HEAT

1. HEAT

The energy that is being transferred between two bodies or between adjacent parts of a body as a result of temperature difference is called heat. Thus, heat is a form of energy. It is energy in transit whenever temperature differences exist. Once it is transferred, it becomes the internal energy of receiving body. If should be clearly understood that the word "heat" is meaningful only as long as the energy is being transferred. Thus, expressions like "heat in a body" or "heat of body" are meaningless.



When we say that a body is heated it means that its molcules begin to move with greater kinetic energy. S.I. unit of heat energy is joule (J). Another common unit of heat energy is calorie (cal).

1.1 Mechanical Equivalent of Heat

In early days heat was not recongnised as a form of energy. Heat was supposed to be something needed to raise the temperature of a body or to change its phase. Calorie was defined as the unit of heat. A number of experimets were performed to show that the temperature may also be increased by doing mechanical work on the system. These experiments established that heat is equivalent to mechanical energy and measured how much mechanical energy is equivalent to a calorie. If mechanical work W produces the same temperature change as heat H, we write,

W = JH

Where J is called mechanical equivalent of heat. J is expressed in joule/calories. The value of J gives how many joules of mechanical work is needed to raise the temperature of 1 g of water by 1°C.

1 calorie : The amount of heat needed to increase the temperature of 1 gm of water from 14.5 to 15.5 °C at one atmospheric pressure is 1 calorie.

1 calorie = 4.186 Joule

1.2 Specific Heat

Specific heat of substances is equal to heat gain or released by that substance to raise or fall its temperature by 1°C for a unit mass of substance.

When a body is heated, it gains heat. On the other hand, heat is lost when the body is cooled. The gain or loss of heat is directly proportional to :

- (a) the mass of the body $\Delta Q \propto m$
- (b) rise or fall of temperature of the body $\Delta Q \propto \Delta T$ $\Delta Q \propto m \Delta T$ or $\Delta Q \propto m s \Delta T$

or $dQ \propto m s dT$ or $Q = m \int s dT$

where s is a constant and is known as the specific heat of the body $s = \frac{Q}{m\Delta T}$. S.I. unit of s is joule/kg-kelvin and C.G.S unit is cal/gm °C

Specific heat of water : s = 4200 J/kg°C = 1000 cal/kg°C = 1 Kcal/kg°C = 1 cal/gm°C Specific heat of steam = half of specific heat of water = specific heat of ice

Important Points :

(a) We know, $s = \frac{Q}{m\Delta T}$, if the substance undergoes the change of state which occurs at constant temperature ($\Delta T = 0$), the $s = Q/0 = \infty$. Thus the specific heat of a substance when it melts or boils at constant temprature is infinite.

(b) If the temperature of the substance changes without the transfer of heat (Q = 0) then $s = \frac{Q}{m\Delta T} = 0$.

Thus when liquid in the thermos flask is shaken, its temperature increases without the tranfer of heat and hence and the specific heat of liquid in the thermos flask is zero.

(c) To raise the temperature of saturated water vapour, heat (Q) is withdrawn. Hence, specific heat of saturated water vapour is negative. (This is for your information only and not in the course)

(d) The slight variation of specific heat of water with temperature is shown in the graph at 1 atmosphere pressure. Its variation is less than 1% over the interval form 0 to 100°C.



1.3 Heat capacity or Thermal capacity :

Heat capacity of a body is defined as the amount of heat required to rasie the temperature of that body by 1°C. If `m' is the mass and `s' the specific heat of the body, then

Heat capaicty = m s.

Units of heat capacity in : CGS system is, cal °C-1; SI unit is, JK-1

1.4 Relation between Specific heat and Water equivalent :

It is the amount of water which requires the same amount of heat for the same temperature rise as that of the object

ms $\Delta T = m_w S_w \Delta T \Rightarrow m_w = \frac{ms}{s_w}$

In calorie $s_w = 1$

 $\therefore m_w = ms$

 m_w is also represented by W so W = ms

2. LAW OF MIXTURE :

When two substances at different temperatures are mixed together, the exchange of heat continues to take place till their temperatues become equal. This tempeature is then called final temperature of mixtue. Here, **Heat taken by one substance = Heat given by another substance**

 $\Rightarrow m_1 s_1 (T_1 - T_m) = m_2 s_2 (T_m - T_2)$



3. PHASE CHANGE :

Heat required for the change of phase or state, $\mathbf{Q} = \mathbf{mL}$, $\mathbf{L} =$ latent heat.

- (a) Latent heat (L): The heat supplied to a substance which changes its state at constant temperature is called latent heat of the body.
- (b) Latent heat of Fusion (L_f) : The heat supplied to a substance which changes it from solid to liquid state at its melting point and 1 atm. pressure is called latent heat of fusion.
- (c) Latent heat of vaporisation (L_v): The heat supplied to a substance which changes it from liquid to vapour state at its boiling point and 1 atm. pressure is called latent heat of vaporization. If in question latent heat of water are not mentioned and to solve the problem it require to assume that we should consider following values.

Latent heat of ice : $L = 80 \text{ cal/gm} = 80 \text{ Kcal/kg} = 4200 \times 80 \text{ J/kg}$ **Latent heat of steam :** $L = 540 \text{ cal/gm} = 540 \text{ Kcal/kg} = 4200 \times 540 \text{ J/kg}$ The given figure, represents the change of state by different lines



HEAT TRANSFER

4. INTRODUCTION

Heat is energy in transit which flows due to temperature difference; from a body at higher temperature to a body at lower temperature. This transfer of heat from one body to the other takes place through three routes.

(i) Conduction (ii) Convection

(iii) Radiation

(a) CONDUCTION

(i) Requires Medium

- (ii) Energy is transmitted from one particle to another particle without displaced of particle
- (iii) No transfer of particle

(b) CONVECTION

- (i) Requires Medium
- (ii) Enegy is transfer through movement of the particle of medium.

(c) RADIATION

- (i) Does not requires any medium
- (ii) Enegy is transfer through Electromagnetic waves.



5. CONDUCTION

Figure shows a rod whose ends are in thermal contact with a hot reservoir at temperature T_1 and a cold reservoir at temperature T_2 . The sides of the rod are covered with insulating medium, so the transport of heat is along the rod, not through the sides. The molecules at the hot reservoir have greater vibrational energy. This energy is transferred by collisions to the atoms at the end face of the rod. These atoms in turn transfer energy to their neighbours further along the rod. Such transfer of heat through a substance in which heat is transported without direct mass transport is called conduction.



Most metals use another, more effective mechanism to conduct heat. The free electrons, which move throughout the metal can rapidly carry energy from the hotter to cooler regions, so metals are generally good donductors of heat. The presence of 'free' electrons also causes most metals to be good electrical conductors. A metal rod at 5°C feels colder than a piece of wood at 5°C because heat can flow more

easily from your hand into the metal.

Heat transfer occurs only between regions that are at different temperatures, and the rate of heat flow is $\frac{dQ}{dt}$. This rate is also called the heat current, denoted by H. Experiments show that the heat current is

proportional to the cross-section area A of the rod and to the temperature gradient $\frac{dT}{dx}$, which is the rate of change of temperature with distance along the bar. In general

$$H = \frac{dQ}{dt} = -kA\frac{dT}{dx}$$

The negative sign is used to make $\frac{dQ}{dt}$ a positive quantity since $\frac{dT}{dt}$ is negative. The constant k, called the thermal conductivity is a measure of the ability of a material to conduct heat.

A substance with a large thermal conductivity k is a good heat conductor. The value of k depends on the temperature, increasing slightly with increasing temperature, but k can be taken to be practically constant throughout a substance if the temperature difference between its ends is not too great.

Let us apply Eq. (i) to a rod of length L and constant cross sectional area A in which a steady state has been reached. In a steady state the temperature at each point is constant in time. Hence.

$$-\frac{\mathrm{d}T}{\mathrm{d}t}=\mathrm{T_1}-\mathrm{T_2}$$

Therefore, the heat ΔQ transferred in time Δt is

$$\Delta Q = kA \left(\frac{T_1 - T_2}{L}\right) \Delta t$$

Here, ΔT = temperature difference (TD) and R = $\frac{l}{kA}$ = thermal resistance of the rod.

• Important Points in conduction

1. Consider a section ab of a rod as shown in figure. Suppose Q_1 heat enters into the section at 'a' and Q_2 leaves at 'b', then $Q_2 < Q_1$. Part of the energy $Q_1 - Q_2$ is utilized in raising the tempeature of section ab and the remaining is lost to atmosphere thorugh ab. If heat is continuously supplied from the left end of the rod, a stage comes when temperature of the section becomes constant. In that case, $Q_1 = Q_2$ if rod is insulated from the surroundings (or loss thorugh ab is zero). This is called the **steady state** condition. Thus, in steady state temperature of different sections of the rod becomes constant (but not same).



 $\begin{array}{l} \mathsf{T}_1 = \mathsf{constant}, \ \mathsf{T}_2 = \mathsf{constant} \ \mathsf{etc.} \\ \mathsf{and} \quad \mathsf{T}_1 > \mathsf{T}_2 > \mathsf{T}_3 > \mathsf{T}_4 \end{array}$

Now, a natural question arises, why the temperature of whole rod not becomes equal when heat is being continuously supplied ? The answer is : there must be a temperature difference in the rod for the heat flow, same as we require a potential difference across a resistance for the current flow thorugh it. In steady state, the temperature varies linearly withd \uparrow_{T}

istance along the rod if it is insluated.

2. Comparing equation number (iii), i.e., heat current



$$H = \frac{dQ}{dt} = \frac{\Delta T}{R} \qquad \qquad \left(\text{where } R = \frac{l}{kA} \right)$$

with the equation, of current flow through a resistance,

$$i = \frac{dq}{dt} = \frac{\Delta V}{R}$$
 (where $R = \frac{l}{\sigma A}$)

We find the following similarities in heat flow through a rod and current flow through a resistance.



From the above table it is evident that flow of heat through rods in series and parallel is analogous to the flow of current through resistances in series and parallel. This analogy is of great importance in solving complicated problems of heat conduction.

RADIATION

6. RADIATION

The process of the transfer of heat from one place to another place without heating the intervening medium is called radiation. The term radiation used here is another word for electromagnetic waves. These waves are formed due to the superposition of electric and magnetic fields perpendicular to each other and carry energy.

Propoerties of Radiation :

(a) All objects emit radiations simply because their temperature is above alsolute zero, and all objects absorb some of the radiation that falls on them from other objects.

(b) Maxwell on the basis of his electromagnetic theory proved that all radiations are electromagnetic waves and their sources are vibrations of charged particles in atoms and molecules.

(c) More radiations are emitted at higher temperature of a body and lesser at lower temperature.

(d) The wavelength corresponding to maximum emission of radiations shifts from longer wavelength to shorter wavelength as the temperature increases. Due to this the colour of a body appears to be changing. Radiations from a body at NTP has predominantly infrared waves.

(e) Thermal radiations travels with the speed of light and move in a straight line.

(f) Radiations are electromagnetic waves and can also travel through vacuum.

(g) Similar to light, thermal radiations can be reflected, refracted, diffracted and polarized.

(h) Radiation from a point source obeys inverse square law (intensity $\alpha \frac{1}{r^2}$)

7. STEFAN-BOLITZMANN'S LAW :

Consider a hot body at temperature T placed in an environment at a lower temperature T_0 . The body emits more radiation than it absorbs and cools down while the surroundings absorb radiation from the body and warm up. The body is losing energy by emitting radiations and this rate.

$$\frac{d\theta}{dt} \propto T^4 , \ \frac{d\theta}{dt} \propto A , \quad \frac{d\theta}{dt} \propto e \implies \frac{d\theta}{dt} = \sigma e A T^4$$

 $P_1 = eA\sigma T^4$

and is receiving energy by absorbing radiations and this absorption rate

$$\frac{d\theta}{dt} = P_2 = aA\sigma T_0^4$$

Here, 'a' is a pure number between 0 and 1 indicating the relative ability of the surface to absorbs radiation from its surroundings. Note that this 'a' is different from the absorptive power 'a'. In thermal equilibrium, both the body and the surrounding have the same temperture (say T_c) and,

$$P_{1} = P_{2}$$

or
$$eA\sigma T_c^4 = aA\sigma T_c^4$$

or e = a

Thus, when $T > T_0$, the net rate of heat transfer from the body to the surroundings is,

Net heat loss =
$$\frac{dQ}{dt} = eA\sigma(T^4 - T_0^4)$$

$$ms\left(\frac{dT}{dt}\right) = eA\sigma(T^4 - T_0^4) \implies Rate of cooling$$

$$\left(-\frac{\mathrm{dT}}{\mathrm{dt}}\right) = \frac{\mathrm{eA\sigma}}{\mathrm{mc}}(\mathrm{T}^{4} - \mathrm{T}_{0}^{4}) \quad \mathrm{or} \quad \frac{\mathrm{dT}}{\mathrm{dt}} \propto (\mathrm{T}^{4} - \mathrm{T}_{0}^{4})$$

8. NEWTON'S LAW OF COOLING

According to this law, if the temperature T of the body is not very different from that of the surroundings

 T_0 , then rate of cooling – $\frac{dT}{dt}$ is proportional to the temperature difference between them. To prove it let us assume that

$$T = T_0 + \Delta t$$

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = \sigma \mathrm{Ae} \left[(\mathrm{T} + \Delta \mathrm{T})^4 - \mathrm{T_0}^4 \right]$$

$$\frac{d\theta}{dt} = \sigma AeT_0^4 \left| 1 + \frac{4\Delta T}{T_0} - 1 \right| = 4\sigma AT_0^3 \Delta T$$

if the temperature difference is small. Thus, rate of colling

$$-\frac{dT}{dt} \propto \Delta T \quad \text{or} -\frac{d\theta}{dt} \propto \Delta \theta$$

as $dT = d\theta \quad \text{or} \quad \Delta T = D\theta$

9. CONCEPT OF AN IDEAL GAS

A gas has no shape and size and can be contained in a vessel of any size or shape. It expands indefinitely and uniformly to fill the available space. It exerts pressure on its surroundings.

The gases whose molecules are point massses (mass without volume) and do not attract each other are called **ideal** or **perfect** gases. It is a hypothetical concept which can't exist in reality. The gases such as hydrogen, oxygen or helium which cannot be liquified easily are called **permanent gases.** An actual gas behaves as ideal gas most closely at low pressure and high temperature.

9.1 Ideal gas Equation

According to this equation.

$$PV = nRT = \frac{m}{M}RT$$

In this equation n = number of moles of the gas = $\frac{m}{M}$

m = total mass of the gas.

- M = molecular mass of the gas
- R = Universal gas constant
- = 8.31 J/mol-K
- = 2.0 cal/mol- K

10. KINETIC THEORY OF GASES

Kinetic Theory of gases is based on the following basic assumptions.

(a) A gas consists of very large number of molecules. These molecules are identical, perfectly elastic and hard spheres. They are so small that the volume of molecules is negligible as compared with the volume of the gas.

(b) Molecules do not have any preferred direction of motion, motion is completely random.

(c) These molecules travel in straight lines and in free motion most of the time. The time of the collision between any two molecules is very small.

(d) The collision between molecules and the wall of the container is perfectly elastic. It means kinetic energy is conserved in each collision.

(e) The path travelled by a molecule between two collisions is called free path and the mean of this distance travelled by a molecule is called mean free path.

(f) The motion of molecules is governed by Newton's law of motion

(g) The effect of gravity on the motion of molecules is negligible.

Note :

At higher temperature and low pressure or at higher temperature and low density, a real gas behaves as an ideal gas.

11. EXPRESSION FOR PRESSURE OF A GAS:

Let us suppose that a gas is enclosed in a cubical box having length ℓ . Let there are 'N' identical molecules, each having mass 'm'. Since the molecules are of same mass and perfectly elastic, so their mutual collisions result in the interchange of velocities only. Only collisions with the walls of the container contribute to the pressure by the gas molecules. Let us focus on a molecule having velocity v₁ and

components of velocity v_{X_1} , v_{y_1} , v_{z_1} along x, y and z-axis as shown in figure.



The change in momentum of the molecule after one collision with wall BCHE

 $= m v_{x_1} - (-m v_{x_1}) = 2 m v_{x_1}.$

The time taken between the successive impacts on the face BCHE = $\frac{\text{distance}}{\text{velocity}} = \frac{2\ell}{v_{x_1}}$

Time rate of change of momentum due to collision = $\frac{\text{change in momentum}}{\text{time taken}} = \frac{2\text{mv}_{x_1}}{2\ell/\text{v}_{x_1}} = \frac{\text{mv}_{x_1}^2}{\ell}$ Hence the net force on the wall BCHE due to the impact of n N molecules of the gas is :

$$\mathsf{F}_{x} = \; \frac{mv_{x_{1}}^{2}}{\ell} \; + \; \frac{mv_{x_{2}}^{2}}{\ell} \; + \; \frac{mv_{x_{3}}^{2}}{\ell} \; + \; \ldots \ldots \\ \frac{mv_{x_{n}}^{2}}{\ell} \; = \; \frac{m}{\ell} \Big(v_{x_{1}}^{2} + v_{x_{2}}^{2} + v_{x_{3}}^{2} + \ldots \\ + v_{x_{n}}^{2} \Big) \; = \; \frac{mN}{\ell} < v_{x}^{2} > \ldots \\ \frac{mv_{x_{n}}^{2}}{\ell} \; = \; \frac{mV_{x_{n}}^{2}}{\ell} \; + \; \frac{mv_{x_{n}}^{2}}{\ell} \; = \; \frac{mV_{x_{n}}^{2}}{\ell} = \; \frac{mV_{x_{n}}^{2}}{\ell}$$

where $\langle v_x^2 \rangle =$ mean square velocity in x-direction. Since molecules do not favour any particular direction therefore $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$. But $\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$ $\Rightarrow \langle v_x^2 \rangle = \frac{\langle v^2 \rangle}{2}$. Pressure is equal to force divided by area. $P = \frac{F_x}{\ell^2} = \frac{M}{3\ell^3} < v^2 > = \frac{M}{3V} < v^2 >$. Pressure is independent of x, y, z directions where l^3 = volume of the container = V M = total mass of the gas, $\langle v^2 \rangle$ = mean square velocity of molecules $\Rightarrow \mathbf{P} = \frac{1}{3}\rho < \mathbf{v}^2 >$ from PV = nRT \therefore n = $\frac{Mass}{Molecular Weight} = \frac{M}{M_0}$ (in kg/mole) $P = \frac{M}{M_0 V} RT = \frac{\rho RT}{M_0} \Rightarrow \frac{\rho RT}{M_0} = \frac{1}{3} \rho V_{rms}^2 \Rightarrow V_{rms} = \sqrt{\frac{3RT}{M_0}}$ $V_{\rm rms} = \sqrt{\frac{3RT}{M_0}} = \sqrt{\frac{3RT}{mN_A}} = \sqrt{\frac{3Kt}{m}}$ $K = Boltzman's const. = \frac{R}{N_A}$

11.1 Co-ordinates of a Gas:

(P, V, T) is the coordinate of the gas

If initial condition of gas is given by $(P_1 V_1 T_1)$ and final condition of gas is given by $(P_2, V_2 T_2)$ such as

 $(\mathsf{P}_1 \mathsf{V}_1 \mathsf{T}_1) \Rightarrow (\mathsf{P}_2 \mathsf{V}_2 \mathsf{T}_2)$

Then (P, V, T) define situation of gas. When a gas changes from one coordinate system to another coordinate system, then we have to follow a process.

12. GAS LAWS

Assuming permanent gases to be ideal, through experiments, it was established that gases irrespective of their nature obey the following laws :

12.1 Boyle's Law

or

or

According to this law, for a given mass of a gas the volume of a gas at constant temperature (called isothermal process) is inversely proportional to its pressure, i.e.,

$$V \propto \frac{1}{P}$$

PV = constant $P_i V_i = P_f V_f$

Thus, P – V graph in an isothermal process is a rectangular hyperbola. Or PV versus P or V graph is a straight line parallel to P or V axis.



(T = constant)

12.2 Charle's Law

According to this law, for a given mass of a gas the volume of a gas at constant pressure (called) **isobaric** process) is directly proportional to its absolute temperature, i.e., $V \propto T$

or

 $\frac{V}{T}$ = constant

 $\frac{V_i}{T_i} = \frac{V_f}{T_f}$

or

Thus, V - T graph in an isobaric process is a straight line passing through origin. Or V/T versus V or T graph is a straight line parallel to V or T axis.



12.3 Gay Lussac's Law or Pressure law

According to this law, for a given mass of a gas the pressure of a gas at constant volume (called **isochoric** process) is directly proportional to its absolute temperature i.e., $P \propto T$

PG

or

or

 $\frac{\mathsf{P}_{\mathsf{i}}}{\mathsf{T}_{\mathsf{i}}} = \frac{\mathsf{P}_{f}}{\mathsf{T}_{f}}$

Thus, P - T graph in an isochoric process is a straight line passing through origin or P/T versus P or T graph is a straight line parallel to P or T axis.



12.4 Avogadro's Law

Two gases at same volume pressure and temperature contain equal amount of moles (mass of gas may be different) or we can say contain equal no. of particle. 1 mole = 6.023×10^{-23} Particles

13. DEGREE OF FREEDOM

Total number of independent co-ordinates which must be known to completely specify the position and configuration of dynamical system is known as "degree of freedom f". Maximum possible translational

degrees of freedom are three i.e. $\left(\frac{1}{2}mV_x^2 + \frac{1}{2}mV_y^2 + \frac{1}{2}mV_z^2\right)$

Maximum possible rotational degrees of freedom are three i.e. $\left(\frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I_z\omega_z^2\right)$

Vibrational degrees of freedom are two i.e. (Kinetic energy. of vibration and Potential energy of vibration) Monoatonic

Eg : (all inrent gases, He, Ar, etc.)

$$f = 3$$
 (translational)
 (V_x, V_y, V_Z)

Diatomic

Eg : (gases like H_2 , N_2 , O_2 etc) (3 translational + 2 rotational) f = 5

$$(V_{x'}, V_{y'}, V_{z}; W_{x}, W_{y'}, W_{z})$$

If temp < 70 K for diatomic molecules, then f = 3 If temp is in between 250 K to 5000 K, then f = 5 If temp is very high (> 5000K) f = 7 [3 translational +2 rotational +2 vibrational] Triatomic

(Non - linear)

 $\underbrace{V_x,V_y,V_z}_{3 \text{ Trans.}} , \underbrace{W_x,W_y,W_z}_{3 \text{ Rotational}}$

If linear (CO₂)

Total D.O.f = 5

 $\underbrace{V_x,V_y,V_z}_{3 \text{ Trans.}} , \underbrace{W_y,W_z}_{2 \text{ Rotational}}$

Maxwell's law of equipartition of energy.

Energy associated with each degree of freedom =
$$\frac{1}{2}$$
 KT.

of one pasticle is same and = $\frac{1}{2}$ KT

If degree of freedom of a molecule is f then

total kinetic energy of that molecule = $\frac{t}{2}$ KT

Monoatomic

Energy of one particle = $\frac{3}{2}$ KT, one mde = $\frac{3}{2}$ RT, n mole = $\frac{3}{2}$ nRT Diatomic

Energy of one Barticle = $\frac{5}{2}$ KT, one mole = $\frac{5}{2}$ RT, n mole = $\frac{5}{2}$ nRT



General Degree of Freedom.

Energy of one particle = $\frac{t}{2}$ KT, one mole = $\frac{t}{2}$ RT, n mole = $\frac{t}{2}$ nRT

Internal energy of a gas only dipends on the temperature of the gas desn't depend on the process taken by the gas to reach the tempreature.

14. INTERNAL ENERGY

The internal energy of a system is the sun of kinetic and potential energies of the molecules of the system. It is denoted by U. Internal energy (U) of the system is the function of its absolute temperature (T) and its volume (V). i.e. U = f(T, V)

In case of an ideal gas, intermolecular force is zero. Hence its potential energy is also zero. In this case, the internal energy is only due to kinetic energy. Which depends on the absolute temperature of the gas.

i.e. U = f(T). For an ideal gas internal energy $U = \frac{f}{2} nRT$.

15. THERMODYNAMICS

Thermodynamics is mainly the study of exchange of heat energy between bodies and conversion of the same into mechanical energy and vice versa.

Thermodynamic System

Collection of an extremely large number of atoms or molecules confined within certain boundaries such that it has a certain value of pressure (P),volume (V) and temperature (T) is called a thermodynamic system. Anything outside the thermodynamic system to which energy or matter is exchanged is called its surroundings. Taking into consideration the interaction between a system and its surroundings thermodynamic system is divided into three classes :

(a) **Open system :** A system is said to be an open system if it can exchange both energy and matter with its surroundings.

(b) Closed system : A system is said to be closed system if it can exchange only energy (not matter with its surrounding

(c) **Isolated system :** A system is said to be isolated if it can neither exchange energy nor matter with its surroundings.

Zeroth law of Thermodynamics :

If two systems (B and C) are separately in thermal equilirbrium with a third one (A), then they the mselves are in thermal equilibrium with each other.



Equation of State (for ideal gases) :

The relation between the thermodynamic variables (P, V, T) of the system is called equation of state. The equation of state for an ideal gas of n moles is given by

Work done by a gas :

Let P and V be the pressure and volume of the gas. If A be the area of the piston. then force exerted by gas on the piston is, $F = P \times A$

Let the piston move through a small distance dx during the expansion of the gas. Work done for a small displacement dx is dW = F dx = PA dx

Since A dx = dV, increase in volume of the gas is dV

 \Rightarrow dW = P dV





or $W = \int dW = \int P dV$

Area enclosed under P-V curve gives work done during process

DIFFERENT TYPES OF PROCESSES

(a) Isothermal Process :

T = constant [Boyle's law applicable] **PV = constant**



There is exchange of heat between system and surroundings. System should be compressed or expanded very slowly so that there is sufficient time for exchange of heat to keep the temperature constant. Slope of P-V curve in isothermal process :

PV = constant = C

 $\Rightarrow \qquad \frac{dP}{dV} = -\frac{P}{V}$

Work done in isothermal process :

$$W = nRT \ln \frac{V_{f}}{V_{i}} \qquad \begin{bmatrix} If \ V_{f} > V_{i} \ then \ W \ is \ positive \\ If \ V_{f} > V_{i} \ then \ W \ is \ negative \\ W = \begin{bmatrix} 2.303 \ nRT \log_{10} \frac{V_{f}}{V_{i}} \end{bmatrix}$$

$$P = \begin{bmatrix} 2.303 \ nRT \log_{10} \frac{V_{f}}{V_{i}} \end{bmatrix}$$

$$P = \begin{bmatrix} V_{f} \ V_{f} \ V_{f} \ V_{f} \end{bmatrix}$$

$$P = \begin{bmatrix} V_{f} \ V_{f} \ V_{f} \ V_{f} \ V_{f} \ V_{f} \end{bmatrix}$$

$$P = \begin{bmatrix} V_{f} \ V_{f}$$

 $U = f(T) \Rightarrow \Delta U = 0$

(b) Iso-Choric Process (Isometric Process) :

 $V = constant \Rightarrow Change in volume is zero$

$$\Rightarrow \quad \frac{P}{T} \text{ is constant}$$
$$\frac{P}{T} = \text{const. (Galussac-law)}$$



$$\Delta Q = n \frac{f}{2} R \Delta T + P[V_f - V_i] = n \frac{f}{2} R \Delta T + nR \Delta T$$

Above expression gives an idea that to increase temperature by ΔT in isobaric process heat required is more than in isochoric process.

(d) Cyclic Process :

In the cyclic process initial and final states are same therefore initial state = final state Work done = Area enclosed under P-V diagram.

Change in internal Energy $\Delta U = 0$ $\Delta Q = \Delta U + \Delta W$

$$\Delta Q = \Delta W$$

If the process on P-V curve is clockwise, then net work done is (+ve) and vice-versa. The graphs shown below explains when work is positive and when it is negative



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16. SPECIFIC HEAT

HEAT

The specific heat capacity of a substance is defined as the heat supplied per unit mass of the substance per unit rise in the temperature. If an amount ΔQ of heat is given to a mass m of the substance and its temperature rises by ΔT , the specific heat capacity s is given by equation

$$s = \frac{\Delta Q}{m\Delta T}$$

The molar heat capacities of a gas are defined as the heat given per mole of the gas per unit rise in the temperature. The molar heat capacity at constant volume, denoted by C_v , is :

$$C_{v} = \left(\frac{\Delta Q}{n\Delta T}\right)_{\text{constant volume}} = \frac{f}{2}R$$

and the molar heat capacity at constant pressure, denoted by C_n is,

$$C_{P} = \left(\frac{\Delta Q}{n\Delta T}\right)_{\text{constant Pressure}} = \left(\frac{f}{2} + 1\right)R$$

where n is the amount of the gas in number of moles and f is degree of freedom. Quite often, the term specific heat capacity or specific heat is used for molar heat capacity. It is advised that the unit be carefully noted to determine the actual meaning. The unit of specific heat capacity is J/kg-K whereas that of molar heat capacity is J/mol-K.

MOLAR HEAT CAPACITY OF IDEAL GAS IN TERMS OF R :

(i) For a monoatomic gas f = 3

$$C_v = \frac{3}{2}R$$
, $C_p = \frac{5}{2}R \Rightarrow \frac{C_p}{C_v} = \gamma = \frac{5}{3} = 1.67$

(ii) For a diatomic gas f = 5

$$C_v = \frac{5}{2}R$$
, $C_p = \frac{7}{2}R$, $\gamma = \frac{C_p}{C_v} = 1$

(iii) For a Triatomic gas f = 6 $C_v = 3R$, $C_p = 4R$

$$\gamma = \frac{C_{P}}{C_{V}} = \frac{4}{3} = 1.33$$

[Note for CO_2 ; f = 5, it is linear] In general if f is the degree of freedom of a molecule, then

$$C_{V} = \frac{f}{2}R$$
, $C_{P} = \left(\frac{f}{2}+1\right)R$, $\gamma = \frac{C_{P}}{C_{V}} = \left[1+\frac{2}{f}\right]$

for any general process C = $\frac{fR}{2} + \frac{work \text{ done by gas}}{n\Delta T}$

ADIABATIC PROCESS

When no heat is supplied or extracted from the system the process is called adiabatic. Process is sudden so that there is no time for exchange of heat. If walls of a container are thermally insulated no heat can cross the boundary of the system and

process is adiabatic.



Equation of adiabatic process is given by

 $PV^{\gamma} = constant$ [Poission law]

dT

>Τ

Ρ

Ρ



T V^{γ -1} = constant

Slope of P-V curve in adiabatic process :

Since PV^γ is constant

 $\therefore \qquad \frac{dp}{dV} = -\gamma \left(\frac{P}{V}\right)$

Slope of P – T – curve in adiabatic process :

Since $T^{\gamma} \ P^{1-\gamma}$ is a constant

$$\therefore \quad \frac{dV}{dT} = - \frac{\gamma}{(1-\gamma)} \frac{P}{T} = \frac{(\gamma)}{(\gamma-1)} \frac{P}{T}$$

Slope of T-V-curve :

 $\frac{\mathrm{dV}}{\mathrm{dT}} = -\frac{1}{(\gamma - 1)}\frac{\mathrm{V}}{\mathrm{T}}$





work done by system is (+ve), if $T_i > T_f$ (hence expansion) work done on the system is (-ve) if $T_i < T_f$ (hence compression)

Reversible and Irreversible Process

A process is said to be reversible when the various stages of an operation in which it is subjected can be traversed the back in the opposite direction in such a way that substance passes through exactly the same conditions at every step in the reverse process as in the direct process.

dV dT

→ T

Comparison of slope of Iso-thermal and Adiabatic Curves







In compression up to same final volume :

$$|W_{adia}| > |W_{isothermal}|$$

In Expansion up to same final volume :

$$W_{isothermal} > W_{adia}$$

Limitations of Ist Law of Thermodynamics :

The first law of thermodynamics tells us that heat and mechanical work are interconvertible. However, this law fails to explain the following points :

- (i) It does not tell us about the direction of transfer of heat.
- (ii) It does not tell us about the conditions under which heat energy is converted into work.
- (iii) It does not tell us whether some process is possible or not.

Mixture of non-reacting gases :

(a) Molecular weight = $\frac{n_1 M_1 + n_2 M_2}{n_1 + n_2}$

 $\rm M_{1}\,\&\,M_{2}$ are molar masses.

(b) Specific heat
$$C_v = \frac{n_1 C_{v_1} + n_2 C_{v_2}}{n_1 + n_2}$$
, $C_P = \frac{n_1 C_{P_1} + n_2 C_{P_2}}{n_1 + n_2}$

(c) for mixture,
$$\gamma = \frac{C_{P_{mix}}}{C_{V_{mix}}} = \frac{n_1 C_{P_1} + n_2 C_{P_2} + \dots}{n_1 C_{V_1} + n_2 C_{V_2} + \dots}$$

(d) Degree of freedom for mixture $f=~\frac{n_1f_1+n_2f_2}{n_1+n_2}$

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SOLVED EXAMPLE

Ex.1 Show that the coefficient of area expansions, $(\Delta A/A)/?T$, of a rectangular sheet of the solid is twice its linear expansivity, α_1 Ans.



Consider a rectangular sheet of the solid material of length a and breadth b When the temperature increases by ?T, a increases by $\Delta a = \alpha_1 a \Delta T$ and b increases by ? $\Delta b = \alpha_1 b \Delta T$. From Fig. 11.8, the increase in area $\Delta A = \Delta A_1 + \Delta A_2 + \Delta A_3$ $\Delta A = a \Delta b + b \Delta a + (\Delta a) (\Delta b)$

= a $\alpha_1 b\Delta T$ + $b\alpha_1 a \Delta T$ + $(\alpha_1)^2 ab (\Delta T)^2$ = $\alpha_1 ab \Delta T (2 + \alpha_1 \Delta T) = \alpha_1 A \Delta T (2 + \alpha_1 \Delta T)$ Since $\alpha_1 \cdot 10^{-5} \text{ K}^{-1}$, the product $\alpha_1 \Delta T$ for fractional temperature is small in comparision with 2 and may be neglected.

Hence,

$$\left(\frac{\Delta A}{A}\right)\frac{1}{\Delta A}\approx 2\alpha_1$$

Ex.2 A blacksmith fixes iron ring on the rim of the wooden wheel of a bullock cart. The diameter of the rim and the iron ring are 5.243 m and 5.231 m respectively at 27 °C. To what temperature should the ring be heated so as to fit the rim of the wheel?

Ans. Given, $T_1 = 27^{\circ}C$ $L_{T1} = 5.231 \text{ m}$ $L_{T2} = 5.243 \text{ m}$ So, $L_{T2} = L_{T1} [1 + \alpha_1 (T_2 - T_1)]$ 5.243 m = 5.231 m $[1 + 1.20 \times 10^{-5} \text{ K}^{-1} (T_2 - 27^{\circ}\text{C})]$ or $T_2 = 218^{\circ}\text{C}$.

Ex.3 A sphere of aluminium of 0.047 kg placed for sufficient time in a vessel containing boiling water, so that the sphere is at 100°C. It is then immediately transfered to 0.14 kg copper calorimeter containing 0.25 kg of water at 20°C. Thetemperature of water rises and attains a steady state at 23°C. Calculate the specific heat capacity of aluminium.

Ans. In solving this example we shall use the fact that at a steady state, heat given by an aluminium sphere will be equal to the heat absorbed by the water

and calorimeter. Mass of aluminium sphere (m₁) = 0.047 kg Initial temp. of aluminium sphere = 100°C Final temp. = 23°C Change in temp (Δ T) = (100°C - 23°C) = 77°CLet specific heat capacity of aluminium be S_{AI}. The amount of heat lost by the aluminiumsphere =m₁s_{AI} Δ T = 0.047kg × S_{AI} × 77°C

Mass of water $(m_2) = 0.25 \text{ kg}$

Mass of calorimeter $(m_3) = 0.14 \text{ kg}$ Initial temp. of water and calorimeter = 20°C Final temp. of the mixture = 23°C Change in temp.

$$(\Delta T_2) = 23^{\circ}C - 20^{\circ}C = 3^{\circ}C$$

Specific heat capacity of water (s_w) = 4.18 × 10³ J kg⁻¹ K⁻¹

Specific heat capacity of copper calorimeter = 0.386×10^3 J kg⁻¹ K⁻¹

The amount of heat gained by water and calorimeter

 $= m_2 \operatorname{sw} \Delta T_2 + m_3 S_{Cu} \Delta T_2$ $= (m_2 + m_2) (\Delta T_2)$

$$= 0.25 \text{ kg} \times 4.18 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1} + 0.14 \text{ kg} \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1} \text{ K}^{-1} + 0.14 \text{ kg} \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1} + 0.14 \text{ kg} \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1} \text{ K}^{-1$$

 0.386×10^3 J kg⁻¹ K⁻¹) (23°C – 20°C) state heat lost by the aluminiumsphere = heat gained by water + heat gained by calorimeter.

So, 0.047 kg \times S_{AI} \times 77°C

= $(0.25 \text{ kg} \times 4.18 \times 10^3 \text{ J} \text{ kg}^{-1} \text{ K}^{-1} + 0.14 \text{ kg} \times 0.386 \times 10^3 \text{ J} \text{ kg}^{-1} \text{ K}^{-1})(3^{\circ}\text{C}) \text{ s}_{\text{Al}} = 0.911 \text{ kJ} \text{ kg}^{-1} \text{ K}^{-1}$

Ex.4 When 0.15 kg of ice of 0°C mixed with 0.30 kg of water at 50°C in a container, the resulting temperature is 6.7°C. Calculate the heat of fusion of ice. ($S_{water} = 4186 J kg^{-1} K^{-1}$)

Ans. Heat lost by water = MS_w $(\theta_f - \theta_i)_w$

= $(0.30 \text{ kg}) (4186 \text{ J kg}^{-1} \text{ K}^{-1}) (50.0^{\circ}\text{C} - 6.7^{\circ}\text{C})$ = 54376.14 J

Heat required to melt ice = $m_2Lf = (0.15 \text{ kg}) Lf$ Heat required to raise temperature of ice water to final temperature = mIS_w ($\theta_f - \theta_i$)I

= (0.15 kg) ($4186 \text{ J} \text{ kg}^{-1} \text{ K}^{-1}$) ($6.7^{\circ}\text{C} - 0^{\circ}\text{C}$) = 4206.93 JHeat lost = heat gained 54376.14 J = (0.15 kg) Lf + 4206.93 J $L_{\epsilon} = 3.34 \times 10^{5} \text{ J} \text{ kg}^{-1}$.

Ex.5 Calculate the heat required to convert 3 kg of ice at -12 °C kept in a calorimeter to steam at 100 °C at atmospheric pressure. Given specific heat capacity of ice = 2100 J kg-1 K-1, specific heat capacity of water = 4186 J kg-1 K-1, latent heat of fusion of ice = 3.35×105 J kg⁻¹ and latent heat of steam = 2.256×106 J kg⁻¹.

Ans. We have Mass of the ice, m = 3 kg specific heat capacity of ice, s_{ice} = 2100 J kg⁻¹ K⁻¹

= 2100 J kg⁻¹ K⁻¹ specific heat capacity of water, s_{water} = 4186 J kg⁻¹ K⁻¹

latent heat of fusion of ice, L_{fice} = 3.35 × 10⁵ J kg⁻¹ latent heat of steam, Lsteam $= 2.256 \times 10^{6} \text{ J kg}^{-1}$ Now, Q = heat required to convert 3 kg of ice at -12 °C to steam at 100 °C, Q_1 = heat required to convert ice at -12 °C to ice at 0°C. = m sice ΔT_1 = (3 kg) (2100 J kg⁻¹.K⁻¹) $[0-(-12)]^{\circ}C = 75600 J$ Q_2 = heat required to melt ice at 0°C to water at 0°C = m Lf ice = (3 kg) (3.35 \times 10⁵ J kg) = 1005000 J Q_3 = heat required to convert water at 0 °C to water at 100 °C. $= mS_{w}$ $\Delta T_2 = (3kg) (4186J kg^{-1} K^{-1}) (100°C) = 1255800 J$ Q_a = heat required to convert water at 100 °C to steam at 100°C. = m Lsteam = (3 kg) (2.256 × 106 J/kg⁻¹) = 6768000 J So, $Q = Q_1 + Q_2 + Q_3 + Q_4 = 75600J + 1005000 J$ + 1255800 J + 6768000 J = 9.1×106 J

Ex.6 What is the temperature of the steel-copper junction in the steady state of the system shown in Fig. 11.15. Length of the steel rod = 15.0 cm, length of the copper rod = 10.0 cm, temperature of the furnace = 300°C, temperature of the other end = 0°C. The area of cross section of the steel rod is twice that of the copper rod. (Thermal conductivity of steel = 50.2 J s⁻¹ m⁻¹K⁻¹; and of copper = 385 J s⁻¹m⁻¹K⁻¹).



Ans. The insulating material around the rods reduces heat loss from the sides of the rods. Therefore, heat flows only along the length of the rods. Consider any cross section of the rod. In the steady state, heat flowing into the element must equal the heat flowing out of it; otherwise there would be a net gain or loss of heat by the element and its temperature would not be steady. Thus in the steady state, rate of heat flowing across a cross section of the rod is the same at every point along the length of the combined steel-copper rod. Let T be thetemperature of the steel-copper junction in the steady state. Then,

$$\frac{K_1 A_1(300 T)}{L_1} = \frac{K_2 A_2(T-0)}{L_2}$$

where 1 and 2 refer to the steel and copper rod respectively. For $A_1 = 2 A_2$, $L_1 = 15.0 \text{ cm}$, $L_2 = 10.0 \text{ cm}$, $K_1 = 50.2 \text{ J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$, $K_2 = 385 \text{ J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$, we have $\frac{50.2 \times 2(300 - \text{T})}{15} = \frac{385\text{T}}{10}$ which gives T = 44.4°C

Ex.7 The density of water is 1000 kg m-3. The density of water vapour at 100 °C and 1 atm pressure is 0.6 kg m-3. The volume of a molecule multiplied by the total number gives ,what is called, molecular volume. Estimate the ratio (or fraction) of the molecular volume to the total volume occupied by the water vapour under the above conditions of temperature and pressure.

Ans. For a given mass of water molecules, the density is less if volume is large. So the volume of the vapour is $1000/0.6 = /(6 \times 10^{-4})$ times larger. If densities of bulk water and water molecules are same, then the fraction of molecular volume to the total volume in liquid state is 1. As volume in vapour state has increased, the fractional volume is less by the same amount, i.e. 6×10^{-4} .??

Ex.8 Estimate the volume of a water molecule using the data in Example 13.1.

Ans. In the liquid (or solid) phase, the molecules of water are quite closely packed. The density of water molecule may therefore, be regarded as roughly equal to the density of bulk water = 1000 kg m-3. To estimate the volume of a water molecule, we need to know the mass of a single water molecule. We know that 1 mole of water has a mass approximately equal to (2 + 16)g = 18 g = 0.018 kg. Since 1 mole contains about 6×10^{23} molecules (Avogadro's number), the mass of a molecule of water is $(0.018)/(6 \times 10^{23}) \text{ kg} = 3 \times 10^{-26} \text{ kg}$. Therefore, a rough estimate of the volume of a water molecule is as follows :

Volume of a water molecule

= $(3 \times 10^{-26} \text{ kg})/(1000 \text{ kg m}^{-3})$ = $3 \times 10^{-29} \text{ m3} = (4/3)$? (Radius)3 Hence, Radius ? $2 \times 10^{-10} \text{ m} = 2 \text{ Å}$??

Ex.9 What is the average distance between atoms (interatomic distance) in water? Use the data given in Examples 13.1 and 13.2.

Ans. A given mass of water in vapour state has 1.67 \times 10³ times the volume of the same mass of water in liquid state (Ex. 13.1). This is also the increase in the amount of volume available for each molecule of water. When volume increases by 103 times the radius increases by V₁/3 or 10 times, i.e., 10 \times 2 Å = 20 Å. So the average distance is 2 \times 20 = 40 Å.

Ex.10 A vessel contains two nonreactive gases : neon (monatomic) and oxygen (diatomic). The ratio of their partial pressures is 3:2. Estimate the ratio of (i) number of molecules and (ii) mass density of neon and oxygen in the vessel. Atomic mass of Ne = 20.2 u, molecular mass of $Q_{i} = 22.0 u$

$O_2 = 32.0 u.$

Ans. Partial pressure of a gas in a mixture is the pressure it would have for the same volume and temperature if it alone occupied the vessel. (The total pressure of a mixture of non-reactive gases is the sum of partial pressures due to its constituent gases.) Each gas (assumed ideal) obeys the gas law. Since V and T are common to the two gases, we have

 $P_1V = \mu_1 \text{ RT} \text{ and } P_2V = \mu_2 \text{ RT}, \text{ i.e. } (P_1/P_2) = (\upsilon_1 / \upsilon_2).$ Here

1 and 2 refer to neon and oxygen respectively. Since $(P_1/P_2) = (3/2)$ (given), $(\upsilon_1/\upsilon_2) = 3/2$.

(i) By definition $\upsilon_1 = (N_1/N_A)$ and $\upsilon_2 = (N_2/N_A)$ where N_1 and N_2 are the number of molecules of 1 and 2, and N_A is the Avogadro's number. Therefore,

 $(N_1/N_2) = (v_1 / v_2) = 3/2.$

(ii) We can also write $\mu_1 = (m_1/M_1)$ and $\upsilon_2 = (m_2/M_2)$ where m_1 and m_2 are the masses of 1 and 2; and M_1 and M_2 are their molecular masses. (Both m_1 and M_1 ; as well as m_2 and M_2 should be expressed in the same units). If υ_1 and υ_2 are the mass densities of 1 and 2 respectively, we have

$$\frac{1}{2}\frac{m_1/V}{m_2/V} = \frac{m_1}{m_2} = \frac{\mu_1}{\mu_2} \times \frac{M_1}{M_2} \quad \frac{3}{2} = \frac{20.2}{32.0} = 0.947$$

Ex.11 A flask contains argon and chlorine in the ratio of 2:1 by mass. The temperature of the mixture is 27 °C. Obtain the ratio of

(i) average kinetic energy per molecule, and (ii) root mean square speed vrms of the molecules of the two gases. Atomic mass of argon = 39.9 u; Molecular mass of chlorine = 70.9 u.

Ans. The important point to remember is that the average kinetic energy (per molecule) of any (ideal) gas (be it monatomic like argon, diatomic like chlorine or polyatomic) is always equal to $(3/2) k_{\rm B}T$. It depends only on temperature, and is independent of the nature of the gas.

(i) Since argon and chlorine both have the same temperature in the flask, the ratio of average kinetic energy (per molecule) of the two gases is 1 : 1.

(ii) Now $\frac{1}{2}$ m V²rms² = average kinetic energy per molecule = (3/2)) k_BT where m is the mass of a molecule of the gas. Therefore,

$$\frac{\mathbf{v}_{\rm rms}^2}{\mathbf{v}_{\rm rms}^2} = \frac{m_{\rm Cl}}{m_{\rm Ar}} = \frac{M_{\rm Cl}}{M_{\rm Ar}} = \frac{70.9}{39.9} = 1.77$$

where M denotes the molecular mass of the gas. (For argon, a molecule is just an atom of argon.) Taking square root of both sides,

$$\frac{\mathbf{v}_{rms}}{\mathbf{v}_{rms}} = 1.33$$

*Ex.*12 Uranium has two isotopes of masses 235 and 238 units. If both are present in Uranium hexafluoride gas which would have the larger average speed ? If atomic mass of fluorine is 19 units, estimate the percentage difference in speeds at any temperature.

Ans. At a fixed temperature the average energy

= $\frac{1}{2}$ m < v² > is constant. So smaller the mass of the molecule, faster will be the speed. The ratio of speeds is inversely proportional to the square root of the ratio of the masses. The masses are 349 and 352 units. So

v349 / v352 = (352/ 349)^{1/2} = 1.0044 . Hence difference $\frac{dv}{v} = 0.44$ %.

Ex.13 (a) When a molecule (or an elastic ball) hits a (massive) wall, it rebounds with the same speed. When a ball hits a massive bat held firmly, the same thing happens. However, when the bat is moving towards the ball, the ball rebounds with a different speed. Does the ball move faster or slower? (Ch.6 will refresh your memory on elastic collisions.)

(b) When gas in a cylinder is compressed by pushing in a piston, its temperature rises. Guess at an explanation of this in terms of kinetic theory using (a) above. (c) What happens when a compressed gas pushes a piston out and expands. What would you observe ?

(d) Sachin Tendulkar uses a heavy cricket bat while playing. Does it help him in anyway ?

Ans. (a) Let the speed of the ball be u relative to the wicket behind the bat. If the bat is moving towards the ball with a speed V relative to the wicket, then the relative speed of the ball to bat is V + u towards the bat. When the ball rebounds (after hitting the massive bat) its speed, relative to bat, is V + u moving away from the bat. So relative to the wicket the speed of the rebounding ball is V + (V + u) = 2V + u, moving away from the wicket. So the ball speeds up after the collision with the bat. The rebound speed will be less than u if the bat is not massive. For amolecule this would imply an increase in temperature. You should be able to answer (b) (c) and (d) based on the answer to (a). (Hint: Note the correspondence, piston bat, cylinder wicket, molecule ball.)

Exercise - I

UNSOLVED PROBLEMS

Q.1 A 'thermacole' icebox is a cheap and efficient method for storing small quantities of cooked food in summer in particular. A cubical icebox of side 30 cm has a thickness of 5.0 cm. If 4.0 kg of ice is put in the box, estimate the amount of ice remaining after 6 h. The outside temperature is 45 oC, and co-efficient of thermal conductivity of thermacole is

 $0.01 \,\mathrm{J\,s^{-1}\,m^{-1}\,0}C^{-1}$.

[Heat of fusion of water = $335 \times 103 \text{ J kg}^{-1}$].

Q.2 A brass boiler has a base area of 0.15 m² and thickness 1.0 cm. It boils water at the rate of 6.0 kg/ min when placed on a gas stove. Estimate the temperature of the part of the flame in contact with the boiler. Thermal conductivity of brass = $109 \text{ J s}^{-1} \text{ m}^{-1} \text{ o} \text{ C}^{-1}$.

[Heat of vaporization of water = $2256 \times 10^3 \text{ J kg}^{-1}$].

Q.3 Estimate the temperature of the surface of the Sun from the following data :

average radius of the earth's orbit = 1.5×10^8 km, average radius of the Sun = 7.0×10^5 km, solar radiant power on the earth at noontime = 1400 W m⁻²

Assume the Sun to be a perfect black body. Will your estimate be greater of less than the actual surface temperature of the Sun ? Explain.

Q.4 Explain why :

(a) a body with large reflectivity is a poor emitter

(b) a brass tumbler feels much colder that a wooden tray on a chilly day

(c) an optical pyrometer (for measuring high temperatures) calibrated for an ideal black body radiation gives too low a value for the temperature of a red hot iron piece in the open, but gives a correct value for the temperature when the same piece is in the furnace

(d) the earth without its atmosphere would be inhospitably cold

(e) heating systems based on circulation of steam are more efficient in warming a building than those based on circulation of hot water

Q.5 A body cools from 80 $^{\circ}$ C to 50 $^{\circ}$ C in 5 minutes. Calculate the time it takes to cool from 60 $^{\circ}$ C to 30 $^{\circ}$ C. The temperature of the surroundings is 20 $^{\circ}$ C.

Q.6 The triple points of neon and carbon dioxide are 24.57 K and 216.55 K respectively Express these temperatures on the Celsius and Fahrenheit scales.

Q.2 A constant volume gas themometer using helium records a pressure of 20.0 kPa at the triple-point of water, and pressure of 14.3 kPa at the temperature of 'dry ice' (solid CO^2). What is the temperature of 'dry ice'?

Q.3 Two absolute scale *A* and *B* have triple points of water defined ot be 200 A and 350 B. What is the relation betwwen T_{A} and T_{B} ?

Q.4 The electrical resistance in ohms of acertain thermometer varies with temperature according to the approximate law : $R = R_0 [1 + 5 \times 10^{-3} (T - T_0)]$ The resistance is 101.6 W at the triple-point of water, and 165.5 W at the normalmelting point of lead (600.5 K). What is the temperature when the resistance is 123.4 W?

Q.5 Answer the following :

(a) The trople- point of water is a standard fixed point in modern thermometry. Why ? What is wrong intaking the melting point of ice and the boiling point of water as standard fixed points (as was originally done inthe Celsius scale)?

(b) There were two fixed point in the original Celsius scale as mentioned above which were *assigned* the number 0 $^{\circ}$ C and 100 $^{\circ}$ C respectively. On the absolute scale, one of the fixed points is the triple point of water, which on the kelvin absolute scale is assigned the number 273.16 K. What is the other fixed point on this (Kelvin) scale ?

(c) The absolute temperature (Kelvin scale) T is related to the temperature $t_{\rm c}$ on the Celsius scale by

 $t_{\rm C} = T - 273.15$

Why do we have 273.15 in this relation, and not 273.16 (d) What is thetemperature of the triple-point of water on an absolute scale whose unit interval size is equal to that of Fahrenheit scale ?

Q.6 Two ideal gas thermometers *A* and *B* use oxygen and hydrogen respectively. The following observations are made :

(a) What is the absolute temperature of normal melting point of sulphur as read by thermometers *A* and *B* ?

(b) What do you think is the reason for the slightly different answers from *A* and *B*? (The

thermometers are not faulty). What further procedure is needed in the experiment to reduce the discrepancy between the two readings?

Q.7 A steel tape 1 m long is correctly calibrated for a temperature of 27.0 °C. The length of a steel rod measured by this tape is found to be 63.0 cm on a hot day when the temperature is 45.0 °C. What is the actual length of the steel rod on that day ? What is the length of the same steel rod on a day when the temperature is 27.0 °C ? Coefficient of linear expansion of steel = 1.20×10^{-5} °C⁻¹.

Q.8 A hole is drilled in a copper sheet. The diameter of the hole is 4.24 cm at 27.0 $^{\circ}$ C. What is the change in the diameter of the hole when the sheet is heated to 227 $^{\circ}$ C? Coefficient of linear expansion of copper =1.77 x 10⁻⁵ $^{\circ}$ C⁻¹.

Q.9 A brass wire 1.8 m long at 27 O C is held taut with little tension between two rigid supports. If the wire is cooled to a temperature of -39 O C, what is the tension developed in the wire, if its diameter is 2.0 mm? Co - efficient of linear expansion of brass = 2.0 x 10 $^{-5}$ O C⁻¹; Young's modulus of brass = 0.91 x 10 11 Pa.

Q.10 A brass or d of length 50 cm and diameter 3.0 mm is joined to a steel rod of the same length and diameter. What is the change in length of the combined rod at 250 $^{\circ}$ C, if the original lengths are at 40.0 $^{\circ}$ C? Is there a 'thermal stress' developed at the junction ? The ends of the rod are free to expand (Co-efficient of linear expansion of brass = 2.0 x 10-5 $^{\circ}$ C⁻¹, steel = 1.2 x 10⁻⁵ $^{\circ}$ C⁻¹).

Q.11 The coefficient of volume expansion of glycerin is $49 \times 10^{-5} {}^{\circ}C^{-1}$. What is the fractional change in its density for a 30 ${}^{\circ}C$ rise in temperature ?

Q.12 A 10 kW drilling machine is used to drill a bore in a small aluminium block of mass 8.0 kg. How much is the rise in temperature of the block in 2.5 minutes, assuming 50% of power is used up in heating the machine itself or lost to the surroundings. Specific heat of aluminium = $0.91 \text{ Jg}^{-1} \text{ C}^{-1}$.

Q.13 A copper block of mass 2.5 kg is heated in a furnace to a temperature of 500 ^OC and then placed on a large ice block. What is the maximum amount of ice the can melt ?

(Specific heat of copper = $0.39 \text{ Jg}^{-10} \text{ C}^{-1}$; heat of fusion of water = 335 Jg^{-1}).

Q.14 In an experiment on the specific heat of a metal, a 0.20 kg block of the metal at 150 $^{\circ}$ C is dropped in a copper calorimeter (of water equivalent 0.025 kg) containing 150 cm³ of water at 27 $^{\circ}$ C. The final temperature is 40 $^{\circ}$ C. Compute the specific heat of the metal. If heat losses to the surroundings are not negligible, is your answer greater of smaller than the actual value for specific heat of the metal ? **Q.15** A geyser heats water flowing at the rate of 3.0 liters per minute from 27 $^{\circ}$ C to 77 $^{\circ}$ C. If the geyser operates on a gas burner, what is the rate of consumption of the fuel is its heat of combustion is 4.0 x 104 J/g ?

Q.16 In an experiment, the specific heats of some inert gases (at ordinary temperatures are measured to be as follows :

Try to discover a regularity in the data and explain it on the basis of kinetic theory.

Q.17 Given below are observations on molar specific heats at room temperature of some common gases. The measured molar specific heats of these gases are markedly different from those for monatomic gases. [Typically, molar specific heat of a monatomic gas is 2.92 cal/mol K, as you must have worked out in 12.16.] Explain this difference. What can you infer from the somewhat larger (then the rest) value for chlorine ?

Q.18 The molar specific heat of hydrogen (H_2) is about (5/2) *R* in the temperature range of about 250 K to 750 K. At lower temperatures, molar specific heat of hydrogen decreases to the value typical of monatomic gases: (3/2) *R*. At higher temperatures, it tends to the value (7/2) *R*. What do you think is happening ?

Q.19 What amount of heat must be supplied to 2.0 x 10^{-2} kg of nitrogen (at room temperature) to raise its temperature by 45 $^{\circ}$ C at constant pressure ?(Molecular mass of N₂ = 28; R = 8.3 J mol⁻¹ K⁻¹.)

Q.20 Answer the following questions bases on the P-T phase diagram of carbon dioxide [Fig. 12.11 (b)] :

(a) At what temperature and pressure can the solid, liquid and vapour phases of CO₂ co-exist in equilib rium?

(b) What is the effect of decrease of pressure on the fusion and boiling point of CO_2 ?

(c) What are the critical temperature and pressure for CO_2 ? What is their significance?

(d) Is CO₂ solid, liquid or gas at (a) -70 $^{\circ}$ C under 1 atm, (b) -60 $^{\circ}$ C under 10 atm, (c) 15 $^{\circ}$ C under 56 atm ?

Q.21 Answer the following questions based on the P-T phase diagram of CO₂ [Fig. 12.11 (b)] :

(a) CO_2 at 1 atm pressure and temperature -60 $^{\circ}C$ is compressed isothermally. Does it go through a liquid phase ?

(b) What happens when CO^2 at 4 atm pressure is cooled from room temperature at constant pres sure (c) Describe qualitatively the changes in a give mass of solid CO_2 at 10 atm pressure and tempera ture -65 °C as it is heated up to room temperature at constant pressure.

(d) CO^2 is heated to a temperature 70 $^{\circ}C$ and

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compressed isothermally. What changes in its proper ties do you expect to observe ?

Q.22 A fat man is used to consuming about 3000 kcal worth of food everyday. His food contains 50 g of butter plus a plate of sweets everyday, besides items which proved him with other nutrients (proteins, vitamins, minerals, etc) in addition to fats and carbohydrates. The caloric value of 10 g of butter is 60 kcal and that of a plate of sweets is averagely 700 kcal. What dietary strategy should be adopt to cut down his calories to about 2100 kcal per day ? Assume the man cannot resist eating the full plate of sweets once it is offered to him !

Q.23 A child running a temperature of 101 O F is given an antipyrin (i.e. a medicine that lowers fever) which causes an increase in the rate of evaporation of sweat from his body. If the fever is brought down to 98 O F in 20 min, what is the average rate of extra evaporation causes, by the drug. Assume the evaporation mechanism to be the only way by which heat is lost. The mass of the child is 30 kg. The specific heat of human body is approximately the same as that of water, and latent heat of evaporation of water at that temperature is about 580 cal g⁻¹.

Q.24 What is the relative humidity on a day in July in Mumbai when the partial pressure of water vapour is 0.013×10^5 Pa and the temperature is $15 {}^{\rm O}$ C? The vapour pressure of water at this temperature is 0.0169×10^5 Pa.

Q.25 Answer the following questions:

(a) A vessel with a movable piston maintained at a constant temperature by a thermostat contains a certain amount of liquid in equilibrium with its vapour. Does this vapour obey Boyle's law ? In other words, what happens when the volume of vapour is decreases ? Does the vapour pressure increase ?

(b) What is meat by 'superheated water' and 'supercooled vapour'? Do these states of water lie on its *P-V-T* surface? Give some practical applications of these state of water.

Q.26 Explain why

(a) Two bodies at different temperature T_1 and T_2 if brought in thermal contact do not necessarily settle to the mean temperature $(T_1 + T_2)/2$. (b) The coolant in a chemical or a nuclear plant (i.e.

(b) The coolant in a chemical or a nuclear plant (i.e. the liquid used to prevent the different parts of a plant from getting too hot) should have high specific heat.

(c) Air pressure in a car tyre increases during driving.(d) The climate of a harbour town is more temperate than that of town in a desert at the same latitude.

Q.27 A cylinder with a movable piston contains 3 moles of hydrogen at standard temperature and pressure. The walls of the cylinder are made of a heat insulator, and the piston is insulated by having a pile of sand on it. By what factor does the pressure of the gas increase if the gas is compressed to half its original volume?

Q.28 In changing the state of a gas *adiabatically* from an equilibrium state *A* to another equilibrium state *B*, an amount of work equal to 22.3 J is done on the system. If the gas is take from state *A* to *B* via a process in which the net heat absorbed by the system is 9.35 cal, how much is the net work done by the system in the latter case ? (Take 1 cal = 4.19 J)

Q.29 Two cylinders *A* and *B* of equal capacity are connected to each other via a stopcock. *A* contains a gas at standard temperature and pressure. *B* is completely evacuated. The entire system is thermally insulated. The stopcock is suddenly opened. Answer the following :

(a) What is the final pressure of the gas in A and B

(b) What is the change in internal energy of the gas?

(c) What the change in the temperature of the gas
(d) Do the intermediate states of the system (before settling to the final equilibrium state) lie on its *P-V-T* surface ?

Q.1 Estimate the fraction of molecular volume to the actual volume occupied by oxygen gas at STP. Take the radius of an oxygen molecule to be roughly 3 Å.

Q.2 Molar volume is the volume occupied by 1 mol of any (ideal) gas at standard temperature and pressure (STP : 1 atmosphere pressure, 0 °C). show that it is 224. litres.

Q.3 Figure shows plot of PV/T versus P for

 $1.00~\times~10^{-3}$ kg of oxygen gas at two different temperatures.

(a) What does the dotted plot signify ?]

(b) Which is true : $T_1 > T_2$ or $T_1 < T_2$?

(c) What is the value of PV / T where the curves meet on the y-axis ?

(d) If we obtained similar plots for 1.00×10^{-3} kg of hydrogen, would we get the same value of PV/T at the point where the curves meet on the y-axis ? If not, what mass of hydrogen yields the same value of PV/T (for low pressure high temperature region of the plot) ?

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HEAT

(Molecular mass of $H_2 = 2.02 \text{ u}$, of $O_2 = 32.0 \text{ u}$, $R = 8.31 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$).



Q.4 An oxygen cylinder of volume 30 litres has an initial gauge pressure of 15 atm and a temperature of 27°C. After some oxygen is withdrawn from the cylinder, the gauge pressure drops to 11 atm and its temperature drops to 17°C. Estimate the mass of oxygen taken out of the cylinder. (R = 8.31 J mol⁻¹ K⁻¹, molecular mass of O₂ = 32 u)

Q.5 An air bubble of volume 1.0 cm³ rises from the bottom of a lake 40 m deep at a temperature of 12°C. To what volume does it grow when it reaches the surface, which is at a temperature of 35°C ?

Q.6 Estimate the total number of air molecules (inclusive of oxygen, nitrogen, water vapour and other constituents) in a room of capacity 25.0 m³ at a temperature of 27°C and 1 atm pressure.

Q.7 Estimate the average thermal energy of a helium atom at (i) room temperature (27°C), (ii) the temperature on the surface of the sun (6000 K), (iii) the temperature of 10 million kelvin (the typical core temperature in the case of a star).

Q.8 Three vessel of equal capacity have gases at the same temperature and pressure. The first vessel contains noon (monoatomic), the second contains chlorine (diatomic), equal number of respective molecules ? Is the root mean square speed of molecules the same in the three cases ? If not, in which case is v_{rms} the largest ?

Q.9 At what temperature does the root mean square speed of an atom in an argon gas cylinder equal to the rms speed of a helium gas atom at -20° C? (Atomic mass of Ar = 40 u, of He = 4.0 u).

Q.10 Estimate the mean free path and collision frequency of a nitrogen molecule in a cylinder containing nitrogen at 2.0 atm and temperature 17°C. Take the radius of a nitrogen molecule to be roughly 1.0 Å. Compare the collision time with the time the molecule moves freely between two successive collisions (Molecular mass of $N_2 = 28.0 \text{ u}$).

Q.11 A metre long narrow bore held horizontally (and closed at one end) contains at 76 cm long mercury thread, which traps a 15 cm column of air. What happens if the tube is held vertically with the open end at the bottom ?

Q.12 Estimate the root mean square speed of the suspended particles in Brownian motion if the particle mass is 10^{-6} kg and the temperature of the liquid is 27°C. Would you expect the answer the change if the liquid were replaced by another liquid of different density and viscosity keeping the temperature fixed ?

Q.13 Explain qualitatively how the extent of Brownian motion is affected by the

(a) Size of the Brownian particle

(b) Density of the medium,

(c) Temperature of the medium

(d) Viscosity of the medium ?

Q.14 In an experiment on Brownian motion using a torsion pendulum a small mirror of area 1 mm² mounted on a thin torsion fibre with torsion constant = 1.8×10^{-17} J/rad²) the mean value of angular displacement θ was found to by nearly zero, and the fluctuation in θ , that is the mean square of was found to be 2.0×10^{-4} rad². Estimate the value of Boltzmann constant from this data and compare it with the correct value. The temperature is 300 K,

[Hint : Use the relation (1/2) $\alpha < \theta^2 > = (1/2) k_B T$ where a is the torsion constant. The mean potential energy of the torsion pendulum is $(1/2)\alpha < \theta^2 >$. In thermal equilibrium it equals 1/2 $k_B T$ according the law of equipartition of energy.]

Q.15 The specific heat at constant volume of a certain metal is approximately 0.1 cal/g °C. Write the chemical formula of its chloride if it contains 0.345 fraction of the metal.

[**Hint :** Use Dulong and Petit's law to get an approximate atomic mass of the metal. Then use the second piece of data to arrive at a simple solution for its chemical formula. You can feed this back to get a more correct value of its atomic mass. The atomic mass of chlorine is 35.5 u]

Q.16 From a certain apparatus, the diffusion rate of hydrogen has an average value of $28.7 \text{ cm}^3 \text{ s}^{-1}$. The diffusion of another gas under the same conditions is measured to have an average rate of $7.2 \text{ cm}^3 \text{ s}^{-1}$. Identify the gas.

[**Hint :** Use Graham's law of diffusion $R_1/R_2 = \sqrt{M_2/M_1}$. where R_1 , R_2 are diffusion rates of gases 1 and 2, and M_1 and M_2 their respective molecular masses. The law is a simple consequence of kinetic theory.]

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Q.17 For Brownian motionof particles of suspensions in liquids, answer the following :

(a) What should be the typical size o suspended particles ? Whjy should not the size of the particles too small (say of atomic dimensions 10^{-10} m) or too large (say of the order of 1 m) ?

(b) Bombardments of the suspended particle by molecules of the liquid are suspended particle from all directions. Why is not the net impact zero ?

(c) Can the assembly of suspended particles be, considered a gas' of 'heavy molecules' ? If so, what isthe temperature of this 'gas', if the temperature of the liquid is T ?

Q.18 (a) Brownian motion is generally regarded as one of the most compelling evidences (through necessarily indirect since we can never hope to 'see' the atoms directly) of the existence of atoms. Do you appreciate this claim ?

Why is it a better evidence than that obtained from the laws of chemical combinations or from the specific heats of gases and solids at ordinary temperatures ? (b) "Brownian motion is observable since Avogadro's number is finite". Comment on this statement.

Q.19A gas in equilibrium has uniform density and pressure throughout its volume. This is strictly true only if there are no external influences. A gas column under gravity, for example, does not have uniform density (and pressure). As you might expect, its density decreases with height. The precise dependence is given by the so-called 'law of

atmospheres' $n_2 = n_1 \exp \left[-\frac{mg}{k_BT}(h_2 - h_1)\right]$ where n_2 , n_1 refer to number density at heights h_2 and h_1 respectively. Use this relation to derive the equation for sedimentation equilibrium of a suspension in a liquid column : $n_2 = n_1 \exp \left[\frac{-mgN_A}{RT}\left(1 - \frac{\rho'}{\rho}\right)(h_2 - h_1)\right]$ where ρ is the density of the suspended particle, and ρ' that of surrounding medium. [N_A is Avogadro's

number, and R the universal gas constant].

Q.20 Given below are data on a gum-resin suspension in water at 22°C. Average radius of a grain of suspension = $0.2 \mu m. 1 \mu m = 10^{-6} m$, average mass of a grain = 6.2×10^{-17} kg, average concentration in a layer = 43 particles per unit area at some reference level, average concentration in a layer = 100.3 particles per unit area at a level 11 μm lower. Estimate the value of Avogadro's number from this data and compare you answer with the correct value.

Q.21 Given below are densities of some solids and liquids. Give rough estimates of the size of their atoms

Substance	Atomic mass(u)	Density (10 ³ kgm ⁻³)
Carbon (diamond	12.01	2.22
Gold	197	19.32
Nitrogen (Liquid)	14.01	1
Lithium	6.94	0.53
Fluorine (liquid)	19	1.14

[Hint : Assume the atoms to be 'tightly packed' in a solid or liquid phase, and use the known value Avogadro's number. You should, however, not take the actual numbers you obtain for various atomic sizes too literally. Because of the crudeness of the tight packing approximation, the results only indicate that atomic sizes are in the range of a few Å]

Q.22 (a) What is the simplest evidence in nature that you can think of to suggest that atoms are not point particles, but have finite (non-zero) size ? (b) Does atomic size increase monotonically with increase in atomic mass. If not, can you guess why not ? (c) What determines fundamentally the size of, say, a hydrogen atom ?

(0.5) Å ? [Note, this question, among other things, had puzzled Niels Bohr before he arrived at his famous quantum model of the hydrogen atom].