UNIT VIII

THERMODYNAMICS

KEY CONCEPTS

- The ratio of work done (W) to the amount of heat produced (Q) is always a constant, represented by J.

  i.e., $$\frac{W}{Q} = J$$

  where J is called **Joule's mechanical equivalent of heat.** The value of J = 4.186 joule/calorie.

- If temperature of a body of mass m rises by ΔT, then $Q = mc\,\Delta T$ where c is *specific heat* of the material of the body,

  When the state of body of mass m changes at its melting point/boiling point, then $Q = m\,L$, where L is *latent heat* of the body.

- All solids expand on heating. The coefficient of linear expansion (α), coefficient of superficial expansion (β) and coefficient of cubical expansion (γ) are related as

  $$\alpha = \frac{\beta}{2} = \frac{\gamma}{3}.$$

- In case of liquids, $\gamma_r = \gamma_a + \gamma_c$ where γ_r is coefficient of real expansion of a liquid, γ_a is coefficient of apparent expansion of the liquid and γ_r is coefficient of cubical expansion of the vessel.

- **Principle of calorimetry :** When two substances at different temperatures are mixed together, they exchange heat. If we assume that no heat is lost to the surroundings, then according to principle of calorimetry.

  Heat lost by one substance = Heat gained by another substance

- **Specific Heat of Gases :** Specific heat of a gas is the amount of heat required to raise the temperature of one gram of gas through 1°C.

  Principal specific heat of a gas :

  (*i*) Specific heat at constant volume (c_v)

  (*ii*) Specific heat at constant pressure (c_p)

  $C_v \rightarrow$ molar heat capacity at constant volume

  $C_p \rightarrow$ molar heat capacity at constant pressure

  $$C_p - C_V = R/J \qquad R = 8.314 \ \frac{J}{\text{Mole-K}}$$

- Coefficient of thermal conductivity (K) of a solid conductor is calculated from the relation

  $$\frac{\Delta Q}{\Delta t} = KA\left(\frac{\Delta T}{\Delta t}\right)$$

  where A is area of hot face, Δx is distance between the hot and cold faces, ΔQ is the small amount of heat conducted in a small time (Δt), ΔT is difference in temperatures of hot and cold faces.

  Here ($\Delta T/\Delta x$) *temperature gradient, i.e.,* rate of *fall* of temperature with distance in the direction of flow of heat.

  All liquids and gases are heated by convection. Heat comes to us from the sun by radiation.

- **Newton's Law of Cooling :** It states that the rate of loss of heat of a liquid is directly proportional to difference in temperatures of the liquid and the surroundings provided the temperature difference is small (≈ 30°C).

  $$-\frac{dQ}{dt} \propto (T - T_0) \qquad \text{or} \qquad \frac{dQ}{dt} = -K(T - T_0)$$

  As, $\dfrac{dQ}{dt} = \dfrac{ms\ dT}{dt} = -K(T - T_0)$ or $\dfrac{dT}{dt} \propto (T - T_0)$.

- When the temperature difference between body and surroundings is large, then Stefan's law for cooling of body is obeyed. According to it,

  $E = \sigma\ (T^4 - T_0^4)$

where E is the amount of thermal energy emitted per second per unit area of a black body. T is the temperature of black body and T_0 is the temperature of surroundings, σ is the Stefan's constant.

Wien's Displacement Law : The wavelength λ_{max} at which the maximum amount of energy is radiated decreases with the increase of temperature and is such that

$$\lambda_{max}T = b \text{ (b wem's constant) } b = 2.88 \times 10^{-3} \text{ m-k}$$

where T is the temperature of black body in Kelvin.

- **Thermodynamical system :** An assembly of extremely large number of gas molecules is called a thermodynamical system. The pressure P, volume V, temperature T and heat cotent Q are called *Thermodynamical parameters.*

- **Zeroth Law of Thermodynamics :** (Concept of temperature) According to this law, when thermodynamic systems A and B are separately in thermal equilibrium with a third thermodynamic system C, then the systems A and B are in thermal equilibrium with each other also.

- **Internal Energy of a Gas** is the sum of kinetic energy and the potential energy of the molecules of the gas.

  K.E./molecule $= \frac{1}{2}mc^2 = \frac{3}{2}k\,T$ where k is Boltzmann's constant.

  internal energy of an ideal gas is wholly kinetic.

- **First Law of Thermodynamics** (principle of conservation of energy)

  According to this law $dQ = dU + dW$

  where dQ is the small amount of heat energy exchange with a system, dU is small change in internal energy of the system and dW is the small external work done by or on the system.

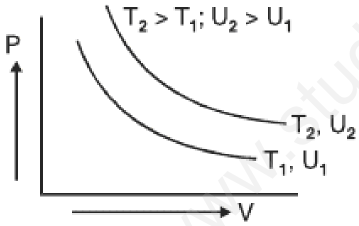
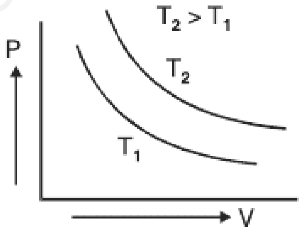
- *Sign conventions* used in thermodynamics.

  (a) Heat *absorbed* by the system = *positive* and heat rejected by the system = *negative.*

  (b) When temperature of the system rises, its internal energy increases ΔU = *positive.*

When temperature of the system falls, its internal energy decreases, ΔU = *negative.*

(c) When a gas expands, work is done by the system. It is taken as positive. When a gas is compressed, work is done *on* the system. It is taken as negative.

Isothermal changes	Adiabatic changes
• Temperature (T) remains constant, *i.e.,* $\Delta T = 0$	1. Heat content and entropy are constant, *i.e.,* Q = const ; S = constant, $\Delta Q = 0$; $\Delta S = 0$
• Changes are slow.	2. Changes are fast.
• System is thermally conducting.	3. System is thermally insulated.
• Internal energy, U = constant $\therefore \Delta U = 0$	4. Internal energy changes, *i.e.,* $\Delta U \neq 0$
• Specific heat, $c = \infty$	5. Specific heat, $c = 0$
• Equation of isothermal changes, PV = constant.	6. Eqn. of adiabatic changes (*i*) PV^{γ} = constant (ii) $TV^{\gamma-1}$ = constant (*iii*) $P^{1-\gamma}T^{\gamma}$ = constant
	
• Slope of isothermal curve, $\frac{dP}{dV} = -\left(\frac{P}{V}\right)$	7. Slope of adiabatic curve, $\frac{dP}{dV} = -\gamma\left(\frac{P}{V}\right)$
• Coeff, of isothermal elasticity, $K_i = P$	8. Coeff. of adiabatic elasticity, $K_a = \gamma P$
• Work done in isothermal expansion	9. Work done in adiabatic expansion
$W = 2.303\ nRT \log_{10}(V_2/V_1)$	$W = \frac{nR(T_2 - T_1)}{1-\gamma}$
n → number of mole	
$W = 2.303\ P_1 V_1 \log_{10}(V_2/V_1)$	$\frac{P_2V_2 - P_1V_1}{1-\gamma}$
$W = 2.303\ nRT \log_{10}(P_1/P_2)$	$W = C_v(T_1 - T_2)$

- **Second Law of Thermodynamics :** It is impossible for self acting machine, unaided by an external agency to convey heat from the body at lower temperature to another at higher temperature. This statement of the law was made by **Clausius.**

According to **Kelvin,** it is impossible to derive a continuous supply of work by cooling a body to a temperature lower than that of the coldest of its surroundings.

Heat Engines : A heat engine is a device which converts heat energy into mechanical energy. Efficiency of a heat engine is the ratio of work done (W) by the engine per cycle to the energy absorbed from the source (Q_1) per cycle.

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$ where Q_2 = heat rejected to the sink

- **Carnot Engine :** is an ideal heat engine which is based on Carnot's reversible cycle. Its working consists of four steps. (Isothermal expansion, Adiabatic expansion isothermal compression and adiabatic compression).

The efficiency of Carnot engine is given by $\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$

where Q_1 is heat energy absorbed from the source maintained at high temperature $T_1 K$ and Q_2 is amount of heat energy rejected to the sink at low temperature $T_2 K$.

A Refrigerator absorbs heat Q_2 from a sink (substance to be cooled) at lower temperature TK. Electric energy W has to be supplied for this purpose

$$Q_1 = Q_2 + W$$

Coefficient of performance (β) *of a refrigerator is the ratio of the heat absorbed per cycle from the sink (Q_2) to the electric energy supplied (W) for this purpose per cycle, i.e.,*

$$\beta = \frac{Q_2}{W}, \quad i.e., \quad \beta = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2} = \frac{1-\eta}{\eta}$$

QUESTIONS

1. Why spark is produced when two substances are struck hard against each other?

2. What is the specific heat of a gas in an isothermal process.
3. On what factors, does the efficiency of Carnot engine depend?
4. What are two essential features of Carnot's ideal heat engine.
5. Plot a graph between internal energy *U* and Temperature (T) of an ideal gas.
6. Refrigerator transfers heat from cold body to a hot body. Does this violate the second law of thermodynamics?
7. What is heat pump?
8. Give two example of heat pump?
9. What is heat engine?
10. Why a gas is cooled when expanded?
11. Can the temperature of an isolated system change?
12. Which one a solid, a liquid or a gas of the same mass and at the same temperature has the greatest internal energy.
13. Under what ideal condition the efficiency of a Carnot engine be 100%.
14. Which thermodynamic variable is defined by the first law of thermodynamics?
15. Give an example where heat be added to a system without increasing its temperature.
16. What is the efficiency of carnot engine working between ice point and steam point?
17. Two blocks of the same metal having masses 5g and 10g collide against a target with the same velocity. If the total energy used in heating the balls which will attain higher temperature?
18. What is the specific heat of a gas in an adiabatic process.

SHORT ANSWER (1 MARK)

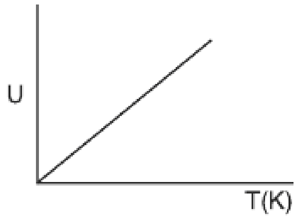
1. Work is converted into heat

2. Infinite

3. $\eta = 1 - T_2/T_1$

4. (i) Source and sink have infinite heat capacities.

   (ii) Each process of the engine's cycle is fully reversible

5. 

6. No, External work is done

7. A heat pump is a device which uses mechanical work to remove heat.

8. Refrigerator, Air Conditioner.

9. Heat engine is a device which convert heat energy into mechanical energy.

10. Decrease in internal energy.

11. Yes in an adiabatic process

12. Gas has greatest internal energy and solid has least internal energy.

13. If the temperature of sink is OK.

14. Internal energy.

15. Melting.

16. $\eta = 1 - T_2/T_1 = 1 - 273/373 = 26.8\%$

17. Both the balls will undergo the same rise in temperature.

18. Zero.

SHORT ANSWER TYPE QUESTION (2 MARKS)

1. A thermos bottle containing tea is vigorously shaken. What will be the effect on the temperature of tea.

2. Write two limitation of the first law of thermodynamics.

3. Write the expressions for C_v and C_p of a gas in terms of gas constant R and γ where

$$\gamma = C_p/C_v$$

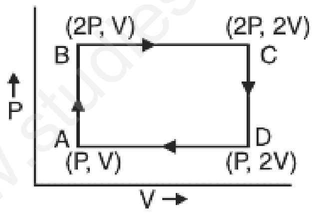
4. No real engine can have an efficiency greater that of a carnot engine working between the same tow temperatures. Why?

5. Why water at the base of a waterfall is slightly warmer than at the top?

6. When ice melts, the change in internal energy is greater than the heat supplied. Why?

7. Explain why two isothermal curves never intersect.

8. An ideal monatomic gas is taken round the cycle ABCDA as shown. Calculate the work done during the cycle.



9. Can a room be cooled by opening the door of refrigerator in a closed room?

10. Explain what is meant by isothermal and adiabatic operations.

11. Two bodies at different temperatures T_1 and T_2, if brought in thermal contact do not necessarily settle to the mean temperature $(T_1 + T_2)/2$ Explain?

SHORT ANSWERS (2 MARKS)

1. Temperature of tea will rise.

2. (i) It does not give the direction of flow of heat.

   (ii) It does not explain why heat cannot be spontaneously converted into work.

3. $\gamma = C_p/C_v$

$C_p - C_v = R$

$C_p = \gamma C_v$

$$(\gamma - 1)C_v = R; C_v = \frac{R}{\gamma - 1}$$

$$C_p = \frac{\gamma R}{\gamma - 1}$$

4. In carnot engine.

(i) There is absolutely no friction between the wall of cylinder and piston.

(ii) Working substance is an ideal gas

In real engine these condition cannot be fulfilled.

5. Potential energy converted in to kinetic energy, some part of kinetic energy is converted in to heat.

6. dq = du + dw

du = dq – pdv

When ice melt change in volume is negative.

7. PV

8. PV

9. No, It a voilets seconds law.

10. Adiabatic a Process – Pressure, volume and temperature of the system changes but there is no exchange of heat.

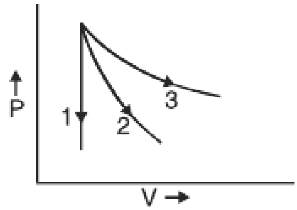
Isothermal Process – Pressure, volume changes temperature remain constant.

11. Heat flows from higher temperature to lower temperature until the temperature become equal only where the thermal capacities of two bodies are equal.

SHORT ANSWER TYPE QUESTIONS (3 MARKS)

1. Obtain an expression for work done in an isothermal process.

2. Identify and name the Thermodynamic processes 1,2,3 as shown in figure.



3. Two samples of gas initially at the same temperature and pressure are compressed from volume V to V/2 one sample is compressed isothermally and the other adiabatically in which case the pressure will be higher? Explain?

4. Explain briefly the principle of a heat pump. What is meant by coefficient of performance?

5. When you blow on the back of your hand with your mouth wide open your breath feels warm about if you partially close your mouth form an "O" and then blow on your hand breath fells cool. Why?

6. Is it a violation of the second law of thermodynamics to convert

   (a) Work completely in to heat?

   (b) Heat completely in to work?

   Why or why not?

7. State first law of thermodynamics on its basis establish the relation between two molar specific heat for a gas.

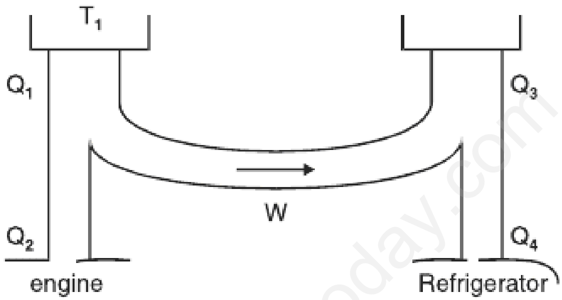
8. Explain briefly the working principle of a refrigerator and obtain an expression for its coefficient of performance.

9. State zeroth law of thermodynamics. How does it lead to the concept of temperature?

10. What is a cyclic process? Show that the net work done during a cyclic process is numerically equal to the area of the loop representing the cycle.

11. State second law of thermodynamics.

12. An ideal engine works between temperatures T_1 and T_2 . It drives an ideal refrigerator that works between temperatures T_3 and T_4. Find the ratio Q3/Q1 in terms of T_1, T_2, T_3 and T_4



LONG ANSWER TYPE QUESTIONS (5 MARKS)

1. Describe briefly carnot engine and obtain an expression for its efficiency.

2. Define adiabatic process. Derive an expression for work done during adiabatic process.

3. Why a gas has two principal specific heat capacities? What is the significance of $C_p - C_v$ and C_p/C_v where symbols have usual meaning.

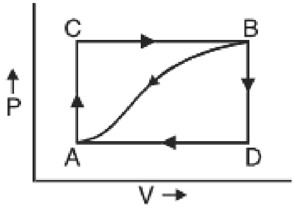
NUMERICALS

1. When a system is taken from state A to state B along the path ACB, 80 k cal of heat flows into the system and 30 kcal of work is done.

   (a) How much heat flows into the system along path ADB if the work done is 10 k cal?

   (b) When the system is returned from B to A along the curved path the work done is 20 k cal. Does the system absorb or librate heat.

   (c) If $U_A = 0$ and $U_D = 40$ k cal, find the heat absorbed in the process AD



2. $\frac{1}{2}$ mole of helium is contained in a container at S.T.P. How much heat energy is needed to double the pressure of the gas, keeping the volume constant? Heat capacity of gas is 3 J g^{-1} K^{-1}.

3. The volume of steam produced by 1g of water at 100°c is 1650 cm^3. Calculate the change in internal energy during the change of state given

   $J = 4.2 \times 10^7$ erg cal^{-1} g = 98 J cm/s^2

   latent heat of steam = 540 cal/g

4. What is the coefficient of performance (β) of a carnot refrigerator working between 30°C and 0°C?

5. Calculate the fall in temperature when a gas initially at 72°C is expanded suddenly to eight times its original volume. (γ = 5/3)

6. A steam engine intake steam at 200°C and after doing work exhausts it directly in air at 100°C calculate the percentage of heat used for doing work. Assume the engine to be an ideal engine?

7. A perfect carnot engine utilizes an ideal gas the source temperature is 500K and sink temperature is 375K. If the engine takes 600k cal per cycle from the source, calculate

   (i) The efficiency of engine

   (ii) Work done per cycle

   (iii) Heat rejected to sink per cycle.

8. Two carnot engines A and B are operated in series. The first one A receives heat at 900 K and reject to a reservoir at temperature T K. The second engine B receives the heat rejected by the first engine and in turn rejects to a heat reservoir at 400 K calculate the temperature T when

   (i) The efficiencies of the two engines are equal

   (ii) The work output of the two engines are equal

9. Ten mole of hydrogen at NTP is compressed adiabatically so that its temperature become 400°C How much work is done on the gas? what is the increase in the internal energy of the gas

$$R = 8.4 \text{ J mol}^{-1}\text{K}^{-1} \quad \gamma = 1.4$$

10. The temperature T_1 and T_2 of the two heat reservoirs in an ideal carnot engine be 1500°C and 500°C respectively. which of these increasing T_1 by 100°C or decreasing T_2 by 100°C would result in a greater improvement in the efficiency of the engine.

ANSWERS

1. (a) $dw_{ADB} = +10$ k cal

Internal energy is path independent

$du_{ADB} = du_{ACB} = 50$ k cal

$dQ_{ADB} = 50 + 10 = 60$ k cal.

(b) $dw_{BA} = -20$ k cal

$du_{BA} = -du_{ADB}$

$dQ_{BA} = du_{BA} + dW_{BA}$

$= -50 - 20 = -70$ k cal

(c) $U_A = 0 \; U_D = 40$ k cal

$du_{AD} = 40$ k cal

$dw_{ADB} = 10$ k cal

$dw_{DB} = 0$ since $dV = 0$

$dQ_{AD} = 40 + 10 = 50$ k cal

2. $n = \frac{1}{2}$, $C_v = 3$J/gK. $M = 4$

$C_v = MC_v = 12$ J/mole k M → Molecular mass

$\frac{P_2}{P_1} = \frac{T_2}{T_1} = 2$

$\Delta T = 2T_1 - T_1 = 273$ k

$\Delta Q = n\ c_v\ \Delta T = 1638$ J

3. Mass of water = 1 g = 10^{-3} kg

$$\text{volume of water} = \frac{\text{Mass}}{\text{Density}} = \frac{10^{-3}}{10^{3}} = 10^{-6} m^3$$

$= 1\ cm^3$

Change in volume = 1650 – 1 = 1649 cm^3

$dQ = m\ L = 540$ cal $= 540 \times 4.2 \times 10^7$ erg

$P = 1$ atm $= 76 \times 13.6 \times 981$

$du = dQ - pdv = 22.68 \times 10^9 - 1.67 \times 10^9$

$= 21.01 \times 10^9$ erg.

4. $$\beta = \frac{T_2}{T_1 - T_2} = \frac{273}{303 - 273} = 9.1$$

5. $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} = 345\left(\frac{x}{8x}\right)^{2/3}$$

$$= 345 \times \frac{1}{4} = 86.25 \text{ k}$$

6. $T_1 = 200°C = 473$ K $T_2 = 100°C = 373$ K

$$\eta = \frac{w}{Q_1} = \frac{T_1 - T_2}{T_1} = \frac{473 - 373}{473}$$

$$= \frac{100}{473} = 0.21$$

= 21%

7. $T_1 = 500$ K $T_2 = 375$ K

Q_1 = Heat absorbed = 600 k cal

$$\eta = 1 - T_2/T_1 = \frac{125}{500} = 0.25$$

$$= 25\%$$

(b) $$\eta = \frac{w}{Q_1}$$

$$W = \eta Q_1 = 0.25 \times 60 \text{ k cal} = 150 \text{ k cal}$$

$$= 450 \text{ k cal}$$

(c) $$w = Q_1 - Q_2 \; Q_2 = Q_1 - W = 600 - 150$$

$$= 450 \text{ k cal}$$

8. $W_A = W_B$

$$\frac{W}{Q_1} = \left(1 - \frac{T_2}{T_1}\right)$$

$$W = Q_1(1 - T_2/T_1)$$

$$Q_2\left(1 - T_3/T_2\right) = Q_1\left(1 - T_2/T_1\right)$$

$$\left(1 - T/900\right) \quad Q_1 = \left(1 - \frac{400}{T}\right) Q_2$$

$$\left(1 - T/900\right) \quad Q_1 = \left(1 - \frac{400}{T}\right) T/900$$

$$1 - T/900 = \frac{T}{900} - \frac{400}{900}$$

$$\frac{2T}{900} = 13/9$$

$$T = 650 \text{ K}$$

$$\eta_A = \eta_B$$

$$1 - T/900 = \frac{1 - 400}{T}$$

$$T^2 = 900 \times 400$$

$= 600\ K$

$T_1 = 273\ K\ T_2 = 673\ K$

mass of gas = 10 mole

$$W_{adia} = \frac{10\ R}{(\gamma - 1)}(T_1 - T_2)$$

$$= \frac{10 \times 8.4}{(1.4 - 1)}(273 - 673)$$

$= -8.4 \times 10^4$ J work being done on the gas

$du = -dw = 8.4 \times 10^4$ J

10. $\eta = 1 - T_2/T_1$

(i) T_1 is increased from 1500°C to 1600°C

$T_1 = 1873$ K

T_2 remain constant $T_2 = 773$ k

$$\eta_1 = \frac{1873 - 773}{1873} = 58.73\%$$

(ii) T_1 remain constant 1500°C

$T_1 = 1500 + 273 = 1773$ k

T_2 is decreased by 100 i.e. 400°C

$T_2 = 400 + 273 = 673$ k

$$\eta_2 = \frac{1773 - 673}{1773} = \frac{1100}{1773} = 62.04\%$$

$\eta_2 > \eta_1$

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