CHARACTERISTICS AND SPECTRA OF LOW VOLTAGE ARCS IN H_2, N_2 AND IN MIXTURES OF H_2 WITH Hg AND N_2

By C. T. Kwei

Abstract

I. *Arc characteristics.*—The tube used was a spherical bulb containing a Ni disk electrode and a W spiral filament and provided with a quartz window and an appendix in which could be placed liquid Hg. By applying corrections for filament drop and for initial velocities, approximately measured by use of a high resistance voltmeter, remarkably consistent values for the breaking voltages were obtained. (1) *With pure hydrogen*, there were no oscillations; the arc broke at the *ionization potential* 16.2 volts; and by plotting the 2/3 power of the current as a function of the voltage, the ionization potential of the atom was located at 13.7 volts. These voltages are subject to a correction of about −0.5 volt for contact potential difference. (2) *With pure nitrogen*, the breaking potential 16.2 is not the ionization potential since oscillations occur below 16.9, the actual ionization potential, as shown by oscillograph observations. (3) *In mixtures of H_2 with Hg*, a careful study was made for pressures of H_2 from 0.1 to 3.0 mm, and with the Hg appendix at room temperature and at 100°C. Below a critical pressure of H_2, depending on the Hg pressure, oscillations of one or two types occurred. With the filament not too hot, 0.8 mm of H_2 and Hg at 20°C, two arcing and two breaking potentials were observed. The curve as far as the second arcing potential, was reversible. The difference between the two arcing potentials is about 10.4 volts, the ionization potential of Hg. When a single breaking potential was observed, it decreased with the pressure of H_2, being approximately a weighted mean of the breaking potentials in the pure gases. (4) *Mixtures of H_2 and N_2* behaved similarly to the mixtures with Hg. The breaking potential reached a minimum value for equal pressures of H_2 and N_2. Under some circumstances two arcing potentials (3 volts apart) and two breaking potentials were observed. Oscillations of two types were likewise obtained. A break was observed at 22.7 volts which seems to be a critical potential for N_2.

II. *Spectroscopic observations.*—(1) *In H_2*, the Balmer lines and secondary spectrum appeared together. (2) *In mixtures of H_2 with Hg*, the Hg lines ($2p-ms$) and ($2p-md$) were weak below the second arcing potential and much intensified above it, while the secondary H_2 spectrum and other bands were weakened or disappeared. (3) *In mixtures of H_2 with N_2*, evidence was obtained which indicates that the *ultraviolet band of ammonia*, associated with the 22.5 volt critical potential, is due to a molecule NH_x, where x is probably 3, and that the *Schuster band* is emitted only in the presence of oxygen and is due to a molecule $N_xH_yO_z$, possibly NH_4OH. This band was observed only at voltages higher than the critical voltage for "active nitrogen," 70.

Introduction

Recent experiments in low-voltage arcs have yielded a number of interesting, though in some cases puzzling, results. It is now known that arcs may be maintained in gases and vapors at voltages as low as their ionizing potentials and in certain monatomic gases as low as their radiating potentials. The latter phenomenon is generally accounted for by the theory[1] that cumulative action is largely responsible for the ionization of partially ionized or excited atoms. Cases were also observed in which arcs were maintained at voltages too far below the radiating potentials to be accounted for by the velocity distribution of electrons. These were found to be due to oscillations in the arc such that the maximum voltage peaks would always be higher than the radiating potentials. This fact was independently discovered by Bär, v. Laue, and Meyer[2] and Eckart and Compton.[3] The last mentioned authors[4] were also able to maintain abnormal low voltage arcs in argon, helium and mercury vapor without oscillations and demonstrated by means of an exploring electrode that the cathode drop was invariably near the radiating potential and that the abnormal low voltage was due to a reverse field between the cathode drop and the anode, which they attribute to the diffusion of electrons, maintained by concentration gradient, against an electric field.

Duffendack[5] studied the low voltage arcs and the associated spectra in several diatomic gases—hydrogen, nitrogen, and iodine. He was able to determine the ionization potential for atomic hydrogen by maintaining an arc in the gas dissociated by means of an electrically heated tungsten tube furnace, and the value thus determined was in good agreement with Bohr's predictions. Similar results were obtained in iodine. In nitrogen, the dissociation was not appreciable when the arc struck, but above 70 volts the conductivity of the arc rapidly increased, and a brilliant flare appeared which Duffendack identified with the formation of "active nitrogen" as described by Strutt.[6] More recently Richardson and Tanaka[7] studied the striking and breaking potentials in hydrogen and concluded, as did Duffendack, that the breaking potential was a critical potential for the gas, but they differed from him in attributing it, from spectroscopic considerations, to the ionization of the hydrogen molecule as against dissociation plus ionization of one of the atoms. A recent important experiment by Smyth,[8] in which the positive ray method was employed in analyzing the ions formed in the hydrogen discharge,

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[1] K. T. Compton, Phys. Rev. **20**, 283 (1922); Van der Bijl, ibid, **10**, 645 (1917).

[2] Bär. v. Laue and Meyer, Zeits. f. Phys. **20**, 82 (1923).

[3] Eckart and Compton, Phys. Rev. **24**, 97 (1924).

[4] Eckart and Compton, Phys. Rev. **25**, 139 (1925).

[5] Duffendack, Phys. Rev. **20**, 665 (1922).

[6] Strutt, Roy. Soc. Proc. **85A**, 219 (1911) et seq.

[7] Richardson and Tanaka, Roy. Soc. Proc. **106A**, 640 (1924).

[8] Smyth, Roy. Soc. Proc. **105A**, 116 (1924); Phys. Rev. **25**, 452 (1925).

seems to have decided definitely in favor of the ionization of the hydrogen molecule.

The work on low voltage arcs has now been extended to mixtures of gases and has already proven itself a promising method for investigating certain chemical properties of elements, such as combination and dissociation. In particular, although the synthesis of ammonia from hydrogen and nitrogen by electrical excitation was discovered over fifty years ago,[9] only a beginning toward analyzing the process has been made through the work of Andersen[10] and of Storch and Olson.[11] These authors detected the formation of ammonia in low voltage arcs in mixtures of hydrogen and nitrogen and by noting the rate of reaction concluded that the formation of ammonia in any appreciable amount occurred only after the arc was struck. Thus the critical potentials of the constituent gases and the rates of reaction as well as the spectra observed at various voltages afford several co-ordinating lines of approach towards a clearer understanding of chemical reaction.

To attack a slightly different problem, Duffendack and Compton[12] studied low voltage arcs in mixtures of hydrogen and mercury vapor and found that the dissociation of the hydrogen molecules in mercury arcs increased ten times in the 5 volt arc and three times in the 10 volt arc as a result of the presence of the mercury. This increase was explained as being due to "collisions of the second kind," in which the hydrogen molecules received the requisite energy of dissociation from excited mercury atoms in the $2p$ states. In mixtures of nitrogen and mercury vapor, the dissociation (or perhaps activation) was found to be only one tenth as large.

Aside from the possibilities of studying combination and dissociation, the low voltage arc offers a convenient method for exciting spectra, for it removes certain objections usually connected with the flame or high voltage excitation. Thus the flame is incapable of excluding impurities present in it and may not furnish enough energy for excitation, and the high voltage discharge is likely to cause dissociation and release of occluded gases from the electrodes and walls. The purpose of our experiment then is to correlate the arcing characteristics in mixtures of gases with the spectra observable at various potentials.

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[9] W. F. Donkin, Roy. Soc. Proc. **21,** 281 (1873).

[10] Andersen, Zeits. f. Physik, **10,** 64 (1922).

[11] Storch and Olson, Jour. Am. Chem. Soc. **45,** 1605 (1923).

[12] Duffendack and Compton, Phys. Rev. **23,** 583 (1924).

APPARATUS AND METHOD

The apparatus consisted of a simple two-electrode discharge tube in the form of a spherical bulb 9 cm in diameter. The anode was a round nickel plate about 3 cm in diameter. The cathode was a hot filament made of 15 mil (38 mm) tungsten wire wound closely in the middle into a helical spring of three turns. The electrodes were welded to tungsten leads which were sealed into ground glass stoppers and these in turn were sealed to the experimental tube by means of hard DeKhotinsky cement which was disposed so as to reduce to a minimum the presence of cement vapor in the tube. Vertically attached to the bottom of the bulb was a small glass appendix. When a mixture of mercury vapor and another gas was desired, this was filled 4 or 5 mm deep with mercury and could be heated up to the boiling point of water by immersing the tube in a water bath.

For spectroscopic observations, a side tube 15 cm in length and 1.7 cm in diameter was horizontally attached to one side of the bulb and a quartz window was fastened to it at the end. The light from any region between the target and filament or behind the filament was brought to a focus on the spectrometer slit by means of a quartz lens. The spectrum was observed with a direct reading constant deviation spectrometer for the visible region and photographs were taken with a small Hilger quartz spectrograph for the ultraviolet region.

The filament was heated through an adjustable carbon resistance by means of storage batteries. The voltage impressed on the plate was tapped from a potentiometer arrangement which was connected at will, by means of a double-pole double-throw reversing switch, to either the positive or negative side of the filament. It was found that the mean value of a critical potential from readings at the two positions was not always equal to the voltmeter reading plus or minus one half the filament drop of potential. In this experiment, only the mean values were taken.

The hydrogen and oxygen used in this experiment were prepared by electrolysis of dilute sulfuric acid. The nitrogen was prepared by dropping liquid bromine into concentrated ammonia, and was then made to pass through a wash bottle containing dilute ammonia and a second wash bottle containing dilute sulfuric acid to remove traces of bromine and ammonia, respectively. Each of these gases was stored in a drying tube for at least 24 hours over phosphorus pentoxide before it was admitted through a stop cock and a mercury cut off into a large reservoir 120 cm high and about 30 cm^2 in cross section. The large volume of the reservoir proved to be very convenient for adjustments at low pressures and reduced the rate of pressure change due to "clean-up." Another mercury cut off was inserted between the reservoir and two liquid air traps connected in series leading to the experimental bulb so that a small change in the pressure of the gas would be sensitively noticed by cutting off the large volume. The system was evacuated by means of a mercury diffusion pump backed by a high vacuum oil pump. For the identification of the ultraviolet and Schuster bands of ammonia, this gas was generated by evaporating a strong ammonia solution and the gas was dried by storing it over potassium hydroxide sticks.

Before a new gas was tried, the experimental bulb was usually baked for three or four hours in an electric furnace at a temperature between 300° and 350°C. The traps were constantly immersed in liquid air to condense any moisture or mercury vapor in the system, except when ammonia was used.

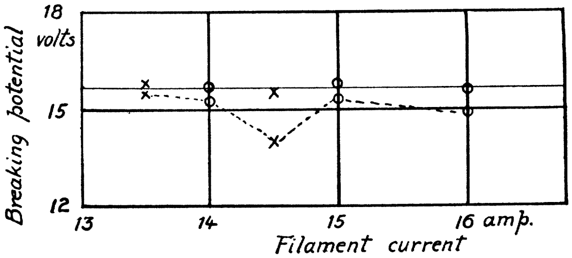

Fig. 1. Breaking potential in a mixture of N_2 and H_2. Pressure for crosses was 0.8 mm, for circles 0.5 mm. The lower curve is uncorrected for "initial voltmeter" reading.

In agreement with Richardson and Tanaka[7] the writer found that when the filament current remained constant, the breaking potential of the arcs tended toward a minimum at a definite pressure. The minimum voltage was found at a pressure of about 0.5 mm, and the breaking voltages did not exceed this minimum by more than 0.25 volt between pressures 0.2 and 1.0 mm. The excess voltage at low pressures must be due to an insufficient supply of molecules to be ionized and at high pressures to energy losses which do not contribute to ionization. It was also found that with the increase of filament temperature, the breaking potential tended to diminish, probably due to the increase in initial velocities of the electrons. To correct this effect to a first approximation, a Cambridge and Paul universal test set was used as a high resistance voltmeter to measure the potential difference of the electrodes, acquired as a result of the thermionic emission only, before the impressed voltage was applied. When this reading, designated as the "initial voltmeter reading" was added, the various breaking potentials became much more uniform. Fig. 1 illustrates this point. This correction was made for all determinations except those of a second arcing potential, where the variation of the second jump exceeded the value of the correction.

Since some of the apparent current-voltage characteristics were due to oscillations in the arc, these were detected and studied by use of a Western Electric cathode ray oscillograph, which was used so as to measure current and voltage along mutually perpendicular axes on the fluorescent screen.

ARC CHARACTERISTICS IN HYDROGEN AND IN MIXTURES OF MERCURY VAPOR AND HYDROGEN

Before the mixtures were tried, preliminary runs were made with hydrogen. The voltage-current characteristics were found to be very similar to those observed by Duffendack: 1. The potential of the break was always lower than the striking potential, usually by several volts, the difference being greater at higher pressures. In each case the varying factor was the striking potential while the breaking potential remained practically constant at 16 volts. 2. The breaking potential, pressure remaining the same, became slightly less with increasing filament temperature. This effect was corrected for by taking the "initial voltmeter" reading as described in the preceding section.

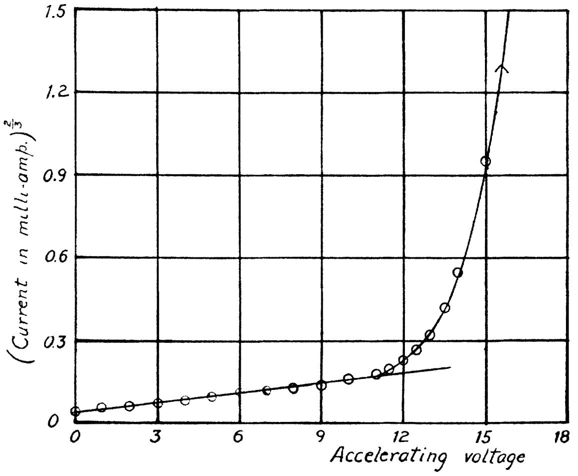

Fig. 2. Ionization potential of atomic hydrogen. Value observed 11.0 volts; with connections reversed 15.0 volts; mean value 13.0 volts. Initial voltmeter reading 0.5 volt. Corrected value 13.5 volts.

Limiting the pressure range to 0.4 to 1.0 mm, the corrected breaking potential as an average of sixteen runs was found to be 16.17 ± .05 volts. An independent series of eleven runs was made several months later with different electrodes and the average was found to be 16.23 ± .03 volts.

Both of these results are in excellent agreement with Duffendack's value of 16.18±.05 volts. We shall take 16.2 as our experimental value for the ionization potential of the hydrogen molecule.

It was suspected that thermal dissociation due to the filament might furnish enough atoms to make the effect of atomic ionization detectable. Graphs were plotted on a magnified scale to see if the increase of current with voltage deviated from the $i \propto V^{3/2}$ relationship. The point of departure of the curve from a straight line was taken as the value for the ionization potential for the hydrogen atom. Six graphs similar to Fig. 2 were plotted and the average potential came out to be 13.67±.14 volts, which is near the 13.5 volt value calculated from the limit of the Lyman series.

When mercury was introduced into the appended tube, as described in the preceding section, and immersed in a water bath at room temperature, it was found that the *breaking potential* was systematically reduced in proportion as the relative amount of hydrogen in the presence of mercury vapor was diminished. The first two columns of Table I contain the experimental data.

TABLE I

Arc in mixture of hydrogen with Hg vapor at room temperature

Pressure of hydrogen	Breaking potential (observed)	(calculated)
1.1 mm	16.34 volts	15.8 volts
.7	15.90	15.6
.35	15.22	15.1
.25	14.61	14.7
.15	14.27	14.2
.09	13.30	13.5

When the filament temperature was not too high, it was possible, in the mixture of hydrogen and mercury vapor maintained at room temperature, to locate a second striking potential when the pressure of hydrogen was at or below 1 mm. This is shown in Fig. 3. Very often when the voltage was lowered there were two breaking potentials, the first one being a volt or so lower than the second. Table II contains a summary of the readings.

It is seen that the two arcing and breaking potentials were observable at higher hydrogen concentrations. When the curve was retraced before the second arcing potential was reached, there was a marked approach to reversibility which is a prominent attribute of arcs with oscillations, as will be shown below. This is shown in Fig. 4. The breaking point here corresponds to the one observed in pure hydrogen.

Interpretation of current-voltage relations in mercury-hydrogen mixtures. It is rather surprising that two distinct breaks were not observed corresponding to the ionization potential for the hydrogen molecule at 16.2

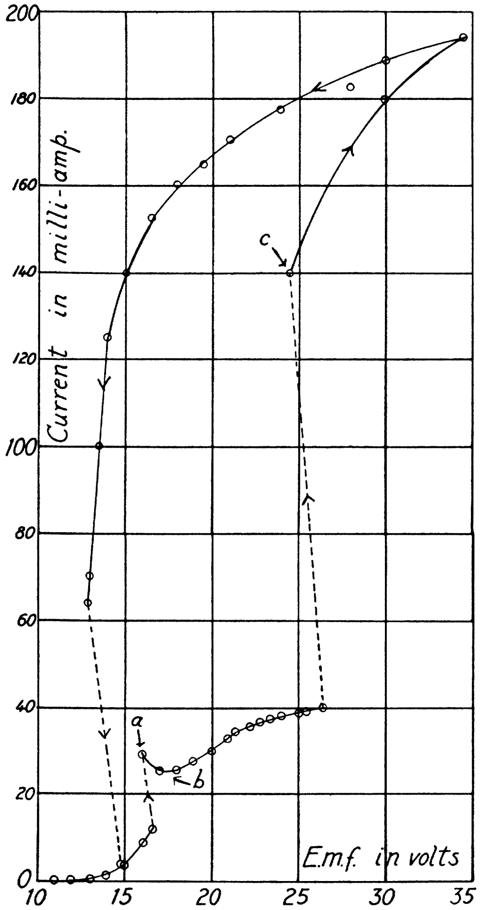

Fig. 3. Showing two striking potentials. Mercury appendix kept at room temperature. Pressure of hydrogen 0.75 mm. Readings uncorrected for filament drop.

TABLE II

Arc in mixture of hydrogen and mercury vapor, with mercury appendix at room temperature

Pressure of hydrogen	Striking potential 1st	Striking potential 2nd	Breaking potential 1st	Breaking potential 2nd
mm	volts	volts	volts	volts
0.9	19.5	28.6	15.3	16.9
0.8	18.9	28.2	15.0	16.1
0.7	25.5		15.1	
0.5	19.1		15.3	
0.35	19.7		15.2	

volts and for the mercury atom at 10.4 volts. An examination of the data suggests that the potential observed may be a weighted mean of the two critical potentials, depending upon the relative effectiveness of each constituent in neutralizing space charge around the filament. This depends upon the number of molecules of each gas present to be ionized, as well as the effective duration of the respective types of positive ions in the region of the space charge around the cathode.[13]

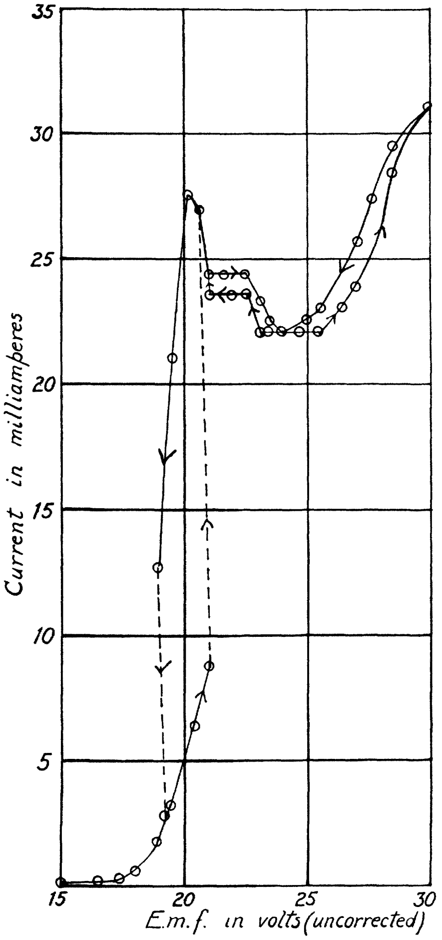

Fig. 4. Arc characteristics in mixture of mercury and hydrogen, when process was reversed before reaching the second striking potential.

Let N_1, N_2 be the concentrations of mercury atoms and hydrogen molecules, respectively; T_1, T_2 be the average durations of the respective

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[13] For theory of the low voltage arc consult K. T. Compton, Phys. Rev. **20,** 183 (1922).

ions; V_1, V_2 their respective ionizing potentials. Then the weighted mean breaking voltages may be taken as

$$V'=\frac{N_1T_1V_1+N_2T_2V_2}{N_1T_1+N_2T_2}=\frac{T_1V_1+(N_2/N_1)T_2V_2}{T_1+(N_2/N_1)T_2}. \tag{1}$$

Now in an electric field of given potential drop, the hydrogen and the mercury ions will move in such a way that

$$\tfrac{1}{2}M_1v_1{}^2=\tfrac{1}{2}M_2v_2{}^2\,, \tag{2}$$

where M_1v_1 and M_2v_2 refer to the mass and velocity of the mercury and hydrogen ions respectively. Therefore,

$$v_1/v_2=\sqrt{M_2/M_1}=T_2/T_1\,. \tag{3}$$

In the present case $M_1=200.6$ and $M_2=2.016$. Thus $T_1=10T_2$ approximately.

The ratio N_1/N_2 may be found by taking the ratio p_1/p_2 where p_1 represents the partial pressure of mercury vapor and p_2 that of hydrogen. Hence Eq. (1) may be written in this form

$$V'=\frac{10V_1+(p_2/p_1)V_2}{10+(p_2/p_1)}. \tag{4}$$

The values of V' thus calculated are tabulated in column 3 of Table I. The assumed pressure was .008 mm, which is the vapor pressure of mercury at 46°C. This is about 20° higher than the temperature of the water bath in which the mercury was immersed, but is a reasonable value owing to the heat from the filament.

The calculated values are in fairly good agreement with the observed values, except for higher pressures. This is perhaps due to the effect of increased hydrogen in reducing the amount by which the mercury is warmed by the filament.

Oscillograph study. An oscillograph study of the current-voltage characteristics further confirmed the reasonableness of this view. It was observed that when oscillations appeared in the arc of the mixture, there was a tendency for the arc to stay at either the maximum or minimum points for the longer time, depending upon the relative amount of hydrogen present. In general when the pressure of hydrogen was reduced, the oscillations extended in the direction of the lower voltage.

When hydrogen alone was used, no oscillations were observed under varying conditions of pressure and filament temperature and the arc was found to break at 16.2 volts.

When mercury in the trap was kept at room temperature (the actual temperature in the tube as we have explained must have been higher), the arcing characteristics for pressure higher than 0.8 mm were similar to those in pure hydrogen. Below this pressure there were two distinct types of oscillations, one being of greater amplitude and at a higher voltage than the other. Fig. 5A is a schematic diagram illustrating the behavior. It will be noted that the process was reversible.

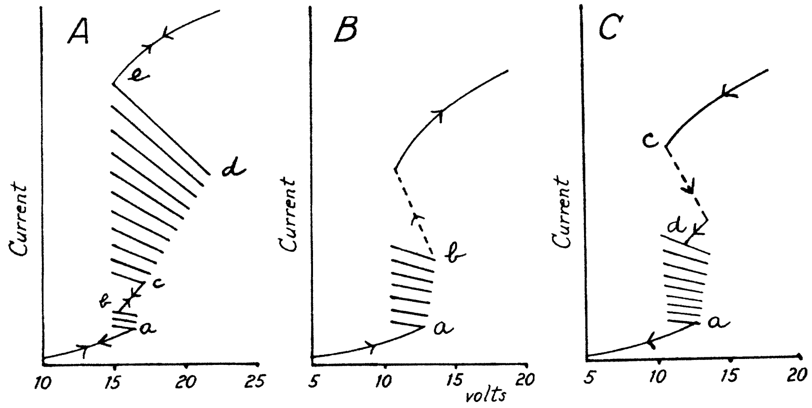

Fig. 5. Types of oscillations in mixtures of mercury vapor and hydrogen.
5A: *a* at 16.5, *b* at 15.3, *c* at 17.2, *d* at 21.8, *e* at 14.5 volts;
5B: *a* at 13.0, *b* at 13.3 volts;
5C: *a* at 13.0, *c* at 10.8, *d* at 12.0 volts.

The oscillations were more difficult to excite when the mercury trap was immersed in the water bath at the boiling point of water (actual temperature much lower of course in the tube owing to condensation in liquid air traps and cool parts of the tube). No oscillations were observed until the hydrogen pressure was reduced to 0.4 mm. The results are tabulated in Table III. The results in the fourth column were calculated from Eq. (4), assuming the pressure of mercury vapor to be 0.4 mm at an assumed bulb temperature of 65°C. Here the larger discrepancies at high

TABLE III

Arc in mixture of hydrogen with mercury vapor with mercury appendix at 100°C

Pressure of hydrogen	Striking potential	Breaking potential (observed)	Breaking potential (calculated)
3.0 mm	33.1 volts	16.7 volts	15.5 volts
2.1	31.0	16.0	15.3
1.5	27.3	15.0	15.0
1.1	25.1	14.6	14.7
0.8	20.7	14.1	14.3
0.4		oscillations set in	

pressures may be attributed to the fact that these pressures are beyond the range in which the arc breaks at the minimum voltage.

Figures 5B and 5C show the type of oscillations which set in at about 0.4 mm with this concentration of mercury vapor. The amplitude of oscillations was evidently larger than in the case of lower concentration and the type that previously appeared at a higher voltage was not present.

In order to account for the peculiar behavior of the oscillations with the two pressures of mercury vapor, let us assume the following cycle of operations. The arc in the mixture was struck only after a sufficient number of hydrogen molecules was ionized under the unfavorable conditions of negative space charge around the filament, since the number of mercury atoms present was always a small fraction of the mixed gases. The increased arc current would now ionize a number of mercury atoms and excite a sufficient number that would dissociate hydrogen molecules by means of "collisions of the second kind," the evidence of which is amply given by the experiments of Cario and Franck,[14] Duffendack and Compton,[12] and Compton and Turner,[15] as well as by the spectroscopic data in this experiment to be presented in the sequel. Both of these effects would further increase the arc current, as was observed. When the voltage was lowered, there might be a sufficient number of positive ions of mercury and of atomic hydrogen effectively to maintain the arc at a lower voltage than in pure hydrogen. However, if these atomic ions could not be sufficiently replaced, as probably would be the case with lower pressure of mercury vapor and therefore less dissociation of the hydrogen molecules, then the current would tend to diminish until the accompanying rise in voltage was enough to again ionize the hydrogen molecules and the cycle was repeated in the form of oscillations.

SPECTROSCOPIC OBSERVATIONS ON MERCURY VAPOR AND HYDROGEN

In pure hydrogen the Balmer lines and the secondary spectrum always appeared together, as soon as the arc was struck, with the Balmer lines more intense than the secondary spectrum. This is due, judging by Smyth's conclusions, to the ionization of the hydrogen atoms formed as a result of secondary collisions. Richardson and Tanaka used lower pressures (.2 mm) than those the writer employed (0.4 to 3.0 mm) and succeeded in actually observing the relative absence of the Balmer lines in the region of bluish glow in front of the anode on the side nearest the

[14] Cario and Franck, Zeits. f. Phys. **11**, 161 (1922).

[15] Compton and Turner, Phil. Mag. **48**, 360 (1924).

cathode. On the anode side the glow was pink and the Balmer lines were relatively more intense.

In mixtures of mercury vapor and hydrogen, the mercury lines and the Balmer series lines were very much enhanced relative to the secondary spectrum after passing the second arcing potential. We shall further examine this in detail. On the return path of voltage change the mercury as well as the hydrogen lines were visible above the upper break. Only the hydrogen spectrum was observable between the upper and lower breaks. Hg line 5461 showed this effect in a most striking manner. When there was only one striking and one breaking potential, the mercury and the hydrogen lines appeared and disappeared together.

Photographs were taken with the type of arc shown in Fig. 3 at the first and second arcing potentials and at the lowest current point between the two. We shall designate these points *a*, *c*, and *b* respectively. The result of examining the photographs may be summarized thus:

1. The mercury lines 5461, 4358, and 4047 were very faint at *a*, not found at *b*, and very much intensified at *c*.
2. The mercury lines 3650, 3132, 3022, 2967, 2803, 2652, and 2537 were more reduced in intensity relative to the rest of the spectrum at *b* compared with the lines at *a*. They were also very much intensified above the higher break.
3. A number of additional Hg lines including 3367, 3352 and 3343 appeared above the higher break.
4. Most of the secondary spectrum lines were reduced in intensity above the higher break.
5. Bands, probably mercury hydride, at 3572, 3531, 3154 were present at *a* and *b* but disappeared at *c*.
6. A band at 3388 was found at *a* and *b* and disappeared at *c*.

One conclusion seems to be unavoidable from these facts, that between the first and second breaks hydrogen molecules were dissociated into atoms. It is significant to note also that the *2p-ms* lines 5461, 4358, 4047 were absent and the *2p-md* lines 3132, 3126, 2967, 3022, 2562 and the 1*S*-2*p* line 2537 were greatly reduced in intensity at *b*, the lowest current point between the two arcing potentials. It seems reasonable to suppose that excited mercury atoms in the 2*p* states lost their energy through impact with hydrogen molecules in dissociating them into atoms, as the reduced intensity of the line 2537 would imply that instead of radiating in returning from the 2*p* state to the normal orbit, the energy of the electrons was absorbed by "collisions of the second kind." Further, it is probable that very few of the mercury atoms were ionized or excited to a higher level than the 2*p* state owing to a large probability of losing their energy in this state. This very probably accounts for the reduced intensity of lines corresponding to transitions from the *s* or *d* states to the 2*p* states.

In this connection it may be suggested that the two reproducible points of discontinuity above the break of Fig. 4 are probably significant of the process of interchange of energy between the hydrogen and mercury vapor, which is proved by the spectra. No very satisfactory interpretation of them has, however, been made.

The relative intensification of the entire mercury spectrum above the upper break lends further support to our assumption that the mercury atoms were increasingly ionized at this point. From Fig. 3 it will be seen that the difference between the two arcing potentials happened to be exactly 10.4 volts, the ionization potential of mercury atoms. Five independent trials gave about the same value for this difference.

The bands observed at *a* and *b* are probably mercury hydride bands. They were not observed by Compton and Turner in the positive columns, and the bands observed by them were not detected by the writer; but the origin of the bands in this experiment arose from a region more similar to negative glow than to positive column.

A comparison of the particular lines of the secondary spectrum which were present in a mixture of mercury vapor and hydrogen at the first arcing potential (see Fig. 3) but disappeared at the higher arcing potential leads to the following results. The lines enclosed in brackets were observed after both breaks whereas those without brackets were visible between the two breaks but not above the higher one. 5014, 4930, (4782), 4724, 4684, (4633), (4581), 4555, 4525, 4492, 4449, (4413), (4304), 4254, (4205), (4178), (4158), (4133), 4099, (4064), 3991, 3944, (3890), (3873), (3861), 3804.

This classification has been compared with those based on Zeeman effect, pressure effect, Stark effect and admixture with helium. Unfortunately most of these classifications have not been extensive enough to give a very thorough comparison. In general it may be said that there is no striking agreement between any two of them, a result which emphasizes our ignorance regarding the real origin of the hydrogen secondary spectrum. Unfortunately, the writer did not extend this study to the lines between 5000 and 6400.

When this experiment was in progress, Duffendack published his findings in a similar experiment.[16] He found that practically the entire secondary hydrogen spectrum appeared in full intensity at 15 volts in pure hydrogen and at 14 volts in a mixture of mercury vapor and hydro-

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[16] Duffendack, Astrophys. Jour. **60**, 122 (1924).

gen, and concluded that the spectrum must be due to the neutral molecule, as the potential is distinctly below 16 volts. The writer, while agreeing with the findings of his experiment, is unable to concur in the necessity for his interpretation. Duffendack did not take into consideration initial velocity distribution which amounted in the present experiment to as much as one and one half volts for hot filament temperatures as shown in the "initial voltmeter reading." When this correction is made, the result in pure hydrogen can be adequately explained as being due to the ionization of the molecule. When mercury vapor was present, the increased thermionic current involves an increase in the number of high velocity electrons in the same proportion, and the ionization of the hydrogen molecules apparently can be accomplished at a lower weighted mean voltage. Duffendack's observations with respect to the lowering of the breaking potentials in the arcs of the mixtures are in perfect agreement with our results.

Arc Characteristics in Mixtures of Nitrogen and Hydrogen

Preliminary runs in nitrogen alone confirmed Duffendack's[17] conclusion that the arc broke at about 16 volts, which Smyth by his positive ray experiments[18] has conclusively shown to refer to the ionization potential of the nitrogen molecule. It was found that for maintaining a given thermionic current, the filament need not be as hot as in the case of hydrogen, and the voltage current curve was more nearly reversible. Taking the average of eight runs, the breaking potential of the nitrogen arc was found to be 16.18 ± .05 volts, which is in excellent agreement with Duffendack's value at 16.17 volts.

There is considerable disagreement among the values reported by various investigators for the ionizing potential of nitrogen,[19] ranging between 15.8 and 18 volts. If the breaking voltage for the arc and the ionizing potential of the gas are identical, both Duffendack's and the present results *seem* to place the potential at 16.2 volts, so that within the errors of experiment the ionization potentials for the hydrogen and for the nitrogen molecules seem to be indistinguishable from each other.

The above result is however quite misleading, for when the arcing characteristics were studied by means of the oscillograph, it was found that the lowest voltage at which the arc could be maintained *without oscillations* was 16.9. Below this voltage oscillations set in with an amplitude of about two volts extending in the direction of lower voltage.

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[17] Duffendack, Phys. Rev. **20,** 665 (1922).

[18] Smyth, Roy. Soc. Proc. **A104,** 121 (1923).

[19] Consult for instance Duffendack's table, Phys. Rev. **20,** 681 (1922).

This accounts for our low value in nitrogen, since the voltmeter reading corresponded to the weighted mean of the high and low peaks of the oscillations.

As in the case of the oscillations in the mixture of mercury vapor and hydrogen, the process of making and breaking the arc was nearly reversible. Fig. 6 is a schematic diagram representing the observations. The oscillations started in at about 17.5 volts or above until the current reached a suitable value and then the arc was maintained at 16.9 volts or above without oscillations. When the voltage was gradually diminished, the oscillations again appeared at 16.9 volts. From eight independent trials, the point *c* in the figure was located at 16.90 ± .07 volts. Further evidence in support of the 16.9 value for the ionization potential of the nitrogen molecule will be given when we take up oscillations in the mixture of the two gases.[20]

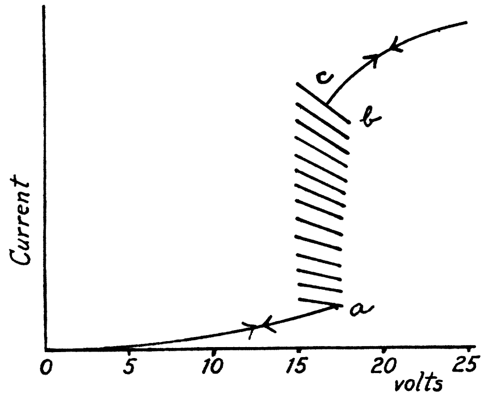

Fig. 6. Oscillations in pure nitrogen; *a* at 17.5, *b* at 18.0, *c* at 16.9 volts.

When nitrogen was mixed with hydrogen, the breaking potential of the arc was consistently lowered with the increase of nitrogen until the ratio to hydrogen was unity. Further increase in nitrogen raised the breaking potential again until finally it reached the breaking potential in nitrogen alone as the limit. These points are illustrated in Fig. 7. As in the case of mercury vapor and hydrogen, we again assume that the voltmeter recorded only the mean of oscillations. If this view is correct, we would expect that the points of lowest breaking potential would correspond to

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[20] *Note on ionizing potentials.* It should be noted that the values here reported do not include a correction for contact difference of potential between electrodes. Probably the most accurate determinations are those by Mackay (Phil. Mag. **46**, 828, 1923) who referred them to the ionizing potential of mercury as a known standard value. His values for H_2 and N_2 are 15.8 and 16.3 respectively. The present values of 16.2 and 16.9 compare well relatively and suggest a correction of about 0.5 volts.

oscillations of greatest amplitude (in the direction of lower voltage), which the oscillograph showed to be the case.

The oscillograph characteristics, Fig. 8, for the mixtures of the two gases, further strengthened the evidence for fixing the ionization potential

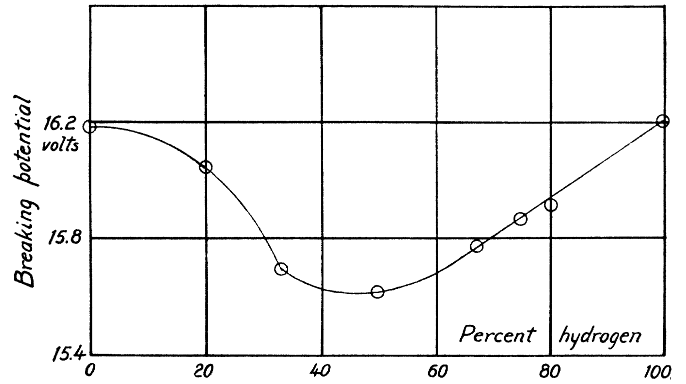

Fig. 7. Breaking potentials in mixtures of H_2 and N_2 in varying proportions.

of nitrogen at about a volt higher than that for the hydrogen molecule. The oscillations of two or three volts amplitude began with the voltmeter reading about 17.0 volts and usually stopped a little below 16.0 volts.

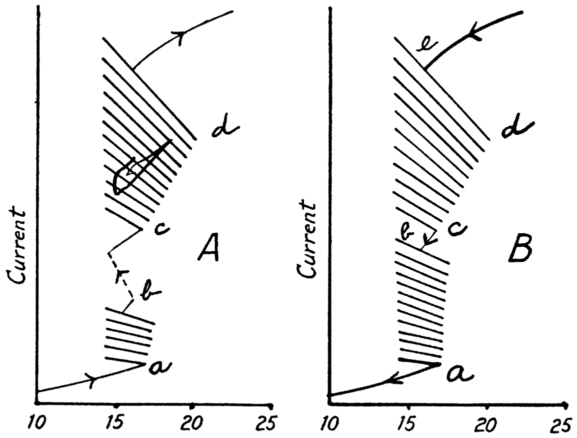

Fig. 8. Oscillations in mixtures of H_2 and N_2.
8A: *a* at 17.0, *b* at 16.0, *c* at 16.9, *d* at 20.2, or 22.8 volts.
8B: *e* at 16.2 volts; other values same as in 8A.

(The decrease in voltage was due to the increase in the arc current of course.) On reaching 16.0 volts, the current increased with a sudden jump and the voltage correspondingly lowered. When the potential was further increased to 16.9 volts, the oscillations started again with a larger amplitude with its maximum at about 20 or 22.5 volts. Higher filament temperature and excess of hydrogen seemed to favor the higher voltage. When the path was reversed the oscillations came in at 16.2 volts, stopped at 16.9 volts, began again at 16.0 volts, and finally stopped altogether at 17.0 volts, the very point where the oscillations set in in the direction of increasing voltage. This characteristic of reversibility has also been found in mercury[21] and in helium[22] for both of which oscillations have been observed in the low voltage arc.

It seems plausible to account for these phenomena as follows. It is known that the "efficiency" of ionization is much greater in nitrogen than in hydrogen. Thus, at the striking point *a* it is the nitrogen ions which are chiefly responsible for the neutralization of space charge, in spite of the higher ionizing potential of nitrogen. At the breaking point *e*, on the other hand, the electron emission is so great that the necessary amount of ionization can be obtained from the hydrogen. Thus the striking voltage *a* is characteristic of nitrogen and the breaking voltage *e* of hydrogen. It should be noted that the oscillations always set in with increasing current at 16.9 volts (nitrogen) rather than the 16.2 volts (hydrogen) in agreement with the fact that they could be found in pure nitrogen but not in pure hydrogen.

At pressures higher than 1 mm, when there was an excess of hydrogen and when the filament temperature was moderate, there were usually two striking and two breaking potentials, as is shown in Fig. 9. These breaks were accompanied by oscillations and the value of the second striking potential was also determined by means of an oscillograph by observing the maximum peaks in the higher voltage oscillations. The calibration did not give readings more accurately than within half of a volt. The average for 21 trials was 22.7 volts. This agrees unexpectedly well with the result from direct voltmeter reading.

It is not easy to decide just what this potential stands for. Horton and Davis[23] located a critical potential for hydrogen at 22.8 volts, and they attributed it to the ionization of the hydrogen molecule. Brandt[24] and Bazzoni and Waldie[25] observed a critical potential near this value (25.4 volts) in nitrogen. Finally, Smyth observed a critical potential in nitrogen at 24.1 ± 1.0 volts at which doubly charged atomic ions appeared. We shall see that the spectroscopic data suggest that this is

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[21] Y. T. Yao, Phys. Rev. **21**, 1 (1923).

[22] Compton, Lilly and Olmstead, Phys. Rev. **16**, 282 (1920).

[23] Horton and Davis, Phil. Mag. **26**, 872 (1923).

[24] Brandt, Zeits. f. Phys. **8**, 32 (1921).

[25] Bazzoni and Waldie, Jour. Frank. Inst. **197**, 57 (1924)

actually a critical potential of nitrogen. Probably the reason for not detecting it in pure nitrogen is that the currents in the latter case were so large that additional effects associated with the second critical potential were masked.

SPECTROSCOPIC OBSERVATIONS IN NITROGEN AND HYDROGEN

There are three bands usually associated with the spectrum of ammonia; the ultraviolet band between 3295 and 3432A, the Schuster bands at 5635 and 5682A and the alpha band which extends throughout the greater part of the visible spectrum.

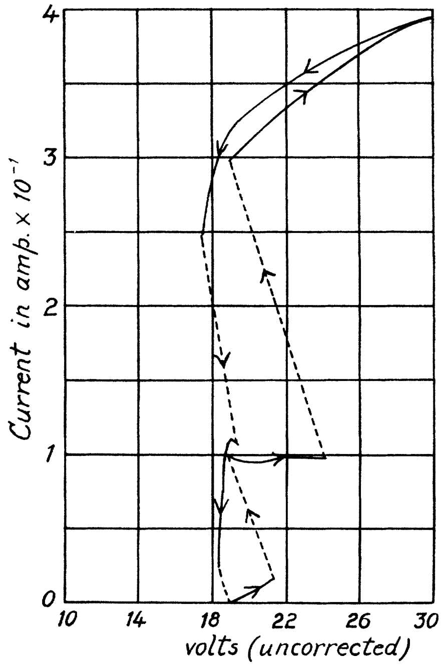

Fig. 9. The two striking potentials in mixtures of H_2 and N_2.

Over ten years ago E. P. Lewis[26] found in vacuum tube experiments that the above mentioned ultraviolet band was present in a mixture of hydrogen and nitrogen with all proportions of the two gases, whereas in each gas alone this band was not found. At the time he attributed it to ammonia. More recently Fowler and Gregory[27] took very precise measurements of the wave-lengths of this band and arranged them into seven series according to their frequency differences. They found by comparison that the ultraviolet band is represented in the solar spectrum.

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[26] E. P. Lewis, Astrophys. Jour. **40,** 154 (1914).

[27] Fowler and Gregory, Phil. Trans. **A218,** 351 (1919).

Bair[28] studied the ammonia spectrum by means of transformer discharges and found that the ultraviolet band appeared when the gas was flowing but not when it was at rest. He reported also that the insertion of a small capacity increased the intensity of the band when the gas was at rest and that "mixtures of flowing ammonia and oxygen gave the ultraviolet band with uncondensed discharge." Still more recently W. B. Rimmer[29] measured the more prominent lines of the alpha band and studied the appearance of the various bands under a variety of experimental conditions. He found (1) "no record of the existence of the Schuster bands in the ammonia flame"; (2) "the Schuster bands have given no sign of resolution under high dispersion," and (3) "the effect of a condensed discharge seemed to be to increase the intensity of the ultraviolet band with respect to the Schuster bands."

Rimmer summarized the conclusions reached by the various investigators and his own as follows: "Lewis suggested (corroborated by Barratt and Bair) that the Schuster bands probably represent the true spectrum of ammonia and that the ultraviolet band is probably due to another emission center arising from a more stable combination of N and H other than the normal molecule of ammonia. In addition the present investigation (Rimmer's own work) suggests that the alpha band is due to an emission center which represents a first stage of dissociation of the normal ammonia molecule into more stable forms and the ultraviolet band to an emission center which represents a still more advanced stage of dissociation into constituent atoms."

The writer in studying the spectra in the low voltage arc obtained results similar to those observed by Lewis, namely, that the ultraviolet band was present in the mixtures of the two gases in all proportions but not in each gas alone. The least amount of nitrogen in the presence of hydrogen would cause the appearance of this band. In fact the writer had considerable difficulty in getting rid of this band after the mixture was tried in the tube. When ammonia either wet and dried was used instead of the mixtures, the same band was observable after the arc was struck at about 20 volts.

This ultraviolet band was observable as soon as the arc was struck at about 17 volts, provided there was only one arcing potential observable, and its intensity increased rapidly. It was distinctly observable at between 20 and 25 volts. In such cases, the oscillographs showed that the maximum peaks of oscillations were at about 22 or 23 volts. Under conditions where there were two striking and two breaking potentials,

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[28] Bair, Astrophys. Jour. **52,** 301 (1920).

[29] Rimmer, Roy. Soc. Proc. **A103,** 696 (1923).

the ultraviolet band appeared only with the second striking potential, estimated at 22.8 volts, whereas before the second jump, the band was entirely invisible. If the voltage was diminished after passing the second striking potential, faint traces of the band could be seen as low as the first breaking potential at about 15.5 volts. We shall assume that the 22.8 volt potential is responsible for the excitation of the ultraviolet band.

In accordance with the quantum theory of band spectra, the writer has employed Fowler and Gregory's measurements in calculating the moment of inertia of the corresponding molecule based upon the relationship $\Delta\nu = h/4\pi^2 I$, where h is the Planck constant, $\Delta\nu$ the frequency difference, and I the moment of inertia of the molecule. Taking the wave-number difference to be 28.5, I comes out to be $1.95(10)^{-40}$ gm cm^2. This is well within the range of values attributed to the ammonia molecule from measurements of the infrared absorption spectrum of ammonia. Schierkolk[30] found two values: (1) From the band at 10.5μ, I was found to be $1.48(10)^{-40}$ gm cm^2; and (2) from the band at 6.1μ, $I = 2.72(10)^{-40}$ gm cm^2. The difference in these two values Schierkolk attributed to the different orientation of the ammonia molecule. The writer also calculated the moment of inertia from B. J. Spence's[31] measurements of the absorption spectrum at 3μ. Taking the average $\Delta\nu = C \times 19.5$, I would be $2.83(10)^{-40}$ gm cm^2, which is in agreement with Schierkolk's higher value within errors of experiment.

Taking the moment of inertia as $2.8(10)^{-40}$ gm cm^2, if we assume a model for NH in which a nitrogen nucleus and a hydrogen nucleus rotate around their center of mass, the distance between the nuclei is $1.17(10)^{-8}$ cm. If a model for NH_2 were assumed in which the heavy nitrogen nucleus is located at the center of mass and a hydrogen nucleus symmetrically placed on each side, the distance between the hydrogen nuclei would be $1.54(10)^{-8}$ cm. Finally, if we assumed a model for NH_3 to be such that the nitrogen nucleus is situated at the center of a circle in which an equilateral triangle is inscribed at whose vertices the hydrogen nuclei are located, the diameter of such a circle is $1.25(10)^{-8}$ cm. All three values agree reasonably with kinetic theory predictions and therefore, with our present knowledge about molecular arrangements, we cannot decide which of the three types of molecules is responsible for the band. The one conclusion which we *can* draw is that the *molecule cannot contain more than one atom of nitrogen.* If two atoms of nitrogen were present in such a molecule, the molecular diameter would have to be of the order of $(10)^{-9}$ cm. We therefore conclude that at 22.8 volts some atomic

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[30] Schierkolk, Zeits. f. Phys. **29**, 277 (1924).

[31] Spence, Jour. Opt. Soc. Amer. & R.S.I. **2**, 127 (1925).

nitrogen ions must be present and this is well supported by Smyth's positive ray experiments in which doubly charged atomic ions were found at this potential.

Now to come back to the origin of the 22.8 volt break. In the light of the above discussion we must attribute it to nitrogen and as we shall see later to a production of atomic ions of nitrogen, in all probability. For ionized molecules and atoms (formed by secondary collisions and dissociation due to the filament) of hydrogen were in abundance at the first arcing potential whereas atomic nitrogen ions have never been observed below 22.8 volts. In further support of this view, the negative band of nitrogen at 3914 was observed to come out simultaneously with the ultraviolet band of ammonia and with the appearance of a line. Possibly this is due to a process related to the dissociation of the nitrogen molecule into atomic ions. L. and E. Bloch[32] also observed the appearance of this band at about 22.5 volts.

The so-called Schuster bands, between 5635 and 5822 were entirely absent from the spectrum in the mixtures of the two gases as long as the last trace of water vapor was condensed in the liquid air traps; but when the liquid air flasks were taken away, in three out of four instances, with a different filament each time, the Schuster bands were unmistakably present when the light from a point very near the target was examined. The failure to observe the bands during one of the trials is attributed to the insufficient amount of water vapor present and to the comparatively short distance between the electrodes which made the combination of atoms into more complicated molecules difficult. The writer feels certain that the bands were not due to any material coming out of the target, for in every trial with dry gases, the Schuster and alpha bands were absent when the light from the same part of the arc was focussed on the spectrometer slit.

Thus far our experiment does not tell us whether water vapor or mercury vapor was responsible for the bands. To test this point a few drops of mercury were put in the attached tube and the traps were again immersed in liquid air. We are now sure that mercury vapor alone was present. The Schuster bands were still missing in the spectrum.

Ammonia prepared by evaporation from concentrated solution and stored over potassium hydroxide sticks was next admitted into the system. Well dried gas showed no trace of the Schuster bands. When either water vapor or oxygen in small amount was mixed with it, the Schuster bands invariably came out. The filament at this stage, as would be expected, burnt out very rapidly.

[32] L. and E. Bloch, Comptes Rendus, **175**, 225 (1921).

A further point of interest is the fact that the Schuster bands appeared only when the potential was raised to 70 volts or over, which in Duffendack's experiments was the critical potential for the formation of "active nitrogen."

In the light of these facts, the writer is not able to concur with Rimmer and Bair as to the origin of these bands, namely that the Schuster bands originate from the normal ammonia molecules and the ultraviolet band belongs to a more stable combination of N and H, possibly other than ammonia. The test in dry ammonia with and without a small oxygen content seems conclusive with respect to this point.

Moreover, if these bands were due to ammonia, the high voltage at which these bands appeared would not harmonize with the experiments of Andersen and of Storch and Olson, who found that ammonia was produced at the striking of the arc. The potential difference cannot be accounted for by any theory of secondary collisions.

A study of the conditions under which the Schuster bands have been previously observed unmistakably supports the writer's point of view. Schuster,[33] the discoverer of these bands, observed them for the first time when he introduced "a few drops of a strong solution in water" into the vacuum tube and the discharge was passed while the tube was being evacuated. Lewis and Bair maintained the visible bands only when a continuous stream was allowed to pass through the tube. Under such conditions traces of water vapor were likely to be present. Rimmer's best results were obtained when he evaporated ammonia from a strong solution, employing a water pump for evacuation. In general these experiments did not show that water vapor was not present.

The writer therefore ventures to suggest that the Schuster bands are due to a heavy molecule containing atoms of hydrogen, nitrogen and oxygen, possibly NH_4OH, which is extremely unstable and can be formed only when there are nitrogen atoms in a highly excited state such as are obtainable at 70 volts in the low voltage arc. This type of molecule will explain some of Rimmers observations and account for the unresolved character of the band as due to its large moment of inertia. Then too, we would not expect these bands to be present under conditions of low excitation such as in the oxygen flame.

The above analysis suggest as a consequence that the ultraviolet band originates from the anhydrous ammonia molecule itself. Since there were no other bands observable in dry mixtures of nitrogen and hydrogen up to 120 volts in addition to the hydrogen and nitrogen

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[33] Schuster, Report British Association (1872).

spectra, although ammonia is formed, it is reasonable to attribute it to ammonia rather than to NH or NH_2 which up to the present have not been observed as temporary products of such arcs.

Perhaps a question may be raised in reference to Storch and Olson's experiments in which they found that ammonia was formed as soon as the arc was struck whereas in our experiment the ultraviolet band is associated with 22.8 volts. There are two possible answers to such an objection. In the first place it is possible that N_2H_6 molecules may be formed which finally dissociate into NH_3 molecules. Such a process would, of course, be much less probable than the direct formation of ammonia at 22.8 volts and may account for the marked increase in the rate of reaction at 23 volts in all of the curves that were published by Storch and Olson. The coincidence of the first and most distinct jump after the arcing potential in the curves of these authors with our 22.8 volt potential is probably not accidental. In the second place, the discrepancy may be due to a difference in the sensitivity of the two methods of detection.

In conclusion, the writer takes this opportunity to express his sincere thanks and grateful appreciation to Professor K. T. Compton for suggesting this problem and for his constant guidance and inspiration throughout this investigation. He acknowledges also with pleasure his indebtedness to Mr. C. C. Van Voorhis and Dr. L. A. Turner for their help in several matters of technique.

Palmer Physical Laboratory,
Princeton, New Jersey,
June 6, 1925.