Suggestions for Further Work

There are indications of the presence of faint bands in part of the region obscured by the background. It would be interesting to examine this region for such bands, and to determine whether they are to be classed with those observed in the ultraviolet, or with those in the visible region.

The rotational analysis of the ultraviolet bands should be feasible if undertaken with a stronger source and somewhat greater resolution than here. Such an analysis may be facilitated by the work of Dieke and Mauchly[3] on the probably similar third positive group of CO.

No explanation can be offered for the diffuse appearance of the bands in the visible region. It may be caused by predissociation in the upper state, or perhaps these bands are due to BF_2 or BF_3, and not to the diatomic molecule BF.

The writer wishes to acknowledge the suggestions and helpful advice which Professor R. S. Mulliken has given in the course of this work.

MARCH 15, 1935 PHYSICAL REVIEW VOLUME 47

Spectral and Impact Phenomena in the Faraday Dark Space

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(Received December 17, 1934)

Observations on the spectra of the negative glow and Faraday dark space in pure helium and in helium containing a trace of nitrogen lead to the conclusion that in the negative glow the phenomena are due mainly to collisions of fast (primary) electrons with normal atoms while in the Faraday dark space impacts of the second kind between normal and metastable atoms are of primary importance. The metastable atoms present in the latter region are probably produced by the absorption of resonance radiation from the negative glow and are thus in the 2^1S state. The negative glow proper emits the He I and He II lines strongly and a band spectrum of He_2. The band spectrum is, relatively, much stronger in the region of transition between the negative glow and the Faraday dark space and this last region emits only the He I line λ5016 (2^1S-3^1P) in sufficient intensity to be observed. When a trace of nitrogen is added to the helium, the N I spectrum replaces the He_2 bands in the transition region. A consideration of the phenomena observed leads to the conclusion that $He_2 2^{1,3}\Sigma$ molecules are formed by the union of a 1^1S atom and a $2^{1,3}S$ atom in a three body collision and that the possibility of observing the visible He_2 bands at all depends on the metastable nature of the $2^3\Sigma$ level of the He_2 molecule. These metastable molecules are excited to higher levels by slow electron impacts in pure helium, whereas when nitrogen is present, they are destroyed by impacts of the second kind with nitrogen molecules before they can be excited. N_2 molecules may be dissociated in these collisions, the dissociation occurring as a secondary consequence of the molecule's being raised to a higher electronic level from which dissociation occurs through predissociation or because the upper level is repulsive or simply because the molecule is excited to a degree above its dissociation asymptote. The effects from admixtures of oxygen and of carbon monoxide to helium and similar experiments on neon and argon support the conclusions drawn from the phenomena observed with helium and helium-nitrogen mixtures.

Introduction

THE Faraday dark space is the name given to the feebly luminous space between the two regions of strong luminosity in the fully developed glow discharge. It is bounded fairly sharply at its anode end by the positive column and passes without sharp demarcation into the negative glow at its negative end. Early measurements on the electric field in this region indicated that the field is very small, or even reversed[1] for electrons, and more recent measurements[2] confirm this observation, the current being due to a concentration gradient[3] of ions and electrons. The properties of the negative glow and the Faraday dark space together approximate those

[1] J. J. Thomson, Phil. Mag. **18**, 441 (1909).
[2] McCurdy, Phil. Mag. **46**, 524 (1924); Compton, Turner and McCurdy, Phys. Rev. **24**, 597 (1924).
[3] Emeleus and Harris, Phil. Mag. **4**, 49 (1927).

of a plasma,[4] but an attempt to formulate an exact quantitative theory of these regions on this basis proved unsatisfactory,[5] the fundamental difficulty being that the rate of ion formation at different distances from the cathode was unknown. The nature of the ionizing agent was uncertain, it being improbable that fast electrons from the cathode dark space could penetrate far into the negative glow in any considerable numbers, although probe analyses[6] indicate that such are present. It now appears that a too simple model had been adopted.

From the spectra emitted by different regions the negative glow and Faraday dark space may be divided into four merging regions, *viz.*, I the negative glow proper, II the region of transition from negative glow to Faraday dark space, III the main Faraday dark space and IV the region of transition from the Faraday dark space to the positive column. In IV there is a considerable accelerating field for electrons toward the anode, a case that has been treated theoretically by Sir J. J. Thomson and G. P. Thomson.[7] The existence of a difference in the spectra of II and III (usually treated together) and I has been recognized for some time, a part of II and III often being called the "aureole." From a spectroscopic study of this in neon and argon, Druyvesteyn[8] concluded that its special properties were due to the presence of metastable atoms formed as a secondary result of the absorption of ultraviolet resonance radiation from I.

In the present work we have studied the regions I, II and III mainly by spectroscopic methods and used the three lightest inert gases, both pure and with controlled contaminations. We believe that, in I, collisions of fast electrons with normal atoms are of primary importance,[9] in III, impacts of the second kind with metastable atoms, and in II, the combined effects of electrons and metastable atoms. The investigation has proved of interest in other connections: (1) Since diffusing resonance radiation occurs in

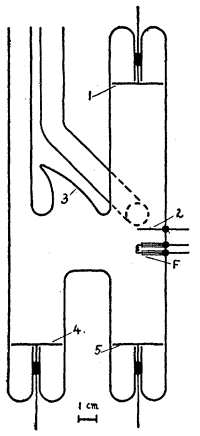

FIG. 1. Glow discharge tube. 1, 4, 5, circular disk electrodes; 2, semicircular disk electrode; 3, light trap; *F*, filament.

III, spectroscopic studies on this region give rather direct information about secondary effects of this diffusion in inert gases obtained otherwise only by indirect electrical methods.[10] (2) Some information has been obtained which bears on two molecular problems, namely, the formation of helium molecules and the dissociation of nitrogen. (3) The results lead to a clearer understanding of the mechanism of chemical reactions in this part of the discharge. This will be dealt with elsewhere.

EXPERIMENTAL ARRANGEMENTS

The tubes used were (i) a cylinder 3.5 cm in diameter with two disk electrodes of nickel and one copper wire electrode between the two disks; (ii) the tube shown in Fig. 1 with a variety of tungsten electrodes, which, used in turn, enabled us to avoid sputtered regions and thus prolong the life of the tube; (iii) a bulb 8 cm in diameter, stemmed with a vertical tube 3 cm in diameter and containing a small anode at the center of the bulb and a nickel disk cathode movable vertically in the stem. Tube (ii) proved very useful and most data were taken with it. Direct-current discharges of from 0.1 to 10 milliamperes per cm^2 at 150 to 1000 volts were run in helium, neon and argon, respectively, at pressures from 0.5 to 7 mm. The helium and the neon were purified

[4] Langmuir and Tonks, Phys. Rev. **34**, 896 (1929).
[5] Cowan, Thesis, Belfast (1931).
[6] Emeleus and Brown, Phil. Mag. **7**, 17 (1929); Emeleus, Brown and Cowan, Phil. Mag. **17**, 146 (1934).
[7] Thomson and Thomson, *Conduction of Electricity through Gases* Vol. II, p. 361.
[8] Druyvesteyn, Zeits. f. Physik **57**, 292 (1929).
[9] Emeleus, Brown and Cowan, Nature **127**, 593 (1931).
[10] Kenty, Phys. Rev. **44**, 891 (1933); Duffendack and Smith, Phys. Rev. **43**, 586 (1933).

by prolonged standing over charcoal cooled by liquid air and the argon was purified by the use of mischmetal arcs. During use with tubes (ii) and (iii), the gas was circulated, and the final purification of the gas was effected by passing it, immediately before admitting it into the discharge tube, through a strong glow discharge between tungsten plate electrodes. The criterion aimed at was freedom from spectroscopic impurities in the visible and near ultraviolet. The only contaminant found was neon in the helium used with (ii) and (iii) and this was probably present to less than 0.05 percent. When required, nitrogen from sodium azide, or oxygen from potassium permanganate was added. In this case, the auxiliary discharge in the circulating system was discontinued. In the observation of the spectra final recourse was always had to photography.

Spectroscopic Data

1. *Pure helium.* Our results are essentially similar to those of Seeliger and Mierdel,[11] who first investigated this case, and of Keyston.[12] Region I (green) is a strong source of the singlet He I and He II lines by virtue of the excitation by high speed electrons. Bands are present also and these include some from high electronic levels so that it is possible that a recombination spectrum of He_2 is present. This can, however, account for only a part of the band spectrum. Region II (peach) is a strong source of He_2 bands which are relatively far less intense in I in comparison with the He I lines than they are in II. The light from III is very feeble and we are certain only that it emits the He I line 5016 (2^1S-3^1P).

Formation and excitation of He_2 molecules

A consideration of our results in comparison with those of other observers and in the light of present knowledge of kinetic and spectral theories, leads us to the conclusion that He_2 molecules are formed in three body collisions involving two normal 1^1S atoms and one metastable $2^{1,3}S$ atom. The resulting molecule will be in the $2^1\Sigma$ or $2^3\Sigma$ state, depending upon whether the metastable atom is 2^1S or 2^3S. $2^3\Sigma$ molecules are metastable and are therefore subject to higher excitation by electron impact. It is this metastable character of the $2^1\Sigma$ molecules that enables us to observe the visible helium bands at all.

To discuss these results we need certain numerical data, *viz.*, (1) the mean life of an excited He atom or He_2 molecule, about 10^{-7} sec. if in an unstable, excited state, and infinitely large, for present purposes, if metastable; (2) the mean time between kinetic theory collisions of the He atoms, about $10^{-7}p^{-1}$ sec. under discharge condition ($\sim 350°K$) at a pressure of p mm; (3) the fundamental vibration time[13] of the lowest $^3\Sigma$ state of He_2, approximately 2×10^{-14} sec. We cannot carry out better than order of magnitude calculations, and to that approximation (2) will also give the time between the collision of normal He atoms and excited atoms or molecules, and (3) the effective time of contact of 2^3S and 1^1S He atoms on impact when they separate again without permanent molecule formation.

Seeliger and Mierdel supposed the relative weakness of bands in I was due (a) to the He_2 molecule's being formed from one metastable and one normal atom, and (b) to the loss of metastable atoms by their reverting to the normal state by impacts of the second kind with slow electrons. These processes are compatible with data now available. The chance of two atoms uniting to form a molecule in a two-body collision in the gas phase is known to be very small, and hence the approximate equality of the times (1) and (2) under typical discharge conditions shows that most unstable excited atoms will revert to the normal or to a lower excited state by radiation in preference to disappearing by molecule formation. Assuming that (b) is correct, in the form that metastable atoms are removed by either first or second type collisions with slow electrons, probe analyses of discharges enables an estimate to be made of the chance of molecule formation on collision between a metastable atom and a normal atom. From simple kinetic theory considerations, the relative chances that an electron will collide with the metastable atom and that a normal atom will collide with

[11] Seeliger and Mierdel, Zeits. f. Physik **19**, 230 (1923).
[12] Keyston, Phil. Mag. **15**, 1162 (1933).
[13] Jevons, *Report on Band Spectra.*

it are about in the ratio $0.2n_e/n_{He}(m_{He}/m_e)^{\frac{1}{2}} \times (T_e/T_{He})^{\frac{1}{2}}$, where n denotes concentration, m mass, T temperature of the electrons and atoms, respectively, and the numerical factor allows roughly for the difference in mean free path for an electron and an atom neglecting Ramsauer effects. Under typical negative glow conditions,[6] ($n_e=10^{10}$ per cc, $T_e=7000°K$) this is of the order 10^{-5} at 1 mm pressure. Hence, if metastable atoms are preferentially destroyed by electron collisions, the chance of molecule formation on atom collisions must be of this order or less. This, again, is compatible with a three-body process for the formation of He_2 (the third atom taking off excess kinetic energy), the chance of a third 1^1S atom colliding with a potentially combining $1^1S+2^{1,3}S$ pair during the time (3) being, from (2), about $10^{-7}p$. This chance being proportional to p is in accord with the well-known high pressure character of the He_2 bands and their absence from stellar spectra,[14] which are produced under essentially low-pressure conditions.

Seeliger and Mierdel's process (a) is not in itself sufficient to account for the production of the visible band spectrum, since it gives rise to He_2 molecules only in the $2^{1,3}\Sigma$ states, whereas the bands arise in transitions from higher levels. A second process must be involved in reaching the higher levels. This process is, fairly certainly, electron collision with $2^{1,3}\Sigma$ He_2 molecules. From the numerical considerations already advanced it is clear electron collision can only be of importance if these molecules are metastable. Since the ground state of He_2 is $1^1\Sigma$ (a repulsive level) and radiative intercombinations do not occur in this light molecule, the $2^3\Sigma$ state is metastable, the $2^1\Sigma$ not. The possibility of observing the visible He_2 bands at all appears to depend, then, on the metastable nature of the $2^3\Sigma$ level, a result which has a bearing on the spectroscopic properties of Ne_2.[14a]

The part played by this level also enables us to understand the preponderance of triplet bands in the visible spectrum, particularly in the "uncondensed" positive column.[12] The reason is that changes in multiplicity produced as a result of electron impact occur most readily when the electron energy available is not much in excess of the minimum required to effect the transition, whereas inelastic impacts which do not involve a change in multiplicity take place most efficiently when there is considerable excess energy. The excitation energy of higher states[13] from $2^3\Sigma$, the effective ground state in this case, is of the order of 3 volts, whereas to produce the metastable 2^3S parent atom from the normal 1^1S atom requires 19.7 volts. In a simple system such as the uncondensed positive column, where most of the free electrons are included in a single group of rather high mean energy, comparable with that of the least excitation potential of the gas, or rather less, the conditions for the formation of 2^3S atoms in quantity is thus incompatible with that for producing excited singlet molecular states. It is only when the distribution of energy amongst the free electrons is more complex, with one group of high energy and one of low energy present simultaneously, as in the negative glow at medium pressures, that conditions are right for producing, first 2^3S atoms, and second both excited singlet and triplet molecular states from the $2^3\Sigma$ molecules. Conditions in a condensed positive column appear to approximate to those in the negative glow.[15] The importance of having very pure helium to obtain the bands can now be understood, since it is necessary not only that the metastable 2^3S atoms be not quenched by collisions with impurities, but also that the metastable 2^3S molecules are not lost likewise.

The spectrum of the Faraday dark space

The spectrum of III in impure helium indicates that it contains metastable atoms. So far as they are produced by absorption of resonance radiation, they must be in the 2^1S state, since there is no intercombination resonance line in He I. The observed emission of 5015 (2^1S-3^1P) can be ascribed to fluorescence of these metastable atoms in the green light from the negative glow with probably also a stronger infrared fluorescence of 2^1S-2^1P. Absence of He_2 bands would go with the absence of 2^3S atoms, or, if these were present (produced by electron impact with 1^1S or 2^1S atoms), with the known small concentration of electrons to excite them to higher

[14] Struve and Christy, Astrophys. J. **71**, 277 (1930).

[14a] Emeleus and Duffendack, Phys. Rev. **44**, 945 (1933); Druyvesteyn, Nature **128**, 1026 (1932), has obtained bands which he attributed to a HeNe molecule.

[15] K. G. Emeleus and F. M. Emeleus, Phil. Mag. **8**, 383 (1929).

molecular states. The bands are strong in II because there is a large concentration of both fast electrons to produce 2^3S atoms, and slow electrons to excite the $2^3\Sigma$ molecules. We were unable to excite bands in III by injecting electrons from the filament F of tube (ii). Positive space charge sheaths in II were observed to be green, emitting the 5016 line but not the bands. The origin of this singlet line in these sheaths may be the same as in III, but perhaps also partly due to direct excitation of 3^1P by electrons emitted by secondary processes at the walls and accelerated in the sheath. In any event, the absence of bands follows from the small concentration of electrons in the sheaths.

The excitation of gas admixtures

2. *Helium, neon and argon+nitrogen.* When nitrogen is added to pure helium, the N I spectrum replaces the band spectrum of He_2. Lines of N I are visible with 0.05 percent nitrogen, N I lines and He_2 bands are about equally intense with one percent nitrogen, and the He_2 bands disappear when the percentage of nitrogen is increased to three percent. Concentrations of nitrogen greater than five percent were not studied but cannot result in much further increase in the strength of N I. This spectrum is not observed in I, II or III with pure nitrogen.[16] The negative bands of N_2^+ appeared in the same parts of the tube as the N I lines, and, in addition, were the only spectrum observed from III and the space charge sheaths. These latter turned blue on account of these bands. The intensity of the bands in III was a maximum for some two percent nitrogen, and they were not visible with five percent nitrogen. Neither N I lines nor N_2^+ bands were observed with neon-nitrogen and argon-nitrogen mixtures.

The initial levels of the N_2^+ bands are probably excited by second type collisions between metastable He atoms and normal $^1\Sigma N_2$ molecules, as follows:

$$He(MS)+N_2 \rightarrow He(1^1S)+N_2^+\delta(B\Sigma^2)+e.$$

The energy discrepancy is much less than one volt, the energy of ionization and excitation of N_2 being 19.6 volts,[17] and the process thus likely. It is not known if one or both of the metastable states of He are involved, although it is probably mainly the singlet state in III. The weakness of the negative bands in II for higher concentrations of N_2 may be ascribed to the absorption of He resonance radiation by nitrogen between I and III, or to the quenching of metastable He atoms by collision with N_2 molecules in the same region. The energy of metastable Ne and A is too small for the excitation of the N_2 bands.

The production of N I is more complicated. Duffendack and Wolfe[18] have already shown it to be a two stage process, the first being supposed to be the dissociation of N_2 into two normal (^4S) atoms. Dissociation by electron impact, although possible,[19] can be ruled out as an important factor in the present case from the absence of N I lines in a similar discharge in pure N_2[16] and, furthermore, that metastable He is involved one may deduce from the observed steady replacement of He_2 bands by N I lines on adding N_2 to He. It cannot, however, be decided from this observation whether the metastable systems are $2^{1,3}S$ He atoms or $2^3\Sigma He_2$ molecules. In any case, if the resulting atoms of nitrogen are in the normal state, the difficulty arises that there is a large energy discrepancy, as the heat of dissociation of N_2 is less than 8 volts and the energy of the metastable He atoms about 20 volts and that of the metastable He_2 molecules about 17.5 volts.[20] The evidence that the N atoms are in the normal state is itself not conclusive, as the dissociation $N_2 \rightarrow N(^4S)+N(^4P)$ is possible, it being only that the intensity distribution in the N I spectrum is much the same when it is produced in a heavy current arc at high pressure,[21] on the cathode of the glow discharge in the pure gas,[16] and in the present case and in the presence of argon.[22] This similarity is understandable if in each case the excitation, after the atoms have once been formed, is by electron collisions with them in the ground state.

We attempted to decide this by examining the line width of the stronger visible N I lines with a Fabry-Perot interferometer. They might be

[16] Emeleus and Hall, Proc. Roy. Irish Acad. **A40**, 1 (1931).
[17] Smyth, Rev. Mod. Phys. **3**, 347 (1931).
[18] Duffendack and Wolfe, Phys. Rev. **34**, 409 (1929).
[19] Kondratew, Zeits. f. Physik **38**, 346 (1926); Turner and Samson, Phys. Rev. **34**, 743 (1929).
[20] Mullikan, Rev. Mod. Phys. **4**, 61 (1932).
[21] Ryde, Proc. Roy. Soc. **A117**, 164 (1927).
[22] Anderson and More, Phys. Rev. **38**, 1995 (1931).

expected to be broadened if there were the large energy discrepancy mentioned going into kinetic energy of the N and He atoms. No broadening was found with a 17.5 mm etalon, nor was any found with a slightly different form of $He-N_2$ discharge by Bacher.[23] However, calculations like those made for pure helium show that even if the N atoms were formed in the ground state with high kinetic energy, they would make some million collisions with other atoms or molecules before excitation by electron impact and would by that time be in thermal equilibrium with the gas.

Cameron[24] obtained N I lines in $Ne–N_2$ discharges. His observations are, however, unreliable, since his neon probably contained helium.[25] Anderson and More[22] produced the N I lines in a low voltage arc in $A–N_2$ mixtures, contrary to a negative result under similar conditions by Duffendack.[26] The only obvious difference in the experiments is that Anderson and More used an oxide coated filament and Duffendack bare tungsten. In view of the rapid interaction between hot tungsten and N atoms, it is possible that in Duffendack's tube the tungsten filament kept the N atom concentration low. Whatever the reason, it is clearly much easier to produce the N I spectrum in helium than it is in argon or in neon.

An ultimate explanation may be looked for on the following lines. The dissociation of N_2 to 2N on impact with a metastable atom of sufficient energy may occur either by increase in vibrational energy in the $1^1\Sigma$ ground state of N_2 or as a secondary consequence of the molecule's being raised to a higher electronic level from which dissociation occurs either through predissociation or because the upper level is repulsive, or simply because it is excited above its dissociation asymptote. So far as energy considerations go, any upper level can be reached in the latter manner if some one of its sublevels has less energy than is possessed by the metastable particles. Since, however, the changes involved are electronic, we might expect the internuclear distance to be fairly closely conserved as in Franck-Condon transitions. Thus the transition becomes comparable to an atomic energy interchange in requiring fairly close energy resonance for the transition to be a probable one. Compared with an electronic change at close resonance, the direct vibrational dissociation is unlikely.[27] The experimental evidence points, then, to the dissociation of N_2 in He being due to an electronic transition in N_2 with close resonance, followed by a separation of the atoms, and in Ne and in A to any dissociation either through an electronic transition with less close resonance or by vibrational dissociation. Knowledge of the electronic levels of N_2 is too fragmentary to make further discussion worth while, but it may be noted that when once a case of dissociation through an electronic change has been established, it provides a way for obtaining a point on a $V-r$ curve for a molecule which it may not be possible to obtain otherwise.

3. *Helium and oxygen.* With about one percent O_2 in He, III turns a brilliant apple-green and shows the first negative bands of O_2^++. No such effect was observed with Ne or A. The initial state of the O_2^+ bands ($b\,^4\Sigma$?) requires about 19.5 volts[28] for excitation from the normal $(^3\Sigma)O_2$, so that the interaction

$$He(MS)+O_2=He(1^1S)+O_2^+(b\,^4\Sigma?)+\text{electron}$$

is likely. Metastable Ne and A have again too little energy to effect the transition.

4. *Helium and carbon monoxide.* This mixture was studied by Seeliger and Mierdel[11] who found that the Baldet-Johnson bands of CO^+ replaced those of He_2 in the aureole. The upper state of these is $B\Sigma^2$, with its state of least vibrational energy about 19.6 volts above the normal state of CO,[17] and hence the resonance:

$$He(MS)+CO=He(1^1S)+CO^+(B\Sigma^2)+\text{electron}$$

is again likely. Seeliger and Mierdel did not observe the ultraviolet $B\,^2\Sigma-X\,^2\Sigma$ negative bands of CO^+, but they must certainly have been present as they are enhanced in other discharges in He–CO mixtures.[29] It is noticeable that with both CO and N_2, the foot of the $V-r$ curve for the ionized state excited by metastable helium is almost directly above the foot of the curve for

[23] Bacher, Phys. Rev. **43**, 1001 (1933).
[24] Cameron, Phil. Mag. **1**, 405 (1926).
[25] According to later work by one of us (K.G.E.) with the same specimen of neon.
[26] Unpublished observation.
[27] Dr. H. S. W. Massey informs us this is the case.
[28] Roy. Phil. Mag. **15**, 421 (1933).
[29] Weizel, *Bandenspektren*, p. 393.

the normal molecule. The same may also be true of O_2 and O_2^+.

5. *Helium and mercury and molybdenum.* These provide apparent exceptions to the principle of resonance. With a trace of the vapor of either metal in helium, a strong development of its arc spectrum was observed in the aureole. The energy discrepancy, if the initial states are produced by impacts with metastable helium atoms in a single act, would be in each case greater than 10 volts. Insufficient data are available to make an attempt at an explanation of these cases profitable.

Mechanism of the discharge

The results of the last section, taken with those obtained by Druyvesteyn,[8] show the importance of resonance radiation and metastable systems in II and III. In several cases (e.g., O_2 admixture in He), new ions result through their action, and it was, in fact, observed in these cases that there was a great increase in conductivity relative to the conductivity of the pure gas. With O_2 in He at 2 mm this was some fivefold for a one percent admixture; with N_2 rather less. However, beyond the recognition of the importance of such processes, the general theory of the Faraday dark space is not advanced quantitatively since we do not know either the concentration of metastable systems or the efficiency of their second type interactions in any individual case. The discharge properties of gases of extreme purity[10] become an interesting problem, and also the question of whether such purity can be attained in a glow discharge. More generally, the difficulty in the way of formulating an exact theory in this and many other cases comes from our very incomplete knowledge of the extent to which the system as a whole departs from a state of thermal equilibrium. We merely know that this is approached in certain unit processes occurring (such as those effecting energy interchanges amongst the free electrons of low energy which have almost a Maxwellian energy distribution),[6] and must, therefore, pick out the individual atomic and molecular acts which seem likely to be of most significance under the circumstances and examine their consequences as far as we are able. The model of the discharge then errs on the side of simplicity, and it is to the neglect of important factors (perhaps the formation of negative ions) that we may attribute the failure of the present theory to explain, in the present case, such phenomena as the occasional appearance of striations in the Faraday dark space.[30]

A consideration of all the data at present available seems to point to the following conclusions. The negative glow proper, region I, is produced by the excitation of the gas molecules by high speed primary electrons. Simultaneous ionization and the excitation of the resultant ion is responsible for the spark spectra and negative bands observed in the negative glow. In the transition region II the effects of electron impacts are of less importance and the effects of the absorption of resonance radiation and of impacts of the second kind with metastable atoms and molecules become important. In region III, the phenomena are due almost wholly to these latter effects. The current through the Faraday dark space is a diffusion current of electrons and positive ions giving a resultant electron current toward the anode.

The results have an application in spectroscopy. A common method for exciting spectra of an element is to volatilize it in a hollow cathode tube in an inert gas, when excitation of the added material occurs through second type collisions between the metastable atoms and ions of the inert gas and the added atoms.[31] The somewhat different properties of I, II and III suggest that differential excitation might be observed if the three regions, or some of them, were observed separately instead of, as in the usual form of hollow cathode tube, effectively together.

The greater part of the experimental work was done at the University of Michigan during 1932–33. One of us (K.G.E.) gratefully acknowledges the facilities put at his disposal by Professor H. M. Randall during this time while he was a guest of the University. Mr. A. Helz gave much help with the experiments.

[30] Holm, Phil. Mag. **11**, 194 (1931); Zeleny, Nature **125**, 562 (1930).

[31] Duffendack, Henshaw and Goyer, Phys. Rev. **34**, 1132 (1929).