# THE EXCESS ENERGY AT COLLISIONS BETWEEN RARE GAS IONS AND NEUTRAL ATOMS IN A LOW VOLTAGE ARC

Thesis for the Degree of M. S.

Earl Kenneth Van Tassel

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Physics

# THESIS

# ON THE EXCESS ENERGY AT COLLISIONS BETWEEN RARE GAS IONS AND NEUTRAL ATOMS IN A LOW VOLTAGE ARC.

by

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I am indebted to and very grateful for the services of Mr. J. G. Black who suggested the problem and blew the glass for the vacum system and aided greatly with timely advice. I further wish to express my appreciation for the personal interest and co-operation given by Professor C. W. Chapman at all times during my work. I am indebted to Professor W. E. Laycock for the help that he offered in connection with the photographic work.

# INTRODUCTION

In an attempt to uncover mother nature's secrets man has only a few tools with which to work. Some of the tools merely probe the cloak of mystery that surrounds the structure which he is studying. Other tools blow the structure to pieces and then he can watch it build up again; noting as it builds up the laws that govern its behavior and fitting a physical concept that will obey these laws. One of these tools is the low voltage arc. A device in which man can shoot high velocity bullets at atoms and find what happens when they strike. As an electron, the shooting bullet, hits an atom, the atom sends out messages called radient energy. When we can properly interpret these messages we will be a long way towards the end of our task of uncovering the secrets of mother nature. It is the purpose of this investigation to make a study of colliding electrons, ions, and atoms.

# PART I

## IMPACTS OF THE FIRST KIND

The term "impact of the first kind" applies to collisions between electrons and molecules and collisions between two molecules when there is a transfer of kinetic energy into atomic energy. The most common method by which electrons can obtain energy is by falling through an electric field. The electron will acquire kinetic energy equal to

$$\tfrac{1}{2}mv^2 = eV$$

where e is the charge on the electron and V is the potential difference through which the electron falls. If the electron collides with a molecule, while passing through space and has not gained enough energy to place the molecule in one of its excited states, the electron will lose practically no energy and the collision is said to be an elastic impact. If, however, the electron has sufficient energy to lift the molecule into one of its excited states, then the electron loses the necessary energy and goes on with a diminished velocity. Such impacts are inelastic and are the most common impacts of the first kind.

A molecule which has been excited or put into a higher energy state will usually dissipate this energy in the form of electromagnetic waves or radiation, as it returns to its normal configuration. The energy going out

is equal to

$$h\nu$$

where h is Planck's constant of radiation and v is the frequency of the emitted light.

## IMPACTS OF THE SECOND KIND

"Impacts of the second kind" is a term first used by Klein and Rosseland[1] to describe a collision which is just the reverse of an impact of the first kind. Klein and Rosseland show that, in a region where we have impacts of the first kind which result in excited molecules and slow moving electrons, it is possible to have a collision between these two in such a manner that the excited molecule returns its energy to the electron.

Franck[3] extended the meaning of the term impact of the second kind to include impacts between excited molecules and neutral molecules. This impact can explain some cases of fluorescence, and photo chemical processes.

Cario[3], working under Franck, discusses two experiments in which he has used the term impact of the second kind. Both of these experiments are dealing with impacts between excited molecules and neutral molecules. The first experiment is of interest to us because he was using a mixture of the same two elements that were used in this investigation. He had a mixture of argon and mercury. He excited

the mercury by flooding it with monochromatic light of wavelength 2536.7 angstroms. This wavelength is one of the resonance lines and will place mercury in an excited state. The light from this mercury vapor was then analyzed by a spectrograph and it was found that the emitted radiation was weakened in the presence of argon. The article states that this proves that all of the energy of excitation may be taken up as kinetic energy of translation. It must be remembered that argon does not have an energy level equal to or less than the energy level which he was using in mercury.

In the second experiment Cairo mixed mercury and thallium vapors and analyzed the radiation from these vapors in a spectrograph. Besides the strong mercury line 2536.7, he obtained six thallium lines. The energies of all six of these lines were less than 4.9 volts, which corresponds to the mercury resonance line 2536.7 angstroms. This experiment shows that energy can be transferred from an excited molecule over to a neutral molecule having lower energy levels and then be emitted by radiation.

## POSITIVE ION IMPACTS

In a region where electrons possess energy sufficient to tear an electron completely away from the molecule, they are said to ionize the molecule. In this region we have ions,

fast and slow moving electrons, and neutral molecules. When an ion collides with a free electron, the atom goes through a series of decreasing energy values and upon each change in energy the difference goes out in the form of radiation. The composite radiation is known as the arc spectrum. The other possibilities for collisions fall into two classes:

1. Impacts between positive ions and molecules of the same kind, or molecules with larger ionizing potential. Out of such a collision very little can happen.

2. Impacts between positive ions and molecules with smaller ionizing potential. It is this class of impacts with which this investigation is chiefly concerned.

## IMPACTS BETWEEN SLOW MOVING POSITIVE IONS OF GREATER IONIZATION POTENTIAL WITH MOLECULES OF SMALLER ENERGY OF IONIZATION

Franck[4] discusses an impact between a slow moving mercury ion with energy equivalent to 10.3 volts with a ceasium molecule which only requires energy carried by an electron after falling through 3.5 volts to ionize it. In this case he suggests that the ion could lose 5.4 volts of energy of the 10.3 volts and be left in the excited state. In the loss of this 5.4 volts, ceasium would use 3.5 volts

in ionization and Franck says that the remaining 1.9 volts of energy goes into kinetic energy of translation. Further, this excited atom of mercury possessing only 4.9 volts of energy could collide with another ceasium molecule and ionize it, using 3.5 volts and dissipating 1.4 volts into kinetic energy of translation of the two molecules.

Further proof that rare gas ions can rob other neutral atoms of an electron is given by an article written by Smyth and Hornwell[5]. In this experiment they used a Demster positive ray apparatus with a mixture of rare gases. As a result they stated that the rare gas ion of helium would rob the neon of an electron.

At the same time Smyth and Hornwell were working at Princeton on their experiment, there were two other men working in the University of California, by the names of Hogness and Lunn. Hogness and Lunn[6] published their work and reported that their results checked those of Smyth and Hornwell.

Very shortly O. S. Duffendack of the University of Michigan conceived the idea that when a rare gas ion robbed another atom of smaller ionizing potential, that the excess energy, if large enough, might go to excite the first spark spectrum of the atom that is being robbed. It should be called to mind at this place, that the composite light emitted by an electron configuration in which all of the

electrons are present is known as the arc spectrum. The light emitted from an electron configuration in which one electron is missing, and the energy changes take place in the remaining electrons, is called the first spark spectrum. If we obtain light from a configuration in which two electrons have been removed from the original nucleus, this series of wavelengths of light is called the second spark spectrum. Dr. Duffendack's idea relative to an impact between a neutral atom and a positive ion possessing sufficient energy to ionize and excite the first spark spectrum, can be easily proven or disproven. The critical potentials and energy levels of the various elements are fairly well known. By careful selection from these different elements we can choose two elements, one of which when ionized will possess enough energy to ionize the other and change the remaining electron configuration. Black[7] of Michigan State College, in connection with Duffendack has recently published an article in Science which contained the results of an experiment using mixtures of neon and copper, and neon and mangenese. The results of this experiment show very clearly that when a neon ion collides with a copper or mangenese atom that the neon will rob it of one electron and shift the remaining configuration into an excited state which upon returning to the normal state emits the first spark spectrum. Smith and Duffendack[8] also have performed work of a similar nature and

have given proof that positive ions upon collision with atoms of smaller ionizing potential will transfer energy in the above manner.

The question now opens up: what would be the result if we should choose two elements; the ionizing potential of one being greater than the other but the excess energy not being sufficient to excite the first spark spectrum? Franck, Duffendack, Smyth, Hornwell, Hogness, Lunn, and many others have all predicted that the excess energy would go into kinetic energy of translation of the two molecules. It is the purpose of this investigation to find out what becomes of this energy. For this purpose we selected two easily accessible elements, argon and mercury. The ionizing potential of argon is about 15.2 volts and that of mercury is 10.392 volts. The difference between these two is 4.808 volts of excess energy. This is insufficient to excite the first spark spectrum of mercury so that the energy could not be used in this manner.

## THE MECHANISM OF IMPACT

If we can picture an atom of argon which has lost one electron and which by induction is distorting the fields about a normal mercury atom and making a dipole of it, we can see how an ion can attract a neutral body. As we reason about

the matter we can see that there are several possible ways for these two bodies to collide and for the argon to rob the mercury of an electron.

The simplest way in which we can picture the argon robbing the mercury of an electron is to have the argon exert a greater force on the nearest outer electron than it exerts on the other electrons. This greater force will pull the electron away from the mercury while the two atoms are at a relatively great distance. There will be an instant in which the electron is in neither the mercury atom nor the argon atom and we will have two ions repelling each other. Some energy must be spent in the throwing of these two ions apart. When we have an electron that does not belong to any particular atom we call this a free electron. Whenever a free electron is captured by an ion and moves in to the normal state the arc spectrum of the element is given off. In this mechanism just described there is an instant in which the electron is a free electron and when it takes its place in the argon atom it should emit the argon arc spectrum. But from thermodynamic considerations we see that this type of collision is impossible. Because at the instant the electron is a free electron we have stored in the system, 15.2 volts in the argon, 10.392 volts in the mercury, plus an additional unknown amount of kinetic energy in the two masses, making a total of over 25.792 volts of energy. This amount of energy is more than we started

with and there is no source from which to obtain this energy.

A second possible series of events that might take place in the chamber would be for the argon ion to pick up a free electron which it might get from the chamber walls or in space. Then as this electron made its way in to the normal level, it would emit a quantum of energy. This radiant energy would be sufficient to ionize the mercury atom and therefore we would get the transfer of energy from the argon over to the mercury by Photo-electric action and any physical impacts as we have been discussing would not have to occur. The excess energy referred to above, would probably be tied up in some unabsorbed argon radiation and in kinetic energy of the electron ejected from the mercury. The photo-electric effect will be almost impossible to eliminate because we cannot remove all the free electrons from the collision chamber.

Still a third way might be thought of as a possible means of exchanging this electron and energy. This would be a collision in which the atoms would come very close together and the electrons of the mercury would intermingle with the electrons around the argon nucleus. If this is the case, at some time or other, an electron originally associated with the mercury will find itself located with respect to all the other electrons in a position that is not permitted by the argon configuration. The argon will then have 4.808 volts of

excess energy. This energy will be given off in one of two ways;

1. As kinetic energy of translation.
2. As radiant energy.

If the excess energy should go into kinetic energy, it is shown in the computations, that the velocity of the molecules would have to increase by $1.99 \times 10^5$ cm/sec. which is rather unreasonable. On the other hand if the energy was to be radiated a wave 2551 angstroms long would be sent out.

## PART II

## THE LOW VOLTAGE ARC

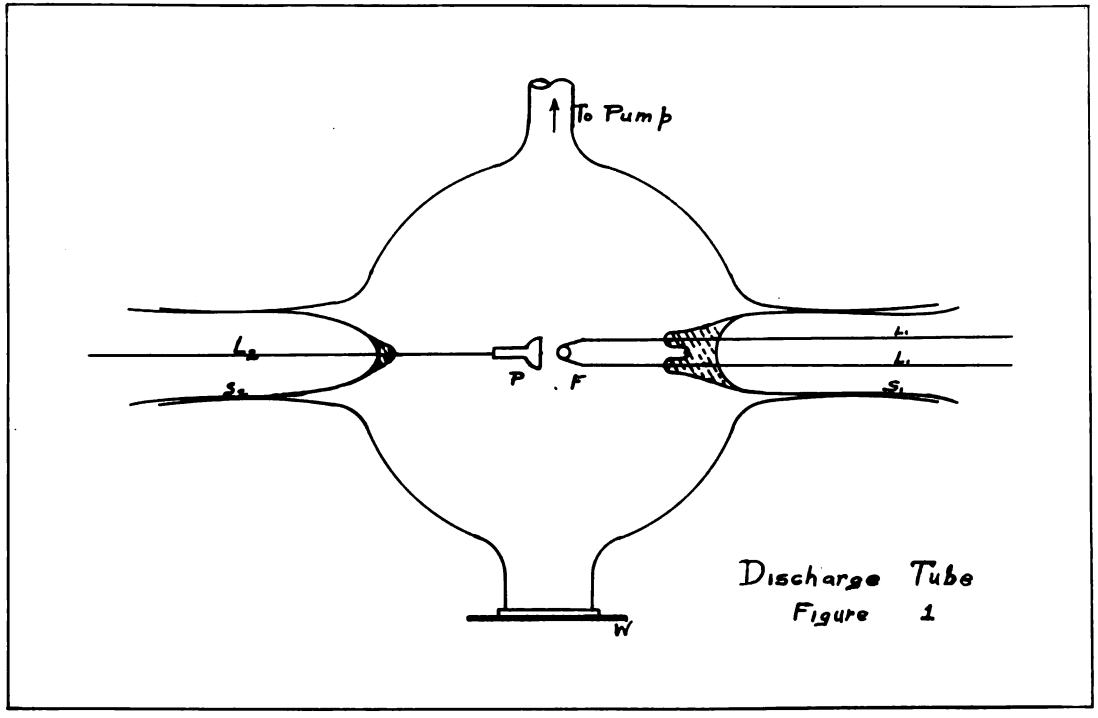
In the early development of the study of atomic structure glow discharges or geissler tubes were used. This type of discharge is unsatisfactory and very difficult to control or interpret. Franck and Hertz[9] in 1914 first published articles on critical potentials and inelastic impacts, describing at the same time the low voltage arc. Franck was given the Nobel Prize for this work which was a direct test of Bohr's theory of atomic structure. In the low voltage arc conditions can be more easily and definitely controlled and measurements more easily taken. This is the type of discharge that was used for this experiment.

The cathode or negative terminal is a hot filament, the filament consists of a 12 mil tungsten wire coiled in 3 or 4 turns of 2 m.m. diameter. The electron emission from this hot filament may be controlled by the current through it. The anode can be of any design necessary to meet the needs of the particular experiment. They can, however, be placed in two general classes,

1. Anode in the form of a plate or flat surface.

2. Anode in the form of a hollow box with one or more sides made of gauze. This produces a constant potential chamber.

In this experiment it was only necessary to use an anode of the first type. The speed of the electron is controlled and hence the kinetic energy is determined by the potential between the anode and the cathode or plate and filament. Therefore we have a large stream of electrons flowing between the filament and plate and we can control the approximate number of these and the energy carried by each. As these electrons travel across this space between the filament and plate, which is from 4 to 7 m.m. long, they encounter numerous impacts with molecules such as we have just described. If the potential through which the electron has fallen is insufficient to give the electron energy enough to lift a molecule to one of its excited states the impact is an elastic impact. If, however, the electron possess sufficient energy to lift the molecule to a state of higher energy, the impact




Discharge Tube
Figure 1

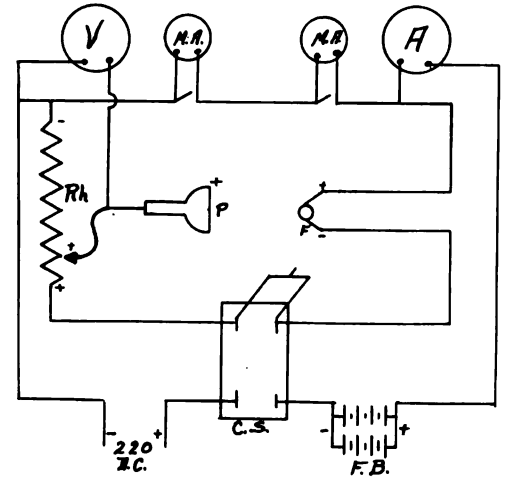
is inelastic. The amount of energy gained by an electron between collisions is determined by the mean free path of the electron (or the pressure of the gas) and the potential gradient. If the electron has acquired sufficient energy before impact to tear an electron completely away from the molecule we have ionization taking place.

## PART III

## APPARATUS

A diagram of the discharge tube is given in Figure 1. $S_1$ and $S_2$ are the two electrodes with ground glass joints sealed in place by De Khotinsky cement, then water cooled to prevent the cement from softening while the tube was in operation. $L_1$ and $L_2$ are tungsten leads sealed in pyrex glass. F is the filament made of #12 mil tungsten wire obtained from the General Electric Company. The filament was spot welded on to the tungsten leads. P is an aluminum plate located a short distance from the filament; usually 7 m.m. or less. W is a quartz window through which the light emitted from the space between the filament and plate was sent to a spectrograph. A small Gaertner quartz spectrograph which takes the whole ultra-violet region on a four inch plate was used.

Figure 2. shows the wiring diagram. FB is a group of Edison batteries furnishing the current to heat the filament. This current amounted to about 9 or 10 amperes at six volts.

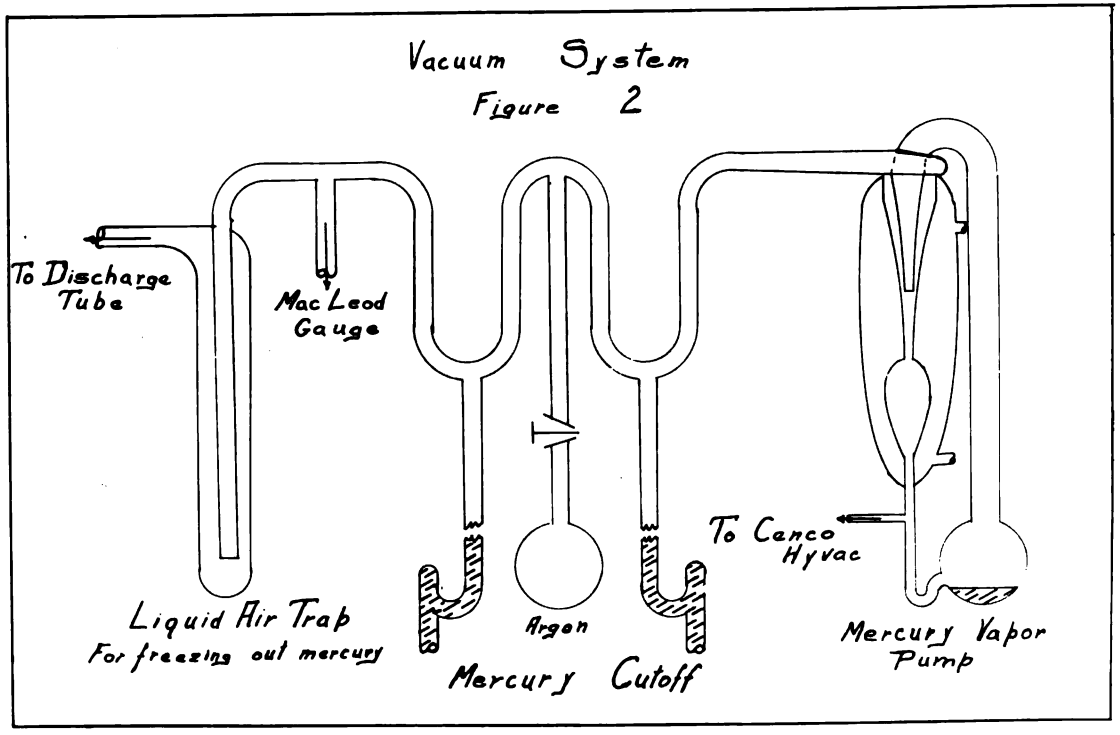



Wiring Diagram
Figure 3

CS is the main control switch having both the filament and plate circuit on it. Rh is a potentiometer used as the source of D. C. potential with which we accelerated the electrons from the filament F to the plate P. The plate voltage was measured by the voltmeter V and the plate current was noted by one of the two milliammeters M.A. As a source of D.C. voltage we used the 220 from the college generator, since it did not have to be extremely constant. A self explanatory diagram of the vacuum system used in connection with the discharge tube is shown in Figure 3.

## MANIPULATION

The pumps were kept running for a period of 10 or 12 hours before the gas was admitted. In the first series of trials a drop of mercury was placed in the discharge tube and at 20° C would furnish a vapor with a pressure of .0013 m.m. But it was found that radiation from the hot filament would increase the temperature many times and the operating temperature was above 100° C. This excess temperature on the mercury increased the vapor pressure tremendously until the pressure 1.5 m.m. This increased pressure, of course, decreased the mean free path of the electron to such an extent that the electron never gained over 4.9 volts of energy without colliding with a mercury molecule and giving up its energy. This


Vacuum System
Figure 2
To Discharge Tube
Mac Leod Gauge
To Canco Hyvac
Liquid Air Trap
For freezing out mercury
Argon
Mercury Cutoff
Mercury Vapor Pump

difficulty was overcome by reducing the quantity of mercury present and allowing the electrons to be accelerated over a greater distance before collision. After removing all of the free mercury from the discharge tube we found that the mercury vapor pump furnished far too much by diffusion. We then bought some liquid air at the University of Michigan and placed it on the liquid air trap. This was left for some time before the argon was introduced into the system, allowing time for diffusion of the vapor out of the discharge tube into the trap. The distance between the plate and filament was about 4 m.m. The argon was introduced until there was a pressure of 1 m.m. The plate voltage was adjusted to about 180 volts and the plate current to 300 milliamperes. Under these conditions a Cramer contrast plate was exposed for six minutes. A pocket spectroscope was used by the operator to observe the nature of the emitted light. At this time a strong argon spectrum stood out superimposed upon the mercury spectrum. The next exposure was made with the same conditions except that the plate voltage was reduced to 40 volts. The second gave practically the same result as the first. Other trials were made with lower argon pressure but with a different result. The plates were then developed and placed on a comparator where the distance between lines could be accurately measured. From their distance from known lines the wave length could be computed.

## PART IV

## RESULTS

In the region between the filament and the plate where these accelerated electrons are bombarding the mercury and argon atoms, we will find the following;

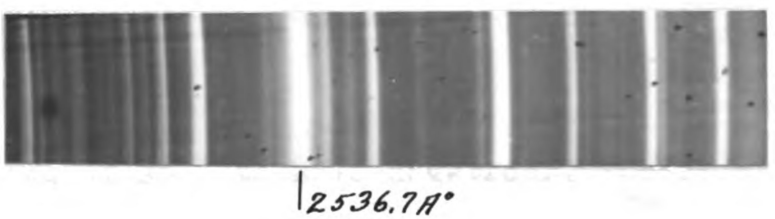
1. Excited mercury atoms with 4.9 volts of energy,
2. Ionized mercury atoms with 10.392 volts of energy,
3. Neutral mercury atoms,
4. Excited argon atoms with 11.5 volts of energy,
5. Ionized argon atoms with 15.2 volts of energy,
6. Neutral argon atoms,
7. Free electrons.

There will be collisions between any two of these seven. As this investigation is interested in the particular impact when ionized argon containing 15.2 volts of energy collides with a neutral atom and robs the mercury of one electron and still possess 4.808 volts, we must, however, consider what the other impacts will do. We must find the mercury spectrum which is emitted whenever an excited atom returns to its normal state or a mercury ion picks up a free electron. We must also find the argon spectrum which is given off when an excited argon atom returns to its normal state. However, there is a second means by which the excited argon may dissipate its energy and that is by impacts with a neutral mercury atom.

PLATE 1


Spectrum of pure mercury


Spectrum of argon and mercury mixed




Spectrum of argon and mercury mixed

The excited argon contains 11.5 volts and will ionize the mercury and still have 1.108 volts of excess energy to radiate. This small quantity of energy, when radiated, produces a line way down in the infra-red and hence cannot be observed on this apparatus. The argon spectrum is further quenched by any impacts between argon ions and mercury atoms. This all decreases the intensity of the argon spectrum, but it will faintly appear.

On Plate 1. are shown three spectra taken on the small quartz spectrograph. Figure 1. is the spectrum of pure mercury obtained from a lab. arc. Figure 2. is the spectrum of argon and mercury mixed in the proper proportions and shows the line 2545 angstroms. Figure 3. is the spectrum of argon and mercury mixed, in which the mean free path of the electrons was too short and the mercury pressure was too great. These two factors reduce the probability of an ionization of argon, and hence decrease the chance for an impact between an argon ion and a neutral mercury atom.

Chart 1. is the data taken from the comparator in which I measured the distance between the lines on the plate in the region of 2536 to 2575 angstroms. Chart 1, is is clear has no line which has a difference in distance from the 2536.7 line of mercury of 26 to 29 scale divisions. Yet as shown in Charts 2, 3, and 4, when I measured the lines in the region of 2536.7 I find a line that is 26 to 29 scale divisions away from the resonant line of mercury. This stray line has a wave-

length of 2545 angstroms and is not easily classified as an argon line. The appearence of this 2545 angstrom line, some people would say, gives unquestionable proof that the excess energy from an impact between an argon ion and a neutral mercury atom goes into radiation, while others would only concede that it is strong evidence for the theory that the excess energy goes into radiation instead of kinetic energy of translation of the two atoms.

The second phase of this investigation is fundamentally important. At the present time the exact and correct value for the ionizing potential of argon is not known. Values have been obtained from 15.0 to 15.7 volts. This experiment opens a very good way of determining the ionization potential of argon. The line 2545 is equivalent to energy of 4.813 volts. This quantity of energy added to the known ionization potential of mercury which is 10.392 volts from spectroscopic evidence, gives a total of 15.205 volts which would be the new and correct ionization potential of argon.

The third fundamentally important feature of this investigation is the possible prediction of the mechanism of impacts: a feature in the study of atomic structure that has not been dealt with to any great extent. I refer to the previous discussion on mechanism of impacts, where I developed the different possibilities and their results. This experiment quite decisively selects one as the possible mechanism

by which two atoms can collide and transfer their energies. It is quite clear that in order to produce this line 2545 the two electron configurations must intermingle and at some instant an electron originally in the mercury configuration, must find itself in an unstable position with respect to the argon. It then emits this 4.813 volts of energy and lands in a stable normal position in the argon atom.

Comparator Data from Plate $(5\text{-}12\text{-}28)_B$

Exposure no. 1

Plate voltage of 150 volts.

Plate current 300 M.A.

Time of exposure 6 minutes.

High argon pressure. Spectrograph focused between the filament and plate.

| Readings | Average Reading | Difference | Wave-Length |
|---|---|---|---|
| 2091, 2080, 2083, 2083, 2088, 2087, 2083, 2083,. | 2083.7 | | 2536.7 |
| 2055, 2055, 2055, 2058, 2058, 2056,. | 2057.4 | 26.3 | 2545.1 |
| 2034, 2033, 2036, 2033, 2033, 2034, 2033, 2034,. | 2033 | 48.7 | 2552 |
| 1997, 1995, 1994, 1996, 1995 1996,. | 1995.5 | 88.2 | 2564.2 |
| 1940, 1939, 1938, 1940, 1940,. | 1939.5 | 144.2 | 2581.5 |

Comparator Data from Plate $(5\text{-}12\text{-}28)_B$

Exposure no. 2

Plate voltage of 40 volts.

Plate current 300 M.A.

Time of exposure 5 minutes.

High argon pressure. Spectrograph focused between the filament and plate.

| Readings | Average Reading | Difference | Wave-Length |
|---|---|---|---|
| 1980, 1980, 1984, 1985, 1984,. | 1984.5 | | 2536.7 |
| 1954, 1955, 1956, 1956, 1957, 1954, 1955,. | 1955.4 | 29.1 | 2545.9 |
| 1937.5, 1937, 1938, 1937, 1937,. | 1937.3 | 47.2 | 2552 |
| 1897, 1897.5, 1897,. | 1897 | 87.5 | 2564 |
| 1845, 1844, 1844, 1844, 1846, 1846, 1845,. | 1845 | 139.5 | 2580 |

Comparator Data from Plate $(5\text{-}11\text{-}28)_B$

Exposure no. 4

Plate voltage of 180 V

Plate current 550 M.A.

Time of exposure 5 minutes.

High argon pressure. Spectrograph focused between the filament and plate.

| Readings | Average Readings | Difference | Wave-Length |
|---|---|---|---|
| 2360, 2357, 2364, 2360, 2358, 2358, 2365,. | 2360 | | 2536.7 |
| 2390, 2388, 2389,. | 2389 | 28.7 | 2545.8 |
| 2411, 2410, 2411, 2410 | 2410.6 | 50.3 | 2552 |
| 2447, 2446, 2446.4, 2447,. | 2446.6 | 86.3 | 2563.6 |
| 2495, 2495, 2494, 2495,. | 2495 | 134.7 | 2577.4 |

Comparator Data from Lab. Arc.

Pure mercury spectrum.

| Readings | Average Readings | Difference | Wave-Length |
|---|---|---|---|
| 2135, 2150, 2132, 2124, 2125, 2134, 2132, 2148, 2132,. | 2134.7 | | 2536.7 |
| 2087, 2086, 2087.5, 2087.5,. | 2087 | 47.7 | 2552 |
| 2043, 2043, 2044, 2043, 2043,. | 2043.3 | 91.4 | 2565 |
| 2007, 2007, 2007,. | 2007 | 127.7 | 2576 |
| 1992, 1992, 19905, 1992,. | 1992 | 142.7 | 2581 |
| 1985, 1985, 1985,. | 1985 | 149.7 | 2583 |

The energy of an electron falling through one volt.

Potential x charge = energy

$\frac{\text{Volts}}{300}$ x e in e.s.u. = ergs

$\frac{1}{300}$ x $4.774 \times 10^{-12}$ ergs.

Velocity of an electron falling through one volt.

$\frac{1}{2}mv^2 = 1.59 \times 10^{-12}$

$$v^2 = \frac{2 \times 1.59 \times 10^{-12}}{9.04 \times 10^{-28}} = 3.517 \times 10^{12}$$

$$v = 3.517 \times 10^{6} \text{ cm/sec.}$$

From Einstein we have that

$$h\nu = \Delta E = 1.59 \times 10^{-12}$$

$$h c \bar{\nu} = 1.59 \times 10^{-12}$$

$\bar{\nu}$ = wave number to 1 volt.

$$\bar{\nu} = \frac{1.59 \times 10^{-12}}{2.99 \times 10^{-10}} \times 6.55 \times 10^{-27} = 8153$$

The change in relative velocity of the two atoms if this excess energy of 4.808 volts went into kinetic energy.

$$\frac{V}{300} \times e = \frac{1}{2}mv^2$$

$$\frac{4.808}{300} \times 4.774 \times 10^{-10} = \frac{1}{2}(1.6 \times 200 + 1.6 \times 40) \times 10^{-24} v^2$$

$$v^2 = \frac{7.65}{192} \times 10^{12} = .03984 \times 10^{12} = 3.984 \times 10^{10}$$

$$v = 1.996 \times 10^{5} \text{ cm./sec.}$$

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