



**Discipline Course-I  
Semester-II**

**Paper No: Thermal Physics : Physics-IIA**

**Lesson: Change in Entropy and Third Law of  
Thermodynamics**

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## Objectives

In this chapter, you will learn how to calculate;

- ✓ The change in entropy of an ideal gas
- ✓ The change in entropy of a system undergoing reversible/irreversible changes
- ✓ The change in entropy of a system having external mechanical irreversibility
- ✓ The change in entropy of a system having Internal mechanical irreversibility
- ✓ The change in entropy of a system having Thermal irreversibility
- ✓ The change in entropy of a system having Chemical irreversibility

## 9.1 Introduction

In the previous chapter, we familiarized ourselves with the concept of entropy. We found entropy as a thermodynamic state function change in which is given by the equation  $dS = dQ/T$ . The defining function of entropy, however, does not enable us to have a single value of the function for a particular state of a system. We can only calculate the change (or difference) of the two values of the same *i.e.* mathematically, we determine the change in entropy for a system when it taken from one (reference) to another (final) state by some means. For thermodynamic processes occurring at constant temperature and pressure such as melting of a solid in expense of thermal energy (as latent heat), the change in entropy can easily be calculated using formulad $S = dQ/T = mL/T$ . However, for the processes such as adiabatic transformation ( $dQ = 0$ ) of work into internal energy of a system due to change in temperature, the change in entropy can not be calculated directly. In the present chapter, we will discuss how to calculate the change in entropy for different thermodynamic processes.

## 9.2 Entropy change of ideal gas

If a system absorbs an infinitesimal amount of heat  $dQ$  reversibly at temperature  $T$ , then, from the definition, the change (increase) in the entropy of the system is given by equation (9.1);

$$dS = \frac{dQ}{T} \quad (9.1)$$

Though, the quantity  $dQ$  is an inexact differential, the ratio  $\frac{dQ}{T}$  is exact. It follows therefore, if the quantity  $dQ$  is expressed in terms of thermodynamic differentials, the quantity  $1/T$  can be integrated to give the net change in entropy of the system.

Consider a mole of ideal gas having pressure  $P$ , temperature  $T$ , and volume  $V$  is given a small amount of heat  $dQ$ . If  $dU$  and  $dW$  be the change in internal energy and work done by the gas respectively, then from equation (9.1), we may write;

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$$dS = \frac{dU + dW}{T} \quad (9.2)$$

Now if  $dV$  be the change in volume and,  $C_v$  molar heat capacity at constant volume of the gas then,  $dU$  and  $dW$  can be expressed as;

$$dU = C_v dT$$

but

$$dW = PdV$$

With the substitution of values for  $dU$  and  $dW$ , equation (9.2) takes the form;

$$dS = \frac{C_v dT + PdV}{T}$$

Now, if the gas is taken from an initial state  $i$  to a final one  $f$ , then the net change in the entropy of the gas can be obtained as;

$$\int_i^f dS = \int_i^f \frac{C_v dT + PdV}{T}$$

$$S_f - S_i = \int_i^f \frac{C_v dT}{T} + \int_i^f \frac{PdV}{T} \quad (9.3)$$

Equation (9.3) expresses a general way to calculate the change in entropy of ideal gas. By expressing the thermodynamic variable accordingly for a given process, one can find out the change in the entropy of the gas for that process.

### 9.2.1 Entropy change in terms of temperature and volume

From the ideal gas equation,  $PV = nRT$  we may write for a mole of ideal gas;

$$P = \frac{RT}{V}$$

Putting this value of  $P$  in equation (9.3),

$$\begin{aligned} S_f - S_i &= \int_i^f \frac{C_v dT}{T} + \int_i^f \frac{RdV}{V} \\ &= C_v \int_i^f \frac{dT}{T} + R \int_i^f \frac{dV}{V} \\ &= C_v \log_e \frac{T_f}{T_i} + R \log_e \frac{V_f}{V_i} \end{aligned}$$

But, from  $C_p - C_v = R$ ;

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$$S_f - S_i = C_v \log_e \frac{T_f}{T_i} + (C_p - C_v) \log_e \frac{V_f}{V_i}$$

This is the required expression for change in entropy in terms of temperature and volume.

### 9.2.1 Entropy change in terms of temperature and pressure

Differentiation of ideal gas equation gives;

$$PdV + VdP = RdT$$

or

$$PdV = RdT - VdP$$

But,  $V = \frac{RT}{P}$  and  $C_p - C_v = R$ ; so

$$PdV = (C_p - C_v)dT - RT \frac{dP}{P}$$

Putting this value of  $PdV$  in equation (9.3);

$$\begin{aligned} S_f - S_i &= \int_i^f C_v \frac{dT}{T} + \int_i^f (C_p - C_v) \frac{dT}{T} - \int_i^f R \frac{dP}{P} \\ &= C_p \int_i^f \frac{dT}{T} - R \int_i^f \frac{dP}{P} \end{aligned}$$

$$S_f - S_i = C_p \log_e \frac{T_f}{T_i} - R \log_e \frac{P_f}{P_i}$$

This is the required expression for change in entropy in terms of temperature and pressure.

### 9.2.1 Entropy change in terms of pressure and volume

Differentiation of ideal gas equation gives

$$PdV + VdP = RdT$$

or

$$\frac{PdV + VdP}{R} = dT$$

putting this value of  $dT$  in equation (9.3), we get;

$$\begin{aligned} S_f - S_i &= \int_i^f C_v \frac{PdV + VdP}{RT} + \int_i^f \frac{PdV}{T} \\ &= C_v \int_i^f \frac{PdV + VdP}{PV} + R \int_i^f \frac{dV}{V} \end{aligned}$$

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$$= C_v \int_i^f \frac{dV}{V} + C_v \int_i^f \frac{dP}{P} + (C_p - C_v) \int_i^f \frac{dV}{V}$$

$$= C_p \int_i^f \frac{dV}{V} + C_v \int_i^f \frac{dP}{P}$$

$$= C_p \log_e \frac{V_f}{V_i} + C_v \log_e \frac{P_f}{P_i}$$

**Example 1: Obtain an expression for the change in entropy when ice having mass  $m$  gram is changed into steam.**

**Solution:** The net change in the entropy will be the sum of the changes in entropy during melting of ice into water (1), heating of water to its boiling temperature (2) and its vaporization (3).

So, the net change in entropy  $(\Delta S) = \Delta S_1 + \Delta S_2 + \Delta S_3$

$$(\Delta S) = \frac{mL_i}{T} + mc \log_e \frac{T_2}{T_1} + \frac{mL_s}{T} \text{ cal/K}$$

where  $L_i$  and  $L_s$  are the latent heats of melting (of ice) and vaporization (of water).

**Example 2:  $m$  gram of a liquid (having specific heat  $c$ ) at temperature  $T_1$  is mixed with the same mass of the same liquid at temperature  $T_2$ . Assuming the system thermally insulated, prove that the change in entropy of the universe in above process is equal to;**

$$\Delta S = 2mc \log_e \frac{T_1 + T_2}{2\sqrt{T_1 T_2}}$$

**Solution:** let us suppose that the equilibrium temperature of the mixture becomes  $T$ , then from calorimetric principle;

$$mc (T_1 - T) = mc (T - T_2)$$

or

$$T = \frac{T_1 + T_2}{2}$$

Now, change in entropy of hotter liquid  $(\Delta S_1)$  can be obtained as;

$$\Delta S_1 = mc \int_{T_1}^T \frac{dT}{T}$$

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$$= mc \log_e \frac{T}{T_1}$$

Similarly, change in entropy of colder liquid ( $\Delta S_2$ ) can be obtained as;

$$\Delta S_2 = mc \log_e \frac{T}{T_2}$$

Hence the net change in entropy of the system ( $\Delta S$ ) is given by;

$$\begin{aligned}\Delta S &= \Delta S_1 + \Delta S_2 \\ &= mc \log_e \frac{T}{T_1} + mc \log_e \frac{T}{T_2} \\ &= mc \log_e \frac{T^2}{T_1 T_2} \\ &= mc \log_e \left( \frac{T}{\sqrt{T_1 T_2}} \right)^2 \\ &= 2mc \log_e \left( \frac{T}{\sqrt{T_1 T_2}} \right)\end{aligned}$$

### 9.3 Entropy change in reversible processes

To understand deeply the significance, the study about all the entropy changes taking place when a system undergoes a reversible process is necessary. Here, all entropy changes refers to net change in the entropy of the universe which equals to the sum of the entropy changes of the system and its surroundings due to the reversible process in concern.

Suppose, during a reversible process, heat  $Q$  is absorbed (or) rejected by a heat reservoir at constant temperature  $T$ . Then the entropy change of the reservoir will be  $Q/T$ . The sign of  $Q$  will be **positive** when heat is absorbed and **negative** in case of heat rejected. It is noticeable here that, in general, most of the reversible processes takes place in such a way that the temperature of the system changes from an initial ( $T_i$ ) to a final ( $T_f$ ) value. So, for such reversible processes, a flow of heat between a system and a set of reservoirs having temperature range from initial to final temperature takes place. If  $dQ_R$  be the heat transferred between the system and one of the reservoirs (at temperature  $T$ ) during any infinitesimal portion of the process then;

The change in entropy of the system,

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$$dS = +\frac{dQ_R}{T}$$

and change in entropy of the reservoir

$$dS = -\frac{dQ_R}{T}$$

The entropy change of the universe will be equal to the sum of the entropy changes of system and reservoir *i.e.*

$$(dS)_{universe} = +\frac{dQ_R}{T} - \frac{dQ_R}{T} = 0$$

Similarly it can be shown that the entropy change of the universe comes out to be zero when heat is rejected reversibly from the system. In above expressions, we calculated the entropy changes for infinitesimally small portions of reversible processes and found no entropy change. So, clearly, *the entropy of the universe remains constant for a reversible process.*

### 9.3 Entropy change in irreversible processes

As we know that all the natural processes are irreversible, it is quite important to calculate the entropy changes in irreversible processes. For a system undergoing an irreversible process between two equilibrium states (initial and final), due to the definition of the entropy, the given irreversible process is replaced by some arbitrary reversible process occurring between the same equilibrium states of the system. If  $S_f$  and  $S_i$  be the entropies of the final and initial states of the given irreversible process then the change in entropy for the process is given by;

$$S_f - S_i = \int_{i,R}^f \frac{dQ}{T}$$

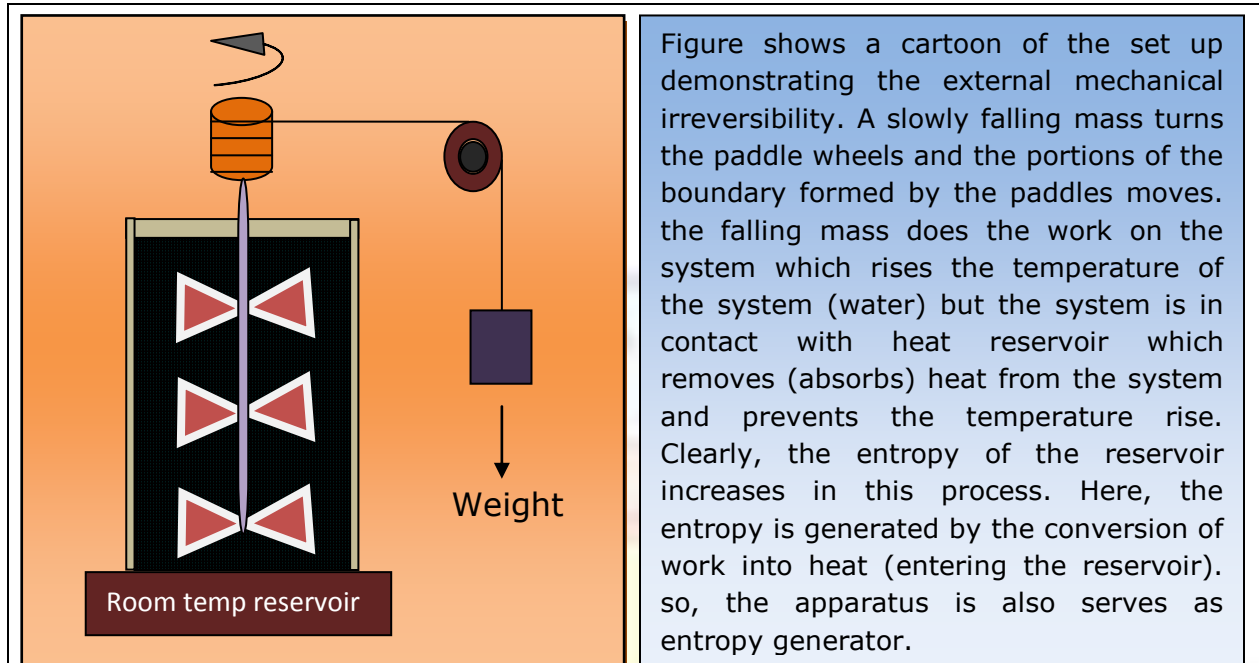
Here R, denotes any arbitrarily chosen reversible process.

Below are given some irreversible processes and the expression for entropy changes for the same;

Nature of irreversibility	Examples
External mechanical irreversibility	<ul style="list-style-type: none"><li>✓ Heat dissipation due to friction from solids in contact with reservoir</li><li>✓ Irregular stirring of viscous liquid in contact with reservoir</li><li>✓ Heat transfer to reservoir due to magnetic hysteresis</li><li>✓ Magnetic hysteresis of a material in contact with a reservoir</li><li>✓ Inelastic deformation of a solid in contact with a reservoir</li></ul>



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**Figure 9.1:** Joule-paddle experimental set-up, also known as entropy generator. Here, the reservoir is in contact with the water by diathermic wall and the surroundings of the water are adiabatic cylindrical walls.

### Calculations for the entropy change:

These processes involve isothermal and adiabatic transformation of work into internal energy of the reservoir. Let us calculate entropy changes for processes involving *isothermal transformation of work into internal energy*.

The change in the entropy of the system will be zero because no change take place in the thermodynamic co-ordinates of the system during above process *i.e.*

$$dS_{\text{system}} = 0$$

the change in the entropy of the reservoir will be

$$dS_{\text{reservoir}} = +\frac{Q}{T} \text{ or } +\frac{W}{T}$$

Where Q (W) and T is the amount of heat (work) transferred into the internal energy and temperature of the reservoir.

Clearly, the change in the entropy of the universe will be;

$$dS_{\text{universe}} = +\frac{Q}{T}$$

Which is a positive value indicating the fact that entropy always increases in irreversible processes.

For the processes involving adiabatic transformation of work in to internal energy, the

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entropy change can be calculated as following;

Consider for any thermodynamic process occurring adiabatically, the temperature of the system rises from  $T_i$  to  $T_f$  (say) at constant atmospheric pressure. As there will be no any heat flow to or from the surroundings (adiabatic), the change in entropy of the surroundings will be zero. The change in entropy of the system can be determined by replacing the original irreversible process by a reversible one that will take system from temperature  $T_i$  to  $T_f$  at constant pressure by means of a series of reservoirs ranging in temperature from  $T_i$  to  $T_f$ .

The entropy change of the system, then, will be;

$$S_f - S_i = \int_{T_{i,R}}^{T_f} \frac{dQ}{T}$$

As the process is isobaric,  $dQ = C_p dT$ , so that;

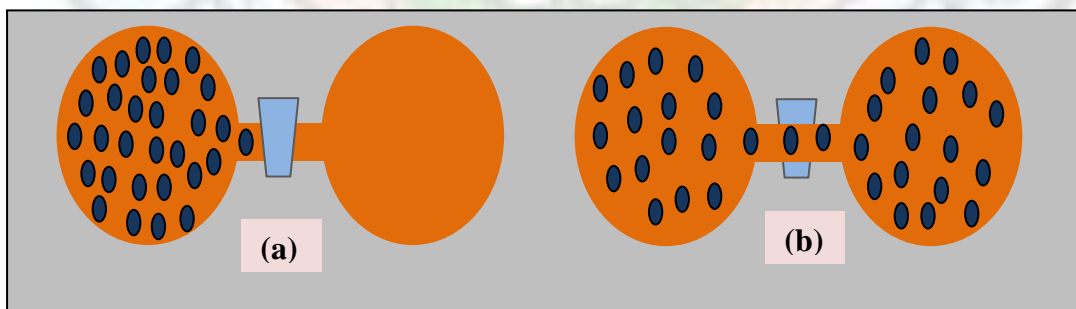
$$S_f - S_i = \int_{T_{i,R}}^{T_f} \frac{C_p dT}{T}$$

Now, if we assume that  $C_p$  is independent of the temperature for given range, then the entropy change of the system will be;

$$S_f - S_i(\text{system}) = C_p \log_e \frac{T_f}{T_i}$$

which will also be equal to the entropy change of the universe and, obviously is positive.

Nature of irreversibility	Examples
Internal mechanical irreversibility	<ul style="list-style-type: none"> <li>✓ Free expansion of ideal gases (Joule expansion)</li> <li>✓ Throttling process (Joule-Thomson expansion)</li> <li>✓ Collapse of soap film when punctured</li> </ul>



**Figure 9.2:** Free expansion of ideal gas. If  $V$  be the volume of each vessel then can you approximate the entropy change of the universe in this process?

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### Calculations for the entropy change:

These processes involve transformation of internal energy of a system enclosed by adiabatic walls into mechanical energy and then again into internal energy. For the calculation of entropy change in a process exhibiting internal mechanical irreversibility, consider a case of free expansion of the ideal gas. In this process, an ideal gas enclosed by adiabatic walls expands in vacuum from an initial volume  $V_i$  to a final volume  $V_f$  (where  $V_f > V_i$ ) at constant temperature. In order to calculate the entropy changes, the original process must be replaced by a reversible one that will take the system from  $V_i$  to  $V_f$  at constant temperature. So, it is convenient to replace the original process by a reversible isothermal expansion (from  $V_i$  to  $V_f$ ) of the gas at temperature  $T$ . The entropy change of the system is given by

$$S_f - S_i(\text{system}) = \int_{V_i,R}^{V_f} \frac{dQ}{T}$$

For an isothermal process of ideal gas,

$$dQ = dU + PdV$$

Or

$$dQ = PdV \text{ (as } dU = 0\text{)}$$

And hence

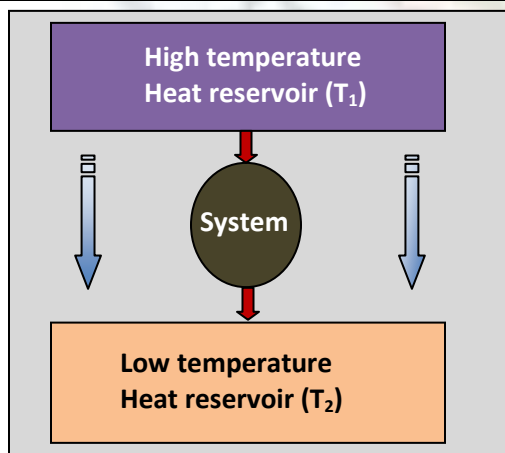
$$\frac{dQ}{T} = nR \frac{dV}{V}$$

So, the entropy change of the system is given by,

$$\begin{aligned} S_f - S_i(\text{system}) &= nR \int_{V_i,R}^{V_f} \frac{dV}{V} \\ &= nR \log_e \frac{V_f}{V_i} \end{aligned}$$

Which is, obviously, equal to the entropy change of the universe. It is clear again that the change in entropy of the universe is positive.

Nature of irreversibility	Examples
Thermal irreversibility	<ul style="list-style-type: none"> <li>✓ Conduction of heat or radiation from a system to its surroundings</li> <li>✓ Conduction of heat or radiation from hotter to cooler reservoir</li> </ul>



**Figure 9.2:** Conduction of heat from hotter reservoir to colder one by means of radiation due to temperature difference. Can you guess whether entropy of the system alter (increase or decrease) or remain the same?

## Change in entropy

### Calculations for the entropy change:

Generally, in thermodynamic process, the heat reservoirs of different temperatures are used as high temperature heat reservoir and low temperature heat sink coupled with the system. There exists always a possibility of heat transfer from system to the colder sink (or to its surroundings) by virtue of finite temperature difference between them. This heat transfer may take place by means of conduction and/or radiation through the system. In this heat transfer process, however, the system remains unchanged and hence poses no entropy changes *i.e.*

$$S_f - S_i(\text{system}) = 0$$

Now, if we assume that heat  $Q$  is transferred from a hotter reservoir at temperature  $T_1$  to a colder reservoir at temperature  $T_2$ , then the change in entropy of the hotter and colder reservoirs will be;

$$S_f - S_i(\text{hotter reservoir}) = -\frac{Q}{T_1}$$

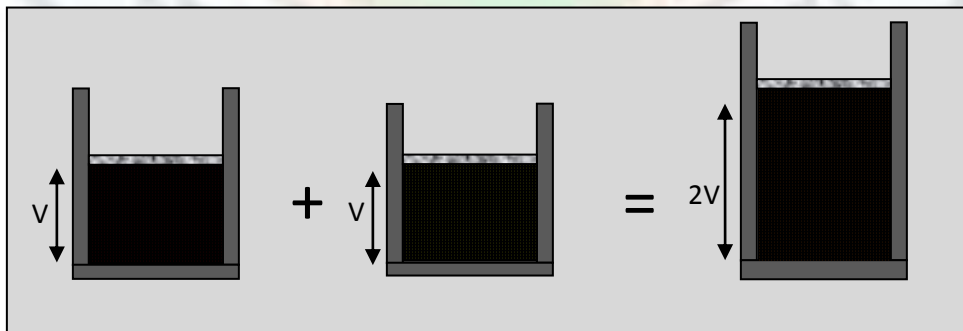
$$S_f - S_i(\text{colder reservoir}) = +\frac{Q}{T_2}$$

Obviously, the entropy change of the universe will be;

$$S_f - S_i(\text{universe}) = \frac{Q}{T_2} - \frac{Q}{T_1}$$

Clearly, since  $T_2 < T_1$ , the entropy change of the universe will be positive.

Nature of irreversibility	Examples
Chemical irreversibility	<ul style="list-style-type: none"> <li>✓ Osmosis</li> <li>✓ Diffusion of two unlike ideal gases</li> <li>✓ Mixing of alcohol and water</li> <li>✓ Condensation of super saturated vapor</li> <li>✓ A chemical reaction</li> </ul>



**Figure 9.4:** Equal amount (volume) of two unlike liquids is added to get a mixture as shown. The walls of the containers are thermally insulated and the mixing has also been carried out in the adiabatic environment. Can you calculate the entropy change of the universe?

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### Calculations for the entropy change:

The thermodynamic phenomena involving the mixing of two or more than two substance to get a resultant one. These processes introduce spontaneous changes of internal structure, density and chemical composition etc.

To calculate the entropy changes in such process, let us assume the mixing of two dissimilar inert ideal gases. This process may be treated equivalent to that of free expansions of the given gases in an adiabatic enclosure having chambers of equal volume. here, our system contains two dissimilar inert gases and hence the change in entropy of the system will be;

$$S_f - S_i(\text{system}) = \text{Change in entropy of the two gases}$$

$$\begin{aligned} S_f - S_i(\text{system}) &= nR \log_e \frac{V_f}{V_i} + nR \log_e \frac{V_f}{V_i} \\ &= 2nR \log_e \frac{V_f}{V_i} \end{aligned}$$

Clearly, the entropy of the system increases as  $V_f > V_i$ . since there will be no change in entropy of the surroundings (reservoir), the entropy change of the universe will be;

$$S_f - S_i(\text{universe}) = 2nR \log_e \frac{V_f}{V_i}$$

Which is a positive number. it can be shown for the processes exhibiting chemical irreversibility that the net change in the entropy of the universe is positive.

## 9.4 Summary

In this chapter, we have been familiarized with various methods to estimate the entropy changes of the system, surroundings and universe for different thermodynamic processes. We may summarize the main results of this chapter in the form of the following points:

- ✓ The general expression for the entropy change of an ideal gas can be written as:

$$S_f - S_i = \int_i^f \frac{C_v dT}{T} + \int_i^f \frac{P dV}{T}$$

- ✓ The expression for change in entropy of an ideal gas in terms of temperature and volume can be expressed as:

$$S_f - S_i = C_v \log_e \frac{T_f}{T_i} + (C_p - C_v) \log_e \frac{V_f}{V_i}$$

- ✓ The expression for change in entropy of an ideal gas in terms of temperature and pressure can be expressed as:

$$S_f - S_i = C_p \log_e \frac{T_f}{T_i} - R \log_e \frac{P_f}{P_i}$$

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- ✓ The expression for change in entropy of an ideal gas in terms of temperature and pressure can be expressed as:

$$S_f - S_i = C_p \log_e \frac{V_f}{V_i} + C_v \log_e \frac{P_f}{P_i}$$

- ✓ We found that the entropy of the universe remains the same (does not change) during any reversible process.
- ✓ The entropy of the universe always increases during any irreversible process. It is clear therefore that the entropy of the universe increases during natural processes.

### 9.5 Exercises

#### 9.5.1 Subjective questions

1. Derive an expression for the entropy change of an ideal gas in terms of temperature and volume.
2. Calculate the net change in the entropy when m gram of ice at 0°C is converted into steam at 100°C in terms of temperature, specific heat and latent heat.
3. Show that the entropy of the universe remains unchanged during a reversible process.
4. Define mechanical irreversibility with some examples and obtain an expression for the entropy change of the universe for such processes.
5. Name the processes exhibiting chemical irreversibility. Show that entropy of the universe increases during the process of osmosis.
6. Explain how Joule-paddle experiment can be used as an entropy generator. Explain which type of irreversibility it exhibits.
7. Give examples of some processes in which entropy decreases.

#### 9.5.2 Objective questions

##### 1. True or false

- a) When the temperature of a gas is reduced, its entropy increases.
- b) When a system takes some heat from a reservoir, the entropy of the reservoir does not change.
- c) In b), the entropy of the system increases.
- d) Melting of ice is an isentropic process.

<b>Correct answer/option (s)</b>	(a) False (b) False (c) True (d) False
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### Justification/feedback for correct answer (s)

- a) On decreasing the temperature of gas, the random motion of gas molecules approaches towards less randomization (more ordered) and hence entropy decreases.
- b) As reservoir rejects some heat, its entropy decreases.
- c) As system absorbs heat, its entropy increases.
- d) During the process of melting, the system (ice) absorbs heat and hence its entropy increases.

### 2. True or false

- a) The change of entropy of the universe is zero for a reversible process.
- b) The entropy of the universe remains unchanged in all natural processes.
- c) The process of friction from two solids in contact with a reservoir is an example of internal mechanical irreversibility.
- d) Transfer of charge through a resistor in contact with a reservoir is an example of external mechanical irreversibility.

<b>Correct answer/option (s)</b>	(a) True (b) False (c) False (d) True
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### Justification/feedback for correct answer (s)

- a) Entropy remains unchanged during a reversible process.
- b) All natural processes are irreversible and entropy of the universe always increases in such processes.
- c) It is an example of external mechanical irreversibility.
- d) Here, the system *i.e.* resistor remains unchanged and heat generated due to charge flow is dissipated into the internal energy of the reservoir. It is an example of external mechanical irreversibility.

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### 9.5.3 Multiple choice questions

1. Whenever a reservoir absorbs heat  $Q$  at the temperature  $T$  from any system during any kind of process, the entropy change of the reservoir is

- (a) Zero
- (b)  $+\frac{Q}{T}$
- (c)  $-\frac{Q}{T}$
- (d) None of the above

2. During the isothermal dissipation of work ( $W$ ) through a system into internal energy of a reservoir (at temp.  $T$ ), the entropy change of the system is

- (a) Zero
- (b)  $+\frac{W}{T}$
- (c)  $-\frac{W}{T}$
- (d) None of the above

3. In above question no. 2, the entropy change of the local surroundings is

- (a) Zero
- (b)  $+\frac{W}{T}$
- (c)  $-\frac{W}{T}$
- (d) None of the above

4. In above question no. 2, the entropy change of the universe is

- (a) Zero
- (b)  $+\frac{W}{T}$
- (c)  $-\frac{W}{T}$
- (d) None of the above

5. In a process of free expansion (from initial volume  $V_i$  to final volume  $V_f$ ) of an ideal gas, the entropy change of the system is

- (a)  $+R \log_e \frac{V_f}{V_i}$
- (b)  $-R \log_e \frac{V_f}{V_i}$
- (c) Zero
- (d) None of the above

6. Which of the following processes exhibits chemical irreversibility?

- (a) Irregular stirring of a viscous liquid in contact with a reservoir



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- (b) Collapse of a soap film after it is punctured
- (c) Mixing of alcohol and water
- (d) None of the above

7. Which of the following processes exhibits internal mechanical irreversibility?

- (a) Irregular stirring of a viscous liquid in contact with a reservoir
- (b) Inelastic deformation of a thermally insulated solid
- (c) Inelastic deformation of a solid in contact with a reservoir
- (d) Collapse of a soap film after it is punctured

8. The entropy of the system during the processes exhibiting thermal irreversibility is

- (a) Zero
- (b)  $>0$
- (c)  $\geq 0$
- (d) Could not be decided

### 9.6 Glossary

**System:** A thermodynamic system may be defined as a certain portion of the universe selected for some investigation e.g. a gas, a vapour (steam), and a mixture etc.

**Surroundings:** Everything outside the system that may affect its behavior is termed as surroundings.

**Universe:** The portion of space which contains both system and its surroundings is termed as universe.

**Magnetic Hysteresis:** In the process of magnetization, the magnetic induction lags behind the applied magnetic field intensity and due to this, some loss of applied magnetic energy occurs. This phenomenon is termed as hysteresis.

**Inelastic deformation:** When a system is subjected to some external stress, it gets deformed but due to its elasticity, it attains its original state on the removal of the stress. However, if the system does not attain its original state, the deformation is called as inelastic.

**Throttling process:** The process of flow (expansion) of a gas from a region of higher pressure to a lower one through a thin porous wall in a thermally insulated container is called as throttling process. A throttling process is also known as Joule-Thomson expansion.

**Diffusion:** The movement of molecules from region of higher concentration to regions of lower one is called as diffusion (transport of mass).

### 9.7 References

#### Book cited:

Heat and Thermodynamics: An Intermediate Text Book by Mark W. Zemansky and Richard H. Dittman (McGra-Hill, 1993).

#### Further readings

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# Change in entropy

## Objectives

After reading this chapter, you will be able to understand about;

- ✓ The definition of the third law of thermodynamics
- ✓ The significance of the third law
- ✓ The mathematical formulation of the third law
- ✓ The un-attainability of absolute zero temperature
- ✓ Few other consequences of the third law

## 10.1 Introduction

In previous chapters (chap. 8 and 9), we studied about an important state function 'entropy' of the thermodynamic systems and calculated the change in this function during some reversible/irreversible processes. We had been familiarized with the fact that entropy (of the universe) remains the same during a reversible process and always increases whenever the process occurs irreversibly. Let us consider a thermodynamic system which absorbs an infinitesimal amount of heat  $dQ$  reversibly at temperature  $T$ , then, from the definition, the change in the entropy of the system is given by equation

$$dS = dQ/T \quad (10.1)$$

Now, for the processes involving unit mass occurring at constant pressure  $dQ$  may be written as;

$$dQ = \frac{C_p dT}{T} \quad (10.2)$$

And, the entropy  $S$  can be obtained by integration, so that

$$S = \int \frac{C_p}{T} dT + \text{Constant of integration} \quad (10.3)$$

Writing above equation as a definite integral, we have that the entropy of a system measured at some temperature  $T$  is given by;

$$S(T) = \int_{T_0}^T \frac{C_p}{T} dT + S(T_0) \quad (10.4)$$

$$\text{Or} \quad S(T) - S(T_0) = \int_{T_0}^T \frac{C_p}{T} dT \quad (10.5)$$

where  $T_0$  is some different temperature. Thus from above equation, it seems that we are only able to find the *change in entropy* and not the absolute measurement of entropy itself at a given temperature. On the other hand, with the fact that the entropy decreases with temperature, what value will it take when temperature is absolute zero? The answer of this question is given by the third law of thermodynamics. Below are given some of the statements of the third law.

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## 10.2 Statements of the third law

While Walter Nernst's ingenious intuition was led to the establishment of third law of thermodynamics, some other distinguished people, most notably Max Planck, Albert Einstein, and Simon contributed significantly in the development of this important scientific venture. The third law of thermodynamics has evolved from the Nernst observations on the chemical thermodynamics of electro-chemical cells. After his statement of third law, the discussions were made between him, Planck and Einstein regarding his analysis on an entropy change in a reacting system at temperatures approaching absolute zero. Even after 100 years since this discussion took place, there is still no satisfactory universal formulation of the third law thermodynamics. The development of the understanding about the third law by different scientists based on their own experimental/theoretical analysis is briefly presented below.

**Walter H. Nernst** (1864-1941) had carried out some experiments on electro-chemical cells and analyzed the data based on chemical thermodynamics. His conclusions were mainly concerned with the changes in enthalpy ( $\Delta H$ ) and Gibb's function ( $\Delta G$ ). According to the relation:  $G = H - TS$ , the change in the Gibb's free energy could be obtained as  $\Delta G = \Delta H - T\Delta S$  so that, theoretically,  $\Delta G \longrightarrow \Delta H$  as  $T \longrightarrow 0$ . Experimentally, it was found true, but he observed that  $\Delta G$  and  $\Delta H$  not only came closer together on cooling, but they approached each other asymptotically. He also postulated that  $\Delta S \longrightarrow 0$  as  $T \longrightarrow 0$ .



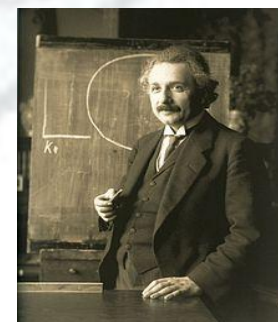
**Walther Nernst**  
(Image from Wikipedia)

**Max Planck** (1858-1947) made a hypothesis in 1911 that the entropy of a perfect crystal is zero and further it is believed to be true about any system which is in **internal equilibrium**. For example, the systems such as  $^4\text{He}$  and  $^3\text{He}$  which are liquids at very low temperature, and electrons in a metal can be treated as a gas even at temperature down to  $T = 0$ . Here, the zero entropy could be understood by taking into account its statistical definition *i.e.*  $S = k_B \log \Omega$ .  $S=0$  implies that  $\Omega=1$ , meaning by at absolute zero, the system is in its ground state which is non-degenerate.



**M. Planck**  
(Image from Wikipedia)

**Einstein (1879-1955)** was first to investigate the entropy of quantum systems at low temperatures. He, on the basis of theoretical calculations, proposed that heat capacities should vanish at absolute zero which implies that  $S$  is finite as  $T$  tends to 0. Later on, Nernst and his group at University of Berlin undertook experimental investigation of physical properties at low temperatures and the results were in agreement (almost) with Einstein's prediction. The quantum theory of heat capacity led by Einstein was later corrected by Debye to produce a better quantitative match with Nernst's experimental results.



**A. Einstein**  
(Image from Wikipedia)

## Change in entropy

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Now, let us discuss one by one the statements made by different physicists about the third law of thermodynamics;

**Planck's statement:** The entropy of any pure crystalline substance tends to a universal constant (which can be taken to be zero) When temperature falls to absolute zero *i. e.*

$$S \longrightarrow 0 \text{ as } T \longrightarrow 0$$

**Explanation:** As we have learned from the previous lessons that entropy is related with the degree of ordering of the constituents of a system *i.e.* lower the ordering, higher the entropy and vice-versa. For a solid substance, the lowest-energy (highest ordering) phase, which could be achieved by cooling it down to zero, is the perfect crystal. Planck chose zero value for the entropy of a perfect crystal. It was further motivated by the development of statistical mechanics, according to which entropy can also be defined as  $S = k_B \log \Omega$ . From this definition of entropy, zero entropy is equivalent to  $\Omega = 1$  which implies that, at absolute zero temperature, a system finds its ground state (lowest energy state) and this ground state is non-degenerate. Planck actually made his statement about third law for perfect crystals. However, with the condition that all parts of a system being in the **internal equilibrium** with each other, it could be true about any system *e.g.* electrons in metal and liquid helium ( $^3\text{He}$ ,  $^4\text{He}$ ) at temperatures down to zero.

One can have an **apparent objection** on the Planck's formulation of third law. Consider a system of  $N$  spinless atoms forming a perfect crystal. According to the Planck statement, the entropy of the considered system, being a perfect crystal, should be zero. However, if we assume that the nucleus of each atom possesses angular momentum  $I$  and in the absence of applied magnetic field, the degeneracy of the nuclear spin will be  $(2I + 1)$ . Now, if  $I > 0$ , the degeneracy will not be equal to 1 and we will have  $S = Nk_B \log(2I + 1) \neq 0$  which contradicts the statement ( $S = 0$ ) for perfect crystals. The **answer** to above contradiction is hidden in the term *internal equilibrium*. It implies that the individual components of the system must be able to exchange energy with each other *i.e.* to interact with each other. So, for the above example, the nuclear spins feel a tiny magnetic field due to their dipolar fields and this lifts the degeneracy of the system to give non-degenerate ground state at absolute zero which corresponds to ( $S = 0$ ).

**Simon's statement:** In internal thermodynamic equilibrium, the contribution to the entropy by each aspect of the system tends to zero as temperature (of the system) approaches to 0.

**Explanation:** Here the term "aspect" indicates about different sub-systems of the main thermodynamic system under study. For a crystal, the subsystems like electrons, nuclear spins, and nucleons *etc.* are called as aspects. The introduction of the term aspect by Simon made his statement convenient by allowing one to focus on a particular aspect of interest while ignoring the aspects that we do not care about. When we cool a crystal, we extract energy from the lattice and its entropy drops towards zero as temperature approaches to zero. However, the nuclear spins may still retain their entropy and it require further cooling to a much lower temperature to have zero entropy. Moreover, if we find method of cooling the nuclei, there might still be some residual entropy associated with the individual nucleons.

**Einstein's statement:** As the temperature falls to absolute zero, the entropy of any substance remains finite.

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$$S(T, y) \longrightarrow S_0(y) \text{ Where } |S_0| < \infty \text{ as } T \longrightarrow 0, |y| < \infty \quad (10.6)$$

The limiting value  $S_0$  may depend on  $y$ ; which is supposed to remain finite at  $T \longrightarrow 0$ .

**Explanation:** In his theory about heat capacities of solids, Einstein proposed that the heat capacities should vanish at absolute zero. Considering expression for the entropy change in a constant pressure heating process;

$$S = \int_0^T \frac{C_p}{T} dT \quad (10.7)$$

In above equation,  $C_p$  stands for  $y$  and equation (10.7) presumes heat capacity to vanish i.e.  $C_p \longrightarrow 0$ , as  $T \longrightarrow 0$ ,

Since otherwise,  $S$  will diverge to  $-\infty$  as  $T \longrightarrow 0$ . A similar conclusion can be obtained for  $C_v$  by considering the heating process with constant volume.

**Nernst's statement:** According to Nernst, the change in entropy of a system undergoing any reversible isothermal process approaches to zero as temperature tends to  $0^\circ\text{K}$ . In other words,

All reactions in a system being in internal equilibrium occur without any change in entropy at temperature near to absolute zero.

Mathematically, we can express it as:

$$\lim_{T \rightarrow 0} \Delta S \rightarrow 0 \quad (10.8)$$

### 10.3 Consequences of the third law

Having familiarized with the third law of thermodynamics in terms of the statements given by different learned physicists, let us discuss some of its consequences;

#### 10.3.1 Heat capacities near absolute zero?

It can be easily shown that the value of any heat capacity will tend to 0, as temperature approaches absolute  $0^\circ\text{K}$  e.g.

The heat capacity  $C$  can be expressed in terms of entropy as;

$$C = T \left( \frac{\partial S}{\partial T} \right) \quad (10.8)$$

$$C = T \left( \frac{\partial S}{\partial \ln T} \right) \quad (10.9)$$

Now from above equation, when  $T \rightarrow 0$ ,  $\ln T \rightarrow -\infty$  and hence  $C$  will tend to zero. Recall that this result defers from the classical predictions according to which  $C = R/2$  per mole per degree of freedom (for gases). However, the classical theory based on equipartition theorem is a high temperature phenomenon which fails at low temperatures. The quantum mechanical treatment by Debye conveniently explained the behavior of heat capacities for

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both high and low temperature limits. Variation of heat capacity as  $T^3$  at low temperatures predicted by Debye is known as  **$T^3$  Law**.

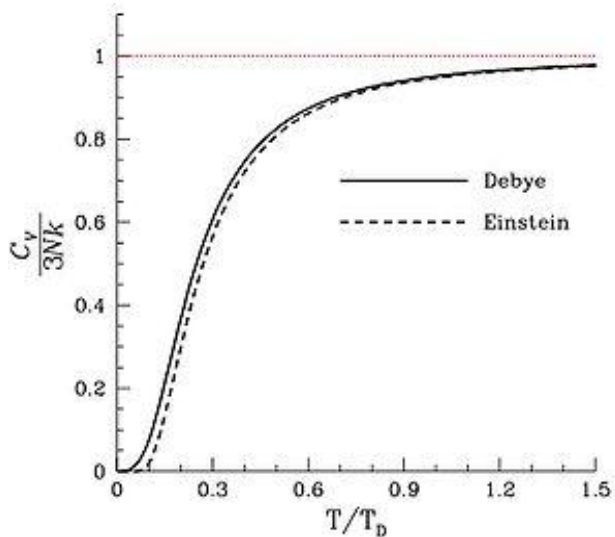


Figure 1 (taken from Wikipedia): Variation of dimensionless heat capacity as a function of temperature as predicted by classical (red line), quantum mechanically (the Debye model and by Einstein's models). The horizontal axis is the temperature divided by the Debye temperature. Note that, the dimensionless heat capacity is zero at absolute zero, and rises to a value of three as the temperature becomes much larger than the Debye temperature.

### 10.3.2 No gases remain ideal as $T \rightarrow 0$

We are familiar with the fact that no any real gas behaves as an ideal gas. The concept of ideal gas is just a combination of some idealized conditions extracted from the theoretical/experimental observations made by some scientists such as Boyle, Charles, and Gay-Lussac. However, the ideal gas equation describes the real gases quite well under quite a wide range of conditions.

We know that for a mole of mono-atomic ideal gas, the difference between its heat capacities equals a constant *i.e.*

$C_p - C_v = R$ ; However, both  $C_p$  and  $C_v \rightarrow 0$  as  $T \rightarrow 0$  and the relation can not be satisfied. Moreover, from the expression for the entropy for an ideal gas;

$$S = C_v \ln T + R \ln V + \text{constant} \quad (10.10)$$

As  $T \rightarrow 0$ , the above equation yields  $S \rightarrow -\infty$  which is as far from zero as you can get! Thus the third law limits the ideal gas model when temperature approaches zero. Of course, at low temperatures, the interactions between gas molecules become important which were ignored during ideal gas modeling. It requires more sophisticated models describing the behavior of gases at low temperatures.



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### 10.3.3 Thermal expansion stops as $T \rightarrow 0$

From the Maxwell's relations, it can be shown that;

$$\left(\frac{\partial S}{\partial p}\right)_T = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p \quad (10.11)$$

where  $\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p = \beta_p$  is the isobaric expansivity. It is clear that  $\beta_p \rightarrow 0$  as  $T \rightarrow 0$  (because  $S \rightarrow 0$  when  $T \rightarrow 0$  and when  $S \rightarrow 0$ ,  $\left(\frac{\partial S}{\partial p}\right)_T \rightarrow 0$  which implies the result).

### 10.3.4 Curie's law breaks down as $T \rightarrow 0$

This law states that the magnetic susceptibility ( $\chi$ ) is inversely proportional to temperature *i.e.*

$$\chi = \frac{M}{B} = \frac{C}{T} \quad (10.2)$$

where  $M$  is magnetization,  $B$  applied magnetic field and  $C$  is a material specific constant. From equation (10.2), it is clear that  $\chi \rightarrow \infty$  as  $T \rightarrow 0$ . However, third law implies that *i.e.*

$\left(\frac{\partial S}{\partial B}\right)_T \rightarrow 0$  and hence

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial m}{\partial T}\right)_B = \frac{VB}{\mu_0} \left(\frac{\partial \chi}{\partial T}\right)_B \rightarrow 0$$

Thus  $\left(\frac{\partial \chi}{\partial T}\right)_B \rightarrow 0$ , this is in disagreement with Curie's law. The reason to this disagreement lies in the development of the law itself. Curie's law is derived by assuming the magnetic moments to be entirely independent and their properties were determined by considering only the interactions between the applied magnetic field (to align the moments) and the temperature (which randomize the moments). The magnetic susceptibility  $\chi$  is a measure of responses of these independent moments to the applied magnetic field which will, obviously, become infinite (maximum) in the complete absence of randomizing force *i.e.* at  $T = 0$ .

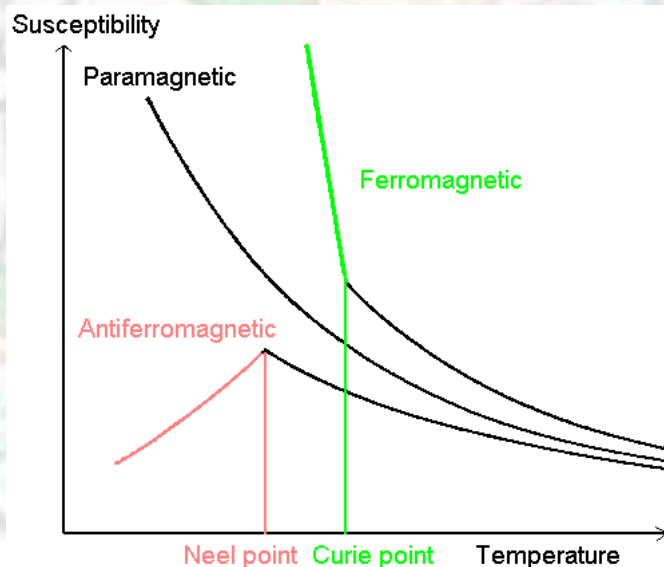


Figure 2: Variation of magnetic susceptibility with temperature (image taken from Wikipedia)

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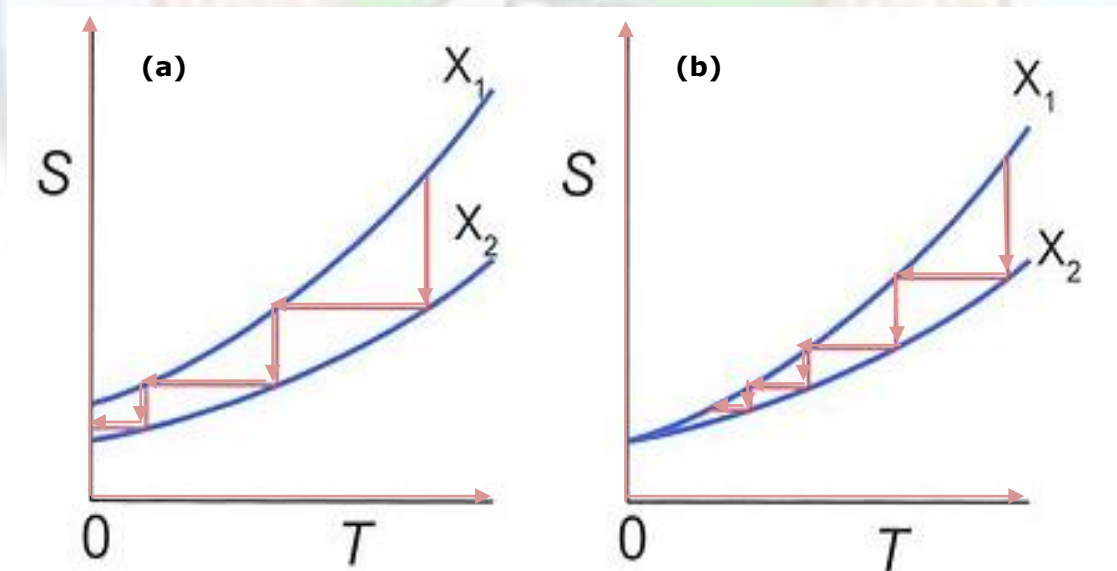
However, at very low temperatures ( $T \rightarrow 0$ ), for the real magnetic systems, the interactions between the magnetic moments can not be ignored. Due to their mutual non-zero interactions these magnetic moments will be driven into some partially ordered state by each other and an applied magnetic field will have much less of an effect. It could be briefly stated as: the microscopic constituents of a system can behave independently at higher temperatures where the thermal energy ( $k_B T$ ) is much larger than any interaction energy. The mutual interactions between the microscopic constituents become significant and their independence breaks down at low temperatures.

### 10.3.5 Unattainability of absolute zero

It is the main consequence of the third law, according to which "It is impossible to cool any system to  $T = 0$  °K in finite number of steps".

Let us understand above statement by considering the cooling behavior of a system in terms of the parameters entropy ( $S$ ) and Temperature ( $T$ ). Figure 3(a) shows the plot of  $S$  against  $T$  for different parameter  $X$  of the system.

Here, the cooling is produced by isothermal increase and adiabatic decrease in  $X$  respectively. If the third law were not to be followed, it would be possible to cool the system to absolute zero by proceeding according to figure 3 (a). However, due to the restriction caused by the third law (*i.e.*  $S \rightarrow 0$ , as  $T \rightarrow 0$ ), the situation will be like as given in figure 3 (b). Clearly, the number of steps (isothermal increase and adiabatic decrease) needed to get absolute zero becomes infinite.



**Figure 3:** The entropy of as a function of temperature for two different values of a parameter  $X$  of a system.

### ***Interesting fact***

#### **Is third law a consequence of the second law?**

In above discussion, we have been familiarized with the fact that we can not attain absolute zero in a finite number of steps as a consequence of the third law. This makes a constraint on the maximum efficiency of the Carnot engine. Let us consider a Carnot engine operating between reservoirs with temperatures  $T_S$  and  $T_H$  where the subscripts S and H represents the low temperature *i.e.* sink and high temperature heat reservoirs respectively. Now, from the expression for the efficiency of Carnot engine *i.e.*  $\eta = 1 - \frac{T_H}{T_S}$ , if  $T_S \rightarrow 0$ , the efficiency  $\eta$  will tend to 1 (maximum value). The Carnot engine when operated under this condition, we will have a complete conversion of heat into work, in violation of Kelvin's statement of the second law. From here, it seems at first sight that un-attainability of absolute zero (an outcome of third law) is simply a consequence of the second law itself.

**Explanation:** We have considered in above example, the Carnot engine operating between two reservoirs, one of which is at absolute zero. The difficulty lies in our consideration *i.e.* how can one perform an isothermal process at absolute zero. Once a system is at absolute zero, it is not possible to change its state without heating it. Thus, the third law is indeed a separate postulate independent from the second law.

### **10.4 Summary**

- The third law of thermodynamics can be stated in various ways:
- According to **Planck**: The entropy of any pure crystalline substance tends to a universal constant (which can be taken to be zero) When temperature falls to absolute zero.
- According to **Simon**: In internal thermodynamic equilibrium, the contribution to the entropy by each aspect of the system tends to zero as temperature (of the system) approaches to 0.
- According to **Einstein**: As the temperature falls to absolute zero, the entropy of any substance remains finite.
- According to **Nernst**: All reactions in a system being in internal equilibrium occur without any change in entropy at temperature near to absolute zero.
- Heat capacities tends to zero as  $T \rightarrow 0$
- The ideal gas model breaks down at temperature  $T \rightarrow 0$
- The coefficient of Thermal expansivity tends to zero as  $T \rightarrow 0$
- Curie's law breaks down as  $T \rightarrow 0$
- It is impossible to cool to absolute zero in finite number of steps.

### 10.5 Exercises

#### 10.5.1 Subjective questions

- 1) Define third law of thermodynamics. Discuss the importance of third law of thermodynamics.
- 2) Give the explanation of Planck's statement of the third law of thermodynamics. How is it modified by Simon?
- 3) State and explain the Nernst statement of the third law.
- 4) Is it possible to cool a substance to absolute zero? Justify your answer.
- 5) Is Curie's law applicable for temperatures tending to absolute zero? Explain.
- 6) Why there is a need to modify the ideal gas model, especially near absolute zero?
- 7) What is the significance of the third law of thermodynamics?

#### 10.5.2 Objective questions

1. **The measure of disorder of the molecules of the system is**
  - (a) Enthalpy
  - (b) Entropy
  - (c) Both these
  - (d) None of these
2. **The statement that the total amount of energy in the universe is constant is governed by**
  - (a) First Law of Thermodynamics
  - (b) Second Law of Thermodynamics
  - (c) Third Law of Thermodynamics
  - (d) None of these
3. **The entropy of a perfectly crystalline structure is Zero. This statement is governed by**
  - (a) First Law of Thermodynamics
  - (b) Second Law of Thermodynamics
  - (c) Third law of Thermodynamics
  - (d) Hess law of constant heat summation

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4. **According to the Einstein when temperature falls to absolute zero, the entropy**
- (a) Becomes zero
  - (b) Remains finite
  - (c) Becomes infinite
  - (d) remains unaffected
5. **The ideal gas model fails at temperatures near absolute zero because**
- (a) The gases becomes solid
  - (b) The interaction between gas molecules vanishes
  - (c) The gas molecules are no longer independent
  - (d) None of these
6. **The low temperature behavior of heat capacities is conveniently explained by**
- (a) The third law of thermodynamics
  - (b) Debye law
  - (c) Dulong-petit's law
  - (d) Einstein's law

### 10.6 Glossary

**Gibbs free energy:** It is defined as the thermodynamic potential that measures the usefulness work that can be obtained from a thermodynamic system at a constant temperature and pressure.

**Enthalpy:** It is a measure of the total energy (sum of the internal energy and energy required to make room for pressure and volume) of a thermodynamic system.

**Degeneracy:** This term is related with the quantum mechanics which could be understood as the property of the states sharing same energy level. If for a given temperature, the two states of a thermodynamic system are in same energy level, then the states are said to be degenerate with degeneracy of 2.

**Perfect crystal:** It is the lowest energy phase of the solids that could be achieved by cooling it down to zero. This phase of the matter indicates the ground state having maximum possible ordering.

**Internal equilibrium:** A condition in which all parts of the system are in equilibrium with each other.

**Thermal expansion:** It is the tendency of matter to change in volume in response to a change in temperature.

**Magnetic susceptibility:** It is the quantitative measure of the extent to which a material may be magnetized in relation to a given applied magnetic field.

**Neel point:** It is the transition temperature above which an anti-ferromagnetic substance becomes paramagnetic.

**Curie point:** It is the transition temperature above which a ferromagnetic substance becomes paramagnetic.

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