

# Classical Principle of Equipartition of Energy

When a large number of indistinguishable, quasi-independent particles whose energy is expressed as the sum of  $f$  squared terms come to equilibrium the average energy per particle is  $f$  times  $\frac{1}{2}kT$ , where  $k$  is Boltzmann constant and  $T$  is absolute temperature.

Both kinetic theory and statistical mechanics, when applied to the molecules of an ideal gas (each having three translational degree of freedom) yield the result that at equilibrium the energy per particle associated with each degree of translational freedom is  $\frac{1}{2}kT$ . The method of kinetic theory can not be applied to rotational and vibrational degree of freedom, but the simple statistical method can deal with all types of molecular energy.

Energy of a molecule can be expressed as sum of independent terms each referring to a different degree of freedom.

$$E = E' + E'' + E''' + \dots$$

then

$$Z = \sum e^{-E/kT} = \sum e^{-(E' + E'' + E''' + \dots)/kT}$$

$$= \sum e^{-E'/kT} \cdot \sum e^{-E''/kT} \cdot \sum e^{-E'''/kT} \dots$$

$$= Z' \cdot Z'' \cdot Z''' \dots$$

If the various types of energy are calculated from classical physics, it is a simple matter to derive the classical principle of the equipartition of energy.

We know that

$$U = NkT^2 \left[ \frac{\partial (\ln Z)}{\partial T} \right]_V$$

and rewrite it as

$$\langle E \rangle = \frac{U}{N} = - \frac{\partial \ln Z}{\partial (\beta/kT)}$$

$$\text{or } \langle E \rangle = - \frac{\partial \ln Z}{\partial \beta}$$

Suppose  $\epsilon$  consists of terms representing kinetic energy of the type  $\frac{1}{2}mv^2$ , those representing rotational energy of the type  $\frac{1}{2}I\omega^2$ , those representing vibrational energy  $\frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2$  etc. All these forms of energy are expressed as squared terms of the type  $b_i p_i^2$ . Let there be  $f$  such terms, or

$$\epsilon = b_1 p_1^2 + b_2 p_2^2 + \dots + b_f p_f^2$$

Then, since the partition function is the product of the separate partition function

$$Z = \int_0^\infty e^{-\beta b_1 p_1^2} dp_1 \int_0^\infty e^{-\beta b_2 p_2^2} dp_2 \dots \int_0^\infty e^{-\beta b_f p_f^2} dp_f$$

$$\text{Let } y_i = \sqrt{\beta} p_i, \quad dy_i = \sqrt{\beta} dp_i$$

$$\text{Then } \int_0^\infty e^{-\beta b_i p_i^2} dp_i = \frac{1}{\sqrt{\beta}} \int_0^\infty e^{-b_i y_i^2} dy_i = \beta^{-1/2} k_i$$

where  $k_i$  does not contain  $\beta$ . The partition function becomes

$$\begin{aligned} Z &= \beta^{-1/2} k_1 \cdot \beta^{-1/2} k_2 \dots \beta^{-1/2} k_f \\ &= \beta^{-f/2} \cdot k_1 k_2 \dots k_f \end{aligned}$$

$$\text{Since } \langle E \rangle = - \frac{\partial \ln Z}{\partial \beta} = - \frac{\partial}{\partial \beta} \left[ -\frac{f}{2} \ln \beta + \ln k_1 + \ln k_2 + \dots + \ln k_f \right]$$

Hence

$$\langle E \rangle = \frac{f}{2\beta} = \frac{f}{2} kT$$

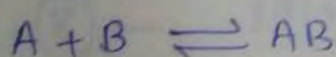
It has therefore been proved that, when a large number of non-distinguishable, quasi-independent particles whose energy is expressed as the sum of square terms come to equilibrium the average energy per particle is  $f$  times  $\frac{1}{2}kT$

The principle breaks down badly when applied to polyatomic molecules which have many vibrational degrees of freedom.

## Saha's Ionisation formula:-

It is to be expected that at very high temperatures the atoms will come into violent collision with each other, and as a result their valency electrons will either jump to higher quantum orbits, or will be altogether knocked off. *vice-versa*, when an ionised atom and electron come together, the ion may capture the electron, and may become a normal or an excited atom. This process is just analogous to chemical reaction. We shall use the law of mass action to derive the ionisation formula.

Consider the reaction



Let us consider a thermodynamic system in which  $N_a$  molecules of reactant A and  $N_b$  molecules of reactant B are mixed with  $N_{ab}$  molecules of the product AB. If the species A, B and AB were inert, then any composition  $N_a$ ,  $N_b$  and  $N_{ab}$  would be allowed. However, since a chemical reaction as given above may take place in the system, a state of equilibrium between the reactant and the product will be achieved eventually. According to the law of mass action

$$K_N = \frac{N_{ab}}{N_a N_b}, \text{ where } K_N \text{ is the equilibrium for the reaction based on the number of molecules present.}$$

$N_a^0$ ,  $N_b^0$  and  $N_{ab}^0$  represents the equilibrium values of  $N_a$ ,  $N_b$  and  $N_{ab}$ , respectively. In terms of the partition function we can write the above expression as

$$K_N = \frac{N_{ab}^0}{N_a^0 N_b^0} = \frac{Z_{ab}}{Z_a Z_b} \quad \text{--- (1)}$$

Thus the equilibrium constant is only a function of the partition function of the individual species. Once the partition functions are evaluated, the equilibrium constant may be determined and eq<sup>n</sup> (1) then provides a relationship between the species concentration at equilibrium.

For the reaction considered here, the equilibrium constant based on partial pressures at equilibrium,

$p_a^0$ ,  $p_b^0$  and  $p_{ab}^0$ , is obtained from eq<sup>n</sup> (1).

Using the eq<sup>n</sup> of state for an ideal gas

$$K_p = \frac{p_{ab}^0}{p_a^0 p_b^0} = \left(\frac{N}{P}\right) \frac{Z_{ab}}{Z_a Z_b} \quad \text{--- (2)}$$

Furthermore if  $\epsilon_0$  is the energy difference between the arbitrary zero-point energy level for the reactive system and the actual zero point energy level of a particular constituent, then,

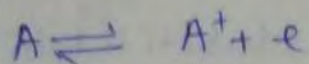
$$Z = Z_0 e^{-\epsilon_0/kT} \quad \text{--- (3)}$$

where  $Z$  is the partition function for the particular species based on the arbitrary zero point energy level and  $Z_0$  is the partition function referred to the actual zero point energy level of the constituent. The energy  $\epsilon_0$  takes account of the energy gained by the rest of the system when a chemical bond is broken. The energy is not included in the rotational, vibrational, translational, electronic or nuclear contribution which are now associated with the partition function  $Z_0$ . Comparison of eq<sup>n</sup> (3) and (1) show that

$$K_N = \frac{Z_{0ab}}{Z_{0a} Z_{0b}} \exp\left(-\frac{\Delta E_0}{kT}\right) \quad \text{--- (4)}$$

where  $\Delta E_0 = \epsilon_{0ab} = \epsilon_{0a} = \epsilon_{0b}$

Ionisation of atom can be represented by the chemical reaction.



The ion  $A^+$  combines with an electron to give the atom  $A$ . In this case the atom  $A$  is equivalent to the molecule  $A_2$ .

The law of mass action expressed in terms of the equilibrium constant in eq<sup>n</sup> (1) and (4) gives

$$K_N = \frac{N_A}{N_{A^+} N_e} = \frac{Z_A}{Z_{A^+} Z_e} \exp(-\Delta E_0 / kT) \quad \text{--- (5)}$$

For ionisation it is appropriate to treat each of the species as a non-atomic, ideal gas partition function are given by:-

$$Z_A = g_A \frac{V}{h^3} (2\pi m_A kT)^{3/2} \quad \text{--- (6)}$$

$$Z_{A^+} = g_{A^+} \frac{V}{h^3} (2\pi m_{A^+} kT)^{3/2} \quad \text{--- (7)}$$

$$\begin{aligned} Z_e &= g_e \frac{V}{h^3} (2\pi m_e kT)^{3/2} \\ &= \frac{2V}{h^3} (2\pi m_e kT)^{3/2} \quad \text{--- (8)} \end{aligned}$$

Under conditions for ionization of atoms, only the ground state contributes to the electronic partition function i.e. very few of the atoms are in an excited electron state. For this reason, only the ground-state statistical weights for the atom and ion,  $g_A$  and  $g_{A^+}$ , are included in the partition function. For electron the statistical weight is 2, corresponding to the two spin of an atom.

The energy difference for this reaction  $\Delta E_0$  (known as the heat of ionisation) is ordinarily expressed in terms of an ionisation potential  $V_i$  by

$$\Delta E_0 = -eV_i \quad \text{--- (9)}$$

Since the mass of the electron is so small, it is a good approximation to assume  $m_A = m_{A^+}$ . Substitution of eqn (6) to (9) into eqn (5) with this approximation gives

$$K_N = \frac{N_A}{N_{A^+} N_e} = \frac{g_A}{2g_{A^+}} \frac{h^3}{V} \frac{1}{(2\pi m_e kT)^{3/2}} \exp\left(\frac{eV_i}{kT}\right) \quad (10)$$

In terms of partial pressure, using eqn (2) gives

$$K_p = \frac{p_A}{p_{A^+} p_e} = \frac{N}{p} \frac{g_A}{2g_{A^+}} \frac{1}{V} \left(\frac{h^2}{2\pi m_e kT}\right)^{3/2} \exp\left(\frac{eV_i}{kT}\right) \quad (11)$$

If we suppose that we had originally started with A and gone on heating it in a confined space to a temperature T, and  $\alpha$  was the fraction ionised, we would have

$$p_e = p_{A^+} = \frac{N}{V} \alpha kT$$

$$p_A = \frac{N}{V} (1-\alpha) kT$$

$$\text{Total Pressure } p = p_A + p_e + p_{A^+} = \frac{N}{V} (1+\alpha) kT$$

$$\frac{p_A}{p} = \frac{1-\alpha}{1+\alpha}, \quad \frac{p_e}{p} = \frac{p_{A^+}}{p} = \frac{\alpha}{1+\alpha}$$

$$\therefore p_A = \left(\frac{1-\alpha}{1+\alpha}\right) p, \quad p_e = p_{A^+} = p \left(\frac{\alpha}{1+\alpha}\right)$$

$$K_p = \frac{p_A}{p_{A^+} p_e} = \left(\frac{1-\alpha}{1+\alpha}\right) p \cdot \left(\frac{1+\alpha}{\alpha}\right)^2 \frac{1}{p^2} = \frac{1-\alpha^2}{\alpha^2} \cdot \frac{1}{p} \quad (12)$$

Combining Eqn (11) and (12) we get

$$\frac{1-\alpha^2}{\alpha^2} = \frac{g_A}{2g_{A^+}} \frac{N}{V} \left(\frac{h^2}{2\pi m_e kT}\right)^{3/2} \exp\left(\frac{eV_i}{kT}\right)$$

$$\text{or } \frac{\alpha^2}{1-\alpha^2} = \frac{2g_{A^+}}{g_A} \frac{V}{N} \left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} \exp\left(\frac{eV_i}{kT}\right)$$

$$= \frac{2g_A^+}{g_A} \frac{(2\pi m_e)^{3/2}}{h^3} (kT)^{5/2} \exp\left(-\frac{eV_i}{kT}\right) \quad (13)$$

This is known as Saha's Ionisation formula. As this equation shows the fraction ionised depends upon  $V_i$ ,  $p$  and  $T$ . Eq<sup>n</sup> (13) can be rewritten as

$$\log\left(\frac{x^2}{1-x^2} p\right) = -\frac{U}{2.3RT} + \frac{5}{2} \log T - 6.459 \quad (14)$$

where  $p$  is now expressed in atmospheres and  $U$  is the heat of ionisation. This is the original form of equation given by Prof. Saha in 1919. The equation shows that the fraction ionised depends upon  $U$ ,  $p$  and  $T$ .

Eq<sup>n</sup> (13) and (14) have been widely applied to diverse fields, some of which are mentioned below:-

(1) Astro physics (physics of stars and sun).

(2) Electrical conductivity of flames.

(3) Formation of the electric arc.

(4) Formation of the ionosphere.

(5) Determination of the electron affinity of halogens.

Actually electrons arise from many other sources and therefore it is better to take its concentration as an independent constituent.

The complete form of the equation is therefore:-

$$\ln\left(\frac{n^+}{n} p_e\right) = -\frac{U}{RT} + \frac{5}{2} \ln T + \ln\left[\frac{(2\pi m_e)^{3/2}}{h^3} k^{5/2}\right] + \ln\left[\frac{2Ze(N^+)}{Z_e(N)}\right] \quad (15)$$

The formula is also applicable at any state  $M^r$  to  $M^{r+1}$  where  $M^r$  denotes the atom which has lost  $r$  electrons. If the heat of ionisation from  $M^r$  to  $M^{r+1}$ ,  $Z_e(M^r)$ ,  $Z_e(M^{r+1})$  the corresponding electronic partition function. we have

$$\ln\left(\frac{n_{r+1}}{n_r} p_e\right) = -\frac{U_r}{RT} + \frac{5}{2} \ln T + \ln\left[\frac{(2\pi m_e)^{3/2} (kT)^{5/2}}{h^3}\right] + \ln\left[\frac{2Z_e M^{r+1}}{Z_e M^r}\right] \quad (16)$$

$$\text{where } Z_e(M^r) = g_{r,0} + \sum g_{rs} e^{-X_{rs}/kT}$$

$g_{r,0}$  being the weight of ground state of  $M^r$ ,  $g_{rs}$  the weight of any excited state 's',  $X_{rs}$  the excitation energy of the excited state 's'. If we express  $p_e$  in bars, heat of ionisation in ionisation potentials, we obtain the Equation.

$$\log\left(\frac{n_{r+1}}{n_r} p_e\right) = -\chi_r \frac{5040}{T} + \frac{5}{2} \log T - 0.48 + \log \frac{2Z_e M^{r+1}}{Z_e(M^r)} \quad (17)$$

From this formula, the value of  $\frac{n_{r+1}}{n_r}$  can be calculated for any atom, either neutral or r-times ionised, provided  $\chi_r$  is known.  $Z_e(M^{r+1})$ ,  $Z_e(M^r)$  can be written out from the electronic structure but the actual values of  $\chi_r$ ,  $X_{rs}$  and excitation potentials have to be obtained from spectroscopic data.

Formula (1) is widely used in stellar physics.

Saha applied his Equation to the determination of the temperature of a stellar atmosphere. The spectrum of a star contains lines which originate from atoms (arc lines) and also those which originate from ions (spark lines). A comparison of the intensity of a spark line with that of an arc line, both referring to the same element, gives rise to a value of the degree of ionisation  $\alpha$ . Treating a star as a sphere of ideal gas, it is possible to obtain an estimate of the pressure of a stellar atmosphere. Since all the other quantities are known, the temperature can be calculated.