Problem Set 5

Chemistry 448

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You may assume that the following data are factual:

Lowest electronic state of nitrogen atom is ^4S

First excited state of nitrogen atom is ^2D, 19,202 cm^{-1} above the ground state.

Second excited state of nitrogen atom is ^2P, 28,808 cm^{-1} above the ground state

Lowest electronic state of nitrogen molecule N_2 is $^1\Sigma_g^+$

First excited electronic state of N_2 is $^3\Sigma_u^+$, approximately 6 eV above the ground state.

Internuclear distance of N_2 is 1.094 Å

Vibrational frequency of N_2 is 2350 cm^{-1}

Ionization potential of N = 14.53 eV

Ionization potential of N_2 = 15.58 eV

Atomic mass of N = 14.0067 amu

Boltzmann constant $k = 1.38047 \times 10^{-16}$ erg deg^{-1}

Planck's constant $h = 6.624 \times 10^{-27}$ erg sec

Energy conversion table

unit	cm^{-1}	erg $molecule^{-1}$	cal $mole^{-1}$	eV
1 cm^{-1}	1	1.9855×10^{-16}	2.8584	1.23941×10^{-4}
1 erg $molecule^{-1}$	5.0364×10^{15}	1	1.43965×10^{16}	6.2422×10^{11}
1 cal $mole^{-1}$	0.34983	6.94612×10^{-17}	1	4.3359×10^{-5}
1 eV	8068.3	1.60199×10^{-12}	23063	1

STATEMENT OF THE PROBLEM

You are to determine whether the following statements and/or experimental results are mutually consistent or not. If they are not consistent, discuss possible sources of discrepancy. In either event, you should indicate WHAT CONCLUSIONS YOU WOULD DRAW FROM THESE EXPERIMENTS, AND DEFEND YOUR CONCLUSIONS BY EXPLORING EACH STATEMENT AND/OR EXPERIMENT QUANTITATIVELY

I. With reference to the molecule N_2, "... two ... predissociations have been observed, one in the $B^3\Pi_g$ state with a limit at 9.839 eV, another in the $a^1\Pi_g$ state with a limit at about 9.8 eV. In the former, a breaking-off is observed in the rotational structure of one vibrational level, in the latter thus far only a breaking off of the vibrational structure. In either case, therefore, the figure given is only an upper limiting value for the corresponding dissociation limit. ... In both predissociations the breaking-off is complete, (that is, affects both Λ-type components) and, therefore, the states causing these predissociations must be Π or Δ states which cannot result from normal atoms (^4S + ^4S). Depending on whether the dissociation products at the predissociation limit, 9.839 eV, are $^4S + {}^2D$, $^4S + {}^2P$, $^2D + {}^2D$, $^2D + {}^2P$, or $^2P + {}^2P$, we obtain for $D_0(N_2)$ the upper limiting values 7.46, 6.27, 5.07, 3.88, or 2.69 eV, respectively. However, since the last observed vibrational state of the ground state lies at 6.6 eV, only the first of these need be considered." [1]

II. " ... an alternative explanation of the predissociation ius possible. Normal nitrogen atoms, $^4S + {}^4S$, can produce a $^5\Sigma$ level which might predissociate $B^3\Pi_g$. The predissociation would, owing to the change of multiplicity, be weak, as is observed, and would increase in intensity with increasing rotational quantum number. ... both Λ-doubling components of the $B^3\Pi_g$ state can be affected by the predissociation. This explanation can apparently be made to explain all the features of the predissociation at least as well as that of (the other) and has the advantage that it explains the incompleteness of the predissociation rather more satisfactorily. With this explanation, values for $D_0(N_2)$ of 9.76, 8.57, and 7.38 eV remain possible..... Comparison shows that in Herzberg's energy level scheme of N_2 the non-crossing rule is not observed." [2]

III. " The purpose of the present work is to choose between the values 7.385 eV and 9.765 eV for D0(N2) by observation of the thermal dissociation of N_2 at high temperatures and low pressures. The general procedure is as follows: Nitrogen at pressures of the order of 1 mm Hg is heated to temperatures up to the limit of a tungsten oven, about 3450 K. A beam of the hot gas, effusing from the tungsten oven mounted in the source chamber of a molecular beams apparatus, passes through the evacuated apparatus toa detector. A strong inhomogeneous magnetic field perpendicular to the beam may be turned on to deflect particles of large magnetic moment away from the detector. The field strength is adjusted so that nitrogen atoms, having magnetic moments of the order of one Bohr magneton, are deflected away from the detector while nitrogen molecules whose moments are of the order of a nuclear magneton, are not sufficiently deflected to miss the detector. A comparison of the beam intensity at the detector with the magnetic field off and on permits the fractional content of nitrogen atoms in a beam of hot nitrogen gas to be determined. .... Two high temperature runs were made with niotrogen. No measureable dissociation was observed in either of them. These runs reached the following oven conditions: 3410 K at 0.61 mm Hg, 3530 K at 1.11 mm Hg." You may assume that the detection limit was ca. ±1%. [3]

IV. "In figure1 is shown the ionization efficiency curve for the formation of nitrogen ions from molecular nitrogen by the impact of electrons which are essentially mono-energetic to about 0.1 eV. This curve shows clearly that there are three distinct processes leading to the formation of N^+ ions. Thee three processes occur at the appearance potentials of 24.32±0.02; 26.66±0.05; and 27.93±0.05 eV.

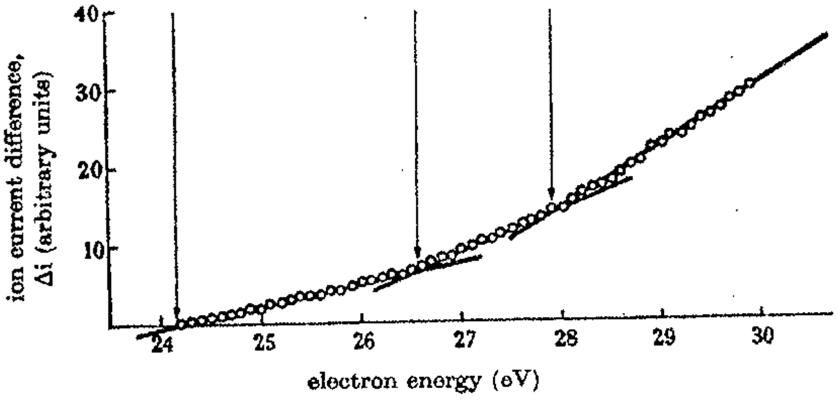

FIGURE 1. Ionization efficiency curve for the production of N^+ ions.

Hagstrum’s (1951) work demonstrated clearly that when nitrogen molecules are bombarded with electrons with 24.3 eV energy they decompose to form atomic nitrogen ions and nitrogen atoms, and that these particles are formed without excess kinetic energy. The dissociation process is thus known to be

$$N_2 + e = N^+ + N + 2e \qquad (1)$$

Since no negative ions are formed and the results quoted earlier show that process (1) occurs at 24.32 eV, the only problem which remains is to decide whether the N^+ ion and the nitrogen atom are produced in their ground states, or in one of their many possible excited states.” [4]

Sources:
[1] G. Herzberg, *Spectra of Diatomic Molecules*, (D. van Nostrand, N.Y., 1950) p. 450.
[2] A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules*, (Chapman and Hall, London, 1947) p. 157.
[3] J. M. Hendrie, *J. Chem. Phys*. **22**, 1503 (1954).
[4] D. C. Frost and C. A. McDowell, *Proc. Roy. Soc. A* **236**, 278 (1956).

You may find one or more of the following formulas useful:

$$Q_t = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} V$$

$$Q_v = \frac{1}{1 - e^{h\nu/kT}}$$

$$Q_r = \frac{8\pi^2 IkT}{\sigma h^2}$$

$$G = -RT \ln \frac{Q}{N}$$

$$E = RT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_V$$

$$H = RT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_V + RTV \left(\frac{\partial \ln Q}{\partial V}\right)_T$$