EXPERIMENTAL

The methanation reaction on ruthenium thin films was studied using a variety of experimental techniques. The kinetics of the reaction were studied over a wide pressure range and under different catalyst pretreatment conditions. Isotopic exchange studies, as well as studies involving the flash desorption of carbon monoxide from ruthenium, were conducted. The catalyst surface was characterized before and after exposure to carbon monoxide and hydrogen under reaction conditions by Auger electron spectroscopy (AES), electron spectroscopy for chemical analysis (ESCA) and low energy electron diffraction (LEED). All kinetic and related studies were conducted in an ultra-high vacuum system designed and constructed specifically for this work. The LEED/Auger and ESCA studies were performed in commercial surface analysis systems built by Varian Associates (Palo Alto, California) and AEI Scientific Apparatus, Inc. (Elmsford, New York) respectively. Since each of these systems required the attainment and maintenance of ultra-high vacuum (10^{-9} to 10^{-10} torr range), UHV techniques were used extensively in the collection of these data. Several excellent reviews of the theory and attainment of ultra-high vacuum are available [57,58], therefore this discussion will be limited to the systems and procedures used specifically in this work.

Vacuum System Design

A diagram of the ultra-high vacuum system used in the kinetic and flash desorption studies is shown in Figure 2. Functionally the system

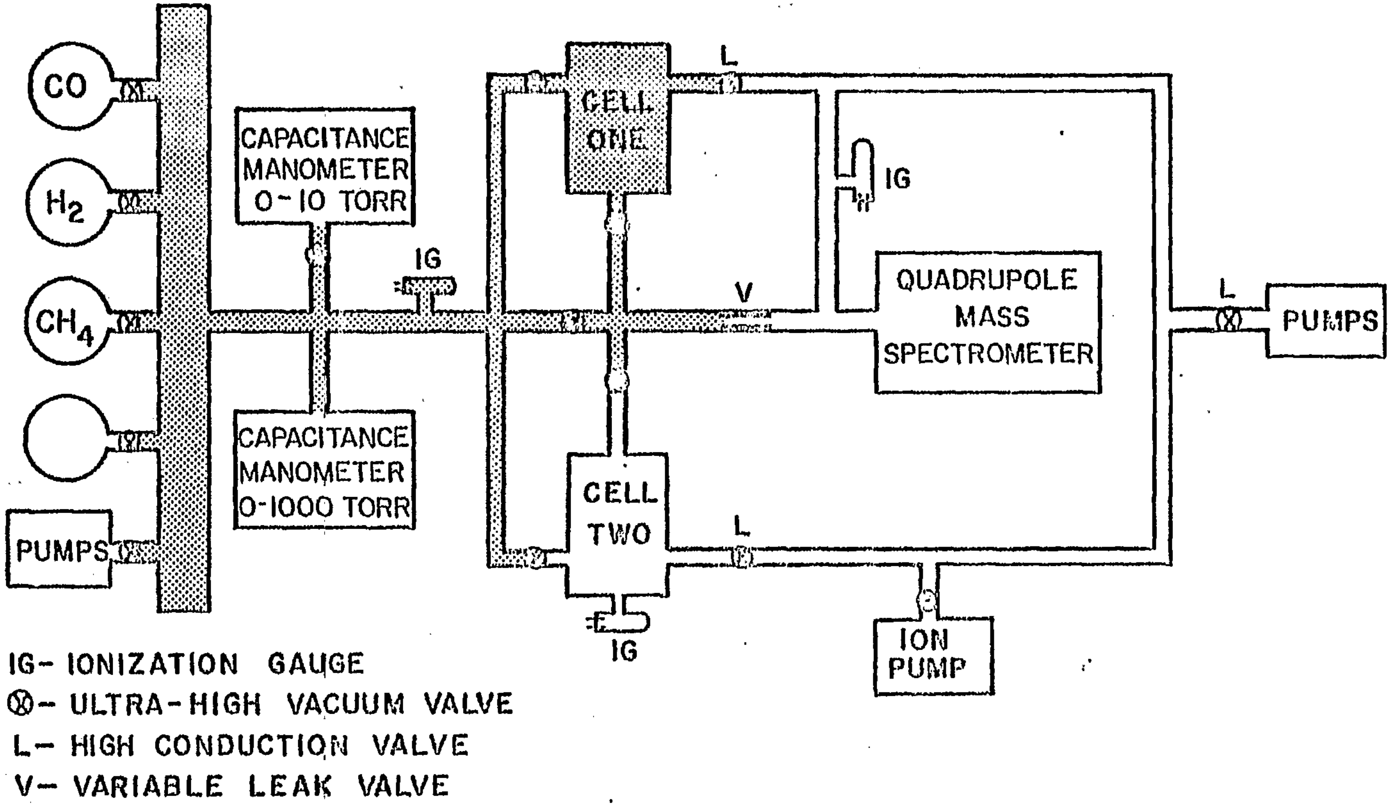

Figure 2. Diagram of ultra-high vacuum system used in kinetic and flash desorption experiments. (Shaded area = reaction volume ≅ 2.0 liters).

consisted of three portions. A gas manifold was used to premix the desired amounts of reactant gases. The reaction cell contained the catalyst which was maintained at an elevated temperature during the kinetic studies. The mass spectrometer was connected to the reaction cell via a leak valve to permit continual sampling of the gas mixture.

The gas manifold was constructed of 14 mm. (o.d.) pyrex tubulation. It was pumped by a two stage mercury diffusion pump to a base pressure of about 1×10^{-7} torr. The pressure in the empty manifold was measured by a conventional Bayard-Alpert ionization gauge. Connected to the manifold were several glass bulbs of high purity gases used in this study. These gases were generally predosed into the manifold prior to dosing onto the catalyst. The gas pressure in the manifold was measured by one of two capacitance manometers attached to the manifold. A low pressure capacitance manometer (Granville Phillips Co., series 212, Boulder, Colorado) was used to measure gas pressures between 1 μ and 10 torr. The reference side of this manometer was continually pumped to 10^{-6} to 10^{-7} torr to provide a stable baseline. The sensor head was water thermostated at 305.4K to prevent drift due to changes in the ambient temperature. The manometer was calibrated against a McLeod gauge (Consolidated Vacuum Corp., Rochester, New York) using argon. Pressure changes were recorded as a meter deflection on the manometer control unit. Five ranges were used with maximum pressures of approximately 100 μm, 300 μm, 1 torr, 3 torr and 10 torr (1 μm = 10^{-3} torr). Each range yielded a linear calibration of the form:

$$\text{Pressure } (\mu\text{m}) = A \times \text{Scale deflection} + B$$

The calibration was repeated periodically and never varied by more than 10 per cent from the initial calibration.

A high pressure capacitance manometer (MKS Instruments, type 107M, Burlington, Mass.) was used to measure gas pressures greater than 10 torr. The reference side of the manometer was pumped to 10^{-6} to 10^{-7} torr by the same pump used on the low pressure manometer. The higher pressure manometer had five ranges with maximum pressures of 10, 30, 100, 300 and 1000 torr. This manometer was factory calibrated such that the actual pressure could be read directly from the instrument meter. The factory calibration was checked twice during the course of this work and did not change by more than 2 per cent. In conjunction these capacitance manometers gave an effective manifold pressure range of 0.1 μm to 1000 torr (seven orders of magnitude). The manifold volume was measured by argon expansion from a standard volume attached to one of the gas inlet valves and was found to be 1087.1 cm^3.

The system had two reaction cells which were connected to the gas manifold. Initially, each cell consisted of a 500 ml. round bottom flask with three feedthroughs for electrical contact to a ruthenium crystal and a thoria coated iridium filament placed in the center of the bulb. Since no procedure for the deposition of ruthenium thin films was available when this project was begun, one of the early goals was to develop such a procedure. This necessitated the deposition of many films under slightly different conditions and the comparison of their activities and stabilities. After use the film was removed and a new round bottom flask was glass blown onto the system. A bakeout was required before the reattainment of UHV conditions and the deposition of another ruthenium thin film. Having two cells allowed the deposition of two films between bakeouts resulting in more rapid data collection since half of the time lost during bakeouts was eliminated. The procedure developed for film deposition will be discussed in another section.

During the experiments a tube furnace (S. B. Lindberg, type SP, Watertown, Wis.) was placed around the reaction bulbs. The bottom of the vertical furnace was sealed and the top was covered to prevent air conduction through the furnace. In this manner, the bulbs could be conveniently heated to any temperature between room temperature and 775K (the approximate softening point of pyrex). The temperature was monitored by a chromel-alumel thermocouple which was inside the furnace and in direct thermal contact with the glass bulb. Once thermal equilibrium was reached, the temperature was stable to within $\pm 2^{\circ}$. The vertical temperature variation over the 12 inch long furnace was about 3°.

After the procedure for film deposition had been developed, cell two was changed from a reaction cell to a flash desorption cell. This added versatility to the system in that both kinetic studies and flash desorption studies could be conducted without modification of the system. A description of the flash cell will be made in a subsequent section. The volume of the reaction cell and connecting tubulation was measured by argon expansion from the manifold and was found to be 889.4 cm^3. The total reaction volume was 1976.5 cm^3.

A variable leak valve (Granville Phillips Co., series 203, Boulder. Colorado) was used to control the flow of gases from the reaction cell (several torr) to the mass spectrometer (10^{-5} torr). The valve was set such that during the duration of an experiment (up to 30 minutes) no detectable pressure drop due to the leak occurred. The pressure in the mass spectrometer chamber was at all times maintained at 10^{-5} torr or below. This volume was pumped by a 20 l/s differential ion pump (Ultek, model 203-2000, Palo Alto, Ca.) and by two 2-stage mercury diffusion pumps attached in series. High conductance valves connected each cell to these pumps so that they could be pumped to a base pressure of 10^{-9} torr before film deposition. These high conductance valves were closed at all other times (except when flash desorption studies were performed in cell two).

A Finnigan Spectrascan 400 quadrupole mass spectrometer (Finnigan Corp., Sunnyvale, Ca.) was used to analyze the gas composition. A range of 1 to 60u was normally scanned once every 3.5 seconds. Periodically the range was widened to scan from 1 to 200u to check for changes in high mass peaks which might be suggestive of higher hydrocarbon formation. No changes past (m/z)=44 were ever detected. The output of the mass spectrometer was directed onto either a 2-channel strip chart recorder (Hewlett-Packard, model 7402A, Palo Alto, Ca.) or an oscilloscope (Tektronix, Inc., type R.M. 503, Portland, Oregon).

The entire system, with the exception of the mercury diffusion pumps, could be baked to 623K. The minimum base pressure was 3×10^{-10} torr. All valves were ultra-high vacuum valves (Granville Phillips, Co., series 202, 203 and 204, Boulder, Co.). All glass was Corning 7740 borosilicate glass.

Thin Film Deposition Techniques

The usual procedure for deposition of thin metal films is to resistively heat a thin wire of the metal until a film is deposited. Unfortunately, ruthenium wires are not commercially available. The metal is so brittle that when thin wires are drawn they tend to break very easily. Three procedures for the production of ruthenium thin films were considered,"in house" production of ruthenium wires, argon ion bombardment of polycrystalline ruthenium and electron bombardment of polycrystalline ruthenium. The electron bombardment technique was ultimately chosen to produce the films used in this work. Since several discussions of thin film techniques are available [59,60], only those procedures used to produce these ruthenium thin films will be mentioned.

An attempt was made to produce ruthenium thin wires so that the more traditional procedure for the production of thin films could be used. A 3.0 gram sample of 99.95% ruthenium powder (Engelhard Industries, Inc., Carteret, N. J.) was melted in vacuum to produce two ruthenium rods (0.7 cm. x 10 cm.). One of the rods was sliced lengthwise several times to produce 20 mil thick slabs of ruthenium metal (1 mil = 0.001 inch). The slabs were sliced lengthwise to produce 20 mil "wires" of ruthenium. The cutting was done on a diamond wheel cutter (Buehler, Ltd., model 11-1180, Evanston, Ill.).

Many of the "wires" were broken in the cutting procedure. Some were ruined during efforts to spotweld them to the support rods in the reaction cell. Of the two or three that were actually put into the system and heated resistively, none resulted in a thin film. The "wires" would repeatedly fracture (presumably along grain boundaries). This procedure was eliminated as a feasible method of producing ruthenium thin films.

Figure 3 shows a diagram of the cell used for production of ruthenium thin films by electron bombardment. A ruthenium polycrystalline disc (Materials Research Corp., Orangeburg, N. Y.) was spotwelded to a tungsten support rod in the center of the glass bulb. The geometric surface area of the sample was approximately 1 cm^2. Auger as well as x-ray fluorescence spectroscopies indicated that the sample was pure ruthenium with no detectable impurities. Located adjacent to the ruthenium sample was a thoria coated iridium filament.

During electron bombardment the ruthenium disc was maintained at +400V with a regulated high voltage power supply (Heath Company, model SP-17A, Benton Harbor, Mi.). Current from a modified dc power supply (Hewlett-Packard, model 6286A, Palo Alto, California) was passed through the throia coated iridium filament. The dc power supply was modified to regulate the electron emission from the filament to the ruthenium sample. The electrons impacting the ruthenium disc caused it to be heated. The background pressure was maintained in the low 10^{-8} torr range. The temperature of the disc was maintained at 2223K for 3 hours while a fairly even ruthenium film was deposited.

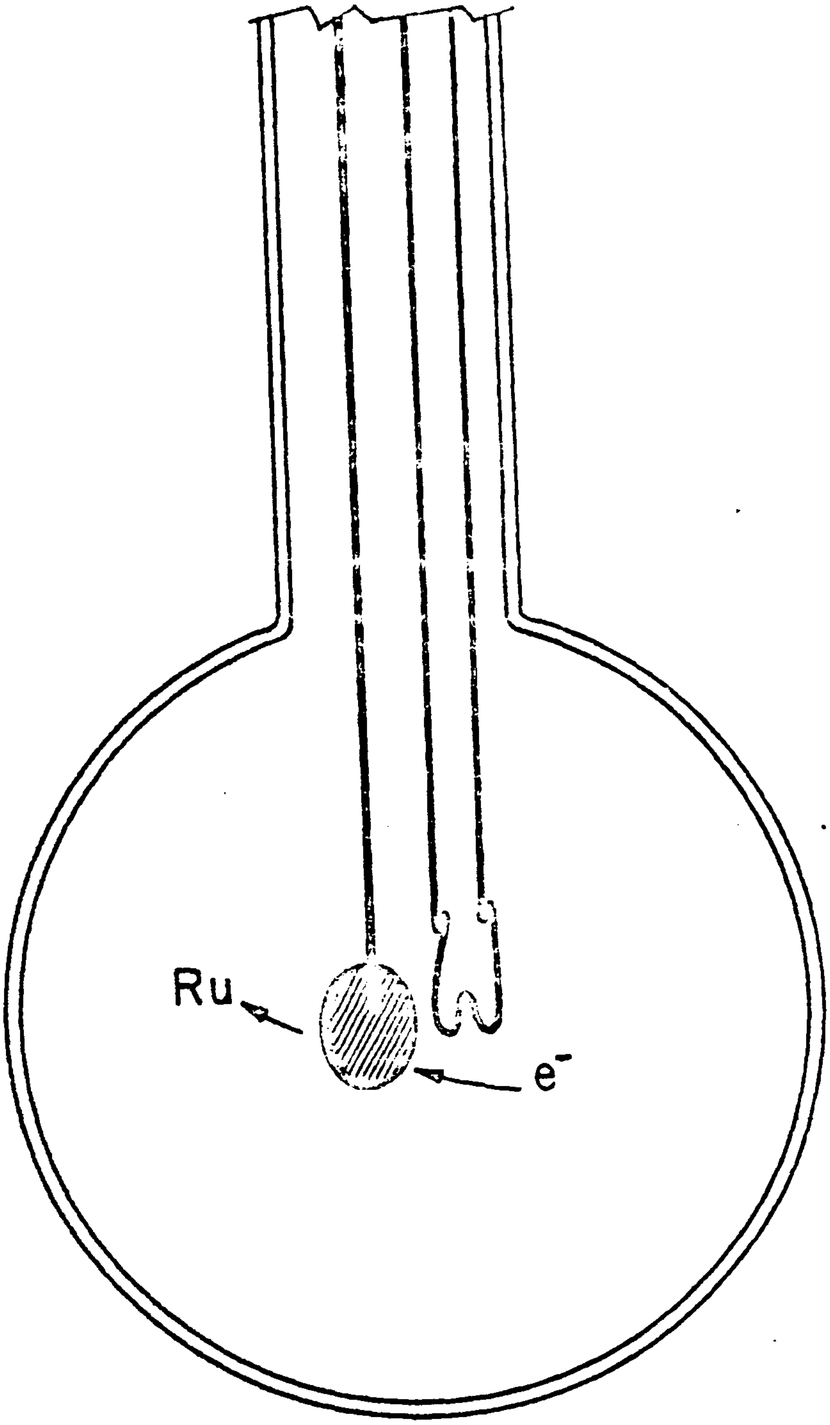

Figure 3. Diagram of the cell used for the production of ruthenium thin films on glass by electron bombardment.

During this entire process, the pyrex bulb was submerged in a large beaker of water. Sufficient heat was transmitted radiatively to the bulb to cause the water to boil. Therefore, the film was deposited with the glass at 373K. The film was then sintered at 673K for 1 hour. Films deposited in this manner were found to be fairly active and quite stable.

It was thought that argon ion bombardment might be a better technique for depositing the film in that deposition would occur without heating the disc quite so hot. This would allow deposition at a lower background pressure and with the glass bulb at a temperature less than 373K. The set-up for this work was essentially the same as with the electron bombardment study except that an additional electrode was located near the disc. The filament was heated while the extra electrode was maintained at +400V. The disc was at a -600V potential. Argon was dosed into the system to a pressure of 2×10^{-4} torr. Argon ions were produced between the filament and the electrode. They were attracted by the -600V potential to the disc. The ion emission to the ruthenium disc was monitored. After a couple of hours at an ion emission of 80 mA a fairly thin, uneven film was produced. The electron bombardment technique produced higher quality films as judged by activity, stability and appearance. All films used in the collection of the data presented were deposited by electron bombardment of a ruthenium disc.

Kinetics Procedure

The kinetic studies were conducted in the temperature range 548 to 623K. Most of the data were collected at 573 to 583K. Mixtures of carbon monoxide and hydrogen were prepared in the manifold. Hydrogen was always present in excess. The initial pressure of each gas was measured using the capacitance manometer. The final pressures (after expansion into the reaction cell) were calculated from the initial pressures and the known volume ratio of the manifold and the reaction cell. At very low carbon monoxide pressures (manifold pressure under 200 μm) a substantial portion of the gas adsorbed onto the film upon exposure. Corrections for this pressure change were made using the data from Figure 4. In this figure an r, which is a factor that converts the pressure of carbon monoxide in the manifold to the pressure of carbon monoxide in the reaction cell, is plotted against the manifold carbon monoxide pressure. Deviations from constancy are due to carbon monoxide adsorption on the film.

The reaction rate was always determined from the change in the methane concentration in the mass spectral chamber as a function of time. Equilibration of the methane across the leak usually occurred quite rapidly (5 seconds or less). It was observed that water did not equilibrate across the leak rapidly enough to give reliable rate information. With each set of data collected, a calibration of the mass spectrometer with respect to methane was made. A known pressure of methane was dosed into the reaction cell and the intensity of the $(m/z)=15$ peak was monitored. This peak was used to measure the methane

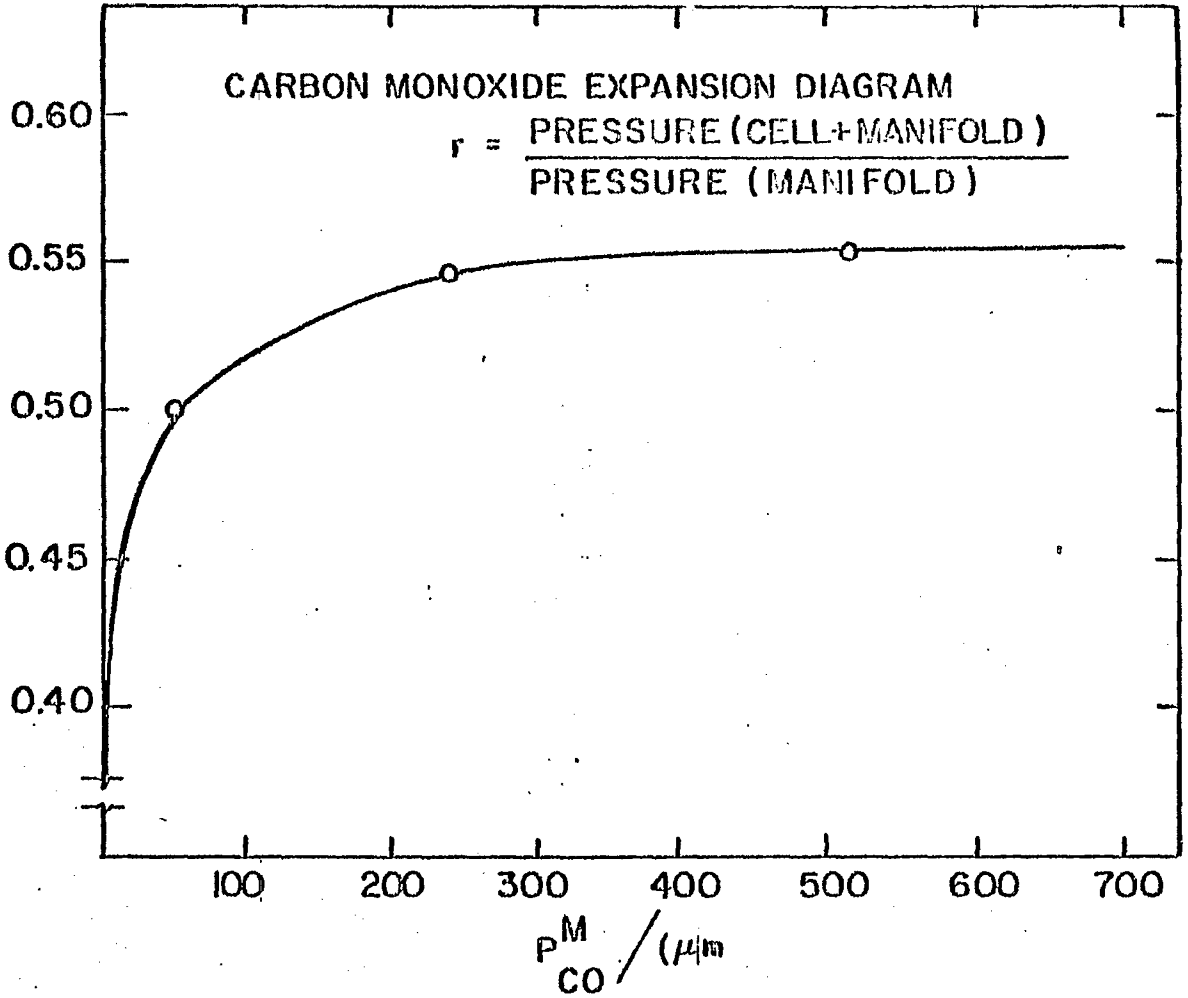

Figure 4. The variation of the carbon monoxide pressure conversion factor as a function of the pressure of carbon monoxide in the manifold.

produced rather than the $(m/z)=16$ because of oxygen interference from carbon monoxide and water. It was found that the mass spectrometer sensitivity to methane varied with the amount of hydrogen present in the reaction cell. As the hydrogen pressure was increased the intensity of the methane peaks in the mass spectrum also increased at constant methane pressure. The change in mass spectrometer response expressed as μm of methane per mv ($(m/z)=15$) is shown in Figure 5 as a function of hydrogen pressure in the cell. The quantity s, which is inversely proportional to the mass spectrometer sensitivity, is observed to decrease with increased hydrogen pressure. This sensitivity change is routinely seen in systems which have a high pressure volume connected to the mass spectrometer via a leak or capillary tube. The cause of this effect has been discussed by Masterson [61]. Ion/molecule interactions might also be involved.

Initial rates were measured in all cases. In general all rates were determined within the first 60 seconds after the initiation of the reaction. After a rate was determined, the reaction cell was pumped through the manifold. When the pressure dropped below 10^{-4} torr as measured by the more sensitive capacitance manometer, 3.5 torr of hydrogen (standard hydrogen dose) was dosed into the reaction cell which was at the reaction temperature, usually 573K. This hydrogen dose had the effect of removing any reactive carbon left on the surface from the previous run so that the initial catalyst surface was regenerated for the next run. It was observed that the amount of methane produced during this standard hydrogen dose depended upon not

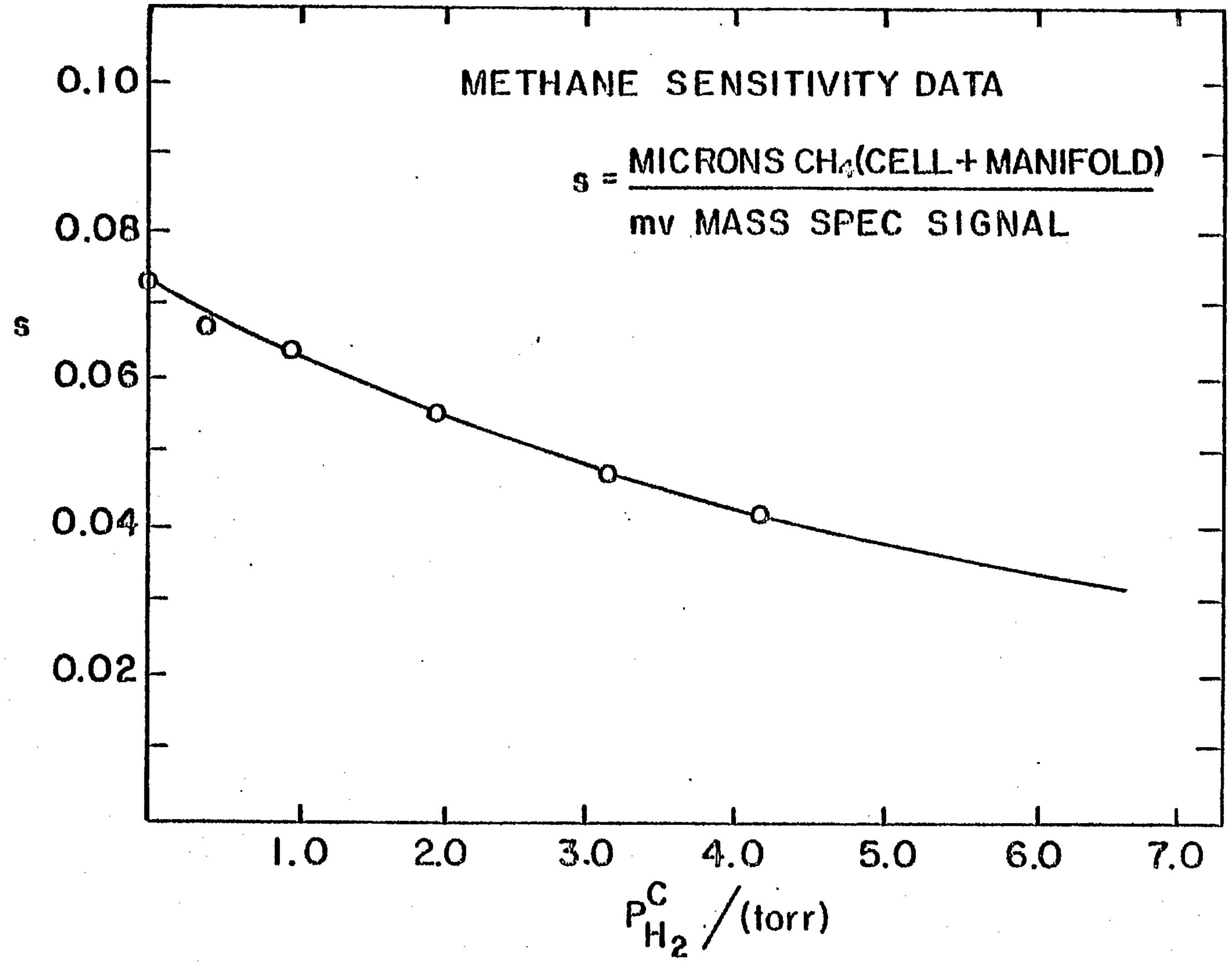

Figure 5. Variation in mass spectrometer response ((m/z)=15) as a function of the pressure of hydrogen in the reaction cell.

only the amounts of carbon monoxide and hydrogen present in the previous kinetic run but also upon the length of time that the reaction cell had been pumped prior to the standard hydrogen dose. This observation will be discussed in more detail in a subsequent section.

Experiments were performed to measure the reaction order with respect to carbon monoxide, hydrogen, water and methane. All of these studies were conducted using the techniques summarized earlier. Calibration rates were always run with each set of data to allow the absolute comparison of data from day to day. When not in use the films were stored in 3.5 torr of hydrogen at room temperature. All rates are reported as turnover numbers (molecules of methane/site·s). This rate is explicitly independent of the catalyst surface area and allows a more direct comparison of the data to literature values obtained under similar conditions.

Studies of the exchange rates of $^{13}C^{18}O$ and $^{12}C^{16}O$ as well as hydrogen and deuterium were performed on the ruthenium thin films at 573K.

Surface Pretreatment Studies

Several experiments were performed to determine the dependence of rate on several kinds of surface pretreatment. Prior to a kinetic run, the surface was predosed with carbon monoxide. The disproportionation reaction (6) occurred, leaving a carbon deposit on the surface. The disproportionation reaction was allowed to proceed for different lengths of time producing different fractional coverages by carbon. The effect of this carbon overlayer upon the kinetics of the methanation reaction was then determined. Studies were also made to attempt to establish the effect of predosing the catalyst with $^{13}C^{18}O$. The mass spectrum was carefully analyzed to see if $^{13}CH_4$ or $^{12}CH_4$ was produced first when the isotopic predose was followed by a kinetic run. The effect of removing the standard hydrogen dose from the kinetic studies was also determined.

Flash Desorption Studies

A few flash desorption experiments were conducted to elucidate the bonding of carbon monoxide to a polycrystalline ruthenium surface. A flash desorption cell was mounted in the position of cell two on the system. A diagram of the flash cell is shown in Figure 6. The cell was constructed entirely of pyrex. A polycrystalline ruthenium disc was spotwelded to a 40 mil support rod. The geometric surface area of the disc was approximately 1 cm^2. A nearby thoria coated iridium filament supplied electrons so that the sample could be heated by electron bombardment. A thermocouple was spotwelded to the disc for temperature measurement. The thermocouple wires were 3 mil W/5%Re, W/26%Re (Hoskins Manufacturing Co., Detroit, Michigan). Two pyrex faceplates were positioned parallel to the faces of the ruthenium disc. This enabled the disc to be heated using a well-focused light beam. Heating by light was chosen over heating by electron bombardment for the flash studies because the latter technique would very likely produce results indicative of the adsorbate-electron interaction rather

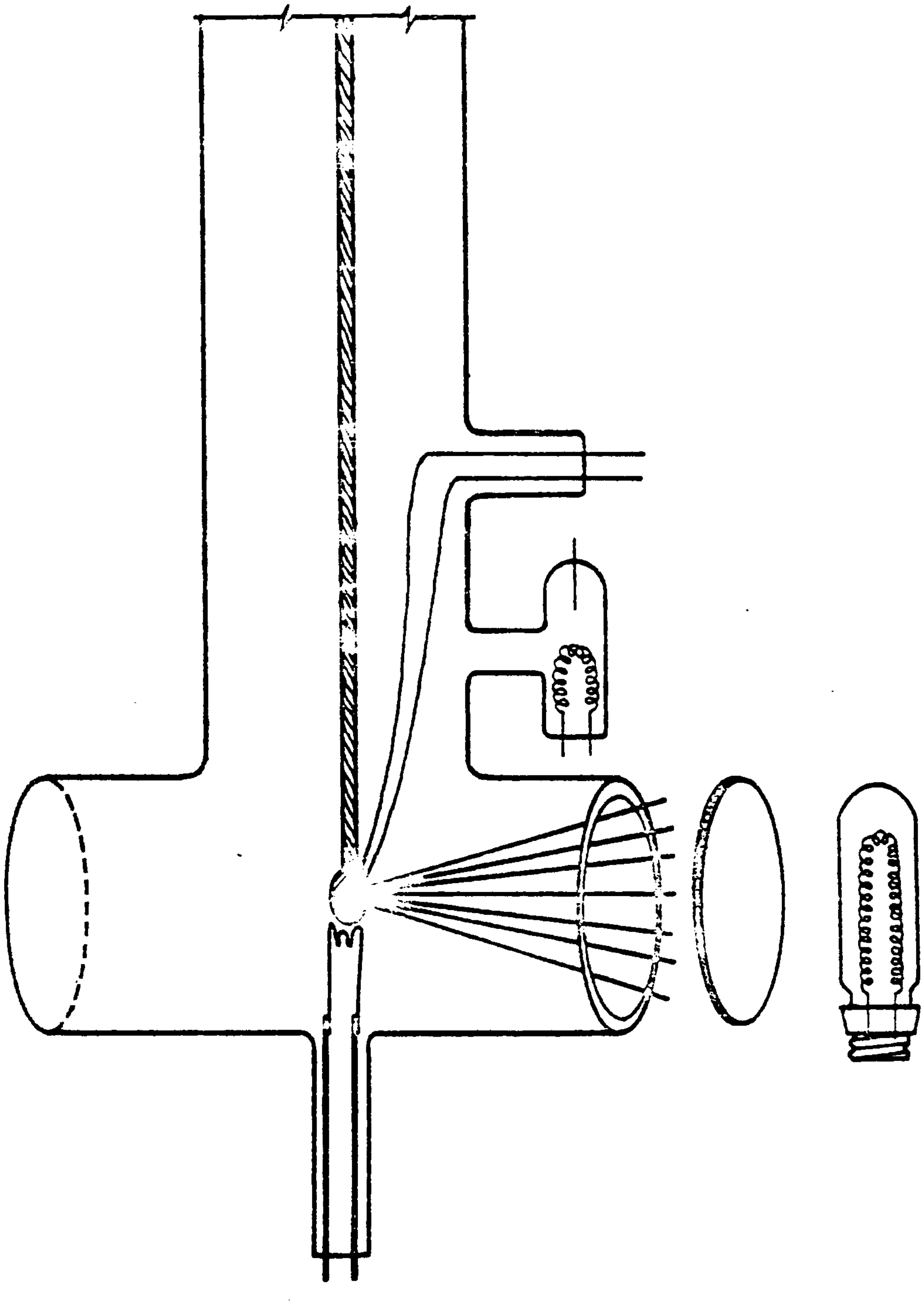

Figure 6. Diagram of the flash desorption cell showing the disc being heated by a well-focused beam of light.

than the adsorbate-substrate interaction. A 1000 watt projector bulb was used to produce a well-focused light beam which could heat the crystal linearly from room temperature to 723K in 30 seconds. The light could be used to heat the crystal to a maximum temperature of 973K.

The disc was cleaned by heating for several days at 1173K using electron bombardment. Several 1×10^{-6} torr oxygen and hydrogen cleaning cycles followed. The oxygen was effective in removing phosphorus and sulfur. The hydrogen removed any remaining oxygen. Flashing to 1773K removed any remaining surface carbon. The experiments were performed by dosing carbon monoxide into the pumped cell with the disc at room temperature (300K). The dose was measured with an gauge attached to the cell and was expressed as Langmuirs (1 Langmuir= 1×10^{-6} torr·s). The dose was stopped and the remaining carbon monoxide was pumped out. The flash was begun by turning on the light. The desorbed gas was monitored on the ion gauge and the mass spectrometer. The output of both the ion gauge and the thermocouple were directed onto two X-Y recorders (Hewlett-Packard, model 7044A, Palo Alto, Ca.) so that a temperature could be assigned to the peak maximum.

Surface Characterization Studies

LEED, Auger and ESCA studies were performed under a variety of conditions to characterize the ruthenium surface before, during and after the methanation reaction had occurred. LEED can be used to predict the symmetry of any ordered adlayer relative to the symmetry of the substrate. Auger electron spectroscopy establishes which atoms are present on the surface and in the first five or so layers of the bulk. ESCA is useful in predicting the sorts of bonding involved between the metal and the adsorbed species. Excellent reviews of the theory and application of LEED [62], Auger [63] and ESCA [64-68] are available.

The LEED/Auger experiments were performed in a Varian 981-2000 vacuum system with 4 grid LEED optics and cylindrical mirror Auger electronics. The system was bakeable to 623K and operated at a base pressure of 2×10^{-10} torr. A circular polycrystalline ruthenium disc was used for the Auger work. The disc had a diameter of 0.6 cm. and a thickness of 0.1 cm. The disc was polished with silicon carbide covered paper. A polished ruthenium $(10\bar{1}2)$ crystal was used for the LEED study. The crystals were mounted to an offset manipulator with movement in the x, y and z directions. A W/5%Re, W/26%Re thermocouple was spotwelded to the face of the disc to permit temperature measurement. The sample was heated by an indirect heater block. The maximum temperature was 1500K. The discs could be flashed to 1400K in 60 seconds. All Auger spectra were run with 10 μa. emission to the sample at a beam energy of 2000 eV. It is predicted that with this fairly low emission only 5 to 10 layers were being sampled. A scan width of 50 to 550 eV was usually used with a 1.67 $\mathrm{eV{\cdot}s^{-1}}$ scan speed. Studies were made to develop an understanding of the interaction of ruthenium with carbon monoxide and hydrogen as well as to characterize the catalyst before and after methanation.

Gases were dosed into the Auger system from a gas handling system through a Granville Phillips leak valve. When carbon monoxide-hydrogen mixtures were dosed, the mixing was done in the gas manifold prior to actual dosing. The manifold pressure was measured with a mercury manometer which could be valved off when not in use. During all doses the poppet valve was closed to prevent flooding of the ion pumps. At the end of each experiment the gases were roughed out with the VacSorb pumps. High vacuum (10^{-8} torr range) was restored in 3 to 5 minutes by opening the poppet valve to the ion pumps. All Auger studies were performed with the catalyst at 573K unless otherwise noted. The Auger spectrometer was also used routinely to characterize the purity of thin films that were removed form the kinetic system.

One result that was immediately evident from the Auger work was that a ruthenium catalyst exposed to carbon monoxide and hydrogen always had carbon associated with it under the conditions of the kinetic studies. An attempt was made to use ESCA and LEED to characterize further this carbon. After the Auger studies were completed the polycrystalline ruthenium sample was placed in an AEI model ES 100B XPS/UPS spectrometer (Associated Electronics Industries, Westwood, New Jersey). The Al K_{α} line (1486.6 eV) was used as an energy source for the XPS work. An attempt was made to determine whether the carbon had formed graphite. Some XPS studies were also made to further characterize the interaction of polycrystalline ruthenium with carbon monoxide and with methanol. These studies involved low pressure doses of each adsorbate onto clean ruthenium.

A LEED study was undertaken to see if the carbon left on the catalyst surface after methanation formed an ordered overlayer with respect to the ruthenium substrate. A ruthenium $(10\bar{1}2)$ crystal was used in this study. The crystal was cleaned and then exposed to carbon monoxide and hydrogen at 573K so that methanation would occur. LEED patterns were taken before and after methanation. Presumably, if graphite had formed, the LEED pattern should show a hexagonal structure characteristic of graphite.

Materials

Most of the gases used in the kinetic and isotopic studies were research grade ultra-high purity gases. The hydrogen (99.9995%), carbon monoxide (99.97%), methane (99.99%), argon (99.9995%) and carbon dioxide (99.998%) were purchased from the Linde division of Union Carbide (Chicago, Ill.) The deuterium (99.99%) was purchased from Air Products and Chemicals, Inc. (Los Angeles, Ca.). The $^{13}C^{18}O$ (90% C, 95% O) was purchased from Prochem Isotopes (Summit, New Jersey). All of these gases were purchased in pyrex bulbs with breakable seals. The water was doubly distilled tap water which was further distilled several times under vacuum. The water was boiled while under vacuum to remove any dissolved gases. A mass spectral analysis indicated that there were no detectable impurities in the water.

The hydrogen used in the LEED/Auger studies was taken from a cylinder and purified by passing through a Pd/25% Ag diffuser. The methanol used in the XPS study was spectral quality distilled in glass

(Burdick & Jackson Laboratories, Inc., Muskegon, Mi.). This was distilled in vacuum several times before using. All other gases used in the LEED/Auger and ESCA studies were identical to those used in the kinetic studies.