



ICT 1107: Physics

Dr M Mahbubur Rahman

Associate Professor

Department of Physics

Jahangirnagar University, Savar, Dhaka 1342

Email: M.Rahman@juniv.edu



ICT 1107: Physics

2. Heat and Thermodynamics

Principle of temperature measurements: platinum resistance thermometer, thermoelectric thermometer, pyrometer; Kinetic theory of gases: Maxwell's distribution of molecular speeds, mean free path, equipartition of energy, Brownian motion, Van der Waal's equation of state, review of the First Law of thermodynamics and its application, reversible and irreversible processes, Second Law of thermodynamics, Carnot cycle; Efficiency of heat engines, Carnot's Theorem, entropy and disorder, thermodynamic functions, Maxwell relations, Clausius-Clapeyron Equation, Gibbs Phase Rule, Third Law of thermodynamics.

8 Lectures



ICT 1107: Physics

Chapter 2

Heat and Thermodynamics



Heat & Thermodynamics

Thermometry

&

Temperature Measurements



ICT 1107: Physics

Chapter 2: Heat and Thermodynamics

The following Topics: Study by yourself

Principle of Temperature Measurements

Platinum Resistance Thermometer

Thermoelectric Thermometer



Chapter 2: Heat & Thermodynamics

Thermometry

The branch of heat relating to the measurement of temperature of an object is called the thermometry.

Thermometer is an instrument used to measure the temperature of a body. The essential requisites of a thermometer are:

1. Construction
2. Calibration, and
3. Sensitiveness



Chapter 2: Heat & Thermodynamics

Thermometers

A **thermometer** is a device that is used to measure the temperature of a system.

Thermometers are based on the principle that some physical property of a system changes as the system's temperature changes.



Chapter 2: Heat & Thermodynamics

Thermometers

These properties include:

- The volume of a liquid
- The dimensions of a solid
- The pressure of a gas at a constant volume
- The volume of a gas at a constant pressure
- The electric resistance of a conductor
- The color of an object

A temperature scale can be established on the basis of any of these physical properties.



Chapter 2: Heat & Thermodynamics

How the Thermometers Work?

Many thermometers work on the basis of expansion and contraction.

Expansion: An increase in volume of an object. Adding heat results to expand.

Contraction: A decrease in volume of an object. Take away/Removal of heat causes to contract.



Chapter 2: Heat & Thermodynamics

Types of Thermometers

There are different types of thermometers:

1. Liquid thermometers (mercury, alcohol)
2. Gas thermometers (Constant pressure, constant volume)
3. Resistance thermometers (platinum resistance)
4. Thermoelectric thermometers (**details given later**)
5. Radiation thermometers (pyrometers)
6. Vapor pressure thermometers (helium vapor pressure thermometer)
7. Bimetallic thermometers (to measure temperatures at high altitudes)
8. Magnetic thermometers (for low temperature measuring)^o



Chapter 2: Heat & Thermodynamics

Resistance Thermometers

A platinum resistance thermometer (PRT) is a piece of platinum wire which determines the temperature by measuring its electrical resistance. It is referred to as a temperature sensor. When manufactured carefully, these devices offer an excellent combination of sensitivity, range and reproducibility.



Chapter 2: Heat & Thermodynamics

PRTs work in the following way. The electrical resistance of many metals (e.g., copper, silver, aluminium, platinum) increases approximately linearly with absolute temperature and this feature makes them useful as temperature sensors. The resistance of a wire of the material is measured by passing a current through it and measuring the voltage across it with a suitable voltmeter.



Chapter 2: Heat & Thermodynamics

Resistance Thermometer





Chapter 2: Heat & Thermodynamics

Platinum Resistance Thermometer

A platinum resistance thermometer consists of a pure platinum wire wound in a double spiral to avoid inductive effects. The wire is wound on a mica plate. The two ends of the platinum wire are connected to thick copper leads (for lower temperatures) and connected to the binding terminals B_1 , B_2 . For higher temperatures the leads are of platinum. C_1 and C_2 are the compensating leads exactly similar and of the same resistance as the leads used with the platinum wire. The platinum wire and the compensating leads are enclosed in a glazed porcelain tube. The tube is sealed and binding terminals are provided at the top. The leads pass through mica discs which offer the best insulation and also prevent convection currents (Fig. 1·6).

The resistance of a wire at $t^\circ\text{C} = R_t$ and at $0^\circ\text{C} = R_0$. These resistances are connected by the relation

$$R_t = R_0 (1 + \alpha t + \beta t^2). \quad \dots(i)$$



Chapter 2: Heat & Thermodynamics

Here α and β are constants. The values of α and β depend on the nature of the material used. To find the values of α and β , the resistance of the platinum wire is determined at three fixed points (i) melting point of ice, (ii) boiling point of water, (iii) boiling point of sulphur $444\cdot6^{\circ}\text{C}$ for high temperature measurement and (iv) boiling point of oxygen $-182\cdot5^{\circ}\text{C}$ for low temperature measurement.

Using these values of resistance in equation (i)

$$R_{100} = R_0[1 + \alpha 100 + \beta 100^2] \quad \dots(ii)$$

and $R_{444\cdot6} = R_0[1 + \alpha 444\cdot6 + \beta(444\cdot6)^2] \quad \dots(iii)$

The values of α and β can be determined by solving the simultaneous equations (ii) and (iii).

From (i) $R_t = R_0[1 + \alpha t + \beta t^2]$



Chapter 2: Heat & Thermodynamics

Neglecting βt^2 (because β is very small)

$$R_t = R_0 [1 + \alpha t] \quad \dots(iv)$$

and

$$R_{100} = R_0 [1 + \alpha \times 100]$$

$$\therefore R_t - R_0 = R_0 \alpha t \quad \dots(v)$$

$$R_{100} - R_0 = R_0 \alpha \cdot 100 \quad \dots(vi)$$

Dividing (v) and (vi)

$$\frac{R_t - R_0}{R_{100} - R_0} = \frac{t}{100}$$

$$t = \left(\frac{R_t - R_0}{R_{100} - R_0} \right) \times 100 \quad \dots(vii)$$

Knowing the values of R_0 , R_{100} and R_t , t can be calculated.



Chapter 2: Heat & Thermodynamics

IR/Radiation Thermometers

IR thermometers are also known as 'thermal radiation thermometers' or 'pyrometers' or 'radiation thermometers' are non-contact thermometers, which measure the temperature of a body based on its emitted thermal radiation

Infrared thermometers are great for checking surface temperature, however, they do not measure the internal temperature of an object. Infrared thermometers are extremely fast, typically giving a reading in a fraction of a second, or the time it takes for the thermometer's processor to perform its calculations.



Chapter 2: Heat & Thermodynamics

Basic Principle of IR/Radiation Thermometers

Infrared thermometers measure temperature from a distance. This distance can range between miles or a fraction of an inch. Infrared thermometers are often used in circumstances where other sorts of thermometers are not practical. For example if an object is very fragile or dangerous to be near, an infrared thermometer is a good way to get a temperature from a safe distance. Infrared thermometers work based on a phenomenon called black body radiation.



Chapter 2: Heat & Thermodynamics

Basic Principle of IR/Radiation Thermometers

Anything at a temperature above absolute zero has molecules inside of it moving around. The higher the temperature, the faster the molecules move. As they move, the molecules emit infrared radiation, a type of electromagnetic radiation below the visible spectrum of light. As they get hotter, they emit more infrared, and even start to emit visible light. That is why heated metal can glow red or even white. Infrared thermometers detect and measure this radiation. Infrared light works like visible light it can be focused, reflected or absorbed.



Chapter 2: Heat & Thermodynamics

Basic Principle of IR/Radiation Thermometers

Infrared thermometers usually use a lens to focus infrared light from one object onto a detector called a thermopile. The thermopile absorbs the infrared radiation and turns it into heat. The more infrared energy, the hotter the thermopile gets. This heat is turned into electricity. The electricity is sent to a detector, which uses it to determine the temperature of whatever the thermometer is pointed at. The more electricity, the hotter the object is.



Chapter 2: Heat & Thermodynamics

Radiation/IR Thermometers





Chapter 2: Heat & Thermodynamics

Sample Questions (Self-Study)

1. Write short notes on the measurements of high and low temperatures.
2. State with reasons the type of thermometer which you consider most suitable for use at temperatures (a) -250°C (b) 700°C , and (c) 2000°C . Indicate briefly the methods of their use.
3. Describe a resistance thermometer. Explain how it is used to measure temperatures accurately. Discuss its advantages over a thermoelectric thermometer.



Chapter 2: Heat & Thermodynamics

Sample Questions (Self-Study)

4. Describe a platinum resistance thermometer. How would you calibrate and use it for measuring temperature of an object. Mention its advantages.

5. Briefly state the principle underlying the working of a thermo-electric thermometer.

6. If the platinum temperature corresponding to 60°C on the gas scale is 60.25°C , what will be the temperature on the platinum scale corresponding to 120°C on the gas scale?



Chapter 2: Heat & Thermodynamics

Sample Questions (Self-Study)

7. If the platinum temperature corresponding to 60°C on the gas scale is 60.36°C , what will be the temperature on the platinum scale corresponding to 151.7°C on the gas scale?



Chapter 2: Heat & Thermodynamics

Kinetic Theory of Gases



Chapter 2: Heat & Thermodynamics

Kinetic Theory of Matter

According to Kinetic theory of matter, every substance (in the form of solid, liquid or gas) consists of a very large number of very small particles called the molecules. The molecules are the smallest particles of a substance that can exist in free state. The molecules possess the characteristic properties of the parent substance. The molecules are in a state of continuous motion with all possible velocities. The velocity of the molecules increases with rise in temperature.



Chapter 2: Heat & Thermodynamics

Kinetic Theory of Matter

The energy possessed by the molecules can be of two forms, kinetic or potential. When the stop-cock of an evacuated flask is opened, air rushes in quickly to fill in the space. This shows that the molecules possess rapid motion and hence they possess kinetic energy. When a solid expands on heating, the molecules are pulled apart against the forces of intermolecular expansion. The amount of work done in separating the molecules to larger distances manifests itself as the potential energy of the molecules. Thus the amount of heat given to a solid substance increases the energy of the molecules and this increase in energy is partly kinetic and partly potential.

Thus, the kinetic theory of matter is based on the following three points : (i) matter is made up of molecules, (ii) molecules are in rapid motion, and (iii) molecules experience forces of attraction between one another.



Chapter 2: Heat & Thermodynamics

Kinetic Theory of Gases

The continuous collision of the molecules of the gas with the walls of the containing vessel and their reflection from the walls results in the change of momentum of the molecules. According to Newton's second law of motion, the rate of change of momentum per unit area of the wall surface corresponds to the force exerted by the gas per unit area. The force per unit area measures the pressure of the gas.



Chapter 2: Heat & Thermodynamics

Basic Postulates of the Kinetic Theory of Gases

1. The molecules in a gas are small and very far apart. Most of the volume which a gas occupies is empty space.
2. A gas consists of molecules in constant random motion.
3. Gas molecules influence each other only by collision; they exert no other forces on each other.
4. All collisions between gas molecules are perfectly elastic; all kinetic energy is conserved. (no loss in KE).



Chapter 2: Heat & Thermodynamics

5. Molecules can collide with each other and with the walls of the container. Collisions with the walls account for the pressure of the gas.
6. The molecules exert no attractive or repulsive forces on one another except during the process of collision. Between collisions, they move in straight lines.
7. The gas is composed of small indivisible particles called molecules. The properties of the individual molecules are the same as that of the gas as a whole.



Chapter 2: Heat & Thermodynamics

8. The distance between the molecules is large as compared to that of a solid or liquid and hence the forces of inter-molecular attraction are negligible.
9. The size of the molecules is infinitesimally small as compared to the average distance traversed by a molecule between any two consecutive collisions. The distance between any two consecutive collisions is called free path and the average distance is called the mean free path. The mean free path is dependent on the pressure of the gas. If the pressure is high the mean free path is less and if the pressure is low the mean free path is more.
10. The molecules are perfectly hard elastic spheres, and the whole of their energy is kinetic.



Chapter 2: Heat & Thermodynamics

11. The time of impact is negligible in comparison with the taken to traverse the mean free path.



Chapter 2: Heat & Thermodynamics

Sample Question

Q. Applying the kinetic theory of gases, the following expression for the pressure of a gas in terms of the properties of its molecules can be derived:

$$P = \frac{MC^2}{3V}$$
$$P = \frac{1}{3} \rho C^2$$



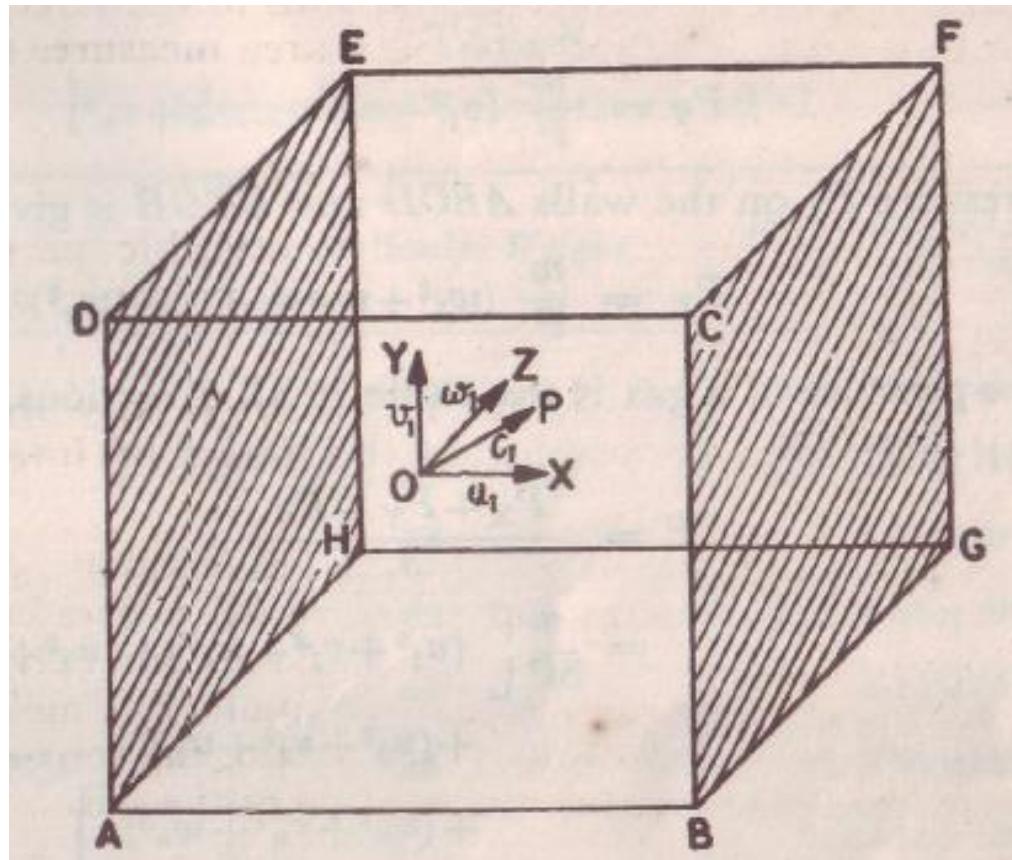
Chapter 2: Heat & Thermodynamics

Answer



Chapter 2: Heat & Thermodynamics

Expression for the Pressure of a Gas





Chapter 2: Heat & Thermodynamics

Consider a cubical vessel $ABCDEFGH$ of side l cm containing the gas. The volume of the vessel and hence that of the gas is l^3 cc. Let n and m represent the very large number of molecules present in the vessel and the mass of each molecule respectively.

Consider a molecule P moving in a random direction with a velocity C_1 . The velocity can be resolved into three perpendicular components u_1 , v_1 and w_1 along the X , Y and Z axes respectively. Therefore,

$$C_1^2 = u_1^2 + v_1^2 + w_1^2$$



Chapter 2: Heat & Thermodynamics

The component of the velocity with which the molecule P will strike the opposite face $BCFG$ is u_1 and the momentum of the molecule is mu_1 . This molecule is reflected back with the same momentum mu_1 in an opposite direction and after traversing a distance l will strike the opposite face $ADEH$.

The change in momentum produced due to the impact is

$$mu_1 - (-mu_1) = 2mu_1$$

As the velocity of the molecule is u_1 , the time interval between two successive impacts on the wall $BCFG$ is

$$\frac{2l}{u_1} \text{ seconds}$$



Chapter 2: Heat & Thermodynamics

∴ No. of impacts per second

$$= \frac{1}{2l} \\ = \frac{u_1}{2l}$$

Change in momentum produced in one second due to the impact of this molecule is

$$2mu_1 \times \frac{u_1}{2l} = \frac{mu_1^2}{l}$$

The force F_x due to the impact of all the n molecules in one second

$$= \frac{m}{l} [u_1^2 + u_2^2 + \dots + u_n^2]$$



Chapter 2: Heat & Thermodynamics

Force per unit area on the wall $BCFG$ or $ADEH$ is equal to the pressure P_X

$$P_X = \frac{m}{l \times l^2} (u_1^2 + u_2^2 + u_3^2 + \dots + u_n^2)$$

Similarly the pressure P_Y on the walls $CDEF$ and $ABGH$ is given by

$$P_Y = \frac{m}{l^3} (v_1^2 + v_2^2 + \dots + v_n^2)$$

and the pressure P_Z on the walls $ABCD$ and $EFGH$ is given by

$$P_Z = \frac{m}{l^3} (w_1^2 + w_2^2 + \dots + w_n^2)$$



Chapter 2: Heat & Thermodynamics

As the pressure of a gas is the same in all directions, the mean pressure P is given by

$$\begin{aligned} P &= \frac{P_x + P_y + P_z}{3} \\ &= \frac{m}{3l^3} \left[(u_1^2 + v_1^2 + w_1^2) + (u_2^2 + v_2^2 + w_2^2) \right. \\ &\quad + (u_3^2 + v_3^2 + w_3^2) + \dots \dots \\ &\quad \left. + (u_n^2 + v_n^2 + w_n^2) \right] \\ &= \frac{m}{3l^3} \left[C_1^2 + C_2^2 + C_3^2 + \dots \dots C_n^2 \right] \dots (i) \end{aligned}$$

But volume, $V = l^3$. Let C be the root-mean-square velocity of the molecules (R.M.S. velocity).

Then

$$C^2 = \frac{C_1^2 + C_2^2 + C_3^2 + \dots \dots C_n^2}{n}$$

or

$$nC^2 = C_1^2 + C_2^2 + C_3^2 + \dots \dots C_n^2$$

Substituting this value in equation (i), we get

$$P = \frac{m \cdot n C^2}{3V} \dots (ii)$$



Chapter 2: Heat & Thermodynamics

But $M = mn$ where M is the mass of the gas of volume V , m is the mass of each molecule and n is the number of molecules in a volume V .

∴

$$P = \frac{MC^2}{3V}$$

or

$$P = \frac{1}{3} \rho C^2 \quad \dots(iii)$$

∴

$$\frac{M}{V} = \rho \text{ the density of the gas.}$$

From equation (iii)

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

$$C = \sqrt{\frac{3P}{\rho}}$$

...(iv)



Chapter 2: Heat & Thermodynamics

Self Study

Kinetic Interpretation of Temperature



Chapter 2: Heat & Thermodynamics

Self Study

Derivation of Gas Laws from Kinetic Theory of Gases



Chapter 2: Heat & Thermodynamics

Sample Questions

1. Give the kinetic interpretation of temperature.
2. Applying the kinetic theory of gases derive the ideal gas equations



Chapter 2: Heat & Thermodynamics

Brownian Motion (Robert Brown in 1827)

You might well have studied Brownian Motion before. It is unlikely that you fully appreciated or understood it!!!

One of the first pieces of evidence for how gases move was discovered by Robert Brown a botanist who noticed that pollen grains in water moved about randomly.

Robert Brown noticed that small grains of pollen (clarkia) suspended in water, moved in a haphazard or random fashion.



Chapter 2: Heat & Thermodynamics

Brownian Motion

It was only visible under a microscope (he used fairly low magnification).

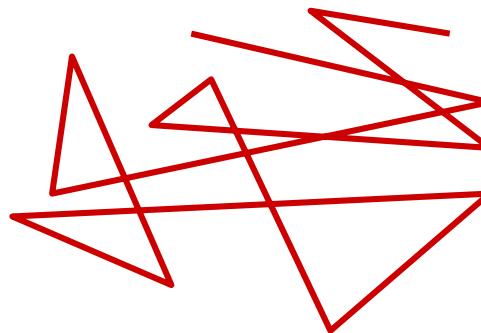
Being a botanist he logically thought that the grains of pollen were alive.

He then tried various other small particles such as carbon (in ink) and realized that the motion was not truly due to life.



Chapter 2: Heat & Thermodynamics

Brownian Motion



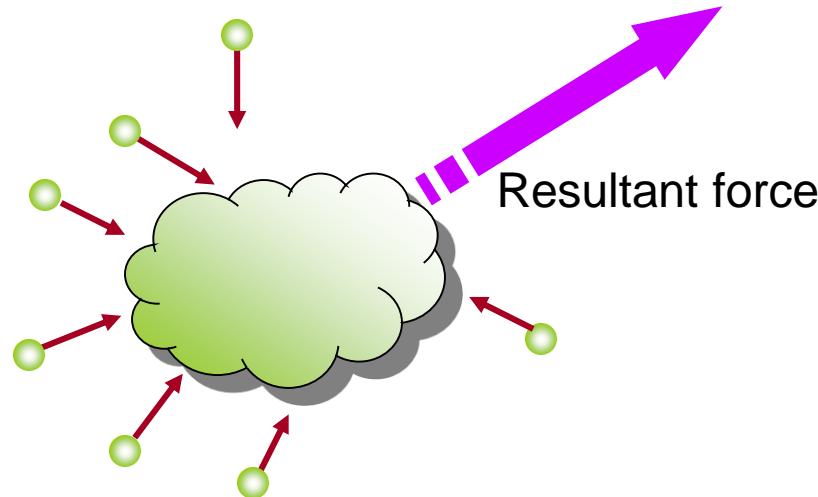
Remember

- There is no appreciable displacement of the particle
- The particle travels more or less in straight lines
- The motion is RANDOM



Chapter 2: Heat & Thermodynamics

Brownian Motion



At any point of time the forces on the particles are uneven causing a net force and therefore acceleration in that direction.

Their light mass means they change direction quickly and easily.



Chapter 2: Heat & Thermodynamics

Brownian Motion

The non-stop, random, perpetual, spontaneous, and haphazard motion of a colloidal solution is called the Brownian motion.



Chapter 2: Heat & Thermodynamics

Essential Features of Brownian Motion

1. The motion of each particle is completely irregular, and random. No two particles are found to execute the same motion.
2. The motion is continuous and takes place for ever.
3. The smaller particles appear to be more agitated than the longer ones.
4. The motion is independent of the nature of the suspended articles. Two particles of the same weight and size move equally fast at the same temperature.



Chapter 2: Heat & Thermodynamics

5. The motion becomes more vigorous when the temperature is increased.
6. The motion is more conspicuous in a liquid of lower viscosity.
7. The motion is not modified due to the shaking of the containing vessel.



Chapter 2: Heat & Thermodynamics

Basis of Brownian Motion

Brownian motion is due to the bombardment of the dispersed particles by molecules of the medium which are themselves in a state of continuous haphazard motion. When the particles are sufficiently large, the forces due to molecular impact is nearly balanced. This is why Brownian motion cannot be observed with particles of large size. But when the size of the particles is very small each particle will be acted upon by a resultant unbalanced force and will consequently move in a haphazard manner in response to the magnitude and direction of this force.



Chapter 2: Heat & Thermodynamics

In other words, the particles move in response to the molecules of the liquid in a completely haphazard manner. The motion of the molecules of a gas is similar to Brownian movement if suspended particles in colloidal solution. Thus, the laws of kinetic theory of gases are applicable to Brownian motion.



Chapter 2: Heat & Thermodynamics

Question

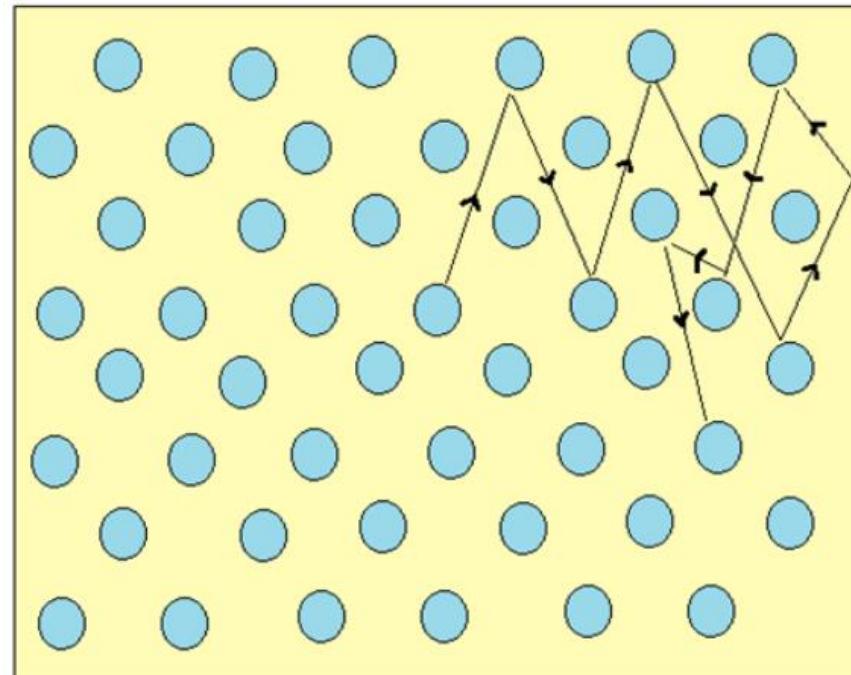
Q. Define Brownian motion with its essential features. Explain the basis of Brownian motion.



Chapter 2: Heat & Thermodynamics

Mean Free Path of Gases

The mean free path λ of a gas molecule is its average path length between collisions.



The random path followed by a gas molecule.



Chapter 2: Heat & Thermodynamics

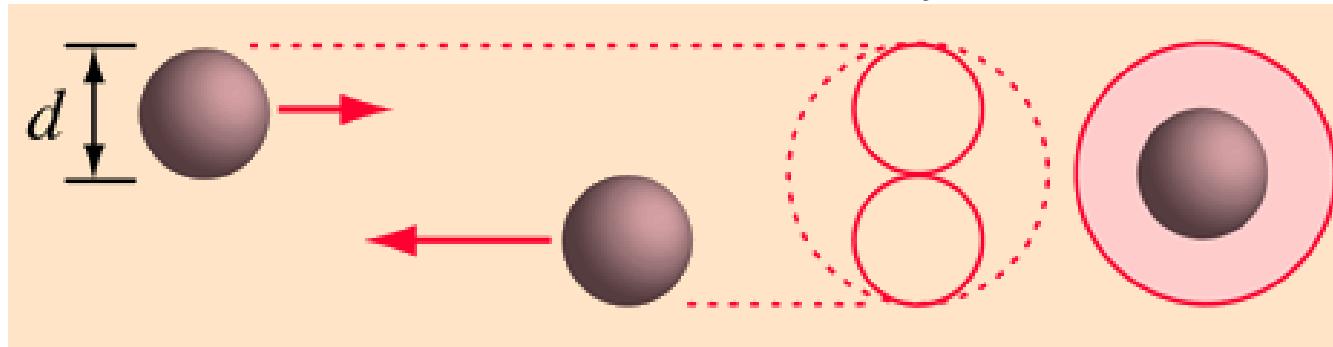
- On the basis of kinetic theory of gases, it is assumed that the molecules of a gas are continuously colliding against each other.
- Molecules move in straight line with constant speeds between two successive collisions.
- Thus path of a single molecule is a series of zig-zag paths of different lengths as shown in figure.

These paths of different lengths are called free paths of the molecule. Mean free path is the average distance traversed by molecule between two successive collisions.



Chapter 2: Heat & Thermodynamics

If the molecules have diameter d , then the effective cross-section for collision can be defined by,

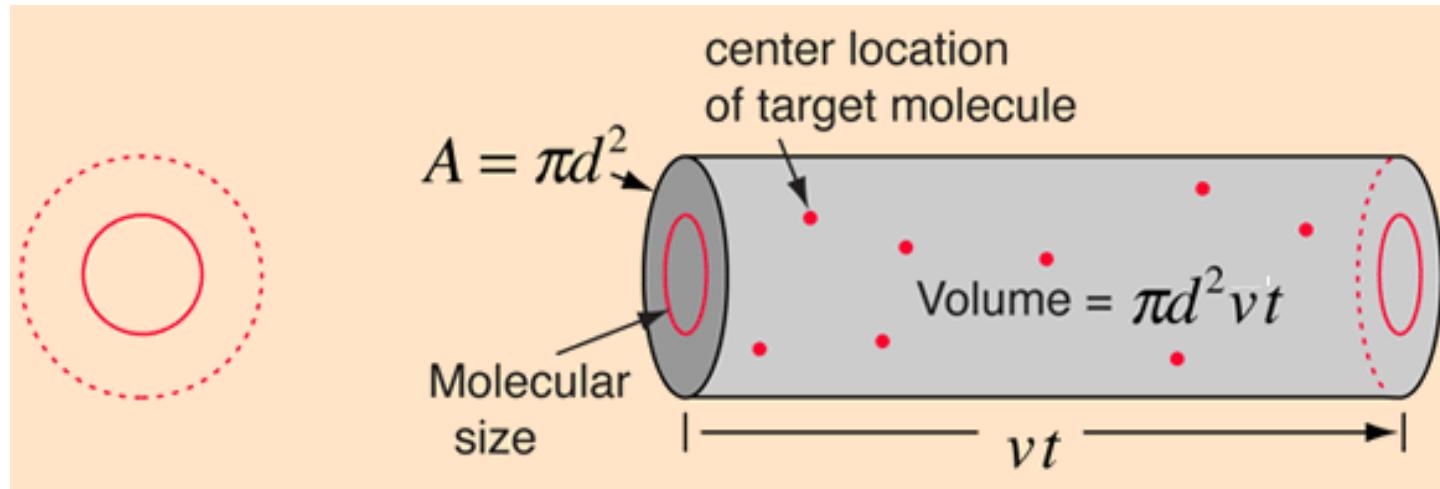


The effective cross-section for collision, $A = \pi d^2$.

Using a circle of diameter $2d$ to represent a molecule's effective collision area while treating the 'target' molecules as point masses. In time t , the circle would sweep out the volume shown and the number of collisions can be estimated from the number of gas molecules available in that volume.



Chapter 2: Heat & Thermodynamics



The mean free path could then be taken as the length of the path divided by the number of collisions. Mathematically,

$$\lambda = \frac{\text{Distance traveled in time } t}{\text{No of collisions suffered in time } t}$$



Chapter 2: Heat & Thermodynamics

The mean free path,

$$\begin{aligned}\lambda &= \frac{vt}{\pi d^2 v t \cdot \frac{N}{V}} \\ &= \frac{1}{\pi d^2 n}\end{aligned}$$

This is the expression for the mean free path of a gas molecule.

This equation was deduced by Clausius.

$$\therefore \lambda \propto \frac{1}{d^2}$$

The mean free path is inversely proportional to the square of the diameter of the molecules.



Chapter 2: Heat & Thermodynamics

Here, we have assumed that all the particles are stationary with respect to the particle we are studying, but in reality all the molecules are moving relative to each other, we have cancelled two velocities in the equation but actually the v in the numerator is the average velocity and v in the denominator is relative velocity hence they both differ from each other with a factor $\sqrt{2}$ therefore the final expression of the mean free path would be,

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 n}$$

This is known as the Maxwell's mean free path based on the law of equipartition of energy.



Chapter 2: Heat & Thermodynamics

Let m be the mass of each molecule.

Then, $m \times n = \rho$

$$\lambda = \frac{m}{\pi d^2 \rho}$$

The mean free path is inversely proportional to the density of the gas.

The expression for the mean path according to Boltzmann is

$$\lambda = \frac{3}{4\pi d^2 n}$$

He assumed that all molecules have the same average speed.



Chapter 2: Heat & Thermodynamics

Law of Equipartition of Energy

A molecule in a gas can move along any of the three co-ordinate axes. It has three degrees of freedom. Degrees of freedom mean the number of independent variables that must be known to describe the state or the position of the body completely. A monoatomic gas molecule has three degrees of freedom. A diatomic gas molecule has three degrees of freedom of translation and two degrees of freedom of rotation. It has in all five degrees of freedom.

According to kinetic theory of gases, the mean kinetic energy of a molecule at a temperature T is given by

$$\frac{1}{2}mC^2 = \frac{3}{2} kT \quad \dots(i)$$

But

$$C^2 = u^2 + v^2 + w^2$$



Chapter 2: Heat & Thermodynamics

As x , y and z are all equivalent, mean square velocities along the three axes are equal

$$\therefore u^2 = v^2 = w^2$$

or

$$\frac{1}{2} m(u^2) = \frac{1}{2} m(v^2) = \frac{1}{2} m(w^2)$$

$$\begin{aligned}\therefore \frac{1}{2} mC^2 &= 3 [\frac{1}{2} m(u^2)] = 3 [\frac{1}{2} m(v^2)] \\ &= 3 [\frac{1}{2} m(w^2)]\end{aligned}$$

$$= \frac{3}{2} kT$$

$$\therefore \frac{1}{2} mu^2 = \frac{1}{2} kT \quad \dots(i)$$

$$\frac{1}{2} mv^2 = \frac{1}{2} kT \quad \dots(ii)$$

$$\frac{1}{2} mw^2 = \frac{1}{2} kT \quad \dots(iii)$$

Therefore, the average kinetic energy associated with each degree of freedom
 $= \frac{1}{2} kT$



Chapter 2: Heat & Thermodynamics

Thus the energy associated with each degree of freedom (whether translatory or rotatory) is $\frac{1}{2} kT$.

This represents the theorem of equipartition of energy.



Chapter 2: Heat & Thermodynamics

(i) *Mono-atomic gas.* A mono-atomic gas molecule has one atom. Each molecule has three degrees of freedom due to translatory motion only.

$$\text{Energy associated with each degree of freedom} = \frac{1}{2} kT$$

Energy associated with three degrees of freedom

$$= \frac{3}{2} kT$$

Consider one gram molecule of a gas.

Energy associated with one gram molecule of a gas

$$= N \times \frac{3}{2} kT$$

$$= \frac{3}{2} (N \times k) T$$



Chapter 2: Heat & Thermodynamics

[But, $N \times k = R$]

$$\therefore U = \frac{3}{2} RT$$

This energy of the gas is due to the energy of its molecules. It is called internal energy U . For an ideal gas, it depends upon temperature only.

$$\therefore C_v = \frac{dU}{dT} = \frac{3}{2} R$$

$\left(\frac{dU}{dT} \right)$ is the increase in internal energy per unit degree rise of temperature)

But

$$C_p - C_v = R$$

$$C_p = C_v + R$$

$$= \frac{3}{2} R + k = \frac{5}{2} R$$



Chapter 2: Heat & Thermodynamics

For a mono-atomic gas

$$\begin{aligned}\gamma &= \frac{C_p}{C_v} \\ &= \frac{\frac{5}{2}R}{\frac{3}{2}R} = 1.67\end{aligned}$$

The value of γ is found to be true experimentally for mono-atomic gases like argon and helium.



Chapter 2: Heat & Thermodynamics

(ii) *Diatom gas.* A diatomic gas molecule has two atoms. Such a molecule has three degrees of freedom of translation and two degrees of freedom of rotation.

- Energy associated with each degree of freedom

$$= \frac{1}{2} kT$$

Energy associated with 5 degrees of freedom = $\frac{5}{2} kT$

Consider one gram molecule of gas.

Energy associated with 1 gram molecule of a diatomic gas

$$= N \times \frac{5}{2} kT = \frac{5}{2} RT$$

$$U = \frac{5}{2} RT$$

$$C_V = \frac{dU}{dT}$$

$$= \frac{5}{2} R$$



Chapter 2: Heat & Thermodynamics

But

$$C_p - C_v = R$$

$$C_p = C_v + R$$

$$= \frac{5}{2}R + R = 7/2R$$

$$\gamma = \frac{C_p}{C_v}$$

$$= \frac{\frac{7}{2}R}{\frac{5}{2}R} = 1.40$$

The value of $\gamma = 1.40$ has been found to be true experimentally for diatomic gases like hydrogen, oxygen, nitrogen etc.



Chapter 2: Heat & Thermodynamics

(iii) *Triatomic gas.* (a) A triatomic gas having 6 degrees of freedom has an energy associated with 1 gram molecule

$$= N \times \frac{6}{2} kT = 3RT$$

$$U = 3RT$$

$$C_V = \frac{dU}{dT} = 3R$$

But

$$C_P - C_V = R$$

$$C_P = C_V + R$$

$$= 3R + R = 4R$$

$$\begin{aligned}\gamma &= \frac{C_P}{C_V} \\ &= \frac{4R}{3R} = 1.33\end{aligned}$$



Chapter 2: Heat & Thermodynamics

(b) A triatomic gas having 7 degrees of freedom has an energy associated with 1 gram molecule = $N \times \frac{7}{2} kT = \frac{7}{2} R$

$$U = \frac{7}{2} RT$$

$$C_V = \frac{dU}{dT} = \frac{7}{2} R$$

But

$$C_P - C_V = R$$

$$C_P = C_V + R$$

$$= \frac{7}{2} R + R = \frac{9}{2} R$$

$$\gamma = \frac{C_P}{C_V}$$

$$= \frac{9/2 R}{7/2 R} = 1.28$$

Thus the value of γ , C_P and C_V can be calculated depending upon the degrees of freedom of a gas molecule.



Chapter 2: Heat & Thermodynamics

Ideal Gas Equation

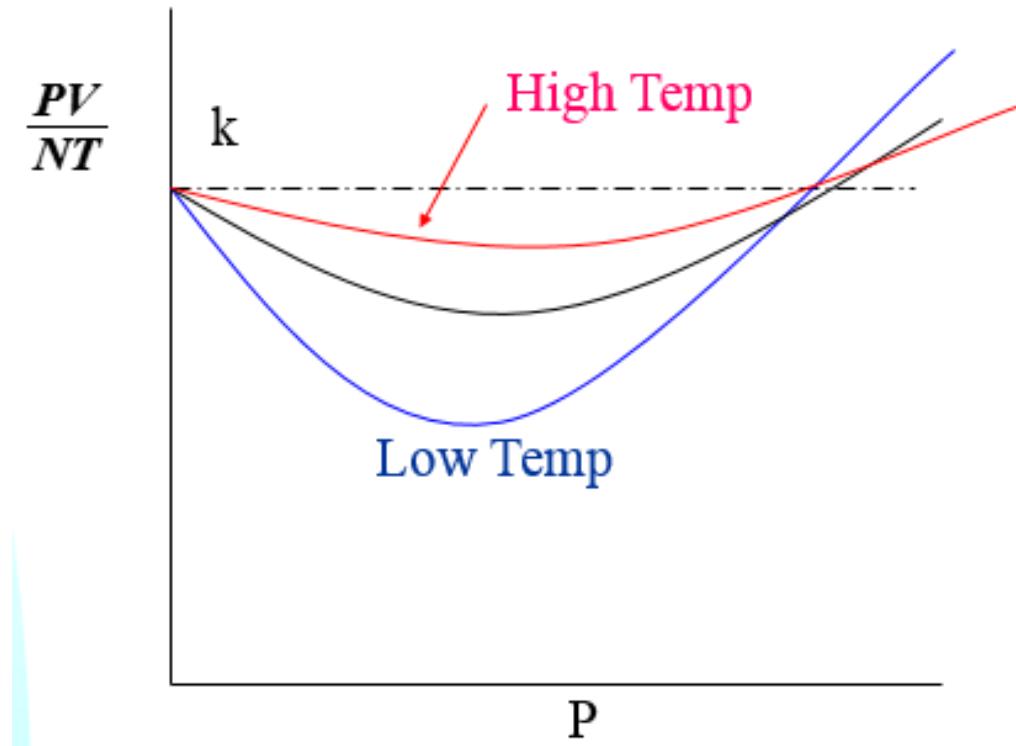
&

Van der Waal's Modifications of the Ideal Gas Equation



Chapter 2: Heat & Thermodynamics

If P , V , and T measurements are made on a sample of a real gas, if the results are plotted graphically, it is found that (N =number of molecules),





Chapter 2: Heat & Thermodynamics

As the pressure decreases $\frac{PV}{NT}$ approaches a fixed value. Furthermore this fixed value is found to be the same for all gases. This experimental number is called Boltzmann's constant and the measured value is:

$$k = 1.3806504 \times 10^{-23} \frac{J}{K}$$

Thus, at low pressure, $\frac{PV}{NT} \approx k$ $PV \approx NkT$

By definition, an ideal gas, obeys this equation of state exactly.

$$PV = NkT$$

and a real gas behaves like an ideal gas when its pressure is low.



Chapter 2: Heat & Thermodynamics

The universal gas constant R is defined as,

$$R \equiv N_A k = \left(6.02214179 \times 10^{23} \frac{\text{molecules}}{\text{mole}} \right) \left(1.3806504 \times 10^{-23} \frac{\text{J}}{\text{K}} \right)$$

$$R = 8.314472 \frac{\text{J}}{\text{moleK}} \quad n = \text{number of moles}$$

$$R = N_A k = \left(\frac{N}{n} \right) k, \quad nR = Nk$$

Thus for ideal gas, $PV = nRT$

This is the ideal gas equation.



Chapter 2: Heat & Thermodynamics

Van der Waal's Equation of State



Chapter 2: Heat & Thermodynamics

The ideal gas equation: $PV = nRT$, derived using the KTG assuming that

1. The size of the molecules of the gas is negligible and
2. The forces of intermolecular attraction are absent

However, at high pressure (at higher densities), the size of the molecules of the gas becomes significant and can't be neglected in comparison with the gas volume.



Chapter 2: Heat & Thermodynamics

In the same way, at high pressure, the gas molecules come closer and the forces of intermolecular attraction are appreciable. Thus, corrections are needed to the ideal gas equation.



Chapter 2: Heat & Thermodynamics

The ideal gas equation is modified based on:

- ✓ Attractive forces between gas particles/
Correction for pressure
(*attractive effect*)

- ✓ Non-zero volumes of gas particles/ Correction
for volume
(*repulsive effect*)



Chapter 2: Heat & Thermodynamics

Attractive effect (Correction for Pressure)

A molecule in the interior of a gas experiences forces of attraction in all directions and the resultant cohesive force is zero. A molecule near the walls of the container experiences a resultant force inwards. For this reason, the observed pressure of the gas is less than the actual pressure. The correction for p depends on:

- (i) The number of molecules striking unit area of the walls of the container/sec
- (ii) The number of the molecules present in a given volume.



Chapter 2: Heat & Thermodynamics

Both factors depend on the density of the gas.
Hence the correction for pressure,

$$p \propto \rho^2 \propto \frac{1}{V^2}$$

or, $p = \frac{a}{V^2}$

Here, a is a constant and V is the volume of the gas. Thus, the correct pressure of the gas will be

$$P + p = P + \frac{a}{V^2}, \text{ where } P \text{ is the observed pressure.}$$



Chapter 2: Heat & Thermodynamics

Repulsive effect (correction for Volume)

- Gas molecules behave like small, impenetrable spheres
- Actual volume available for gas smaller than volume of container, V
- The molecules have the sphere of influence around them and due to this factor, the correction for volume b is approximately 4 times actual volume of the gas molecules.



Chapter 2: Heat & Thermodynamics

Thus, the corrected volume of gas = $V - b$.

Let the radius of one molecule be r . The volume of the molecule,

$$x = \frac{4}{3}\pi r^3$$

The volume of the sphere of influence of each molecule,

$$S = \frac{4}{3}\pi(2r)^3 = 8x$$



Chapter 2: Heat & Thermodynamics

Consider a container of volume V and the molecules are allowed to enter one by one.

The volume available for the first molecule = V

The volume available for the 2nd molecule = $V-S$

The volume available for the 3rd molecule = $V-2S$

.....

.....

Volume available for the n th molecule = $V-(n-1)S$



Chapter 2: Heat & Thermodynamics

Thus, the average space available for each molecule

$$= \frac{V + (V - S) + (V - 2S) + \dots + \{V + (n-1)S\}}{n}$$

$$= V - \frac{S}{n} \{1 + 2 + 3 + \dots + (n-1)\}$$

$$= V - \frac{S}{n} \cdot \frac{(n-1)n}{2}$$

$$= V - \frac{nS}{2} + \frac{S}{2}$$

As the number molecule is very high, we can ignore the last term $\frac{S}{2}$.

Hence, the space available for each molecule

$$= V - \frac{nS}{2} = V - \frac{n(8x)}{2} = V - 4(nx) = V - b, \text{ where } b = 4nx, 4 \text{ times the actual volume of the gas molecules}$$



Chapter 2: Heat & Thermodynamics

Combining both derivations, we get the Van der Waal's Equation of State

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT$$

Where a and b are Van der Waal's constants. From Van der Waal's equation of state, we can write

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$



Chapter 2: Heat & Thermodynamics

$\frac{a}{V^2}$ comes from interactions among gas molecules.

b comes from volume of the gas molecules.

a and b are different for different gases.



Chapter 2: Heat & Thermodynamics

The Van der Waal's constant a

- ✓ Gives a rough indication of magnitude of intermolecular attraction. Usually, the stronger the attractive forces, the higher is the value of a



Chapter 2: Heat & Thermodynamics

The Van der Waal's constant b

Gives a rough indication of the size of gas molecules. Usually, the bigger the gas molecules, the higher is the value of b



A Brief Summary

- ✓ Ideal gas equation combines Avogadro's, Boyle's and Charles' Laws.

- ✓ Assumptions of ideal gas equation fail for real gases, causing deviations.

- ✓ Van der Waals gas equation accounts for attractive and repulsive effects ignored by ideal gas equation.



A Brief Summary

- ✓ Constants a and b represent the properties of a real gas
- ✓ A gas with higher a value usually has stronger IMF
- ✓ A gas with higher b value is usually bigger
- ✓ A gas cannot be condensed into liquid at temperatures higher than its critical temperature



Chapter 2: Heat & Thermodynamics

Van der Waal's Constants



Chapter 2: Heat & Thermodynamics

Self Study

Calculate the Van der Waal's
Constants (a , and b)



Chapter 2: Heat & Thermodynamics

Critical Constants



Chapter 2: Heat & Thermodynamics

Self Study

Calculate the Critical Constants

P_c , V_c and T_c



Chapter 2: Heat & Thermodynamics

Laws of Thermodynamics



Chapter 2: Heat & Thermodynamics

0th Law of Thermodynamics



0th Law of Thermodynamics

When two systems are put in contact with each other, there will be a net exchange of energy between them unless or until they are in thermal equilibrium, that is, they are at the same temperature

“If A and C are each in thermal equilibrium with B , A is also in thermal equilibrium with C .”

Single temperature and pressure can be attributed to the whole system



Chapter 2: Heat & Thermodynamics

1st Law of Thermodynamics



First Law of Thermodynamics

- ✓ Energy is conserved

- **FIRST LAW OF THERMODYNAMICS**

- Examples:

- Engines (Heat \rightarrow Mechanical Energy)
 - Friction (Mechanical Energy \rightarrow Heat)

- ✓ All processes must increase *entropy*

- **SECOND LAW OF THERMODYNAMICS**

- Entropy is measure of disorder
- Engines can not be 100% efficient



Chapter 2: Heat & Thermodynamics

Adding heat Q can:

- ✓ Change temperature
 - ✓ Change state of matter
 - ✓ Can also change ΔU by doing work on the gas
- Change of
Internal Energy ΔU



Chapter 2: Heat & Thermodynamics

The internal energy $\Delta U (=Q + W)$ of a gas can be changed, by

- Adding heat to gas: Q
- Doing work on gas: $W = -P\Delta V$

Note:

(Work done by the gas) = - (Work done on the gas)

$$W_{\text{by the gas}} = +P\Delta V$$

$$Q = \Delta U + W_{\text{by the gas}}$$

Add heat => Increase Int. Energy + Gas does work¹⁰²



Chapter 2: Heat & Thermodynamics

What is INTERNAL ENERGY?

The internal energy of the system is the sum of the kinetic and potential energies of the atoms and molecules making up the system.



Another Definition of 1st Law of Thermodynamics

The increase in the internal energy of a system is equal to the amount of heat added to the system, plus the amount of work done **on** the system.

The increase in the internal energy of a system is equal to the amount of heat added to the system, minus the amount of work done **by** the system.

$$\Delta U = Q - W$$

Q = heat add to system

W = work done by system



Chapter 2: Heat & Thermodynamics

The 1st Law of thermodynamics is an empirical statement regarding the conservation of energy.



Chapter 2: Heat & Thermodynamics

Reversible & Irreversible Processes



Chapter 2: Heat & Thermodynamics

Reversible (Ideal) Process: A system process is defined as reversible if a system, after having experienced several transformations, can be returned to its original state without alteration of the system itself or the system's surroundings.

- ✓ it should occur infinitely slowly due to infinitesimal gradient
- ✓ all the changes in state occurred in the system are in thermodynamic equilibrium with each other

Remember:

In a reversible process, the entropy of the universe (i.e.,¹⁰⁷ the system plus surroundings) remains constant.



Chapter 2: Heat & Thermodynamics

Example of reversible processes:

A change that can go forwards or backwards,
for example melting and freezing



Chapter 2: Heat & Thermodynamics

Irreversible (natural) Processes:

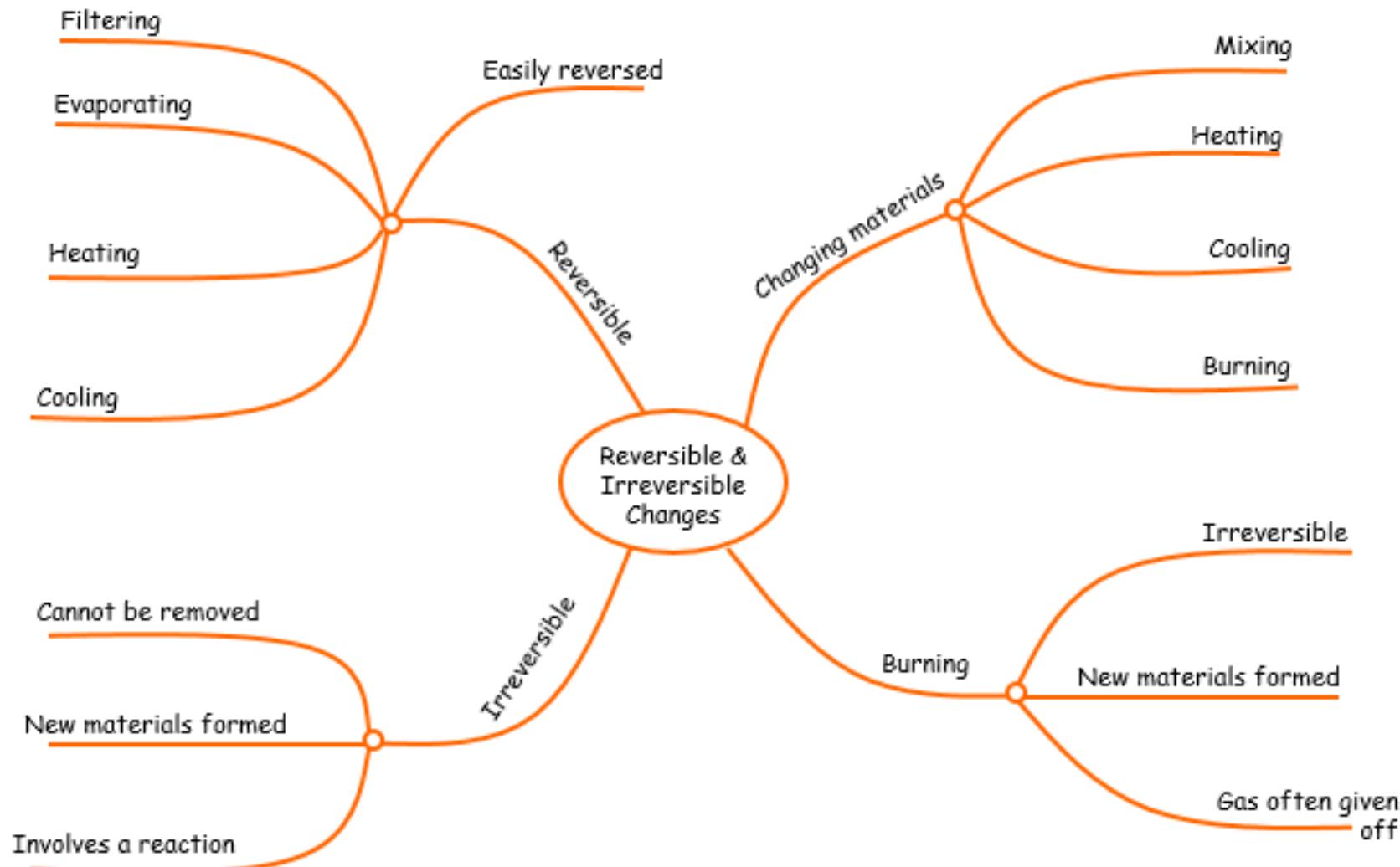
- ✓ All processes in nature are irreversible
- ✓ Finite gradient between the two states of the system
 - heat flow between two bodies occurs due to temperature gradient between the two bodies;

Example of Irreversible Processes:

All processes in nature are irreversible, a change that cannot go back, for example burning



Chapter 2: Heat & Thermodynamics





Chapter 2: Heat & Thermodynamics

2nd Law of Thermodynamics



2nd Law of Thermodynamics

- ✓ The 2nd Law of thermodynamics is concerned with the maximum fraction of heat that can be converted into useful work.

The 2nd law may be stated in several different ways, such as :

1. Thermal energy will not spontaneously flow from a colder to a warmer object. (What is thermal energy?)
 2. The *entropy* (defined below) of the universe is constantly increasing.
- ✓ Thus, the 2nd law is not a conservation principle (as in the 1st law), but rather is a law defining the direction of flow of energy.



Chapter 2: Heat & Thermodynamics

In a system, a process that occurs will tend to increase the total entropy of the universe

1. It is impossible to make heat flow from a material at a lower temperature to a material at a higher temperature without doing external work on the working substance (**Clausius Statement**)

2. It is impossible to convert heat completely into work in a cyclic process (**Definition by Kelvin**)



Chapter 2: Heat & Thermodynamics

If a process occurs in a closed system, the entropy of the system increases for irreversible processes and remains constant for reversible processes. It never decreases.

$$\Delta S \geq 0 \quad (\text{second law of thermodynamics})$$

Here the greater-than sign applies to irreversible processes and the equals sign to reversible processes. This relation applies only to closed systems.



Summary

0th Law of Thermodynamics

- ✓ Definition of temperature
- ✓ Systems at different temperatures exchange energy until reaching a thermal equilibrium

1st Law of Thermodynamics

- ✓ Conservation of energy
- ✓ heat is a form of energy

2nd Law of Thermodynamics

- ✓ Entropy of an isolated system never decreases
- ✓ perpetual motions of machines is impossible



Chapter 2: Heat & Thermodynamics

3rd Law of Thermodynamics

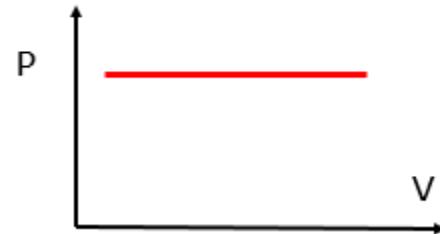
- ✓ Entropy at absolute zero temperature (0K)



Chapter 2: Heat & Thermodynamics

Isobaric

- $P = \text{constant}$



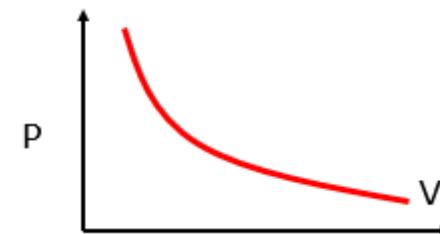
Isovolumetric/Isometric

- $V = \text{constant}$
- $W = 0$



Isothermal

- $T = \text{constant}$
- $\Delta U = 0$ (ideal gas)



Adiabatic

- $Q = 0$

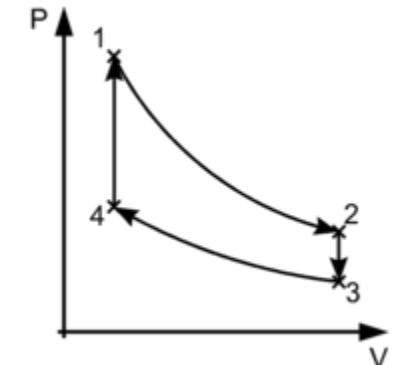




Chapter 2: Heat & Thermodynamics

Cyclic

- ✓ If clockwise – heat engine
- ✓ If counterclockwise – heat pump





Chapter 2: Heat & Thermodynamics

Carnot's Theorem

No engine operating between two heat reservoirs can be more efficient than a Carnot engine operating between those same reservoirs

Not only there are no perfect engines and refrigerators, but also their efficiency has an upper limit!

Carnot's theorem (Alternative definition)

- (1) All reversible engines operating between two given reservoirs have the same efficiency.
- (2) No engines have an efficiency higher than that of a reversible engine.



Chapter 2: Heat & Thermodynamics

“All the reversible engines working between the same temperature limits have the same efficiency. No engine can be more efficient than a Carnot’s reversible engine working between the same two temperatures.”

- ✓ Ideal engines = Reversible engines
- ✓ A Carnot engine is an ideal engine undergoing a Carnot cycle.



Chapter 2: Heat & Thermodynamics

Consider two reversible engines *A* and *B*, working between the temperature limits T_1 and T_2 (Fig. 6-15). *A* and *B* are coupled. Suppose *A* is more efficient than *B*. The engine *A* works as a heat engine and *B* as a refrigerator. The engine *A* absorbs an amount of heat H_1 from the source at a temperature T_1 . It does external work W and transfers it to *B*. The heat rejected to the sink is H_2 at a temperature T_2 . The engine *B* absorbs heat H_2' from the sink at temperature T_2 and W amount of work is done on the working substance. The heat given to the source at temperature T_1 is H_1' .

Suppose the engine *A* is more efficient than *B*.

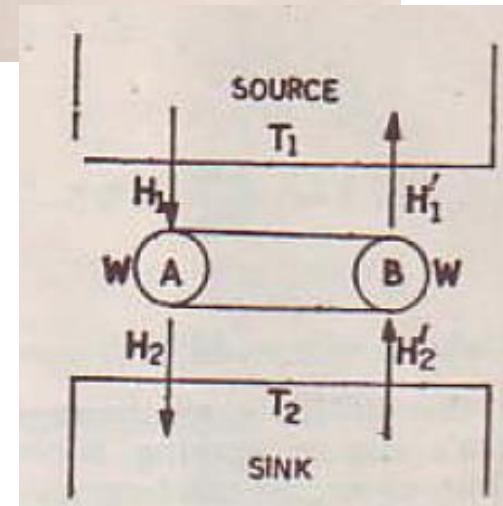


Fig. 6-15.



Chapter 2: Heat & Thermodynamics

Efficiency

Efficiency of the engine A

$$= \eta = \frac{H_1 - H_2}{H_1} = \frac{W}{H_1}$$

Efficiency of the engine B

$$= \eta' = \frac{H_1' - H_2'}{H_1'} = \frac{W}{H_1'}$$

Since $\eta > \eta'$; $H_1' > H_1$

Also, $W = H_1 - H_2 = H_1' - H_2'$

$\therefore H_2' > H_2$



Carnot's Theorem

Thus, for the two engines A and B working as a coupled system, $(H_2' - H_2)$ is the quantity of heat taken from the sink at a temperature T_2 , and $(H_1' - H_1)$ is the quantity of heat given to the source at a temperature T_1 . Both $(H_2' - H_2)$ and $(H_1' - H_1)$ are positive quantities. It means heat flows from the sink at a temperature T_2 (lower temperature) to the source at a temperature T_1 (higher temperature) i.e., heat flows from a body at a lower temperature to a body at a higher temperature. But, no external work has been done on the system. This is contrary to the second law of thermodynamics. Thus, η cannot be greater than η' . The two engines (reversible) working between the same two temperature limits have the same efficiency. Moreover, in the case of a Carnot's engine, there is no loss of heat due to friction, conduction or radiation (irreversible processes). Thus, the Carnot's engine has the maximum efficiency. Whatever may be the nature of the working substance, the efficiency depends only upon the two temperature limits.

In a practical engine there is always loss of energy due to friction, conduction, radiation etc. and hence its efficiency is always lower than that of a Carnot's engine.



Carnot's Reversible Engine

Heat engines are used to convert heat into mechanical work. Sadi Carnot (French) conceived a theoretical engine which is free from all the defects of practical engines. Its efficiency is maximum and it is an ideal heat engine.

For any engine, there are three essential requisites :

(1) **Source.** The source should be at a fixed high temperature T_1 from which the heat engine can draw heat. It has infinite thermal capacity and any amount of heat can be drawn from it at constant temperature T_1 .

(2) **Sink.** The sink should be at a fixed lower temperature T_2 to which any amount of heat can be rejected. It also has infinite thermal capacity and its temperature remains constant at T_2 .

(3) **Working Substance.** A cylinder with non-conducting sides and conducting bottom contains the perfect gas as the *working substance*.



Chapter 2: Heat & Thermodynamics

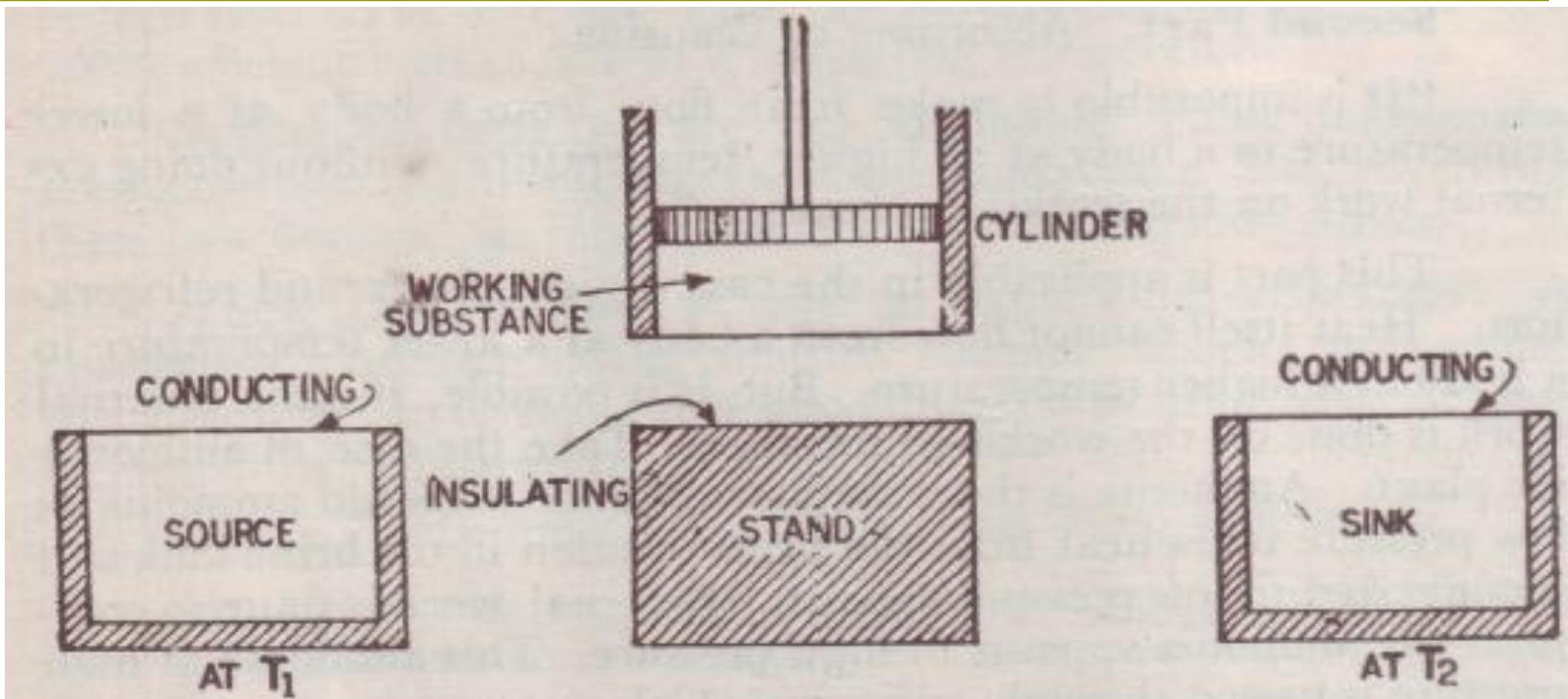


Fig. 6.12

A perfect non-conducting and frictionless piston is fitted into the cylinder. The working substance undergoes a complete cyclic operation (Fig. 6.12).

A perfectly non-conducting stand is also provided so that the working substance can undergo adiabatic operation.



Chapter 2: Heat & Thermodynamics

Carnot's Cycle

(1) Place the engine containing the working substance over the source at temperature T_1 . The working substance is also at a temperature T_1 . Its pressure is P_1 and volume is V_1 , as shown by the point A in Fig. 6.13. Decrease the pressure. The volume of the working substance increases. Work is done by the working substance. As the bottom is perfectly conducting to the source at temperature T_1 , it absorbs heat. The process is completely isothermal. The temperature remains constant. Let the amount of heat

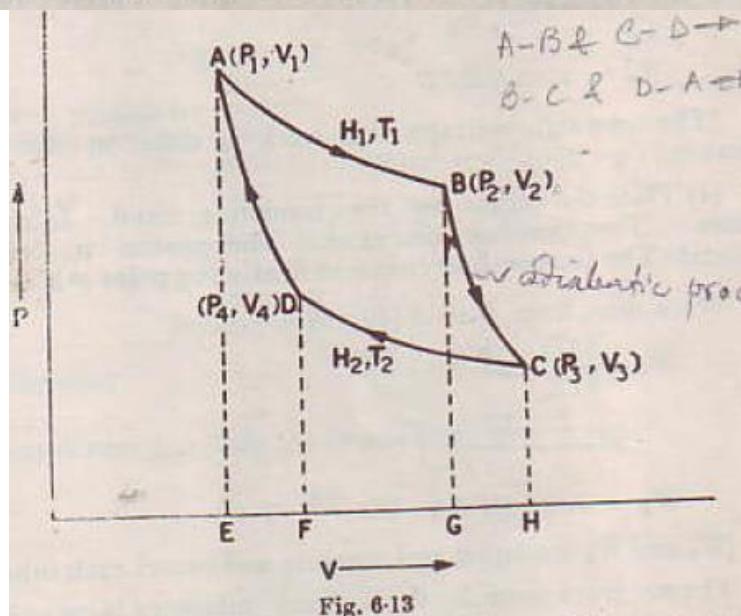


Fig. 6.13



Chapter 2: Heat & Thermodynamics

absorbed by the working substance be H_1 at the temperature T_1 .
The point B is obtained.

Consider one gram molecule of the working substance.

Work done from A to B (isothermal process)

$$W_1 = \int_{V_1}^{V_2} P_1 dV = RT_1 \log \frac{V_2}{V_1} \quad [P_1 V_1 =$$

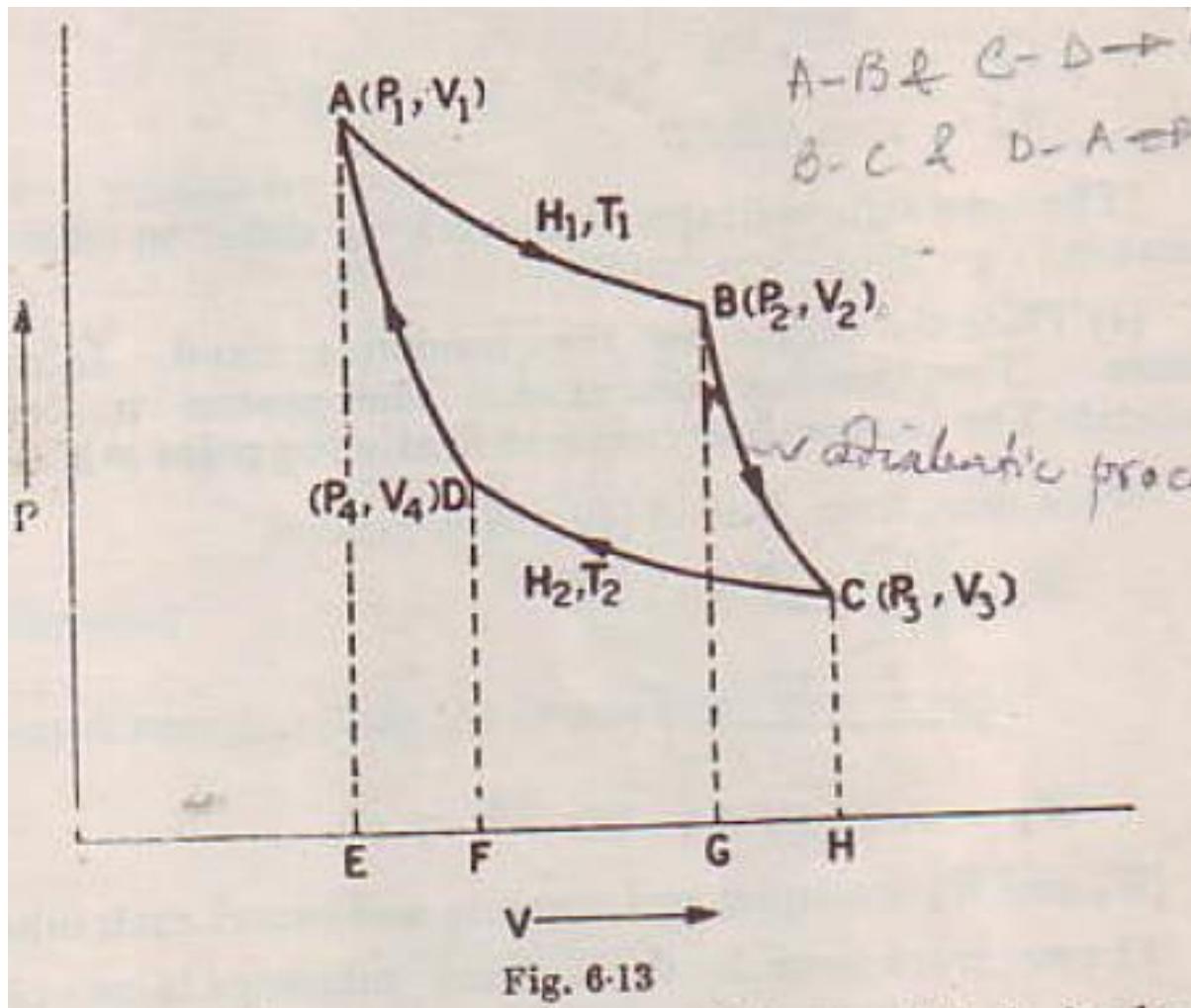
... (i)

$P_1 V_1 = RT_1$

(2) Place the engine on the stand having an insulated top.
Decrease the pressure on the working substance. The volume



Chapter 2: Heat & Thermodynamics





Chapter 2: Heat & Thermodynamics

increases. The process is completely adiabatic. Work is done by the working substance at the cost of its internal energy. The temperature falls. The working substance undergoes adiabatic change from B to C . At C the temperature is T_2 (Fig. 6.13).

Work done from B to C (adiabatic process)

$$\begin{aligned}
 W_2 &= \int_{V_2}^{V_3} P \cdot dV \\
 &= K \int_{V_2}^{V_3} \frac{dV}{V^\gamma} \\
 &= \frac{KV_3^{1-\gamma} - KV_2^{1-\gamma}}{1-\gamma} \\
 &= \frac{P_3V_3 - P_2V_2}{1-\gamma} \\
 &= \frac{R[T_2 - T_1]}{1-\gamma} = \frac{R[T_1 - T_2]}{\gamma-1} \\
 W_2 &= \text{Area } BOHG
 \end{aligned}$$

But $PV^\gamma = \text{constant} = K$
 $P_2V_2 = RT_1$

$P_3V_3 = RT_2$ ✓

$P_3V_3^\gamma = P_2V_2^\gamma = K$

... (ii)



Chapter 2: Heat & Thermodynamics

(3) Place the engine on the sink at temperature T_3 . Increase the pressure. The work is done on the working substance. As the base is conducting to the sink, the process is isothermal. A quantity of heat H_2 is rejected to the sink at temperature T_3 . Finally the point D is reached.

Work done from C to D (isothermal process)

$$\begin{aligned}W_3 &= \int_{V_3}^{V_4} PdV \\&= RT_3 \log \frac{V_4}{V_3} \\&= -RT_3 \log \frac{V_3}{V_4} \quad \dots(iii)\end{aligned}$$

$$W_3 = \text{area } CHFD$$

(The -ve sign indicates that work is done on the working substance.)



Chapter 2: Heat & Thermodynamics

(4) Place the engine on the insulating stand. Increase the pressure. The volume decreases. The process is completely adiabatic. The temperature rises and finally the point *A* is reached.

Work done from *D* to *A* (adiabatic process).

$$W_4 = \int_{V_4}^{V_1} P dV$$
$$= - \frac{R(T_1 - T_4)}{\gamma - 1}$$

$$W_4 = \text{Area } DFEA \quad \dots(iv)$$

[W_2 and W_4 are equal and opposite and cancel each other.]

The net work done by the working substance in one complete cycle

$$\begin{aligned} &= \text{Area } ABGE + \text{Area } BCHG - \text{Area } CHFD \\ &\quad - \text{Area } DFEA \\ &= \text{Area } ABCD \end{aligned}$$



Chapter 2: Heat & Thermodynamics

The net amount of heat absorbed by the working substance

$$= H_1 - H_2$$

Net work = $W_1 + W_2 + W_3 + W_4$

$$= RT_1 \log \frac{V_2}{V_1} + \frac{R(T_1 - T_2)}{\gamma - 1} - RT_2 \log \frac{V_3}{V_4} - \frac{R(T_1 - T_2)}{\gamma - 1}$$

$$W = RT_1 \log \frac{V_2}{V_1} - RT_2 \log \frac{V_3}{V_4} \quad \dots(v)$$

The points A and D are on the same adiabatic

$$T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_4} \right)^{\gamma-1} \quad \dots(vi)$$



Chapter 2: Heat & Thermodynamics

The points B and C are on the same adiabatic

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$
$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_3} \right)^{\gamma-1} \quad \dots(vii)$$

From (vi) and (viii)

$$\left(\frac{V_1}{V_4} \right)^{\gamma-1} = \left(\frac{V_2}{V_3} \right)^{\gamma-1}$$

or

$$\frac{V_1}{V_4} = \frac{V_2}{V_3}$$

or

$$\frac{V_3}{V_1} = \frac{V_2}{V_4}$$

From equation (v)

$$W = RT_1 \log \frac{V_2}{V_1} - RT_2 \log \frac{V_3}{V_1}$$

$$W = R \left[\log \frac{V_2}{V_1} \right] [T_1 - T_2]$$

$$W = H_1 - H_2$$



Chapter 2: Heat & Thermodynamics

Efficiency

$$\eta = \frac{\text{Useful output}}{\text{Input}} = \frac{W}{H_1}$$

Heat is supplied from the source from A to B only.

$$H_1 = RT_1 \log \frac{V_2}{V_1}$$

$$\therefore \eta = \frac{W}{H_1} = \frac{H_1 - H_2}{H_1}$$

$$= \frac{R[T_1 - T_2] \log\left(\frac{V_2}{V_1}\right)}{RT_1 \log\left(\frac{V_2}{V_1}\right)}$$

$$\eta = 1 - \frac{H_2}{H_1}$$

$$\eta = 1 - \frac{T_2}{T_1}$$

....(viii) 134



Chapter 2: Heat & Thermodynamics

The Carnot's engine is perfectly reversible. It can be operated in the reverse direction also. Then it works as a refrigerator. The heat H_2 is taken from the sink and external work is done on the working substance and heat H_1 is given to the source at a higher temperature.

The isothermal process will take place only when the piston moves very slowly to give enough time for the heat transfer to take place. The adiabatic process will take place when the piston moves extremely fast to avoid heat transfer. Any practical engine cannot satisfy these conditions.

All practical engines have an efficiency less than the Carnot's engine.



Chapter 2: Heat & Thermodynamics

Problem

Imagine a Carnot engine that operates between the temperatures $T_H = 850\text{ K}$ and $T_L = 300\text{ K}$. The engine performs 1200 J of work each cycle, which takes 0.25 s.

- (a) What is the efficiency of this engine?

- (b) What is the average power of this engine?

- (c) How much energy $|Q_H|$ is extracted as heat from the high-temperature reservoir every cycle?

- (e) By how much does the entropy of the working substance change as a result of the energy transferred to it from the high-temperature reservoir? From it to the low-temperature reservoir?



Chapter 2: Heat & Thermodynamics

Solution

$$\varepsilon = 1 - \frac{T_L}{T_H} = 1 - \frac{300 \text{ K}}{850 \text{ K}} = 0.647 \approx 65\%. \text{ (Answer)}$$

$$P = \frac{W}{t} = \frac{1200 \text{ J}}{0.25 \text{ s}} = 4800 \text{ W} = 4.8 \text{ kW}. \text{ (Answer)}$$

$$|Q_H| = \frac{W}{\varepsilon} = \frac{1200 \text{ J}}{0.647} = 1855 \text{ J}. \text{ (Answer)}$$
$$|Q_L| = |Q_H| - W \\ = 1855 \text{ J} - 1200 \text{ J} = 655 \text{ J}. \text{ (Answer)}$$

$$\Delta S_H = \frac{Q_H}{T_H} = \frac{1855 \text{ J}}{850 \text{ K}} = +2.18 \text{ J/K}. \text{ (Answer)}$$

Similarly, for the *negative* transfer of energy Q_L to the low-temperature reservoir at T_L , we have

$$\Delta S_L = \frac{Q_L}{T_L} = \frac{-655 \text{ J}}{300 \text{ K}} = -2.18 \text{ J/K}. \text{ (Answer)}$$

Note that the net entropy change of the working substance for one cycle is zero, as we discussed in deriving Eq. 20-10.



Chapter 2: Heat & Thermodynamics

Entropy

If an irreversible process occurs in a closed system, the entropy S of the system always increases; it never decreases.

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T} \quad (\text{change in entropy defined}).$$

Here Q is the energy transferred as heat to or from the system during the (reversible) process, and T is the temperature of the system in kelvins.



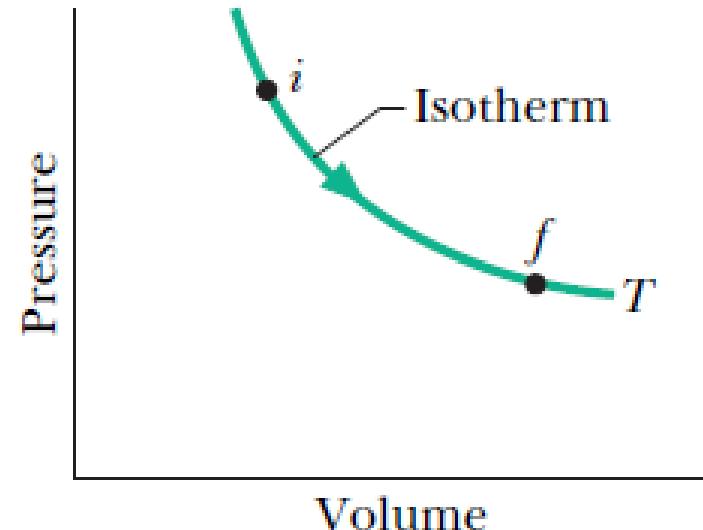
Chapter 2: Heat & Thermodynamics

Entropy of an Isothermal Process

$$\Delta S = S_f - S_i = \frac{1}{T} \int_i^f dQ.$$

$$\int dQ = Q,$$

$$\Delta S = S_f - S_i = \frac{Q}{T} \quad (\text{change in entropy, isothermal process}).$$





Chapter 2: Heat & Thermodynamics

Entropy & 2nd Law of Thermodynamics



Chapter 2: Heat & Thermodynamics

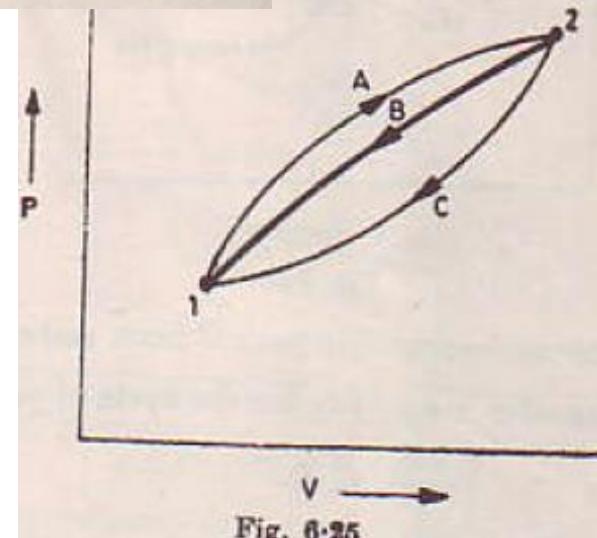
Entropy and 2nd Law of Thermodynamics

Consider a closed system undergoing a reversible process from state 1 to state 2 along the path A and from state 2 to state 1 along the path B (Fig. 6.25). As this is a reversible cyclic process

$$\oint \frac{\delta H}{T} = 0$$

$$\therefore \int_{1A}^{2A} \frac{\delta H}{T} + \int_{2B}^{1B} \frac{\delta H}{T} = 0$$

... (i)





Chapter 2: Heat & Thermodynamics

Now consider the reversible cycle from state 1 to state 2 along the path A and from state 2 to state 1 along the path C .

For this reversible cyclic process

$$\int_{1A}^{2A} \frac{\delta H}{T} + \int_{2C}^{1C} \frac{\delta H}{T} = 0 \quad \dots(iii)$$

From equations (i) and (iii)

$$\int_{2B}^{1B} \frac{\delta H}{T} = \int_{2C}^{1C} \frac{\delta H}{T} \quad \dots(iv)$$



Chapter 2: Heat & Thermodynamics

This shows that $\int \frac{\delta H}{T}$ has the same value for all the reversible paths from state 2 to state 1. The quantity $\int \frac{\delta H}{T}$ is independent of the path and is a function of the end states only, therefore it is a property.

This property is called entropy. Entropy is a thermodynamical property and is defined by the relation

$$dS = \frac{\delta H}{T} \quad \dots(iv)$$

or $S_2 - S_1 = \int_1^2 \frac{\delta H}{T} \quad \dots(v)$

The quantity $S_2 - S_1$ represents the change in entropy of the system when it is changed from state 1 to state 2.



Chapter 2: Heat & Thermodynamics

Change of Entropy in an Irreversible Process



Consider a reversible cycle where the state is changed from 1 to 2 along the path A and 2 to 1 along the path B (Fig. 6.26).

For a reversible cyclic process

$$\oint \delta H = 0$$

$$\therefore \int_{1A}^{2A} \frac{\delta H}{T} + \int_{2B}^{1B} \frac{\delta H}{T} = 0 \quad \dots(i)$$

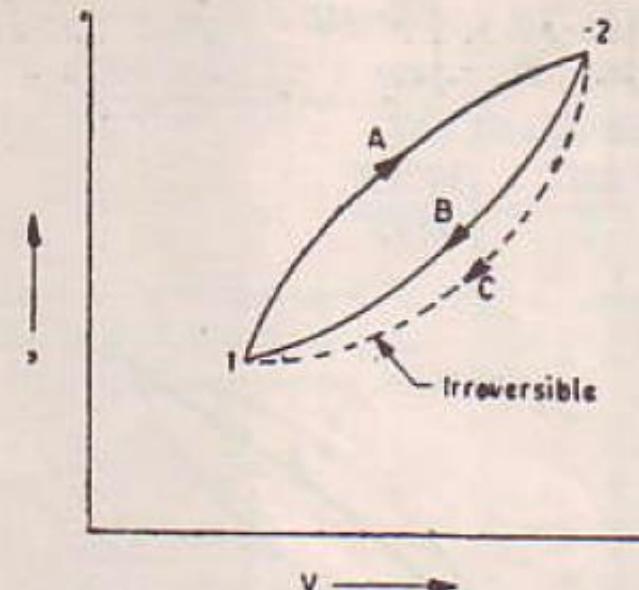


Fig. 6.26



Now consider an irreversible path C from state 2 to state 1.

Applying Clausius inequality for the cycle of processes A and C

$$\int \frac{\delta H}{T} < 0$$

$$\therefore \int_{1A}^{2A} \frac{\delta H}{T} + \int_{2C}^{1C} \frac{\delta H}{T} < 0 \quad \dots(iii)$$

From equations (i) and (ii)

$$\int_{2B}^{1B} \frac{\delta H}{T} - \int_{2C}^{1C} \frac{\delta H}{T} > 0$$

Since path B is reversible and entropy is a property

$$\int_{2B}^{1B} \frac{\delta H}{T} = \int_{2B}^{1B} dS = \int_{2C}^{1C} dS$$

$$\therefore dS > \frac{\delta H}{T} \quad \dots(iv)$$

or $S_2 - S_1 > \int_1^2 \delta H \quad \dots(iv)$



Chapter 2: Heat & Thermodynamics

To conclude,

For a reversible process

$$S_2 - S_1 = \int_1^2 \frac{\delta H}{T}$$

and for an irreversible process

$$S_2 - S_1 > \int_1^2 \frac{\delta H}{T}$$

Equation (4) clearly states that the irreversible process always tends to enhance the entropy of a system.



Chapter 2: Heat & Thermodynamics

Change of Entropy in a Reversible Process



Chapter 2: Heat & Thermodynamics

Consider a complete reversible process [Carnot's cycle] $ABCD A$ (Fig. 6.28). From A to B , heat energy H_1 is absorbed by the work-

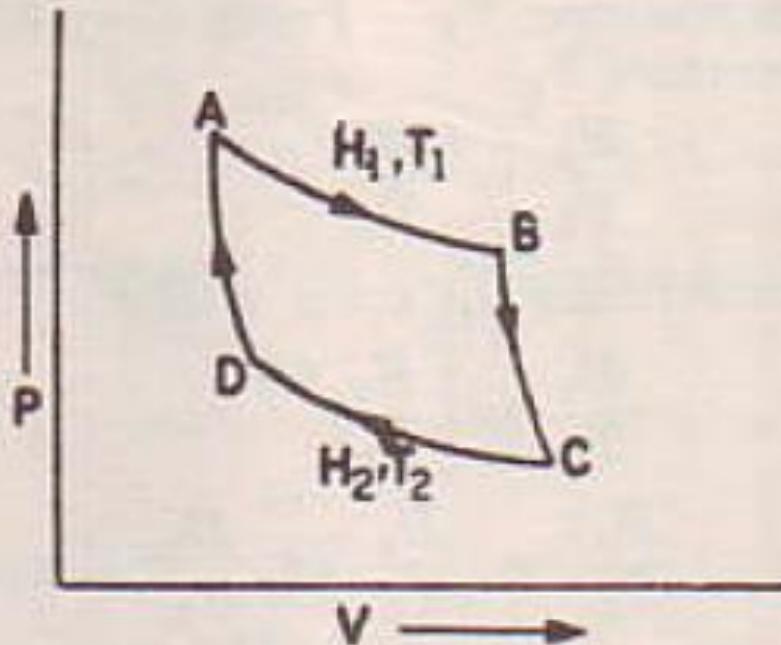


Fig. 6.28



Chapter 2: Heat & Thermodynamics

ing substance at temperature T_1 . The gain in entropy of the working substance from A to $B = H_1/T_1$. (H_1/T_1 is the decrease in entropy of the source from which the amount of heat H_1 is drawn at a temperature T_1). From B to C there is no change in entropy because BC is an adiabatic. From C to D , heat energy H_2 is rejected by the working substance at a temperature T_2 . The loss in entropy of the working substance from C to $D = H_2/T_2$. (H_2/T_2 is also the gain in entropy of the sink to which the amount of heat H_2 is rejected at a temperature T_2). From D to A there is no change in entropy. Thus



Chapter 2: Heat & Thermodynamics

the total gain in entropy by the working substance in the cycle *ABCDA*

$$= \frac{H_1}{T_1} - \frac{H_2}{T_2}$$

But for a complete reversible process

$$\frac{H_1}{T_1} = \frac{H_2}{T_2}$$

Hence the total change in entropy of the working substance in a complete reversible process

$$= \oint dS = \frac{H_1}{T_1} - \frac{H_1}{T_2} = 0.$$



Chapter 2: Heat & Thermodynamics

Maxwell's Thermodynamic Relations



Chapter 2: Heat & Thermodynamics

From the two laws of thermodynamics, Maxwell was able to derive six fundamental thermodynamical relations. The state of a system can be specified by any pair of quantities viz. pressure (P), volume (V), temperature (T) and entropy (S). In solving any thermodynamical problem, the most suitable pair is chosen and the quantities constituting the pair are taken as independent variables.

From the first law of thermodynamics

$$\delta H = dU + \delta W$$

$$\delta H = dU + PdV$$

$$dU = \delta H - PdV$$

or

From the second law of thermodynamics,

$$dS = \frac{\delta H}{T}$$

$$\delta H = TdS$$

or



Chapter 2: Heat & Thermodynamics

Substituting this value of δH in the first equation

$$dU = TdS - PdV \quad \dots(1)$$

Considering S , U and V to be functions of two independent variables x and y [here x and y can be any two variables out of P , V , T and S],

$$dS = \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy$$

$$dU = \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy$$

$$dV = \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy$$



Chapter 2: Heat & Thermodynamics

Substituting these values in equation (i)

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = T \left[\left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy \right] - P \left[\left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy \right]$$

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = \left[T \left(\frac{\partial S}{\partial x}\right)_y - P \left(\frac{\partial V}{\partial x}\right)_y \right] dx + \left[T \left(\frac{\partial S}{\partial y}\right)_x - P \left(\frac{\partial V}{\partial y}\right)_x \right] dy$$

Comparing the coefficients of dx and dy , we get

$$\left(\frac{\partial U}{\partial x}\right)_y = T \left(\frac{\partial S}{\partial x}\right)_y - P \left(\frac{\partial V}{\partial x}\right)_y \quad \dots(ii)$$

$$\left(\frac{\partial U}{\partial y}\right)_x = T \left(\frac{\partial S}{\partial y}\right)_x - P \left(\frac{\partial V}{\partial y}\right)_x \quad \dots(iii)$$



Chapter 2: Heat & Thermodynamics

Differentiating equation (ii) with respect to y and equation (iii) with respect to x

$$\begin{aligned}\frac{\partial^2 U}{\partial y \cdot \partial x} = & \left(\frac{\partial T}{\partial y} \right)_x \left(\frac{\partial S}{\partial x} \right)_y + T \frac{\partial^2 S}{\partial y \partial x} \\ & - \left(\frac{\partial P}{\partial y} \right)_x \left(\frac{\partial V}{\partial x} \right)_y - P \frac{\partial^2 V}{\partial y \partial x}\end{aligned}$$

and

$$\begin{aligned}\frac{\partial^2 U}{\partial x \partial y} = & \left(\frac{\partial T}{\partial x} \right)_y \left(\frac{\partial S}{\partial y} \right)_x + T \frac{\partial^2 S}{\partial x \partial y} \\ & - \left(\frac{\partial P}{\partial x} \right)_y \left(\frac{\partial V}{\partial y} \right)_x - P \frac{\partial^2 V}{\partial x \partial y}\end{aligned}$$

The change in internal energy brought about by changing V and T whether V is changed by dV first and T by dT later or vice versa is the same.



Chapter 2: Heat & Thermodynamics

It means dU is a perfect differential

$$\therefore \frac{\partial^2 U}{\partial x \partial y} = \frac{\partial^2 U}{\partial y \partial x} \text{ and}$$

$$\begin{aligned} & \left(\frac{\partial T}{\partial y} \right)_z \left(\frac{\partial S}{\partial x} \right)_y + T \frac{\partial^2 S}{\partial y \partial x} - \left(\frac{\partial P}{\partial y} \right)_z \left(\frac{\partial V}{\partial x} \right)_y - P \frac{\partial^2 V}{\partial y \partial x} \\ &= \left(\frac{\partial T}{\partial x} \right)_y \left(\frac{\partial S}{\partial y} \right)_x + T \frac{\partial^2 S}{\partial x \partial y} \\ & \quad - \left(\frac{\partial P}{\partial x} \right)_y \left(\frac{\partial V}{\partial y} \right)_z - P \frac{\partial^2 V}{\partial x \partial y} \end{aligned}$$

Simplifying,

$$\begin{aligned} & \left(\frac{\partial T}{\partial y} \right)_z \left(\frac{\partial S}{\partial x} \right)_y - \left(\frac{\partial P}{\partial y} \right)_z \left(\frac{\partial V}{\partial x} \right)_y \\ &= \left(\frac{\partial T}{\partial x} \right)_y \left(\frac{\partial S}{\partial y} \right)_x - \left(\frac{\partial P}{\partial x} \right)_y \left(\frac{\partial V}{\partial y} \right)_z \quad ... (iv) \end{aligned}$$

Here x and y can be any two variables out of P, V, T and S .



Chapter 2: Heat & Thermodynamics

(1) Taking T and V as independent variables and

$$x = T$$

and

$$y = V$$

$$\frac{\partial T}{\partial x} = 1, \quad \frac{\partial V}{\partial y} = 1,$$

$$\frac{\partial T}{\partial y} = 0, \quad \frac{\partial V}{\partial x} = 0$$

Substituting these values in equation (iv)

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \quad \text{...}(v)$$

But

$$dS = \frac{\partial H}{T}$$

$$\therefore \left(\frac{\partial H}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V \quad \text{...}(vi)$$



Chapter 2: Heat & Thermodynamics

(2) Taking T and P as independent variables and

$$x = T$$

and

$$y = P$$

$$\frac{\partial T}{\partial x} = 1, \quad \frac{\partial P}{\partial y} = 1,$$

$$\frac{\partial T}{\partial y} = 0, \quad \frac{\partial P}{\partial x} = 0$$

Substituting these values in equation (iv)

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P \quad | \quad \dots \text{(vii)}$$

or

$$\left(\frac{\partial H}{\partial P} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_P \quad | \quad \dots \text{(viii)}$$



Chapter 2: Heat & Thermodynamics

(3) Taking S and V as independent variables and

$$x = S$$

and

$$y = V$$

$$\frac{\partial S}{\partial x} = 1, \quad \frac{\partial V}{\partial y} = 1$$

$$\frac{\partial S}{\partial y} = 0, \quad \frac{\partial V}{\partial x} = 0$$

Substituting these values in equation (iv)

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V \quad \cancel{\text{Eq}}$$

or

$$\left(\frac{\partial T}{\partial V} \right)_S = -T \left(\frac{\partial P}{\partial H} \right)_V \quad ... (x)$$



Chapter 2: Heat & Thermodynamics

✓ (4) Taking S and P as independent variables and

$$x = S$$

and

$$y = P$$

$$\frac{\partial S}{\partial x} = 1, \quad \frac{\partial P}{\partial y} = 1,$$

$$\frac{\partial S}{\partial y} = 0, \quad \frac{\partial P}{\partial x} = 0$$

Substituting these values in equation (iv)

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P \text{ |||} \quad \dots (xi)$$

or

$$\left(\frac{\partial T}{\partial P} \right)_S = T \left(\frac{\partial V}{\partial H} \right)_P \quad \dots (xi)$$



Chapter 2: Heat & Thermodynamics

(5) Taking P and V as independent variables and

$$x = P \quad \text{and} \quad y = V$$

$$\frac{\partial P}{\partial x} = 1, \frac{\partial V}{\partial y} = 1, \frac{\partial P}{\partial y} = 0, \frac{\partial V}{\partial x} = 0$$

Substituting these values in equation (iv)

$$\left(\frac{\partial T}{\partial P} \right)_V \left(\frac{\partial S}{\partial V} \right)_P - \left(\frac{\partial T}{\partial V} \right)_P \left(\frac{\partial S}{\partial P} \right)_V = 1 \quad \dots \text{(xiii)}$$



Chapter 2: Heat & Thermodynamics

(6) Taking T and S as independent variables and
 $x = T$ and $y = S$

$$\frac{\partial T}{\partial x} = 1, \frac{\partial S}{\partial y} = 1, \frac{\partial T}{\partial y} = 0, \frac{\partial S}{\partial x} = 0$$

Substituting these values in equation (iv)

$$\left(\frac{\partial P}{\partial T} \right)_S \left(\frac{\partial V}{\partial S} \right)_T - \left(\frac{\partial P}{\partial S} \right)_T \left(\frac{\partial V}{\partial T} \right)_S = 1 \quad \dots(iv)$$



Chapter 2: Heat & Thermodynamics

Sample Questions

8. Outline the essential features of the kinetic theory of gases.

9. Derive an expression for the pressure of an ideal gas on the basis of the kinetic theory of gases. Prove that the pressure of a gas is equal to $\frac{2}{3}$ of the translational kinetic energy of the molecules in a unit volume of gas.



Chapter 2: Heat & Thermodynamics

Sample Questions

10. Apply the kinetic theory of gases to account for the simple gas laws.
11. Find an expression for the energy of a gas on the kinetic theory of gases. Give the kinetic interpretation of the temperature.
12. What is meant by mean free path of a gas molecule? Applying the assumptions of the kinetic theory of gases show that the mean free path is equal to $\lambda = \frac{kT}{\sqrt{2.\pi p d^2}}$, where the symbols carry their standard meanings.



Chapter 2: Heat & Thermodynamics

Sample Questions

13. Show that the mean free path of a gas molecule is directly proportional to its absolute temperature, inversely proportional to its pressure, and inversely proportional to its density.
14. Explain the essential features of the Brownian motion.
15. Explain the terms ‘degrees of freedom’ and ‘the law of equipartition of energy’.
16. Applying the kinetic theory of gases, find the ratio of the two specific heats (is given by $1 + \frac{2}{f}$, where f is the degrees of freedom of the gas) for a monatomic, diatomic, and triatomic gases.



Chapter 2: Heat & Thermodynamics

Sample Questions

17. Briefly discuss the considerations which led Van der Waal's to modify the gas equations. Derive the Van der Waal's equation of state and hence find the expressions for the critical constants in terms of Van der Waal's constants a and b .
18. Derive the Van der Waal's equation of state and hence find the expressions for the Van der Waal's constants a and b .
19. What are meant by critical constants of a gas? Calculate the values of these constants.



Chapter 2: Heat & Thermodynamics

Sample Questions

20. Explain the corrections introduced by Van der Waal's in the gas equation. Show that for a gas obeying Van der Waal's equation: $\frac{RT_c}{P_c V_c} = \frac{8}{3}$, where the symbols carry their standard meanings.
21. Derive the adiabatic gas equation: $PV^\gamma = \text{constant}$, where the symbols carry their standard meanings.
22. Define entropy. Write up its physical significance. Show that the entropy of a perfect gas remains constant in a reversible process but increases in an irreversible process.



Chapter 2: Heat & Thermodynamics

Sample Questions

23. Discuss the second law of thermodynamics and the principle of increase of entropy.
24. Define entropy. Show that the change of entropy of a substance in a cyclic process is zero.
25. State and prove Carnot's theorem.
26. Define entropy. State and prove the principle of increase of entropy.



Chapter 2: Heat & Thermodynamics

Sample Questions

25. What is meant by a reversible process? Define the Carnot's theorem, and show that all reversible engines working between the same two temperatures have the same efficiency.
26. State the first law of thermodynamics. Express it mathematically and explain its physical significance.
27. Prove that the efficiency of a Carnot engine using an ideal gas as a working substance is $\eta = \frac{T_1 - T_2}{T_1}$, where the symbols carry their standard meanings.



Chapter 2: Heat & Thermodynamics

Sample Questions

28. State and explain third law of thermodynamics.
29. State and explain the second law of thermodynamics.
30. Define adiabatic, isothermal, isobaric, and isochronic processes.
31. Derive a relation between the volume and temperature for a perfect gas during an adiabatic transformation ($TV^{\gamma-1} = \text{Constant}$).



Chapter 2: Heat & Thermodynamics

Sample Questions

32. For a perfect gas during an adiabatic transformation, derive the relationship between the pressure and temperature ($T^\gamma P^{1-\gamma} = \text{Constant}$).

33. Derive the following Maxwell's thermodynamic relations:

$$(i) \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_P$$

$$(ii) \left(\frac{\partial H}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V$$

$$(iii) \left(\frac{\partial H}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P$$



Chapter 2: Heat & Thermodynamics

Sample Questions

$$(IV) \left(\frac{\partial T}{\partial V} \right)_S = -T \left(\frac{\partial P}{\partial H} \right)_V$$

$$(V) \left(\frac{\partial T}{\partial P} \right)_S = T \left(\frac{\partial V}{\partial H} \right)_P$$

$$(VI) \left(\frac{\partial T}{\partial P} \right)_V \left(\frac{\partial S}{\partial V} \right)_P - \left(\frac{\partial T}{\partial V} \right)_P \left(\frac{\partial S}{\partial P} \right)_V = 1$$

$$(VII) \left(\frac{\partial P}{\partial T} \right)_S \left(\frac{\partial V}{\partial S} \right)_T - \left(\frac{\partial P}{\partial S} \right)_T \left(\frac{\partial V}{\partial T} \right)_S = 1$$



Chapter 2: Heat & Thermodynamics

Home Work

Solve a few problems related to the theory we have studied in this chapter



Thank You for Listening

Physics is hopefully simple but Physicists are not

