

Different Statements of the second law:-

1. It is impossible to construct a machine working in cycles which can convert heat completely into an equivalent amount of work without producing changes elsewhere.
2. It is impossible for a self acting machine, without the help of some external agency, to transfer heat from one body at a lower temperature to a higher temperature.
3. All other forms of energy can be completely converted into heat, whereas complete conversion of heat into any other form of energy is not possible.
4. All spontaneous processes are irreversible.
5. In a reversible process the entropy change, ΔS , of the system and the surroundings taken together remains constant. In an irreversible process it increases. i.e., $\Delta S > 0$.
6. In a reversible process the free energy change ΔG , of the system and surroundings taken together remains constant. In an irreversible process it decreases. i.e., $\Delta G > 0$.

Carnot cycle and its efficiency :- ②

Carnot's cycle.

Some definitions :-

(1) Carnot engine: The hypothetical heat engine designed by Carnot is known as Carnot engine. In a Carnot engine the working substance is one mole of an ideal gas. The engine is capable of working between two temperatures T_2 and T_1 where $T_2 > T_1$.

(2) Cycle process: When a system, after completing a series of changes returns to its original state, it is said to have completed a cycle. Such a process is known as a cyclic process. We know that internal energy E depends only upon the state of a system.

In a cyclic process, as the system returns back to its original state,

$$\Delta E = 0; \quad \text{i.e., } \Delta E = Q - W = 0$$

$$Q - W = 0; \quad \text{i.e., } Q = W.$$

(3) Carnot cycle: A single cycle of the Carnot's engine is referred to as the Carnot cycle. For a single cycle of Carnot engine, the ideal gas undergoes the following changes.

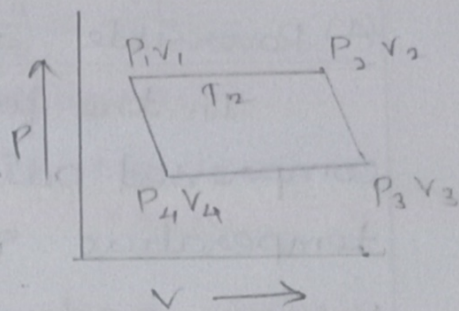
1. Reversible isothermal expansion,
2. Reversible adiabatic expansion
3. Reversible isothermal compression and
4. Reversible adiabatic compression

Carnot's cycle is used to show the maximum convertibility of heat into work

(4) Efficiency of heat engine (η)

$$\eta = \frac{\text{work done}}{\text{Heat absorbed}} = \frac{W}{Q}$$

Derivation of an expression for the efficiency of Carnot's engine:



Carnot's reversible cycle: The pressure and volume of the ideal gas change during the Carnot cycle as shown by figure

(1) Reversible isothermal expansion:

One mole of the ideal gas absorbs heat from the reservoir at T_2 and expands isothermally and reversibly. The volume of the gas changes from V_1 to V_2 . During this change;

Heat change = Q_2 ; Work done = W_1

$W_1 = RT_2 \ln \frac{V_2}{V_1}$ Since the gas is ideal $Q_2 = W_1$;

(2) Reversible adiabatic expansion:

In the second stage, the ideal gas at T_2 is allowed to expand adiabatically. The volume changes from V_2 to V_3 and temperature reduces to T_1 .

heat change = 0

Work done $W_2 = C_v \int_{T_2}^{T_1} dT = -C_v(T_1 - T_2)$

$W_2 = C_v(T_2 - T_1)$

(3) Reversible isothermal compression:

In the third stage, the gas is placed in the reservoir at T_1 and is compressed isothermally and reversibly such that it gives heat Q_1 to the reservoir; There by the

volume decreases from V_3 to V_4 . \oplus

heat change = $-Q_1$.

$$\text{Work done, } W_3 = RT_1 \ln \frac{V_4}{V_3} \quad W_3 = -Q_1$$

(4) Reversible adiabatic compression:

In the fourth stage the gas is compressed adiabatically and the temperature increases from T_1 to T_2 . The volume reduces from V_4 to V_1 . Thus one cycle is completed and the gas returns to the initial state. During the fourth stage.

heat change = 0.

$$\text{Work done, } W_4 = -C_V (T_2 - T_1)$$

The total work done in the cycle is the sum of works done in the four stages.

$$W = W_1 + W_2 + W_3 + W_4$$

$$W = RT_2 \ln \frac{V_2}{V_1} - C_V (T_2 - T_1) + RT_1 \ln \frac{V_4}{V_3} - C_V (T_2 - T_1)$$

$$W = RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_4}{V_3}$$

The heat absorbed from the reservoir at T_2

$$Q_2 = RT_2 \ln \frac{V_2}{V_1}$$

Efficiency of the engine = $\frac{W}{Q_2}$

$$\frac{W}{Q_2} = \frac{-RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_4}{V_3}}{RT_2 \ln \frac{V_2}{V_1}}$$

When we consider the adiabatic expansion in the cycle.

$$T_2 V_2^{\gamma-1} = T_1 V_3^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left[\frac{V_3}{V_1} \right]^{\gamma-1} \quad (5)$$

comparing (2) and (3)

$$\frac{V_3}{V_2} = \frac{V_4}{V_1}; \quad \text{i.e.,} \quad \frac{V_4}{V_3} = \frac{V_1}{V_2}$$

Substituting these in equation (1)

$$\frac{W}{Q_2} = \frac{RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_1}{V_2}}{RT_2 \ln \frac{V_2}{V_1}}$$

$$\frac{W}{Q_2} = \frac{(T_2 - T_1)}{T_2} \times \frac{R \ln \frac{V_2}{V_1}}{R \ln \frac{V_2}{V_1}}$$

$$\frac{W}{Q_2} = \frac{T_2 - T_1}{T_2}$$

Thus the efficiency of the Carnot engine is given by the working temperature. Any other heat engine working reversibly between these temperatures will have the same efficiency.

This efficiency does not depend upon the working substances, design of the engine etc., because as per the above equation efficiency depends on only the temperature of source and sink and nothing else.

Efficiency of a heat engine is always less than one :-

We know that

$$\text{Proof: } \eta = \frac{T_2 - T_1}{T_2} = \frac{T_2}{T_2} - \frac{T_1}{T_2}$$

$$\text{i.e., } \eta < 1$$

Reason: We know that $\eta = \frac{T_2 - T_1}{T_2}$ (b)

If $T_1 = 0$ then

$$\eta = \frac{T_2 - 0}{T_2} = \frac{T_2}{T_2} = 1.$$

i.e., If we use a sink in the Carnot cycle, whose temperature is absolute zero (i.e., 0K) then efficiency will be 1. But 0K is unattainable. So η will always be less than 1.

A heat engine cannot work between two reservoirs with same temperature.

Reason: If $T_2 = T_1$, then efficiency is zero. That means the machine cannot work.

Concept of Entropy:-

Definition of entropy from the efficiency of Carnot's engine:-

Based on second law, we define a new thermodynamic property called entropy. We express the efficiency of a heat engine by the following expression.

$$\frac{W}{Q_2} = \frac{T_2 - T_1}{T_2} \quad \text{We know } W = Q_2 - Q_1$$

Neglecting the signs of heat quantities it may be said that W is equal to the algebraic sum of Q_2 and Q_1 . Therefore,

$$W = Q_2 + Q_1$$

$$\frac{Q_2 + Q_1}{Q_2} = \frac{T_2 - T_1}{T_2}; \quad 1 + \frac{Q_1}{Q_2} = 1 - \frac{T_1}{T_2}$$

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

This tells that in a reversible cycle sum of (Q/T) terms is equal to zero. This is stated as

$$\oint \frac{q_{rev}}{T} = 0. \quad \text{①}$$

We know that the cyclic integral of an exact differential is zero so $\frac{q_{rev}}{T}$ is an exact differential. $\frac{q_{rev}}{T}$ is denoted as dS .

$$\therefore dS = \frac{q_{rev}}{T}$$

S is called the entropy. It is a state property, If S_1 is the entropy of the system in its initial state and S_2 at the final state

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

ΔS is entropy change. It does not depend upon the path in which the system undergoes the change. It depends upon the initial and final states only. Entropy is an extensive property similar to internal energy.

Definition:-

Change of entropy (ΔS) of a system is defined as the integral of all the terms involving heat change (q) divided by the absolute temperature (T) during each infinitesimally small change of the process carried out reversibly.

$$\text{Mathematically } \Delta S = \int_1^2 \frac{q_{rev}}{T}$$

Entropy as a Function of P and T :- (a)

consider the general expression for the change in entropy.

$$ds = \frac{1}{T} dE + \frac{P}{T} dv \quad \text{--- (1)}$$

consider also the definition of enthalpy

$$E = H - Pv; \quad dE = dH - pdv - vdp$$

$$ds = \frac{dH}{T} - \frac{pdv}{T} - \frac{vdp}{T} + \frac{P}{T} dv$$

$$ds = \frac{dH}{T} - \frac{v}{T} dp \quad \text{--- (2)}$$

If we consider enthalpy as a function of temperature and pressure

$$dH = C_p dT + \left(\frac{dH}{dP} \right)_T dp$$

Substituting this value of dH in (2)

$$ds = \frac{C_p}{T} dT + \frac{1}{T} \left[\left(\frac{dH}{dP} \right)_T - v \right] dp$$

At constant pressure $dp = 0$

$$\therefore ds = \frac{C_p}{T} dT; \quad \Delta S = \int \frac{C_p}{T} dT$$

This equation relates entropy change with temperature, at constant pressure.

At constant temperature the above eqn. reduces to

$$ds = -v \alpha dp; \quad \left(\frac{ds}{dp} \right)_T = -v \alpha$$

v is molar volume and α is coefficient of expansion.

Entropy change in ideal gases :-

Entropy change in isothermal expansion of an ideal gas :-

$$\text{From first law} \quad \Delta E = Q - W$$

In an isothermal reversible expansion of an ideal gas $\Delta E = 0$.

(10)

$\therefore Q_{rev} - W = 0$; i.e., $Q_{rev} = W$

We know work done in such a case

$$W = nRT \ln \frac{V_2}{V_1}; \therefore Q_{rev} = nRT \ln \frac{V_2}{V_1}$$

Dividing through out by T $\frac{Q_{rev}}{T} = nR \ln \frac{V_2}{V_1}$

But by definition $\frac{Q_{rev}}{T} = \Delta S$; $\Delta S = nR \ln \frac{V_2}{V_1}$

~~But by~~

Entropy change when V and T are the variables:

The general expression for the entropy change of any system give below.

$$dS = \frac{1}{T} dE + \frac{P}{T} dV \quad \text{--- (1)}$$

For an ideal gas $dE = C_V dT$

$$\therefore dS = \frac{C_V}{T} dT + \frac{P}{T} dV$$

For one mole of an ideal gas $P = \frac{RT}{V}$

Substituting this value of P in the above equation

$$dS = \frac{C_V}{T} dT + \frac{R}{V} dV$$

Integrating the equation between limits.

$$\int_1^2 dS = \int_{T_1}^{T_2} \frac{C_V}{T} dT + R \int_{V_1}^{V_2} \frac{1}{V} dV$$

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

Entropy change when P and T are the variables:

We know, from definition $E = H - PV$

$$dE = dH - PdV - VdP$$

Substituting this value of dE_{Pn} equation (1)

$$ds = \frac{1}{T} (dH - PdV - vdp) + \frac{P}{T} dv.$$

$$ds = \frac{1}{T} dH - \frac{v}{T} dp.$$

For this and ideal gas $dH = c_p dT$;

$$ds = \frac{1}{T} c_p dT - \frac{v}{T} dp$$

For one mole of an ideal gas $v = RT/p$

$$ds = \frac{1}{T} c_p dT - \frac{R}{p} dp.$$

Integrating between limits

$$\Delta s = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}.$$

Entropy of mixing of ideal gases :-

Consider the expression for the entropy change of an ideal gas.

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

General integration of the above gives.

$$S = c_v \ln T + R \ln v + S_0 \quad \text{--- (1)}$$

S_0 is the integration constant

Now consider a number of ideal gases placed in a vessel separately using partitions. Let n_i be number of moles of the gas i and v_i be its volume. If the gases are at the same temperature, the total entropy is given as

$$S_T = \sum n_i (c_v \ln T + R \ln v_i + S_i) \quad \text{--- (2)}$$

If the partitions are removed, the gases mix together. Now the volume of each gas is the total volume. The

total entropy ⁽¹²⁾ is given as
after mixing,

$$S_2 = \sum n_i (C_v \ln T + R \ln V + S_i) \quad \text{--- (3)}$$

If the gases, before mixing were at the same pressure

$$\frac{V_i}{V} = \frac{n_i}{n} = x_i$$

n is the total number of moles, x_i is the mole fraction of i the gas.

Rearranging

$$V_i = x_i V$$

Substituting this value of V_i in (2)

$$S_1 = \sum n_i (C_v \ln T + R \ln x_i + R \ln V + S_i) \quad \text{--- (4)}$$

The increase in entropy due to mixing of gases is obtained as

$$\Delta S_m = S_2 - S_1 = (4) - (3)$$

For one mole of the gases,

$$\Delta S_m = -R \sum \frac{n_i}{n} \ln x_i = -R \sum x_i \ln x_i$$

For two gases the above equation becomes

$$\Delta S_m = -R (x_1 \ln x_1 + x_2 \ln x_2)$$

Entropy changes in isothermal transformation:

$$\Delta S_T = R \ln \frac{V_2}{V_1} = 2.303 R \log \frac{V_2}{V_1}$$

(or)

$$\Delta S_T = R \ln \frac{P_1}{P_2} = 2.303 R \log \frac{P_1}{P_2}$$

Entropy changes in isobaric (constant pressure) process.