The reactivity toward carbon of oxygen gas excited by electron impact was studied. There was no reaction below 7.9 volts, but between 7.9 and 10.6 volts a reaction commenced and increased in rapidity up to the highest potentials investigated. The product of the reaction is carbon dioxide, at least in large part.

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THE HEATS OF DISSOCIATION OF THE MOLECULES, CH, NH, OH AND HF

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In an investigation on the dissociation energetics of the molecule of hydrogen cyanide, it was necessary to make an estimate of the heats of dissociation of its different possible decomposition products. Although it sounds strange to the chemist to speak of the molecules, CH, NH and OH, still their existence is definitely proved by the observation of band spectra[1] which are ascribed to them. The molecules, unsaturated chemically, are most probably extremely reactive, but we should not consider them unstable, in the sense that they have a tendency to decompose. The knowledge of the heats of dissociation of these molecules has great theoretical importance in studying the dissociation of other compounds, as well as hydrogen cyanide.

In order to calculate these heats, I have made use of two empirical principles discovered by band spectroscopists. First, Kuhn[2] has shown that the restoring force constant, C, in the equation for the vibration of a harmonic oscillator is approximately proportional to the heat of dissociation of the molecule.

$$C \equiv \mu\omega_0^2 = kD \qquad (1)$$

ω_0 is the frequency of vibration for infinitely small displacement and is determined experimentally by the difference between the first and second vibrational energy levels of the molecule as measured from its band spectrum; μ is the resultant mass and equals $m_1m_2/(m_1 + m_2)$ for a diatomic molecule. Second, Mecke[3] has shown that molecular constants vary with the atomic number in much the same manner as other physical and chemical constants. The method of estimation, then, is to determine

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[1] CH: Heurlinger and Hulthén, *Z. wiss. Phot.*, **18**, 241 (1919); *Compt. rend.*, **173**, 524 (1921); *Z. Physik*, 11, 284 (1922). NH: Hulthén and Nakamura, *Nature*, 119, 235 (1927). OH: Grebe and Holtz, *Ann. Physik*, **39**, 1243 (1912); Heurlinger, "Dissertation," Lund, 1918; Fortrat, *J. phys.*, **5**, 20 (1924); Jack, *Proc. Roy. Soc. London*, 11**5A**, 373 (1927); 11**8A**, 647 (1928).

[2] Kuhn, *Z. Physik*, **39**, 77 (1926).

[3] Mecke, *Physik. Z.*, **28**, 483 (1927).

k in (1) and to calculate D from this, making use of ω_0, obtained already or interpolated by applying Mecke's principle.

Birge[4] gives the following values of ω_0 which he calculated for the molecules CH, OH and HF: ω_0'' HF, 3962 cm.$^{-1}$; OH, 3570 cm.$^{-1}$; CH, 2797 cm.$^{-1}$. Interpolating for ω_0 of NH gives 3188 cm.$^{-1}$. Figure 1 shows that all of the points lie on a perfectly straight line.

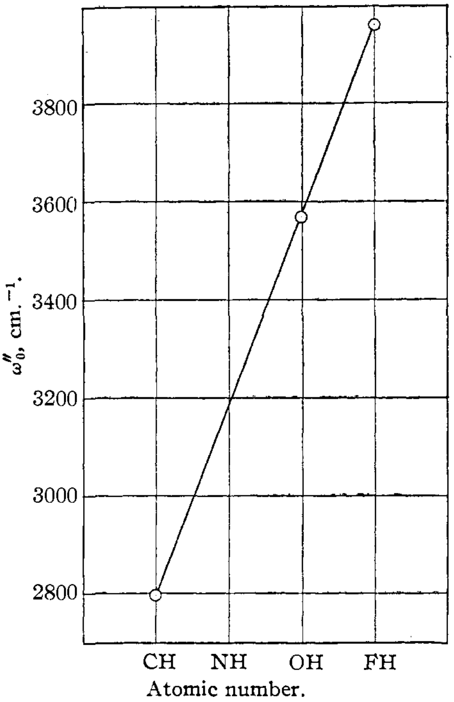

Fig. 1.

The next step made in the approximation process is to tabulate C and D (see Equation 1) for several different molecules and to calculate therefrom the proportionality constant, k. This is given in Table I, the values in parentheses being the results of estimation. It will be immediately evident that k varies also with the atomic number for the similar molecules, H_2, HCl, HBr. Plotting k against atomic number in Fig. 2, we may interpolate and get the values given in parentheses under k. Knowing k and ω_0, one may immediately calculate D and this, too, is given in Table I. If this interpolation is justified, it can be seen that the error involved in our value of D is at most not over 3%.

We can compare these calculated heats of dissociation with some quasi-experimental ones which may be obtained from the work of Ellis.[5] According to him, the bonding power (C in the above notation) of the C–H

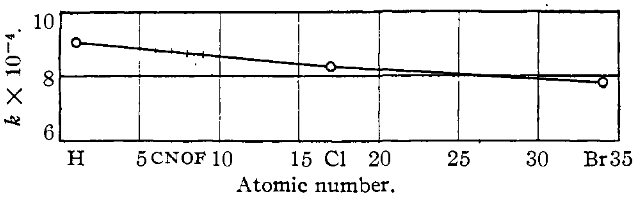

Fig. 2.

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[4] Birge, "Molecular Spectra in Gases," *Bulletin National Research Council,* Washington, D. C., **11,** No. 57, 230 (1926).

[5] Ellis, *Phys. Rev.,* **33,** 35 (1929).

Table I

Heat of Dissociation

			D		
Molecule	μ	ω_0'', cm.$^{-1}$	Volts	Kilocal.	k
Cl_2	17.73	555	2.5	58.5	9.36 × 10^4
Br_2	39.95	326	2.0	45.2	9.42
I_2	63.45	214	1.5	35.2	8.14
N_2	7.00	2345	9.5	219.0	17.6
NO	7.46	1892	7.3	169.0	15.86
CO	6.85	2150	11.2	258.0	12.3
CN	6.47	2060	9.5	219.0	12.1
H_2	0.50	4264	4.4	101.0	9.10
CH	.923	2797	(3.55)	(82.0)	(8.81)
NH	.933	3188	(4.65)	(108.3)	(8.76)
OH	.942	3570	(5.98)	(138.0)	(8.71)
HF	.950	3962	..	(172.0)	(8.68)
HCl	.972	2941	4.4	101.7	8.29
HBr	.976	2559	..	81.7	7.82

linkage is 23% greater in hexane (heat of dissociation, 97 kilocal.) than in the CH molecule. If C is proportional to the heat of dissociation, D, then

$$\frac{C_1}{C_2} = 1.23 = \frac{k_1D_1}{k_2D_2} = \frac{97}{D_{\mathrm{CH}}} \qquad (2)$$

where the subscripts 1 and 2 refer to hexane and CH, respectively. If we neglect the fact that k_1 (9.15) is different from k_2 (8.81 according to Table I) we can calculate D_{CH}

$$D_{\mathrm{CH}} = 79 \text{ kilocal.}$$

which agrees very well with the value 82 kilocal. obtained above. To say that the ratio $k_1/k_2 = 1$ is, of course, inconsistent with our other method of calculation and any results obtained in this manner can only indicate the order of magnitude. Likewise, an application of Equation 2 with the same assumption concerning the ratio k_1/k_2 gives us a value for the heat of dissociation of Cl_3C–H. Using Ellis' data for ω_0, this is found to be 105 kilocal., which agrees with his observed value of 108 kilocal.

Ellis also obtained values for the linkage heat of the N–H bond. In aniline he reports it as being 113 (±15%) kilocal. He compared this spectroscopic value with a chemical value obtained by dividing the "atomic" heat of formation (referred to the gaseous atoms) of ammonia by three. He found 101 kilocal. but this should be 93 if we accept the new value[6] for the heat of dissociation of nitrogen, $D_{N_2} = 9.5$ volts or 219 kilocal. This checks well the value obtained from Equation 2 (*i. e.*, 91.4 kilocal.)

$$\frac{3440^2 \times 0.989}{3188^2 \times 0.933} = \frac{k_a\,113}{k_{\mathrm{NH}}\,D_{\mathrm{NH}}}$$

$$D_{\mathrm{NH}} = 91.4 \text{ kilocal. or } 4.0 \text{ volts if } k_a/k_{\mathrm{NH}} = 1$$

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[6] Mulliken, *Phys. Rev.*, **32**, 761 (1928); Birge, *Nature*, **122**, 842 (1928).

Here k_a = 10.36 and the discrepancy may be ascribed to its difference from k_{NH}.

In view of the above discussion concerning the empirical variation of k with atomic number, it seems best to choose as values for D those given in Table I.

The heat of dissociation of CN has already been calculated to be 9.5 volts[7] (1 volt = 23 kilocal.). Recent work has indicated that it is probable that one of the products of this dissociation is an excited atom.[6] If it is a characteristic of odd molecules that their normal states will dissociate, resulting in an excited atom, while their next excited molecular states dissociate into normal atoms,[8] then some doubt is thrown on the meaning of our above value for D_{CH}, as it must represent only an upper limit for the heat of dissociation into *normal* atoms. As yet there has been no evidence advanced that this is true for the hydride molecules under consideration.[9] However, even were this true, we still have obtained the *actual* energy necessary to break up the molecule, a quantity which has very interesting theoretical implications.

Our value for the heat of dissociation of OH agrees in order of magnitude with other existent data. If the "atomic" heat of formation of water is 238.8 kilocal., then the heat of dissociation of water into H and OH is 238.8 − 138 = 100.8. Senftleben and Rehren[10] estimate it to be less than 112 kilocal. Bonhoeffer and Reichardt[11] obtain a value in agreement with theirs. Bates and Taylor[12] find that the efficiency of excited mercury (113 kilocal.) is much less in its dissociation of water vapor than in its action on other molecules. An explanation, accessory to that advanced by Bates and Taylor, might be that the amount of energy available from the mercury is in excess of that necessary to dissociate the water molecule by 12 kilocal. and that we have here a resonance phenomenon such as is observed elsewhere in collisions of the second kind.[13]

Summary

Data from band spectra have been interpolated by Mecke's method and the magnitude of the heat of dissociation of the molecules, CH, NH, OH and HF was calculated to be, respectively, 82.0, 108.3, 138.0 and 172 kilocalories.

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[7] Mulliken, *Phys. Rev.*, **32**, 206 (1928).

[8] Heitler and Herzberg, *Z. Physik*, **53**, 52 (1929).

[9] *Cf.* Mulliken, *Phys. Rev.*, **33**, 738 (1929), Table I.

[10] Senftleben and Rehren, *Z. Physik*, **37**, 529 (1926).

[11] Bonhoeffer and Reichardt, *Z. Elektrochem.*, **34**, 652 (1928); *Z. physik. Chem.*, **139**, 92 (1928).

[12] Bates and Taylor, THIS JOURNAL, **49**, 2450 (1927).

[13] Beutler and Josephy, *Naturwissenschaften*, **15**, 540 (1927); Webb and Wang, *Phys. Rev.*, **33**, 329 (1929).