

Change of Entropy in a Reversible Process

If we calculate the entropy change of the system and add the calculated entropy change of the surrounding, then we obtain the sum of the entropy changes brought about by this particular process. We may call this sum the entropy change of the universe due to this process.

Consider now the entropy change of the universe that is brought about by the performance of any reversible process. The process will, in general, be accompanied by the flow of heat between a system and a set of reservoir.

During any infinitesimal portion of the process, an amount of heat δQ_R is transferred between the system and one of the reservoirs at the temperature T .

If δQ_R is absorbed by the system, then

$$dS \text{ of the system} = + \frac{\delta Q_R}{T}$$

$$dS \text{ of the reservoir} = - \frac{\delta Q_R}{T}$$

and the entropy change of the universe, which is the sum of these two changes is zero.

If δQ_R is rejected by the system, then obviously

$$dS \text{ of the system} = - \frac{\delta Q_R}{T}$$

$$dS \text{ of the reservoir} = + \frac{\delta Q_R}{T}$$

and the entropy change of the universe is again zero.

If no heat is transferred then δQ_R is zero. Neither the system nor the reservoir will have an entropy change and the entropy change of the universe is still zero.

Since there is no change in entropy of the universe for any infinitesimal portion of reversible process, then there is no entropy change for all such portions. In general, **the change of entropy of the universe is zero for a reversible process**. In other words, **when a reversible process is performed, the entropy of the universe remain unchanged**.

Change of Entropy in a Irreversible Process

In order to relate change of entropy to heat in irreversible processes, consider a cycle in which a system begins in an initial equilibrium state i , passes during an irreversible process I to a final equilibrium state f , and then returns by a reversible process R to the initial state i as shown in figure 16. Since entropy is a state function, its closed integral is always zero:

$$\oint dS = \int_I^f dS + \int_R^i dS = 0 \quad (63)$$

From eq. (58), we obtain

$$\oint \frac{\delta Q}{T} = \int_I^f \frac{\delta Q}{T} + \int_R^i \frac{\delta Q}{T} < 0 \quad (64)$$

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From eq. (62) we can write

$$\int_{R}^i \frac{\delta Q}{T} = \int_{R}^i dS \quad (65)$$

Subtract the eq. (64) from (63) and substitute the eq. (65), then

$$\int_i^f dS - \int_i^f \frac{\delta Q}{T} > 0$$

or,
$$\int_i^f dS > \int_i^f \frac{\delta Q}{T} \quad (66)$$

which means that the change of entropy during an irreversible process is greater than the integral of the heat divided by the temperature of the auxiliary reservoirs.

For small change in state, eq. (66) can be written as

$$dS > \frac{\delta Q}{T} \quad \text{(irreversible)} \quad (67)$$

In general, from eq. (62) and (67), we have

$$dS \geq \frac{\delta Q}{T} \quad (68)$$

where the equality applies to reversible processes and the inequality applies to irreversible processes.

Figure 16 An irreversible process followed by a reversible process to complete an irreversible cycle.

The Physical Significance of Entropy

The entropy of a substance is a real physical quantity defined by eq. (61) and (62) and can be easily evaluated for a solid or a perfect gas. The entropy remains constant when the substance undergoes a reversible adiabatic compression or expansion. It is a definite single valued state function of the thermodynamical coordinates defining the state of the system like the temperature, pressure, volume, internal energy, etc. It is difficult to form a clearly visible conception of entropy because there is nothing physical to represent it; it cannot be felt like temperature or pressure. We can, however, easily understand that it is a measure of the disorder or randomness in the molecular arrangement of the system. The addition of heat to a system increases its entropy; from the kinetic point of view addition of heat produces a more violent agitation to the molecules. Thus by the continuous abstraction of heat the entropy of the system decreases and the molecular motion tends to vanish and the molecular arrangement attains a state of great order. Hence increase of entropy implies a transition from an ordered to a less ordered state of affairs.

Entropy and Disorder

Unlike most quantities in physics and chemistry, the change of entropy of the system and its surrounding is not conserved, rather, it increases. In order to understand the concept of entropy, let us consider various processes:

1. As latent heat is supplied to a solid, the process of sublimation changes the solid into vapour with no change in temperature. The change of entropy increases as expected. The material in solid phase retains its size and shape, i.e., solid is in state of order. Meanwhile a vapour has no fixed size and shape, i.e., vapour particles are not arranged into any organized structure, i.e., the vapour is in state of disorder, relative to its solid phase.
2. The temperature of an ideal gas does not change and heat is not added to the system during a free expansion, yet the entropy increases. An increase of volume which provides the gas particles with more space for their motion is a measure of disorder.
3. When the temperature of a ferromagnet material is raised above its Curie point it becomes paramagnetic. The magnetic moment of the ferromagnetic material are mostly aligned in one direction (ordered). At temperature above the Curie point, the magnetic moments are randomly oriented (disordered) to produce paramagnetic behaviour. The entropy increases in the transition from ferro to paramagnetism.

Thus, an increase in entropy of a system can be described as an increase in the disorder of the system. ***Any isolated system or systems plus surrounding experiences irreversible processes proceed towards a state of greater disorder.*** The increase of entropy of the universe during natural processes is an expression of this tendency. So in a metaphorical sense,

“Entropy is the arrow of time , it points forward into the future.”

Principle of Increase of Entropy

In all of the irreversible processes studied so far, it was found that the entropy of the universe increased. This is found to be the case in any irreversible process that may be analysed, and we conclude that it is true for all irreversible processes. This conclusion is known as the ***principle of increases of entropy*** and is considered as a part of the second law of thermodynamics: *The entropy of the universe increase in every irreversible process.*

If all systems that interact in a process are enclosed in a rigid adiabatic boundary, they form a completely isolated system and constitute their own universe. Hence we can say that *in every process taking place in an isolated system, the entropy of the system either increases or remains constant*

To understand the concept, consider the process in which a quantity of heat δQ flows from the surrounding at temperature T_{sur} to the system at temperature T_{sys} . Let δW be the work done by the system during this process.

From the inequality of Clausius, we can write

$$\Delta S_{sys} \geq \frac{\delta Q}{T_{sys}}$$

For the surrounding, δQ is negative and we can write

$$\Delta S_{sur} \geq -\frac{\delta Q}{T_{sur}}$$

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The net change of entropy of the universe is therefore

$$\Delta S = \Delta S_{sys} + \Delta S_{sur} \geq \frac{\delta Q}{T_{sys}} - \frac{\delta Q}{T_{sur}}$$

or,

$$\Delta S = \delta Q \left[\frac{1}{T_{sys}} - \frac{1}{T_{sur}} \right]$$

Since, $T_{sur} > T_{sys}$, the quantity in bracket is positive and we conclude that

$$\Delta S \geq 0 \quad (69)$$

If $T_{sur} < T_{sys}$, the heat transfer is from the system to the surrounding, and both δQ and the quantity in bracket will be negative, yielding the same result.

We may therefore conclude that for all possible processes that a system in a given surrounding can undergo, the increase in entropy is always positive, i.e., $\Delta S \geq 0$. In the eq. (69) the equality sign holds for reversible and greater than holds for irreversible processes. Since natural processes are irreversible, therefore, the entropy of the universe is increasing. This result is known as the principle of increase of entropy.

Entropy and The Second Law of Thermodynamics

We may call this principle of increase of entropy itself as the second law of thermodynamics. In fact Clausius summed up the first law by saying that the energy of the universe remains constant and the second law by saying that the entropy of the universe tends to a maximum.

A more formal statement of the second law of thermodynamics can now be made in terms of the properties of the system itself without reference to any process. This involves the following two statements:

1. For any system a characteristic thermodynamical function called entropy may be defined which is such that

the difference of entropies between two states is given by $\int_1^2 \delta Q/T$ where the integral is to be taken over any reversible path connecting the two states and which is a variable of state. If two states are very near to each other, then $\delta Q = T dS$.

2. The entropy of a closed system (one that has no interaction with the surrounding) can never decrease, i.e., $dS \geq 0$.

Thermodynamic Scale of Temperature

Kelvin's Absolute Scale: Independent of any Working Substance

Lord Kelvin showed in 1848 that with the help of the ideal Carnot engine, it was possible to define temperature in terms of energy, and the scale so obtained is independent of the nature of any particular substance. *A temperature scale that is independent of the nature of the working substance* is known as an **absolute scale** or **thermodynamic temperature scale**. The Carnot engine provides the basis for the thermodynamic temperature scale because it was proven that the efficiency of a Carnot engine working between two temperatures depends only on the two temperatures and is independent of the nature of the working substance. This may be mathematically stated in the form

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$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = \phi(T_H, T_L)$$

where $W = Q_H - Q_L$ is the work done by the Carnot engine, Q_H is the heat taken and Q_L is the heat rejected by the engine, and T_H and T_L are the temperature between which the engine works. Hence

$$\frac{Q_H}{Q_L} = \frac{1}{1 - \phi(T_H, T_L)} = f(T_H, T_L) \quad (85)$$

where, ϕ and f are unknown function of the two temperatures T_H and T_L .

Figure 17 Carnot engines used to demonstrate the thermodynamic temperature scale.

Let us apply eq. (85) to the three Carnot engines operating between the three reservoirs shown in figure 17, where $T_1 > T_3 > T_2$. For engine R_A

$$\frac{Q_1}{Q_2} = f(T_1, T_2)$$

Now consider the second Carnot engine R_B and third Carnot engine R_C . Since the heat Q_3 rejected by the second Carnot engine R_B is absorbed by the third Carnot engine R_C , both engines working together are equivalent to the first Carnot engine R_A . Thus, engine R_B absorbed the same amount of heat Q_1 from the reservoir at T_1 that engine R_A absorbs. So, for engine R_B

$$\frac{Q_1}{Q_3} = f(T_1, T_3)$$

Engine R_A rejects heat Q_2 to the cold reservoir. Thus for engine R_C

$$\frac{Q_3}{Q_2} = f(T_3, T_2)$$

Since,

$$\frac{Q_1}{Q_2} = \frac{Q_1/Q_3}{Q_2/Q_3}$$

We have the result that,

$$f(T_1, T_2) = \frac{f(T_1, T_3)}{f(T_2, T_3)}$$

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Now, we know the temperature T_3 is chosen arbitrarily and since it does not appear in left hand term, T_3 must, therefore, cancel out of the ratio on the right hand terms. Thus

$$\frac{Q_1}{Q_2} = \frac{\psi(T_1)}{\psi(T_2)} \quad (86)$$

where, ψ is another unknown function of one temperature only. Thus, the ratio on the right hand side is defined as the ratio of two thermodynamic temperatures and is denoted by T_1/T_2 . We have therefore

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad (87)$$

Thus, eq. (87) is used to define a new scale of temperature, which is called the **thermodynamic scale** or **Kelvin's absolute scale of temperature**. *The ratio of any two temperature on thermodynamic scale is equal to the ratio of the absolute values of the heat absorbed and rejected; respectively by a Carnot engine operating between reservoirs at these temperatures.*

Thermodynamic temperature scale is independent of the characteristic of any particular substance. Finally, *the thermodynamic temperature are called absolute temperature because they are independent to the nature of any material.*