

KINETIC THEORY OF GASES

Assumption of kinetic theory:

- All gases are made of very small particles called molecules. The molecules of gas are identical and different from the molecules of the other gases
- The size of the molecules is very small and considered as point masses
- The force of cohesion between the gas molecules is negligible
- The molecules are in a state of continuous random motion moving with all possible velocities from zero to infinity in all directions
- The collision of molecules is perfectly elastic colliding with one another and with the walls of the container. There is no energy loss due to collision
- Molecules move in a straight line with uniform velocities between two successive collision
- The time spent in collision is negligible compared with the time spent in travelling between successive collisions
- During collision, the number of molecules per unit volume of the gas remains constant.

Gas Laws

Boyle's law: $P \propto \frac{1}{V}$ or $P = \frac{k}{V}$ or $k = PV$ 2.1a

Charles law: $V \propto T$ or $V = kT$ or $k = \frac{V}{T}$ 2.1b

Pressure law: $P \propto T$ or $P = kT$ or $k = \frac{P}{T}$ 2.1c

General Gas law: $k = \frac{PV}{T}$

Universal gas equation: $PV = nRT$

$R = 8.314 \text{ J/mol.K}$ or 1.99 Cal/mol.K

At standard temperature and pressure (S.T.P) or normal temperature and pressure (N.T.P), $P = 760 \text{ mmHg} = 1.03 \times 10^5 \text{ N/m}^2 = 1 \text{ atm}$, $T = 273.15 \text{ K}$ and volume of an ideal gas = 22.4 m^3

Ideal Gases: An ideal or perfect gas is composed of tiny, moving, non-interacting particles and it obeys the ideal gas laws. Almost all chemically stable gas behaves ideally if it is far removed from conditions under which it will liquefy or solidify. Conversely, a real gas behaves like an ideal gas when its atoms and molecules are so far apart that they do not appreciably interact with one another.

Terms Associated with Gas Molecules

Mole (mol): one mole is the amount of substance that contains as many elementary molecules as there are atoms in 0.012 kg of carbon 12.

Avogadro's number (N_A): This is the number of molecules in a mole

$$N_A = 6.022 \times 10^{23} \text{ molecules/mol}$$

Molar mass (m): mass of one mole of a substance

Total mass (M) of a substance is given by:

$$M = Nm \quad 2.2$$

Where M= total mass, m = mass per molecule, N = no of molecules

Velocity of Gas Molecules

- Mean or Average velocity: This velocity is the mean or average value of the velocities possessed by the molecules;

$$C_{av} = \frac{C_1 + C_2 + C_3 + \dots + C_N}{N} \quad 2.3$$

Where C_1, C_2, \dots, C_N = velocity and N = no of molecules

- Root mean square (rms) velocity(C_{rms}): This velocity is the square root of the mean value of the squares of the individual velocities:

$$C_{rms} = \sqrt{\frac{C_1^2 + C_2^2 + C_3^2 + \dots + C_N^2}{N}} \quad 2.4$$

Individual velocities of molecules may change due to repeated encounters but the rms velocity C_{rms} remains constant so long as the temperature remains constant. Thus it can be expressed as

$$C_{rms} = \sqrt{\frac{3KT}{m}} \quad 2.5$$

Where T = temperature, K = Boltzmann constant and m = mass per molecule of the gas

- Most Probable Velocity: This is the velocity with which the largest number of molecules of the gas at any given temperature move.

$$C_m = \sqrt{\frac{2KT}{m}} \quad 2.6$$

$$C_{rms} > C_{av} > C_m$$

Forms of Ideal Gas Equation

- $PV = nRT$ 2.7a
- $PV = \frac{1}{3}mNC^2$ 2.7b
- $P = \frac{1}{3}\rho C^2$ 2.7c
- $PV = NKT$ 2.7d
- $P = nKT$ 2.7e
- $P = \frac{m}{M}KT$ 2.7f

Pressure Exerted by an Ideal Gas:

The pressure exerted by an ideal gas is given by;

$$P = \frac{mNC^2}{3V} \quad 2.8$$

$$\text{Also, } P = \frac{mNC^2}{3} \quad 2.9$$

Where the no of moles $n = \frac{N}{V}$.

$$\text{Recall, } M = mN, \rho = \frac{M}{V} = \frac{mN}{V} \quad 2.10$$

Substitute eqn. 2.10 in eqn. 2.8

$$P = \frac{1}{3} \rho C^2 \quad 2.11$$

Where ρ = density, m = mass per molecule, N = no of molecules, P = pressure,
 V = volume, M = total mass of gas, C = rms velocity

Relationship between Pressure and Kinetic Energy of Gas Molecules

For a unit volume of gas, $M = \rho$

$$\text{Hence, K.E of the gas} = \frac{1}{2} MC^2 = \frac{1}{2} \rho C^2 \quad 2.12$$

Eqn. 2.11 can be rewritten in the form

$$P = \frac{2}{3} \times \frac{1}{2} \rho C^2 \quad 2.13$$

Substitute eqn. 2.12 in eqn. 2.13

$$P = \frac{2}{3} E \quad 2.14$$

Where E = K.E of the gas molecules

Relationship between C_{rms} and Temperature

$$\text{Using eqn. 2.8; } PV = \frac{mNC^2}{3} = \frac{1}{3} MC^2 \quad 2.15$$

$$\text{Recall, } PV = nRT \text{ or } PV = RT \text{ (for 1 mole)} \quad 2.16$$

Equating eqn. 2.15 and 2.16

$$\frac{1}{3} MC^2 = RT$$

$$C = \sqrt{\frac{3RT}{M}} \quad 2.17$$

For molar volume; $M = mN_A$ where N_A = Avogadro's no, M = molar mass and m = mass of single molecule

$$C = \sqrt{\frac{3RT}{mN_A}}$$

$$C = \sqrt{\frac{3KT}{m}} \quad 2.18$$

Where $K = \frac{R}{N_A}$, R = universal gas constant and K = Boltzmann constant

$$\text{Also, } C = \sqrt{\frac{3RT}{M}} = \sqrt{3R'T} \quad 2.19$$

Where $R' = \frac{R}{M}$ is called characteristics gas constant

Kinetic Energy and Temperature

$$\frac{1}{3} MC^2 = RT$$

$$\frac{1}{3} mN_A C^2 = RT$$

$$\frac{1}{3} mC^2 = \frac{R}{N_A} T = KT$$

$$mC^2 = 3KT$$

$$\frac{1}{2} mC^2 = \frac{3}{2} KT \quad 2.20$$

Eqn. 2.20 is the K.E. per molecule

Density of an Ideal gas

Recall, $P = \frac{1}{3} \rho C^2$

Hence, $\rho = \frac{3P}{C^2}$ 2.21

Question:

Find the r.m.s velocity of hydrogen molecules at 0°C. Given that the molecular mass of hydrogen is 2×10^{-3} kg and molar gas constant is 8.3 J/mol.K.

Solution:

$$C = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.3 \times 273}{2 \times 10^{-3}}} = 1843.60 \text{ m/s}$$

Question:

At what temperature is the average translational K.E of a molecule equal to the K.E of an electron accelerated from rest through a p.d of 0.5Volts (that is, an energy of 0.5eV)?

Solution:

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}, K = 1.38 \times 10^{-23} \text{ J/K}$$

$$\text{K.E} = \frac{3}{2} KT = \text{eV}$$

$$\frac{3}{2} KT = 0.5 \text{ eV}$$

$$T = \frac{2 \times 0.5 \times 1.6 \times 10^{-19}}{3 \times 1.38 \times 10^{-23}} = 3864.7 \text{ K}$$

Question:

Calculate the mean translational kinetic energy per molecule of a gas at 727 °C, given R = 8.32 J/mol.K, $N_A = 6.02 \times 10^{23}$

Solution

$$T = 727 + 273 = 1000 \text{ } ^\circ\text{C}$$

$$\text{KE per molecule} = \frac{3}{2} KT = \frac{3}{2} \frac{RT}{N_A} = \frac{3 \times 8.32 \times 1000}{2 \times 6.02 \times 10^{23}} = 2.073 \times 10^{-29} \text{ J}$$

THERMODYNAMICS

What is thermodynamics?

Thermodynamics is the study of the relationship between matter and energy and the energy changes.

Introduction

Thermodynamics focuses largely on how a heat transfer is related to various energy changes within a physical system undergoing a thermodynamic process. Such processes usually result in work being done by the system and are guided by the laws of thermodynamics.

Thermal contact: This is when objects are in touch such that heat flows from one body to another.

Thermal equilibrium: This is when there is no net flow or transfer of heat from one body to another and the two bodies have the same temperature i.e two systems are in thermal equilibrium if and only if they have the same temperature.

Total energy: This is the sum of all forms of energy. In thermodynamics we have two types of energy

- **Macroscopic energy:** Energy a system possesses with respect to some outside reference frame like K.E and P.E.
- **Microscopic energy:** Energy of the molecular structure of a system and the degree of the molecular activity

Internal energy: The sum of all the forms of energy possessed by the atoms and molecules in a system. It is denoted by U .

Latent energy: Internal energy associated with the phase of a system.

Sensible energy: Internal energy associated with K.E of the molecules.

Terms Used in Thermodynamics

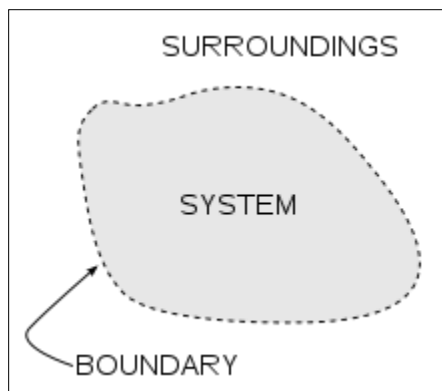


Fig. 3.1: A generic thermodynamic system

System or thermodynamics system: It is the quantity of matter or region in space chosen for study.

Surroundings: The region outside the system.

Boundary: The real or imaginary surface that separate a system from its surroundings. It has zero thickness, thus it can neither contain any mass nor occupy any volume in space. It can be fixed or movable.

Closed system (control mass): It consist a fixed amount of mass and no mass can cross it boundary. But energy in form of heat or work can cross the boundary.

Open system (control volume): It is a system that both mass and energy can cross the boundary but the volume is fixed.

Isolated system: It is a system in which nothing enters or leaves the system. It is mass and volume control

Process: It is any change that a system undergoes from one equilibrium state to another. The series of states through which a system passes during a process is called the path of the process.

Quasi-static process: This is when a process proceeds in such a manner that the system remains infinitesimally close to an equilibrium state all the time. It is viewed as a sufficiently slow process that allows the system to adjust itself internally so that properties in one part of the system do not change any faster than those at other parts.

Reversible process or change: It is a process in which the values of P, V, T and U are well defined during the change i.e, P,V, T and U will take on their original values when the system is returned to where it started. For a system to be reversible, the process must usually be slow, and the system must be close to equilibrium during the entire change.

Laws of Thermodynamics

Zeroth law of Thermodynamics:

It states that if objects A and B are separately in thermal equilibrium with a third object C, then objects A and B are in thermal equilibrium with each other.

First Law of Thermodynamics:

- It states that a definite amount of mechanical work is needed to produce definite amount of heat. That is, the ratio of work done and the heat produced is always a constant
- It states that heat is a form of energy and in a closed system the total amount of energy of all kinds is constant. That is, the total heat energy is the sum of the internal energy and work done.

$$\Delta Q = \Delta U + \Delta W$$

$$\Delta U = \Delta Q - \Delta W \quad 3.1$$

$$\text{But } \Delta W = P\Delta V \quad 3.2$$

$$\Delta U = \Delta Q - P\Delta V \quad 3.3$$

Where U = internal energy, W= work, Q = heat, P = pressure and V = volume

Thermodynamics Processes

Isobaric Process: It is a process carried out at constant pressure ($\Delta P = 0$). The heat transferred to the system does work but also changes the internal energy of the system:

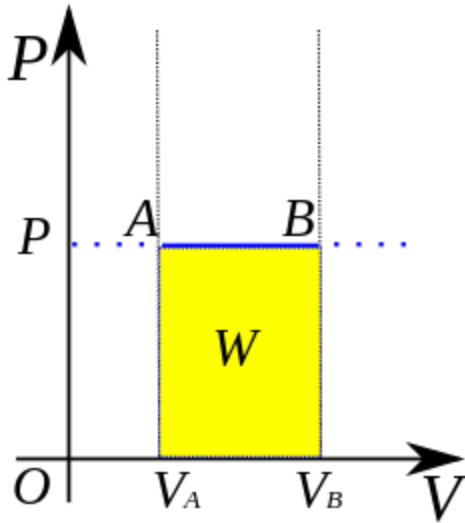


Fig. 3.2: Isobaric process

Pressure-volume work by the closed system is given by

$$W = \int p dV$$

$$W = p\Delta V \quad 3.4$$

Where Δ means change over the whole process, whereas d denotes a differential.

$$\text{From ideal gas law, } PV = nR\Delta T \quad 3.5$$

According to the equipartition theorem, the change in internal energy is related to the temperature of the system by

$$\Delta U = nC_V\Delta T \quad 3.6$$

$$\text{Recall, } \Delta Q = \Delta U + P\Delta V$$

Substituting equations 3.5 and 3.6 produces:

$$\Delta Q = nC_V\Delta T + nR\Delta T \quad 3.7$$

$$\Delta Q = n(C_V + R)\Delta T$$

$$\Delta Q = nC_P\Delta T \quad 3.8$$

Where C_V is specific heat at constant volume, C_P is specific heat at a constant pressure

Isochoric or Isometric or Isovolumic Process: It is a process carried out at constant volume.

$$\Delta V = 0$$

Hence, $\Delta U = \Delta Q$. Any heat that flows into the system appears as increased internal energy of the system.

Isothermal Process: It is a process carried out at constant temperature. For an ideal gas where the constituent atoms and molecules do not interact $\Delta U = 0$ and $\Delta Q = \Delta W$

However, this is not true for many other systems. For example, $\Delta U \neq 0$ as ice melts to water at 0°C even though the process is isothermal.

For an ideal gas changing isothermally from P_1V_1 to P_2V_2

$$\Delta Q = \Delta W = P_1V_1 \ln\left(\frac{V_2}{V_1}\right) \quad 3.2$$

Adiabatic Process: It is a process in which no heat enters or leaves the system $\Delta Q = 0$ and $0 = \Delta U + \Delta W$ 3.3

Any work done by the system is done at the expense of the internal energy and any work done on the system serves to increase the internal energy.

For an ideal gas changing from $P_1V_1T_1$ to $P_2V_2T_2$ in an adiabatic process,

$$P_1V_1^\gamma = P_2V_2^\gamma \text{ and } T_1V_1^\gamma = T_2V_2^\gamma \text{ where } \gamma = \frac{C_P}{C_V} \quad 3.4$$

C_p (pdV) = specific heat of gas at constant pressure

C_v (vdP) = specific heat of gas at constant volume

Specific Heat of Gases: When a gas is heated at constant volume, heat supplied goes to increase the internal energy of the gas molecules but when a gas is heated at constant pressure, the heat supplied not only increases the internal energy of the molecules but also increases the mechanical work in expanding the gas against the opposing constant pressure. Hence, $C_P > C_V$.

For an ideal gas, $C_P - C_V = \frac{R}{M}$ where R = universal constant and M = molecular weight

Question:

Find the change in internal energy of a system if 1200 Cal is removed from a gas held at constant volume.

Solution:

$$Q = 1200 \text{ Cal} = -1200 \times 4.186 = -5023.2 \text{ J}, V = 0$$

$$\Delta U = \Delta Q = -5023.2 \text{ J}$$

Question:

One kilogram of steam at 100°C and 101 kPa occupies 1.68 m^3 (a) calculate the work done by the expansion of water into steam (b) determine the increase in internal energy of 1.0 kg of water as it is vaporized at 100°C . (Latent heat of vaporization of water = $2.26 \times 10^6 \text{ J/kg}$)

Solution:

$$Q = mL_v = 1 \times 2.26 \times 10^6 = 2.26 \times 10^6 \text{ J} = 2260000$$

$$W = PdV = 101 \times 10^3 \times 1.68 = 169680$$

$$U = Q - W = 2260000 - 169680 = 2090320 \text{ J}$$

SECOND LAW OF THERMODYNAMICS

It can be stated in three equivalent ways:

1. Heat flows spontaneously from a hotter to a colder object but not vice versa
2. No heat engine that cycle continuously can change all its heat-in to useful work-out.
3. If a system undergoes spontaneous change, it will change in such a way that its entropy will increase or at best remain constant.

The 2nd law tells us the manner in which a spontaneous change will occur while the 1st law tells us whether or not the change is possible. The 1st law deals with the conversion of energy, the 2nd law deals with the dispersal of energy.

Entropy (S): It is a measure of disorder. It is a state of variable for a system in equilibrium.

$$\Delta S = \frac{\Delta Q}{T} \quad 3.5$$

A state that can occur in only one way is a state of high order but, a state that can occur in many ways is a more disordered state.

The most probable state: It is a state with the largest entropy. It is a state with the most disorder and the state that can occur in the largest number of ways.

Exercise:

1. Compute the rms speed of a gas of helium atoms at 300 K. At what temperature will oxygen have the same rms speed?
2. An ideal gas expands adiabatically to three times its original volume. In doing so, the gas does 720 J of work. (a) How much heat flows from the gas? (b) What is the change in internal energy of the gas? (c) Does the temperature rise or falls?
3. A student is trying to decide what to wear. The surroundings (his bedroom) are at 20.0 °C. If the skin temperature of the unclothed student is 35 °C, what is the net energy loss from his body in 10.0 min by radiation? Assume that the emissivity of skin is 0.900 and that the surface area of the student is 1.50 m².
4. The glass windows of a room have a total area of 10 square metres and the glass is 4.1 mm thick. Calculate the rate at which heat escapes from the room by conduction when the inside surface of the windows are at 25 °C and the outside surface at 10 °C. K is 8.4 W/m.K.
5. If the Avogadro's no $N_A = 6.02 \times 10^{23}$ and Boltzmann constant $K = 2.36 \times 10^{-6}$ ergs/degree, calculate the r.m.s. velocity of oxygen molecule at 27 °C