



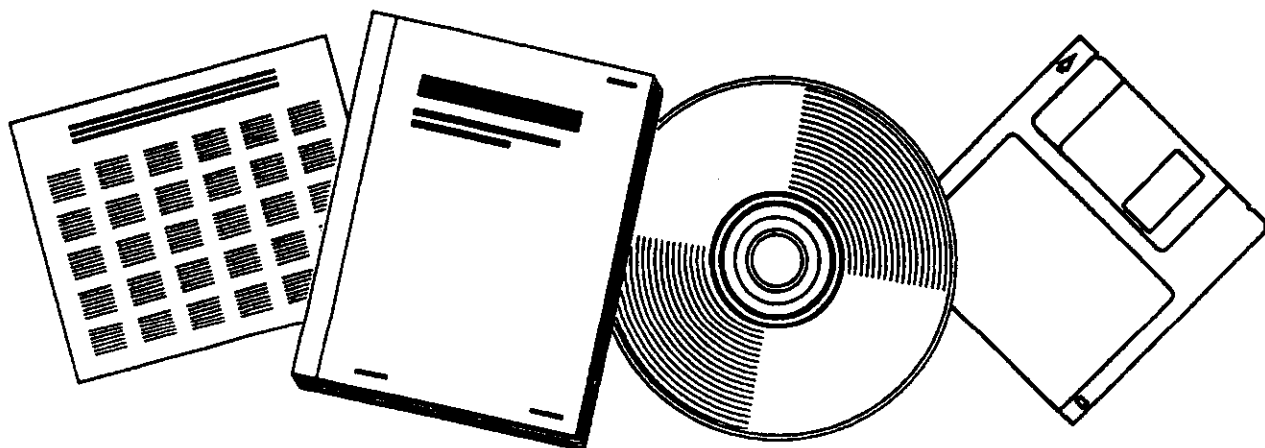
COO25791

NTIS[®]
Information is our business.

**AUGER AND REACTION STUDIES OF POISONING BY
SULFUR AND REGENERATION OF METAL SYNTHESIS
GAS CATALYSTS. PROGRESS REPORT, APRIL 1,
1975--DECEMBER 15, 1975**

DELAWARE UNIV., NEWARK. DEPT. OF
CHEMICAL ENGINEERING

DEC 1975



U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

COO-2579-1

AUGER AND REACTION STUDIES OF POISONING BY SULFUR AND
REGENERATION OF METAL SYNTHESIS GAS CATALYSTS

Progress Report

For Period April 1, 1975 - December 15, 1975

James R. Katzer

Department of Chemical Engineering
University of Delaware
Newark, Delaware 19711

MASTER

December, 1975

NOTICE
This report was prepared as an account of work sponsored by the United States Government, neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Prepared For

The U.S. Energy Research and Development Administration
Under Contract No. E(11-1)-2579

Ep

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

A.

ABSTRACT

The objective of this work is to determine the rate and mechanism of sulfur poisoning and of regeneration of metal catalysts used in synthesis gas conversion to hydrocarbon products.

Auger electron spectroscopy (AES) is being used for surface analysis, and in situ reaction studies of deactivation and regeneration are being combined with microreactor studies to quantify sulfur poisoning. An all-glass internal recirculation microreactor has been designed, fabricated and debugged and has been integrated into a metal-free feed gas and G. C. analysis system for kinetic studies of sulfur deactivation in CO hydrogenation. An UHV antechamber has been designed, built and connected with the Auger electron spectrometer to allow sample treatment at high temperature and pressure with subsequent AES analysis without atmospheric contamination. A gas-dosing molecular-leak system has been installed on the AES vacuum chamber to allow in situ sample treatment to bridge the high-pressure low-pressure gap. A mass spectrometer has been added to the system, and a computer is being interfaced with the spectrometer for improved data treatment and analysis at nano-ampere beam currents. The procedures for film preparation and cleaning have been developed; films are being used in all parts of the work.

B.

OBJECTIVES AND SCOPE

The main objective is to improve our currently incomplete understanding of the rate and mechanism of sulfur poisoning and of regeneration of metal catalysts used in converting synthesis gas ($\text{CO} + \text{H}_2$) to gaseous and liquid hydrocarbon products. Improved understanding of deactivation and of regeneration resulting from the data generated in this work should result in development of catalysts with improved sulfur tolerance and the designation of improved operating procedures. A second objective is to bridge the gap between reaction studies at practical conditions and surface studies carried out under ultra-high vacuum conditions.

Rates of sulfur adsorption on and of deactivation of metal film catalysts are to be quantitatively measured, and mechanisms of sulfur deactivation are to be postulated, based on the data obtained. Rates and mechanisms of regeneration of sulfided metal foils and films in O_2 and H_2 as a function of temperature and gas-phase composition will be determined. The work will concentrate on Ni, Co and Fe but will also include other elements and combinations thereof (alloys).

Auger electron spectroscopy (AES) is being used to measure surface concentrations and component depth profiles with both metal foils and films for H_2S singly and in the presence of CO and H_2 . Residual gas analysis (RGA) is being

used to help uniquely define surface processes, to determine the occurrence and rate of surface reactions producing desorbable species and to monitor the partial pressure of gases in multi-component mixtures. AES studies will involve comparison of surface conditions present under the ultra-high vacuum environment of the Auger electron spectrometer vacuum chamber with the surface conditions present under the high-pressure conditions of catalytic reactions. These studies will provide a link between the surface conditions at high pressures and those at low pressures and will thus show us how to use results obtained with modern surface analysis tools under ultra-high vacuum conditions to interpret the catalytic behavior of the surface. Development of an understanding of how to bridge this large gap is essential to the effective use of electron spectroscopy tools in catalytic studies.

Microreactor studies of sulfur poisoning of CO hydrogenation activity of the same catalysts used in the AES studies and of in situ regeneration of these catalysts will be carried out concurrently with the AES studies. These studies will use the same catalysts as those used in the AES studies and will use the same conditions as used in the high-pressure AES studies to make the link between the AES (high and low pressure) measured sulfur concentration and the catalytic activity of the surface. Results of this part of the work should assist in the development of catalysts

more resistant to sulfur and in the specification of in situ regeneration procedures.

C. ACCOMPLISHMENTS TO DATE

The surface analysis is being done with a Physical Electronics Auger electron spectrometer which has undergone several modifications to allow us to obtain the data required for this work. To carry out the low-pressure surface studies within the Auger electron spectrometer vacuum chamber a molecular leak system similar to that used by Professor Somorjai has been constructed and connected into the vacuum chamber. Figure 1 is a schematic of this system, which is operational and in use.

For high-pressure surface studies an ante-chamber which connects to the vacuum chamber of the Auger electron spectrometer has been designed and constructed. This chamber is shown schematically in Figure 2. It is separated from the main vacuum chamber of the Auger electron spectrometer by a viton-sealed ultra-high vacuum gate valve, which can be opened to allow the sample to be moved directly into the vacuum chamber into position for Auger surface analysis. The ante-chamber is an ultra-high vacuum chamber composed of a 6-way cross and a metal bellows which compresses when the rod carrying the sample holder is moved into the main vacuum chamber. The sample on the sample holder can be heated to high temperatures, and gas of any composition

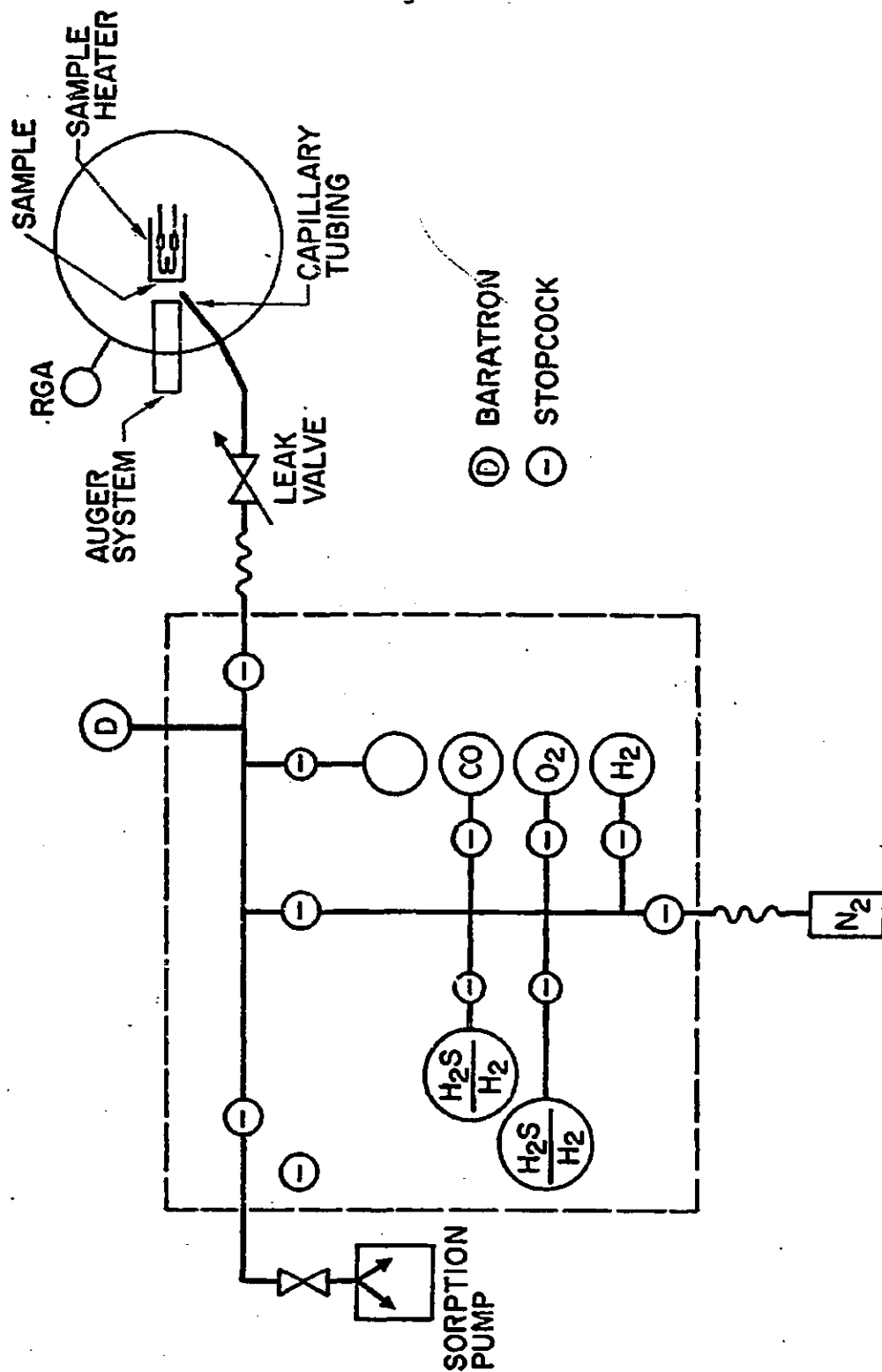


Fig. 1 MOLECULAR LEAK SYSTEM INTO AUGER CHAMBER

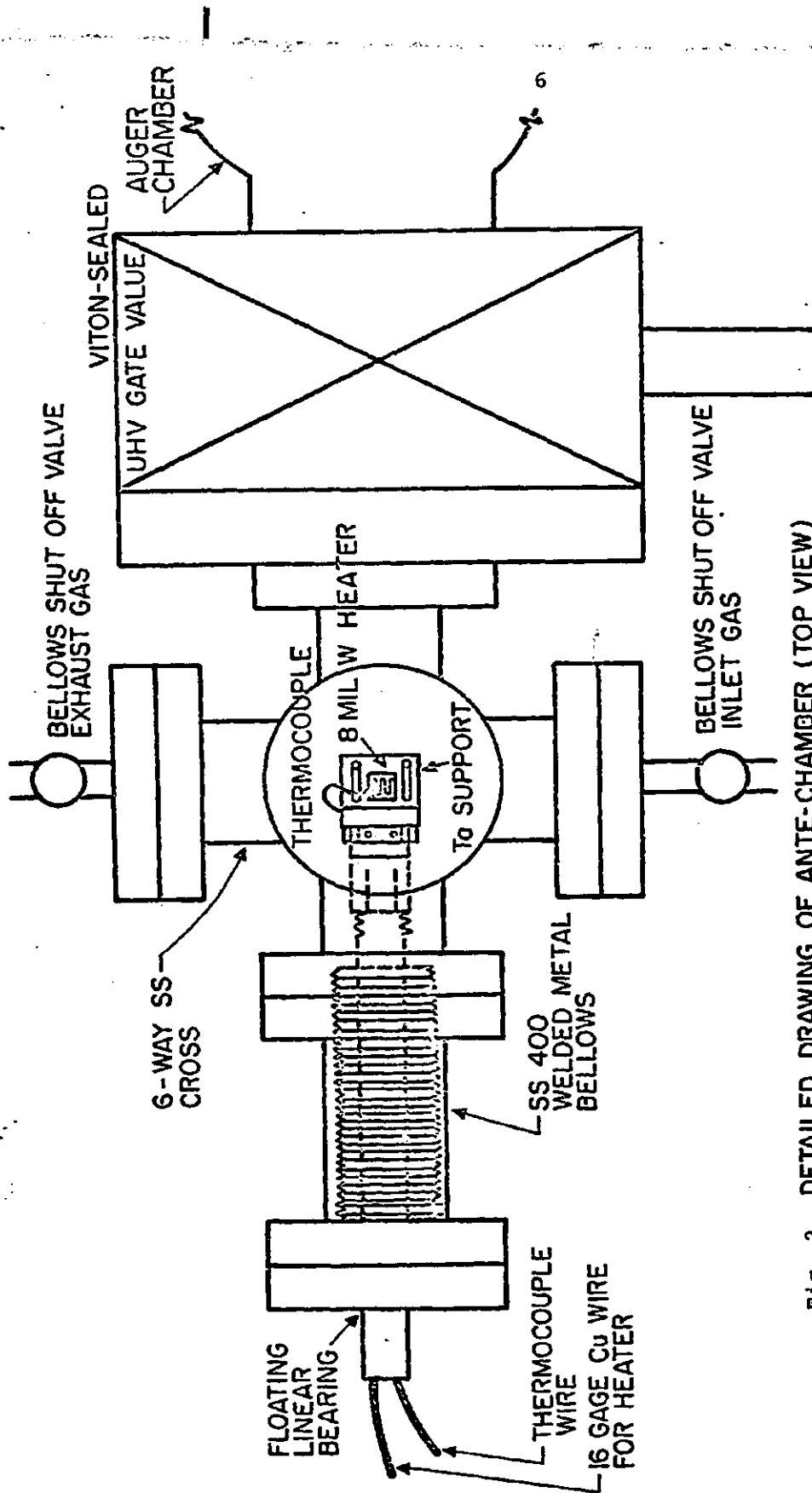


Fig. 2. DETAILED DRAWING OF ANTE-CHAMBER (TOP VIEW)

desired can be flowed through the chamber at pressures to several atmospheres. Thus samples can be treated under practical reaction conditions including the presence and absence of sulfur, and the rate of reaction over the sample can be determined. Then the system can be evacuated (The ante-chamber is cryo-pumped.), and the sample can be moved, without contact with or contamination by air or other gases, into the vacuum chamber of the Auger electron spectrometer where the surface analysis is carried out. These results can then be compared with those obtained under the ultra-high vacuum conditions of the main chamber using the molecular leak apparatus. They can also be compared with the kinetic measurements made with the micro-reactor system described below. The combination of these three measurements is, I believe, the key to bridging the gap between UHV surface studies and high-pressure kinetic studies; the bridging of this gap is extremely important in making these new surface analysis techniques more useful in the interpretation of catalytic behavior.

All component parts for the ante-chamber system have been obtained, and the chamber has been assembled, attached to the main vacuum chamber of the Auger electron spectrometer and leak tested. We are now taking initial data with the ante-chamber to determine the best mode of operation. Questions that we are now working on resolving include: (a) how can we best avoid or minimize cross and back con-

tamination of the sample in the chamber?, (b) what are the most effective cleaning procedures to be used with each fresh metal film before it is used in a study?, (c) what is the best procedure to use in going from steady-state gas-flow reaction conditions to the evacuated state so that the sample can be moved into the main vacuum chamber for surface analysis? and (d) how significant are the changes that occur in the surface composition of the metal catalyst upon evacuation and translation into the main vacuum chamber?

A schematic of the gas flow system to the ante-chamber and of its orientation on the main vacuum chamber of the Auger electron spectrometer is shown in Figure 3. All lines leading to the ante-chamber which carry H_2S are teflon to avoid problems due to sulfur loss on and contamination of the metal. The gas-feed system is constructed and in operation on the system.

Figure 3 is a schematic of the complete Auger electron spectrometer analysis and treatment system. A UTI mass spectrometer (RGA) has been added to the system to monitor partial pressures of gases in multi-component mixtures in the chamber to help define surface reaction processes and to determine the occurrence and rate of surface reactions producing desorbable species. A leak is to be installed between ante-chamber and the main vacuum chamber so that the mass spectrometer can be used to determine rates of reaction

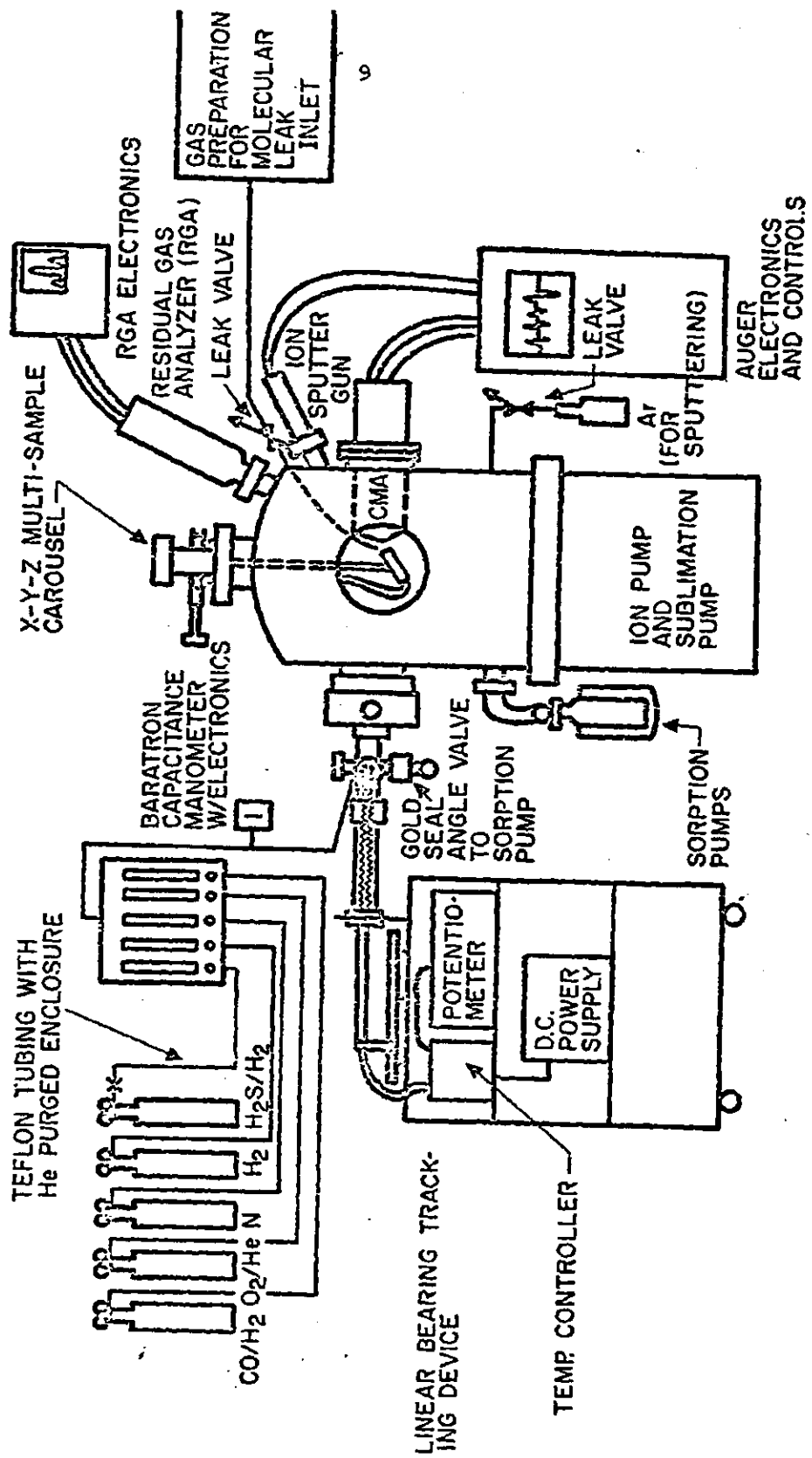


FIG. 3 SCHEMATIC OF AUGER ELECTRON SPECTROMETER WITH ANTE-CHAMBER

on the catalyst in the ante-chamber. Ion-sputtering capabilities allow component depth profiling. We are in the process of interfacing a PDP-11 computer to the spectrometer so that electron beam currents can be reduced from the micro-ampere range to the nano-ampere range. This three-order of magnitude reduction in the electron beam energy should markedly reduce the extent of damage done to the surface by the electron beam and thus increase the utility of the analysis results. The computer will also be used to obtain directly $N(E)$ peaks rather than the derivative $(dN(E)/dE)$ data typically obtained in Auger electron spectroscopy. This will allow direct integration of the data and more accurate quantification of it.

An all-glass internal recirculation reactor has been designed, fabricated and debugged (Figure 4); and we are at the stage of carrying out our initial reaction studies with it. The reactor was designed to utilize the same catalytic films used in the experiments to be done with the Auger electron spectrometer and the ante-chamber. Thus the results should be translatable from one system to the other. Adequate mixing and operation to 400°C and three atmospheres have been demonstrated. The all-glass construction prevents any losses of sulfur fed at very low concentrations (~ 1 ppm) on metal surfaces or cross contamination from run to run.

Figure 5 shows the entire system for the reaction studies.

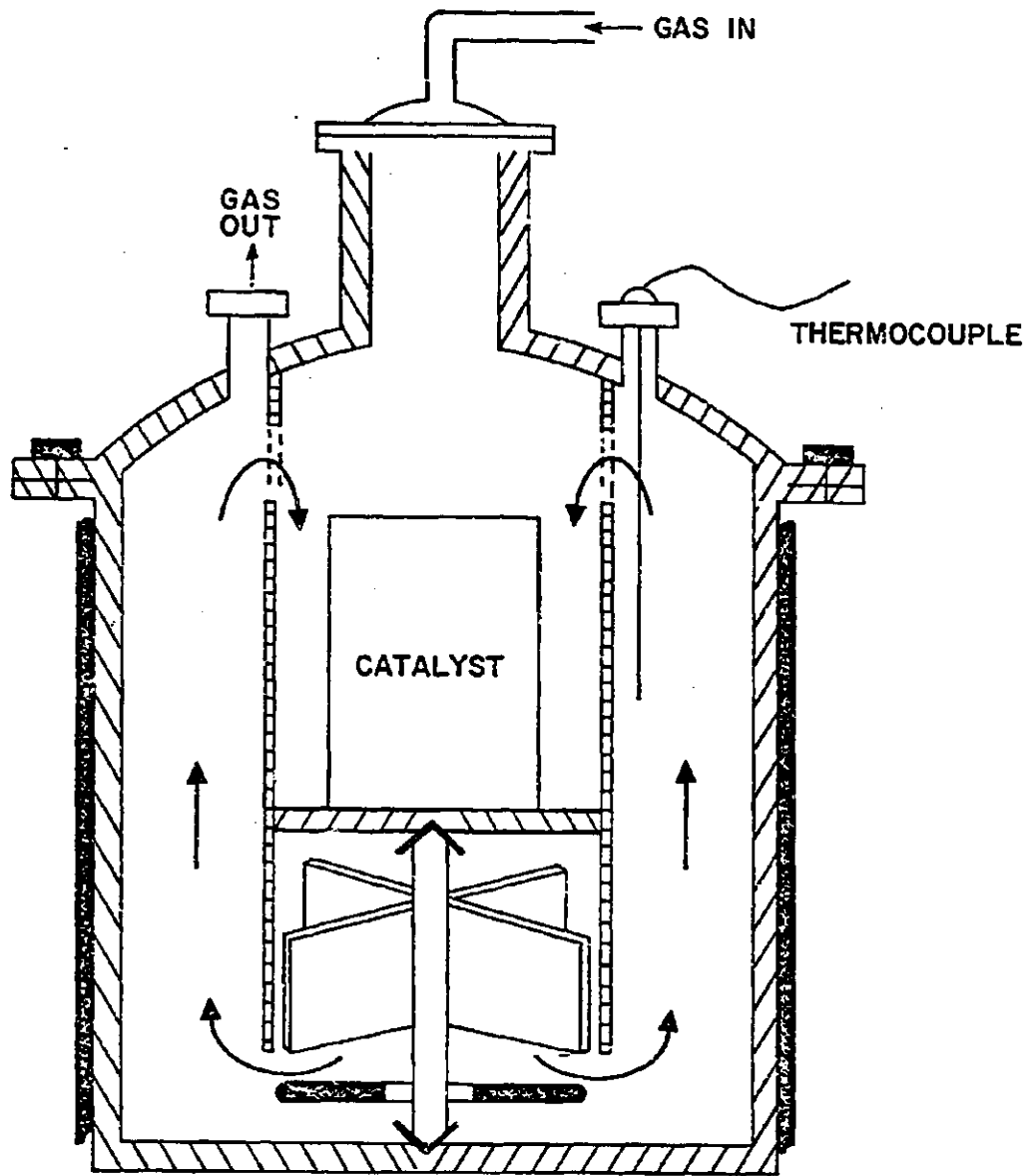


Fig. 4. SCHEMATIC OF MAGNETICALLY-DRIVEN
INTERNAL RECYCLE REACTOR

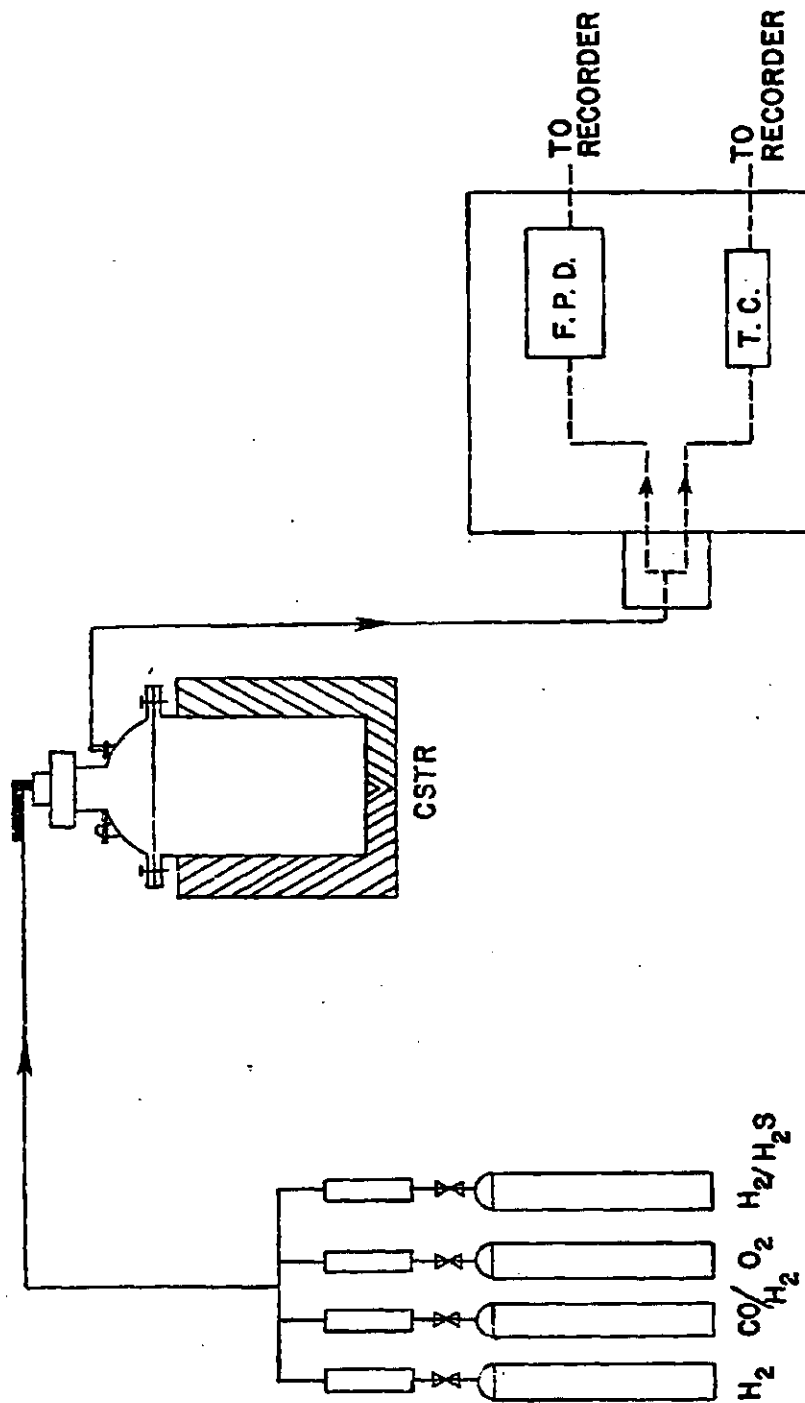
GAS
CHROMATOGRAPH

Fig. 5. SCHEMATIC FLOW REACTOR SYSTEM

Again any lines handling H_2S are teflon to prevent sulfur losses and cross contamination. Analysis is by gas chromatography with a sulfur-specific detector to allow sulfur concentrations in the PPB range to be quantitatively measured. A thermal conductivity detector is used for CO , H_2 , CH_4 and hydrocarbon analysis.

Film forming (Figure 6) and cleaning techniques have been developed for both systems. All measurements are to be carried out on the same films of the metal evaporated onto alumina. Ni, Co, Fe are the primary metals to be considered, but other metals will also be investigated singly and in combination (alloys). Thus we can study thick films which cover the support completely or study thin films which should approximate supported metal catalysts reasonably well. Formation and cleaning techniques have been satisfactorily developed and demonstrated.

Metal surfaces are typically contaminated by sulfur and carbon as shown for nickel foil in Figure 7. Oxidation and reduction cycles can reduce the level of these contaminants to very low values. A single oxidation and reduction at $500^\circ C$ reduces the carbon and sulfur levels to almost immeasurable values (Figure 7). The oxygen is only on the surface due to contact with air as shown by the complete reduction in the oxygen signal upon sputtering with argon for less than one minute. Figure 8 shows the depth profiling

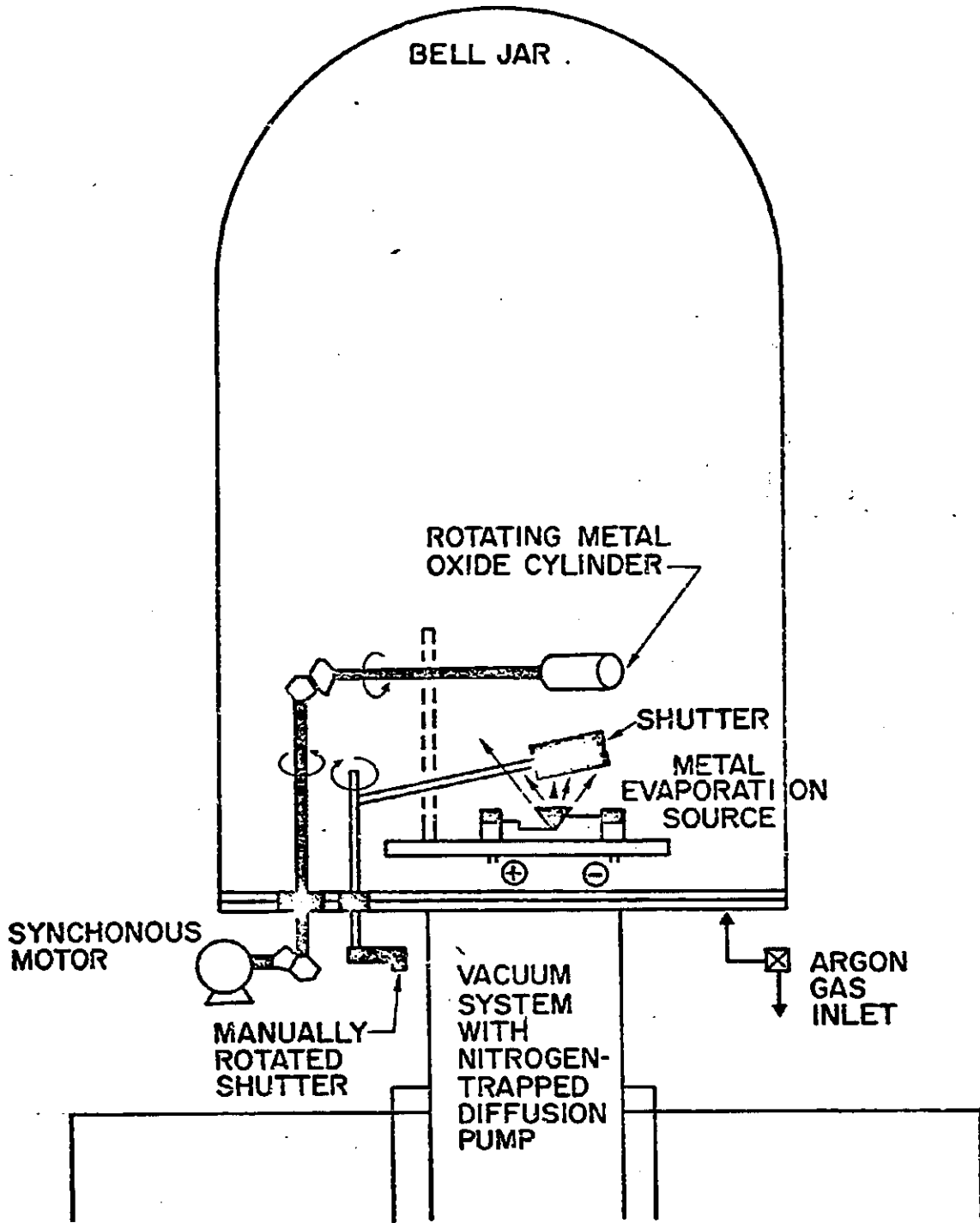


Fig. 6. Film formation on Al_2O_3 cylinder by evaporation

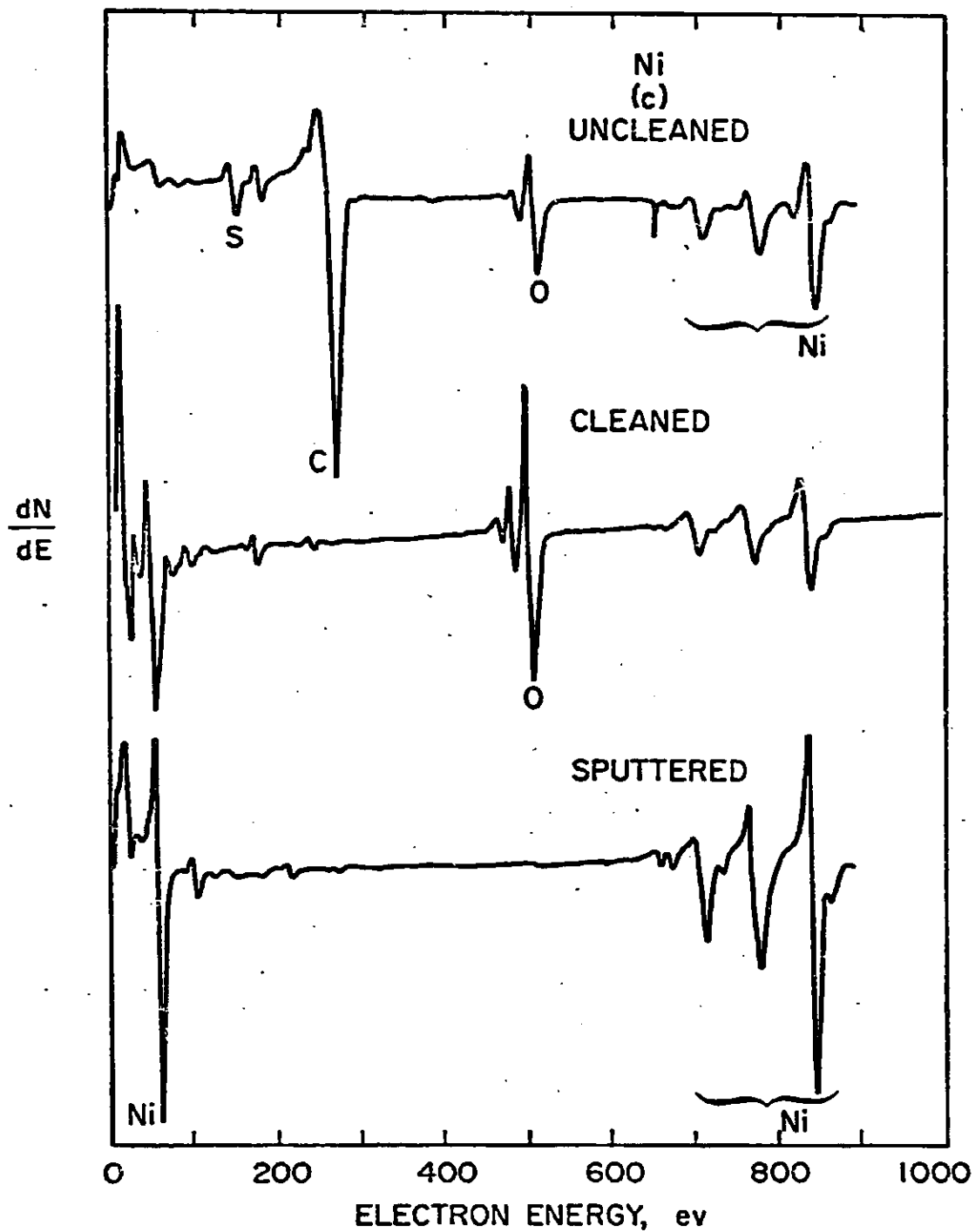


Fig. 7. Effects of oxidation reduction cycle for cleaning nickel foil.

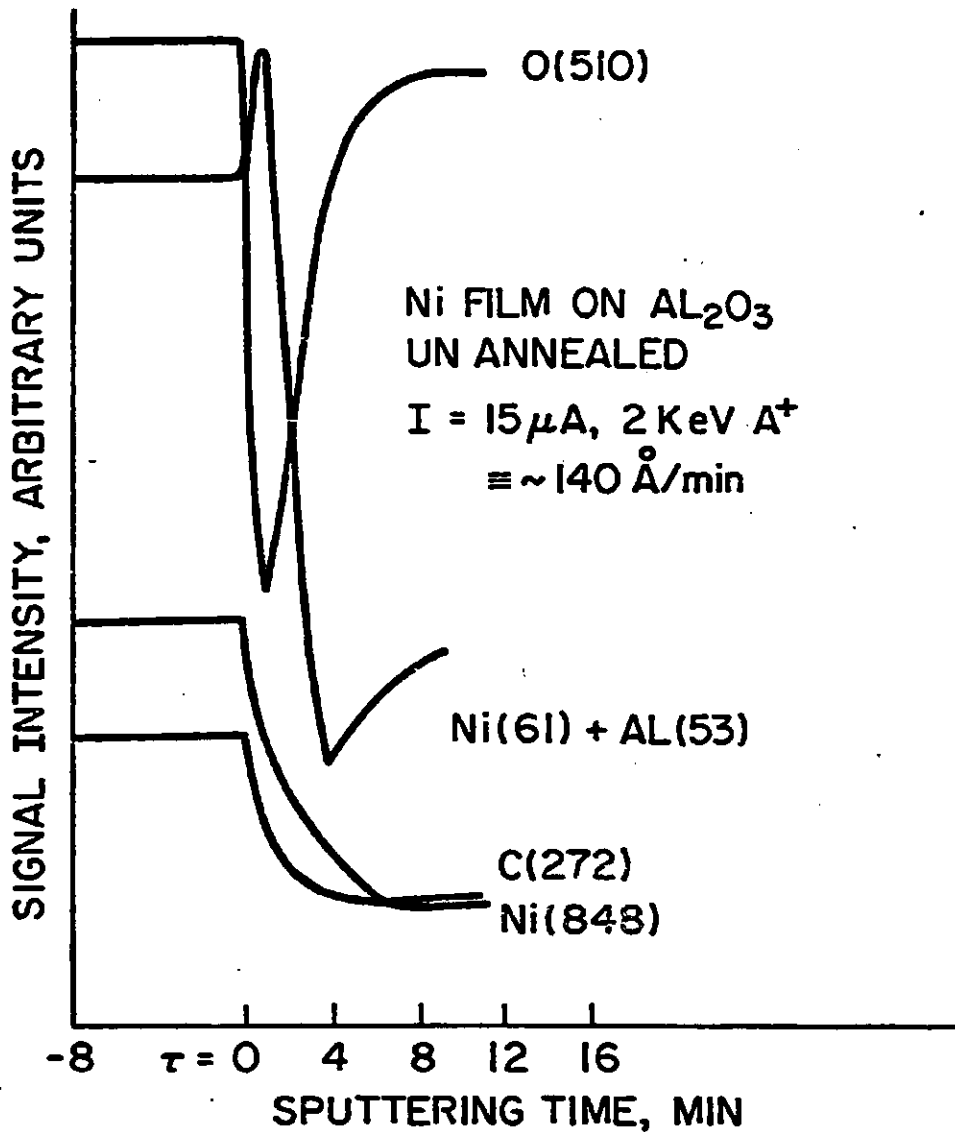


Fig. 8. Depth profile of a thin Ni on Al₂O₃ film.

by sputtering of a thin film of Ni on alumina. This film is about 300-400Å thick. The high carbon level is due to carbon (oil) in the evaporating system and is completely removed by an oxidation-reduction cycle. The sulfur level is very low in prepared films.

The advantage of using films rather than foils is that the sulfur level in films is controllable by our preparation and is much below that in foils. Annealing results in less than monolayer coverage with our films, but foils have sufficient sulfur for many monolayers because of their large bulk. One cleaning cycle reduces the film sulfur level to almost acceptable levels; foils or single crystals require many cycles. Similarly in reaching steady state under reaction conditions there must be an equilibration between the surface and the bulk of the metal; this equilibration occurs much more rapidly with films than with foils or single crystals, and this should be more characteristic of the behavior expected for actual supported metal catalysts.

Preliminary studies also suggest that carbon and oxygen peak shape can be used to distinguish chemisorbed CO from carbon on the surface and oxygen on surface. Figure 9 shows what is observed for carbon and oxygen on the surface; Figure 7b shows the signal for CO. Carbon and oxygen may also be present in Figure 7b. We are presently attempting to clarify this further. Such peak-shape information may allow us to

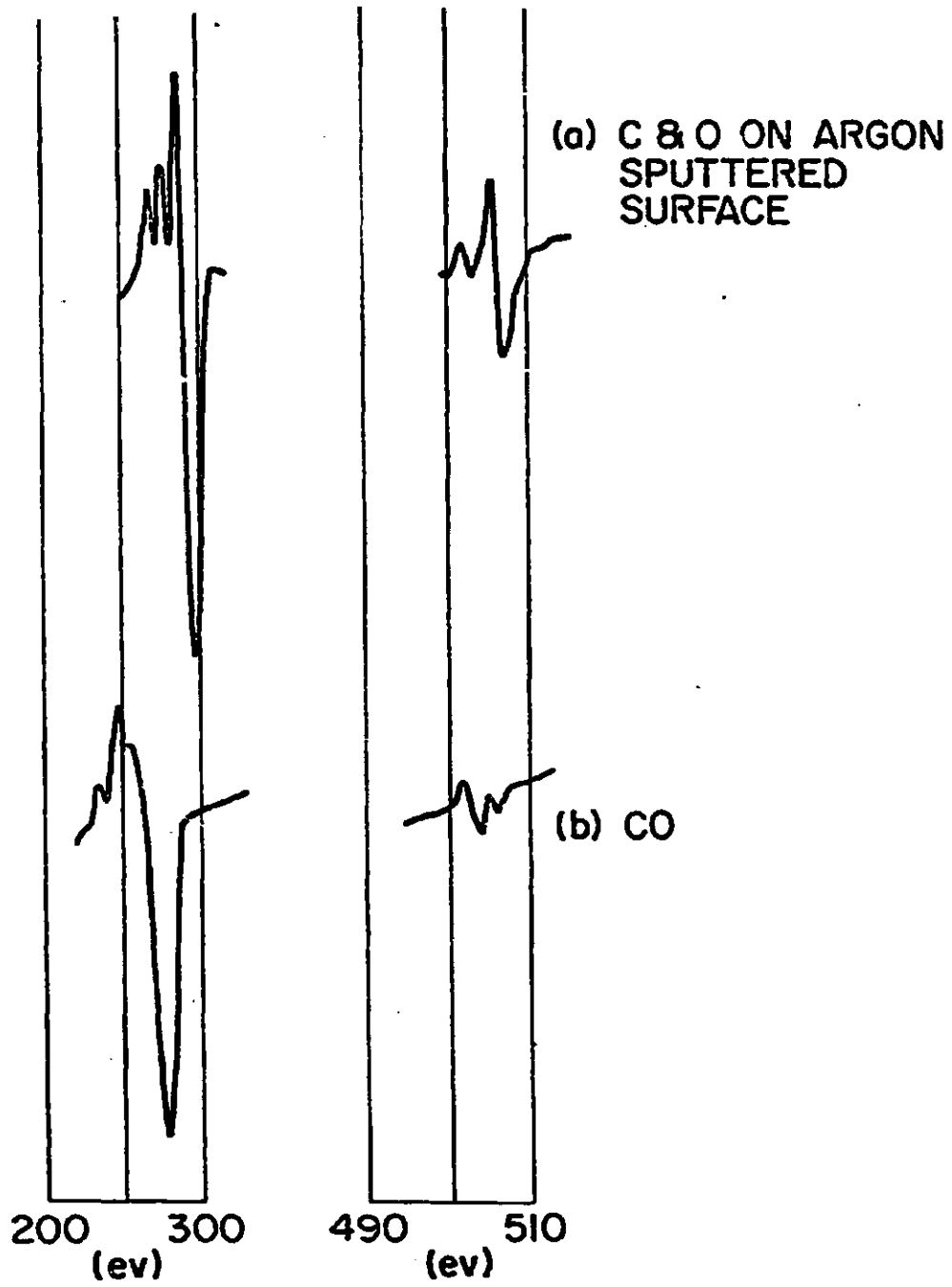


Fig. 9. Peak shape for surface carbon and oxygen (a) and for chemisorbed CO (b).

distinguish between different types of carbon on the surface.

Progress to date has been in accord with the time plan set forth in the proposal submitted for this work. We were held up somewhat during August and September because of the very slow delivery of a UHV leak valve, a Baratron pressure transducer head, the all-glass reactor and because of the presence of a leaking conflat flange on the ante-chamber upon completion. These problems have all been overcome, and we now have all parts of the system operating. To the best of my knowledge we have complied with all phases of the contract to this point.

D. CONTINUING WORK

The work for the remainder of the current term of the agreement will concentrate on nickel. Ni will be used in the studies we are now starting to determine the rates and extents of adsorption of sulfur using the molecular leak and various temperatures and ratios of H_2-H_2S-CO . Simultaneously studies in the ante-chamber will be carried out at similar temperatures and ratios of H_2-H_2S-CO . The objectives of this work are: (a) to determine how the system behaves at high and at low (in situ) pressures; (b) to determine how best to go from the high-pressure steady-state environment and surface condition in the ante-chamber through evacuation and movement into the main vacuum chamber of the Auger electron spectrometer for analysis with the least alteration of the steady-state surface condition; (c) to determine (to the extent possible) what changes in the surface condition occur upon evacuation and movement into the main vacuum chamber; and (d) to develop correlations between the observed surface composition in the Auger chamber and that under actual reaction conditions. A broad variety of experiments will need to be performed, and the results of each carefully evaluated to allow us to determine what actually happens to the surface during evacuation and movement for analysis and thus to be able to say what UHV measurements mean with respect to higher-pressure steady-state surface conditions during reaction. The results of this work are important because they provide the base for our future work and because they may be useful to the

efforts of many other groups around the country doing surface analysis and attempting to relate it to catalytic observations.

When we feel we have a reasonably good understanding of how to translate from high-pressure conditions to UHV conditions, we will begin studies of the surface sulfur level on Ni as a function of reaction conditions using the ante-chamber. If possible we will measure rates of reaction in these studies to relate to observed sulfur concentration.

We are starting to do a substantial study of the effect of sulfur on the methanation activity in the all-glass internal recycle reactor system described earlier. This will provide quantitative information on the rates of deactivation caused by several H_2S concentration levels in the feed gas and on the steady-state methanation activity as a function of feed gas H_2S concentration. This study will exactly duplicate the conditions studied in the ante-chamber so that a quantitative relationship between sulfur level and activity can be determined.

The third activity to be pursued during the remainder of the contract is a study of the regeneration of sulfur-deactivated nickel catalysts. This will involve the films used in the ante-chamber poisoning studies and those used in the all-glass micro-reactor studies. The emphasis of this work will be to determine the rate and mechanism of regeneration and to determine the optimum conditions for regeneration. We strongly feel that regeneration of sulfur-deactivated catalysts is possible.

D. PERSONNEL

The principal investigator (James R. Katzer) has spent approximately one-third of his summer (about one month) and about 15% of his time during the academic year working on the project. It is anticipated that this level (15%) of effort will continue through the rest of the current term of the agreement.

Dr. Hassan Windawi, who has a Ph.D. in Physics (Sputtering from Surfaces), joined the project as a Post-Doctoral Fellow July 1, 1975, and he has been devoting full time effort to the project. His responsibilities are mainly with the application of the Auger electron spectrometer to the work, and he will be continuing to work on the project. Mr. William Fitzharris, who is beginning his Ph.D. program in Chemical Engineering, joined the project April 1 and is devoting about one-half time to the effort; the other half of his time is spent on course work. He will continue to work on the project and is mainly responsible for the film preparation and micro-reactor studies. His future work will concentrate on coupling the reaction kinetic studies in the microreactor with the studies carried out in the high-pressure ante-chamber on the Auger electron spectrometer. Mr. Steve Colby also joined the project in April and has been responsible for the design, construction and operation of the ante-chamber on the Auger spectrometer. His future studies

will center around the question of defining appropriate re-generation procedures.

There was some supplementation of Bill Fitzharris' and Steve Colby's stipends with Departmental funds for Teaching Assistance (laboratory) duties rendered (Colby) and from unrestricted funds from private companies (Fitzharris) because the salaries and wages in the grant were insufficient to cover all three people completely. None of these funds were Federal funds nor were other Federal monies used in this work in any way.

COO - 2579

AUGER AND REACTION STUDIES OF POISONING BY SULFUR AND
REGENERATION OF METAL SYNTHESIS GAS CATALYSTS

Renewal Request

For Period April 1, 1976 - March 31, 1977

James R. Katzer

Department of Chemical Engineering
University of Delaware
Newark, Delaware 19711

December 1975

Request for continuation of Contract

No. E(11-1)-2579

PRINCIPAL INVESTIGATOR

UNIVERSITY OF DELAWARE BY:

James R. Katzer 12-17-75
Dr. James R. Katzer, Associate
Professor of Chemical Eng.

Arnold L. Lippert
Dr. Arnold L. Lippert, Associate
Provost for Research and Dean of the
College of Graduate Studies