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CALORIMETRY, KINETIC THEORY of GASES \& THERMODYNAMICS

## GUPTA CLASSES

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## CALORIMETRY

## Specific heat

When a substance does not undergo a change of state (i.e., liquid remains liquid or solid remains solid), then the amount of heat required to raise the temperature of mass ' $m$ ' of the substance by an amount ' $\Delta \mathrm{T}$ ' is:
$\Delta Q=m c \Delta \mathrm{~T}$, where ' c ' is the specific heat capacity (or specific heat in short) of substance.

1. Specific heat of hydrogen is maximum $\left(=3.5 \mathrm{cal} / \mathrm{g}{ }^{\circ} \mathrm{C}\right)$. For all other substances specific heat is less than $1 \mathrm{cal} / \mathrm{g}^{\circ} \mathrm{C}$ and is minimum for radon and actinium ( $\cong 0.022 \mathrm{cal} / \mathrm{g}^{\circ} \mathrm{C}$ ).
2. All specific heats have been found to vary with temperature, particularly at low temperatures.
3. Specific heat of substance at its melting point or boiling point is infinite (because $\Delta T=0$ ).
4. Specific heat of a substance undergoing an adiabatic change is zero (because $\Delta Q=0$ ).
5. A substance can also possess a negative value of specific heat. For example, specific heat of saturated water vapours is negative.
6. Water has large specific heat, so if used as coolant, it takes away large amount of heat energy and this property makes it a useful coolant. Sodium too has high specific heat and molten sodium is used as coolant in nuclear reactors.

## Thermal capacity

Thermal capacity of a body is defined as the quantity of heat energy required to raise the temperature of the body by unity.

## Molar specific heat

1. The molar specific heat of a substance is defined as the amount of heat energy needed to raise the temperature of one mole of the substance by 1 K . SI unit of molar specific heat is J/mol-K.
2. If $M$ be the molecular weight of a substance then molar specific heat. $C=M c=\frac{Q}{n \Delta T}$
3. For metals, it is found that the molar specific heat is about 25 joule/mol-K for almost all metals (Dulong - Petit's law). Thus the amount of heat required to raise the temperature of a metal depends on the number of particles in the sample and not on the mass of each molecule.

## Water equivalent

The water equivalent of a body is the amount of water that absorbs or gives out the same amount of heat as is done by the body when heated or cooled through $1^{\circ} \mathrm{C}$. If m be the mass of the body and c be its specific heat, then water equivalent is given by: $\mathbf{W}=\mathbf{m c}$. Its unit is kilogram or gram.

## Latent heat

When a substance changes from one state to another state (say from solid to liquid or liquid to gas or from liquid to solid or gas to liquid) then energy is either absorbed or liberated. This heat energy is called latent heat.

1. No change in temperature is involved when the substance changes its state. That is, phase transformation is an isothermal change. Ice at $0^{\circ} \mathrm{C}$ melts into water at $0^{\circ} \mathrm{C}$. Water at $100^{\circ} \mathrm{C}$ boils to form steam at $100^{\circ} \mathrm{C}$.
2. The amount of heat required to change the mass $m$ of the substance is written as: $\Delta \mathrm{Q}=\mathrm{mL}$, where L is the latent heat. Latent heat is also called as Heat of Transformation.
3. Any material has two types of latent heats: (a) Latent heat of fusion: for a change from solid to liquid (melting) or for a change from liquid to solid (freezing), (b) Latent heat of vaporisation: for a change from liquid to vapour (boiling) or for a change from vapour to liquid (condensation).

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4. In the process of melting or boiling, heat supplied is used to increase the internal potential energy of the substance and also in doing work against external pressure while internal kinetic energy remains constant. This is the reason that internal energy of steam at $100^{\circ} \mathrm{C}$ is more than that of water at $100^{\circ} \mathrm{C}$,

## Evaporation

Conversion of liquid into gaseous state at all the temperatures is called evaporation. It is a phenomenon that occurs at the surface of liquids. The rate of evaporation increases with rise in temperature. Heat required to change unit mass of liquid into vapour at a given temperature is called heat of evaporation at that temperature.

## Sublimation

Sublimation is the conversion of a solid directly into vapours. Sublimation takes place when boiling point is less than the melting point. A block of ice sublimates into vapours on the strface of moon because of very - very low pressure on its surface. Heat required to change unit mass of solid directly into vapours at a given temperature is called heat of sublimation at that temperature.

## Hoar frost

Direct conversion of vapours into solid is called hoar frost. This process is just reverse of the process of sublimation, e.g., formation of snow by freezing of clouds.

## Effect of pressure on boiling point and melting point

1. Boiling point of every liquid increases with increase in pressure.
2. For substances like wax and sulphur, which expand on melting, melting point rises with increase in pressure; and for substances like ice and rubber, which contract on melting, melting point decreases with increase in pressure.

## Principle of calorimetry

When two bodies at different temperatures are placed in contact with each other then heat will pass from the body at higher temperature to the body at lower temperature until both reach to a common temperature. In this process,

> i.e., principle of calorimetry is an alternative form of the law of conservation of energy.

1. When two bodies at different temperatures are mixed together, then equilibrium temperature of mixture T is always $\geq$ lower temperature ( $\mathrm{T}_{\mathrm{L}}$ ) and $\leq$ higher temperature ( $\mathrm{T}_{\mathrm{H}}$ ), i.e., a body cannot be cooled below the temperature of cooling body, and also a body cannot be heated above the temperature ofbeating body.
2. Rise intemperature of one body is not equal to the fall in temperature of the other body.

## Some more points

1. There will be no exchange of heat between two bodies when they attain the same temperature, e.g., if we put the beaker containing water in melting ice, the water in the beaker will cool to $0^{\circ} \mathrm{C}$ but will never freeze.
2. Amount of steam at $100^{\circ} \mathrm{C}$ required to just melt ' m ' $g$ of ice at $0^{\circ} \mathrm{C}$ is $(\mathrm{m} / 8) \mathrm{g}$.
3. If equal amounts of ice and water are mixed and if the temperature of water is $\leq 80^{\circ} \mathrm{C}$, resultant temperature $=0^{\circ} \mathrm{C}$.
(a) If temperature of water $=80^{\circ} \mathrm{C}$, resultant is all water at $0^{\circ} \mathrm{C}$.
(b) If temperature of water $<80^{\circ} \mathrm{C}$, some ice is left unmelted.
4. If equal amounts of ice and steam are mixed then resultant temperature is $100^{\circ} \mathrm{C}$.
5. If equal amounts of water and steam are mixed, then resultant temperature is $100^{\circ} \mathrm{C}$.

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6. If a given mass $m$ of a solid is supplied heat continuously at a constant rate and a graph is plotted between temperature (on y - axis) and time (on x - axis), then the curve so obtained is called as heating curve. Following important conclusions are obtained from this curve:
(a) specific heat in any state $\propto 1$ / slope of curve in that state
(b) latent heat in any state $\propto$ length of curve in that state.

## Kinetic Theory of Gases

## Assumptions of kinetic theory of gases

1. A gas consists of a large number of identical, tiny, spherical, neutral and elastic particles called molecules.
2. In a gas molecules are moving in all possible directions with all possible speeds in accordance with Maxwell's distribution law.
3. The space occupied by the molecules is much smaller than the volume of the gas.
4. There is no force of attraction among the molecules.
5. The pressure of a gas is due to elastic collision of gas molecules with the walls of the container.
6. The time of contact of a moving molecule with the walls of the container is negligible as compared to the time interval between two successive collisions on the same wall of the container

## Different types of speeds of gas molecules

1. Root mean square speed: It is defined as the square root of mean of squares of the speed of different molecules, i.e., $\mathrm{v}_{\mathrm{rms}}=\sqrt{\left(\mathrm{v}_{1}^{2}+\mathrm{v}_{2}^{2}+\ldots \ldots \ldots \ldots\right) / \mathrm{N}} \quad=\sqrt{\frac{3 \mathrm{RT}}{\mathrm{M}}}=\sqrt{\frac{3 \mathrm{kT}}{\mathrm{m}}}$
2. Most probable speed: It is the speed which maximum number of molecules in a gas have at constant temperature and is given by: $\mathrm{v}_{\mathrm{mp}}=\sqrt{\frac{2 \mathrm{RT}}{\mathrm{M}}}=\sqrt{\frac{2}{3}} \mathrm{v}_{\mathrm{rms}}=0.816 \mathrm{v}_{\mathrm{rms}}$
3. Average speed: It is the arithmetic mean of the speed of molecules in a gas at a given temperature,

$$
\text { i.e., } \mathrm{v}_{\mathrm{av}}=\left(\mathrm{v}_{1}+\mathrm{v}_{2}+\mathrm{v}_{3}+\ldots \ldots\right) / \mathrm{N}=\sqrt{\frac{8 \mathrm{RT}}{\pi \mathrm{M}}}=\left(\sqrt{\frac{8}{3 \pi}}\right) \mathrm{v}_{\mathrm{rms}}=0.92 \mathrm{v}_{\mathrm{rms}}
$$

4. It is thus evident that (a) $v_{r m s}>v_{a v}>\nu_{m p}$.
5. A planet or satellite will have atmosphere only and only if $\mathrm{v}_{\text {rms }}<\mathrm{v}_{\text {escape }}\left[=(2 \mathrm{gR})^{1 / 2}\right]$

## Some points concerning root méan square speed

1. $v_{\mathrm{rm},}-\mathrm{oc}(1 / \sqrt{\rho})$, which is called as Graham's Law of Diffusion.
2. $v_{\text {rms }} \propto \sqrt{ }$ Ti.e., with rise in temperature (in Kelvin) rms speed of gas molecules increases.
3. For a given temperature $\mathrm{V}_{\text {rms }} \propto(1 / \sqrt{ } \mathrm{M})$ i.e., with increase in molecular weight rms speed of gas molecules decreases.
4. RMS speed of gas molecules is of the order of $\mathrm{km} / \mathrm{s}$.
5. As speed of sound in a gas $\mathrm{v}_{\mathrm{S}}=\sqrt{\frac{\gamma \mathrm{RT}}{\mathrm{M}}}$; hence $\frac{\mathrm{v}_{\mathrm{S}}}{\mathrm{v}_{\mathrm{rms}}}=\sqrt{\frac{\gamma}{3}}$, i.e. speed of sound in a gas is of the same order as rms speed of its molecules.

## Mean kinetic energy of gases

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Mean Kinetic energy of gas per molecule, $\mathrm{E}=\frac{3}{2} \mathrm{kT}$, Average translational KE of a gas molecule depends only on its temperature and is independent of its nature, Mean kinetic energy of molecules is zero at absolute zero if gas continues to remain a gas at that temperature.

## Pressure exerted by an ideal gas and root mean square speed

1. Pressure ' $P$ ' exerted by an ideal gas is given by: $\quad P=\frac{1}{3} \frac{\mathrm{mN}}{\mathrm{V}} \mathrm{v}_{\mathrm{rms}}^{2}$, where $\mathrm{v}_{\mathrm{rms}}=$ the root mean square velocity, $m=$ mass of each molecule and $N=$ total number of molecules in the vessel having volume $V$.
2. Also $\mathrm{P}=\frac{1}{3} \rho \mathrm{v}_{\mathrm{rms}}^{2}$; and $\mathrm{v}_{\mathrm{rms}}=\sqrt{(3 \mathrm{P} / \rho)}=\sqrt{\frac{3 \mathrm{RT}}{\mathrm{M}}}=\sqrt{\frac{3 \mathrm{kT}}{\mathrm{m}}}$ where $\rho$ is density of gas; M is molecular mass of gas , R universal gas constant and k Boltzman constant.
3. Pressure of a gas is numerically equal to $(2 / 3)$ of its $K E$ per unit volume. i.e $P=\frac{2}{3} E$

## Degrees of freedom

The term degrees of freedom of a system refers to the possible independent motions a system can have or number of possible independent ways in which a system can have energy. The independent motions of a system can be translational, rotational or vibrational or any combination of these.
In general no. of degree of freedom are given by relation $f=3 \mathrm{~A}-\mathrm{R}$, where A is atomicity of molecule and R is relation among atoms of molecules.

## Law of equipartition of energy

According to law of equipartition of energy, energy of a gas molecule is equally distributed among its various degrees of freedom and each degree of freedom is associated with energy $1 / 2 \mathrm{kT}$, where k is Boltzmann constant and T temperature of the gas in Kelvin.

## Gas-Iaws

1. Boyle's law: $\mathrm{V} \propto 1 / \mathrm{P}$ if mass of gas and $\mathrm{T}=\mathrm{constant}$
2. Charles' law: $\mathrm{V} \propto \mathrm{T}$ if m and $\mathrm{P}=$ constant
3. Gay-Lussac's law: $\mathrm{P} \propto \mathrm{T}$ if m and $\mathrm{V}=$ constant,
4. Avogadro's law: According to it, at same temperature and pressure, equal volumes of all the gases contain equal number of molecules, i.e., $\quad N_{1}=N_{2}$ if $\bar{P}, \mathrm{~V}$ and T are same
5. Graham's law: According to it, at constant pressure and temperature, the rate of diffusion of a gas is inversely proportional to the square root of its density, i.e., Rate of diffusion $\propto 1 / \sqrt{ } \rho$
6. Dalton's law: According to it, the pressure exerted by a gaseous mixture is equal to the sum of partial pressure of each component present in the mixture, i.e., $\mathrm{P}=\mathrm{P}_{1}+\mathrm{P}_{2}+\ldots$
7. Ideal gas equation: A relation connecting macroscopic properties pressure, volume and temperature of a gas describes the state, i.e., physical condition of the system and is called equation of state, $\mathrm{PV}=\mathrm{nRT}$ with $\mathrm{R}=$ $8.31 \mathrm{~J} / \mathrm{mol} \mathrm{K}$

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## Thermodynamics

## Thermodynamics

1. A system whose state is completely defined by the variables like Pressure ( P ), Volume ( $V$ ), Temperature ( $T$ ), Internal energy ( $U$ ), is called a thermodynamic system. These variables are called thermodynamic variables.
2. A P-V diagram for a system is called an indicator diagram.
3. The area under a curve on P-V diagram shows work done on or by the system.
4. Work done on or by a gas or system depends upon the initial state, final state and the path adopted between these two states.
5. Like work done, heat exchanged by the system or a gas also depends upon the initial state, the final state and the path.
6. Change in internal energy of a gas depends only upon the initial and the final state but not on the path. It is a unique function of the point on the indicator diagram

## Zeroth law of thermodynamics

When two bodies A and B are in thermal equilibrium with a third body C , then A and B are in thermal equilibrium mutually, i.e; if $\mathrm{T}_{\mathrm{A}}=\mathrm{T}_{\mathrm{C}} \mathrm{T}_{\mathrm{B}}=\mathrm{T}_{\mathrm{C}}$, then $\mathrm{T}_{\mathrm{A}}=\mathrm{T}_{\mathrm{B}}$.

## First law of thermodynamics

First law of thermodynamics is equivalent to law of conservation of energy. According to this law $\Delta \mathrm{Q}=$ $\Delta U+\Delta \mathrm{W}$, Where $\Delta \mathrm{Q}$ is heat added or rejected by system, $\Delta \mathrm{W}$ is work done by or on the system and $\Delta \mathrm{U}$ is the change in internal energy of system.

1. $\Delta \mathrm{Q}$ is +ive if heat is added to system and -ive if heat is rejected by system.
2. $\Delta \mathrm{W}$ is +ive if work is done by system and -ive if work is done on system.
3. $\Delta U$ is +ive if internal energy os system increases and -ive if decreases.

## Specific heats of a gas

1. Specific heat of a gas at constant volume ( $\mathbf{C}_{v}$ ): It is the amount of heat that must be added to unit mass of a gas to increase its temperature by $1^{\circ} \mathrm{C}$ or 1 K when the volume is kept constant. If the amount of mass considered is one mole, then $C_{v}$ is called molar specific heat at constant volume. If we consider $n$ moles of a gas at constant volume, then $d Q=\mathrm{n} C_{V} d T=d U$ $(\cdot d W=P d V=0)$
2. Specific heat of a gas at constant pressure ( $\mathrm{C}_{p}$ ): It is the amount of heat that must be added to unit mass of gas to increase its temperature by $1^{\circ} \mathrm{C}$ when the pressure of gas is kept constant. If the amount of mass considered is 1 mole, then $C_{p}$ is called molar specific heat at constant pressure. If we consider n moles of a gas at constant pressure, then $d Q=\mathrm{n} C_{p} d T=$ $d U+d W$
3. Mayor's relation between $\mathbf{C}_{p}$ and $\mathbf{C}_{v}$ : For one mole of a gas $C_{p}-C_{\nu}=R$
4. For any gas: $\gamma=\frac{\mathrm{C}_{\mathrm{p}}}{\mathrm{C}_{\mathrm{v}}}=1+\frac{2}{\mathrm{f}}$, (where $\gamma$ depends on atomicity of gas and $f$ is degree of freedom).
5. $\mathbf{C}_{p}$ and $\mathbf{C}_{v}$ in terms of $\boldsymbol{\gamma}$ and $\boldsymbol{R}: \mathrm{C}_{\mathrm{v}}=\frac{\mathrm{R}}{\gamma-1} \quad$ and $\quad \mathrm{C}_{\mathrm{p}}=\gamma \mathrm{C}_{\mathrm{v}}=\frac{\gamma \mathrm{R}}{\gamma-1}$
6. $\quad \mathrm{C}_{\boldsymbol{p}}$ and $\mathrm{C}_{v}$ in terms of $\boldsymbol{f}$ and $\boldsymbol{R}: \mathrm{C}_{\mathrm{v}}=\frac{\mathrm{f}}{2} \mathrm{R} \quad$ and $\quad \mathrm{C}_{\mathrm{p}}=\left[\frac{\mathrm{f}}{2}+1\right] \mathrm{R}$

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## Work done in thermodynamic process

If there occurs an infinitesimal change in volume $d V$ at a pressure $P$, work done $d W$ is given by : $d W=$ PdV. Total work done in a variable pressure process in going from some initial state $\left(P_{i}, V_{i}\right)$ to final state $\left(P_{f}, V_{f}\right)$ is: $\mathrm{W}=\int_{\mathrm{V}_{\mathrm{i}}}^{\mathrm{V}_{\mathrm{f}}} \mathrm{PdV}$.

1. Work done is equal to area under the curve on $\mathrm{P}-\mathrm{V}$ diagram.
2. Work done by a gas during expansion is taken as positive while during compression it is taken as negative.
3. For a cyclic process: $\mathrm{W}=$ area enclosed in the cycle. Work done is positive when the cycle is traced out in clockwise direction and work is negative when the cycle is traced out in anticlockwise direction.
4. Work done in Isobaric process: $\quad \mathrm{W}=\mathrm{P}\left(\mathrm{V}_{f}-\mathrm{V}_{i}\right)$
5. Work done in Isometric process: $W=0 \quad(\Delta V=0)$
6. Work done in Isothermal process: $W=\mu R T \log _{e}\left(\frac{V_{f}}{V_{i}}\right)=\mu R T \log _{e}\left(\frac{P_{f}}{P_{i}}\right)=P_{i} V_{i} \log _{e}\left(\frac{V_{f}}{V_{i}}\right)$
7. Work done in Adiabatic process:

$$
\mathrm{W}=\frac{\mathrm{P}_{\mathrm{i}} \mathrm{~V}_{\mathrm{i}}-\mathrm{P}_{\mathrm{f}} \mathrm{~V}_{\mathrm{f}}}{\gamma-1}=\frac{\mu \mathrm{R}\left(\mathrm{~T}_{\mathrm{i}}-\mathrm{T}_{\mathrm{f}}\right)}{\gamma-1}=\mu \mathrm{C}
$$

## Heat added or removed from a thermo dynamical system

The amount of heat involved with (added or removed from) n moles of a gas is given by: $\Delta Q=\mathrm{nC}_{\mathrm{v}} \Delta T$ (for isometric or isochoric process) and $\Delta Q=\mathrm{nC}_{\mathrm{p}} \Delta T$ (for isobaric process)

## Internal energy of a gas

1. According to kinetic theory of gases, mean kinetic energy of a molecule is; $(\mathrm{KE})_{\text {mean }}=(3 / 2) \mathrm{kT}$. A gas contains a large number of molecules. The internal energy of agas is equal to sum of the kinetic and potential energies of all the molecules of the gas. In practice, we ignore potential energies of the molecules and neglect intermolecular forces. Thus the total KE of all the molecules of the gas is equal to the internal energy of the gas.
2. For $n$ moles of gas, if the system undergoes any thermodynamic process in which temperature changes by $\Delta T$, the change in the internal energy is: $\Delta U=n_{V} \Delta T$.

## Different types of thermodynamical processes

Isobaric process: It is a thermodynamic process in which pressure is kept constant. The equation of state for the process is: $(\mathrm{V} / \mathrm{T})=$ constant

1. In isobaric compression, temperature decreases and internal energy flows out in the form of heat energy, while in isobaric expansion, temperature increases and heat flows into the system.
2. The amount of heat energy transferred is given by: $\Delta Q=\mathrm{nC}_{\mathrm{p}} \Delta T$

3. In the adjoining figure, graphs I and II represent isobaric expansion and compression respectively.
4. The slope of the isobaric curve on a P-V diagram is zero.

Isochoric (Isometric) process: It is a thermodynamic process in which the volume of the system is kept constant.

1. The equation of state for the process is: $(\mathrm{P} / \mathrm{T})=$ constant.
2. For isochoric process: $\Delta Q=\mu \mathrm{C}_{V} \Delta T$ and $\Delta \mathrm{W}=0$
3. In the adjoining figure, graphs I and II represent isometric decrease in pressure
 at volume $V_{1}$ and isometric increase in pressure at volume $V_{2}$ respectively.
4. The slope of the isometric curve is infinite on a $\mathrm{P}-\mathrm{V}$ diagram.

Isothermal process: It is a thermodynamical process in which the temperature of the system remains constant.

1. The equation of state for the process is: $\mathrm{PV}=$ constant.
2. During isothermal expansion of a gas, its volume increases while pressure decreases, while in isothermal compression, the volume decreases while pressure increases.


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3. The isothermal curve on P-V diagram is like a hyperbola and is shown in the figure.
4. The slope of the isothermal curve at any point $M$ is given by: $d P / d V=-(P / V)$

Adiabatic process: It is a process in which heat exchanged by the system to or from the surroundings is zero, i.e., $\Delta Q=0$

1. The equation of state for this process is: $\mathrm{PV}^{\gamma}=$ const. where $\gamma$ is the ratio of specific heats of the gas.
2. Other equation are $\mathrm{TV}^{\gamma-1}=$ const. and $\mathrm{P}^{1-\gamma} \mathrm{T}^{\gamma}=$ const.


3. The adiabatic curve on the $\mathrm{P}-\mathrm{V}$ diagram is shown in the adjoining figure. The slope of the curve at any point is given by: $\mathrm{dP} / \mathrm{dV}=-\gamma(\mathrm{P} / \mathrm{V})$
4. Slope of adiabatic curve is more in magnitude in comparison to the slope of the Isothermal curve.
5. When a gas expands from some initial volume to final volume, then final pressure is less for adiabatic expansion. But, when a gas compresses from some initial volume to a final volume, then the final pressure is more in case of adiabatic compression.
6. In adiabatic expansion, temperature decreases while in adiabatic compression, temperature increases.
7. Isothermal and adiabatic bulk modulus of a gas are given by: $B_{i \text { iso }}=P$ and $B_{\text {adi }}=\gamma P$

## Second law of thermodynamics

1. Kelvin's statement: It is impossible for an engine operating in a cyclic process to extract heat from a reservoir and convert it completely into work, i.e., whole of heat can never be converted into work though whole of work can be converted into heat, i.e., a perfect heat engine can never be constructed.
2. Clausius statement: It is impossible for a self-acting machine unaided by any external agency to transfer heat from a cold to hot reservoir, i.e., heat by itself cannot pass from a colder to hotter body.

## Heat engine

1. It is a device which converts heat into work continuously through a cyclic process.
2. Every heat engine consists : (a) a hot body called source (b) a working substance (c) a cold body called sink
3. In a heat engine working substance absorbs heat $\left(Q_{1}\right)$ from the source at a higher temperature $T_{H}$, converts a part of it into useful work (W) and rejects the rest $\left(\mathrm{Q}_{2}\right)$ to the sink (usually atmosphere) at a lower temperature $T_{L}$ and comes back tơ its initial state.
4. Efficiency of a heat engine, $\quad \eta=\frac{\text { work done }}{\text { heat absorbed }}=\frac{\mathrm{W}}{\mathrm{Q}_{1}}=\frac{\mathrm{Q}_{1}-\mathrm{Q}_{2}}{\mathrm{Q}_{1}}=1-\frac{\mathrm{Q}_{2}}{\mathrm{Q}_{1}}$
5. A perfect heat engine is one which converts all heat into work, i.e., $W=Q_{1}$ so that $Q_{2}=0$ hence, for it $\eta=1$.
Carnot heat engine: It consists of four parts:
6. A cylinder with perfectly insulating walls and a perfectly conducting base containing a perfect gas as working substance and fitted with an insulating frictionless piston;
7. A source of infinite thermal capacity maintained at a constant higher temperature $T_{H}$;
8. A sink of infinite thermal capacity maintained at constant lower temperature $T_{L}$, and
9. A perfectly non-conducting stand for cylinder.

Carnot cycle: It consists of four operations in succession: (i) isothermal expansion at higher temperature $T_{H}$. (ii) adiabatic expansion between temperatures $T_{H}$ and $T_{L}$. (iii) isothermal compression at constant lower temperature $T_{L}$ and (iv) adiabatic compression between temperatures $T_{L}$ and $T_{H}$.

1. Efficiency of the engine: $\eta=1-\frac{T_{L}}{T_{H}}=1-\frac{Q_{1}}{Q_{2}}, \eta$ depends only on temperatures of source and sink and is independent of all other factors.
2. As on kelvin scale, temperature can never be negative and $T_{H}$ and $T_{L}$ are finite, efficiency of a heat engine is always lesser than unity, i.e., whole of heat can never be converted into work which is in accordance with second law.

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## Refrigerator or heat pump

1. A refrigerator or heat pump is basically a heat engine run in reverse direction. In it working substance takes heat $Q_{2}$ from a body at a lower temperature $T_{L}$, has a net amount of work done $W$ on it by an external agent (usually compressor) and gives out a larger amount of heat $Q_{1}\left(=Q_{2}+W\right)$ to a hot body at temperature $T_{H}$ (usually atmosphere).
2. A refrigerator or heat pump transfers heat from a cold to a hot body at the expense of mechanical energy supplied to it by an external agent. The working substance here is called refrigerant.
3. The coefficient of performance of a refrigerator is defined as:

$$
\beta=\frac{\text { heat extracted from the reservoir at low temperature } T_{L}}{\text { work done to transfer the heat }} \text { i.e. } \beta=\frac{Q_{2}}{W}=\frac{Q_{2}}{Q_{1}-Q_{2}}=\frac{T_{L}}{T_{H}-T_{L}}
$$

4. A perfect refrigerator is one which transfers heat from a cold to a hot body without doing any work, i.e., $\mathrm{W}=0$ so that $Q_{1}=Q_{2}$, and hence for it $\mathrm{K}=\infty$.


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## Calorimetry, Kinetic Theory, thermodynamics

1. A lead bullet strikes a steel armour plate with a velocity of $300 \mathrm{~m} / \mathrm{s}$ and is completely stopped. If the heat produced is shared equally between the bullet and the target, the rise in the temperature of the bullet is (specific heat of lead $0.03 \mathrm{cal} / \mathrm{g}^{\circ} \mathrm{C}$ )
(a) $89.3^{\circ} \mathrm{C}$
(b) $49.3^{\circ} \mathrm{C}$
(c) $178.6^{\circ} \mathrm{C}$
(d) $357.2^{\circ} \mathrm{C}$
2. The temperatures of equal masses of three different liquids $\mathrm{A}, \mathrm{B}$ and C are $12^{\circ} \mathrm{C}, 19^{\circ} \mathrm{C}$ and $28^{\circ} \mathrm{C}$, respectively. When A and B are mixed, the temperature is $16^{\circ} \mathrm{C}$ and when B and C are mixed, it is $23^{\circ} \mathrm{C}$. The temperature when A and C are mixed is
(a) $10.1^{\circ} \mathrm{C}$
(b) $20.2^{\circ} \mathrm{C}$
(c) $30.3^{\circ} \mathrm{C}$
(d) $40.4^{\circ} \mathrm{C}$
3. A perfect gas at $27^{\circ} \mathrm{C}$ is heated at constant pressure so as to double its volume. The temperature of the gas becomes
(a) $54^{\circ} \mathrm{C}$
(b) 150 K
(c) $327^{\circ} \mathrm{C}$
(d) 327 K
4. Two identical cylinders contain helium at 2.5 atmospheres and argon at 1 atmosphere. If both the gases are filled in one of the cylinders, the pressure would be (in atmosphere)
(a) 1.75
(b) 3.5
(c) 4.75
(d) 7.
5. The temperature at the bottom of a 40 m deep lake is $12^{\circ} \mathrm{C}$ and that at the surface is $35^{\circ} \mathrm{C}$. An air bubble of volume $1.0 \mathrm{~cm}^{3}$ rises from the bottom to the surface. Its volume becomes (atmospheric pressure $=10 \mathrm{~m}$ of water)
(a) $2.0 \mathrm{em}^{3}$
(b) $3.2 \mathrm{~cm}^{3}$
(c) $5.4 \mathrm{~cm}^{3}$
(d) $8.0 \mathrm{~cm}^{3}$
6. Oxygen and hydrogen gases are at the same temperature. The ratio of the average kinetic energy of an oxygen molecule and that of a hydrogen molecule is
(a) 16
(b) 4
(c) 1
(d) $1 / 4$
7. Two gases are enclosed in a container at constant temperature. One of the gases, which is diatomic, has relative molecular mass eight times the other, which is monoatomic. The ratio of the r.m.s speed of the molecules of the monoatomic gas to that of the molecules of the diatomic gas is
(a) 8
(b) 4
(c) $2 \sqrt{ } 2$
(d) 2
8. When an ideal gas undergoes an isothermal expansion, the pressure of the gas in the enclosure falls. This is due to
(a) decrease in the change of momentum per collision
(b) decrease in the frequency of collision
(c) decrease in both the frequency of collision and the change of momentum per collision
(d) decrease in neither the frequency of collision nor the change of momentum per collision.
9. A jar A is filled with an ideal gas characterised by parameters $\mathrm{P}, \mathrm{V}$ and T and another jar B is filled with an ideal gas with parameters $2 \mathrm{P}, \mathrm{V} / 4$ and 2 T . The ratio of number of molecules in jars A and B is
(a) 1 :
(b) $1: 2$
(c) $2: 1$
(d) $4: 1$
10. The pressure of a gas contained in a closed vessel is increased by $0.4 \%$ when heated by $1^{\circ} \mathrm{C}$. The initial temperature was
(a) 250 K
(b) $250^{\circ} \mathrm{C}$
(c) 500 K
(d) $500^{\circ} \mathrm{C}$

Two different ideal gases are enclosed in two different vessels at the same pressure. If $\rho_{1}$ and $\rho_{2}$ are their densities and $c_{1}$ and $c_{2}$ are their rms speeds, respectively, then $c_{1} / c_{2}$ is equal to
(a) $\rho_{1}{ }^{2} / \rho_{2}{ }^{2}$
(b) $\rho_{2}{ }^{2} / \rho_{1}{ }^{2}$
(c) $\left(\rho_{1} / \rho_{2}\right)^{1 / 2}$
(d) $\left(\rho_{2} / \rho_{1}\right)^{1 / 2}$
12. If the inter molecular forces vanish the volume occupied by the molecules of 4.5 kg water at S.T.P. will be
(a) $5.6 \mathrm{~m}^{3}$
(b) 11.2 litre
(c) $4.5 \mathrm{~m}^{3}$
(d) $11.2 \mathrm{~m}^{3}$.
13. Four molecules have speeds $2 \mathrm{~km} / \mathrm{s}, 3 \mathrm{~km} / \mathrm{s}, 4 \mathrm{~km} / \mathrm{s}$ and $5 \mathrm{~km} / \mathrm{s}$. The rms speed of these molecules in $\mathrm{km} / \mathrm{s}$ is
(a) $\sqrt{ } 54 / 3$
(b) $\sqrt{ } 54 / 2$
(c) 3.5
(d) $3 \sqrt{ } 3$
14. The equation of state corresponding to 8 g of $\mathrm{O}_{2}$ is
(a) $\mathrm{PV}=8 \mathrm{RT}$
(b) $\mathrm{PV}=\mathrm{RT} / 4$
(c) $\mathrm{PV}=\mathrm{RT}$
(d) $P V=R T / 2$
15. Van der Waals gave the following equation of state for real gases $\left(\mathrm{P}+\frac{\mathrm{a}}{\mathrm{V}^{2}}\right)(\mathrm{V}-\mathrm{b})=\mathrm{RT}$. The quantity $\mathrm{a} / \mathrm{V}^{2}$ relates to
(a) effective area of the molecules
(b) volume of the molecules
(c) average speed of the molecules
(d) force of attraction between the molecules.
16. Internal energy is a unique function of a state because change in internal energy
(a) does not depend on path

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(b) depends on path
(c) corresponds to an adiabatic process
(d) corresponds to an isothermal process.
17. An ideal gas is taken around the cycle ABCA as shown in the PV diagram. The net work done by the gas during the cycle is

(a) 12 PV
(b) 6 PV
(c) 3 PV
(d) PV
18. If the amount of heat given to a system be 35 J and the amount of work done by the system be -15 J , then change in internal energy of system is
(a) -50 J
(b) 20 J
(c) 30 J
(d) 50 J
19. Two samples $A$ and $B$ of the same mass of a gas, initially at the same pressure, temperature and volume are compressed to half the original volume, A isothermally and B adiabatically. The final pressure of A is
(a) greater than that of $B$
(b) equal to that of B
(c) less than that of B
(d) twice that of B
20. During the adiabatic expansion of 2 moles of a gas, the change in internal energy was found to be -100 J . The work done during the process was
(a) zero
(b) -100 J
(c) 200 J
(d) 100 J
21. For an adiabatic expansion of a perfect gas, the value of $\Delta \mathrm{P} / \mathrm{P}$ is equal to
(a) $-\gamma^{1 / 2}(\Delta V / V)$
(b) $-(\Delta \mathrm{V} / \mathrm{V})$
(c) $-\gamma(\Delta \mathrm{V} / \mathrm{V})$
(d) $\gamma^{2}(\Delta \mathrm{~V} / \mathrm{V})$
22. The pressure - volume graph of an ideal gas cycle consisting of isothermal and adiabatic processes i shown in the figure. The adiabatic process is described by
(a) AB and BC
(b) $A B$ and $C D$
(c) BC and CD
(d) AD and BC
23. During an adiabatic expansion, increase in volume is associated with
(a) decrease in pressure and decrease in temp.
(b) increase in pressure and decrease in temp.
(c) increase in pressure and increase in temp.
(d) decrease in pressure and increase in temp.
24. The pressure and density of a diatomic gas ( $\gamma=$ 715 ) change adiabarically from ( $\mathrm{P}, \rho$ ) to ( $\mathrm{P}^{\prime}, \rho \rho^{\prime}$. If $\left(p^{\prime} / \rho\right)=32$. The ( $p / p$ ) is
(a) 128
(b) $1 / 128$
(c) 32
(d) none of these
25. A gas hasone specific heat (b) two specific heats (c) three specific heats
(d) infinite specific heats.
26. A system changes from the state $\left(\mathrm{P}_{1}\right.$, $\left.\mathrm{V}_{1}\right)$ to the state $\left(\mathrm{P}_{2}\right.$, $V_{2}$ ) as shown in the figure. The work done by system is

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(a) $7.5 \times 10^{5} \mathrm{~J}$
(b) $7.5 \times 10^{5} \mathrm{ergs}$
(c) $12 \times 10^{5} \mathrm{~J}$
(d) $6 \times 10^{5} \mathrm{~J}$
27. When a monoatomic gas expands at constant pressure, the percentage of heat supplied that increases the internal energy of the gas and that which is involved in expansion is
(a) $75 \%, 25 \%$
(b) $25 \%, 75 \%$
(c) $60 \%, 40 \%$,
(d) $40 \%, 60 \%$,
28. 70 calories of heat are required to raise the temperture of 2 moles of an ideal gas at constant pressure from $30^{\circ} \mathrm{C}$ to $35^{\circ} \mathrm{C}$. The amount of heat required (in calories) to raise the temperature of the same gas through the same range $\left(30^{\circ} \mathrm{C}\right.$ to $\left.35^{\circ} \mathrm{C}\right)$ at constant volume is
(a) 30
(b) 50
(c) 70
(d) 90
29. The maximum possible efficiency of an engine that absorbs heat at $327^{\circ} \mathrm{C}$ and exhausts heat at $127^{\circ} \mathrm{C}$ is
(a) $1 / 3$
(b) ${ }^{1 / 2}$
(c) $2 / 3$
(d) $1 / 4$
30. An ideal refrigerator is used to transfer heat from a freezer at $-23^{\circ} \mathrm{C}$ to the surroundings at $27^{\circ} \mathrm{C}$. Its coefficeint of performance is
(a) 2
(b) 5
(c) 7.5
(d) 10
31. The temperatures of the source and the sink in a Carnot engine are 400 K , and 300 K respectively. If the engine receives 600 cal of heat from the source per cycle, the heat rejected to the sink per cycle is
(a) 150 cal
(b) 300 cal
(c) 400 cal
(d) 450 cal
32. A Carnot engine working, between 300 K and 600 K has a work output of 800 J per cycle. The amount of heat energy supplied to the engine from the source per cycle is
(a) 1200 J
(b) 2400 J
(c) 1600 J
(d) 3200 J
33. The temperature below which a gas should be cooled, before it can be liquified by applying pressure, is termed the
(a) dew point
(b) critical temperature
(c) Boyle temperature
(d) saturation point.
34. The water on the surface of a lake is just about to freeze. The most likely temperature at the bottom of the lake is
(a) $4^{\circ} \mathrm{C}$
(b) $0^{\circ} \mathrm{C}$
(c) $-4^{\circ} \mathrm{C}$
(d) $-273^{\circ} \mathrm{C}$
35. A refrigerator, with its power on, is kept in a closed room with its door open. The temperature of the room will
(a) rise
(b) fall
(c) remains the same
(d) rise or fall depending on the area of the room.
36. When a gas expands adiabatically
(a) no energy is required for expansion
(b) energy is required and it comes from the wall of the container of the gas
(c) internal energy of the gas is used in doing work
(d) law of conservation of energy does not hold.

## ANSWERS

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,14b , 15d ,16a , 17c , 18d ,19c , 20d ,21c , 22d ,23a , 24a
,25d ,26c , 27c , 28b , 29a , 30b , 31d , 32c , 33b , 34a , 35a
,36c


