.0494 g of the gas occupies a volume of 0.100 L at a temperature 26°C and a pressure of 307 torr?

Example 3 - Answer

- What is the molar mass of a gas if 0.0494 g of the gas occupies a volume of 0.100 L at a temperature 26°C and a pressure of 307 torr?

  ➢ $m = 0.0494 \ g = 0.0494 \times 10^{-3} kg$

  ➢ $V = 0.1 \ L = 0.1 \times 10^{-3} m^3$

  ➢ $T = 26°C = 299 \ K$

  ➢ $p = 307 \ torr = 307 \ torr \times 133.322 \frac{Pa}{torr} = 40929.854 Pa$

  ➢ $\rho = \frac{m}{V} = \frac{0.0494 \times 10^{-3} kg}{0.1 \times 10^{-3} m^3} = 0.494 \frac{kg}{m^3}$

  ➢ $p = \rho RT / M$

  ➢ $M = \frac{\rho RT}{p} = \frac{0.494 \frac{kg}{m^3} \times 8.314462 \frac{J}{K.mol} \times 299K}{40929.854 Pa} = 0.03 \frac{kg}{mol}$

Example 4

- At 1.70 atm, a sample of gas takes up 4.25L. If the pressure in the gas is increased to 2.40 atm, what will the new volume be?

Example 4 - Answer

- At 1.70 atm, a sample of gas takes up 4.25L. If the pressure in the gas is increased to 2.40 atm, what will the new volume be?

  ➢ $p_1 = 1.7 \text{ atm} = 1.7 \text{ atm} \times 101325 \frac{\text{Pa}}{\text{atm}} = 172252.5 \text{ Pa}$

  ➢ $V_1 = 4.25 \ L = 4.25 \times 10^{-3} m^3$

  ➢ $p_2 = 2.4 \text{ atm} = 2.4 \text{ atm} \times 101325 \frac{\text{Pa}}{\text{atm}} = 243180 \text{ Pa}$

  ➢ Boyle's Law

  ➢ $p_1 V_1 = p_2 V_2$

  ➢ $V_2 = p_1 V_1 / p_2$

  ➢ $V_2 = {172252.5 Pa \times (4.25 \times 10^{-3} m^3)}/{243180 \text{ Pa}} = 3.01 \times 10^{-3} m^3 = 3.01 L$

Example 5

- A 40.0L balloon is filled with air at sea level (1.00 atm, 25.0°C). It is tied to a rock and thrown in a cold body of water, and it sinks to the point where the temperature is 4.0°C and the pressure is 11.0 atm. What will its new volume be?

Example 5 - Answer

- A 40.0L balloon is filled with air at sea level (1.00 atm, 25.0°C). It is tied to a rock and thrown in a cold body of water, and it sinks to the point where the temperature is 4.0°C and the pressure is 11.0 atm. What will its new volume be?

  ➢ $p_1 = 1 \text{ atm} = 1 \text{ atm} \times 101325 \frac{\text{Pa}}{\text{atm}} = 101325 \text{ Pa}$

  ➢ $V_1 = 40 \ L = 40 \times 10^{-3} m^3$

  ➢ $T_1 = 298K$

  ➢ $p_2 = 11 \text{ atm} = 11 \text{ atm} \times 101325 \frac{\text{Pa}}{\text{atm}} = 1114575 \text{ Pa}$

  ➢ $T_1 = 277K$

  ➢ Using Combined Law, $\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$

  ➢ $V_2 = \frac{T_2 p_1 V_1}{T_1 p_2} = \frac{277K \times 1 \ atm \times 40L}{298K \times 11 \ atm} = 3.38L = 3.38 \times 10^{-3} m^3$

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