Thermodynamics

Branch of Physics which deals with concepts of heat and temperature.

It is a macroscopic science which deals with bulk system without going to the molecular constitution of the matter.

Deals with macroscopic variable like pressure, volume, temperature, mass etc called thermodynamic co ordinate.

Thermal equilibrium

A system is said to be in thermal equilibrium, if temperature at all points are equal and is equal to the temperature of the surroundings. Any two independent thermodynamic co ordinates of the system remains constant.

Heat

Energy which is transferred from one body (point) to another by conduction, convection and radiation on account of temperature difference. SI unit is J calorie = 4.186 JBtu = 1055 JCalorie = 4186 J

Note : Total energy content of a system is called internal energy.

There are two types of internal energy i) ordered IE

ii) Disordered IE

Only disordered energy will be transferred due to the temperature difference and it is the heat energy.

Temperature

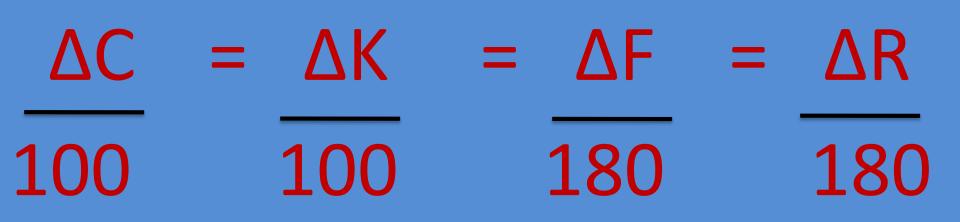
Measure of degree of hotness or coldness of an object (mean KE of random motion of the molecules) which determines direction of heat flow.

Scales of temperature. i) Celsius (Anders Celsius) ii) Farenheit (Gabriel Farenheit) iii)Absolute scale or Kelvin scale (Lord Kelvin) iv)Rankine scale (John Mac Quorn Rankine) 492 to 672 with 180 equal parts.

Conversion equation

$\frac{C-0}{100} = \frac{F-32}{180} = \frac{K-273}{100} = \frac{R-492}{180}$

To find difference in temperature from one scale to another



Kelvin Scale or Absolute scale

- It does not depend upon any physical property of thermometric substance used.
- Since heat and temperature are directly connected (does not depend on the properties of any thermometric substance), it is called ideal scale.

Standard fixed point used is triple point of water (273.16 K at 4.58 mm of Hg pressure). One Kelvin is defined as 1/273.16 of the temperature of triple point of water. Method: Let the gas pressure measured using constant volume gas thermometer at triple point of water be P_{tr}. If P is the press of the gas at unknown temperature T, Then $T/T_{tr} = P/P_{tr}$. Unknown temp. T = 273.16 (P/P_{tr})

Adiabatic wall: ideal insulating wall. (no heat exchange is permitted through it) Eg: fibre glass, wood, plastic etc.

Diathermal wall: partition that allows two systems on its opposite sides to exchange heat. Eg: copper, aluminium etc.

Zeroth law of thermodynamics

- Two systems in thermal eqbm with a third are in thermal eqbm with each other.
- Note: temperature of a system can be defined as a property which determines whether or not the system is in thermal eqbm with other systems, when brought into contact.

Specific heat capacity of gases - C_p and C_v .

Molar sp.heat at constant volume is defined as the quantity of heat reqd to raise the temperature of one mole of a gas through 1K keeping volume (or prssure as the case be).

Unit is J/mole/K

Why $C_p > C_v$?

 C_v – heat absorbed – used for increase in internal energy.

C_p – increase in internal energy + work done in expansion.

So.

Mayer's relation

- 1 mole of a gas enclosed in a cylinder fitted with a tight frictionless piston of area of cross section 'a'. (press P, volume V)
- Heat reqd to rise temp by $1^{\circ}C \Delta Q_1 = C_v$. (used for increasing the internal energy)

If gas is heated at constant press,

$$\Delta Q = C_p = \Delta Q_1 + W$$

= $C_v + P a dx$ = $C_v + P dv$
PV = RT
P(V+dv) = R (T+1)
PV + Pdv = RT + R

Ratio of specific heats

- $\gamma = C_p/C_v$ is a constant for a gas and depends on the atomicity of the gas.
- i. Monoatomic gas
- $C_v = dU/dT = \frac{d(1.5 \text{ RT})}{dT} = 1.5 \text{ R}$ $C_p = C_v + R = 2.5 \text{R}$
- $\gamma = C_p/C_v = 2/3 \ x \ 5/2 = 5/3 = 1.67$

ii. Diatomic gas

 $\gamma = C_p / C_v = 3.5 R / 2.5 R = 1.4$

iii. Triatomic gas $\gamma = C_p / C_v = 4R / 3R = 1.33$ (For linear triatomic gas U = 7/2 RT) $\gamma = C_p / C_v = 9 / 7 = 1.28$ (as degree of freedom increases , γ approaches unity) iv. Polyatomic gas having n degree of freedom . For 1 mole, U = nRT/2

- Cv = dU/dT = nR/2Cp = nR/2 + R
- $\gamma = Cp/Cv = nR/2 + R$ nR/2
 - = 1 + 2/n

Thermodynamic system

Assembly of extremely large no. of particles (atoms or molecules) which has certain value of P,V and temperature.

Can be a solid, a liquid, or a gas or a combination of two or more of these .(no.of particles should be very large).

Surroundings.

Everything outside the

system which has a direct

effect on the system is

called its surroundings.

Thermodynamic variables or parameters or co-ordinates

Quantities like, pressure, volume, temperature which help us to study the behavior of a thermodynamic system.

Thermodynamic process.

A process in which, some changes occur in the state of a thermodynamic system. ie. thermodynamic variable change with time

Eg: isothermal, adiabatic, isobaric, isochoric, cyclic, non cyclic, quasistatic or eqbm process etc.

Cyclic process

A thermodynamic process in which a system, after undergoing a series of changes, comes back to the original state is called a cyclic process.

Work done in a cyclic process is, numerically equal to the area enclosed in indicator diagram.

Quasi – Static Process

A change in any of the parameter which takes place at such a slow speed that the values of P,V and T can be taken to be, practically, constant, is called a quasistatic or eqbm process.

First law of thermodynamics The energy supplied to a system (ΔQ) is used to raise the internal energy (ΔU) and for doing external work (ΔW) .

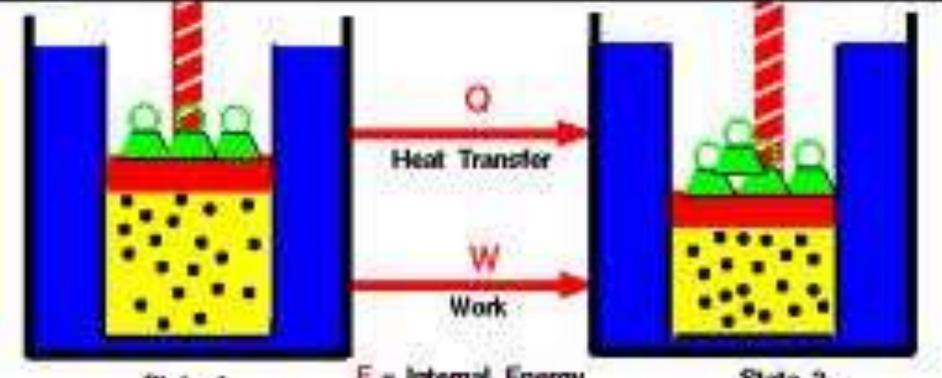
ie. $\Delta Q = \Delta U + \Delta W$

For infinitesimally small change dQ = dU + dW (differential form)



First Law of Thermodynamics

Glenn Research Center



State 1

E = Internal Energy E, - E, = Q - W

State 2

Any thermodynamic system in an equilibrium state possesses a state variable called the internal energy (E). Between any two equilibrium states, the change in internal energy is equal to the difference of the heat transfer into the system and work done by the system.

Note:

- i. It is law of conservation of energy and hence applicable to every process in nature.
- ii. It introduce concept of internal energy .
- iii. dQ and dW are path fns. So dQ cannot be written as Q_1 Q_2 , similarly initial work and final work are meaningless.

Note:

- iv. Sign convention .
- Heat gained by the system dQ is +ve
- Heat lost by the system dQ is -ve
- Work done by the sytem dW is +ve
- Work done on the system dW is -ve
- Increase in internal energy dU is +ve
- Derease in internal energy dU is -ve.

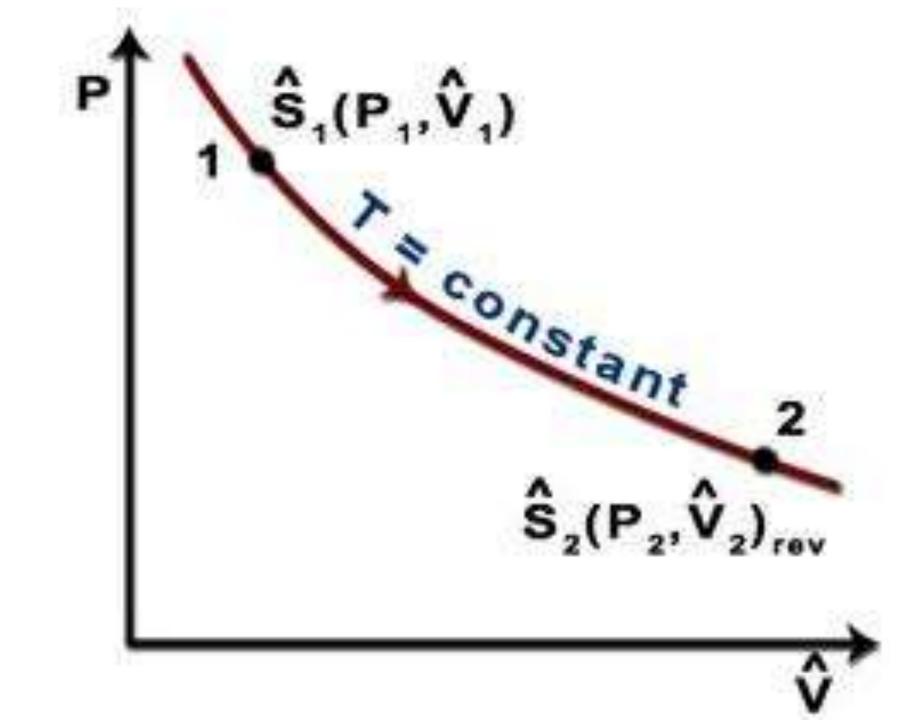
Indicator diagram or P-V diagram

- Graph connecting Pressure and volume. Helps to calculate amount of work done by the gas or on the gas during expansion or compression.
- Area work done.
- For small area abcd, dW = Pdv
- Total work $W = \int P dv$ limit v_1 to v_2 .

Eqn for isothermal process PV = RT

- Isothermal process, T = constant.
- ie. PV = constant.
- Isothermal process obey Boyle's law.
- $\mathrm{d}\mathrm{U}=\mathrm{0}.$
- So, dQ = dW

ie. ideal gas when expands isothermally, does mechanical work dW and absorbs equivalent amount heat from surroundings.



When a system goes from state A to state B, it is supplied with 400J of heat and it does 100J of work.

i) For this transition, what is ΔU ?

ii) If the system moves from B to A , ΔU ?

iii) If in moving from A to B along a different path in which W' = 400J of work is done on the system , how heat does it absorb?

i) $\Delta U_{AB} = 400 - 100 = 300$ J

ii) If system comes back to A, $\Delta U = \Delta U_{AB} + \Delta U_{BA} = 0$ $\Delta U_{BA} = -300 J$ iii) ΔU is same for all the paths having same initial and final states. $\Delta U_{AB} = Q' - W'$ $Q' = \Delta U_{AB} + W' = 300 + (-400) = -100J$

-ve sign indicates that system loses heat .

Cyclic process

A thermodynamic process in which a system, after undergoing a series of changes, comes back to the original state is called a cyclic process. Work done in a cyclic process is, numerically equal to the area enclosed in indicator diagram (dU = 0)dO = dW

Isolated system

Neither take heat from outside, nor do work is called isolated system. $d\mathbf{Q} = \mathbf{0} = d\mathbf{W}$ dU = 0

Free expansion

Membrane separate two compartments of a container, one ideal gas, other vacuum. Membrane breaks, gas expands. dQ = 0, dW = 0 (into vacuum) dU = 0

Name two thermodynamic process no change in internal energy

Isothermal process

 $\Delta T = 0$ does not mean that ΔU is zero.

Energy change appear as PE. dQ = dU + dW

Adiabatic process

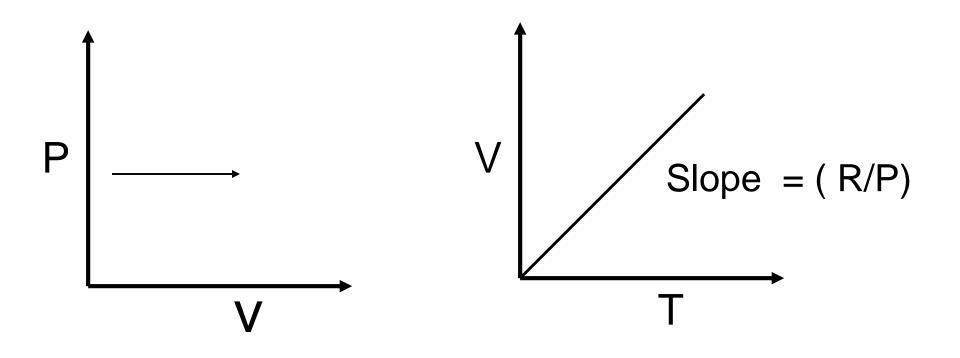
- No heat exchange with surroundings.
- $dQ = 0 \qquad dU = dW$
 - Eg. i) vigorous shaking a thermos containing tea.
 - ii) cycle pump gets heated up (piston moves fast ,work on the gas dU +ve).
 - iii) propagation of sound in air.
 - iv) deposition of CO_2 particles on a cloth held at the nozzle of a vessel containing CO_2 , due to cooling and solidification.

Isobaric process - at constant pressure.

$\mathbf{dW} = \mathbf{P}\left(\mathbf{V}_2 - \mathbf{V}_1\right)$

$dQ = (U_2 - U_1) + P(V_2 - V_1)$ Melting dU = 0, boiling, du and dV are there .

Isobaric process

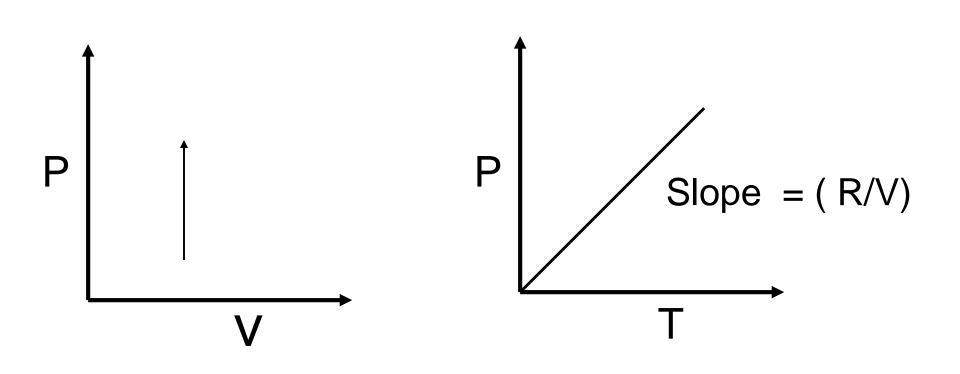


Isochoric process - at constant volume

- No work is done dW = 0dQ = dU
- Eg. Explosion in a petrol engine.

Sudden rise in T and associated P, before start of power stroke, cause explosion .





Application of First law of thermodynamics i. Cooling caused in an adiabatic process. Expansion of 1 mole of gas in perfectly insulating cylinder. $\overline{dW} = \overline{PdV}$ dU = Cv dTCvdT + PdV = 0dT = - PdV/Cv-ve sign shows cooling.

Application of First law of thermodynamics

- ii. Melting
- $dQ = mL_{f}$.
- Since no appreciable change in volume during melting, dV = 0. dW = PdV = 0. $mL_f = dU + 0$. $dU = mL_f$.
- ie. whole of the supplied heat is used in raising the internal energy of the substance, inspite of the fact that there is no rise of temperature.

Application of First law of thermodynamics

- iii. Boiling
- $dQ = mL_v$.
- Volume change V_i to V_f . $dW = P(V_f V_i)$
- dU = dQ PdV
 - $= mL_v P(V_f V_i)$

ie. total heat supplied to the system is utilized in raising the internal energy as well as in doing external work. Application of First law of thermodynamics

iv. Derivation of Mayer's relation 1 mole of gas heated at const volume, $dQ = C_v dT = dU$ (dW = 0)If heated at constant pressure, for same dT, $dQ' = C_p dT$ dW' = PdV $dU' = C_p dT - PdV = dU$ (U point fn) $C_v dT = C_p dT$ - PdV $C_p dT = C_v dT + P dV$ PdV = RdT

Note:

- i. It is law of conservation of energy and hence applicable to every process in nature.
- ii. It introduce concept of internal energy .
- iii. dQ and dW are path fns. So dQ cannot be written as Q_1 Q_2 , similarly initial work and final work are meaningless.
- iv. dU is path independent.

Salary(dQ) = Expenditure(dw) + Savings(dU)

Work done in isothermal process 1 mole of ideal gas enclosed in a cylinder having perfectly non conducting walls and conducting bottom. $W = \int P dv$ limit v_1 to v_2 . $=\int (RT/V) dv$ PV = RT $= \operatorname{RT} \log_{e} \left[V_2 / V_1 \right]$ $P_1V_1 = P_2V_2$. $= 2.303 \text{ RT } \log_{10} [P_1/P_2]$

Equation For Adiabatic process.

- 0 = dU + PdV
- 0 = CvdT + PdV
- PV = RT PdV + VdP = RdT dT = [PdV + VdP] /R
- $0 = Cv \left[PdV + VdP \right] / R + PdV$
- 0 = Cv [PdV + VdP] + RPdV
- $0 = \mathbf{C}\mathbf{v} \left[\mathbf{P}d\mathbf{V} + \mathbf{V}d\mathbf{P}\right] + \left[\mathbf{C}\mathbf{p} \mathbf{C}\mathbf{v}\right]\mathbf{P}d\mathbf{V}$
- 0 = Cv VdP + Cp PdV
- $0 = dP/P + \gamma dV/V$
- Integrating, $logP + \gamma logV = constant$.
- $Log(PV^{\gamma}) = constant$ or $PV^{\gamma} = constant$

Equation For Adiabatic process.

 $PV^{\gamma} = constant.$

 $\gamma = C_p / C_v$ P = RT/V

- $RT V^{\gamma} = constant$
- $V = T V^{\gamma-1} = constant$

 $P (RT / P)^{\gamma} = constant$

V = RT/P

 $T^{\gamma}P^{1-\gamma} = constant$

Work done in Adiabatic process Adiabatic process dQ = 0, $dW = -dU = -C_v dT$ $W = \int -C_v dT$ limit T_1 to T_2 . $= -C_{v} [T_{2} - T_{1}]$ $= C_{v} [T_{1} - T_{2}]$ {Mayer's relation ÷ Cv and solving, $C_v = R/(\gamma - 1)$ } $= R [T_1 - T_2]$ **γ** -1 W $\alpha [T_1 - T_2]$

Comparison of slopes of isothermal and adiabatic.

- Isothermal. PV = RT, PdV + VdP = 0dP/dV = - P/V gives slope of isothermal Adiabatic $PV^{\gamma} = constant.$ $V^{\gamma} dP + P \gamma V^{\gamma-1} dV = 0$ $dP/dV = -\gamma P/V$ gives slope of adiabatic. ie. Slope of adiabatic = γ^* slope of isothermal (under same conditions of pressure and volume.)
- Since $\gamma > 1$, slope of adiabatic is steeper.

Isothermal Process $\Delta T = 0$ System is thermally conducting to the surroundings. Change occur slowly ΔU may or maynot be 0 Sp.heat – infinite Eqn PV = constant. Isotherm slope dP/dV = -(P/V) **Adiabatic process** $\Delta Q = 0$ Thermally insulated. Sudden change $\Delta U \neq 0$ Sp.heat = 0Eqn PV^{γ} = constant. Adiabatic slope $dP/dV = -\gamma(P/V)$

Adiabatic elasticity = γP

Reversible process. One that is performed in such a way that, at the conclusion of the process, both the system and its surroundings are restored to their initial states, without producing ay change in the rest of the universe.

Conditions reqd for reversible process
i. P and V of system undergoing process, must not be very different from those of surroundings. ie. thermal eqbm with surroundings.

ii. Slow

iii. Working parts must be frictionlesss

iv. No loss due to conduction, radiation.

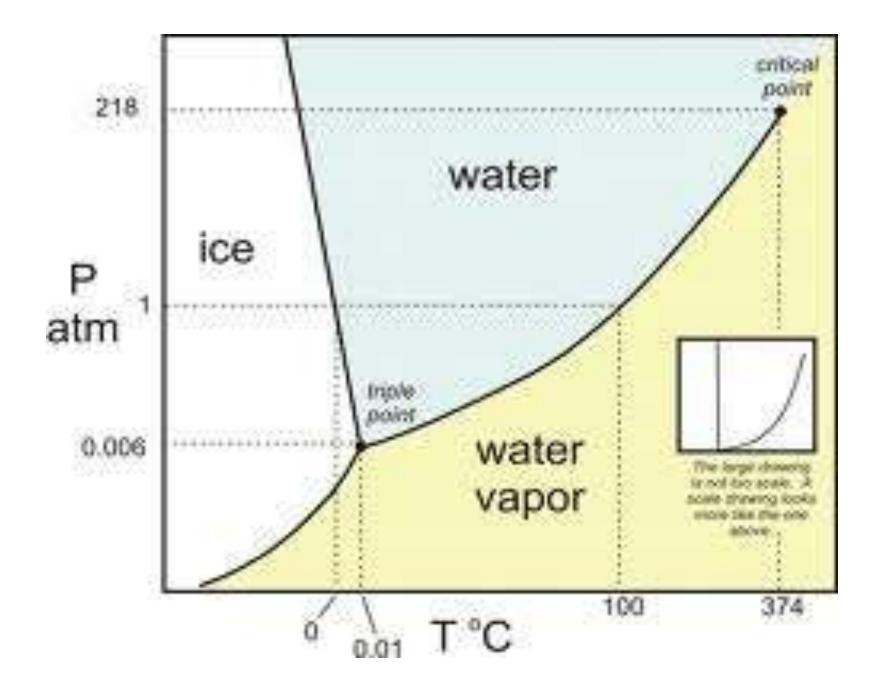
Irreversible process.

One in which, at the conclusion of the process, the system cannot be restored to its initial state when the process is reversed.

A permanent change is left somewhere.

Eg. Chemical reaction, heat loss due to friction, heat conduction, radiation

etc.



What is the angle which the curve of P-V diagram of an isobaric change makes with the positive direction of V-axis ?

It has been observed that air coming out of the hole of a punctured foot ball is cooler. Why is it so ?

The climate of a harbour town is more termperate than that of a town in desert at the same latitude? Relative humidity is high. So does not go to extreme condition.

Super heated water and super cooled vapour

Water above its boiling point and water vapour below boiling point.

Unstable states, donot lie on P-V-T surface. Used in cloud chamber, and bubble chamber for detection of charged nuclear particles.

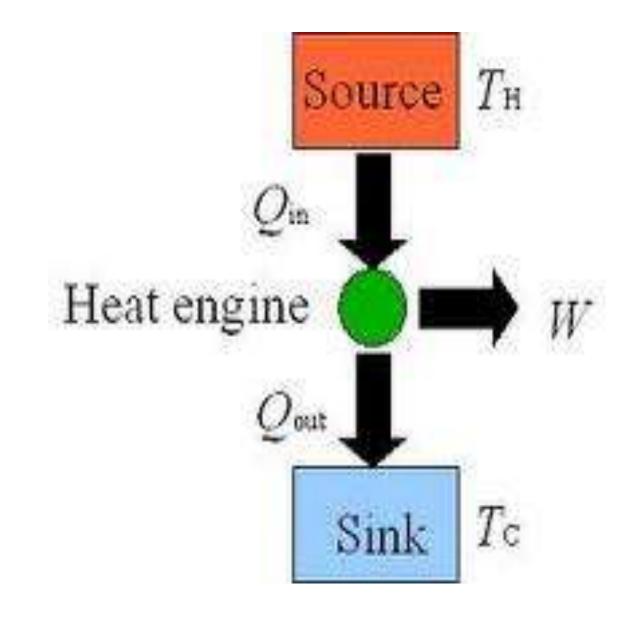
Limitations of First law of thermodynamics

- Does not indicate the direction in which 1. the change can occur. ($H \rightarrow C$ and $C \rightarrow H$) a) why no flow of heat from cold to hot. ? b) Applying car brake - work – friction – heat. Why – cools - does not move ?
- First law silent about reverse conversion.

Limitations of First law of thermodynamics

- ii. No idea about extent of change.(100 % heat \rightarrow Work. But not possible)
 - a) any amount of work to heat . Eg. Friction. But restriction on reverse.
 - b) extenrnal agency is reqd for reverse .
 - c) no heat engine can covert all heat received into mechanical energy.

First law detes quality thet into mechanical quality for statement of beating work. But nature hasimposed restrictions. Which heat is extracted So require a device Working substance. Called heat engine and a mediumacialiedworking



 Q_1 – amount absorbed. Q_2 – rejected. W – work done. Efficiency $\eta = \text{work out put}$ Heat in put $= W/Q_1$ $= 1 - Q_2$ $= Q_1 - Q_2$ 01 vary from 5% to 60% ie. $\eta < 1$

Note: it is not possible to covert heat derived from a single body into work.

- i) So ship cannot run with enormous energy available in sea water.
- ii) Factories cannot run with vast amount of heat available in the atmosphere.

CARNOT ENGINE

It is an ideal theoretical engine devised by Sadi Carnot.

Parts:

i) Source - reservoir of heat having conducting top at T_1 Kwih infinite thermal capacity.

CARNOT ENGINE

ii) Body or engine-1mole of ideal gas (working substance) taken in an adiabatic cylinder with frictioless piston, having conducting bottom. iii) Sink – like source (at $T_2K < T_1K$) Working of Carnot engine

Carnot's cycle : working substance is subjected to a cycle of operations consisting of two isothermal operations and two adiabatic operations. This cycle of operations is

called carnot's cycle.

Working of Carnot engine

Working substance is 1 mole of ideal gas at temperature T_1 K same as that of

source.

 P_1 – pressure V_1 – volume.

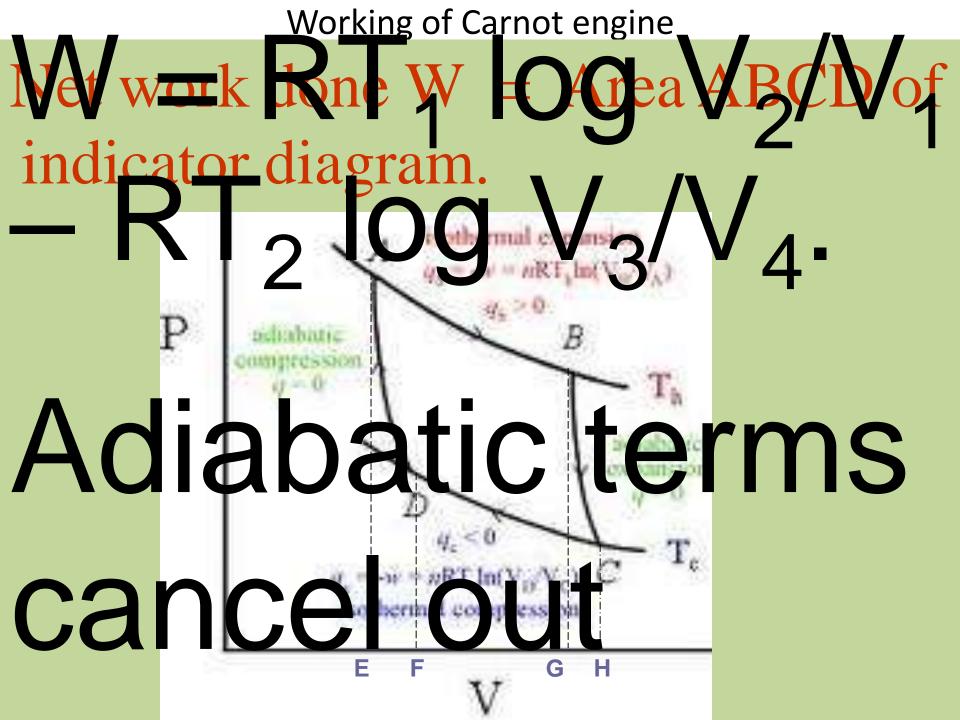
i)Isothermal expansion :

Cylinder on source. Pressure on piston is slowly reduced and allowed to expand. ie P_1 , V_1 , $T_1 \rightarrow P_2$, V_2 , T_1 . $Q_1 = W_1 = RT_1 \log V_2 / V_1$. = Area BCHGB

- ii) Adiabatic expansion :
 - Cylinder on platform. Pressure on piston is slowly reduced and allowed to expand until temp T_2K . ie P_2 , V_2 , $T_1 \rightarrow P_3$, V_3 , T_2 . $W_2 = R (T_1 - T_2)$ $(\gamma - 1)$ = Area BCHGB

iii) Isothermal compression: Cylinder on sink. Pressure on piston is slowly increased and gas inside is compressed to V_3 at T_2K . ie P_3 , V_3 , $T_2 \rightarrow P_4$, V_4 , T_2 . $-Q_2 = -W_3 = -RT_2 \log V_3 / V_4.$ = - Area CDFHC

iv) Adiabatic compression : Cylinder on platform. Pressure on piston is slowly increased so that gas regains initial conditions. ie P_4 , V_4 , $T_2 \rightarrow P_1$, V_1 , T_1 . $-W_{4} = -R (T_{1} - T_{2})$ $(\gamma - 1)$ = - Area DAEFD



Note: Points A and D are on same adiabatic $T_1 V_1^{\gamma - 1} = T_2 V_4^{\gamma - 1}$ $T_2/T_1 = [V_1/V_A]^{\gamma-1}.$ Points B and C are on same adiabatic $T_1V_2^{\gamma-1} = T_2V_3^{\gamma-1} \qquad T_2/T_1 = [V_2/V_3]^{\gamma-1}.$ $V_1/V_4 = V_2/V_3 = 0r = V_2/V_1 = V_3/V_4$ Since initial and final state are same dU = 0 $W = Q_1 - Q_2.$ $= RT_1 \log V_2/V_1 - RT_2 \log V_3/V_4.$ $=R(T_1 - T_2) \log V_2/V_1.$

 η in terms of temperature of source and sink

 $\eta = W/Q_1 = (Q_1 - Q_2)$ \mathbf{O}_1 $= R(T_1 - T_2) \log V_2/V_1.$ $RT_1 \log V_2/V_1$ $= (T_1 - T_2)$ T_1 $= 1 - (Q_2/Q_1) = 1 - (T_2/T_1).$ η

Q: Show that efficiency of a heat engine depends on the temperature of the source and sink and not on the properties of the working substance?



Nicolas Léonard Sadi Carnot (1796-1832)

Characteristics of Carnot's Engine

- i) Operations are perfectly reversible
- ii)η is independent of the working substance.
- iii)η depends only on the temperature of the source and sink .

Reversibility of carnot's engine is possible due to following reasons.

i) Slow

ii) frictionless piston.

iii) source and sink are at

constant temperatures.

iv)No loss of heat.

Characteristics of Carnot's Engine

Canene verabere alised reversible in practice. Carnot's in reversible in reversible in reversible in practice. Carnot's in reversible in reversi in reversible in reversible in reversible in aistandardotoyjudge the performance of actual and sink engine. • <u>F:\1212\video\adiabatic process.flv</u>

Refrigerator : device used to transfer heat from a cold region to a relatively hotter region .

(A carnot's engine works in the reverse order)

When external work is put on the working substance, it extracts an amount of heat Q₂ from a body at a lower temperature T₂K and rejects a larger amount of heat Q₁ to a body at a higher temp T_1K .

Coefficient of performance β : Defined as the ratio of the heat taken Orbitain the refigerator. $b_{I} = b_{I} = b_{I$? $Q_2/Q_1 = T_2/T_1$ $\beta = \frac{Q_2}{W} = \frac{Q_2}{(Q_1 - Q_2)} = \frac{1}{(Q_1/Q_2) - 1} = \frac{1}{(T_1/T_2) - 1}$

Second law of thermodynamics It is a generalisation of certain experiences and observations and is mainly concerned with the direction in which heat transfer takes place.

Stated in a number of ways, but all the statements are logically equivalent to one another. Based on Heatengined ynamics Steam engine takes hot steam and reject comparatively cold steam to sink (surrounding or atmosphere) lie Mechanical work is derived due to the flow of heat from a hotter source to a colder sink. Or colder sink is a

Basedtomrefrigerator. "It is impossible for a self – acting Nondirect proof of the law isernal available, but it is acknowledged to be universally trueserature to a Proof of this law is that it has never been possible to construct a machine which disobey the

Carnot's theorm :

 i) No engine can be more efficient than a reversible engine working b/w the same limits of temperature.

ii) All reversible engines working b/w the same limits of temperature have the same efficiency . Practical heat engines: i) External combustion engine (STEAM ENGINE). Steam is produced outside in separate boiler. Widely used in industry and for

locomotion .

Cycle in ideal – Rankine's cycle.

Practical heat engines: ii) Internal combustion engines. a) Otto engine (petrol) – heat is absorbed at constant volume. b) Diesel engine - at const Pressure.

<u>F:\1212\video\YouTube - The BEST OLD</u>
 <u>STEAM LOCOMOTIVE VIDEO from Sibley Iowa</u>
 <u>2008 PART 1.flv</u>

An ideal gas is compressed at constant temperature. Will its internal energy increase or decrease?

No Change, (T constant) Can a room be cooled by leaving the door of an electric refrigerator open ?

No.

Room will be heated up.

Is it possible for the internal energy of a substance to increase without showing any increase in its temperature? Illustrate by giving example.

Change of Phase.

Give the value of mechanical equivalent of heat. Is it a physical quntity ?

Mechanical eqvnt J = 4.186 J/cal.
It is not a physical quantity, but a conversion factor.

Why are the brake drums of a car heated when the car moves down a hill at constant speed ?

Force is applied to cancel the acceleration which does work and produce heat.

The internal latent heat of ice is equal its latent heat; while internal latent heat of vapourisation is less than its total latent heat. Why? Latent heat consists of true (internal) latent heat and work of evaporation. Since work is done in liquid – vapor phase change, internal LH is less.

The internal energy of a substance can be increases by two ways - by performing work on it or adding heat to it. Can you distinguish whether the internal energy has been increases by doing work or by transfer of heat? Explain.

<u>F:\1212\video\YouTube - nordic skiing stunts</u>
 <u>HD - fun.flv</u>

Draw schematically the isobaric process in (V,T) (P,V) and (P, T) diagrams.

A given quantity of gas has an initial state P1,V1 and T1. The expands V1 to V2 under i) const temp ii) constant Press. In which case is the work done by the gas more? Hint: second case. Area under hyperbola < area under

straight line parallel to V axis in the second case.