Sparking Potentials at Low Pressures

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At low pressures where only a few electrons produce ions, the number of electrons set free at the cathode by the impact of the positive ions formed in the gas is of primary importance in determining the minimum sparking potentials. Using the data for the efficiency of ionization by electrons of various velocities, and recent observations of sparking potentials in air, we may deduce the number of electrons set free by the impact of a positive ion on a nickel cathode for any velocity. This number increases with the velocity of the ion from approximately 4 at 3000 volts to 85 at 30,000 volts. These numbers are much greater than those given by direct observations. The explanation is suggested that the spark originates at small spots where the emission is especially abundant, whereas the direct observations of secondary electron emission give an average value for the surface.

IT is well known that at low pressures the potential required to produce a discharge between electrodes that are closer together than the cathode dark space may amount to many thousand volts. The theories of the sparking potential that are based on the occurrence of repeated ionization by collisions of the electrons, or of the positive ions, with the gas molecules, are not applicable to this case of low pressure and high voltage. For example, in air at a pressure of 0.06 mm a potential difference of 20,000 volts is required to produce a discharge between nickel electrodes 1 cm apart. Now from experiments on the number of ions made by an electron in going 1 cm we find that only one-tenth of the electrons leaving the cathode would produce even one positive particle. These positives at low speeds are much less efficient ionizers than the electrons, and at high velocities possibly do not produce any free electrons at all, but merely neutralize themselves by detaching an electron from a neutral molecule. Photoelectrons would also become relatively unimportant as the pressure is reduced and in general the probability of excitation by fast electrons is small compared with the probability of ionization.[1] Photoelectric emission due to radiation excited by the impact of the electrons on the anode must be small as it is negligible in high voltage kenotrons and x-ray tubes.

We are thus led to consider the possibility of interpreting the electrical break down at low pressures and high potentials as due primarily to the release of electrons from the cathode under the impact of the positive ions. This phenomenon has been used, along with repeated ionization by collision, in some theories to account for the sparking potentials at higher pressures instead of relying entirely on ionization phenomena in the gas itself, as originally suggested by Townsend.[2] In this paper the numerical results obtained in recent years on the efficiency of ionization by electrons of various velocities, will be made use of in calculating the number of positives produced in the gas. If the efficiency of the production of secondary electrons at the cathode by positive ion bombardment were known for all ion and metal combinations, we could then deduce the sparking potentials. Our knowledge of this subject is still, however, very incomplete, especially at high velocities.[3] More precise experimental observations can be made of the sparking potentials with various gases and metal electrodes, and the connection between the two phenomena discussed below allows us to deduce the number of electrons emitted under the bombardment of positive ions of any velocity from the minimum sparking potential.

Minimum Sparking Potential and Probability of Ionization

The number of secondary electrons s produced by an electron in going 1 cm through a gas at a pressure of 1 mm of mercury has been determined by several observers. Buchmann[4] gives a sum-

[1] K. K. Darrow, *Electrical Phenomena in Gases*, p. 98.

[2] G. Holst and E. Oosterhuis, Phil. Mag. **46**, 1117 (1923). For a discussion of these theories and observations see: K. K. Darrow, *Electrical Phenomena in Gases*, p. 280.

[3] For references and some experiments with alkali ions see W. S. Stein, Phys. Rev. **40**, 425 (1932).

[4] E. Buchmann, Ann. d. Physik **87**, 524 (1928).

mary in which $s(V)$ is recorded for air for various electron voltages V up to 29,000 volts. If the potential applied between two electrodes 1 cm apart is V_0, and the potential gradient is uniform, an electron leaving the cathode will produce in 1 cm at 1 mm pressure, a number of positive ions given by $(1/V_0)\int_0^{V_0} s(V)dV$. If the distance is d cm this number is multiplied by d. The positive ions will reach the cathode with various energies depending on the position at which they were formed, and on impact will set free various numbers of electrons. Suppose a positive ion of energy V releases $m(V)$ electrons on striking the cathode. Since the number of positives with energy between V and $V+\Delta V$ is $(1/V_0)s(V)\Delta V$, and these release $(1/V_0)s(V)m(V)\Delta V$ electrons from the cathode, we have for the total number of new electrons, released by all the positives, the expression $(1/V_0)\int_0^{V_0} s(V)m(V)dV$. If this is greater than unity a spark will occur, as the number of electrons is multiplied indefinitely. If the pressure is p mm of Hg and the distance is d cm the minimum potential V for a spark is given by $(pd/V)\int_0^V s(V)m(V)dV=1$. This relation connects the minimum sparking potential V with the efficiency of production of electrons $m(V)$ by positive ion impact, when $s(V)$ is sufficiently well known.

We shall use some as yet unpublished observations by S. S. Cerwin on the minimum sparking potentials in air at low pressures with carefully outgassed nickel electrodes, to illustrate how the function $m(V)$ may be deduced. Cerwin's observations for low pressures (p, mm) and short distances (d, cm) such that $p.d.<0.095$ may be shown to agree with the formula, $pde^{V/43,500}=0.10$. If we equate this expression involving V to the above integral expression for the same value of $p.d.$, and differentiate we find,

$$10e^{V/43,500}\left(1+\frac{V}{43,500}\right)=s(V)m(V).$$

Using Buchmann's values for $s(V)$ we deduce the values of $m(V)$ given in Table I. It is of interest that for voltages above 10,000, the number $m(V)$ increases approximately linearly with the voltage. It is quite unnecessary for the observations of V to be expressed in a formula. The experiments give V directly in terms of $p.d.$, and we may plot $1/pd$ as a function of V, say $f(V)$. From this a second curve $Vf(V)$ may be drawn which gives the value of the integral in the above expression for sparking potentials, so that the slope of this curve at any V is the value of $s(V)m(V)$.

TABLE I. *$s(V)$ ionizing collisions in 1 cm at 1 mm pressure; $m(V)$ secondary electrons set free by a positive ion of energy V.*

V (volts)	$s(V)$	$m(V)$
3000	2.70	4.0
5800	2.03	6.35
10600	1.27	12.7
14200	0.90	21.2
18000	0.625	34.7
26000	0.425	71.2
30000	0.40	84.5

When we compare the values of $m(V)$ deduced in this manner, with the direct observations of secondary electron emission we are struck by the fact that Fuchtbauer,[5] Campbell,[6] Baerwald,[7] Stein,[3] and Schneider[8] all found much smaller values. Schneider, for example, found between 4 and 4.6 electrons set free by a hydrogen ion impinging on various metals with energies between 23 and 46 kilovolts.

The most reasonable explanation for the larger numbers in Table I, is that the electron emission in sparking potential observations occurs under very special conditions. A strong field acts at the surface and would be expected to reduce the work function as in thermionic emission. Furthermore a spark will begin at the most favorable spot on the cathode if a sensitive point should exist. On the other hand, the direct observations of secondary electron emission under positive ion bombardment have hitherto been made with very weak fields at the surface of the metal, and the observations give only the average electron emission over the surface.

It is known that in thermionic emission of electrons, sensitive spots on the cathode exist, from which the emission is very much stronger than from other areas at the same tempera-

[5] C. Fuchtbauer, Phys. Zeits. **7**, 153 (1906).
[6] N. Campbell, Phil. Mag. **29**, 783 (1915).
[7] H. Baerwald, Handb. d. Physik, **24**, p. 106.
[8] G. Schneider, Ann. d. Physik **11**, 382 (1931).

ture,[9,10] and it is quite reasonable to suppose that the electron emission under positive ion bombardment is also much greater from some spots on the cathode than from others. There is thus no disagreement with the above theory of the sparking potential, and the values in Table I can be taken as applying to the emission from these sensitive areas.

[9] H. Seemann, Zeits. f. Physik **79**, 742–752 (1932).
[10] A. J. Dempster, Phys. Rev. **46**, 165 (1934).

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Vibrations of Tetrahedral Pentatomic Molecules
Part III. Comparison with Experimental Data. Part IV. Isotopic Shifts

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Part III. Various specific assumptions as to intramolecular forces are discussed from the point of view of the general theory and are compared with experimental data. CH_4 is found to be the only molecule even approximately to obey valence forces. For some other molecules satisfactory results are obtained by postulating an additional repulsive force inversely proportional to some power of the distance between the corner atoms.

Part IV. Certain relations between the frequencies of the isotopic molecules are found to be independent of the values of the force constants. For YX_4* definite upper and lower limits may be predicted for the values of the active frequencies.

Part III

The expressions for the normal frequencies of the molecule YX_4 derived in Part II of this paper,[1] may be applied to experimental data with a view of determining the actual values of the constants in the potential energy function V. It has been shown that in the most general case V involves five arbitrary constants, while only four frequencies are observed in the absence of isotopic shifts. From these four frequencies we may evaluate four of the constants as functions of the fifth one, considered as a variable parameter. The notation will in general be the same as used previously, but, in conformity with general usage, the normal vibrations will be designated by ω_1, ω_2, ω_3 and ω_4; $(\omega_3>\omega_4)$. The notational connection between these and the $\omega_{(\rho),\ (\sigma)}$, $\omega_{(\tau)}$, etc., introduced in Part II is as follows:

$$\omega_1\rightarrow\omega_{(\tau)};\qquad \omega_2\rightarrow\omega_{(\rho),\ (\sigma)};\qquad \omega_3,\ \omega_4\rightarrow\omega_{(\xi\alpha),\ (\eta\beta),\ (\zeta\gamma)}.$$

Of the five constants A, B, C, D and E used in the potential energy expression, two are directly given by the frequencies:

$$C/4\pi^2=m\omega_2^2/4;\qquad E/4\pi^2=m\omega_1^2/16. \tag{32}$$

Choosing D as the variable parameter, we obtain from Eqs. (31) the following expressions for A and B:

$$\begin{aligned} A/4\pi^2&=2m\mu\{\omega_3^2+\omega_4^2\pm[(\omega_3^2-\omega_4^2)^2-(8/\mu m^2)(D/4\pi^2)^2]^{\frac{1}{2}}\};\\ B/4\pi^2&=\tfrac{1}{16}m\{\omega_3^2+\omega_4^2\mp[(\omega_3^2-\omega_4^2)^2-(8/\mu m^2)(D/4\pi^2)^2]^{\frac{1}{2}}\}, \end{aligned} \tag{33}$$

where

$$\mu=M/(4m+M).$$

The sign of the square root is undetermined but, however, is different, for A and B. Since all constants are essentially real, it follows from Eqs. (33) that A, B and D have to lie within certain definite

[1] Jenny Rosenthal, Phys. Rev. **45**, 538 (1934).