THE ENERGY OF GASEOUS MOLECULES.

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1. The configuration and structure of the atomic nucleus has no appreciable influence on the molecular heats of gases, since the monatomic molecules of the five inert gases (with the possible exception of helium), of mercury vapour, and of dissociated iodine vapour, which have totally different nuclear structures, have identical energies, $2 \cdot 98 T$ g. cal. per g. mol. The determining factor is the manner in which the molecule is built up of the nuclei of its constituent atoms and of surrounding electrons. The contribution of the electrons themselves, on account of their small mass, is negligible under all ordinary circumstances. The configuration of the molecule as a whole mainly determines its behaviour to impulsive forces of collision, but the internal motions of the parts of more complicated molecules may contribute an appreciable fraction to the energy.

The behaviour of a molecule in collisions depends almost entirely on the shape of the outer shell of electrons : the nuclei never approach within a distance appreciably less than the sum of the radii of the outer shells of the two molecules. (If the radii calculated from Bohr's theory are those of the outer electron orbits, we must, as will be shown presently, assume that on collision the nuclei do not come together within a distance less than twice the sum of the radii of the outer orbits.) During collisions, therefore, the molecules may be regarded as elastic solids with shapes determined by the intense but probably highly localised fields of force of the outer electron shells. This assumption seems to retain its validity when the collision is between a molecule and a slow moving electron (*e.g.*, one with a velocity of the order of 1 volt ; see K. Ramsauer and H. F. Mayer,[1] and H. F. Mayer[2]). With increasing velocity of the colliding electron, penetration into successive electron shells occurs, with the emission of characteristic types of spectra regulated by the quantum relation $Ve = h\nu$. The speculation suggests itself that the exchange of energy in ordinary collisions may be in quanta, which are proportional to the collision frequencies. The wave lengths corresponding with these frequencies would lie in the region of the short Hertzian waves. The effects on matter of such waves, and of those in the region between them and the Reststrahlen, have as yet scarcely been investigated. The abnormal conductivities of solid dielectrics for high frequency currents, a maximum conductivity occurring for a definite frequency for each dielectric, are suggestive in this connection. At any rate, the actual mechanism of the purely fictitious "elastic collisions" postulated in the dynamical theory

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[1] *Ann. Physik*, 1921, **64**, 513.   [2] *Ibid.*, 451.

of gases is, so far, almost unconsidered. It is possible that the laws of collision of molecules are not covered by a purely dynamical theory.

2. The exchange of energy by collisions is assumed to be divided up among the *degrees of freedom* of the molecules, and a determination of the number of degrees of freedom of a molecule is an appreciable step in the way of a knowledge of its structure, as understood by chemists. The Theory of Equipartition provides a key which unlocks many problems of this kind, but it is restricted in application and is definitely known to be inapplicable in connection with the atoms of solid bodies. The equal share of energy associated, on this theory, with each degree of freedom is $\epsilon = \frac{1}{2}k T$, where k is Boltzmann's constant and T the absolute temperature: $k = R/N_o$, where R is the gas constant per g. mol. in absolute units, and N_o the number of molecules in 1 g. mol. If f is the number of degrees of freedom, the energy of 1 g. mol. is $N_o f \epsilon$ and the ᴅ ᴅlar heat at constant volume is

$$C_v = d(N_o f \epsilon)/dT = 0.992\left(f + T\frac{df}{dT}\right) = f + T\frac{df}{dT} \text{ g. cal.,}$$

very approximately. As a very rough approximation we can put:

$$df/dT = a_o + b_o T + c_o T^2 + \ldots$$

so that
$$C_v = f_o + aT + bT^2 + \ldots$$

which satisfies the experimental results over a wide range of temperature. A more detailed investigation[1] shows that with a more exact value of df/dT the experimental results, to the lowest temperatures investigated, may be covered without recourse to the quantum theory. In this case, however, it is necessary to assume $f_o = 3$ for the diatomic gas hydrogen, a result difficult to interpret, since it corresponds only with the translational energy, and rotations would inevitably be set up by collisions if there were no restraining influence at work such as is postulated by the theory of quanta.

3. In considering the experimental results, it must be remembered that the latter usually require corrections of various kinds.[2] In what follows these corrections have been applied. The results may be summarised as follows:—

Monatomic Gases.—With the possible exception of helium, C_v for all monatomic gases is equal to $0.992 \times 3 = 2.98$, and is quite independent of temperature up to 3000° abs. Thus $f = 3$; the molecule behaves as a hard smooth elastic sphere. Rotation may or may not be present; it could in any case have no influence on C_v. Scheel and Heuse[3] report a slight diminution in C_v for helium from 3.008 at 18° C. to 2.949 at – 180° C. If this is confirmed it would indicate that helium, a gas of low molecular weight and small molecular diameter, behaves like hydrogen, a diatomic gas with the same characteristics, in exhibiting a more marked dependence of C_v on temperature than similar gases of higher molecular weight and diameter.

Diatomic Gases.—These may be divided into three groups: (*a*) One gas, hydrogen, having C_v appreciably lower than the equipartition value ($f = 5$; $C_v = 4.98$) corresponding with a rigid molecule symmetrical about an axis. For hydrogen, C_v diminishes with temperature fairly rapidly

[1] G. W. Todd, *Phil. Mag.*, 1920, **40**, 357.
[2] See *Proc. Roy. Soc.*, 1921, **100** (A), 27.
[3] *Ann. Physik*, 1912, **37**, 79; 1913, **40**, 473.

from 4·87 at 0° C. to 2·98 at − 200° C., remaining at the latter value to the lowest temperatures investigated (*c.* 30° abs.). (*b*) A group of diatomic gases, including oxygen, nitrogen, carbon monoxide, nitric oxide, and halogen hydracids, for which C_v at ordinary temperatures is almost exactly the equipartition value and is constant over a fairly wide range of temperature. The different members of this group, however, exhibit small but apparently well established differences from the equipartition value, which will be considered later. (*c*) The free halogens, Cl_2, Br_2, and I_2, which have appreciably higher values of C_v, approximating to 6 at ordinary temperatures, but dependent on temperature.[1] This value gives $f = 6$ on the theory of equipartition, and the extra degree of freedom may consist in a non-oscillatory extension of the molecular axis, a supposition which receives some support from the much larger molecular diameters of gases of this group as compared with those of groups (*a*) and (*b*). The change in the wave length of sound in chlorine exposed to light of particular wave length is also of interest in this connection, although it is not yet clearly established whether this is due to heating or to a change of C_v. The case of hydrogen cannot be explained on the theory of equipartition.

It is convenient to speak of the *internal energy* of a molecule as the difference between C_v and 2·98, the translational energy on the theory of equipartition. In the normal diatomic gases the value of C_v^{int}, *viz.* 1·986 cal., might be equally well explained by assuming that the molecule as a whole had no rotation, but that the two atoms were oscillating in the line of the axis. This appears less probably true for at least two reasons: (i) It is extremely difficult to explain the absence of rotations. (ii) The difference between molecules of types (*b*) and (*c*) would be difficult to explain.

The effect of the introduction of a second halogen atom into a molecule, as exemplified by the types HX and X_2, and in organic derivatives, is of interest.

Polyatomic Molecules.—The data in this field are very incomplete, and the values of C_v depend on temperature in a manner which, although more marked than in the case of diatomic molecules, is even less accurately known. The following typical results are, with the exception of N_2O, taken from my own measurements or those of my students, and refer to the temperatures stated.

Gas.	Temperature C.	C_v.	f_i (Internal).
CO_2	17	6·76	3·76
SO_2	13	7·27	4·27
NH_3	14·5	6·71	3·71
N_2O	20	7·01	4·01

The value of C_v for CO_2 at 20°, calculated from that at 17° by the known temperature coefficient, would be 6·98, so that CO_2 and N_2O have, at 20°, practically identical molecular heats and, presumably practically identical external electronic structures. If the values of f_i are diminished by 3, the rotational part, the remainder may be assumed to be a measure of the *residual energy*, which may be expected to run parallel with the chemical activities of the molecules. If polar molecules (*e.g.*, HCl), the activities of

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[1] The value for F_2 is not known.

which depend on the electrical structure, are excluded, the following table gives the order of the residual energies (" activities ") of four gases :—

Gas.	CH_4.	CO_2.	N_2O.	C_2H_4.
Activity . . .	1	2	3	5
Mol. diam. $\times 10^8$ cm.	3·9	4·4	4·6	4·7
$b \times 10^3$ . . .	1·62	1·91	1·84	2·51
$a \times 10^3$ . . .	3·57	7·17	7·10	8·77
$(n-1) \times 10^4$ . .	4·4	4·5	5·2	7·0
$(D-1) \times 10^4$ . .	—	9·85	9·9	14·6

a and b are the constants of Van der Waals' equation; n is the refractive index for the D-line ; D is the dielectric constant.

5. The quantum theory assumes that energy exchange occurs discontinuously, in whole multiples of the quantum $\epsilon = h\nu$, where h is Planck's constant and ν is a characteristic frequency. The probability of the exchange of a quantum is all the less the larger the quantum ; when the quantum is very small the exchange occurs practically continuously according to the law of equipartition. The frequency ν may be a mean value. In the case of the translational energy of gaseous molecules it is of interest to examine the results obtained when ν is identified with the collision frequency $\nu = \Omega/L$, where Ω = mean velocity, L = mean free path. If η is the viscosity, $L = \eta/0\cdot31\ \rho\Omega$, where ρ is the density ; and one of the many formulæ connecting viscosity with molecular diameter is $\eta = 0\cdot44\ \rho\Omega/\sqrt{2}\ N\pi\sigma^2$ (Jeans, " Dynamical Theory of Gases ") where N = number of molecules per c.c., σ = molecular diameter in cm.

The expression of the effect of temperature on η is a problem of some difficulty. On the theory of equipartition ν is proportional to $\sqrt{T}$, since $G = \sqrt{3RT}$, where $\Omega = 0\cdot921\ G$. But the viscosity results show that the relation which follows, that η is proportional to $\sqrt{T}$, is incorrect ; for a number of gases the effect of temperature on viscosity is represented empirically, with very tolerable accuracy, by the formula : $\eta = \eta_0(T/273)^n$, where n varies from 0·68 to 0·98.[1] I find that n can, with good approximation, be represented as a function of the critical pressure p_c atm. by the formula:—

$$n = 0\cdot642 + 0\cdot00116p_c + 0\cdot0000399p_c{}^2$$

except possibly for values of n approaching unity.

Gas.	He.	H_2.	N_2.	CO.	O_2.	A.	N_2O.	CO_2.
p_c atm.	2·3	20	33	36	50	53	75	73
n obs.	0·65	0·7	0·74	0·74	0·8	0·82	0·93	0·98
n calc.	0·65	0·08	0·72	0·74	0·8	0·82	0·95	0·95

The limiting value of n for very complex molecules may be unity. For a number of gases at 0° C. and 76 cm. we find from the formula $\nu = \Omega/L$ values of $\beta\nu = h\nu/k$, varying from 0·1 to 0·44(H_2 as a maximum). Although the values of C_v^{tr}, i.e., the translational part of C_v, for the various gases are, within the limits of experimental error, all equal to the equiparti-

[1] Jeans, " Dynamical Theory of Gases," 2nd edit., p. 302.

tion value with these small quanta, the values of $\beta\nu$ are in the order to be expected, at least in the case of diatomic gases, from the values of C_v :—

Gas.	C_v Obs.	$\beta\nu$.	$\sigma \times 10^8$ cm.
H_2	4·87	0·442	2·68
N_2	4·95	0 231	3·80
O_2	5·00	0·205	3·62
CO	5·00	0·235	3·76
NO	4·97	0·232	3·72

This suggests that, although the translational part of the energy is almost exactly equal to the equipartition value, at ordinary temperatures, the rotational part may depend on the former through a whole multiple relation between the frequencies, since the observed deviations would then depend on the rotational energies. The values for O_2 and CO could not be obtained with only five degrees of freedom, on the theory of equipartition, and the quantum theory would require still more. In the case of helium the value of $\beta\nu$, 0·203, is larger than that for the other monatomic gases, which corresponds with the greater dependence of C_v for helium on temperature, in which respect helium resembles hydrogen among the diatomic gases.

Gas.	C_v Obs.	$\beta\nu$.	$\sigma \times 10^8$ cm.
He	3·008	0·203	1·68
Ne	—	0·129	2·04
A	2·98	0·183	2·56
Kr	2·98	0·133	2·76
Xe	3·06	—	—

On the assumption that $\beta\nu \propto \sqrt{T}$, we can calculate at what temperature C_v^{tr} will begin to fall appreciably below the equipartition value 2·98. This will appear when $\beta\nu/T = 0·01$. In the case of hydrogen ($\beta\nu = 0·44$ at 0° C.) we should expect "freezing" of the translational energy to begin at a temperature T, where $0·44\sqrt{T}/T \cdot \sqrt{273} = 0·01$, viz. T = 7° abs. Other gases would require still lower temperatures.

6. In the case of rotational and vibrational frequencies we may provisionally assume that :—

(i) rotational frequencies are whole multiples of translational frequencies, and

(ii) vibrational frequencies are independent of T, as in the case of solid bodies.

There is some indirect evidence for both assumptions. Sackur [1] finds that the H_2O molecule may be regarded as having two moments of inertia related as 1 : 2, and since $2\pi^2\nu = nh/I$, the multiple relation between the rotational frequencies follows. A whole number relation between the various frequencies of a molecule has also been proposed by Professor E. C. C. Baly in numerous communications relating to absorption spectra and more recently in another field by Professor Perrin. Since the translational frequency depends ultimately on molecular weight

[1] *Ann. Physik*, 2913, **40**, 95.

and diameter, we may expect all the characteristic frequencies with the possible exception of vibrational frequencies, and magnitudes dependent on them, to be simply related to these two magnitudes.

The wave length of the rotational frequency of the H_2O molecule, $\lambda = c/v$ is given by Bjerrum[1] as 10^{-3} cm., approximately. The translational wave length is about 10 cm., hence the multiplier is of the order of 10^4. If we take v' (rotational) $= 1000v$ (translational), in the case of hydrogen ($\beta v = 0.442$) we find at $0°$ C. $\beta v' = 442$, whereas Eucken[2] represented his results for C_v by a constant frequency $\beta v'$ of 430 in Einstein's equation ($f = 2$):—

$$C_v^{int} = Rx^2 \frac{e^x}{(e^x - 1)^2} \text{ where } x = \beta v'/T.$$

Nernst[3] assumes $\beta v' = 450$. A constant value of $\beta v'$ would imply a vibrational, not a rotational, motion. Eucken's calculations are, however, of a provisional character. His results show that Einstein's formula with $\beta v' = 430$ gives too high values at lower temperatures and too low values at higher temperatures. The results, according to Eucken, are still worse represented by the Nernst-Lindemann formula :—

$$C_v^{int} = \tfrac{1}{2}Rx^2 \frac{e^x}{(e^x - 1)^2} + \tfrac{1}{2}Ry^2 \frac{e^y}{(e^y - 1)^2} \text{ where } y = \tfrac{1}{2}x; \ x = \beta v',$$

with $\beta v' = 570$. This would seem to increase the probability that the energy is vibrational, since Nernst[4] has shown with some degree of success that, in the case of solid bodies, the *molecular* motion is more correctly given by the Nernst-Lindemann (or still more accurately, by the Debye), formula, whilst the *atomic vibrations* are represented by the Einstein formula. The results of the X-ray examination of solids, however, throw some doubt on this interpretation of the specific heats. In an earlier communication,[5] Nernst assumed that the rotational energies of gas molecules are represented by the Einstein formula, but that the frequency $\beta v'$ is proportional to the square root of the absolute temperature, as on the classical theory. If $\beta v' = a\sqrt{T}$, where a is a constant, the following equation gives the contribution of one degree of freedom to C_v for the rotations :—

$$C_v^{int} = \frac{R}{4} \cdot \left[\frac{x}{e^x - 1} + e^x \left(\frac{x}{e^x - 1}\right)^2 \right] (f = 1),$$

where $x = a/\sqrt{T}$.

The table below gives the values of C_v^{int} found experimentally by Eucken and those calculated (i) by Einstein's formula with $\beta v' = 430$; (ii) by the Nernst-Lindemann formula with $\beta v' = 570$; (iii) by Nernst's formula with $a = 37$; (iv) by an empirical method of the author with $\beta v' = 6541/\sqrt{T}$.

In the latter method of calculation, the values of $x = \beta v'/T$ are substituted in the Debye formula with $f = 2$. The good agreement with experiment points to some extension of the theory which is not clear at present. The method is stated with proper reserve as of possible use as an interpolation formula.

[1] *Nernst Festschrift*, 1912, 90.   [2] *Berl. Ber.*, 1912, 141.
[3] *Verh. d. D. phys. Ges.*, 1916, **18**, 83.   [4] " Theory of the Solid State," 1913.
[5] *Zeit. Elektrochem.*, 1911, **17**, 270.

TABLE OF MOLECULAR HEATS OF HYDROGEN (INTERNAL).

T.	C_v^{int} Obs.	C_v^{int} Calculated.			
		(i)	(ii)	(iii)	(iv)
40	0·00	0·00	0·04	0·10	0·008
50	0·03	0·02	0·11	0·16	0·024
80	0·16	0·26	0·43	0·35	0·21
100	0·44	0·51	0·67	0·44	0·45
196·5	1·41	1·34	1·33	0·74	1·51
273	1·86	1·61	1·60	0·91	1·79

7. The only theory of atomic structure which at present appears competent to give us any *quantitative* information as to the internal motions of molecutes is that of Bohr, and even in this case the results are far from precise. The energy of the hydrogen molecule has been considered from the point of view of Bohr's theory by T. Krüger.[1] He regards the hydrogen molecule as a minute gyrostat, the axis of which is the line joining the two positive nuclei, around which the two electrons are spinning in a perpendicular circular orbit midway between the nuclei. The result (see Macdougall),[2] is not wholly satisfactory if only two degrees of freedom are assumed, although Eucken's value of $\beta\nu'$ is approximately found.

The structure of more complicated molecules according to Bohr's theory is at present largely a matter of speculation. Consider the nitrogen molecule. The nitrogen atom has a nucleus of mass 14 and charge + 7, and there will be seven electrons in the outer orbits, almost certainly distributed between two rings. Bohr puts four electrons in the inner ring and three in the outer. If we take Bohr's arrangement, we have to consider what rearrangement of the orbital electrons of two nitrogen atoms occurs when coalescence to form the molecule occurs. We may expect the formation of an outer ring of eight electrons bisecting the axis of the nuclei at right angles, since the nitrogen molecule is very stable. The remaining six electrons may be arranged in various ways. One possible arrangement is the addition of two more rings coplanar with the 8 ring, with four and two electrons, respectively. This would give an inner ring of 2, also corresponding with the stability of the N_2 molecule. Let a_1, a_2, a_3, be the radii of the three rings, in the above order. The equation for the orbits may be assumed to be $a = h^2/4\pi e^2 m F_o$ (Bohr), where h is Planck's constant, e the charge of the electron, m the mass of the electron, and F_o a function of the structure of the particle :—

$$F_o = \frac{N^2}{2n}\left[\left(\frac{4n}{N}\right)^{\frac{2}{3}} - 1\right]^{\frac{3}{2}} - s_n,$$

where $s_n = \frac{1}{4}\sum_{s=1}^{s=n-1}\operatorname{cosec}\frac{s\pi}{n}$, N being the net nuclear charge, n the number of electrons in the orbit. We may note in passing that $a_o = h^2/4\pi e^2 m$ is identical with the constant k of the "quantum force," k/a^3, of Dr. Langmuir[3] when $t = 1$, and with the constant c of the law of force assumed by Sir J. J. Thomson :—[4]

"Quantum force" $= \frac{1}{ma^3}\left(\frac{th}{2\pi}\right)^2$ independent of the nuclear charge

[1] *Ann. Phys.*, 1916, **50**, 346 ; **51**, 450.　　[2] *J. Amer. Chem. Soc.*, 1921.
[3] *Science*, March 25th, 1921.　　[4] *Phil. Mag.*, 1921.

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