

{ B.Sc Part I (Physics Hons) }
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Question :- State the law of equipartition of energy. Deduce the law and using it account for the specific heat of gas

Ans :- Equipartition of Energy :-

The total number of independent quantities which are necessary to specify the configuration of any dynamical system is called the nos of degree of freedom of the system. The number depends upon the capacities for the motion of the system and not on the motion. It is determined solely by the geometrical and not the mechanical properties of the system. Thus an atom considered as a point, which is the actual practice, has three degrees of freedom, considered as a rigid sphere has six degree of freedom. A diatomic molecule will have five degree of freedom, three of translational and two of rotational. If the distance between the two atom is fixed, a triatomic molecule will have six degree of freedom, three of translation, and three of rotation. A pair of compasses has got seven degree of freedom while two rigid arms connected by a universal joint has nine.

Statement :-

In a dynamical system in thermal equilibrium the energy is equally distributed between various degree of freedom and for each of them is equal to $\frac{1}{2} kT$. Here $k =$ Boltzmann constant, $T =$ Absolute temp)

This law was first arrived at by Maxwell in 1859 and was later shown by Boltzmann to hold for the energies of rotation and vibration also.

Deduction :- we start with energy Expression

$$E = \frac{1}{2} \alpha_1 p_1^2 + E'$$

Here p_1, p_2, \dots are the new variables called 'more momentoids', $\alpha_1, \alpha_2, \dots$ are co-efficient which may depend on position co-ordinates q_1, q_2, \dots

E' represents the energy corresponding to the

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other momentoids and co-ordinates, and $\frac{1}{2} \alpha p_1^2$ denoted ⁽²⁾ the part of energy corresponding to the momentoid p_1 , α_1 is independent of p_1 but in ~~gen~~ general it may be a function of the q 's.

with the aid of generalized dynamical treatment Boltzmann showed that the law of distribution of particles having their motion defined by any set of $P+Q$ and contained within the range $q, q+dq, P+dP$ may be

$$dn = n A e^{(-\frac{1}{2} \alpha_1 p_1^2 + E')/KT} dp_1 dp_2 \dots dq \dots \dots \dots (2)$$

where $A =$ constant is given as

$$\int \dots \int = A e^{(-\frac{1}{2} \alpha_1 p_1^2 + E')/KT} dp_1 dp_2 \dots dq = 1 \dots \dots \dots (3)$$

$$\therefore A = \frac{1}{\int e^{-\frac{1}{2} \alpha_1 p_1^2 / KT} dp_1 \int \dots \int e^{-E'/KT} dp_2 \dots dq} \dots \dots \dots (4)$$

For the variables $p_1, p_2 \dots q_1, q_2 \dots$ are all independent, and hence the integral may be regarded as a product of two integrals.

The mean energy corresponding to the momentoid p_1 is

$$\frac{1}{n} \int \frac{1}{2} \alpha_1 p_1^2 dn = \int \frac{1}{2} \alpha_1 p_1^2 A e^{(-\frac{1}{2} \alpha_1 p_1^2 + E')/KT} dp_1 dp_2 \dots dq$$

$$= \frac{\frac{1}{2} \alpha_1 p_1^2 e^{-\frac{1}{2} \alpha_1 p_1^2 / KT} dp_1 \int \dots \int e^{-E'/KT} dp_2 \dots dq}{\int e^{-\frac{1}{2} \alpha_1 p_1^2 / KT} dp_1 \int \dots \int e^{-E'/KT} dp_2 \dots dq}$$

Since the 2nd integral in both the numerator and denominator are identical they cancel out and the expression for the mean energy becomes

$$\frac{\int_{-\infty}^{\infty} \frac{1}{2} \alpha_1 p_1^2 e^{-\frac{1}{2} \alpha_1 p_1^2 / KT} dp_1}{\int_{-\infty}^{\infty} e^{-\frac{1}{2} \alpha_1 p_1^2 / KT} dp_1} = \frac{1}{2} KT$$

$$\therefore E = \frac{1}{2} KT \dots \dots \dots (5)$$

The mean energy for the momentoid (p_1) is $\frac{1}{2} KT$. Similarly for the other momentoids also. Thus we observe that there is equipartition of energy between the different momentoids.



It is always possible to identify three momentoids with the translational motion of the C.O.G of a molecule and hence the energy of translational motion or to each degree of freedom is $\frac{1}{2}KT$. It ~~shd~~ should be borne in mind that the momentoid 'p' may refer to vibration also. By suitable transformations it can be shown that this result is also applicable to rotational K.E

Molecular and Atomic Energy :->

Equation (5) is very useful in calculating the total molecular energy of substances.

For monoatomic Gases :- Nos of degree of freedom = 03

Total number of degree of freedom = $3N$ (N being the nos of molecules) in a gram-molecule of the gas)

$$E = 3N \times \frac{1}{2}KT = \frac{3}{2}NKT$$

one molar specific heat at constant volume is

$$C_v = \frac{\delta}{\delta T}(E) = \frac{3}{2}NK = \frac{3}{2}R \quad (K = \frac{R}{N} \text{ or } R = KN)$$

$$= 2.98 \text{ cal degree}^{-1}$$

For all perfect gases $C_p - C_v = R$

$$\text{or } C_p = C_v + R$$

$$= \frac{3}{2}R + R = \frac{5R}{2} = 4.96 \text{ cal degree}^{-1}$$

$$\therefore \gamma = \frac{C_p}{C_v} = \frac{5}{3} = 1.66$$

These theoretical conclusions agree with experimental results for monoatomic gases like Argon, Helium etc

For Diatomic gases :->

$$E = 5N \times \frac{1}{2}KT = \frac{5}{2}RT \text{ and } \gamma = 1.4$$

For Triatomic gases :-

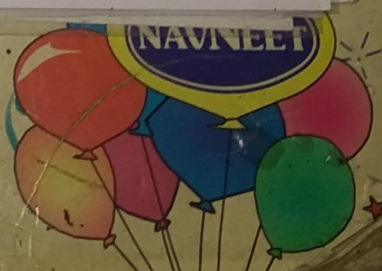
$$E = 6N \times \frac{1}{2}KT = \frac{6}{2}RT \text{ and } \gamma = 1.33$$

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Thank You



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