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## THE ELECTRON

# THE ELECTRON

ITS ISOLATION AND MEASUREMENT AND THE  
DETERMINATION OF SOME OF  
ITS PROPERTIES

By

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TO  
ALBERT A. MICHELSON  
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THIS SMALL OUTGROWTH OF THEIR  
INSPIRATION AND GENEROSITY  
IS RESPECTFULLY DEDICATED

## PREFACE

It is hoped that this volume may be of some interest both to the physicist and to the reader of somewhat less technical training. It has been thought desirable for the sake of both classes of readers, not to break the thread of the discussion in the body of the book with the detailed analyses which the careful student demands. It is for this reason that all mathematical proofs have been thrown into appendixes. If, in spite of this, the general student finds certain chapters, such as vii and viii, unintelligible, it is hoped that without them he may yet gain some idea of certain phases at least of the progress of modern physics.

R. A. MILLIKAN

May 18, 1917

## PREFACE TO THE SECOND EDITION

In the present edition of this book I have endeavored to present a simple treatment of all the developments in physics to date which have caused a modification or extension of any of the viewpoints expressed just seven years ago. In its preparation I have been very much impressed to find how uniformly the changes represent additions rather than subtractions—a striking illustration of the great truth that science, like a plant, grows in the main by the process of accretion. If I have succeeded in interesting some old friends and making a few new ones for one of the most fascinating of subjects, I shall be content.

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May 18, 1924

# CONTENTS

	PAGE
INTRODUCTION . . . . .	I
CHAPTER	
I. EARLY VIEWS OF ELECTRICITY . . . . .	6
II. THE EXTENSION OF THE ELECTROLYTIC LAWS TO CONDUCTION IN GASES . . . . .	25
III. EARLY ATTEMPTS AT THE DIRECT DETERMINATION OF $e$ . . . . .	45
IV. GENERAL PROOF OF THE ATOMIC NATURE OF ELECTRICITY . . . . .	66
V. THE EXACT EVALUATION OF $e$ . . . . .	90
VI. THE MECHANISM OF IONIZATION OF GASES BY X-RAYS AND RADIIUM RAYS . . . . .	125
VII. BROWNIAN MOVEMENTS IN GASES . . . . .	145
VIII. IS THE ELECTRON ITSELF DIVISIBLE? . . . . .	158
IX. THE STRUCTURE OF THE ATOM . . . . .	182
X. THE NATURE OF RADIANT ENERGY . . . . .	232
APPENDIX A. $ne$ FROM MOBILITIES AND DIFFUSION COEFFICIENTS . . . . .	262
APPENDIX B. TOWNSEND'S FIRST ATTEMPT AT A DETERMINATION OF $e$ . . . . .	265
APPENDIX C. THE BROWNIAN-MOVEMENT EQUATION . . . . .	268
APPENDIX D. THE INERTIA OR MASS OF AN ELECTRICAL CHARGE ON A SPHERE OF RADIUS $a$ . . . . .	272

	PAGE
APPENDIX E. MOLECULAR CROSS-SECTION AND MEAN FREE PATH . . . . .	275
APPENDIX F. NUMBER OF FREE POSITIVE ELECTRONS IN THE NUCLEUS OF AN ATOM BY RUTHERFORD'S METHOD . . . . .	277
APPENDIX G. BOHR'S THEORETICAL DERIVATION OF THE VALUE OF THE RYDBERG CONSTANT . . . . .	282
APPENDIX H. A. H. COMPTON'S THEORETICAL DERIVA- TION OF THE CHANGE IN THE WAVE-LENGTH OF ETHER-WAVES BECAUSE OF SCATTERING BY FREE ELECTRONS . . . . .	284
APPENDIX I. THE ELEMENTS, THEIR ATOMIC NUMBERS, ATOMIC WEIGHTS, AND CHEMICAL POSITIONS . . . . .	286
INDEXES . . . . .	289

## INTRODUCTION

Perhaps it is merely a coincidence that the man who first noticed that the rubbing of amber would induce in it a new and remarkable state now known as the state of *electricity* was also the man who first gave expression to the conviction that there must be some great unifying principle which links together all phenomena and is capable of making them rationally intelligible; that behind all the apparent variety and change of things there is some primordial element, out of which all things are made and the search for which must be the ultimate aim of all natural science. Yet if this be merely a coincidence, at any rate to Thales of Miletus must belong a double honor. For he first correctly conceived and correctly stated, as far back as 600 B.C., the spirit which has actually guided the development of physics in all ages, and he also first described, though in a crude and imperfect way, the very phenomenon the study of which has already linked together several of the erstwhile isolated departments of physics, such as radiant heat, light, magnetism, and electricity, and has very recently brought us nearer to the primordial element than we have ever been before.

Whether this perpetual effort to reduce the complexities of the world to simpler terms, and to build up the infinite variety of objects which present themselves to our senses out of different arrangements or motions of the least possible number of elementary substances, is a



modern heritage from Greek thought, or whether it is a native instinct of the human mind may be left for the philosopher and the historian to determine. Certain it is, however, that the greatest of the Greeks aimed at nothing less than the complete banishment of caprice from nature and the ultimate reduction of all her processes to a rationally intelligible and unified system. And certain it is also that the periods of greatest progress in the history of physics have been the periods in which this effort has been most active and most successful.

Thus the first half of the nineteenth century is unquestionably a period of extraordinary fruitfulness. It is at the same time a period in which for the first time men, under Dalton's lead, began to get direct, experimental, quantitative proof that the atomic world which the Greeks had bequeathed to us, the world of Leucippus and Democritus and Lucretius, consisting as it did of an infinite number and variety of atoms, was far more complex than it needed to be, and that by introducing the idea of molecules built up out of different combinations and groupings of atoms the number of necessary elements could be reduced to but about seventy. The importance of this step is borne witness to by the fact that out of it sprang in a very few years the whole science of modern chemistry.

And now this twentieth century, though but twenty-four years old, has already attempted to take a still bigger and more significant step. By superposing upon the molecular and the atomic worlds of the nineteenth century a third electronic world, it has sought to reduce the number of primordial elements to not more than two, namely, positive and negative electrical charges. Along

with this effort has come the present period of most extraordinary development and fertility—a period in which new viewpoints and indeed wholly new phenomena follow one another so rapidly across the stage of physics that the actors themselves scarcely know what is happening—a period too in which the commercial and industrial world is adopting and adapting to its own uses with a rapidity hitherto altogether unparalleled the latest products of the laboratory of the physicist and the chemist. As a consequence, the results of yesterday's researches, designed for no other purpose than to add a little more to our knowledge of the ultimate structure of matter, are today seized upon by the practical business world and made to multiply tenfold the effectiveness of the telephone or to extract six times as much light as was formerly obtained from a given amount of electric power.

It is then not merely a matter of academic interest that electricity has been proved to be atomic or granular in structure, that the elementary electrical charge has been isolated and accurately measured, and that it has been found to enter as a constituent into the making of all the seventy-odd atoms of chemistry. These are indeed matters of fundamental and absorbing interest to the man who is seeking to unveil nature's inmost secrets, but they are also events which are pregnant with meaning for the man of commerce and for the worker in the factory. For it usually happens that when nature's inner workings have once been laid bare, man sooner or later finds a way to put his brains inside the machine and to drive it whither he wills. Every increase in man's knowledge of the way in which nature works must, in the long run, increase by just so much man's ability to

control nature and to turn her hidden forces to his own account.

The purpose of this volume is to present the evidence for the atomic structure of electricity, to describe some of the most significant properties of the elementary electrical unit, the electron, and to discuss the bearing of these properties upon the two most important problems of modern physics: the structure of the atom and the nature of electromagnetic radiation. In this presentation I shall not shun the discussion of exact quantitative experiments, for it is only upon such a basis, as Pythagoras asserted more than two thousand years ago, that any real scientific treatment of physical phenomena is possible. Indeed, from the point of view of that ancient philosopher, the problem of all natural philosophy is to drive out qualitative conceptions and to replace them by quantitative relations. And this point of view has been emphasized by the farseeing throughout all the history of physics clear down to the present. One of the greatest of modern physicists, Lord Kelvin, writes:

When you can measure what you are speaking about and express it in numbers, you know something about it, and when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind. It may be the beginning of knowledge, but you have scarcely in your thought advanced to the stage of a science.

Although my purpose is to deal mostly with the researches of which I have had most direct and intimate knowledge, namely, those which have been carried on during the past fifteen years in this general field, first in the Ryerson Laboratory at the University of Chicago, and later at the Norman Bridge Laboratory of Physics at

the California Institute at Pasadena, I shall hope to be able to give a correct and just review of the preceding work out of which these researches grew, as well as of parallel work carried on in other laboratories. In popular writing it seems to be necessary to link every great discovery, every new theory, every important principle, with the name of a single individual. But it is an almost universal rule that developments in physics actually come about in a very different way. A science, like a plant, grows in the main by a process of infinitesimal accretion. Each research is usually a modification of a preceding one; each new theory is built like a cathedral through the addition by many builders of many different elements. This is pre-eminently true of the electron theory. It has been a growth, and I shall endeavor in every case to trace the pedigree of each research connected with it.

## CHAPTER I

## EARLY VIEWS OF ELECTRICITY

## I. GROWTH OF THE ATOMIC THEORY OF MATTER

There is an interesting and instructive parallelism between the histories of the atomic conception of matter and the atomic theory of electricity, for in both cases the ideas themselves go back to the very beginnings of the subject. In both cases too these ideas remained absolutely sterile until the development of precise quantitative methods of measurement touched them and gave them fecundity. It took two thousand years for this to happen in the case of the theory of matter and one hundred and fifty years for it to happen in the case of electricity; and no sooner had it happened in the case of both than the two domains hitherto thought of as distinct began to move together and to appear as perhaps but different aspects of one and the same phenomenon, thus recalling again Thales' ancient belief in the essential unity of nature. How this attempt at union has come about can best be seen by a brief review of the histories of the two ideas.

The conception of a world made up of atoms which are in incessant motion was almost as clearly developed in the minds of the Greek philosophers of the School of Democritus (420 B.C.), Epicurus (370 B.C.), and Lucretius (Roman, 50 B.C.) as it is in the mind of the modern physicist, but the idea had its roots in one case in a mere speculative philosophy; in the other case, like most of

our twentieth-century knowledge, it rests upon direct, exact, quantitative observations and measurement. Not that the human eye has ever seen or indeed can ever see an individual atom or molecule. This is forever impossible, and for the simple reason that the limitations on our ability to see small objects are imposed, not by the imperfections of our instruments, but by the nature of the eye itself, or by the nature of the light-wave to which the eye is sensitive. If we are to see molecules our biological friends must develop wholly new types of eyes, viz., eyes which are sensitive to waves one thousand times shorter than those to which our present optic nerves can respond.

But after all, the evidence of our eyes is about the least reliable kind of evidence which we have. We are continually seeing things which do not exist, even though our habits are unimpeachable. It is the relations which are seen by the mind's eye to be the logical consequences of exact measurement which are for the most part dependable. So far as the atomic theory of matter is concerned, these relations have all been developed since 1800, so that both the modern atomic and the modern kinetic theories of matter, in spite of their great antiquity, are in a sense less than one hundred years old. Indeed, nearly all of our definite knowledge about molecules and atoms has come since 1851, when Joule<sup>1</sup> in England made the first absolute determination of a molecular magnitude, namely, the average speed with which gaseous molecules of a given kind are darting hither and thither at ordinary temperatures. This

<sup>1</sup> *Mem. of the Manchester Lit. and Phil. Soc.* (1851; 2d series), 107; *Phil. Mag.*, XIV (1857), 211.

result was as surprising as many others which have followed in the field of molecular physics, for it showed that this speed, in the case of the hydrogen molecule, has the stupendous value of about a mile a second. The second molecular magnitude to be found was the mean distance a molecule of a gas moves between collisions, technically called the mean free path of a molecule. This was computed first in 1860 by Clerk Maxwell.<sup>1</sup> It was also 1860 before anyone had succeeded in making any sort of an estimate of the number of molecules in a cubic centimeter of a gas. When we reflect that we can now count this number with probably greater precision than we can attain in determining the number of people living in New York, in spite of the fact that it has the huge value of 27.05 billion billion, one gains some idea of how great has been our progress in mastering some at least of the secrets of the molecular and atomic worlds. The wonder is that we got at it so late. Nothing is more surprising to the student brought up in the atmosphere of the scientific thought of the present than the fact that the relatively complex and intricate phenomena of light and electromagnetism had been built together into moderately consistent and satisfactory theories long before the much simpler phenomena of heat and molecular physics had begun to be correctly understood. And yet almost all the qualitative conceptions of the atomic and kinetic theories were developed thousands of years ago. Tyndall's statement of the principles of Democritus, whom Bacon considered to be "a man of mightier metal than

<sup>1</sup> *Phil. Mag.*, XIX (1860; 4th series), 28. Clausius had discussed some of the relations of this quantity in 1858 (*Pogg. Ann.*, CV [1858], 239), but Maxwell's magnificent work on the viscosity of gases first made possible its evaluation.

Plato or Aristotle, though their philosophy was noised and celebrated in the schools amid the din and pomp of professors," will show how complete an atomic philosophy had arisen 400 years B.C. "That it was entirely destroyed later was not so much due to the attacks upon it of the idealistic school, whose chief representatives were Plato and Aristotle, as to the attacks upon all civilization of Genseric, Attila, and the barbarians." That the Aristotelian philosophy lasted throughout this period is explained by Bacon thus: "At a time when all human learning had suffered shipwreck these planks of Aristotelian and Platonic philosophy, as being of a lighter and more inflated substance, were preserved and came down to us, while things more solid sank and almost passed into oblivion."

Democritus' principles, as quoted by Tyndall, are as follows:

1. From nothing comes nothing. Nothing that exists can be destroyed. All changes are due to the combination and separation of molecules.
2. Nothing happens by chance. Every occurrence has its cause from which it follows by necessity.
3. The only existing things are the atoms and empty space; all else is mere opinion.
4. The atoms are infinite in number and infinitely various in form; they strike together and the lateral motions and whirlings which thus arise are the beginnings of worlds.
5. The varieties of all things depend upon the varieties of their atoms, in number, size, and aggregation.
6. The soul consists of fine, smooth, round atoms like those of fire. These are the most mobile of all. They interpenetrate the whole body and in their motions the phenomena of life arise.

These principles with a few modifications and omissions might almost pass muster today. The great advance which has been made in modern times is not so

much in the conceptions themselves as in the kind of foundation upon which the conceptions rest. The principles enumerated above were simply the opinions of one man or of a school of men. There were scores of other rival opinions, and no one could say which was the better. Today there is absolutely no philosophy in the field other than the atomic philosophy, at least among physicists. Yet this statement could not have been made even as much as twenty years ago. For in spite of all the multiple relationships between combining powers of the elements, and in spite of all the other evidences of chemistry and nineteenth-century physics, a group of the foremost of modern thinkers, until quite recently, withheld their allegiance from these theories. The most distinguished of this group was the German chemist and philosopher, Wilhelm Ostwald. However, in the preface to the last edition of his *Outlines of Chemistry* he now makes the following clear and frank avowal of his present position. He says:

I am now convinced that we have recently become possessed of experimental evidence of the discrete or grained nature of matter for which the atomic hypothesis sought in vain for hundreds and thousands of years. The isolation and counting of gaseous ions on the one hand . . . and on the other the agreement of the Brownian movements with the requirements of the kinetic hypothesis . . . justify the most cautious scientist in now speaking of the experimental proof of the atomic theory of matter. The atomic hypothesis is thus raised to the position of a scientifically well-founded theory.

## II. GROWTH OF ELECTRICAL THEORIES

The granular theory of electricity, while unlike the atomic and kinetic theories of matter in that it can boast

no great antiquity in any form, is like them in that the first man who speculated upon the nature of electricity at all conceived of it as having an atomic structure. Yet it is only within very recent years—thirty at the most—that the modern electron theory has been developed. There are no electrical theories of any kind which go back of Benjamin Franklin (1750). Aside from the discovery of the Greeks that rubbed amber had the power of attracting to itself light objects, there was no knowledge at all earlier than 1600 A.D., when Gilbert, Queen Elizabeth's surgeon, and a scientist of great genius and insight, found that a glass rod and some twenty other bodies, when rubbed with silk, act like the rubbed amber of the Greeks, and he consequently decided to describe the phenomenon by saying that the glass rod had become electrified (amberized, electron being the Greek word for amber), or, as we now say, had acquired a charge of electricity. In 1733 Dufay, a French physicist, further found that sealing wax, when rubbed with cat's fur, was also electrified, but that it differed from the electrified glass rod, in that it strongly attracted any electrified body which was repelled by the glass, while it repelled any electrified body which was attracted by the glass. He was thus led to recognize two kinds of electricity, which he termed "vitreous" and "resinous." About 1747 Benjamin Franklin, also recognizing these two kinds of electrification, introduced the terms "positive" and "negative," to distinguish them. Thus, he said, we will arbitrarily call any body positively electrified if it is repelled by a glass rod which has been rubbed with silk, and we will call any body negatively electrified if it is repelled by sealing wax which has been rubbed with cat's

fur. *These are today our definitions of positive and negative electrical charges.* Notice that in setting them up we propose no theory whatever of electrification, but content ourselves simply with describing the phenomena.

In the next place it was surmised by Franklin and indeed asserted by him in the very use of the terms "positive" and "negative," although the accurate proof of the relation was not made until the time of Faraday's ice-pail experiment in 1837, that when glass is positively electrified by rubbing it with silk, the silk itself takes up a negative charge of exactly the same amount as the positive charge received by the glass, and, in general, *that positive and negative electrical charges always appear simultaneously and in exactly equal amounts.*

So far, still no theory. But in order to have a rational explanation of the phenomena so far considered, particularly this last one, Franklin now made the assumption that something which he chose to call the electrical fluid or "electrical fire" exists in normal amount as a constituent of all matter in the neutral, or unelectrified state, and that more than the normal amount in any body is manifested as a positive electrical charge, and less than the normal amount as a negative charge. Aepinus, professor of physics at St. Petersburg and an admirer of Franklin's theory, pointed out that, in order to account for the repulsion of two negatively electrified bodies, it was necessary to assume that matter, when divorced from Franklin's electrical fluid, was self-repellent, i.e., that it possessed properties quite different from those which are found in ordinary unelectrified matter. In order, however, to leave matter, whose independent existence was thus threatened, endowed with its familiar old properties,

and in order to get electrical phenomena into a class by themselves, other physicists of the day, led by Symmer, 1759, preferred to assume that *matter in a neutral state shows no electrical properties because it contains as constituents equal amounts of two weightless fluids which they called positive and negative electricity, respectively.* From this point of view a positively charged body is one in which there is more of the positive fluid than of the negative, and a negatively charged body is one in which the negative fluid is in excess.

Thus arose the so-called two-fluid theory—a theory which divorced again the notions of electricity and matter after Franklin had taken a step toward bringing them together. This theory, in spite of its intrinsic difficulties, dominated the development of electrical science for one hundred years and more. This was because, if one did not bother himself much with the underlying physical conception, the theory lent itself admirably to the description of electrical phenomena and also to mathematical formulation. Further, it was convenient for the purposes of classification. It made it possible to treat electrical phenomena in a category entirely by themselves, without raising any troublesome questions as to the relation, for example, between electrical and gravitational or cohesive forces. But in spite of these advantages it was obviously a makeshift. For the notion of two fluids which could exert powerful forces and yet which were absolutely without weight—the most fundamental of physical properties—and the further notion of two fluids which had no physical properties whatever, that is, which disappeared entirely when they were mixed in equal proportions—these notions were in a



high degree non-physical. Indeed, Sir J. J. Thomson remarked in his Silliman Lectures in 1903 that

the physicists and mathematicians who did most to develop the fluid theories confined their attention to questions which involved only the law of forces between electrified bodies and the simultaneous production of equal quantities of plus and minus electricity, and refined and idealized their conception of the fluids themselves until any reference to their physical properties was considered almost indelicate.

From the point of view of economy in hypothesis, Franklin's one-fluid theory, as modified by Aepinus, was the better. Mathematically the two theories were identical. The differences may be summed up thus. The modified one-fluid theory required that matter, when divorced from the electrical fluid, have exactly the same properties which the two-fluid theory ascribed to negative electricity, barring only the property of fluidity. So that the most important distinction between the theories was that the two-fluid theory assumed the existence of three distinct entities, named positive electricity, negative electricity, and matter, while the one-fluid theory reduced these three entities to two, which Franklin called matter and electricity, but which might perhaps as well have been called positive electricity and negative electricity, unelectrified matter being reduced to a mere combination of these two.

Of course, the idea of a granular structure for electricity was foreign to the two-fluid theory, and since this dominated the development of electrical science, there was seldom any mention in connection with it of an electrical atom, even as a speculative entity. But with Franklin the case was different. His theory was essen-

tially a material one, and he unquestionably believed in the existence of an electrical particle or atom, for he says: "The electrical matter consists of particles extremely subtle, since it can permeate common matter, even the densest, with such freedom and ease as not to receive any appreciable resistance." When Franklin wrote that, however, he could scarcely have dreamed that it would ever be possible to isolate and study by itself one of the ultimate particles of the electrical fluid. The atomic theory of electricity was to him what the atomic theory of matter was to Democritus, a pure speculation.

The first bit of experimental evidence which appeared in its favor came in 1833, when Faraday found that the passage of a given quantity of electricity through a solution containing a compound of hydrogen, for example, would always cause the appearance at the negative terminal of the same amount of hydrogen gas irrespective of the kind of hydrogen compound which had been dissolved, and irrespective also of the strength of the solution; that, further, the quantity of electricity required to cause the appearance of one gram of hydrogen would always deposit from a solution containing silver exactly 107.1 grams of silver. This meant, since the weight of the silver atom is exactly 107.1 times the weight of the hydrogen atom, that the hydrogen atom and the silver atom are associated in the solution with exactly the same quantity of electricity. When it was further found in this way that all atoms which are univalent in chemistry, that is, which combine with one atom of hydrogen, carry precisely the same quantity of electricity, and all atoms which are bivalent carry twice

this amount, and, in general, that valency, in chemistry, is always exactly proportional to the quantity of electricity carried by the atom in question, it was obvious that the atomic theory of electricity had been given very strong support.

But striking and significant as were these discoveries, they did not serve at all to establish the atomic hypothesis of the nature of electricity. They were made at the very time when attention began to be directed strongly away from the conception of electricity as a substance of any kind, and it was no other than Faraday himself who, in spite of the brilliant discoveries just mentioned, started this second period in the development of electrical theory, a period lasting from 1840 to about 1900. In this period electrical phenomena are almost exclusively thought of in terms of stresses and strains in the medium which surrounds the electrified body. Up to this time a more or less definite something called a charge of electricity had been thought of as existing *on* a charged body and had been imagined to exert forces on other charged bodies at a distance from it in quite the same way in which the gravitational force of the earth acts on the moon or that of the sun on the earth. This notion of action at a distance was repugnant to Faraday, and he found in the case of electrical forces experimental reasons for discarding it which had not then, nor have they as yet, been found in the case of gravitational forces. These reasons are summed up in the statement that the electrical force between two charged bodies is found to depend on the nature of the intervening medium, while gravitational pulls are, so far as is known, independent of intervening bodies. Faraday, therefore, pictured to himself

the intervening medium as transmitting electrical force in quite the same way in which an elastic deformation started at one end of a rod is transmitted by the rod. Further, since electrical forces act through a vacuum, Faraday had to assume that it is the ether which acts as the transmitter of these electrical stresses and strains. The properties of the ether were then conceived of as modified by the presence of matter in order to account for the fact that the same two charges attract each other with different forces according as the intervening medium is, for example, glass, or ebonite, or air, or merely ether. These views, conceived by Faraday and put into mathematical form by Maxwell, called attention away from the electrical phenomena in or on a conductor carrying electricity and focused it upon the stresses and strains taking place in the medium about the conductor. When in 1886 Heinrich Hertz in Bonn, Germany, proved by direct experiment that electrical forces are indeed transmitted in the form of electric waves, which travel through space with the speed of light exactly as the Faraday-Maxwell theory had predicted, the triumph of the ether-stress point of view was complete. Thereupon textbooks were written by enthusiastic, but none too cautious, physicists in which it was asserted that an electric charge is nothing more than a "state of strain in the ether," and an electric current, instead of representing the passage of anything definite along the wire, corresponds merely to a continuous "slip" or "breakdown of a strain" in the medium within the wire. Sir Oliver Lodge's early book, *Modern Views of Electricity*, was perhaps the most influential disseminator and expounder of this point of view.



Now what had actually been proved was not that electricity is a state of strain, but that when any electrical charge appears upon a body the medium about the body does indeed become the seat of new forces which are transmitted through the medium, like any elastic forces, with a definite speed. Hence it is entirely proper to say that the medium about a charged body is in a state of strain. But it is one thing to say that the electrical charge on the body *produces* a state of strain in the surrounding medium, and quite another thing to say that the electrical charge *is nothing but* a state of strain in the surrounding medium, just as it is one thing to say that when a man stands on a bridge he produces a mechanical strain in the timbers of the bridge, and another thing to say that the man is nothing more than a mechanical strain in the bridge. The practical difference between the two points of view is that in the one case you look for other attributes of the man besides the ability to produce a strain in the bridge, and in the other case you do not look for other attributes. So the strain theory, although not irreconcilable with the atomic hypothesis, was actually antagonistic to it, because it led men to think of the strain as distributed continuously about the surface of the charged body, rather than as radiating from definite spots or centers peppered over the surface of the body. Between 1833 and 1900, then, the physicist was in this peculiar position: when he was thinking of the passage of electricity through a solution, he for the most part, following Faraday, pictured to himself definite specks or atoms of electricity as traveling through the solution, each atom of matter carrying an exact multiple, which might be anywhere between one and eight, of a

definite elementary electrical atom, while, when he was thinking of the passage of a current through a metallic conductor, he gave up altogether the atomic hypothesis, and attempted to picture the phenomenon to himself as a continuous "slip" or "breakdown of a strain" in the material of the wire. In other words, he recognized two types of electrical conduction which were wholly distinct in kind—electrolytic conduction and metallic conduction; and since more of the problems of the physicist dealt with metallic than with electrolytic conduction, the atomic conception, as a general hypothesis, was almost, though not quite, unheard of. Of course it would be unjust to the thinkers of this period to say that they failed to recognize and appreciate this gulf between current views as to the nature of electrolytic and metallic conduction, and simply ignored the difficulty. This they did not do, but they had all sorts of opinions as to the causes. Maxwell himself in his text on *Electricity and Magnetism*, published in 1873, recognizes, in the chapter on "Electrolysis,"<sup>1</sup> the significance of Faraday's laws, and even goes so far as to say that "for convenience in description we may call this constant molecular charge (revealed by Faraday's experiments) one molecule of electricity." Nevertheless, a little farther on he repudiates the idea that this term can have any physical significance by saying that "it is extremely improbable that when we come to understand the true nature of electrolysis we shall retain in any form the theory of molecular charges, for then we shall have obtained a secure basis on which to form a true theory of electric currents and so become independent of these provisional hypotheses."

<sup>1</sup> I, 375-86.

And as a matter of fact, Faraday's experiments had not shown at all that electrical charges on metallic conductors consist of specks of electricity, even though they had shown that the charges on ions in solutions have definite values which are always the same for univalent ions. It was entirely logical to assume, as Maxwell did, that an ion took into solution a definite quantity of electricity because of some property which it had of always charging up to the same amount from a charged plate. There was no reason for assuming the charge *on the electrode* to be made up of some exact number of electrical atoms.

On the other hand, Wilhelm Weber, in papers written in 1871,<sup>1</sup> built up his whole theory of electromagnetism on a basis which was practically identical with the modified Franklin theory and explained all the electrical phenomena exhibited by conductors, including thermoelectric and Peltier effects, on the assumption of two types of electrical constituents of atoms, one of which was very much more mobile than the other. Thus the hypothetical molecular current, which Ampere had imagined fifty years earlier to be continually flowing inside of molecules and thereby rendering these molecules little electromagnets, Weber definitely pictures to himself as the rotation of light, positive charges about heavy negative ones. His words are:

The relation of the two particles as regards their motions is determined by the ratio of their masses  $e$  and  $e'$ , on the assumption that in  $e$  and  $e'$  are included the masses of the ponderable atoms which are attached to the electrical atoms. Let  $e$  be the positive electrical particle. Let the negative be exactly equal and opposite

<sup>1</sup> See *Werke*, IV, 281.

and therefore denoted by  $-e$  (instead of  $e'$ ). But let a ponderable atom be attracted to the latter so that its mass is thereby so greatly increased as to make the mass of the positive particle vanishingly small in comparison. The particle  $-e$  may then be thought of as at rest and the particle  $+e$  as in motion about the particle  $-e$ . The two unlike particles in the condition described constitute then an Amperian molecular current.

It is practically this identical point of view which has been elaborated and generalized by Lorentz and others within the past three decades in the development of the modern electron theory, with this single difference, that we now have experimental proof that it is the negative particle whose mass or inertia is negligible in comparison with that of the positive instead of the reverse. Weber even went so far as to explain thermoelectric and Peltier effects by differences in the kinetic energies in different conductors of the electrical particles.<sup>1</sup> Nevertheless his explanations are here widely at variance with our modern conceptions of heat.

Again, in a paper read before the British Association at Belfast in 1874, G. Johnstone Stoney not only stated clearly the atomic theory of electricity, but actually went so far as to estimate the value of the elementary electrical charge, and he obtained a value which was about as reliable as any which had been found until within quite recent years. He got, as will be more fully explained in the next chapter,  $3 \times 10^{-10}$  absolute electrostatic units, and he got this result from the amount of electricity necessary to separate from a solution one gram of hydrogen, combined with kinetic theory estimates as to the number of atoms of hydrogen in two grams, i.e., in one

<sup>1</sup> *Op. cit.*, p. 294.

gram molecule of that element. This paper was entitled, "On the Physical Units of Nature," and though read in 1874 it was not published in full until 1881.<sup>1</sup> After showing that all physical measurements may be expressed in terms of three fundamental units, he asserts that it would be possible to replace our present purely arbitrary units (the centimeter, the gram, and the second) by three natural units, namely, the velocity of light, the coefficient of gravitation, and the elementary electrical charge. With respect to the last he says:

Finally nature presents us with a single definite quantity of electricity which is independent of the particular bodies acted on. To make this clear, I shall express Faraday's law in the following terms, which, as I shall show, will give it precision, viz.: *For each chemical bond which is ruptured within an electrolyte a certain quantity of electricity traverses the electrolyte which is the same in all cases.* This definite quantity of electricity I shall call  $E_1$ . If we make this our unit of electricity, we shall probably have made a very important step in our study of molecular phenomena.

Hence we have very good reason to suppose that in  $V$ ,  $G$ , and  $E_1$  we have three of a series of systematic units that in an eminent sense are the units of nature, and stand in an intimate relation with the work which goes on in her mighty laboratory.

Take one more illustration from prominent writers of this period. In his Faraday lecture delivered at the Royal Institution in 1881, Helmholtz spoke as follows:

Now the most startling result of Faraday's law is perhaps this, if we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions which behave like atoms of electricity.<sup>2</sup>

<sup>1</sup> *Phil. Mag.*, XI (1881, 5th series), 384.

<sup>2</sup> *Wissenschaftliche Abhandlungen*, III, 69.

This looks like a very direct and unequivocal statement of the atomic theory of electricity, and yet in the same lecture Helmholtz apparently thinks of metallic conduction as something quite different from electrolytic when he says:

All these facts show that electrolytic conduction is not at all limited to solutions of acids or salts. It will, however, be rather a difficult problem to find out how far the electrolytic conduction is extended, and I am not yet prepared to give a positive answer.

The context shows that he thought of extending the idea of electrolytic conduction to a great many insulators. But there is no indication that he thought of extending it to metallic conductors and imagining these electrical atoms as existing as discrete individual things on charged metals or as traveling along a wire carrying an electrical current. Nevertheless, the statement quoted above is one of the most unequivocal which can be found anywhere up to about 1899 as to the atomic nature of electricity.

The foregoing quotations are sufficient to show that the atomic theory of electricity, like the atomic theory of matter, is not at all new so far as the conception alone is concerned. In both cases there were individuals who held almost exactly the modern point of view. In both cases, too, the chief new developments have consisted in the appearance of new and exact *experimental* data which has silenced criticism and compelled the abandonment of other points of view which up to about 1900 flourished along with, and even more vigorously than, the atomic conception. Even in 1897 Lord Kelvin, with a full knowledge of all the new work which was appearing on X-rays and cathode rays, could seriously raise the

question whether electricity might not be a "continuous homogeneous liquid." He does it in these words:

Varley's fundamental discovery of the cathode rays, splendidly confirmed and extended by Crookes, seems to me to necessitate the conclusion that resinous electricity, not vitreous, is *The Electric Fluid*, if we are to have a one-fluid theory of electricity. Mathematical reasons prove that if resinous electricity is a continuous homogeneous liquid it must, in order to produce the phenomena of contact electricity, which you have seen this evening, be endowed with a cohesive quality. It is just conceivable, though it does not at present seem to me very probable, that this idea may deserve careful consideration. I leave it, however, for the present and prefer to consider an atomic theory of electricity foreseen as worthy of thought by Faraday and Clerk-Maxwell, very definitely proposed by Helmholtz in his last lecture to the Royal Institution, and largely accepted by present-day workers and teachers. Indeed Faraday's laws of electrolysis seem to necessitate something atomic in electricity, . . . .<sup>1</sup>

What was the new experimental work which already in 1897 was working this change in viewpoint? Much of it was at first little if at all more convincing than that which had been available since Faraday's time. Nevertheless it set physicists to wondering whether stresses and strains in the ether had not been a bit overworked, and whether in spite of their undoubted existence electricity itself might not after all be something more definite, more material, than the all-conquering Maxwell theory had assumed it to be.

The result of the past twenty-five years has been to bring us back very close to where Franklin was in 1750, with the single difference that our modern electron theory rests upon a mass of very direct and convincing evidence, which it is the purpose of the next chapters to present.

<sup>1</sup> Kelvin, "Contact Electricity and Electrolysis," *Nature*, LVI (1897), 84.

## CHAPTER II

### THE EXTENSION OF THE ELECTROLYTIC LAWS TO CONDUCTION IN GASES

#### I. THE ORIGIN OF THE WORD "ELECTRON"

The word "electron" was first suggested in 1891 by Dr. G. Johnstone Stoney as a name for the "natural unit of electricity," namely, that quantity of electricity which must pass through a solution in order to liberate at one of the electrodes one atom of hydrogen or one atom of any univalent substance. In a paper published in 1891 he says:

Attention must be given to Faraday's Law of Electrolysis, which is equivalent to the statement that in electrolysis a definite quantity of electricity, the same in all cases, passes for each chemical bond that is ruptured. The author called attention to this form of the law in a communication made to the British Association in 1874 and printed in the *Scientific Proceedings of the Royal Dublin Society* of February, 1881, and in the *Philosophical Magazine* for May, 1881, pp. 385 and 386 of the latter. It is there shown that the amount of this very remarkable quantity of electricity is about the twentietheth (that is  $\frac{1}{10^{20}}$ ) of the usual electromagnetic unit of electricity, i.e., the unit of the Ohm series. This is the same as 3 eleventheths ( $\frac{3}{10^{21}}$ ) of the much smaller C.G.S. electrostatic unit of quantity. A charge of this amount is associated in the chemical atom with each bond. There may accordingly be several such charges in one chemical atom, and there appear to be at least two in each atom. These charges, which it will be convenient to call "electrons," cannot be removed from the atom, but they become disguised when atoms chemically unite. If an

electron be lodged at the point  $P$  of the molecule which undergoes the motion described in the last chapter, the revolution of this charge will cause an electromagnetic undulation in the surrounding ether.<sup>1</sup>

It will be noticed from this quotation that the word "electron" was introduced to denote simply a definite elementary quantity of electricity without any reference to the mass or inertia which may be associated with it, and Professor Stoney implies that every atom must contain at least two electrons, one positive and one negative, because otherwise it would be impossible that the atom as a whole be electrically neutral. As a matter of fact the evidence is now altogether convincing that the hydrogen atom does indeed contain just one positive and one negative electron.

It is unfortunate that all writers have not been more careful to retain the original significance of the word introduced by Professor Stoney, for it is obvious that a word is needed which denotes merely the elementary unit of electricity and has no necessary implication as to where that unit is found, to what it is attached, with what inertia it is associated, or whether it is positive or negative in sign; and it is also apparent that the word "electron" is the logical one to associate with this conception. Further, there is no difficulty in retaining this original and derivative significance of the word "electron," and at the same time permitting its common use as a convenient abridgment for "the free negative electron." In other words, in view of the omnipresence of the negative electron in experimental physics and the extreme rarity of

<sup>1</sup> *Scientific Transactions of the Royal Dublin Society*, IV (1891, 11th series), 563.

the isolated positive electron, it may be generally agreed that the negative is understood unless the positive is specified. The case is then in every way identical with that found in the use of the word "man," which serves admirably both to designate the genus "homo" and also to denote the male representative of that genus, the female being then differentiated by the use of a prefix. The terms "electron" and "positive electron" would then be used altogether conveniently precisely as are the terms "man" and "woman." Indeed, the most authoritative writers—Thomson, Rutherford, Campbell, Richardson, etc.—have in fact retained the original significance of the word "electron" instead of using it to denote *solely* the free negative electron, the mass of which is  $1/1,845$  of that of the hydrogen atom. All of these writers in books or articles written since 1913<sup>1</sup> have treated of positive as well as negative electrons, although the mass associated with the former is never less than that of the hydrogen atom. Nor is this altogether logical use confined at all to English. Prentiss has approved it, and Nernst in the 1921 edition of his *Theoretische Chemie*, on pp. 197 and 456, definitely and unambiguously defines the positive and negative electrons, precisely as has been done above, as the elementary positive and negative electrical charges, respectively.

## II. THE DETERMINATION OF $\frac{e}{m}$ AND $N_e$ FROM THE FACTS OF ELECTROLYSIS

Faraday's experiments had of course not furnished the data for determining anything about how much

<sup>1</sup> See particularly Rutherford's presidential address at the recent Liverpool meeting of the British Association, *Science*, LVIII (1923), 213.

electricity an electron represents in terms of the standard unit by which electrical charges are ordinarily measured in the laboratory. This is called the coulomb, and represents the quantity of electricity conveyed in one second by one ampere. Faraday had merely shown that a given current flowing in succession through solutions containing different univalent elements like hydrogen or silver or sodium or potassium would deposit weights of these substances which are exactly proportional to their respective atomic weights. This enabled him to assert that one and the same amount of electricity is associated in the process of electrolysis with an atom of each of these substances. He thought of this charge as carried by the atom, or in some cases by a group of atoms, and called the group with its charge an "ion," that is, a "goer," or "traveler." Just how the atoms come to be charged in a solution Faraday did not know, nor do we know now with any certainty. Further, we do not know how much of the solvent an ion associates with itself and drags with it through the solution. But we do know that when a substance like salt is dissolved in water many of the neutral NaCl molecules are split up by some action of the water into positively charged sodium (Na) ions and negatively charged chlorine (Cl) ions. The ions of opposite sign doubtless are all the time recombining, but others are probably continually forming, so that at each instant there are many uncombined ions. Again, we know that when a water solution of copper sulphate is formed many of the neutral  $\text{CuSO}_4$  molecules are split up into positively charged Cu ions and negatively charged  $\text{SO}_4$  ions. In this last case too we find that the same current which will deposit in a

given time from a silver solution a weight of silver equal to its atomic weight will deposit from the copper-sulphate solution in the same time a weight of copper equal to exactly one-half its atomic weight. Hence we know that the copper ion carries in solution twice as much electricity as does the silver ion, that is, it carries a charge of two electrons.

But though we could get from Faraday's experiments no knowledge about the quantity of electricity,  $e$ , represented by one electron, we could get very exact information about the ratio of the ionic charge  $E$  to the mass of the atom with which it is associated in a given solution.

For, if the whole current which passes through a solution is carried by the ions—and if it were not we should not always find the deposits exactly proportional to atomic weights—then the ratio of the total quantity of electricity passing to the weight of the deposit produced must be the same as the ratio of the charge  $E$  on each ion to the mass  $m$  of that ion. But by international agreement one absolute unit of electricity has been defined in the electromagnetic system of units as the amount of electricity which will deposit from a silver solution 0.01118 grams of metallic silver. Hence if  $m$  refers to the silver ion and  $E$  means the charge on the ion, we have

$$\text{for silver } \frac{E}{m} = \frac{1}{0.01118} = 89.44 \text{ electromagnetic units;}$$

or if  $m$  refers to the hydrogen ion, since the atomic weight of silver is  $\frac{107.88}{1.008}$  times that of hydrogen,

$$\text{for hydrogen } \frac{E}{m} = \frac{1}{0.01118} \times \frac{107.88}{1.008} = 9,573,$$

which is about  $10^4$  electromagnetic units.

Thus in electrolysis  $\frac{E}{m}$  varies from ion to ion, being for univalent ions, for which  $E$  is the same and equal to one electron  $e$ , inversely proportional to the atomic weight of the ion. For polyvalent ions  $E$  may be 2, 3, 4, or 5 electrons, but since hydrogen is at least 7 times lighter than any other ion which is ever found in solution, and its charge is but one electron, we see that the largest value which  $\frac{E}{m}$  ever has in electrolysis is its value for hydrogen, namely, about  $10^4$  electromagnetic units.

Although  $\frac{E}{m}$  varies with the nature of the ion, there is a quantity which can be deduced from it which is a universal constant. This quantity is denoted by  $Ne$ , where  $e$  means as before an electron and  $N$  is the Avogadro constant or the number of molecules in 16 grams of oxygen, i.e., in one gram molecule. We can get this at once from the value of  $\frac{E}{m}$  by letting  $m$  refer to the mass of that imaginary univalent atom which is the unit of our atomic weight system, namely, an atom which is exactly  $1/16$  as heavy as oxygen or  $1/107.88$  as heavy as silver. For such an atom

$$\frac{E}{m} = \frac{e}{m} = \frac{107.88}{0.01118} = 9649.4.$$

Multiplying both numerator and denominator by  $N$  and remembering that for this gas one gram molecule means 1 gram, that is  $Nm=1$ , we have

$$Ne = 9649.4 \text{ absolute electromagnetic units, } \dots\dots\dots (1)$$

and since the electromagnetic unit is equivalent to  $3 \times 10^9$  electrostatic units, we have

$$Ne = 28,948 \times 10^9 \text{ absolute electrostatic units.}$$

Further, since a gram molecule of an ideal gas under standard conditions, i.e., at  $0^\circ \text{C}$ . 76 cm. pressure, occupies 22412 c.c., if  $n$ , represents the number of molecules of such a gas per cubic centimeter at  $0^\circ \text{C}$ ., 76 cm., we have

$$n_e e = \frac{28,948 \times 10^9}{22,412} = 1.292 \times 10^9 \text{ electrostatic units.}$$

Or if  $n$  represent the number of molecules per cubic centimeter at  $15^\circ \text{C}$ . 76 cm., we should have to multiply the last number by the ratio of absolute temperatures, i.e., by  $273/288$  and should obtain then

$$ne = 1.225 \times 10^9 \dots\dots\dots (2)$$

Thus, even though the facts of electrolysis give us no information at all as to how much of a charge one electron  $e$  represents, they do tell us very exactly that if we should take  $e$  as many times as there are molecules in a gram molecule we should get exactly 9,650 absolute electromagnetic units of electricity. This is the amount of electricity conveyed by a current of 1 ampere in 10 seconds. Until quite recently we have been able to make nothing better than rough guesses as to the number of molecules in a gram molecule, but with the aid of these guesses, obtained from the kinetic theory, we have, of course, been enabled by (1) to make equally good guesses about  $e$ . Those guesses, based for the most part on quite uncertain computations as to the average



radius of a molecule of air, placed  $N$  anywhere between  $2 \times 10^3$  and  $20 \times 10^3$ . It was in this way that G. Johnstone Stoney in 1874 estimated  $e$  at  $3 \times 10^{-10}$  E.S. units. In O. E. Meyer's *Kinetische Theorie der Gase* (p. 335; 1899),  $n$ , the number of molecules in a cubic centimeter, is given as  $6 \times 10^{19}$ . This would correspond to  $e = 2 \times 10^{-10}$ . In all this  $e$  is the charge carried by a univalent ion in solution and  $N$  or  $n$  is a pure number, which is a characteristic gas constant, it is true, but the analysis has nothing whatever to do with gas conduction.

### III. THE NATURE OF GASEOUS CONDUCTION

The question whether gases conduct at all, and if so, whether their conduction is electrolytic or metallic or neither, was scarcely attacked until about 1895. Coulomb in 1785 had concluded that after allowing for the leakage of the supports of an electrically charged conductor, some leakage must be attributed to the air itself, and he explained this leakage by assuming that the air molecules became charged by contact and were then repelled—a wholly untenable conclusion, since, were it true, no conductor in air could hold a charge long even at low potentials, nor could a very highly charged conductor lose its charge very rapidly when charged above a certain potential and then when the potential fell below a certain critical value cease almost entirely to lose it. This is what actually occurs. Despite the erroneousness of this idea, it persisted in textbooks written as late as 1900.

Warburg in 1872 experimented anew on air leakage and was inclined to attribute it all to dust particles. The real explanation of gas conduction was not found until

after the discovery of X-rays in 1895. The convincing experiments were made by J. J. Thomson, or at his instigation in the Cavendish Laboratory at Cambridge, England. The new work grew obviously and simply out of the fact that X-rays, and a year or two later radium rays, were found to discharge an electroscope, i.e., to produce conductivity in a gas. Therefore no agencies had been known by which the electrical conductivity of a gas could be controlled at will.

Thomson and his pupils found that the conductivity induced in gases by X-rays disappeared when the gas was sucked through glass wool.<sup>1</sup> It was also found to be reduced when the air was drawn through narrow metal tubes. Furthermore, it was removed entirely by passing the stream of conducting gas between plates which were maintained at a sufficiently large potential difference. The first two experiments showed that the conductivity was due to something which could be removed from the gas by filtration, or by diffusion to the walls of a metal tube; the last proved that this something was electrically charged.

When it was found, further, that the electric current obtained from air existing between two plates and traversed by X-rays rose to a maximum as the P.D. between the plates increased, and then reached a value which was thereafter independent of this potential difference; and, further, that this conductivity of the air died out slowly through a period of several seconds when the X-ray no longer acted, it was evident that the qualitative proof was complete that gas conduction must be due to charged particles produced in the

<sup>1</sup> J. J. Thomson and E. Rutherford, *Phil. Mag.*, XLII (1896), 302.



air at a definite rate by a constant source of X-rays, and that these charged particles, evidently of both plus and minus signs, disappear by recombination when the rays are removed. The maximum or *saturation* currents which could be obtained when a given source was ionizing the air between two plates whose potential difference could be varied were obviously due to the fact that when the electric field between the plates became strong enough to sweep all the ions to the plates as fast as they were formed, none of them being lost by diffusion or recombination, the current obtained could, of course, not be increased by further increase in the field strength. Thus gas conduction was definitely shown about 1896 to be electrolytic in nature.

#### IV. COMPARISON OF THE GASEOUS ION AND THE ELECTROLYTIC ION

But what sort of ions were these that were thus formed? We did not know the absolute value of the charge on a univalent ion in electrolysis, but we did know accurately *ne*. Could this be found for the ions taking part in gas conduction? That this question was answered affirmatively was due to the extraordinary insight and resourcefulness of J. J. Thomson and his pupils at the Cavendish Laboratory in Cambridge, both in working out new theoretical relations and in devising new methods for attacking the new problems of gaseous conduction. These workers found first a method of expressing the quantity *ne* in terms of two measurable constants, called (1) the mobility of gaseous ions and (2) the coefficient of diffusion of these ions. Secondly, they devised new methods of measuring these two

constants—constants which had never before been determined. The theory of the relation between these constants and the quantity *ne* will be found in Appendix A. The result is

$$ne = \frac{e}{D} P \dots\dots\dots (3)$$

in which *P* is the pressure existing in the gas and *e*, and *D* are the mobility and the diffusion coefficients respectively of the ions at this pressure.

If then we can find a way of measuring the mobilities *e* of atmospheric ions and also the diffusion coefficients *D*, we can find the quantity *ne*, in which *n* is a mere number, viz., the number of molecules of air per cubic centimeter at 15° C., 76 cm. pressure, and *e* is the average charge on an atmosphere ion. We shall then be in position to compare this with the product we found in (2) on p. 31, in which *n* had precisely the same significance as here, but *e* meant the average charge carried by a univalent ion in electrolysis.

The methods devised in the Cavendish Laboratory between 1897 and 1903 for measuring the mobilities and the diffusion coefficients of gaseous ions have been used in all later work upon these constants. The mobilities were first determined by Rutherford in 1897,<sup>1</sup> then more accurately by another method in 1898.<sup>2</sup> Zeleny devised a quite distinct method in 1900,<sup>3</sup> and Langevin still another method in 1903.<sup>4</sup> These observers all agree closely in finding the average mobility (velocity in unit

<sup>1</sup> *Phil. Mag.*, XLIV (1898), 422.

<sup>2</sup> *Proc. Camb. Phil. Soc.*, IX, 401.

<sup>3</sup> *Phil. Trans.*, A 195, p. 193.

<sup>4</sup> *Annale de Chimie et de Physique*, XXVIII, 289.

field) of the negative ion in dry air about 1.83 cm. per second, while that of the positive ion was found but 1.35 cm. per second. In hydrogen these mobilities were about 7.8 cm. per second and 6.1 cm. per second, respectively, and in general the mobilities in different gases, though not in vapors, seem to be roughly in the inverse ratio of the square roots of the molecular weights.

The diffusion coefficients of ions were first measured in 1900 by Townsend, now professor of physics in Oxford, England,<sup>1</sup> by a method devised by him and since then used by other observers in such measurements. If we denote the diffusion coefficient of the positive ion by  $D+$  and that of the negative by  $D-$ , Townsend's results in dry air may be stated thus:

$$D+ = 0.028$$

$$D- = 0.043.$$

These results are interesting in two respects. In the first place, they seem to show that for some reason the positive ion in air is more sluggish than the negative, since it travels but about 0.7 ( $= 1.35/1.81$ ) as fast in a given electrical field and since it diffuses through air but about 0.7 ( $= 28/43$ ) as rapidly. In the second place, the results of Townsend show that an ion is very much more sluggish than is a molecule of air, for the coefficient of diffusion of oxygen through air is 0.178, which is four times the rate of diffusion of the negative ion through air and five times that of the positive ion. This sluggishness of ions as compared with molecules was at first universally considered to mean that the gaseous ion is not a single molecule with an attached electrical charge, but

<sup>1</sup> Phil. Trans., A 193, p. 129.

a cluster of perhaps from three to twenty molecules held together by such a charge. If this is the correct interpretation, then for some reason the positive ion in air is a larger cluster than is the negative ion.

It has been since shown by a number of observers that the ratio of the mobilities of the positive and negative ions is not at all the same in other gases as it is in air. In carbon dioxide the two mobilities have very nearly the same value, while in chlorine, water vapor, and the vapor of alcohol the positive ion apparently has a slightly larger mobility than the negative. There seems to be some evidence that the negative ion has the larger mobility in gases which are electro-positive, while the positive has the larger mobility in the gases which are strongly electro-negative. This dependence of the ratio of mobilities upon the electro-positive or electro-negative character of the gas has usually been considered strong evidence in favor of the cluster-ion theory.

Very recently, however, Loeb,<sup>1</sup> who has worked at the Ryerson Laboratory on mobilities in powerful electric fields, and Wellish,<sup>2</sup> who, at Yale, has measured mobilities at very low pressures, have concluded that their results are not consistent with the cluster-ion theory, but must rather be interpreted in terms of the so-called Atom-ion Theory. This theory seeks to explain the relative sluggishness of ions, as compared with molecules, by the additional resistance which the gaseous medium offers to the motion of a molecule through it when that

<sup>1</sup> Leonard B. Loeb, *Proc. Nat. Acad.*, II (1916), 345, and *Phys. Rev.*, 1917.

<sup>2</sup> Wellish, *Amer. Jour. of Science*, XXXIX (1915), 583.

molecule is electrically charged. According to this hypothesis, the ion would be simply an electrically charged molecule.

So far as the negative ion is concerned, the situation at the moment seems to be in favor of the atom-ion theory. There has recently developed strong evidence<sup>1</sup> that although in some very pure gases, such as helium, argon, and even nitrogen, the negative electron cannot find attachment at all, when it does attach so as to form ions of the mobility mentioned above, it carries with it thereafter but a single molecule.

On the other hand, Erikson<sup>2</sup> and Wahlm<sup>3</sup> have apparently shown quite conclusively that if the mobility of the positive ion in air is measured within .03 second of the time of its formation, its value is identical with that of the negative, namely, 1.8 cm. per second, while a short time thereafter it has sunk to about 1.4 cm. per second because of the addition of one more molecule, thus forming a very stable two-molecule-ion group.

Fortunately, the quantitative evidence for the electrolytic nature of gas conduction is in no way dependent upon the correctness of either one of the theories as to the nature of the ion. It depends simply upon the comparison of the values of  $ne$  obtained from electrolytic measurements, and those obtained from the substitution in equation (3) of the measured values of  $v_0$  and  $D$  for gaseous ions.

As for these measurements, results obtained by Franck and Westphal,<sup>4</sup> who in 1908 repeated in Berlin

<sup>1</sup> L. B. Loeb, *Jour. Franklin Inst.*, CXCVII (1924), 45.

<sup>2</sup> H. A. Erikson, *Phys. Rev.*, XX (1922), 118.

<sup>3</sup> H. B. Wahlm, *ibid.*, p. 267.

<sup>4</sup> *Verh. der deutsch. phys. Ges.*, XI (1909), 146 and 276.

both measurements on diffusion coefficients and mobility coefficients, agree within 4 or 5 per cent with the results published by Townsend in 1900. According to both of these observers, the value of  $ne$  for the negative ions produced in gases by X-rays, radium rays, and ultra-violet light came out, within the limits of experimental error, which were presumably 5 or 6 per cent, the same as the value found for univalent ions in solutions, namely,  $1.23 \times 10^{10}$  absolute electrostatic units. This result seems to show with considerable certainty that the negative ions in gases ionized by X-rays or similar agencies carry on the average the same charge as that borne by the univalent ion in electrolysis. When we consider the work on the positive ion, our confidence in the inevitableness of the conclusions reached by the methods under consideration is perhaps somewhat shaken. For Townsend found that the value of  $ne$  for the positive ion came out about 14 per cent higher than the value of this quantity for the univalent ion in electrolysis, a result which he does not seem at first to have regarded as inexplicable on the basis of experimental uncertainties in his method. In 1908, however,<sup>1</sup> he devised a second method of measuring the ratio of the mobility and the diffusion coefficient and obtained this time, as before, for the negative ion,  $ne = 1.23 \times 10^{10}$ , but for the positive ion twice that amount, namely,  $2.46 \times 10^{10}$ . From these last experiments he concluded that the positive ions in gases ionized by X-rays carried on the average twice the charge carried by the univalent ion in electrolysis. Franck and Westphal, however, found in their work that Townsend's original value for  $ne$  for the

<sup>1</sup> *Proc. Roy. Soc.*, LXXX (1908), 207.

positive ions was about right, and hence concluded that only about 9 per cent of the positive ions could carry a charge of value  $2e$ . Work which will be described later indicates that neither Townsend's nor Franck and Westphal's conclusions are correct, and hence point to errors of some sort in both methods. But despite these difficulties with the work on positive ions, it should nevertheless be emphasized that Townsend was the first to bring forward strong quantitative evidence (1) that the mean charge carried by the negative ions in ionized gases is the same as the mean charge carried by univalent ions in solutions, and (2) that the mean charge carried by the positive ions in gases has not far from the same value.

But there is one other advance of fundamental importance which came with the study of the properties of gases ionized by X-rays. For up to this time the only type of ionization known was that observed in solution and here it is always some compound molecule like sodium chloride (NaCl) which splits up spontaneously into a positively charged sodium ion and a negatively charged chlorine ion. But the ionization produced in gases by X-rays was of a wholly different sort, for it was observable in pure gases like nitrogen or oxygen, or even in monatomic gases like argon and helium. Plainly, then, the neutral atom even of a monatomic substance must possess minute electrical charges as constituents. Here we had the first direct evidence (1) that an atom is a complex structure, and (2) that electrical charges enter into its make-up. *With this discovery, due directly to the use of the new agency, X-rays, the atom as an ultimate, indivisible thing was gone, and the era of the study of the*

*constituents of the atom began.* And with astonishing rapidity during the past twenty-five years the properties of the subatomic world have been revealed.

Physicists began at once to seek diligently and to find at least partial answers to questions like these:

1. What are the masses of the constituents of the atoms torn asunder by X-rays and similar agencies?
2. What are the values of the charges carried by these constituents?
3. How many of these constituents are there?
4. How large are they, i.e., what volumes do they occupy?
5. What are their relations to the emission and absorption of light and heat waves, i.e., of electromagnetic radiation?
6. Do all atoms possess similar constituents? In other words, is there a primordial subatom out of which atoms are made?

The partial answer to the first of these questions came with the study of the electrical behavior of rarefied gases in so-called vacuum tubes.

This field had been entered and qualitatively explored with amazing insight as early as 1879 by Sir William Crookes, who in describing in that year some of his experiments said:

The phenomena in these exhausted tubes reveal to physical science a new world—a world where matter exists in a fourth state. . . . In studying this fourth state of matter we seem at length to have within our grasp and obedient to our control the little indivisible particles which with good warrant are supposed to constitute the physical basis of the universe.<sup>1</sup>

<sup>1</sup> Fournier d'Albe, *Life of Sir William Crookes*, 1924.

Further, by 1890 Sir Arthur Schuster<sup>1</sup> had gone a step farther and shown how the ratio of the charge to the mass  $\left[\frac{e}{m}\right]$  of these same hypothetical particles might be determined. Indeed he had experimentally evaluated this ratio, obtaining, however, a value very much too small, namely,  $1.1 \times 10^{-6}$  electromagnetic units.

But it was J. J. Thomson<sup>2</sup> who in 1897 first introduced a more reliable method of determining this ratio, namely, one which combines a measurement of the magnetic deflectability of a beam of cathode rays with the electrostatic deflectability of the same beam. The value which he obtained, namely,  $7 \times 10^6$  electromagnetic units, was nearly a thousand times the value of  $\frac{e}{m}$  for the hydrogen ion in solutions. Also since the approximate equality of  $me$  in gases and solutions meant that  $e$  was at least of the same order in both, the only possible conclusion was that the negative ion which appears in discharges in exhausted tubes has a mass, i.e., an inertia, only one-thousandth of the mass of the lightest-known atom, namely, the atom of hydrogen. Later more accurate experiments have fixed the correct value of  $\frac{e}{m}$  for cathode rays at  $1.768 \times 10^7$  electromagnetic units.

Furthermore, J. J. Thomson and after him other experimenters showed that  $\frac{e}{m}$  for the negative carrier is always the same whatever be the nature of the residual gas in the discharge tube. This was an indication of an affirmative answer to the sixth question above—an

<sup>1</sup> *Proc. Roy. Soc.*, XL (1890), 526.

<sup>2</sup> *Phil. Mag.*, XLIV (1897), 298.

indication which was strengthened by Zeeman's discovery in 1897 of the splitting by a magnetic field of a single spectral line into two or three lines; for this, when worked out quantitatively, pointed to the existence *within* the atom of a negatively charged particle which had approximately the same value of  $\frac{e}{m}$ .

The study of  $\frac{e}{m}$  for the *positive* ions in exhausted tubes was first carried out quantitatively by Wien,<sup>1</sup> and was later most elaborately and most successfully dealt with by J. J. Thomson<sup>2</sup> and his pupils at the Cavendish Laboratory. The results of the work of all observers up to date seem to show quite conclusively that  $\frac{e}{m}$  for a positive ion in gases is never larger than its value for the hydrogen ion in electrolysis, and that it varies with different sorts of residual gases just as it is found to do in electrolysis.

In a word, then, the act of ionization in gases appears to consist in the detachment from a neutral atom of one or more negatively charged particles, called by Thomson corpuscles. The residuum of the atom is of course positively charged, and it always carries practically the whole mass of the original atom. The detached corpuscle must soon attach itself, in a gas at ordinary pressure, to a neutral atom, since otherwise we could not account for the fact that the mobilities and the diffusion coefficients of negative ions are usually of the same order of magnitude as those of the positive ions. It is because of this tendency of the parts of the dissociated atom to

<sup>1</sup> W. Wien, *Wied. Ann.*, LXV (1898), 440.

<sup>2</sup> *Rays of Positive Electricity*. London: Longmans, 1913.

form new attachments in gases at ordinary pressure that the inertias of these parts had to be worked out in the rarefied gases of exhausted tubes.

The foregoing conclusions as to the masses of the positive and negative constituents of atoms had all been reached before 1900, mostly by the workers in the Cavendish Laboratory, and subsequent investigation has not modified them in any essential particulars.

The history of the development of our present knowledge of the charges carried by the constituents will be detailed in the next chapters.

### CHAPTER III

#### EARLY ATTEMPTS AT THE DIRECT DETERMINATION OF $e$

Although the methods sketched in the preceding chapters had been sufficient to show that the mean charges carried by ions in gases are the same or nearly the same as the mean charges carried by univalent ions in solution, in neither case had we any way of determining what the absolute value of that mean charge is, nor, indeed, had we any proof even that all the ions of a given kind, e.g., silver or hydrogen, carry the same charge. Of course, the absolute value of  $e$  could be found from the measured value of  $ne$  if only  $n$ , the number of molecules in 1 c.c. of gas under standard conditions, were known. But we had only rough guesses as to this number. These guesses varied tenfold, and none of them were based upon considerations of recognized accuracy or even validity.

#### I. TOWNSEND'S WORK ON $e$

The first attempt at a direct determination of  $e$  was published by Townsend in a paper read before the Cambridge Philosophical Society on February 8, 1897.<sup>1</sup> Townsend's method was one of much novelty and of no little ingenuity. It is also of great interest because it contains all the essential elements of some of the subsequent determinations.

<sup>1</sup> *Proceedings*, IX (1897), 244.

It had been known, even to Laplace and Lavoisier a hundred years before, that the hydrogen gas evolved when a metal dissolves in an acid carries with it an electrical charge. This "natural method" of obtaining a charge on a gas was scarcely studied at all, however, until after the impulse to the study of the electrical properties of gases had been given by the discovery in 1896 that electrical properties can be artificially imparted to gases by X-rays. Townsend's paper appeared within a year of that time. Enright<sup>1</sup> had indeed found that the hydrogen given off when iron is dissolving in sulphuric acid carries with it a positive charge, but Sir Oliver Lodge<sup>2</sup> had urged that it was not the gas itself which carries the charge but merely the spray, for the frictional electrification of spray was a well-known phenomenon. Indeed, it has always been assumed that the gas molecules which rise from the electrodes in electrolysis are themselves neutral. Townsend, however, first showed that some of these molecules are charged, although there are indeed a million million neutral ones for every one carrying a charge. He found that both the oxygen and the hydrogen which appear at the opposite electrodes when sulphuric acid is electrolyzed are positively charged, while when the electrolyte is caustic potash both the oxygen and the hydrogen given off are negative. Townsend's electrolyzing currents were from 12 to 14 amperes. He got in this way many more ions per cubic centimeter than he could produce with X-rays, the total charge per cubic centimeter being as large as  $5 \times 10^{-3}$  electrostatic units.

<sup>1</sup> *Phil. Mag.*, XXIX (1890; 5th series), 56.

<sup>2</sup> *Ibid.*, p. 292; *Nature*, XXXVI, 412.

When these charged gases were bubbled through water they formed a cloud. This cloud could be completely removed by bubbling through concentrated sulphuric acid or any drying agent, but when the gas came out again into the atmosphere of the room it again condensed moisture and formed a stable cloud. Townsend says that "the process of forming the cloud in positive or negative oxygen by bubbling through water, and removing it again by bubbling through sulphuric acid, can be gone through without losing more than 20 or 25 per cent of the original charge on the gas." This means simply that the ions condense the water about them when there is an abundance of moisture in the air, but when the cloud is carried into a perfectly dry atmosphere, such as that existing in a bubble surrounded on all sides by concentrated sulphuric acid, the droplets of water evaporate and leave the charge on a molecule of air as it was at first. The 20 or 25 per cent loss of charge represents the fraction of the droplets with their charges which actually got into contact with and remained in the liquids through which the gas was being bubbled.

In order to find the charge on each ion, Townsend took the following five steps:

1. He assumed that in saturated water vapor each ion condensed moisture about it, so that the number of ions was the same as the number of droplets.
2. He determined with the aid of a quadrant electrometer the total electrical charge per cubic centimeter carried by the gas.
3. He found the total weight of the cloud by passing it through drying tubes and determining the increase in weight of these tubes.



4. He found the average weight of the water droplets constituting the cloud by observing their rate of fall under gravity and computing their mean radius with the aid of a purely theoretical law known as Stokes's Law.

5. He divided the weight of the cloud by the average weight of the droplets of water to obtain the number of droplets which, if assumption 1 is correct, was the number of ions, and he then divided the total charge per cubic centimeter in the gas by the number of ions to find the average charge carried by each ion, that is, to find  $e$ .

A brief description of the way in which these experiments were carried out is contained in Appendix B.

One of the interesting side results of this work was the observation that clouds from negative oxygen fall faster than those from positive oxygen, thus indicating that the negative ions in oxygen act more readily than do the positive ions as nuclei for the condensation of water vapor. This observation was made at about the same time in another way by C. T. R. Wilson,<sup>1</sup> also in the Cavendish Laboratory, and it has played a rather important rôle in subsequent work. Wilson's discovery was that when air saturated with water vapor is ionized by X-rays from radioactive substances and then cooled by a sudden expansion, a smaller expansion is required to make a cloud form about the negative than about the positive ions. Thus when the expansion increased the volume in a ratio between 1.25 and 1.3, only negative ions acted as nuclei for cloudy condensation, while with expansions greater than 1.3 both negatives and positives were brought down.

<sup>1</sup> *Proc. Camb. Phil. Soc.*, IX (1897), 333.

Townsend first obtained by the foregoing method, when he worked with positive oxygen,

$$e = 2.8 \times 10^{-10} \text{ electrostatic units,}$$

and when he worked with negative oxygen,

$$e = 3.1 \times 10^{-10} \text{ electrostatic units.}$$

In later experiments<sup>1</sup> he obtained 2.4 and 2.9, respectively, in place of the numbers given above, but in view of the unavoidable errors, he concluded that the two charges might be considered equal and approximately  $3 \times 10^{-10}$  electrostatic units. Thus he arrived at about the same value for  $e$  as that which was then current because of the kinetic theory estimates of  $n$ , the number of molecules in a cubic centimeter of a gas.

The weak points in this first attempt at a direct determination of  $e$  consisted in: (1) the assumption that the number of ions is the same as the number of drops; (2) the assumption of Stokes's Law of Fall which had never been tested experimentally, and which from a theoretical standpoint might be expected to be in error when the droplets were small enough; (3) the assumption that the droplets were all alike and fell at a uniform rate wholly uninfluenced by evaporation or other causes of change; (4) the assumption of no convection currents in the gas when the rate of fall of the cloud was being measured.

## II. SIR JOSEPH THOMSON'S WORK ON $e$

This first attempt to measure  $e$  was carried out in Professor J. J. Thomson's laboratory. The second attempt was made by Professor Thomson himself<sup>2</sup> by a method

<sup>1</sup> *Ibid.*, p. 345.

<sup>2</sup> *Phil. Mag.*, XLVI (1898), 528.



which resembled Townsend's very closely in all its essential particulars. Indeed, we may set down for Professor Thomson's experiment precisely the same five elements which are set down on p. 47 for Townsend's. The differences lay wholly in step 2, that is, in the way in which the electrical charge per cubic centimeter carried by the gas was determined, and in step 3, that is, in the way in which the total weight of the cloud was obtained. Thomson produced ions in the space *A* (Fig. 1) by an X-ray bulb which ran at a constant rate, and measured first the current which, under the influence of a very weak electromotive force *E*, flows through *A* between the surface of the water and the aluminum plate which closes the top of the vessel. Then if *n'* is the whole number of ions of one sign per cubic centimeter, *n* the velocity of the positive and *v* that of the negative ion under unit electric force, i. e., if *n* and *v* are the mobilities of the positive and negative ions, respectively, then the current *I* per unit area is evidently given by

$$I = n'e(u+v)E \dots \dots \dots (4)$$

*I* and *E* were easily measured in any experiment; *n*+*v* was already known from Rutherford's previous work, so that *n'e*, the charge of one sign per cubic centimeter of gas under the ionizing action of a constant source of X-rays, could be obtained at once from (4). This then simply replaces Townsend's method of obtaining the charge per cubic centimeter on the gas, and in principle the two methods are quite the same, the difference in experimental arrangements being due to the fact that Townsend's ions are of but one sign while Thomson's are of both signs.

Having thus obtained *n'e* of equation (4), Thomson had only to find *n'* and then solve for *e*. To obtain *n'* he proceeded exactly as Townsend had done in letting the ions condense droplets of water about them and weighing the cloud thus formed. But in order to form the cloud, Thomson utilized C. T. R. Wilson's discovery

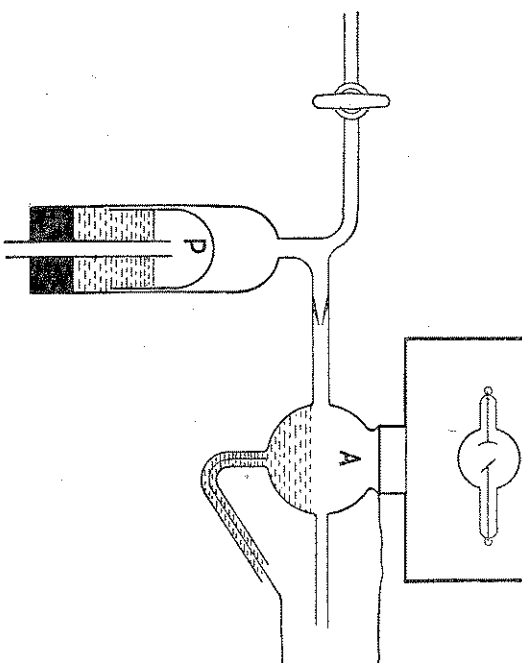


FIG. 1

just touched upon above, that a sudden expansion and consequent cooling of the air in *A* (Fig. 1) would cause the ions in *A* to act as nuclei for the formation of water droplets. To produce this expansion the piston *P* is suddenly pulled down so as to increase the volume of the space above it. A cloud is thus formed about the ions in *A*. Instead of measuring the weight of this cloud directly, as Townsend had done, Thomson computed it by a theoretical consideration of the amount of cooling

produced by the expansion and the known difference between the densities of saturated water vapor at the temperature of the room and the temperature resulting from the expansion. This method of obtaining the weight of the cloud was less direct and less reliable than that used by Townsend, but it was the only one available with Thomson's method of obtaining an ionized gas and of measuring the charge per cubic centimeter on that gas. The average size of the droplets was obtained precisely as in Townsend's work by applying Stokes's Law to the observed rate of fall of the top of the cloud in chamber *A*.

The careful consideration of Thomson's experiment shows that it contains the theoretical uncertainties involved in Townsend's work, while it adds some very considerable experimental uncertainties. The most serious of the theoretical uncertainties arise from (1) the assumption of Stokes's Law, and (2) the assumption that the number of ions is equal to the number of droplets. Both observers sought for some experimental justification for the second and most serious of these assumptions, but subsequent work by H. A. Wilson, by Quincke, and by myself has shown that clouds formed by C. T. R. Wilson's method consist in general of droplets some of which may carry one, some two, some ten, or almost any number of unit charges, and I have never been able, despite quite careful experimenting, to obtain conditions in which it was even approximately true that each droplet carried but a single unit charge. Quincke has recently published results from which he arrives at the same conclusion.<sup>1</sup>

<sup>1</sup> *Verh. der deutsch. phys. Ges.*, XVI (1914), 422.

Again, when we compare the *experimental* uncertainties in Townsend's and Thomson's methods, it is at once obvious that the assumption that the clouds are not evaporating while the rate of fall is being determined is even more serious in Thomson's experiment than in Townsend's, for the reason that in the former case the clouds are formed by a sudden expansion and a consequent fall in temperature, and it is certain that during the process of the return of the temperature to initial conditions the droplets must be evaporating. Furthermore, this sudden expansion makes the likelihood of the existence of convection currents, which would falsify the computations of the radius of the drop from the observed rate of fall, more serious in Thomson's work than in Townsend's. The results which Thomson attained in different experiments gave values ranging from  $5.5 \times 10^{-10}$  to  $8.4 \times 10^{-10}$ . He published as his final value  $6.5 \times 10^{-10}$ . In 1903, however,<sup>1</sup> he published some new work on  $e$  in which he had repeated the determination, using the radiation from radium in place of that from X-rays as his ionizing agent and obtained the result  $e = 3.4 \times 10^{-10}$ . He explained the difference by the assumption that in his preceding work the more active negative ions had monopolized the aqueous vapor available and that the positive ions had not been brought down with the cloud as he had before assumed was the case. He now used more sudden expansions than he had used before, and concluded that the assumption made in the earlier experiments that the number of ions was equal to the number of particles, although shown to be incorrect for the former case, was correct for these

<sup>1</sup> *Phil. Mag.*, V (1903; 6th series), 354.

second experiments. As a matter of fact, if he had obtained only half the ions in the first experiments and all of them in the second, his second result should have come out approximately one-half as great as the first, which it actually did. Although Thomson's experiment was an interesting and important modification of Townsend's, it can scarcely be said to have added greatly to the accuracy of our knowledge of  $e$ .

The next step in advance in the attempt at the determination of  $e$  was made in 1903 by H. A. Wilson,<sup>1</sup> also in the Cavendish Laboratory.

### III. H. A. WILSON'S METHOD

Wilson's modification of Thomson's work consisted in placing inside the chamber  $A$  two horizontal brass plates  $3\frac{1}{2}$  cm. in diameter and from 4 to 10 mm. apart and connecting to these plates the terminals of a 2,000-volt battery. He then formed a negative cloud by a sudden expansion of amount between 1.25 and 1.3, and observed first the rate of fall of the top surface of this cloud between the plates when no electrical field was on; then he repeated the expansion and observed the rate of fall of the cloud when the electrical field as well as gravity was driving the droplets downward. If  $mg$  represents the force of gravity acting on the droplets in the top surface of the cloud and  $mg + Fe$  the force of gravity plus the electrical force arising from the action of the field  $F$  on the charge  $e$ , and if  $v_1$  is the velocity of fall under the action of gravity alone, and  $v_2$  the velocity when both gravity and the electrical field are acting, then, if the ratio between the force acting and

<sup>1</sup> *Op. cit.*, p. 429.

the velocity produced is the same when the particle is charged as when it is uncharged, we have

$$\frac{mg}{mg + Fe} = \frac{v_1}{v_2} \dots \dots \dots (5)$$

Combining this with the Stokes's Law equation which runs

$$v_1 = \frac{2}{9} \frac{g a^2 \sigma}{\eta} \dots \dots \dots (6)$$

in which  $a$  is the radius,  $\sigma$  the density,  $v_1$  the velocity of the drop under gravity  $g$ , and  $\eta$  is the viscosity of the air, and then eliminating  $m$  by means of

$$m = \frac{4}{3} \pi a^3 \sigma \dots \dots \dots (7)$$

Wilson obtained after substituting for  $\eta$  and  $\sigma$  the appropriate values (not accurately known, it is true, for saturated air at the temperature existing immediately after the expansion),

$$e = 3.1 \times 10^{-9} \frac{g}{F} (v_1 - v_2) v_1^{\frac{1}{2}} \dots \dots \dots (8)$$

Wilson's method constitutes a real advance in that it eliminates the necessity of making the very awkward assumption that the number of droplets is equal to the number of negative ions, for since he observes only the rate of fall of the *top* of the cloud, and since the more heavily charged droplets will be driven down more rapidly by the field than the less heavily charged ones, his actual measurements would always be made upon the *least heavily charged droplets*. All of the other difficulties and assumptions contained in either Townsend's or Thomson's experiments inhere also in Wilson's, and in addition one fresh and rather serious assumption

is introduced, namely, that the clouds formed in successive expansions are identical as to size of droplets. For we wrote down the first equation of Wilson's method as though the  $v_1$  and  $v_2$  were measurements made upon the same droplet, when as a matter of fact the measurements are actually made on wholly different droplets. I have myself found the duplication of cloud conditions in successive expansions a very uncertain matter. Furthermore, Wilson's method assumes uniformity in the field between the plates, an assumption which might be quite wide of the truth.

Although the elimination of the assumption of equality of the number of droplets and the number of ions makes Wilson's determination of  $e$  more reliable as to method than its predecessors, the accuracy actually attained was not great, as can best be seen from his own final summary of results. He made eleven different determinations which varied from  $e = 2 \times 10^{-10}$  to  $e = 4.4 \times 10^{-10}$ . His eleven results are:

TABLE I

$e$	$e$
$2.3 \times 10^{-10}$	$3.8 \times 10^{-10}$
"	"
"	3.0
4.4	"
"	3.5
2.7	"
"	2.0
3.4	"
"	2.3
3.8	"
Mean	$3.1 \times 10^{-10}$

In 1906, being dissatisfied with the variability of these results, the author repeated Wilson's experiment without obtaining any greater consistency than that which the latter had found. Indeed, the instability, distortion, and indefiniteness of the top surface of the cloud were some-

what disappointing, and the results were not considered worth publishing. Nevertheless, it was concluded from these observations that the accuracy might be improved by using radium instead of X-rays for the ionizing agent, by employing stronger electrical fields, and thus increasing the difference between  $v_1$  and  $v_2$ , which in Wilson's experiment had been quite small, and by observing the fall of the cloud through smaller distances and shorter times in order to reduce the error due to the evaporation of the cloud during the time of observation. Accordingly, a 4,000-volt storage battery was built and in the summer of 1908 Mr. Begeman and the author, using radium as the ionizing agent, again repeated the experiment and published some results which were somewhat more consistent than those reported by Wilson.<sup>1</sup> We gave as the mean of ten observations which varied from 3.66 to 4.37 the value  $e = 4.06 \times 10^{-10}$ . We stated at the time that although we had not eliminated altogether the error due to evaporation, we thought that we had rendered it relatively harmless, and that our final result, although considerably larger than either Wilson's or Thomson's (3.1 and 3.4, respectively), must be considered an approach at least toward the correct value.

#### IV. THE BALANCED-DROP METHOD

Feeling, however, that the amount of evaporation of the cloud was still a quite unknown quantity, I next endeavored to devise a way of eliminating it entirely. The plan now was to use an electrical field which was strong enough, not merely to increase or decrease slightly the speed of fall under gravity of the top surface of the

<sup>1</sup> *Phys. Rev.*, XXVI (1908), 198.

cloud, as had been done in all the preceding experiments, but also sufficiently strong to hold the top surface of the cloud stationary, so that the rate of its evaporation could be accurately observed and allowed for in the computations.

This attempt, while not successful in the form in which it had been planned, led to a modification of the cloud method which seemed at the time, and which has actually proved since, to be of far-reaching importance. *It made it for the first time possible to make all the measurements on individual droplets*, and thus not merely to eliminate ultimately all of the questionable assumptions and experimental uncertainties involved in the cloud method of determining  $e$ , but, more important still, it made it possible to examine the properties of individual isolated electrons and to determine whether different ions actually carry one and the same charge. That is to say, it now became possible to determine whether electricity in gases and solutions is actually built up out of electrical atoms, each of which has exactly the same value, or whether the electron which had first made its appearance in Faraday's experiments on solutions and then in Townsend's and Thomson's experiments on gases is after all only a *statistical mean* of charges which are themselves greatly divergent. This latter view had been strongly urged up to and even after the appearance of the work which is now under consideration. It will be given further discussion presently.

The first determination which was made upon the charges carried by individual droplets was carried out in the spring of 1909. A report of it was placed upon the program of the British Association meeting at Winni-

peg in August, 1909, as an additional paper, was printed in abstract in the *Physical Review* for December, 1909, and in full in the *Philosophical Magazine* for February, 1910, under the title "A New Modification of the Cloud Method of Determining the Elementary Electrical Charge and the Most Probable Value of That Charge."<sup>1</sup> The following extracts from that paper show clearly what was accomplished in this first determination of the charges carried by individual droplets.

#### THE BALANCING OF INDIVIDUAL CHARGED DROPS BY AN ELECTROSTATIC FIELD

My original plan for eliminating the evaporation error was to obtain, if possible, an electric field strong enough exactly to balance the force of gravity upon the cloud and then by means of a sliding contact to vary the strength of this field so as to hold the cloud balanced throughout its entire life. In this way it was thought that the whole evaporation-history of the cloud might be recorded, and that suitable allowances might then be made in the observations on the rate of fall to eliminate entirely the error due to evaporation. It was not found possible to balance the cloud, as had been originally planned, but it was found possible to do something much better: namely, to hold individual charged drops suspended by the field for periods varying from 30 to 60 seconds. I have never actually timed drops which lasted more than 45 seconds, although I have several times observed drops which in my judgment lasted considerably longer than this. The drops which it was found possible to balance by an electrical field always carried multiple charges, and the difficulty experienced in balancing such drops was less than had been anticipated.

The procedure is simply to form a cloud and throw on the field immediately thereafter. The drops which have charges of the same sign as that of the upper plate or too weak charges of the opposite sign rapidly fall, while those which are charged with too many multiples of the sign opposite to that of the upper plate are

<sup>1</sup> *Phil. Mag.*, XIX (1910), 209.

jerked up against gravity to this plate. The result is that after a lapse of 7 or 8 seconds the field of view has become quite clear save for a relatively small number of drops which have just the right ratio of charge to mass to be held suspended by the electric field. These appear as perfectly distinct bright points. I have on several occasions obtained but one single such "star" in the whole field and held it there for nearly a minute. For the most part, however, the observations recorded below were made with a considerable number of such points in view. Thin, flocculent clouds, the production of which seemed to be facilitated by keeping the water-jackets  $J_1$  and  $J_2$  (Fig. 2) a degree or two above the temperature of the room, were found to be particularly favorable to observations of this kind.

Furthermore, it was found possible so to vary the mass of a drop by varying the ionization, that drops carrying in some cases two, in some three, in some four, in some five, and in some six, multiples could be held suspended by nearly the same field. The means of gradually varying the field which had been planned were therefore found to be unnecessary. If a given field would not hold any drops suspended it was varied by steps of 100 or 200 volts until drops were held stationary, or nearly stationary. When the P.D. was thrown off it was often possible to see different drops move down under gravity with greatly different speeds, thus showing that these drops had different masses and correspondingly different charges.

The life-history of these drops is as follows: If they are a little too heavy to be held quite stationary by the field they begin to move slowly down under gravity. Since, however, they slowly evaporate, their downward motion presently ceases, and they become stationary for a considerable period of time. Then the field gets the better of gravity and they move slowly upward. Toward the end of their life in the space between the plates, this upward motion becomes quite rapidly accelerated and they are drawn with considerable speed to the upper plate. This, taken in connection with the fact that their whole life between plates only 4 or 5 mm. apart is from 35 to 60 seconds, will make it obvious that during a very considerable fraction of this time their motion must be exceedingly slow. I have often held drops through a

period of from 10 to 15 seconds, during which it was impossible to see that they were moving at all. Shortly after an expansion I have seen drops which at first seemed stationary, but which then began to move slowly down in the direction of gravity, then become stationary again, then finally began to move slowly up. This is probably due to the fact that large multiply charged drops are not in equilibrium with smaller singly charged drops near them, and hence, instead of evaporating, actually grow for a time at the expense of their small neighbors. Be this as it may, however, it is by utilizing the experimental fact that there is a considerable period during which the drops are essentially stationary that it becomes possible to make measurements upon the rate of fall in which the error due to evaporation is wholly negligible in comparison with the other errors of the experiment. Furthermore, in making measurements of this kind the observer is just as likely to time a drop which has not quite reached its stationary point as one which has just passed through that point, so that the mean of a considerable number of observations would, even from a theoretical standpoint, be quite free from an error due to evaporation.

#### THE METHOD OF OBSERVATION

The observations on the rate of fall were made with a short-focus telescope  $T$  (see Fig. 2) placed about 2 feet away from the plates. In the eyepiece of this telescope were placed three equally spaced cross-hairs, the distance between those at the extremes corresponding to about one-third of the distance between the plates. A small section of the space between the plates was illuminated by a narrow beam from an arc light, the heat of the arc being absorbed by three water cells in series. The air between the plates was ionized by 200 mg. of radium, of activity 20,000, placed from 3 to 10 cm. away from the plates. A second or so after expansion the radium was removed, or screened off with a lead screen, and the field thrown on by hand by means of a double-throw switch. If drops were not found to be held suspended by the field, the P.D. was changed or the expansion varied until they were so held. The cross-hairs were set near the lower plate, and as soon as a stationary drop was found somewhere above the upper cross-hair, it was watched for a few seconds to make sure that it was not moving.

and then the field was thrown off and the plates short-circuited by means of the double-throw switch, so as to make sure that they retained no charge. The drop was then timed by means of an accurate stop watch as it passed across the three cross-hairs, one of the two hands of the watch being stopped at the instant of

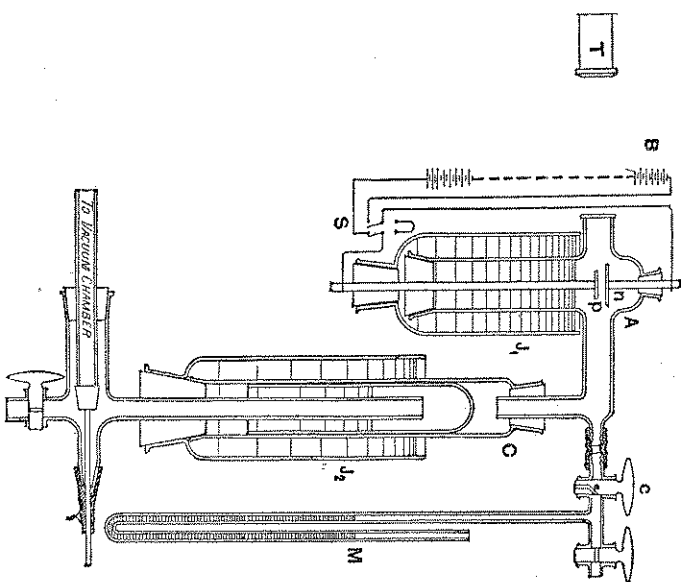


FIG. 2

passage across the middle cross-hair, the other at the instant of passage across the lower one. It will be seen that this method of observation furnishes a double check upon evaporation; for if the drop is stationary at first, it is not evaporating sufficiently to influence the reading of the rate of fall, and if it begins to evaporate appreciably before the reading is completed, the time required to pass through the second space should be greater than that required

to pass through the first space. It will be seen from the observations which follow that this was not, in general, the case.

It is an exceedingly interesting and instructive experiment to watch one of these drops start and stop, or even reverse its direction of motion, as the field is thrown off and on. I have often caught a drop which was just too light to remain stationary and moved it back and forth in this way four or five times between the same two cross-hairs, watching it first fall under gravity when the field was thrown off and then rise against gravity when the field was thrown on. The accuracy and certainty with which the instants of passage of the drops across the cross-hairs can be determined are precisely the same as that obtainable in timing the passage of a star across the cross-hairs of a transit instrument.

Furthermore, since the observations upon the quantities occurring in equation (4) [see (8) p. 55 of this volume] are all made upon the same drop, all uncertainties as to whether conditions can be exactly duplicated in the formation of successive clouds obviously disappear. There is no theoretical uncertainty whatever left in the method unless it be an uncertainty as to whether or not Stokes's Law applies to the rate of fall of these drops under gravity. The experimental uncertainties are reduced to the uncertainty in a time determination of from 3 to 5 seconds, when the object being timed is a single moving bright point. This means that when the time interval is say 5 seconds, as it is in some of the observations given below, the error which a practiced observer will make with an accurate stop watch in any particular observation will never exceed 2 parts in 50. The error in the mean of a considerable number of concordant observations will obviously be very much less than this.

Since in this form of observation the  $v_2$  of equation (5) [(8) of this volume] is zero, and since  $F$  is negative in sign, equation (5) reduces to the simple form:

$$e = 3.422 \times 10^{-9} \times \frac{d^2}{\lambda} (v_1)^3 \dots \dots \dots (6)^*$$

\* I had changed the constant in Wilson's equation from 3.1 to 3.422 because of careful measurements on the temperature existing in the cloud chamber about 10 seconds after expansion and because of new measurements on the viscosity of the saturated air.

It will perhaps be of some interest to introduce two tables from this paper to show the exact nature of these

TABLE II

SERIES 1 (BALANCED POSITIVE WATER DROPS)			SERIES 2 (BALANCED POSITIVE WATER DROPS)		
Distance between plates .545 cm.			Distance between plates .545 cm.		
Measured distance of fall .155 cm.			Measured distance of fall .155 cm.		
Volts	Time 1 Space	Time 2 Spaces	Volts	Time 1 Space	Time 2 Spaces
2.285.....	2.4 sec.	4.8 sec.	2.365.....	1.8 sec.	4.0 sec.
2.285.....	2.4	4.8	2.305.....	1.8	4.0
2.275.....	2.4	4.8	2.365.....	2.2	3.8
2.325.....	2.4	4.8	2.365.....	1.8	4.0
2.325.....	2.6	4.8	2.395.....	2.0	4.0
2.325.....	2.2	4.8	2.395.....	2.0	4.0
2.365.....	2.4	4.8	2.395.....	2.0	3.8
			2.305.....	1.8	4.0
			2.365.....	1.8	4.0
			2.365.....	1.8	4.0
			2.374.....	1.90	3.96

Mean time for .155 cm.=4.8 sec.

$$e_3 = 3.422 \times 10^{-9} \times \frac{980.3}{14.14} \times \left( \frac{.155}{4.8} \right)^3$$

$$= 13.77 \times 10^{-10}$$

Therefore  $e = 13.85 \times 10^{-10} \div 3$

$$= 4.59 \times 10^{-10}$$

Mean time for .155 cm.=3.91 sec.

$$e_4 = 3.422 \times 10^{-9} \times \frac{980.3}{14.52} \times \left( \frac{.155}{3.91} \right)^3$$

$$= 18.25 \times 10^{-10}$$

Therefore  $e = 18.25 \div 4$

$$= 4.56 \times 10^{-10}$$

TABLE III

Series	Charge	Value of $e$	Weight Assigned
1.....	3e	4.59	7
2.....	4e	4.56	7
3.....	2e	4.64	6
4.....	5e	4.83	4
5.....	2e	4.87	1
6.....	6e	4.69	3

Simple mean  $e = 4.70 \times 10^{-10}$

Weighted mean  $e = 4.65 \times 10^{-10}$

earliest measurements on the charges carried by individual particles.

In connection with these experiments I chanced to observe a phenomenon which interested me very much at the time and suggested quite new possibilities. While working with these "balanced drops" I noticed on several occasions on which I had failed to screen off the rays from the radium that now and then one of them would suddenly change its charge and begin to move up or down in the field, evidently because it had captured in the one case a positive, in the other a negative, ion. This opened up the possibility of measuring with certainty, not merely the charges on individual droplets as I had been doing, but the charge carried by a single atmospheric ion. For by taking two speed measurements on the same drop, one before and one after it had caught an ion, I could obviously eliminate entirely the properties of the drop and of the medium and deal with a quantity which was proportional merely to the charge on the captured ion itself.

Accordingly, in the fall of 1909 there was started the series of experiments described in the succeeding chapter.

The problem had already been so nearly solved by the work with the water droplets that there seemed no possibility of failure. It was only necessary to get a charged droplet entirely free from evaporation into the space between the plates of a horizontal air condenser and then, by alternately throwing on and off an electrical field, to keep this droplet pacing its beat up and down between the plates until it could catch an atmospheric ion in just the way I had already seen the water droplets do. The change in the speed in the field would then be exactly proportional to the charge on the ion captured.



### I. ISOLATION OF INDIVIDUAL IONS AND MEASUREMENT OF THEIR RELATIVE CHARGES

In order to compare the charges on different ions, the procedure adopted was to blow with an ordinary commercial atomizer an oil spray into the chamber *C* (Fig. 3).

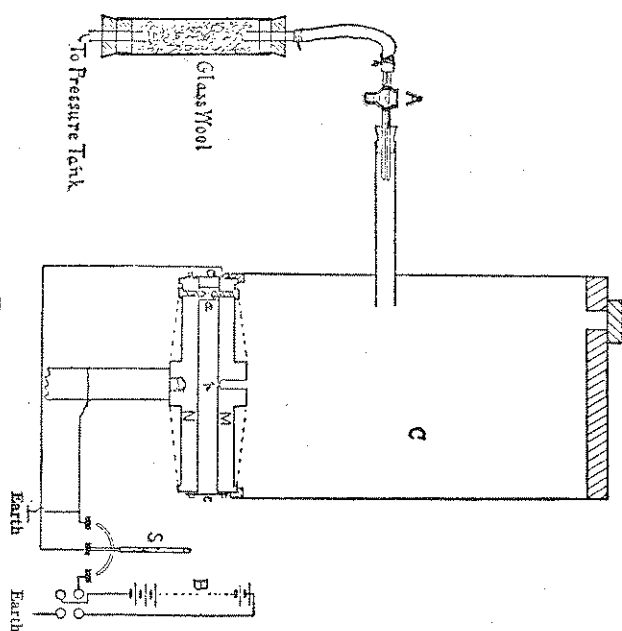


FIG. 3

The air with which this spray was blown was first rendered dust-free by passage through a tube containing glass wool. The minute droplets of oil constituting the spray, most of them having a radius of the order of a one-thousandth of a millimeter, slowly fell in the chamber *C*, and occasionally one of them would find its way

## CHAPTER IV GENERAL PROOF OF THE ATOMIC NATURE OF ELECTRICITY

Although the "balanced-droplet method" just described had eliminated the chief sources of uncertainty which inhered in preceding work on *e* and had made it possible to assert with much confidence that the unit charge was a real physical entity and not merely a "statistical mean," it was yet very far from an exact method of studying the properties of gaseous ions. The sources of error or uncertainty which still inhered in it arose from (1) the lack of stagnancy in the air through which the drop moved; (2) the lack of perfect uniformity of the electrical field used; (3) the gradual evaporation of the drops, rendering it impossible to hold a given drop under observation for more than a minute or to time a drop as it fell under gravity alone through a period of more than five or six seconds; and (4) the assumption of the validity of Stokes's Law.

The method which was devised to replace it was not only entirely free from all of these limitations, but it constituted an entirely new way of studying ionization and one which at once yielded important results in a considerable number of directions. This chapter deals with some of these by-products of the determination of *e* which are of even more fundamental interest and importance than the mere discovery of the exact size of the electron.

through the minute pinhole  $p$  in the middle of the circular brass plate  $M$ , 22 cm. in diameter, which formed one of the plates of the air condenser. The other plate,  $N$ , was held 16 mm. beneath it by three ebonite posts  $a$ . By means of the switch  $S$  these plates could be charged, the one positively and the other negatively, by making them the terminals of a 10,000-volt storage battery  $B$ , while throwing the switch the other way (to the left) short-circuited them and reduced the field between them to zero. The oil droplets which entered at  $p$  were illuminated by a powerful beam of light which passed through diametrically opposite windows in the encircling ebonite strip  $c$ . As viewed through a third window in  $c$  on the side toward the reader, it appeared as a bright star on a black background. These droplets which entered  $p$  were found in general to have been strongly charged by the frictional process involved in blowing the spray, so that when the field was thrown on in the proper direction they would be pulled up toward  $M$ . Just before the drop under observation could strike  $M$  the plates would be short-circuited and the drop allowed to fall under gravity until it was close to  $N$ , when the direction of motion would be again reversed by throwing on the field. In this way the drop would be kept traveling back and forth between the plates. The first time the experiment was tried an ion was caught within a few minutes, and the fact of its capture was signaled to the observer by the change in the speed with which it moved up when the field was on. The significance of the experiment can best be appreciated by examination of the complete record of one of the early experiments when the timing was done merely with a stop watch.

The column headed  $t_g$  gives the successive times which the droplet required to fall between two fixed cross-hairs in the observing telescope whose distance apart corresponded in this case to an actual distance of fall of .5222 cm. It will be seen that these numbers are all the same within the limits of error of a stop-watch measurement. The column marked  $t_f$  gives the successive times

TABLE IV

$t_g$	$t_f$
13.6	12.5
13.8	12.4
13.4	21.8
13.4	34.8
13.6	84.5
13.6	85.5
13.7	34.6
13.5	34.8
13.5	16.0
13.8	34.8
13.7	34.6
13.8	21.9
13.6	
13.5	
13.4	
13.8	
13.4	

Mean 13.595

which the droplet required to rise under the influence of the electrical field produced by applying in this case 5,051 volts of potential difference to the plates  $M$  and  $N$ . It will be seen that after the second trip up, the time changed from 12.4 to 21.8, indicating, since in this case the drop was positive, that a negative ion had been caught from the air. The next time recorded under  $t_f$ , namely, 34.8, indicates that another negative ion had been caught. The next time, 84.5, indicates the capture

of still another negative ion. This charge was held for two trips, when the speed changed back again to 34.6, showing that a positive ion had now been caught which carried precisely the same charge as the negative ion which before caused the inverse change in time, i.e., that from 34.8 to 84.5.

In order to obtain some of the most important consequences of this and other similar experiments we need make no assumption further than this, that the velocity with which the drop moves is proportional to the force acting upon it and is independent of the electrical charge which it carries. Fortunately this assumption can be put to very delicate experimental test, as will presently be shown, but introducing it for the time being as a mere assumption, as Townsend, Thomson, and Wilson had done before, we get

$$\frac{v_1}{v_2} = \frac{m_g}{F e_n - m_g} \text{ or } e_n = \frac{m_g}{F v_1} (v_1 + v_2) \dots \dots \dots (9)$$

The negative sign is used in the denominator because  $v_2$  will for convenience be taken as positive when the drop is going up in the direction of  $F$ , while  $v_1$  will be taken as positive when it is going down in the direction of  $g$ .  $e_n$  denotes the charge on the drop, and must not be confused with the charge on an ion. If now by the capture of an ion the drop changes its charge from  $e_n$  to  $e_n'$ , then the value of the captured charge  $e_i$  is

$$e_i = e_n' - e_n = \frac{m_g}{F v_1} (v_1' - v_2) \dots \dots \dots (10)$$

and since  $\frac{m_g}{F v_1}$  is a constant for this drop, any charge which it may capture will always be proportional to

$(v_1' - v_2)$ , that is, to the change produced in the velocity in the field  $F$  by the captured ion. The successive values of  $v_2$  and of  $(v_2 - v_1)$ , these latter being obtained by subtracting successive values of the velocities given under  $v_1$ , are shown in Table V.

TABLE V  
 $v_2$   $(v_1' - v_2)$

$\frac{.5222}{12.45} = .04196$	$.01866 \div 2 = .00903$
$\frac{.5222}{21.5} = .02390$	$.00885 \div 1 = .00885$
$\frac{.5222}{34.7} = .01505$	$.00891 \div 1 = .00891$
$\frac{.5222}{85.0} = .006144$	$.00891 \div 1 = .00891$
$\frac{.5222}{34.7} = .01505$	$.01759 \div 2 = .00880$
$\frac{.5222}{16.0} = .03264$	$.01759 \div 2 = .00880$
$\frac{.5222}{34.7} = .01505$	$.00891 \div 1 = .00891$
$\frac{.5222}{21.85} = .02390$	

It will be seen from the last column that within the limits of error of a stop-watch measurement, all the charges captured have exactly the same value save in three cases. In all of these three the captured charges were just twice as large as those appearing in the other changes. Relationships of exactly this sort have been found to hold absolutely without exception, no matter in what gas the drops have been suspended or what sort of droplets were used upon which to catch the ions. In

many cases a given drop has been held under observation for five or six hours at a time and has been seen to catch not eight or ten ions, as in the experiment above, but hundreds of them. Indeed, I have observed, all told, the capture of many thousands of ions in this way, and in no case have I ever found one the charge of which, when tested as above, did not have either exactly the value of the smallest charge ever captured or else a very small multiple of that value. *Here, then, is direct, unimpeachable proof that the electron is not a "statistical mean," but that rather the electrical charges found on ions all have either exactly the same value or else small exact multiples of that value.*

## II. PROOF THAT ALL STATIC CHARGES BOTH ON CONDUCTORS AND INSULATORS ARE BUILT UP OF ELECTRONS

The foregoing experiment leads, however, to results of much more fundamental importance than that mentioned in the preceding section. The charge which the droplet had when it first came under observation had been acquired, not by the capture of ions from the air, but by the ordinary frictional process involved in blowing the spray. If then ordinary static charges are built up of electrons, this charge should be found to be an exact multiple of the ionic charge which had been found from the most reliable measurement shown in Table V to be proportional to the velocity .00891. This initial charge  $e_n$  on the drop is seen from equations (9) and (10) to bear the same relation to  $(v_1 + v_2)$  which the ionic charge  $e_i - e_n$  bears to  $(v_2 - v_1)$ . Now,  $v_1 = .5222/13.595 = .03842$ , hence  $v_1 + v_2 = .03842 + .04196 = .08038$ . Dividing this by 9 we obtain .008931, which is within about

one-fifth of 1 per cent of the value found in the last column of Table V as the smallest charge carried by an ion. *Our experiment has then given us for the first time a means of comparing a frictional charge with the ionic charge, and the frictional charge has in this instance been found to contain exactly 9 electrons.* A more exact means of making this comparison will be given presently, but suffice it to say here that experiments like the foregoing have now been tried on thousands of drops in different media, some of the drops being made of non-conductors like oil, some of semi-conductors like glycerin, some of excellent metallic conductors like mercury. In every case, without a single exception, the initial charge placed upon the drop by the frictional process, and all of the dozen or more charges which have resulted from the capture by the drop of a larger or smaller number of ions, have been found to be exact multiples of the smallest charge caught from the air. Some of these drops have started with no charge at all, and one, two, three, four, five, and six elementary charges or electrons have been picked up. Others have started with seven or eight units, others with twenty, others with fifty, others with a hundred, others with a hundred and fifty elementary units, and have picked up in each case a dozen or two of elementary charges on either side of the starting-point, so that, in all, drops containing every possible number of electrons between one and one hundred and fifty have been observed and the number of electrons which each drop carried has been accurately counted by the method described. When the number is less than fifty there is not a whit more uncertainty about this count than there is in counting one's own fingers and toes. It

is not found possible to determine with certainty the number of electrons in a charge containing more than one hundred or two hundred of them, for the simple reason that the method of measurement used fails to detect the difference between 200 and 201, that is, we cannot measure  $v'_2 - v_2$  with an accuracy greater than one-half of 1 per cent. But it is quite inconceivable that large charges such as are dealt with in commercial applications of electricity can be built up in an essentially different way from that in which the small charges whose electrons we are able to count are found to be. Furthermore, since it has been definitely proved that an electrical current is nothing but the motion of an electrical charge over or through a conductor, it is evident that the experiments under consideration furnish not only the most direct and convincing of evidence that all electrical charges are built up out of these very units which we have been dealing with as individuals in these experiments, but that all electrical currents consist merely in the transport of these electrons through the conducting bodies.

In order to show the beauty and precision with which these multiple relationships stand out in all experiments of this kind, a table corresponding to much more precise measurements than those given heretofore is here introduced (Table VI). The time of fall and rise shown in the first and second columns were taken with a Hipp chronoscope reading to one-thousandth of a second. The third column gives the reciprocals of these times. These are used in place of the velocities  $v_2$  in the field, since distance of fall and rise is always the same. The fourth column gives the successive changes in speed due

to the capture of ions. These also are expressed merely as time reciprocals. For reasons which will be explained in the next section, each one of these changes may correspond to the capture of not merely one but of several distinct ions. The numbers in the fifth column represent

TABLE VI

$t_g$ Sec.	$t_P$ Sec.	$\frac{1}{t_P}$	$\left(\frac{1}{t_P} - \frac{1}{t_g}\right)$	$n'$ $\frac{1}{n} \left( \frac{1}{t_P} - \frac{1}{t_g} \right)$	$\left(\frac{1}{t_g} - \frac{1}{t_P}\right)$	$n$	$\frac{1}{n} \left( \frac{1}{t_g} + \frac{1}{t_P} \right)$
11.848	80.708	.01236	.03234	6	.00655	18	.005366
11.890	22.366	.04470	.03751	7	.12887	24	.005371
11.908	22.309	.04470	.03751	7	.005358		.005371
11.924	22.368	.04470	.03751	7	.00138	17	.005375
11.882	140.505	.007192	.005348	1	.00673	18	.005374
11.906	79.600	.01254	.005348	1			
11.838	34.748	.02870	.01016	3	.005387	21	.005376
11.816	34.846	.02870	.01016	3	.11289	21	.005376
11.776	34.846	.02870	.01016	3			
11.840	29.286	.03414	.026872	5	.11833	22	.005379
11.924	29.236	.03414	.026872	5	.09146	17	.005380
11.870	137.308	.007268	.021572	4	.11303	17	.005382
11.860	34.638	.02884	.01023	3	.005410	24	.005386
11.800	22.104	.04507	.04307	8	.12026	24	.005386
11.912	500.1	.002000	.04307	8	.08619	16	.005387
11.846	22.268	.04507	.04307	8			
11.918	19.704	.05079	.04879	9	.005421	25	.005390
11.870	19.668	.05079	.04879	9	.13498	25	.005390
11.888	77.630	.01285	.03794	7	.00704	18	.005390
11.894	77.806	.01285	.03794	7	.10783	20	.005392
11.878	42.302	.02364	.01079	2	.005305		.005392
11.880				Means	.005386		.005384

Duration of exp. = 45 min.  
 Plate distance = 16 mm.  
 Fall distance = 10.21 mm.  
 Initial volts = 5,088.8  
 Final volts = 5,081.2  
 Temperature = 22.82° C.  
 $e = 4.991 \times 10^{-10}$   
 Pressure = 75.62 cm.  
 Air density = .0190  
 Air viscosity =  $1.824 \times 10^{-7}$   
 Radius ( $a$ ) = .000276 cm.  
 $f = .034$   
 Speed of fall = .08584 cm./sec.

simply the small integer by which it is found that the numbers in the fourth column must be divided in order to obtain the numbers in the sixth column. These will be seen to be exactly alike within the limits of error of the experiment. The mean value at the bottom of the sixth column represents, then, the smallest charge ever caught

from the air, that is, it is the elementary *ionic* charge. The seventh column gives the successive values of  $v_1 + v_2$  expressed as reciprocal times. These numbers, then, represent the successive values of the *total* charge carried by the droplet. The eighth column gives the integers by which the numbers in the seventh column must be divided to obtain the numbers in the last column. These also will be seen to be invariable. The mean at the bottom of the last column represents, then, the *electrical unit out of which the frictional charge on the droplet was built up, and it is seen to be identical with the ionic charge represented by the number at the bottom of the sixth column.*

It may be of interest to introduce one further table (Table VII) arranged in a slightly different way to show

TABLE VII

#	$4.917 \times n$	Observed Charge	#	$4.917 \times n$	Observed Charge
1.....	4.917	.....	10.....	49.17	49.41
2.....	9.834	.....	11.....	54.09	53.91
3.....	14.75	.....	12.....	59.00	59.12
4.....	19.66	19.66	13.....	63.92	63.68
5.....	24.59	24.60	14.....	68.84	68.65
6.....	29.50	29.62	15.....	73.75	.....
7.....	34.42	34.47	16.....	78.67	78.34
8.....	39.34	39.38	17.....	83.59	83.22
9.....	44.25	44.42	18.....	88.51	.....

how infallibly the atomic structure of electricity follows from experiments like those under consideration.

In this table  $4.917$  is merely a number obtained precisely as above from the change in speed due to the capture of ions and one which is proportional in this experiment to the ionic charge. The column headed  $4.917 \times n$  contains simply the whole series of exact mul-

tiples of this number from 1 to 18. The column headed "Observed Charge" gives the successive observed values of  $(v_1 + v_2)$ . It will be seen that during the time of observation, about four hours, this drop carried all possible multiples of the elementary charge from 4 to 18, save only 15. *No more exact or more consistent multiple relationship is found in the data which chemists have amassed on the combining powers of the elements and on which the atomic theory of matter rests than is found in the foregoing numbers.*

Such tables as these—and scores of them could be given—place beyond all question the view that an electrical charge wherever it is found, whether on an insulator or a conductor, whether in electrolytes or in metals, has a definite granular structure, that it consists of an exact number of specks of electricity (electrons) all exactly alike, which in static phenomena are scattered over the surface of the charged body and in current phenomena are drifting along the conductor. Instead of giving up, as Maxwell thought we should some day do, the "provisional hypothesis of molecular charges," we find ourselves obliged to make all our interpretations of electrical phenomena, *metallic as well as electrolytic*, in terms of it.

### III. MECHANISM OF CHANGE OF CHARGE OF A DROP

All of the changes of charge shown in Table IV were spontaneous changes, and it has been assumed that all of these changes were produced by the capture of ions from the air. When a negative drop suddenly increases its speed in the field, that is, takes on a larger charge of its own kind than it has been carrying, there seems to be no other conceivable way in which the change can be

produced. But when the charge suddenly *decreases* there is no a priori reason for thinking that the change may not be due as well to the direct loss of a portion of the charge as to the neutralization of this same amount of electricity by the capture of a charge of opposite sign. That, however, the changes do actually occur, when no X-rays or radioactive rays are passing between the plates, only by the capture of ions from the air, was rendered probable by the fact that drops not too heavily charged showed the same tendency on the whole to increase as to decrease in charge. This should not have been the case if there were two causes tending to decrease the charge, namely, direct loss and the capture of opposite ions, as against one tending to increase it, namely, capture of like ions. The matter was very convincingly settled, however, by making observations when the gas pressures were as low as 2 or 3 mm. of mercury. Since the number of ions present in a gas is in general directly proportional to the pressure, spontaneous changes in charge should almost never occur at these low pressures; in fact, it was found that drops could be held for hours at a time without changing. The frequency with which the changes occur decreases regularly with the pressure, as it should if the changes are due to the capture of ions. For the number of ions formed by a given ionizing agent must vary directly as the pressure.

Again, the changes do not, in general, occur when the electrical field is on, for then the ions are driven instantly to the plates as soon as formed, at a speed of, say, 10,000 cm. per second, and so do not have any opportunity to accumulate in the space between them. When the field is off, however, they do so accumulate, until, in

ordinary air, they reach the number of, say, 20,000 per cubic centimeter. These ions, being endowed with the kinetic energy of agitation characteristic of the temperature, wander rapidly through the gas and become a part of the drop as soon as they impinge upon it. It was thus that all the changes recorded in Table IV took place.

It is possible, however, so to control the changes as to place electrons of just such sign as one wishes, and of just such number as one wishes, within limits, upon a given drop. If, for example, it is desired to place a positive electron upon a given drop the latter is held with the aid of the field fairly close to the negative plate, say the upper plate; then an ionizing agent—X-rays or radium—is arranged to produce uniform ionization in the gas between the plates. Since now all the positive ions move up while the negatives move down, the drop is in a shower of positive ions, and if the ionization is intense enough the drop is sure to be hit. In this way a positive charge of almost any desired strength may be placed upon the drop.

Similarly, in order to throw a negative ion or ions upon the drop it is held by the field close to the lower, i.e., to the positive, plate in a shower of negative ions produced by the X-rays. It was in this way that most of the changes shown in Table VI were brought about. This accounts for the fact that they correspond in some instances to the capture of as many as six electrons.

When X-rays are allowed to fall directly upon the drop itself the change in charge may occur, not merely because of the capture of ions, but also because the rays eject beta particles, i.e., negative electrons, from the molecules of the drop. That changes in charge were



actually produced in this way in our experiments was proved conclusively in 1910 by the fact that when the pressure was reduced to a very low value and X-rays were allowed to pass through the air containing the drop, the latter would change readily in the direction of increasing positive or decreasing negative charge, but it could almost never be made to change in the opposite direction. This is because at these low pressures the rays can find very few gas molecules to ionize, while they detach negative electrons from the drop as easily as at atmospheric pressure. *This experiment proved directly that the charge carried by an ion in gases is the same as the charge on the beta or cathode-ray particle.*

When it was desired to avoid the direct loss of negative electrons by the drop, we arranged lead screens so that the drop itself would not be illuminated by the rays, although the gas underneath it was ionized by them.<sup>1</sup>

#### IV. DIRECT OBSERVATION OF THE KINETIC ENERGY OF AGITATION OF A MOLECULE

I have already remarked that when a drop carries but a small number of electrons it appears to catch ions of its own sign as rapidly as those of opposite signs—a result which seems strange at first, since the ions of opposite sign must be attracted, while those of like sign must be repelled. Whence, then, does the ion obtain the energy which enables it to push itself up against this electrostatic repulsion and attach itself to a drop already strongly charged with its own kind of electricity? It cannot obtain it from the field, since the phenomenon of capture occurs when the field is not on. It cannot

<sup>1</sup> See *Phil. Mag.*, XXI (1911), 757.

obtain it from any explosive process which frees the ion from the molecule at the instant of ionization, since in this case, too, ions would be caught as well, or nearly as well, when the field is on as when it is off. Here, then, is an absolutely direct proof that the ion must be endowed with a kinetic energy of agitation which is sufficient to push it up to the surface of the drop against the electrostatic repulsion of the charge on the drop.

This energy may easily be computed as follows: Let us take a drop, such as was used in one of these experiments, of radius .000197 cm. The potential at the surface of a charged sphere can be shown to be the charge divided by the radius. The value of the elementary electrical charge obtained from the best observations of this type, is  $4.774 \times 10^{-10}$  absolute electrostatic units. Hence the energy required to drive an ion carrying the elementary charge  $e$  up to the surface of a charged sphere of radius  $r$ , carrying 16 elementary charges, is

$$\frac{16e^2}{r} = \frac{16 \times (4.774 \times 10^{-10})^2}{.000197} = 1.95 \times 10^{-14} \text{ ergs}$$

Now, the kinetic energy of agitation of a molecule as deduced from the value of  $e$  herewith obtained, and the kinetic theory equation,  $\bar{p} = \frac{1}{2} m \bar{c}^2$ , is  $5.75 \times 10^{-14}$  ergs. According to the Maxwell-Boltzmann Law of the partition of energy, which certainly holds in gases, this should also be the kinetic energy of agitation of an ion. It will be seen that the value of this energy is approximately three times that required to push a single ion up to the surface of the drop in question. Hence the electrostatic forces due to 16 electrons on the drop are too weak to exert much influence upon the motion of an approaching

ion. But if it were possible to load up a drop with negative electricity until the potential energy of its charge were about three times as great as that computed above for this drop, then the phenomenon here observed of the catching of new negative ions by such a negatively charged drop should not take place, save in the exceptional case in which an ion might acquire an energy of agitation considerably larger than the mean value. Now, as a matter of fact, it was regularly observed that the heavily charged drops had a very much smaller tendency to pick up new negative ions than the more lightly charged drops, and, in one instance, we watched for four hours another negatively charged drop of radius .000658 cm., which carried charges varying from 126 to 150 elementary units, and which therefore had a potential energy of charge (computed as above on the assumption of uniform distribution) varying from  $4.6 \times 10^{-14}$  to  $5.47 \times 10^{-14}$ . In all that time this drop picked up but one single negative ion when the field was off, and that despite the fact that the ionization was several times more intense than in the case of the drop of Table I. Positive ions too were being caught at almost every trip down under gravity. (The strong negative charge on the drop was maintained by forcing on negative ions by the field as explained above.)

#### V. POSITIVE AND NEGATIVE ELECTRONS EXACTLY EQUAL

The idea has at various times been put forth in connection with attempts to explain chemical and cohesive forces from the standpoint of electrostatic attractions that the positive and negative charges in a so-called neutral atom may not after all be exactly equal, in other

words, that there is really no such thing as an entirely neutral atom or molecule. As a matter of fact, it is difficult to find decisive tests of this hypothesis. The present experiments, however, make possible the following sort of test. I loaded a given drop first with negative electrons and took ten or twelve observations of rise and fall, then with the aid of X-rays, by the method indicated in the last section, I reversed the sign of the charge on the drop and took a corresponding number of observations of rise and fall, and so continued observing first the value of the negative electron and then that of the positive. Table VIII shows a set of such observations taken in air with a view to subjecting this point to as rigorous a test as possible. Similar, though not quite so elaborate, observations have been made in hydrogen with the same result. The table shows in the first column the sign of the charge; in the second the successive values of the time of fall under gravity; in the third the successive times of rise in the field  $F$ ; in the fourth the number of electrons carried by the drop for each value of  $t_F$ ; and in the fifth the number, characteristic of this drop, which is proportional to the charge of one electron. This number is obtained precisely as in the two preceding tables by finding the greatest common divisor of the successive values of  $(\tau_1 + \tau_2)$  and then multiplying this by an arbitrary constant which has nothing to do with the present experiment and hence need not concern us here (see chap. v).

It will be seen that though the times of fall and of rise, even when the same number of electrons is carried by the drop, change a trifle because of a very slight evaporation and also because of the fall in the potential

TABLE VIII

Sign of Drop	$t_g$ Sec.	$t_p$ Sec.	$n$	$e$
-	63.118 63.050 63.186 63.332 62.328 62.728 62.926 62.900 63.214 Mean = 62.976	41.728 41.590 25.740 25.798 25.510 25.806	8   11	$e_1 = 6.713$
+	63.538 63.244 63.114 63.242 63.362 63.136 63.226 63.764 63.280 63.530 63.208 Mean = 63.325	22.694 22.830 25.870 25.876 25.484 10.830 10.682 10.756 10.778 10.672 10.646	12  11  22	$e_2 = 6.692$
+	63.642 63.020 62.820 63.514 63.312 63.776 63.300 63.156 63.126 Mean = 63.407	71.664 71.248 52.668 52.800 52.496 52.860 71.708	6  7  6	$e_3 = 6.702$

TABLE VIII—Continued

Sign of Drop	$t_g$ Sec.	$t_p$ Sec.	$n$	$e$
-	63.228 63.204 63.184 63.260 63.478 63.074 63.306 63.414 63.450 63.446 63.556 Mean = 63.335	42.006 41.920 42.108 53.210 52.922 53.034 53.438 12.888 12.812 12.748 12.824	8  7  19	$e_1 = 6.686$

Duration of experiment 1 hr. 40 min.

Initial volts = 1723.5

Mean  $e_+ = 6.697$   
Mean  $e_- = 6.700$ 

Final volts = 1702.1

Pressure = 53.48 cm.

of the battery, yet the mean value of the positive electron, namely, 6.697, agrees with the mean value of the negative electron, namely, 6.700, to within less than 1 part in 2,000. Since this is about the limit of the experimental error (the probable error by least squares is 1 part in 1,500), we may with certainty conclude that there are no differences of more than this amount between the values of the positive and negative electrons. This is the best evidence I am aware of for the exact neutrality of the ordinary molecules of gases. Such neutrality, if it is actually exact, would seem to preclude the possibility of explaining gravitation as a result of electrostatic forces of any kind. The electromagnetic effect of moving charges might, however, still be called upon for this purpose.

VI. RESISTANCE OF MEDIUM TO MOTION OF DROP THROUGH  
IT THE SAME WHEN DROP IS CHARGED AS WHEN  
UNCHARGED

A second and equally important conclusion can be drawn from Table VIII. It will be seen from the column headed " $n$ " that during the whole of the time corresponding to the observations in the third group from the top the drop carried either 6 or 7 electrons, while, during the last half of the time corresponding to the observations in the second group from the top, it carried three times as many, namely, 22 electrons. Yet the mean times of fall under gravity in the two groups agree to within about one part in one thousand. The time of fall corresponding to the heavier charge happens in this case to be the smaller of the two. We may conclude, therefore, that in these experiments the resistance which the medium offers to the motion of a body through it is not sensibly increased when the body becomes electrically charged. This demonstrates experimentally the exact validity for this work of the assumption made on p. 70 that the velocity of the drop is strictly proportional to the force acting upon it, whether it is charged or uncharged.

The result is at first somewhat surprising since, according to Sutherland's theory of the small ion, the small mobility or diffusivity of charged molecules, as compared with uncharged, is due to the additional resistance which the medium offers to the motion through it of a charged molecule. This additional resistance is due to the fact that the charge on a molecule drags into collision with it more molecules than would otherwise hit it. But with oil drops of the sizes here used

( $a = 50 \times 10^{-9}$ ) the total number of molecular collisions against the surface of the drop is so huge that even though the small number of charges on it might produce a few more collisions, their number would be negligible in comparison with the total number. At any rate the experiment demonstrates conclusively that the charges on our oil drops do not influence the resistance of the medium to the motion of the drop. This conclusion might also have been drawn from the data contained in Table VI. The evidence for its absolute correctness has been made more convincing still by a comparison of drops which carried but 1 charge and those which carried as many as 68 unit charges. Further, I have observed the rate of fall under gravity of droplets which were completely discharged, and in every case that I have ever tried I have found this rate precisely the same, within the limits of error of the time measurements, as when it carried 8 or 10 unit charges.

VII. DROPS ACT LIKE RIGID SPHERES

It was of very great importance for the work, an account of which will be given in the next chapter to determine whether the drops ever suffer—either because of their motion through a resisting medium, or because of the electrical field in which they are placed—any appreciable distortion from the spherical form which a freely suspended liquid drop must assume. The complete experimental answer to this query is contained in the agreement of the means at the bottom of the last and the third from the last columns in Table VI and in similar agreements shown in many other tables, which

may be found in the original articles.<sup>1</sup> Since  $\frac{1}{f_g}$  is in this experiment large compared to  $\frac{1}{f_p}$ , the value of the greatest common divisor at the bottom of the last column of Table VI is determined almost wholly by the rate of fall of the particle under gravity when there is no field at all between the plates, while the velocity at the bottom of the third from the last column is a difference between two velocities in a strong electrical field. If, therefore, the drop were distorted by the electrical field, so that it exposed a larger surface to the resistance of the medium than when it had the spherical form, the velocity due to a given force, that is, the velocity given at the bottom of the third from the last column, would be less than that found at the bottom of the last column, which corresponds to motions when the drop certainly was spherical.

Furthermore, if the drops were distorted by their motion through the medium, then this distortion would be greater for high speeds than for low, and consequently the numbers in the third from the last column would be consistently larger for high speeds than for low. No such variation of these numbers with speed is apparent either in Table VI or in other similar tables.

We have then in the exactness and invariableness of the multiple relations shown by successive differences in speed and the successive sums of the speeds in the third from the last and the last columns of Table VI complete experimental proof that in this work the droplets act under all circumstances like undeformed spheres. It is of interest that Professor Hadamard,<sup>2</sup> of the University of

Paris, and Professor Lunn,<sup>3</sup> of the University of Chicago, have both shown from theoretical considerations that this would be the case with oil drops as minute as those with which these experiments deal, so that the conclusion may now be considered as very firmly established both by the experimentalist and the theorist.

<sup>1</sup> *Phys. Rev.*, XXXV (1912), 227.

<sup>2</sup> *Phys. Rev.*, Series I, XXXII (1911), 349; Series 2, II (1913), 109.

<sup>3</sup> *Comptes rendus* (1911), 1735.