

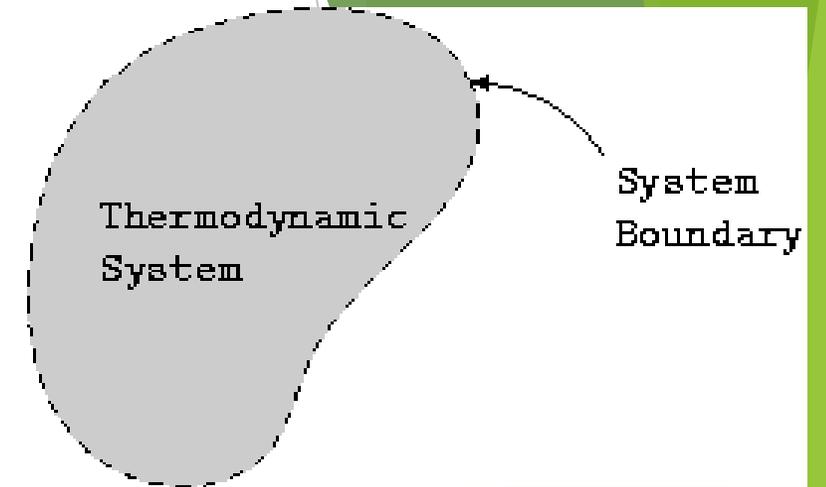
# THERMODYNAMICS

## THERMODYNAMICS

# INTRODUCTION

- ▶ Thermodynamics is that branch of physics which is concerned with transformation of heat into mechanical work.
- ▶ It deals with the concepts of heat, temperature and inter conversion of heat into other forms of energy i.e., electrical, mechanical, chemical and magnetic etc.
- ▶ Thermodynamics does not take any account of atomic or molecular constitution of matter and it deals with the bulk systems.
- ▶ State of any thermodynamic system can be described in terms of certain known macroscopic variables known as thermodynamic variables.

PREPARED BY : S D KHOBRAJADE PGT PHYSICS JNV OSMANABAD



Thermochemistry: Basic Concepts

Raja Mafaa  
Lizardi Institution  
Zarouk2

**SURROUNDINGS**

A diagram showing a pink oval labeled 'SYSTEM' containing two water molecules (H<sub>2</sub>O) and two oxygen molecules (O<sub>2</sub>). The oval is surrounded by a white area labeled 'SURROUNDINGS'. A box labeled 'boundary' is positioned at the bottom of the oval.

**System and Surroundings**

The **system** is a well-defined part of the universe that we single out for study.

Everything else is called the **surroundings**.

Between the system and surroundings is a **boundary**, across which transfers of matter, energy, or both may take place.

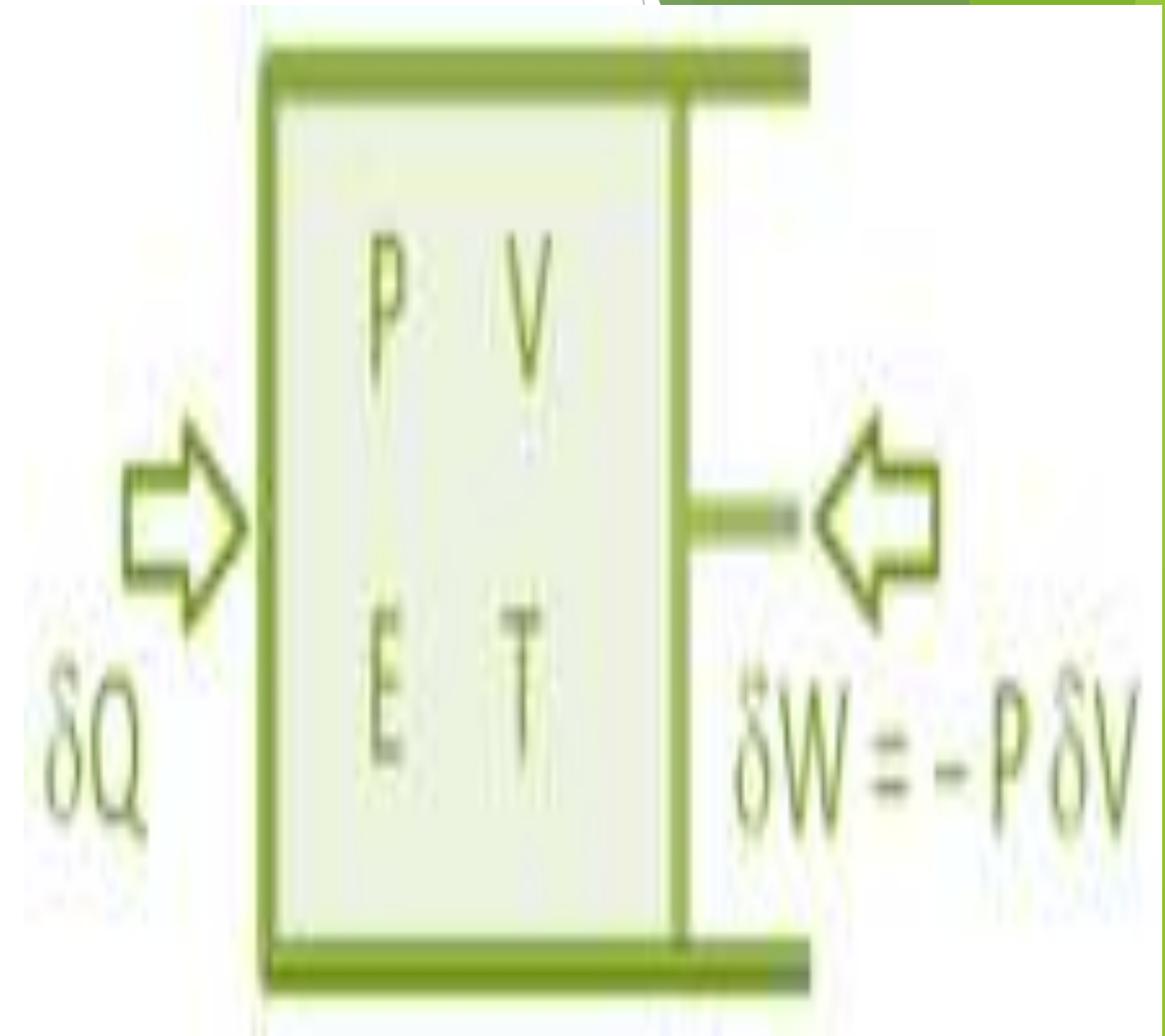
A system may be **open**, **closed**, or **isolated**.

A diagram showing a box labeled 'system' with a vertical line separating it from a box labeled 'surroundings'.

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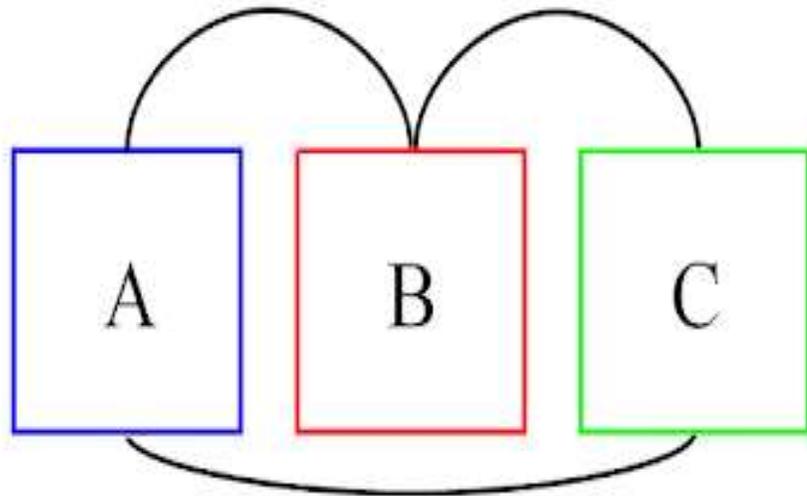
- ▶ Thermodynamic variables determine the thermodynamic behaviour of a system. Quantities like **pressure (P)**, **volume (V)**, and **temperature (T)** are thermodynamic variables.
- ▶ Some other thermodynamic variables are **entropy**, **internal energy** etc. described in terms of **P, V and T**.
- ▶ A thermodynamic system is said to be in thermal equilibrium if all parts of it are at same temperature.
- ▶ Thus two systems are said to be in thermal equilibrium if they are at same temperature.



# ZEORTH LAW OF THERMODYNAMICS

Two systems in thermal equilibrium with a third system separately are in thermal equilibrium with each other.

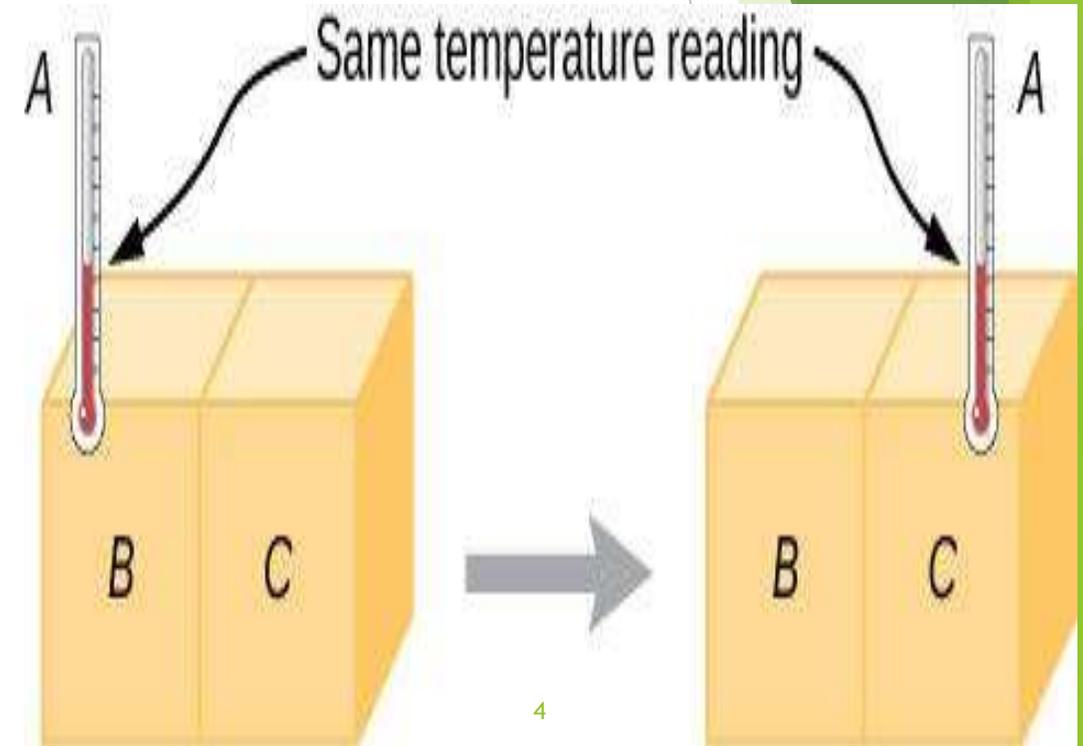
If A and B are separately in equilibrium with C.  $T_A = T_C$  and  $T_B = T_C$  then  $T_A = T_B$  i.e. systems A and B are also in thermal equilibrium



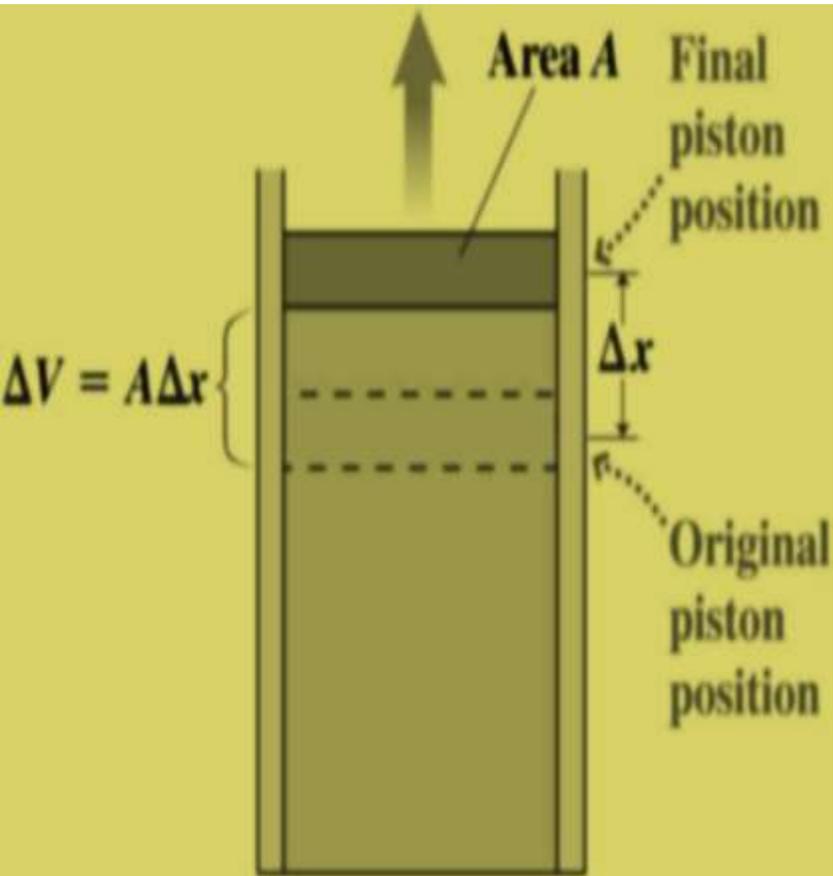
The Zeroth Law of Thermodynamics

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and The Principles of Sufficiency and Equivalency



# FIRST LAW OF THERMODYNAMICS



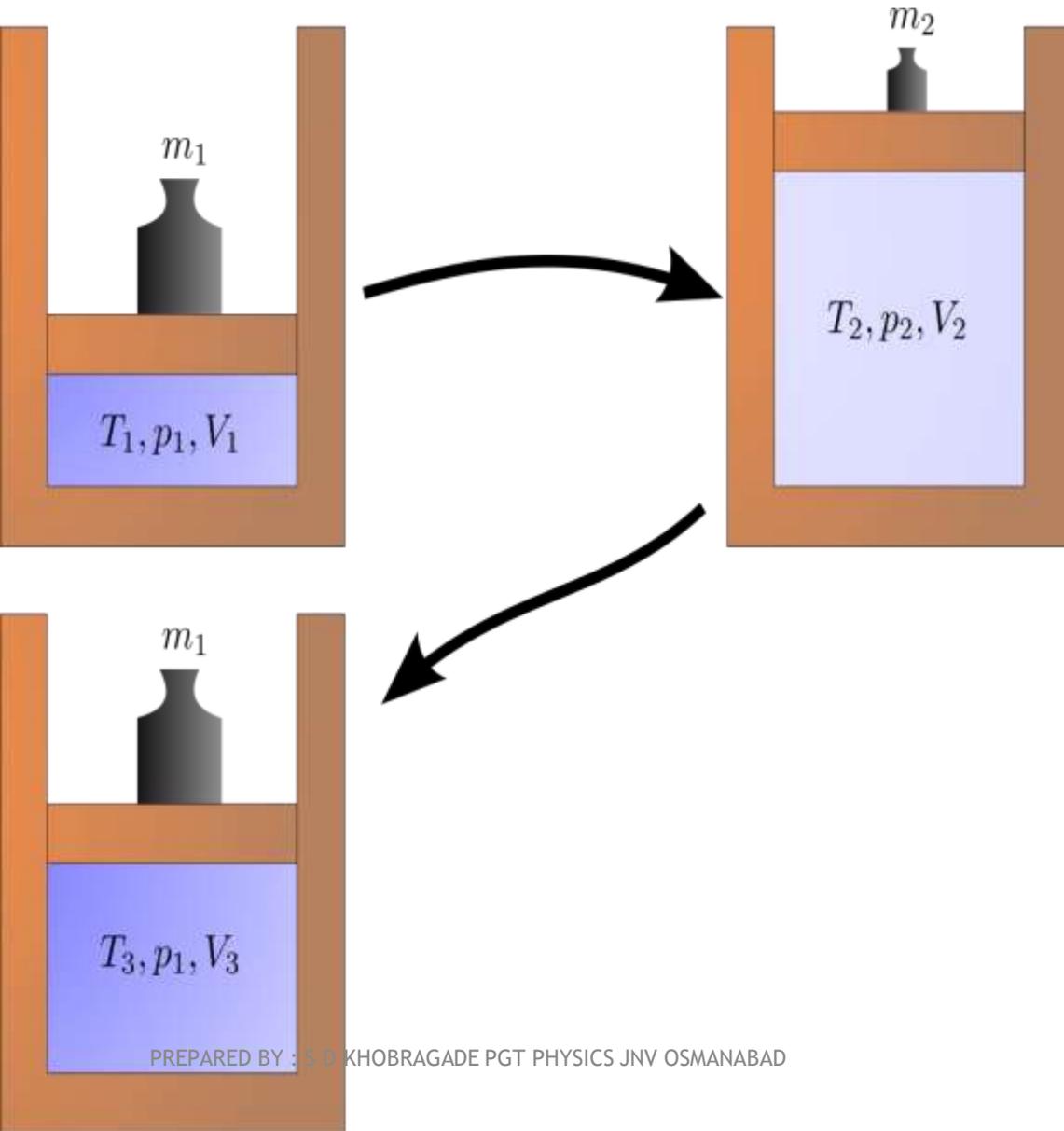
- ▶ It is based on the law of conservation of energy.
- ▶ When heat is added to the system then a part of heat is used to increase the internal energy of the system and other part is used to work done by the system.

- ▶  $dQ = dU + dW$

## SIGN CONVENTIONS

- ▶  $dQ = -Ve$  heat given by the system.
- ▶  $dQ = +Ve$  heat added to the system.
- ▶  $dU = +Ve$  if internal energy increase the temperature.
- ▶  $dU = -Ve$  if internal energy decrease the temperature.
- ▶  $dW = +Ve$  if work is done by the system (volume increases)
- ▶  $dW = -Ve$  if work is done on the system (volume decreases)

# QUASI STATIC PROCESS



- ▶ The system changes its variables so slowly that it remains in thermal and mechanical equilibrium with its surroundings throughout. At every stage the difference in the pressure of the system and external pressure is infinitesimally small and the temperature is also small.
- ▶ In quasi static process we change the external pressure by a small amount allow the system to equalise its pressure with that of the surroundings and continue the process infinitely slowly until the system achieves the required pressure.
- ▶ Similarly to change the temperature we introduce an infinitesimal temperature difference between the system and the surrounding reservoirs and by choosing reservoirs of progressively different temperature.

# WORK DONE IN AN ISOTHERMAL PROCESS

- ▶ A process in which the temperature of the system is kept fixed throughout is called an isothermal process.
- ▶ Ideal gas equation for isothermal process  $PV = \text{constant}$
- ▶ Consider an ideal gas goes isothermally from its initial state  $(P_1, V_1)$  to the final state  $(P_2, V_2)$  in this process at any stage with pressure  $P$  and volume change from  $V$  to  $V + \Delta V$

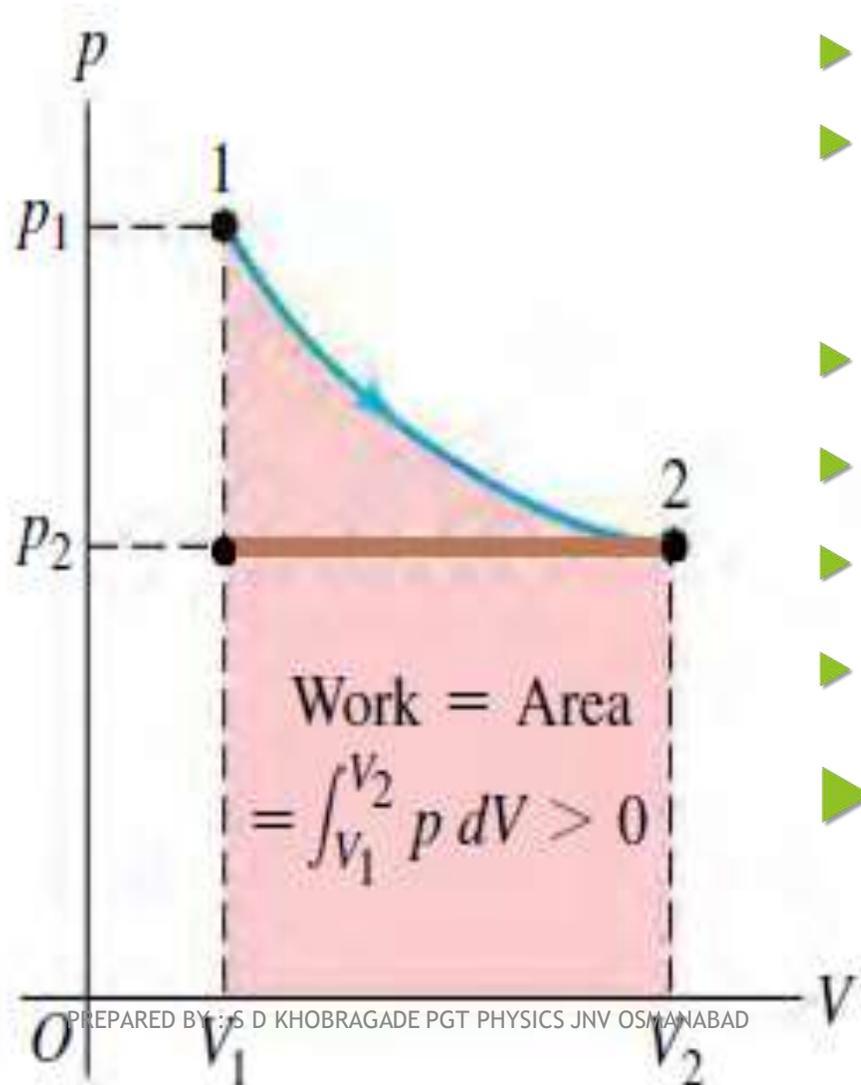
▶ Work done  $\Delta W = P \Delta V$

▶ To the entire process the work done  $W = \int_{V_1}^{V_2} P \Delta V$

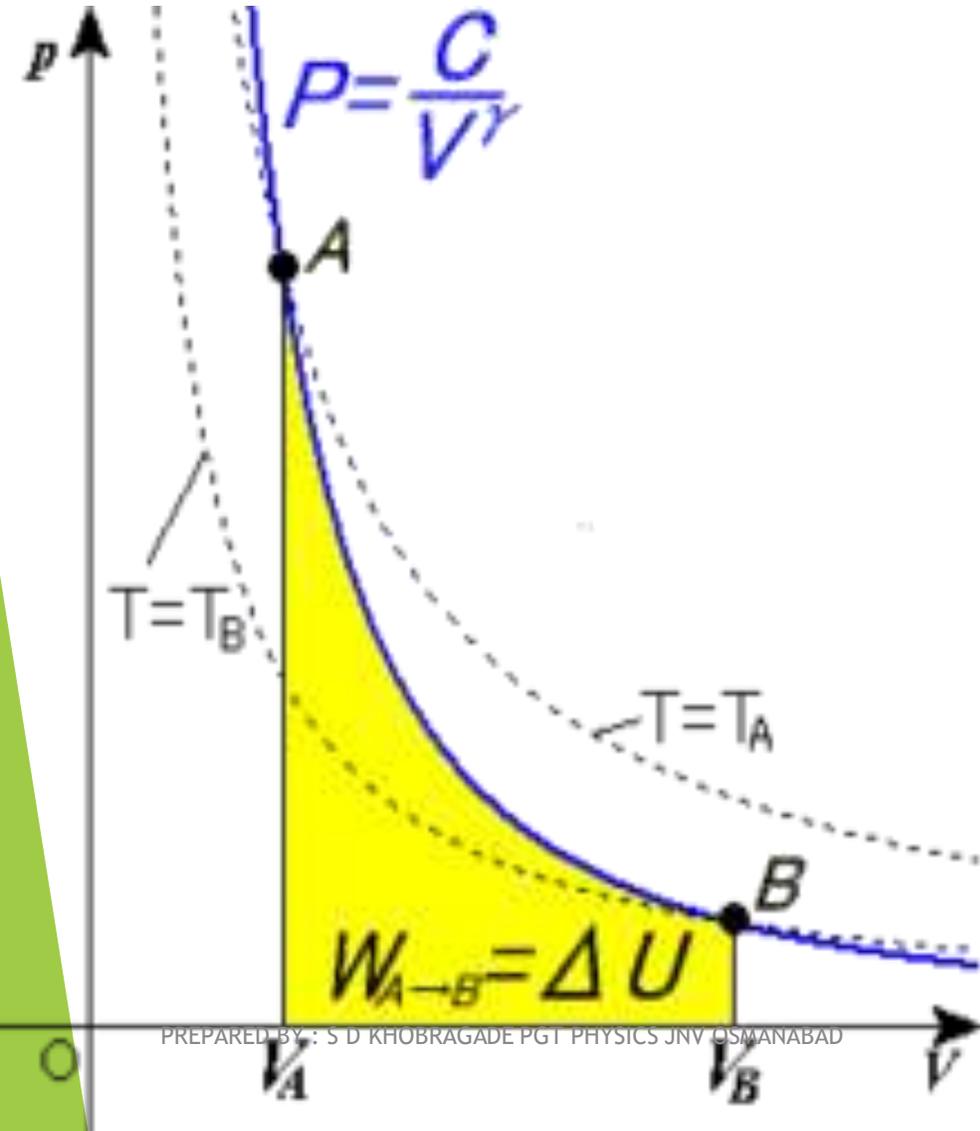
▶ From an ideal gas  $PV = \mu RT$

▶ So  $W = \mu RT \int_{V_1}^{V_2} \left(\frac{\Delta V}{V}\right) = \mu RT \ln(V_2/V_1)$

▶  **$W = 2.303 \mu RT \log(V_2/V_1)$**

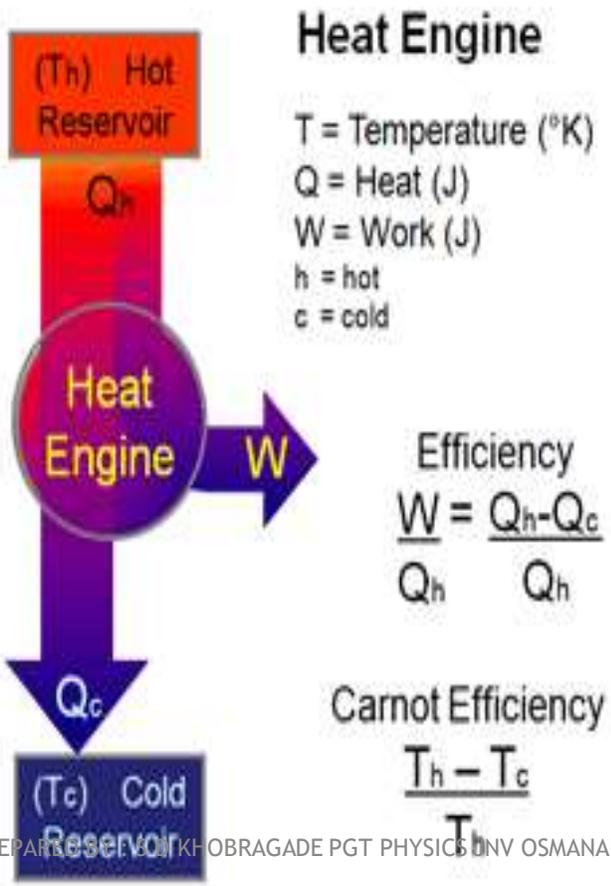


# WORK DONE IN AN ADIABATIC PROCESS



- ▶ If the system is insulated from the surroundings and no heat flows between the system and the surroundings then the process is called adiabatic process.
- ▶ An adiabatic process of an ideal gas equation is  **$PV^\gamma = \text{constant}$** .
- ▶ Work done in an adiabatic process:
- ▶ Consider an ideal gas change adiabatically from its initial state  $(P_1, V_1, T_1)$  to the final state  $(P_2, V_2, T_2)$
- ▶ Work done  $W = \int_{V_1}^{V_2} P \Delta V = \text{constant} \times \int_{V_1}^{V_2} \Delta V / V^\gamma$
- ▶  $= \frac{\text{constant}}{1-\gamma} \times (1/V_1^{\gamma-1} - 1/V_2^{\gamma-1})$
- ▶  $P_1 V_1^\gamma = P_2 V_2^\gamma = \text{constant}$
- ▶  $W = \frac{1}{1-\gamma} (P_2 V_2^\gamma / V_2^{\gamma-1} - P_1 V_1^\gamma / V_1^{\gamma-1})$
- ▶  **$W = \frac{1}{1-\gamma} (P_2 V_2 - P_1 V_1) = \mu R (T_1 - T_2) / \gamma - 1$**

# HEAT ENGINE



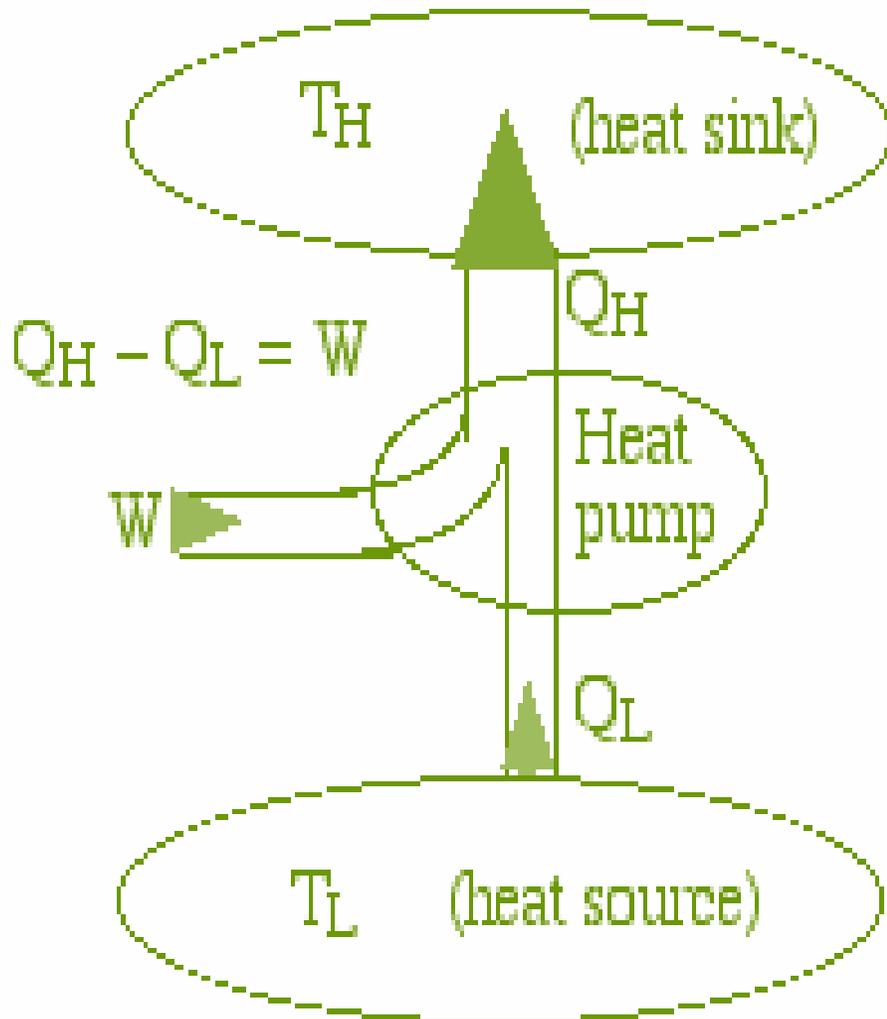
- ▶ Heat engine is a device to undergo cyclic process in conversion of heat into work.
- ▶ A mixture of fuel vapour and air in a gasoline or diesel engine or steam in a steam engine are the working substances. The working substance goes to cyclic process and absorbs a total amount of **heat  $Q_h$**  from an external reservoir at high **temperature  $T_h$**  and converted into work done. In some other process the remaining **heat  $Q_c$**  releases to an external reservoir at **temperature at  $T_c$** .

▶ The efficiency of heat engine  $\eta = W/Q_h$

▶  $W = Q_h - Q_c$

▶  $W = 1 - Q_c/Q_h$

# REFRIGERATOR



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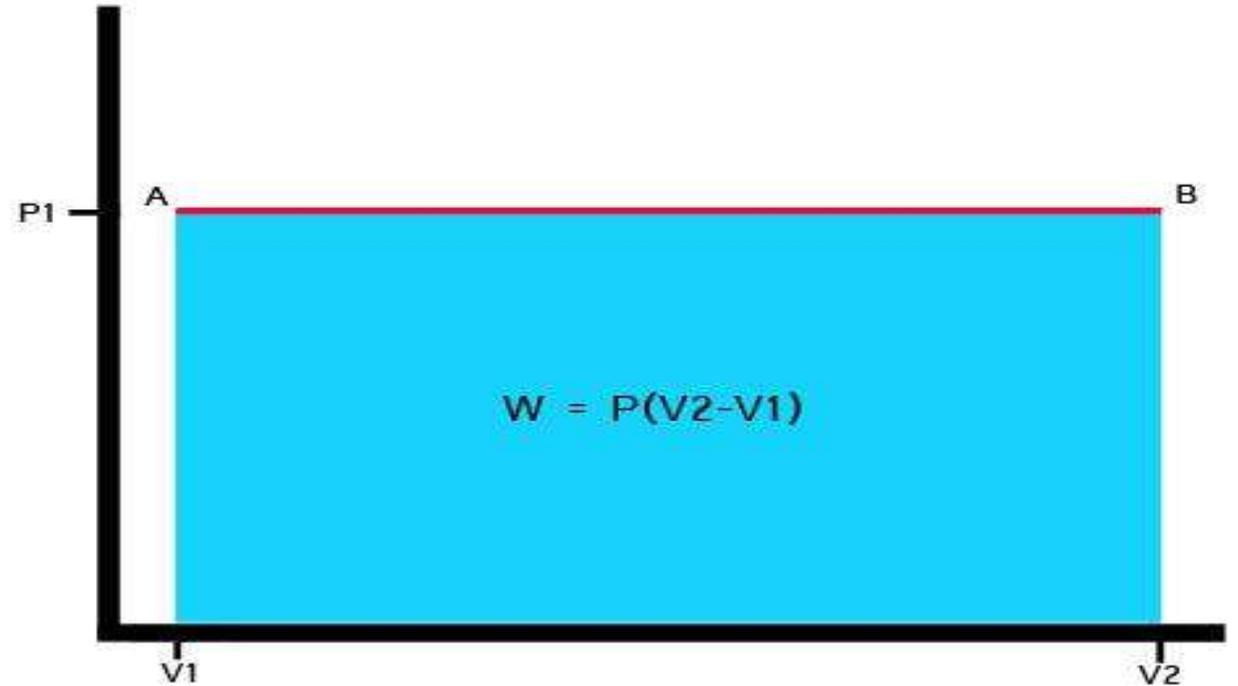
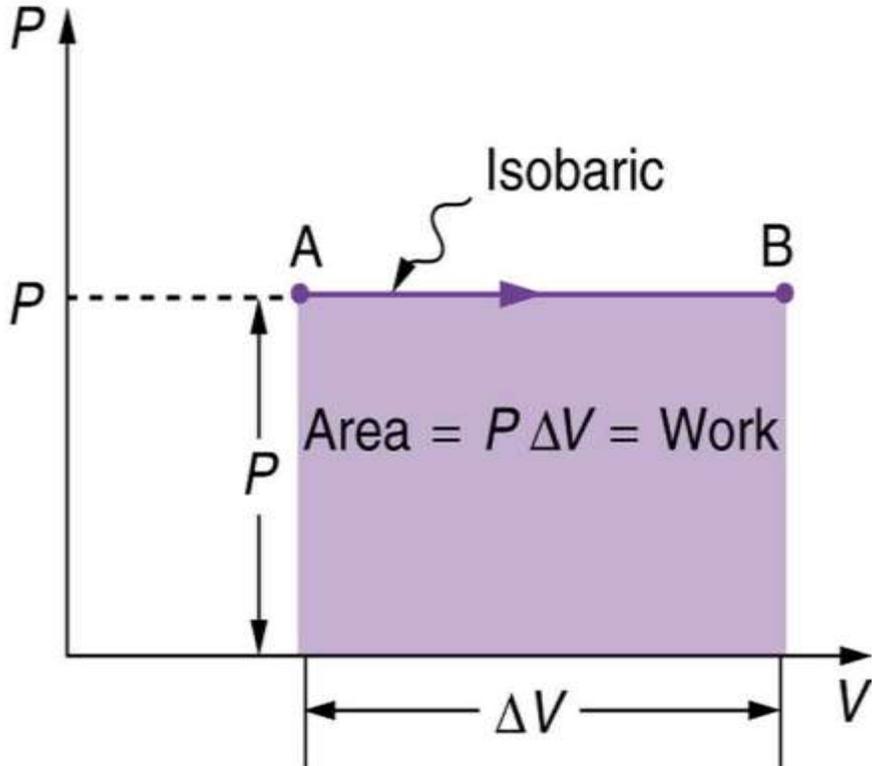
- ▶ A refrigerator is the reverse of a heat engine.
- ▶ In a refrigerator the working substance extracts heat  $dE_1$  from the cold reservoir at temperature  $T_1$  some external work is done on it and heat  $dE_2$  is released to the hot reservoir at temperature  $T_2$ .
- ▶ In a refrigerator the working substance goes through the following steps
- ▶ (a) sudden expansion of gas from high to low pressure (b) absorption of heat by cold fluid (c) heating up the vapour
- ▶ The coefficient of performance of a refrigerator  $\alpha = Q_2/dW$
- ▶  $Q_1 = dW + Q_2$
- ▶  $\alpha = \frac{Q_2}{Q_1 - Q_2}$

# ISOCHORIC PROCESS

In this process  $V$  is constant and no work is done on or by the gas.

# ISOBARIC PROCESS

In this process  $P$  is constant and work is done it is  $W = P(V_2 - V_1) = \mu RT(T_2 - T_1)$



# REVERSIBLE AND IRREVERSIBLE PROCESSES

## REVERSIBLE PROCESS

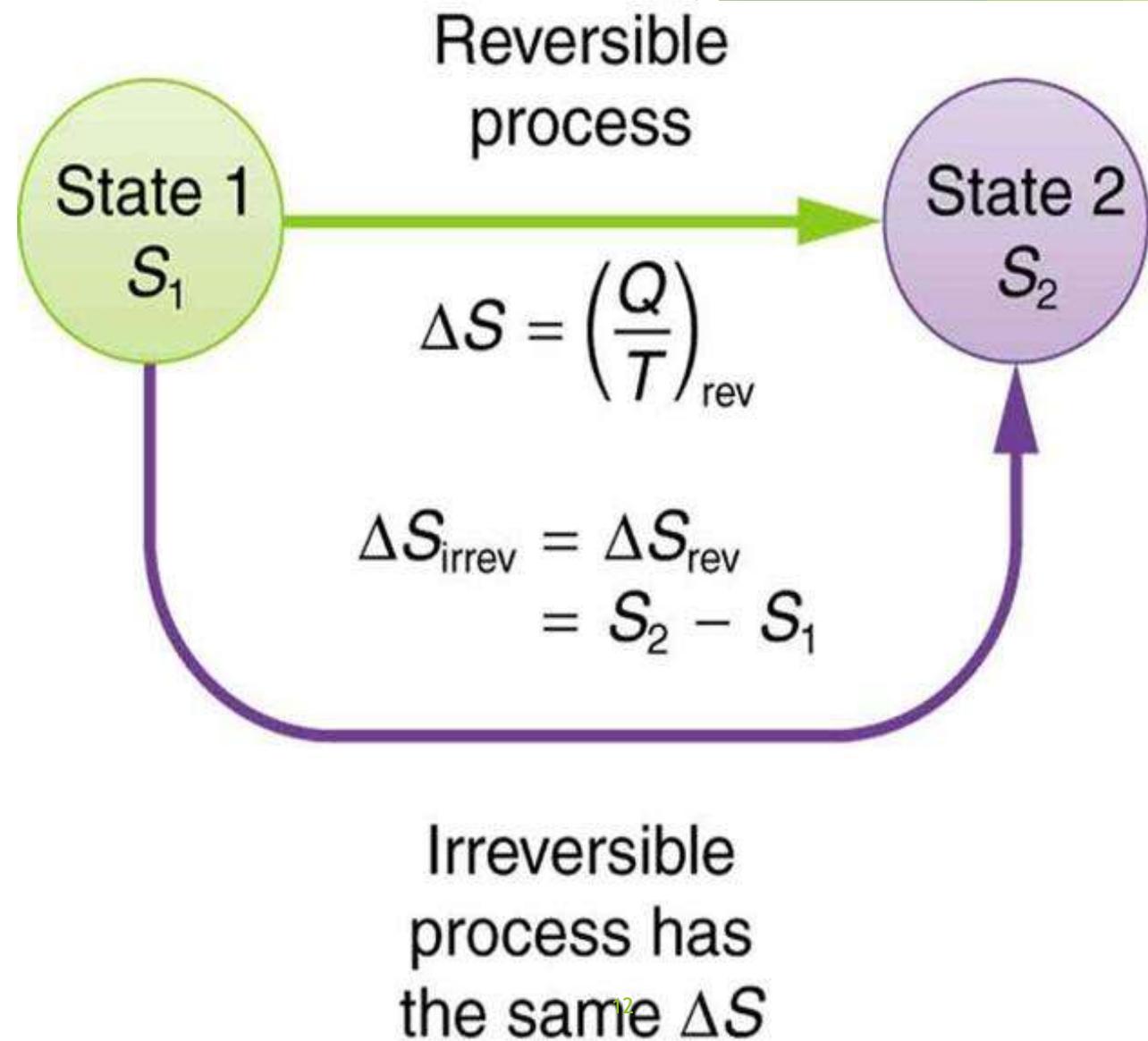
If the process can be turned back such that both the system and the surroundings return to their original states without any other change.

A quasi-static isothermal expansion of an ideal gas in a cylinder fitted with a frictionless movable piston is a reversible process.

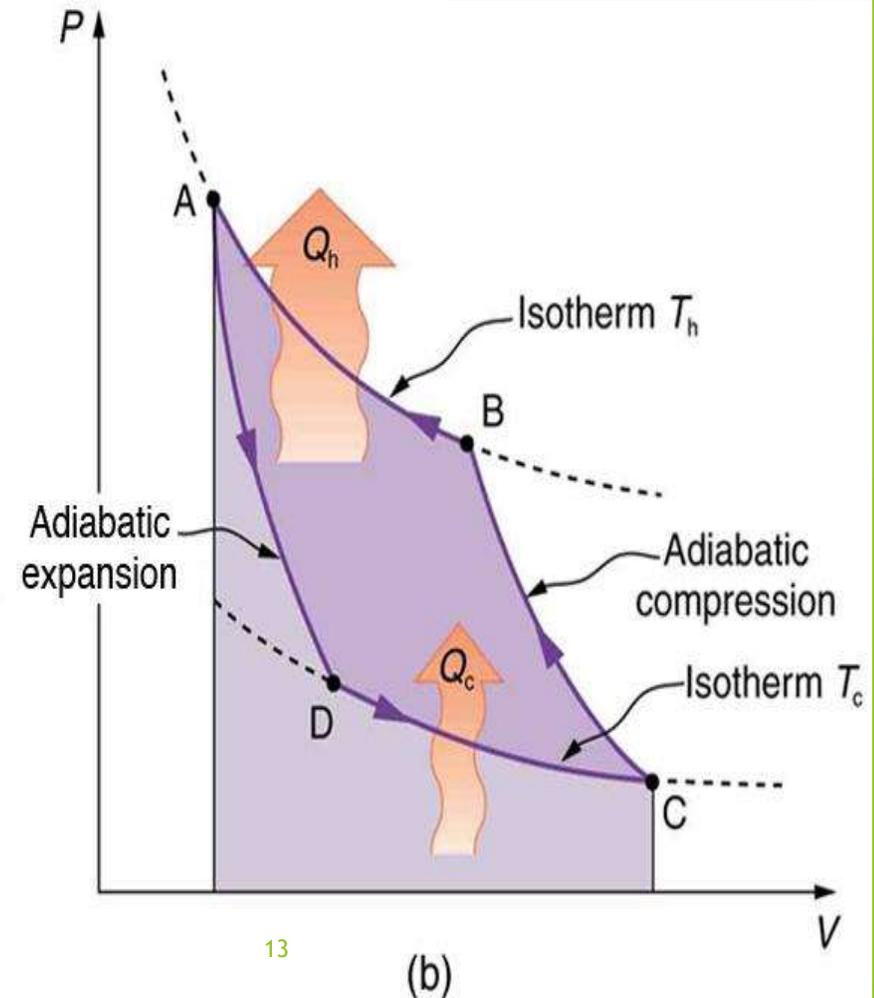
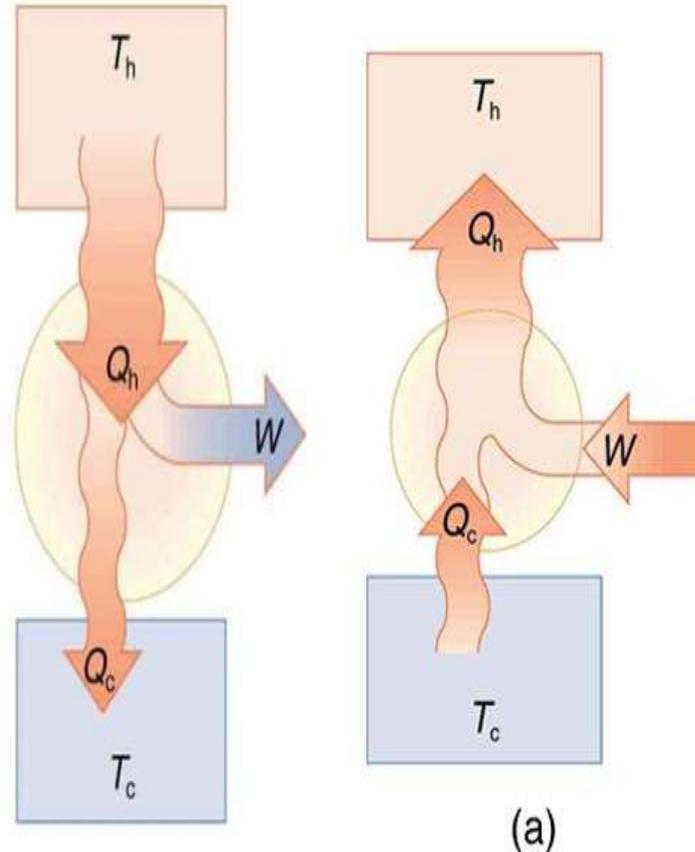
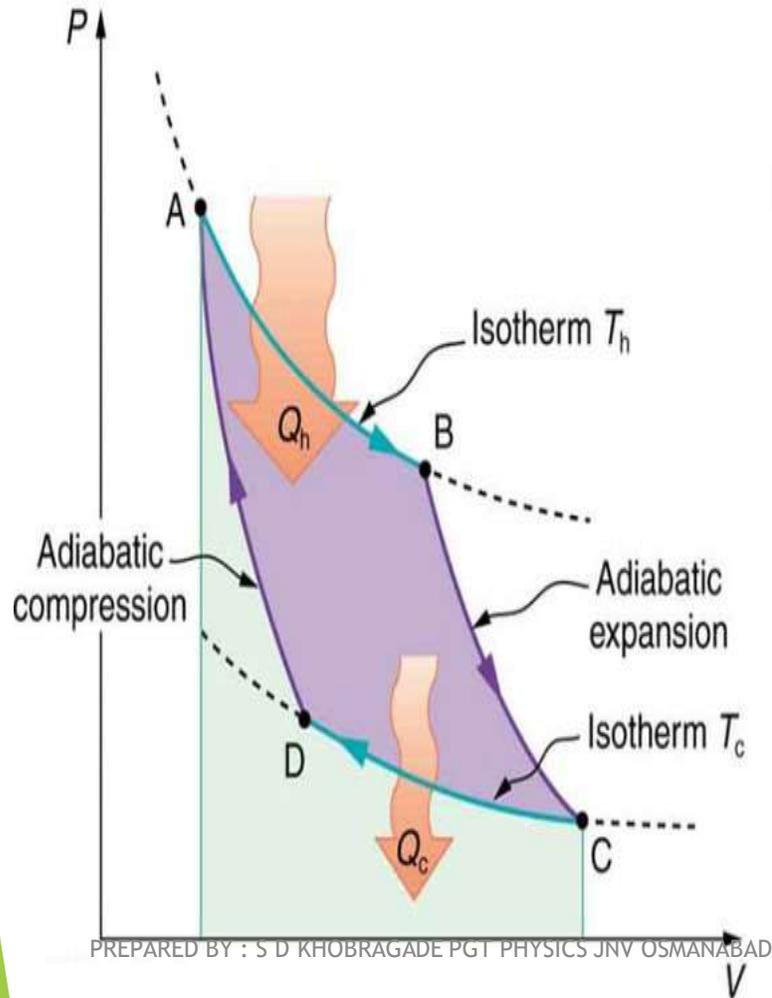
## IRREVERSIBLE PROCESS

If the process cannot be reversed is called irreversible process. The spontaneous processes of nature are irreversible.

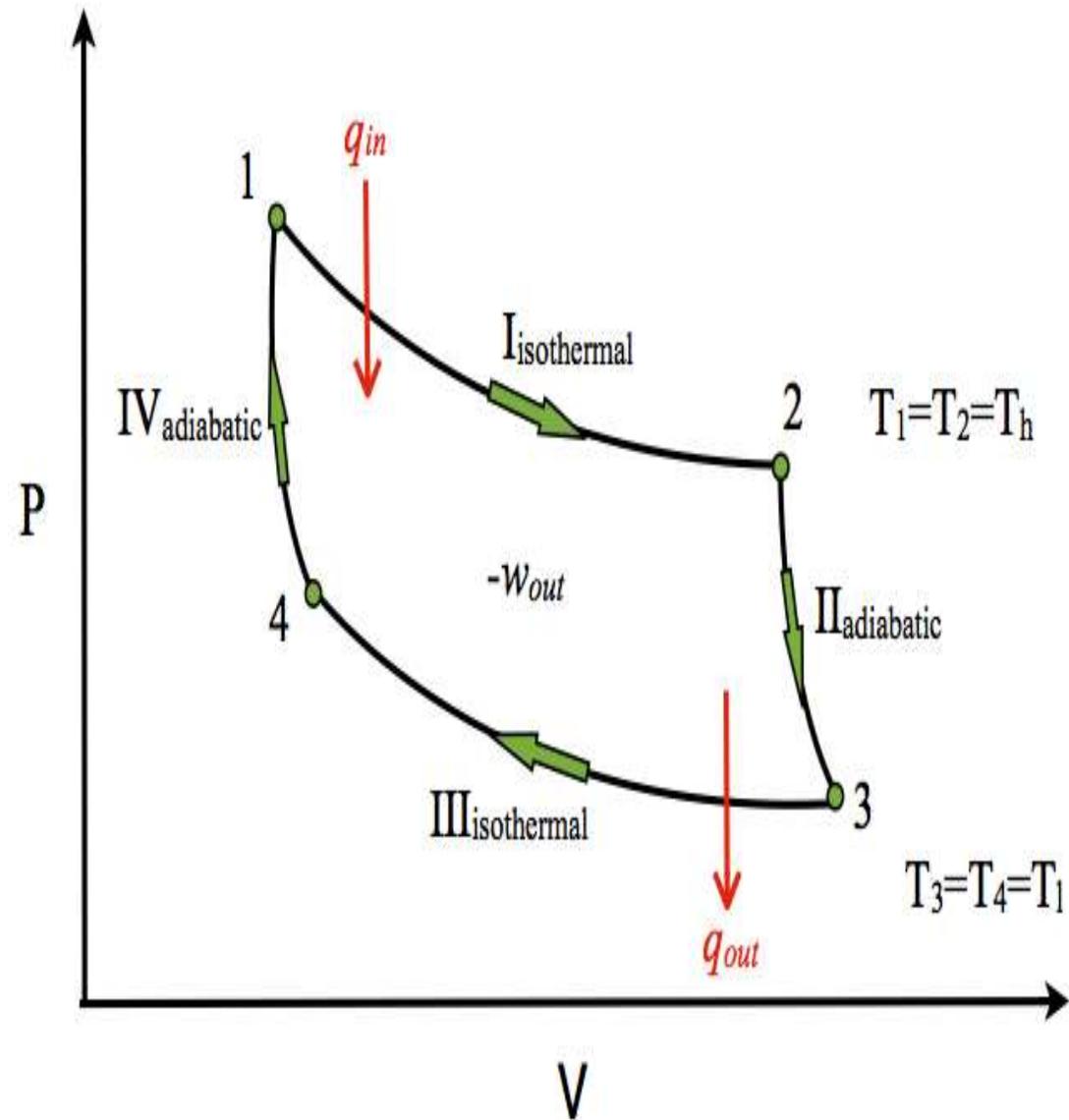
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# CARNOT ENGINE



- ▶ According to second law of thermodynamics, no heat engine can have 100% efficiency
- ▶ Carnot's heat engine is an idealized heat engine that has maximum possible efficiency consistent with the second law.
- ▶ Cycle through which working substance passed in Carnot's engine is known as Carnot's Cycle.
- ▶ Carnot's engine works between two temperatures
  - $T_1$  - temperature of hot reservoir
  - $T_2$  - temperature of cold reservoir
- ▶ In a Complete Carnot's Cycle system is taken from temperature  $T_1$  to  $T_2$  and then back from temperature  $T_2$  to  $T_1$ .
- ▶ We have taken ideal gas as the working substance of Carnot's engine.





# Ideal Carnot Cycle p-V diagram

Glenn  
Research  
Center

► In step b→c isothermal expansion of gas taken place and thermodynamic variables of gas changes from  $(P_1, V_1, T_1)$  to  $(P_2, V_2, T_1)$

► If  $Q_1$  is the amount of heat absorbed by working substance from the source and  $W_1$  the work done by the gas

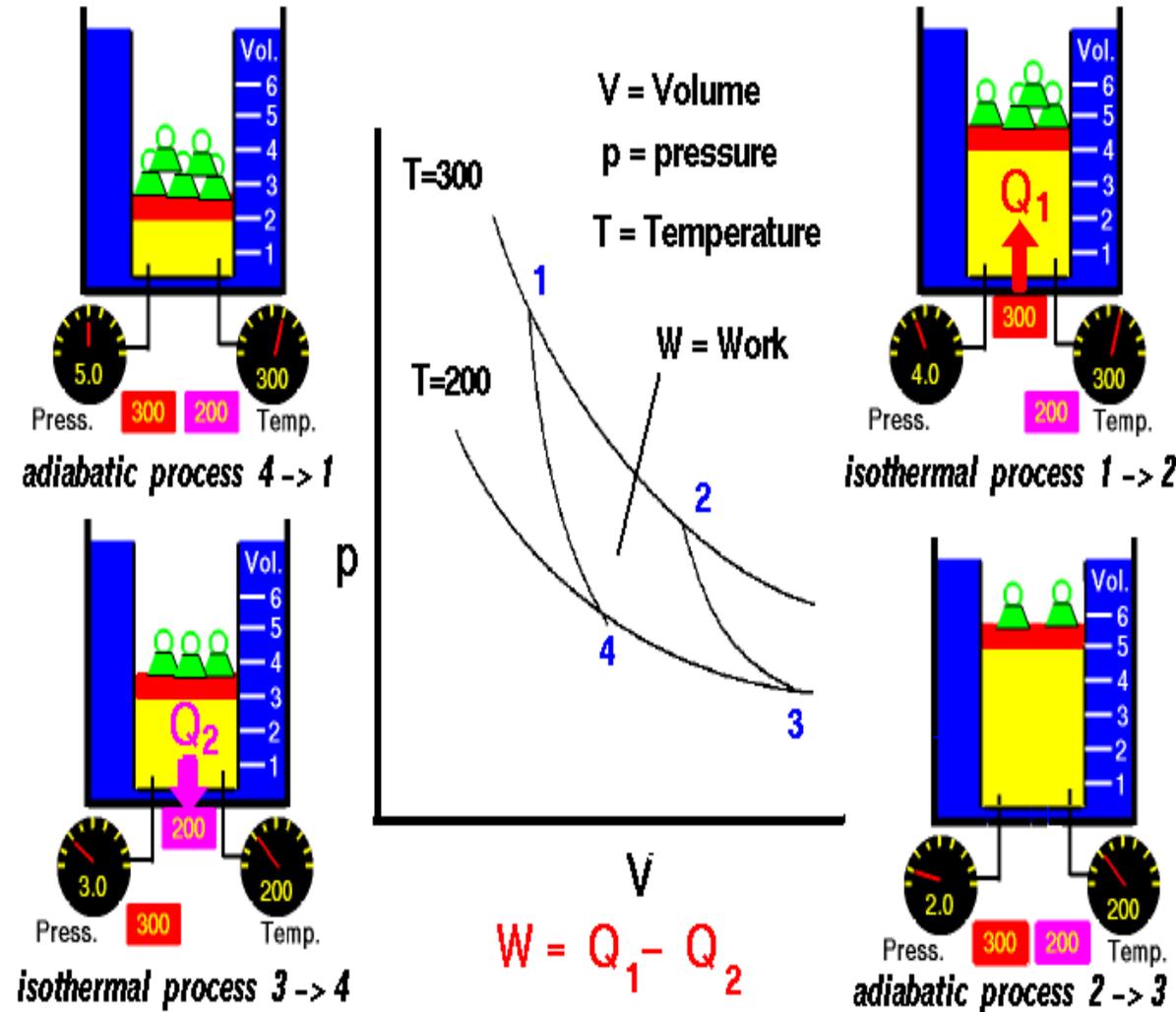
$$Q_1 = W_1 = nRT_1 \ln(V_2/V_1)$$

as process is isothermal.

► (ii) Step c→d is an adiabatic expansion of gas from  $(P_2, V_2, T_1)$  to  $(P_3, V_3, T_2)$ . Work done by gas in adiabatic expansion is given by

$$W_2 = nR(T_1 - T_2) / (\gamma - 1)$$

► (iii) Step d→a is isothermal compression of gas from  $(P_3, V_3, T_2)$  to  $(P_4, V_4, T_2)$ . Heat  $Q_2$  would be released by the gas to the at temperature  $T_2$



- ▶ Work done on the gas by the environment is

$$W_3 = Q_2 = nRT_2 \ln(V_3/V_4)$$

- (iv) Step a → b is adiabatic compression of gas from  $(P_4, V_4, T_2)$  to  $(P_1, V_1, T_1)$

- ▶ Work done on the gas is

$$W_4 = nR (T_1 - T_2) / (\gamma - 1)$$

- ▶ Now total work done in one complete cycle is

$$W = W_1 + W_2 - W_3 - W_4$$

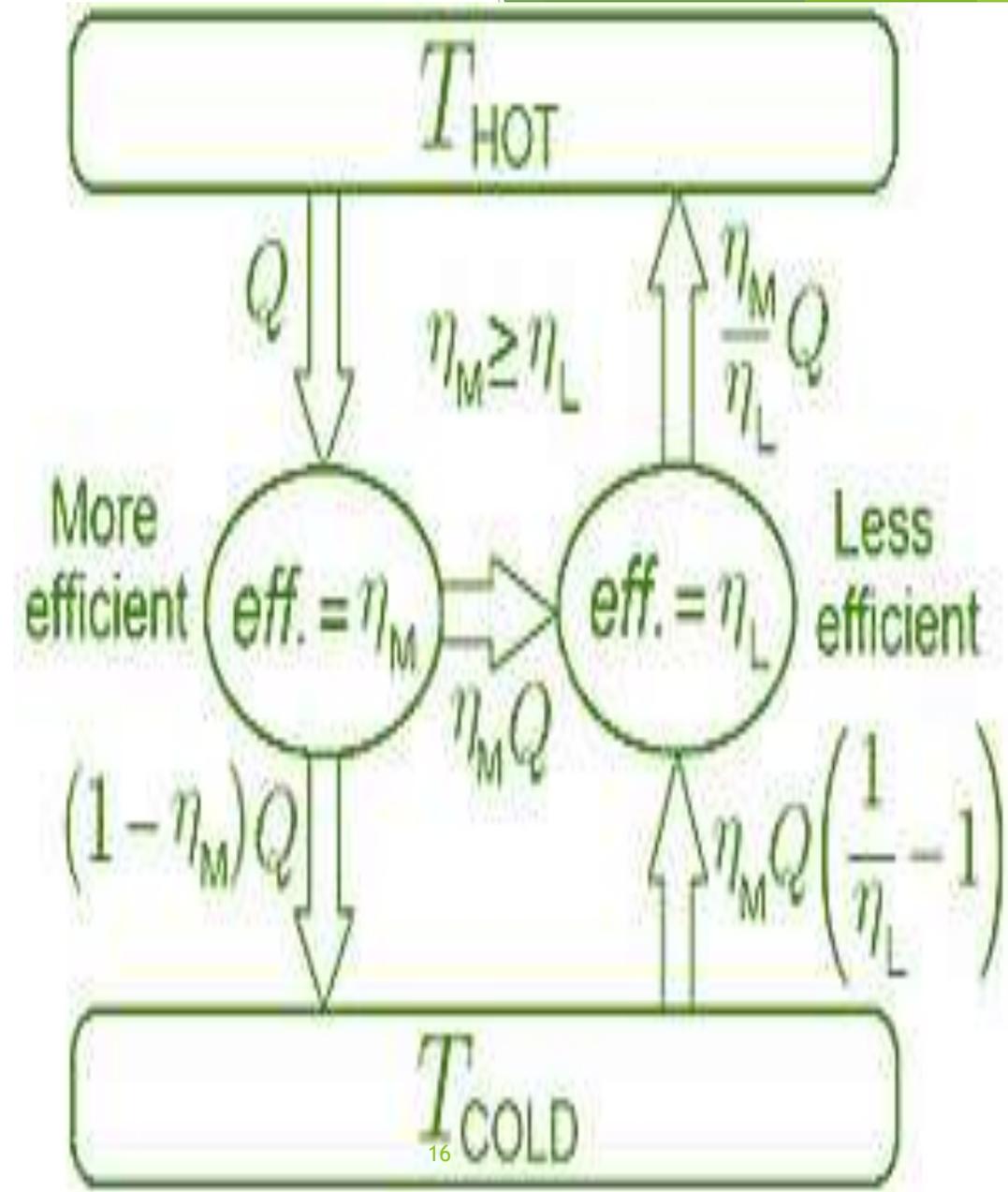
- ▶  $= nRT_1 \ln(V_2/V_1) - nRT_2 \ln(V_3/V_4)$   
as  $W_2 = W_4$

- ▶ Efficiency of Carnot engine

$$\eta = W/Q_1 = 1 - (Q_2/Q_1)$$

$$= 1 - (T_2/T_1) \ln(V_3/V_4) / \ln(V_2/V_1)$$

$$\text{or } \eta = 1 - [T_2 \ln(V_3/V_4) / T_1 \ln(V_2/V_1)]$$



► Since points b and c lie on same isothermal  
 $\Rightarrow P_1V_1=P_2V_2$ . Also points c and d lie on same  
 adiabatic.

$\Rightarrow P_2(V_2)^\gamma=P_3(V_3)^\gamma$

Also points d and a lie on same isothermal and  
 points a and b on sum adiabatic thus,

$P_3V_3=P_4V_4$

$P_4(V_4)^\gamma=P_2(V_1)^\gamma$

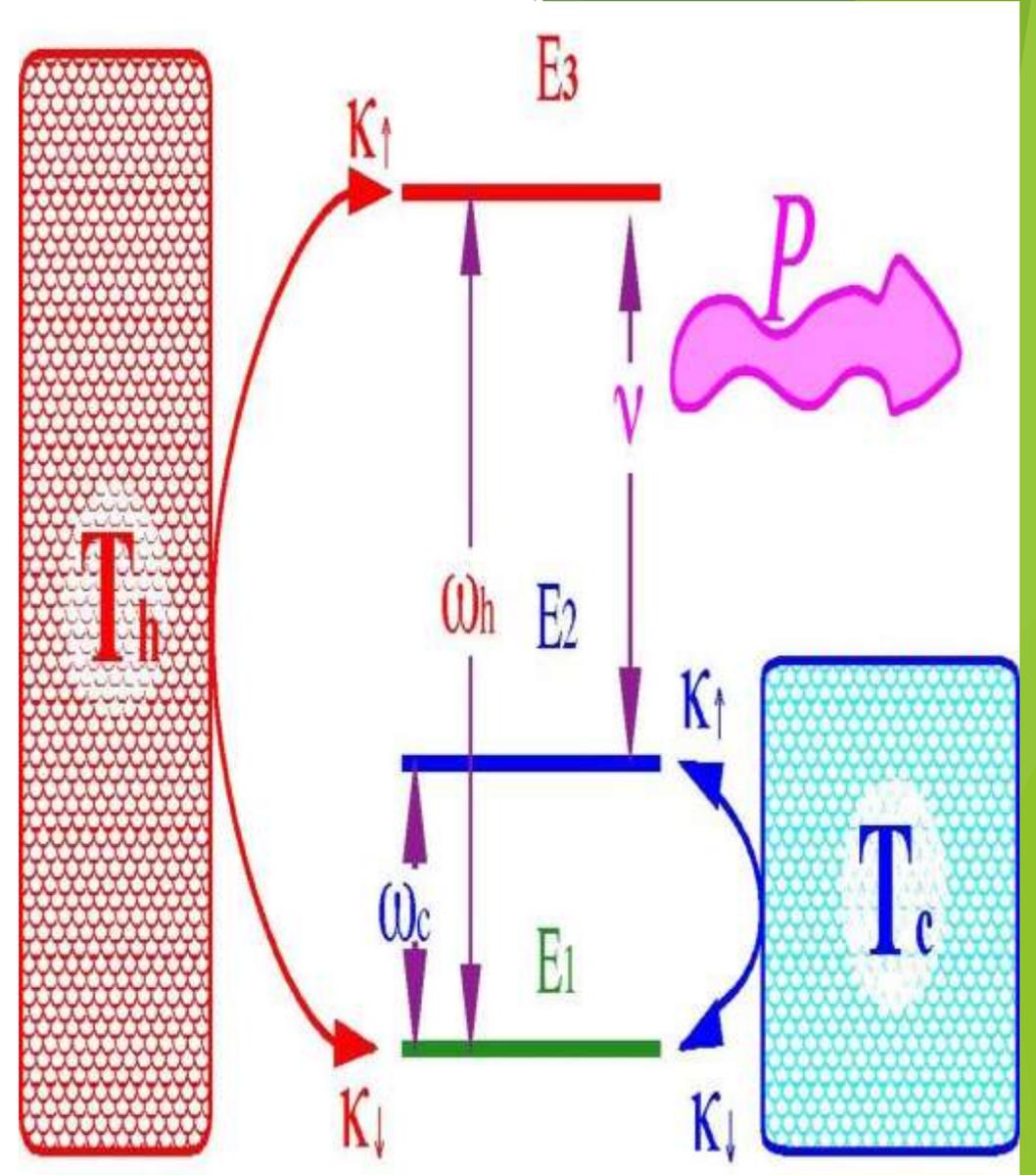
Multiplying all the above four equations may get

$V_3/4 = V_2/V_1$

Putting this in equation

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

From above equation we can draw following  
 conclusions that efficiency of Carnot engine is  
 (i) independent of the nature of working substance  
 (ii) depend on temperature of source and sink



# SPECIFIC HEAT CAPACITY OF AN IDEAL GAS

- ▶ There are two specific heats of ideal gases.
  - (i) Specific heat capacity at constant volume
  - (ii) Specific heat capacity at constant pressure

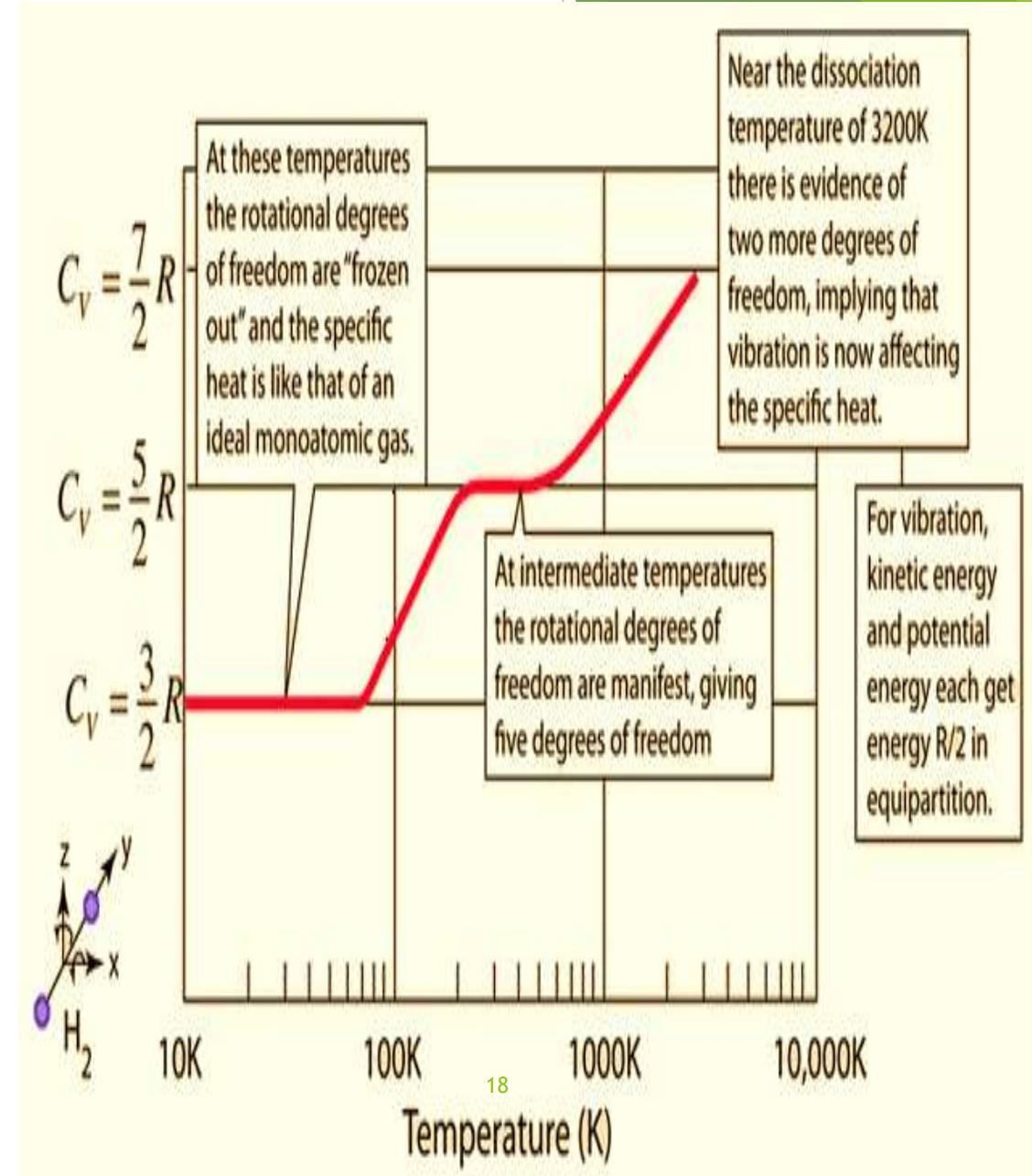
- ▶  $C_p$  and  $C_v$  are molar specific heat capacities of ideal gas at constant pressure and volume respectively. For  $C_p$  and  $C_v$  of ideal gas, there is a simple relation

$$C_p - C_v = R$$

where R- universal gas constant

- ▶ This relation can be proved as follows:  
From first law of thermodynamics for 1 mole of gas we have

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



► If heat is absorbed at constant volume then,  
 $\Delta V = 0$  and  $C_V = (\Delta Q/\Delta T)_V = (\Delta U/\Delta T)_V$

► If Q is absorbed at constant pressure then  
 $C_p = (\Delta Q/\Delta T)_p = (\Delta U/\Delta T)_p + P(\Delta V/\Delta T)_p$

Now ideal gas equation for 1 mole of gas is

$$PV = RT$$
$$= P(\Delta V/\Delta T) = R$$

From above equations

$$C_p - C_V = (\Delta U/\Delta T)_p - (\Delta U/\Delta T)_V + P(\Delta V/\Delta T)_p$$

► Since internal energy U of ideal gas depends only on temperature so subscripts P and V have no meaning.

$$C_p - C_V = R$$

which is the desired relation.

$$dh = du + d(Pv) = du + R dT$$

$$C_p dT = C_V dT + R dT \Rightarrow C_p = C_V + R$$

Define:  $k = \frac{C_p}{C_V}$  (ratio of specific heat capacities)

# EVALUATION

- ▶ Q1. What is zeroth law of thermodynamics?
- ▶ Q2. State the 1<sup>st</sup> law of thermodynamics?
- ▶ Q3. Give an example for isothermal process?
- ▶ Q4. Give an example for adiabatic process?
- ▶ Q5. Which process is called quasi-static process?
- ▶ Q6. How the efficiency of heat engine increases?
- ▶ Q7. State the 2<sup>nd</sup> law of thermodynamics?
- ▶ Q8. Say the relation between specific heat capacities?
- ▶ Q9. Why  $C_p > C_v$ .
- ▶ Q10. If it is possible to get 100% efficiency by any engine?

# RECAPTULATION

- ▶ **Thermodynamic Process** : A thermodynamic process is said to be taking place, if the thermodynamic variable of the system change with time.
- ▶ **Types of thermodynamic Process:-**
- ▶ (1) *Isothermal process*: process taking place at constant temperature.
- ▶ (2) *Adiabatic process*: process where there is no exchange of heat.
- ▶ (3) *Isochoric process*: process taking place at constant volume
- ▶ (4) *Isobaric process*: Process taking place at constant Pressure.
- ▶ (5) *Cyclic process*: Process where the system returns to its original state.
- ▶ **First law of Thermodynamics** : It states that if an amount of **heat  $dQ$**  added to a system , a part of heat is used in increasing its **internal energy** while the remaining part of heat may be used up as the **external work done  $dW$**  by the system.
- ▶ **Mathematically**      $dQ=dU+dW$
- ▶  $dQ=dU+ PdV.$

Thermodynamic processes are

**(1) Isothermal process :** A thermodynamic process that takes place at constant temperature is called an isothermal process.

Equation of state for isothermal process :  **$PV = \text{constant}$** .

Work done during an isothermal process  $W_{\text{iso}} = \mu RT \ln (V_2/V_1) = 2.303 \mu RT \log (V_2/V_1)$

**(2) Adiabatic process:** A thermodynamic process that takes place in such a manner that no heat enters or leaves the system is called adiabatic process .Equation of state for adiabatic process **(i)  $PV^\gamma = \text{constant}$  (ii)  $TV^{\gamma-1} = \text{constant}$**

**(3) Work done during adiabatic change**

$$W = \frac{1}{1-\gamma}(P_2V_2 - P_1V_1) = \mu R(T_1 - T_2) / \gamma - 1$$

**(4) Efficiency of heat Engine:** It is defined as the ratio of the external work obtained to the amount of heat energy absorbed from the heat source.

Mathematically  **$\eta = 1 - Q_2/Q_1$**

**(5) Carnot's heat Engine:** It is an ideal heat Engine which is based on carnot's reversible cycle.

**Efficiency of carnot's heat Engine  $\eta = 1 - T_2/T_1$**

**(6) Refrigerator or Heat pump:** It is heat engine working backward.

**(7) Co-efficient of performance:** It is the ratio of heat absorbed from cold body to the work done by the refrigerator.

Mathematically  **$B = Q_1 / (Q_1 - Q_2)$**

**THANK YOU**

**PREPARED BY:**

**S D KHOBRAKAGE**

**PGT PHYSICS**

**JNV OSMANABAD**