

**CORRELATION BETWEEN VARIOUS PHYSICAL AND  
CHEMICAL PROPERTIES OF OXIDE SURFACES  
AND THEIR CONSTITUTION**

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SEPTEMBER 1961  
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DIRECTORATE OF MATERIALS & PROCESSES  
CONTRACT AF 33(616)-6188  
PROJECT No. 7022

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UNITED STATES AIR FORCE  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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## FOREWORD

This report was prepared by the Department of Research at the State University of New York College of Ceramics at Alfred University under USAF Contract No. AF 33 (616)-6188. This contract was initiated under Project No. 7022, "Surface and Interface Phenomena of Matter", Task No. 73664, "Interaction of Surfaces With Extreme Environments". This work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with Dr. R. J. Barton acting as project engineer.

This report covers work conducted from December 1958 to November 1960.

Personnel associated with this program are Professor Thomas J. Gray, Project Director; Samuel F. Hulbert, Senior Research Fellow; and David Benson, Junior Assistant.

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## ABSTRACT

A study has been inaugurated to elucidate the correlation between physical and chemical properties of oxide and other surfaces and their constitution. A mass spectrometer is under construction to investigate the kinetic aspects of surface properties at high temperature under various incident radiations or under molecular beam impact. Preliminary work using associated equipment concerns the preparation and modification of thin films of oxide by metal evaporation and oxidation techniques during the course of which oxidation characteristics are studied.

## PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



J. READ HOLLAND, Actg. Chief,  
Advanced Metallurgical Studies Branch  
Metals & Ceramics Laboratory  
Directorate of Materials & Processes

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## I. INTRODUCTION

The correlation between the defect constitution of solids and their surface activity has been developed extensively by Gray, Hauffe, Volkenshtein and others, and is now generally accepted as the basis for qualitative and semi-quantitative description of surface reactions. This correlation is based on an electronic energy band model in which electronic contribution of various defects can be considered, both independently and collectively. The model is applicable to a wide variety of processes such as chemisorption of gases, catalytic activity, photocatalytic phenomena, corrosion processes, and physical characteristics such as optical absorption, and reflectivity, thermal diffusivity, and mechanical characteristics. While many of the qualitative aspects have been considered, particularly in respect to catalysis and dry corrosion processes, it is essential that a quantitative appraisal is undertaken in order that the theoretical aspects should be better understood.

To derive adequate information to establish a satisfactory model for quantitative development, it is essential to measure simultaneously as many as possible of the following characteristics:

- (a) Semiconductivity characteristics, activation energy and variation with gas atmosphere are an initial requirement. Both d.c. and a.c. measurements are essential, the latter enabling a differentiation to be achieved between surface and bulk contribution, while the former yields evidence of rectifying characteristics, and in certain instances can indicate long-term polarization phenomena.
- (b) Photoconductivity and P.E.M. determinations assist in locating the various discrete electronic impurity energy levels and indicate the lifetime of free current carriers. Optical absorption and reflection should be correlated with these measurements, particularly infrared determinations which can be employed to elucidate the nature of chemical bonding in the surface and of the surface with an absorbed species (after Eischens).
- (c) Contact potential measurements can be employed to ascertain the characteristics of electron release under a variety of conditions.

The program on the investigation of the properties of calcogenides for formulate general theories relating the correlation between the optical, semiconducting, photoconducting, and other associated properties for thin films with their composition commenced in our laboratory in February 1959. The program has been devoted to the design and construction of equipment capable of a wide variety of measurements under very flexible, precisely controlled conditions.

The equipment has been designed so that it may be used in conjunction with the mass spectrometer currently being built with funds provided by the State University of New York College of Ceramics at Alfred. It is planned to study the

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Manuscript released for publication 1 January 1961 as a WADD Technical Report.

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emission products from the films by means of this instrument. Valuable correlation between emission product studies and the aforementioned properties should then be possible. In particular, reaction kinetics will be studied at high temperatures under stationary state conditions.



## II. EVAPORATED FILM REACTION UNIT

In the majority of investigations currently in progress on surface properties there has been a tendency to emphasize unduly either the physical or chemical aspects, and many programs have suffered accordingly. Furthermore, since surface reactions are essentially structure sensitive, results are frequently prejudiced by an inadequate definition of the surface constitution, purity of material and history. In order to obtain information of optimum value, these aspects must be accurately defined in a system under stringent vacuum or gas atmosphere conditions and should be derived in such a manner that one single aspect can be independently varied such as surface dislocation density, impurity concentration, or gas adsorption.

These considerations necessitated exacting gas handling and vacuum conditions. The films being studied under this program are metal oxides, sulfides, and other chalcogenides deposited on substrates of single crystal alumina, quartz, sapphire, periclase and fluorite. Studies on Cu, Zn, Fe, Ni, Ti, and V will commence shortly. The films are prepared by the evaporation of the parent metal with subsequent in situ combination with oxygen, nitrogen, sulfur or carbon, as desired. The electrical conductivity is measured under controlled conditions of radiation, temperature, pressure, and gas atmosphere in such a manner that kinetic rate data will be obtained. Semiconductivity, photoconductivity, magnetic and thermoelectric effect on properties are also to be studied as a function of the composition, temperature, pressure, gaseous environment, and defect structure.

The temperature range of investigation will be from 50°K to 1500°K with a stability of 0.1°K; the pressure is continuously variable from  $10^{-7}$  mm to  $10^{-1}$  mm Hg. Radiation will consist of monochromatic light, monochromatic and white x-radiation, electrons and, possibly at a later stage, neutrons. The atmosphere is controlled through a gas-handling station integrally connected to the test apparatus (see figure 2).

A complex reaction unit has been designed by Hulbert and constructed by Benson to facilitate the accurate measurement of those properties discussed. The test cell consists of a stainless steel (#316) bell jar, 12 inches high and 4-1/2 inches in diameter, sealed at the top and flanged at the lower end. The inner assembly consists of a platen upon which the substrate is mounted, a resistance heater, thermal evaporation unit, and glass-to-metal seals for electrical leads. These are shown in detail in figure 1a and b.

Temperature variation of the platen is made possible by a resistance heater and circulating liquid nitrogen passing through tubular channels. Control of the temperature to within 0.1°K is maintained by a sensitive temperature controller designed and built in these laboratories.

The vacuum system comprises a glass mercury diffusion pump, backed by a Welch duoseal mechanical pump, liquid nitrogen trap,  $P_2O_5$  traps, and a suitable glass system. This can be seen in detail in figure 2. With this vacuum apparatus, static pressures of  $10^{-7}$  mm Hg have been obtained and a dynamic vacuum of  $10^{-8}$  mm Hg can be realized. A precision double McLeod gauge and an ionization gauge in the vacuum circuit permit accurate measurements of the pressure from  $10^{-1}$  mm to below  $10^{-8}$  mm Hg.

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The atmosphere within the test cell is rigidly controlled by means of a gas-handling system provided with reservoirs.  $P_2O_5$  drying tubes and purification systems will be added. Pressure, volume, and composition of the atmosphere can thus be carefully controlled. Gases currently being used for these investigations are helium, oxygen, and hydrogen.

The films are deposited on the substrate by a thermal evaporation process. Films of high purity are readily produced and with a minimum of interfering conditions. The mean free path of the volatilizing atom is large compared with the dimensions of the system or, more specifically, with the source-to-target distance. The source-to-target distance is 3 cm and since the evaporation is being performed at  $10^{-7}$  mm Hg, the mean free path is very large compared with this distance. The substrates are ultrasonically cleaned when possible, and precautions are taken to maintain the substrate at a constant temperature during the deposition of the metal film. Low rates of evaporation of metals tend to produce non-crystalline layers, or layers in which the crystal size is very small, whereas high rates of evaporation yield films of large crystallites. In this work, tungsten, tantalum, or molybdenum heaters are used to minimize contamination by the heater material.

Evaporated platinum contacts on the substrate serve as the electrical contacts for measurements of resistivity, Hall coefficient, photoconductivity, and various other measurements readily adapted to standard electrical procedures. It is also anticipated that measurements of dielectric loss, work function, and contact potential will later be made with existing equipment after appropriate modification.

At present, the work includes the study of kinetics of oxidation and examination of oxidation products since this data becomes available during the preparation of the oxide films. The electrical resistivity method is employed to determine the rate of oxidation with time. The products will be examined by electron diffraction, x-ray diffraction, and metallograph techniques when product information of this nature is desired, full facilities for these techniques being already available.

In conjunction with the design and construction work, literature surveys and theoretical examinations of the phenomena to be studied are also being conducted.

The evaporated film reaction unit is shown in block diagrams in figures 1 and 2.

### III. MASS SPECTROMETER FOR STUDYING CORRELATION BETWEEN CHEMICAL PROPERTIES OF CALCOGENIDE SURFACES

A mass spectrometer for studying the correlation between properties of calcogenide surfaces and their constitution is under construction with funds provided by the State University of New York. The mass spectrometer will facilitate the observation of solid surface characteristics as affected by various types of radiation used to promote the emission of electrons and ions from the solid surfaces, i.e., irradiation by electrons, monochromatic light, monochromatic and white x-radiation, and neutrons (thus giving a separation of the different types of primary particles).

The studies of structure-sensitive phenomena such as semiconductivity and associated phenomena has been inherently handicapped for the most part by a very deficient knowledge of the chemical constituents present in the materials studied. The composition of surfaces is not only uncontrollable within desired limits (because of diffusion exchange within the interior of the solid, and because of absorption of foreign materials from the vacuum system), but it is also undeterminable by an currently known analytical technique except mass spectroscopy. The goal of the mass spectrometer in this research project is therefore as follows: surface analysis, ultimately of mono-molecular layers, made concurrently with measurements of semiconductivity, without appreciably damaging the surface itself.

The mass spectrometer is of the Nier type (first order direction focusing mass analyzer). The theory describing the operation of this type of analyzer is described by Inghram in his Handbook on Mass Spectroscopy<sup>1</sup>. The mass spectrometer has a 60° sector field with a 12-inch radius inconel tube. The ion source will be in the form of an evaporated film which will be subjected to ionization initially by electron bombardment. Ion source for the mass spectrometer is known as secondary ion, ion source.

The secondary ion source is based on the fact that when electrons or ions impinge on a surface they produce at that surface secondary ions characteristic of the surface and of the impinging ions. In our source, electrons are formed by thermionic emission, accelerated through a potential maintained between the filament and the case assembly and focused onto the sample to be studied. Secondary ions formed at this surface are accelerated and focused onto the collimating slits by the accelerating and collimating plates.

The sample bombarding region is to be separated from the ionizing region by a tungsten mesh. The structure, therefore, allows neutral particles evaporated from the sample to be analyzed in the usual gas analysis fashion, and charged particles from the sample region to be restrained, by suitable potential, from entering the spectrometer analyzer. On the other hand, if so desired, charged particles from the sample may be accelerated through the spectrometer along with the ions from the analyzing beam region. These features are described in figures 3 through 6.

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1. Mark G. Inghram, National Academy of Sciences, NRC Publication No. 311.

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The mass spectrometer is provided with separate vacuum systems for source and detector to facilitate preliminary setup. Gold-gasket vacuum seals are used. A glass, two-stage mercury diffusion pump capable of pumping speeds in excess of 80 liters per second at  $10^{-7}$  mm is used with each system. The rest of the vacuum system is comprised of a Welch duoseal mechanical pump, liquid nitrogen trap, double McLeod gauge, and an ionization gauge, thermocouple gauge (enabling measurement of the pressure with accuracies of one part in  $10^5$ ), brass valves with Teflon seats, and a suitable glass system (see figure 7). The entire spectrometer is free of wax and grease joints so it can be out-gassed readily by electric furnaces wrapped around the various parts. The magnet is on a track and can be moved aside during baking.

The ion collector is a simple electrical ion detector. It consists of four major parts: (1) a defining slit, (2) a secondary electron suppressor, (3) a cage-type ion collector, and (4) an electron multiplier. The defining slit is adjustable from outside the vacuum system in order to set the machine for optimum operation in any mass range. The secondary electron repeller is placed in such a fashion as to suppress the secondary electrons formed when the ion beam strikes the surface. It is important for most applications that these secondaries be suppressed since without the suppression the collector is not linear, because the number of secondaries is a function of the mass and energy of the ions and of the strength of the stray magnetic field. The cage type ion collector used is one in which secondary ion and ion reflection errors are minimized. It consists of a small box covered with a slight transmission grid. The electron multiplier will be a converted Du Mont multiplier phototube.

Electronic control and supplies include an electron emission regulator, magnet control and stabilized supply, a unit providing a stabilized voltage supply for the electrodes of the electron and ion gun systems, ionizing gauge, magnet safety circuit, preamplifier, d.c. feedback amplifier, and automatic recorder.

Provision is being incorporated for 0.25 MeV electrons at high intensity. These can also be employed for the generation of x-rays and alternately for the excitation of a neutron-producing zirconium-tritium target which it is hoped to incorporate at a later stage.

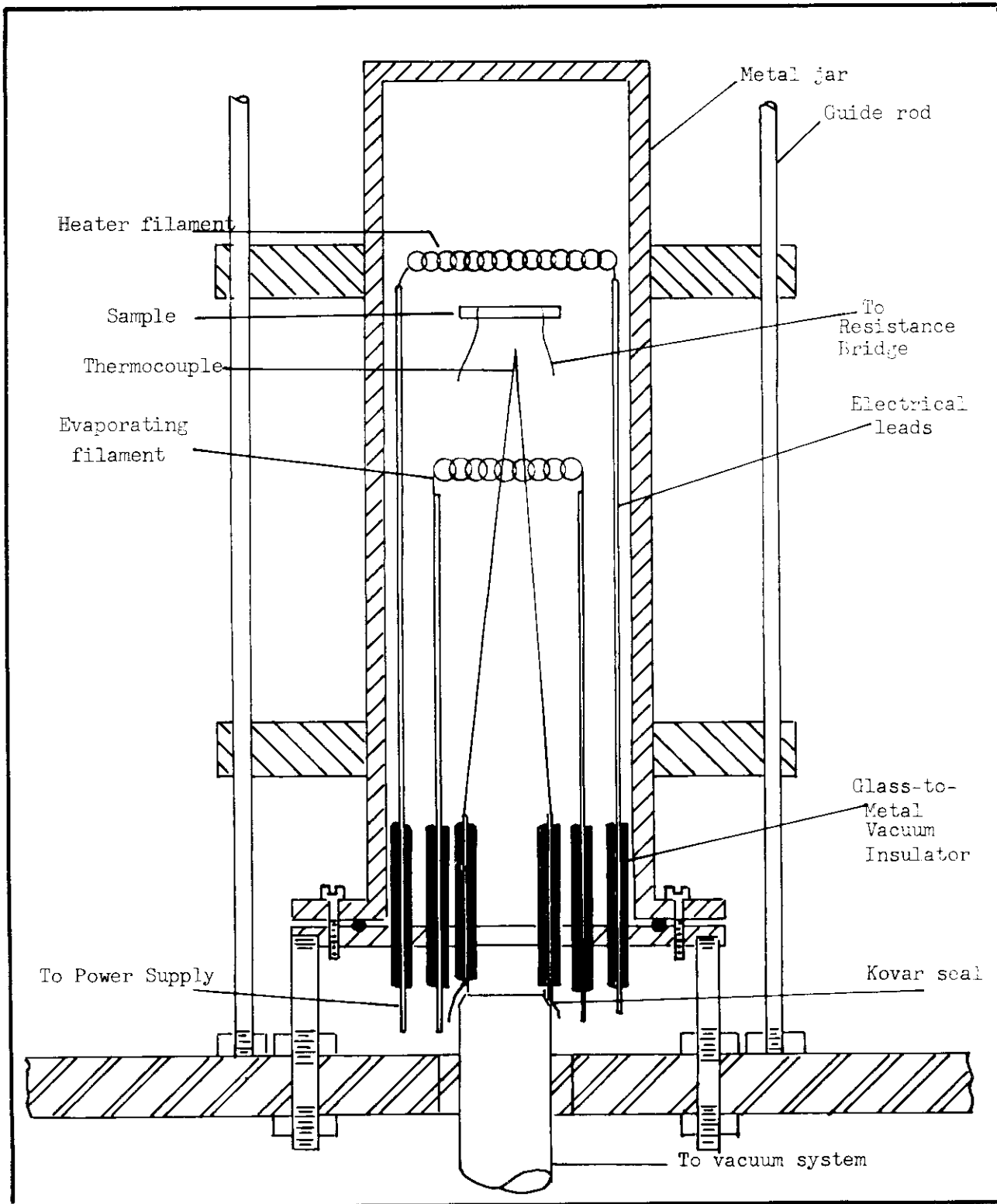


Figure 1a. Evaporating and Reaction Unit.

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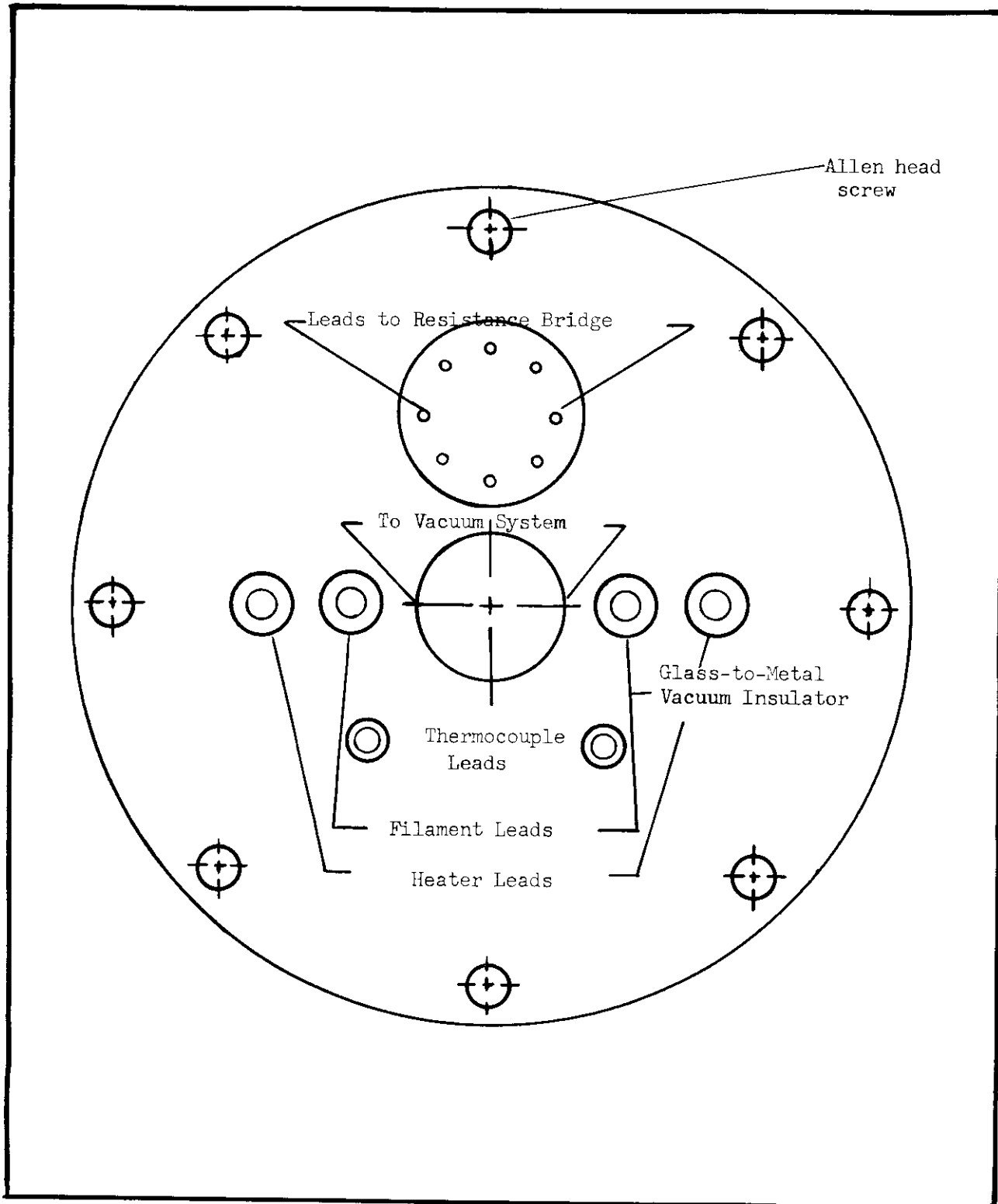


Figure 1b. Reaction Unit Bottom Plate, Top View.

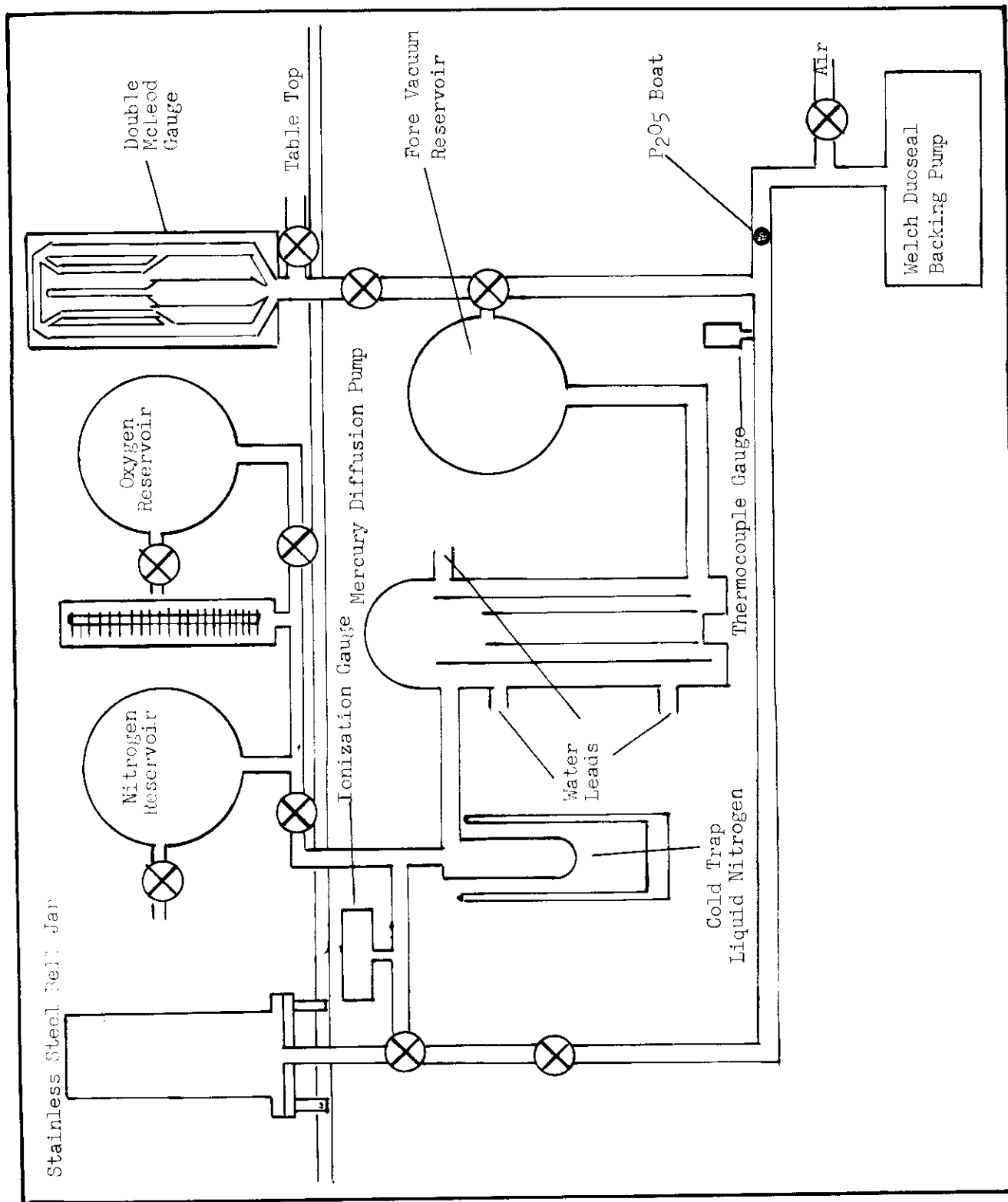


Figure 2. Evaporated Film Reaction Unit.

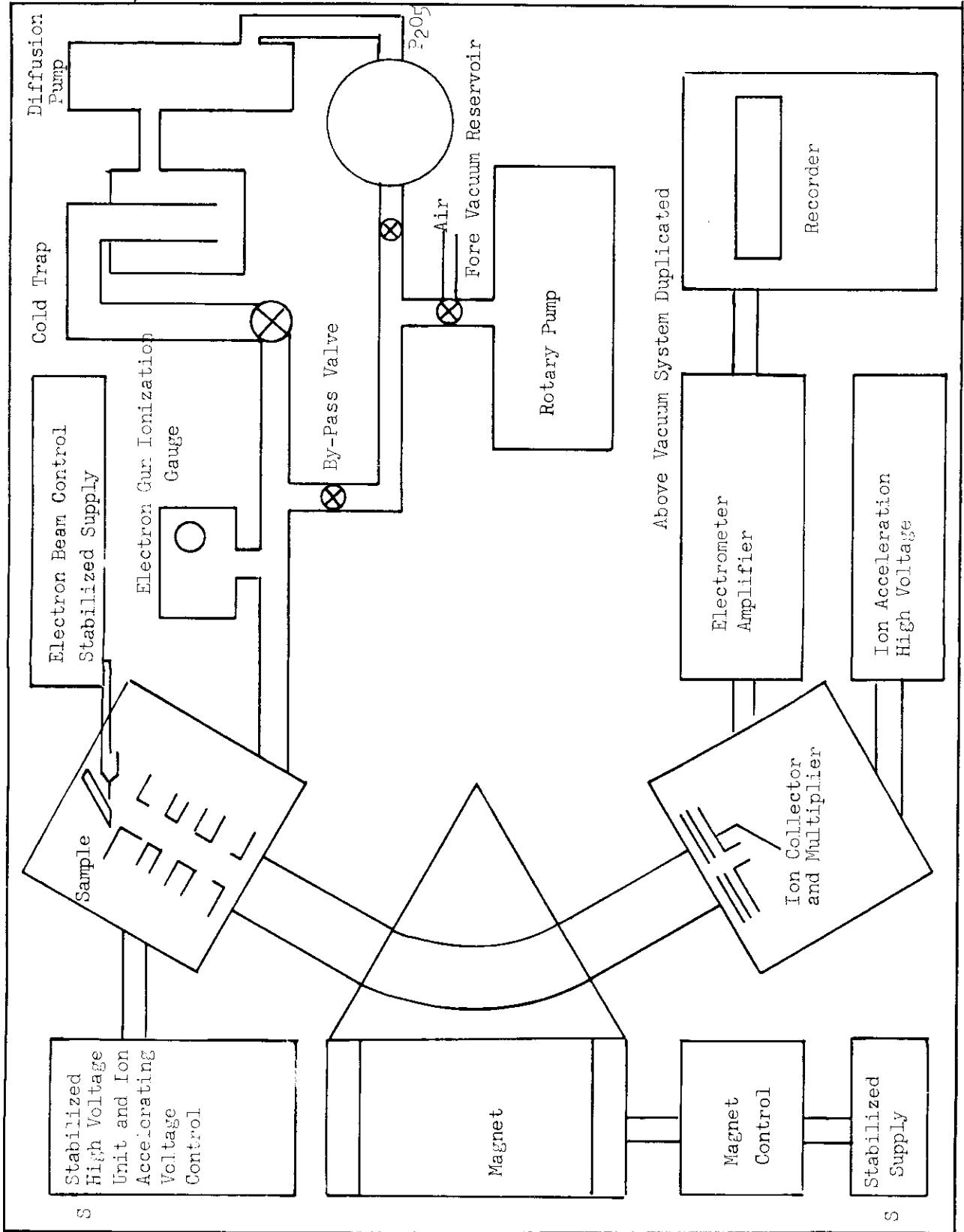


Figure 3. Mass Spectrometer.



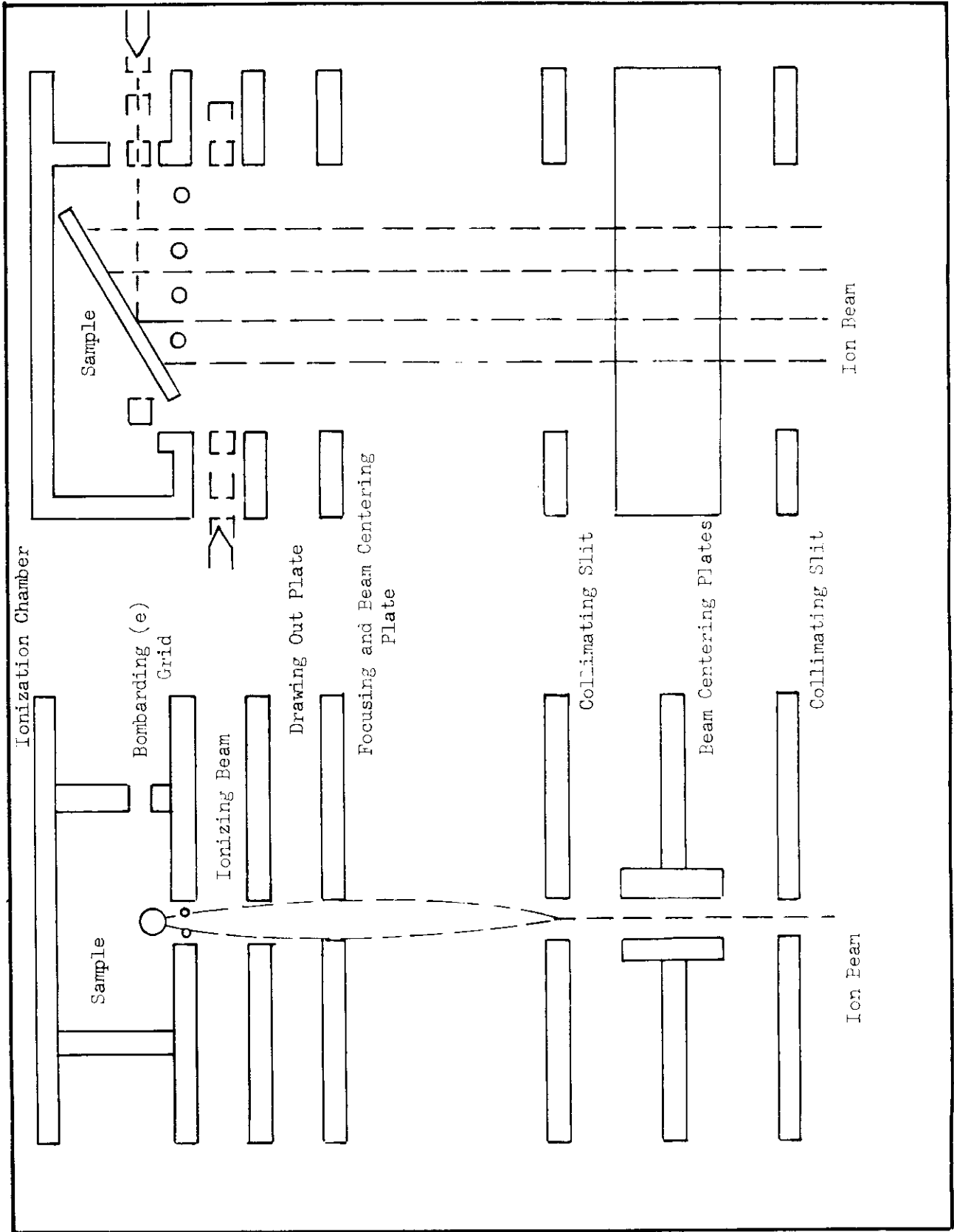


Figure 4. Ion Source.

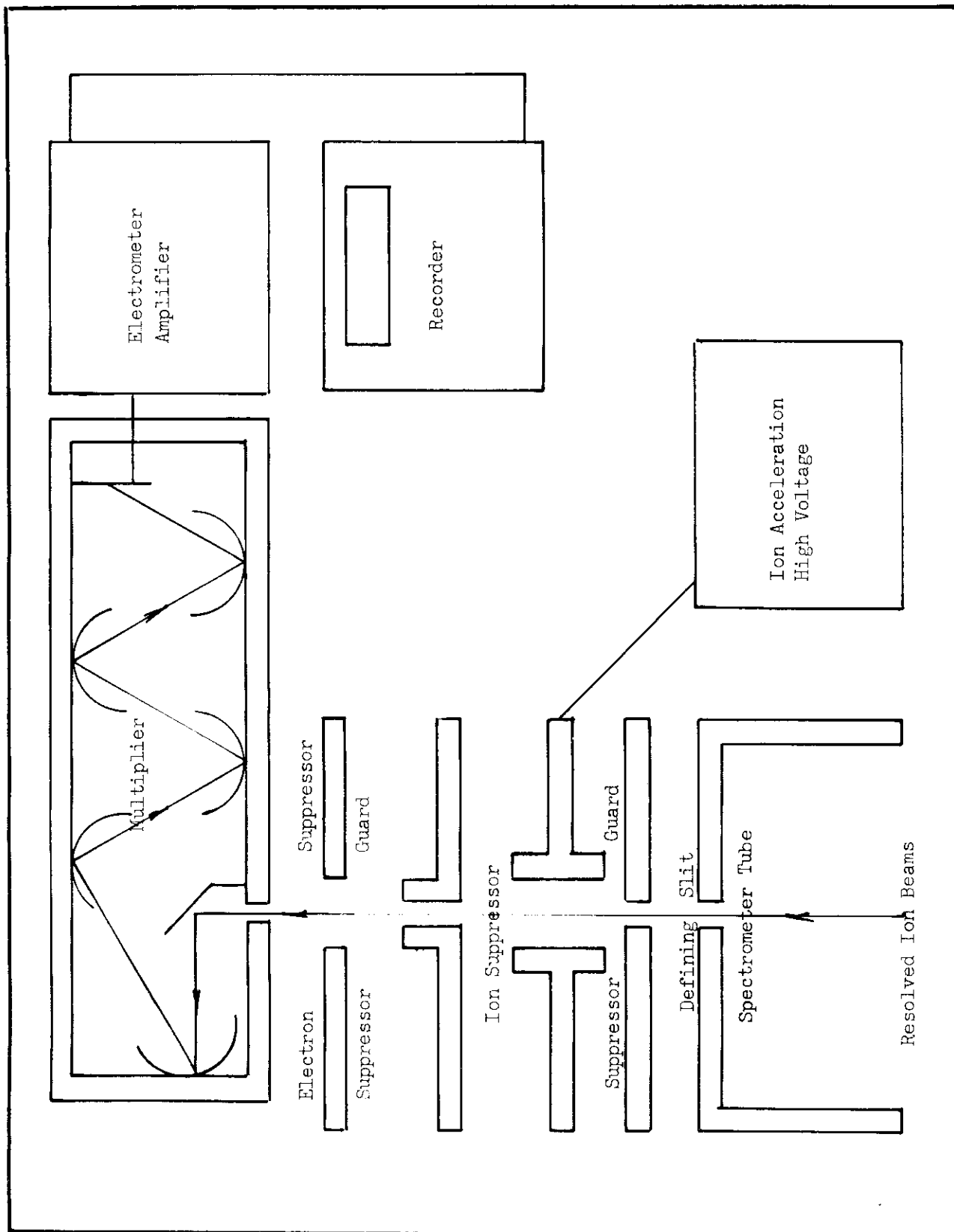


Figure 5. Collector System.

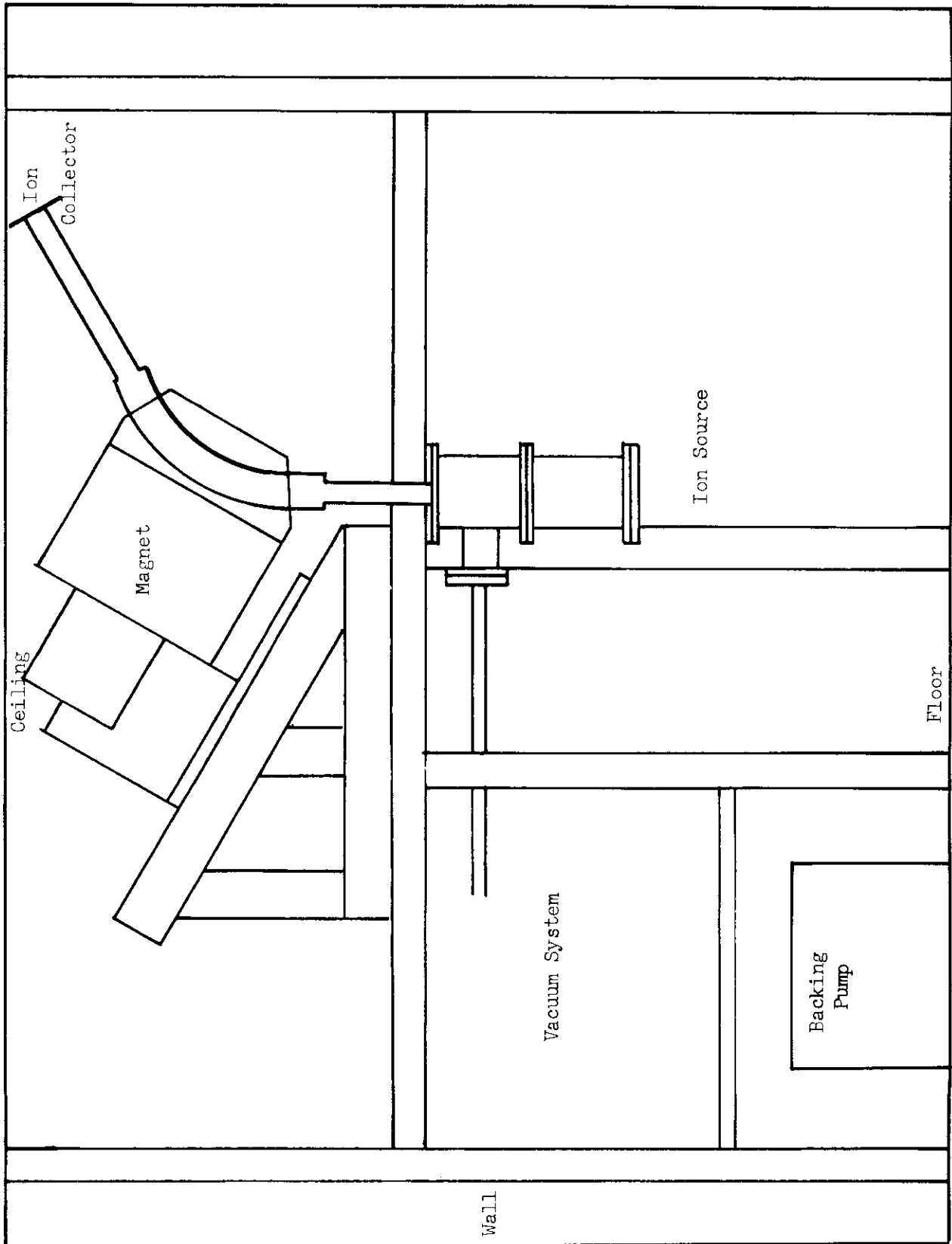


Figure 6. Mass Spectrometer.

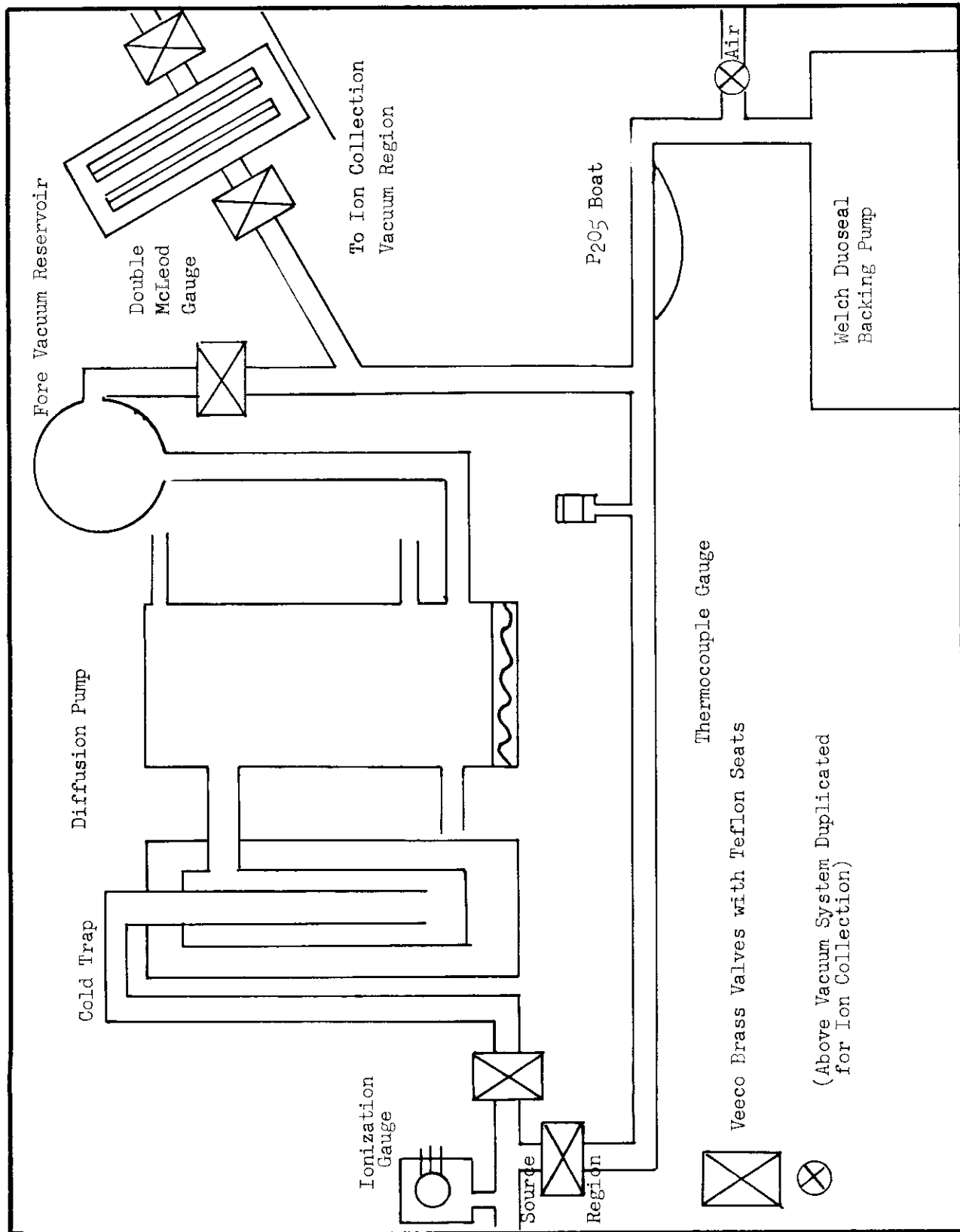


Figure 7. Ion Source Vacuum System.