A SIMPLE DERIVATION OF PLANCK-EINSTEIN'S FORMULA.

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A monatomic solid containing n atoms is considered. It is assumed that each atom oscillates with a fixed frequency ν, its energy being distributed equally for each of three degrees of freedom of atomic motion, and that the energy exchanges for one degree of freedom take place only in integral multiples of a quantum $h\nu$, where h denotes a universal constant. The difference between atoms having different quanta of energy can be regarded, from the standpoint of energetics, similar to the difference of isomeric molecules. The equilibrium between these atoms can be treated in the same way as a chemical equilibrium between isomers.

The energy of each kind of atom in the solid is uniquely determined by ν, and therefore the energy of a system composed of several kinds of atoms is equal to the sum of energy of each kind taken separately. The volume of each atom is constant at a given temperature, and therefore the total volume is also additive. Now a homogeneous mixture in which the energy and volume are additive is known as an ideal solution, the dilute solution being its special case. A chemical equilibrium in such a system follows the law of dilute solutions, and the equilibrium constant can be calculated in the ordinary way.

Let molar fractions of atoms whose energy for one degree of freedom is equal to 0, $h\nu$, $2h\nu$, $3h\nu$,...... $mh\nu$...... be respectively n_0/n, n_1/n, n_2/n, n_3/n...... ......n_m/n....... The equilibrium constant of the transformation of atoms having energy zero to those having energy $mh\nu$ is n_m/n_0. The energy absorbed in the change is $mh\nu N$ for one gram atom, N being Avogadro's constant. Then we have for a small change of absolute temperature T,

$$\frac{d\, ln\frac{n_m}{n_0}}{d\,T}=\frac{mh\nu N}{R\,T^2}, \qquad \text{R : Gas constant.}$$

Since ν is assumed to be constant independent of temperature, the following relation is obtained by integration.

$$ln\frac{n_m}{n_0}=-\frac{mh\nu N}{RT}+C.$$

The integration constant C can be easily known to be zero. For in the limiting case $m=0$, we have

$$n_m = n_0, \quad mh\nu = 0, \qquad \text{so} \quad C = 0.$$

Then the result of integration can be transformed to the following form.

$$\frac{n_m}{n_0} = e^{-\frac{mh\nu}{kT}},$$

k denoting Boltzmann's constant which is equal to R/N.

The number of each kind of atoms, $n_0, n_1, n_2, n_3 \ldots\ldots n_m \ldots\ldots$, can now be expressed as follows:

$$n_0,\ n_0 e^{-\frac{h\nu}{kT}},\ \ n_0 e^{-\frac{2h\nu}{kT}},\ \ n_0 e^{-\frac{3h\nu}{kT}},\ \ \ldots\ldots n_0 e^{-\frac{mh\nu}{kT}},\ \ldots\ldots$$

The total number n is equal to the sum of these values:

$$n = n_0 (1 + e^{-\frac{h\nu}{kT}} + e^{-\frac{2h\nu}{kT}} + e^{-\frac{3h\nu}{kT}} \ldots\ldots) = n_0 \frac{1}{1 - e^{-\frac{h\nu}{kT}}}.$$

Now the total energy E for all three degrees of freedom is equal to

$$3(0 + h\nu n_1 + 2h\nu n_2 + 3h\nu n_3 + \ldots\ldots),$$

i.e.

$$E = 3h\nu n_0 e^{-\frac{h\nu}{kT}} (1 + 2e^{-\frac{h\nu}{kT}} + 3e^{-\frac{2h\nu}{kT}} + \ldots\ldots).$$

If the mean energy of an atom be denoted with ε, we have

$$E = \varepsilon n = \varepsilon n_0 (1 + e^{-\frac{h\nu}{kT}} + e^{-\frac{2h\nu}{kT}} + \ldots\ldots).$$

The series in bracket in the former equation for E is evidently equal to the square of that in the latter equation. We have thus by equating these two equations,

$$3h\nu e^{-\frac{h\nu}{kT}} (1 + e^{-\frac{h\nu}{kT}} + e^{-\frac{2h\nu}{kT}} + \ldots\ldots) = \varepsilon,$$

i.e.

$$\varepsilon = 3h\nu \frac{e^{-\frac{h\nu}{kT}}}{1 - e^{-\frac{h\nu}{kT}}} = 3 \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}.$$

This is the equation of Planck-Einstein for the mean energy of an atom in a monatomic solid.

In the transformation of one gram atom of a certain kind of atom having energy $mh\nu$ to another kind having $m'h\nu$, in the same concentration, the maximum work or the decrease of free energy is equal to $RTln\frac{n_{m'}}{n_m}$, while the increase of energy is $(m'-m)h\nu N$. Now it is easily seen from the above results that

$$ln\frac{n_{m'}}{n_m} = -\frac{(m'-m)h\nu}{kT} = -\frac{(m'-m)h\nu N}{RT}.$$

This shows that the change of free energy and total energy is always equal to each other for such transformations. The theory of the action quantum, *i.e.* of the energy quantum proportional to frequency, is equivalent to the assumption that the equilibrium of interatomic exchange of energy in a solid can be treated as a chemical equilibrium and Berthelot-Thomsen's principle can be applied to this equilibrium.

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