MEDICAL UNIVERSITY – PLEVEN
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LECTURE No3

EQUILIBRIUM THERMODYNAMICS

The laws of thermodynamics. Mathematical formulation of the first law. Limitations of the first law. Second law. Phenomenological definition of entropy

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EQUILIBRIUM THERMODYNAMICS

(Latin: aequalis = level and libra = weight or balance + Greek: thermos = heat and dynamis = power).

Equilibrium thermodynamics is the systematic study of transformations of matter and energy in systems as they approach equilibrium.

The word equilibrium implies a state of balance.

- **Zeroth law** - thermodynamic equilibrium is an equivalence relation. If two thermodynamic systems are in thermal equilibrium with a third, they are also in thermal equilibrium with each other.

- **First law** - about the conservation of energy.

- **Second law** - about entropy.

- **Third law** - about absolute zero temperature. As a system asymptotically approaches absolute zero of temperature all processes virtually cease and the entropy of the system asymptotically approaches a minimum value.

FIRST LAW OF THERMODYNAMICS

1. The total energy of an isolated system always remains constant, although there may be a change from one form to another.

Or 2. The energy of an isolated system remains constant and whenever a quantity of some form of energy disappears, an exactly equivalent quantity of some other form of energy must be produced.

Or 3. Any gain or loss of energy by the system must be exactly equivalent to the loss or gain, respectively, by the surroundings of the system.

Or 4. Whenever a certain quantity of energy is produced, an equivalent amount of other form of energy must be used up.

Or 5. Energy can neither be created nor destroyed, the only change which energy can undergo is a transformation from one form to another.

Or 6. The total energy of a system, plus its surroundings remains constant.

Mathematical formulation of the First law

$$dQ=dU+dW$$

Limitations of the first law

- While the first law establishes the equivalence between heat and work, it imposes no condition on their mutual convertibility. It never tells us under what circumstances and to what extent it is possible to convert one form of energy into another.
- First law tells us that the amount of heat lost by the hot body must be equial to that gained by the cold body but there is nothing in the first law which tells us that the heat has to flow spontaneously from the hotter to the colder body and not in the reverse direction.
- When we examine the relationship between heat and work, we notice that whereas different forms of energy can be readily and completely converted into heat, it is not possible to convert back heat completely into work.

Second law of thermodynamics

Phenomenological definition of entropy

1. It is impossible for a self-acting machine unaided by any external agency to convey heat from a lower to a higher temperature.

Or, 2. It is impossible to lift a weight and cool a body without leaving any other change.

Or, 3. It is impossible to convert heat into an equivalent amount of work without producing other changes in some parts of the system.

Or, 4. The total entropy of a system must increase if a process is to occur spontaneously. Entropy is a state function.

- $dS = S_2 - S_1 = \frac{dQ}{T}$ for reversible processes
- $dS > \frac{dQ}{T}$ for irreversible processes

For an isolated system:

1. Entropy does not change during reversible processes ($dS=0$) and increases during irreversible processes.

2. Only those processes can naturally take place where entropy will increase. All real processes are irreversible.

3. Entropy of closed and open systems may decrease ($dS<0$) if these systems give off heat to the environment ($dQ<0$).