

ENTROPY AND 2ND LAW OF THERMODYNAMICS

Heat Engine and 2nd Law of Thermodynamics

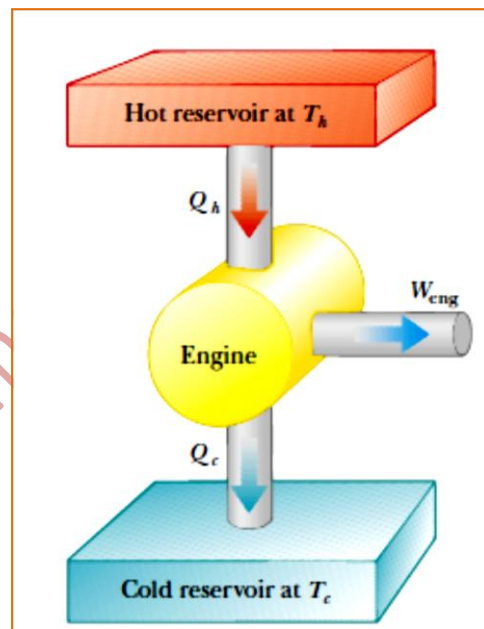
It is a device that converts heat energy into mechanical energy. Every heat engine takes heat from a hot body (source), converts a part of it into work and rejects the remaining part to a cold body (sink).

A heat engine carries some working substance through a cyclic process during which:

- 1) The working substance absorbs energy by heat from a high-temperature energy reservoir
- 2) Work is done by the engine,
- 3) Energy is expelled by heat to a lower-temperature reservoir.

Example

Consider the operation of a steam engine, which uses water as the working substance. The water in a boiler absorbs energy from burning fuel and evaporates to steam, which then does work by expanding against a piston. After the steam cools and condenses, the liquid water produced returns to the boiler and the cycle repeats.



Efficiency of Heat Engine

Suppose a heat engine takes heat Q_h from hot body at temperature T_h , converts a part of it into work and rejects the remaining heat Q_c to cold body at temperature T_c .

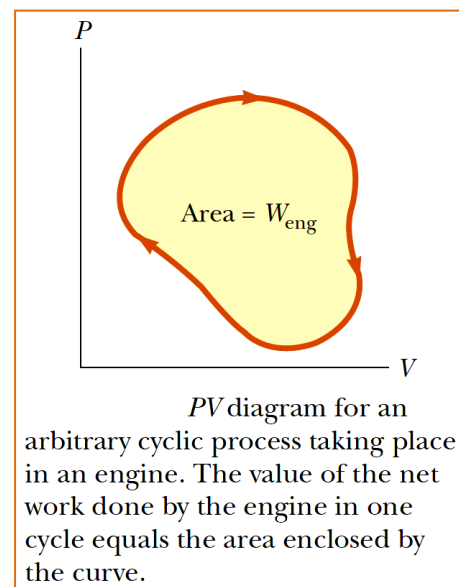
After completing one complete cycle, the system returns to the initial state. So its internal energy remains constant in a cycle. So work done by the engine in one cycle is $W = Q_h - Q_c$ and the change in internal energy is zero. So, the net work done W by a heat engine is equal to the net energy transferred to it.

If the working substance is a gas, the net work done in a cyclic process is the area enclosed by the curve representing the process on a PV diagram.

The efficiency of the heat engine is defined as:

“Ratio of work done by the engine in one cycle to the heat absorbed in one cycle”

Mathematically, it is described as:



$$e = \frac{\text{Work Done}}{\text{Heat Absorbed}}$$

$$e = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = \frac{Q_h}{Q_h} - \frac{Q_c}{Q_h}$$

$$e = 1 - \frac{Q_c}{Q_h}$$

From this equation, it is clear that efficiency of heat engine is not 100% or 1. The efficiency can be 100% if $Q_c = 0$ i.e., no heat is transferred to the cold body and heat Q_h taken from hot body is completely converted into work. The engine which will do so is called perfectly efficient heat engine. But the experiments show that no such heat engine can be made which can convert whole heat drawn from a single body to work.

Kelvin Statement of Second Law of Thermodynamics

It is impossible to make a heat engine which operating in a cycle can go on doing work by taking heat from a single body, without other body at lower temperature.

This law tells that two bodies at different temperature are necessary for the working of a heat engine. The hot body is called source while the cold body is called sink.

Refrigerator and 2nd law of Thermodynamics

A heat engine run in reverse is known as refrigerator. A refrigerator needs work to transfer heat from cold body to hot body.

If Q_c is the amount of heat removed from the cold body at temperature T_c and Q_h is the amount of heat given to the hot body at temperature T_h , then the difference $Q_h - Q_c$ is the external work required to drive the refrigerator.

Co-Efficient of Performance

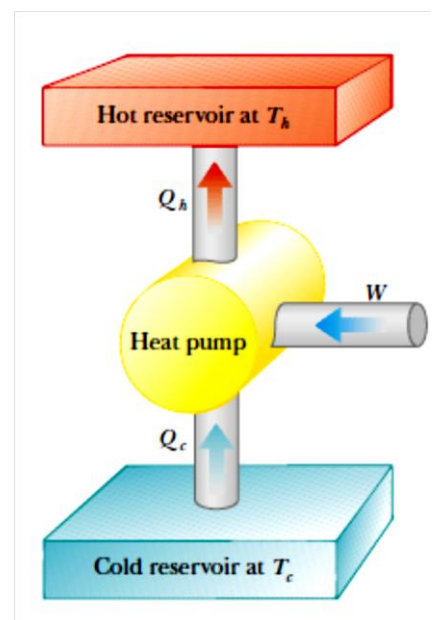
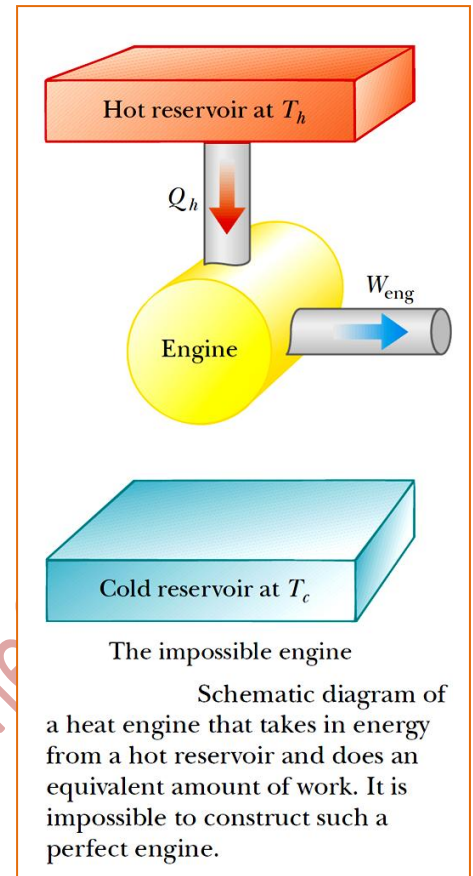
In a refrigerator, instead of efficiency, we use the term co-efficient of performance K, which is defined as:

$$K = \frac{\text{Desired Output}}{\text{Required Input}}$$

i.e., co-efficient of performance is the ration of heat removed from the cold body to the mechanical work required to operate the refrigerator.

$$K = \frac{Q_c}{Q_h - Q_c}$$

In a perfect refrigerator $W = 0$ and so $Q_c = Q_h$. So the coefficient of performance of perfect refrigerator is infinity.



In an ordinary house hold refrigerator, the working substance is the liquid (Freon) that circulated within the system. The cold body is the interior of the refrigerator and hot body is the room in which refrigerator is kept. Typical refrigerator have the coefficient of performance around 5.

Clausius Statement of 2nd Law of Thermodynamics

It is impossible to cause heat to flow from cold body to the hot body without expenditure of energy.

So from this, we find that heat can't flow by itself from cold to hot body. So we have to do work to make this flow. So this statement can also be stated as:

Perfect refrigerator is impossible

Equivalence of Clausius and Kelvin Statement

The two statement of the end law of thermodynamics can be shown to be identical by supposing that if one of the statements is false, the other is also false.

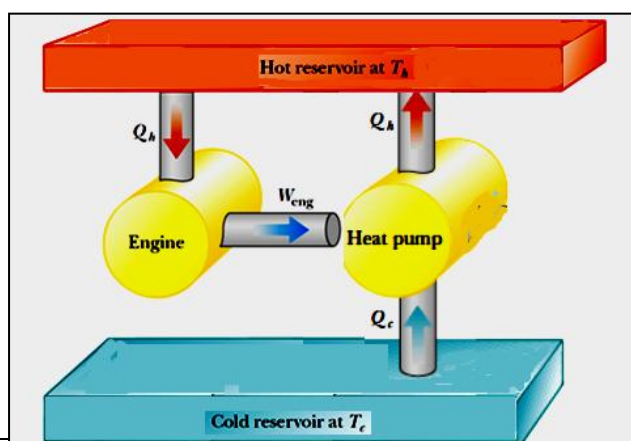
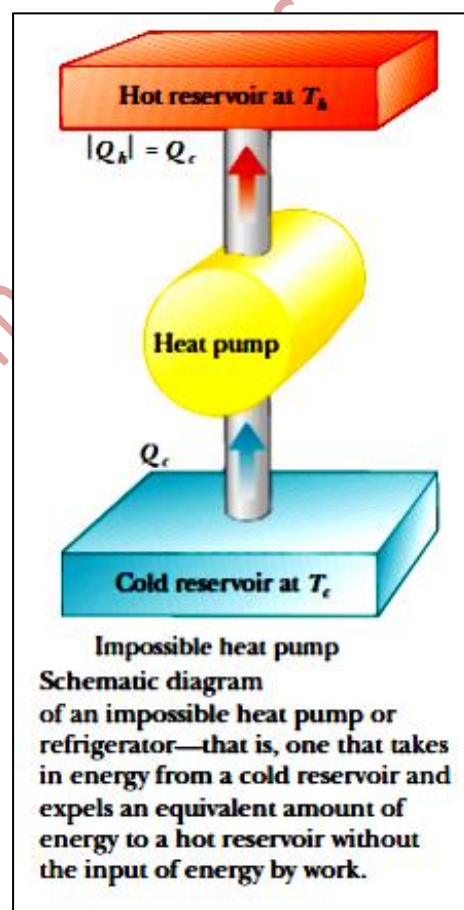
We suppose that Kelvin statement is false i.e., we can construct a heat engine, which can convert the heat of a single body into work without a cold body.

Suppose this engine is used to run a refrigerator as shown in the figure:

In refrigerator, the heat flows from cold body to hot body. So work done by the engine is used operate the refrigerator which transfer heat from cold body to hot body.

Thus, the heat engine and the refrigerator both from a system which transfer heat from cold body to hot body without any external work. But it is against the Clausius Statement. So the Clausius statement is also false if the Kelvin statement is false. So a violation of Kelvin statement gives the violation of Clausius statement.

So we see that violation of one statement gives a violation of the other. Hence from the above discussion, we find that these two statements are logically identical.



Carnot Engine

It is an ideal heat engine free from all heat losses and all the processes are reversible.

Construction of Carnot Engine

It consists of the following parts:

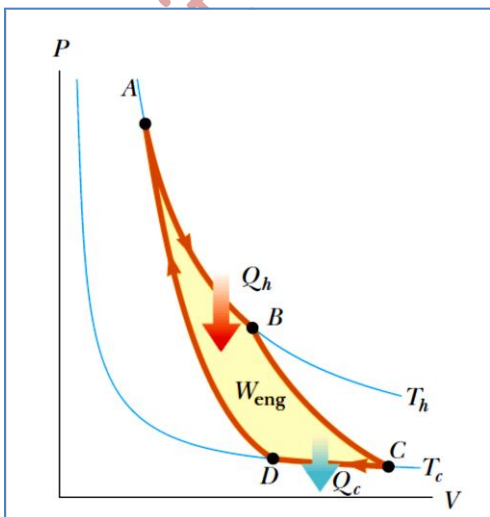
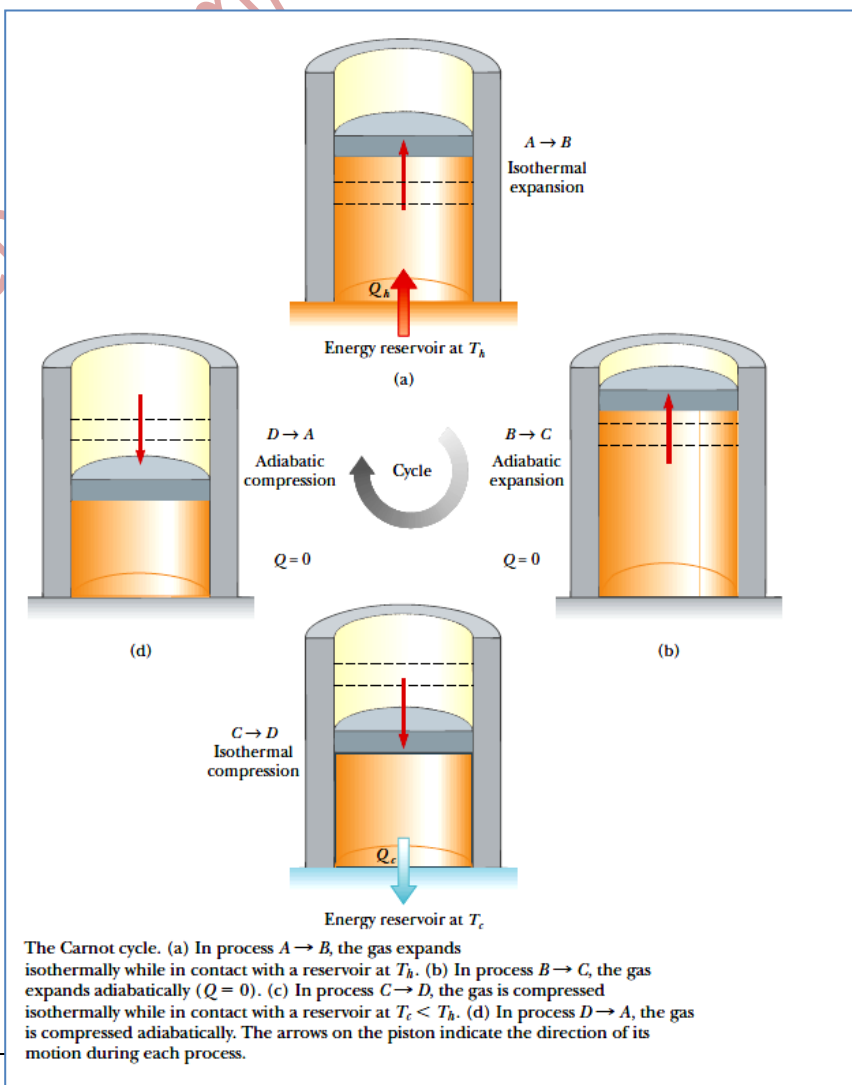
1. A cylinder containing perfect gas having non-conducting walls and piston and only base conducting
2. A source of heat at temperature T_h
3. A sink at temperature T_c
4. A non-conducting stand

Carnot Cycle

The operating cycle of Carnot engine is called Carnot cycle. The Carnot cycle consists of the following four processes:

Isothermal Expansion

The cylinder is placed on the source of heat at temperature T_h and gas is allowed to expand very slowly by removing weights on the piston. The gas expands and tends to cool down but it absorbs heat Q_h from the source of heat so that its temperature remains constant (Q_h). This process is isothermal, so $\Delta E_{int} = 0$ and all the heat added appears as negative work done on the gas. This process is shown on a PV diagram by the curve AB.



Adiabatic Expansion

The cylinder is now placed on the non-conducting stand so that heat does not enter or leave the gas. The gas is allowed to expand slowly by removing more weights from the piston. The process is adiabatic and $Q = 0$. The piston does negative work on the gas and the work is done at the cost of internal energy of the gas. So the temperature of gas decreases to T_c . This process is shown on the PV diagram by the curve BC.

Isothermal Compression

The cylinder is now placed on the sink and the gas is compressed by adding weights on the piston. During this process the gas rejects heat Q_c to sink at T_c . This process is isothermal compression and positive work is done on gas during compression. The process is shown in the PV diagram by the curve CD.

Adiabatic Compression

The cylinder is finally placed on the non-conducting stand. The gas is compressed by adding more weights on the piston. As heat can't leave gas so the process is adiabatic. The process is such that temperature of the gas rises to T_h and the gas goes back to its initial state. The process is shown on the PV diagram by curve DA.

So the gas undergoes a cycle ABCDA. It is a reversible cycle and is called Carnot cycle.

Efficiency of Carnot Engine*Isothermal Processes*

Along the isothermal path AB, temperature remains constant, so $\Delta E_{int} = 0$. So by the first law of thermodynamics, heat transferred Q_h from source is equal to magnitude of work.

$$Q_h = W_{AB} = nR T_h \ln \left(\frac{V_B}{V_A} \right) \quad \text{----- (1)}$$

Similarly for isothermal compression CD, the heat energy rejected Q_c to the sink is

$$Q_c = W_{CD} = nR T_c \ln \left(\frac{V_C}{V_D} \right) \quad \text{----- (2)}$$

Dividing equation (1) and (2), we get:

$$\frac{Q_c}{Q_h} = \frac{nR T_c \ln \left(\frac{V_C}{V_D} \right)}{nR T_h \ln \left(\frac{V_B}{V_A} \right)} = \frac{T_c \ln \left(\frac{V_C}{V_D} \right)}{T_h \ln \left(\frac{V_B}{V_A} \right)} \quad \text{----- (A)}$$

Adiabatic Processes

For an adiabatic process, we have:

$$T V^{\gamma-1} = \text{constant}$$

For adiabatic path BC, we can write:

$$\begin{aligned} T_h V_B^{\gamma-1} &= T_c V_C^{\gamma-1} \\ \Rightarrow \frac{T_h}{T_c} &= \frac{V_C^{\gamma-1}}{V_B^{\gamma-1}} \quad \text{-----} \quad (3) \end{aligned}$$

For adiabatic path DA, we have:

$$\begin{aligned} T_c V_D^{\gamma-1} &= T_h V_A^{\gamma-1} \\ \Rightarrow \frac{T_h}{T_c} &= \frac{V_D^{\gamma-1}}{V_A^{\gamma-1}} \quad \text{-----} \quad (4) \end{aligned}$$

Comparing equation (3) and (4), we get:

$$\begin{aligned} \frac{V_D^{\gamma-1}}{V_A^{\gamma-1}} &= \frac{V_C^{\gamma-1}}{V_B^{\gamma-1}} \\ \Rightarrow \left(\frac{V_D}{V_A}\right)^{\gamma-1} &= \left(\frac{V_C}{V_B}\right)^{\gamma-1} \\ \Rightarrow \frac{V_D}{V_A} &= \frac{V_C}{V_B} \\ \Rightarrow \frac{V_B}{V_A} &= \frac{V_C}{V_D} \end{aligned}$$

Putting this value in equation (A), we get:

$$\begin{aligned} \frac{Q_c}{Q_h} &= \frac{T_c \ln\left(\frac{V_C}{V_D}\right)}{T_h \ln\left(\frac{V_C}{V_D}\right)} \\ \Rightarrow \frac{Q_c}{Q_h} &= \frac{T_c}{T_h} \end{aligned}$$

So, the efficiency of the Carnot engine is:

$$\begin{aligned} e &= 1 - \frac{Q_c}{Q_h} \\ \Rightarrow e &= 1 - \frac{T_c}{T_h} \end{aligned}$$

From this expression, we find that efficiency of Carnot engine only depend upon temperature of source and sink between which it operate.

The efficiency is increased by decreasing T_c . The efficiency will be 100% if $T_c = 0 K$ which is not possible. Thus, the efficiency of the Carnot engine can't be 100%.

Thermodynamic Temperature Scale

The scale of temperature which is independent of the nature of working substance is called thermodynamic temperature scale or Kelvin temperature scale. Thermodynamic temperature scale has been derived by Kelvin by the law of thermodynamics.

The efficiency of Carnot reversible heat engine does not depend on the working substance and depend on the working temperature θ_1 and θ_2 of the source and sink, where θ_1 and θ_2 are measured on the perfect gas scale.

So the efficiency of Carnot engine is the function of θ_1 and θ_2 :

$$e = 1 - \frac{Q_2}{Q_1} = \phi(\theta_1, \theta_2)$$

$$\Rightarrow 1 - \frac{Q_2}{Q_1} = \phi(\theta_1, \theta_2)$$

$$\Rightarrow 1 - \phi(\theta_1, \theta_2) = \frac{Q_2}{Q_1}$$

$$\Rightarrow \frac{Q_2}{Q_1} = 1 - \phi(\theta_1, \theta_2)$$

$$\Rightarrow \frac{Q_1}{Q_2} = \frac{1}{1 - \phi(\theta_1, \theta_2)}$$

$$\Rightarrow \frac{Q_1}{Q_2} = f(\theta_1, \theta_2)$$

Now we consider three Carnot engines working between the temperatures (θ_1, θ_2) , (θ_2, θ_3) and (θ_1, θ_3) , where $\theta_1 > \theta_2$ and $\theta_2 > \theta_3$. Then

$$\frac{Q_1}{Q_2} = f(\theta_1, \theta_2)$$

$$\frac{Q_2}{Q_3} = f(\theta_2, \theta_3)$$

$$\frac{Q_1}{Q_3} = f(\theta_1, \theta_3)$$

Now

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

$$\frac{Q_1}{Q_2} = \frac{f(\theta_1, \theta_3)}{f(\theta_2, \theta_3)}$$

As $\frac{Q_1}{Q_2}$ is a function of (θ_1, θ_2) only, so θ_3 can be omitted

$$\therefore \frac{Q_1}{Q_2} = \frac{\psi(\theta_1)}{\psi(\theta_2)}$$

Let $\frac{\psi(\theta_1)}{\psi(\theta_2)} = \frac{T_1}{T_2}$

$$\therefore \frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

Or

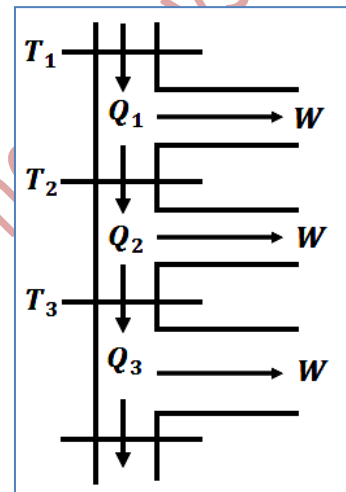
$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

Where T_1 and T_2 are called Kelvin temperatures or absolute temperatures.

Now consider a series of Carnot engines coupled together such that each engine does the same amount of work and also sink of proceeding engine becomes the source of next engine and so on.

It means that

- The first engine received heat Q_1 from the source at temperature T_1 , performs the work W and rejects heat Q_2 to the second engine.
- The second engine receives heat Q_2 at temperature T_2 and rejects heat Q_3 to the third engine and so on



As each engine does the same amount of work, therefore we can write:

$$W = Q_1 - Q_2 = Q_2 - Q_3 = Q_3 - Q_4 = \dots \dots \dots$$

So,

$$Q_1 \left(1 - \frac{Q_2}{Q_1}\right) = Q_2 \left(1 - \frac{Q_3}{Q_2}\right) = Q_3 \left(1 - \frac{Q_4}{Q_3}\right) = \dots \dots \dots$$

$$\Rightarrow Q_1 \left(1 - \frac{T_2}{T_1}\right) = Q_2 \left(1 - \frac{T_3}{T_2}\right) = Q_3 \left(1 - \frac{T_4}{T_3}\right) = \dots \dots \dots$$

$$\Rightarrow \frac{Q_1}{T_1} (T_1 - T_2) = \frac{Q_2}{T_2} (T_2 - T_3) = \frac{Q_3}{T_3} (T_3 - T_4) = \dots \dots \dots$$

As $\frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_3}{T_3}$

$$\therefore (T_1 - T_2) = (T_2 - T_3) = (T_3 - T_4) = \dots \dots \dots$$

It shows that the temperature difference for each Carnot engine is the same. If there are 100 Carnot engines working between boiling point of water and melting point of ice, then

$$T_b - T_i = 100 \text{ degrees}$$

Where

- T_b = Temperature corresponding to the boiling point of water
- T_i = Temperature corresponding to the melting point of ice

Kelvin scale was derived on the basis of laws of thermodynamics, so it is also called thermodynamic temperature scale.

Question. Show that thermodynamic scale of temperature and perfect gas scale are identical.

Ans. Consider a Carnot engine working between the temperatures T_1 and T_2 on Kelvin scale.

Then by Kelvin scale:

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad \text{----- (1)}$$

Let these temperatures be θ_1 and θ_2 on the perfect gas scale. Therefore

$$\frac{Q_1}{Q_2} = \frac{\theta_1}{\theta_2} \quad \text{----- (2)}$$

Combining (1) and (2), we get:

$$\frac{T_1}{T_2} = \frac{\theta_1}{\theta_2}$$

$$\therefore \frac{T_b}{T_i} = \frac{\theta_b}{\theta_i}$$

$$\text{As } T_b - T_i = 100 \Rightarrow T_b = T_i + 100$$

$$\text{Similarly } \theta_b - \theta_i = 100 \Rightarrow \theta_b = \theta_i + 100$$

$$\frac{T_i + 100}{T_i} = \frac{\theta_i + 100}{\theta_i}$$

$$\Rightarrow \frac{T_i \left(1 + \frac{100}{T_i}\right)}{T_i} = \frac{\theta_i \left(1 + \frac{100}{\theta_i}\right)}{\theta_i}$$

$$\Rightarrow 1 + \frac{100}{T_i} = 1 + \frac{100}{\theta_i}$$

$$\Rightarrow \frac{100}{T_i} = \frac{100}{\theta_i}$$

$$\Rightarrow \frac{1}{T_i} = \frac{1}{\theta_i}$$

$$\Rightarrow T_i = \theta_i$$

Similarly $T_b = \theta_b$

Or $T = \theta$

It shows that temperature of melting point of ice and boiling temperature of water are same on both scales. Hence the Kelvin scale and perfect gas scale are identical.

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Absolute zero and negative temperature

We can't have a gas below 1 K and so we can't measure temperature below 1 K using constant volume gas thermometer. But by the thermodynamic temperature scale, we can measure temperature below 1 K.

Consider a system at temperature T_2 . We want to measure the temperature of the system. For this we consider the system around a Carnot cycle. First we do work on the gas adiabatically and temperature of the gas increases to T_1 which is supposed to be known. Then heat Q_1 is transferred isothermally. Then doing work adiabatically to decrease the temperature back to T_2 . Then in the last Q_2 is rejected isothermally to bring the system to its initial state.

So by the relation:

$$\frac{T_2}{T_1} = \frac{Q_2}{Q_1}$$

$$\Rightarrow T_2 = \frac{Q_2}{Q_1} T_1$$

So, knowing T_1 and measuring Q_1 and Q_2 , we can measure T_2 . Similarly we can take the system around another Carnot cycle to a still lower temperature T_3 . We can continue this process to the absolute zero temperature.

But smaller the temperature, small is heat transferred in the isothermal process between two adiabatic process. Near absolute zero, the system will undergo an isothermal process without the transfer of heat.

It is found experimentally that lower the temperature, the more difficult it is to go still lower. So we can state 3rd law of thermodynamics as follows:

It is impossible by any procedure, no matter how idealized, to reduce any system to the absolute zero of temperature in a finite number of operations.

Hence we can't have a sink at absolute zero or a heat engine with 100% efficiency is impossible.

Entropy Function

Entropy is a Greek terms means change. It is a measure of disorder or randomness of molecular motion of the system. It is a thermal property of a system which remains constant as long as no heat enters or leaves the system. It is a real physical quantity. Entropy of a system increases if heat flows into the system at constant temperature and decreases if leaves the system at constant temperature.

It is a state function and depends on the state of system. The absolute value of entropy can't be determined however change in entropy dS can be determined by the relation:

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

This expression shows that entropy of a system increases if heat flows into the system at constant temperature and decreases if leaves the system at constant temperature. The SI unit of entropy is J/K.

Entropy in Reversible Process

As we know that for a Carnot cycle:

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

As Q_1 and Q_2 always have opposite signs, so the above expression can be written as:

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \quad \text{----- (1)}$$

This equation shows that the sum of algebraic quantity $\frac{Q}{T}$ is zero for a Carnot cycle.

For a finite number of cycles, equation (1) becomes:

$$\sum \frac{Q}{T} = 0 \quad \text{----- (2)}$$

For infinite number of cycles, equation (1) becomes:

$$\oint \frac{dQ}{T} = 0 \quad \text{----- (3)}$$

Here \oint indicates that the integral is calculated over a close path and quantity dQ is the small quantity of heat which enters or leave the system. Equation (3) is called **CLAUSIUS THEOREM**.

The Clausius theorem gives the definition of entropy function. Consider a reversible cycle represented by the close curve as shown in the figure.

Let i and f denote the initial and final states of a system. Let the system undergo a change from i to f along path-1 and back to i along path-2. These two path form a reversible cycle. By Clausius theorem,

$$\oint \frac{dQ}{T} = 0$$

This integral can be written as the sum of two integrals:

$$\oint \frac{dQ}{T} = \int_i^f \frac{dQ}{T} + \int_f^i \frac{dQ}{T} = 0$$

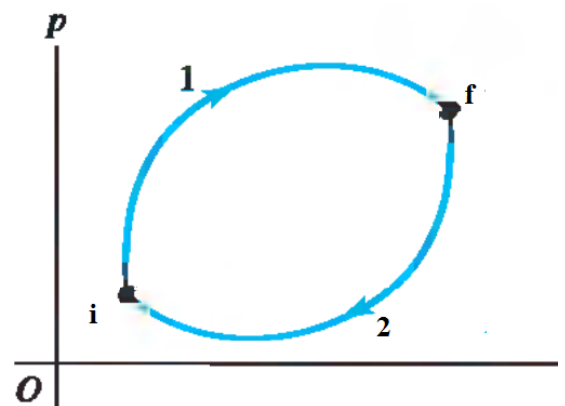
$$\int_i^f \frac{dQ}{T} = - \int_f^i \frac{dQ}{T}$$

$$\int_i^f \frac{dQ}{T} = \int_i^f \frac{dQ}{T}$$

This shows that the integrals on two reversible paths are equal. It means that the integral $\int \frac{dQ}{T}$ is same along the reversible paths from i to f . In the language of mathematics,

the integrand $\frac{dQ}{T}$ is an exact differential of some function S i.e.,

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



$$\int_i^f \frac{dQ}{T} = \int_i^f dS = S_f - S_i$$

This quantity S is called entropy of the system. It should be noted that dQ is an inexact differential but $\frac{dQ}{T}$ is an exact differential. Change in entropy dS is independent of path and only depends on the initial and final states.

Entropy in Irreversible Process

In nature there is no reversible process due to friction and heat transfer. So every thermodynamic process is irreversible.

To find the entropy change for an irreversible process, we choose a path by connecting the initial and final state and calculate the entropy change by the equation:

$$S = \int_i^f \frac{dQ}{T}$$

Examples of Irreversible Process

Free Expansion

Consider an ideal gas enclosed in an insulated container. When the ideal gas rushes into evacuated chamber, its temperature and internal energy remains constant i.e., $\Delta E_{int} = 0$ and by 1st law of thermodynamics:

$$Q + W = 0$$

$$\Rightarrow Q = -W$$

The free expansion is an irreversible process. There is an entropy change between initial and final states. To find the entropy change, we choose a path from i to f . Let us consider an isothermal expansion that takes the gas from initial state (P_i, V_i, T_i) to (P_f, V_f, T_f) . Now

$$S = \int_i^f \frac{dQ}{T} = \frac{1}{T} \int_i^f dQ = \frac{1}{T} (Q) = \frac{Q}{T}$$

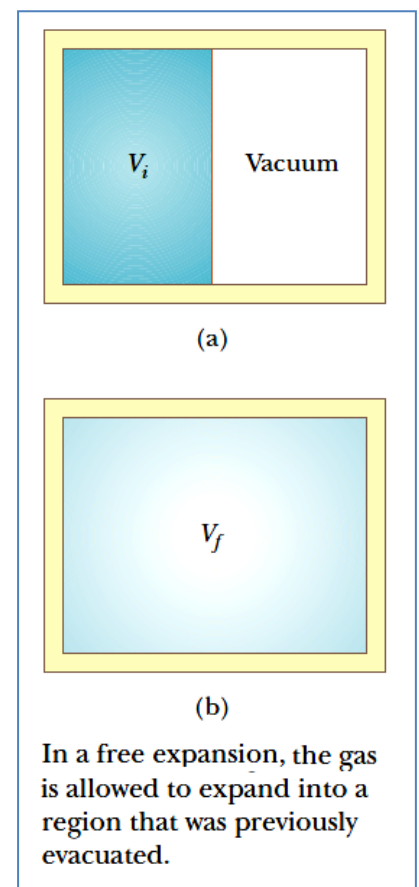
Putting the value of Q , we get:

$$S = -\frac{W}{T}$$

In an isothermal process, $W = -nRT \ln\left(\frac{V_f}{V_i}\right)$. Therefore,

$$S = nR \ln\left(\frac{V_f}{V_i}\right)$$

This is equal to the entropy change irreversible free expansion. It should be noted that entropy change is positive for an irreversible



process. As there is no heat transfer to environment in free expansion, so entropy change for environment is zero. Thus the total entropy of *system + environment* increases during free expansion.

Irreversible Heat Transfer

Consider two block at temperatures T_1 and T_2 . Both the blocks have same mass and specific heat. We bring the blocks into thermal contact. After some time, they reach common temperature T_e . Like free expansion, this is also irreversible process.

To find the entropy change in this irreversible process, we consider block 1 at lower temperature T_1 and imagine a series of thermal reservoirs at temperatures $T_1, T_1 + dT, T_1 + 2dT, \dots, T_e - dT, T_e$. We first start with block 1 in contact with the 1st reservoir and move it one step at a time along a sequence. In each step, a small amount of heat $dQ = Cm dT$ enters the block. Entropy change for block 1 is given by:

$$\Delta S_1 = \int_i^f \frac{dQ}{T} = Cm \int_{T_1}^{T_e} \frac{dT}{T} = Cm(\ln|T|_{T_1}^{T_e}) = Cm(\ln T_e - \ln T_1) = Cm \left(\ln \frac{T_e}{T_1} \right)$$

Similarly, for block 2 between temperatures T_2 and T_e , the entropy change is given by:

$$\Delta S_2 = \int_i^f \frac{dQ}{T} = Cm \int_{T_2}^{T_e} \frac{dT}{T} = Cm(\ln|T|_{T_2}^{T_e}) = Cm(\ln T_e - \ln T_2) = Cm \left(\ln \frac{T_e}{T_2} \right)$$

The total entropy change is given by:

$$\begin{aligned} \Delta S &= \Delta S_1 + \Delta S_2 \\ \Rightarrow \Delta S &= Cm \left(\ln \frac{T_e}{T_1} \right) + Cm \left(\ln \frac{T_e}{T_2} \right) \\ \Rightarrow \Delta S &= Cm \left(\ln \frac{T_e}{T_1} + \ln \frac{T_e}{T_2} \right) \\ \Rightarrow \Delta S &= Cm \left[\ln \left(\frac{T_e}{T_1} \times \frac{T_e}{T_2} \right) \right] \\ \Rightarrow \Delta S &= Cm \left[\ln \left(\frac{T_e^2}{T_1 T_2} \right) \right] \end{aligned}$$

Now, we can show that the total entropy change ΔS is positive. For this purpose, we have to prove that $\frac{T_e^2}{T_1 T_2} > 1$.

We first find T_e by considering the total heat flow equal to zero.

$$\begin{aligned} Q_1 + Q_2 &= 0 \\ \Rightarrow Cm(T_e - T_1) - Cm(T_2 - T_e) &= 0 \\ \Rightarrow 2CmT_e - Cm(T_1 + T_2) &= 0 \end{aligned}$$

$$\Rightarrow 2CmT_e = Cm(T_1 + T_2)$$

$$\Rightarrow T_e = \frac{T_1 + T_2}{2}$$

Now

$$\frac{T_e^2}{T_1 T_2} = \frac{\left(\frac{T_1 + T_2}{2}\right)^2}{T_1 T_2} = \frac{T_1^2 + T_2^2 + 2T_1 T_2}{4T_1 T_2} = \frac{T_1^2 + T_2^2 - 2T_1 T_2 + 4T_1 T_2}{4T_1 T_2}$$

$$\Rightarrow \frac{T_e^2}{T_1 T_2} = \frac{(T_1 + T_2)^2 + 4T_1 T_2}{4T_1 T_2} = \frac{4T_1 T_2}{4T_1 T_2} + \frac{(T_1 + T_2)^2}{4T_1 T_2}$$

$$\Rightarrow \frac{T_e^2}{T_1 T_2} = 1 + \frac{(T_1 + T_2)^2}{4T_1 T_2}$$

This expression shows that $\frac{T_e^2}{T_1 T_2} > 1$. So $\ln\left(\frac{T_e^2}{T_1 T_2}\right)$ is greater than zero and so the entropy change is positive.

Hence by placing two block in thermal contact produces no change at all in the environment and so $\Delta S = 0$ for environment. But the total entropy of *system + environment* increases in this irreversible heat transfer.

Entropy and the 2nd law of thermodynamics

The 2nd law of thermodynamics can be stated in terms of entropy as:

In any thermodynamic process, that proceeds from one equilibrium state to another, the entropy of the system + environment either remains unchanged or increases.

For reversible process, the entropy does not change. For irreversible processes i.e., for all natural processes, the total entropy of the *system + environment* must increase. It is possible that the entropy of system might decrease, but entropy of environment shows increase of greater magnitude, so that the total change in entropy is always positive.

No natural process can ever shown decrease in the total entropy of the *system + environment*. This is another statement of 2nd law of thermodynamics. Let us consider this statement of 2nd law for the following cases.

Free Compression.

The reverse process of free expansion is called free compression.

The change in entropy in free expansion is given by:

$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right)$$

In free compression, $V_f < V_i$, so $\ln\left(\frac{V_f}{V_i}\right)$ is negative. So ΔS is negative. Which means entropy decreases. But this violates the 2nd law according to which entropy of *system + environment* is always positive.

In free compression, there is no change in entropy of environment like free expansion. So the 2nd law of thermodynamics in terms of entropy denies the process of free compression.

The Kelvin-Planck Form of 2nd Law of Thermodynamic

Because all engines operates in cycle, so entropy change for the system in complete cycle is zero. In a perfect engine, the environment (source) releases heat Q at temperature T and its entropy change is $\frac{Q}{T}$, a negative quantity. The total entropy change of *system + environment* is therefore negative in a perfect heat engine which violates the 2nd law in terms of entropy. So the 2nd law of thermodynamics denies the possibility of perfect engine.

Clausius form of 2nd law

In a perfect refrigerator, there is no change entropy of the system in one complete cycle. But the environment (cold body) releases heat ($-Q$) at temperature T_c and absorbs heat Q at temperature T_h . The total change entropy of the environment is:

$$\Delta S = \frac{Q}{T_h} - \frac{Q}{T_c} = Q \left(\frac{1}{T_h} - \frac{1}{T_c} \right)$$

Because $T_h > T_c$, so ΔS is negative which violates the second law in terms of entropy. So the 2nd law denies the possibility of perfect refrigerator.

The Arrow of Time

All the natural processes are taking place in such direction that the change in entropy of *system + environment* is always positive i.e., if in any process the entropy of the system decreases then there is large increases in the environment such that total entropy change is positive.