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Applied Physics

Lecture-13 & 14

Unit III-Thermal Properties of solids

Topics to be discussed in this lecture:

- Thermodynamic system
- Thermal equilibrium and concept of temperature (**Zeroth law of thermodynamics**)
- **First law of thermodynamics**
- **Entropy and Second law of thermodynamics**
- **Third law of thermodynamics**

Thermodynamic System

A thermodynamic system is one which can be described in terms of the thermodynamic co-ordinates. The coordinates of a thermodynamic system can be specified by any pair of quantities viz., pressure (P), volume (V), temperature (T) and entropy (S). The thermodynamic systems in engineering are gas, vapour, steam, mixture of gasoline vapour and air, ammonia vapours and its liquid. In Physics, thermodynamics includes besides the above, systems like stretched wires, thermocouples, magnetic materials, electrical condenser, electrical cells, solids and surface films.

Examples :

1. **Stretched wire**

In a stretched wire, to find the Young's modulus of a wire by stretching, the complete thermodynamic co-ordinates are

(a) The stretching force F

(b) The length of the stretching wire and

(c) The temperature of the wire.

The pressure and volume are considered to be constant.

2. **Surface Films**

For liquid films, in the study of surface tension, the thermodynamic co-ordinates are

(a) The surface tension

(b) The area of the film and

(c) The temperature.

Thermal equilibrium and Concept of Temperature(Zeroth law of thermodynamics

A thermodynamic system is said to be in thermal equilibrium if any two of its independent thermodynamic coordinates X and Y remain constant as long as the external conditions remain unaltered. Consider a gas enclosed in a cylinder fitted with a piston. If the pressure and volume of the enclosed mass of gas are P and V at the temperature of the surroundings, these values o P and V will remain constant as long as the external conditions viz. temperature and pressure remain unaltered. The gas is said to be in thermal equilibrium with the surroundings.

The **zeroth law of thermodynamics** was formulated after the first and the second laws of thermodynamics have been enunciated. **This law helps to define the term temperature of a system.**

This law states that if, of three systems, A, B and, C, A and B are separately in thermal equilibrium with C, then A and B are also in thermal equilibrium with one another.

Therefore, the **temperature** of a system can be defined as the property that determines whether or not the body is in thermal equilibrium with the neighboring systems. If a number of systems are in thermal equilibrium, this common property of the system can be represented by a single numerical value called the temperature, it means that if two systems are not in thermal equilibrium, they are at different temperature.

Example: In mercury glass thermometer, the pressure above the mercury column is zero and volume of mercury measures the temperature. If a thermometer shows a constant reading in two systems A and B separately, it will show the same reading even when A and B are brought in contact.

Concept of Heat (H) and Work (W)

Heat is defined as energy in transit. As it is not possible to speak of work in a body, it is also not possible to speak of heat in a body. Work is either done on a body or by a body. Similarly, heat can flow from a body or to a body. If a body is at a constant temperature, it has both mechanical and thermal energies due to the molecular agitations and it is not possible to separate them. So, in this case, we cannot talk of heat energy. It means, if the flow of heat stops, the word heat cannot be used. It is only used when there is transfer of energy between two or more systems.

So to summarize:

- Heat and work are both transient phenomena. Systems do not possess heat or work.
- When a system undergoes a change, heat transfer or work done may occur.
- Heat and work are boundary phenomena. They are observed at the boundary of the system.
- Heat and work represent the energy crossing the boundary of the system.
- Heat and work are path functions and hence they are inexact differentials. They are written as ∂H and ∂W.
- Heat is defined as the form of energy that is transferred across a boundary by virtue of difference of temperature or temperature gradient.

  Whereas Work is said to be done by a system if the sole effect on things external to the system could be the raising of a weight.

It is customary to represent, work done by the system as +ve, and work done on the system as -ve, heat flowing into the system as + ve, and heat flowing out of the system as -ve.

First Law of Thermodynamics

Joule's law gives the relation between the work done and the heat produced. It is true when the whole of the work done is used in producing heat or vice-versa. Here, W = JH where J is the Joule's mechanical equivalent of heat. But in practice, when a certain quantity of heat is supplied to a system the whole of the heat energy may not be converted into work. Part of the heat may be used in doing external work and the rest of the heat might be used in increasing the internal energy of the molecules. Let the quantity of heat supplied to a system be ∂H, the amount of external work done be ∂W and the increase in internal energy of the molecules be ∂U. The term U represents the internal energy of a gas due to molecular agitation as well as due to the forces of inter-molecular attraction.

Mathematically,

$$\boldsymbol{\partial H = \partial W + \partial U} \qquad (1)$$

Equation 1 represents the **first law of thermodynamics**. All the quantities are measured in heat units. The first law of thermodynamics states that the amount of heat given to the system is equal to the sum of the increase in the internal energy of the system and the external work done.

For a cyclic process, the change in the internal energy of the system is zero because the system is brought back to the original condition. Therefore for a cyclic process $\oint \partial U$=0

and $\oint \partial H = \oint \partial W$ (2)

This equation represents joule's law.

Second Law of Thermodynamics

A heat engine is chiefly concerned with the conversion of heat energy into mechanical work. A refrigerator is a device to cool a certain space below the temperature of its surroundings. The first law of thermodynamics is a qualitative statement which does not preclude the possibility of the existence of either a heat engine or a refrigerator. The first law does not contradict the existence of either a heat engine or a self-acting refrigerator.

In practice, these two are not attainable. These phenomena are recognized and this led to the formulation of a law governing these two devices. It is called **second law of thermodynamics.**

A new term reservoir is used to explain the second law. A reservoir is a device having infinite thermal capacity and which can absorb, retain or reject unlimited quantity of heat without any change in its temperature.

Kelvin-Plank statement of the second law is as follows;

"It is impossible to get a continuous supply of work from a body (or engine) which can transfer heat with a single heat reservoir. This is a negative statement. According to this statement, a single reservoir at a single temperature cannot continuously transfer heat into work. It means that there should be two reservoirs for any heat engine. One reservoir (called the source) is taken at a higher temperature and the other reservoir (called the sink) is taken at a lower temperature.

According to this statement, zero degree absolute temperature is not attainable because no heat is rejected to the sink at zero degree Kelvin. If an engine works between any temperature higher than zero degree Kelvin and zero degree kelvins, it means it uses a single reservoir which contradicts Kelvin Planck's statement of the second law. Similarly, no engine can be 100% efficient.

In a heat engine, the engine draws heat from the source and after doing some external work, it rejects the remaining heat to the sink. The source and sink are of infinite thermal capacity and they maintain constant temperature.

First Part.

According to Kelvin, the second law can also be stated as follows: "it is impossible to get continuous supply of work from a body by cooling it to a temperature lower than that of its surroundings".

In a heat engine the working substance does some work and rejects the remaining heat to the sink. The temperature of the source must be higher than the surroundings and the engine will not work when the temperatures of the source and the sink are the same.

Take the case of a steam engine. The steam (working substance) at high pressure is introduced into the cylinder of the engine. Steam expands, and it does external work. The contents remaining behind after doing work are rejected to the surroundings. The temperature of the working substance rejected to the surroundings is higher than the temperature of the surroundings.

If this working substance rejected by the first engine is used in another engine, it can do work and the temperature of the working substance will fall further.

It means that the working substance can do work only if its temperature is higher than that of the surroundings.

Second Part.

According to Clausius:

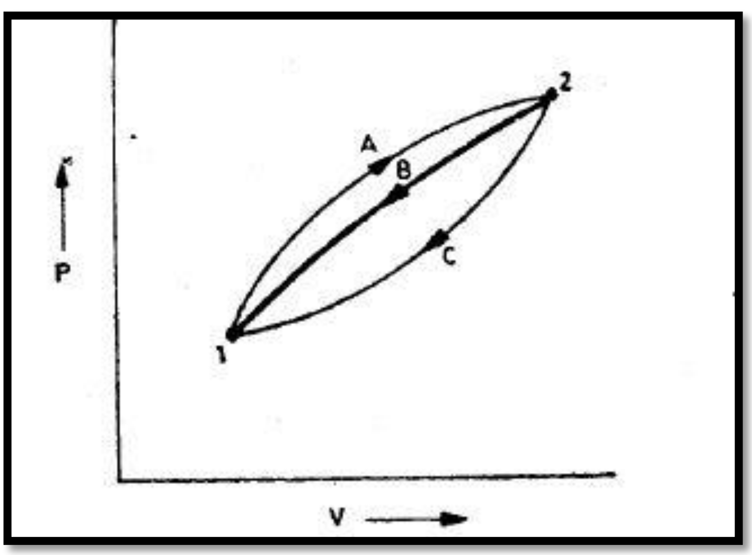
"It is impossible to make heat flow from a body at a lower temperature to a body at a higher temperature without doing external work on the working substance."

This part is applicable in the case of ice plants and refrigerators. Heat itself cannot flow from a body at a lower temperature to a body at a higher temperature. But, it is possible, if some external work is done on the working substance. Take the case of ammonia ice plant. Ammonia is the working substance. Liquid ammonia at low pressure takes heat from the brine solution in the brine tank and is converted to low pressure vapour. External work is done to compress the ammonia vapours to high pressure. This ammonia at high pressure is passed through coils over which water at room temperature is poured. Ammonia vapour gives heat to water at room temperature and gets itself converted into liquid again. This high pressure liquid ammonia is throttled to low pressure liquid ammonia. In the whole process ammonia (the working substance) takes heat from brine solution (at a lower temperature) and gives heat to water at room temperature (at a higher temperature). This is possible only due to the external work done on ammonia by the piston in compressing it. The only work of electricity in the ammonia ice plant is to move the piston to do external work on ammonia. If the external work is not done, no ice plant or refrigerator will work. Hence, it is possible to make heat flow from a body at a lower temperature to a body at a higher temperature by doing external work on the working substance.

Thus, the second law of thermodynamics plays an important part for practical devices e,g., heat engines and-refrigerators'. The first law of thermodynamics only gives the relation between the work done and the heat produced. But the second law of thermodynamics gives the conditions under which heat can be converted into work.

Entropy and the second law of thermodynamics

Consider a closed system undergoing a reversible process from state 1 to state 2 along the path A and from state 2 to state 1 along the path B as shown in figure below.



As this is a reversible process

$$\oint \frac{\partial H}{T} = 0$$

Therefore, $\oint_{1A}^{2A} \frac{\partial H}{T} + \oint_{2B}^{1B} \frac{\partial H}{T} = 0$ (3)

Now consider the reversible cycle from state 1 to state 2 along the path A and from state 2 to state 1 along the path C,

For the reversible cyclic process,

$$\oint_{1A}^{2A} \frac{\partial H}{T} + \oint_{2C}^{1C} \frac{\partial H}{T} = 0 \qquad (4)$$

From equations 3 and 4,

$$\oint_{2B}^{1B} \frac{\partial H}{T} = \oint_{2C}^{1C} \frac{\partial H}{T} \qquad (5)$$

This shows that $\oint \frac{\partial H}{T}$ has the same value for all the reversible paths from state 2 to state 1. The quantity $\oint \frac{\partial H}{T}$ is independent of the path and is a function of the end states only, therefore it is a property.

This property is called **entropy. Entropy** is a thermodynamical property and is defined by the relation

$$dS = \frac{\partial H}{T} \qquad (6)$$

or $$S_2 - S_1 = \oint_1^2 \frac{\partial H}{T} \qquad (7)$$

The quantity $S_2 - S_1$ represents the change in entropy of the system when it is changed from state 1 to state 2.

Third law of thermodynamics

In all heat engines, there is always loss of heat in the form of conduction, radiation and friction. Therefore, in actual heat engines $\frac{H_1}{T_1}$ is not equal to $\frac{H_2}{T_2}$.

Therefore, $\frac{H_1}{T_1} - \frac{H_2}{T_2}$ is not zero but it is not positive quantity. When cycle after cycle is repeated, the entropy of the system increases and tends to a maximum value. When the system has attained a maximum value, a stage of stagnancy is reached and no work can be done by the engine at this stage. In this universe the entropy is increasing and ultimately the universe will also reach a maximum value of entropy where no work is possible. With the increase in the entropy, the disorder of the molecules of a substance increases. The entropy is also a measure of the disorder of the system. With decrease in entropy, the disorder decreases. *At absolute zero temperature, the entropy tends to zero and the molecules of a substance or a system are in perfect order (welt arranged). This is the **third law of thermodynamics.***

Example-

The molecules are more free to move in the gaseous state than in the liquid state. The enropy is more in the gaseous state than in the liquid state. The molecules are more free to move in the liquid state than in the solid state. The enropy is more in the liquid state than in the solid state. Thus when a substance is converted from a solid to a liquid and then from the liquid to solid state, the entropy increases and vice versa. When ice is converted into water and then into steam, the entropy and disorder of the molecules increase. When the steam is converted into water and then into ice, the entropy and disorder of the molecules decrease. **Hence entropy is a measure of the disorder of the molecules of the system.**

By any ideal procedure, it is impossible to bring any system to absolute zero temperature performing a finite number of operations. This is called the **principle of unattainability of absolute zero.** Thus according to Fowler and Guggenheim, the **unattainability principle** is called the **third law of thermodynamics.**