

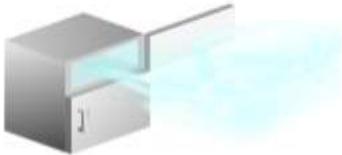
Thermodynamics

Introduction

- Thermodynamics is that branch of physics which deals with concepts of heat and temperature and their relation to energy and work.
- We can also consider it as a macroscopic science which deals with bulk systems and tells us about system as a whole.
- In this chapter we will learn about the laws of thermodynamics which describes the system in terms of macroscopic variables, reversible and irreversible processes. Finally we will also learn on what principle heat engines, refrigerators and Carnot engine work.

Examples: - Refrigerator, steam engine

Refrigerator



Thermodynamics vs. Mechanics

- In Thermodynamics we consider only the state of the object which means we will only consider macroscopic variables like pressure, volume and temperature.
- In mechanics we consider the motion, velocity and acceleration of the object.

For eg: -

- In mechanics if a bullet is fired from a gun we will consider the motion of bullet and its velocity, acceleration etc.



Bullet getting fired from gun

Consider a second scenario where bullet is fired on a wall. When it hits the wall its kinetic energy gets converted to heat. Due to heat generation there will be a change in temperature and the internal energy of the bullet. These are the macroscopic variables which we will study in Thermodynamics.



Bullet fired from the gun and hitting a wall

Thermal Equilibrium

- Two systems are said to be in thermal equilibrium if the temperatures of the two systems are equal.
- In mechanics if the net force on a system is zero, the system is in equilibrium.
- In Thermodynamics equilibrium means all the macroscopic variables (pressure, temperature and volume) don't change with time. They are constant throughout.

For Example: -

- Consider two bodies at different temperatures one is at 30°C and another at 60°C then the heat will flow from body at higher temperature to the body at lower temperature.
- Heat will flow till both bodies acquire same temperature.
- This state when there is no heat flow between two bodies when they acquire the same temperature is known as thermal equilibrium.



In the above case if consider a hot cup of coffee will become cold after sometime if it is kept on the table as there will heat flow between the hot coffee and surroundings. When the cup of coffee attains the same temperature as of room temperature then there will be no flow of heat.

Types of Equilibrium

Thermal Equilibrium: - Two systems are said to be in thermal equilibrium with each other if the temperatures of both the systems do not change with time.

Chemical Equilibrium: - Two systems are said to be in chemical equilibrium with each other if the composition of the system does not change over time.

Mechanical Equilibrium: - Two systems are said to be in mechanical equilibrium with each other if the pressure of the system doesn't change with time.

A system is said to be in **Thermodynamic equilibrium** when all of its macroscopic variables are constant.

System and Surroundings

System: - System is defined as any part of universe enclosed by some boundary through which exchange of heat or energy takes place.

Surroundings: - Any part of the universe which is not a system.

- For example: - If we consider a hot coffee in a kettle then the kettle is the system and everything else is the surroundings.
- System and surroundings constitute Universe.



Kettle with hot coffee constitutes System and everything else around it is surroundings.

A system is in thermal equilibrium or not depends on:-

- Surroundings

For example:-A cup of hot coffee after some time becomes cold due to the exchange of heat between the system and surroundings.



Hot Coffee

Hot coffee becoming cold

- The nature of the wall dividing the system and surroundings.
- If the wall is adiabatic then there will be no flow of heat between the system and surroundings. As it is an insulating wall.
- If the wall is diathermic then the flow of heat will take place between the system and surroundings. As it is a conducting wall.

Isolated System: - In this system there is neither change in matter nor change in energy. For example: - Any closed insulated vessel like thermos flask. In thermos tea can be kept hot for many hours because the walls of thermos are insulated and it does not allow heat to flow out of the flask.

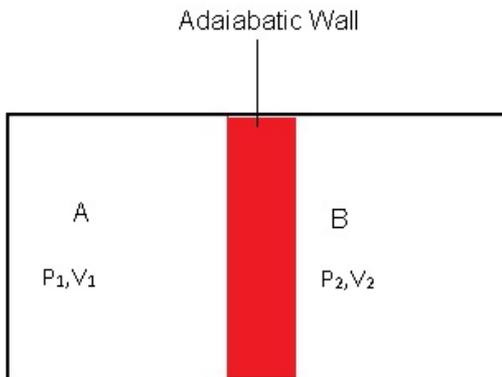


Thermos Flask

Types of Walls

Adiabatic wall: - It is an insulating wall which doesn't allow heat to flow from one system to another. This means temperature of both the systems won't change with time.

- Consider 2 systems A and B as shown in the figure, which are separated by adiabatic wall. Let pressure and volume of A be (P_1, V_1) and B be (P_2, V_2)
- Both are at the same temperature as there is no change in temperature with time.
- There is no heat flow between A and B as they are separated by an adiabatic wall.
- Both these systems are also separated from the surroundings by adiabatic wall which means there is no flow of heat between A and surroundings and also B and surroundings.



Two systems A and B are separated by an adiabatic wall from each other as well as from surroundings.

For example: - Thermos Flask. In which tea or coffee remains hot for a long time as it is made of insulating walls due to which there is no heat flow between tea and surroundings.

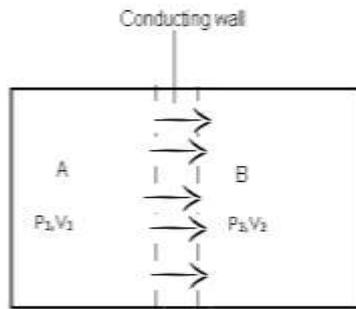


Thermos Flask

Diathermic Wall: - It is a conducting wall which allows the flow of heat between any 2 systems.

- Consider two systems A and B which are separated by a conducting wall. System A is at higher temperature T_1 , pressure P_1 and volume V_1 and System B is at lower temperature T_2 , pressure P_2 and volume V_2 .
- There is flow of heat from a system at a higher temperature to the system at a lower temperature till the systems reach thermal equilibrium.

- For Example: - A vessel made up of metals like copper or aluminium has diathermic walls.



Two systems are separated by a conducting wall.

- For example:-Hot tea in a cup. It will become cold after sometime as there will be flow of heat between tea and surroundings. And when temperature of the tea is in thermal equilibrium then there will be no heat flow.

Cup of Tea

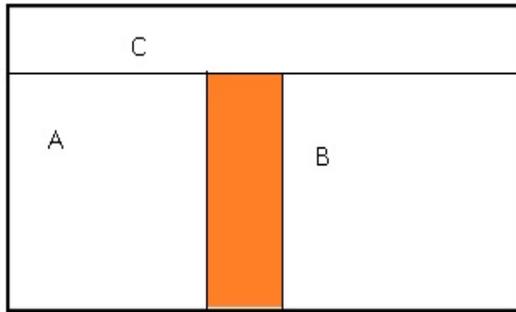


Copper vessels



Zeroth Law of Thermodynamics

- Zeroth law of thermodynamics states that when two systems are in thermal equilibrium through a third system separately then they are in thermal equilibrium with each other also.
- Foreg: - Consider two systems A and B which are separated by an adiabatic wall. Heat flow happens between systems A and C, and between B and C, due to which all 3 systems attain thermal equilibrium.



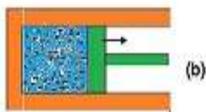
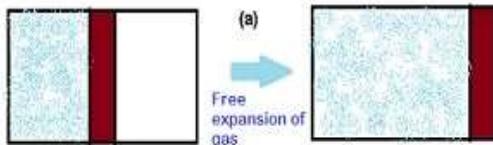
Systems A and B are in thermal equilibrium with C. Then they will be in equilibrium with each other also.

- Zeroth Law of Thermodynamics suggested that there should be some physical quantity which should have same value for the system to be in thermal equilibrium.
- This physical quantity which determines whether system is in equilibrium or not is Temperature.
- Temperature is the quantity which determines whether the system is in thermal equilibrium with the neighbouring system.
- When the temperature becomes equal then the flow of heat stops.

Thermodynamic state variables

Thermodynamic state variables are the macroscopic quantities which determine the thermodynamic equilibrium state of a system.

- These macroscopic quantities are known as thermodynamics state variables.
- Since these macroscopic quantities describe the behaviour of thermodynamic system it is known as thermodynamic.
- As they determine the state of the system that is pressure, volume and temperature, at one particular time they are known as thermodynamic state variables.
- Pressures (P), Volume (V), Temperature (T), mass (m), Internal energy (U) are the thermodynamic state variables.
- These variables can tell us the position or the condition of any gas at that particular time.
- A system not in equilibrium cannot be described by state variables. It means the macroscopic variables are changing with time and they are not constant.



(a) The partition in the box is suddenly removed leading to free expansion of the gas. (b) A mixture of gases undergoing an explosive chemical reaction. In both situations, the gas is not in equilibrium and cannot be described by state variables.

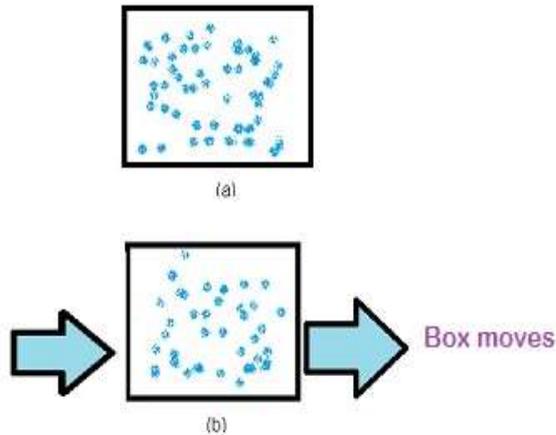
Types of thermodynamic state variables:-

Extensive variables: - They indicate the size of the system, which means extensive variables are those that depend on the mass of the system or the number of particles in the system. Example: volume, mass, internal energy. If we consider a system whose mass is greater than the size of that system is greater. All these depend on the size of the system.

Intensive variables: -

- They don't depend on size of the system.
- Pressure and Temperature are known as intensive variables.

- It only depends on the state of the system at that particular time.
- It does not depend on how the system has reached that state.



In figure(a) shows a box at rest then the Internal energy of a gas inside the box is sum of the kinetic and potential energies of its molecules.

In figure (b) if the same box is pushed and it starts moving as a whole with some velocity, the kinetic energy of the box is not to be included in U .

Two different modes to change Internal energy are:-

Heat
Work

Heat: - Consider a bottle and a balloon are tied at the neck of the bottle. When we heat the bottle, due to the difference in temperature heat flow takes place, as a result balloon blows up. That is due to transfer of heat kinetic energy and potential energy changes from bottle to the balloon. This results in the change of internal energy.



Deflated Balloon

Inflated Balloon

Work: - We can do some work on the system (in this case system is bottle with a balloon tied) as a result the internal energy of the system changes.

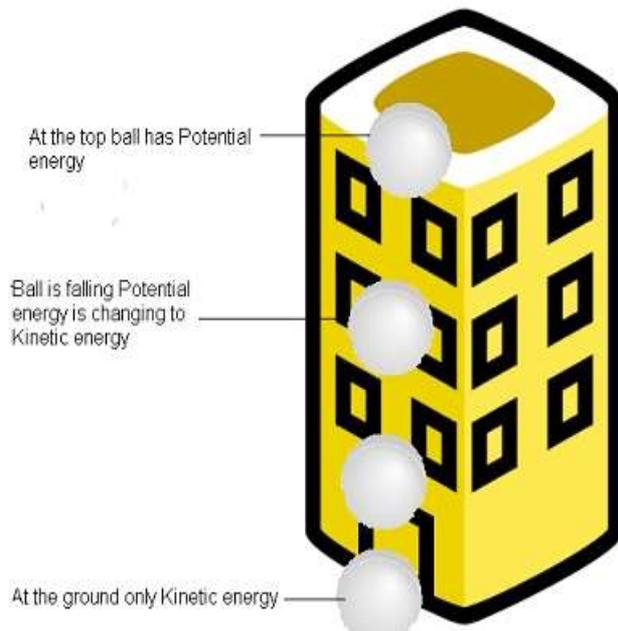
Internal energy increases when the system absorbs heat and some work is done on the system similarly internal energy decreases if we change the conditions.

How Internal energy is different from Work and Heat

- Heat and work are not state variables unlike internal energy.
- They are modes of energy transfer to system resulting in change in internal energy.

First Law of Thermodynamics

- The First law of thermodynamics is same as law of conservation of energy.
- According to law of energy conservation: - Energy can neither be created nor be destroyed, only transformed to other forms.
- According to first law of thermodynamics:- The change in the internal energy of a closed system is equal to the amount of heat supplied to the system, minus the amount of work done by the system on its surroundings.
- Examples:- Consider a ball falling from the roof of the building when at top of the building the ball has only potential energy and when it starts falling potential energy decreases and kinetic energy starts increasing. At the the ground it has only kinetic energy.



A ball falling from the roof of the building

Mathematically:-

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

Where:

- ΔQ is the heat supplied to the system by the surroundings
- ΔW is the work done by the system by the surroundings
- ΔU is the change in internal energy of the system
- Some part of heat supplied gets lost and remaining part is the work done on the surroundings. This remaining part is used up to increase or change the internal energy of the system.

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

Consider a system whose initial state is (P_1, V_1) and final state (P_2, V_2)

ΔU is the change in the energy of the system to change from initial state to final state.

- Internal energy is a state variable which means it is path independent. It does not depend how state changes from initial to final.
- But the work done and heat is path dependent. It depends on how the path changes from initial to final.
- Consider a system whose initial state is defined as (P_1, V_1) and Final state is defined as (P_2, V_2) .
- The internal energy doesn't depend on how the system has changed from initial state to final state. It only depends on how it has reached from initial state to final state.

Therefore:-

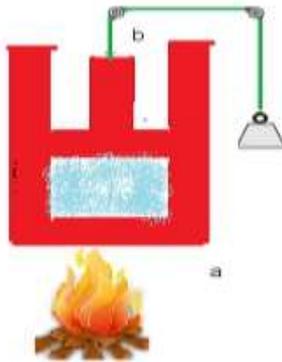
$$\Delta Q - \Delta W = \Delta U \quad \text{where}$$

- (ΔQ and ΔW are path dependent quantities whereas ΔU is path independent quantity)
- This concludes $\Delta Q - \Delta W$ is path independent quantity.
- Case 1:- System undergoes a process such that $\Delta U = 0$ which means internal energy is constant. From first law of thermodynamics

$$\Delta Q = \Delta U + \Delta W \quad \text{putting } \Delta U = 0$$
- This implies **$\Delta Q = \Delta W$** this means heat supplied by the surroundings is equal to the work done by the system on the surroundings.
- Case 2:- System is a gas in a cylinder with movable piston, by moving the piston we can change the volume of the gas.
- If we move the piston downwards some work is done and it can be given as:-

- Work done = ΔW
- = Force x displacement
- = $P \times \text{Area} \times \text{displacement}$
- $\Delta W = P\Delta V$ ($\Delta V = \text{Area} \times \text{displacement}$) (Equation 1)
- Therefore by first law of thermodynamics
- **$\Delta Q = \Delta U + P\Delta V$** where $\Delta V = \text{change in volume}$

(From Equation 1)



Heat and work are two distinct modes of energy transfer to a system that results in change in its internal energy. (a) Heat is energy transfer due to temperature difference between the system and the surroundings. (b) 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.

Specific heat capacity

- Specific heat is defined as the amount of heat required to raise the temperature of a body per unit mass.
- It depends on:-
- Nature of substance
- Temperature
- Denoted by 's'

Mathematically:-

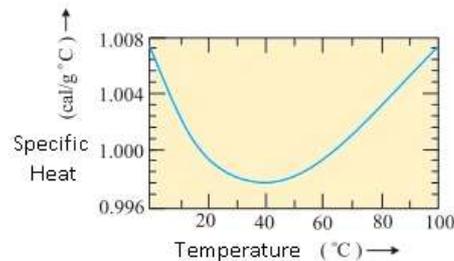
$$s = (\Delta Q / m\Delta T)$$

- where m= mass of the body
- ΔQ = amount of heat absorbed or rejected by the substance
- ΔT = temperature change
- Unit - $J\ kg^{-1}\ K^{-1}$
- If we are heating up oil in a pan, more heat is needed when heating up one cup of oil compared to just one tablespoon of oil. If the mass s is more the amount of heat required is more to increase the temperature by one degree.

Specific heat capacity of water

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.

- In SI units, the specific heat capacity of water is $4186 \text{ J kg}^{-1} \text{ K}^{-1}$.
- $4.186 \text{ J g}^{-1} \text{ K}^{-1}$.
- The specific heat capacity depends on the process or the conditions under which heat capacity transfer takes place.



Variation of specific heat capacity of water with temperature

- Water has highest specific heat of capacity because of which it is used as a coolant in automobile radiators and in hot water bags.

Molar Specific Heat Capacity

- Heat capacity per mole of the substance is defined as the amount of heat (in moles) absorbed or rejected (instead of mass m in kg) by the substance to change its temperature by one unit.

$$C = S / \mu = \Delta Q / \mu \Delta T$$

Where

- μ = amount of substance in moles
- C = molar specific heat capacity of the substance.
- ΔQ = amount of heat absorbed or rejected by a substance.
- ΔT = temperature change
- Depends on :
 - nature of substance
 - Temperature
 - Conditions under which heat is supplied
- SI Unit: J/mol/K

Molar Specific heat capacity at constant pressure (Cp)

- If the gas is held under constant pressure during the heat transfer, then the corresponding molar specific heat capacity is called molar specific heat capacity at constant pressure (Cp).

Problem: - What amount of heat must be supplied to 2.0×10^{-2} kg of nitrogen (at room temperature) to raise its temperature by 45°C at constant pressure?

(Molecular mass of $\text{N}_2 = 28$; $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$.)

Answer:-

Mass of nitrogen, $m = 2.0 \times 10^{-2} \text{ kg} = 20 \text{ g}$

Rise in temperature, $\Delta T = 45^\circ\text{C}$

Molecular mass of N_2 , $M = 28$

Universal gas constant, $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$

Number of moles, $n = m/M$

$$= 2.0 \times 10^{-2} \times 10^3 / 28 = 0.714$$

Molar specific heat at constant pressure for nitrogen = $C_p = 7/2R$

$$= 7/2 \times 8.3 = 29.05 \text{ J mol}^{-1} \text{ K}^{-1}$$

The total amount of heat to be supplied is given by the relation:

$$\Delta Q = nC_p \Delta T$$

$$= 0.714 \times 29.05 \times 45$$

$$= 933.38 \text{ J}$$

Therefore, the amount of heat to be supplied is 933.38 J.

Molar Specific heat capacity at constant volume (C_v):

- If the volume of the gas is maintained during the heat transfer, then the corresponding molar specific heat capacity is called molar specific heat capacity at constant volume (C_v).

To Prove: - $C_p - C_v = R$ for an ideal gas

From First Law: - $\Delta Q = \Delta U + \Delta W$.

- Consider the case a gas is enclosed in a cylinder fitted with piston. Then the work done changes to

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

- At constant volume $\Delta Q = \Delta U$ (where $\Delta V=0$)

Therefore

$$C_v = (\Delta Q / \Delta T)_v = (\Delta U / \Delta T)_v = \Delta U / \Delta T$$

- At constant pressure: - $C_p = (\Delta Q / \Delta T)_p = (\Delta U + P\Delta V) / \Delta T$

By solving and doing all calculations:

$$C_p - C_v = R$$

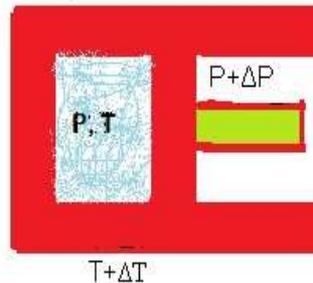
Hence proved.

Specific Heat Ratio: -

- It is denoted by γ .
- $\gamma = C_p/C_v$
- For Mono atomic gas:-
 - $C_v = 3/2R$
 - $C_p = 5/2R$
 - $\gamma = 1.67$
- For Diatomic gas: -
 - $C_v = 5/2 R$
 - $C_p = 7/2R$
 - $\gamma = 1.4$

Thermodynamic processes – Quasi Static Process

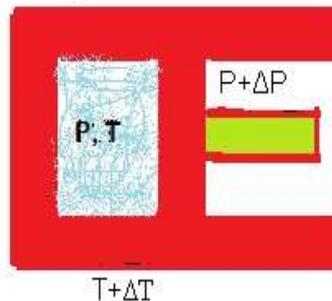
- Quasi static term means semi static .It is not purely moving.
- It is a hypothetical construct which means it is not in real.
- It is an infinitely slow process which means change from its original position is not at all significant.
- System changes its variables (P, T, and V) so slowly that it remains in equilibrium with its surroundings throughout.
- Consider a gas initially at Pressure (P) and Temperature (T) changes it to a new state whose Pressure is (P') and Temperature (T').
- If we change the surrounding pressure to P by very small amount then allow the system to reach that system.
- The characteristics for a system to be Quasi-static process
- Extremely very slow process.
- There should not be any accelerated motion. Not large temperature gradient. Temperature gradient means the



difference in temperature ($T_1 - T_2$).

In a quasi-static process, the temperature of the surrounding reservoir and the external pressure differ only infinitesimally

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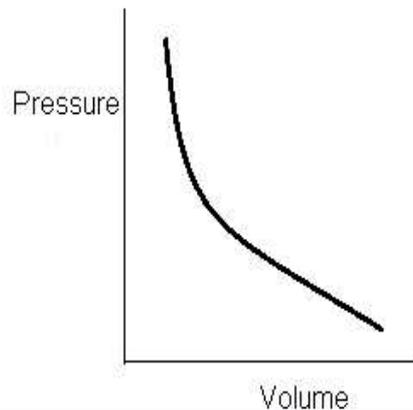


difference in temperature ($T_1 - T_2$).

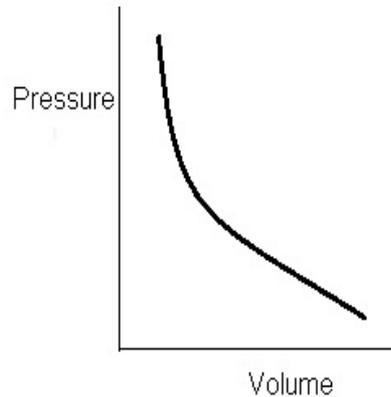
In a quasi-static process, the temperature of the surrounding reservoir and the external pressure differ only infinitesimally from the temperature and pressure of the system.

Isothermal Processes

- Isothermal: - Iso means same and thermal related to temperature. In Isothermal process the temperature remains constant throughout while all other variables change.
- Temperature is constant throughout.
- For an ideal gas
 - $PV = nRT$ where
 - n =no. of moles (constant), R = universal gas constant, T =constant for isothermal process.
 - This implies PV =constant
 - Pressure and volume are inversely proportional to each other.
 - Graphically if we plot pressure and volume



- This implies $PV = \text{constant}$
- Pressure and volume are inversely proportional to each other.
- Graphically if we plot pressure and volume



- We will get decreasing curve because if we increase pressure volume decreases and vice versa.
- This curve is known as Isothermal Curve.

Isothermal Expansion of an Ideal gas

- It can be described as amount of work done during isothermal expansion of an ideal gas under constant temperature.
- Initially ideal gas is at Pressure P_1 and Volume V_1 .

- At constant temperature the gas will expand from pressure P_1 to P_2 and volume changes from V_1 to V_2 . So the final state (P_2, V_2) .
- These all expansions are QuasiStatic processes.
- Consider any intermediate stage ,
 - Pressure is P and volume is $V_1 + \Delta V$ where ΔV increase in volume.
 - $\Delta W = P \Delta V$ where ΔW = small work done
 - By solving and doing calculation the above equation the work done for an ideal gas the work done will be given as

∴

$$W = RT \ln V_2 / V_1$$

- In an isothermal expansion there is no change in the internal energy of an isothermal process. As there is no change in temperature as a result there is no change in internal energy.
- From First law of thermodynamics
- $\Delta Q = \Delta U + \Delta W$ (putting $\Delta U = 0$ as $\Delta T = 0$)
- $\Delta Q = \Delta W$. This means the amount of heat supplied to the gas is equal to the amount of work done by the gas on the surroundings.

Isothermal expansion and contraction

- The expression of isothermal process for the work done is:
- $W = RT \ln V_2/V_1$
- In isothermal expansion the work is done by the gas whereas in isothermal contraction the work is done on the gas.
- Case 1: Isothermal expansion : $V_2 > V_1$
- This implies $W > 0$, work is positive which means work is done by the gas that is heat is absorbed by the gas.
- Case 2: Isothermal contraction : $V_2 < V_1$
- This implies $W < 0$, work is negative which means work is done on the gas that is heat is released.

Adiabatic Processes

- Adiabatic is a process in which there is no heat flow takes place between the system and the surroundings.
- These processes are sudden.
- The walls of the container should be adiabatic
- For an adiabatic process of an ideal gas
- From Boyle's law
- $PV^\gamma = \text{constant}$

Where $\gamma = C_p/C_v$ Specific heat ratio

Example: - Hot tea in Thermos flask. It will remain hot as there is no exchange of heat takes place because the walls of thermos is insulating.



Adiabatic change of an ideal gas

- It implies how much work is done during adiabatic change of an ideal gas.
- Initially ideal gas is at Pressure P_1 , Volume V_1 and Temperature T_1 (P_1, V_1, T_1)
- Final state of an ideal gas Pressure P_2 , Volume V_2 and Temperature T_2 (P_2, V_2, T_2)
- $P V^\gamma = \text{const}$
- $\gamma = C_p/C_v$
- If an ideal gas undergoes a change in its state adiabatically from (P_1, V_1) to (P_2, V_2)
- $P_1 V_1^\gamma = P_2 V_2^\gamma$
- The work done in an adiabatic change of an ideal gas from the state (P_1, V_1, T_1) to the state (P_2, V_2, T_2).

$$W = \int P V dV = P \int V dV \text{ (Integrating between the limits } V_2 \text{ and } V_1)$$

For Adiabatic Process

- $P V^\gamma = \text{constant}$ This implies $P = \text{constant} / V^\gamma$

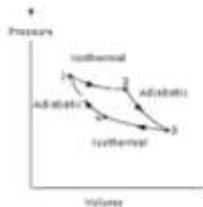
- $W = \text{constant} \int dV / V^\gamma$
- $\text{constant} [V^{\gamma-1} / -\gamma + 1]$
- $\text{constant} / 1 - \gamma [V_2^{1-\gamma} - V_1^{1-\gamma}]$
- $= \text{constant} / 1 - \gamma [1 / V_2^{1-\gamma} - 1 / V_1^{1-\gamma}]$
- By solving Work done $W = R / (\gamma - 1)(T_2 - T_1)$, where
- T_2 = final Temperature
- T_1 = initial temperature
- R = Universal gas constant
- γ = Specific heat ratio
- This is the work done during adiabatic change.
- Consider $W = R / (\gamma - 1)(T_2 - T_1)$

Case 1: $W > 0$ (when $T_1 > T_2$)

Temperature of the gas decreases.

Case 2: $W < 0$ ($T_1 < T_2$)

Temperature of the gas increases.



P-V curves for isothermal and adiabatic processes of an ideal gas.

Isochoric Processes

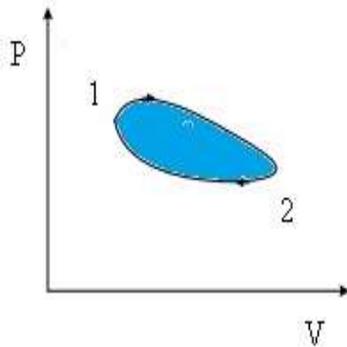
- Isochoric process means volume is constant while all other variables change.
- As volume is kept constant therefore no work is done on or by the gas.
- Heat absorbed by the gas is completely used to change its internal energy and its temperature.
- From First law of Thermodynamics
- $\Delta Q = \Delta U + \Delta W$ ($\Delta W = 0$)
- $\Delta Q = \Delta U$
 - This means whatever heat is supplied to the system that is used up completely to change the internal energy and temperature of the system.
- $C_V = \Delta U / \Delta T$

Isobaric Processes

- Iso means same and baric is related to pressure.
- In this process pressure is constant while all other variables change.
- Process in which pressure is constant.
- Work done is given as :
 - $W = P (V_2 - V_1)$
 - $= \mu R (T_2 - T_1)$
- From First law of thermodynamics
- $\Delta Q = \Delta U + \Delta W$
- $\Delta Q = \Delta U + \mu R (T_2 - T_1)$
- We can see from the above equation that the heat absorbed goes partly to increase internal energy and partly to do work.

Cyclic Processes

- A Process in which the system will come back to its initial state.
- $\Delta U=0$ this means the total heat absorbed equals the work done by the system.



The system started from point 1 it went through series of processes reached its final position 2 and then it comes back to its initial position 1.

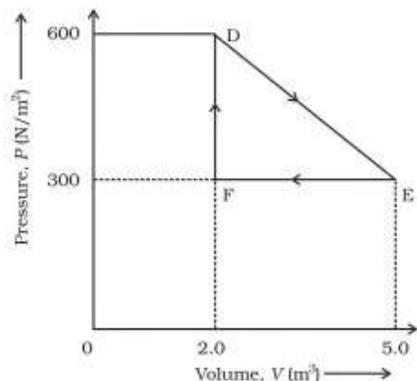
- The total internal energy is 0.
- By applying First law of thermodynamics:

- $\Delta E = Q + W$ as ($\Delta E=0$),
- Therefore
- $W=Q$
- The work done by the system in a cyclic process is equal to the heat absorbed by the system.

Example: - Heat Engine, Heat Pump



Problem: - A thermodynamic system is taken from an original state to an intermediate state by the linear process shown in Fig.?



Its volume is then reduced to the original value from E to F by an isobaric process. Calculate the total work done by the gas from D to E to F?

Answer:

Total work done by the gas from D to E to F = Area of ΔDEF

Area of $\Delta DEF = \frac{1}{2} \times DE \times EF$

$DF = \text{Change in pressure} = 600 \text{ N/m}^2$

$- 300 \text{ N/m}^2$

$= 300 \text{ N/m}^2$

$FE = \text{Change in volume}$

$= 5.0 \text{ m}^3$

$- 2.0 \text{ m}^3$

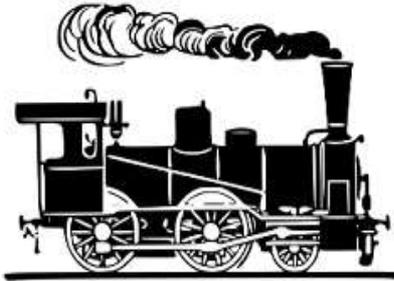
$= 3.0 \text{ m}^3$

Area of $\Delta DEF = \frac{1}{2} \times 300 \times 3 = 450 \text{ J}$

Therefore, the total work done by the gas from D to E to F is 450 J.

Heat Engines

- In a heat engine a body is configured to do work when placed in alternating contact with hot and cold bodies so that heat can be supplied and absorbed. In simple terms heat engine is a device which converts thermal energy to mechanical energy.



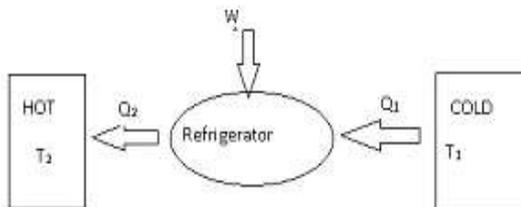
Steam Engine

- Basic Components : -
- Working substance For Example: - a mixture of fuel vapour and air in a steam engine.
- External Reservoir which is at higher temperature.
- External Reservoir which is at lower temperature.
- The reservoirs are at different temperature so that there is flow of energy from higher level to lower level.
- Consider a hot reservoir having a temperature T_1 and a cold reservoir having a temperature T_2 .

Refrigerators

- It works on principle which is reverse of a heat engine.
- In refrigerators we have 2 bodies lower temperature (cold) body which is freezer and higher temperature (hot) body which is surroundings.
- It takes heat from the cold reservoir and then some work is done on the refrigerator and then the amount of heat is transferred to heat reservoir.
- Let Q_2 be the takes from the cold reservoir, W is the work done on the system and then releases Q_1 amount of heat to the hot reservoir.
- Mathematically $Q_2 + W = Q_1$

Simple Representation of Refrigerators



Working of a refrigerator or a heat pump is based on same principle which is the reverse of a heat engine.

Coefficient of Performance (COP) of the refrigerator

- It is denoted by α .
- Mathematically given as :
 - **$\alpha = Q_2/W$**
 - where Q_2 is the heat extracted from the cold reservoir
 - W is the work done on the system—the refrigerant
- α can be greater than 1
- Using Law of energy conservation :- $Q_2 + W = Q_1$
- This implies $W = Q_1 - Q_2$
- Therefore:-
- $\alpha = Q_2 / (Q_1 - Q_2)$
- $W \neq 0$ then $Q_1 - Q_2 \neq 0$
- This implies $\alpha \neq \infty$

Problem: A refrigerator is to maintain eatables kept inside at 9°C. If room temperature is 36° C, calculate the coefficient of performance?

Answer:

Temperature inside the refrigerator, $T_1 = 9^\circ\text{C} = 282\text{ K}$

Room temperature, $T_2 = 36^\circ\text{C} = 309\text{ K}$

Coefficient of performance = $T_1 / T_2 - T_1$

$$= 282 / (309 - 282) = 10.44$$

Therefore, the coefficient of performance of the given refrigerator is 10.44.

Heat Pump

In a heat pump heat is supplied into system when the surroundings are cold.

Second law of Thermodynamics

There are 2 statements of second law of thermodynamics given by two scientists:

- **Kelvin-Planck Statement**: - No process is possible whose 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 result is the transfer of heat from a colder object to a hotter object.

Explanation of Kelvin-Planck Statement: It is always impossible that the total amount of heat which is supplied to system will get converted to work, and there will always be loss of heat. Complete conversion of heat into work is not possible.

Explanation of Clausius statement: - Transfer of heat from colder body to hotter body won't take place until some external work is done on the system.

Reversible and Irreversible processes

Reversible Process

- A thermodynamic process is reversible if the process can be turned back such that the system and surroundings return to their original states, with no other change anywhere else in the universe.
- This means in the Reversible processes if a process starts from initial state then it goes to final state and then it can be reversed back from final state to initial state.
- Examples:- Isothermal expansion and compression, Electrolysis
- A process is reversible if :-

It is quasi-static

No dissipative forces (that is no loss of heat by friction etc.).

Both initial and final states of the system are in thermodynamic equilibrium with each other.

Irreversible Process

- Irreversible processes are those that cannot be reversed.
- Two causes which give rise to irreversible processes
 - Irreversible processes take place at a very fast rate.
 - Dissipative Effects.
- Examples:- Plastic deformation, Combustion, Diffusion, Falling of water from hill.

Carnot engine

- A Carnot engine is named after Carnot scientist.
- It is a reversible heat engine operating between two temperatures.
- It has a maximum efficiency which no other engine can have.

Cycle of processes in a Carnot engine

Basic Function of any heat engine is it will take heat Q_1 from a hot reservoir at temperature T_1 and give heat Q_2 to a cold reservoir at temperature T_2 .

- As system is absorbing heat so it is isothermal expansion. Engine absorbs heat Q_1 at temperature T_1 .
- An adiabatic process takes place inside the engine because of which there is increase in the temperature of the engine from T_1 to T_2 but no flow of heat.
- As system is releasing heat so it is isothermal contraction. Engine releases heat Q_2 at temperature T_2 .
- An adiabatic process takes place again which changes the temperature of the system from T_2 to T_1 .
- One cycle of Carnot engine will have Isothermal expansion then adiabatic process, and then isothermal contraction followed by adiabatic process.
- This will keep on repeating.

The efficiency of Carnot engine is given by:-

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

The graph below depicts the Carnot cycle for a heat engine with an ideal gas as the working substance.

