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[45] Patented **Jan. 12, 1971**
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[56] **References Cited**
UNITED STATES PATENTS
3,254,209 5/1966 Fite et al. 250/41.9
OTHER REFERENCES

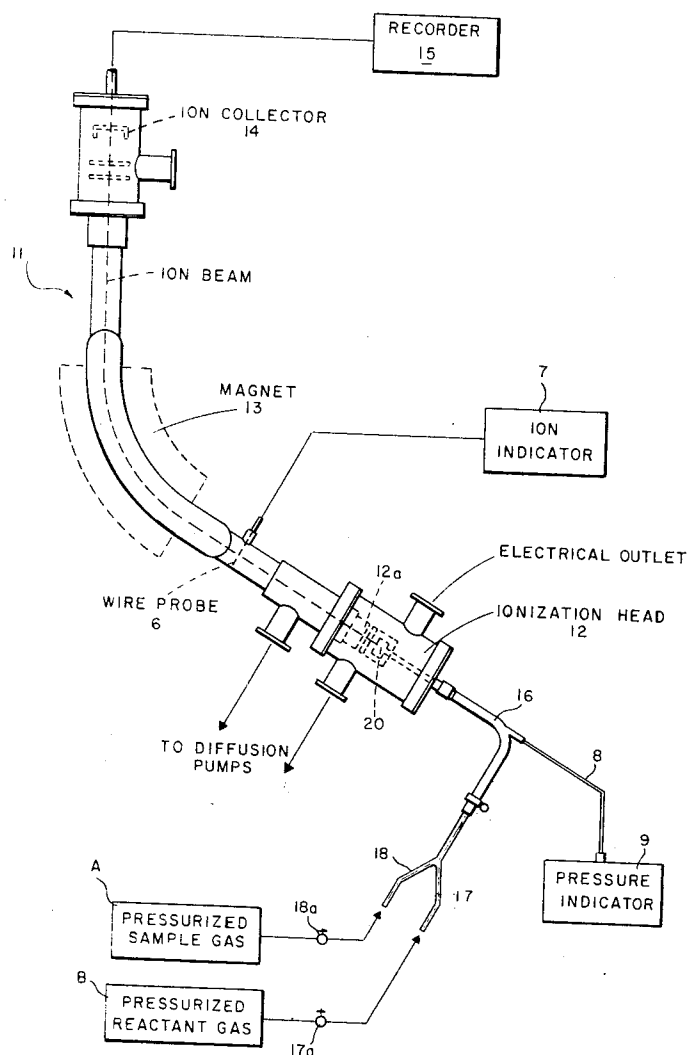
"Mass Spectrometer For the Study of Ion-Molecule Collision Processes" by G. F. Wells et al. from "The Review of Scientific Instruments," Vol. 28, No. 12, Dec., 1957, Pages 1065 to 1069.

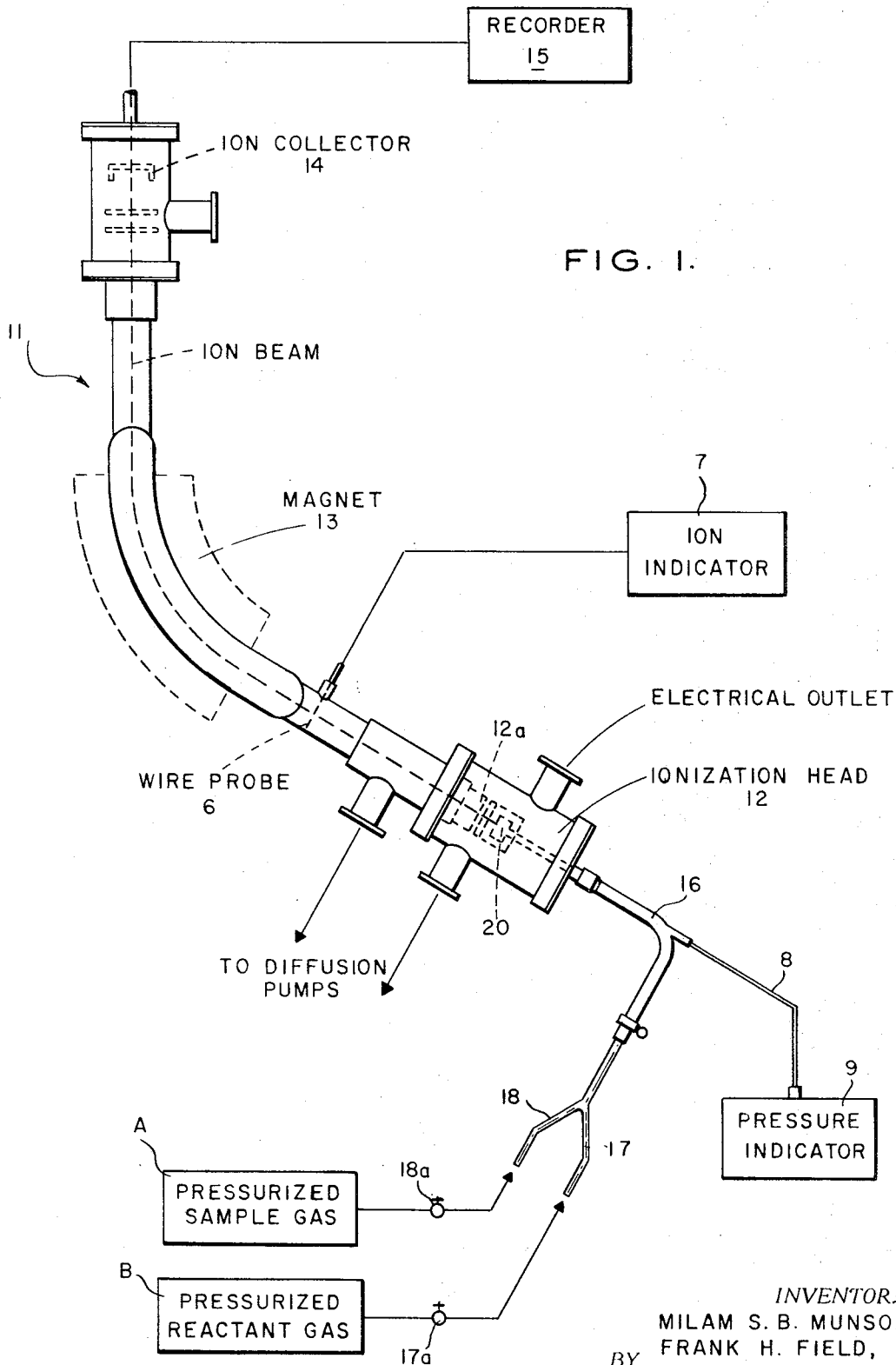
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[54] **PROCESS FOR CHEMICAL IONIZATION FOR
INTENDED USE IN MASS SPECTROMETRY AND
THE LIKE**
31 Claims, 5 Drawing Figs.

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[51] Int. Cl. B01d 59/44,
H01j 39/34
[50] Field of Search 250/41.9G,
41.9ISB, 41.9ISE, 41.9S; 313/63, 230, 231

ABSTRACT: Ionizable substances are reacted by continuously ionizing a mixture of a first gasform material and second gasform material to form stable ions from the first gasform material which undergo ion-molecule reactions with the second gasform material to produce ions characteristic of the second material. The reaction may be conducted in a mass spectrometer which provides a volume of high pressure relative to the pressure in the mass spectrometer envelope.



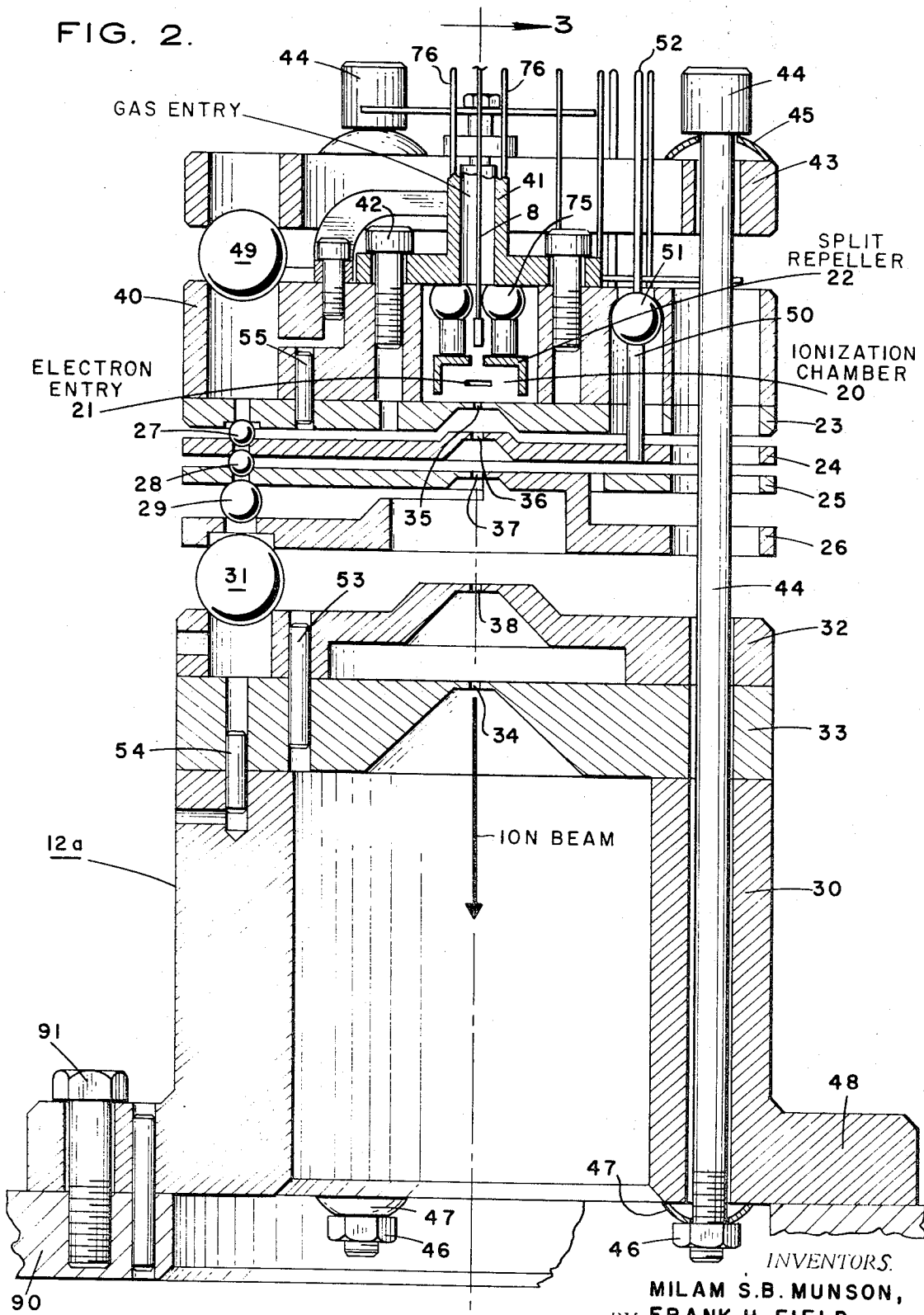


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FIG. 2.



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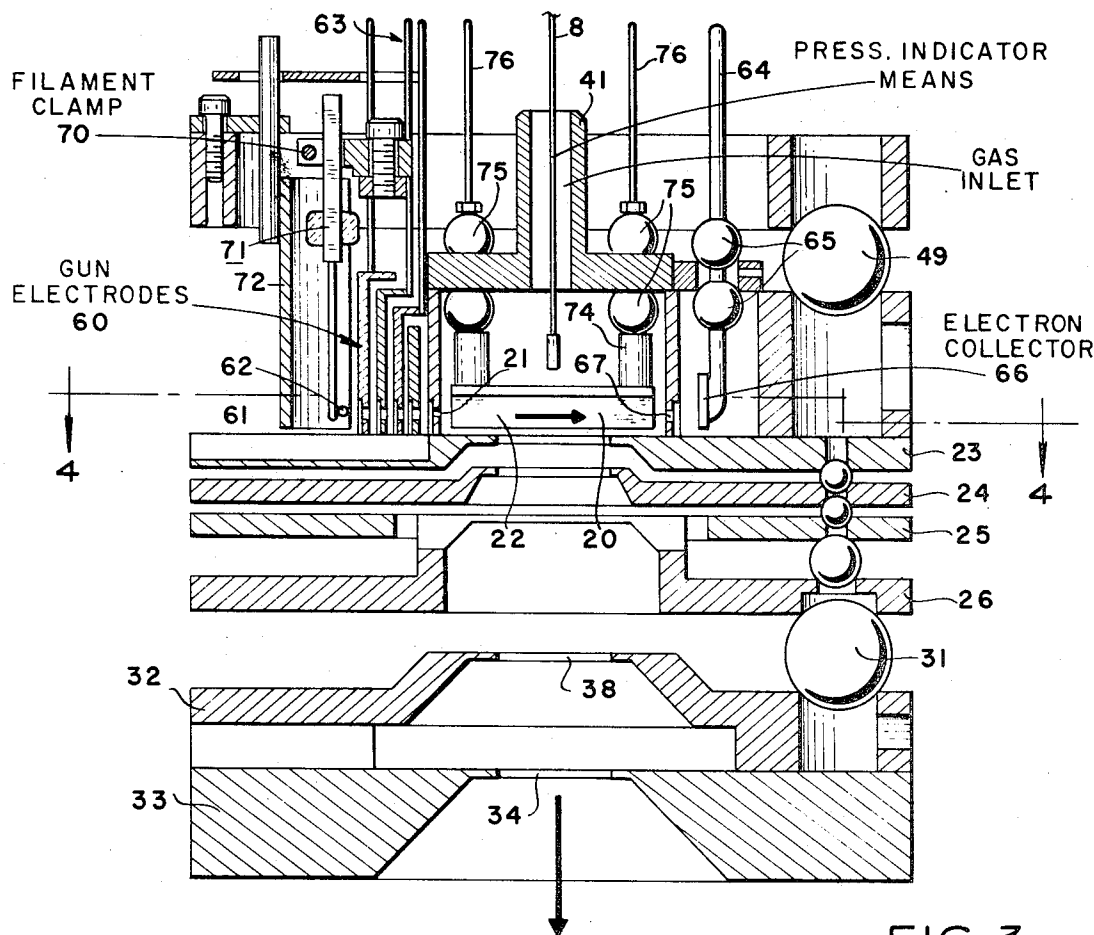


FIG. 3.

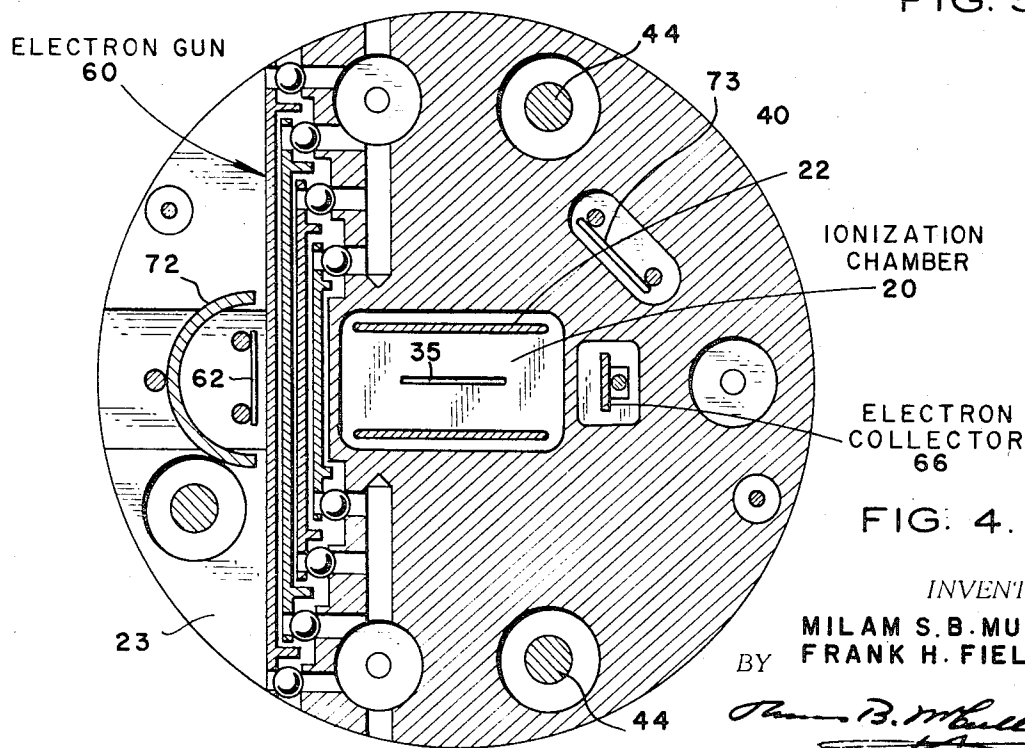
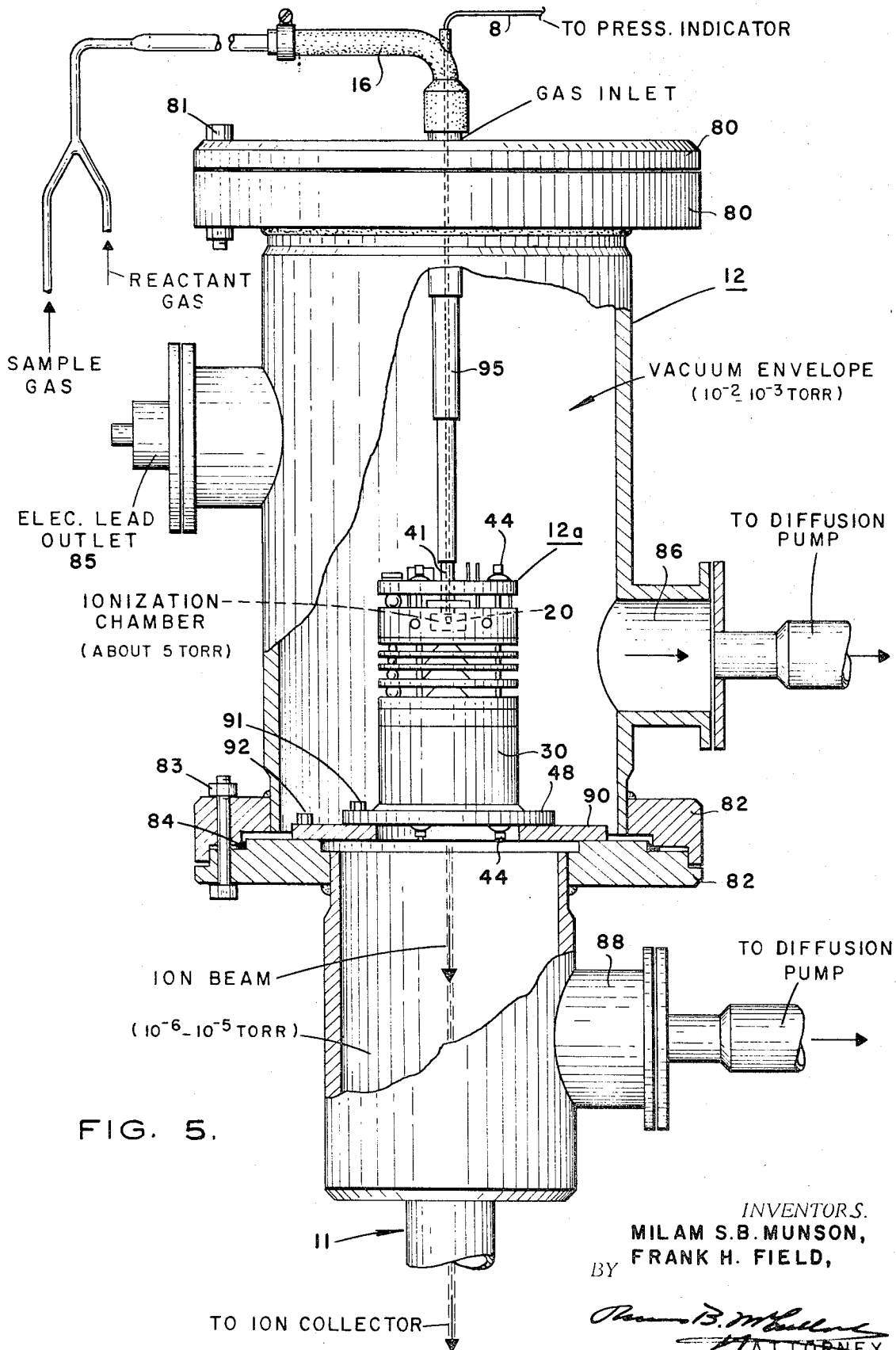


FIG. 4.

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PROCESS FOR CHEMICAL IONIZATION FOR INTENDED USE IN MASS SPECTROMETRY AND THE LIKE

This application is a continuation-in-part of Ser. No. 512,599, filed Nov. 1, 1965 for Milam S. B. Munson and Frank H. Field, now abandoned.

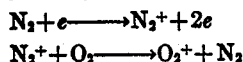
BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention is directed to mass spectrometry. More particularly, the invention is concerned with method and apparatus in which chemical ionization is obtained. In its more specific aspects, the invention is concerned with chemical ionization of a second gasform material by a first gasform material in a mass spectrometer.

2. Description of the Prior Art

Heretofore, it has been known to conduct ionization of certain gases under pulsed or discontinuous conditions and under pressures somewhat higher than is conventional. However, the pulsed ionization conditions require special equipment and the results may not be as accurate and useful as desired. Additionally, the prior art where pulsed ionization has been employed at pressures higher than conventional is concerned with ionization of certain gases involving electron transfer processes as exemplified by:



For such an electron transfer process to occur as exemplified by the prior art, it is necessary that the ionization potential of one gas such as O_2 be lower than that for another gas such as N_2 . In the present invention, this is unnecessary in that the mechanism involved is heavy particle transfer, the more important heavy particles being, but not limited thereto, H^+ , H^- , alkyl ions (R^+), alkide ions (R^-), and the like. In contrast to the prior art where the gases undergo little or no reaction after electron impact, except for the well known unimolecular decomposition reactions which are undesirable, in the present invention, a complex set of reactions occur to produce ions that effect ionization of added material which is quite advantageous and useful as brought out further hereinafter.

Specific prior art considered with respect to this invention includes:

U.S. Pat. No. 3,254,209 (Fite et al. Wells and Melton, "Mass Spectrometer for the Study of Ion-Molecule Collision Processes," The Review of Scientific Instruments, Vol. 28, No. 12, Dec. 1957, pages 1065-1069.

SUMMARY OF THE INVENTION

The present invention may be briefly summarized as involving reaction ionizable substances in which a mixture of a first gasform material and a second gasform material at a pressure within the range from about 0.2 to about 5 torr (torr = mm. Hg) is ionized under continuous ionizing conditions to form stable ions from the first gasform material. The stable ions and the second gasform material undergo ion-molecule reactions under said pressure and ionizing conditions to produce ions characteristic of the second gasform material.

The present invention also involves improved apparatus in a mass spectrometer having a tube provided with means for introducing a gasform sample thereto and means for generating and collecting ions from an ion beam formed in the mass spectrometer tube, said tube providing an envelope of reduced pressure. A feature of the present invention is a housing in the mass spectrometer tube forming a substantially gastight ionization chamber to provide a volume of high pressure relative to the pressure of the envelope with means in the housing separating the ionization chamber from at least a second chamber. The housing is provided with an electron entrance orifice having a width within the range from about 0.025 to about 0.05 mm. and a length within the range from about 1 to about 3 mm., the separation means being provided with an ion exit orifice having a width from about 0.025 to about 0.05 mm. and a length within the range from about 4 to about 5 mm.

A barrier means in the mass spectrometer tube is provided with an orifice having a width within the range from about 0.005 to about 0.25 mm. and a length from about 5 to about 10 mm., the barrier means separating a first region in the envelope surrounding the housing from a second region in the envelope wherein the ion beam is deflected and collected to minimize gas flow between the housing and the collection means. It is within the purview of this invention to provide a plurality of regions in the envelope and which may be three, four or more regions as desired.

A first pump means is connected to the first region and a second pump means is connected to the second region. The first and second pump means may suitably be diffusion pumps of high capacity which are capable of maintaining a differential pressure from the first region to the second region. As stated, a plurality of three or more pressure regions may be provided.

VARIABLES OF THE INVENTION

The second gasform material is employed in an amount sufficient to provide a concentration less than about 1 percent by volume of the mixture. A suitable concentration range may be from about 0.001 to about 1 percent by volume of the mixture.

The first gasform material may be any compound or substance which is capable of transferring protons or more massive positively or negatively charged molecular or atomic entities or may be any substance or compound which has the capability of abstracting hydride ions from more massive molecular entities. Similarly, the compound or substance may be one which ionizes by energy transfer from excited states such as by the Penning process.

The second gasform material may be any substance which will undergo ion-molecule reactions under the pressure and ionizing conditions to which the mixture is subjected.

Without limiting the present invention to the particular examples, examples of the first gasform material are hydrogen, methane, propane, isobutane, water, hydrogen sulfide, methanol, ammonia, and the like.

The second gasform material may be exemplified by way of illustration, and not by way of limitation, by paraffinic, olefinic, naphthenic and aromatic hydrocarbons having from 1 to 50 carbon atoms in the molecule and boiling in the range from about -160° to about $+600^\circ$ C. Specific examples of such compounds are: hexadecane, eicosane, 2, 2, 4 trimethyl pentane, toluene, butyl cyclohexane, 1-dodecene, and the like. Other organic and inorganic compounds may also be employed, the only limitation being that the compound must be placed in a gasform condition. By way of illustration and not by way of limitation, specific examples of such compounds are: alcohols (1-decanol), ketones (CH_3COCH_3), acids (H-COOH), aldehydes (CH_3CHO), amines [$(\text{C}_4\text{H}_9)_3\text{N}$], organic halides ($\text{C}_7\text{H}_{15}\text{Br}$), perfluorinated compounds ($\text{n.C}_6\text{F}_{14}$), and the like.

BRIEF DESCRIPTION OF THE DRAWING

The present invention will be further described and illustrated by reference to the drawing in which:

FIG. 1 is a general view of the mass spectrometer of the present invention;

FIG. 2 is a cross-sectional view of the ionization head of FIG. 1;

FIG. 3 is a view taken along the line 3-3 of FIG. 2;

FIG. 4 is a view taken along the line 4-4 of FIG. 3; and

FIG. 5 is a view in greater detail of the ionization head of FIG. 1.

DESCRIPTION OF THE PREFERRED MODE AND EMBODIMENTS RELATIVE TO THE DRAWING AND EXAMPLES

Referring now to the drawing in which a best mode and embodiment contemplated are set forth, and in which identical numerals will identify identical parts, and specifically with

reference to FIG. 1, numeral 11 generally designates a mass spectrometer tube provided with an ionization end 12 having an ionization head 12a arranged therein, a magnet 13, an ion collector 14 and a recorder 15. Leading into the ionization end 12 is a sample introduction means 16 provided with branches 17 and 18 controlled, respectively, by valves 17a and 18a and connecting to pressurized sample gas A and pressurized reactant gas B.

A wire probe 6 is inserted into the tube 11 so as to project into the path of the ion beam. The probe 6 is electrically connected to an ion indicator 7.

A pressure responsive means 8 is inserted through the introduction means 16 and projects into the ionization chamber 20 of head 12a (see FIGS. 2 and 3). The pressure in chamber 20 is thus indicated on indicator 9.

Referring now to FIG. 2, the ionization head 12a is provided with an ionization chamber 20 which in turn is provided with an electron entry slit or orifice 21 and a repeller 22. The ionization head 12a is suitably comprised of a plurality of plate members, one of which is plate member 23 which defines the exit orifice from chamber 20 for the ion beam. Other plate members provide a kinetic energy analyzer 24 and focusing electrodes 25 and 26, each of the several members 23, 24 25 and 26 being spaced apart by beads 27, 28 and 29, the plate 26 being spaced from the upper end of a housing base 30 by beads 31.

A ground electrode member 32 rests on the base 30 of head 12a above a plate member 33 in which is formed the analyzer entrance slit 34. Members 23, 24 and 25 are each provided respectively with orifices 35, 36 and 37 and the ground electrode 32 is likewise provided with an orifice 38. The orifice 35 in plate 23 is the ion exit orifice, the dimensions of which are selected in accordance with the present invention.

The ionization chamber 20 is enclosed within a member 40 which rests on the member 23. Arranged on the member 40 is an inlet member 41 which connects to the inlet 16 as will be described further. This member 41 is bolted to the member 40 by threaded bolts 42. Arranged on the member 40 is another member 43 through which threaded bolts 44 extend. The head of bolts 44 rests on spring members 45 which in turn rest on member 43. The threaded bolts 44 extend through the several plate members and the base member 30 and are secured by hex-nuts 46 which bear against spring member 47 which in turn bears against the base flange 48 of the base 30. The plate 43 is spaced from the member 40 by glass beads 49.

An electrical lead 50 connects to the member 24 and is insulated by bead 51 through which it extends and in turn connects to electrical lead 52.

Dowel pins 53 and 54 maintain the relative positions of the ground electrode 32 relative to member 33 and member 33 relative to the base 30. Likewise, dowel pin 55 maintains the member 40 in its relationship to the member 23.

Referring now to FIGS. 3 and 4, the ionization chamber 20 is provided with gun electrodes 60 and with slits 61 adjacent to filament 62 which on energizing electrodes 60 causes a continuous beam of electrons to be directed into the ionization chamber 20 through the electron entry slit 21. The electrons are produced from a heated wire filament 62. The gun electrodes 60 are connected by electrical leads 63 to a source of electrical energy outside the mass spectrometer tube 11 which will be described further. Electrical lead 64 is provided with glass insulator beads 65 and lead 64 connects to an electron collector 66 receiving electrons through orifice 67 from the ionization chamber 20. A clamp 70 supports the filament assembly 71 to which the filament 62 is connected. The filament 62 and the filament assembly 71 are arranged within a semicylindrical member 72 which serves to protect same.

In FIG. 4 a heater for the ionization chamber block is provided and is identified by the numeral 73.

It is noted in FIG. 3 that the repeller 22 is spaced from the member 23 and this distance is carefully selected and should range from about 1 to about 25 mm. Provision is made for selecting this distance by spacing the repeller by spacing

means 74 and insulation means, such as bead 75, which rests against the inlet member 41. Leads 76 pass through beads 77 and 75, support 74 and connect to repeller 22.

Referring now to FIG. 5, the ionization end 12 is closed by suitable flange members 80 which are bolted together by threaded bolts 81. The ionization end 12 is bolted to the mass spectrometer tube assembly 11 by flange members 82 connected by threaded bolts 83. It is to be noted that there is a gold seal 84 between the flange members 82 to form a gastight connection. The ionization end 12 is provided with an electrical lead outlet 85 through which the electrical leads are collected and taken to the outside to a suitable source of electrical energy. Likewise, the ionization end 12 is provided with an outlet 86 to which a diffusion pump (not shown) is connected. The mass spectrometer tube assembly is connected by flange member 82 to the ionization end 12 and is provided with a flanged outlet member 88 which also connects to a diffusion pump (not shown). It is to be noted that the base 30 of ionization head 12a and flange 48 rest on a plate 90 which in turn rests on the lower portion of flange members 82. The base 30 is connected as has been described by threaded bolts 44 and the flange 48 connects to the plate 90 by threaded bolts 91 while the plate 90 connects to the lower portion of the flange member 82 by threaded bolts 92. The inlet member 41 shown more clearly in FIGS. 2 and 3 connects by a tubular member 95 to the inlet 16 shown in FIG. 1.

In the practice of the present invention with reference to the drawing, a first gasiform material, which may be called a reactant gas, and a second gasiform material, which may be called a sample gas, are connected respectively to branch members 17 and 18 and lead into inlet 16 by tubular member 95 and thence to inlet 41. A suitable pressure is maintained on the sources of the reactant and sample gases to provide in the ionization chamber a pressure of about 0.2–5 torr while the high capacity diffusion pump 87 maintains a pressure in the envelope surrounding the ionization chamber in the range from about 10^{-2} to about 10^{-3} torr. Likewise, the diffusion pumps maintain a pressure in the deflecting and collection section of the mass spectrometer in the range from about 10^{-6} to about 10^{-5} torr. Under these pressures and ionizing conditions caused by a voltage within the range from about 50 to about 1000 volts on the electrode gun 60, stable ions are continuously formed from the reactant gas which in turn undergo ion-molecule reactions with the sample gas to form ions which are separated, collected and recorded to allow identification of the components of the sample gas.

Thus, the present invention is based on the occurrence of ionic reactions in the gaseous phase and it is to these reactions that the term "chemical ionization" refers. In accordance with the present invention, a mass spectrometer is operated at pressures in the ionization chamber as high as about 5 torr. Under these pressures, certain gases, which are referred to as reactant gases, are continuously ionized to produce ions which are stable in the gas; that is, they react with the gas at a negligibly slow rate. It has been found that if a second substance is added to the reactant gas in small concentrations which may range up to about 1 percent by volume, the stable ions formed from the reaction gas will then undergo ion-molecule reactions with the added substance to produce a set of ions which is characteristic of the second substance. This set of ions may be used to provide information about the chemical structure of compounds of the substance added and also may be employed to determine the composition of mixtures. Thus, the present invention is quite important and useful.

The wire probe 6 projecting into the ion beam serves as a monitor on the total ionization. The current collected by this wire probe 6 may, if desired, be used to actuate a control circuit which maintains the total ionization constant. Such a device makes the method described herein applicable to quantitative analysis.

The pressure responsive means 8 measures and indicated on indicator 9 the pressure within the ionization and reaction chamber 20. This device may also be used to actuate a control

circuit to maintain the chamber pressure constant and may be quite advantageous in accurate quantitative work.

The reactant gas may be any one of several gases and it is intended that the present invention is not to be limited by the specific examples. These gases may be chosen to produce desired characteristics of the distribution of ions formed from the added compound, that is, the chemical ionization mass spectrum. As stated, the second compound is added in low concentration to minimize ionization of the compound and reactions of the ions formed by direct ionization of the compound itself. Briefly, the present invention achieves a situation where a very large majority of the ions formed from the added compound are produced by chemical ionization reactions with the stable ions from the reactant gas.

In accordance with the present invention, the ions of the reactant gas may be produced by any suitable method or combination of methods such as ionization by electron impact, photo-ionization, ionization with products of radioactive decay, thermal ionization, and the like. If the reactant ions are produced by reactions of primary ions which are produced, for example, by electron impact ionization with the reactant gas, conditions must be selected such that a large fraction of the primary ions have reacted yielding a distribution of stable ions which does not depend strongly on pressure or lifetime of the ions in the ionization chamber. It has been found in the present invention that source pressures of about 0.2 to 5.0 torr with ion path lengths of 0.5 to 20 mm will satisfy these conditions.

In order to illustrate the invention further, in the following examples, relative ion currents are given for several different compounds which are analyzed by electron impact in comparison with the chemical ionization of the present invention.

EXAMPLE I.—2,2 DIMETHYLBUTANE (M.W.=86)

Ion mass:	Relative intensity	
	P(CH ₄)=1 torr	Electron impact
86.....		.05
85.....	330	.20
71.....	343	74.00
57.....	100	100.00
56.....	27	30.00
43.....	37	103.00
41.....	40	62.00
39.....	3	27.00

In the first column, the ion mass is given. In the second column, the relative intensity generated by chemical ionization with methane as the reactant gas at 1 torr is presented and in the third column, the relative intensity by electron impact at a pressure of about 10^{-4} torr is shown.

EXAMPLE II.—2,2,5 Trimethylhexane (M.W.=128)

Ion mass:	Relative intensity	
	P(CH ₄)=1 torr	Electron impact
127.....	46	.01
113.....	102	4.00
99.....	0	0.00
85.....	19	.20
71.....	108	18.00
57.....	100	100.00

EXAMPLE III.—2-Propanol (M.W.=60)

Ion mass:	Relative intensity	
	P(CH ₄)=1 torr	Electron impact
61.....	240	0.0
60.....	5	.5
59.....	91	4.0
47.....	180	0.0
45.....	100	100.0
43.....	200	19.0

EXAMPLE IV.—N-BUTYL BUTANOATE (M.W.=144)

Ion mass:	Relative intensity	
	P(CH ₄)=1 torr	Electron impact
145.....	101.	0.00
144.....	9	.07
143.....	47	0.00
117.....	66	.10
101.....	34	6.00
89.....	400	51.00
87.....	117	0.00
75.....	90	0.00
71.....	100	100.00
57.....	63	23.00

EXAMPLE V.—TRI-N-BUTYLAMINE (M.W.=185)

Ion mass:	Relative intensity	
	P(CH ₄)=1 torr	Electron impact
186.....	106	0.0
185.....	54	5.0
184.....	116	0.0
170.....	18	0.0
156.....	13	1.0
142.....	100	100.0

EXAMPLE VI.—EPICHLOROHYDRIN, 3-CHLORO-1,2-EPOXY-PROPANE (M.W.=92 & 94)

Ion mass:	Relative intensity	
	P(CH ₄)=1 torr	Electron impact
95.....	26	0.0
94.....	0	0.1
93.....	81	0.0
92.....	0	0.3
69.....	5	0.0
64.....	0	6.0
63.....	14	0.0
62.....	0	19.0
59.....	11	0.0
57.....	100	100.0

It will be seen from an examination of the data provided in the foregoing examples that the present invention is broadly applicable to all types of compounds which may be subjected to chemical ionization in accordance with the present invention where stable ions from the reactant gas undergo ion-molecule reactions with the added material. Thus, the present invention allows identification of parent compounds which heretofore were identified only with difficulty, if at all, and also allows the bringing about of selective ionization of compounds and mixtures of substances. Thus, the present invention is quite important and useful and represents a substantial advance in the art.

While the present invention has been described and illustrated by reference to ionizing a mixture of a first gasiform material with a second gasiform material, the present invention may be practiced by ionizing a first gasiform material under the conditions set forth herein and then admixing a second gasiform material with the stable ions to produce ions characteristic of the second gasiform material. This is possible because the ions of the reactant gas are stable and will exist for a period of time up to about 10^{-3} seconds and thus advantage thereof will be taken.

The nature and objects of the present invention having been fully described and illustrated and the best mode and embodiment contemplated set forth, what we wish to claim as new and useful and secure by Letters Patent is:

We claim:

1. A method for reacting ionizable organic substances which comprises: continuously ionizing a mixture of a first gasiform organic material and a second gasiform organic material to form stable ions from said first gasiform material, said stable ions and said second gasiform material undergoing ion-molecule reactions under said continuous ionizing conditions to produce ions characteristic of said second material.

2. A method in accordance with claim 1 in which the mixture is ionized at a pressure within the range from about 0.2 to about 5 torr.

3. A method in accordance with claim 1 in which the ionizing conditions include an electrical discharge within the range from about 50 to about 1000 volts.

4. A method in accordance with claim 1 in which the second gasiform material is in an amount sufficient to provide a concentration less than about 1 percent by volume of the mixture.

5. A method in accordance with claim 1 in which the first gasiform material is a proton transferring substance.

6. A method in accordance with claim 1 in which the first gasiform material is a compound having the capability of abstracting hydride ions.

7. A method in accordance with claim 1 in which the first gasiform material is a compound which ionizes by energy transfer from excited states.

8. A method in accordance with claim 1 in which the stable ions are formed by subjecting said first gasiform material to electron impact.

9. A method in accordance with claim 1 in which the stable ions are formed by subjecting said first gasiform material to photo-ionization.

10. A method in accordance with claim 1 in which the stable ions are formed by subjecting said first gasiform material to ionization with products of radioactive decay.

11. A method in accordance with claim 1 in which the stable ions are formed by subjecting said first gasiform material to thermal ionization.

12. A method in accordance with claim 1 in which the mixture is formed under ionizing conditions.

13. A method in accordance with claim 1 in which the mixture is formed under nonionizing conditions.

14. A method in accordance with claim 1 in which said ions characteristic of said second material are collected and measured.

15. A method in accordance with claim 1 in which the first gasiform material is methane.

16. A method for reacting ionizable substances which comprises:

continuously ionizing a first gasiform organic material to form stable ions from said first gasiform organic materials; and

admixing a second gasiform organic material with said stable ions whereby said stable ions and said second gasiform organic material undergo ion-molecule reactions to produce ions characteristic of said second material.

17. A method in accordance with claim 16 in which the first gasiform material is ionized at a pressure within the range from about 0.2 to about 5 torr.

18. A method in accordance with claim 16 in which the first gasiform material is methane.

19. A method for reacting ionizable organic substances which comprises: contacting a second gasiform organic material with stable ions continuously formed from a first gasiform organic material under conditions to produce ions characteristic of said second gasiform material.

20. A method in accordance with claim 19 in which the first gasiform material is methane.

21. A method in accordance with claim 19 in which the stable ions are formed by admixing the first and second gasiform materials under ionization conditions.

22. A method in accordance with claim 19 in which the stable ions are formed by ionizing the first gasiform material prior to said contacting.

23. A method in accordance with claim 19 in which the first gasiform material is a substance having the characteristic under said ionizing conditions of transferring protons.

24. A method in accordance with claim 19 in which the first gasiform material is a substance having the characteristic under said ionizing conditions of transferring more massive positively charged molecular or atomic entities.

25. A method in accordance with claim 19 in which the first gasiform material is a substance having the characteristic under said ionizing conditions of transferring more massive negatively charged molecular or atomic entities.

26. A method in accordance with claim 19 in which the first gasiform material is a substance having the characteristic under said ionizing conditions of abstracting hydride ions from more massive molecular entities.

27. A method in accordance with claim 19 in which the first gasiform material is a substance having the characteristic of ionizing by energy transfer from excited states.

28. A method in accordance with claim 27 in which the energy transfer from excited states is by the Penning process.

29. A method for reacting ionizable substances which comprises: contacting a second gasiform organic material with stable ions continuously formed from a gasiform material selected from the group consisting of organic materials, hydrogen, water, hydrogen sulfide, and ammonia under conditions to produce ions characteristic of said second gasiform material.

30. A method in accordance with claim 29 in which the conditions include an ion source pressure of 0.2 to 5.0 torr and an ion path length of 0.5 to 20 mm.

31. A method for a reacting ionizable substances which comprises: contacting a second gasiform organic material with stable ions continuously formed from a gasiform material selected from the group consisting of hydrogen, methane, propane, isobutane, water, hydrogen sulfide, methanol, and ammonia under conditions to produce ions characteristic of said second gasiform material.