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On the rotation — vibration entropy of diatomic gases

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The rotation — vibration entropy results from the rotations of molecules and the vibrations of the atoms. The author has already published some papers on the rotation — vibration entropy of diatomic gases. In the present paper calculations will be made under more general conditions. The assumptions are the following: 1. The muclei do not generally vibrate along the line joining them. The nuclei perform small harmonic vibrations. The „harmonic" attribute signifies that nuclei of all molecules vibrate with the same frequency. The influence of the centrifugal force and the force of Coriolis are neglected. 3. The cohesive force of the molecules is very little. 4. The changes of the arrangement of electrons of the molecules and their effects may be neglected. I suppose that the resultant momentum of the in molecules rotating electrons may be neglected in proportion to the momentum of the rotating nuclei. In this case the molecule rotates about an equatorial axis which is perpendicular to the line joining the two nuclei.

1. The entropy is defined by the Planck equation

$$S = k \ln P, \tag{1}$$

where P is the number of all the stationary states which the system can assume.

Let us consider a diatomic gas having the energy E. To calculate the number of all stationary states, let us take, starling from some stationary state, the products of the volumes of the molecule cells belonging to this stationary state and add these products with respect to all the possible stationary states and divide, for each molecule by h^f, the whole sum by h^{fN} where f denotes the number of degrees of freedom of a molecule.

The number of all possible stationary states is defined by

$$P = \frac{1}{h^{fN} N!} \iiint \ldots dx_1\, dy_1\, dz_1 \ldots\ldots d\vartheta_1\, d\varphi_1 \ldots\ldots$$

$$\ldots\ldots dp_{x_1}\, dp_{y_1}\, dp_{z_1} \ldots\ldots dp_{\vartheta_1}\, dp_{\varphi_1} \ldots\ldots \tag{2}$$

where the indices 1,2... refer to the first, second... molecule; the integration has to be extended over those values of the coordinates which correspond to the given macroscopic state. One must divide by N!, for with any state fixed by a system of coordinates, there are N! different state points to be considered.

The rotational and vibrational energy of the gas molecules, as well as the rotational and vibrational coordinates change in first approximation independently of the translation energy and the translations coordinates. To determine the rotation vibration entropy in (1), the part referring to the rotational and vibrational coordinates must be computed.

2. Let the origin of the coordinates be the center of gravity of the molecule under consideration. Let the polar coordinates of the two nuclei of the molecule be: $r_1\ \vartheta_1\ \varphi_1$, $r_2\ \vartheta_2\ \varphi_2$, respectively. r_1 and r_2 are vectors in the direction of inreasing r; m_1 m_2 are the masses of the nuclei,

$$\vartheta_1 = \pi - \vartheta_2 = \vartheta,\ \varphi_1 = \varphi_2 + \pi = \varphi.$$

The energy of the molecule is

$$E = \frac{m_1}{2}\left(\dot{r}_1^2 + r_1^2\,\dot{\vartheta}_1^2 + r_1^2 \sin^2\vartheta_1\,\dot{\varphi}_1^2\right)$$
$$+ \frac{m_2}{2}\left(\dot{r}_2^2 + r_2^2\,\dot{\vartheta}_2^2 + r_2^2 \sin^2\vartheta_2\,\dot{\varphi}_2^2\right) + E_h, \tag{3}$$

where E is the potential energy of the molecule. It follows from the definition of the center of gravity, that

$$m_1 r_1 = - m_2 r_2. \tag{4}$$

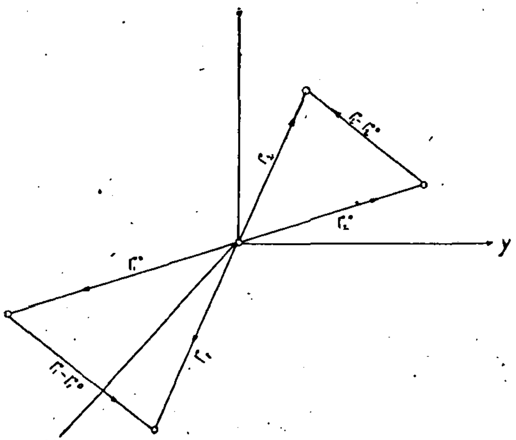

Fig. I.

According to the laws of mechanics, the interior forces of the molecule have no influence on the center of gravity. Therefore the vibration of the nuclei of the molecule has no effect to the place of the center of gravity. According to (4), the greater the distance of the nucleus m_2 from the center of gravity r_2 is, the greater will be r_1. The two nuclei and the center of gravity are always in a straight line and the two nuclei move in the same plane. The linear harmonic vibrations of the two nuclei are parallel with each other (Fig. 1).

Let $r = r_1 - r_2$. Equation (4) becomes $m_1 r_1 (m_1 + m_2) = m_1 m_2 r$

$$m_1 r_1 = \mu r, \tag{5}$$

in like manner

$$m_2 r_2 = - \mu r, \tag{6}$$

where $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$ is the reduced mass of the two nuclei. The restoring force of the nuclei is proportional to their distance from their origin, i. e.

$$p_1 = -c_1 \ (r_1 - r_1^0) \tag{7}$$

$$p_2 = -c_2 \ (r_2 - r_2^0), \tag{8}$$

where r_1^0 and r_2^0 denote the vector distances of the places of equilibrium of the nuclei from the center of gravity (Fig. 1), c_1 and c_2 are constants.

The period of oscillation of the nuclei is

$$t = 2\pi \sqrt{\frac{m_1}{c_1}} = 2\pi \sqrt{\frac{m_2}{c_2}}.$$

Introducing the frequency of oscillation, we get

$$c_1 = m_1 (2\pi\nu)^2. \quad c_2 = m_2 (2\pi\nu)^2. \tag{9}$$

The potential energy of the two nuclei is, from equations (7), (8) and (9),

$$E_{h_1} = \frac{m_1 (2\pi\nu)^2 (r_1 - r_1^0)^2}{2}, \quad E_{h_2} = \frac{m_2 (2\pi\nu)^2 (r_2 - r_2^0)^2}{2}. \tag{10}$$

From the equations (5), (6) and (10), the potential energy of the molecule is

$$E_h = \frac{\mu}{2} (2\pi\nu)^2 (r - r_0)^2, \tag{11}$$

where $r_0 = r_1^0 - r_2^0$ is the vector distance of the places of equilibrium of the nuclei.

Consequently we have for the energy (3) of the molecule by the equations (5), (6) and (11)

$$E = \frac{\mu}{2} \left\{ \dot{r}^2 + r^2 \dot{\vartheta}^2 + r^2 \sin^2 \vartheta \, \dot{\varphi}^2 + (2\pi\nu)^2 (r - r_0)^2 \right\} \tag{12}$$

Substitute $r - r_0 = l$, since r_0 is constant, the energy is

$$E = \frac{\mu}{2} \left\{ \dot{l}^2 + (r_0 + l)^2 \dot{\vartheta}^2 + (r_0 + l)^2 \sin^2 \vartheta \, \dot{\varphi}^2 + (2\pi\nu)^2 l^2 \right\}. \tag{13}$$

3. On the basis of (13) the rotation and the harmonic vibration of any molecule may be considered together as a quasi harmonic oscillator of mass μ, the equilibrium place of which is at a constant distance from the origin of the system of coordinates. The mass μ in the distance r_0 vibrates around the equilibrium place parallel to the vibrations of the nuc nuclei; furthermore the mass μ and the distance r_0 are rotating. To calculate the rotation — vibration entropy of the diatomic gas, we have to compute the entropy of such a system which consists of N molecules of the mass μ rotating and vibrating in the given manner.

4. On account of vibrations of nuclei the moments of inertia of the molecules referring to the equatorial axes are different. Let the moment of inertia of the molecule be I, when the mass μ and therefore also the nuclei, are in the equilibrium position. Let the intervals of the different moments of inertia be

$$I \longrightarrow I + \Delta I = I_1, \ I_1 \longrightarrow I_1 + \Delta I_1 = I_2, \ldots\ldots.$$

$$I \longrightarrow I - \Delta I = I_{m+1}, \ I_{m+1} \longrightarrow I_{m+1} - \Delta I_{m+1} = I_{m+1} \ldots\ldots$$

The partitions of the molecules among the different moments of inertia can be different in consequence of vibrations of nuclei. In the case of the most probable partition of the molecules, let the number of the molecules be N', $N_1' \ldots\ldots$, having moments I and $I + \Delta I = I_1$, I_1 and $I_1 + \Delta I_1 = I_2 \ldots$ etc. In the case of the most probable partition it can be supposed that there are so many molecules with a moment of inertia between $I \longrightarrow I + \Delta I = I_1$, $I_1 \longrightarrow I_1 + \Delta I_1 = I_2 \ldots\ldots$ as there are molecules with a moment of inertia between $I \longrightarrow I - \Delta I = I_{m+1}$,

$$I_{m+1} \longrightarrow I_{m+1} - \Delta I_{m+1} = I_{m+2} \ldots\ldots$$

It follows from the equation (13), introducing impulse coordinates and substituting $\bar{p}_\varphi = \frac{p_\varphi}{\sin\vartheta}$, that, in the case of the most probable partition of the molecules, the energy of the gas is

$$\begin{aligned} E = {} & \frac{1}{2I} \sum_{n=1}^{N'} (p_{\vartheta_n}^2 + \bar{p}_{\varphi n}^2) + \frac{1}{2I_1} \sum_{n=1}^{N_1'} (p_{\vartheta_n}^2 + \bar{p}_{\varphi n}^2) + \ldots \\ & + \frac{1}{2I} \sum_{n=1}^{N'} (p_{\vartheta_n}^2 + \bar{p}_{\varphi n}^2) + \frac{1}{2I_{m+1}} \sum_{n=1}^{N_2'} (p_{\vartheta_n}^2 + \bar{p}_{\varphi n}^2) + \ldots \\ & + \frac{1}{2} \sum_{n=1}^{N} \left(\frac{p_{l_n}^2}{\mu} + \mu (2\pi\nu)^2 l_n^2 \right) = E_r + E_v. \end{aligned} \tag{14}$$

5. In our case the number of all the possible stationary states is, from (2),

$$\begin{aligned} P & = \frac{1}{h^{3N}} \iiint \ldots\ldots dl_1\, d\vartheta_1\, d\varphi_1 \ldots dp_{l_1}\, dp_{\vartheta_1}\, dp_{\varphi_1} \ldots \\ & = \left(\frac{4\pi}{h^3}\right)^N \iiint \ldots\ldots dl_1 \ldots dp_{l_1}\, dp_{\vartheta_1}\, dp_{\varphi_1} \ldots, \end{aligned} \tag{15}$$

where the indices 1 2 ... refer to the first, second ... molecule. The integration has to be extended over those values of coordinates that correspond to the given state between E and $E + \Delta E$. The division by $N!$ is already effected by the translation coordinates. Thus

$$\iiint \ldots dl_1 \ldots dp_{l_1}\, dp_{\varphi_1} \ldots = \frac{\Delta V_r}{\Delta E_r} \frac{\Delta V_v}{\Delta E_v} \Delta E_r \Delta E_v,$$

where V_r and V_v denote in the phase space the volume surrounded by the surface of energy E_r and E_v, respectively. Considering the volume of the sphere of f dimensions[2] and equation (14), we get

$$\frac{\Delta V_r}{\Delta E_r} \Delta E_r = \frac{(2\pi)^N I^{2N'} (I_1 I_{m+1})^{N_1'} (I_2 I_{m+2})^{N_2'} \ldots E_r^{N-1} \Delta E_r}{(N-1)!}$$

$$\frac{\Delta V_v}{\Delta E_v} \Delta E_v = \frac{E_v^{N-1}}{(N-1)!\,\nu} \Delta E_v.$$

We have at high temperatures $E_r = E_v = kNT$; in the last equation ΔE_r, ΔE_v may be neglected in comparison with E_r^N, E_v^N. Consequently, it follows from the given equations

$$S = kN \ln \frac{8\pi^2 e^2 I_0 (kT)^2}{h^3 \nu}$$

$$\text{where } I_0^N = I^{2N'} (I_1 I_{m+1})^{N_1'} (I_2 I_{m+2})^{N_2'} \ldots\ldots \qquad (16)$$

is the equation of the average momentum of inertia.

References.

1. K. Széll, Matem. és Természettud. Értesitő, 44, 99 (1927) and 45, 210 (1928), Phys, Zeitschrift, 28, 546 (1927).

2. The volume of an f dimensional sphere of radius f is

$$V = \frac{\sqrt{\pi f}\, rf}{\Gamma\left(\frac{f}{2}+1\right)}.$$

Cf. T. H. Schonte, Mehrdimensionale Geometrie, Sammlung Schubert 1905. II. 289.

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Über den Einfuss der Ionisation auf die Extinktionskurven von Benzolderivaten.

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1. *Einleitung.*

Es wurde wiederholt gezeigt, dass die Extinktionskurven von organischen Verbindungen in ionisierten und nicht ionisierten Zustand oft grosse Unterschiede aufweisen (1). Da die Erklärung der Versuchsdaten nach einer umfassenden Theorie bisher nicht gelungen ist, so wurde die systematische Untersuchung dieser Frage in Begriff genommen.

2. *Zur Elektronenverteilung der Benzolderivate.*

Die Elektronenverteilung des Benzolmoleküls im Grundzustand geben die zwei Kekuléschen Formeln (Ia) an. Die Dewarsche Grenzformeln (Ib) spielen eher in dem Anregungszustand eine Rolle.

Die symmetrische Ladungsverteilung der lockerer gebundenen π-Elektronen beeinflussen die Substituenten stärker, als dies der fester gebundenen σ-Elektronen. Nach der Quantentheorie kann diese Störung der σ-Elektronenverteilung im Grund- und Anregungszustand berecchnet werden (2). Bringt auch der Substituent π-Elektronen mit sich, so werden diese mit den π-Elektronen des Ringes zusammen behandelt. Das Mitspielen der π-Elektronen der Substituenten hängt von deren Bindungsfeste ab, indem bei einer festeren Bindung ihre Beteiligung geringer ist. Eifachheits halber behandelt die Quantentheorie die Störung der Elektronen des Benzolringes und der Substituenten gesondert. Die beiden Effekte sind aber voneinander nicht unabhängig, sind auch nicht additiver Art, sondern überlagern sich komplizierter Weise.

Die auf die Ladungsverteilung der π-Elektronen ausgeübte Wirkung der Substituenten wird, als ihre induktive Wirkung bezeichnet (2b). Während die Beteiligung der π-Elektronen der Substituenten in der Mesomerie