Chemical Physics of Discharges

Wade L. Fite
University of Pittsburgh

Introduction

The gas discharge as a chemical tool is of interest for the environment which it provides, an environment which in many respects is very close to and in others very far away from thermal and chemical equilibrium. Since achieving this situation in the gas discharge is a result of the physical processes occurring to sustain the electrical characteristics of the discharge it is appropriate to consider some of the basic physical aspects of gas discharges before examining the chemical consequences.

In attempting to understand the physics of discharges one would like first to understand the microscopic processes in discharges and then construct a reasonably complete and accurate synthesis to describe the macroscopic characteristics. This approach of course implies that one has a detailed understanding of the processes involves and know the rates and cross sections for the processes. While one can use this approach succesfully up to a point, the extreme complexity of discharge phenomena forces one also to formulate a macroscopic description and work toward a juncture with the microscopic point of view.

In this brief review, the microscopic point of view will be used primarily. Also, in view of the fact that other participants at this symposium will discuss extensively the heavy particle aspects of discharges, i.e., the chemistry, it would appear appropriate to emphasize in this paper the role of the electron in discharges. In the final analysis, the electron is the essential ingredient, the sine qua non of a gas discharge, the agent which transfers energy from an electrical power supply to the gas.

Following some microscopic considerations, some of the macroscopic description of discharges is reviewed briefly and finally the afterglow of a gas discharge is discussed.

II Electron Motion and Behavior

Be it supposed that a gas is enclosed in a container and that a free electron has been produced--perhaps by a cosmic ray, or by the radiation from the experimenter's watch dial, or from that little piece of uranium glass in a graded seal, or by cold cathode emission by the very strong electric fields around a sharp point on an electrode in the discharge tube.

If a dc electric field is imposed, the electron will respond according to Newton's law,

$$\dot{v} = \frac{q}{m} E \tag{1}$$

and begin to accelerate in free fall. This acceleration will continue until it has a collision with a gas molecule. If the energy of the electron at the time of collision is very low, only elastic scattering will be admitted. At higher energies large amounts of energy can be lost by the electron in exciting the molecule to high-lying states of internal energy and at higher energies yet, ionization can occur. The latter process is, of course, essential to achieve the electron multiplication and convert the gas with a single electron in it into a gaseous medium of high electrical conductivity.

Since each type of collision has separate consequences for the discharge we consider them in turn. The collisions are of course statistical and we must incorporate statistics with particle mechanics in their treatment.

A. Elastic Collisions: Transfer of Energy

In elastic collisions of electrons with heavy gas molecules, two effects are of importance. First there is a redistribution of directions of travel of the electrons and second there is a very slight loss of energy (and therefore speed) as a very small amount of momentum and energy are transferred to the molecule by the electron.

At low energies, i.e., a few ev and less, electron scattering tends to be isotropic in angle in the center of mass coordinates. This implies that if we examine many electrons immediately after they have had a collision the average vector velocity will be zero, but of course the average scalar speed will not be zero. The probability per unit time that an electron will have a collision (i.e. the collision frequency) is given by

$$Z(c) = n\, Q(c)\, c \tag{2}$$

where n is the number density of molecules, c is the electron's speed and Q(c) is the total cross section for elastic collisions. The cross section generally diminishes with increasing speed, although resonances in scattering impart considerable structure in the functional form of the cross section in the case of most gases.

We suppose that an electric field, E, is imposed in the z direction, and inquire about the component of velocity in the z direction, averaged over all electrons, $\langle v_z \rangle$, which is identical to $\langle \vec{v} \rangle$. Since each electron responds to the field in the same way, the average acceleration due to the field is that of each electron separately. Further, because the average velocity is zero following a collision, the loss of average velocity due to collisions is to good approximation just the product of the average collision frequency $\langle Z \rangle$ and the average velocity. Thus we can write that for the average velocity in the z direction

$$\frac{d\langle v_z \rangle}{dt} = \frac{q}{m} E - \langle Z \rangle \langle v_z \rangle. \tag{3}$$

When the steady state is achieved the left side vanishes, which implies that the pickup of directed velocity from the field is just balanced by the loss of directed velocity due to the randomization of direction of motion by the collisions. Under steady state collisions, then,

$$\langle v_z \rangle = \frac{q}{m} \cdot \frac{1}{\langle Z \rangle} E = \mu E \tag{4}$$

where μ is designated the mobility.

Equation (4) can be re-written in terms of Eq. (2) as

$$\langle v_z \rangle = \frac{q}{m} \cdot \frac{1}{\langle c Q(c) \rangle} \cdot \frac{E}{n}. \tag{5}$$

In this expression the second term gives all the information about the interaction between the electron and the particular gas molecule and the third term contains the parameters available to the experimenter, i.e., the electron field and the gas number density. Since the number density is proportional to the gas pressure, the experimental quantity of major relevance is the ratio E/p.

Randomization of directions of velocity says nothing whatever about average speeds of the particles. For this we turn to other considerations. Conservation of momentum requires that the energy loss from an electron of mass m and kinetic energy W in collision with a heavy particle of Mass M is given by

$$\Delta W = W \frac{2m}{M} (1 - \cos\Theta) \tag{6}$$

where θ is the angle of deflection of the electron in the collision. If the scattering is isotropic (as it closely approximates at low energies) then the energy loss in a collision averaged over angle is

$$\overline{\Delta W} = \frac{2m}{M} W = hW \tag{7}$$

where for convenience we let $2m/M = h$.

We would expect a steady state ultimately to be achieved between the electron energy picked up from the electric field between collisions and the energy transmitted from the electron to the heavy particles through the collisions. We proceed to evaluate these separately. For simplicity we assume that the collision frequency is independent of speed of the electrons.

Since the electric field acts only in the z direction, all the increase in kinetic energy of an electron will occur through increasing the z component of its velocity which is given by

$$v_z = v_{oz} + at \tag{8}$$

where v_{0z} is the value of v_z immediately following the collision and t is the time elapsed since the last collision and $a = (q/m)E$. The energy picked up will be

$$\Delta W = qE \int dz = ma \int v_z dt = ma\left\{ v_{oz}t + \tfrac{1}{2}at^2 \right\}. \tag{9}$$

If we now average over all angles of direction of motion immediately following the last collision, $\overline{v_{oz}} = 0$ so that

$$\overline{\Delta W} = \tfrac{1}{2} m a^2 t^2. \tag{10}$$

If we now average over all collision times, Eq. (10) becomes

$$\overline{\Delta W}_{av} = \tfrac{1}{2} m a^2 (t^2)_{av}. \tag{11}$$

To find $(t^2)_{av}$, we assume that collisions are random events and the collision frequency is independent of speed. We can then write that the probability of a collision occurring in the interval t to t + dt following the precdding collision is

$$p(t)dt = Z e^{-Zt} dt \tag{12}$$

for which the average value of t^2 is $2\tau^2$ where $\tau = 1/Z$ is the mean collision time. Eq. (11) then becomes

$$\overline{\Delta W}_{av} = m a^2 \tau^2 \tag{13}$$

If we also average over all speeds of electrons and neglect some of the finer points of statistics, Eq. (13) becomes

$$\langle \overline{\Delta W}_{av} \rangle \simeq m a^2 \frac{\lambda^2}{\bar{c}^2} \tag{14}$$

where λ is the mean free path and $\bar{c}$ is the mean speed of the electrons.

This quantity, in the steady state, will equal the right hand side of Eq. (7) averaged over all electrons. If we let $W \simeq \frac{1}{2} m \bar{c}^2$

$$\frac{1}{2} h m \bar{c}^2 \simeq m a^2 \frac{\lambda^2}{\bar{c}^2} \tag{15}$$

Thus we would expect that the mean speed would be given by

$$\bar{c}^4 \simeq 2 \frac{a^2 \lambda^2}{h^2} \tag{16}$$

and the mean energy of the electrons in the steady state by

$$\frac{1}{2} m \overline{c^2} \simeq \frac{1}{2} m \bar{c}^2 \simeq \frac{1}{2} \sqrt{\frac{M}{m}}\, g E \lambda . \tag{17}$$

The remarkable aspect of this result comes on the insertion of numbers in Eq. (17). If for example, one has electrons moving through a gas with $M \sim 30$ AMU, at pressures giving $\lambda \sim 1$mm (i.e. $p \lesssim 1$ torr) then the mean energy in ev is around 25 times the field strength in volts/cm. With as little as a few tenths of v/cm fields, mean electron energies are several ev. We can thus understand the appearance of high electron "tempreatures" in gas discharges.

It is beyond the scope of this review to go further and question the distribution of electrcn energies. It is sufficient to indicate that if one takes assumptions similar to those made in this simplified argument and utilizes them in the Boltzmann equation, one can obtain an approximate solution for the distribution of speeds. The result is not the Maxwell-Boltzmann distribution, but rather that known as the Druyvesteyn distribution whose dependence on speed is given by

$$f(c)\,dc \propto c^2 e^{-\frac{3hc^4}{8\lambda^2 a^2}}. \tag{18}$$

This distribution function is similar in shape to the Maxwell-Boltzmann distribution for a given mean speed, except that the most probable speed is slightly higher and the high energy tail is diminished in the Druyvesteyn distribution. Nonetheless, the distributions are sufficiently similar that one can, to good approximation, think of the electrons as having a temperature in the Maxwellian sense which is much higher than the neutral gas temperature; i.e. typically 30,000°K vs 300°K. It is this dichotomy of temperatures which is perhaps the most striking of the non-equilibrium aspects of a gas discharge.

This general effect of collisions randomizing the direction of motion of electrons which have picked up energy from the field between collisions has another important manifestation. It is responsible for the operation of microwave electrodeless discharges. If we consider an electron moving in an ac field which is of the form $E(t) = E_o \cos \omega t$, then Newton's law for the electron becomes, in the absence of collisions,

$$\dot{v} = \frac{q}{m} E_o \cos \omega t \tag{19}$$

which solves to give

$$\left\{ \begin{aligned} v &= \frac{qE_o}{m\omega} \sin \omega t \\ x &= -\frac{qE_o}{m\omega^2} \cos \omega t \end{aligned} \right\}. \tag{20}$$

The rate of energy pickup from the field i.e. the power, P is given by

$$P = qEv = \frac{q^2 E_o^2}{m\omega} \cos\omega t \sin\omega t = \frac{1}{2}\frac{q^2E_o^2}{m\omega} \sin 2\omega t, \tag{21}$$

which, it is noted can be negative as well as positive. If we consider the total power pickup over a complete cycle, the sine-cosine product integrates to zero, indicating that there is no net transferral of energy from the electric field to the electron. This is of course a result of the fact that the applied field and the electron velocity are 90° out of phase.

Furthermore, we can note from (20) that the maximum electron velocity will be $qE_0/m\omega$ and the maximum kinetic energy will be

$$W_{max} = \frac{1}{2}\frac{q^2 E_0^2}{m\omega^2}. \tag{22}$$

It is noted that if one has a field oscillating at say 10^9 cps and a maximum field strength of say 300 volts/cm, equation (22) indicates that the maximum kinetic energy of the freely oscillating electron will be only about 2 ev. This is insufficient energy to ionize gases, and yet breakdown will occur for this type of field.

It is collisions of the type which lead to the Druyvestryn distribution which are responsible for ionization. An electron will be accelerated by the field during a portion of its cycle and then be deflected in a collision. The energy parallel to the electric field is thus converted to energy perpendicular to the field. The field then proceeds to give the electron additional energy in the direction of the field. Energy is pumped from kinetic energy of motion parallel to the field to kinetic energy in all directions.

If we write Newton's law for an electron, adding a collision term, we are left with Eq. (3), except now, E is time-dependent. Writing $E = E_0 \cos \omega t$

$$\frac{d\langle v_z\rangle}{dt} = \frac{qE_0}{m}\cos\omega t - \langle Z\rangle\langle v_z\rangle. \tag{23}$$

The power delivered to an electron by the field, averaged over a cycle, is

$$\overline{P} = \frac{1}{2}\frac{q^2E_0^2}{m}\frac{\langle Z\rangle}{\langle Z\rangle^2+\omega^2} \tag{24}$$

This equation shows directly the role of collisions of electrons in conversion of electrical energy to energy of the gas.

Again if this power gain is equated to the loss of energy of electrons in elastic collisions with the gas molecules, as would occur in the steady state, then

$$\frac{1}{2} m \bar{c}^2 h \langle z \rangle \simeq \frac{q^2}{m} E_o^2 \frac{\langle z \rangle}{\langle z \rangle^2 + \omega^2} \tag{25}$$

or since $\langle z \rangle \simeq \frac{\bar{c}}{\lambda}$

$$\frac{1}{2} m \bar{c}^2 \simeq \frac{\lambda a}{\sqrt{h}} \left\{ \sqrt{1 + \frac{\lambda^2 \omega^2}{a^2 h}} - \frac{\lambda \omega}{a \sqrt{h}} \right\} \tag{26}$$

where $a \equiv \frac{qE_o}{m}$.

From (26) one would expect the electron "temperature" for fixed E_o to diminish with increasing frequency, but for pressures of the order of one torr and gas masses of around 30 AMU the electron temperature will remain near the dc value for frequencies usually employed for gas discharge work.

B. Elastic Collisions, and Diffusion

Since in either dc or ac discharges, the electrons will have high temperatures, one can expect that all the manifestations of a kinetic temperature will be present. Particularly important among these is diffusion through elastic collisions. If only electrons are present in a neutral gas they will tend to diffuse as would any other gaseous component with a current density

$$\vec{S}_e = n \langle \vec{v}_e \rangle = - D_e \nabla n_e \tag{27}$$

where n_e is the number density of the electrons and D_e is the diffusion coefficient of the electrons through the gas. If a field is also superposed, the current density will contain a mobility term as well so that

$$\vec{S}_e = - D_e \nabla n_e - n_e \mu_e \vec{E} \tag{28}$$

where the minus sign in the second term indicates that because of the negative charge on the electrons, their motion will try to be in the direction opposite to that of the applied field. μ_e is taken to be a positive number. Whether the electron motion is diffusion-dominated or field dominated depends on whether the first term is larger than or smaller than the second.

In a gas discharge, the electrons will have produced ions and these also will tend to diffuse through the neutral gas as well as respond to any electric fields. The current density of ions will be given therefore by a similar equation

$$\vec{S}_+ = -D_+ \nabla n_+ + n_+ \mu_+ \vec{E}. \tag{29}$$

From Eq. (4) the mobility of either type of particle is $\mu = |q|/(m\langle z\rangle)$ and from kinetic theory, the diffusion coefficient is given by $D = \kappa T/(m\langle z\rangle)$. Since both these parameters have the mass appearing in the denominator the electron will diffuse and respond to an electric field much more rapidly than will the heavy ions.

The case of major interest for discharge physics is that where the number density of ions is very nearly equal to that of the electrons. Clearly because the electron mass is very light these will try to diffuse away from the ions. However, as soon as they do this, an electric field is set up between the electrons and ions so that the electrons are held back by the ions and the ions are dragged along by the electrons. We would thus expect that the current fluxes S_e and S_+ would be equal.

If we set $S_e = S_+ \equiv S$, and $n_e = n_+ \equiv n$, to indicate an electrically neutral plasma, Eqs. (28) and (29) can be combined to eliminate the electric field with the result that

$$S = -D_a \nabla n \tag{30}$$

where

$$D_a = \frac{\dfrac{D_+}{\mu_+} + \dfrac{D_e}{\mu_e}}{\dfrac{1}{\mu_+} + \dfrac{1}{\mu_e}}. \tag{31}$$

Since $\dfrac{D_+}{\mu_+} = \dfrac{\kappa T_+}{|q_+|}$ and $\dfrac{D_e}{\mu_e} = \dfrac{\kappa T_e}{|q_e|}$

and $\dfrac{1}{\mu_+} \gg \dfrac{1}{\mu_e}$, $|q_e| = |q_+| = e$ we can write

$$D_a \simeq \frac{\kappa\mu_+}{e}(T_+ + T_e) \tag{32}$$

or

$$D_a \simeq \frac{\kappa\mu_+ T_+}{e}\left(1 + \frac{T_e}{T_+}\right) = D_+\left(1 + \frac{T_e}{T_+}\right). \tag{33}$$

If the electron temperature is equal to the ion temperature, as in the case of late in an afterglow, the ambipolar diffusion coefficient is just twice the value of D_+. In the active discharge, however, as we have seen T_e will be large, perhaps of the order of 30,000°K. On the other hand the ion temperature will deviate little from the neutral gas temperature. The reason is that the ion mass is comparable to the mass of the neutral molecules; thus by arguments similar to those leading to Eq. (7) the ion will in a single collision be able very effectively to give to the neutral gas the energy it picks up from the field between collisions. The temperature of the ions will therefore remain very close to the neutral gas temperature. The ratio T_e/T_+ will be of the order of 100 typically in an active discharge and rapid diffusion of the plasma through the neutral gas and to the walls of the container will result.

Summary of the Remainder of the Paper

C. Electron production and loss mechanisms are discussed and the plasma balance equation is formulated.

D. Excitation to radiating and metastable states is summarized and some of their consequences for the operation of a discharge are presented.

E. Wall phenomena.

III. Macroscopic phenomena.

A. Plasma polarization and the Debye length are discussed.

B. Characteristics of certain types of discharges are reviewed; Glow Discharges, Arc Discharges and rf discharges.

IV. Afterglows. The effects of suddenly reducing the electron temperature are briefly reviewed.