THERMODYNAMICS

heat motion

Bismah Noor
Batch I Fsc
@Sochbadlobymak

General Concepts

↳ Thermal Equilibrium : Effect produced in which two bodies have the same temprature due to flow of energy from hotter body to colder body is called as thermal equilibrium. (It's not necessary for bodies to be in direct contact with each other).

↳ Heat : Heat is a form of energy which flows from a hot body to a cold body.

↳ Work : Work is said to be done by the system when it expands (positive work) and work is said to be done on thy system when it contracts. (negative work) work is simply $\vec{F} \cdot \Delta\vec{S}$.

↳ Internal Energy : The sum of the kinetic and potential energies associated with the random motion of the atoms of the substance is the internal energy of the substance.

↳ Relation ship between heat, work and internal energy : Heat flows to a body and that increases the internal energy of the body which is in turn responsible for the work that a body performs.

↳ Heat in transit / Energy in transit : Once heat enters a system it become a part of the system called heat in transit or energy in transit.

↳ Units used for heat : SI unit = Joule. A common unit is calorie.

↳ Calorie : Energy needed to change the temprature of 1g water by 1 °C specifically between 14.5°C and 15.5°C. 1 cal = 4.18 J.

↳ Difference between heat and work : Work can be exchanged between an object and its surroundings without requiring the difference of temprature whereas for the transfer of heat, temprature difference is compulsory.

↳ Thermodynamic system : Thermodynamic system includes anything whose thermodynamic properties are of interest.

↳ Thermodynamic process : Any change or a series of changes in a thermodynamic system is called thermodynamic process.

↳ Boundary : A hypothetical or imaginary line differenciating between system and surroundings.

↳ Surroundings: Everything other than the system in the universe is called the surroundings of the system i.e., the whole universe

↳ Closed system: System in which there is no transfer of mass across its boundary is called closed system. (transfer of heat takes place).

↳ Open system: The system in which there is a transfer of mass across its boundary along with heat.

↳ Isolated system: The system in which there is no transfer of heat and matter (mass) across its boundary is called an isolated system.

↳ Reversible process: Process which can be retraced exactly in reverse direction without producing any change in surroundings. (The change produced in surroundings during forward process is counteracted by the changes produced in surrounding during reverse process).

↳ Irreversible process: A process which can not be retraced in the backward direction by reversing the controlling factors is called irreversible.

↳ Cyclic Process: A series of processes which bring the system back in its initial state is called a cyclic process.

↳ Thermodynamic state: The particular condition when a system has specified values of pressure P, volume V and temprature T etc is called the state of system.

↳ State variables: certain variables which determine the state of system are called state variables. P, V, T, U, S are some state variables. (S = entropy, U = internal energy).

↳ Equation of state: Mathematical relationship between the parametres defining a homogenous system is called equation of state i.e., $PV = nRT$ (ideal gas equation).

↳ Equivalence of Heat and work: According to Joule, when a given amount of work is done, the same amount of heat is always produced

$W \propto Q$, $W = JQ$

↳ Mechanical Equivalent of heat (Joule's constant): Ratio of work done in Joules to heat produced in calories is called mechanical equivalent of heat 'J'. If both are measured in joules then $J = 1$.

FIRST LAW OF THERMODYNAMIS

↳ Statement : This law states that every thermodynamic system has a state variable (U) called internal energy

↳ Mathematical form : $\Delta Q = \Delta U + \Delta W$ or $\Delta U = \Delta Q - \Delta W$

where $\Delta U' = U_B - U_a$ thus $U_B - U_A = \Delta Q - \Delta W$

↳ Cyclic process : In a cyclic process all the heat energy is absorbed by the system is used in doing some useful work

thus $\Delta Q = \Delta W$ as $U_B = U_A$, $(\Delta U = 0)$

APPLICATIONS

• Isochor Process

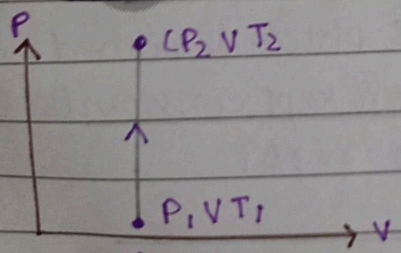
↳ The thermodynamic process during which the volume of the system remains constant.

↳ system consists of a gas filled in a cylinder having a conducting base and non-conducting walls & w/ a fixed piston.

↳ In an isochor process entire amount of heat supplied to the gas is converted to internal energy i.e, no work.

↳ $\Delta Q = \Delta U$

↳



isochor

• Isobar Process

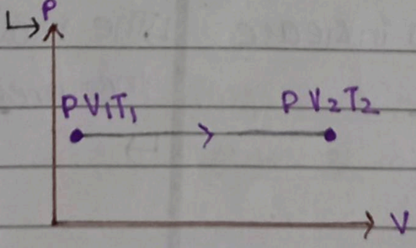
↳ The thermodynamic process during which the pressure is kept constant.

↳ A gas contained in a cylinder having a conducting base and non-conducting walls and frictionless piston of cross-sectional area 'A' is considered.

↳ Entire heat is converted into Pressure-volume work + internal energy with $P_1 = P_2$ (no delta sign w/ P).

↳ $\Delta Q = \Delta U + P\Delta V$

↳



isobar

• Isothermal Process

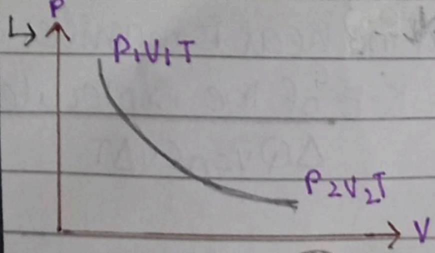
↳ The thermodynamic process during which temprature remains constant.

↳ A gas contained in a cylinder having conducting base and nonconducting walls with a moveable piston is considered. The cylinder is placed on a heat reservoir T_1

↳ Entire heat is converted into work done, no change in internal energy takes place

↳ $\Delta Q = \Delta W$

↳



isotherm

• Adiabatic Process

↳ The thermodynamic process during which no heat enters or leaves a system is called an adiabatic process.

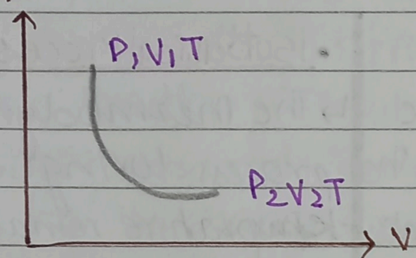
↳ The flow of heat requires finite time, so any process performed quickly enough will be practically adiabatic.

↳ $\Delta Q = \Delta U + \Delta W$ $(\Delta Q = 0)$

$\Delta U = -\Delta W$

↳ system does work at the cost of internal energy.

↳



MOLAR SPECIFIC HEAT OF A GAS

↳ **Statement:** The quantity of heat required to raise the temprature of one mole of gas by 1K is called molar specific heat or molar specific heat capacity of that gas.

↳ Mathematical form: $C_M = \frac{\Delta Q}{n\Delta T}$ (CM is called as molar specific heat)

↳ SI unit : $J\,mole^{-1}K^{-1}$

TYPES

• **Constant Volume Molar Specific Heat C_v**

↳ The amount of heat required to raise the temprature of one mole of a gas by 1K while keeping its volume constant is called the constant volume MSH C_v of that gas.

↳ All the heat is manifested to increase the K.E of the molecules.

↳ $\Delta Q_v = nC_v\Delta T$

• **Constant Pressure Molar Specific Heat C_p**

↳ The amount of heat required to raise the temprature of one mole of a gas by 1K while keeping its pressure constant pressure M.S.H C_p of that gas.

↳ The moveable piston is pushed while the pressure is kept constant.

↳ $\Delta Q_p = nC_p\Delta T$

Date:............/............/20.......... M☐ T☐ W☐ T☐ F☐ S☐

RELATION B/W 'Cp' AND 'Cv'

↳ Heating at constant volume : When the gas is heated at constant volume, there is no work done by the gas against the surroundings. All the heat is converted into the internal energy, raising the temprature.

↳ Heating at constant pressure : When the gas is heated at constant pressure, the gas will expand on being heated. It does work against the surroundings.

↳ Reason why 'Cp' is greater than Cv : Change in internal energy is same for both. The extra heat in the case of Cp accounts for the work done on the surroundings. As there's no work involved in 'Cv' thus $C_p > C_p$.

↳ Mathematical interpretation : We know that $\Delta Q_v = nC_v\Delta T$ and $\Delta Q_p = nC_p\Delta T$.

↳ For constant volume :

$\Delta W_v = 0$

$\Delta Q_V = \Delta U + \Delta W_v$

$\Delta Q_V = \Delta U$

$\Delta U = nC_v\Delta T$

↳ For constant Pressure

$\Delta W_p =$ Force x distance $= F\Delta Y$

$\Delta W_p = PA\Delta Y = P\Delta V$ $(\Delta Y \times A = \Delta V)$

$\Delta W_p = P\Delta V = nR\Delta T$ (by general gas eq.)

$\Delta Q_p = \Delta U + \Delta W_p$

↳ Substituting values

By constant Pressure ; $\Delta Q_P = nC_p\Delta T$

By constant volume ; $\Delta U = nC_v\Delta T$

By general gas equation ; $\Delta W_p = nR\Delta T$

Putting values in highlighted equation.

$nC_p\Delta T = nC_v\Delta T + nR\Delta T$ (n and ΔT are common)

$C_p - C_v = R$ where R equals $8.315 J mol^{-1} K^{-1}$

$C_p = \gamma C_v$ (important for numericals)

HEAT ENGINE

↳ Definition : A heat engine is a device that converts heat energy into mechanical work.

↳ Construction : 1. Heat source or Heat reservoir at temprature T_1. 2. Heat sink or cold reservoir at temprature 3. An engine 4. A working substance normally a gas.

↳ Working: The working substance is taken through a cyclic process ($\Delta U = 0$). Heat Q_1 is absorbed by the working substance. Certain quantity of heat absorbed is utilized in doing work and the remaining heat Q_2 is rejected to the LTR. Net change in ΔU remains zero this way.

↳ Mathematical Form: $\Delta W = \Delta Q$ or $\Delta W = Q_1 - Q_2$

Thermal efficiency; $\eta = \frac{\Delta W}{Q_1}$ where Q_1 = heat absorbed by engine.

Ideal heat engine ; $Q_2 = 0$ thus $\eta = 100\%$

It's impossible to construct a heat engine that converts all heat absorbed into work done.

SECOND LAW OF THERMODYNAMICS

↳ Distinction from 1st law: First law of thermodynamics tells us about the interconversion of heat and mechanical work but second law of thermodynamics tells us about under what parameters heat is converted into work.

↳ Lord Kelvin Statement: It is impossible to construct a heat engine, operating continuosly in a cycle which takes heat from a heat source at higher temprature and performs an equivalent amount of work without rejecting any heat to a sink at low temprature.

CARNOT CYCLE & CARNOT HEAT ENGINE

↳ Introduction: Carnot heat engine is free from all sorts of heat losses and thus it enables us to understand lord kelvin statement in the manner that the efficiency of an actual heat engine is always less than that of carnot heat engine.

↳ Construction: 1. a gas cylinder with perfectly insulating walls and perfectly conducting base 2. A perfectly insulated weight less and frictionless piston in cylinder.

↳ Cycle: A cycle is completed when system comes back to its initial state. The cycle consists of four processes.

↳ Rudolf Clausius Statement: It is impossible to cause heat to flow from a cold body to a hot body without the expenditure of work.

REFRIGERATOR

↳ Definition: The device which will either cool or maintain a body temprature below that of the surroundings is called refrigerating machine.

↳ Construction: 1 HTR at T_1 2 LTR at T_2 3 radiator. refrigerant

↳ Working: The refrigerant is taken through a cycle in such a way that some amount of heat is removed from LTR at T_2 (Q_2). For this purpose work W is performed. The quantity rejected to HTR is Q_1 by the radiator. The sole purpose of a refrigerator is to extract as much heat Q_2 as possible from the cold reservoir with as little work as possible.

↳ Mathematical interpretation:

$Q_1 = W + Q_2$ (Q_2 is heat absorbed from LTR and W is the work done to transfer heat from low temp to high temp).

Coefficient of performance for heating

$$E_{heating} = \frac{Q_1}{W}$$

$$= Q_1 / Q_1 - Q_2$$

$$E_{heating} = T_1 / T_2 - T_1$$

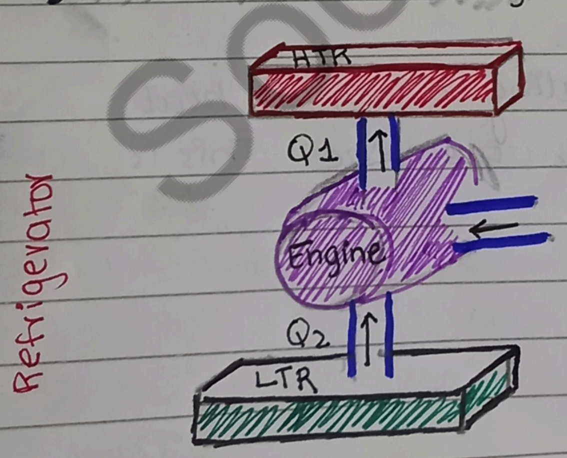
Coefficient of performance for cooling

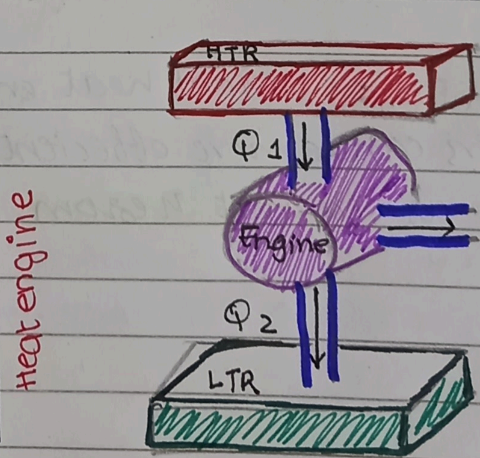
$$E_{cooling} = \frac{Q_2}{W}$$

$$= Q_2 / Q_1 - Q_2$$

$$E_{cooling} = T_2 / T_2 - T_1$$

↳ Contrast b/w heat engine and refrigerator:





↳ 2nd law of Thermodynamics is obeyed
↳ Heat flows from HTR to HTR

↳ First law of thermodynamics is obeyed
↳ Heat flows from H.TR to LTR

ENTROPY

↳ Statement: Entropy is the measure of disorder or randomness in a system. The more disordered or random a system is, the higher is entropy.
(shaheer's point Batch II)

↳ Main points:

→ When heat is absorbed by a system, its entropy increases and will have positive value

→ When heat is left a system its entropy decreases and will have negative value.

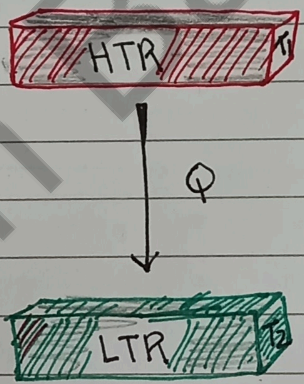
→ Degradation of energy Energy pass from more useful form to less useful form is called degradation of energy

→ Entropy of a system during any natural process increases.

↳ Mathematical Form: $\Delta S = \Delta Q / T$

↳ Unit: JK^{-1}

↳ Diagramatic Interpretation from PKMZ:



S_1 (-S) Q/T_1 (decrease in entropy)

S_2 (+S) Q/T_2 (increase in entropy)

$$\Delta S = +S_2 - S_1$$

$$\Delta S = \frac{Q}{T_2} - \frac{Q}{T_1}$$ (where $Q/T_2 > Q/T_1$)

Bismah Noor
Batch I Fsc
@Sochbadlobymak

→ Heat death of universe The point at which universe will reach a maximum value of entropy is called as heat death of universe. No heat for useful work will be present.