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INSTRUMENTS AND TECHNIQUES

Higher-Pressure Mass Spectrometry

A basic physics tool finds new chemical uses when modified to study reactions up to 1-millimeter pressure.

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It is now half a century since J. J. Thomson, in 1912, developed the first instrument for measuring mass spectra and discovered two of the isotopes of neon. Following this great work, A. J. Dempster, F. W. Aston, and others constructed several different types of mass spectrometers which were devoted almost entirely to the discovery of new isotopes and to the determination of the relative isotopic abundances and isotopic masses for each of the stable chemical elements. About 1940, the mass spectrometer took on a new function—that of quantitative chemical analysis of hydrocarbons and other gaseous mixtures. Since then the mass spectrometer has been applied to an increasing number of fundamental problems in chemistry and physics.

This article is concerned primarily with the development of the mass spectrometer to probe the kinetics and mechanism of various elementary reactions of vital interest to research in the fields of radiation and catalytic chemistry. In the past this type of study has been limited, principally because of the pressure range within which conventional instruments are designed to operate—that is, between 10^{-5} and 10^{-8} millimeter in the reaction chamber. With the development of a higher-pressure mass spectrometer capable of studying reactions up to a pressure of 1 millimeter, the practical feasibility of the mass spectrometer for studying gaseous reactions of ions and other transient species having lifetimes of about 1 microsecond has begun to be recognized. We cite examples of its successful application to a variety of chemical problems in order to demonstrate the immense research potential of this basic and very versatile experimental method.

General Instrumentation

Higher-pressure mass spectrometers usually have the following general features: (i) maximum detection sensitivity; (ii) a corrosion-resistant ionizing electron filament; (iii) precise control of the energy of the ionizing radiation (electrons, photons, and so on); (iv) differential pumping; and (v) an adaptable ion source assembly.

Feature (i), maximum detection sensitivity, is necessary for the general detection of short-lived chemical species such as free radicals and transient ions which are present in minimal concentrations in a given reaction system. The measurement of negative ions is critical, because the production rate is usually 10^2 to 10^4 times lower for negative than for positive ions from a given compound under the same operating conditions. Using a 10- to 20-stage electron multiplier as the detector in conjunction with either a pulse counter or an electrometer-recorder read-out device for the mass spectrometer, one can achieve a maximum detection sensitivity of about 1 ion per second, or a 10^{-19}-ampere ion beam current.

Feature ii, a corrosion-resistant ionizing electron filament, is required to withstand attack by reactive gases. For example, hot tungsten, which is used as a filament in conventional mass spectrometers, would burn out quickly in an atmosphere of 1 millimeter of oxygen or other corrosive gases. Fortunately, the thoria-iridium filament (*1*) has proved to be a relatively inert filament under these stringent conditions, and consequently it is becoming more widely used in research instruments.

Feature iii, precise control of the ionizing radiation, is useful in detecting the presence of certain transient species such as free radicals, in controlling the concentration and types of primary ions formed by the ionizing source, and in measuring or estimating the energetics of various molecular transitions. It is often desirable to vary both the intensity and the energy of the ionizing radiation. Such control is comparatively easy with electron and photon sources but is not possible with radioactive sources. Ideally for ion-molecule work, the energy of the ionizing source is slowly decreased until only one type of primary ion is formed in a given sample gas A—for example, A ⤁ $A^+ + e^-$, where the symbol (⤁) indicates that a generalized ionizing radiation source has initiated the transition. Secondary collision reactions by this primary ion with various added neutral species can then be observed. In mass spectrometry, the minimum energy needed to transform a particular neutral molecule in its ground state to an ion in a detectable ionic state is called the appearance potential for that transition. If the change is from the ground state of the neutral molecule to the ground state of the ion, the appearance potential is identical with the ionization potential for that transition.

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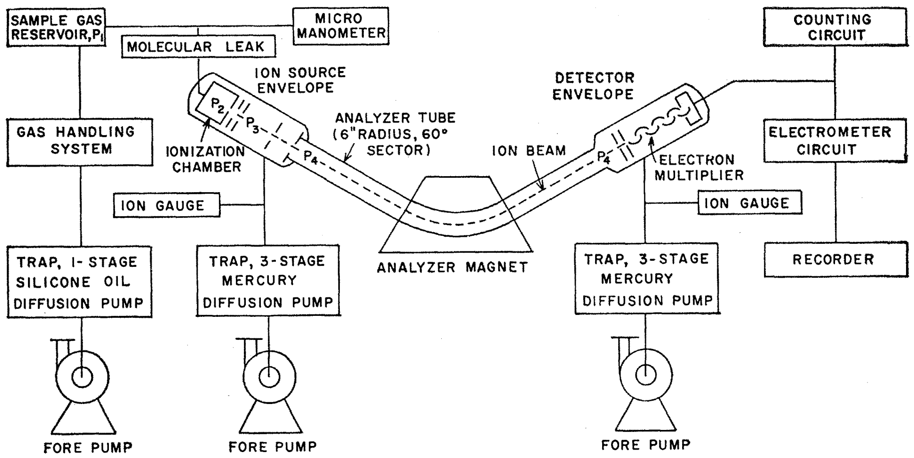


Fig. 1. Schematic diagram of the higher-pressure mass spectrometer.

To illustrate how one makes use of these ideas to study ion-molecule reactions, let us consider two gases, A and B, to be irradiated by an electron beam, and let us assume that gas B has a higher ionization potential than gas A. First, the electron energy is adjusted so that only one type of primary ion, A^+, is detected, and both the partial pressure of A and the electron beam intensity are set to obtain a sufficient intensity of A^+ ions. Second, the partial pressure of B is independently increased, and the secondary ion AB^+, with an intensity directly proportional to the partial pressure of B in the mixed system, begins to be detected. Concurrently, the intensity of the primary ions decreases as the intensity of the secondary ions increases, in such a way that the sum of the two ion intensities is roughly constant. These observations are convincing evidence for the ion-molecule reaction $A^+ + B \rightarrow AB^+$. In a similar fashion, the rates and pathways of many consecutive bimolecular collision reactions of primary, secondary, tertiary, and even higher-order ions have been measured by mass spectrometry.

Feature iv, differential pumping, is necessary to attain higher pressures in the reaction chamber so that consecutive ion-molecule reactions can be observed. A block diagram of the type of mass spectrometer we use is shown in Fig. 1. The different steady-state pressures P_1, P_2, P_3, and P_4 indicated for the sample reservoir, the ionization or reaction chamber, the ion source envelope, and the analyzer tube-detector envelope sections, respectively, can be maintained because either a molecular leak or a tiny slit is employed to partially isolate one section from another. In actual practice, the arrangement shown, in which two stages of differential or parallel pumping are used, achieves roughly the following relative pressures: $P_1 \simeq 500$, $P_2 \simeq 1$, $P_3 \simeq 0.02$, and $P_4 \simeq 0.0003$, as estimated by a method reported elsewhere (*2*). Hence, there is at least a 3000-fold drop in pressure between the ionization chamber and the analyzer tube. In accord with considerations of mean free path, we observe appreciable ion-beam losses in the analyzer tube at pressures above 10^{-5} millimeter because of charge transfer and collision scattering. It is perhaps more obvious now why higher-pressure mass spectrometers must have the maximum detection sensitivity (feature i) plus efficient differential pumping to operate effectively up to a pressure of 1 millimeter in the ionization chamber.

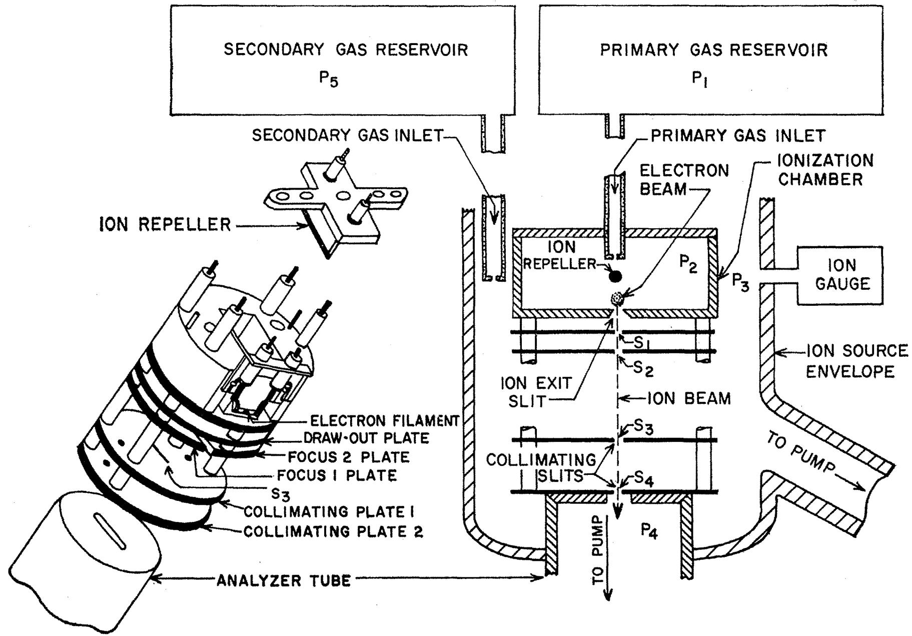


Fig. 2. Ion source assembly.

Feature v, an adaptable ion source assembly, is perhaps the most critical element in successful application of the mass spectrometer to a particular chemical problem. Figure 2 illustrates the kind of ion source we have found quite useful in previous work. Such a source has been used to study ion-molecule reactions over a wide range of pressures and temperatures. This source assembly has been modified, with alpha- and beta-particle sources for problems of radiation chemistry, with light sources used for photochemical problems, and with catalytic sources for problems of surface chemistry; some specific modifications of the assembly are mentioned in connection with several research studies cited later in this article. In general, the gases to be irradiated are passed from the primary reservoir through a molecular leak into the ionization chamber. Ions of the same charge type, formed either on primary collision with the radiation source or by subsequent ion-molecule reactions, are repelled through the ion exit slit because of a small potential (variable from 0 to ± 2 volts with respect to the chamber wall) applied to the ion repeller. Ion-molecule reactions can then occur between the primary ions and the neutral molecules within the ionization chamber in the time it takes for the primary ions either to drift out the ion exit slit or to become neutralized at the chamber wall. It is also possible to observe ion-molecule reactions by a second technique—by letting the emerging ions from the primary gas collide with neutral molecules of a secondary gas let into a "field-free" region between the ion exit slit and slit S_1 by a secondary leak system in the ion source envelope (*3*). This technique is especially convenient when the secondary gas has a lower ionization potential than molecules of the primary gas. A third method of studying ion-molecule reactions, by introducing the secondary gas into the analyzer tube through a leak in the detector envelope, has also been used (*4*). The electrostatic lens system composed of circular plates with slits S_1, S_2, S_3, and S_4 imparts a fixed kinetic energy to each ion and collimates the ion beam as it passes into the analyzer tube. The field of the analyzer magnet separates the ions according to their momenta. By electronic changes in the magnet current in our spectrometer, ions of the same momentum are successively brought to focus on the detector slit system, whence they strike the first dynode of the electron multiplier. The resulting current pulses are either counted directly or further amplified, integrated, and measured by standard electrical techniques.

The Vanderbilt and Oak Ridge Spectrometers

Figure 3 shows the higher-pressure mass spectrometer built last year at Vanderbilt University (*5*). This instrument, except for the kind of diffusion pumps employed, is a copy of the first such instrument, which was designed and built by Melton and his co-workers (*2*) at the Oak Ridge National Laboratory in 1956.

The gas-handling system, sample reservoir, molecular leak, and spectrometer envelopes (Fig. 1) are fabricated of borosilicate glass. The analyzer tube, of 6-inch radius and 60-degree sector, is made of copper and is joined through Kovar seals to the glass end pieces. The complete tube, with envelopes, was fabricated by specialized methods developed at the K-25 Oak Ridge Facility. The glass envelopes enclosing the ion source and detector are separately evacuated through similar all-metal pumping systems consisting of a Kovar seal (of 1.5 inches inside diameter) silver-soldered to a stainless steel bellows of the same diameter and a stainless steel bucket trap (15 inches high and of 5-inch inside diameter) fitted on top of a three-stage mercury diffusion pump (Consolidated Vacuum Corporation model MHG-180, with a speed rated at 200 liter per second). Teflon gaskets are used with the flanged high-vacuum connections on both trap and pump. With this pumping arrangement the lowest base pressure in the spectrometer is about 2×10^{-9} millimeter with liquid N_2 and about 5×10^{-7} millimeter with a dry ice–acetone slush in the traps. The gas-handling network is evacuated by a Consolidated Vacuum Corporation pump (model VMF-10) filled with Dow-Corning 702 silicone fluid. Quantitative pressures in both spectrometer envelopes are measured by means of an RG-75 ionization gauge with an RG-3A gauge control, from the Vacuum-Electronics Corporation. Pressures in the gas-handling and sample reservoir are determined by using either a thermocouple gauge with the RG-3A supply or a calibrated micromanometer (Consolidated Electrodynamics Corporation model 41550).

The analyzer magnet was designed and built at Vanderbilt (*6*). It is made entirely of Armco magnet iron and

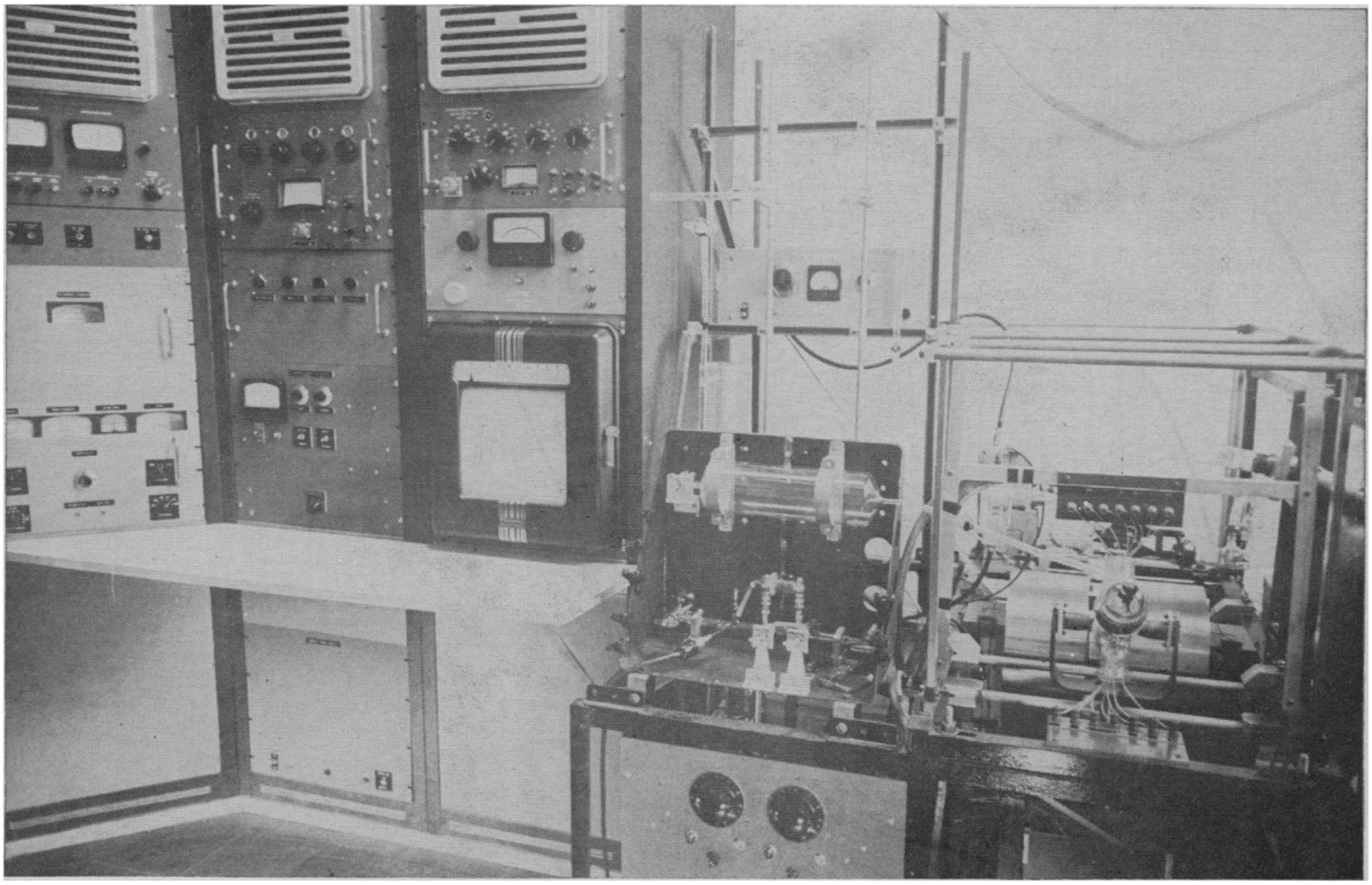
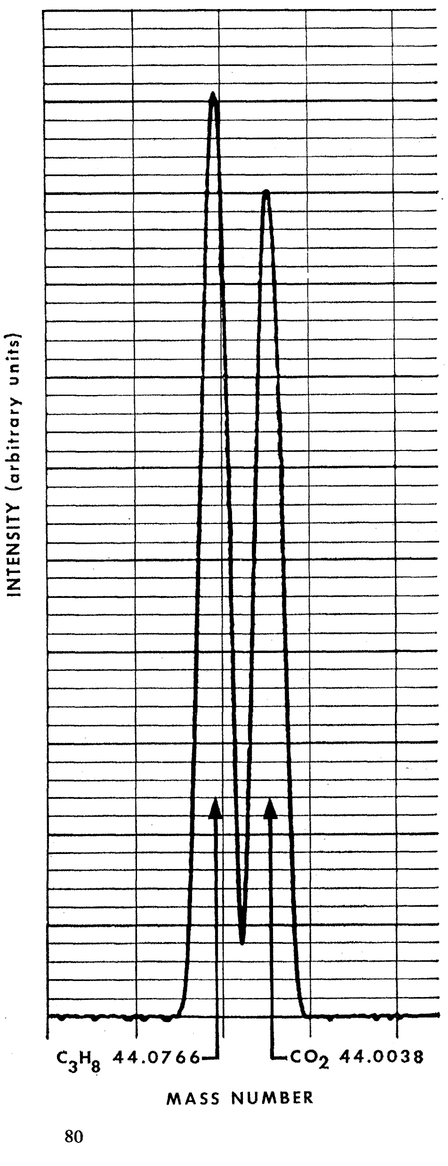


Fig. 3. The Vanderbilt higher-pressure mass spectrometer.

consists of a three-piece yoke of 3- by 6-inch stock with two coil pieces, 6- by 5-inch outside diameter, with shaped pole faces having a 9/16-inch gap to fit the analyzer tube. Each of the two coils wrapped on these coil pieces consists of about 22,000 turns of No. 22 copper wire triple-coated with Formvar; the combined series impedance is about 1600 ohms. This magnet develops a field of 11.5 kilogauss at 350 milliamperes. A General Electric Company direct-current magnet power supply and sweep regulator capable of delivering a total of 450 milliamperes through an impedance of 1250 ohms is used to control the magnet current, with negligible ripple for either electronic or manual scanning.

A modified Nier-type source (*7*) made of stainless steel with alumina insulators (Fig. 2) was equipped with smaller slits and with a tightly fit molecular leak to improve the differential pressure characteristics of our instrument. The electron beam collimating hole was made 0.031 inch in diameter, and the ion exit slit, 0.250 by 0.005 inch to attain higher relative pressures in the ionization chamber. The ion draw-out plate slit S_1 is 0.250 by 0.020 inch. The focus plate consists of two half plates, focus 1 and focus 2, separated from each other by a 0.020-inch gap S_2. The collimating slits S_3 and S_4 were made the same size as the ion exit slit to obtain better differential pumping between the tube and source sections. These changes produced two other desirable results: back diffusion into the ionization chamber by the products of any filament pyrolysis was minimized, and the overall resolution of the instrument was improved. Good mass resolution is important in the study of chemical systems at higher pressure because of beam "blow-up," elastic scattering, and other factors (*8*). Photographs of our recorder scans (Figs. 4 and 5) illustrate quite clearly the resolving powers at different masses attainable with this spectrometer.

The direct-current potentials applied to the various parts of the ion source come from a suitable voltage distribution network activated by a ± 10 kilovolt power supply (Fluke model 410A). The relative voltages in the ion source, for our standard operating voltage of ± 5000 volts applied to the ionization chamber, are listed for comparison in Table 1, together with the approximate spacings, along the ion beam axis, for various parts of the ion source pictured in Fig. 2. These are typical voltage values for studying ion-molecule reactions by the first method described in our discussion of the ion source assembly. It should be understood that we use the +5000 volts for positive ion work and the −5000 volts for negative ion studies, both voltages with



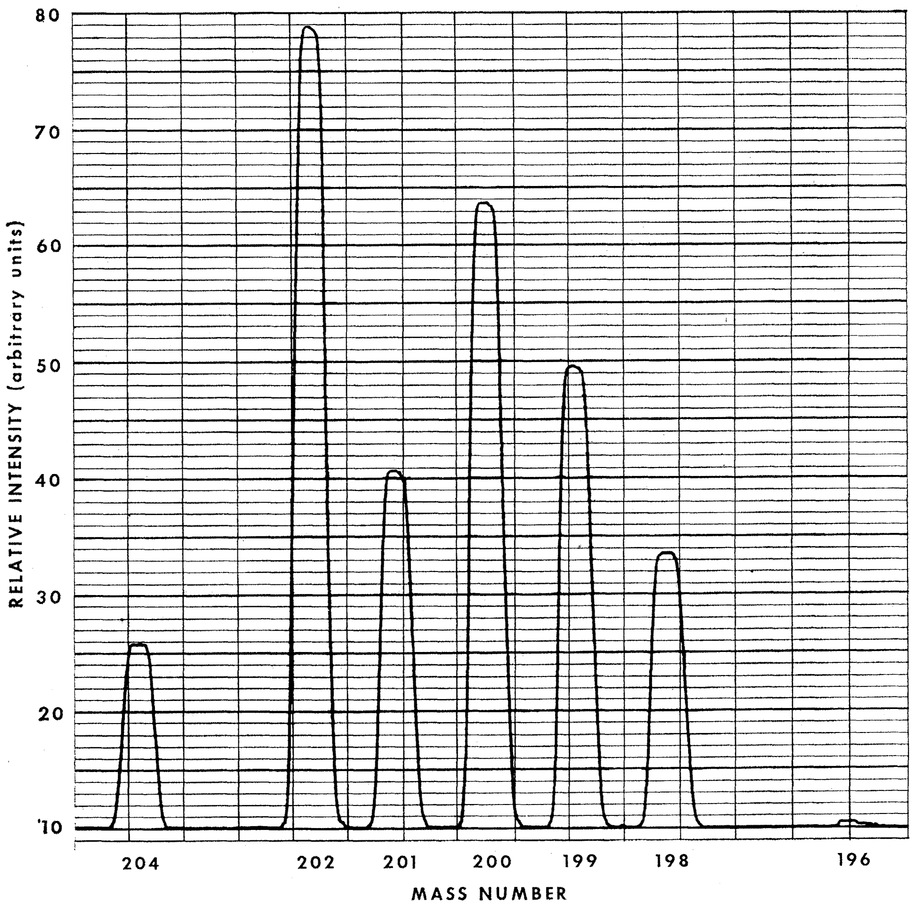
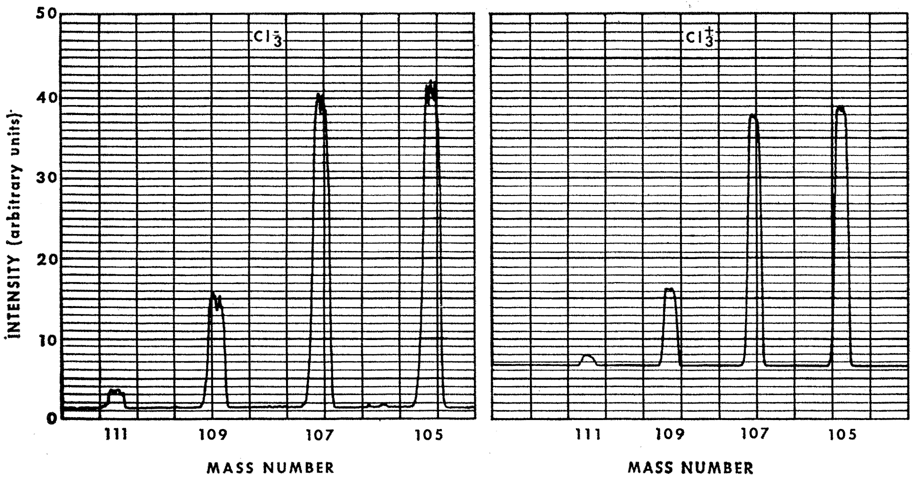


Fig. 4 (left). Resolution of the mass-44 peaks of CO_2 and C_3H_8. Fig. 5 (above). Resolution of the mercury isotopes.



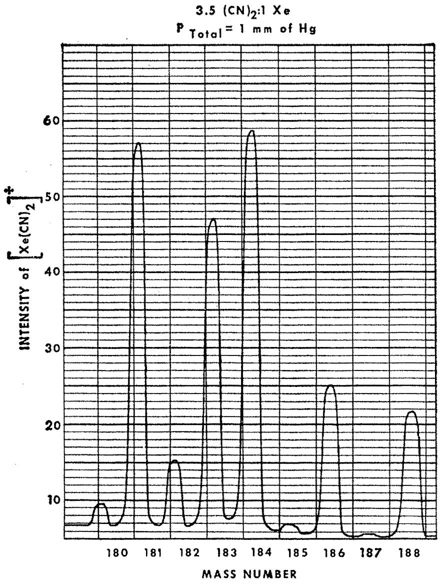


Fig. 6 (above). The Cl_3 positive and negative ion spectra. [Reproduced from the *Journal of Chemical Physics*, with permission] Fig. 7 (right). The isotopic pattern of $Xe(CN)_2^+$ at 1-millimeter pressure in the ionization chamber. [Reproduced from the *Journal of Chemical Physics*, with permission]

respect to the analyzer tube, which is always at earth ground.

When the electron beam is used as the ionizing source, both the energy and the intensity of the beam are controlled simultaneously by a Hutchison-Wolff emission regulator (*9*), which must float at the source potential. The use of the thoria-iridium filament makes it possible to operate this electron source for several months in the presence of reactive gases such as Cl_2 and O_2 at a pressure in excess of 1 millimeter without detrimental change in the filament emission characteristics.

The ion detection system consists of one fixed and one adjustable slit mechanism, a modified 14-stage electron multiplier (RCA-6810A) operated by a Fluke model 408A direct-current ± 6-kilovolt power supply (*10*), a vibrating reed electrometer (Cary model 31), and a 5-millivolt recorder (Leeds and Northrup, Speedomax G) having 1-second full-scale response. The minimum dependable signal with this arrangement is about 5 ions per second, or 8×10^{-19} ampere. The adjustable slit is set to match the collimating slits of the ion source for maximum-resolution work.

One of the most important functions of the higher-pressure mass spectrometer is that of finding evidence of short-lived species to better understand the pathways and rates of basic chemical processes. Because it takes about 1 microsecond for an ion once formed in the ionization chamber and accelerated with 5000 volts to reach the electron multiplier, any chemical intermediate having a lifetime at least this long can be detected. It is even possible to gain some information about shorter-lived species from an analysis of metastable ion spectra which are obtained from transient ions which decompose to smaller fragments on entering the analyzer tube (*11*).

The Cl_3 molecule is an example of a neutral transient species for which there is good mass-spectral evidence. It was proposed as an intermediate in a number of photochemical reactions, and Rollefson and Eyring (*12*) predicted its existence from theoretical considerations. However, there was no experimental evidence of the presence of Cl_3 until the first higher-pressure mass spectrometer was constructed; photographs of the Cl_3 positive and negative ion spectra (*13*) taken by combined use of the Oak Ridge instrument and a suitable light source are shown in Fig. 6. Although observation of these charged chlorine species is not direct proof that Cl_3 was present in the reaction system, the fact that both positive and negative ions are found suggests strongly that the common precursor for these ions was the Cl_3 molecule. Similarly, the best experimental evidence thus far reported for the existence of the important HO_2 free radical was obtained by mass spectrometry (*14*).

In addition to unusual neutral species, charged intermediates of unfamiliar valence are commonly observed in ion-molecule work. These ions are of value in explaining certain problems in radiation chemistry. For example, the ion $Xe(CN)_2^+$ was first postulated by Eyring (*15*) to account for the increased rate of polymerization of C_2N_2 due to admixed xenon. In 1960 Melton and Rudolph (*16*) observed this species, as presented in Fig. 7. This photograph is a typical scan taken at 1-millimeter pressure in the ionization chamber. Note that even at this high pressure the resolution of our higher-pressure mass

Table 1. Comparative voltages and spacings along the ion beam axis for the ion source assembly.

Item	Relative voltage: With respect to ionization chamber	Relative voltage: With respect to analyzer tube at earth ground	Separation distance (in.) with respect to ion exit slit
Ion repeller	Variable, 0 to ±2		0.2
Electron beam	Variable, 0 to −150		0.1
Ionization chamber		±5000	0
Drawout plate*		±4500, but variable ±110	0.1
Focus 1 plate		Same as drawout	0.2
Focus 2 plate		Variable ±50 with respect to drawout and focus 1-voltage	0.2
Collimating plate 1		Same as tube	0.80
Collimating plate 2		Same as tube	1.10

* All plates are 0.06 inch thick and 1.44 inch in diameter.

spectrometer is adequate to resolve the individual isotopic masses of xenon.

We have also observed some unexpected species and ion-molecule reactions with negative ion spectra at higher pressure. Figure 8 is a typical scan taken with a 50:50 mixture of HCOOH and DCOOH irradiated by the electron beam. Note that the $HCOO^-$ and $DCOO^-$ ion intensities are about equal, in accord with the composition of the primary gas mixture, but that the distribution of the 91, 92, and 93 ions formed by ion-molecule reactions of the type

$$HCOO^- + HCOOH \rightarrow HCOOHCOOH^- \quad \text{(mass 91)}$$

$$HCOO^- + DCOOH \rightarrow HCOODCOOH^- \quad \text{(mass 92)}$$

$$DCOO^- + HCOOH \rightarrow DCOOHCOOH^- \quad \text{(mass 92)}$$

$$DCOO^- + DCOOH \rightarrow DCOODCOOH^- \quad \text{(mass 93)}$$

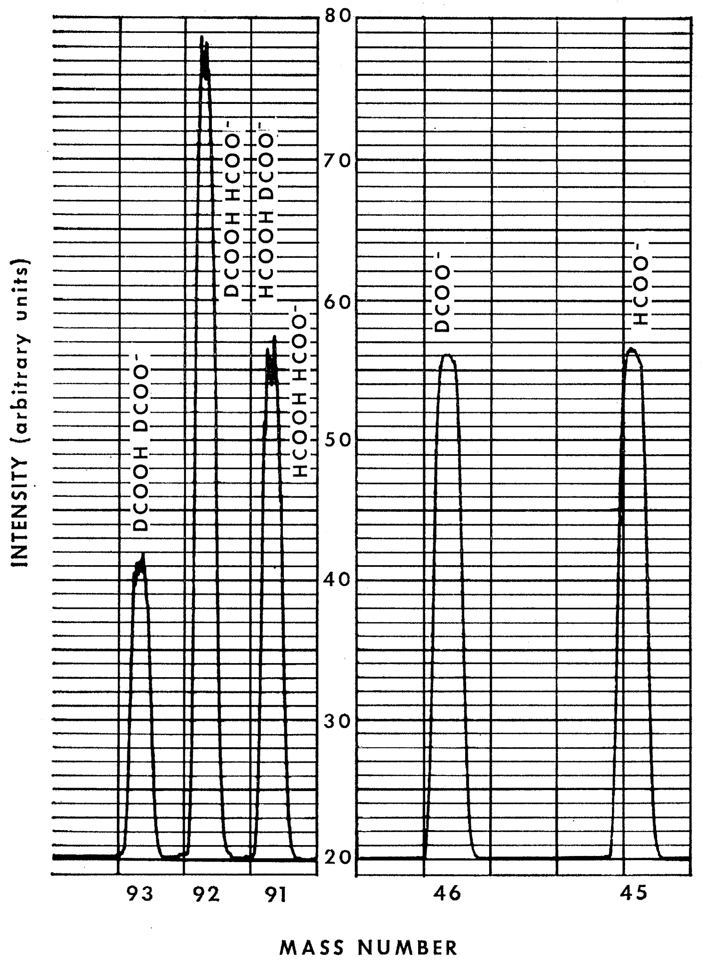
is not what would be predicted on a statistical basis, where the 91, 92, and 93 peaks should be in the ratio 1:2:1. This atypical behavior suggested an interesting isotope effect, which was shown to be consistent with a molecular rearrangement associated with the migration of the hydrogen atom on the primary ion (*17*).

In the field of chemical catalysis, several investigators have reported that free radicals are formed on, and possibly desorb from, catalytic surfaces during heterogeneous reactions. With the advent of the higher-pressure spectrometer it became practical to test whether such species were in fact desorbed into the gas phase. Since our instruments are sensitive enough to detect primary ions from concentrations of neutral molecules as low as 10^7 molecules per cubic centimeter ($\approx 10^{-14}M$) at the lowest operating pressure of $\cong 10^{-9}$ millimeter in the ionization chamber, this concentration also represents the lowest concentration level at which intermediate free radicals can be detected. This excellent detection sensitivity was used to great advantage in observing the positive and negative ions from free radicals and other neutral intermediates produced in the

Table 2. Transient species detected in the reaction $D_2 + CO_2 \xrightarrow[\text{hot Pt}]{} D_2O + CO$ (products from ion-molecule reactions are not included).

M/e	Ion*	Probable precursor	Suggested source of precursor
2	D^+, D^-	D	$D_2 \xrightarrow[\text{Pt}]{} D + D$
30	CDO^+	CDO	CDO desorbed off Pt
46	$DCOO^-$	DCOOD, DCO_2	$CO_2 + D_2 \xrightarrow[\text{Pt}]{} DCOOD$ or DCO_2
60	CO_3^-	D_2CO_3, CO_3	$D_2O + CO_2 \xrightarrow[\text{Pt}]{} D_2CO_3$ or CO_3
62	DCO_3^-	D_2CO_3, DCO_3	$D_2O + CO_2 \xrightarrow[\text{Pt}]{} D_2CO_3$ or DCO_3

* The intensities of the negative ions listed here were less by two to three orders of magnitude than those of the positive ions. The intensities of all these transient species were less than 1 percent of the intensities observed for each of the product ions, CO^+ and D_2O^+.



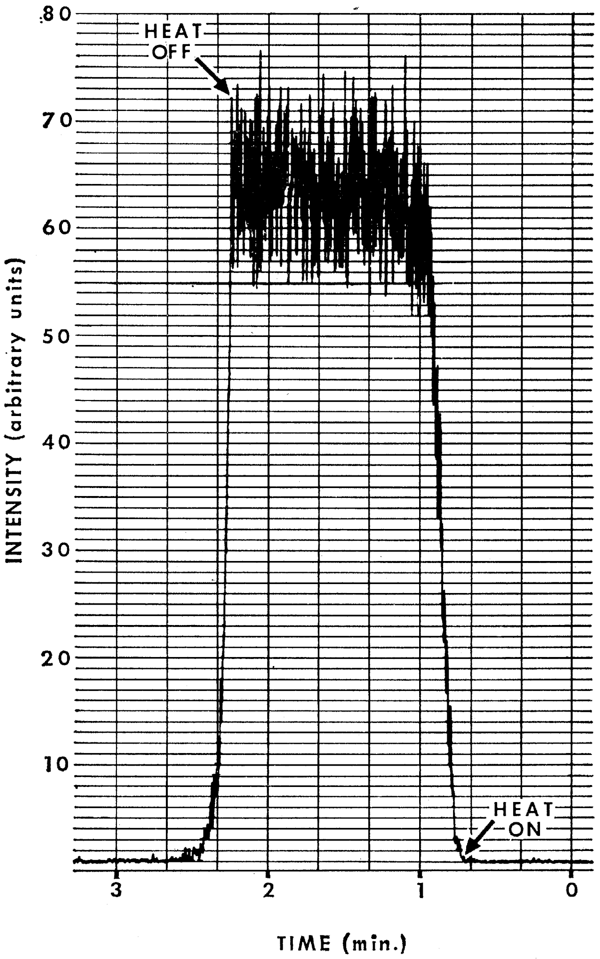


Fig. 8 (left). Isotope effect in a negative ion-molecule reaction. Fig. 9 (right). NH_4^+ ions produced in the catalytic decomposition of NH_3 on platinum.

catalyzed reaction of CO_2 and D_2 listed in Table 2. These neutral species desorbed from the hot platinum catalyst during the course of the reaction and were identified by means of higher-pressure mass spectrometry (*18*). The application of the mass spectrometer to catalytic reactions furnishes, in at least four ways, information outside the scope of other chemical kinetic methods: (i) transients are observed within a few microseconds of desorption; (ii) positive, neutral, and negative transients can be detected; (iii) reactions are studied primarily in one direction, since final products have little opportunity to back-react; and (iv) tests for stable chemical precursors to identified intermediates can be made by independently exposing the catalyst to stable compounds of similar molecular configuration.

The mass spectrometer catalytic technique has been utilized also to identify ions released from the catalyst surface during reaction. In a recent study of the decomposition of NH_3 over platinum (*19*), the NH_4^+ species was discovered to desorb at the surprisingly low temperature of 500°C. A temperature-time scan from this work is given in Fig. 9.

The higher-pressure instrument can be modified readily with radioactive ionizing sources for studying processes in radiation chemistry. Melton and Rudolph (*20*) used a polonium-208 source to study ion-molecule reactions initiated by alpha ionization, and Baldock and Martin (*21*) used a nickel-63 sample in a similar way to test for possible new chemical effects of beta radiation, as compared to effects of electrons of lower energies in the electron beam. Recently an improved source design has permitted more definitive study of the energy effects of electrons on ionization processes up to 6000 electron volts (*22*). Thus far there appears to be no observable influence of either the energy or the type of radiation source used to initiate a specific ion-molecule reaction. The kinetic behavior of the ensuing chemical reactions appears to be quite independent of their method of initiation. For example, we observe no significant differences in the rates of specific reactions over a wide range of energy and type of ionizing radiation. Furthermore, ions of the same atom composition and charge appear to have no distinguishable differences in kinetic behavior when formed from different primary gases—for example, $C_2H_4^+$ from ethylene and $C_2H_4^+$ from ethane behave chemically in the same way.

Finally, the method by which the rates of specific ion-molecule reactions are measured by the mass spectrometer should be mentioned. Let us consider the known reaction

$$C_2H_3N^+ + D_2 \xrightarrow{k} C_2H_3ND^+ + D$$

which we have proved to be a case of hydrogen atom abstraction by the methyl cyanide parent ion-radical $C_2H_3N^+$ (*23*). The bimolecular rate constant k, in cubic centimeters per molecule per second, is estimated in the following manner (*8*):

$$k = \frac{R}{C\bar{t}} = \frac{R\bar{v}}{C\bar{d}} = \frac{R[1.39 \times 10^6 (E\bar{d}/M_i)^{\frac{1}{2}}]}{2C\bar{d}} \qquad (1)$$

where R is the experimental ion current ratio of product ion to reactant ion; C is the concentration (in molecules per cubic centimeter) of D_2; $\bar{t}$ is the average time (in seconds) that the primary ion spends in the ion chamber; $\bar{d}$ is the average distance (in centimeters) from electron beam to exit slit; $\bar{v}$ is the average velocity (in centimeters per second) of the primary ion; E is the potential gradient (in volts per centimeter) of the ion repeller with respect to the exit slit; and M_i is the gram-atomic weight of the reactant ion. Because of uncertainties in pressure and in estimating the values of the various average quantities in the foregoing calculation, the rate constants calculated in this way may have an absolute instrumental uncertainty of at least a factor of two, whereas relative k's on the same instrument can be measured with a precision of ± 10 percent. In order to compare the kinetic results obtained with different instruments, it is customary to choose some accepted reference reaction by which the data can be compared. The reaction

$$CH_4^+ + CH_4 \xrightarrow{k^*} CH_5^+ + CH_3$$

with $k^* = 1.30 \times 10^{-9}$ cubic centimeter per molecule per second is a convenient one and has been used for this purpose (*23*).

We have attempted to describe some of the recent accomplishments and some of the major instrumentation features necessary for a basic understanding of the current field of higher-pressure mass spectrometry. As is true in all science, the present workers in a field are there largely by standing on the shoulders of those who have preceded them. We have tried to acknowledge our indebtedness to many of these individuals in the more extensive bibliographies listed in the references cited. We hope this article will lead other scientists to take a more active and creative interest in the applicability of mass spectrometric methods to their research problems. We wish them great success.

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