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IMPROVED INSTRUMENTATION TO CARRY OUT SURFACE ANALYSIS AND TO MONITOR CHEMICAL SURFACE REACTIONS IN SITU ON SMALL AREA CATALYSTS OVER A WIDE PRESSURE RANGE (10-8-105 torr)

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IMPROVED INSTRUMENTATION TO CARRY OUT SURFACE ANALYSIS AND TO MONITOR CHEMICAL SURFACE REACTIONS IN SITU ON SMALL AREA CATALYSTS OVER A WIDE PRESSURE RANGE (10^{-8}-10^{5} torr)

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ABSTRACT

Improved one-tier and two-tier designs for a high pressure-low pressure (HPLP) apparatus are described together with some of their recent applications. These instruments are used for surface analysis and in situ monitoring of catalytic reactions on small samples with a geometrical surface area of ~1 cm^2. Catalytic reactions are studied over a wide range of pressures (10^{-8}-10^{5} torr) and temperatures (273-1273 K). The apparatus incorporates surface analysis methods such as Electron Spectroscopy for Chemical Analysis (ESCA), High Resolution Electron Energy Loss Spectrometry (HREELS) and ^{14}C-radiotracer labeling in addition to Low Energy Electron Diffraction (LEED), Auger Electron Spectroscopy (AES) and mass spectrometry. Facilities are also available for argon sputter-ion cleaning, deposition of adsorbates by evaporation and coverage calibration by means of a thickness monitor.

INTRODUCTION

We have successfully studied a variety of reactions over single crystal and polycrystalline surfaces of low surface area (~1 cm^2)[1-8] using our previously reported high pressure-low pressure apparatus.[9] The basic design philosophy was to enable high pressure reaction monitoring and catalyst surface characterization to be carried out in the same apparatus. Thus, since the sample is not removed from the UHV system, contamination of the catalyst by ambient gases can be kept to a minimum. Nevertheless, in a number of these studies, LEED and AES did not provide sufficient information to characterize the surface completely and the ability to combine many available techniques including ESCA, HREELS, ^{14}C-radiotracer labeling, among others, with high pressure catalysis appears highly desirable. The combination of many surface analysis techniques provides a better understanding of a catalytic process. LEED is used for surface and adsorbate structure determinations and AES for surface composition mesurements. ESCA gives information about the oxidation state and electronic structure of the surface and chemisorbed species, whereas HREELS allows the investigation of the bonds of chemisorbed molecules at the surface. Finally radiotracer methods are among the most powerful techniques for measuring very low concentrations of materials in a transient environment.

The design of the improved HPLP apparatus allows for the easy exchange of surface analysis techniques and has a suitable geometry for rapid sample turnaround. Sensitivity to products has been maximized by making the high pressure cell as small as possible. Two designs were needed (one-tier and two-tier) to satisfy the compatibility requirements of the electron spectrometers, evaporation stations and other instruments.

One Tier-HPLP System

A photograph and a schematic diagram of this system are shown in Figures 1 and 2, respectively. It consists of a conventional stainless steel UHV chamber within which an isolation cell for high pressure studies is situated. The chamber is cylindrical in shape and has a diameter of 12". Ultra high vacuum is obtained by a mechanically-backed Varian 1,200 liters/sec diffusion pump with a liquid nitrogen trap, in combination with a water-cooled titanium sublimation pump. The background pressure of the system is lower than 1×10^{-9} Torr.

The sample is placed on the central axis of the chamber and is accessible to LEED, AES, ESCA, ion bombardment, mass spectrometry, deposition by evaporation and beta radiation detection facilities. Moreover, the sample can be rotated through 360°, thus allowing both front and back faces to be cleaned and inspected with the various surface science techniques.

The sample may be enclosed in a small high pressure cell. This cell is displaced up and down by a hydraulic piston. In order to close the cell, a sealing pressure of 2,000 lb/in^2 is applied via the piston, the seal being made by an oxygen-free copper gasket. The cell is externally (to the UHV system) connected to a circulation pump, a pressure gauge, a gas manifold and a gas sampling valve of a gas chromatograph. These units are connected in series forming a loop that starts at one end of the cell and is completed at the other end. The cell can be pressurized up to 100 atm with no significant increase in the background pressure of the vacuum chamber.

In the high pressure mode, the isolation cell is closed and the reactants are admitted to the reaction loop. The reactants are continuously pumped by a mechanical circulation pump, and flow through the reaction loop and repeatedly over the sample. The gas mixture is sampled and analyzed by the gas chromatograph.

The sample can be heated resistively by a high-current AC power supply and its temperature monitored by a chromel-alumel thermocouple.

One of several innovations in this apparatus consists of a LEED optics and a cylindrical mirror analyzer (CMA) mounted on bellows, thus allowing these instruments to move back and forth relative to the sample. The optimum performance of the CMA is achieved when the end of the instrument is at a distance of 0.4" from the sample. Since the radius of the high pressure cell is greater than this distance, the CMA would obstruct the cell while it was moving towards the closed position, unless the CMA were withdrawn. The LEED optics are also mounted on bellows, since otherwise they would obstruct the CMA. The operation of ESCA/AES, LEED and the closing of the high pressure cell are thus all mutually exclusive. Withdrawal of the LEED optics and the CMA is carried out by the same hydraulic system that controls the high pressure cell.

Two Tier-HPLP System

A photograph of this system is shown in Figure 2 and consists of a stainless steel ultra high vacuum (UHV) chamber built in two levels with an isolation cell for high pressure studies (a schematic diagram of the system is displayed in Figure 3). The upper portion of the UHV chamber contains the standard single crystal surface analysis equipment (four grid LEED/Auger optics, glancing incidence electron gun, sputter ion gun for specimen cleaning and quadrupole mass spectrometer). The lower part of the UHV system contains the electron energy loss spectrometer (HREELS). The samples are lowered from the upper to the lower level by an extended travel precision manipulator. A similar system without the high pressure isolation cell has been described in detail elsewhere.[10]

The high pressure cell is identical to that in the one tier-HPLP system

but in this case both sides of the cell can be moved up and down. The top section of the cell has x and y displacement facilities, and, therefore, the sample can be precisely positioned in the x, y and z-directions and rotated through 360°. Nevertheless, when the cell is closed this upper part of the cell must be locked in one position in order to withstand the sealing force. Due to the size of the top section, the LEED/Auger optics are mounted on bellows in order to facilitate easy withdrawal when the sample is lowered to the HREELS position. This system contains all the other features mentioned in the description of the one tier-HPLP system.

Surface Analysis

As we mentioned previously, the UHV chambers of the HPLP apparatus can incorporate combinations of many kinds of surface analysis techniques, thus providing very valuable information about surface composition and structure. As an example we list some of them which we have used and others that could be easily adapted: low energy electron diffraction (LEED), Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS), high resolution electron energy loss spectroscopy (HREELS), secondary ion mass spectroscopy (SIMS) and ^{14}C-radiotracer labeling. Moreover, instruments such as mass spectrometer, sputter-ion gun, evaporators and thickness monitor can be easily fitted.

Use of HPLP Apparatus as a Catalytic Reactor

During high pressure operation, the reaction cell can either be attached to a closed loop and run as a batch reactor, or used in a one-pass manner as a flow-reactor. By removing the reaction products with a suitable condenser, the closed-loop system may also function as a flow reactor, and an example of this will be described below.

High pressure photocatalytic reaction studies can be undertaken by incorporating a sapphire window into the reaction cell. This allows the sample to be illuminated by an external light source (UV or visible), when the sapphire window is aligned with another window in the UHV chamber. Product gases may be detected and analysed by the use of a gas chromatograph attached to the sample loop. By the use of suitable chromatographic columns and detectors (such as flame ionization, thermal conductivity or photoionization), most likely product combinations may be separated and analyzed. Moreover, a more direct analysis can be made if the product stream is throttled (by means of a leak valve) into a separately-pumped mass spectrometer.

Application of the High Pressure-Low Pressure Apparatus to Catalytic Systems

The principal advantage of the type of apparatus discussed in the present paper over the more traditional catalytic reactor, is that the structure and composition of the catalyst surface can be readily ascertained both before and after the catalytic reaction has taken place. Thus, it is possible to investigate the catalytic properties of well-defined, ultra-clean samples and observe the effects of the catalytic reaction on the sample surface.

The HPLP apparatus has been used to study the hydrogenation of carbon monoxide on iron and rhodium polycrystalline specimens[2,6] as well as on single crystals[4] and various rhodium compounds.[11] Post-reaction surface analysis revealed the presence of a catalytically active carbonaceous layer on all the samples investigated. In addition, precise control of the rhodium surface oxidation state by oxygen pre-treatment in the UHV chamber was found to have a marked effect on the product distribution of the rhodium catalyzed reaction.

An investigation of the catalytic effects of adsorbing gold on platinum surfaces has recently been undertaken.[12] A Knudsen oven and quartz crystal

thickness monitor[13] have been attached to a HPLP system, enabling accurate, reproducible dosing of submonolayer quantities of gold under the ultra-clean conditions of the UHV chamber. Results indicate that atoms of gold inhibit the catalytic activity of the platinum in heptane isomerization. However, annealing to form a 2-D alloy (and the consequent separation of surface platinum into small ensembles), actually led to an increase in isomerization activity over the clean platinum value.

The HPLP apparatus has enabled the study of catalytic reactions over a pressure range covering many orders of magnitude. The reaction of cyclohexane with hydrogen has been studied between 10^{-7} and 10^{2} torr.[5] It was found that at low pressure the principal product was benzene, and at high pressure the reaction predominantly formed cyclohexane. It was also observed that while the low pressure reaction took place on an essentially clean surface, the high pressure reaction occurred in the presence of a near-monolayer of carbonaceous species. In an effort to investigate this overlayer more fully, a ^{14}C-radioisotope technique was employed.[14] It was observed that when the platinum surface was dosed with ^{14}C-labelled hydrocarbons, the lability of the deposited radioactive carbonaceous layer varied with deposition temperature.[15]

At temperatures below 300 K, hydrocarbons were found to adsorb reversibly on platinum, i.e. with no carbon build-up. At temperatures greater than 750 K multilayer carbon build-up was observed, with poisoning of the platinum's catalytic activity by graphitic carbon. However, at temperatures between these extremes, a mixture of hydrocarbon fragments appeared to exist on the platinum surface. This deposit was found to play an important role in hydrocarbon rearrangement reactions when they were carried out on the platinum surface under these conditions. The surface radioactivity was measured with

a surface barrier detector mounted inside the UHV chamber on a rotatable feedthrough.

Ammonia synthesis from nitrogen and hydrogen on iron single crystal surfaces has been recently studied in a HPLP apparatus and yielded the interesting result that Fe(111) appears to be some 2 1/2 orders of magnitude more active at catalyzing this reaction than the close-packed Fe(110) plane (at 798 K and 20 atm total pressure).[16,17] This work has been the highest-pressure application of the HPLP apparatus to date, ammonia synthesis being thermodynamically favored at high pressures. During catalytic runs on the HPLP apparatus at 20-25 atm, the base pressure in the UHV chamber did not exceed 10^{-8} torr, even after many closings of the cell on the same copper gasket. Indeed, it is clear that this seal would function satisfactorily at much higher pressures. Although the same can be said for most of the external circulation loop of the apparatus, some care must be exercised before subjecting electrical feedthroughs to high pressure operation. Most of these feedthroughs are designed for use on UHV chambers, and are not capable of withstanding high pressures on what is normally their vacuum side. This situation is exacerbated by the large heating current required to maintain the catalyst temperature at high gas pressures, since this leads to a warming and consequent weakening of the electrical feedthrough seals. This problem has been partially solved by directing a cooling fan onto the feedthroughs during a catalytic run. Feedthroughs capable of withstanding high internal pressure have been developed recently, however, and it is hoped that these will soon be readily available.

It was found during studies of ammonia synthesis on iron that the incorporation of a condenser downstream of the sample valve in the external circulation loop of the HPLP apparatus (Figure 5), enabled the system to be run as a

flow- rather than a batch-reactor. This is true for any reaction system where the reactants are more volatile than the products, since the condenser temperature can be adjusted to trap the products almost exclusively, allowing a nearly pure stream of reactants to impinge on the catalyst. In the case of ammonia synthesis, (where, next to the product, nitrogen at a partial pressure of 5 atm was the most condensable species) a slurry of isopentane (-159.9°C) was found to be the ideal condenser medium. During a study of rhenium-catalyzed ammonia synthesis,[18] the isopentane condenser was switched in periodically, in order to reduce the ammonia partial pressure to below that at which it appeared to poison the catalyst. In this way, the rhenium was able to produce ammonia in excess of the amount ususally leading to poisoning.

The ability to predose catalysts with controlled, submonolayer quantities of promoters is clearly an advantage of the HPLP apparatus over more conventional reactors. The effects of potassium on iron-catalyzed ammonia synthesis and CO hydrogenation are currently being investigated and there is evidence to suggest that the alkali metal plays a role in maintaining a clean catalyst surface. Potassium and other alkali metals are readily dispensed as ions from heated aluminosilicates.[19] The use of submonolayer quantities of potassium as a catalyst itself has also been recently studied by Cabrera et. al.,[8] who produced methane by reacting water (20 torr) with graphite in the presence of potassium at 200°C.

Sulfur and halogens are important in catalysis, being capable of behaving as poisons and promoters in different catalytic systems. A study of the effect of submonolayer quantities of these elements on the performance of several catalysts is currently in progress. Both sulfur[20] and halogens[21] may be conveniently and reproducibly deposited on the catalyst surface by the in situ solid state electrolysis of the respective silver compound.

Summary

A new generation of high pressure-low pressure apparatus has been described. As with the previously described equipment, high pressure catalytic experiments may be carried out on samples which have been prepared and characterized in a UHV environment. Significant improvements have been made in the HPLP design. These include the mounting of the CMA and LEED optics on precision displacement, hydraulically-driven 8" bellows, a more versatile manipulation design to allow easy specimen mounting and exchange, together with precise sample positioning during surface analysis, and the addition of a sapphire window to the reactor cell, to permit sample illumination in photocatalytic studies.

The HPLP apparatus has been applied to studies of the hydrogenation of carbon monoxide on iron and rhodium compounds, the catalytic effect of gold adsorption on platinum surfaces, the hydrogenation and dehydrogenation of cyclobenzene, the iron and rhodium catalyzed synthesis of ammonia and the potassium catalyzed methanation of graphite.

Acknowledgment

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FIGURE CAPTIONS

Figure 1: Photograph of a one tier-HPLP system.

Figure 2: (a) Schematic diagram of a one tier-HPLP system with high pressure cell closed.
(b) Detail with high pressure cell open.

Figure 3: Photograph of a two tier-HPLP system.

Figure 4: (a) Schematic diagram of a two tier-HPLP system with high pressure cell open.
(b) Detail with high pressure cell closed.

Figure 5: Schematic diagram of a freeze-trap used in studies of ammonia synthesis that was attached to the external reaction loop.

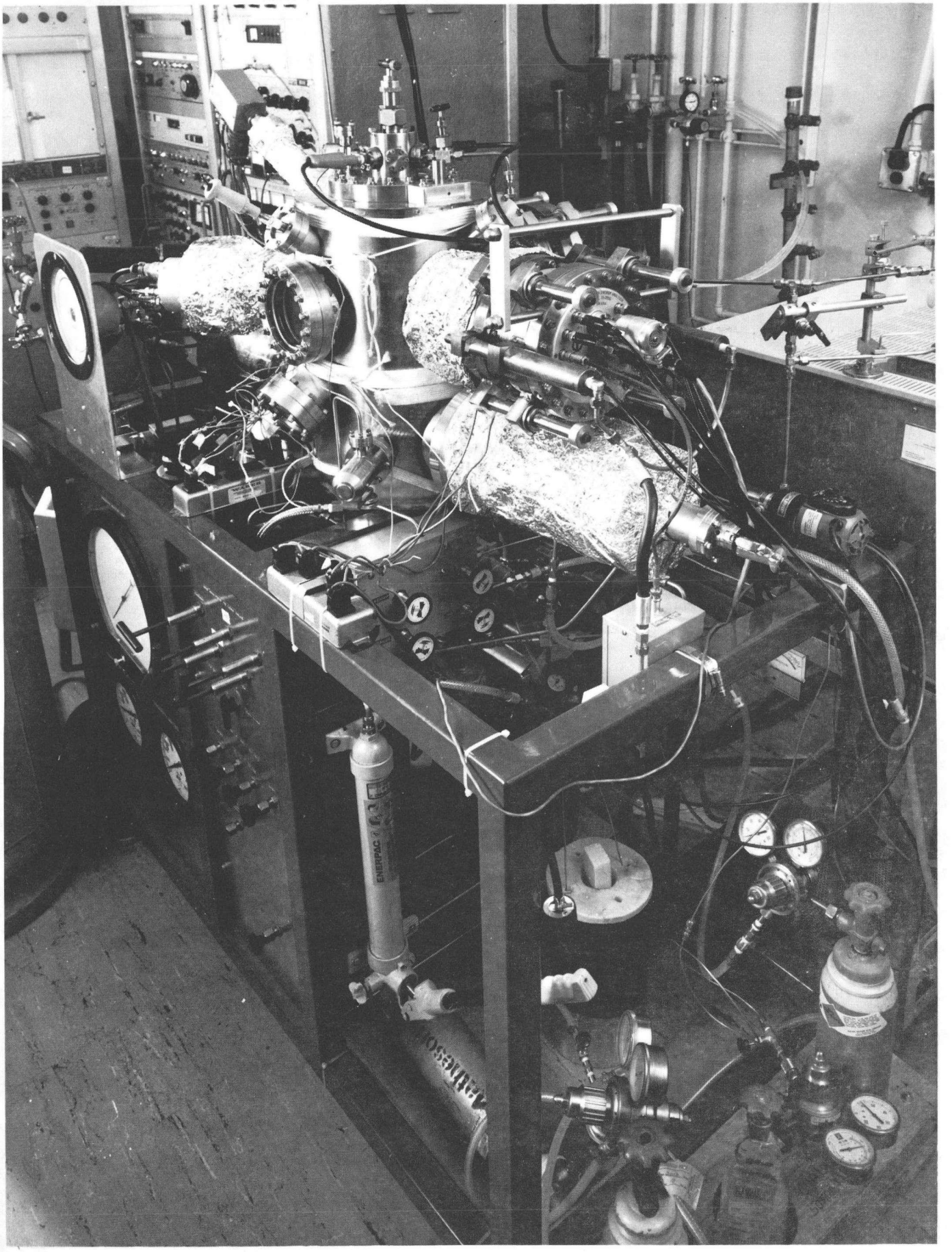

Fig. 1

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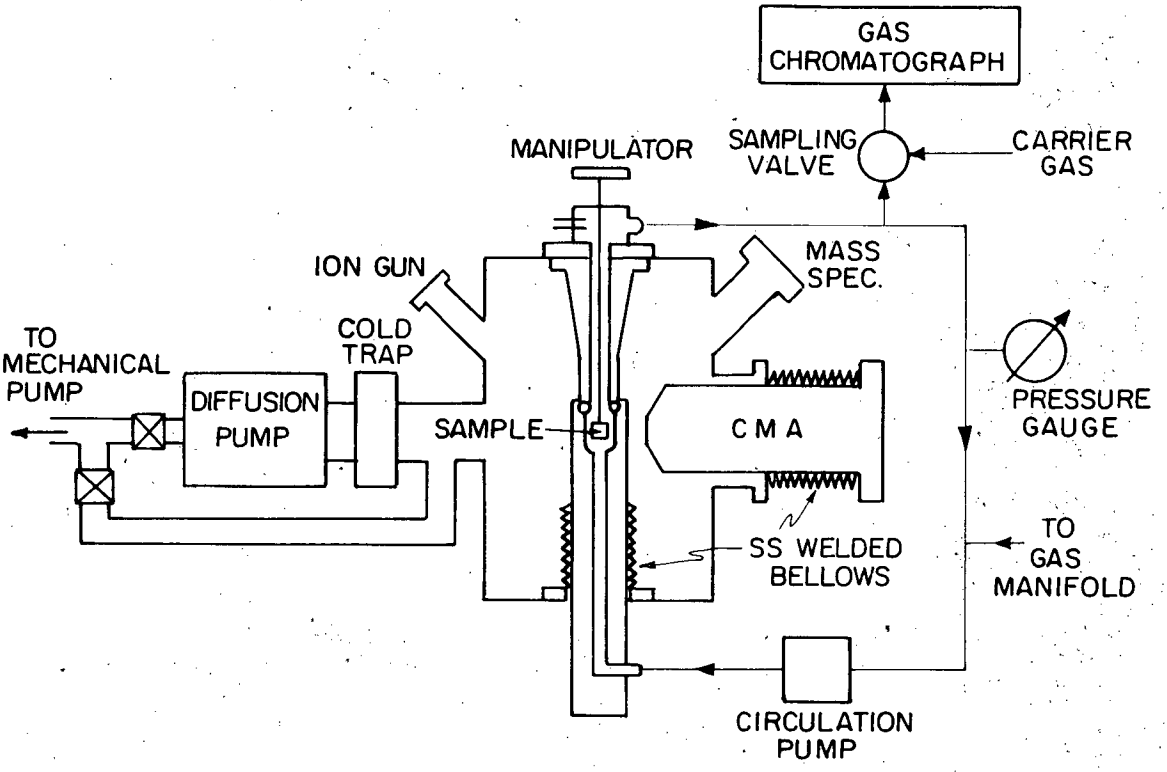

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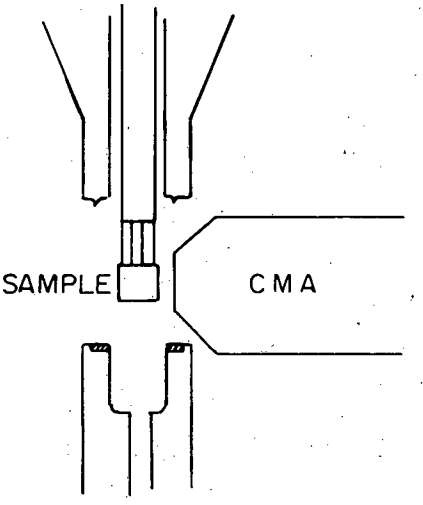

(b)

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Fig. 2

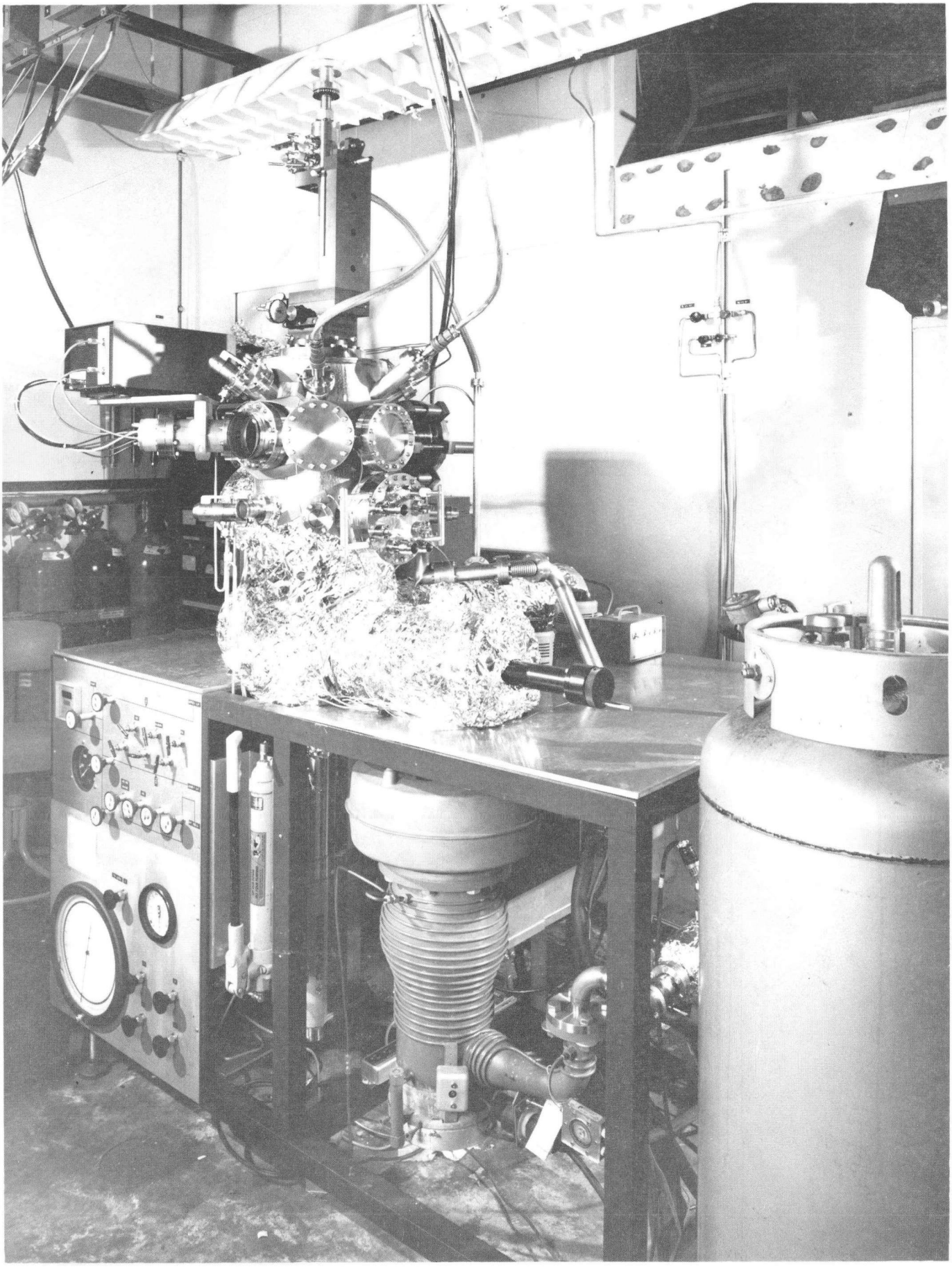

Fig. 3

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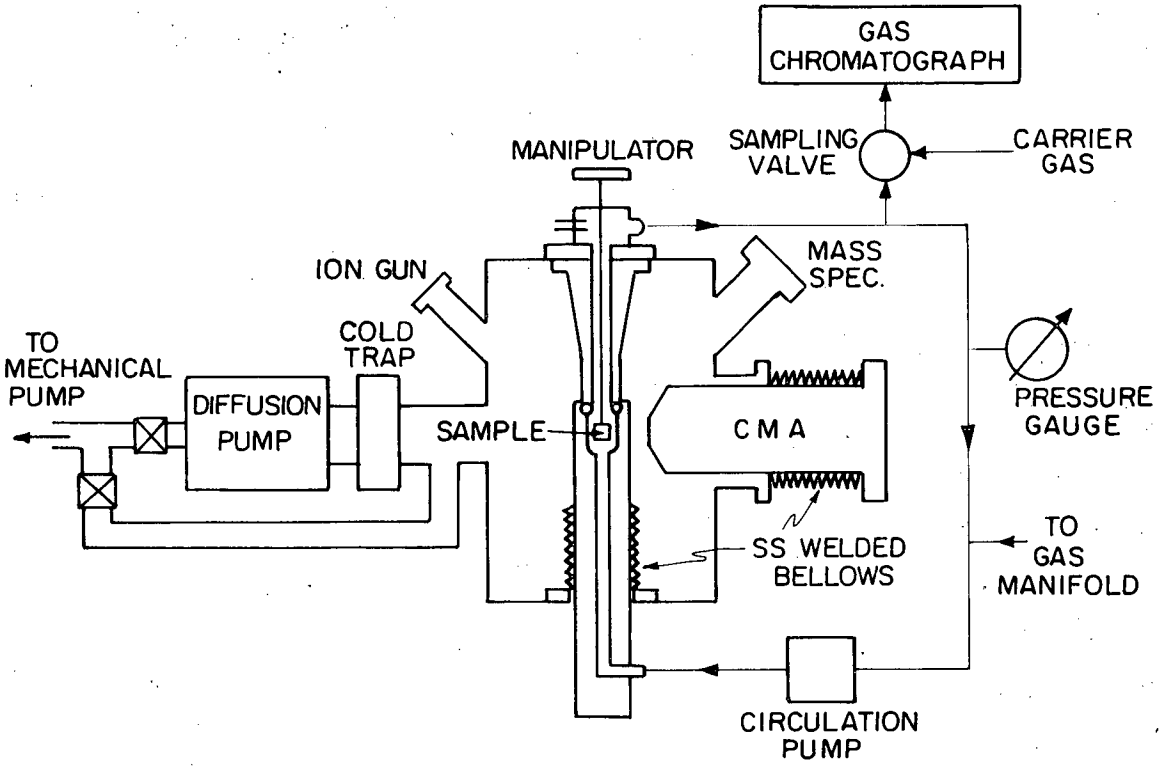
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Fig. 4

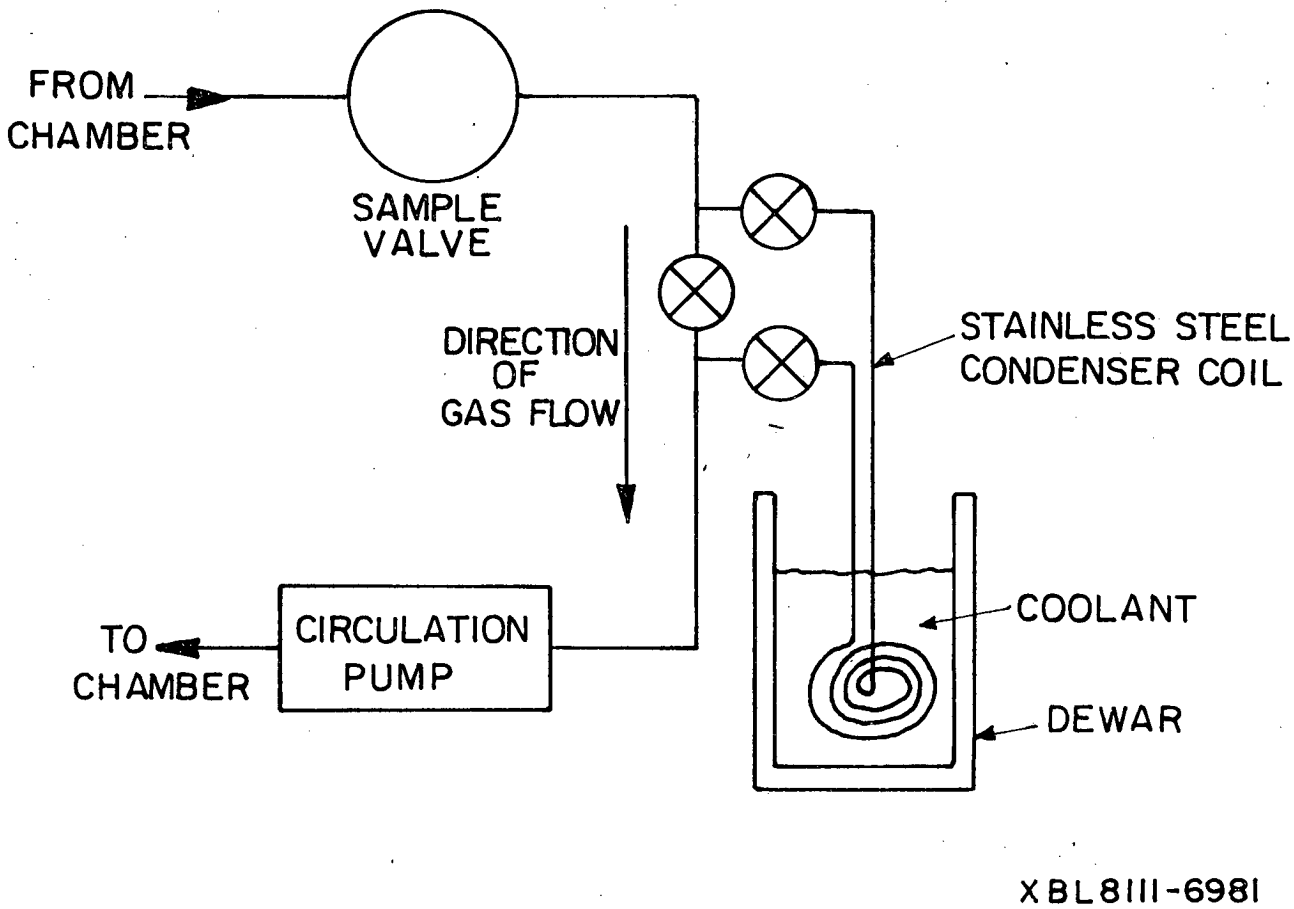
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Fig. 5

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