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The Heats of Dissociation of Hydrogen and Nitrogen

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A method previously described has been employed to determine the heats of dissociation of the normal molecule and the molecular ion for H_2 and N_2. A new apparatus has been constructed of tantalum, which eliminates previous difficulties, believed due to contact potentials. As previously shown, electrons passing through diatomic gases are able to produce atomic ions possessing kinetic energies of several volts. Simultaneous measurements of the electron energy necessary to produce atomic ions and the kinetic energy of the ions permit the determination of the heats of dissociation. The values obtained are $D(H_2^+) = 2.59 \pm 0.03$ v, $D(H_2) = 4.43 \pm 0.03$ v, $D(N_2^+) = 6.73 \pm 0.02$ v, $D(N_2) = 7.90 \pm 0.02$ v. It is concluded that these results are free from systematic errors to ±0.1 v. A critical comparison of these data is made with the results of other methods, mainly spectroscopic.

INTRODUCTION

A PROBLEM which has interested physical scientists for many years has been the determination of heats of dissociation of diatomic molecules; i.e., the energy requisite to separate the normal molecule into unexcited atoms. Of the many different methods of attack the following are examples: thermochemical methods, band spectral extrapolations of vibration levels, sensitized fluorescence, absorption spectra, predissociation and electron bombardment. While some heats of dissociation, such as those of H_2, O_2 and the halogens are known with considerable accuracy, for most molecules the results of various methods are neither precise nor in good agreement.

At one time attempts were made to interpret the energy losses of electrons in diatomic gases in terms of heats of dissociation.[1] This was however unsuccessful and with the formulation of the Franck-Condon principle[2] it was immediately seen why this was not generally possible. On the basis of previous quantum mechanical calculations, Condon[3] drew up in 1930 a set of predictions of the products of ionization of H_2 by electron impact. These predictions were strikingly verified by Bleakney[4] using a mass-spectrograph.

Among these predictions was the one that H^+ ions should be formed with kinetic energies of several volts. To test the detailed theoretical predictions concerning these, an apparatus was built by the writer.[5] Within the precision of the apparatus these were completely verified. Later, it was shown[6] how the heats of dissociation of CO and N_2 could be determined from a study by using this type of apparatus. The procedure can briefly be reviewed as follows. One measures the minimum kinetic energy of the bombarding electrons, which are able to produce atomic ions; simultaneously the kinetic energy of the dissociating products is measured. According to the Franck-Condon principle the kinetic energy lost by the impacting electron is converted into potential energy of the molecule, which finds itself in an unstable state and immediately dissociates, part of the potential energy being converted into kinetic energy. Subtracting the kinetic energy of the dissociation products from the electron energy loss, there results the potential energy increase of the dissociated molecule with respect to the normal molecule. From another side this is equal to the heat of dis-

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[1] K. T. Compton and F. L. Mohler, *Critical Potentials*, Nat. Res. Council Bull., p. 117 (1924).

[2] J. Franck, Trans. Far. Soc. **21**, 536 (1925) and Zeits. f. physik. Chemie **120**, 144 (1926); E. U. Condon, Phys. Rev. **28**, 1182 (1926) and **32**, 858 (1928).

[3] E. U. Condon, Phys. Rev. **35**, 658A (1930). See also E. U. Condon and H. D. Smyth, Proc. Nat. Acad. Sci. **14**, 871 (1928) for an earlier comparison of theory and experiment.

[4] W. Bleakney, Phys. Rev. **35**, 1180 (1930).

[5] W. Wallace Lozier, Phys. Rev. **36**, 1285 (1930).

[6] John T. Tate and W. Wallace Lozier, Phys. Rev. **39**, 254 (1932).

sociation of the molecule plus the ionization potential of the atom which is ionized plus any energy of excitation of the dissociation products. The last two quantities are accurately known from atomic spectra and thus allow the calculation of the heat of dissociation.

It must be mentioned that in the work on CO and N_2 the precision was not altogether satisfactory. Furthermore, Arnot[7] pointed out a possible disturbing effect in this work which could account for certain unexpected results that we obtained in regard to the electron affinity of oxygen atoms. Arnot, on the basis of some of his earlier work on Hg vapor[8] suggested that space charge might have built up radial potential gradients which invalidated our measurement of the kinetic energy of the ions. After reexamining some data taken with that apparatus, the writer is of the opinion that radial potential gradients (other than applied fields) were present but that these were due to contact potentials and not to space charge.[9] It must be said the older apparatus was constructed of copper, which in the course of the research passed through various stages of oxidation. To avoid surface effects a new apparatus was constructed of tantalum and it is believed the following results on H_2 and N_2 show that these disturbing influences have been avoided and a satisfactory precision has been attained. In particular we have made tests on this apparatus which show that the kind of potential gradients mentioned by Arnot are not present. Our purpose in studying H_2 is to determine the precision of the apparatus; for the heats of dissociation of H_2 and H_2^+ and the ionization potentials of H_2 and H are accurately known. The accuracy of the result obtained shows that disturbing influences in this apparatus are truly negligible.

Apparatus

Fig. 1 is a longitudinal cross section of the apparatus which is constructed entirely of tantalum mounted on Pyrex rods. *A*, *B* and *C* illustrate the filament assembly which is housed in a separate compartment exhausted by a separate mercury pump; this compartment is connected to the remainder of the apparatus by a 0.3 mm hole in *A*, through which the bombarding electrons are admitted. Electrons are accelerated (12 volts) from the oxide coated cathode *B*, retarded (10 volts) from *D* to *E*, then pass through field free space to *H*,[10] are accelerated by a variable potential between *H* and *I*, then pass through field free space to *T* where they are collected by a potential of 100 volts.

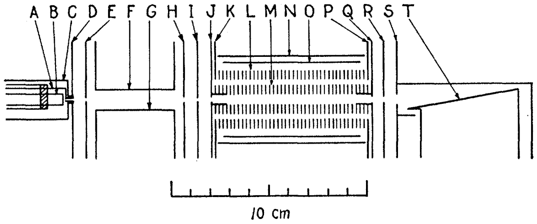

FIG. 1. Diagram of apparatus.

The center part of the apparatus (from *H* to *R*) possesses cylindrical symmetry about the line of the electron beam. *L* and *M* are concentric sets of thin disks, each supported by three tantalum rods (not shown) spot-welded to *K* and *J* respectively. The cylinder *O* is suspended from the guard cylinder and shield *N* by Pyrex beads. The action of this center part is as follows. If gas molecules are present the electrons will produce ions in the region *J* to *Q*. The electrons are confined to the axis by a magnetic field of 150 gauss, applied by an external solenoid, along their direction of motion. However, a fraction of the ions formed will travel almost perpendicularly to the electron beam and pass between the defining disks *L* and *M* and reach the collector *O* where their currents are measured. By the application of suitable

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[7] F. L. Arnot, Nature **129**, 617 (1932).

[8] F. L. Arnot, Proc. Roy. Soc. **A129**, 361 (1930).

[9] This conclusion was based on a study of the energy distribution of positive molecular ions which should possess only thermal velocities which are of the order of a few hundredths of a volt. The data in one case showed a most probable energy of about 0.5 volt. This did not change with the accelerating potential of the electrons as it should if due to the conditions mentioned by Arnot. Tests of this kind on the new apparatus show a most probable energy very close to zero, as it should be.

[10] The parallel plates *FG* were originally included for the purpose of preventing ions, by the application of a small cross-field, from bombarding the filament. On finding this precaution unnecessary *E*, *F*, *G* and *H* were connected together.

electric fields in the intervals L–M and O–L negative and positive ions can be separated and the kinetic energy of either can be measured. The entire apparatus is mounted on four Pyrex rods (not shown) and enclosed in a Pyrex tube without stopcocks or wax joints. The whole can be baked out at 450°C.

The ion currents are measured by a vacuum tube electrometer connected to O. This electrometer is constructed of two FP-54 tubes arranged according to the circuit described by DuBridge.[11] It is used at a voltage sensitivity of 20,000 mm/volt. All the data shown here were taken by the rate of drift method with which the residual fluctuations of the amplifier correspond to grid current changes of 5×10^{-17} amp.

The nitrogen was generated by the action of bromine on ammonia, the hydrogen electrolytically. Both were purified by P_2O_5 and liquid air. The gases were so admitted to the apparatus through a capillary leak that with the mercury pumps running continuously, pressures of from 10^{-5} to 10^{-4} mm Hg could be maintained in the experimental tube. Electron currents of from 10^{-7} to 10^{-6} amp. were used.

Regarding the purity of the gases, it may be said that the gases generated in this same way have previously been analyzed by mass-spectrographs and showed no appreciable impurities. Therefore the writer feels certain the currents measured were due to N_2 and H_2.

PROCEDURE

In this research we have confined ourselves to a determination of the minimum electron energies needed to form ions which can traverse definite retarding potentials.

As has been shown,[5] the magnetic field exerts a stopping effect on ions. For H^+ and N^+ it turns out, by using the dimensions of the apparatus and $H=150$ gauss, that ions, which are barely able to traverse a retarding potential V_R and reach the collector O, must originally have started from the center of the tube with an energy V_F greater than V_R by 0.98 and 0.07 volt, respectively.

The procedure was to place in the interval L–M 5 or 10 volts drawing out positive ions; connect this potential reversed to the interval O–L; and in addition place here any desired potential retarding positive ions. The current reaching O was studied as a function of the variable accelerating potential in the region H–I.

In order to determine the voltage correction to the electron beam, the appearance potential of molecular ionization was observed. This was accomplished by making the above-mentioned retarding potential in the interval O–L one which accelerated positive ions toward O.

Resistance-box potentiometers, accurate to 0.1 percent, were used to apply the potentials and the voltmeters measuring the total drop across the potentiometers were checked at frequent intervals against a standard voltmeter.

It is well to point out, before passing to a discussion of the results, some of the defects and advantages of this method. It has the advantage over the mass-spectrograph in that it measures and corrects for the kinetic energy of the dissociation products. It has the defect that it does not determine the masses of the dissociation products; however, it does measure the ratio of the masses.[6] In gases so simple as H_2 and N_2 there appears little chance for error in this respect. This method, as well as the mass-spectrograph is unable to identify the state of excitation of the dissociated particles. Therefore, as will be seen in the following discussion, supplementary information is needed to permit this identification. The method does have the advantage that the measured energy quantity itself arises directly from the use of the conservation principles of energy and momentum and does not depend on the extrapolation of physical regularities beyond the range of their known validity.

RESULTS ON HYDROGEN

Fig. 2 shows the results obtained with hydrogen at a pressure of 5×10^{-5} mm Hg and with an electron current of 10^{-6} amp. The curves show the current reaching the collector O as a function of accelerating potential for five different retarding voltages (corrected for the effect of the magnetic field). The inset shows the onset of molecular ionization. From the results of Fig. 2, without any knowledge of the true ionization potential of H_2, we can determine the difference between the appearance potential V_i of the

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[11] L. A. DuBridge, Phys. Rev. **37**, 396 (1931).

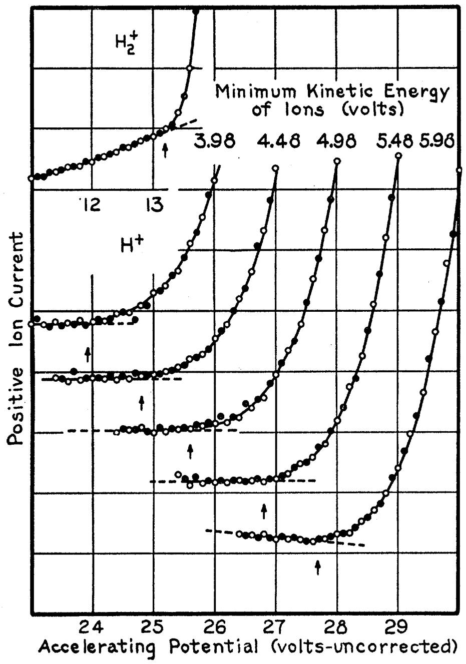

FIG. 2. Curves showing the H^+ current, as a function of electron energy, which is able to traverse the indicated retarding potentials. The inset shows the appearance of H_2^+ ionization. The open and closed circles represent data taken some fifteen minutes apart.

kinetic energy ions and that of the molecular ions V_M. These results are given in Table I for the data of Fig. 2 as well as some other data not shown.

Of this difference in energy a part goes into increase of potential energy of the molecular ion on dissociation, and the remainder into kinetic energy of the dissociation products. We have measured the kinetic energy of one product of dissociation, the ion. From the principle of conservation of momentum we know the dissociating partner of the ion must carry an equal energy; so, if we subtract twice the measured kinetic energy of the ion from $(V_i - V_M)$ we should obtain the potential energy increase of the dissociated molecule over the normal molecular ion. This is shown in Table I and the value is 2.59 volts. This measures the heat of dissociation of the H_2^+ ion plus any excitation energy of the dissociation products. The first excited state of H lies at 10.14 v; thus the possibility of excitation is excluded and we conclude 2.59±0.03 v represents the heat of dissociation of H_2^+.

TABLE I. *Results for hydrogen.*

Minimum K.E. of ions (volts)	$V_i - V_M$ (volts)	$(V_i - V_M) - 2$(K.E.) (volts)
1.48	5.5	2.54
1.98	6.6	2.64
3.98	10.7	2.74
4.48	11.6	2.64
4.98	12.5	2.54
4.98	12.4	2.44
5.48	13.6	2.64
5.98	14.5	2.54
		Average 2.59±0.03

To compare with this value of 2.59±0.03 v for the heat of dissociation of H_2^+ we have the quantum mechanical calculation of Burrau[12] corrected by Condon[13] to give 2.62±0.03 v. The writer believes the good agreement of these values furnishes a vauable check on the functioning of this apparatus and it gives confidence in regard to the results to be given with reference to N_2.

To calculate the heat of dissociation of H_2 we need the ionization potentials of molecular and atomic hydrogen. The second of these is well known to be 13.53 v. For the molecular ionization potential we have the spectroscopic value of 15.37 v determined by Richardson and Davidson[14] which was subsequently substantiated when Bleakney[15] experimentally obtained 15.37±0.03 v. The combination of these data gives $D(H_2) = 4.43 \pm 0.03$ v to compare with the Richardson and Davidson value[14] of 4.46±0.04 v. According to Birge[16] the extrapolation of vibration levels gives very nearly this same value.

It has been known that the calculated vibration constants for H_2^+ agreed with the experimentally determined ones;[14] but, so far as the writer knows this is the most accurate direct confirmation of the quantum mechanical calculation of the binding energy of the H_2^+ ion.

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[12] Burrau, K. Danske Vid. Selsk. Math-fys. **7**, No. 14 (1927).

[13] R. T. Birge, Proc. Nat. Acad. Sci. **14**, 14 (1928).

[14] O. W. Richardson and P. M. Davidson, Proc. Roy. Soc. **A123**, 483 (1929).

[15] W. Bleakney, Phys. Rev. **40**, 496 (1932).

[16] R. T. Birge, *Molecular Spectra and Molecular Structure*, Faraday Society, p. 713 (1929).

RESULTS ON NITROGEN

In Fig. 3 are shown results for N_2 corresponding to those given for H_2 in Fig. 2. The pressure of nitrogen in the lower set of curves was about 2×10^{-5} mm Hg while that in the upper was twice as great. In both cases the electron current was about 10^{-6} amp. The curves show the appearance of N_2^+ ions (in the insets) and that of high speed ions (N^+) as a function of their minimum energy. In the upper curve are seen traces of ionization below the designated appearance potentials. This was due to residual gases in the tube, remaining after incomplete baking out. This ionization remained even when the N_2 was pumped out. Thus we can disregard this as it is without significance for N_2. The lower set of data taken some weeks earlier shows no such ionization.

As in the treatment of H_2 we can, without any knowledge of the ionization potential of N_2, calculate the voltage difference (V_i-V_M) between the appearance of N^+ and N_2^+ ions. This is given in Table II for ions of different kinetic energy including other data as well as those of Fig. 3. The quantity in the third column, as before, represents the potential energy increase of the dissociated products relative to N_2^+.

The average value is 8.62±0.02 v. For reasons that follow we hesitate to call this the heat of dissociation of N_2^+. It is equal to this plus any excitation energy of the products N^+ and N.

TABLE II. *Results for nitrogen.*

Minimum K.E. of ions (volts)	V_i-V_M (volts)	$(V_i-V_M)-2(\text{K.E.})$ (volts)
1.07	10.7	8.56
	10.8	8.66
	10.6	8.46
1.27	11.1	8.56
1.57	11.8	8.66
	11.8	8.66
2.07	12.8	8.66
	12.7	8.56
	12.8	8.66
2.57	13.8	8.66
	13.8	8.66
	13.8	8.66
3.07	14.8	8.66
		Average 8.62±0.02

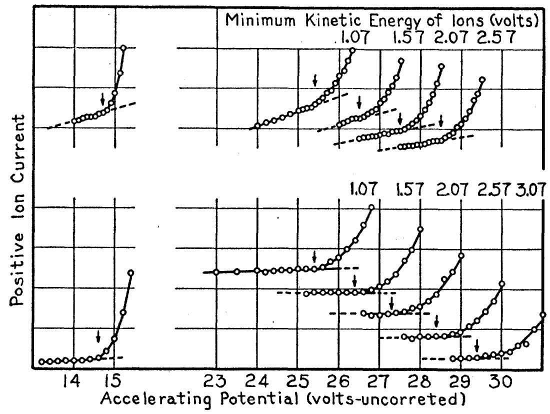

FIG. 3. Curves showing N^+ current, as a function of electron energy, which is able to traverse the indicated retarding potentials. The curves at the extreme left represent N_2^+ ionization. The two sets of data were taken several weeks apart.

To show why we believe one of the products to be excited it is necessary to determine the potential energy of the dissociated products relative to N_2. To do this we need the ionization potential of N_2. For some time the accepted value for this was about 16.5 v but several investigations in the last few years[17] have given results in the neighborhood of 15.8 v. Finally, in a careful research with a mass-spectrograph and argon as the calibrating gas Tate, Smith and Vaughan[18] showed the I.P. of N_2 to be lower than that of argon by 0.04 v corresponding to an ionization potential of 15.65±0.02 v. Adding to this 8.62 v we see 24.27±0.02 v represents the potential energy of the dissociation products.

As confirmatory evidence of the correctness of our value 24.27 v for the potential energy of the dissociation products may be cited the mass-spectrograph measurements. The older mass-spectrograph measurements,[19] while making no claim to high accuracy, concurred in a value of 24 volts for the energy necessary to form N^+ ions. Recently, Vaughan[20] has found N^+ ions appear-

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[17] L. A. Turner and E. W. Samson, Phys. Rev. **34**, 750 (1929); A. L. Vaughan, Phys. Rev. **38**, 1687 (1931); John T. Tate and P. T. Smith, Phys. Rev. **39**, 273 (1932).

[18] John T. Tate, P. T. Smith and A. L. Vaughan, Phys. Rev. **43**, 1054A (1933).

[19] H. D. Smyth, Rev. Mod. Phys. **3**, 371 (1931).

[20] A. L. Vaughan, Phys. Rev. **38**, 1687 (1931). In this work with Hg as the calibrating gas, the I.P. of N_2 was found to be 15.8 v. If all Vaughan's results are lowered to

ing at 24.5 ± 0.1 v. Of course, mass-spectrograph measurements would be expected to agree with our value only if N^+ ions are formed with a minimum of zero kinetic energy. From the discussion of Smyth[19] it seems probable that one can form N^+ ions with zero kinetic energy by electron impact. It is pleasing to find Vaughan's value agreeing to within 0.2 v.

If this energy represents the energy of N^+ and N (unexcited), then $24.27 - 14.48 = 9.79$ v represents the heat of dissociation of N_2. There are several lines of evidence militating against such a high value. First, can be mentioned the observations of Kaplan[21] that several electronic levels of N_2 show predissociation. Most of these occur in the triplet levels whose exact energy is unknown. However, one of these intensity irregularities occurs in the a $^1\Pi$ level at 9.3 v. Granting the interpretation as predissociation we can say with certainty that $D(N_2) \leqq 9.3$ v. Secondly, there is the observation by Kaplan[21] of a similar irregularity in certain bands of NO occurring at an energy of 6.15 v which is interpreted as predissociation and thus requires $D(NO) \leqq 6.15$ v. From the known heat of dissociation of O_2 and certain thermochemical data[22] it can easily be shown that $D(N_2) = 2D(NO) - 3.20$ v. From the result above we arrive at $D(N_2) \leqq 9.1$ v. Thirdly, there is the work of Datta,[23] who studied the continuous absorption spectra of N_2O and obtained from its interpretation, combined with the results of thermochemical measurements, $D(N_2) = 8.7$ v. This was later corrected by Sutton[24] to 9.0 v. This value also can only represent an upper limit; for continuous absorption in general will, just as in the experiments described in this paper, produce dissociation products with kinetic energy. We have cited three lines of evidence which indicate respectively $D(N_2) \leqq 9.3$, 9.1, 9.0 v. This seems to the writer to be strong evidence against normal dissociation products N and N^+ in our experiment, for we have shown this assumption leads to $D(N_2) = 9.79$ v.

We must then ascertain the state of excitation of the dissociation products. As possibilities we may state that the N^+ ion has the following low levels ^1D at 1.89 v and ^1S at 4.03 v. The N atom has as low-lying levels $^2D^\circ$ at 2.37 v and $^2P^\circ$ at 3.56 v.[25]

Let us consider again the heat of dissociation of N_2^+. If we assume our dissociation products are N^+ (normal) and $N(^2D^\circ)$ then $D(N_2^+) = 6.25$ v. However if they are assumed to be $N^+(^1D)$ and N (normal), $D(N_2^+) = 6.73$ v. Supplementary evidence for $D(N_2^+)$ comes from band spectra. The negative bands of N_2^+ $(A' \rightarrow X')$ correspond to an energy difference of 3.15 in the (0, 0) band. Herzberg's analysis[26] allows an extrapolation of the vibrational levels of the upper (A') state. According to Herzberg the maximum value of $D(A') = 3.7$ v with a most probable value of 3.5 v. On the basis of observations on the general behavior of vibration level spacings, Birge[27] came to the conclusion $D(A') \leqq 3.9$ v. But later, after finding a new method of treating the data—this method has proved very successful in the case of O_2 and H_2^-. Birge[28] obtained $D(A') = 3.67$ estimated as accurate to 0.1 v. This gives $D(N_2^+) = 3.67 + 3.15 = 6.82 \pm 0.1$ v which agrees, within the estimated reliability, with our value of 6.73 v obtained by assuming our dissociation products to be N^+ (^1D) and N (normal). The assumption of any other excitation energy appears to give far too low an energy of dissociation for N_2^+. It is very difficult after carefully considering the work of Herzberg and Birge to see how $D(A')$ can be less than 3.5 v. The possibility of its being a few tenths of a volt higher is not unreasonable. But the assumption that our products of dissociation are unexcited would lead to $D(N_2^+) = 8.62$ v and require $D(A') = 5.47$ v. It seems extremely unlikely that the extrapolations of Herzberg and Birge are in error by 75 percent when the vibration levels

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bring this into agreement with the new value 15.65, his value, 24.5 v, for N^+ becomes 24.35 and is in even better agreement with our value, 24.27 v.

[21] J. Kaplan, Phys. Rev. **37**, 1406 (1931) and **42**, 97 (1932).

[22] The thermochemical data needed are $\frac{1}{2}N_2 + \frac{1}{2}O_2 + 0.94\text{ v} \rightarrow NO$. See Landolt-Börnstein, p. 1490 (1923).

[23] A. K. Datta, Nature **129**, 870 (1932) and Proc. Roy. Soc. **A138**, 85 (1932).

[24] T. C. Sutton, Nature **130**, 132 (1932).

[25] Bacher and Goudsmit, *Atomic Energy States*, McGraw-Hill (1932). Professor A. G. Shenstone has kindly pointed out to me that the ^5S term from the configuration $2s(2p)^3$ of N^+ has never been located.

[26] G. Herzberg, Ann. d. Physik **86**, 189 (1928).

[27] R. T. Birge, Nature **122**, 842 (1928).

[28] See reference 16, also Phys. Rev. **34**, 1062 (1929).

themselves have been followed to 75 percent of the energy of the estimated convergence point. Therefore we conclude with some confidence that $D(N_2^+) = 6.73 \pm 0.02$ v.

Carrying out this interpretation, $D(N_2) = 15.65 + 6.73 - 14.48 = 7.90 \pm 0.02$ v. The writer believes this result is free from systematic errors to within 0.1 v.

A table of the older values of $D(N_2)$ is available in the paper of Datta.[23] Of these we will mention only a few. Kaplan[21] has interpreted the predissociations in N_2, which we have already mentioned, as occurring with very little kinetic energy giving $D(N_2) \leqq 9.0$. Most of his work also rests on Sponer's questionable determination of the energy of the triplet levels of N_2. Datta,[23] whose result (9.0 v) we have already used, takes much the same position in regard to dissociation of N_2O by continuous absorption. He believes this occurs with production of dissociation products of zero kinetic energy. A strong argument against his viewpoint comes from his own work. The employment of his method[29] on the absorption spectra of SO_3 yielded $D(O_2) = 5.57$ v whereas it is accurately known to be 5.09 v. We believe the early extrapolations of Birge and Sponer on the X level of N_2 merit no comment—the extrapolations were far too long.

However, the results of Birge and Herzberg on the N_2^+ bands, which we have discussed above, have been quoted as giving for $D(N_2)$ from 9.0 to 9.5 v depending on the value assumed for the I.P. of N_2. From the latest value for this quantity, 15.65 v, and from Birge's latest extrapolation for $D(A')$ there results $D(N_2) = 7.99 \pm 0.1$ v which is in satisfactory agreement with our value.

CONCLUSIONS

We have obtained $D(H_2) = 4.43 \pm 0.03$ v, $D(H_2^+) = 2.59 \pm 0.03$ v, $D(N_2) = 7.90 \pm 0.02$ v and $D(N_2^+) = 6.73 \pm 0.02$ v. The probable errors have been calculated from the variation of the data according to the usual formulae. It is believed the results are free from systematic errors to within 0.1 v.

The author is glad to acknowledge his indebtedness to the National Research Council for a grant for carrying on this work and to the Palmer Physical Laboratory for the generous facilities provided. He is also grateful to Professor H. D. Smyth and Dr. Walker Bleakney for their helpful discussions.

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[29] A. K. Datta, Proc. Roy. Soc. **A137**, 367 (1932).