

Question: → (a) Give two statements of the 2nd law of thermodynamics.

(b) Prove the Clausius inequality $\sum_i \frac{Q_i}{T_i} \leq 0$

Ans: → (a) Second law of thermodynamics is the direct consequence of Carnot's theorem. This involves the principle of convertibility of heat to work which arose out of Carnot's speculations.

Lord Kelvin stated the law in this form: →

"It is impossible to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects."

Clausius stated in the form: -

"It is impossible for a self-acting machine unaided by any external agency to convey heat from any body to another at a higher temperature, a heat can not itself pass from a colder to warmer body."

(b) Let η and η' be the efficiencies of a reversible and irreversible cycle operating between same two limits of temp. T_1 and T_2 respectively.

Then $\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$ and since $\eta' < \eta$

$$\frac{Q_1 - Q_2}{Q_1} < \frac{T_1 - T_2}{T_1}$$

or $\frac{Q_1}{T_1} - \frac{Q_2}{T_2} < 0$ and taking account of the signs we get

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} < 0$$

in general $\oint \frac{dQ}{T} < 0$

Therefore combining the expression for reversible and irreversible process we get

$$\int \frac{dQ}{T} \leq 0 \quad \left\{ \int \frac{dQ}{T} = 0 \right\}$$

This equation is known as Clausius equation of inequality.

Let us consider a system whose particles can exchange energy and interact only with one another such a system neither loses nor gains energy from outside and is therefore known as an isolated system. If all the

parts of the system are at the same temp, it is said to be in thermal equilibrium. This means that the system is in the state of maximum thermodynamic probability. The ~~prob~~ probability of the system existing in a microstate having even a small deviation from the state of maximum probability is negligible. Hence if the system initially exists in some state other than the equilibrium state due to natural collision between the particles constituting the system, the entropy 'S' of a system is proportional to the thermodynamic probability ω . Hence the system is moving from a state of lower probability to the state of maximum entropy. It is not possible for the system to itself move in opposite direction when the system is in equilibrium entropy S has the maximum value.

For the state of equilibrium change in entropy

$$\Delta S = 0$$

when moves from a state of lower probability to the state of maximum probability there is an increase in entropy.

Hence the entropy of an isolated system remains constant or increasing according as the change it undergoes are reversible or irreversible.