

CHAPTER TWELVETHERMODYNAMICS

- **Thermodynamics** is a branch of physics which deals with the study of heat, temperature and the inter conversion of heat energy into other forms of energy.
- The various terms involved in thermodynamics are:-

Thermodynamic System

- A thermodynamic system consists of a large number of atoms or molecules at a particular temperature, pressure and volume
- The system may exist in solid, liquid and gaseous state.

Surroundings

- Everything outside a thermodynamic system is its surrounding.

Thermodynamic Variables or Parameters

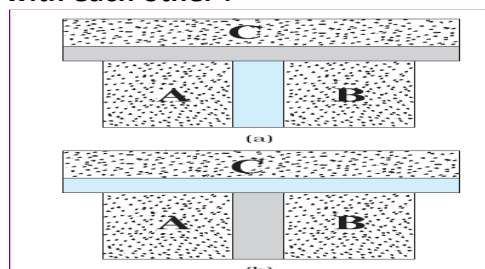
- These are quantities like pressure, volume and temperature which help us to study the behaviour of thermodynamic system.

THERMAL EQUILIBRIUM

- An insulating wall that does not allow flow of energy (heat) from one to another is called an **adiabatic wall**.
- A conducting wall that allows energy flow (heat) from one to another is called a **diathermic wall**.
- In thermal equilibrium, the temperatures of the two systems are equal.

ZEROth LAW OF THERMODYNAMICS

- R.H. Fowler formulated this law
- The **Zeroth Law of Thermodynamics** states that 'two systems in thermal equilibrium with a third system separately are in thermal equilibrium with each other'.



- Thus if $T_A = T_B$ and $T_A = T_C$, then $T_A = T_B$

HEAT, INTERNAL ENERGY AND WORK

- **Heat** is that part of internal energy which is transferred from one body to another on account of the temperature difference
- **Internal energy** is the sum of the kinetic energies and potential energies of the molecules. It is denoted by U .
- **Work** is energy transfer brought about by means (e.g. moving the piston by raising or lowering some weight connected to it) that do not involve such a temperature difference

FIRST LAW OF THERMODYNAMICS

- The amount of heat given to a system is equal to the sum of the increase in the internal energy of the system and the external work done.

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

- ΔQ = Heat supplied to the system by the surroundings
- ΔW = Work done by the system on the surroundings
- ΔU = Change in internal energy of the system
- At constant pressure

$$\Delta W = P \Delta V$$

- Thus

$$\Delta Q = \Delta U + P \Delta V$$

Specific heat of a substance

- Specific heat of a substance is the quantity of heat required to raise the temperature of unit mass of the substance through one Kelvin

$$s = \frac{1}{m} \frac{\Delta Q}{\Delta T}$$

- Unit: J/ kg /K.

Molar Specific Heat (C)

- It is the amount of heat energy required to raise the temperature of one mole of a substance through one degree celsius or one kelvin.

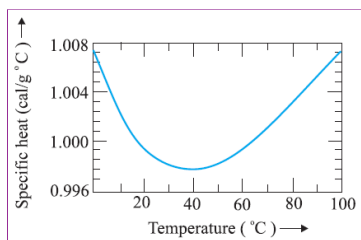
$$C = \frac{1}{\mu} \frac{\Delta Q}{\Delta T}$$

- Where μ = number of moles, ΔQ = Heat absorbed to raise the temp by an amount ΔT .

Unit: J/mol/K.

Specific heat capacity of water

- The old unit of heat was calorie.
- One calorie is defined to be the amount of heat required to raise the temperature of 1g of water from 14.5 °C to 15.5 °C
- The specific heat of water varies slightly with temperature



- In SI units, the specific heat capacity of water is $4186 \text{ J kg}^{-1} \text{ K}^{-1}$

Molar Specific Heat of gas.

Molar specific heat at constant volume (C_V)

- Molar specific heat of a gas at constant volume is the amount of heat required to raise the temperature of one mole of the gas through 1K when its volume is kept constant.*

Molar Specific heat at constant pressure (C_P)

- Molar specific heat of the gas at constant pressure is defined as the amount of heat required to raise the temperature of one mole of the gas through 1K, when its pressure is kept constant.*

Relation between C_P and C_V . (Mayer's relation)

$$C_P - C_V = R$$

Proof

- From first law of thermodynamics we have

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

- If ΔQ heat is absorbed at constant volume ($\Delta V = 0$)

$$C_V = \left[\frac{\Delta Q}{\Delta T} \right]_V = \left[\frac{\Delta U}{\Delta T} \right]_V = \frac{\Delta U}{\Delta T} \dots\dots\dots(1)$$

- Since internal energy of ideal gas depends only on temperature,
- Similarly we get



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$$C_P = \left[\frac{\Delta Q}{\Delta T} \right]_P = \left[\frac{\Delta U}{\Delta T} \right]_P + P \left[\frac{\Delta V}{\Delta T} \right]_P \dots\dots\dots(2)$$

- From ideal gas equation for one mole $PV = RT$.
- Differentiating w.r.t. temperature (at constant pressure)

$$P \left[\frac{\Delta V}{\Delta T} \right]_P = R \dots\dots\dots(3)$$

- Substituting in (2)

$$C_P = \frac{\Delta U}{\Delta T} + R \dots\dots\dots(4)$$

- Eqn 4 – eqn 1 gives

$$C_P - C_V = R$$

- This is Mayer's relation

C_P is greater than C_V . Why?

- When one mole of the gas is heated at constant volume, the heat is used only to increase the internal energy of the gas.
- But when the gas is heated at constant pressure, the heat is used not only for increasing the internal energy but also for doing external work during expansion.
- For same rise of temp, the increase in internal energy is same in both cases. Hence C_P is greater than C_V .

THERMODYNAMIC STATE VARIABLES

- Every **equilibrium state** of a **thermodynamic system** is completely described by specific values of some macroscopic variables called state variables.
- The thermodynamic state variables are of two kinds: **extensive and intensive**.
- Extensive variables** indicate the 'size' of the system.
- Internal energy U , volume V , and total mass M are *extensive variables*.
- Intensive variables** do not indicate the size of the system.
- Pressure P , temperature T , and density ρ are *intensive variables*.

EQUATION OF STATE

- The connection between the state variables is called the equation of state.
- For an ideal gas, the equation of state is

$$P V = \mu R T$$

- The pressure-volume curve for a fixed temperature is called an **isotherm**.

THERMODYNAMIC PROCESSES

- It is any process in which there is some change in pressure, volume or temperature of a system.

| Type of processes | Feature |
|-------------------|---|
| Isothermal | Temperature constant |
| Isobaric | Pressure constant |
| Isochoric | Volume constant |
| Adiabatic | No heat flow between the system and the surroundings ($\Delta Q = 0$) |

Quasistatic process

- It is a process in which a thermodynamic system proceeds extremely slowly such that at every instant of time, the temperature and pressure are the same in all parts of the system.

Isothermal process

- A process in which the temperature of the system is kept fixed throughout is called an isothermal process.
- In such a process, if heat is developed in the system, it is given out to the surroundings or if heat is lost, it is taken from the surroundings.
- Eg: Melting, boiling, the expansion of a gas in a metallic cylinder placed in a large reservoir of fixed temperature etc.

Equation of state of isothermal process

$$P V = \text{constant}$$

Work done by an ideal gas during an isothermal process

- Suppose one mole of an ideal gas goes isothermally (at temperature T) from its initial state (P_1, V_1) to the final state (P_2, V_2).
- Let the volume of a gas having pressure P change by dV .
- Then work done, $dW = P dV$.
- Thus the total work done

$$W = \int_{V_1}^{V_2} P dV \quad \text{But } P V = R T. \text{ Or } P = \frac{R T}{V}$$

$$\therefore W = \int_{V_1}^{V_2} \frac{R T}{V} dV. = R T \int_{V_1}^{V_2} \frac{dV}{V}$$

$$W = R T \ln \frac{V_2}{V_1}$$

- For an ideal gas, internal energy depends only on temperature.
- Thus, there is no change in the internal energy of an ideal gas in an isothermal process.
- For $V_2 > V_1$, $W > 0$; and for $V_2 < V_1$, $W < 0$.
- That is, in an **isothermal expansion**, the **gas absorbs heat and does work** while in an **isothermal compression**, **work is done on the gas by the environment and heat is released**.

Adiabatic process

- In an adiabatic process, the system is insulated from the surroundings and heat absorbed or released is zero.

Equation of state for adiabatic process

- For an adiabatic process of an ideal gas

$$P V^\gamma = \text{const}$$

- where γ is the ratio of specific heats at constant pressure and at constant volume.

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

- Also

$$T V^{\gamma-1} = \text{Constant}$$

$$P^{1-\gamma} T^\gamma = \text{Constant}$$

Work done in an adiabatic process

- Let an ideal gas undergoes adiabatic change from (P_1, V_1, T_1) to (P_2, V_2, T_2).

$$W = \int_{V_1}^{V_2} P dV$$

$$W = k \int_{V_1}^{V_2} \frac{dV}{V^\gamma} \quad \left(\text{since } P = \frac{k}{V^\gamma} \right)$$

- Here k is a constant

$$W = k \left[\frac{V_2^{-\gamma+1}}{-\gamma+1} - \frac{V_1^{-\gamma+1}}{-\gamma+1} \right] = \frac{k}{1-\gamma} \left[\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}} \right] = \frac{1}{1-\gamma} \left[\frac{k}{V_2^{\gamma-1}} - \frac{k}{V_1^{\gamma-1}} \right] = \frac{1}{1-\gamma} \left[\frac{P_2 V_2^\gamma}{V_2^{\gamma-1}} - \frac{P_1 V_1^\gamma}{V_1^{\gamma-1}} \right]$$

$$W = \frac{1}{1-\gamma} [P_2 V_2 - P_1 V_1]$$

$$W = \frac{1}{1-\gamma} [P_2 V_2 - P_1 V_1] = \frac{R}{1-\gamma} (T_2 - T_1)$$

- That is

$$W = \frac{1}{\gamma-1} [P_1 V_1 - P_2 V_2] \quad \text{or} \quad W = \frac{R}{\gamma-1} [T_1 - T_2]$$

- If work is done by the gas in an adiabatic process ($W > 0$) then $T_2 < T_1$.
- If work is done on the gas ($W < 0$), we get $T_2 > T_1$ i.e., the temperature of the gas rises.

Isochoric process

- In an isochoric process, V is constant.
- Thus work done on or by the gas is zero.
- The heat absorbed by the gas goes entirely to change its internal energy and its temperature.

Isobaric process

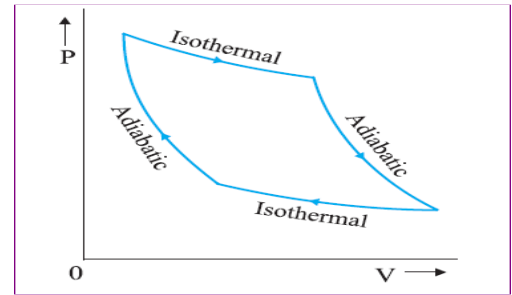
- In an isobaric process, P is fixed. Work done by the gas is
- $$W = P (V_2 - V_1) = \mu R (T_2 - T_1)$$
- The heat absorbed goes partly to increase internal energy and partly to do work.
 - The change in temperature for a given amount of heat is determined by the specific heat of the gas at constant pressure.

Cyclic process

- In cyclic process, the system returns to its initial state such that change in internal energy is zero.
- That is $\Delta U = 0$ for a cyclic process
- Thus the total heat absorbed equals the work done by the system
- The P - V diagram for cyclic process will be closed loop and area of this loop gives work done or heat absorbed by system.

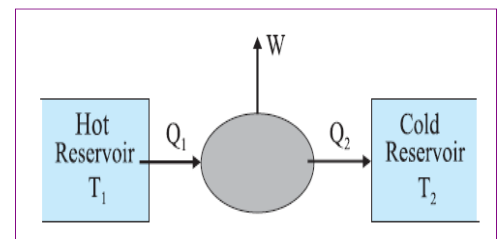


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HEAT ENGINES

- Heat engines convert heat energy into mechanical energy.
- Heat engine is a device by which a system is made to undergo a cyclic process that results in conversion of heat to work
- Heat engines consists of :**
- Working substance** (the system which undergoes cyclic process) eg: mixture of fuel vapour and air in diesel engine, steam in steam engine.
- An external reservoir at a high temperature** (T_1) - it is the source of heat.
- An external reservoir at low temperature** (T_2) or sink



Working

- The working substance absorbs an energy Q_1 from source reservoir at a temperature T_1 .
- It undergoes cyclic process and releases heat Q_2 to cold reservoir.
- The change in heat ($Q_1 - Q_2$) is converted into work (mechanical energy)

Efficiency of heat engine (η)

- The efficiency (η) of a heat engine is defined by

$$\eta = \frac{W}{Q_1}$$

- where Q_1 is the heat input i.e., the heat absorbed by the system in one complete cycle and W is the work done on the environment in a cycle.
- Thus

$$W = Q_1 - Q_2$$

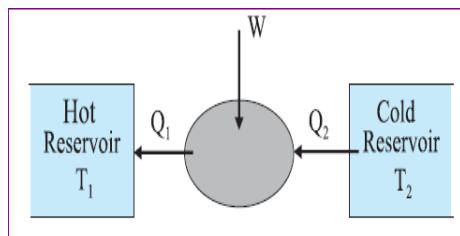
i.e.,

$$\eta = 1 - \frac{Q_2}{Q_1}$$

- In an external combustion engine, say a steam engine the system is heated by an external furnace.
- In an internal combustion engine, it is heated internally by an exothermic chemical reaction.

REFRIGERATORS

- Refrigerator is the reverse of a heat engine.
- It is a device used to cool a portion of space (inside a chamber)



- The working substance extracts heat Q_2 from the cold reservoir at temperature T_2 , some external work W is done on it and heat Q_1 is released to the hot reservoir at temperature T_1 .
- The working substance in refrigerator is termed as refrigerant
- In a refrigerator the working substance (usually, in gaseous form) goes through the following steps :
 - **Sudden expansion of the gas** from high to low pressure which cools it and converts it into a vapour-liquid mixture.
 - **Absorption by the cold fluid of heat** from the region to be cooled converting it into vapour.
 - **Heating up of the vapour** due to external work done on the system.
 - **Release of heat** by the vapour to the surroundings, bringing it to the initial state and completing the cycle.

The coefficient of performance (α)

- The coefficient of performance (α) of a refrigerator is given by

$$\alpha = \frac{Q_2}{W}$$

HEAT PUMPS

- The device used to pump heat into a portion of space (to warm-up room) is called heat pump.
- A heat pump is the same as a refrigerator.
- The coefficient of performance for heat pump is defined as Q_1/W .

SECOND LAW OF THERMODYNAMICS

Kelvin-Planck statement

- No process is possible whose sole result is the absorption of heat from a reservoir and the complete conversion of the heat into work.

Clausius statement

- No process is possible whose sole result is the transfer of heat from a colder object to a hotter object.

REVERSIBLE AND IRREVERSIBLE PROCESSES

- A reversible process is one, which can be retraced in the reverse order, so that it passes exactly through the same state as in the direct process.

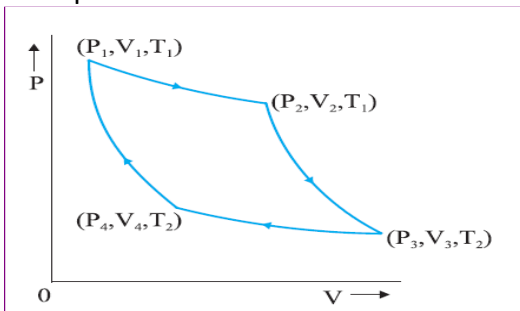
Condition for a process to be reversible:

- All steps of the process must be infinitely slow.
- Loss of heat due to friction, viscosity, resistance etc should be completely absent.
- The temp and pressure of the system must not change considerably from the surrounding at any stage.
- Eg:- Slow evaporation of substance in an insulated container., The slow compression of a spring, Melting and boiling, Ideal case of adiabatic and isothermal process.
- Any process, which cannot be retraced in the opposite direction by reversing, controlling factors, is called **an irreversible process.**

- Eg: (1) Almost all process in nature are irreversible. (2) Rusting of iron, dissolving of soap in water etc.

CARNOT ENGINE

- A **reversible heat engine** operating between two temperatures is called a Carnot engine.
- Developed by Sadi Carnot
- The working substance of the Carnot engine is an ideal gas.
- The **Carnot cycle** consists of the following steps:



- Step 1 → 2 Isothermal expansion** of the gas taking its state from (P_1, V_1, T_1) to (P_2, V_2, T_1) .
- The work done ($W_{1 \rightarrow 2}$) by the gas on the environment is

$$W_{1 \rightarrow 2} = Q_1 = \mu R T_1 \ln \left(\frac{V_2}{V_1} \right)$$

- Step 2 → 3 Adiabatic expansion** of the gas from (P_2, V_2, T_1) to (P_3, V_3, T_2)
- Work done by the gas,

$$W_{2 \rightarrow 3} = \frac{\mu R}{\gamma - 1} [T_1 - T_2]$$

- Step 3 → 4 Isothermal compression** of the gas from (P_3, V_3, T_2) to (P_4, V_4, T_2) .
- The work done ($W_{3 \rightarrow 4}$) on the gas by the environment is

$$W_{3 \rightarrow 4} = Q_2 = \mu R T_2 \ln \left(\frac{V_4}{V_3} \right)$$

Or

$$W_{3 \rightarrow 4} = Q_2 = -\mu R T_2 \ln \left(\frac{V_3}{V_4} \right)$$

- Step 4 → 1 Adiabatic compression** of the gas from (P_4, V_4, T_2) to (P_1, V_1, T_1) .
- Work done on the gas,

$$W_{4 \rightarrow 1} = -\frac{\mu R}{\gamma - 1} [T_1 - T_2]$$

- The total work done by the gas in one complete cycle is

$$W = W_{1 \rightarrow 2} + W_{2 \rightarrow 3} + W_{3 \rightarrow 4} + W_{4 \rightarrow 1}$$

$$= \mu R T_1 \ln \left(\frac{V_2}{V_1} \right) - \mu R T_2 \ln \left(\frac{V_3}{V_4} \right)$$

Efficiency of a Carnot Engine

- The efficiency η of a heat engine is

$$\eta = 1 - \frac{Q_2}{Q_1}$$

- But for a Carnot engine $\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$
- Thus

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

- Reversing the steps in the Carnot cycle will amount to taking heat Q_2 from the cold reservoir at T_2 , doing work W on the system, and transferring heat Q_1 to the hot reservoir. This will be a reversible refrigerator.

Carnot's Theorem

- (a) working between two given temperatures T_1 and T_2 of the hot and cold reservoirs respectively, no engine can have efficiency more than that of the Carnot engine and
- (b) The efficiency of the Carnot engine is independent of the nature of the working substance.



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