

hot moist air and the cool air of the moist monsoon current, so that when the monsoon wind advances under the heated air we shall have the essential conditions of a cold front with its attendant squalls and its tendency to produce the vortices of waterspouts. It will facilitate the production of rain if the hot air which is lifted by the cold is moist, at any rate in its lower layers; and it may be that cyclones only form when this moisture exceeds some limit. Also it would be interesting to see whether the direction of the front between these two air-masses is related with the direction in which the cyclone, when formed, begins to move—a matter on which light is badly needed.

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The Heat of Dissociation of Nitrogen.

IN a recent letter to NATURE (122, 313; Sept. 1, 1928) E. Gaviola has presented some evidence indicating that the heat of dissociation (D) of N_2 is not more than 9.8 volts, as contrasted with the 11.4 volt value calculated by Birge and Sponer (*Phys. Rev.*, 28, 259; 1926). It seems desirable to state that some months ago R. S. Mulliken and I independently reached the conclusion that the value of D for N_2 is probably about 9.5 volts. The evidence on which I reached this conclusion, which seems to me quite direct and unambiguous, is contained implicitly in a recent article by G. Herzberg (*Ann. d. Physik*, 86, 189; 1928) on the negative N_2 bands.

Herzberg has greatly extended this system, obtaining 12 levels in the excited state (A'), as compared to the 5 levels available to Birge and Sponer. He is thus able to get a fairly trustworthy curve for the variation of the frequency of vibration with the vibrational quantum number (p. 205, loc. cit.). He then obtains, from this curve, 3.5 volts as the probable value of the heat of dissociation for this excited (A') level, with 3.7 volts as an upper limit. However, plots made by me of all known vibration curves indicate that they probably always have a point of inflection, and the true value of D for level A' is therefore slightly more than 3.7 volts, rather than less.

For a reason appearing below, I will assume 3.9 volts as an upper limit. Adding the electronic energy 3.2 volts, one obtains 7.1 volts as an upper limit for the total energy difference between the normal (X') level of N_2^+ and dissociation from state A' . If the products of dissociation from state A' are two normal atoms (N^+ and N), then 7.1 volts is also, within a few tenths of a volt, the normal heat of dissociation (D') of N_2^+ . If the products of dissociation from state A' include one excited atom, D' is at least 2.4 volts less than 7.1 volts. By the argument presented below, this would give $D = 9.5 - 2.4 = 7.1$ volts, an unreasonably low value. The probable products of dissociation from the various electronic levels are discussed in the accompanying letter by Prof. Mulliken.

The total energy necessary to obtain normal N^+ and N from normal N_2 is then given by either $I_m + D'$ or $D + I_a$, where I_m and I_a are the respective ionisation potentials of the neutral molecule (N_2) and neutral atom (N). Hence, by conservation of energy, $I_m + D' = D + I_a$, a relation used repeatedly by Birge and Sponer. I_m can scarcely be more than 16.9 volts (the experimental values range from 16.3 to 16.9 volts). We have just seen that D' can scarcely be more than 7.1 volts. Hence $7.1 + 16.9 = 24.0$ volts, giving an upper limit for the potential at which N^+ ions might first appear, starting with normal N_2 . Hogness and Lunn (*Phys. Rev.*, 26, 786; 1925) observed N^+ ions at a minimum potential of 24 volts. Considering now the right side of the equation, we

know that I_a is 14.5 volts (J. J. Hopfield, *Phys. Rev.*, 27, 801; 1926). Hence D cannot well be greater than 9.5 volts.

This new value of 9.5 volts (or a few tenths of a volt less) is consistent with Sponer's theory of the origin of the α -group bands observed in the afterglow of active nitrogen, provided that one assumes that association to form the nitrogen molecule occurs only between one normal and one 2.4 volt (metastable) excited atom. It is also consistent with the quite different recent ideas on this subject given by Kaplan and Cario (NATURE, 121, 906; June 9, 1928). This, however, is a matter which can more appropriately be discussed by those actively at work in the field.

Birge and Sponer used the value of D for N_2 in calculating indirectly the value of D for NO. The above lowering from 11.4 to 9.5 volts lowers the D of NO by half this difference, the new indirect calculation being thus 7.3 volts (or less). This agrees better with the later more reliable direct calculation of 6.8 volts, by Jenkins, Barton, and Mulliken (*Phys. Rev.*, 30, 150; 1927). All recent work seems to indicate the approximate correctness of the value 7.0 volts for the D of O_2 , given by Birge and Sponer. Hogness and Harkness (unpublished work) have recently checked the Birge and Sponer value of about 11 volts for CO. The probable values for the heat of dissociation of these molecules are therefore, in the opinion both of Prof. Mulliken and myself, O_2 , 7.0 volts; CO, 11 volts; N_2 , 9.5 volts (or slightly less); NO, 7 volts.

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IN connexion with the assignment of quantum numbers for electrons in molecules (R. S. Mulliken, *Phys. Rev.*, 32, 186; 1928), it is important, in considering a molecule in a specified electronic state, to know in what electronic states the atoms or ions resulting from its adiabatic dissociation would be (R. S. Mulliken, *Phys. Rev.*, November 1928). I have thus been led to a study of dissociation products and heats of dissociation for various molecules, and among other results have reached conclusions essentially the same as those stated in the accompanying letter by Prof. Birge. Only a few points concerning the nitrogen molecule will be given here; further discussion will be found in the articles cited.

As Prof. Birge points out, data on N_2^+ furnish strong evidence for a value of about 9.5 volts for the heat of dissociation (D) of neutral N_2 . Three electron levels of N_2^+ are known at present, namely, two 3S levels at about 16.9 and 20.1 volts (X' and A' levels of Birge), and a third, probably also 3S , level at 24 volts, which is known from the work of Hogness and Lunn. The transition $A' \rightarrow X'$ corresponds to the 'negative nitrogen bands.' If we confine ourselves to a consideration of adiabatic processes of dissociation, definite theoretical limitations exist in regard to possible dissociation products. Thus, as Hund has shown (*Z. f. Physik*, 42, 93; 1927), an unexcited (4S) N atom and an unexcited (3P) N^+ ion can give only one 3S state of N_2^+ on adiabatic union. Other 3S states must involve an excited atom or ion.

As Birge notes in the accompanying letter, Herzberg's work leads to the conclusion that the best experimental value for the total energy ($T.E.$) required to ionise an N_2 molecule, excite it to state A' , and dissociate it adiabatically, is (not more than) 24.0 volts. This value leads to $D = 9.5$ volts, if the dissociation products of state A' are an unexcited atom and ion. If the latter supposition is correct, the dissociation products from the normal state X'