VOLUME-13 Part B and C

CONTENTS

V. Thermodynamic and Statistical Physics

V. Thermodynamic and Statistical Physics

1.1 Laws of thermodynamics and their consequences

1. The Zeroth Law of Thermodynamics

Consider three system A, B and C which are separately in equilibrium. Suppose that no heat transfer occurs when C is placed in thermal contact with A and that no heat transfer occurs when C is placed in thermal contact with B. We know that $\beta_C = \beta_A$ and $\beta_C = \beta_B$. Where $\beta_A, \beta_B, \beta_C$ denotes the β parameter of system A, B, and C respectively. From these two equalities we conclude that,

$$\beta_A = \beta_B$$

Hence no heat transfer will occur if systems A and B are placed in thermal contact with each other. "If two systems are in thermal equilibrium with a third system then they must be in thermal equilibrium with each other". This statement is called as "zeroth law of thermodynamics".

$$\beta = \frac{1}{kT}$$

$$\therefore \qquad \beta = \frac{\partial \ln \Omega(U)}{\partial U}$$

$\Omega(U)$ is an increasing function of U.

$$\therefore \qquad \beta > 0 \text{ or } T > 0$$

Thus absolute temperature can never be negative. The lowest attainable temperature is therefore 0^0 absolute.

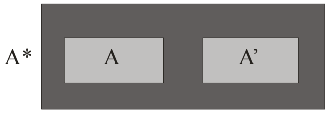
$$T^{-1} = k\frac{\partial \ln \Omega(U)}{\partial U}$$

The above equation gives the statistical definition of temperature.

Adiabatic Interaction

When two systems thermally insulated from each other, they can still interact and thus exchange energy with each other, provided that at least some of their external parameters change in the process, such an interaction is called as 'adiabatic interaction'. The increase of the mean energy of an adiabatically isolated system is called work done on the system and is denoted by W. The decrease of the mean energy of a system is called the work done by the system and is denoted by –W.

Since the interaction involves changes in some of the external parameter, at least some of the energy levels of the system are changed in the process which change the energy of the system.



Consider two systems A and A^1 which are insulated from each other and also from their environment. So the composite system A* is isolated A and A^1 are separated by an adiabatic frictionless movable piston. Initially, this piston is held in same position. When it is released, the volumes of A and A^1 change. Let w be the work done by A and W^1 be the work done on A^1.

Let ΔU be the change in energy of the system A and ΔU^1 be the change in energy of system A^1. Then

$$W = \Delta U$$

$$W^1 = \Delta U^1$$

But $\Delta U + \Delta U^1 = 0 \quad \because$ (A* is isolated)

$$\therefore \qquad W + W^1 = 0$$

$$\therefore \qquad W = -W^1$$

This shows that work done on one system is equal to the work done by the other system.

System in Contact with Heat Reservoir

Consider an object in a room. A heat reservoir is supposed to have infinite heat capacity. It has very large energy compared to energy of any system interacting with it. As a result, the temperature of the reservoir remain constant when it interacts with any system in it. Let us consider a system A in a heat reservoir A^1 at temperature T. The composite system A* is isolated and its energy U* must be constant. Let U and U^1 be the energies of A and A^1 respectively.

$$U^* = U + U^1$$

Let $U_1, U_2, U_3, \ldots$ be the energy states of the system and let them be non-degenerate. Under the conditions of equilibrium, what is the probability of finding the system A in any one particular state r? When A is in this one definite state r of energy Ur, then reservoir A^1 must have energy $U^* - Ur$. Since A is only in one definite state, the number of states accessible to A* is simply the number of states accessible to A^1. i.e. $\Omega^1\left(U^* - Ur\right)$.

Therefore, Probability that system A has energy *Ur*.

$$P(Ur) = \frac{\Omega^1\left(U^* - Ur\right)}{\sum \Omega^1\left(U^* - U^1\right)} \qquad \left(\because \Omega^1\left(U^1\right) = \Omega^1\left(U^* - Ur\right)\right)$$

$$P(Ur) = C.\Omega^1\left(U^* - Ur\right)$$

Where $\qquad P(Ur) = \dfrac{1}{\sum \Omega^1\left(U^* - U^1\right)}.$

$$ln\, P(Ur) = ln\, C + ln\, \Omega^1\left(U^* - Ur\right)$$

Now, $Ur << U^*$

$$\therefore \qquad ln\, \Omega^1\left(U^* - Ur\right) = ln\, \Omega^1\left(U^*\right) - \frac{\partial\, ln\, \Omega^1}{\partial U^1} Ur + \ldots\ldots\ldots\ldots$$

$$= ln\, \Omega^1\left(U^*\right) \frac{Ur}{kT} \left(\because \frac{\partial\, ln\, \Omega^1}{\partial U^1} = \beta = \frac{1}{kT}\right)$$

$$\therefore \qquad \ln P(Ur) = \ln C + \ln \Omega^1(U^*) - \frac{Ur}{kT}.$$

Let $\ln C + \ln \Omega^1 \ (U^*) = \ln A$

$$\ln P(Ur) = \ln A - \frac{Ur}{kT}$$

$$\therefore \qquad \ln P(Ur) = \ln A - \frac{Ur}{kT}$$

$$\therefore \qquad \ln\left(\frac{P(Ur)}{A}\right) = -\frac{Ur}{kT}$$

$$\therefore \qquad \frac{P(Ur)}{A} = e^{-Ur/kT}$$

$$\therefore \qquad P(Ur) = A \ e^{-Ur/kT}$$

Normalizing P(Ur) to unity, we get

$$\sum_r P(Ur) = \sum_r A \, e^{-Ur/kT}$$

$$\therefore \qquad \sum A \,.\, e^{-Ur/kT} = 1$$

$$\therefore \qquad A = \frac{1}{\sum e^{-Ur/kT}}$$

$$\therefore \qquad P(Ur) = \frac{e^{-Ur/kT}}{\sum_r e^{-Ur/kT}} \qquad \ldots 1$$

The exponential factor $e^{-Ur/KT}$ is called Boltzmann factor, the corresponding probability distribution equation (1) is known as canonical distribution or canonical ensemble. Equation (1) gives the relative probability of a system occupying a state *r* in a heat both at temperature T.

The probability distribution equation (1) allows us to calculate very simply the mean values of various parameters characterizing the system A in contact with the heat reservoir at absolute temperature T.

Let y be the quantity assuming y_r in state *r* of the system A.

$$\bar{y} = \sum y_r \, Pr$$

$$\therefore \qquad \bar{y} = \frac{\sum y_r . e^{-\beta Ur}}{\sum e^{-\beta Ur}}$$

What happen's when energy states are degenerate? Let g_r be the degeneracy of the state *r* in which a system has energy *Ur*. i.e. *gr* is the number of microstate each corresponding to energy *Ur* and they are 1, 2, 3,…… g_r. Then our system A will have the same energy. *Ur* whether it is in degenerate state or 1 or 2 or 3 or g_r.

$$\therefore \qquad P(Ur) = A \, g_r . e^{-Ur/kT}$$

Normalizing *P*(*Ur*) to unity,

$$\therefore \qquad P(Ur) = \frac{g_r . e^{-Ur/kT}}{\sum_r g_r . e^{-Ur/kT}}$$

This is the expression for the probability of a system being instate *Ur* of degeneracy *gr* in an environment of constant temperature *T*. For non-degenerate state $g_r = 1$.

It should be noted that the above discussion holds for any system A which has a very small energy compound to the energy of heat reservoir A^1. Hence it applies equally well to a molecule in an insulated macrosystem. Thus, the probability that a particle has energy Er is a system at temperature T is given by,

$$\therefore \qquad \Pr = \frac{e^{-Er/kT}}{\sum e^{-Er/kT}}$$

Entropy and Probability

We know that the number of microstates accessible to an isolated system increases in an irreversible process and remains same in a reversible process. Similarly we can say about a thermodynamic variable entropy. Entropy must be related to the number of microstates accessible to a system.

Consider a composite isolated system with two subsystems A and A^1 in thermal contact. Entropy is an additive function (extensive parameter). Therefore, Entropy of the composite system.

$$S^* = S_A + S_A^{\ 1} \qquad \ldots 1$$

Number of microstates accessible to A*

$$\Omega^* = \Omega_A \, \Omega_A^{\ 1} \qquad \ldots 2$$

S^*, S_A and SA^1 are entropies of the composite system A^*, A and A^1 respectively.

Ω^*, Ω_A and $\Omega_A^{\ 1}$ are the number of states accessible to A^*, A and A^1 respectively.

Entropy has to be some function of accessible microstates. Therefore, from equation (2).

$$f(\Omega^*) = f(\Omega_A \, \Omega_A^{\ 1})$$

$$f(\Omega^*) = f(\Omega_A) + f(\Omega_A^{\ 1})$$

This equation is possible if *f* is a logarithmic function of Ω.

$$\therefore \qquad S = A \ln \Omega \qquad \ldots 3$$

$$\left(\frac{\partial S}{\partial U}\right)_V = A . \frac{\partial \ln \Omega}{\partial U} = A\beta$$

$$= k . \frac{1}{kT}$$

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \ldots\ldots\ldots\ldots \left(\because A = k \text{ and } \beta = \frac{1}{kT}\right)$$

Continued with...Page 5 Onwards.... It's So Goooood!!!, Buy it now...!