ABSTRACTS

Ninth Annual Meeting

ASTM COMMITTEE E-14 ON MASS SPECTROMETRY

June 4-9, 1961
Hotel Sherman
Chicago, Illinois

(1) HIGH TEMPERATURE STUDIES AT THE BRUSSELS MASS-SPECTROMETRY LABORATORY, Paul Goldfinger, *University of Brussels*.

Several sulfide and intermetallic diatomic molecules have been investigated using the Knudsen cell mass spectrometric techniques described at the June 1960 Meeting.

A method for measuring relative ionization cross sections for monoatomic and diatomic species has been developed and applied.

Correlations between stabilities of various molecules and the electronic structure of the component atoms have been found.

(2) CONTROLLED ATMOSPHERE HIGH TEMPERATURE VAPORIZATION STUDIES, R. T. Grimley and R. P. Burns, *Department of Physics, University of Chicago, Chicago, Illinois*.

In certain cases the standard mass spectrometric Knudsen technique has been found unsuited for gas phase equilibrium and vaporization studies. This is especially true in the vaporization of compounds such as CuO and ZnO which evolve sufficiently high oxygen partial pressures at low temperatures such that examination of any high temperature vapor species is prevented. Frequently, however, examination of such systems is made possible by the use of controlled atmosphere experiments. The vaporization of Cr₂O₃, In₂O₃, NiO and the Cu-O system has been studied in

the presence of independently variable oxygen partial pressures. As a consequence of the ability to shift the equilibria, vapor species were found which could not be detected under neutral conditions; accuracy in the measurement of equilibrium constants was improved; and previously undetected fragmentation processes were observed.

(3) THERMODYNAMIC STUDY OF CaO AND OF T_a, T. Babeliowsky and A. J. H. Boerboom, (to be read by J. Kistemaker). *FOM—Laboratorium voor Massaspectrografie, Amsterdam, The Netherlands*.

Values for the heat of vaporization and dissociation of CaO were found by mass spectrometrically analyzing the vapor effusing from a Knudsen cell. ZrO₂ linings were found to be satisfactory sample containers.

No other masses could be detected than are attributable to CaO Ca and O.

The following results have been obtained for CaO.

$$\Delta H_{298}^{\text{vap}} = 139 \pm 14 \text{ kcal/mole and}$$

$$D_0^\circ = 4.5 \pm 1.2 \text{ eV.}$$

The latter value is based on a heat of reaction $\Delta H_{1900}^\circ = 234 \pm 25 \text{ kcal/mole}$ for the reaction

as determined from ion intensity dependence on temperature.

Measurements on the vaporization products of a Tantalum wire provided for the heat of vaporization of Ta and for the dissociation energy of Ta₂. No

other species were found.

The following results are obtained.

For the reaction

These values lead to a dissociation energy for Ta_2 at 2600 °K of 7.8 ± 1.4 eV.

This value seems to be rather high. Therefore measurements are continued.

(4) MASS SPECTROMETRIC STUDIES OF ION PROFILES IN LOW PRESSURE FLAMES, H. F. Calcote and J. L. Reuter, *AeroChem Research Laboratories, Inc., P. O. Box 12, Princeton, New Jersey.*

An rf mass spectrometer is used to identify the ions produced in low pressure flames and to determine ion profiles through the flame front. Flat flames are produced on burners at 2 mm Hg and the ions allowed to diffuse into the mass spectrometer through a small orifice in a cone shaped probe. The geometry employed causes only a minimum disturbance to the flame and the maintenance of an orifice diameter of approximately the ion mean free path reduces the effect of ion-wall reactions to a minimum.

The formation and removal of various ions have been observed through several hydrocarbon-oxygen flames. Contrary to expectations, the maximum for the C_3H_3^+ ion appears before the maximum for the H_3O^+ ion. Neither of these is believed to be the ion first formed from neutral species; they are probably produced by rapid ion-molecule reactions which suppress the concentration of the ion initially formed.

This work has been supported by the Air Force, Contract AF 04(647)-157.

(5) THE PRODUCTION OF NH_4^+ and NO^+ IONS IN FLAMES, K. Bascombe, D. Jenkins, H. I. Schiff, T. M. Sugden, *Cambridge University.*

The principal ion produced in the reaction zone of flames of premixed hydrogen, oxygen and nitrogen is H_3O^+ . When small amounts (less than 1 %) of NO and NH_3 are added to the flame supply, large quantities of NH_4^+ and NO^+ ions are produced

in both cases. These ions have been studied as functions of distance from the reaction zone, amount of additive, mass spectrometer leak size, and presence of metallic elements. The conclusions are:

(1) NH_4^+ ions are produced by the reaction:

(2) NO^+ ions are produced independently of H_3O^+ by thermal ionization.

(3) The dependence of the ion intensities on the concentration of additive can be explained in terms of known flame reactions, in particular

(4) The rate of the reaction $\text{HO}_3^+ + \text{e}^- \rightarrow \text{H}_2\text{O} + \text{H}$ is about $2 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$ and the recombination rate of $\text{NO}^+ + \text{e}^-$ has a very similar value.

(6) MASS SPECTROMETRIC STUDIES OF LOW PRESSURE PYROLYSIS REACTIONS OF SIMPLE CHLORO AND FLUOROCARBONS IN GRAPHITE OVENS, Dino R. Bidinosti and Richard F. Porter, *Department of Chemistry, Cornell University, Ithaca, New York.*

The reaction products formed when simple chloro and fluorocarbons are passed through heated graphite inlet systems have been analyzed mass spectrometrically. Information concerning the mechanism can be inferred from ion current measurements obtained as a function of pressure or leak rate and temperature.

The pyrolysis of CCl_4 to C_2Cl_4 and Cl_2 has been studied as a function of temperature and pressure. When either CCl_4 or C_2Cl_4 is passed through the leak system, at temperatures above 900°K, $\text{C}_2\text{Cl}_2(\text{g})$ is formed. This latter species is identified by observation of the $\text{C}_2\text{Cl}_4^+/\text{C}_2\text{Cl}_2^+$ ratio as a function of temperature and by the appearance potential for C_2Cl_2^+ . This potential is several volts below that required to form C_2Cl_2^+ by fragmentation of C_2Cl_4 . The C_2Cl_4^+ current shows a first order pressure dependence on C_2Cl_4 but appears to be independent of Cl_2 pressure. The mechanism of formation of C_2Cl_2 is attributed to a surface reaction

Tetrachloroethane is found to pyrolyze mainly to dichloroethylene. The mechanism is attributed to a surface reaction similar to that observed for C_2Cl_4 .

Pentachloroethane similarly yields trichloroethylene.

Mixed fluoro-chloromethanes pyrolyze to ethylenes and are found to undergo halogen exchange.

(7) THE ADAPTION OF A BENDIX TIME-OF-FLIGHT MASS SPECTROMETER FOR HIGH TEMPERATURE STUDIES, H. J. Foster, *National Bureau of Standards, Washington 25, D. C.*

Of current interest in this laboratory is the use of a Bendix, Model 12-101, Time-of-Flight (TOF) mass spectrometer and combination Knudsen source, incorporating a slit-shutter arrangement and differential pumping, for studies of equilibrium vapor composition above the condensed phase of thermally stable materials at temperatures above 2000°C . From these studies, partial pressures of the evaporating molecular species are obtained, and from this information thermodynamic constants are derived. The design, construction, and performance of a slit and shutter arrangement used in the modification of the Bendix, 12-101 TOF mass spectrometer for high-temperature studies are described. The desirability of this feature, which provides for differential pumping, and its general usefulness for high-temperature gas analysis, in connection with discrimination between interfering residual and out-gassed sources of molecules and those molecules representative of the sample composition will be emphasized,

(8) ION-MOLECULE REACTIONS OF METHANOL AND ETHANOL WITH VERY SLOW POSITIVE IONS, E. Lindholm and P. Wilmenius, *Physics Department, Royal Institute of Technology, Stockholm 70, Sweden.*

In a double mass spectrometer methanol or ethanol gas was bombarded with positive ions, produced in a mass spectrometer. From the alcohol molecules ionized fragments were obtained, which were analyzed in a second mass spectrometer. Usually, the ionized fragments are due to charge exchange, but

at very low velocity of the incident ion (≈ 5 eV) ion-molecule reactions have been observed. Proton transfer seems to occur nearly always when the incident molecular ion (e.g. CH_4^+ , H_2S^+ , SH^+ , $\text{C}_2\text{H}_5\text{OH}^+$, $\text{C}_2\text{H}_5\text{OH}^+$) contains hydrogen, but hydride ion transfer seems to be of importance only in a few cases ($\text{CH}_3^+ \rightarrow \text{CH}_3\text{OH}$ or $\text{C}_2\text{H}_5\text{OH}$; $\text{SH}^+ \rightarrow \text{CH}_3\text{OH}$; $\text{P}^+ \rightarrow \text{CH}_3\text{OH}$). The reason seems to be that the competitive process, charge exchange, usually has a greater probability, so that hydride ion transfer can be important only when charge exchange cannot take place. This means that the recombination energy of the incident ion must be lower than the ionization potential of the molecule.

(9) DISSOCIATION OF ALCOHOL MOLECULE IONS FORMED IN CHARGE EXCHANGE COLLISIONS WITH POSITIVE IONS, H. Von Koch, E. Lindholm and P. Wilmenius, *Physics Department, Royal Institute of Technology, Stockholm 70, Sweden.*

Mass spectra of CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ have been obtained after charge exchange with slow positive ions. As the energy absorbed by the alcohol equals the recombination energy of the incident ion it is possible to plot the peaks as a function of the energy absorbed by the molecule. The graph accordingly corresponds to similar graphs obtained by means of the statistical theory of mass spectra (1). The electron impact mass spectrum can be computed from the curves by integration of the curves. The "energy distribution function" is assumed to be constant up to 18 eV for CH_3OH and 17 eV for $\text{C}_2\text{H}_5\text{OH}$. Reasonable agreement is then obtained with the observed electron impact mass spectra.

A comparison between the theoretical curves by Friedman, Long, and Wolfsberg (1) and our experimental curves shows disagreement in several respects. In all cases where it can be decided our curves rise steeply from the appearance potential while the theoretical curves rise very slowly.

From the curves some information about the dissociation processes can be obtained.

(1) L. Friedman, F. A. Long, and M. Wolfsberg, *J. Chem. Phys.* 27, 613 (1957).

(10) REACTIONS OF GASEOUS IONS

IX. CHARGE EXCHANGE REACTIONS OF RARE GAS IONS WITH ETHYLENE,

J. L. Franklin and F. H. Field, *Humble Oil & Refining Company, Baytown, Texas.*

Using a mass spectrometer ion source as a reactor, ions of all of the rare gases have been shown to under charge exchange reactions with ethylene. The rates of these reactions are in the order of 10^{-10} – 10^{-9} cc: molecule $^{-1}$ sec $^{-1}$ and thus are typical of the other ion-molecule reactions. Xenon and argon ions, respectively, produce $C_2H_4^+$ and $C_2H_3^+$ predominantly. Krypton ions produce $C_2H_4^+$, $C_2H_3^+$, and $C_2H_2^+$ in approximately the ratio 1:2:1. Helium and neon ions react somewhat more slowly than the others and produce CH_2^+ predominantly.

(11) CHARGE EXCHANGE PHENOMENA IN A MASS SPECTROMETER,

G. F. Crable and G. L. Kearns, *Gulf Research & Development Company, Pittsburgh, Pennsylvania.*

Ion currents observed well below the ionization potential are explained as the result of charge transfer between ions produced in the electron trap, or catcher region, and molecules within the normal ionization region of the ion chamber. Electrons which enter the ionization chamber with energies as much as 5 to 10 volts below the ionization potential are accelerated to relatively high energies in the electron collector region and can produce ionization there. Secondary ions produced by this mechanism should depend on the square of the number of molecules per cm 3 in the ion chamber and directly on the ionizing electron current. Experimental data from a number of molecule ions agree with predictions.

A more stringent test of a charge exchange reaction can be made through the fact that cross section for such a process is a maximum when the energy required to produce the secondary ion equals the recombination energy of the bombarding ion. The change in charge exchange spectrum of H_2S was observed when argon was added. The A^+ (I.P. = 15.76 v.) ions produced a maximum enhancement of the HS^+ (A.P. = 15.2 v.) ions as compared to intensity changes of the H_2S^+ (I.P. = 10.47 v.) ions and S^+ (A.P. = 14.0 v.) ions.

Relative cross sections for charge exchange for

aromatic compounds will be discussed.

(12) RECONSIDERATION OF THE ENERGY DEPENDENCE OF ION MOLECULE CROSS SECTIONS,

D. A. Kubose and W. H. Hamill, *Department of Chemistry and Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana.*

The energy dependence of gaseous ion molecule reaction cross sections, Q , have been re-examined. It has been found that a number of these reactions do not follow the predicted dependence,

$$Q = \frac{a}{E^{1/2}},$$

where E is the ion exit energy. Experimental data from this laboratory and values reported in the literature indicate for low ion energies

$$Q = \frac{a}{E^{1/2}} + b \text{ and } Q = \frac{aE_i^{1/2} + cE_i}{E} + d$$

for high ion energies, the transition occurring at E_i . These equations have been applied to several organic systems, to reactions of D_2^+ on D_2 , K_r^+ on H_2 and others involving D_2 or H_2 . The adequate description obtained indicates these equations are of general applicability.

(13) ION-NEUTRAL REACTIONS IN THE HELIUM-HYDROGEN SYSTEM SECONDARY PRODUCTION OF PROTONS BY ION-NEUTRAL REACTIONS,

M. Hertzberg and D. Rapp, *Lockheed Missiles and Space Division, Palo Alto, California.*

The relative yields of H^+ , H_2^+ , H_3^+ , He^+ and HeH^+ ions produced in an electron bombardment ionization source have been measured as a function of electron energy and pressure. The following ion-neutral reactions have been shown to contribute to the yield of secondary ions:

The appearance potential of the HeH^+ ion coincided with the appearance potential of H_2^+ . Since the appearance potential of the secondary protons

was displaced above the appearance potential of H_2^+ by an energy approximately equal to the dissociation energy of H_2^+ , it is concluded that the protons formed by the endoenergetic reactions (2) and (6) involve H_2^+ ions in highly excited vibrational energy states. The extent to which existing measurements verify the classical polarizability theory is critically reviewed, and a modified theory is proposed.

(14) MORE FUN WITH ASTON BANDS, Wm. McGowan and Larkin Kerwin, *University Laval, Quebec, Canada*.

By examining the products of ion-molecule collisions in a mass spectrometer (e. g. Aston bands), information can be obtained about the process of the initial ion formation by electron bombardment. When collision cross-sections are known, this technique leads in some cases to the determination of metastable states in which the ions were formed. Data will be presented for argon, nitrogen, and oxygen.

(15) ION-MOLECULE REACTIONS IN ELECTRON-IMPACT TYPE ION SOURCES*, Dwight Hutchison and Louis Pobo, *Argonne National Laboratory, Argonne, Illinois*.

Recent studies of ion-molecule reactions have been made which may be represented as $M_1^+ + M_2 \rightarrow S^+ + N$, where M_1^+ is the reactant ion, M_2 is the reactant neutral species, S^+ is the product secondary ion, and N is the product neutral species. It has been assumed in past work that either M_1 or M_2 carries the positive charge. The possibility that two reactions occur in which M_1^+ and M_2^+ react simultaneously with M_2 and M_1 , respectively, to form the same secondary ions S^+ has not been considered. We have shown that both reactions may occur simultaneously. We present a method for the determination of the fraction of each reaction occurring and a method for obtaining the average total cross section for each reaction. We illustrate the methods by experimental data taken for N_2D^+ formed in mixtures of N_2 and D_2 , by ArH^+ formed Ar and H_2 , and by COD^+ formed from CO and D_2 .

*Based on work performed under the auspices of the U.S. Atomic Energy Commission.

(16) FRANCK-CONDON FACTORS AND THE SHAPE OF IONIZATION EFFICIENCY CURVES, Morton E. Wacks and Morris Krauss, *Physical Chemistry Division, National Bureau of Standards, Washington, D. C.*

Theoretical calculations of the vibrational overlap integrals for the following transitions have been completed:

- a) $O_2(X^3\Sigma_g^-, v=0, 1) \rightarrow O_2^+(X^2\pi_g, v'=0 \rightarrow 10;$
 $a \ ^4\pi, v=0 \rightarrow 15; A^2\pi_u, v'=0 \rightarrow 20; b \ ^4\Sigma_g^-, v'=0 \rightarrow 10)$
- b) $NO(X^2\pi, v=0) \rightarrow$
 $NO^+(X' \Sigma^+, v'=0 \rightarrow 10; A' \pi, v'=0 \rightarrow 10)$
- c) $CO(X' \Sigma^+, v=0) \rightarrow CO^+(X^2\Sigma^+,$
 $v'=0 \rightarrow 10; A^2\pi, v'=0 \rightarrow 10;$
 $B^2\Sigma^+, v'=0 \rightarrow 10).$

These results have been used to construct theoretical ionization efficiency curves assuming an energy dependence for the electronic transition integral for both photoionization and ionization by electron impact.

The O_2 curve for electron impact is compared with previously published experimental data¹. A similar comparison is made between experimental photoionization data² and the theoretical curve for NO .

A cursory examination of the situation for polyatomic molecules will be made. It is evident that the large number of final vibrational states will profoundly affect the shape of the ionization efficiency curves.

In particular, it may be noted that lack of an extensive vibrational foot on an ionization efficiency curve does not necessarily indicate an adiabatic transition or *vice-versa*.

1D. C. Frost and C. A. McDowell, J. Am. Chem. Soc., 80, 6183 (1958).

2"Final Report on Ionization Potential of Molecules by a Photoionization Method," K. Watanabe, T. Nakayama and J. Mottl, Department of Physics, University of Hawaii, December, 1959.

(17) RECENT ELECTRON IMPACT EXPERIMENTS, James D. Morrison.

The study of ionization efficiency curves leads not only to the determination of threshold energies, but to the measurement of relative electronic transition probabilities and the lifetimes of transient

excited states. The way in which excess energy is removed from the collision complex can be determined, and enables a given process to be identified. The study of multiply charged molecular ions indicates that the potential energy functions describing their energy states are often of unusual form. Some recent electron impact experiments carried out in a mass spectrometer employing a beam of ionizing electrons with low spread in energy will be described.

(18) CURRENT STATUS OF THE STATISTICAL THEORY OF MASS SPECTRA, Morris Krauss, Henry Rosenstock and Merrill B. Wallenstein, *Physical Chemistry Division, National Bureau of Standards, Washington 25, D. C.*

A critical review of the present status of the theory of mass spectra will be given. Special emphasis will be given to the statistical mechanical foundations of the theory. The semiclassical approximation to the vibrational density of states is shown to produce large errors in the computed rate constants. Significance of the effective number of oscillators is discussed. The degree of accuracy to be expected from assumptions of the structure of the activated complex is analyzed. Current knowledge of the details of the primary ionization process is reviewed and related to the interpretation of mass spectral data.

The above considerations are applied especially to problems of metastable transitions, competing reactions and kinetic shifts of appearance potentials.

(19-I) AN IMPROVED INTEGRAL APPROXIMATION IN QUASI-EQUILIBRIUM MASS SPECTRAL THEORY, Marvin Vestal, Austin L. Wahrhaftig¹ and William H. Johnston, *William H. Johnston Laboratories, Inc.², Baltimore, Maryland.*

The basic equation of the quasi-equilibrium theory of mass spectra is

$$k_i = \frac{1}{h} \int_0^{E-\epsilon_0} \frac{p^{\ddagger}(E, \epsilon_0, \epsilon_i)}{p(E)} d\epsilon_i$$

where k_i is the rate of the i^{th} reaction of an ion and p , $p^{\ddagger}$ are energy state density functions for the ion in normal and activated complex states,

respectively³. All calculations to date have involved (1) the assumption that the ion can be represented by a collection of harmonic oscillators (and possibly free internal rotors) in both normal and activated states and (2) the evaluation of the number of states for such a collection of oscillators by the Dirichlet integral.

In the present work it is shown that the evaluation, (2), is completely invalid at ion energies only slightly above the activation energy for a dissociation process and is, at best, a very poor approximation. Over the energy range of interest practically all of the states have several oscillators unexcited; the usual expression neglects these states.

A method is presented which explicitly considers the assignment of zero vibrational quantum numbers and provides an integral approximation for other quantum numbers. The application of this method to the dependence of reaction rate upon ion energy is briefly discussed.

(1) University of Utah, Salt Lake City, Utah.

(2) This research project was supported by U.S. Air Force Contract AF 33(616) - 7638.

(3) Rosenstock, Wallenstein, Wahrhaftig and Eyring, *Proc. Nat. Acad. Sci. U.S.* 38, 667 (1952).

(19-II) THE APPLICATION OF THE IMPROVED INTEGRAL APPROXIMATION TO QUASI-EQUILIBRIUM THEORY OF MASS SPECTRA¹, Austin L. Wahrhaftig², Marvin Vestal² and William H. Johnston³.

The previous abstract has described an improved integral approximation for use in the calculation of rates of unimolecular decomposition reactions in mass spectrometry. When this method is used to derive the rate expression for a simple harmonic oscillator model, the rate constant for the i^{th} reaction is given by

$$k_i(E) = \frac{\sum_{p=1}^{N-1} a_{ip}(E-\epsilon_i)^p}{\sum_{Q=0}^{N-1} b_Q E^Q} \quad (1)$$

where the b_Q are known functions of the oscillator frequencies for the normal state of the ion and the a_{ip} are known functions of the oscillator frequencies of the i^{th} activated complex form the ion.

A number of interesting consequences are described which arise from the application of this equation

instead of the equation previously used

$$k_i(E) = Z_i \left(\frac{E - \epsilon_i}{E} \right)^{N-1} \quad (2)$$

Thus Equation (1) gives a variation of rate constant with energy using physically significant parameters which is similar to the results obtained over a small energy range with the previous equation, (2), using empirical parameters, such as those reported by Chupka and by Inghram. Also, the difficulty noted by Friedman *et al*, that the strict application of equation (2) would make the direct experimental observation of appearance potentials impossible, is resolved within the framework of the theory.

Some calculations using the new rate expression will be presented.

- (1) Work performed at the William H. Johnston Laboratories, Inc. Baltimore, Maryland, was supported by U.S. Air Force Contract AF 33(616)-7638. Work performed at University of Utah was supported in part by U.S. Atomic Energy Commission Contract AT(11-1)-82.
- (2) University of Utah, Salt Lake City, Utah, and William H. Johnston Laboratories, Inc., Baltimore, Maryland.
- (3) William H. Johnston Laboratories, Inc., Baltimore, Maryland.

(20) ENERGY RANDOMIZATION AND THE STATISTICAL THEORY OF MASS SPECTRA*, William A. Chupka, *Argonne National Laboratory, Argonne, Illinois.*

The critical assumption of energy randomization in excited molecular ions is examined. The results of luminescence studies of organic molecules are used to estimate the efficiency of inter-conversion among excited electronic states of molecular ions. Mass spectral evidence for lack of such conversion in certain cases is cited. The process of randomization of energy among vibrational modes is examined in terms of Fermi resonance. Optical and mass spectroscopic and chemical kinetic data are used to estimate the efficiency of this randomization. Metastable ion peak shapes are analyzed and provide support for certain qualitative features of the statistical theory of mass spectra.

*Work performed under the auspices of the U.S. Atomic Energy Commission.

(21) EQUILIBRATION IN THE STATISTICAL THEORY OF MASS SPECTRA*, Max Wolfsberg, *Chemistry Department, Brookhaven National Laboratory, Upton, Long Island, New York.*

Equilibration of excitation energy among the degrees of freedom of the parent molecule ion prior to dissociation into fragments is one of the fundamental hypotheses of the statistical theory of mass spectra. The theoretical implications of this hypothesis will be discussed in detail. Information to be gained on the hypothesis from various experimental data will also be discussed. These data include mass spectral patterns under usual experimental conditions, mass spectral patterns as a function of energy of ionizing electrons, and the forms of ionization efficiency curves.

*Research carried out under the auspices of the U. S. Atomic Energy Commission.

(22) PHOTOIONIZATION OF FREE RADICALS AND THE KINETICS OF UNIMOLECULAR DISSOCIATION, Fred A. Elder, C. Giese, Mark G. Inghram and Bruce Steiner, *Department of Physics, University of Chicago, Chicago, Illinois.*

Methyl, ethyl, n-propyl and sec-propyl radicals have been studied by photoionization techniques in a mass spectrometer¹. The study was undertaken in order to provide more precise information on the threshold energies for these radicals and thereby to furnish evidence on the role of kinetics in the fragmentation of paraffin ions².

Tetramethyl lead, tetra-n-propyl lead, diethyl mercury, disecpropyl mercury, tertbutyl nitrite, secbutyle nitrite, n-butyl nitrite and isobutyl nitrite were introduced, through a greaseless glass-metal system, into the ionization chamber of the mass spectrometer, where they were pyrolyzed on a hot platinum filament. The free radicals were ionized by an approximately mono energetic photon beam which crossed the ionization chamber. The radical parent ions and ions of the same mass produced by fragmentation of the parent molecule ions were observed. No fragment ions from the radical parent ions were observed in the energy range 7.2-11.9 ev.

The ionization efficiency curves of these radicals indicate that the vertical transition for the methyl radical, which is believed to correspond to the adiabatic transition, occurs at 9.84 ± 0.04 ev. This value is in agreement with the adiabatic transition reported by Herzberg³. The interpretation of

the transitions for the other radicals will be discussed.

1. H. Hurler, Mark G. Inghram and J. D. Morrison, *J. Chem. Phys.* 28, 76-82 (1958).
2. Bruce Steiner, Clayton F. Cies and Mark G. Inghram, *J. Chem. Phys.* 34, 189-220 (1961).
3. G. Herzberg and J. Shoosmith, *Canad. J. Phys.* 34, 523 (1956).

(23) TEMPERATURE DEPENDENCE OF METASTABLE TRANSITIONS, H. Ehrhardt, *University of Bonn, Bonn, Germany*.

(24) CHARGE STATES OF MOLECULAR FRAGMENTS FOLLOWING NUCLEAR DECAY*, Sol Wexler, *Argonne National Laboratory*.

The patterns of positively charged fragments from dissociation of molecules following nuclear decay of bound radioactive atoms are characteristic of the mode of nuclear decay. After negative beta emission the mass pattern of the ions is composed almost entirely of singly-charged species, and the modes of molecular disruption appear to be insensitive to the nuclear charge of the radioactive atom, and hence to the size of its surrounding electron cloud. On the other hand, nuclear isomeric transition accompanied by internal conversion leads to mass patterns dominated by multiply-charged atomic species. The data indicate that extensive electron transfer occurs in the molecule prior to rupture. The molecules are apparently shattered as a result of multicenter Coulombic repulsion of separated positive charges.

*Work performed under the auspices of the U.S. Atomic Energy Commission.

(25) A NON-STATISTICAL APPROACH TO THE CALCULATION OF MASS SPECTRA, J. C. Lorquet (*).

The processes occurring during ionization and fragmentation of a molecule bombarded by monoenergetic electrons are considered. The absolute calculation of the mass spectrum of this molecule requires the solution of two problems: 1) calculation of the electronic levels of the ion and 2) study of the transition probabilities to each of these levels.

1) The electronic levels of an ion can be either determined experimentally, as ionization and appearance potentials, or calculated by quantum me-

chanical methods. If the latter procedure is used, it must be complemented by an assumption about the probability of rupture of the different chemical bonds in each electronic state. We assume in this work that the chemical bond with the lowest bond order will dissociate.

2) An empirical expression is then proposed, which relates the transition probabilities from the ground state of a neutral molecule to electronically excited states of the corresponding positive ion and the energy required by the transition as well as the acceleration voltage of the impinging electrons. It is concluded that for a given energy of the bombarding electrons, the transition probability decreases regularly when levels more and more excited are considered. Transitions requiring 30 ev. or more occur to a negligible extent, whatever energy the impinging electrons may have.

The mass spectrum of small molecules, for which all ionization and appearance potentials have experimentally determined (N_2 , O_2 , NO , CO , CO_2 , H_2O) are calculated by means of these relations, and a satisfactory agreement with experiment is found. The mass spectrum of butadiene is also calculated by the same method, using the electronic levels calculated for the ion by means of a LCAO/SCF/CI treatment.

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(26) COMPARISON OF MASS SPECTRAL REGULARITIES FOR n-PARAFFINS AND n-TERMINAL OLEFINS, Norman D. Coggeshall, *Gulf Research & Development Company, Pittsburgh, Pennsylvania*.

The mass spectra of n-paraffins and n-terminal olefins in the C_{10} to C_{20} range, inclusive, have been studied to establish the quantitative relationships that must be predicted by a satisfactory theory of mass spectra. The n-terminal olefin spectra are generically similar to those for the n-paraffins but systematically have a higher center of gravity (based on $C(M,n)$ plots). The linear behavior of classes upon M (carbon number of parent molecule) previously observed for n-paraffins has been confirmed by this investigation. The same

type of class dependence upon M was observed for the olefins. Subclasses defined by $Y(M, n, j)$, each of which represents specific ions, showed, for both classes of compounds, a linear dependence on M expressible as

$$Y(M, n, j) = f_j(n) (M - n_j)$$

The data showed that the probability of formation of different ion species may be essentially independent of, increase with, or decrease with, M . The postulate that the molecules first dissociate into C_nH_{2n+1} ions with subsequent dissociation into ions of different stoichiometry is shown to be untenable. The data indicate that the presence of the double bond affects the molecule as a whole in all its dissociation modes rather than just those modes not involving the double bond. Classes of ions defined by particular stoichiometric relationships and summed over all n are shown to be independent of or linearly dependent upon M . This suggests that the molecules may first dissociate to a particular stoichiometry and then to the final values of n .

(27) THE MASS SPECTRA OF THREE DEUTERATED PROPENES, W. H. McFadden, *Western Regional Research Laboratory**, Albany 10, California.

The mass spectra of 2-d-propene, 1,1-d₂-propene, and 3,3,3-d₃-propene will be presented. The data show that considerable rearrangement of deuterium with hydrogen can occur from all positions. The rate of exchange is sufficient to give a statistical distribution for the ions containing three carbons but ions containing two carbons show only modest exchange. This indicates that the rate of breaking a C-C bond to give $C_2H_3^+$ is of the same order of magnitude as the rate of H-D exchange.

*A laboratory of the Western Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

(28) CORRELATION STUDIES ON SOME OXYGEN CONTAINING COMPOUNDS, P. A. Finan, R. I. Reed, J. S. Shannon and J. M. Wilson, *The Chemistry Department, The University, Glasgow, W.1.*

Following the mass-spectrometric examination of the eight inositols, the studies have been extended

to include some anhydro-sugars and sugar derivatives. Correlations have been sought between these latter spectra and those of some of the inositols.

(29) VARIATIONS OF MASS SPECTRA WITH THMPERATURE BETWEEN -195°C AND $+200^\circ\text{C}$, A. Cassuto and P. LeGoff, *Laboratoire de Spectrometrie de masse, Faculte des Sciences NANCY (France)*.

Variations of mass spectra with temperature between -195°C and $+200^\circ\text{C}$ have been studied. The ionization chamber was either heated electrically or cooled with liquid nitrogen. The experimental technique has been firstly described in a previous paper (1) but recent improvements have been made for better accuracy and reproductibility.

The experimental results may be summarized as follows:

—total ionization of Argon, Neon, CO_2 , N_2 , CH_4 , C_2H_6 , C_3H_8 , C_5H_{12} are unchanged in the whole temperature range.

—Cracking pattern of Argon, Neon, CO_2 and N_2 are unchanged in the same range.

—Relative cracking pattern of the considered hydrocarbons measured with reference to the argon or the neon peak or the total ionization as in internal standard, present thorough change only above 0°C .

These results may be theoretically explained using the Rosenstock et al. theory (2). Particularly, variations of the hydrocarbons parent peaks may be represented by

$$\frac{I(T)}{I(T_0)} = \exp\left(-K(\varepsilon - \varepsilon_0)\right)$$

(T) being the vibrational energy of the molecule.

With the same experimental technique the activation energy of the ion-molecule reaction:

has been measured between -195°C and 200°C . The result is 0 ± 0.2 Kcal/mole, in good agreement with a previous measurement of STEVENSON and SCHISSLER in a higher temperature range.

- (1) L.P. BLANCHARD and P. LEGOFF: *Advances in mass spectrometry* p. 570 Pergamon Press London 1959.
- (2) H. M. ROSENSTOCK M. B. WALLENSTEIN, A.

L. WAHRHAFTIG and H. EYRING, Proc. Natl. Acad. Sci. U. S. 38, (1952).

- (3) STEVENSON D. P. and O. SCHISSLER, J. Chem. Phys. 24, (1956).

(30) METASTABLE IONS IN MASS SPECTROMETRY, G. A. Muccini, W. H. Hamill and R. Barker, *Department of Chemistry, University of Notre Dame, Notre Dame, Indiana.*

The rate of the metastable transition $C_3H_7^+ = C_3H_5^+ + H_2$ or $2H$ in eight normal hydrocarbons was studied by mass spectrometric techniques. The rate constant of this transition appears to be independent of the number of carbon atoms in the hydrocarbons.

In another set of experiments the rate constant of this transition was measured at different energies of the ionizing electrons. Normal hexane was used in these runs. It was found that the rate constant increases with decreasing energy of the ionizing electrons.

A number of suggestions to explain these results are made.

(31) ANOMALIES IN THE MASS SPECTRUM OF HEXACHLOROPROPENE AND ITS RELATION TO BASIC CONCEPTS OF THE PROPENE MOLECULE, H. R. Harless, *Research Department, Union Carbide Chemicals Company, South Charleston, West Virginia.*

The thermodynamic relationships of the carbon-carbon bonds of propene appear to have been clarified by correlation of mass spectral data with the apparent spatial atomic arrangement of hexachloropropene and propene. Spectrum-structure correlations for propenes have added credence to postulations that the configuration of the propene molecule is that of a resonance hybrid. A discussion of various forms of the allyl ion and propenyl derivatives is given and a new concept of the propene molecule is advanced. Rectification of anomalous ionization mechanisms has led to postulations that the two individual carbon-carbon bonds of propene are fundamentally equivalent in respect to each other in a manner that may be analogous to the various bonds of butadiene and benzene. The classical valence-bond structure of hexachloropropene is refuted and a new concept of its structure sugge-

sted. An idea is advanced that the spatial structure of propene should be depicted in a singular mode as yet unpublished.

(32) ANALYTICALLY USEFUL CORRELATIONS OF MASS SPECTRA AND MOLECULAR STRUCTURES OF THIOLS, SULFIDES, AND DISULFIDES, Glenn L. Cook, D. G. Earnshaw and G. U. Dinneen, *U. S. Bureau of Mines, Laramie, Wyo.*

The $C_nH_{2n+1} S^+$ ions in the spectra of the thiols indicate the largest R-group if the formula of the thiol is expressed as $R_1R_2R_3-CSH$. Primary thiols are differentiated from secondary thiols by examination of $C_nH_{2n}^+$ ions and $C_nH_{2n+1}^+$ ions in their spectra. Additional information about the alkyl group is obtained from the intensity of the m/e 35 ion.

The m/e of the base peak, the intensity of the m/e 35 ion, the intensities of the RSH^+ and RSH_2^+ ions, and the intensities of the C_nH_{2n+1} ions show the number of carbon atoms in each of the alkyl groups. The number of possible configurations for the alkyl groups is limited by the intensity of the m/e 35 ion.

The number of carbon atoms in each alkyl group of a disulfide is determined by examination of the C_nH_{2n+1} and $RSSH^+$ ion intensities. An ethyl-alkyl-disulfide is uniquely indicated by the intensity of the $HSSH^+$ peak in its spectrum.

(33) A NEW MASS SPECTROMETER OF MEDIUM SIZE, MASS RANGE 2 TO 100, FOR ISOTOPIC MEASUREMENTS AND FOR GAS ANALYSES, K. Kronenberger, *Atlas-Werke, A.G.*

Construction and performance data of an easily operated mass spectrometer of medium size, mass range 2 to 100, are given. The instrument is suitable for precision measurements of isotopic ratios of gaseous samples, for trace analyses and purity tests as well as for qualitative and quantitative analyses of gaseous mixtures.

Resolving power : $m/M = 100$

Accuracy: 0.02% rel. for isotopic ratios in range
1 : 1 to 1 : 100

0.1% rel. for the D/H ratio of natural

hydrogen.

(34) SENSITIVE TIME-OF-FLIGHT MASS SPECTROMETER FOR GAS ANALYSIS, B. R. F. Kendall, *Radio and Electrical Engineering Division, National Research Council, Ottawa, Canada.*

The design and performance of an all-metal, non-magnetic time-of-flight mass spectrometer are discussed. The instrument is suitable for operation at pressures down to and including the ultra-high-vacuum range. A feature of the instrument is the ease with which different flight tubes and ion detection systems can be fitted, thus allowing the operating characteristics to be readily matched to the needs of specific applications. The mean ion current is approximately 4×10^{-3} amp. per mm Hg of partial pressure. When flight path of 50 cm is used, the amplitudes of adjacent mass peaks of similar height can be measured satisfactorily up to mass 60. The response time of the instrument for a change in gas composition in the ion source can be varied between 10^{-5} second and 1 second. The corresponding variation in minimum detectable partial pressure is from 10^{-10} mm Hg to approximately 2×10^{-10} mm Hg.

(35) DEVELOPMENT OF A BALLOON-BORNE TIME-OF-FLIGHT MASS SPECTROMETER, J. F. Betts, R. A. Fluegge, G. J. O'Halloran, *Bnedix Corporation, Research Labs, and R. S. Narcui, Air Force, Cambridge Research Labs.*

The development of a balloon-borne Time-of-Flight Mass Spectrometer is described. This instrument which employs a servo controlled variable leak to accommodate sample pressure variations from 760 to 1 mm Hg provides six continuously monitored output channels. Performance data for the instrument is presented.

(36) A PANORAMIC RAPID SCANNING MASS SPECTROMETER, D. G. H. Mersden and C. Ouellet, *Department of Chemistry, Laval University, Quebec, P.Q.*

The rapid scanning panoramic sector field mass spectrometer first described in Can. J. Phys. 33, 74 (1955) has been modified and improved consi-

derably. Fast gas reactions may be studied up to 200 mm pressure at temperatures up to 450°C . A mass range up to 10 to 1 ratio may be observed on the screen of a cathode ray tube at repetition rates up to 1000 per second. Limitations in performance and comparison with time of flight panoramic mass spectrometers will be discussed.

(37) A MASS SPECTROGRAPH FOR THE ANALYSIS OF SOLIDS, W. M. Hickam and G. Sweeney, *Westinghouse Research Laboratories, Pittsburgh 35, Pennsylvania.*

A double focusing mass spectrograph of the Mattauch type for the analysis of solids⁽¹⁾ has been constructed. Ions representing the sample are obtained by a radio-frequency spark or thermal ion source. Low permeability gasketing is accomplished through the use of molded teflon films. Operating pressures are obtained by ionic and cryogenic pumping. Negative and positive ion spectra are detected either photographically or electrically.

The apparatus and some experimental results are described. Negative ion spectra, similar to those reported by Honig⁽²⁾ have been obtained using a heated alkali halide coated filament. In part, the atom species associated with the positive and negative ion spectrum from the thermal source are influenced by the introduction of known gases at pressures of 10^{-7} mm Hg into the vacuum system.

(1) Hannay, N. B., Review of Scientific Instruments 25, 644 (1954).

(2) Honig, R. E., J. of App. Physics 29, 549 (1958).

(38) A METHOD OF INCREASING THE RESOLVING POWER OF MASS SPECTROMETERS AND OTHER ANALYTICAL INSTRUMENTS, B. R. F. Kendall, *Radio and Electrical Engineering Division, National Research Council, Ottawa, Canada.*

The basic function of a mass spectrometer is to identify the nuclides present at its input and to indicate their relative abundance. A technique is described which makes possible the automatic and continuous computation of this information from the output of a mass spectrometer, even when the resolving power is much too low for adjacent mass peaks to be resolved. The computed information can be displayed in the form of a mass spectrum in

which adjacent mass peaks are completely resolved. The overall effect can therefore be regarded as a multiplication of the useful resolving power of the mass spectrometer. The method is based on the use of a simple electronic analog mass spectrometer. Results obtained with experimental resolving power multipliers are described. Multiplication factors as high as eight have been achieved. Similar techniques are applicable to other classes of scientific instruments.

(39) MODEL OF A MASS SPECTROMETER FOR THE SIMULTANEOUS DETECTION OF POSITIVE AND NEGATIVE IONS, Gerald D. Flesch and Harry J. Svec, *Ames Laboratory of the United States Atomic Energy Commission*.

A model of a mass spectrometer which detects positive and negative ions simultaneously has been built and tested. The ion source consists of two conventional Nier-type sources arranged back to back in which the electron gun is maintained at ground potential and the ion accelerating electrodes either positive or negative with respect to ground. Positive ions are extracted in one direction and negative ions in the diametrically opposite direction. Mass separation is achieved by means of two 180° magnetic sectors with an ion trajectory radius of $1\frac{1}{2}$ inches. Mass resolution of approximately $1/60$ has been obtained. Mass spectra are scanned magnetically.

The model has served well to aid in the solution of circuit problems which will be encountered in a larger model of the instrument. Results have been obtained on the mass spectra of chromyl fluoride, CrO_2F_2 , and Freon 12, CCl_2F_2 , which satisfy the original design objectives for the model. Some crude appearance potentials have been attempted for the observed positive and negative ions from CCl_2F_2 .

Work performed in the Ames Laboratory of The United States Atomic Energy Commission.

(40) APPLICATIONS OF MASS SPECTROMETRY IN THE STUDY OF ELECTRON TUBE MATERIALS, M. W. Russell and B. I. Grady.

A summary of some gas sorption studies of

electron tube materials and the effects of materials processing on gas content is given. The paper will discuss gas collection and monitoring methods which include the use of a specially designed automatic peak selector for sequentially recording five spectrum peaks and the sample temperature. A typical experiment, statistically designed to optimize process variables for the removal of hydrocarbons and other gaseous contaminants from vacuum tube components, is described.

This technique appears to offer significant advantages in the study of sorption processes in materials.

(41) SEMICONDUCTOR DETECTORS FOR MASS SPECTROSCOPY, S. S. Friedland, *Solid State Radiations, Inc., Culver City, Calif.*

Following a brief description of the principles of the semiconductor charge particle detector the operating characteristics for the detection of the electronic mass through fission fragment mass will be reported. The various techniques for fabricating a one-dimensional array of detectors to make an essential electronic recording photographic plate will be described. Possible methods of application in mass spectroscopy will be shown.

(42) FOX-TYPE ION SOURCE FOR OPERATION WITH THE ATLAS MASS SPECTROMETER CH_4 , C. Brunnee, K. Kronenberger, *Atlas-Werke A. G., Dept. MAT, P. O. Box 9 II, Bremen, Germany*.

For the ATLAS Universal Mass Spectrometer CH_4 a Fox-type ion source has been developed for the performance of appearance potential measurements as well as for studies of molecular and ionic reactions in the ionization chamber. This can easily be exchanged against the normal ion source of the CH_4 . The construction details as well as characteristic measuring data of the ion source are given. The control unit of the ion source permits to adjust, independently from each other,

- a) time between electron pulse and ion pulse
- b) duration of electron pulse
- c) duration of ion pulse.

The frequency can be adjusted between 10 kcps and 100 kcps.

(43) KINETIC ENERGY DISCRIMINATION IN CROSSED-FIELD ION SOURCES, Norman D. Coggeshall, *Gulf Research & Development Co., Pittsburgh 30, Pennsylvania.*

The ion trajectories in crossed-field ion sources are portions of cycloids which precess in a direction perpendicular to both fields. The cycloidal path for any ion depends upon the energy and direction of the initial velocity component lying in a plane perpendicular to the magnetic field and parallel to the electric field. Use of previously developed differential equations for the orbits¹ and the assumption of uniform fields allow a transformation of angle from the isotropic distribution of initial velocity components to the anisotropic distribution of paths that applies at any subsequent slit or point between slits in the system.

At low repeller voltages, ions of very low initial-energy components in the plane referred to above will not be able to pass through the first slit. This is because the cycloids will turn around, i.e., reach a point of maximum advance in the direction of electric field, before they reach the first slit. This results in a collection efficiency which may be calculated and which depends upon the field values, the geometrical instrument parameters and the initial kinetic energy distribution of the ions. Other parameters being held constant the collection efficiency will increase with repeller voltage until it reaches a constant value of unity. The existence of this collection efficiency may render invalid conclusions based on data obtained with very low repeller voltages and which purport to show differences based on different resident times.

The equations used to calculate summation of velocity components, transformation of orbit angles, collection efficiency and distribution of orbits with angular spread will be presented.

1 N. D. Coggeshall, PHYSICAL REVIEW, 70, 270 (1946).

(44) STUDY OF NEGATIVE IONS WITH A CYCLOIDAL INSTRUMENT, W. J. Lange, *Physics Department, Westinghouse*

Research Labs, Pittsburgh 35, Pa.

Negative ions, formed by electron impact on CO, H₂ and H₂O molecules, have been studied with a cycloidal type spectrometer. The results are compared with previously published work. It is found, in general, that mass spectrometer results are in only partial agreement with each other and the results of measurements of total ionization. In the present work the ratio of O⁻ to CO⁺ in CO is observed to be a strong function of spectrometer operating conditions. Possible instrumental effects on collection efficiencies will be discussed.

(45) FRAGMENT PATTERNS AND APPEARANCE POTENTIALS USING THE OMEGATRON MASS SPECTROMETER, David Lichtman and Audrey Hebling, *Vacuum Research Group, Sperry Gyroscope Company, Great Neck, New York.*

The Omegatron mass spectrometer has been used to study reactions of gases in high and ultra high vacuum systems. Calibration data have been accumulated on fragment patterns and appearance potential curves.

The mass spectrometer vacuum system is described, indicating the advantages and disadvantages of an ion pumped station. Fragment patterns and the effects of total pressure on specific patterns is presented for such gases as helium, neon, argon, CO, CO₂, H₂O, etc. Appearance potential curves have been obtained for these parent gases and for their fragment patterns. Correlation with data obtained by other methods is seen to be quite good.

The overall results indicate the usefulness of the Omegatron for general mass spectrometer studies as well as for high vacuum gas analysis.

(46) EFFECTS OF SUBSTITUENT GROUPS ON THE IONIZATION POTENTIALS OF BENZENES, G. F. Crable and G. L. Kearns, *Gulf Research & Development Company, Pittsburgh, Pennsylvania.*

Ionization potentials of a number of substituted benzenes have been measured to determine the effects of substituent groups. Ionization potentials of mono-substituted benzenes are shown to correlate

with Hammett's substituent constants in a linear manner. Exceptions to this correlation, in particular phenol, will be discussed. A simple additivity rule for substituent effects is found to be true to the first approximation. Typical additivity factors are -0.3 v. for $-\text{CH}_3$, -0.5 v. for $-\text{OH}$ and $+0.5$ v. for $-\text{NO}_2$. Data for several sets of ortho, meta, and para isomers of disubstituted benzenes show differences as a function of position which are dependent on the properties of the substituent groups.

(47) THE STRENGTH OF THE N-F BONDS IN NF_3 AND OF THE N-F BONDS AND THE N-N BOND IN N_2F_4 , Al Kennedy and Charles B. Colburn, *Rohm and Hass Co., Redstone Arsenal Research Division*.

Recently three papers have appeared by Colburn and Johnson¹, Herron and Dibeler² and Loughran and Mader³ which give widely divergent values for the strength of the N-N bond in tetrafluorohydrazine. These values are respectively 20 kcal./mole, 52 kcal./mole, and 30 kcal./mole. The values in the latter two papers were determined by appearance potential studies of tetrafluorohydrazine and are dependent upon the value of the N-F bonds in NF_3 as assigned by Reese and Dibeler⁴. Reese and Dibeler distributed the energy of the N-F bonds in NF_3 in a fashion similar to the distribution Altshuller⁵ made for the N-H bond strengths in NH_3 , i.e. the values assigned are $D(\text{NF}-\text{F}_2)=73$ kcal., $D(\text{NF}-\text{F})=62$ kcal. and $D(\text{N}-\text{F})=62$ kcal.

These assignments of N-F bond strengths in NF_3 together with measured appearance potentials lead to the divergence in the values of the N-N bond strength in tetrafluorohydrazine noted above.

If, however, the N-F bond energy assignment in NF_3 is made in the following fashion $D(\text{NF}_2-\text{F})=55$ kcal., $D(\text{NF}-\text{F})=71$ kcal. and $D(\text{N}-\text{F})=71$ kcal. then the work of Herron and Dibeler², Loughran and Mader³, together with that of Reese and Dibeler⁴ are not only internally consistent but are also in agreement with $D(\text{F}_2\text{N}-\text{NF}_2)$ determined thermally together with the measured heats of formation of NF_3 and N_2F_4 .

The values for the bond strengths in tetrafluoro-

hydrazine are then $D(\text{F}_2\text{N}-\text{NF}_2)=20$ kcal. and $D(\text{N}-\text{F})=71$ kcal.

These values are consistent with the known chemical behavior of NF_3 and N_2F_4 .

1C. B. Colburn and F. A. Johnson, *J. Chem. Phys.* 33, 1869 (1960).

2J. T. Herron and V. H. Dibeler, *J. Chem. Phys.* 33, 1595 (1960).

3E. D. Loughran and C. Mader, *Phys. J. Chem.* 32, 1578 (1960).

4R. M. Reese and V. H. Dibeler, *J. Chem. Phys.* 24, 1175 (1956).

5A. P. Altshuller, *J. Chem. Phys.* 22, 2947 (1954).

(48) SOLIDS ANALYSIS BY HIGH RESOLUTION MASS SPECTROMETRY, George D. Perkins and Charles F. Robinson, *Bell & Howell Research Center, Pasadena, California*.

The value of high resolution in the analysis of gases and liquids by mass spectrometry has been demonstrated by several workers.

Recent studies with a spark source high resolution is not only of paramount importance in qualitative identification of constituents but is also necessary if reasonable accuracy in abundance measurements is to be obtained. The high energy conditions in the spark ionization process results in many ionic species in which more than one electron has been removed. These multiply charged ions appear in portions of the spectrum occupied by lower mass singly charged atoms with consequent masking unless the resolution capability of the instrument is sufficient to separate them.

This work was supported in whole or in part by the United States Air Force under Contract AF 33(616) - 5571, monitored by the Materials Central, Wright Air Development Division, Wright-Patterson Air Force Base, Ohio.

(49) MASS SPECTROGRAPHIC ANALYSIS OF COMPOUND SEMICONDUCTORS, Robert K. Willardson and George D. Perkins, *Bell & Howell Research Center, Pasadena, California*.

A spark source, high resolution mass spectrometer was used to determine the presence of ^{12}C , ^{16}O , ^{23}Na , ^{28}Si , and ^{130}Te in compound semiconductors. Compounds studied include InSb , GaSb , InAs , and GaAs . Impurities in semiconductors can be determined in concentrations as low as 1 ppb. Analyses are discussed in terms of the results expected on the basis of the added impurity concentrations and the measured free electron concentrations and

mobilities. Surface contamination, oxides, hydrocarbons, residual gases, and multiple ionization are factors which must be considered in order to obtain more than a semiquantitative analysis.

This work was supported in whole or in part by the United States Air Force under Contract AF 33(616)-5571, monitored by the Materials Central, Wright Air Development Division, Wright-Patterson Air Force Base, Ohio.

(50) THE USE OF THE SPARK SOURCE TIME-OF-FLIGHT MASS SPECTROMETER, R. A. Fluegge, *Bendix Corporation, Research Laboratories.*

The results of solid sample analyses with the Time-of-Flight Mass Spectrometer using a spark-type ion source are presented. Performance data for the instrument is given.

(51) ABSOLUTE ISOTOPIC ABUNDANCE OF TERRESTRIAL SILVER, William R. Shields, Ernest L. Garner and Vernon H. Dibeler, *Mass Spectrometry Section, National Bureau of Standards, Washington 25, D. C.*

Isotopic abundance ratios are reported for a commercial silver nitrate, 13 samples of native silver, and 11 silver minerals of various compositions and from widely distributed deposits. Collateral measurements of known mixtures of nearly pure silver isotopes permit the determination of absolute abundance ratios. The native silver sample from Cobalt, Ontario, previously reported¹ as exhibiting statistically significant variation is re-examined. Additional measurements are reported for samples of the same nugget and from the same region. Except for the original Cobalt sample, no significant variation from normal is observed for any of the samples. The Ag-107/Ag-109 ratio and 95% confidence limit for the pooled data is 1.0759 ± 0.0010 .

1 W. R. Shields, D. N. Craig and V. H. Dibeler, *J. Amer. Chem. Soc.* 82, 5033 (1960).

(52) IMPROVEMENTS IN TRANSMISSION AND SENSITIVITY IN SURFACE IONIZATION ISOTOPIC ANALYSIS USING A 12" RADIUS MASS SPECTROMETER*, C. M. Stevens, B. A. Swartz, *Argonne National Laboratories, Lemont, Illinois.*

The transmission for a 12" radius sector magnet mass spectrometer used in surface ionization isotopic analysis has been increased a factor of eight as a result of three improvements: higher accelerating voltages, 44° sector magnet, and axial electrostatic focusing. The comparison of the sensitivity of three basic surface ionization techniques, single, multiple and canoe filament, are presented.

*This research performed under the auspices of the United States Atomic Energy Commission.

(53) CALIBRATION AND ACCURACY IN SURFACE IONIZATION ANALYSIS*, C. M. Stevens, A. L. Harkness, B. A. Swartz, *Argonne National Laboratories, Lemont, Ill.*

A systematic method of determining correction factors is described for application in isotopic analysis of uranium using surface ionization techniques. The method is based on determining separately the mass discrimination coefficient and non-linearity of the instrument ion current measuring system using NBS isotopic standards. The results of the method as applied to several instruments show that surface ionization processes have negligible mass discrimination, and electron multipliers used as current amplifiers have both considerable mass discrimination and in certain current ranges, non-linearity properties.

*This research performed under the auspices of the United States Atomic Energy Commission.

(54) THE CHEMISTRY OF URANIUM IN SURFACE IONIZATION SOURCES*, M. H. Studier, E. N. Sloth and L. P. Moore, *Argonne National Laboratory, Argonne, Illinois.*

A Bendix time of flight mass spectrometer was modified to permit the measurement of ions emitted from the surface of electrically heated filaments. The uranium system has been studied and it was demonstrated that by control of the oxidizing and reducing agents on a heated filament and in the surrounding atmosphere, the emission of any one of the following ions can be favored.

Reducing Agents (e. g. carbon)

Oxidizing Agents (e g. oxygen)

*Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(55) IMPROVED SAMPLE BONDING AND EMISSION* FROM SURFACE IONIZATION FILAMENTS, Paul Goris, *Phillips Petroleum Company, Atomic Energy Division, Idaho Falls, Idaho.*

A technique for preparing a porous surface on tantalum ribbon filaments will be described. Emission intensity for uranium analysis can be uniformly maintained at very high levels for long periods as a result of this treatment. Reasonable results are obtainable with much smaller quantities of sample due to reduced flaking losses and more efficient ionization. Results from a single filament source will be discussed for the NBS provisional standards, and micro uranium determination by isotope dilution.

*Work done under Contract AT(10-1)-205 to the Idaho Operations Office, U. S. Atomic Energy Commission.

(56) A PROCEDURE FOR THE MASS SPECTROMETRIC ANALYSIS OF BORON IN THE NEAR NORMAL RANGE, H. O. Finley and E. E. Leuang, Jr. *U. S. Atomic Energy Commission, New Brunswick, New Jersey.*

The instrumentation and analytical technique suitable for the detection of possible isotopic shift in the B^{11}/B^{10} ratio due to the chemical processing of boron compounds has been developed and evaluated. A solid source, 12-inch radius mass spectrometer with a single rhenium filament is used. The procedure yields values of the B^{11}/B^{10} ratio with a precision of 0.5% relative or a standard deviation of ± 0.02 . Based upon the analysis of a synthetic standard, the maximum bias in the ratio is 0.004 with standard deviation of ± 0.013 .

Significant differences have been found in the B^{11}/B^{10} ratios of boron metal and boric oxide derived from the same geological origin. The possibility of isotope fractionation during chemical processing is thus indicated. Other differences in the ratios found between other boron compounds could be caused by differences in geological origin. Inter-laboratory data support the ratio values obtained.

(57) A VACUUM LOCK SAMPLE CHANGER FOR SOLID SOURCE MASS SPECTROMETERS, R. F. Mitchell, A. R. Corbett, K. Swanson and G. F. Lindholm.

A vacuum lock sample changer has been designed for use with mass spectrometers employing a surface ionization source. The changer has been designed to eliminate the necessity for close tolerance in machining and the need for differential pumping required in the bayonet-type changer now in common use. The changer consists of three chambers. The first is a chamber of small volume with a screw cap that can be removed for inseting a fresh sample mounted on a mono- or tri-filament source. The chamber is pumped down with a small auxiliary oil diffusion pump.

The second chamber contains the changer mechanism and a stainless steel diaphragm between it and the first chamber. The mechanism consists of a scissors-jack arrangement which is extended or retracted by a rotating shaft. In the extended position the changer seats against the stainless steel diaphragm and isolates the first and second chambers. At the same time the changer seats a filament against the anode plate located in the third chamber. At this point, the first chamber may be opened to atmospheric pressure without affecting the vacuum in the rest of the instrument.

(58) ISOTOPIC OXYGEN RATIO IN BeO BY MASS SPECTROMETRY*, R. A. Meyer, *Atomics International, Research Dept.*

Serially ground samples from a BeO cylinder which was non-uniformly enriched in BeO^{18} were analyzed for $O^{16}-O^{18}$ ratio. The oxygen in the finely ground BeO was converted to CO by a vacuum fusion technique and the resultant gas analyzed for $CO^{16}-CO^{18}$ ratio with a conventional gas inlet mass spectrometer. Results from ten replicate runs on unenriched BeO showed an O^{18} percentage of 0.217 ± 0.004 .

*Work performed under AEC Contract AT-(11)-GEN-8.

(59) LOW-VOLTAGE MASS SPECTROMETER CHARACTERIZATION OF SULFUR CONCENTRATES FROM CRUDE OILS, Norman G. Foster, R. F. Kendall, D. E. Hirsch and B. H. Eccleston,

Bartlesville Petroleum Research Center, Bureau of Mines, U. S. Department of the Interior, Bartlesville, Oklahoma.

The Bureau of Mines is participating in the American Petroleum Institute's Research Project 48A, "The Separation and Identification of Sulfur Compounds in Crude Petroleum." Successful prosecution of this work is facilitated by information on the relative amounts of the various types of sulfur compounds in wide boiling fractions to permit selection of those fractions that contain concentrations favorable for identification. Low-voltage mass spectrometric methods of analysis for hydrocarbon types are reported in the literature, but application of these methods to sulfur concentrates requires special precautions in both treatment of the material and the interpretation of the mass spectra obtained.

The methods used for mass spectrometer characterization of wide boiling-range materials containing sulfur compounds are outlined and typical results are reported. A brief description of the treatment of the crude oil to obtain the sulfur concentrates is given and an example of subsequent handling to lead to an identification is shown.

The methods shown will assist others in solving more efficiently similar problems in the petroleum or chemical field where many classes of compounds are present in a mixture. The specific method outlined for characterization by means of the mass spectrometer is shown to be an important and rapid step in the analysis of such complex mixtures.

(60) A MASS SPECTROMETRIC METHOD FOR ANALYSIS OF PETROLEUM DISTILLATES IN THE FURNACE OIL—KEROSENE BOILING RANGE, M. E. Fitzgerald, V. A. Cirillo, F. Calbraith, *Atlantic Refining Company, Philadelphia, Pa.*

A mass spectrometric method has been developed for a hydrocarbon-type analysis of virgin and cat-cracked furnace oils. The procedure consists of separating a furnace oil sample into saturate and aromatic fractions which are then run separately on the M. S. A total of eleven hydrocarbon types are determined. These include: paraffins,

mono and/or non-condensed polycycloparaffins, condensed dicycloparaffins, condensed tricycloparaffins, alkyl benzenes, indans and/or tetralins and/or cycloparaffinic benzenes, indenenes and/or dihydronaphthalenes, naphthalenes, acenaphthenes and/or diphenyls, acenaphthalenes and/or fluorene, and tricyclic aromatics. To do separations on a routine basis, a rapid small scale elution technique was developed. Coulometric bromine numbers and infrared analyses of the saturate fractions give information of the amount and types of olefins present.

(61) COMPARISON OF THE MASS SPECTRA OF EXTRACTS AND VACUUM PYROLYSIS PRODUCTS FROM COAL, A. G. Sharkey, Jr., J. L. Shultz and R. A. Friedel, *U. S. Bureau of Mines, Pittsburgh, Pa.*

As part of a program to apply mass spectrometric techniques to the investigation of coal and various materials derived from coal, the mass spectra of a vacuum pyrolysis condensate and a methanol-benzene extract of Pittsburgh seam (Hvab) 84 percent carbon coal were obtained. Because of the complexity of the spectra obtained under normal operating conditions and the lack of calibration data, only qualitative interpretations were attempted by Holden and Robb and Reed in previous investigations. In the present investigation, mass spectra obtained at reduced ionizing voltage show, with few exceptions, similar peak distributions for the two materials. Quantitative analyses were carried out based on structural types found in coal carbonization products. Average molecular weights calculated from these data are 195 for the extract and 206 for the condensate. It is interesting that the same molecular weight range is covered for compounds obtained by a single-pass extraction at room temperature as by vacuum pyrolysis at 450°C.

(62) RESOLUTION OF CYCLOPENTANES AND CYCLOHEXANES IN GASOLINE BY MASS SPECTROMETRY, H. E. Howard and W. C. Ferguson, *Union Oil Company, Brea, California.*

A mass spectrometric method has been developed which resolves cyclopentanes from cyclohexanes in any non-olefinic gasoline containing any combination of carbon numbers, C_6 through C_{12} . In addition, the following components are determined: isoparaffins, n -paraffins, dinaphthenes, indans and/or tetralins, and alkylbenzenes by carbon number, C_6 through C_{12} . Cyclopentanes are resolved from cyclohexanes by the selection of peak summation which are characteristic of each of these hydrocarbon types. The validity of this split has been substantiated by the selective catalytic dehydrogenation of cyclohexanes in several typical gasoline samples. These samples were analyzed by the mass method both before and after dehydrogenation with a resultant balance between the loss of cyclohexanes and the gain in aromatics.

(63) HYDROCARBON TYPES IN OLEFINIC GASOLINE BY MASS SPECTROMETRY, D. M. G. Lawry and J. F. Paulson, *Sun Oil Company, Marcus Hook, Pa.*

ASTM D-2, RD-IV, Section M developed a method for hydrocarbon types in olefinic gasoline as a result of cooperative effort. While working with this program the authors have assembled and tested a slightly different procedure. This determines liquid volume percentages of the following hydrocarbon types: paraffins, cycloparaffins, dicycloparaffins, tricycloparaffins, aliphatic monoolefins, cyclic monoolefins, six to twelve carbon alkylbenzenes, nine to twelve carbon alkylindans, and ten to twelve carbon alkyl-naphthalenes.

Total analysis time is about 3.5 man-hours. The repeatability standard deviation is less than 0.22% of each component reported. Agreement with other methods is generally within 2%. These results follow from the use of several special techniques. These include an IBM 650 program, a GLPC "stripper" analysis, separate olefin and cycloparaffin calibration data, and the assembly of saturate and olefin matrices according to the paraffin carbon number distribution for each sample. Calibration data were variously obtained from synthetic blends, averaged API Project 44 spectra, and extrapolation and interpolation using various reference spectra. During the course of this work, rhenium filaments and a

mass spectrum digitizer were placed in service with no noticeable change in results. Generally good agreement between MS and Fluorescent Indicator Adsorption (D1319)-Acid Treat (D1019) results were observed upon running commercial motor fuels.

(64) METHODS FOR THE ANALYSIS OF TAR BASES. T. Kessler and H. A. Barnett, *United States Steel Applied Research Laboratories.*

Instrumental methods have been developed for the complete analysis of two commercial tar-base fractions—a pyridine fractions and a 2-picoline fraction—and for determining pyridine in crude tar-base mixtures. These methods utilize mass spectrometry either as an independent technique or in combination with gas chromatography.

The pyridine fraction was analyzed by using mass spectrometry. This fraction contained pyridine, 2-picoline, 2,6-lutidine and toluene.

To analyze the 2-picoline fraction, both mass spectrometric and gas chromatographic techniques were utilized. The 2-picoline was determined by mass spectrometry. The impurities—pyridine and 2,6-lutidine—were determined by gas chromatography.

Mass spectrometry was used to determine the pyridine concentrations in crude tar bases. No corrections were made to compensate for errors caused by the presence of higher molecular weight compounds, but such errors are very small.

(65) THE MASS SPECTRA OF 2-n-HEXYLIOPHENE AND α - C^{13} -2-n-HEXYLTHIOPHENE, Norman G. Foster, R. F. Kendall and B. H. Eccleston, *Bartlesville Petroleum Research Center, Bureau of Mines, U. S. Department of the Interior, Bartlesville, Okla., and R. W. Higgins, Texas Woman's University, Denton, Texas.*

A Bureau of Mines study of the mass spectra of the alkylthiophenes indicates the presence of rearrangement ion at the m/e 98 ($C_5H_6S^+$ ion) for the monoalkylthiophenes. This investigation was undertaken to examine the fragmentation of a

typical 2-n-alkylthiophene, 2-n-hexylthiophene in detail and to establish firmly the formation of this rearrangement ion.

The mass spectrum of the untagged compound is compared to that of a mixture that had been 60 percent enriched with the C^{13} isotope in the alpha position. The naturally occurring and randomly positioned C^{13} atoms were taken into account in the spectra of both compounds. The various fragmentation paths, as disclosed by the location of the C^{13} tag, are exhibited and discussed. Particular emphasis is given to fragmentation of the side-chain carbon bonds at the alpha, beta, and gamma positions.

The tagged alpha carbon atom is shown to be included in the rearranged ion, thus establishing in part the mechanism of the rearrangement. Several other fragment ions are shown that are sufficiently interesting to merit further investigation.

(66) MASS SPECTROMETRIC STUDY OF REACTIVE MATERIALS, I. CHLORINE TRIFLUORIDE, V. E. Bedwell, E. F. C. Cain, B. L. Tuffly, *Research Department, Rocketdyne, A Division of North American Aviation, Inc., Canoga Park, California*.

A study of the properties of chlorine trifluoride in the Consolidated Mass Spectrometer Model 21-103C is presented. Because of the ease of decomposition of the compound, none of the predicted peaks can be found in the mass spectrum. However, by measuring the rate of formation of various ions, it is possible to differentiate between some of the impurities and decomposition products in commercial chlorine trifluoride. Treatment of the inlet system before and after studies of chlorine trifluoride in order to operate the instrument satisfactorily for other studies is also given.

(67) MASS SPECTROMETRIC STUDY OF REACTIVE MATERIALS, II. PENTABORANE, V. E. Bedwell, E. F. C. Cain, B. L. Tuffly, *Research Department, Rocketdyne, A Division of North American Aviation, Inc., Canoga Park, California*.

In a mass spectrometric study of pentaborane,

B_5H_9 , it was observed that pattern stability could not be obtained consistently with a Consolidated Mass Spectrometer Model 21-103C. The previous history of the inlet system and condition of the oil-diffusion pump determined the amount of decomposition of pentaborane. However, by concurrently introducing anhydrous ammonia with a pentaborane to the mass spectrometer, entirely reproducible patterns for pentaborane could be obtained regardless of the condition of the inlet system. Furthermore, relatively large amounts of air could also be introduced with the ammonia and pentaborane into the mass spectrometer without adverse effect on the pentaborane. The effect of other nitrogen-containing compounds on the pattern of pentaborane is presented.

(68) AUTOMATIC ASSEMBLY OF MATRICES FOR MASS SPECTROMETRIC CALCULATIONS, Mary H. Loeffler and Ruth E. Goodman, *Westinghouse Research Laboratories, Pittsburgh 35, Penna.*

The calculations for determining the composition of a gas mixture by mass spectrometer analysis consist primarily of the solution of a system of simultaneous linear equations. This is a standard mathematical problem for which existing machine programs are readily available. Before such a program is started, however, the matrix of the coefficients of the system must be in storage in the required locations in the machine. To eliminate the manual formulation of this matrix, a machine program which assembles it automatically is being used on the Burroughs Datatron 205.

For each sample, the only input which must be given to the computer is the list of gases involved along with the mixture peak height for each. An executive program uses this information to assemble the matrix from a "dictionary" which is permanently stored on magnetic tape. This dictionary consists of the calibration data for the various gases. Once the matrix is assembled, the program to solve the system of equations and determine the chemical composition of the sample is started automatically. The chemical formula for each gas is printed out, along with its mole concentration.

The dictionary which the executive routine consults is indefinitely expandable. Data for more gases can be added to it easily at any time. Similarly, it can be up-dated readily to accommodate recalibrations.

(69) RAPID MASS SPECTROMETER—GAS CHROMATOGRAPHIC ANALYSIS OF NON-OLEFINIC NAPHTHAS, V. A. Cirillo, D. J. Skahan, B. Hollis, H. Morgan, *Atlantic Refining Co., Philadelphia, Penna.*

Much time is saved in the analysis of non-olefinic naphthas, C_3 to C_{12} , by introducing the total naphtha into the mass spectrometer using a simple probe-silicone rubber technique. Results including a carbon number distribution of paraffins and alkyl benzenes are compared with analyses obtained by Pod distillation and mass where the C_6+ fractions were introduced using a heated indium-covered sintered disk.

(70) COMBINATION OF MASS SPECTROMETER, GAS CHROMATOGRAPH, AND CATALYTIC HYDROGENATION FOR THE ANALYSIS OF OLEFINS, L. P. Lindeman and C. F. Spencer, *California Research Corporation, Richmond, California.* Equipment is described for the analysis of olefin samples using a catalytic hydrogenation microreactor as an integral part of the mass spectrometer-gas chromatograph combination previously described.¹ The hydrogenation is carried out either before the sample reaches the gas chromatograph or after the sample emerges from the chromatograph but before it enters the mass spectrometer. The first situation gives the total amount of olefin isomers with the same skeletal structure in the sample. The second situation gives the skeletal structure for each component separated on the chromatograph and, hence, greater detail of the olefin isomers present. The temperature of the microreactor can be adjusted so that cyclohexane derivatives are selectively dehydrogenated to alkylbenzenes and, therefore, are readily differentiated from cyclopentane derivatives.

The usefulness of the equipment is shown by the analysis of a cracked gasoline for various olefins.

1L. P. Lindeman and J. L. Annis, *Anal. Chem.* 32, 1742 (1960).

(71) COMBINATION OF GAS CHROMATOGRAPH WITH BENDIX TIME-OF-FLIGHT MASS SPECTROMETER, A. A. Ebert, Jr. *Jackson Laboratory, E. I. du Pont de Nemours Company.*

The combination of a gas chromatograph with a time-of-flight (TOF) mass spectrometer has proved to be an extremely useful tool for the rapid and positive identification of chromatograph cuts. The advantage of the TOF mass spectrometer for this use lies in its speed. The entire mass spectrum can be scanned and recorded simultaneously with the appearance of a chromatograph peak.

The spectra obtained are comparable to those obtained in conventional mass spectrometers permitting full use to be made of all available spectral libraries as references. The mass range of the spectrometer is broad and peaks as high as 650 a.m.u. have been recorded with normal operating conditions. Good resolution is achieved over the normal operating range.

An electronic pump has been used successfully to maintain the high vacuum in the spectrometer. This provides a clean system with little background.

The input system to spectrometer is designed to trap the sample from the column and allow it to leak into the spectrometer for a period long enough to allow the analog output system to record the spectrum. This normally requires less than one minute. Usable spectra can be obtained of components in very low concentrations and even when overlapped by a major component in the chromatogram.

(72) A MASS SPECTROMETRIC STUDY OF PARAFFIN WAX COMPOSITION BY ANALYSIS OF GAS CHROMATOGRAPHIC FRACTIONS, E. J. Levy, R. A. Brown*, F. Calbraith, F. W. Melpolder.

The results of a mass spectrometric investigation of gas chromatographic fractions from paraffin wax will be reported. Simplification of the wax mixture by gas chromatography permits the identification of specific hydrocarbon isomers.

The techniques for the mass spectrometric determination of individual wax hydrocarbons and the quantitative relationship between the particular isomers will be discussed in detail. The results of this study are in agreement with the simple structures in paraffin wax proposed by Hood, Clerc and O'Neal.

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(73) INTRODUCTION SYSTEM FOR SOLID SAMPLES USING A STANDARD HEATED INLET, George W. Young and Anders H. Laurene, *Research Department, R. J. Reynolds Tobacco Company, Winston-Salem, North Carolina.*

A technique for the introduction of weighed samples of liquids or solids has been developed for use with a C. E. C. Model 21-103C mass spectrometer equipped with a standard heated inlet system. The method is simple, convenient and precise, and requires no elaborate apparatus. No modification of the standard inlet system is necessary. Sensitivities may be calculated on the basis of divisions/mg. eliminating the need for any pressure measurement and obviating errors due to small amounts of air, water or solvents in samples to be analyzed.

(74) DRY ORIFICE SAMPLING SYSTEMS, D. R. McAdams and R. I. Harris, *Esso Research Laboratories, Humble Oil & Refining Company, Baton Rouge Refinery.*

A simple all-glass sample introduction system included in the sample handling facilities of a mass spectrometer is described. Operation from low

temperatures to 350°C with gases, liquids and solid samples are outlined. Data comparing this new system with conventional arrangements using liquid metal sealants are given. Simplicity of the system is exemplified by the ability to obtain spectra within 30 seconds following receipt of certain solid samples.

(75) CONTINUOUS STREAM MONITORING FOR A TRACE CONSTITUENT, D. R. McAdams, *Esso Research Laboratories, Humble Oil & Refining Company, Baton Rouge Refinery.*

Propylene at the 0.02% level in ethylene was analyzed by a radio-frequency mass spectrometer. The problem of secondary ion-molecule reactions was overcome by controlling the sampling pressure.

(76) ANALYSIS OF HIGH PURITY HELIUM*, W. M. Hickham, I. Marschik and J. Zamaria, *Westinghouse Research Laboratories, Pittsburgh 35, Pennsylvania.*

A method for analyzing the impurities in helium over a concentration range of .03-500 parts per million has been developed. Concentration of the impurities is accomplished by pumping the sample through a coil at 4.2°K similar to that described by Kirkland¹⁾. The concentrated impurities are then analyzed mass spectrometrically. Results on helium atmospheres in fatigue testing equipment are given along with results on helium purified in a charcoal trap at liquid nitrogen temperature.

(1) C. G. Kirkland, L. W. Brandt, and W. M. Deaton, Bureau of Mines, Report No. 5644 (1960).

*Supported in part by the U. S. Atomic Energy Commission.