

The entropy of the universe is continuously increasing.

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ENTROPY AND THE LAWS OF THERMODYNAMICS

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STUDY GUIDE

In the previous unit, you have learnt how to obtain the expression for efficiency of Carnot engine and coefficient of performance of a refrigerator using an indicator diagram. In this unit, you will learn about entropy, which is a variable of state and used to state the second law of thermodynamics. You will learn that entropy is a mathematical tool. That is, unlike temperature and pressure, entropy cannot be measured. You will also learn how to obtain expressions for entropy changes for a few typical thermodynamic systems.

The expression for efficiency of a Carnot engine can be obtained rather easily using the temperature-entropy (T - S) diagram. You will learn that the calculation of the absolute value of entropy is not possible even for a reversible process. However, the behaviour of entropy at low temperatures approaching absolute zero led Nernst to postulate the third law of thermodynamics. This statement was subsequently modified by Planck. You will learn about these developments here. The mathematics used in this unit is very simple but physical concepts are of fundamental importance. Therefore, you should focus on understanding the underlying physics. Answering SAQs and solving TQs on your own would help you enjoy this unit.

“Our greatest weakness lies in giving up. The most certain way to succeed is always to try just one more time.”

***Thomas Alva
Edison***

9.1 INTRODUCTION



Rudolf Julius Emanuel Clausius (1822-1888) was a German physicist, who is famous for his significant contributions to kinetic theory of gases and thermodynamics. His pioneering work on convertibility of heat into work led to the formulation of the second law of thermodynamics in 1850. Later on, he also introduced the concept of entropy.

From experience we know that heat flows from a body at higher temperature to a body at lower temperature spontaneously. But the reverse is not true, i.e., heat does not flow **on its own** from a body at lower temperature to a body at higher temperature. This is because cooling is a **unidirectional** natural process. You may be familiar with many other unidirectional processes occurring in physically diverse systems. We may mention spontaneous expansion of a gas into fixed volume (free expansion), battery discharge when in operation (chemical process), and intermixing of two fluids (diffusion), among others.

Do you know why natural processes take place in a particular direction? To discover an answer to this question, we need to know: What determines the direction of a natural process? Can we give a quantitative thermodynamic criterion which governs this change?

The answer to these and many other such questions was given by Clausius in 1850 when he introduced a new thermodynamic function called **entropy** (from the Greek word *tropos*, which means 'change'). Clausius showed that for natural processes, entropy of the universe always increases. That is, natural processes evolve in the direction of increase of entropy.

But you may now ask: What is entropy? Entropy characterises disorder in a system. It is a mathematical tool, an abstract property and it cannot be measured like temperature, pressure or volume. For simplicity, we first define entropy with reference to a reversible process in Sec. 9.2, though all natural processes are irreversible and this definition holds for these as well.

In Sec. 9.3, we have postulated the second law of thermodynamics in terms of entropy and established the combined form of the first and second laws of thermodynamics. You will learn how to derive expressions for changes in entropy of an ideal gas in Sec. 9.4. This is followed by the derivation of the expression for the efficiency of a Carnot engine using T - S diagram. In Sec. 9.6, you will learn about the behaviour of entropy at absolute zero and the third law of thermodynamics.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ define entropy and state second law of thermodynamics in terms of entropy;
- ❖ calculate entropy change for a system when it undergoes a reversible/irreversible change;
- ❖ represent Carnot cycle on T - S diagram and derive expression for efficiency of a heat engine; and
- ❖ state third law of thermodynamics and discuss its important consequences.

9.2 DEFINING ENTROPY

To define entropy, let us consider n moles of an ideal gas at temperature T and pressure p enclosed in an insulated cylinder fitted with a frictionless piston. On a p - V diagram, this state of the system is represented as shown in Fig. 9.1. Suppose that now an infinitesimal amount of heat δQ is added reversibly along the path 1A2 to the system. Using the first law of thermodynamics, we can write:

$$\delta Q_{rev} = nc_V dT + pdV \quad (9.1a)$$

The subscript *rev* signifies that we are considering a *reversible* process.

On dividing Eq. (9.1a) throughout by T , we can write:

$$\frac{\delta Q_{rev}}{T} = nc_V \frac{dT}{T} + \frac{p}{T} dV \quad (9.1b)$$

Using the equation of state for an ideal gas ($pV = nRT$), we can write:

$$\frac{p}{T} = \frac{nR}{V}$$

Using this result in Eq. (9.1b), we obtain:

$$\frac{\delta Q_{rev}}{T} = nc_V \frac{dT}{T} + nR \frac{dV}{V}$$

Now suppose that as a result of addition of heat, the system changes from initial state 1 to final state 2. Then, the net change in the value of $\frac{\delta Q_{rev}}{T}$ is given by:

$$\int_1^2 \frac{\delta Q_{rev}}{T} = \int_1^2 nc_V \frac{dT}{T} + nR \int_1^2 \frac{dV}{V}$$

Let us now suppose that the initial and final states are characterized by the thermodynamic variables (V_1, T_1) and (V_2, T_2) , respectively. If we assume that c_V does not change when heat is added reversibly, we can readily carry out integration to obtain:

$$\int_1^2 \frac{\delta Q_{rev}}{T} = nc_V \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right) \quad (9.2)$$

Before proceeding further, let us interpret this result. It tells us that the value of $\frac{\delta Q_{rev}}{T}$ depends on V_1, V_2, T_1 and T_2 .

In other words, the value of $\frac{\delta Q_{rev}}{T}$ can be determined by considering the temperatures and volumes corresponding to the initial and final states of the system. We express this by saying that $\frac{\delta Q_{rev}}{T}$ defines a new property of the gas and is characteristic of the state.

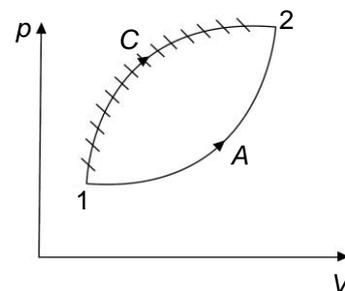


Fig. 9.1: Representation of a reversible process on p - V diagram.

You would recognise that it is immaterial how the system got in that state. How can you justify this?

To this end, we recall from Unit 7 of Block 2 that δQ_{rev} is an inexact differential, i.e., a function of path. But the value of $\frac{\delta Q_{rev}}{T}$, which is the ratio of a path function and a state variable, is determined only by the initial and final states. This is possible only when $\frac{\delta Q_{rev}}{T}$ defines a change in some new function. This function is called **entropy** and is denoted by the symbol S . So, we write:

$$dS = \frac{\delta Q_{rev}}{T} \quad (9.3)$$

You will recognise that we have postulated existence of entropy in Eq. (9.3).

Mathematically, an inexact differential can be made exact by introducing an *integrating factor*. Therefore, we can say that here T^{-1} acts as an integrating factor for δQ_{rev} .

In words, when we add an infinitesimal amount of heat δQ_{rev} reversibly to a system at constant temperature T , its entropy changes by $\frac{\delta Q_{rev}}{T}$.

In SI units, entropy is expressed in joule per kelvin (JK^{-1}). Like pressure, volume and temperature, entropy is also a thermodynamic state variable. Can we classify entropy as an extensive variable? Certainly yes, and we define *specific entropy* as entropy per mole or per unit mass.

$$s = \frac{S}{n} \quad \text{or} \quad s = \frac{S}{m}$$

Let us now pause for a while and ask: How good is the relation contained in Eq. (9.3)? It may be mentioned here that although we arrived at Eq. (9.3) by considering a gaseous system, it holds for every thermodynamic system. Moreover, this equation enables us to write an expression for the change in entropy for any system:

$$S_2 - S_1 \equiv \Delta S = \int_1^2 \frac{\delta Q_{rev}}{T} \quad (9.4)$$

The limits on the integral refer to two thermodynamic states of entropies S_1 and S_2 . You can draw the following inferences from Eq. (9.4):

- i) For a reversible cycle, net change in entropy will be zero, i.e., entropy does not change or is conserved in a reversible process.
- ii) We can calculate change in entropy rather than its absolute value.
- iii) The entropy of a system in a given state relative to some arbitrary intermediate state (n) can be expressed as

$$S = S_n + \int_n^2 \frac{\delta Q_{rev}}{T} \quad (9.5)$$

where S_n signifies entropy of the intermediate state.

- iv) Eq. (9.4) has been derived for a reversible process. You may now ask: How will this equation modify for natural processes like free expansion

Entropy is analogous to gravitational potential energy, which is specified with respect to some reference level.

or heat flow? To discover the answer to this question, refer to Fig. 9.1 again and consider heat flow along the path 1C2, which is an irreversible process. You may like to know as to how the method of calculation of entropy is modified in this case. To this end, we assume that heat is given in infinitesimal steps so that irreversible process between states 1 and 2 can be replaced by a reversible process through infinite quasi-static equilibrium states. It means that we can use Eq. (9.4) to calculate the entropy change for each quasi-static state. Therefore, we can conclude that Eq. (9.4) is valid for irreversible processes as well for the same initial and final states. This is because entropy is a property of state and the entropy difference does not depend on how a system got into that state.

Before proceeding further, you should recapitulate what you have learnt about entropy so far in this section.

ENTROPY

Recap

- Entropy for a reversible process is defined through the relation

$$\Delta S = \frac{\delta Q_{rev}}{T}$$

where δQ_{rev} is the amount of heat given reversibly.

- For a reversible cycle, net change in entropy will be zero, i.e., entropy is conserved in a reversible process.
- Between states 1 and 2, the change in entropy for reversible process for n moles of a gas is given by:

$$S_2 - S_1 \equiv \Delta S = \int_1^2 \frac{\delta Q_{rev}}{T}$$

- We can calculate change in entropy rather than its absolute value.
- Eq. (9.4) can also be used to calculate the change in entropy even for an irreversible process.

Now we would like you to go through the following examples to grasp the concepts discussed above.

EXAMPLE 9.1: ENTROPY CALCULATION

Two blocks of iron are in thermal contact. The temperature of block A is 300K and that of block B is infinitesimally higher than 300K. The blocks are so large that 600 J of heat transferred from B to A leaves their temperatures unchanged. Calculate the entropy change of the individual blocks and also the total entropy change. Take the process to be reversible.

SOLUTION ■ Since block A is at lower temperature, it will absorb heat. You can calculate the entropy change using Eq. (9.3):

The entropy change for block A , $\Delta S_A = \frac{\delta Q_A}{T} = \frac{600 \text{ J}}{300 \text{ K}} = 2 \text{ JK}^{-1}$

The entropy change for block B , $\Delta S_B = \frac{\delta Q_B}{T} = -\frac{600 \text{ J}}{300 \text{ K}} = -2 \text{ JK}^{-1}$

The negative sign is included with ΔS_B as B loses heat. This means that entropy of a system increases when it is heated and vice versa.

Total entropy change, $\Delta S = \Delta S_A + \Delta S_B = 2 \text{ JK}^{-1} - 2 \text{ JK}^{-1} = 0$

That is, when heat transfer is reversible, there is no net change in entropy and you can say that entropy is conserved in a reversible process.

EXAMPLE 9.2: CHANGE IN ENTROPY OF A SYSTEM

A block of copper of mass 1.5 kg is heated from 300 K to 350 K . Calculate the change in entropy of the block. The specific heat capacity of copper is $389 \text{ J kg}^{-1} \text{ K}^{-1}$. Assume that heat is added irreversibly.

SOLUTION ■ Although heat has been added irreversibly, we can calculate ΔS using Eq. (9.4):

$$\Delta S = \int_{300 \text{ K}}^{350 \text{ K}} \frac{\delta Q_{\text{rev}}}{T} \quad (\text{i})$$

The heat absorbed for an infinitesimal rise in temperature is given by:

$$\delta Q_{\text{rev}} = ms\Delta T \quad (\text{ii})$$

where m is mass and s is specific heat capacity of the block. On inserting the given data in Eq. (ii), we find that

$$\delta Q_{\text{rev}} = (1.5 \text{ kg}) \times (389 \text{ J kg}^{-1} \text{ K}^{-1}) \times \Delta T$$

$$\begin{aligned} \therefore \Delta S &= \int_{300 \text{ K}}^{350 \text{ K}} \frac{(1.5 \text{ kg}) \times (389 \text{ J kg}^{-1} \text{ K}^{-1}) \times \Delta T}{T} = 583.5 \ln \left(\frac{350}{300} \right) \text{ JK}^{-1} \\ &= 583.5 \times 2.303 \times \log_{10}(1.67) \text{ JK}^{-1} = 90.0 \text{ JK}^{-1} \end{aligned}$$

You should not confuse small letter s with entropy.

You may now like to answer an SAQ to check your understanding.

SAQ 1 – Entropy change

One kg water at 27°C and 1 atm pressure is heated to 80°C at the same pressure. Calculate the change in entropy. Take specific heat capacity of water as $4.2 \times 10^3 \text{ JK}^{-1} \text{ kg}^{-1}$.

Before proceeding further, you may like to know the physical significance of entropy. So far, we have not said anything about it. We know that when heat

is added to ice, it melts and the molecular arrangement (in water) is somewhat loosened (compared to ice). If you add more heat, water may change to the vapour state. In vapour state, molecules are relatively far apart and molecular motion is quite disordered. So, we can say that **addition of heat (or increase in entropy) creates disorder**. On the other hand, when a gas condenses or a liquid solidifies (giving out heat), the molecular arrangement becomes more ordered. That is, disorder decreases when a gaseous substance changes into the solid state. From this discussion we can conclude that **entropy is a measure of disorder** in the system.

So far, we have introduced the concept of entropy and calculated entropy change in a reversible/irreversible process. You may now ask: How does such a change influence the system, its surroundings and hence the universe? The answer to this question leads us to the second law of thermodynamics. It applies to processes in our body, to combustion of fuel in an automobile, an aeroplane and a rocket as well as to working of refrigerators and other cooling machines. It enables us to specify the direction of evolution of natural processes. We now discuss it in detail.

9.3 ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

Consider that an infinitesimal amount of heat δQ flows from the surroundings at temperature T_{surr} to the system under consideration at temperature T_{sys} .

The net change in the entropies of the system and surroundings is given by

$$\Delta S = \Delta S_{sys} + \Delta S_{surr} = \delta Q \left(\frac{1}{T_{sys}} - \frac{1}{T_{surr}} \right) \geq 0 \quad (9.6)$$

Note that the equality sign holds for reversible heat flow, whereas greater than sign signifies irreversible heat flow. Since all natural processes are irreversible, you may be tempted to conclude that entropy of the universe is continuously increasing. If you think so, you are on the right track. This continuous increase of entropy in natural processes is known as the **principle of increase of entropy**. And the second law of thermodynamics may be stated as follows:

The entropy of the universe can never decrease.

Consider the construction of a building from materials that were initially dispersed in the Earth. In this process, matter goes from a completely disorganized state to a highly ordered state. That is, the entropy decreases. In Unit 7 of Block 2, you have learnt that the internal energy of a growing child or a plant increases. But the growth of a living organism from a random mix of molecules is accompanied by decrease in entropy. These examples may seem to you to contradict the first and second laws of thermodynamics. But it is not so. To understand this, let us enquire: What is responsible for life on the Earth? We can trace it to the energy generated in the Sun's core by nuclear

Recall that the second law has been stated in somewhat different but essentially equivalent forms by Kelvin-Planck and Clausius. You have learnt about these in Unit 8.



Don't forget

fusion ($H_2 \rightarrow He$ cycle). For example, plants use solar energy for photosynthesis and create food. Similarly, humans receive this energy via food chain. So, to answer the above question, you have to consider the Earth-Sun system. When you do so, you will find that the magnitude of entropy decrease associated with life on the Earth is less than the entropy increase associated with nuclear reaction in the core of the Sun. That is, the organisation of matter is governed by a tendency towards greater disorder elsewhere in the universe (Sun in this case). Thus, a more formal statement of the second law in terms of entropy reads as follows:



When an isolated system undergoes a change, its entropy cannot decrease; it increases or remains constant.

In view of the above discussion, can we say that entropy of the universe has continuously increased ever since its creation? Definitely, yes.

You must now be convinced that the second law relates (available) energy to entropy. We can use the integrated statement of these laws to obtain an expression for entropy difference for any process. This is illustrated in the next section.

9.3.1 The Combined Form of the First and Second Laws

The first law of thermodynamics establishes the existence of internal energy (U) as a function of state. Similarly, the second law introduces entropy (S) as a state function. You may now ask: Can we relate these functions? You may recall from Unit 7 that for any change of state, the change in internal energy is given by

$$dU = \delta Q - \delta W \quad (9.7)$$

Similarly, for an infinitesimal reversible process between two equilibrium states, the second law of thermodynamics tells us that

$$dS = \frac{\delta Q}{T} \quad (9.8)$$

These equations may be combined to obtain mathematical expression for the combined form of the first and the second laws of thermodynamics:

$$TdS = dU + \delta W \quad (9.9)$$

This is one of the most important thermodynamic relations. In the next unit, you will use it to derive many useful thermodynamic relations.

Proceeding further, we note that for a gaseous system, $\delta W = pdV$ so that Eq. (9.9) takes the form

$$TdS = dU + pdV \quad (9.10)$$

Note that this equation relates all five thermodynamic variables that you have learnt so far.

Using the results obtained in Unit 8, we can rewrite Eq. (9.10) in three equivalent forms:

$$TdS = nC_V dT + pdV \quad (9.11a)$$

$$TdS = nC_P dT - Vdp \quad (9.11b)$$

and
$$TdS = \frac{1}{R}(C_P pdV + C_V Vdp) \quad (9.11c)$$

where C_P and C_V , respectively, denote molar thermal capacities at constant pressure and constant volume. Note that dS denotes change in molar entropy.

Before proceeding further, you may like to answer the following SAQ.

SAQ 2 – First and second law of thermodynamics

Write the combined mathematical forms of the first and second laws of thermodynamics for a i) stretched wire, ii) surface film, and iii) paramagnetic substance.

Before proceeding further, we recapitulate the important results of this section.

ENTROPY AND THE FIRST AND SECOND LAWS

Recap

- The second law of thermodynamics states that when an isolated system undergoes a change, its entropy either increases or remains constant.
- In the most general form, the combined form of the first and the second laws of thermodynamics can be mathematically expressed as

$$TdS = dU + \delta W$$

We now use Eqs. (9.11a, b, c) to obtain expressions for changes in entropy for an ideal gas under different physical conditions.

9.4 ENTROPY CHANGE OF AN IDEAL GAS

Consider n moles of an ideal gas at temperature T in a cylinder fitted with a frictionless piston. Depending on the physical conditions, we can use one of the relations given in Eqs. (9.11a, b, c) to obtain an expression for change in entropy. Suppose that the gas is given an infinitesimal amount of heat, which induces changes in temperature and volume. We can describe such a change by Eq. (9.11a). On dividing throughout by T and substituting for p from the equation of state ($pV = nRT$), we get

$$dS = nC_V \frac{dT}{T} + nR \frac{dV}{V} \quad (9.12)$$

Let us now suppose that the initial and final states are characterized by the thermodynamic variables (V_1, T_1) and (V_2, T_2) , respectively. If we assume that C_V is independent of temperature, we can readily integrate Eq. (9.12) to obtain the same result as given in Eq. (9.2):

$$\Delta S = nC_V \ln \left(\frac{T_2}{T_1} \right) + nR \ln \left(\frac{V_2}{V_1} \right) \quad (9.13)$$

You should study the following example to learn how to apply this result.

EXAMPLE 9.3: CHANGE IN ENTROPY

Calculate the increase in entropy of 1 g of hydrogen when its temperature is raised from -173°C to 27°C and its volume becomes four times. It is given that $C_V = 2.43 \text{ cal g}^{-1} \text{ K}^{-1}$, $R = 2.01 \text{ cal mol}^{-1} \text{ K}^{-1}$ and molecular weight is 2 g mol^{-1} .

SOLUTION ■ For n moles of an ideal gas, the entropy change is calculated using Eq. (9.13). However, for 1g of the gas, you have to replace nC_V by C_V and nR by $r = R/\text{mol. weight}$:

$$r = \frac{2.01 \text{ cal mol}^{-1} \text{ K}^{-1}}{2 \text{ g mol}^{-1}} = 1.005 \text{ cal g}^{-1} \text{ K}^{-1}$$

From Eq. (9.13) we recall that change in entropy is given by

$$\Delta S = 2.303 \left[C_V \log_{10} \left(\frac{T_2}{T_1} \right) + (1.005 \text{ cal g}^{-1} \text{ K}^{-1}) \log_{10} \left(\frac{V_2}{V_1} \right) \right]$$

Here $T_1 = (-173 + 273)\text{K} = 100\text{K}$, $T_2 = (27 + 273)\text{K} = 300\text{K}$, and $C_V = 2.43 \text{ cal g}^{-1} \text{ K}^{-1}$. On inserting the given values, we get

$$\begin{aligned} \Delta S &= 2.303 \times [(2.43 \text{ cal g}^{-1} \text{ K}^{-1}) \times \log_{10} 3 + (1.005 \text{ cal g}^{-1} \text{ K}^{-1}) \times \log_{10} 4] \\ &= 2.303 \times (2.43 \times 0.4771 + 1.005 \times 0.6021) \text{ cal g}^{-1} \text{ K}^{-1} \\ &= 4.062 \text{ cal g}^{-1} \text{ K}^{-1}. \end{aligned}$$

Starting from Eq. (9.11b), you can easily convince yourself that the entropy change between states defined by (T_1, p_1) and (T_2, p_2) is given by

$$\Delta S = nC_P \ln \left(\frac{T_2}{T_1} \right) - nR \ln \left(\frac{p_2}{p_1} \right) \quad (9.14)$$

Similarly, if reference states are defined by (p_1, V_1) and (p_2, V_2) , the entropy change is given by

$$\Delta S = nC_P \ln \left(\frac{V_2}{V_1} \right) - nC_V \ln \left(\frac{p_2}{p_1} \right) \quad (9.15)$$

A gas may be made to expand or compress isothermally. When n moles of an ideal gas are made to undergo isothermal changes, Eqs. (9.13) and (9.14) predict that entropy changes are, respectively, given by

$$\Delta S_T = nR \ln \left(\frac{V_2}{V_1} \right) \quad (9.16a)$$

and
$$\Delta S_T = R \ln \left(\frac{p_1}{p_2} \right) \quad (9.16b)$$

The subscript T in ΔS_T signifies that temperature remains constant. That is, *when an ideal gas undergoes an isothermal expansion defined by ($V_2 > V_1, p_1 > p_2; T = \text{constant}$), its entropy increases.* When a gas undergoes isothermal compression, entropy will decrease.

For isobaric changes, Eqs. (9.14) and (9.15) predict that

$$\Delta S_P = nC_P \ln \left(\frac{T_2}{T_1} \right) \quad (9.17a)$$

and
$$\Delta S_P = nC_P \ln \left(\frac{V_2}{V_1} \right) \quad (9.17b)$$

These results tell us that when either temperature or volume increases during an isobaric process, the entropy increases and vice versa.

Now you should go through the following example carefully.

EXAMPLE 9.4: ENTROPY CHANGE IN TERMS OF R

One mole of an ideal gas expands isothermally to four times its initial volume. Calculate the entropy change in terms of the gas constant.

SOLUTION ■ For one mole of an ideal gas, Eq. (9.16) implies that

$$\frac{\Delta S_T}{R} = \ln(V_2 / V_1) = 2.303 \log_{10}(V_2 / V_1)$$

Since $V_2 / V_1 = 4$, the entropy change during isothermal expansion, in terms of gas constant, is given by

$$\begin{aligned} \frac{\Delta S_T}{R} &= 2.303 \log_{10} 4 \\ &= 2.303 \times 0.6020 = 1.386 \end{aligned}$$

You may like to answer the following SAQ before studying further.

SAQ 3 – Increase in entropy

Calculate the increase in entropy of one mole of argon heated from 300K to 600K at constant volume.

9.4.1 Entropy of Mixing

Refer to Fig. 9.2. Suppose that the hollow circles depict n_1 moles of oxygen and solid circles denote n_2 moles of nitrogen in two separate containers at constant temperature T and pressure p . The gases are separated by means of a stopcock. We assume that these gases behave as an ideal gas. You may now like to know: What happens when the stopcock is opened and these gases mix? To answer this question, let us assume that partial pressures of oxygen and nitrogen in the mixture are p_1 and p_2 , respectively.

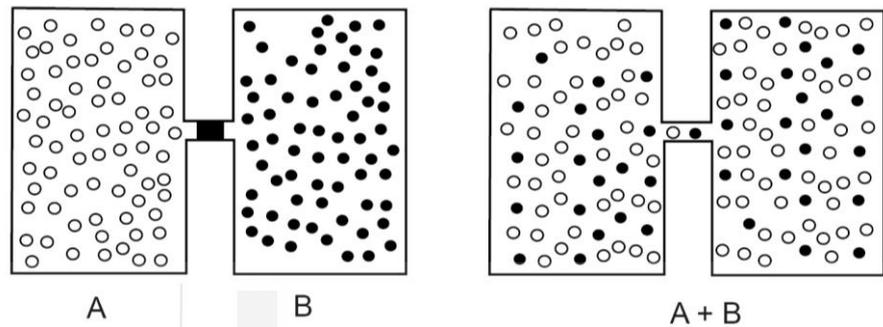


Fig. 9.2: Intermixing of two gases.

The entropy of mixing is equal to the sum of the entropy changes for each gas as it expands from its initial pressure to its partial pressure in the mixture. The changes in entropies ΔS_1 and ΔS_2 for the two gases when mixing takes place at constant T can be obtained using Eq. (9.14):

$$\Delta S_1 = -n_1 R \ln \left(\frac{p_1}{p} \right) = n_1 R \ln \left(\frac{p}{p_1} \right)$$

and

$$\Delta S_2 = n_2 R \ln \left(\frac{p}{p_2} \right)$$

Hence, when the gases have mixed, the entropy of mixing is given by

$$\Delta S_{mix} = \Delta S_1 + \Delta S_2 = n_1 R \ln \left(\frac{p}{p_1} \right) + n_2 R \ln \left(\frac{p}{p_2} \right) \quad (9.18)$$

From your school curriculum in chemistry, you may recall that the partial pressures can be expressed in terms of total pressure as $p_1 = x_1 p$ and $p_2 = x_2 p$, where x_1 and x_2 are mole fractions of two gases. On substituting these values of p_1 and p_2 in Eq. (9.18), we obtain

$$\begin{aligned} \Delta S_{mix} &= n_1 R \ln \left(\frac{p}{x_1 p} \right) + n_2 R \ln \left(\frac{p}{x_2 p} \right) \\ &= -n_1 R \ln x_1 - n_2 R \ln x_2 \end{aligned} \quad (9.19)$$

Now suppose you have to compute the entropy of mixing per mole of the mixture. You can do so easily by dividing both sides of Eq. (9.19) by $n_1 + n_2$.

This gives

$$\frac{\Delta S_{mix}}{n_1 + n_2} = -R \left[\frac{n_1}{n_1 + n_2} \ln x_1 + \frac{n_2}{n_1 + n_2} \ln x_2 \right]$$

The ratios $\frac{n_1}{n_1 + n_2}$ and $\frac{n_2}{n_1 + n_2}$ define the mole fractions of two gases.

Hence, the entropy of mixing per mole of mixture is

$$\Delta S_{mix} = -R[x_1 \ln x_1 + x_2 \ln x_2] \quad (9.20)$$

Note that a negative sign occurs in the expression for entropy of mixing. Does this mean that entropy decreases in the process of mixing of two gases? If you think so, you are not correct.

Since x_1 and x_2 are less than one, the entropy of mixing will be always positive. Note that we have derived Eq. (9.20) for ideal gases. But it holds for liquids also where intermolecular forces between the components are uniform. The concept developed in this section is illustrated in the following example.

EXAMPLE 9.5: ENTROPY OF MIXING

Equal volumes of two gases are mixed under same temperature and pressure. The pressure remains unchanged but the total volume is doubled. Calculate the entropy of mixing for one mole of the mixture.

SOLUTION ■ Since the gases are initially at the same temperature and pressure, Avogadro's hypothesis tells us that equal volume will have equal number of molecules, i.e., $n_1 = n_2 = n$, say. Therefore, the mole fraction of each gas in one mole of the mixture is 0.5. Hence, the entropy of mixing is given by

$$\begin{aligned} \Delta S_{mix} &= -R[x_1 \ln x_1 + x_2 \ln x_2] \\ &= -(8.31 \text{ JK}^{-1} \text{ mol}^{-1})[0.5 \ln 0.5 + 0.5 \ln 0.5] = 5.76 \text{ JK}^{-1} \text{ mol}^{-1} \end{aligned}$$

We know that matter can change its state from solid to liquid (ice to water) and liquid to gas (water to steam) or solid to gas (dry ice, i.e., solid carbon dioxide to CO_2 gas) under appropriate conditions of temperature and pressure. Such a transformation is called **phase transition**. Conversion of ice to water is an example of first order phase transition. You will now learn to obtain expressions for entropy changes accompanying a phase transition.

9.4.2 Entropy Change of Phase Transition

We know that at atmospheric pressure, water boils at 100°C . But on hill stations, boiling begins below 100°C . In a physics laboratory also, you can make water boil below 100°C through a simple activity. Put some boiling water in a flask and allow it to cool. Then pour some water over the flask. You will observe that water begins to boil again even though it is below 100°C . It means that phase transition is determined by pressure. However, it is accompanied by absorption or evolution of heat. For an isobaric-isothermal process, the quantity of heat evolved or absorbed by a system defines enthalpy, H . Hence, the entropy change for an isothermal-isobaric process can be calculated using the relation

$$\Delta S = \frac{\delta Q_{rev}}{T} = \frac{\Delta H}{T} \quad (9.21)$$

You can use this result to compute the entropy change accompanying the transition of a solid to a liquid or a liquid to a vapour and vice versa.

When n mole of a solid melts to the liquid phase, the entropy of fusion is given by

$$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_{fusion}} \quad (9.22)$$

where ΔH_{fusion} is molar enthalpy of fusion and T_{fusion} is the melting point.

Similarly, for n mole of a substance, the entropy of evaporation is given by

$$\Delta S_{evap} = \frac{\Delta H_{evap}}{T_{evap}} \quad (9.23)$$

where ΔH_{evap} is molar enthalpy of vaporisation and T_{evap} is the boiling point.

In the following example, we have illustrated the use of some of these relations to compute entropy changes.

EXAMPLE 9.6: ENTROPY OF VAPORISATION

The enthalpy of vaporisation of ethanol is 43.5 kJ mol^{-1} at its normal boiling point of 351.5 K . Compute the entropy of vaporisation. The enthalpy of fusion of ethanol is 4.6 kJ mol^{-1} at its normal melting point of 156 K . Calculate the entropy of fusion.

SOLUTION ■ From Eq. (9.23), we recall that entropy of vaporisation is given by

$$\Delta S_{evap} = \frac{\Delta H_{evap}}{T_{evap}} = \frac{43500 \text{ J mol}^{-1}}{351.5 \text{ K}} = 124 \text{ JK}^{-1} \text{ mol}^{-1}$$

From Eq. (9.22), we note that entropy of fusion is given by

$$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_{fusion}} = \frac{4600 \text{ J mol}^{-1}}{156 \text{ K}} = 29.5 \text{ JK}^{-1} \text{ mol}^{-1}$$

You will note that $\Delta S_{evap} \gg \Delta S_{fusion}$. This difference shows that entropy increases as a system becomes less restricted. When a solid melts, its atoms become less ordered in their locations and motion. When a liquid vaporises, molecules gain considerably greater freedom of movement.

We would now like you to solve an SAQ.

SAQ 3 – Entropy of solidification

The melting point of water at 1 atm pressure is 273.16 K and the specific latent heat of melting is 334.4 Jg^{-1} . Calculate the entropy of solidification for one mole of water.

Before proceeding further, we would like you to recapitulate what you have learnt in this section.

Recap

ENTROPY CHANGE, ENTROPIES OF MIXING, FUSION AND EVAPORATION

- When n moles of an ideal gas undergo an isothermal transformation, the change in entropy is given by:

$$\Delta S_T = nR \ln \left(\frac{V_2}{V_1} \right) = nR \ln \left[\frac{p_1}{p_2} \right]$$

- For an isobaric process, change in entropy of a gas made up of n moles is given by:

$$\Delta S_P = nC_P \ln \left(\frac{V_2}{V_1} \right) = nC_P \ln \left[\frac{T_2}{T_1} \right]$$

- The entropy of mixing per mole of mixture of two gases is always positive:

$$\Delta S_{mix} = -R[x_1 \ln x_1 + x_2 \ln x_2]$$

where x_1 and x_2 are mole fractions.

- For one mole of a substance, the entropy of fusion is given by:

$$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_{fusion}}$$

and the entropy of evaporation is: $\Delta S_{evap} = \frac{\Delta H_{evap}}{T_{evap}}$.

Having established that entropy is a thermodynamic property of a system, we now discuss its significance in various reversible processes and draw corresponding T - S diagrams. These diagrams are often useful in engineering. As you know, the simplest and the most important reversible cycle is the **Carnot cycle**. You have learnt how to obtain an expression for the efficiency of a Carnot engine in Unit 8. Here we will show how the same result can be obtained more elegantly using a T - S diagram.

9.5 REPRESENTATION OF CARNOT CYCLE ON ENTROPY-TEMPERATURE DIAGRAM

Refer to Fig. 9.3. It is a schematic representation of the Carnot cycle on the T - S diagram.

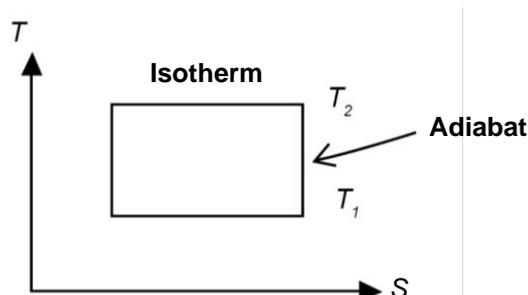


Fig. 9.3: Representation of Carnot cycle on T - S diagram.

You will recall that Carnot cycle consists of four reversible processes:

i) isothermal expansion, ii) adiabatic expansion, iii) isothermal compression, and iv) adiabatic compression.

You will note that the isotherms are horizontal straight lines for a given temperature, whereas the adiabats are vertical straight lines corresponding to constant S ($\delta Q = 0 = dS$). So, Carnot cycle is a rectangle on the T - S diagram. To obtain the expression for net entropy change in one cycle, let us consider n moles of an ideal gas is enclosed in a cylinder.

Step I: The gas absorbs heat Q_1 reversibly at temperature T_1 and expands isothermally. (The pressure decreases from p_1 to p_2 .) Using Eq. (9.3), we can write the increase in entropy of the gas as

$$\Delta S_1 = \frac{Q_1}{T_1} \quad (9.24a)$$

Step II: The gas expands adiabatically (but pressure falls from p_2 to p_3). We know that no heat exchange takes place between the system and its surroundings in an adiabatic process. Therefore, according to the first law of thermodynamics, expansion occurs at the expense of internal energy of the system. This, in turn, implies drop in temperature of the gas. Suppose that temperature drops from T_1 to T_2 . Since no heat transfer occurs, entropy does not change and we can write

$$\Delta S_2 = 0 \quad (9.24b)$$

Step III: The gas at temperature T_2 is now compressed isothermally. In this process, work is done on the gas and it gives up heat Q_2 to the environment. Then change in entropy is given by

$$\Delta S_3 = -\frac{Q_2}{T_2} \quad (9.24c)$$

Step IV: Finally, the gas is compressed adiabatically to its original volume and pressure. As a result, the gas attains its state and its entropy is conserved during the process:

$$\Delta S_4 = 0 \quad (9.24d)$$

Since Carnot cycle is reversible, there will be no net change in its entropy, i.e., $\Delta S = 0$ and we can write

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 = 0$$

On using Eqs. (9.24a to d), we get

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

$$\text{or} \quad \frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad (9.25)$$

This result shows that the ratio of the heat absorbed to the heat given out in a reversible cycle is equal to the ratio of the temperatures of the source and the sink. Since efficiency is ratio of work done and heat absorbed, we can write:

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

Using Eq. (9.25) we can write:

$$\eta = 1 - \frac{T_2}{T_1} \quad (9.26)$$

Note that the expression for efficiency of Carnot engine has been obtained more conveniently using T - S diagram as compared to the indicator diagram.

9.6 ENTROPY AT ABSOLUTE ZERO: THIRD LAW OF THERMODYNAMICS

From experience we know that the basic difficulty with all cooling processes is that it becomes gradually more difficult to achieve and maintain lower and lower temperatures. For example, the cooler a liquid is, the harder it becomes to maintain its temperature or pump it out to produce further cooling.

Suppose that temperature T_{f1} , say 10% of the initial temperature T_i is achieved in one mechanical step. The second step will produce a temperature T_{f2} which is approximately 10% of T_{f1} . This means that even by an infinite number of adiabatic processes, it would not be possible to attain absolute zero. From this we may conclude that

The absolute zero is not attainable by any number of mechanical processes.



Don't forget

Like the second law, the third law can also be stated in terms of entropy. But before giving that statement, we would like you to relook at Eq. (8.5). It can be re-written as

$$S = S_n + \int_n^f \frac{\delta Q_{rev}}{T} \quad \text{where } f \text{ is the final state.}$$

It helps us to determine the change in entropy of a system during a reversible process. But absolute entropy remains indeterminate because of the presence of an additive constant (S_n). You may now ask: Can we determine this constant? The answer to this question constitutes another statement of the third law. It defines the entropy of a system as its temperature tends to absolute zero.

Nernst observed that at low temperatures entropy change of a system is very small when we go from one equilibrium state to another. It is because near absolute zero, all systems are highly ordered and the entropy of all states (of every substance) is almost constant. This prompted Nernst to state the third law as follows:

The entropy changes associated with any reversible isothermal process tend to zero as temperature approaches absolute zero.



Don't forget

Mathematically, this is expressed as:

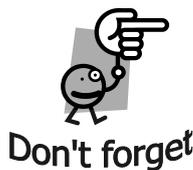
$$\lim_{T \rightarrow 0} \Delta S \rightarrow 0 \quad (9.27)$$

This fact beautifully manifests in the case of liquid helium-II and superconductors. To understand this, we recall Clausius-Clapeyron equation:

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V}$$

You will recognise that $\frac{dp}{dT}$ defines the slope of the melting curve. Eq. (9.27) predicts that the curve should become horizontal ($\Delta S = 0$) as $T \rightarrow 0$.

In 1912, Planck extended this idea by proposing that near absolute zero, entropy of every substance is so small that it can be taken as essentially zero. He stated the third law of thermodynamics as follows:



The entropy of every substance is zero at the absolute zero.

Mathematically, this is expressed as:

$$\lim_{T \rightarrow 0} S \rightarrow 0 \quad (9.28)$$

Today, this law is supported by ample experimental evidences and finds wide applications in low temperature physics. We now discuss some important consequences of the third law.

9.6.1 Consequences of the Third Law

i) Behaviour of thermodynamic potentials

We know that $G = H - TS$ and $F = U - TS$. According to the third law of thermodynamics, as $T \rightarrow 0, S \rightarrow 0$ so that the product $TS \rightarrow 0$. That is, when temperature approaches absolute zero, Gibbs potential equals enthalpy and Helmholtz potential equals internal energy. Physically, it means that there is perfect order and entire energy is available for work.

ii) Iso-thermal volume and pressure expansion coefficients

The changes in entropy of a system due to small changes in pressure during a process near absolute zero may be expressed as

$$\Delta S = \int \left(\frac{\partial S}{\partial p} \right)_T dT \quad (9.29)$$

But according to the third law of thermodynamics, as $T \rightarrow 0, \Delta S \rightarrow 0$. So we can say that

$$\lim_{T \rightarrow 0} \left(\frac{\partial S}{\partial p} \right)_T \rightarrow 0$$

Using Maxwell's relation $\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p$, we can write:

$$\lim_{T \rightarrow 0} \left(\frac{\partial V}{\partial T} \right)_p \rightarrow 0 \quad (9.30)$$

By definition, $\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$ is the coefficient of volume expansivity, α . So,

$$\lim_{T \rightarrow 0} \alpha \rightarrow 0 \quad (9.31)$$

Similarly, you can convince yourself that

$$\lim_{T \rightarrow 0} \left(\frac{\partial p}{\partial T} \right)_V = 0 \quad (9.32)$$

iii) Heat capacities near absolute zero

Recall that specific heat capacity at constant pressure is defined as

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_p$$

Hence, at constant pressure, we can take

$$dS = \frac{C_p dT}{T}$$

By integrating it between finite temperature limits, we can write

$$S(T_1) - S(T) = \int_T^{T_1} \frac{C_p dT}{T} \quad (9.33)$$

In the limit $T \rightarrow 0$, the third law implies that the integral on the right hand side of Eq. (9.33) should be finite. That is, it should not diverge as $T \rightarrow 0$.

Thus, we must have

$$\lim_{T \rightarrow 0} C_p = 0 \quad (9.34)$$

Similarly, it can be shown that as $T \rightarrow 0$

$$\lim_{T \rightarrow 0} C_V = 0 \quad (9.35)$$

It shows that in the limit $T \rightarrow 0$, the specific heat capacities attain the same value. This prediction of the third law is borne out by experiments rather well. Let us recapitulate what you have learnt in this section

THIRD LAW OF THERMODYNAMICS

Recap

Entropy of a system at absolute zero is zero and the system is in perfect order. It essentially implies non-attainability of absolute zero temperature.

9.7 SUMMARY

Concept	Description
Entropy	<ul style="list-style-type: none"> Entropy is defined through the relation $dS = \frac{\delta Q_{rev}}{T}$ Entropy is an extensive variable and a state function.
Second law of thermodynamics in terms of entropy	<ul style="list-style-type: none"> Entropy is a measure of disorder in the system; more chaotic the system, greater will be its entropy. The second law of thermodynamics is essentially the principle of increase of entropy. It states that, when a closed system undergoes a change, its entropy cannot decrease; it either increases or remains constant. Mathematically, it may be expressed as $\Delta S \geq 0$
Entropy change of an ideal gas	<ul style="list-style-type: none"> The entropy change of an ideal gas made up of n moles can be calculated using the relations $\begin{aligned} \Delta S &= nC_V \ln \left(\frac{T_2}{T_1} \right) + nR \ln \left(\frac{V_2}{V_1} \right) \\ &= nC_P \ln \left(\frac{V_2}{V_1} \right) + nC_V \ln \left(\frac{p_2}{p_1} \right) \\ &= nC_P \ln \left(\frac{T_2}{T_1} \right) - nR \ln \left(\frac{p_2}{p_1} \right) \end{aligned}$
Third law of thermodynamics	<ul style="list-style-type: none"> Third law of thermodynamics states that equilibrium entropies of all systems and the entropy changes in all reversible isothermal processes tend to zero as temperature approaches absolute zero.

9.8 TERMINAL QUESTIONS

- A huge copper block at 1000K is joined to another huge copper block at 500K by a copper rod. The rate of heat conduction is 10^4 Js^{-1} . Calculate the increase in entropy of the universe due to this process.
- Eddington proposed that entropy is the arrow of time. Comment.
- m g of water at temperature T_1 is mixed with an equal mass of water at temperature T_2 . Show that the change in entropy is

$$2mC_P \ln \left(\frac{T_{av}}{\sqrt{T_1 T_2}} \right) \text{ where } T_{av} = \frac{T_1 + T_2}{2} \text{ is average temperature.}$$

- 20 g of ice at 0°C is converted into water at the same temperature. Calculate the change in entropy. [Given: Latent heat of fusion (L) = 80 cal/g].

- Calculate the change in entropy when 10 g of ice at 0°C is converted into steam. [Given: latent heat of fusion of ice = 80 cal/g; latent heat of fusion of steam = 540 cal/g].
- Write the third law of thermodynamics in terms of entropy differences.

9.9 SOLUTIONS AND ANSWERS

Self-assessment Questions

- The change in entropy when 1 kg water is heated from 27°C (= 300K) to 80°C (= 353K) is given by

$$\Delta s = \int_{300}^{353} \frac{mcdT}{T} = mc \ln \left(\frac{353}{300} \right)$$

On substituting the given values, we get

$$\begin{aligned} \Delta s &= (1\text{kg}) \times (4.2 \times 10^3 \text{Jkg}^{-1}\text{K}^{-1}) \ln \left(\frac{353}{300} \right) \\ &= (4.2 \times 10^3 \text{Jkg}^{-1}\text{K}^{-1}) \times 0.163 \text{JK}^{-1} = 6.84 \times 10^2 \text{JK}^{-1} \end{aligned}$$

- a) $TdS = dU - Fdl$; b) $TdS = dU - \sigma dA$ and c) $TdS = dU - BdM$

- $\Delta S_V = nC_V \ln \left(\frac{T_2}{T_1} \right) = C_V \ln 2$

Since $C_V = \frac{3}{2}R$, we find that

$$\Delta S_V = \frac{3}{2} \times (8.314 \text{JK}^{-1} \text{mol}^{-1}) \ln 2 = 8.64 \text{JK}^{-1}$$

- $\Delta S_{melt} = \frac{m\Delta\ell}{T_{melt}} = \frac{18\text{g} \times 334.4\text{Jg}^{-1}}{273.16\text{K}} = \frac{6019.2\text{J}}{273.16\text{K}} = 22 \text{JK}^{-1}$

Terminal Questions

- By carrying out the heat transfer reversibly, we can calculate that

$$\Delta S = (q/T_1) - (q/T_2) = 10^4 \text{Js}^{-1} [(1/500\text{K}) - (1/1000\text{K})] = 10 \text{JK}^{-1}\text{s}^{-1}$$

Thus, the entropy of the universe increases by 10 JK⁻¹ per second.

- The statement is justified. If you calculate entropy of the universe at two different times, the point of higher entropy would correspond to the point of later time. This statement is further justified by the fact that the universe has been expanding uniformly ever since its creation. Even if one observed the motion of galaxies, these are found receding with respect to any point of observation. This means that the entropy of the universe is increasing continuously, as does time.
- Since the masses of water being mixed are equal, the temperature of the mixture will be the arithmetic mean of T_1 and T_2 :

$$T_{\text{mix}} = \frac{T_1 + T_2}{2} = T_{\text{av}}$$

Since the process is isobaric, the change in entropy of water sample whose temperature rises from T_1 to T_{av} is given by:

$$\Delta S_1 = \frac{\delta Q}{T} = m C_P \ln \left(\frac{T_{av}}{T_1} \right) \quad (i)$$

Similarly, the change in entropy of water sample whose temperature falls from T_2 to T_{av} is:

$$\Delta S_2 = m C_P \ln \left(\frac{T_{av}}{T_2} \right) \quad (ii)$$

Hence, the net change in entropy is:

$$\Delta S = \Delta S_1 + \Delta S_2 = m C_P \ln \left(\frac{T_{av}}{T_1} \right) + m C_P \ln \left(\frac{T_{av}}{T_2} \right) \quad (iii)$$

Since $\ln a + \ln b = \ln(ab)$, you can write it as $\Delta S = m C_P \ln \left(\frac{T_{av}^2}{T_1 T_2} \right)$

$$= m C_P \ln \left(\frac{T_{av}}{\sqrt{T_1 T_2}} \right)^2 = 2 m C_P \ln \left(\frac{T_{av}}{\sqrt{T_1 T_2}} \right) \text{ since } \ln x^n = n \ln x. \quad (iv)$$

In (iii), T_{av} is the arithmetic mean. $\sqrt{T_1 T_2}$ is geometric mean of T_1 and T_2 . We know that the arithmetic mean of two unequal positive numbers is greater than their geometric mean. So, the argument of logarithmic function is greater than one and the entropy of the system increases:

$$\Delta S > 0 \quad (v)$$

You will recognise that entropy change is not necessarily accompanied by heat flow. That is why, entropy increases in free expansion, intermixing of gases and so on.

4. Total heat is $dQ = mL = 20 \times 80 = 1600$ cal and $T = 0^\circ\text{C} = 273\text{K}$.

$$\text{The increase in entropy } dS = \frac{dQ}{T} = \frac{1600}{273} = 5.86 \text{ cal/K}$$

5. It is given that latent heat of fusion of ice = 80 cal/g, and Latent heat of fusion of steam = 540 cal/g.

Step I: Ice changes into water at 0°C (isothermal change)

$$\Delta S_1 = \frac{mL_1}{T_1} = \frac{10 \times 80}{273} \text{ cal/K} = 2.93 \text{ cal/K}$$

Step II: Water changes its temperature from 0°C to 100°C .

$$\Delta S_2 = \int_{273}^{373} \frac{mcdT}{T} = mc \ln \left(\frac{373}{273} \right) = 10 \times 1 \times \ln \left(\frac{373}{273} \right) = 3.12 \text{ cal/K}$$

Step III: Water at 100°C changes into steam at 100°C .

$$\Delta S_3 = \frac{10 \times 540}{373} = 14.48 \text{ cal/K}$$

\therefore Net change in entropy = $2.93 + 3.12 + 14.48 = 20.53$ cal/K

6. In terms of entropy, third law of thermodynamics can be expressed as

$$\lim_{T \rightarrow 0} S \rightarrow 0$$