May 24, 1960 S. W. BENSON ET AL 2,938,116

MOLECULAR MASS SPECTROMETER

Filed April 2, 1956 2 Sheets-Sheet 1

FIG. 1.

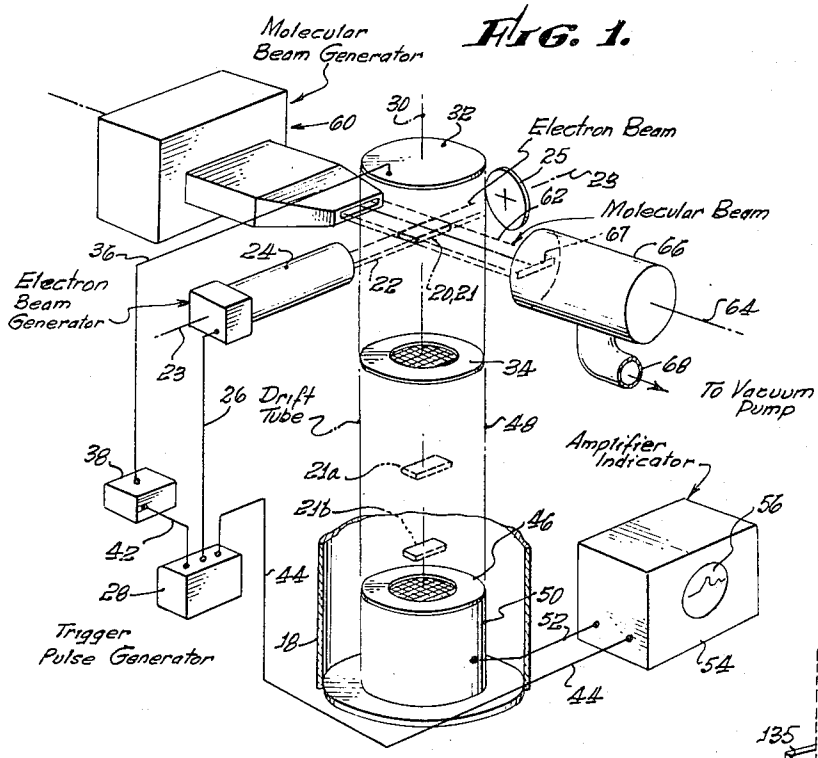


FIG. 7.

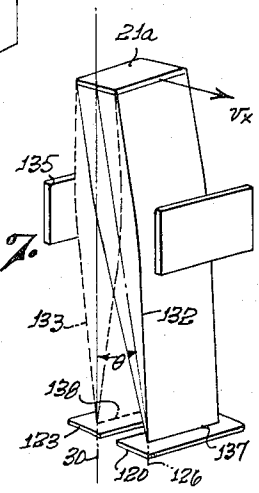


FIG. 6.

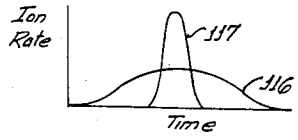


FIG. 10.

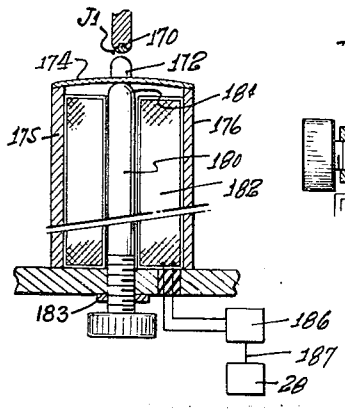


FIG. 11.

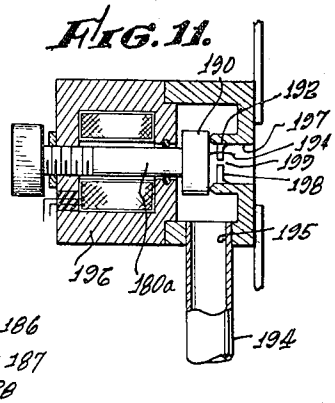
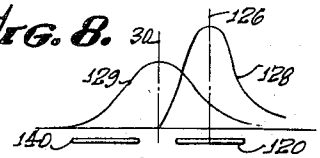


FIG. 8.



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May 24, 1960 S. W. BENSON ET AL 2,938,116

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Filed April 2, 1956 2 Sheets-Sheet 2

FIG. 4.

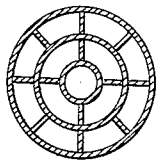


FIG. 3

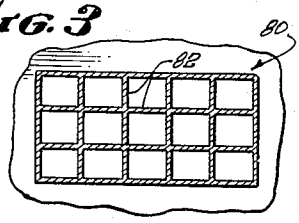


FIG. 2.

FIG. 9.

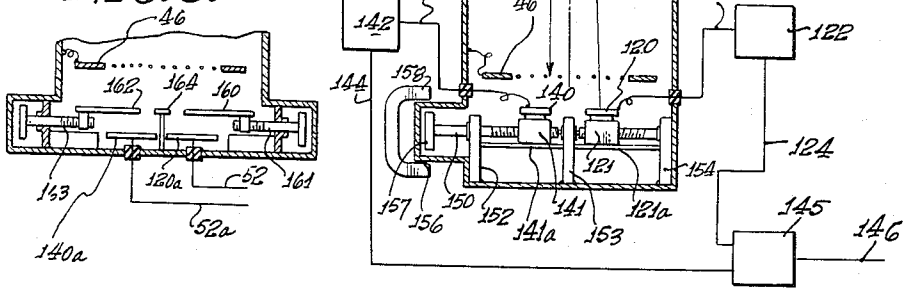
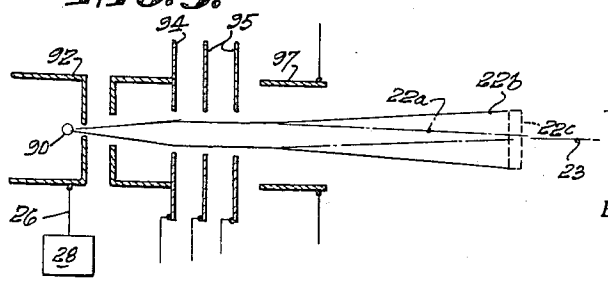


FIG. 5.



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2,938,116

MOLECULAR MASS SPECTROMETER

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18 Claims. (Cl. 250—41.9)

This invention has to do with mass spectrometers, and is concerned more particularly with means for increasing the resolving power of such instruments.

The invention relates particularly to molecular mass spectrometers in which gaseous molecules to be analysed are ionized, the ions are accelerated electrically, and the accelerated ions are separated in accordance with their respective masses and are then detected in some manner that distinguishes with respect to the masses. One of the factors that may seriously limit the effective resolution of such mass spectrometers is the random component of ion movement due to thermal velocity of the initial molecules.

An important object of the present invention is to render the resolving power of mass spectrometers less dependent upon, or substantially independent of, the thermal velocity distribution of the gas to be analyzed.

That is accomplished by selecting for ionization those molecules for which the thermal velocity is directed predominantly perpendicular to a predetermined axis or plane which may be determined for each type of instrument, and which will be referred to as the critical direction. That critical direction corresponds to the direction in which ions of different mass are accelerated.

For example, in conventional resonant mass spectrometers employing a radio-frequency deflecting field, either alone or in combination with a crossed uniform magnetic field, the critical direction is parallel to the plane of movement of the ions. In time-of-flight mass spectrometers the critical direction is parallel to the axis of the ion beam. In conventional magnetic mass spectrometers, in which magnetic focusing ordinarily compensates initial transverse ion movement, the critical direction is parallel to the ion beam. In each instance, the effective mass resolution is limited to a greater or lesser extent by the random ion movement in the critical direction due to the thermal velocity component in that direction of the molecules from which the ions were produced.

In accordance with the present invention, that effect of molecular thermal energy may be greatly reduced by forming the ions initially from molecules having abnormally small random velocity components in the critical direction.

Whereas such selected molecules of abnormally uniform velocity in the critical direction may be made to predominate in the region of ion formation, it is not feasible in practice to exclude completely molecules having substantially random thermal velocities, which will be referred to as background molecules. A further aspect of the invention concerns means for obtaining an output signal that is derived preferentially from ions derived from the described selected molecules rather than from background molecules; and means for compensating, in part or in full, for such background molecules, so that the final output signal may be substantially independent of them.

In accordance with the kinetic theory of gases the molecular translational energy in a gas under equilibrium conditions is independently distributed within each of the velocity components, taken parallel to three Cartesian coordinates, for example. Hence it is impossible to control the distribution of one velocity component by selecting molecules that have a particular distribution in another velocity component. For example, if all molecules are selected for which the velocity component parallel to the x coordinate is large, the selected molecules still ordinarily have a normal random distribution of velocity components parallel to the y and z coordinates.

The present invention, however, provides means for selecting molecules on the basis of the ratio between different components of their velocities. For example, an assemblage of molecules may be produced for which the ratio of the x to the z velocity components is large compared to unity. In such an assemblage, the actual values of the z components of the molecular velocities are abnormally small, and hence abnormally uniform. They are not, of course, precisely determined, but are typically distributed over a range of values that is appreciably smaller than the range normally associated with thermal energy distribution at the existing temperature.

Although the x components of velocity in such an assemblage may, on the average, be larger than normal, that fact does not interfere with the utility of the invention. On the contrary, that fact may be utilized by the invention to further improve the response of the instrument.

In accordance with the invention, molecules having the desired type of velocity distribution may be selected from molecules having normal thermal velocities by forming therefrom a collimated molecular beam. Such a beam may be formed, for example, by allowing molecules to pass through a suitable collimatiing aperture structure from a region at relatively high gas pressure to a region at relatively low pressure. The aperture structure is arranged to pass predominantly only those molecules whose velocities lie within a predetermined range of directions, which typically corresponds to a definite solid angle. That range of directions may be limited only in one coordinate, for example, leading to a molecular beam of sheet form which typically lies substantially in a plane. The molecules in such a beam have velocity components perpendicular to the beam plane that are smaller and more uniform than normal.

Alternatively, the range of molecular directions selected by the aperture structure may be limited in two coordinates, leading typically to a beam of linear form with beam axis parallel to the third coordinate. In such a beam the molecular velocity components in any direction perpendicular to the beam axis are smaller and more uniform than corresponds to normal thermal velocity distribution. The degree of limitation may be different in the two transverse directions, typically leading to a beam of elongated cross section. The molecular velocity components in the transverse directions tend to be more uniform the smaller the beam cross section.

In accordance with the invention, the ion beam of a mass spectrometer is developed from ions produced by ionization of a molecular beam of the described type, the molecular beam being suitably arranged with respect to the critical direction of the particular type of mass spectrograph. That arrangement is such that the molecules of the molecular beam have abnormally uniform velocity components in the critical direction (whether linear or planar) of the spectrometer. Molecules of the beam may be ionized in any suitable manner. An illustrative ionizing means comprises an electron beam of

ionizing energy arranged to intersect the molecular beam at a definite ionizing region. That ionizing region may, for example, be sharply limited longitudinally of the molecular beam, as when the electron beam is sharply defined and the beams intersect substantially perpendicularly; or may comprise substantially the entire volume of the molecular beam, as when the beams intersect substantially parallel.

It is desirable, in carrying out the invention, that the density of molecules in the described molecular beam at the ionization region be as large as possible relative to the density of background molecules, which have substantially normal thermal velocity distribution. The ratio of background molecules to beam molecules may be reduced, for example, by evacuation of the ionizing chamber at a high pumping speed. However, such pumping, to be sufficently effective by itself, requires pumping equipment of such high capacity as to be uneconomical. In accordance with the invention, it is preferred to provide other means for reducing the relative concentration of background ions. In particular, the molecular beam is preferably caused to enter the ionizing chamber through one or more intermediate chambers in which the pressure is maintained at a low value compared to the pressure from which the beam originates. Also, the ionizing chamber is preferably provided with an exit aperture through which the beam may pass into a target chamber which is evacuated sufficiently fast to prevent excessive back flow through the exit aperture. That back flow is preferably further reduced by providing in the exit aperture a novel structure which acts as a unidirectional resistance, passing substantially all of the collimated beam molecules, but obstructing the flow of molecules having normal thermal energy distribution.

The invention further provides novel means for pulsing the molecular beam, whereby flow of molecules into the ionizing region may be limited substantially to the actual periods of ion production. That offers the advantage of greatly reducing the mass of gas that must be removed from the apparatus. Moreover, the amount of sample required for investigation is correspondingly reduced. The very rapid valve action required for effective pulsing of a molecular beam is produced by means of a valve actuated by an element which is magnetostrictive or electrostrictive, and which is driven in turn by suitable pulses of electricity. Rapidly acting valves of that novel type are useful for many purposes other than the control of molecular beams in mass spectrography.

A further aspect of the invention concerns means for preferentially detecting and indicating ions produced by ionization of molecules in the described molecular beam, rather than ions produced by ionization of background molecules. Such selective detection of "beam ions" rather than "background ions" may be accomplished by utilizing the fact that the component of velocity parallel to the molecular beam axis is unidirectional in the direction of the beam for all molecules in the beam, whereas background molecules have velocity components equally divided between the forward beam direction and its reverse. With suitable discriminating means, to be illustratively described, the ion detecting means may be arranged to respond preferentially or solely to ions having a velocity component in the forward direction of the molecular beam, and to be relatively or completely insensitive to ions having a velocity component in the opposite direction. Such preferential response of the system reduces any deleterious effect on resolution caused by the fact that some background molecules are necessarily present and have normal random velocity components in the critical direction.

Furthermore, the effect of background molecules may be substantially eliminated from the final output by providing dual ion-detecting means, typically comprising two detecting channels, each of which develops an electrical signal. The two channels are arranged to be more sensitive and less sensitive, respectively, to ions originating from the molecular beam than to ions originating from background molecules. The two signals are then compared, and a differential signal is developed which represents substantially the effect that would result in absence of any background molecules in the ionizing chamber.

The invention further provides means by which the origin of certain types of ions may be determined with greater convenience and certainty than has previously been possible. For example, a procedure to be described is capable of distinguishing between ions that correspond directly to molecular species in the original gas sample, and ions that have resulted from fragmentation of such initial molecules.

A full understanding of the invention and of its further objects and advantages will be had from the following description, of which the accompanying drawings form a part. That description is intended only as illustration of the invention, and not as a limitation upon its scope, which is defined in the appended claims.

In the drawings:

Fig. 1 is a schematic perspective, representing an illustrative embodiment of the invention in a time of flight mass spectrometer;

Fig. 2 is a schematic axial section illustrating the invention;

Fig. 3 is a section on line 3—3 of Fig. 2, at enlarged scale;

Fig. 4 is a section corresponding to Fig. 3 and showing a modification;

Fig. 5 is a schematic section illustrating electron accelerating means in accordance with the invention;

Fig. 6 is a schematic diagram illustrating typical time distribution of certain types of ions;

Fig. 7 is a schematic perspective representing illustrative ion paths in accordance with the invention;

Fig. 8 is a schematic diagram illustrating typical space distribution of certain types of ions;

Fig. 9 is a fragmentary section corresponding to a portion of Fig. 2 and illustrating a modification;

Fig. 10 is a fragmentary section illustrating means for pulsing a molecular beam; and

Fig. 11 is a fragmentary section corresponding generally to Fig. 10 and illustrating a modification.

An illustrative embodiment of one aspect of the invention is shown in schematic form in Fig. 1 in connection with a mass spectrometer of the type that distinguishes molecular masses in terms of the time of flight of ions between an accelerating field and a collector. For clarity of illustration in Fig. 1, the chamber wall of the vacuum chamber is shown only fragmentarily at **18**. Positive ions are produced within a definite ionizing region **20** of chamber **18**. The ions are then accelerated downward in the direction of main axis **30** by an electric field of definite magnitude and typically very short duration produced between a conductive pusher plate **32** and a grid **34**. The accelerated ions pass through grid **34** into a substantially field free space indicated at **48**, which will be referred to as the drift tube. The time required by an ion to traverse the drift tube depends upon its axial velocity, which in turn is a function of its mass. The total time of flight may thus be utilized as a measure of the mass.

At the farther end of the drift tube, suitable means are provided for detecting the ions, indicated as the collecting grid **46** and electrical detection means **50**. Detector **50** may be directly responsive to the charge of ions passing through defining grid **46**, or may respond, for example, to secondary electrons produced by the ions. What ever type of detection is used, an electrical signal is typically produced on line **52** which corresponds to the instantaneous rate of arrival of ions at the sensitive area of the detector. That signal may be displayed or otherwise utilized by any suitable means, represented illustratively as a cathode ray oscilloscope **54**.

Ionizing region 20 is preferably of flat laminar form, as typically represented in the drawing. The resulting ion assemblage 21 then has substantially the same form. It will be referred to for convenience of designation as an ion lamina, but without thereby intending any necessary limitation upon its shape. Ion lamina 21 may be produced by collisions of electrons in a pulsed electron beam 22 with molecules within the ionizing region 20. Electron beam 22 may be produced by any suitable type of pulsed electron beam generator, indicated schematically at 24 and illustratively described in connection with Fig. 5. Electrons that do not make collisions continue along electron beam axis 23 and are received by a target plate 25, which is preferably held at a suitable positive potential by means not explicitly shown in Fig. 1.

The ions are produced during a very short time period, typically of the order of microseconds, as by a correspondingly short pulse of electrons. The timing of the pulse of ionizing electrons is typically controlled by a periodic ionizing timing pulse, supplied to electron beam generator 24 from a trigger pulse generator indicated schematically at 28. Trigger pulses are typically developed periodically at intervals of a few milliseconds, under any suitable type of timing control, such as a conventional oscillator forming a part of generator 28.

After production of each pulse of ions in lamina 21, an ion accelerating field is produced parallel to main axis 30 and of suitable polarity to accelerate the positive ions in a positive direction along that axis, which is taken as downward in Fig. 1. The ion accelerating field is typically developed between a conductive plate 32 and a field-defining grid 34, which intersect axis 30 perpendicularly above and below region 20, respectively. Grid 34 is preferably maintained continuously at ground potential, the ion accelerating field being produced by applying a suitable positive voltage to plate 32. Plate 32 will be referred to for convenience as a pusher plate, but without implying that the ion accelerating pulse is necessarily applied to it, rather than to grid 34, for example.

The ion accelerating field is initiated in definite time relation to the pulse of ionizing electrons already described. An accelerating voltage pulse may, for example, be developed by suitable means indicated at 38 and delivered via a line 36 to pusher plate 32. Action of accelerating pulse generator 38 may be controlled by a timing pulse supplied via line 42 from trigger pulse generator 28. Either trigger generator 28 or accelerating pulse generator 38 is provided with mechanism of known type to produce the desired time delay, which is preferably adjustable, so that the ion accelerating field is imposed immediately or shortly after the end of the ionizing electron pulse from electron gun 24.

Ion lamina 21 is thus accelerated bodily downward along axis 30. It passes through the apertures of grid 34 into the substantially field-free drift tube 48 between that grid and a defining collector grid 46. For clarity of discussion all ions will ordinarily be considered to have lost a single electron, and hence to have unit positive charge. The velocities with which the individual ions enter drift tube 48 then depend primarily upon their respective masses. If the pusher field is maintained uniform until all ions have passed grid 34, as will be assumed for purposes of illustration, the ion velocities are substantially inversely proportional to the square roots of their respective masses. If the pusher field is reduced to zero before the ions have passed grid 34, the ion velocities are substantially inversely proportional to the first power of the respective masses. In either case, the ions of original lamina 21 become separated into a plurality of sub-laminas, such as 21*a* and 21*b*, which comprise ions of distinct masses and which travel at corresponding distinct velocities.

Any suitable type of ion collector 50 is provided, which is typically responsive to the rate at which ions are received. When the ion sub-laminas of respective masses are completely separated longitudinally of the drift tube, as indicated at 21*a* and 21*b*, the corresponding signals on line 52 are similarly separated in time. The relative amplitude of those signals then provides a measure of the relative abundance of the corresponding ion masses in the initial lamina 21. That information may be indicated or utilized in any suitable manner. For example, the horizontal sweep of oscilloscope 54 may conveniently be triggered by a timing pulse supplied on line 44 from trigger generator 28; and the signal from line 52, after suitable amplification, may be applied to the vertical deflection plates of the oscilloscope, producing directly a graphical plot of relative mass abundances as a function of arrival time at the ion collector, as indicated at 56.

In actual practice, ions having equal mass and charge do not all move down the drift tube at strictly equal velocities, due to factors of many different types. Hence each sub-lamina tends to become diffused as it travels, reducing the effective sharpness with which closely adjacent mass numbers are resolved. The present invention is concerned particularly with means for reducing an important cause of such spreading of the respective laminas, namely, the random thermal velocities of the molecules that are initially ionized in ionizing region 20.

The components of molecular thermal velocities perpendicular to main axis 30 cause relatively little harm, since transverse diffusion of the ion sub-laminas can be compensated by focusing devices or by employing an ion collector of adequate effective area. However, the random velocity components of the initial molecules parallel to main axis 30 persist throughout the ion acceleration and drift phases of the operation, leading to longitudinal diffusion of the ion laminas at collector 50. That type of diffusion affects the time of arrival and tends to cause adjacent sub-laminas to be incompletely separated at the collector. The critical direction for the time of flight spectrometer is thus parallel to the main axis.

In accordance with the invention, molecules are supplied to ionizing region 20 in such manner that their velocities are not completely random, but have been selected in a particular way. In the present embodiment, molecules are selected which have abnormally small ratios of their velocity components parallel to main axis 30 (that is, parallel to the sensitive direction) to their velocity components in a predetermined direction perpendicular to that axis. That is accomplished by forming a collimated beam 62 of molecules with axis 64 which intersects main axis 30 substantially perpendicularly at ionizing region 20. The molecular beam may be formed by suitable means, indicated at 60 and to be described. Molecular beam axis 64 is preferably substantially perpendicular to electron beam axis 23, as well as to main axis 30. Ionizing region 20 is then effectively defined by the volume common to the intersecting molecular and electron beams. Use of a molecular beam thus provides the advantage of limiting the region of effective ion formation longitudinally of the electron beam.

Those molecules of beam 62 which are not ionized, either because they pass through ionizing region 20 while electron beam 22 is cut off or because they do not happen to be struck by an ionizing electron, preferably pass through an aperture 67 into a trap structure indicated schematically at 66, from which they may be evacuated as at 68.

Fig. 2 represents in further detail but also in schematic form an embodiment of the invention, including illustrative means for producing a molecular beam. In Figs. 1 and 2 the same numerals are applied to parts which correspond generally in function. Fig. 2 is a section in the plane defined by molecular beam axis 64 and main axis 30, and is thus typically perpendicular to electron beam axis 23. Several successively communicating chambers, shown typically as five, are represented at C1 to C5, with apertures J1 to J4 between the successive pairs of

chambers. The apertures are all aligned on axis 64. Apertures J1 to J3 may be all identical in size and structure, and will be so considered for clarity of description. They are preferably considerably wider in the direction perpendicular to the plane of Fig. 2 then in that plane, the dimensions shown being somewhat exaggerated for clarity of illustration. Chambers C2 to C5 are provided for purposes of illustration with respective individual vacuum pumps V2 to V5, which are typically of diffusion type and may exhaust to a common mechanical forepump of conventional type. Chamber C4 corresponds generally to the main chamber indicated at 18 in Fig. 1; chambers C1 to C3 comprise molecular beam generator 60 of that figure; and chamber C5 corresponds to tape 66.

Gas molecules to the analyzed are supplied in chamber C1 at a pressure P1 which is ordinarily, although not necessarily, substantially uniform, as from a reservoir 70, which communicates with the chamber via a control valve 72. The molecules in chamber C1 typically have a substantially normal energy distribution corresponding to an existing temperature T. Gas molecules are allowed to issue freely from chamber C1 to chamber C2 through the relatively small aperture J1, the pressure P2 in the second chamber being maintained by pump V2 at a value appreciably less than P1. Pressure P2 is sufficiently low that the molecular mean free path in the second chamber is long compared to the chamber dimensions. That same relation holds also for chambers C3 and C4. The molecules leaving aperture J1 then form a divergent beam, as indicated schematically at Q12, which is distributed substantially uniformly within a solid angle determined by the form of aperture J1.

A relatively small proportion of those beam molecules continues without collision through aperture J2 into the third chamber C3, forming in that chamber a direct beam indicated at Q13. The relatively small solid angle of beam Q13 is determined primarily by the dimensions of aperture J2 and its axial spacing from aperture J1. The remainder of the molecules of the initial beam Q12 strike the walls of chamber C2, acquire substantially random velocities, and are eventually removed, primarily by pump V2. A small proportion of those random molecules in chamber C2 escapes through aperture J2, forming a relatively diffuse secondary beam Q23 in chamber C3. Although the solid angle of that beam is typically much larger than that of the direct beam Q13, its density is determined by the pressure P2, which is typically much smaller than the pressure P1 that determines the density of the primary beam. For example, if P2 is of the order of one twentieth of P1, secondary beam Q23 is typically of the order of one twentieth of the initial beam Q12 and may be approximately equal to Q13. Hence, if pumps V2 and V3 are of equal capacity, the pressure P3 in the third chamber may be approximately one tenth of P2.

Again, a small portion of the direct beam Q13 passes without collision through aperture J3 into the fourth chamber C4, which is shown illustratively as the ionizing chamber of the mass spectrometer. It will be understood, however, that a larger or smaller number of intermediate chambers may be provided between C1 and C4. The number of thermal molecules passing through J3 into the ionization chamber, indicated at Q34, is of the order of one tenth of Q23, corresponding to the pressure ratio P3/P2. The number of molecules per second in direct beam Q14 is typically about one half that in Q13, since the beam solid angle has been further restricted by aperture J3. The direct beam Q14 then contains about five times as many molecules per second as secondary beam Q34. Thus the use of successive collimating apertures, with suitable evacuation of the regions between them, permits the effective intensity of the direct beam to be progressively increased with relation to the intensity of thermal molecules that accompany it. As a result, the pressure P4 of stray or background molecules in chamber C4 can be held by moderate pumping capacity of pump V4 to such a level that within direct beam Q14 the effective pressure of beam molecules predominates over that of background molecules. Under that preferred condition, ionizing region 20, which lies within the direct molecular beam Q14, contains predominantly beam molecules.

The density of background molecules in chamber C4 may be further reduced, for given pumping capacity from that chamber, by providing a suitable beam trap, illustratively shown as target chamber C5 and associated mechanism. Chamber C5 communicates with ionizing chamber C4 via an aperture J4, which is preferably just large enough to receive substantially the entire direct beam Q14. Hence, that beam passes as a direct beam Q15 into target chamebr C5, from which the molecules are removed, as by pump V5, sufficiently fast to maintain a pressure P5 that is preferably not appreciably greater than P4. The back flow of thermal molecules through J4, denoted by Q54, may thereby be held to a satisfactory low level.

The invention also includes means for further reducing the back flow through aperture J4. Structure may be provided at that aperture which causes a differential resistance to passage of background molecules, having randomly distributed velocities, and beam molecules, whose velocities lies predominantly within a relatively small solid angle. Such a differential resistance is represented illustratively at 80 in Fig. 2, and is further illustrated in section in Figs. 3 and 4, which show two illustrative embodiments. Restricting vanes 82 of relatively thin material are inserted in the aperture in mutually spaced positions, extending parallel to the direction of movement of the beam molecules. Those vanes preferably extend longitudinally of the beam through a distance that is large compared to their separation. A great majority of the beam molecules pass between the vanes without obstruction, only a small proportion striking the edges of the thin vanes, or grazing the vane faces because of slight departure from the geometrical beam direction. Hence the vane structure presents substantially the same resistance to the directed molecules of the beam as would result from a bare aperture J4. With respect to background molecules, on the other hand, the vane structure presents a much higher resistance, which corresponds to the normal resistance of a large number of tubes of relatively small effective diameter. With a differential resistance of the described type at aperture J4, reduction of the back flow Q54 to a desired level may be accomplished more economically, for example, by means of a pump of lower capacity at V5.

Ionizing region 20 may be considered to be defined by the intersection of molecular beam Q14 and the ionizing electron beam 22, which is perpendicular to the paper in Fig. 2. The vertical width of the molecular beam, indicated at 62, is preferably equal to or greater than that of the electron beam. The limits of the ionizing region, as seen in Fig. 2, then coincide with the cross section of the electron beam, by which they are defined. The dimension of region 20 perpendicular to the paper is defined by the corresponding dimension of the molecular beam, which is readily controllable by the apertures J1 to J3. That dimension of region 20 is not particularly critical, but is preferably large compared to its height, and may considerably exceed its horizontal dimension as seen in Fig. 2.

Electron beam 22 may be produced by a suitable electron gun structure for accelerating the electrons to ionizing energy, provided with suitable focusing means for concentrating the electrons to the desired relatively small and sharply defined cross section, as indicated at 22 in Fig. 2, for example. Suitable electron gating means are further provided, for production of a sharp electron pulse under control of the timing voltage pulse on line 26 of

Fig. 1, for example. Such structure is illustrated schematically in Fig. 5. A source of electrons, such as a hot tungsten filament, is indicated at **90**. A control grid or apertured electrode **92** is normally held at a negative cut-off potential, and is raised to a positive potential with respect to electron source **90** only during the short timing pulse supplied via line **26**. Electrons accelerated through grid **92** during that pulse are further accelerated along axis **23** by positive electrode **94** the total accelerating potential being typically one or two hundred volts. The resulting beam is preferably focused by suitable electrodes **95** to form a defined beam, indicated schematically by the dashed lines **22***a*. Positively charged deflecting plates **97** may then act as a cylindrical negative lens, widening the electron beam in the plane of Fig. 5, as indicated by the solid lines **22***b*. The resulting elongated beam cross section at ionizing region **20** is typically represented at **22***c*.

Of all the molecules in ionizing region **2**, those which have arrived without collision from the initial beam-defining aperture J1 will be referred to as beam molecules. The velocities of all beam molecules in that region must then lie within a rather small definite solid angle, which includes axis **64** and is determined by the geometry of the apparatus. Since all beam molecules thus have velocities that are nearly perpendicular to main axis **30**, the molecular velocity component parallel to that axis is necessarily small compared to the velocity itself. And since the beam molecules have been selected only with respect to the directions of their velocities, and not with respect to the magnitudes, the distribution of velocity magnitudes is substantially the same as under normal equilibrium conditions. The actual velocity components parallel to main axis **30** are thus necessarily smaller than would correspond to normal thermal distribution. Since those velocity components are distributed about the value zero, and since their magnitudes are abnormally small, the variation of the velocity components is necessarily less than that corresponding to normal random thermal velocity distribution for a given direction. With respect to movement along the main aixs, the beam molecules comprise an abnormally homogeneous group.

That initial homogeneity remains during ionization of the beam molecules, provided the ionization takes place without fragmentization of the molecules, since the momentum of the ionizing electrons is negligible compared to that of the molecules. The homogeneity with respect to thermal energy parallel to axis **30** also persists during accerelation of the ions along that axis. That is to say, although accelerations that are differential with respect to mass may later be produced, the substantial absence of differential thermal velocities in the direction of the main axis persists. The ion sub-lamina corresponding to each molecular mass therefore disperses longitudinally of the main axis less than if normal molecular thermal velocities were involved. The situation when ionization produces molecular fragmentization is discussed below.

The ion lamina **21** produced in ionizing region **20** by each electron pulse is accelerated downward in the direction of main axis **30** by any suitable means. The length of the ion accelerating field is preferably large compared to the axial dimension of ionizing region **20**, so that the energy imparted to an ion is substantially independent of its initial position within region **20**. As illustrated, the field extends from pusher plate **32** to defining grid **34**. Annular guard rings are preferably provided, as indicated at **100**, arranged coaxially with respect to main axis **30** and connected to suitable points of a voltage dividing network. Such a network may comprise the resistances **104**, connected in series between ground and a suitable source of positive voltage indicated at B+. Guard rings **100** are connected to the respective junction points of resistances **104** by the respective lines **102**, which pass through a suitable insulating fitting **103** in the wall of chamber C4. The guard ring **100***a* nearest ionizing region **20** is preferably provided with a grid **105** to provide positive field definition, and is connected directly to B+. Pusher plate **32** is effectively connected to guard ring **100***a* in idle condition of the ion accelerating structure and is made positive with respect to guard ring **100***a* during the relatively short time that an ion lamina is to be accelerated.

As illustratively shown, pusher plate **32** is connected via line **36** to an electronic pulse generator indicated at **106**, which corresponds generally to device **38** of Fig. 1, and receives timing pulses via line **42** from trigger pulse generator **28**. In absence of a timing pulse, pusher plate **32** is held at the same potential as guard ring **100***a*. In response to a timing pulse on line **42**, pulse generator **106** supplies a positive-going pulse via line **36** to pusher plate **32**. That establishes an ion accelerating field between the pusher plate and guard ring **100***a*, which may be regarded as a part of an over-all accelerating field between the pusher plate and defining grid **34**.

In operation, the region between pusher plate and grid **105** is substantially field-free during ion formation in region **20**. After formation of an ion plasma a field is applied which accelerates the ions downward through grid **105** into the main accelerating field which is permanently maintained between grids **105** and **34**. The intensity of the injecting field above grid **105** may be determined by suitable selection of the magnitude of the pulse from generator **106**. It is typically made equal to the field intensity just below grid **105**, but a change of field strength at grid **105** may be provided if desired.

The values of resistances **104** may be directly proportional to the axial spacing of the elements which they connect, producing a uniform accelerating field throughout its length. It is preferred, however, to provide such variations of the accelerating field as will tend to focus the ions toward axis **30**. That may be accomplished by suitable selection of resistances **104**. A preferred arrangement, illustrated in Fig. 2, comprises connection of one or more of the guard rings **100**, shown as the ring **100***b* adjacent grid **34**, to an independent and preferably variable voltage source. Such a source is typically provided by the potentiometer **110**, connected in series with a suitable resistance **111** between ground and B+. The potentiometer voltage, supplied via line **112** to guard ring **100***b*, is typically made sufficiently positive with respect to the adjacent rings to give the desired degree of focusing. The focusing means, whatever its detailed structure, is preferably such that ions initially leaving ionizing region **20** along parallel paths tend to be brought substantially together at the ion receiving means. Focusing means of cylindrical type may be provided in known manner, which tend to bring such ions together at a line perpendicular to the plane of Fig. 2, rather than at a point. The latter type of focusing is illustrated schematically in Fig. 7, and is particularly effective in connection with the present invention.

An advantage in providing a relatively long ion accelerating field is that focusing of the described type can be provided without large variations of field strength and also without introducing appreciable differences of effective path length for ions in different portions of the field cross section.

A further advantage of a relatively long ion accelerating field is that the total time of flight of ions from ionizing region **20** to collector grid **46** is thereby increased, for any given total length of apparatus and total accelerating voltage. In the illustrative case of uniform accelerating field, the time $t1$ required for an ion to move through an accelerating field of length D1 is $2D1/v$, where v represents the velocity gained by the ion in falling through the total accelerating voltage E. For an ion of mass m and charge e, $v=(2eE/m)^{1/2}$. The time $t2$ required by the ion to then move through a drift tube of length D2 is $D2/v$. Hence the total time of flight

$t=(2D1+D2)/v$. The effective length D' of the ion path, which determines the time of flight, is thus given by $2D1+D2$, whereas the actual length D, which determine sthe bulk and to a large extent the cost of the instrument, is only $D1+D2$. The total time of flight is thus directly proportional to D' and to the square root of the ion mass.

The effective path length D' may be visualized with relation to Fig. 2 by considering the ions to be produced at a virtual source indicated at **20***a*, located on main axis **30** at a distance D1 above actual source **20**. The effective length of the instrument, so far as total drift time is concerned, is equivalent to the distance from virtual source **20***a* to collector grid **46**.

The effective path length D' is a factor of great practical importance in determining effective operation of a time of flight mass spectrometer. For the time separation between arrival at the detector of ions of different masses is directly proportional to that length. Assuming that ion sub-laminas corresponding to adjacent mass numbers $m1$ and $m2$, for example, become spatially separated before reaching the ion detector, they cannot be effectively resolved unless the time separation between them is sufficiently large with respect to the response time of the detecting and indicating means. Whereas that response time can theoretically be varied within wide limits, expense and complexity tend to increase rapidly as the response time is reduced. It is therefore highly desirable that the effective path length be increased by making D1 as large as practicable with relation to D2.

Ion receiving means **50** may be of any suitable type, and may, for example, have an effective area of response sufficient to receive all ions produced in ionizing region **20**, whether from beam molecules or from background molecules. Fig. 6 represents schematically illustrative distribution in time of the arrival at receiver **50** of ions of a single mass produced by one electron pulse, the time scale being enlarged to clarify the action. Curve **116** represents such ions produced from background molecules having normal thermal velocity distribution. Such molecules have normally distributed components v_z of thermal velocity parallel to main axis **30**, corresponding on the average to a kinetic energy of $\frac{1}{2}kT$, where k is Boltzmann's constant and T is the absolute temperature in chamber C4. For molecules of mass m, that average energy corresponds to a velocity component v_z of $(kT/m)^{1/2}$. The velocity v_e produced by the accelerating field E is $(2eE/m)^{1/2}$. The time of flight depends upon the total velocity $v=ve_e\pm v_z$, which is either larger or smaller than v_e, according to the direction of v_z. That velocity variation causes each ion sub-lamina to disperse longitudinally of main axis **30**. Arrival of the otherwise homogeneous ions at the receiver is therefore relatively spread out in time, leading to a relatively broad time distribution curve such as **116**.

Ions formed from beam molecules, on the other hand, have random velocity components v_z that are distributed over a far narrower range. Assuming molecular flow, the total velocity of beam molecules, which is substantially equal to the component velocity v_x, corresponds to an average energy of about $2kT$. The component v_z, however, does not correspond on the average to one third of that energy. For each beam molecule the velocity component v_z may be expressed approximately as $v_x \sin\theta$, where θ is the angle between beam axis **64** and the projection of the molecular path on the plane of Fig. 2. Since angle θ is small, $\sin\theta$ is substantially equal to $\tan\theta$, which cannot be larger than about half the vertical width d of ionizing region **20** divided by the distance L of that region from jet orifice J1, the vertical width of J1 being assumed small compared to d. The random thermal velocity in the critical direction is thus reduced for all beam molecules by a fraction which is of the order of d/L, as compared to background molecules. That ratio preferably has a value between about one tenth and about one twentieth, but may be made even smaller if desired. The axial dispersion with which the resulting ions arrive at the receiver is correspondingly reduced, leading to a time distribution curve such as **117** in Fig. 6. The potential improvement in resolution is obvious.

The flow through aperture J1, which forms the molecular beam, is typically partially viscous, and may be made to correspond substantially entirely to viscous flow by selecting the pressure P1 so that the average molecular mean free path in chamber C1 is large compared to the dimensions of aperture J1. For example, if P1 is 1 mm. of Hg and the smallest dimension of aperture J1 is about 0.5 mm., the flow is typically essentially viscous. Viscous flow has the advantage that the ratio of molecular species in the molecular beam corresponds closely to that in chamber C1, whereas with molecular flow molecules of small mass and high velocity tend to be favored. Under conditions of viscous flow, the considerations discussed above apply in principle, although quantitative details are altered. The beam molecules may be considered to have a uniform forward velocity of the order of the velocity of sound, upon which is superposed a random thermal velocity. That random velocity component typically corresponds to a temperature lower than the temperature of chamber C1. As in the case of molecular flow, the action of successive apertures, such as J2 and J3, eliminates molecules for which the thermal velocity component in the critical direction is not small compared to the beam velocity.

Even in the presence of an appreciable proportion of background molecules in ionizing region **20**, provision of a molecular beam of the type described may be highly advantageous. For example, the presence in the output signal of sharp peaks such as **117** may well provide useful information even though superposed upon a background, such as **116**, that is resolved less clearly or not at all.

The described improvement in resolution, however, may be greatly increased by providing suitably arranged ion receiving means of novel type. For that purpose, the primary ion receiver is preferably offset with respect to main axis **30** in the direction of flow of molecular beam **62**. Such an offset receiving surface is illustratively indicated at **120**. The line **126** from the effective center of receiving surface **120** to the center of virtual ionizing region **20***a* will be referred to as the axis of the receiver. The amount of offset of receiver **120** may conveniently be expressed in terms of the angle θ between receiver axis **126** and main axis **30**. That angle may be so chosen that the receiver receives preferentially ions originating from beam molecules rather than ions originating from background molecules. That is because the beam velocity of the former tends to carry them progressively farther to the right from main axis **30** as they drift toward the receiver.

As already pointed out, under conditions of molecular flow the total thermal velocity of molecules in the beam corresponds to an approximate average energy of $2kT$, and the velocity component v_x in the beam direction is substantially equal to the total velocity. The relative number N_1 of beam molecules having a given velocity component v_x may be expressed approximately as

$$N_1=4\pi v_x^2\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv_x^2}{2kT}} \qquad (1)$$

which goes to zero for $v_x=0$. For background molecules, on the other hand, the relative number of molecules having a given velocity component v_x may be expressed theoretically as

$$N_2=\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{mv_x^2}{2kT}} \qquad (2)$$

The approximate ratio of beam molecules to back ground

molecules, expressed as a function of v_x, can therefore be expressed theoretically as

$$\frac{N_1}{N_2}=4\frac{mv_x^2}{2kT} \quad (3)$$

After acceleration through a potential difference E, each ion moves along a path in the drift tube which makes an angle θ with main axis **30** the tangent of which is approximately equal to the ratio of the initial velocity component v_x in the molecular beam direction divided by the acceleration velocity v_e (neglecting the small dependence of θ upon the thermal velocity component v_z along main axis **30**). Since θ is small, the tangent is substantially equal to the angle in radians, so that, approximately,

$$\theta=\frac{v_x}{v_e}=v_x\left(\frac{m}{2eE}\right)^{1/2} \quad (4)$$

Such correction factors as the initial molecular velocity component v_z along main axis **30** may be taken into account if desired, but do not alter the nature of the result. The projection of an ion path on the plane of Fig. 2 can be constructed approximately by drawing a straight line at the angle θ, not through the actual point of origin of the ion in region **20**, but through the corresponding point of virtual ionizing region **20***a*. The line **126** in Fig. 2 represents such a path for an ion originating at the center of region **20**. From the last two equations, the approximate theoretical ratio of beam ions to background ions at a given value of v_x may be expressed in terms of θ as

$$\frac{N_1}{N_2}=8\frac{\theta^2eE}{2kT} \quad (5)$$

which is seen to be independent of the ion mass *m*.

Fig. 7 is a schematic perspective, representing illustrative ion paths for typical beam ions, shown in solid lines at **132**, and for typical background ions, shown in dashed lines at **133**. Suitable focusing means are indicated schematically at **135**, acting as a cylindrical lens so that each lamina component becomes compressed in the direction v_x, forming ideally a line image at the plane of the receiver. Such an image for beam ions, having average v_x corresponding to average kinetic energy of substantially $2kT$, is indicated at **137**, and for background ions, having average v_x equal to zero, at **138**. Separate receivers **120** and **123** are represented, at positions to receive preferentially the respective beam and background component images **137** and **138**. Receiver **123** is shown directly on main axis **30**; and receiver **120** is offset from that axis in the direction of v_x at a radial distance corresponding to the angle θ. The ratio of that radial offset to the axial spacing of the receiver from the ionizing region is given by tan θ, or v_x/v_e. That ratio is approximately equal to the square root of the quotient of $2kT$ divided by the acceleration energy of the ions. That approximate relation may be verified, for example, by replacing v_x and v_e in the ratio v_x/v_e by values derived from the kinetic energy relations: before ionization, the average molecular kinetic energy $mv_x^2/2$ is approximately $2kT$; and after acceleration, the ion acceleration energy is approximately equal to the kinetic energy $mv_e^2/2$.

If ions are considered that have initial velocities different from the average values for the beam and background components, it may be seen that for any specific assumed value of v_x, there is typically a definite transverse position of the corersponding image at the receiver.

Fig. 8 is a schematic drawing representing typical transverse spatial distribution of ions at the ion receiver. The curves **128** and **129** are plots of the relative numbers of ions of a particular mass arriving at the receiving surface, as a function of the distance from main axis **30**, curve **128** representing ions originating from beam molecules, and curve **129** representing ions originating from background molecules. It is assumed for clarity of illustration that equal numbers of ions of the two types are produced. The curves are not necessarily drawn to scale, and are intended only to illustrate qualitative relations. In absence of focusing means such as **135**, or with partial focusing, both curves are considerably broadened, because of the appreciable dimension of ionizing region **20** in the direction of molecular beam axis **64**. Because of that effect, and other practical factors tending to broaden the actual ion distribution, curve **128** does not, in fact, necessarily lie entirely to the right of main axis **30**. Beam ions arrive typically with a spatial distribution such as curve **128** of Fig. 8 and a time distribution such as curve **117** of Fig. 6; while background ions arrive typically with a spatial distribution such as curve **129** of Fig. 8 and a time distribution such as curve **116** of Fig. 6.

It may be seen at once from Fig. 8, that even with the relatively unfavorable assumption that the ratio of total beam ions to background ions is 1:1, the corresponding ratio for ions actually received by a surface such as **120** may be made appreciably larger by suitable placement of the receiver with respect to axis **30**. The farther receiver **120** is moved off axis the larger that ratio becomes. However, the absolute number of beam ions received goes through a maximum at a position close to that shown in Fig. 8, and further increase in the ratio of beam ions to background ions is therefore attained at the expense of signal intensity. The optimum position of a single receiver **120** typically depends upon such factors as the actual ion intensity. It may be considerably farther off axis than the position of maximum signal.

The dispersion due to thermal motion of the background molecules can be substantially eliminated, in accordance with a further aspect of the invention, by correcting the primary signal from receiver **120** for the background ions that are included in it. That can be done by taking advantage of the fact that the background ions tend to be distributed symmetrically with respect to the drift tube axis, whereas the beam ions are distributed unsymmetrically in the plane of the molecular beam in the manner that has been described.

Secondary receiving means are provided, typically positioned on the opposite side of axis **30** from the primary receiving means and in symmetrical relation thereto. Such a secondary receiver is indicated schematically at **140** in Fig. 2 and also in Fig. 8. That position of secondary receiver **140** is distinct from that of receiver **123** in Fig. 7, which illustrates typical placement for receiving a maximum background ion signal.

As seen best in Fig. 8, the flow of background ions **129** to secondary receiver **140** is substantially the same as to primary receiver **120**; whereas the flow of beam ions **128** takes place mainly to primary receiver **120** and only to a minor extent, if at all, to secondary receiver **140**.

The signals from the two receivers **120** and **140** may be separately amplified, as by means indicated schematically in Fig. 2 at **122** and **142**, respectively, and the resulting signals on lines **124** and **144**, respectively, may be supplied to any suitable means responsive to their difference, such, for example, as a differential amplifier of any suitable type, indicated schematically at **145**. The resulting output signal on line **146** from differential device **145** is then typically proportional to the difference between the rates of arrival of ions at receivers **120** and **140**. That difference is substantially equal to the rate of arrival at receiver **120** of beam ions only. The time resolution of that signal with respect to the ion masses corresponds to curve **117** of Fig. 6, and is substantially or wholly unaffected by the lower resolution of the background ions, represented by curve **116**.

Particularly if only a single receiver is employed, it may be desirable to provide deflecting means of any suitable type, either as part of the ion accelerating electrode system or within the drift tube proper, to deflect the ions transversely in a direction opposite to the molecular beam velocity. For example, slightly different voltages may be applied to the two focusing plates **135** of

Fig. 7. In that way, for example, the mean path 132 of beam ions may be made parallel, or more nearly parallel, to the geometrical axis of the drift tube. An electrical axis of the system may then be defined by the mean path 133 of the background ions, which is then no longer parallel to the geometrical axis. Under such conditions, the line 30 in Fig. 8, for example, corresponds to the electrical axis, and the geometrical axis of the instrument may be represented, for example, by the line 126. In any case, receiver 120 is seen to be offset from the electrical axis, and receivers 120 and 140 are typically placed symmetrically with respect to that axis. The term "main axis" as employed with reference to ion reception refers to the electrical axis rather than to the geometrical axis of the system.

In accordance with a further aspect of the invention, primary and secondary receivers 120 and 140 are mounted for co-ordinated movement to permit adjustment of their radial distance from axis 30 while maintaining their symmetrical relation with respect to that axis. Such adjustment facilitates the production of optimum mass resolution under varying conditions of such factors as ion mass, relative intensity of adjacent masses and ratio of beam to background ions. Illustratively shown in Fig. 2, a shaft 150 is journaled within the vacuum chamber diametrally with respect to axis 30, as by the brackets 152, 153 and 154, and is rotatable by external control. For example, an end of the shaft may extend into a side tube 156 of the chamber wall and carry in mutually fixed relation a transverse armature 157 which may be driven by manual rotation of a magnet outside the chamber, as indicated at 158. Portions of shaft 150 on opposite sides of axis 30 carry right and left-handed threads, respectively, on which nuts 121 and 141 are threaded. Receivers 120 and 140 are carried in insulated relation on the respective nuts, which are guided longitudinally of the shaft by suitable ways, indicated schematically at 121*a* and 141*a*. Flexible electrical connections from the respective receivers may be carried through insulating fittings to external leads 52 and 52*a*.

Fig. 9 represents alternative means by which the effective position of one or more receivers may be varied by providing movable shutters that limit the size of the ion beam reaching them. Receivers 120*a* and 140*a* are shown fixedly mounted on insulating fittings on the chamber wall. However they may, for example, be movably mounted as in Fig. 2. Shutters 160 and 162 are mounted in spaced relation above the respective receivers in suitable guideways and are movable radially with respect to axis 30 as by threaded shafts 161 and 163, respectively. Those shafts may be driven from outside the vacuum chamber by any suitable mechanism, shown illustratively as of the same type already described for moving the receivers. A central shield portion 164 may be fixedly mounted to intercept ions close to axis 30. Shutters 160 and 162 may both be driven from the same shaft, as described for receivers 120 and 140 of Fig. 2. Movement of the shutters alters both the effective width and the effective positions of the receiving surfaces. That type of control is particularly convenient when it is desired to utilize receiving means of relatively complex type, which may, for example, incorporate signal amplification of the well-known electron multiplier type.

An important advantage of the invention is that it provides means for distinguishing between ions formed by fragmentation of molecules in the initial gas sample and ions of the same mass and charge originating directly from molecules present in that sample. If a certain ion species is formed by splitting initial molecules into two fragments, for example, the resulting fragments typically receive appreciable translational energy which is divided between them in accordance with the conservation of momentum. The fragments thus require respective velocities which are oppositely directed along a line randomly oriented in space. Hence, the components of those velocities in any particular direction are distributed statistically in somewhat the manner of thermal velocity components. The magnitudes of those velocity components, however, typically have a definite maximum value which depends upon the particular process involved. That velocity is typically of the same order of magnitude as, or somewhat larger than, normal thermal velocities. Hence for ions originating by fragmentation, the fragmentation velocities broaden both the space distribution and time distribution at the receiver. In the case of fragmentation of beam molecules, the space distribution of the resulting fragments is broadened with respect to that indicated, for example, by line 128 of Fig. 8, and typically extends appreciably farther to the left of axis 30 than is true for ions not produced by fragmentation. And the broadened time distribution is clearly distinguishable by comparison with the relatively narrow peaks, such as line 117 of Fig. 6, obtained from similar ions not involving fragmentation.

Moreover, in the case of molecular flow through beam orifice J1, the average beam velocity v_x for any molecular species depends inversely upon the molecular mass. Hence the average angle θ is greater for ions produced directly from beam molecules than for similar ions produced by fragmentation of larger molecules.

Those various types of differences in ion behaviour can readily be distinguished by direct observation of the oscilloscope peaks, or from variations in relative intensity of such peaks as the effective positions of the receivers are varied.

A further aspect of the invention provides means for remarkably rapid control of the flow through an orifice. Such means may be utilized, for example, to control flow of molecules through orifice J1, to cut off the molecular beam during at least a large proportion of the time between ionizing electron pulses. By thus permitting flow primarily or only when molecules are actually required at ionizing region 20, the volume of gas sample required is greatly reduced. Moreover, the pumping capacity required throughout the system to maintain any given pressure distribution is correspondingly reduced. Alternatively, pumps of given capacity can produce lower pressures, reducing the number of background molecules in ionizing region 20.

As shown illustratively in Fig. 10, aperture J1 is formed between a fixed jaw 170 and a movable jaw 172, one of which is preferably of a relatively hard material, such as tool steel, and the other of a relatively soft material, such as nylon or brass. As shown, movable jaw 172 is mounted on a transverse spring 174, the ends of which are fixed to spaced walls 175 and 176. An elongated actuating element 180 is positioned between walls 175 and 176 with one end fixed and the other end engaging the spring at 181 directly below jaw 172 and normally deflecting it into aperture closing position. The fixed end of element 180 is preferably adjustable, as by threads and a lock-nut 183. Element 180 is of a material that changes its length in response to an electric or a magnetic field. For example, element 180 may be of a magnetostrictive material such as nickel, and may be surrounded by an electrical winding 182 capable of producing a magnetic field in response to an applied electrical voltage. That applied voltage produces a current in winding 182, and the resulting magnetic field causes element 180 to constrict longitudinally, opening aperture J1. A suitable source of actuating voltage is indicated schematically at 186, acting to supply a current pulse through winding 182 under time control of a timing pulse received via line 187, as from trigger pulse generator 28. That timing pulse on line 187 is preferably arranged to precede the timing pulse supplied via line 26 to electron beam generator 24 by a definite time period, sufficient to permit a pulse of molecules to reach ionizing region 20. Upon removal of the magnetic

field, element 180 returns to its normal elongation, closing aperture J1 and terminating the molecular pulse.

Alternatively, element 180 may represent a suitably oriented electrostrictive material, such as a quartz crystal or a suitable barium titanate, with electrodes 182 adjacent its longitudinal faces. Application of voltage to such electrodes then causes a reduction in length of element 180, opening aperture J1 for a time period that is controllable by the duration of the applied voltage.

Fig. 11 represents an alternative manner of forming a rapidly acting valve in accordance with the invention. The actuating element 180*a* may be substantially as already described in connection with Fig. 10. Movable jaw 190 comprises a member rigidly mounted on the movable end of element 180*a* with a flat valve face 191 perpendicular to the length of that element. Fixed jaw 192 comprises an annular member, typically circular, adapted to be engaged by face 191 in normal condition of element 180*a*. Constriction of that element then causes the valve to open. Gas may be admitted via a tube 194 through an opening 195 in cylindrical valve housing 196, leaving the valve via the passage 197 along the axis of annular valve jaw 192. A constriction 198 in passage 197 may form a jet aperture 199 of desired size and shape. The chamber formed within fixed jaw 192 and between constriction 198 and movable jaw 190 is preferably small, so that the time required for it to fill and empty as the valve is operated is short compared to the open period of the valve. Aperture 199 may be utilized as a molecular beam forming aperture J1 in accordance with the invention.

The particulars of the described embodiments are intended only as illustration and may be varied in many respects without departing from the scope of the invention, which is defined by the appended claims.

We claim:

1. In a mass spectrometer, structure forming an evacuable chamber, means forming a plurality of apertures spacedly aligned along an axis, the last said aperture opening into said chamber, means for producing in the chamber a beam of electrons of ionizing energy intersecting the axis to ionize molecules emerging from the apertures, means for accelerating the resulting ions in a direction transverse of the axis, and means for distinguishing the accelerated ions in accordance with their respective masses.

2. In a mass spectrometer which comprises structure forming an evacuable chamber, means for producing gaseous ions in the chamber, means for accelerating the ions in a predetermined plane, and means for distinguishing the accelerated ions in accordance with their respective masses; the improvement which is characterized by the fact that said means for producing ions comprises means forming entrance and exit apertures for the chamber aligned along an axis transverse of said plane, means for producing a beam of gaseous molecules which enter the chamber through the entrance aperture along respective paths substantially all of which pass through the exit aperture, means for evacuating the space outward of the exit aperture, and means for producing in the chamber a beam of electrons of ionizing energy intersecting the axis.

3. In a mass spectrometer which comprises structure forming an evacuable chamber, means for producing gaseous ions in the chamber, means for accelerating the ions in a predetermined plane, and means for distinguishing the accelerated ions in accordance with their respective masses; the improvement which is characterized by the fact that said means for producing ions comprises means forming entrance and exit apertures for the chamber aligned along an axis transverse of said plane, means for producing a beam of gaseous molecules which enter the chamber through the entrance aperture along respective paths substantially all of which pass through the exit aperture, a plurality of vanes mounted in the exit aperture substantially parallel to the molecular paths, means for evacuating the space outward of the exit aperture, and means for producing in the chamber a beam of electrons of ionizing energy intersecting the axis.

4. In a mass spectrometer which comprises structure forming an evacuable chamber, means for producing gaseous ions in the chamber, means for accelerating the ions in a predetermined plane, and means for distinguishing the accelerated ions in accordance with their respective masses; the improvement which is characterized by the fact that said means for producing ions comprises means forming entrance and exit apertures for the chamber aligned along an axis transverse of said plane, means for producing a beam of gaseous molecules which enter the chamber through the entrance aperture along respective paths substantially all of which pass through the exit aperture, said exit aperture comprising a plurality of sub-apertures separated by relatively thin walls substantially parallel to the molecular paths and extending longitudinally of the axis for a distance that is long compared to the transverse separation of the walls, means for evacuating the space outward of the exit aperture, and means for producing in the chamber a beam of electrons of ionizing energy intersecting the axis.

5. In a time of flight mass spectrometer, structure forming an evacuable chamber, means for producing in the chamber a beam of gaseous molecules and for causing the beam to be limited to a predetermined limiting dimension in a direction transverse of the beam axis, means for ionizing molecules in the beam, means for producing an electrical field in the chamber to accelerate the resulting ions, the electrical field extending continuously in the said transverse direction throughout a distance from the beam axis that is large compared to the said limiting dimension of the molecular beam, and ion detecting means in the path of the accelerated ions responsive to differences in arrival time of ions having different masses.

6. In a time of flight mass spectrometer, an accelerating grid, an electrode spaced on one side of the grid and parallel thereto, means for admitting gaseous ions between the electrode and the grid, means for producing an electric field between the electrode and the grid to accelerate the ions through the grid, and ion detecting means spaced on the other side of the grid responsive to the time of arrival of the respective ions; the improvement which is characterized by the fact that the means for producing ions comprises means for producing a beam of gaseous molecules having a beam axis which is substantially parallel to the electrode and is spaced between the electrode and the grid, and means for producing a beam of electrons of ionizing energy intersecting the molecular beam.

7. In a time of flight mass spectrometer, an accelerating grid, an electrode spaced on one side of the grid, and parallel thereto, means for admitting gaseous ions between the electrode and the grid, means for producing an electric field between the electrode and the grid to accelerate the ions through the grid, and ion detecting means spaced on the other side of the grid responsive to the time of arrival of the respective ions; the improvement which is characterized by the fact that the means for producing ions comprises means for producing a beam of gaseous molecules having a beam axis which is substantially parallel to the electrode and is spaced between the electrode and the grid, the cross-section of the molecular beam having a dimension perpendicular to the electrode that is small compared to the distance between the molecular beam axis and the grid, and means for producing a beam of electrons of ionizing energy intersecting the molecular beam.

8. In a mass spectrometer, structure forming an evacuable chamber, means for forming the molecules within an ionizing region in the chamber into a first plurality of molecules having substantially random thermal velocities

and a second plurality of molecules having thermal velocities directed predominantly in a predetermined direction, means for ionizing molecules of both said pluralities within the ionizing region, means for accelerating the resulting ions in the direction of an axis that passes through the center of said region transversely of said direction, and means spaced along the axis from the ionizing region for detecting the accelerated ions, said detecting means being responsive to the times of arrival of ions of respective masses, and being offset from the axis in the said direction.

9. In a mass spectrometer, structure forming an evacuable chamber, means for forming the molecules within an ionizing region in the chamber into a first plurality of molecules having substantially random thermal velocities and a second plurality of molecules having thermal velocities directed predominantly in a predetermined direction, means for ionizing molecules of both said pluralities within the ionizing region, means for accelerating the resulting ions in the direction of an axis that passes through the center of said region transversely of said direction, and ion detecting means responsive to ions incident upon a limited effective area transverse of the axis, said effective area being spaced axially from the ionizing region and being offset radially from the axis in the said direction, the ratio of said radial offset to said axial spacing being approximately equal to the square root of the quotient of twice the product of the Boltzman constant k and the absolute temperature divided by the acceleration energy of the ions.

10. In a mass spectrometer, structure forming an evacuable chamber, means for forming the molecules within an ionizing region in the chamber into a first plurality of molecules having substantially random thermal velocities and a second plurality of molecules having thermal velocities directed predominantly in a predetermined direction, means for ionizing molecules of both said pluralities within the ionizing region, means for accelerating the resulting ions in the direction of an axis that passes through the center of said region transversely of said direction, and means spaced along the axis from the ionizing region for detecting the accelerated ions, said detecting means comprising two ion collecting structures transversely spaced on opposite sides of the axis.

11. In a mass spectrometer, structure forming an evacuable chamber, means for forming the molecules within an ionizing region in the chamber into a first plurality of molecules having substantially random thermal velocities and a second plurality of molecules having thermal velocities directed predominantly in a predetermined direction, means for ionizing molecules of both said pluralities within the ionizing region, means for accelerating the resulting ions in the direction of an axis that passes through the center of said region transversely of said direction, and means spaced along the axis from the ionizing region for detecting the accelerated ions, said detecting means comprising two ion collecting structures transversely spaced on opposite sides of the axis, and electrical means for detecting differences between the rates of ion flow to the respective ion collecting structures.

12. In a mass spectrometer, structure forming an evacuable chamber, means for forming the molecules within an ionizing region in the chamber into a first plurality of molecules having substantially random thermal velocities and a second plurality of molecules having thermal velocities directed predominantly in a predetermined direction, means for ionizing molecules of both said pluralities within the ionizing region, means for accelerating the resulting ions in the direction of an axis that passes through the center of said region transversely of said direction, and two ion detecting means spaced along the axis from the ionizing region, said ion detecting means being responsive preferentially to ions resulting from ionization of molecules of said first and second pluralities, respectively.

13. In a mass spectrometer, structure forming an evacuable chamber, means for forming the molecules within an ionizing region in the chamber into a first plurality of molecules having substantially random thermal velocities and a second plurality of molecules having thermal velocities directed predominantly in a predetermined direction, means for ionizing molecules of both said pluralities within the ionizing region, means for accelerating the resulting ions in the direction of an axis that passes through the center of said region transversely of said direction, two ion detecting means for producing electrical signals corresponding to the accelerated ions, said ion detecting means being responsive preferentially to ions resulting from ionization of molecules of said first and second pluralities, respectively, and means differentially responsive to said signals for producing visual indication thereof.

14. In a mass spectrometer comprising structure forming an evacuable chamber, means for producing in the chamber successive ion pulses spaced in time, means for accelerating the ion pulses, and means for distinguishing the accelerated ions in accordance with their respective masses; the improvement characterized by the fact that said means for producing ion pulses comprises means actuable to produce a beam of gaseous molecules having a beam axis, means actuable to produce a beam of electrons of ionizing energy intersecting said axis, and means for actuating the two last said means in predetermined time relation.

15. In a mass spectrometer comprising structure forming an evacuable chamber, means for producing in the chamber successive ion pulses spaced in time, means for accelerating the ion pulses, and means for distinguishing the accelerated ions in accordance with their respective masses; the improvement characterized by the fact that said means for producing ion pulses comprises means actuable in response to a first timing pulse of electrical energy to produce a directed beam of gaseous molecules having a beam axis, means actuable in response to a second timing pulse of electrical energy to produce a beam of electrons of ionizing energy intersecting said axis, and means for supplying timing pulses substantially simultaneously to the two last said means.

16. In a mass spectrometer comprising structure forming an evacuable chamber, means for producing in the chamber successive ion pulses spaced in time, means for accelerating the ion pulses, and means for distinguishing the accelerated ions in accordance with their respective masses; the improvement characterized by the fact that said means for producing ion pulses comprises means forming an aperture opening into the chamber, electrically operated valve means associated with the aperture and operable to control the flow of gaseous molecules therethrough, said valve means being responsive to an electrical signal to open the valve substantially only during the duration of the signal, means for supplying to the valve means periodic electrical signals of duration short compared to the period thereof, and means for ionizing gaseous molecules admitted to the chamber through the aperture during the resulting open periods of the valve means.

17. In a mass spectrometer comprising structure forming an evacuable chamber, means for producing in the chamber successive ion pulses spaced in time, means for accelerating the ion pulses, and means for distinguishing the accelerated ions in accordance with their respective masses; the improvement characterized by the fact that said means for producing ion pulses comprises means forming an aperture opening into the chamber, electrically operated valve means associated with the aperture and operable to control the flow of gaseous molecules therethrough, said valve means comprising two relatively movable valve members, an elongated valve actuating

element composed of a material which changes length in response to an electromagnetic field, means anchoring one of the valve members in fixed relation to one end of the element, means operatively connecting the other valve member to the other end of the element, and means for impressing upon the element an actuating field to open the valve means in response to a voltage signal, means for supplying to the valve means periodic voltage signals, and means for ionizing gaseous molecules admitted to the chamber through the aperture during the resulting open periods of the valve means.

18. In combination with structure forming two evacuable chambers separated by an apertured wall, and means for projecting molecules along predetermined paths through the aperture from the first chamber into the second; means for restricting the return flow of molecules from the second chamber to the first, comprising a plurality of vanes mounted in the aperture substantially parallel to the molecular paths, the dimensions of said vanes longitudinally of said paths being large compared to the transverse dimensions between them.

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