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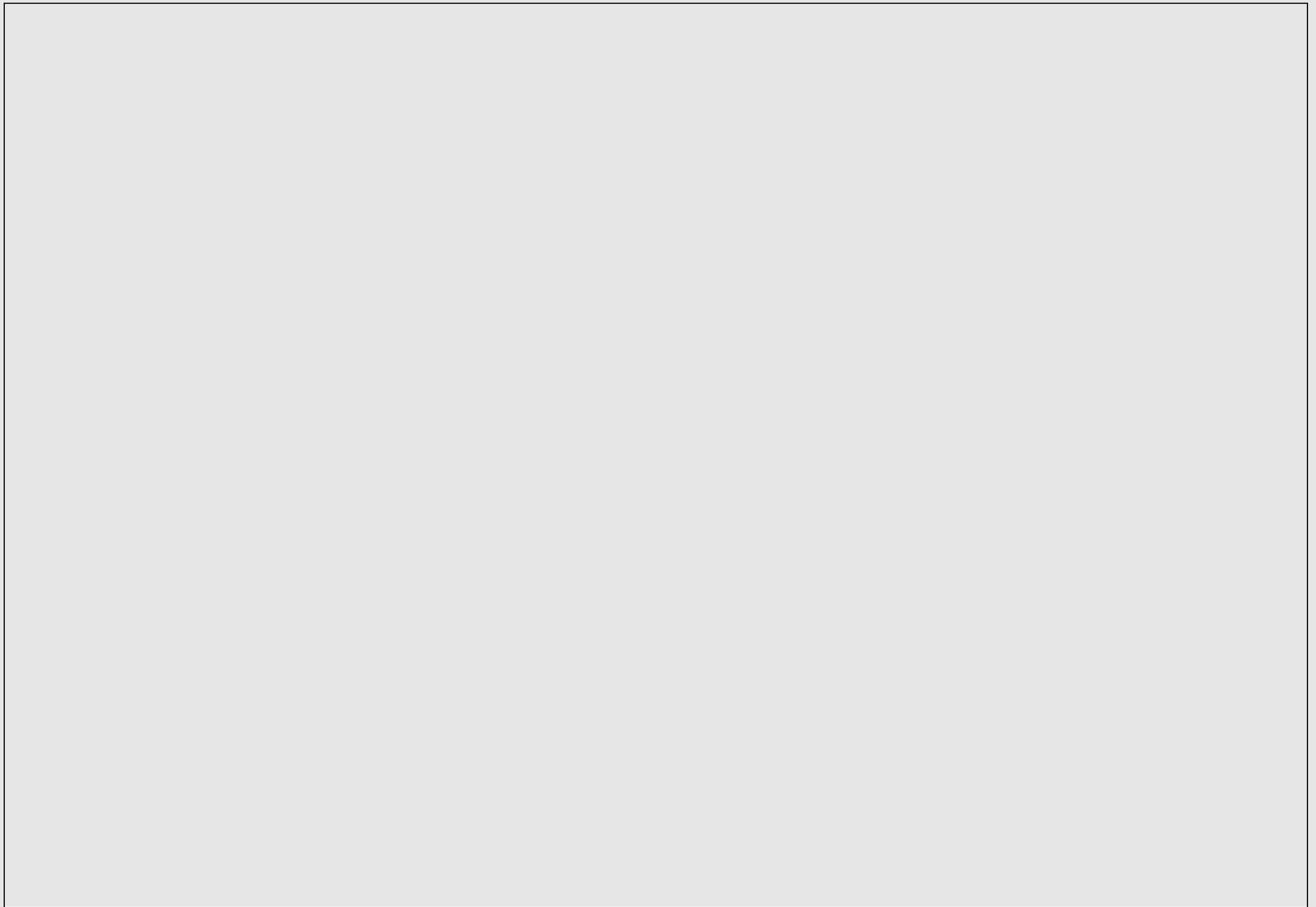
# METALLURGICAL THERMODYNAMICS AND KINETICS

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1st module



MME DEPARTMENT  
Gce kjr



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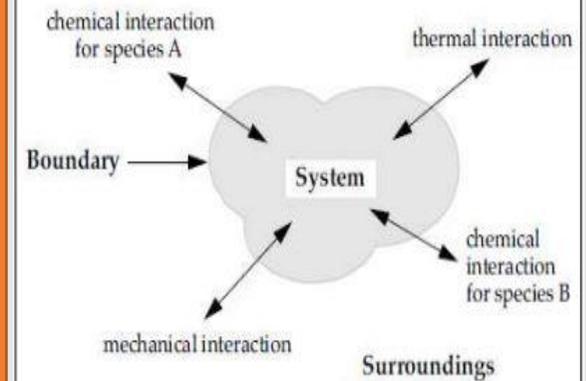
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# THERMODYNAMIC TERMS

## IMPORTANCE OF THERMODYNAMICS

- Thermodynamics is the branch of physics which deals with the relationship between heat and other form of energy
- In physical metallurgy the main aim of the study is to predict whether the alloy will be in equilibrium or not
- This subjects deals with the no. of parameter that made the phases to remain in equilibrium
- it also helps to predict the reaction of any material with other material
- All material depends on thermodynamic in one way or the other

- System : it is any portion of the universe that is separated by rest of the universe and is closed by a boundary wall
- Surrounding : except the system the rest of the universe is called surrounding



## THREE TYPES OF SYSTEM

1. OPEN SYSTEM (MASS AND HEAT TRANSFER POSSIBLE)
2. CLOSED SYSTEM (ONLY HEAT TRANSFER POSSIBLE)
3. ISOLATED SYSTEM (NEITHER HEAT NOR MASS TRANSFER IS POSSIBLE)

## PROPERTY:

EXTENSIVE PROPERTY: THE PARAMETERS THAT DEPENDS ON MASS

INTENSIVE PROPERTY: THE PARAMETERS THAT DOESNOT DEPEND ON MASS

## EQUILIBRIUM

If in a system both thermal & mechanical equilibrium exists simultaneously. Then it is known as in thermodynamic equilibrium.

- i. Thermal Equilibrium: Uniform temperature throughout the system.
- ii. Mechanical Equilibrium: Uniform pressure throughout the system.
- iii. Chemical Equilibrium: Uniform chemical potential throughout the system

## PROCESS

When in a system there is two or more than two parameters get changed then it is known as system gets changed and process occurs.

- i. Cyclic Process: Sequence of processes which return back to its initial point.
- ii. Adiabatic Process: Process in which net heat change ( $Q$ ) is equal to zero.
- iii. Isothermal Process: Process in which net temperature change ( $\Delta T$ ) is equal to zero.
- iv. Isobaric Process: Process in which net pressure change ( $\Delta P$ ) is equal to zero.
- v. Isochoric Process: Process in which net volume change ( $\Delta V$ ) is equal to zero.
- vi. Quasi-static Process: It is the process in which every small steps are in equilibrium, so that entire process is in equilibrium.

# LAW'S OF THERMODYNAMICS

## THE 1<sup>ST</sup> LAW OF THERMODYNAMICS

This states that the change in the internal energy of a system ( $\Delta U$ ) is equal to the sum of the energy added by heating the system ( $\Delta Q$ ) and the energy entering the system through work being done on it ( $\Delta W$ )

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

- This law is an expression of the principle of conservation of energy (the amount of energy in a closed system does not change)
- It is not possible to measure the total internal energy of a body, only changes in it.
- Internal energy is the sum of all energy associated with translational motion, vibrational motion and electronic configuration and it is a state property.

## HEAT CAPACITY

The amount of heat required to raise the temperature of 1 gram of substances by 1 degree Celsius. Is called heat capacity

At least 2 types of heat capacity

- a) Keep volume constant  $C_v$
- b) Keep pressure constant  $C_p$

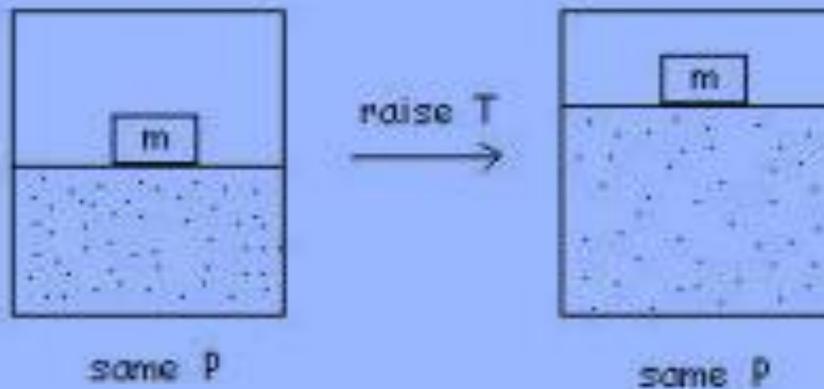
p) keep pressure constant  $C^b$

a) keep volume constant  $C^a$

$$C_V = \left( \frac{\delta q}{dT} \right)_V$$

$$C_P = \left( \frac{\delta q}{dT} \right)_P = \left( \frac{dH}{dT} \right)_P$$

Relation for  $C_P$  and  $C_V$  for ideal gas?



$$V_2 > V_1; T_2 > T_1$$

$$\Delta U = q_P + w = q_P - P_{\text{ext}}(V_2 - V_1) \quad PV = nRT$$

$$\Delta U = q_P - nR(T_2 - T_1) \quad q_P = C_P \Delta T; \Delta U = q_V = C_V \Delta T$$

$$C_P \Delta T = C_V \Delta T + nR \Delta T$$

$$C_P = C_V + nR$$

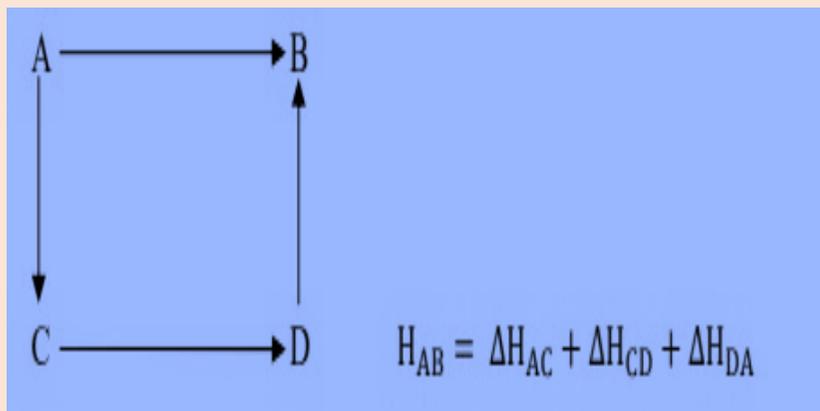
or

$$C_{P,m} = C_{V,m} + R$$

## Hess law

The law states that “The total change of heat in a chemical reaction is same irrespective whether it occurs in a single step or in multiple steps provided that the reaction must be isothermal or isobaric or isochoric.”

If a process occurs from A to B, then using Hess’s law we can write as enthalpy change throughout the path AB is equal to sum of the enthalpies throughout AC, CD and DA.



## KIRCHHOFF'S LAW

Kirchhoff's law states that “If a system undergoes a change from one state to another state then both internal energy & heat occur would alter.”

Mathematically Kirchhoff's law can be expressed as

$$\int_{T_1}^{T_2} d(\Delta H) = \int_{T_1}^{T_2} (\Delta C_p)_{\text{Reaction}} dT$$

$$\Rightarrow [\Delta H_{T_2} - \Delta H_{T_1}] = \int_{T_1}^{T_2} [(\sum C_p)_{\text{Product}} - (\sum C_p)_{\text{Reactant}}] dT$$

$$\Rightarrow [\Delta H_{T_2}] = [\Delta H_{T_1}] + \int_{T_1}^{T_2} [(\sum C_p)_{\text{Product}} - (\sum C_p)_{\text{Reactant}}] dT$$

# ADIABATIC AND ISOTHERMAL PROCESS

## ADIABATIC PROCESS

The net heat content in the system is zero

In Adiabatic system, it obey the following equations

$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$P_1^{1-\gamma} T_1^\gamma = P_2^{1-\gamma} T_2^\gamma$$

## ISOTHERMAL PROCESS

It states that the net temperature change throughout the process is zero i.e.  $\Delta T = 0$ .

### Reversible Isothermal Process:

When an ideal gas of mass  $m$  undergoes a reversible process from state 1 to state 2, and then work done is given by

$$\begin{aligned} \int_1^2 \delta W &= \int_{V_1}^{V_2} P dV \\ \Rightarrow W_{1-2} &= W_1 - W_2 = \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} \frac{mRT}{V} dV \\ &\text{(Since } PV = mRT) \\ \Rightarrow W_{1-2} &= mRT \ln \left( \frac{V_2}{V_1} \right) = mRT \ln \left( \frac{P_1}{P_2} \right) \end{aligned}$$

The heat transfer involved in the process

$$q_{1-2} = mRT \ln \left( \frac{V_2}{V_1} \right) = T(S_2 - S_1)$$

# SECOND LAWS OF THERMODYNAMICS

- Definition by Clausius

There is no thermodynamics transformation whose sole effect is to deliver heat from a reservoir of lower temperature to a reservoir of higher temperature

- Definition by Kelvin

there is no thermodynamic transformation whose effect is to extract heat from a reservoir and convert it entirely to work

From the microscopic point of view

- heat transfer is an exchange of energy due to the random motion of atoms;
- work's performance requires an organized action of atoms.

In these terms, heat being converted entirely into work means chaos changing spontaneously to order, which is a very improbable process.

## 4.1 Heat engines

In a cyclic transformation the final state of a system is by definition identical to the initial state. The overall change of the internal energy  $U$  hence vanishes,

$$\Delta U = 0, \quad \Delta W = -\Delta Q .$$

A cycle transformation is by definition reversible and the *work done* by the system during a cycle is equal to the *heat absorbed*.

**Work.** The (negative) of the work

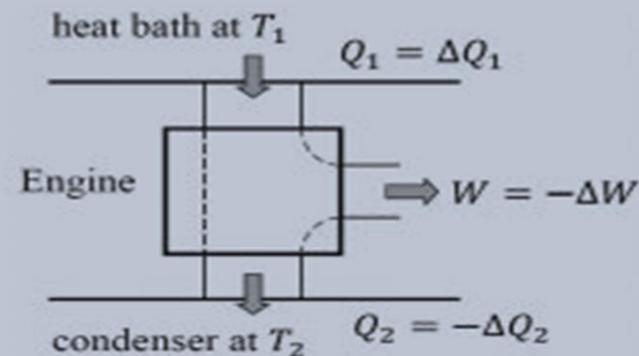
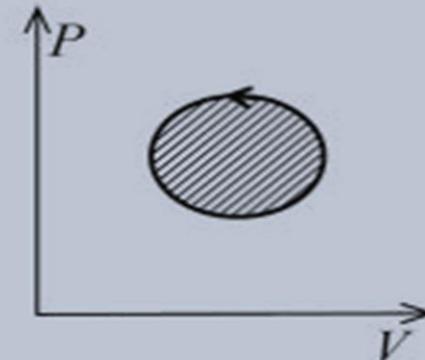
$$-\Delta W = \oint P dV = \text{area enclosed.}$$

corresponds for a reversible cyclic process to the area enclosed by the loop in the  $V - P$  state diagram.

**Heat engine.** Work is converted by a cyclic process into heat, and vice versa. A cyclic process can hence be regarded as an *heat engine*.

Consider a heat engine operating between  $T_1 > T_2$ . Part of the heat that is transferred to the system from a heat bath with temperature  $T_1$ ,  $Q_1$ , is converted into work,  $W$ , and the rest,  $Q_2$ , is delivered to a second bath with  $T_2 < T_1$  (condenser). Following the first law of thermodynamics,

$$|Q_1| - |Q_2| = |W| .$$



# CARNOT CYCLE

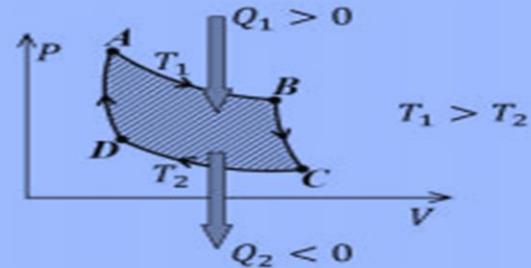
## 4.1.1 Carnot cycle

The *Carnot process* is a reversible cycle process bounded by two *isotherms* and two *adiabatic lines*.



$$PV = nRT$$

$$U = U(T)$$



One Carnot cycle consists of four consecutive thermodynamic processes, which can be realized with an arbitrary working substance. We shall consider here however the case of an ideal gas.

(1)	$A \rightarrow B$	isothermal expansion	$T = T_1$	$V_A \rightarrow V_B$	$Q_1$ absorbed
(2)	$B \rightarrow C$	adiabatic expansion	$T_1 \rightarrow T_2$	$V_B \rightarrow V_C$	$\Delta Q = 0$
(3)	$C \rightarrow D$	isothermal compression	$T = T_2$	$V_C \rightarrow V_D$	$Q_2$ released
(4)	$D \rightarrow A$	adiabatic compression	$T_2 \rightarrow T_1$	$V_D \rightarrow V_A$	$\Delta Q = 0$

**Work.** We note that  $Q_1 > 0$  (absorbed from hot bath) and  $Q_2 < 0$  (released to cold bath). Total energy conservation, viz the first law of thermodynamics, dictates that

$$0 = \oint dU = \oint (\delta Q + \delta W) = Q + W = Q_1 + Q_2 + W,$$

where  $-W$  is the work performed by the system, equal to the area enclosed in the loop.

**Efficiency.** The *efficiency* of the Carnot engine is defined as

$$\eta \equiv \frac{\text{performed work}}{\text{absorbed heat}} = \frac{-W}{Q_1} = \frac{Q_1 + Q_2}{Q_1} = \frac{Q_1 - |Q_2|}{Q_1}.$$

$\eta$  is 100% if there is no waste heat ( $Q_2 = 0$ ). However, we will see that this is *impossible* due to the second law of thermodynamics.

# SPONTANEOUS PROCESS

- THESE PROCESSES ARE THE NATURALLY OCCURRING PROCESSES WHICH CANNOT BE REVERSED WITHOUT THE INTERRUPTION OF EXTERNAL FORCE

Examples of Spontaneous processes: Flow of heat from higher to lower temperature, diffusion process of a species from higher to lower concentration, mixing of acid-base reactions, all natural processes that occurring in nature without external intervention.

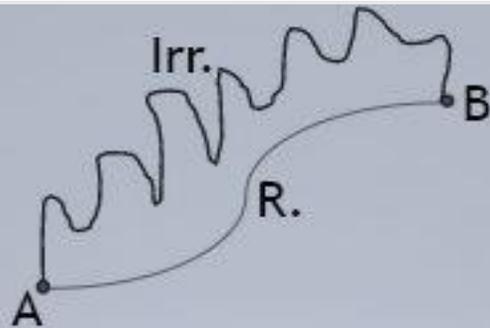
Generally 2nd law of TD mathematically expressed in terms of entropy(S) as

$$dS = \frac{\delta q_{rev}}{T}$$

## Entropy

- It measure the randomness of a system
- Its symbol is S
- Unit:J/K mol

Sl no.	Reversible Process	Irreversible Process
1	It is defined as the hypothetical passage of a system through a series of equilibrium stages.	The process that can't be reversed or changed back (permanent damage).
2	Very slow & mostly impracticable in nature.	Generally at normal condition it occurs. It may be very fast or fast or slow & practically possible.
3	For isolated system $dS_{sys} = 0$	For isolated system $dS_{sys} > 0$



There is an unlimited number of irreversible paths between states A and B but only one reversible path

Comparing the change in entropy of both paths:

Reversible path

$$dS_{system} = \frac{dQ_{rev}}{T}$$

$$dS_{surr} = -\frac{dQ_{rev}}{T}$$

$$dS_{uni} = dS_{system} + dS_{surr} = 0$$

$$dU = TdS_{sys} - dW_{rev}$$

$$TdS_{system} - dW_{rev} = dQ - dW$$

$$dS_{system} = \frac{dQ}{T} + \frac{1}{T}(dW_{rev} - dW)$$

$$dS_{system} > \frac{dQ}{T} \quad \text{since } dW_{rev} > dW$$

Irreversible path

$$dS_{system} > \frac{dQ}{T}$$

$$dS_{surr} = -\frac{dQ}{T}$$

$$dS_{uni} = dS_{system} + dS_{surr} > 0$$

$$dU = dQ - dW$$

$$dS_{system} = \frac{dQ}{T} + \frac{dW_{lost}}{T}$$

Hence the entropy of a system can be altered in two ways:

1. Through heat exchange
2. Through irreversibilities

The work lost due to irreversibility is always greater than zero, so the only way to decrease the entropy of a system is through heat transfer

The total entropy change for any spontaneous process equals the (lost work)/T

$$dS_{surr} = -\frac{dQ}{T}$$

$$dS_{total} = \frac{dQ}{T} + \frac{dW_{lost}}{T} - \frac{dQ}{T} = \frac{dW_{lost}}{T}$$

A thermodynamic cycle is a series of thermodynamic processes transferring heat and work, while varying pressure, temperature and other state variables, eventually returning a system to its initial state

A minimum of 3 such processes are required to construct a cycle.

All processes do not need to have work interactions eg: isochoric process

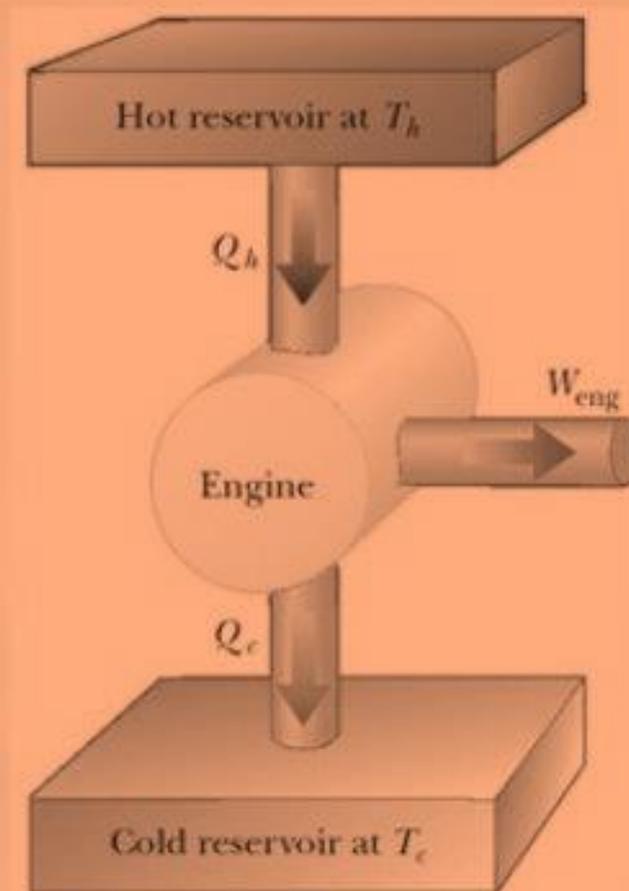
All processes do not need to involve heat interactions eg: adiabatic process

When a system undergoes a thermodynamic cycle, then the net heat supplied to the system from the surroundings is equal to the net work done by the system on its surroundings

$$W_{net} = \sum Q_{supplied} - \sum Q_{rejected}$$

A heat engine takes in energy from a high temperature heat reservoir and partially converts it to other forms by cyclic motion

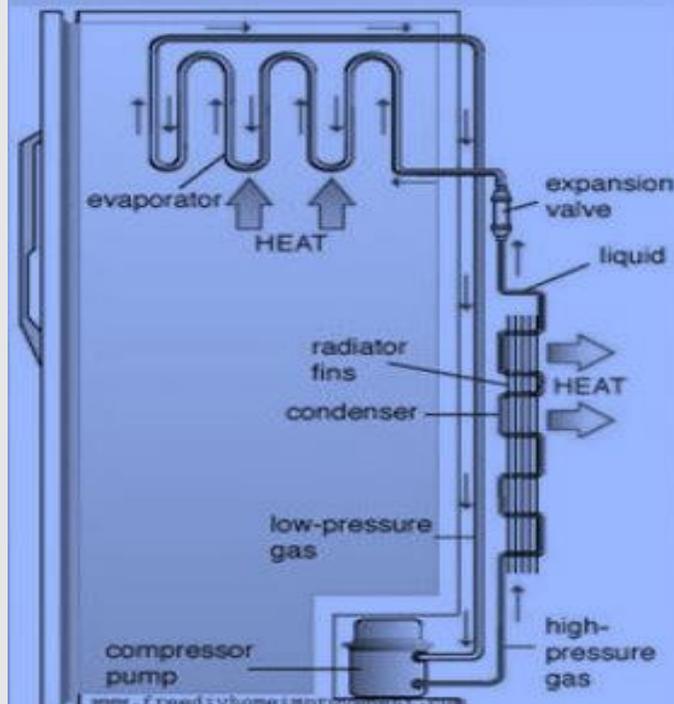
A portion of the heat is rejected to a cold temperature heat reservoir as the last part of the cycle



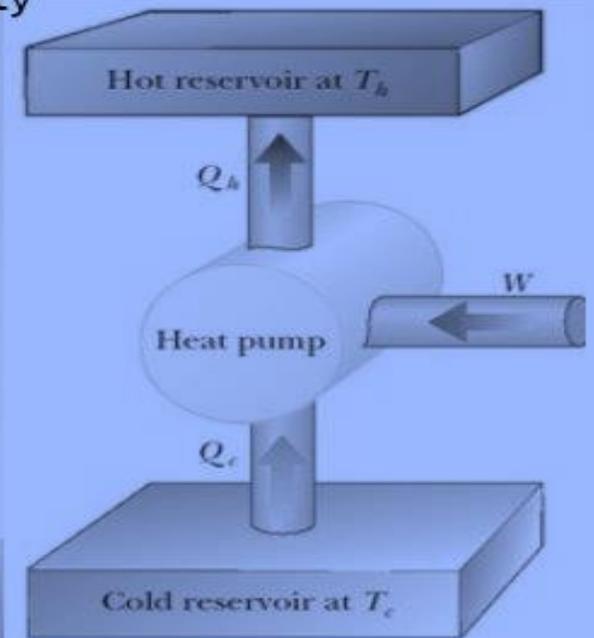
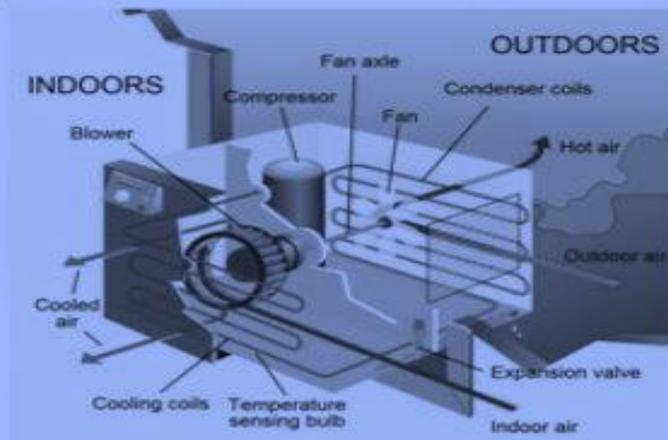
When run in reverse, heat engine operates as a heat pump:

- Energy is given to the system in some form like electricity
- Heat is extracted from the cold reservoir
- Heat is rejected to the hot reservoir

Examples -  
Refrigerator



Air conditioner



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**An alternative statement of the second law by Kelvin and Planck is**

***No heat engine operating in a cycle can absorb energy from a reservoir and use it entirely for the performance of an equal amount of work***

**This means that some heat must be rejected to the surroundings**

**Thermal efficiency of a heat engine cannot reach 100%**

**Thermal efficiency is defined as the ratio of the work done by the engine to the energy absorbed at the higher temperature**

$$\eta = \frac{W_{eng}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|}$$

**For full efficiency, no heat rejected to cold reservoir**

**Recall that first law required that the amount of energy out of a cyclic process cannot be greater than the energy put in**

**The second law requires that energy in cannot be equal to energy out**

## Carnot cycle, step A-B

Reversible isothermal expansion at  $T_h$

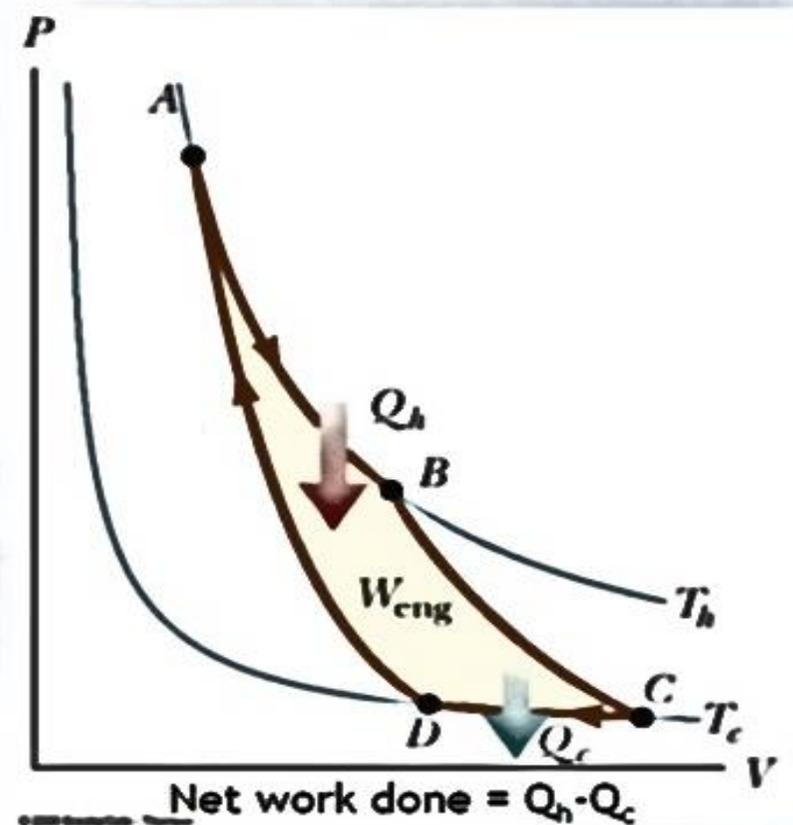
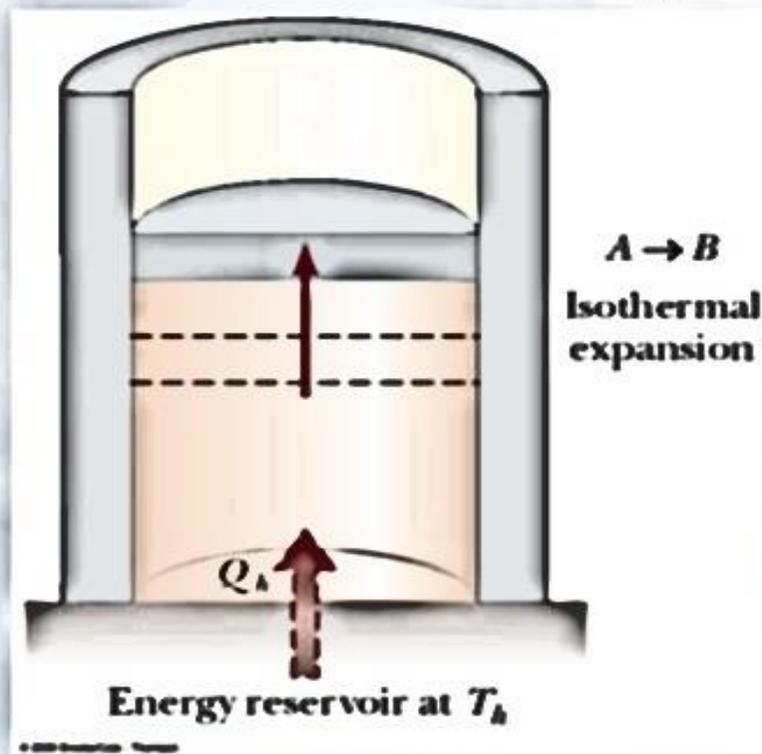
State A - Gas @  $T_h, P_A, V_A$

Gas absorbs heat from high temperature reservoir

State B - Gas @  $T_h, P_B, V_B$

Gas does work to raise the piston

$$\Delta U = 0, Q_{A-B} = W_{A-B} = nRT_h \ln \frac{V_B}{V_A}$$

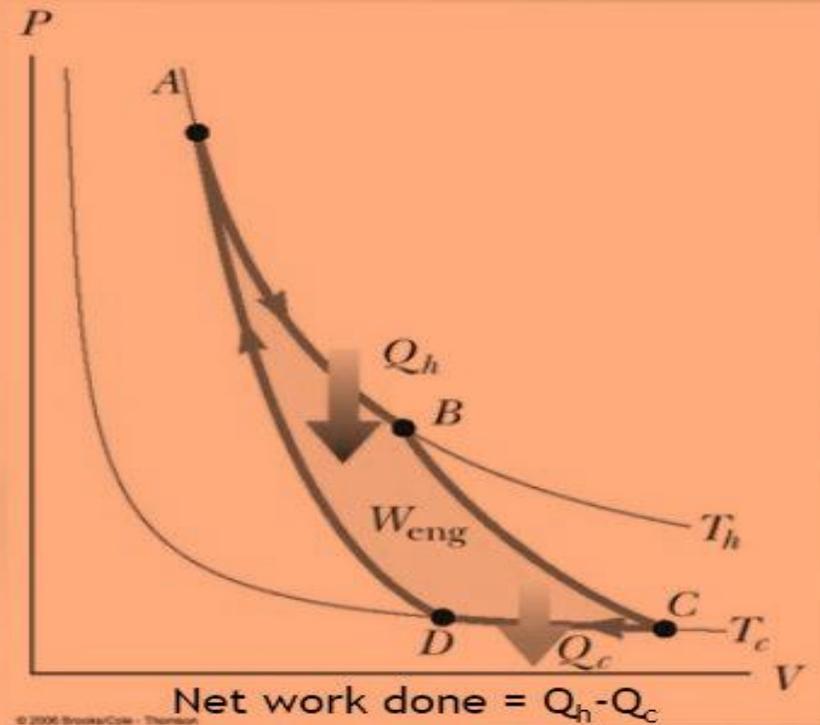
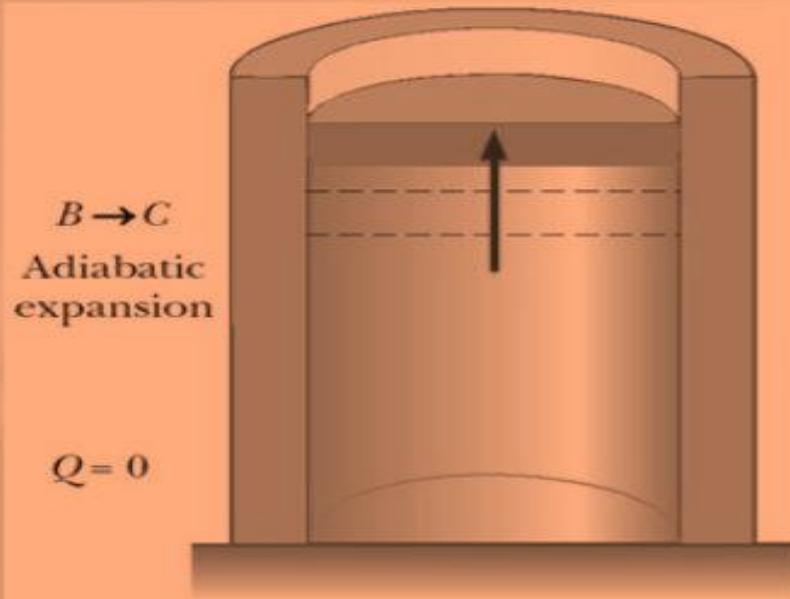


Carnot cycle, step B-C  
Reversible adiabatic expansion

State B - Gas @  $T_h, P_B, V_B$   
State C - Gas @  $T_c, P_C, V_C$

Gas expands further when no heat enters the system  
Gas does work to raise the piston and to decrease T

$$Q_{B-C} = 0, \Delta U_{B-C} = -W_{B-C} = nC_v(T_h - T_c)$$



## Carnot cycle, step C-D

Reversible isothermal compression at  $T_c$

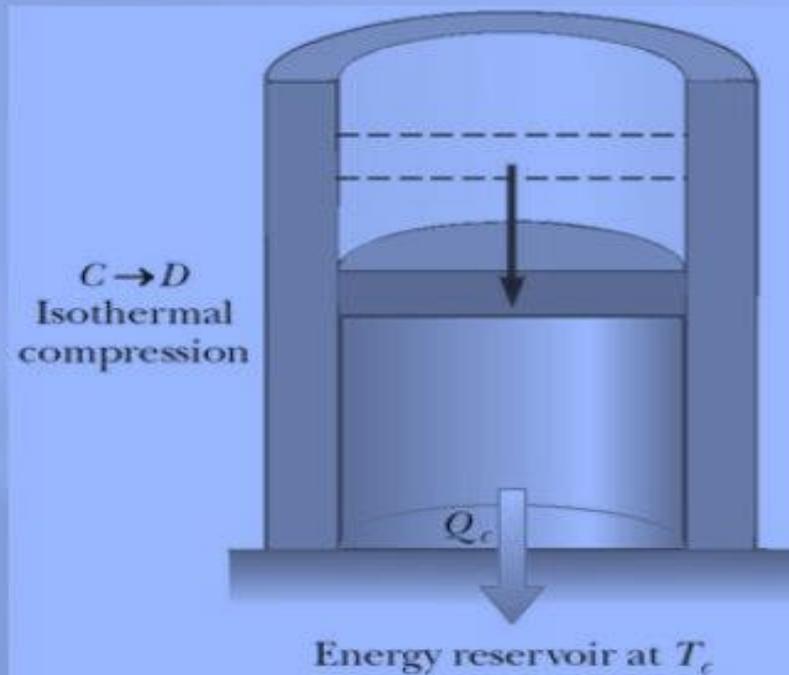
State C - Gas @  $T_c, P_C, V_C$

State D - Gas @  $T_c, P_D, V_D$

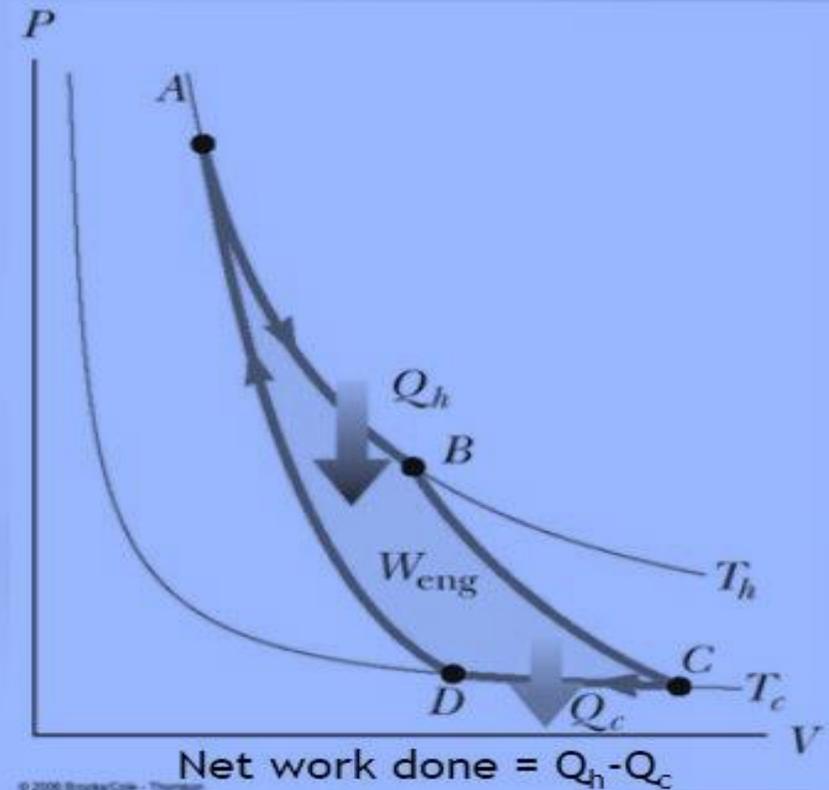
Gas rejects heat to low temperature reservoir

Work is done by the piston on the gas

$$\Delta U = 0, Q_{C-D} = W_{C-D} = nRT_c \ln \frac{V_D}{V_C}$$



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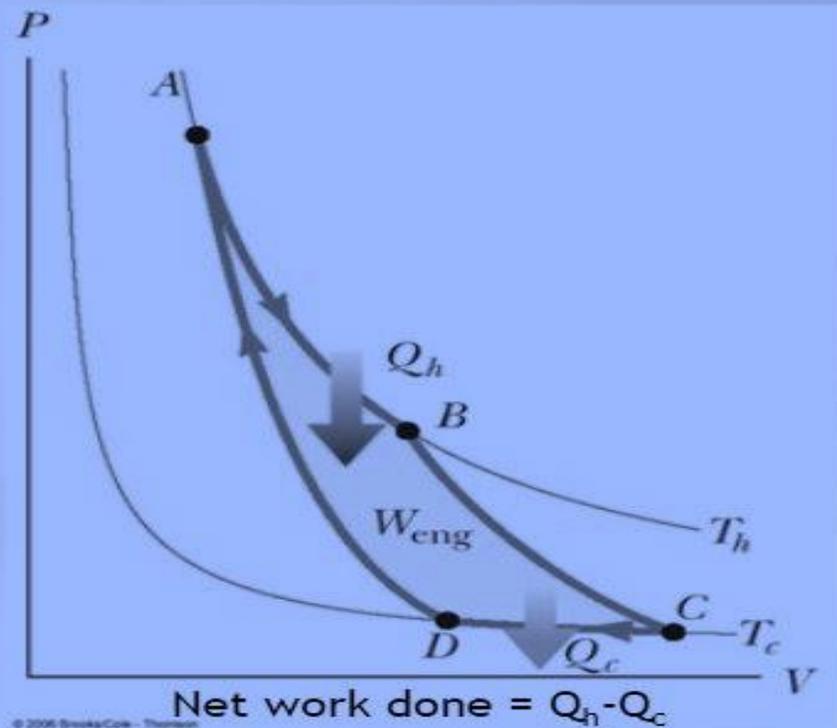
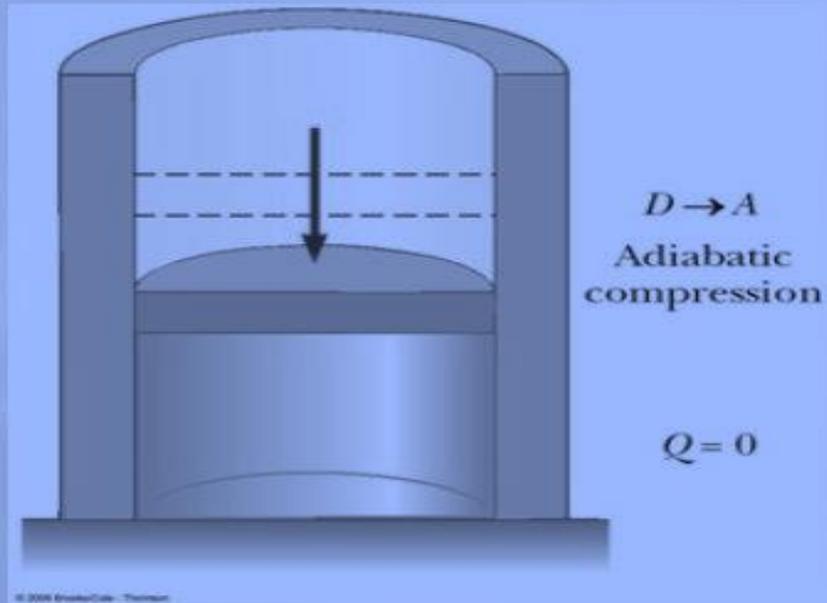
### Carnot cycle, step D-A

Reversible adiabatic compression which brings the system back to the initial state

State D - Gas @  $T_c, P_D, V_D$  Gas is compressed further when no heat leaves the system

State A - Gas @  $T_h, P_A, V_A$  Work is done by the piston on the gas to increase T

$$Q_{D-A} = 0, \Delta U_{D-A} = -W_{D-A} = nC_v(T_c - T_h)$$



Total work done by one cycle

$$W = W_{A-B} + W_{B-C} + W_{C-D} + W_{D-A}$$

$$W = nRT_h \ln \frac{V_B}{V_A} - nC_v(T_c - T_h) + nRT_c \ln \frac{V_D}{V_C} - nC_v(T_h - T_c)$$

$$W = nRT_h \ln \frac{V_B}{V_A} + nRT_c \ln \frac{V_D}{V_C}$$

Since steps B-C and D-A are reversible adiabatic steps,

$$\frac{T_c}{T_h} = \left( \frac{V_B}{V_C} \right)^{R/C_v}, \quad \frac{T_h}{T_c} = \left( \frac{V_D}{V_A} \right)^{R/C_v}$$
$$\frac{V_B}{V_C} = \frac{V_A}{V_D} \quad \text{or} \quad \frac{V_D}{V_C} = \frac{V_A}{V_B}$$

Substituting the equalities in total work equation gives

$$W = Q = nRT_h \ln \frac{V_B}{V_A} + nRT_c \ln \frac{V_A}{V_B}$$

$$W = Q = nR(T_h - T_c) \ln \frac{V_B}{V_A}$$

Total heat consumption by one cycle

$$Q = Q_{A-B} + Q_{C-D} = nRT_h \ln \frac{V_B}{V_A} + nRT_c \ln \frac{V_D}{V_C}$$

$$\ln \frac{V_B}{V_A} = \ln \frac{V_C}{V_D} = \frac{Q_{A-B}}{nRT_h}$$

$$Q = Q_{A-B} + Q_{C-D} = nRT_h \frac{Q_{A-B}}{nRT_h} - nRT_c \frac{Q_{A-B}}{nRT_h}$$

$$Q_{C-D} = -nRT_c \frac{Q_{A-B}}{nRT_h}$$

$$Q_{C-D} + T_c \frac{Q_{A-B}}{T_h} = 0$$

$$\frac{Q_{C-D}}{T_c} + \frac{Q_{A-B}}{T_h} = 0$$

$$\Delta S = \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

Carnot efficiency is the best that can be obtained from any cycle operating between two fixed temperatures

$$\eta = \frac{W_{eng}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|}$$

$$\eta = \frac{Q_{A-B} - Q_{C-D}}{Q_{A-B}} = \frac{nRT_h \frac{Q_{A-B}}{nRT_h} - nRT_c \frac{Q_{A-B}}{nRT_h}}{nRT_h \frac{Q_{A-B}}{nRT_h}} = \frac{T_h - T_c}{T_h}$$

# COMBINED EXPRESSION OF 1<sup>ST</sup> AND 2<sup>ND</sup> LAW

COMBINING 1<sup>ST</sup> AND 2<sup>ND</sup> LAW OF THERMODYNAMICS WITH CONSIDERING THE FOLLOWING ASSUMPTION WE GOT

$$dU = TdS - PdV \quad \Rightarrow \quad \left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V$$

$$dA = -SdT - PdV \quad \Rightarrow \quad \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V$$

$$dH = TdS + VdP \quad \Rightarrow \quad \left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P$$

$$dG = -SdT + VdP \quad \Rightarrow \quad - \left( \frac{\partial S}{\partial P} \right)_T = \left( \frac{\partial V}{\partial T} \right)_P$$

# THIRD LAW'S OF THERMODYNAMICS

In 1906, W. Nernst proposed his heat theory on the basis of experimental evidence. It was later generalized by Max Plank as “The entropy of any substance (which is at complete equilibrium) may take as Zero at 0K.” This is known as Third law of Thermodynamics

## CONSEQUENCES OF 3<sup>RD</sup> LAW

When disorder in a substance completely vanishes, it becomes perfectly ordered and has only one possible arrangement of atoms. Then and only then a complete internal equilibrium is established. The causes for deviation from perfect order are

- i. Thermal energy and resulting motion of atoms and molecules (at  $T = 0\text{K}$ ).
- ii. Non-crystallinity, as in amorphous solids and liquids.
- iii. Crystal defects-vacancies, interstitial atoms, dislocation.
- iv. Disordered compound structure.
- v. Disordered solid solution.

At  $T = 0\text{K}$ , thermal energy is zero. Thus this source of disorder gets eliminated. But other sources remain there. In reality it is difficult to achieve exactly zero entropy at  $T = 0\text{K}$ . Actually, all disorders are caused by thermal energy which get lowered continuously and vanish at  $T = 0\text{K}$  provided internal equilibrium exists.

## DEBYE'S THEORY OF HEAT CAPACITY

In early 20th century, Einstein represents the experimental datas of  $C_v$  of some solid elements using quantum theory. Each atom in the crystal assumes to oscillate independently along three perpendicular directions under the harmonic motion i.e. to-fro motion. The energy of  $i$ th energy level of harmonic oscillation is given as

$$\varepsilon_i = \left(i + \frac{1}{2}\right) h\nu$$

Again, we know

$$U = 3 \sum n_i \varepsilon_i$$

Combining both equation we got

$$U = \frac{3}{2} N_o h\nu + \frac{3N_o h\nu}{\left(e^{h\nu/k_b T} - 1\right)}$$
$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = 3R \left(\frac{\theta_E}{T}\right)^2 \left(\frac{e^{(\theta_E/T)}}{\left(e^{(\theta_E/T)} - 1\right)^2}\right)$$

Where

$$\theta_E = \text{Einstein Temperature} = \frac{h\nu}{k_B}$$

## Debye's Theory of Heat Capacity of Solids:

Einstein's deviation was to be later modified by Debye who assumed a spectrum of vibration frequency in contrast to a single frequency of oscillation of Einstein. Debye arrived at a different equation in terms of Debye temperature. Where

$$\theta_D = \frac{h\nu_D}{k_B}, \nu_D = \nu_{max}$$

At low temperature (near 0K), the Debye equation may be simplified as

$$C_V = 464.5 \times \left(\frac{T}{\theta_D}\right)^3$$

Moreover, it is concerned with elements only, that too in crystalline state. Hence, due to its limited applicability, it is a normal practice to determine heat capacity vs Temperature relationship for solids and liquids.

## REFERENCES

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