

ELECTRON IMPACT  
PHENOMENA  
AND THE PROPERTIES OF GASEOUS IONS

---

*F H. Field and J. L. Franklin*

# ELECTRON IMPACT PHENOMENA

AND THE PROPERTIES OF GASEOUS IONS

F. H. FIELD AND J. L. FRANKLIN

*Refining Research and Development Division  
Humble Oil & Refining Company  
Baytown, Texas*



1957

ACADEMIC PRESS INC • PUBLISHERS • NEW YORK

# **ELECTRON IMPACT PHENOMENA**

## Preface

Because gaseous ions are highly energetic and of a transitory nature in most environments, the observation and measurement of their primary molecular properties is not an easy task. In recent years, however, this task has to a considerable extent been accomplished, and our knowledge of molecular gaseous ionic phenomena has expanded rapidly. But, because the growth in the field has been rapid, this knowledge is for the most part available only in original research papers, which are by their nature generally of limited scope. In this book we have attempted to provide a comprehensive and critical compilation and review of electron impact phenomena and the properties of gaseous ions, placing our primary emphasis on the very interesting chemical physics of the systems studied. In so doing we would like to think that not only do we provide an introduction into the field for those unfamiliar with it, but also that by bringing together in one place data from different sources we may promote the observation of phenomena, trends, and interrelationships which might otherwise pass unnoticed. Indeed, in retrospect we ourselves are somewhat surprised by the extent to which the physics and chemistry of ionic systems constitute a consistent set of phenomena and principles. For expert workers in the field we have tabulated and, where possible, interpreted, all available energetic data pertaining to electron impact phenomena. We have found this tabulation useful in our own work, and we hope that others will have the same experience.

We believe that knowledge concerning gaseous ionic systems is applicable to other fields of chemistry and physics, and we have included in the book several examples of this applicability. While at the present we can only speculate, we feel that other areas of applicability will be discovered. Two of these might be mentioned, namely, radiation chemistry and catalysis. At the time of writing the role played by ions in radiation chemistry phenomena is undergoing a reassessment by many radiation chemists, and a body of thought is growing that ionic processes may be much more important than has previously been realized. Somewhat similarly, a very active field of research is that concerned with the electrical properties of heterogeneous catalysts and the relationship between electrical properties and catalytic properties. If such a relationship exists, it seems to us to imply

that the substance undergoing the catalysis must be charged to one extent or another, in which case a knowledge of ionic systems will very possibly be of interest. Whatever may be the truth in these specific cases, a knowledge of the basic properties of ionic systems will be a stimulus in thinking about ions in other areas. We hope that by better delineating ionic behavior this book will contribute to this end.

In preparing this book we found it desirable to reproduce various figures and diagrams from the literature, and we would like to thank the following organizations and individuals for permitting us to use their material:

The Institute of Petroleum for permission to use figures from several of its publications, and authors Drs. J. D. Waldron and K. Wood, and R. Thompson.

The Faraday Society, and Drs. C. A. McDowell, J. W. Warren, M. Magat, W. C. Price, and T. M. Sugden for permission to use figures from their articles in Faraday Society publications.

The American Institute of Physics for permission to reproduce figures from several articles from *Physical Reviews* and *Journal of Chemical Physics*.  
*Reviews of Modern Physics*.

Drs. H. Eyring, H. M. Rosenstock, and A. L. Wahrhaftig for permission to use material from their technical report entitled "The Mass Spectra of Large Molecules."

Westinghouse Electric Company for permission to reproduce a drawing of their Type LV mass spectrometer.

No book of this kind could ever be completed without the help of one's colleagues and the encouragement of friends and family. It is a pleasure to take this opportunity to acknowledge our manifold indebtedness to our friends in Baytown and elsewhere. We would especially like to acknowledge the encouragement and help of Dean Henry Eyring, Professors F. A. Matsen and W. E. Doering, and our colleague Dr. F. W. Lampe. We wish also to thank the members of our stenographic staff for their invaluable help in preparing the manuscript and correcting the proofs. One of us (JLF) would also like to express his gratitude to his family for help in correcting the proofs. Finally, we thank Humble Oil & Refining Company for support of this work.

F. H. FIELD

J. L. FRANKLIN

Baytown, Texas

May, 1957

# Contents

Preface . . . . .	v
I. Introduction . . . . .	1
II. Apparatus and Methods . . . . .	3
A. Mass Spectrometric Apparatus . . . . .	3
B. Apparatus Not Using Mass Analysis . . . . .	9
C. Ionization Efficiency Curves . . . . .	12
1. Elementary Considerations . . . . .	12
2. Fine Structure in Ionization Efficiency Curves . . . . .	16
3. Ionization Efficiency Curves of Negative Ions . . . . .	24
D. Ionization and Appearance Potentials . . . . .	26
1. Positive Ions . . . . .	26
2. Negative Ions . . . . .	37
E. Instrumental Factors Affecting Electron Energy . . . . .	41
F. Reliability of Ionization and Appearance Potential Measurements . . . . .	50
III. Theoretical . . . . .	53
A. Ionization Cross Sections . . . . .	53
B. Excited Ionic States and Autoionization . . . . .	54
C. Franck-Condon Principle . . . . .	57
D. Ionization and Dissociation of $N_2$ . . . . .	62
E. Ionization and Dissociation of Symmetrical Polyatomic Molecules . . . . .	66
F. Quasi-Equilibrium Theory of Mass Spectra of Large Molecules . . . . .	68
IV. Energetic Considerations . . . . .	80
A. Heat of Formation of Ions . . . . .	80
B. Activation Energies of Molecule-Ion Decompositions . . . . .	88
C. Kinetic Energy of Ions . . . . .	92
D. Ionization Potentials . . . . .	105
E. Bond Strengths . . . . .	128
F. Bond Strengths in Ions . . . . .	141
G. Negative Ions . . . . .	145
H. Heat of Dissociation of $N_2$ and CO and the Heat of Sublimation of Carbon . . . . .	152
V. Mass Spectral Considerations . . . . .	166
A. Mass Spectra . . . . .	166
1. Diatomic Molecules . . . . .	166
2. Polyatomic Molecules . . . . .	168
(a) Paraffins . . . . .	168
(b) Olefins . . . . .	174

(c) Aromatics . . . . .	175
(d) Stabilities of Molecule-Ions . . . . .	176
(e) Fluorocarbons . . . . .	179
(f) Miscellaneous . . . . .	180
B. Total Ionization . . . . .	180
C. Multiply-Charged Ions . . . . .	183
D. Rearrangement . . . . .	185
E. Metastable Ions . . . . .	194
F. Temperature Coefficients of Mass Spectra . . . . .	202
G. Mass Spectra of Isotopically Substituted Molecules . . . . .	204
H. Secondary Processes in the Mass Spectrometer . . . . .	217
<b>VI. Implications for Chemical Reactions . . . . .</b>	<b>225</b>
A. Olefin Addition Reactions . . . . .	225
B. Rearrangement . . . . .	229
C. Catalytic Cracking . . . . .	230
D. Solvolysis of Aromatic Diazonium Salts . . . . .	230
E. Aromatic Substitution . . . . .	233
F. Non-Planar Ions . . . . .	237
G. Charge Transfer Complexes . . . . .	238
<b>Appendix — Compilation of Critical Potential Values . . . . .</b>	<b>239</b>
Part 1. Positive Ions . . . . .	243
Ions Containing H . . . . .	243
Rare Gas Ions . . . . .	244
Ions Containing B . . . . .	246
Carbon and Hydrocarbon Ions . . . . .	247
Ions Containing Halogens . . . . .	285
Ions Containing Alkali Metal Atoms . . . . .	294
Ions Containing Mg . . . . .	296
Ions Containing Al . . . . .	297
Ions Containing Si . . . . .	297
Ions Containing P . . . . .	299
Ions Containing S . . . . .	299
Ions Containing Ti . . . . .	301
Ions Containing V, Cr, Mn, Fe, Co, Ni . . . . .	301
Ions Containing Ge . . . . .	303
Ions Containing As and Sb . . . . .	304
Ions Containing Se and Te . . . . .	305
Ions Containing Ba . . . . .	305
Ions Containing Hg . . . . .	306
Ions Containing U . . . . .	306
Ions of Ambiguous Composition . . . . .	308
Part 2. Negative Ions . . . . .	311
H Ions . . . . .	311
Alkali Metal Ions . . . . .	311
Ions Containing B . . . . .	311

# CONTENTS

ix

Ions Containing C . . . . .	312
Ions Containing N . . . . .	312
Ions Containing O . . . . .	312
Ions Containing Halogen Atoms . . . . .	314
Ions Containing Si . . . . .	315
Ions Containing S, Se, and Te . . . . .	315
Ions Containing Sb and Bi . . . . .	316
Hg Ions . . . . .	317
<b>References . . . . .</b>	<b>318</b>
<b>Author Index . . . . .</b>	<b>332</b>
<b>Subject Index . . . . .</b>	<b>340</b>



## I. Introduction

We consider in this book electron impact phenomena in gases at low pressure ( $10^{-4}$  —  $10^{-6}$  mm Hg) involving low-energy electrons ( $< 100$  v) and resulting in the formation of ions. Within the past 15 to 20 years the number of fundamental studies of such phenomena has undergone a large increase, and this can be taken as a manifestation of a widespread interest in the subject. This interest is to a considerable extent, we think, the result of the fact that mass spectrometers have become available on a commercial basis and have found a very practical use in the field of analytical measurements. Some of the fundamental studies made were undertaken to provide basic information necessary for the development of the practical applications; others resulted from the happy combination of problems of intrinsic scientific merit with relatively easy accessibility to the equipment needed for their attack; still others were part of the auto-catalytic development to be encountered in any scientific field of endeavor.

Under the conditions here considered, information concerning the primary ionization and dissociation behavior of atoms and molecules under electron bombardment can be obtained. The information is pertinent to a number of aspects of physics and chemistry, and in addition there has evolved what might in some respects be considered a new body of knowledge concerning the physics and chemistry of gaseous ionic systems. This knowledge is of value in itself, but also parts of it may be applicable to other fields such as gaseous electrical discharges, ionic chemical reactions in condensed phases, radiation chemistry, etc.

While there have been a number of reviews of the subject in recent years, they either have been fragmentary and/or essentially briefly annotated bibliographies, or they have had as their focal point of interest experimental and apparatus problems. There is a need for as unified and comprehensive a review as can be achieved, and particularly one wherein the primary emphasis is laid upon the behavior of the systems considered. We have striven toward this ideal, but because we are vitally interested in the energetics of electron impact processes, we have seen fit to discuss in detail problems of apparatus and technique involved in making such measurements. We should point out that, while a large majority of the work we consider involves studies with mass spectrometers, this is merely a reflection of the fact that mass spectro-

meters are electron impact devices. We are not primarily interested in the details of the mass analysis nor in the instrumentation of mass spectrometry, so this work does not constitute a review of mass spectrometry as such.

Work done prior to about 1930 has been adequately reviewed by Smyth (455), and only sparing reference has been made to it herein.

## II. Apparatus and Methods

The essentials for making electron impact experiments are a beam of electrons of known energy passing through the gas under investigation and a device for detecting the ions produced and for measuring their quantity. While apparatus of this low degree of complexity has been used in the past for the determination of ionization potentials of molecules, its utility is quite limited, and consequently apparatus designed to provide information concerning the identities and/or kinetic energies of the ions have come into much more widespread use. In the large majority of the experiments conducted in the past twenty-five years or so, the ions have been subjected to mass analysis, which serves partially to identify the ions and is consequently very useful. In this section we will first discuss the mass spectrometers which have been used in electron impact studies (with particular emphasis on studies leading to the determination of ionic energies) made since the appearance of the review article by Smyth (455), following which the instruments not utilizing mass analysis will be considered.

### A. MASS SPECTROMETRIC APPARATUS

It is not necessary here to give any elaborate discussion of the theory, construction, and operation of mass spectrometers in view of their widespread usage and the excellent reviews of the subject which are available (17, 138, 249). It perhaps suffices to say that in almost all the instruments used for electron impact studies, the ions formed by the electron impact are accelerated and collimated into a beam by a system of electrodes at different potentials, and the essentially monoenergetic beam thus formed is passed through some sort of mass analyzer. Although radio-frequency, time-of-flight, etc., methods of mass analysis are presently being developed and are coming into wider use, the magnetic deflection method of analysis predominates, as it has in the past, and we will restrict our discussion to it. A beam of ions passing at right angles through a homogeneous magnetic field is deflected by an amount which is determined by the momentum of the ions. Since, in general, the beam emerging from the ion source is inhomogeneous in momentum, the several types of ions having different momenta will be

deflected by different amounts, and a judiciously placed slit enables one to collect the ions with a single momentum. Since ions of equal charge in the original beam are homogeneous in energy, the momentum depends only on the mass of the ion, and consequently, the collected ions are all of the same mass. Thus, one achieves mass dispersion. The mathematical relationships for the radius of curvature  $R$  of an ion of mass  $m$  and velocity  $v$  (derived from a voltage  $V$ ) moving through a magnetic field of strength  $H$  are:

$$\frac{mv^2}{R} = e_{esu} vH,$$

$$\frac{1}{2}mv^2 = e_{esu} V/300 \quad (\text{where } V \text{ is in practical volts}),$$

$$\begin{aligned} R &= \sqrt{\frac{e_{esu} Vm}{150 e_{esu}^2 H^2}} \\ &= \sqrt{2.072 \times 10^4 MV/H^2} \end{aligned} \quad (\text{II-1})$$

where  $R$  is in cm and  $M$  is the mass in atomic weight units.

For a fixed system of slits one can collect ions of a given mass by appropriately adjusting the magnetic field strength and the ion energy (ion accelerating voltage). In practice, when one wishes to determine the ions formed from a given compound (the mass spectrum) either the magnetic field strength is maintained constant, and the ion accelerating voltage varied continuously (voltage scanning), or conversely (magnetic scanning).

Perhaps of most interest for our purposes is the instrument devised by Bleakney (32, 36) because the general design of its ion source, involving a magnetically collimated beam of electrons transverse to the ion beam, has since been almost universally used in mass spectrometric electron impact studies. Actually, Bleakney constructed two instruments similar except for the type of mass sorting used. A drawing of the second, and more widely used, version is given in Fig. 1. The entire apparatus depicted is placed within a water-cooled solenoid, 1 meter in length and 5 in. in diameter, producing a magnetic field strength of 1500 oersteds. Electrons from the filament  $F$  are accelerated by the first two plates of the electron gun  $G$  into the space between the plates  $A$  and  $B$  and are collected on the inclined plate  $P$ , which is 100 v positive with respect to the rest of the trap  $T$ . The ions formed are accelerated through the slits  $S_1$  and  $S_2$  by a small field between  $A$  and  $B$  and a stronger one between  $B$  and  $C$ . After deflection by the magnetic field they pass through the slit  $S_3$  and are collected by the plate  $K$ . The magnetic field also serves to constrain the electrons to a well-defined

beam. The sensitivity of the apparatus is quite high because the ion slits  $S_1$ ,  $S_2$ , and  $S_3$  are about 5.5 cm in length, much longer than the slits found in conventional present-day mass spectrometers. A number of pioneering

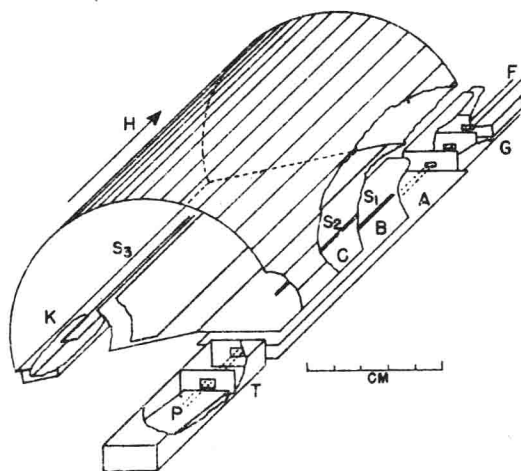


FIG. 1. Bleakney's mass spectrometer (36).

electron impact studies were made with this type of apparatus (36, 274, 373, 450, 493), and quite a few of the results obtained have withstood the passage of time very well. Thus, Bleakney (36) obtained the value of  $15.44 \pm 0.03$  v for the ionization potential of  $H_2$ , to be compared with the presently accepted spectroscopic value of 15.427 v. Similarly, Smith's work on methane (450) is at least as reliable as any of the several more recent studies of this compound.

Bleakney and Hipple (39) later constructed a machine similar to this except for the fact that the ions pass through an electric field perpendicular to the magnetic field of the solenoid and consequently describe a prolate cycloidal path. This apparatus was used for electron impact studies on ethane (219), propane, propylene, and allene (91).

The apparatus used by Tate and Smith (492) is similar to that of Bleakney in that the magnetic field (1000 oersteds) is supplied by a solenoid within which is placed the ion source and mass analyzer. However, the long ion slits used in Bleakney's apparatus are replaced by slits on the order of 5 mm in length, with a corresponding reduction in the length of the apparatus. Nier (369) constructed an apparatus similar to that of Tate and Smith, but utilizing a larger and more powerful solenoid (magnetic field strength

of 2000 oersteds attainable), with the consequence that a resolution of about 100 was achieved. Nier's apparatus was used for electron impact studies on benzene, cyclohexane, and pyridine (247) and on water and ammonia (305). Nier (370) also constructed an apparatus of the same general type except that the magnetic field was supplied by an electromagnet rather than a solenoid. This permitted a larger ionic radius of curvature and a resolving power of 200. A similar apparatus was used by Hagstrum and Tate (198) for an extensive study on energies and modes of decomposition of simple diatomic molecules under electron impact.

An apparatus presumably somewhat similar to that of Tate and Smith was used by Stevenson and Hipple for some of the first extensive studies on hydrocarbons (462, 471, 472, 473, 474). The mass analyzer was of the  $180^\circ$  deflection type, and both the ion source and the mass analyzer were placed within a solenoid providing a magnetic field of 1000 oersteds. A resolving power of about 150 was achieved.

Other home-made machines used for electron impact studies were the  $180^\circ$  deflection instrument of Stueckelberg and Smyth (459) [used for studies on  $\text{H}_2\text{O}$  (457),  $\text{SO}_2$  (458),  $\text{CS}_2$  (456), and  $\text{Br}_2$  (40)] and that of Hogness and Lunn used by Bauer and Hogness (22) for a study on  $\text{CH}_3\text{Cl}$ . Both of these machines are described by Smyth (455). Cummings and Bleakney (88) studied methanol and ethanol with an all-metal  $180^\circ$  deflection instrument.

In the early 1940's mass spectrometers began to be marketed commercially by Westinghouse Electric Company and Consolidated Engineering Corporation, and since then a large majority of the electron-impact experiments made have involved the use of commercial machines. More recently a machine has been manufactured in this country by the General Electric Company and in England by the Metropolitan-Vickers Company, Ltd. The small number of individually constructed machines which have been used have been mostly of the Nier sector-field design (371, 372). In these instruments the Nier (371, 372) modification of the Bleakney (32, 36) ion source is used (the modification consisting of introducing the gas to be subjected to the electron bombardment from a direction normal to the electron beam and collinear to the ion beam, rather than collinear with the electron beam), and the mass analysis is achieved by deflecting the ion beam through  $60^\circ$  (Nier and General Electric),  $90^\circ$  (Westinghouse and Metropolitan-Vickers), or  $180^\circ$  (Consolidated).

To illustrate the details of mass spectrometer operation, a schematic drawing of the Westinghouse mass spectrometer tube (228) is given in Fig. 2. Electrons are emitted by the heated tungsten filament and are accelerated into the ionization chamber by a potential difference of 5 to 105 v between

the filament and electrode 5. Electrodes 3 and 4, maintained at voltages slightly positive with respect to the filament, serve somewhat to collimate the electron beam. The electron beam is collected by electrode 6. The gas

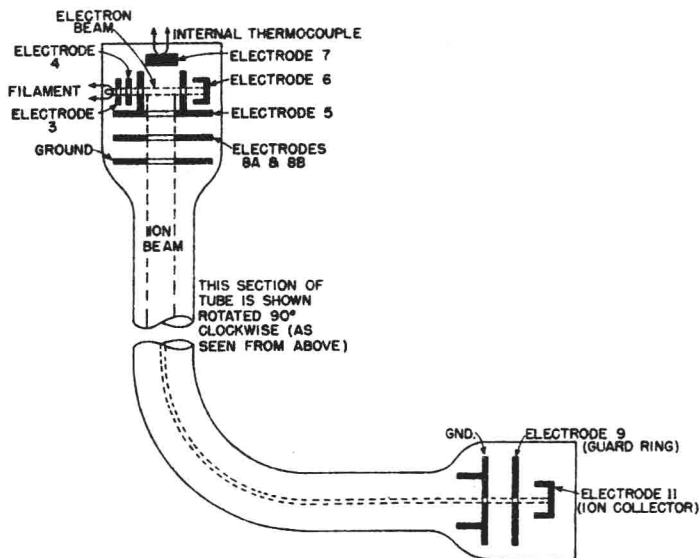


FIG. 2. Westinghouse mass spectrometer tube (228).

under study passes into the ionization chamber from the bottom of electrode 7, and the ions formed in the electron beam are pushed out of the ionization chamber by a small voltage between electrodes 7 and 5 (variously referred to as the ion drawout, ion pusher, or ion repeller voltage). The main ion accelerating voltage (300 to 1300 v) is applied between electrode 5 and the ground electrode. Electrodes 8a and 8b provide some focusing effect on the ion beam. After deflection by the magnetic field the resolved ion beam emerges from the slit in the ion exit electrode and is collected by the collector electrode. The intermediate electrode operated at a negative voltage serves to turn back secondary electrons knocked out of the ion collector by the ion bombardment. The ion current is measured by means of a vacuum tube electrometer the ultimate sensitivity of which is usually on the order of  $10^{-14}$  to  $10^{-15}$  amp.

It is perhaps of interest to compare the commercial instruments (which, as has been mentioned, are now widely used for electron impact studies)

with the older, individually constructed instruments described previously. Such a comparison can also be used as a basis for evaluating the relative reliability of the results obtained with the two classes of instruments. The commercial instruments are designed mostly for routine analytical work, rather than for making electron impact experiments as such. They are well-engineered pieces of equipment which will operate day in and day out with as little trouble as can be expected from apparatus of such a degree of complexity. However, the advances which they embody are in the direction of improving their utility and accuracy for analytical work, and it is our opinion that little or no improvement has been made in the basic problem of electron impact work; namely, that of producing ions by electrons of very well-defined energy. In certain respects the commercial instruments are inferior to the older instruments. Thus, almost all of the individually constructed instruments described above utilized differential pumping on the filament chamber to prevent diffusion of the products of pyrolysis on the filament back into the ionization chamber. While the commercial ion sources are designed to keep pyrolysis at a minimum, it has been recognized that certain electron impact energy measurements made in commercial mass spectrometers are of little or no significance because of the occurrence of pyrolysis (94, 143, 468). Similarly, many of the older instruments used oxide-coated filaments, which, since they operate at a relatively low temperature, serve further to decrease the possibility of pyrolysis; but more important, the very bothersome Maxwellian spread of the energies of the electrons emitted by the filament is appreciably reduced. The commercial instruments in the interest of longer life and less troublesome operation invariably use tungsten filaments.

Thus, with regard to the problem of evaluating the relative merits of the results of earlier work (up to about 1940) and the more recent work done with commercial instruments, we are inclined toward the opinion that there is little basis for general preference. However, it is probably necessary to make the reservation that early work done without the benefit of vacuum-tube amplification of the ion current must be considered as suspect. Also, some of the energies obtained in the 1930's were derived from the experimental ionization efficiency curves by a method (the linear extrapolation method) which is now thought to be unreliable. When this is the case the results obtained must be considered as doubtful. Furthermore, it is possible that the technique (or art) involved in making the measurements was somewhat less advanced then than now, although this factor, of course, depends completely upon the workers involved. To sum up, in cases where the results of later work are in disagreement with those of earlier work, we



do not think it justifiable to conclude, as some workers have done, that the earlier work is *ipso facto* in error.

### B. APPARATUS NOT USING MASS ANALYSIS

At present, apparatus not subjecting the ions formed to mass analysis are very little used. Apparatus of this type are mostly of historical interest, and will be described as briefly as possible.

Perhaps the most useful of the non-mass analysis apparatus is that of Tate and Lozier (489) depicted in Fig. 3 (see also Lozier (296) for an earlier, less elaborate version). Electrons from the filament *F* are accelerated by

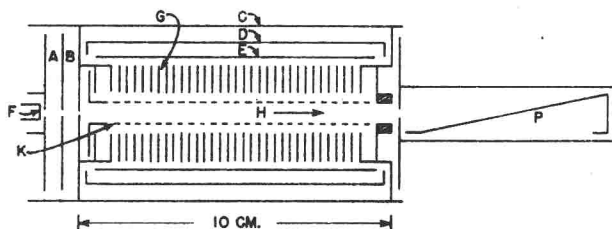


FIG. 3. Retarding potential apparatus of Tate and Lozier (489).

electrodes *A* and *B* down the axis of the apparatus to the electron collector *P*. A magnetic field provided by an external solenoid prevents the electron beam from diverging. The ions formed in the axial chamber diffuse through the cylindrical gauze *K*, and those moving perpendicular to the electron beam are able to traverse the spaces between the thin cylindrical discs *G* and are collected by the ion collecting cylinder *E*. *D* is a guard cylinder and *C* a shield. By applying a voltage of appropriate polarity between *G* and *K*, one can determine whether positive or negative ions are to be collected, by *E*; and by applying an appropriate voltage between *G* and *E*, one can prevent the collection by *E* of ions initially formed with less than any arbitrarily chosen amount of kinetic energy. By varying the energy applied to the electron gun, one can determine the minimum electron energy required to produce ions of a specific kinetic energy and also the relative efficiency of producing ions of a specified minimum kinetic energy as a function of the electron energy. The electron energies must be calibrated by measuring the threshold voltage for the appearance of the molecule-ion of a gas of known ionization potential (which is usually the gas under investigation).