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Clausius theorem and clausius inequality :→

→ Clausius theorem → For any reversible cyclic process

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

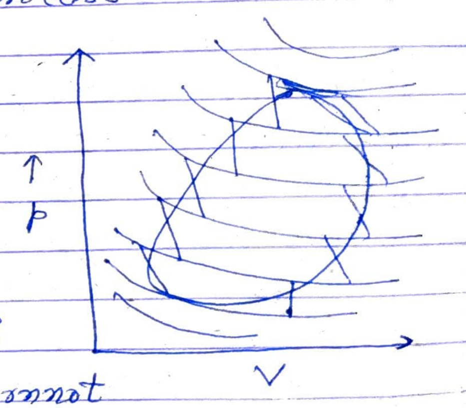
We have $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$

Here Q_1 is the heat absorbed by the working substance and so it is positive and Q_1 is the heat rejected by it and so it is negative. Hence for reversible carnot cycle we have

$$\frac{Q_1}{T_1} + \left(-\frac{Q_2}{T_2}\right) = 0$$

$$\text{or,} \quad \sum \frac{Q}{T} = 0 \quad \text{------ (1)}$$

This equation states that the algebraic sum of quantities $\frac{Q}{T}$ is zero in a reversible cyclic process.



Now Consider an arbitrary reversible cyclic process, Draw a set of closely spaced isotherms and then Join them by short adiabatic lines cutting the cycle given in figure. ~~P~~

This way, arbitrary cyclic is divided into large number of tiny carnot cycles. Now, first traverse the individual carnot cycles and then go once round the cycle along the Jagged path. Note that the two traversals are exactly equivalent to each other because adjacent carnot cycles have a common isotherm and its traversal in opposite directions in the two adjacent carnot cycles cancel each other. Thus heat transfer and workdone along the Jagged path are the same as the heat transfer and the workdone in transversing the Carnot cycles. If ΔQ is the heat transfer at temp. T then for the Carnot cycles we have from (1)

$$\sum \frac{\Delta Q}{T} = 0$$

In the limiting case when the Carnot cycles are infinitesimally small, the Jagged path coincides exactly with the arbitrary reversible cyclic process. Thus for any reversible cyclic process,

$$\oint_R \frac{dQ}{T} = 0 \quad \text{--- (2)}$$

where $\oint$ indicates the integral over a cyclic path and 'R' stands for reversible cycle. This is called Clausius theorem.

→ Clausius Inequality theorem :→

Statement → For any reversible cyclic process

$$\oint_R \frac{dQ}{T} \leq 0$$

Let us consider the cycle of an irreversible engine which absorbs Q_1 amount of heat at temp T_1 and rejects Q_2 amount of heat at temp. T_2 then efficiency of this engine is $\frac{Q_1 - Q_2}{Q_1}$ and the efficiency of a reversible Carnot engine working between the same two temp. is $1 - \frac{T_2}{T_1}$. Since the efficiency of an irreversible engine is less than a reversible one working between the same temp. we have for an irreversible cycle,

$$1 - \frac{Q_2}{Q_1} < 1 - \frac{T_2}{T_1}$$

$$\text{or,} \quad \frac{Q_2}{Q_1} > \frac{T_2}{T_1}$$

or, $$\frac{Q_1}{T_1} + \left(-\frac{Q_2}{T_2}\right) < 0$$

or, $$\sum \frac{Q}{T} < 0 \quad \text{------} \quad (1)$$

Now any arbitrary irreversible cyclic process may be divided into large number of infinitesimal small irreversible cyclic process. Hence arguing in the same way as before we have for any irreversible cyclic process.

$$\oint_I \frac{dQ}{T} < 0 \quad \text{----} \quad (2)$$

This relation combined with (1) gives

$$\int \frac{dQ}{T} \leq 0$$

Where the inequality sign holds for irreversible cyclic processes and the equality sign holds for reversible cyclic processes. This is known as clausius inequality.

Entropy → From clausius inequality we have

$$\Delta S \geq \int \frac{dQ}{T}$$

where inequility for irreversible process and equility for reversible process.

Since the inequality sign holds for irreversible processes, it is prove that in all irreversible processes in this universe entropy increases and in the reversible process $\Delta S = 0$, that is, entropy of the universe remains unchanged. The result $\Delta S \geq 0$ is of great importance. This fixes up the criterion or reversibility of any process. The process, in which $\Delta S > 0$, that is, ~~therefore~~ is increase in entropy of the Universe is irreversible and the one in which $\Delta S = 0$, that is, entropy remains constant, is reversible. This also gives criterion for any process to occur. In this universe all natural processes are taking place irreversibly and hence by all processes going around us the entropy of the universe is ever increasing. The natural direction of any process is therefore towards irreversibility. Thus the second law fixes up the direction of a physical or chemical change as the direction in which entropy of the universe increases.

The second law of thermodynamics can now be stated in terms of entropy in this way –

" A Physical or chemical process will proceed in the direction that causes the entropy of the universe to increase."

This is also known as the principle of entropy of the universe.

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