Active Hydrogen

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value. Thus the use of Bourgin's revised figures together with the application of the above correction factor slightly increases the discrepancy previously noted.

Let us now return to the criticisms of Bourgin's method. As regards adsorbed vapor, one may note that the vapor pressure of HCl at room temperature is about 45 atmospheres. Since the pressure of the gas actually used was one atmosphere, one may reasonably assume that the adsorbed layer would not be much more than one molecule deep. Taking the cross section of the molecule standing on end to be 10^{-16} sq. cm, one readily calculates that the number of adsorbed molecules per square centimeter on the front and back quartz surfaces is equal to the number per sq. cm in a layer of gas less than a hundredth of a millimeter thick. Even if the adsorbed molecules were free to rotate normally and contribute as much to the absorption as free molecules, their contribution would have been too small to detect experimentally. Moreover, the base-line readings were taken without removing the adsorbed gas by heating, so that most of its contribution to the absorption must have been eliminated by subtraction.

Finally an examination of the A, x curves (cf. Fig. 4 in the first paper and Fig. 1 of the second paper) should make it evident that Bourgin's estimate that the extrapolated value of the initial slope is reliable within 20 percent, is a fair one. These estimates were made with the aid of two-parameter semitheoretical curves which were fitted to the complete absorption curve and gave due weight to the observations made with long tubes. In fact we can derive from the A, x curves a lower bound to the value of B_{01}^{+1} which is several times as large as that given by Bartholomé. From the fundamental formula for the area, viz., $A(x) = \int(1-e^{-\mu x})d\nu$, it follows that $dA/dx = \int \mu(\nu)e^{-\mu x}d\nu$. Hence dA/dx and all the higher derivatives of $A(x)$ are monotonically decreasing functions of x. It follows that *the initial slope must be greater than the slope of any chord connecting two points on the curve.* Joining the origin with the points for the two shortest tubes and using the data for the third line of the R branch (the strongest in the band) one obtains the lower bounds 7.05×10^{15} and 5.84×10^{15} for B_{01}^{+1}. The other lines yield similar bounds. Thus it is quite impossible to reconcile Bourgin's data with Bartholomé's low value of the transition probability.

Let us next consider the possibility of error in Bartholomé's experiment. The observations consisted in measuring the absorption with a relatively wide spectrometer slit and an absorption tube containing one atmosphere of HCl mixed with air at total pressures up to 60 atmospheres. The theory of the experiment is that at sufficiently high pressures the lines will be broadened enough to destroy the rotational structure of the band and give a smooth curve for the absorption coefficient plotted against frequency. Under these circumstances with a slit-width small enough to cover one line at a time, but not necessarily small enough to resolve rotational structure, the radiation reaching the radiometer should be sensibly homogeneous as regards its absorption coefficient. By means of the exponential absorption law it should then be

possible to determine the smeared-out absorption coefficient curve from observations made with a single tube-length. It is assumed that the transition probability is sensibly independent of the pressure and on that point the evidence is reasonably conclusive.

It is rather difficult and dangerous to criticize an experiment from as meager an account of the experimental details and data as that given by Bartholomé, but one weak point is apparent. He gives his slit width as equivalent to 800A. If we assume that the entrance and exit slits of the spectrometer were of equal width, as is customary in such work, the extreme range of wavelengths reaching the thermopile would be 1600A. As the distance between the points of maximum intensity for the R and P branches is about 1400A, it is quite clear that even when the lines were broadened so as to eliminate the rotational fine structure, the radiation reaching the microradiometer must have been very inhomogeneous as regards its absorption coefficient. In the R branch for example, the 4th line has an intensity five times as great as the 8th line which differs in wavelength by only 750A. Thus it is not permissible to extrapolate to zero tube-length by means of the exponential absorption law and an attempt to determine the transition probability by means of such an extrapolation is sure to underestimate seriously its true value. With higher resolving power Bartholomé's method should be good.

EDWIN C. KEMBLE

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Research Laboratory of Physics,
March 27, 1935.

[1] R. S. Mulliken, J. Chem. Phys. **2**, 400, 712 (1934).
[2] D. G. Bourgin, Phys. Rev. **29**, 794 (1927); **32**, 237 (1928).
[3] J. L. Dunham, Phys. Rev. **34**, 438 (1929).
[4] The value given in Bourgin's first paper was wrong by a factor of two.

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Four years ago I expressed my doubts in what at that time was considered to be proofs for the existence of triatomic hydrogen.[1] It appeared that a final decision had been reached when Conrad in his mass-spectrographical work[2] found an uncharged molecule corresponding to the mass (3). Unfortunately the significance of his investigation was greatly reduced[3] after deuterium was discovered. A strict distinction should be made between HD and H^3 even in mass-spectrograph analysis. This has not been done in every case.[4] Hence positive ray analysis as applied to this problem must take account of the two facts, (1) that the presence of HD may obliterate an unequivocal decision, (2) that only such particles[5] can be considered as a proof of H^3 which were uncharged for some definite length of time and received their charge later on by electron transfer.

The H^3 molecule may have properties identical with those of the H-atom. One would have to assume this, reading the publications of Grubb and co-workers[6] if their argumentations were conclusive in every respect. Only their most weighty argument of their most recent publica-

tion may be considered. Either the decay reaction occurs independently of the surface or their wall reaction is erroneous. Both cannot be assumed at the same time. Conceding for a moment that the wall reaction be negligible, a homogeneous gas reaction of the first order is improbable because it will be difficult to suggest a mechanism which would fit such an assumption. A monomolecular decay should therefore be explained as a wall reaction. It seems possible[7] to oppress this wall reaction even more than Steiner and Wicke[8] were able to do. One may argue that active hydrogen in as small a concentration as 0.001 to 0.025 percent[9] would have exactly the same properties if explained on the basis of the well-known atomic modification. This argumentation may be followed up in every instance.

Wrede's orifice method[10] and Keussler's study of the absorption spectrum of H-atoms[11] would be sufficient proof to substantiate the atomic nature of that hydrogen which is obtained by Wood's method, unless the bulk of other investigations which were based on this assumption is taken as proof in itself. A decision in favor of H^3 appears exceedingly difficult by the use of merely chemical methods.

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        April 15, 1935.

[1] J. Phys. Chem. **35**, 3186 (1931).
[2] Zeits. Physik **75**, 504 (1932); Zeits. f. Electrochemie **38**, 183 (1932).
[3] Zeits. f. physik Chemie **A164**, 30 (1933); Cf. Ann. d. Physik [5] **8**, 456 (1931).
[4] Grubb, Nature **132**, 1001 (1933); J. J. Thompson, Nature **133**, 280 (1934). Cf. Phil. Mag. **17**, 1025 (1934).
[5] O. Luhr, J. Chem. Phys. **3**, 146 (1935); Zeemann and Gier, Proc. Amst. Acad. **36**, 717 (1933). Cf. Bainbridge, Phys. Rev. **44**, 57 (1933). Massey, Proc. Camb. Phil. Soc. **27**, 451 (1931). Zentr.-bl. 1932, I, 636.
[6] J. Chem. Phys. **3**, 139 (1935); Nature **132**, 1001 (1933); J. Phys. Chem. **36**, 2817 (1932).
[7] Amdur and Robinson, Phys. Rev. **43**, 208 (1933); J. Am. Chem. Soc. **55**, 1395, 2115 (1933).
[8] Zeits. f. physik. Chemie, Bodenstein Festband 817 (1931). Cf. Wartenberg and Schultze, ibid. **B6**, 261 (1929).
[9] Grubb, reference 4.
[10] Zeits. f. Physik **54**, 53 (1929).
[11] Ann. d. Physik [5] **7**, 225 (1930).