

# Introduction

- It may be noted that all heat is not equally valuable for converting into work. Heat that is supplied to a substance at high temperature has a greater possibility of conversion into work than heat supplied to a substance at a lower temperature.

# Introduction

- Entropy is a measure of the degree of randomness of the molecules comprising the system. Higher the disorder, greater is the increase in entropy.
- "**Entropy** is a function of a quantity of heat. The increase in entropy is small when heat is added at a high temperature and is greater when heat addition is made at a lower temperature. Thus for maximum entropy, there is minimum availability for conversion into work and for minimum entropy there is maximum availability for conversion into work."

# Introduction

- From Clausius Inequality  $\oint_R \frac{\partial Q}{T} = 0$
- This indicates that  $\frac{\partial Q}{T}$  is a point function hence property of the system. This Property is called entropy (denoted as dS)
- For a Process  $\int_1^2 dS = S_2 - S_1 = \int_1^2 \frac{\partial Q}{T}$
- Entropy is an extensive property.
- Unit KJ/kelvin
- Entropy increase as heat absorb by the system and decrease as the heat rejected by the system.
- For reversible adiabatic process dS=0
- S=Constant for reversible adiabatic process
- So entropy is a property of the system that remains constant during a reversible adiabatic process.

# Entropy—a Property of a System (A Point Function)

- Let us consider a system undergoing a reversible process from state 1 to state 2 along path  $L$  and then from state 2 to the original state 1 along path  $M$ . Applying the Clausius theorem to this reversible cyclic process, we have

$$\oint_R \frac{\partial Q}{T} = 0$$

(Where the subscript  $R$  designates a reversible cycle)

- Hence when the system passes through the cycle 1- $L$ -2- $M$ -1, we have

$$\int_{1(L)}^2 \frac{\partial Q}{T} + \int_{2(M)}^1 \frac{\partial Q}{T} = 0 \quad (1)$$

- Now consider another reversible **cycle** in which the system changes from state 1 to state 2 along path  $L$ , but returns from state 2 to the original state 1 along a different path  $N$ . For this reversible cyclic process, we have

$$\int_{1(L)}^2 \frac{\partial Q}{T} + \int_{2(N)}^1 \frac{\partial Q}{T} = 0 \quad (2)$$

- Subtracting equation (2) from equation (1), we have

$$\int_{2(M)}^1 \frac{\partial Q}{T} - \int_{2(N)}^1 \frac{\partial Q}{T} = 0$$

$$\int_{2(M)}^1 \frac{\partial Q}{T} = \int_{2(N)}^1 \frac{\partial Q}{T}$$

- As no restriction is imposed on paths  $L$  and  $M$ , except that they must be reversible, the quantity  $\frac{\delta Q}{T}$  is a function of the initial and final states of the system and is independent of the path of the process. Hence it represents a property of the system. This property is known as the “**entropy**”.

# Entropy Principle

- We know that the entropy of an isolated system either increase or remains constant, *i.e.*,

$$(dS)_{isolated} \geq 0$$

- By including any system and its surrounding within a single boundary, an isolated system can be formed. The combination of the system and the surroundings within a single boundary is sometimes called the **Universe**. Hence, applying the principle of increase in entropy, we get

$$\text{where } (dS)_{universe} = (dS)_{system} + (dS)_{surroundings}$$
$$(dS)_{universe} \geq 0$$

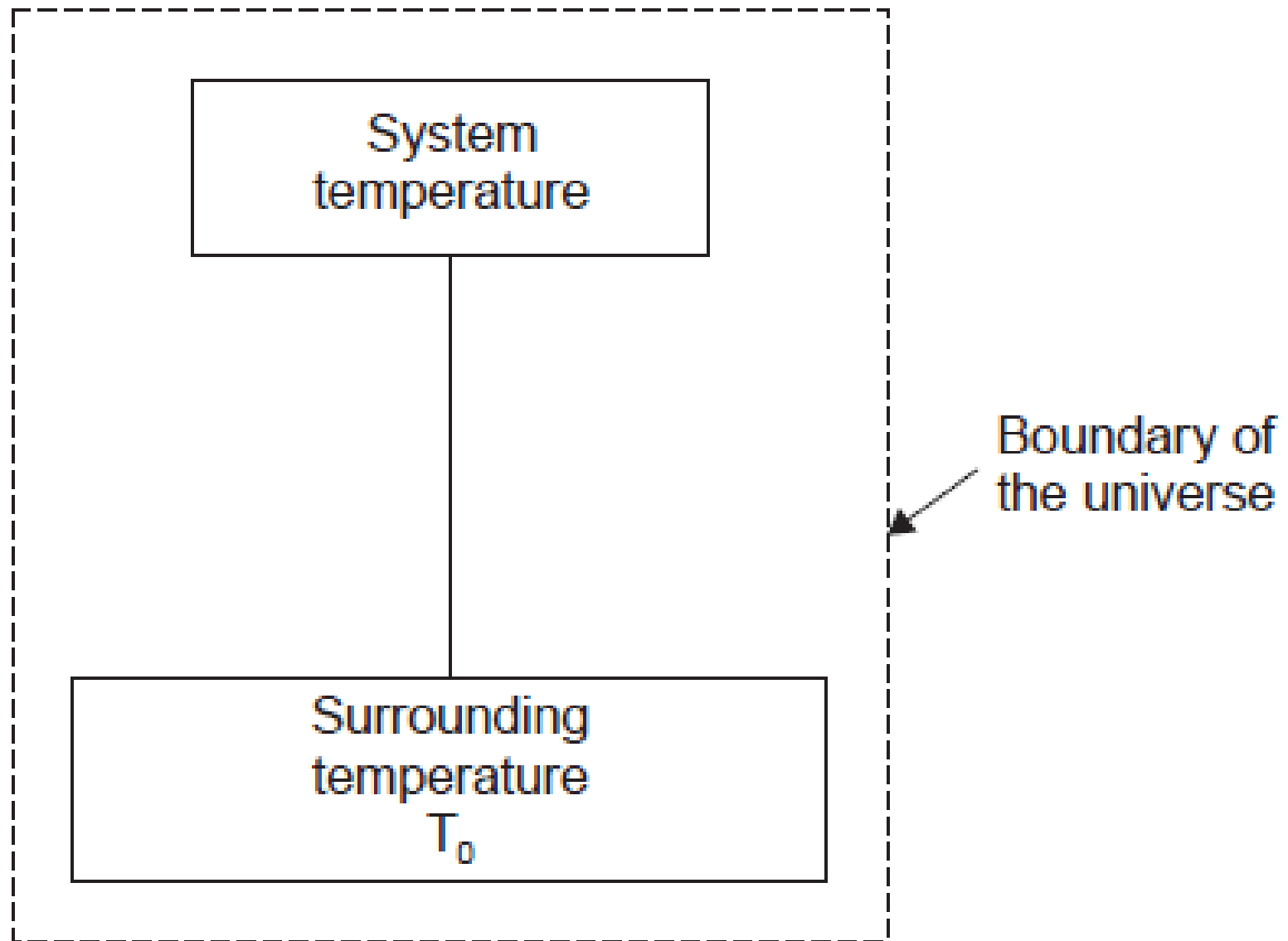


Fig. 5.23. Entropy change of universe.



# Entropy Principle

- In the combined closed system consider that a quantity of heat  $\delta Q$  is transferred from the
- system at temperature  $T$  to the surroundings at temperature  $T_0$ . Applying entropy to this
- process, we can write  $(dS)_{system} > - \frac{\delta Q}{T}$
- And  $(dS)_{surroundings} = \frac{\delta Q}{T_0}$

Hence, the total change in entropy for the combined system

$$(dS)_{system} + (dS)_{surroundings} \geq - \frac{\delta Q}{T} + \frac{\delta Q}{T_0}$$

$$(dS)_{universe} \geq dQ \left( - \frac{1}{T} + \frac{1}{T_0} \right)$$

The same result can be obtained in the case of an open system.

For both closed and open systems, we can write

$$(dS)_{universe} \geq 0$$

# Entropy Principle

- It states that the process involving the interaction of a system and the surroundings takes place only if the net entropy of the combined system increases or in the limit remains constant. *Since all natural processes are irreversible, the entropy is increasing continually.*
- The entropy attains its maximum value when the system reaches a stable equilibrium state from a non-equilibrium state. This is the state of maximum disorder and is one of maximum thermodynamic probability.

# TEMPERATURE-ENTROPY DIAGRAM

- If entropy is plotted-horizontally and absolute temperature vertically the diagram so obtained is called *temperature-entropy (T-s) diagram*. If working fluid receives a small amount of heat  $dQ$ , the entropy will increase from  $S_A$  to  $S_B$  during process  $AB$ .
- This is called '*increment of entropy*' and is denoted by  $dS$ . The total heat received by the operation will be given by the area under the curve  $AB$  and  $(S_B - S_A)$  will be corresponding increase of entropy.
- Heat Transfer during a process  $Q = T(S_B - S_A)$

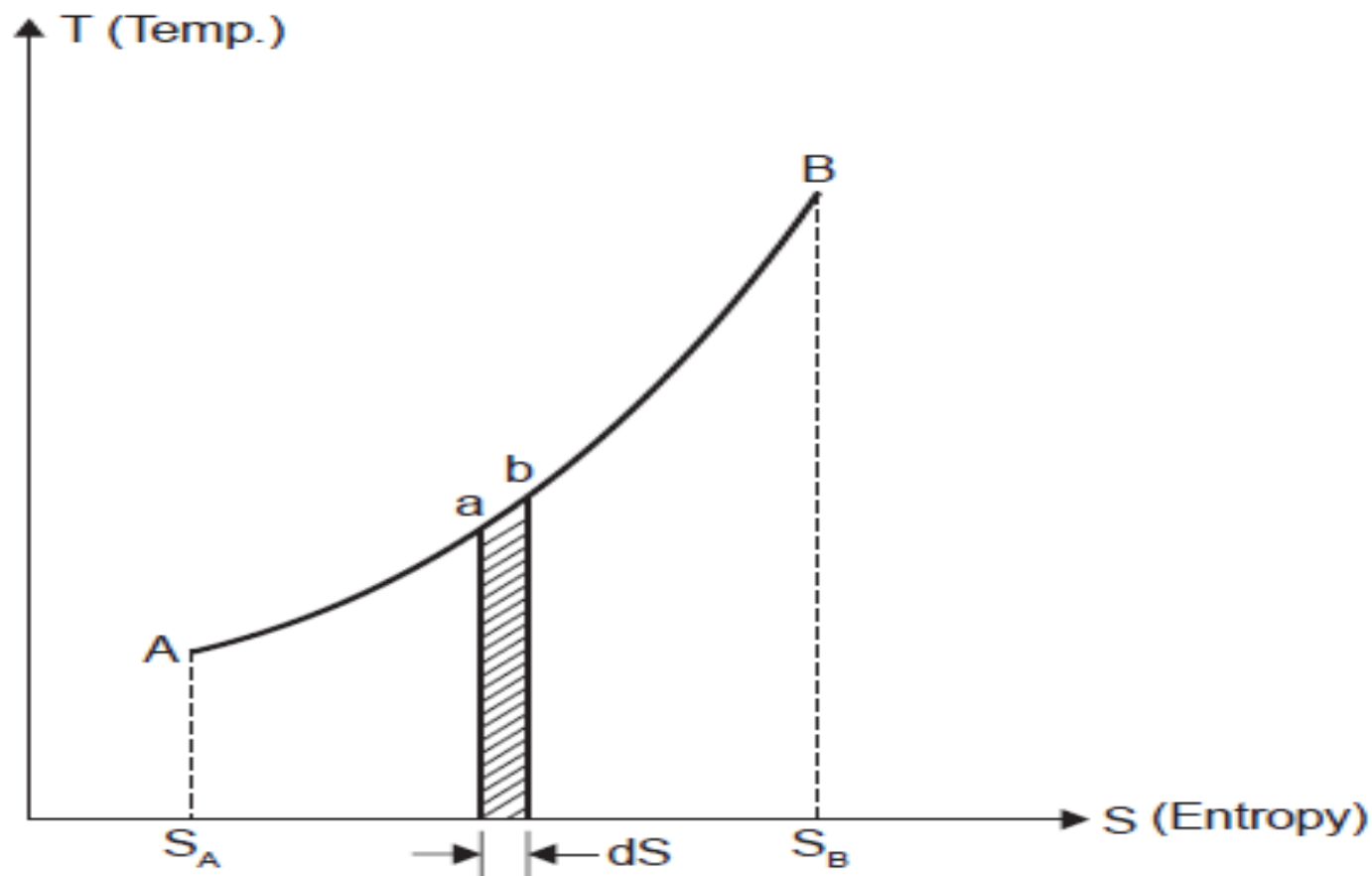


Fig. 5.24. Temperature-entropy diagram.

From above we conclude that :

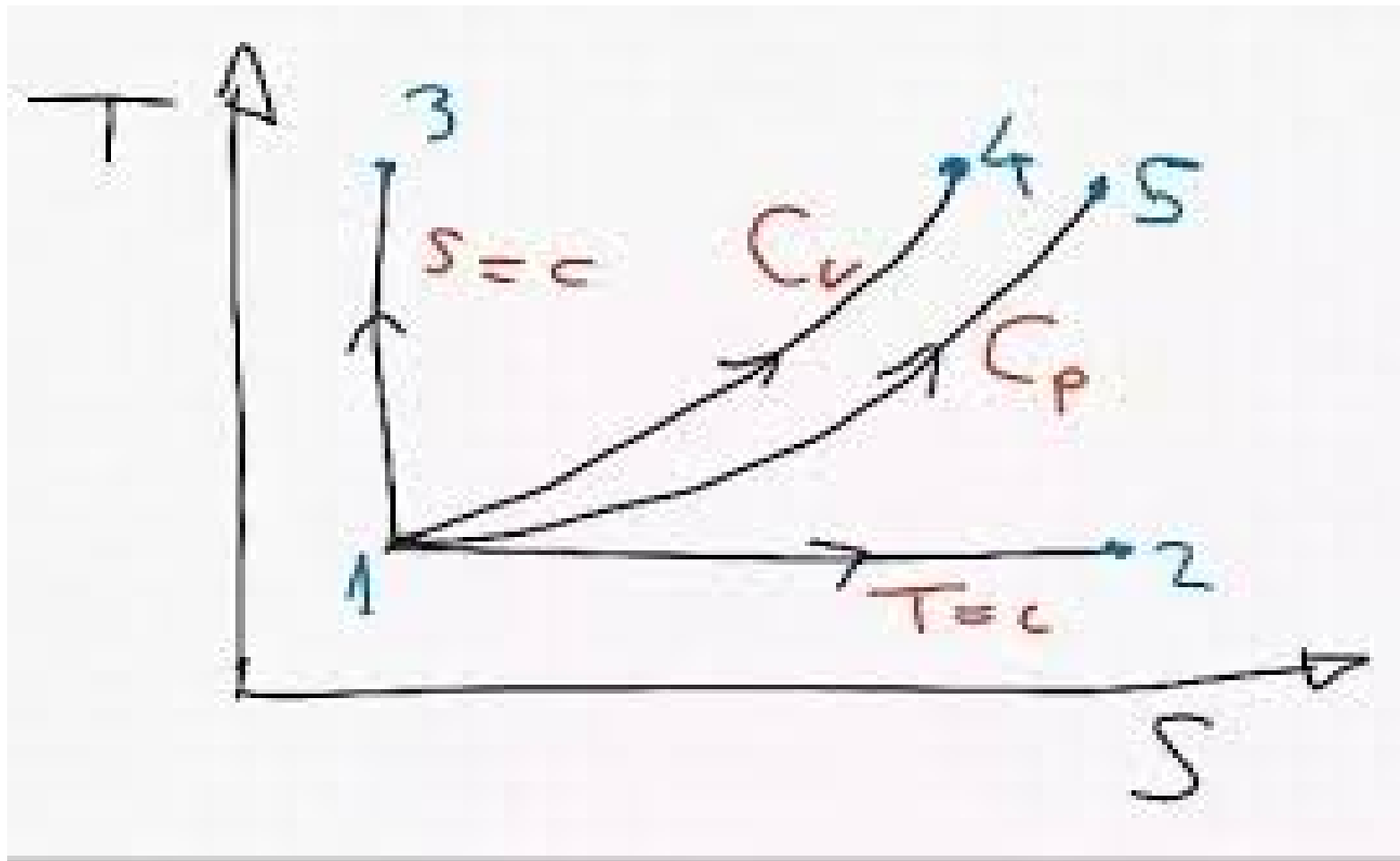
$$\text{Entropy change, } dS = \frac{\text{Heat change (} Q \text{)}}{\text{Absolute temperature (} T \text{)}} .$$

- ***"Entropy may also be defined as the thermal property of a substance which remains constant when substance is expanded or compressed adiabatically in a cylinder".***
- ***Note. 's' stands for specific entropy whereas 'S' means total entropy (i.e.,  $S = ms$ ).***

## **CHARACTERISTICS OF ENTROPY**

The characteristics of entropy in a summarised form are given below :

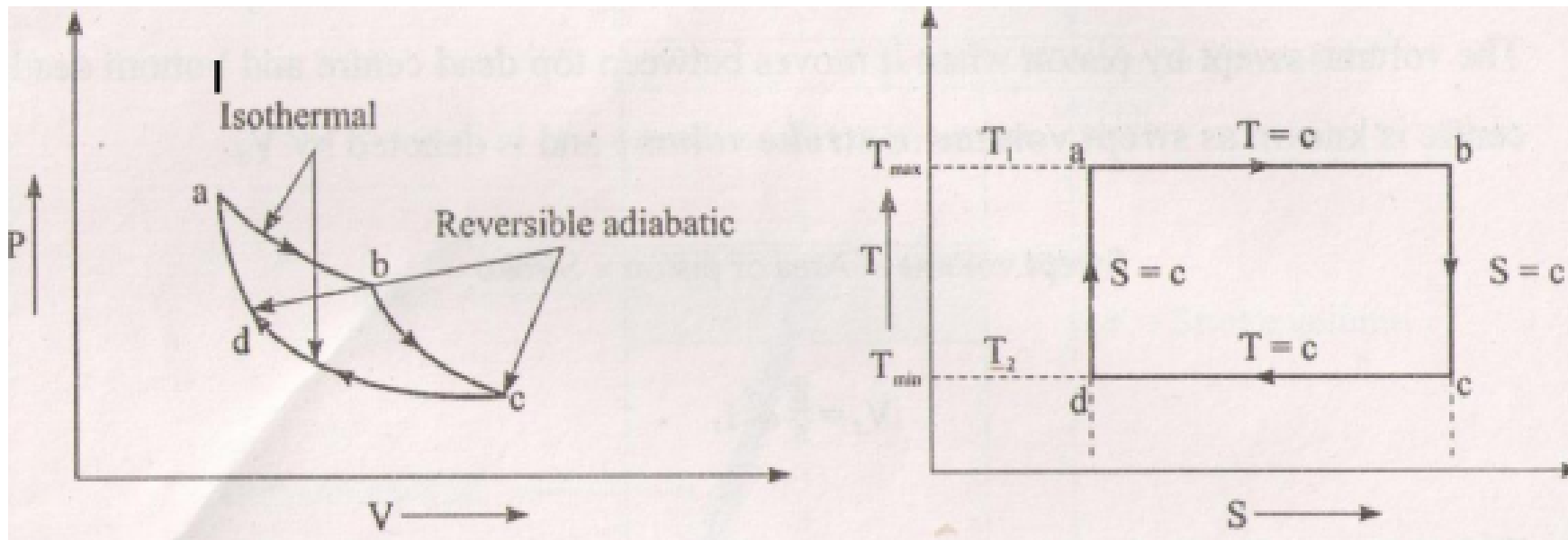
1. It increases when heat is supplied irrespective of the fact whether temperature changes or not.
2. It decrease when heat is removed whether temperature changes or not.
3. It remains unchanged in all adiabatic frictionless processes.
4. It increases if temperature of heat is lowered without work being done as in a throttling process.



Slope of constant volume curve ( $T/C_v$ ) is greater than slope of constant pressure curve ( $T/C_p$ )

# Carnot Cycle

Representation of Carnot Cycle on  $P - V$  and  $T - S$  diagram



**Process 1-2:-** Isentropic or reversible adiabatic Compression process.

**Process 2-3:-** Reversible Isothermal heat addition process.

**Process 3-4:-** Isentropic or reversible adiabatic expansion process.

**Process 4-1:-** Reversible Isothermal heat rejection process.

- Heat added in process ab  $Q_1 = T_1(S_B - S_A)$
- Heat added in process bc = 0
- Heat rejected in process cd  $Q_2 = T_2(S_A - S_B) = -T_2(S_B - S_A)$
- Heat added in process da = 0

For cyclic process  $W_{\text{net}} = T_1(S_B - S_A) - T_2(S_B - S_A)$   
 $= (T_1 - T_2)(S_B - S_A)$

Efficiency of carnot cycle =  $W_{\text{net}} / \text{Heat Supplied}(Q_1)$

$$\eta = \frac{(T_1 - T_2)(S_B - S_A)}{T_1(S_B - S_A)}$$

$$\eta = \frac{(T_1 - T_2)}{T_1}$$

$$\eta = 1 - \frac{T_2}{T_1}$$



# General Case for Change of Entropy of a Gas

- Let 1 kg of gas at a pressure  $p_1$ , volume  $v_1$ , absolute temperature  $T_1$  and entropy  $s_1$ , be heated such that its final pressure, volume, absolute temperature and entropy are  $p_2$ ,  $v_2$ ,  $T_2$  and  $s_2$  respectively. Then by law of conservation of energy (First Law),

$$dQ = du + dW$$

where,  $dQ$  = Small change of heat,

$du$  = Small internal energy, and

$dW$  = Small change of work done ( $p dv$ ).

$$dQ = c_v dT + p dv$$

Dividing both sides by  $T$ , we get

$$\frac{dQ}{T} = \frac{c_v dT}{T} + \frac{p dv}{T}$$

But

$$\frac{dQ}{T} = ds$$

and as

$$pv = RT$$

$\therefore$

$$\frac{p}{T} = \frac{R}{v}$$

Hence

$$ds = \frac{c_v dT}{T} + R \frac{dv}{v}$$

Integrating both sides, we get

$$\int_{s_1}^{s_2} ds = c_v \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{v_1}^{v_2} \frac{dv}{v}$$

or

$$(s_2 - s_1) = c_v \log_e \frac{T_2}{T_1} + R \log_e \frac{v_2}{v_1}$$

This expression can be reproduced in the following way :

According to the gas equation, we have

$$\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2}$$

or

$$\frac{T_2}{T_1} = \frac{p_2}{p_1} \times \frac{v_2}{v_1}$$

Substituting the value of  $\frac{T_2}{T_1}$  in eqn. (5.28), we get

$$\begin{aligned}s_2 - s_1 &= c_v \log_e \frac{p_2}{p_1} \times \frac{v_2}{v_1} + R \log_e \frac{v_2}{v_1} \\&= c_v \log_e \frac{p_2}{p_1} + c_v \log_e \frac{v_2}{v_1} + R \log_e \frac{v_2}{v_1} \\&= c_v \log_e \frac{p_2}{p_1} + (c_v + R) \log_e \frac{v_2}{v_1} \\&= c_v \log_e \frac{p_2}{p_1} + c_p \log_e \frac{v_2}{v_1}\end{aligned}$$

$$\therefore s_2 - s_1 = c_v \log_e \frac{p_2}{p_1} + c_p \log_e \frac{v_2}{v_1}$$

Again, from gas equation,

$$\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2} \quad \text{or} \quad \frac{v_2}{v_1} = \frac{p_1}{p_2} \times \frac{T_2}{T_1}$$

Putting the value of  $\frac{v_2}{v_1}$  in eqn. (5.28), we get

$$\begin{aligned}(s_2 - s_1) &= c_v \log_e \frac{T_2}{T_1} + R \log_e \frac{p_1}{p_2} \times \frac{T_2}{T_1} \\&= c_v \log_e \frac{T_2}{T_1} + R \log_e \frac{p_1}{p_2} + R \log_e \frac{T_2}{T_1} \\&= (c_v + R) \log_e \frac{T_2}{T_1} - R \log_e \frac{p_2}{p_1} \\&= c_p \log_e \frac{T_2}{T_1} - R \log_e \frac{p_2}{p_1}\end{aligned}$$

$$\therefore \quad s_2 - s_1 = c_p \log_e \frac{T_2}{T_1} - R \log_e \frac{p_2}{p_1} .$$

# Heating a Gas at Constant Volume

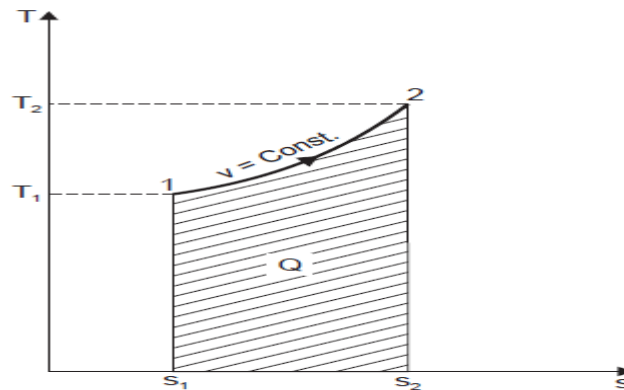


Fig. 5.25. *T-s* diagram : Constant volume process

Let 1 kg of gas be heated at constant volume and let the change in entropy and absolute temperature be from  $s_1$  to  $s_2$  and  $T_1$  to  $T_2$  respectively.

We Know that  $Q = c_v(T_2 - T_1)$

Differentiating to find small increment of heat  $dQ$  corresponding to small rise in temperature  $dT$ .

$$dQ = c_v dT$$

Dividing both sides by  $T$ , we get

$$\frac{dQ}{T} = c_v \cdot \frac{dT}{T}$$

or 
$$ds = c_v \cdot \frac{dT}{T}$$

Integrating both sides, we get

$$\int_{s_1}^{s_2} ds = c_v \int_{T_1}^{T_2} \frac{dT}{T}$$

or 
$$s_2 - s_1 = c_v \log_e \frac{T_2}{T_1}$$

# Heating a Gas at Constant Pressure

Let 1 kg of gas be heated at constant pressure, so that its absolute temperature changes from  $T_1$  to  $T_2$  and entropy  $s_1$  to  $s_2$ .

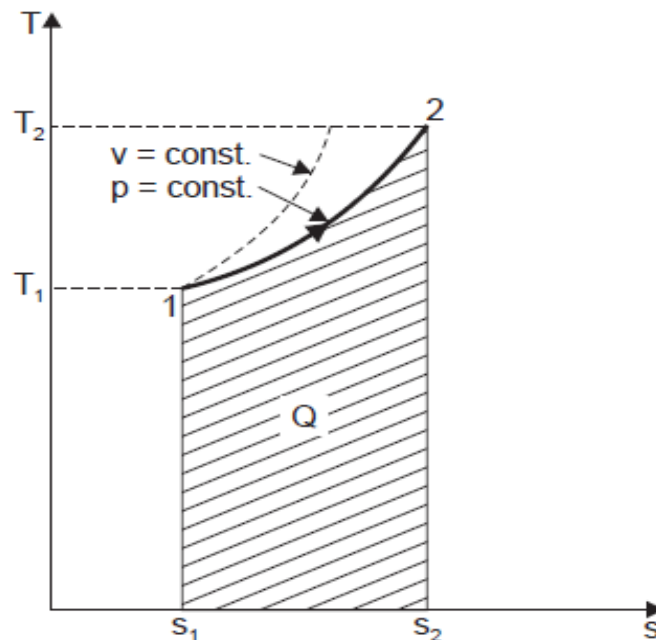


Fig. 5.26.  $T$ - $s$  diagram : Constant pressure process.



Then,  $Q = c_p(T_2 - T_1).$

Differentiating to find small increase in heat,  $dQ$  of this gas when the temperature rise is  $dT$ .

$$dQ = c_p \cdot dT$$

Dividing both sides by  $T$ , we get

$$\frac{dQ}{T} = c_p \cdot \frac{dT}{T}$$

$$ds = c_p \cdot \frac{dT}{T}$$

Integrating both sides, we get

$$\int_{s_1}^{s_2} ds = c_p \int_{T_1}^{T_2} \frac{dT}{T}$$

$$s_2 - s_1 = c_p \log_e \frac{T_2}{T_1}$$

# Isothermal Process

- An isothermal expansion 1-2 occur at constant temperature.
- *For Isothermal process  $du = 0$*
- Entropy changes from  $s_1$  to  $s_2$  when gas absorbs heat during expansion. The heat taken by the gas is given by the area under the line 1-2 which also represents the work done during expansion.
- In other words,  $Q = W$ .

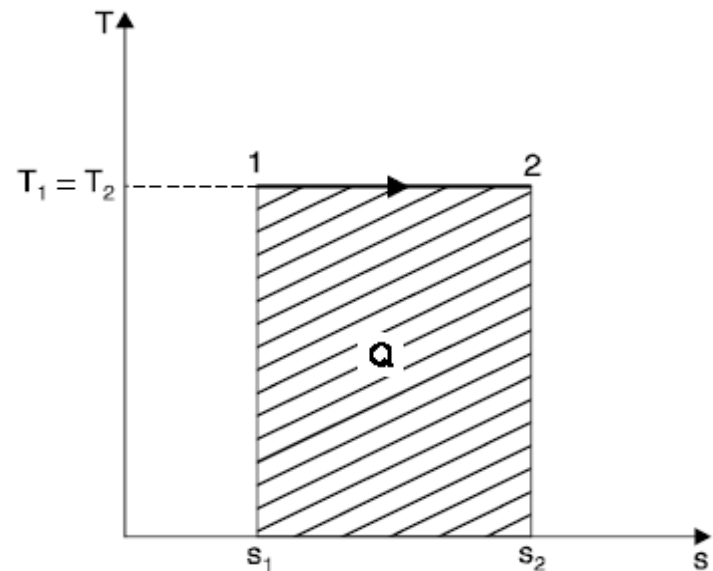


Fig. 5.27. T-s diagram : Isothermal process.

$$Q = \int_{s_1}^{s_2} T ds = T(s_2 - s_1)$$

$$W = p_1 v_1 \log_e \frac{v_2}{v_1} = RT_1 \log_e \frac{v_2}{v_1} \text{ per kg of gas} \quad [\because p_1 v_1 = RT_1]$$

$$T(s_2 - s_1) = RT_1 \log_e \frac{v_2}{v_1}$$

$$s_2 - s_1 = R \log_e \frac{v_2}{v_1} . \quad [\because T_1 = T_2 = T]$$

- An adiabatic process is shown by a vertical line (1-2) and therefore area under this line is nil ; hence heat supplied or rejected and entropy change is zero.
- This shows that there is no change in entropy and hence it is known as *isentropic process*.

During an adiabatic process as heat is neither supplied nor rejected,

$$dQ = 0$$

$$\frac{dQ}{dT} = 0$$

$$ds = 0$$

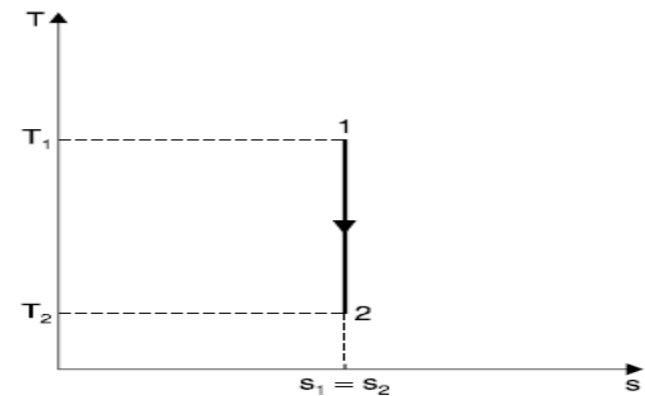


Fig. 5.28. T-s diagram : Adiabatic process.

# Polytropic Process

- The expression for 'entropy change' in polytropic process ( $pv^n = \text{constant}$ ) can be obtained from eqn.

$$s_2 - s_1 = c_v \log_e \frac{T_2}{T_1} + R \log_e \frac{v_2}{v_1}$$

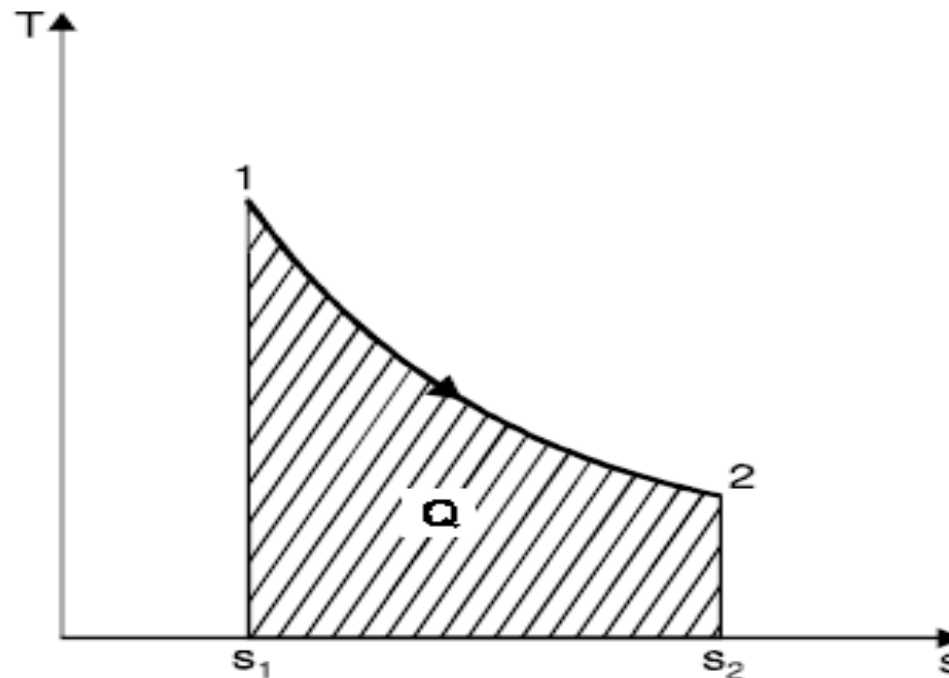


Fig. 5.29. T-s diagram : Polytropic process.

- We know that

$$\left(\frac{v_2}{v_1}\right)^{n-1} = \frac{T_1}{T_2}$$

$$\frac{v_2}{v_1} = \left(\frac{T_1}{T_2}\right)^{\frac{1}{n-1}}$$

- Substituting the value of  $\frac{v_2}{v_1}$  in eqn. of Entropy (Previous Slide)

$$s_2 - s_1 = c_v \log_e \frac{T_2}{T_1} + R \log_e \left(\frac{T_1}{T_2}\right)^{\frac{1}{n-1}} = c_v \log_e \frac{T_2}{T_1} + R \left(\frac{1}{n-1}\right) \log_e \frac{T_1}{T_2}$$

$$= c_v \log_e \frac{T_2}{T_1} - R \left( \frac{1}{n-1} \right) \log_e \frac{T_2}{T_1}$$

$$= c_v \log_e \frac{T_2}{T_1} - (c_p - c_v) \times \left( \frac{1}{n-1} \right) \log_e \frac{T_2}{T_1} \quad [\because R = c_p - c_v]$$

$$= c_v \log_e \frac{T_2}{T_1} - (\gamma \cdot c_v - c_v) \times \left( \frac{1}{n-1} \right) \log_e \frac{T_2}{T_1} \quad [\because c_p = \gamma \cdot c_v]$$

$$= c_v \left[ 1 - \left( \frac{\gamma - 1}{n - 1} \right) \right] \log_e \frac{T_2}{T_1} = c_v \left[ \frac{(n - 1) - (\gamma - 1)}{(n - 1)} \right] \log_e \frac{T_2}{T_1}$$

$$= c_v \left( \frac{n - 1 - \gamma + 1}{n - 1} \right) \log_e \frac{T_2}{T_1}$$

$$= c_v \cdot \left( \frac{n - \gamma}{n - 1} \right) \log_e \frac{T_2}{T_1} \text{ per kg of gas}$$

$$s_2 - s_1 = c_v \left( \frac{n - \gamma}{n - 1} \right) \log_e \frac{T_2}{T_1} \text{ per kg of gas}$$

# Summary of Formulae

<i>S. No.</i>	<i>Process</i>	<i>Change of entropy (per kg)</i>
1.	General case	<p>(i) <math>c_v \log_e \frac{T_2}{T_1} + R \log_e \frac{v_2}{v_1}</math> (in terms of <math>T</math> and <math>v</math>)</p> <p>(ii) <math>c_v \log_e \frac{p_2}{p_1} + c_v \log_e \frac{v_2}{v_1}</math> (in terms of <math>p</math> and <math>v</math>)</p> <p>(iii) <math>c_p \log_e \frac{T_2}{T_1} - R \log_e \frac{p_2}{p_1}</math> (in terms of <math>T</math> and <math>p</math>)</p>
2.	Constant volume	$c_v \log_e \frac{T_2}{T_1}$
3.	Constant pressure	$c_p \log_e \frac{T_2}{T_1}$
4.	Isothermal	$R \log_e \frac{v_2}{v_1}$
5.	Adiabatic	Zero
6.	Polytropic	$c_v \left( \frac{n - \gamma}{n - 1} \right) \log_e \frac{T_2}{T_1}$



# THE THIRD LAW OF THERMODYNAMICS

- The third law of thermodynamics is stated as follow :  
*“The entropy of all perfect crystalline solids is zero at absolute zero temperature”.*
- The third law of thermodynamics, often referred to as *Nernst Law*, provides the basis for the calculation of absolute entropies of substances.

- The ***third law of thermodynamics*** states "*When a system is at zero absolute temperature, the entropy of system is zero*".
- It is clear from the above law that the absolute value of entropy corresponding to a given state of the system could be determined by integrating between the state at absolute zero and the given state. *Zero entropy, however, means the absence of all molecular, atomic, electronic and nuclear disorders.*