STATISTICAL PHYSICS

(Part-3)

B.Sc. III (paper-1)

Unit-II

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THARMODYNAMIC PROBABILITY

The number of microstates corresponding to any given macrostate is called its thermodynamic probability. It represented by W.

For examples n particles and two compartment (or cells),is r is the number of particles in the compartment no. 1 and the remaining (n-r) are in compartment no. 2, then the no. of microstates in a macrostate (r, n-r or thermodynamics probability).

$$W_{(r,\, n-r)} = \frac{\mathbf{n}!}{\mathbf{r}!\ (\mathbf{n}-\mathbf{r})!} = {}^{n}C_{r} \qquad \ldots\ldots (1)$$

Applying this to a system of 4 distinguishable particles, for a macrostate (1,3), r=1,(n-r)=3 and n=4 the number of macrostates,

$$W_{(1,3)} = 4\,!\,/1!\,3!$$

$$=4$$

For macrostate (0, 4) or (4,0) will be

$$\mathbf{W_{(0,\,4)} = W_{(4,0)}}$$

$$= \frac{\mathbf{4}!}{\mathbf{0}!\ \mathbf{4}!}$$

$$=1 \qquad (\mathbf{0}! = \mathbf{1})$$

Most Probable Macrostate

The probability of a macrostate is defined as the ration of the ratio of the number of microstate (i.e. thermodynamic probability W) in it to the total number of possible microstate of the system.

Thus,

$$P_{macro} = \frac{\text{no.of microstates in the macrostate}}{\text{total no.of microstates of the system}} \qquad \ldots(2)$$

The total no. of ways of arranging n distinguishable particles in c numbered compartments=c^n

Ex-if there are only 2 compartments or cell, then the total no. of microstate of the system=$2^{n.}$

For 4 particles system, total no. of microstate will be 2^4=16. Form above eq. (2), we get.

$$P_{macro} = W/c^n$$

$$=W/2^n \qquad \ldots(3)$$

Substituting for W from eq.(1) in eq.(3), we get.

$$P_{(r,\, n-r)} = \frac{n!}{r!\ (n-r)!} \frac{1}{2^n}$$

$$P_{(r,n-r)} = \frac{1}{2^n} * {}^nC_r$$

This gives the probability of macrostate (r, n-r).

Combination Possessing Maximum Probability

We know from elementary algebra that if n is even the value of ^nC_r is maximum when r=n/2, refer eq. hence the maximum value of probability is given by

$$P_{max}=\frac{1}{2^n}\ {}^nC_{n/2}$$

$$=\frac{n!}{\frac{n}{2}!\frac{n}{2}!}*\frac{1}{2^n}$$

$$P_{max}=\frac{n!}{\left(\frac{n}{2}!\right)^2}*\frac{1}{2^n}$$

Combination Possessing Minimum Probability

We know from elementary algebra that ^nC_r is minimum, if r is equal to either zero or n.

If r=0, the probability is

$$P_{min}=\frac{n!}{r!\ (n-r)!}\frac{1}{2^n}$$

$$= \frac{\mathbf{n}!}{\mathbf{0}!\ (\mathbf{n}-\mathbf{0})!} \frac{\mathbf{1}}{\mathbf{2^n}}$$

$$\mathbf{P_{min}} = \frac{\mathbf{1}}{\mathbf{2^n}} \qquad \text{....... (1)}$$

If r=n, the probability is

$$P_{min} = \frac{\mathbf{n}!}{\mathbf{r}!\ (\mathbf{n}-\mathbf{r})!} \frac{\mathbf{1}}{\mathbf{2^n}}$$

$$= \frac{\mathbf{n}!}{\mathbf{r}!\ (\mathbf{n}-\mathbf{n})!} \frac{\mathbf{1}}{\mathbf{2^n}}$$

$$= \frac{\mathbf{n}!}{\mathbf{r}!\ \mathbf{0}!} \frac{\mathbf{1}}{\mathbf{2^n}}$$

$$\mathbf{P_{min}} = \frac{\mathbf{1}}{\mathbf{2^n}} \qquad \text{...... (2)}$$

Thus, from eq. (1) and eq. (2), we conclude that the minimum probability is given by

$$\mathbf{P_{min}} = \frac{\mathbf{1}}{\mathbf{2^n}}$$

Relation Between P and W

The probability of occurrence of a particular microstate is given by

$$\mathbf{P} = \frac{1}{2^n}$$

Because 2^n gives the total no. of microstates of a system of n particles to be arranged in two compartments (or cells) and all the microstates of a system have a priori probability. Thus, from equation, we have

$$P=W*p$$

P = no. of microstates in macrostate *probability of occurrence of a microstate

or $$\mathbf{P \propto W}$$

Therefore, the probability of a macrostate(P) is directly proportional to the thermodynamic probability(W).

Probability with Weightage

The theorem of the probability of a composite event, the probability of r successes and (n-r) failures in a specified order is

$$= (a*a*a*\ldots\ldots r \text{ times})*\{b*b*b\ldots\ldots(n-r) \text{ times}\}$$

$$= a^r\, b^{n-r}$$

But there are C ways in which r success and n-r failures can occur.

Therefore, the probability of exactly r successes out of n trails is

$$\mathbf{P={}^{n}C_{r}\,a^{r}\,.b^{n-r}} \qquad \text{...... (1)}$$

Thus the probability of 0, 1, 2, 3, …….. n successes respectively a

$$b^{n},\ {}^{n}C_{1}\,a.b^{n-1},\ {}^{n}C_{2}\,a^{2}\,.b^{n-2},\ldots..{}^{n}C_{r}\,a^{r.}\,b^{n-r},\ldots\ldots..a^{r}$$

which are the successive terms of the binomial expansion

$$(b+a)^{n} = b^{n}+{}^{n}C_{1}\,a.b^{n-1}+{}^{n}C_{2}\,a^{2}\,.b^{n-2}+\ldots..+{}^{n}C_{r}\,a^{r.}\,b^{n-r}+,\ldots\ldots..+a^{r}$$

Obviously ${}^{n}C_{r}\,a^{r}\,b^{n-r}$ is the $(r+1)^{th}$ term in the binomial expression of $(b+a)^{n}$.

The probability distribution of the number of success thus determined is called **BINOMIAL DISTRIBUTION.**

Thus, if a is the probability of happening of the event and b that of failing of the event then if n events are considered simultaneously, then the probability of happening of r evnts is

$$\mathbf{P(r)=\frac{n!}{r!\ (n-r)!}\ a^{r}\ b^{n-r}}$$

MOST PROBABLE STATE (EQUILIBRIUM STATE)

In Boltzmann distribution, one of the key ingredients is to calculate the most probable distribution. First things first, the most probable distribution is indicating the distribution of energy (distribution**)** that is most probable. On the other hand, we also talked about the probability of the microstates. It is crucial to understand the difference between distribution and microstates.

In the case of N particles distributed in two compartments, the probability of occurrence of the most probable state is given by

$$P_{max} = {}^{N}C_{N/2} / 2^{N}$$

Microstates describe the configurations of the system which is the most detailed view of the system in statistical physics. A distribution of the system describes the number of particles on each energy levels of the particle.

EXPRESSION FOR AVERAGE PROBABILITY

To understand the concept behind expression, consider a discrete random variable with range $R_X=\{x_1, x_2, x_3,...\}$. This random variable is a result of random experiment. Suppose that we repeat this experiment a very large number of times N, and that the trials are independent. Let N_1 be the number of times we observe x_1, N_2 be the number of times we observe x_2, ..., N_k be the number of times we observe x_k, and so on....

Since $P(X= x_k) = PX(x_k)$,

we expect that

$$P_X(x_1) = \frac{N1}{N}$$

$$P_X(x_2) = \frac{N2}{N}$$

....

$$P_X(x_k) = \frac{N_k}{N}$$

....

In other words, we have $N_k = NP_X(x_k)$.

Now, if we take the average of the observed values of X, we obtain

$$\text{AVERAGE} = \frac{N1x1 + N2x2 + N3x3 + \cdots..}{N}$$

$$= \frac{x1NPX(x1) + x2NPX(x2) + x3NPX(x3) + ..}{N}$$

$$=x1PX(x1) + x2PX(x2) + x3PX(x3) + \ldots.$$

$$\textbf{AVERAGE}=\sum \boldsymbol{P_r x_r}$$

The above eq. represents the average value of the properties of x.

Reference books:

Statistical mechanics by **Satya Prakash**.

Relativity and statistical physics by **J.C. Agarwa**l.

Heat thermodynamics and statistical by **Dr. N. Subramaniam Brijlal**.