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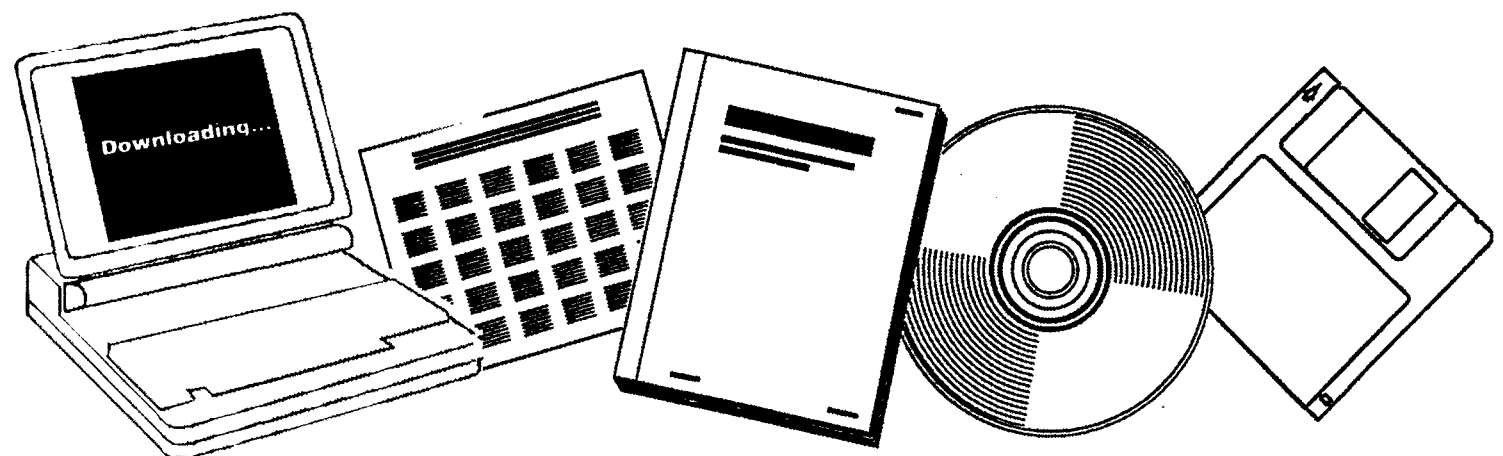
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**ALLOY CATALYSTS WITH MONOLITH SUPPORTS FOR
METHANATION OF COAL-DERIVED GASES. PHASE
I. QUARTERLY TECHNICAL REPORT, APRIL
22--JULY 22, 1975**

BRIGHAM YOUNG UNIV., PROVO, UTAH

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ALLOY CATALYSTS WITH MONOLITH SUPPORTS FOR
METHANATION OF COAL-DERIVED GASES

Phase 1

Quarterly Technical Progress Report
For Period April 22-July 22, 1975

Calvin H. Bartholomew

BRIGHAM YOUNG UNIVERSITY
Provo, Utah 84602

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FOREWORD

This report summarizes technical progress during the first quarter period (April 22, 1975 to July 22, 1975) of a two-year study conducted for the Energy Research and Development Administration (ERDA) under Contract No. E(49-18)-1790. The principal investigator for this work is Dr. Calvin H. Bartholomew; Dr. Paul Scott is the technical representative for ERDA.

The following students contributed to the technical accomplishments and to this report: Graduates - Kyung Sup Chung, Blaine Barton, Don Stowell and Undergraduates - Norman Shipp, Eldon Larsen, Ray Eelsing, and Scott Engstrom.

Mr. Bruno Szalkowski, glassblower, rendered assistance in design and construction of vacuum, reduction, and poisoning systems; Mr. James Hoen, supervisor of the Research Machine Shop, assisted in the design and construction of the reactor and vaporizer. Michael King, Mary Jo F. Schaub and Scott Folster provided typing and drafting services.

TABLE OF CONTENTS

	Page
DISCLAIMER	ii
FOREWORD	iii
LIST OF TABLES	v
LIST OF FIGURES	vi
ABSTRACT	1
I. OBJECTIVES AND SCOPE	2
A. Background	2
B. Objectives	2
C. Technical Approach	3
II. SUMMARY OF PROGRESS	5
III. DETAILED DESCRIPTION OF PROGRESS	7
A. Task 1: Catalyst Preparation and Characterization	7
B. Task 2: Laboratory Reactor Construction	43
C. Task 3: Reactor Screening of Alloy Catalysts	55
D. Task 4: Catalyst Geometry Testing and Design	62
E. Task 5: Technical Visits and Communication	62
IV. CONCLUSIONS	64
V. REFERENCES	65
APPENDICES	67
A. Calculation of Surface Area and Dispersion	68
B. Report Distribution List	73
C. NTIS Bibliographic Data Sheet	74

LIST OF TABLES

Table	Page
1. General Catalyst Preparation Scheme	8
2. Preparation of Alumina-Supported Nickel and Nickel-Alloy Catalysts	9
3. Standard Procedure for Measuring H ₂ Uptake of Nickel Catalysts	16
4. Procedure for Measuring CO Uptake of Nickel Catalysts	17
5. H ₂ Uptake Data (Two Different Reduction Systems)	19
6. H ₂ Chemisorption Data for Alumina-Supported Ni-Ru Catalysts	26
7. CO Chemisorption Data for Ni-A-111	27
8. CO and H ₂ Chemisorption Data for Alumina	33
9. The Effect of H ₂ S Poisoning (450°C) on H ₂ Uptake (25°C)	36
10. Equipment and Materials on Order for Reactor System	46
11. Reactor Test Data Sheet	58
12. Steady-State Activity Data for Nickel and Nickel Alloy Catalysts	59

LIST OF FIGURES

Figure	Page
1. Project Progress Summary	6
2. Volumetric Chemisorption Apparatus	12
3. Chemisorption Sample Cell	14
4. Poisoning Apparatus	15
5. H ₂ Chemisorption on Ni-A-111 at 25°C	20
6. H ₂ Chemisorption on Ni-Ru-A-105 at 25°C	21
7. H ₂ Chemisorption on Ni-Rh-A-100 at 25°C	22
8. H ₂ Chemisorption on Ni-MoO ₃ -A-101 at 25°C	23
9. H ₂ Chemisorption on 0.5% Ru/Al ₂ O ₃ (Engelhard) at 25°C	24
10. CO Chemisorption on Ni-A-111 at -83°C	30
11. Effect of CO Exposure (25°C) on H ₂ Chemisorption for Ni-A-111	31
12. CO Adsorption on Kaiser SAS, Al ₂ O ₃ Beads at 25°C	34
13. CO Chemisorption on Kaiser SAS Al ₂ O ₃ Beads at -84°C	35
14. Poisoning of Ni-MoO ₃ -A-101 with 10 ppm H ₂ S	37
15. Reduction and Passivation System	39
16. New Chemisorption-Vacuum System--Chemisorption Side	41
17. New Chemisorption-Vacuum System--Vacuum Side	42
18. Low Pressure Continuous Flow Reactor System for Methanation Studies	44
19. Proposed High Pressure Laboratory Reactor	45
20. High Pressure H ₂ O Vaporizer	49
21. High Pressure Stainless Steel Reactor for Catalyst Testing	50
22. Concentration - Time Relation for the Gas Concentration Dilution Technique	52

Figure	Page
23. Dilution Calibration Apparatus	53
24. Stirrer for Dilution Calibration Apparatus	54
25. Stainless Steel Catalyst Reactor (0-60 psig operation)	57
26. Integral Activity Test for Ni-A-114 (15% Ni/Al ₂ O ₃)	61

ABSTRACT

This report presents work accomplished during the first quarter of investigation of new pellet- and monolithic-supported alloy catalysts for methanation of coal synthesis gas. Alumina-supported nickel and nickel alloys were prepared, characterized by surface area measurements, and tested for methanation catalyst activity. To determine effects of sulfur poisoning on surface area, the adsorption of hydrogen on these catalysts was measured before and after exposure to hydrogen sulfide. A procedure for measuring adsorption of carbon monoxide on nickel underwent extensive testing and evaluation. In addition, screening and testing procedures to measure methanation catalyst activity were designed and tested. Preparation, adsorption, poisoning and analytical calibration systems were designed, constructed, and tested. Design of a high pressure laboratory reactor was completed and the associated equipment and supplies ordered.

I. OBJECTIVES AND SCOPE

A. Background

Natural gas is a highly desirable fuel because of its high heating value and nonpolluting combustion products. In view of the expanding demand for and depletion of domestic supplies of clean fuels, economical production of synthetic natural gas (SNG) from coal ranks high on the list of national priorities.

Presently there are several gasification processes under development directed toward the production of methane or SNG. Although catalytic methanation of coal synthesis gas is an important cost item in the process, basic technological and design principles for this step are not well advanced. Extensive research and development are needed before the process can realize economical, reliable operation. Specifically, there appears to be important economical advantages in the development of more efficient, stable catalysts.

An extensive general review of the pertinent literature dealing with methanation catalysts was reported in the proposal, including reviews by Greyson¹ and Mills and Steffgen.² From the literature three major catalyst problems are apparent which relate to stability: (1) sulfur poisoning, (2) carbon deposition with associated plugging, and (3) sintering. These problems have received at best only modest attention. There has been very little research dealing with alloy catalysts for methanation, and there are no published investigations of the effects of catalyst support geometry on catalyst performance. This study deals specifically with sulfur poisoning, carbon deposition, and the effects of support (monolith and pellet) geometry on the performance of alloy methanation catalysts.

B. Objectives

The general objectives of this research program are (1) to study nickel and ruthenium alloy catalysts in the search for catalysts resistant to poisoning and carbon deposition and (2) to investigate the effects on catalytic efficiency of support (monolith and pellet) geometry. The work has been divided into five tasks to be completed over a period of two years:

Task 1. Prepare pellet- and monolithic-supported nickel and ruthenium alloy methanation catalysts by impregnation with metal salts of nickel, ruthenium, iron, platinum, etc. followed by reduction in hydrogen. Hydrogen and carbon monoxide chemisorption uptakes will be measured before and after exposure to hydrogen sulfide. Metallic phases of these catalysts will be examined by x-ray diffraction for chemical composition and particle size.

Task 2. Design and construct a continuous flow laboratory reactor system capable of 25-1000°C and 1-25 atm. to be used for screening methanation catalysts and investigating effects of sulfur poisoning on methanation activity.

Task 3. Screen catalysts prepared in Task 1 using a reactor system constructed in Task 2 to determine methanation catalyst activity at various time exposures to 10 ppm H₂S.

Task 4. The most promising catalysts based on the results of Tasks 1 and 3 will be compared for steady-state catalytic activity on different pellet and monolith supports of different hole sizes and geometries under various operating conditions, i.e., temperature, pressure, H₂/CO ratio and H₂S level.

Task 5. Close liaison shall be maintained with organizations doing similar research such as the Bureau of Mines, Bituminous Coal Research, Institute of Gas Technology, and others.

C. Technical Approach

The technical approach which will be used to accomplish the tasks outlined above is presented in the revised proposal dated May 17, 1974. The main features of that approach are reviewed here along with more specific details and modifications which have evolved as a result of progress in related research over the past year. It is expected that various other aspects of this approach will be modified and improved as the project develops and as new data are made available. Nevertheless, the objectives, tasks and principle features of the approach will remain substantially the same.

Task 1: Catalyst preparation and characterization. Alumina pellets and extruded monolithic ceramic supports (provided by Corning Glass Works) coated with high surface area alumina will be impregnated with nickel nitrate and an alloying metal salt. Metals which will be alloyed with nickel include cobalt, iron, molybdenum, rhodium, ruthenium, platinum, and palladium. Ruthenium will be used in combination with nickel, iron, and palladium. Approximately equimolar quantities of base metals will be used in combination with nickel. Only very small amounts of noble metal will be used in combination with nickel or other base metals. Catalyst samples will be dried in vacuum at 70-100°C, reduced at 500°C in flowing hydrogen, and carefully passivated with 1% air in preparation for further testing. A dedicated reduction apparatus will be used to reduce and passivate large batches of pellets and monolithic catalysts. Alloy catalysts will be initially prepared in pellet form for chemisorption, x-ray diffraction, and reactor screening measurements. Only the more promising catalysts will be prepared in monolithic form.

Hydrogen and carbon monoxide chemisorption uptakes will be measured using a conventional volumetric apparatus before and after exposure of each catalyst to hydrogen sulfide. Catalysts will be exposed to 10 ppm H₂S over a period of several hours in a dedicated poisoning apparatus. X-ray diffraction measurements will be carried out to determine the active metallic phases and metal crystallite size where possible. Selected "aged" samples from Task 4 will be analyzed (by x-ray and perhaps ESCA) to determine carbon content and possible changes in phase composition or particle size. More extensive study of

catalyst sintering or thermal degradation will be undertaken as part of a separate study supported by NSF and perhaps as an extension of this work, but is not intended to be within the scope of this two-year study.

Task 2: Laboratory reactor construction. It was initially proposed to construct a combination pulse-continuous flow reactor system for catalyst screening and testing. This apparatus was in fact constructed during the past year as part of a previous methanation study supported by Corning Glass Works and Brigham Young University. The combination was found to be unworkable--unsatisfactory for pulse operation because of pulse broadening in the reactor and for continuous-flow operation due to high flow resistance in the small diameter tubing and sample valve. The reactor system was later modified for continuous-flow operation and collection of steady-state activity data, which were found to be more useful, realistic indicators of catalyst performance than the unsteady-state pulse measurements. Our continuous-flow reactor system, presently capable of 0-60 psig, will be modified for operation to 400 psig and significantly upgraded to enable convenient study of activity as a function of temperature, pressure, and feed composition.

Task 3: Reactor screening of alloy catalysts. Catalyst samples will be screened on the basis of steady-state methanation activity (reaction rate based upon catalyst surface area) measured in a differential flow reactor at atmospheric pressure and 250 or 275°C at a fixed H₂/CO ratio of 3.5-4.0. Samples to be screened will include freshly-reduced catalysts and catalyst samples exposed in a separate poisoning system to 10 ppm H₂S over a period of 6-18 hours.

Task 4: Catalyst geometry testing and design. The most promising catalysts based on the results of screening will be tested for activity and conversion as a function of pressure, temperature, H₂/CO ratio, and H₂S concentration. The conversion of carbon monoxide to methane as a function of temperature will be determined for various pellet and monolith geometries at both high and low pressures. The effects of water addition to the feed stream will also be investigated. Conversion of carbon monoxide to methane during *in situ* exposure to low levels of hydrogen sulfide and at low H₂/CO ratios will be used as a measure of stability toward sulfur poisoning and carbon deposition. A comparison of steady-state conversions at given temperature and pressure conditions for monolithic supports of different hole sizes and geometries will be used to optimize the geometry of the catalyst support.

Task 5: Technical visits and communication. Visits to other methanation laboratories such as the Bureau of Mines and the Institute of Gas Technology are planned. Close communication with other researchers working in methanation catalysis both in industrial and academic locations is also planned. The principal investigator will attend coal and catalysis meetings regularly to communicate with other workers regarding methanation catalysis.

II. SUMMARY OF PROGRESS

A project progress summary is presented in Figure 1 and accomplishments during the past quarter are summarized below. Figure 1 shows that task accomplishments are either on or ahead of schedule. Particularly Task 2, Construction of Reactor System, and Task 3, Catalyst Screening, are well ahead of schedule. This is not unexpected, however, since our previous studies have given us a head start; moreover, our research efforts are in full swing during summer compared to part-time during Fall and Winter.

Accomplishments during the last quarter are best summarized according to task:

Task 1. Alumina-supported Ni, Ni-Ru, Ni-Rh, Ni-MoO₃, Ni-Fe, Ni-Co, Ni-Pt, and Ni-Pd catalysts were prepared in pellet form by impregnation, drying and reduction in hydrogen. Hydrogen adsorption uptakes were measured for Ni, Ni-Ru, Ni-Rh, and Ni-MoO₃ catalysts before and after exposure to 10 ppm H₂S in hydrogen. A method for measuring CO adsorption on nickel was tested extensively on a 3% Ni/Al₂O₃. A catalyst reduction system, a poisoning apparatus, and a new chemisorption-vacuum system were designed, constructed and tested.

Task 2. An atmospheric laboratory reactor used for catalyst testing was redesigned to (1) allow for operation to 400 psia (2) enable more efficient, reproducible operation by addition of mass flow meters, a better furnace with temperature programming, etc. and (3) improve the accuracy of gas phase analysis by addition of analytical equipment and accessories. The associated equipment and supplies for the new system were ordered. A dilution-calibration apparatus was designed and built to be used in preparation of gas calibration standards.

Task 3. Catalyst screening and testing procedures were designed and refined to give rapid, useful comparisons of methanation activity under steady state conditions. In addition, procedures for data collection and reduction were designed and tested. Screening measurements of steady state activity at 275°C were carried out for alumina-supported Ni, Ni-Ru, and Ni-Rh catalysts. Conversion as a function of temperature and the effect of passivation on activity were studied on a 15 wt.% Ni/Al₂O₃ catalyst.

Task 4. Work is scheduled to begin October 22, 1976.

Task 5. The principal investigator has established technical communications with other workers in methanation catalysis. He also attended the Symposium on Catalytic Conversion of Coal held April 21-23 in Pittsburgh.

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Work Statement

- a. Catalyst Preparation
- b. Catalyst Characterization
- c. Lab Reactor Construction
- d. Catalyst Screening
- e. Catalyst Testing and Design
- f. Visits and Technical Communication

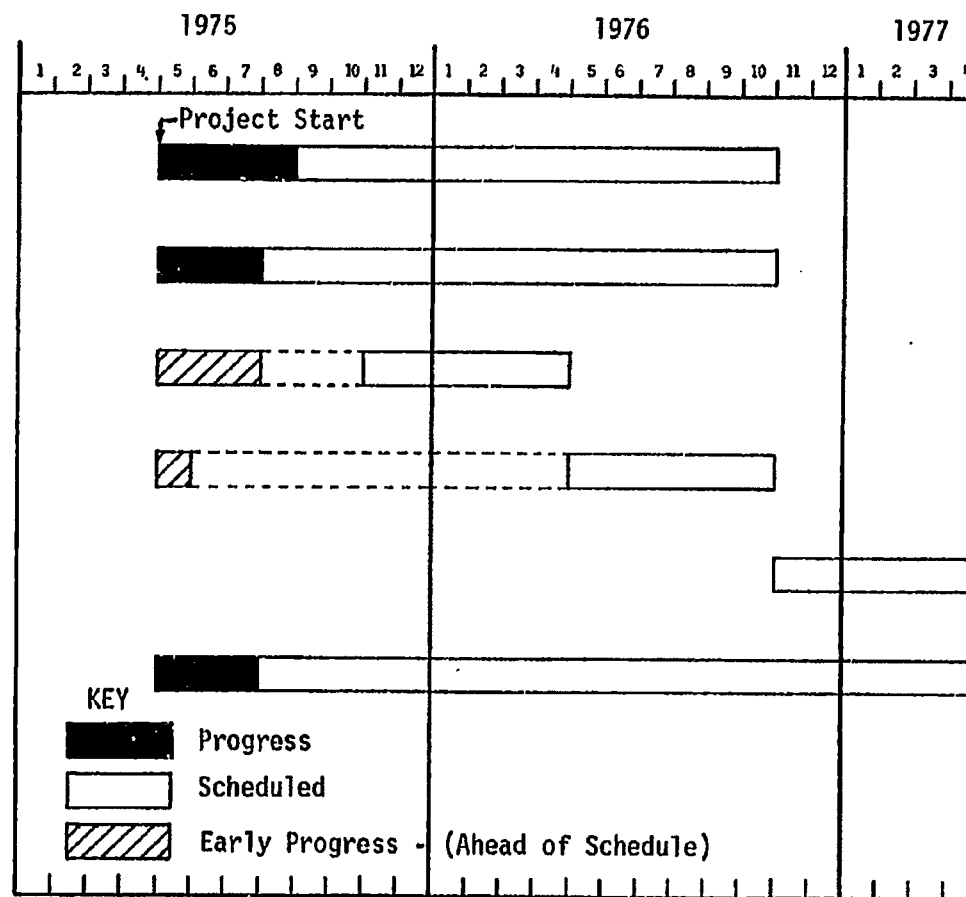


Figure 1. Project Progress Summary

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 1: Catalyst Preparation and Characterization

1. Catalyst preparation. It is well known that subtle differences in preparation techniques or in drying and reduction schedules may affect significantly the ultimate catalytic properties for a given catalyst sample. During the past year the principal investigator has studied the effects of different preparation variables on catalytic surface area for alumina-supported nickel catalysts.³ The results of this study indicate that (1) carefully controlled decomposition of alumina-supported nickel nitrate (at low heating rates) in pure hydrogen results in extensive but not complete reduction to the metal and ensures maximum nickel area, (2) calcination in air at high temperatures prior to reduction results in lower reducibility and metal surface area, (3) a slow heating rate in reduction of alumina-supported nickel nitrate prevents exothermic temperature excursions which might badly sinter the catalyst.

Based on the results of this previous study³ and upon experience in this laboratory over the past year, a general preparation scheme has been developed which has been used in preparation of catalysts in this study. This general preparation scheme is outlined in Table 1; a summary of catalysts prepared during the past quarter is shown in Table 2. Preparation of Ni-A-111 and all but two of the Ni-Ru catalysts was initiated as part of the earlier study just one or two months previous to the start of this contract work. Particular details and modifications to the general preparation scheme are discussed below for each catalyst. Small catalyst samples (less than 20g) were reduced in a special cell described in Section III-A-2 and large samples (50-500g) in a large combustion tube described in Section III-A-3 of this report.

Kaiser SAS 5 x 8 mesh alumina ($301 \text{ m}^2/\text{g}$) was used in all the preparations discussed below, and in each case, the beads were calcined at 600°C for 2.0 hrs. prior to impregnation. All nickel-ruthenium catalysts were prepared by transferring the impregnation solution from a pipet slowly on to the beads; however, the remaining samples were impregnated by stirring the beads while adding the impregnation solution. It is felt the latter approach gives more uniform coverage and less attrition of the support. After impregnation to incipient wetness, the catalysts were dried at $75\text{-}100^\circ\text{C}$ in a forced-air-circulation oven for at least 24 hours. Where more than one impregnation was desired, the beads were dried at $75\text{-}100^\circ\text{C}$ for at least 4 hours prior to the next impregnation. A vacuum oven was used for secondary drying in the more recent preparation of large catalyst batches.

Using the general procedure outlined in Table 1, the Ni-A-111 sample was prepared by two impregnations using an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The Ni-Ru-A-100, Ni-Ru-A-103, and Ni-Ru-A-104 samples were all prepared by impregnation of the pretreated support with an

TABLE 1
General Catalyst Preparation Scheme

Step	Procedure
Drying	<p>Samples are dried:</p> <ol style="list-style-type: none"> 1. In a forced-circulating-air oven at 80-100°C for 24 hours. 2. In a vacuum oven, 100-115°C for 12-24 hours
Reduction	<p>Sample is purged in flowing N₂ or evacuated to 5x10⁻⁴ Torr at 120-150°C. Reduction in flowing hydrogen (700-2000 GHSV) is according to the following temperature schedule:</p> <ul style="list-style-type: none"> • 0-230°C at less than 5°C/min • 230°C hold for 1 hour • 230-450°C or 230-500°C at less than 5°C/min • 450-500°C hold for 10-16 hours
Passivation	<p>Sample is exposed to a stream or doses of less than 1% air in nitrogen or helium over a period of 15 to 20 minutes. The concentration of air is then gradually increased to 100%.</p>

TABLE 2

Preparation of Alumina-Supported
Nickel and Nickel-Alloy Catalysts

Catalyst	Code	Weight	Composition (wt.%)	Preparation
Ni/Al ₂ O ₃	Ni-A-111	500g	3.0% Ni	2 impregnations
Ni-Ru/Al ₂ O ₃	Ni-Ru-A-100	20g	2.5% Ni .5% Ru	acidic 1 impreg.
Ni-Ru/Al ₂ O ₃	Ni-Ru-A-101	20g	2.5% Ni .5% Ru	ion exchange
Ni-Ru/Al ₂ O ₃	Ni-Ru-A-102	20g	2.5% Ni .5% Ru	basic 2 impreg.
Ni-Ru/Al ₂ O ₃	Ni-Ru-A-103	20g	2.5% Ni .5% Ru	Same as Ni-Ru-A-100
Ni-Ru/Al ₂ O ₃	Ni-Ru-A-104	150g	2.5% Ni .5% Ru	acidic 1 impreg.
Ni-Ru/Al ₂ O ₃	Ni-Ru-A-105	150g	2.5% Ni .5% Ru	basic 2 impreg.
Ni-Ru/La/Al ₂ O ₃	Ni-Ru-La-A-100	20g	2.5% Ni .5% Ru 3.0% La	basic 2 impreg.
Ni-Ru/La/Al ₂ O ₃	Ni-Ru-La-A-101	20g	2.5% Ni .5% Ru 3.0% La	acidic 1 impreg.
Ni-Rh/Al ₂ O ₃	Ni-Rh-A-100	70g	2.5% Ni .5% Rh	acidic 2 impreg.
Ni-MoO ₃ /Al ₂ O ₃	Ni-MoO ₃ -A-101	200g	2.5% Ni 3.0 MoO ₃	basic 5 impreg.
Ni-Fe/Al ₂ O ₃	Ni-Fe-A-100	100g	10% Ni 10% Fe	acidic 3 impreg. Incipient wetness
Ni-Co/Al ₂ O ₃	Ni-Co-A-100	100g	10% Ni 10% Co	neutral 2 impreg.

TABLE 2 Continued

Catalyst	Code	Weight	Composition (wt.%)	Preparation
Ni-Pt/Al ₂ O ₃	Ni-Pt-A-100	100g	15% Ni 0.5% Pt	slightly acidic 2 impreg.
Ni-Pd/Al ₂ O ₃	Ni-Pd-A-100	100g	15% Ni 1% Pd	acidic 2 impreg.

acidic solution of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The impregnation solution was acidified ($\text{pH} = 3$ with HCl) to prevent hydrolysis of the RuCl_3 . A ruthenium solution for the basic impregnations was prepared by the addition of the acidic RuCl_3 solution to a 4:1 mixture of H_2O - NH_4OH which was heated overnight at 80°C . After the RuCl_3 had complexed $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added with additional NH_4OH to complex the nickel. The ion-exchanged-sample, Ni-Ru-A-101, was prepared by quickly pouring in enough ammoniacal ruthenium solution to cover the beads; after which the sample was equilibrated 2 days, the excess solution decanted off, and the sample dried at 75°C . The Ni-Ru-A-102 and Ni-Ru-A-105 samples were prepared by impregnation to incipient wetness using an ammoniacal solution similar to that used in the ion exchange preparation.

The lanthanum promoted catalysts, Ni-Ru-La-A-100 and Ni-Ru-La-A-101, were prepared by first impregnating the support with $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (stabilized with HCl to $\text{pH} = 3$) and calcining at 600°C for 2 hrs.; thereafter, the samples were impregnated using basic and acidic solutions as in the preparations described above.

It was observed that in the samples prepared by basic impregnation a uniform distribution of catalyst was obtained throughout each pellet; whereas, samples made using acidic impregnations were found to have a thin shell of catalyst on the outside of each pellet. Hence, it appears that the acidic impregnation results in a catalyst more suitable for mass transfer limited applications while the basic impregnation would be more suited to kinetically limited conditions.

The Ni-Rh-A-100 catalyst was prepared by double impregnation of support with a pH adjusted (HCl) solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Some difficulty was encountered initially in the preparation of Ni-MoO₃-A-100 due to solubility problems, but it was discovered later that the $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was soluble in conc. NH_4OH . Because a number of different acids and bases were added to the initial impregnation solution (Ni-MoO₃-A-100), a new sample, Ni-MoO₃-A-101, was prepared using conc. NH_4OH as the impregnation medium.

Ni-Fe-A-100 and Ni-Co-A-100 were prepared by multiple impregnation of solutions prepared from the hydrated nitrate salts. The pH of the nickel-iron solution was adjusted to prevent iron hydroxide formation. Ni-Pt-A-100 and Ni-Pd-A-100 were prepared by double impregnation using solutions of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{H}_2\text{PtCl}_6 \cdot 9\text{H}_2\text{O}$, and PdCl_2 . One ml each of HNO_3 and HCl was added to 170 ml H_2O to dissolve the PdCl_2 and the solution was stirred overnight.

2. Hydrogen and Carbon Monoxide Chemisorption on Nickel and Nickel Alloys and Effects of Hydrogen Sulfide on Adsorption.

a. Equipment and materials. Gas adsorption measurements were carried out in a conventional Pyrex glass volumetric adsorption apparatus (see Fig. 2) capable of 10^{-6} Torr vacuum, which consisted of an oil diffusion pump and a rotary mechanical pump isolated from the adsorption system by a liquid-nitrogen cooled trap. The pressure was measured with

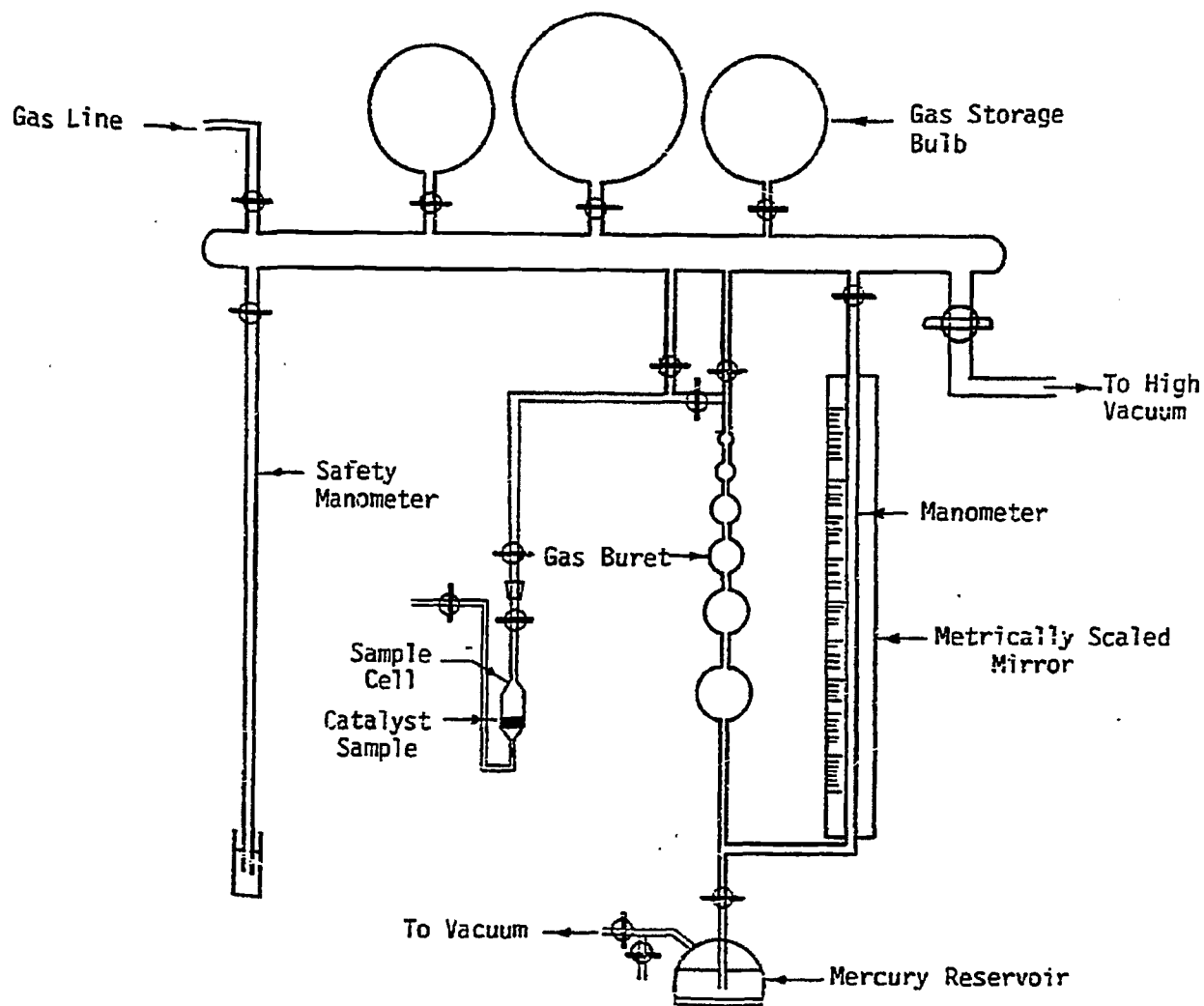


Figure 2. Volumetric Chemisorption Apparatus

a Phillips cold cathode gauge. Each catalyst sample was placed in a Pyrex flow-through cell (Fig. 3) to enable reduction of samples in flowing hydrogen prior to the chemisorption measurement. The amount of gas adsorbed by the catalyst was determined by means of a calibrated gas buret connected to a manometer backed with a metrically-calibrated mirror (see Fig. 2).

In principle it is possible to use the same chemisorption-vacuum system for controlled, *in situ* exposure of catalyst samples to H_2S . However, in practice, there were difficulties encountered with contamination of the system, adsorption in the molecular sieve trap, and significant variations in the flow of the H_2S stream. To avoid these difficulties a separate poisoning apparatus was constructed according to the design sketched in Figure 4.

b. Catalyst pretreatment and procedure. All catalyst samples were prepared in accordance with the general scheme shown in Table 1. Most of the samples used in adsorption measurements were reduced *in situ* using a sample cell of the design shown in Figure 3. Samples pre-reduced and passivated in the large reduction apparatus (Section III-A-3) were again reduced in flowing hydrogen for a minimum of 2 hours at $450^\circ C$ prior to adsorption measurements.

The standard procedure used in measuring hydrogen adsorption uptake is presented in Table 3 and is based upon surveys of the literature^{4,5} and upon adsorption studies³ of nickel catalysts over the past year. This procedure is presently undergoing further investigation and refinement in a related NSF study⁴ in this laboratory.

Catalyst surface area and dispersion (see Appendix A) were calculated using hydrogen uptake data and assuming (1) hydrogen atoms/surface metal atoms = 1, (2) complete reduction of nickel and nickel alloys to the metallic state (except for $NiMoO_3$), (3) a surface metal composition identical to the bulk metal composition, and (4) planar site densities based upon the three lowest index crystallographic planes for each metal. Assumptions 1-3 are currently under investigation as part of the NSF methanation study in this laboratory. The applicability of these assumptions is discussed below in connection with the adsorption results. Sample calculations of surface area and dispersion for alloy catalysts are presented in Appendix A.

The measurement of carbon monoxide adsorption uptake for nickel and nickel alloy catalysts was carried out according to a procedure shown in Table 4. Unfortunately, the uptake data for a given sample were found to vary greatly according to various changes in procedure such as modifications in the equilibration pressure and temperature. In fact, the ratio of adsorbed carbon monoxide atoms to hydrogen atoms varied from 0.5 to 4.7 depending upon modifications in procedure. Moreover, there is apparently formation of nickel carbonyl which further complicates the measurements. These problems are discussed below in relation to adsorption data.

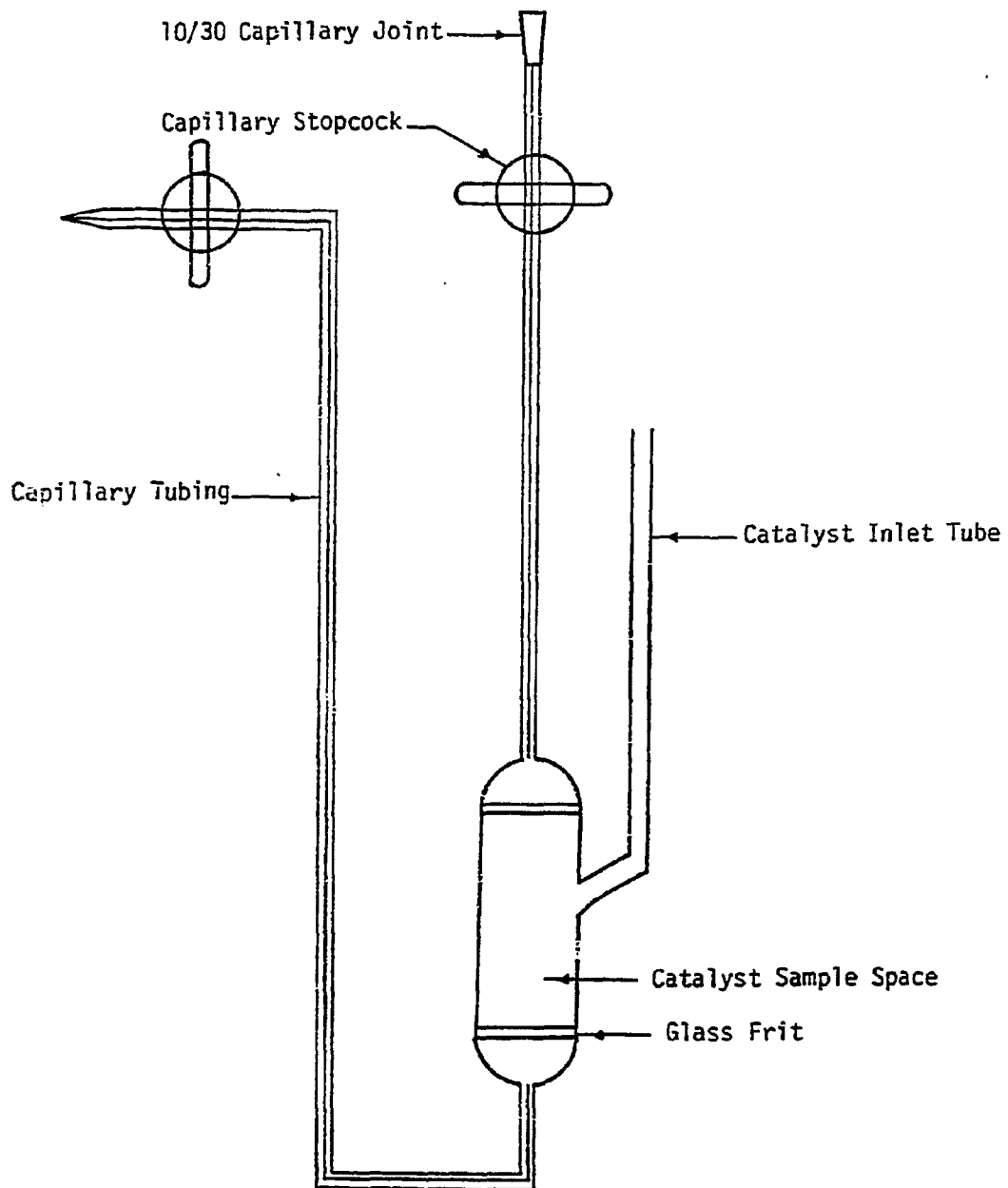


Figure 3. Chemisorption Sample Cell

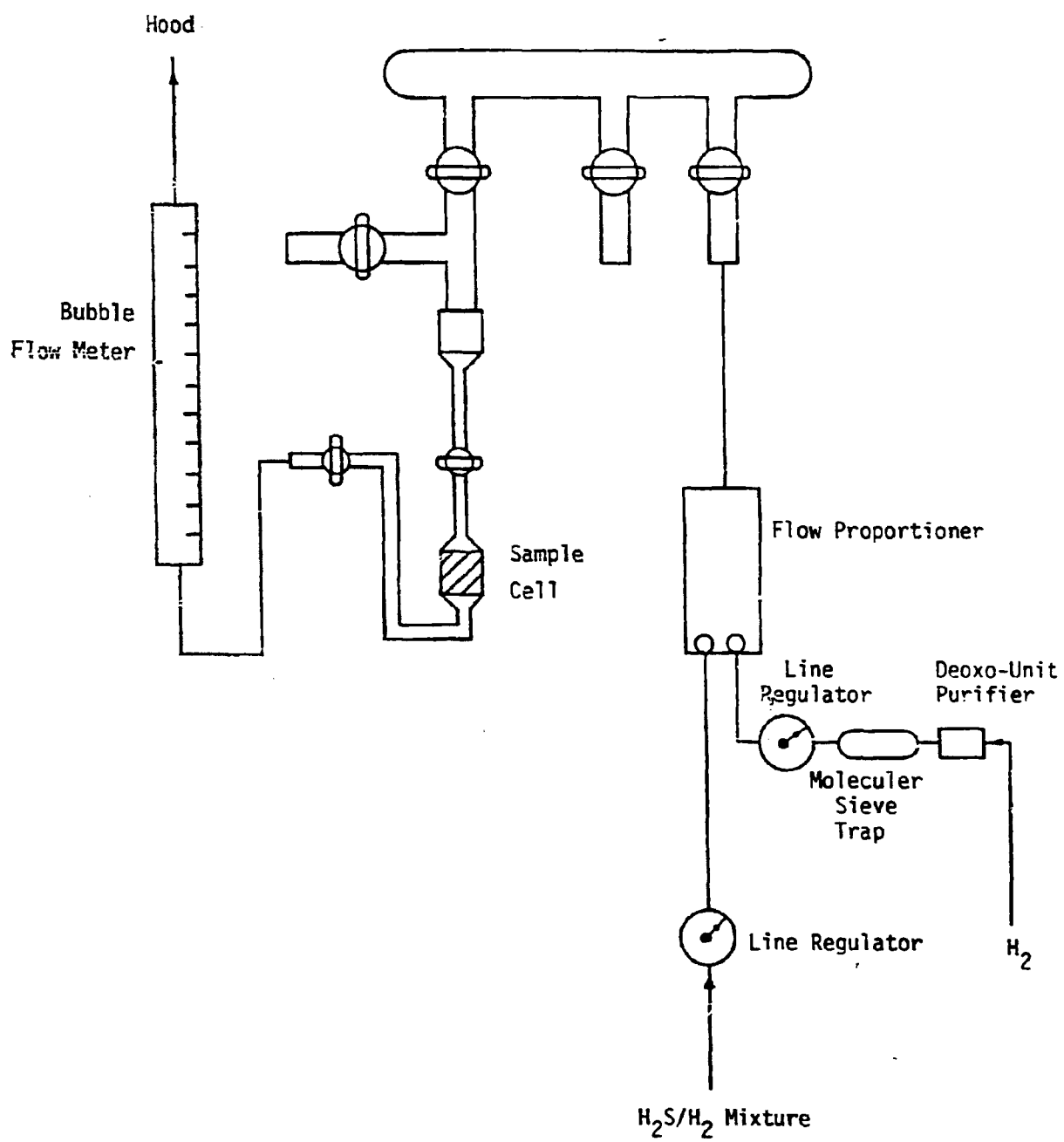


Figure 4. Poisoning Apparatus

TABLE 3
Standard Procedure for Measuring H₂ Uptake
of Nickel Catalysts

Step	Procedure
Reduction	Reduce <u>in situ</u> - 10-16 hrs. at 450-500°C Reduce previously reduced catalysts - 2 hrs. at 450°C
Evacuation	Evacuate - 1-2 hrs. at 400-450°C and usually to about 10 ⁻⁵ Torr.
Adsorption	<ol style="list-style-type: none"> 1. Expose evacuated sample to measured amount of hydrogen at 25°C and 400-500 Torr for 45 minutes (200 minutes for ruthenium containing catalysts). 2. Measure moles of hydrogen as a function of pressure from 0-400 Torr.
Calculation	Plot hydrogen uptake versus pressure and extrapolate to zero pressure to determine uptake due to chemisorption.

TABLE 4
 Procedure for Measuring CO Uptake
 of Nickel Catalysts

Step	Procedure
Reduction (in H ₂)	Reduce <u>in situ</u> - 10-16 hours at 450-500°C Reduce previously reduced catalysts - 2 hrs. at 450°C.
Evacuation 1	Evacuate - 1-2 hrs. at 400-500°C and usually to about 10 ⁻⁵ Torr.
Adsorption 1	<ol style="list-style-type: none"> 1. Expose evacuated sample to measured amount of CO at -85° or 25°C and 400-500 Torr for 30-60 min. 2. Measure moles of CO as a function of pressure from 0-400 Torr.
Evacuation 2	Evacuate 30-60 min. at -85° or 25°C and usually to 10 ⁻³ to 10 ⁻⁴ Torr.
Adsorption 2	<ol style="list-style-type: none"> 1. Expose sample to measured amount of CO at -85° or 25°C and 400-500 Torr for 30-60 min. 2. Measure moles of CO as a function of pressure from 0-400 Torr.
Calculations	Plot both isotherms (moles uptake versus pressure). Correct the first isotherm for chemisorption on the support. Determine the difference between isotherms at zero pressure which corresponds to amount chemisorbed on the metal.

Controlled poisoning of catalysts by H_2S involved 6 or 12 hour exposure of 10-15g samples to a flowing stream of 10 or 50 ppm H_2S in H_2 at $450^\circ C$ using the apparatus sketched in Figure 4.

c. Adsorption data. Hydrogen uptake, percent dispersion, and surface area data are listed in Table 5 for several nickel and nickel alloy catalysts prepared in this study. Hydrogen adsorption isotherms are shown for each of these catalysts in Figures 5-9. Hydrogen adsorption uptakes were determined by extrapolating to zero the straight-line portion of each isotherm above the saturation pressure (about 100 Torr). The relatively small values for the slopes of the isotherms in Figures 5-9 indicate that physical adsorption on the support is a small effect at $25^\circ C$.

Two different values of hydrogen uptake are listed in Table 5 for each catalyst except Ru/Al_2O_3 . The samples for data denoted by A were reduced in small batches (10-15g) in a glass sample cell (see Fig. 3). Samples corresponding to B were reduced in large batches (50-500g) in a combustion tube reduction system described in Section III-A-3. Apparently the surface areas for Ni, Ni-Ru, and Ni-Rh catalysts are larger for samples reduced in large batches. This very likely results from a slower, more uniform temperature rise in the large reduction apparatus. On the other hand, the surface area for the Ni-MoO₃ catalyst is larger for the small sample reduced in a glass cell. The reasons for this discrepancy are not known, but might be related to the chemistry of reduction.

In the calculation of percent dispersion and surface area shown in Table 5 complete reduction of nickel and nickel alloys to the metallic state (except for Ni-MoO₃) was assumed. Data from the literature⁶⁻¹⁴ and this laboratory³ indicate that alumina-supported nickel cannot be reduced completely to the metallic state. Recent measurements (NSF study) show that Ni/Al₂O₃ catalysts prepared by the general method shown in Table I contain 60-90% of the nickel in the metallic state. The addition of noble metals is expected to increase the degree of reduction to the metal.¹⁵⁻¹⁸ The actual values of percent reduction to the metal will be determined for each of these catalysts as part of the NSF study.

One of the objectives of this study is to find catalysts for methanation which are more efficient, active, and stable than nickel. One measure of efficiency is the active catalyst surface area per unit mass or volume. The data in Table 5 indicate that surface areas for Ni-Ru and Ni-Rh catalysts are significantly higher compared to Ni and Ni-MoO₃. No site density data for Ni-MoO₃ were available and thus the surface area could not be calculated. Nevertheless, hydrogen uptake and dispersion values are lower for the molybdate catalyst compared to the other alloys and about the same as for nickel. The Engelhard Ru/Al_2O_3 catalyst has the lowest surface area simply because the metal loading is low; however, its dispersion is the highest for this group of catalysts. Apparently the nickel-ruthenium catalyst has a dispersion intermediate between nickel and ruthenium.

TABLE 5

H₂ Uptake Data (Two Different Reduction Systems)

Catalyst Code	Composition		H ₂ Uptake (μ mole/g)		Percent Dispersion	Surface Area (m ² /g)	Footnotes
	Metal	Wt%	A	B			
Ni-A-111	Ni	3.0	A	12.75	4.97	1.04	A: Reduction of small batch in sample cell B: Reduction of large batch in combustion tube reduction system *Supplied by Engelhard
			B	21.4	8.35	1.75	
Ni-Ru-A-105	Ni Ru	2.5 0.5	A	27.9	11.74	2.32	
			B	44.6	18.78	3.71	
Ni-Rh-A-100	Ni Rh	2.5 0.5	A	31.4	13.24	2.6	
			B	38.3	16.15	3.17	
Ni-MoO ₃ -A-101	Ni Mo	3.0 3.0	A	32.3	8.33		
			B	22.5	5.80		
Ru/Al ₂ O ₃ *	Ru	0.5	A	7.62	30.81	0.75	

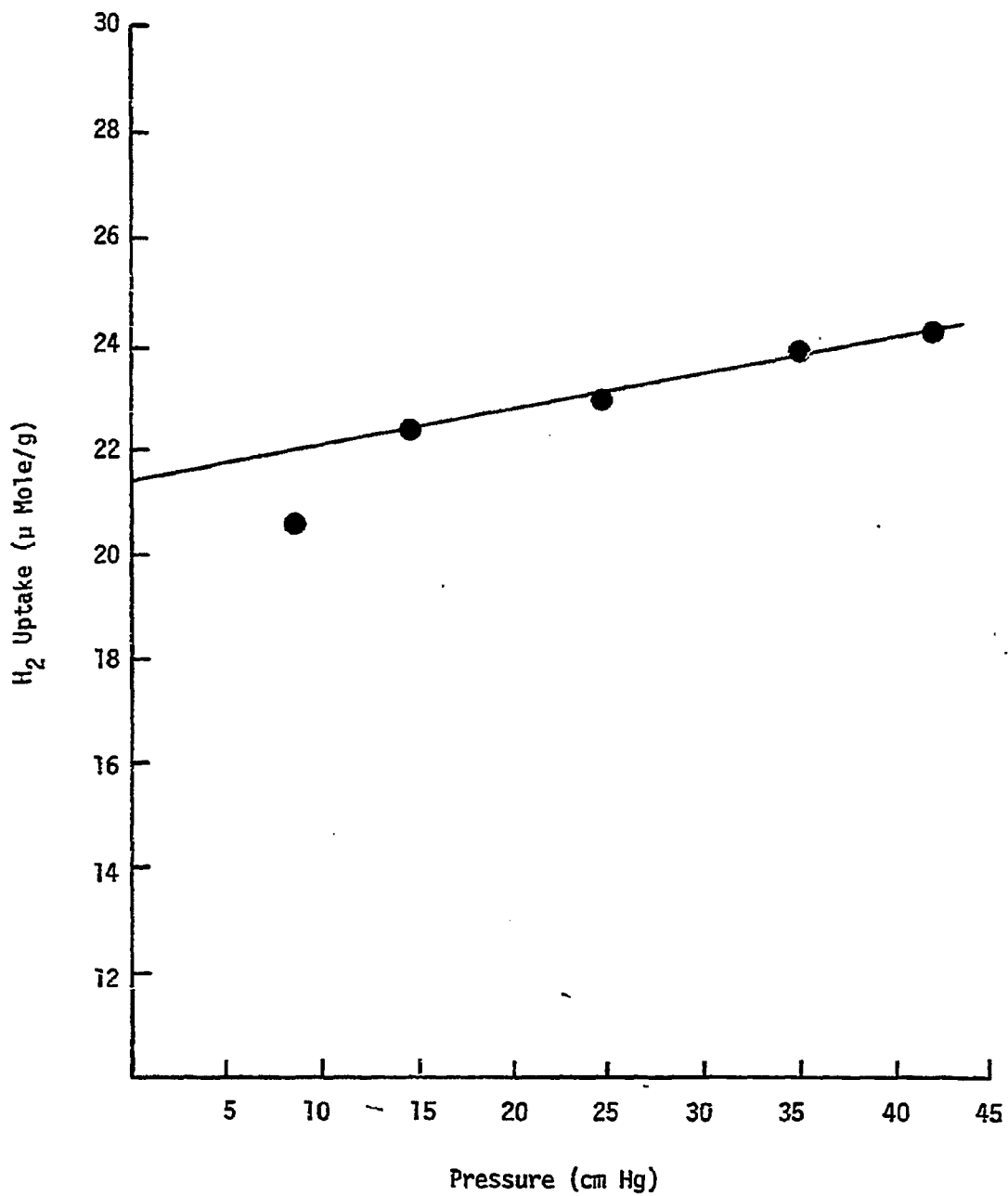


Figure 5. H₂ Chemisorption on Ni-A-111 at 25°C.

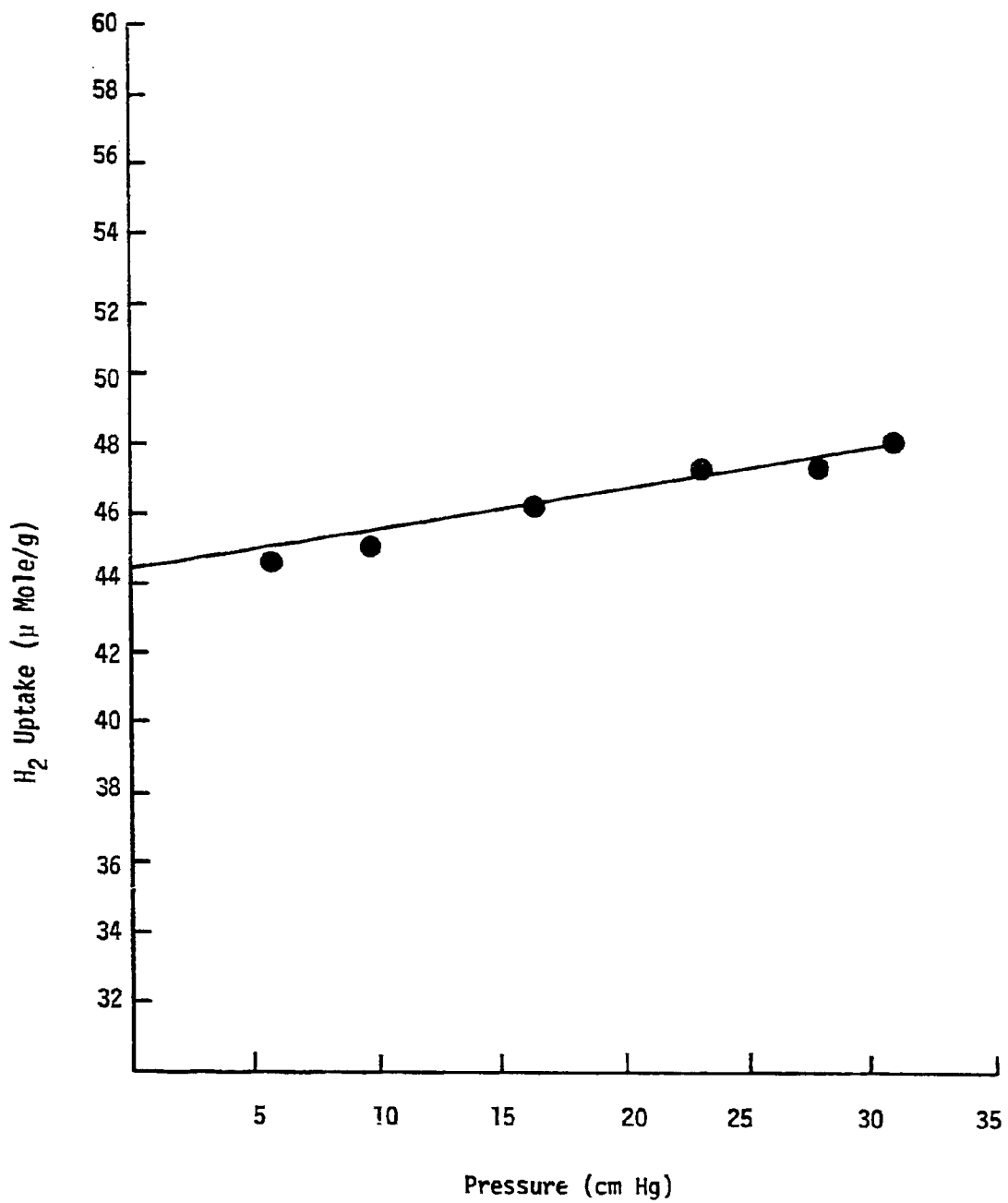


Figure 6. H₂ Chemisorption on Ni-Ru-A-105 at 25°C.

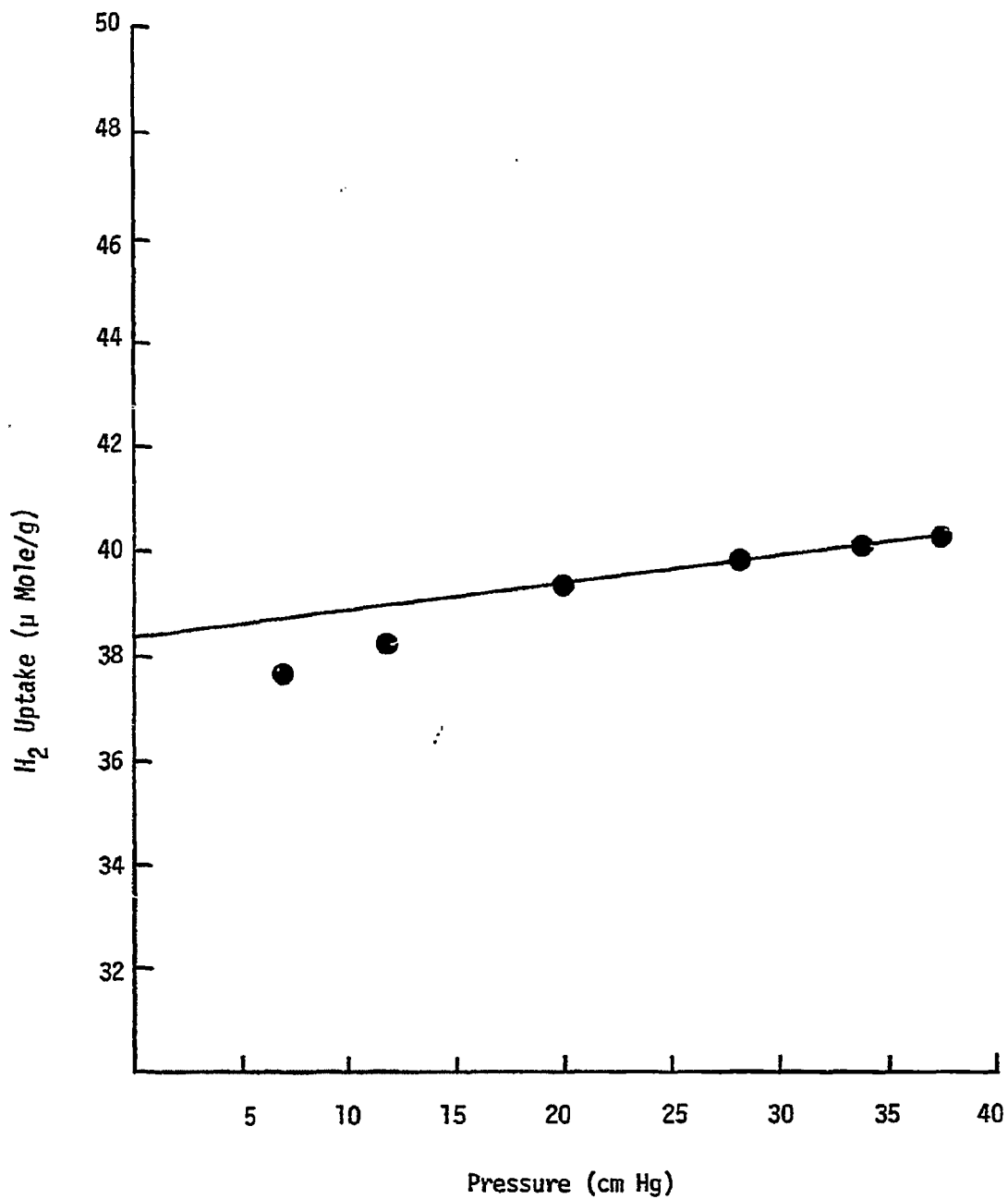


Figure 7. H₂ Chemisorption on Ni-Rh-A-100 at 25°C.

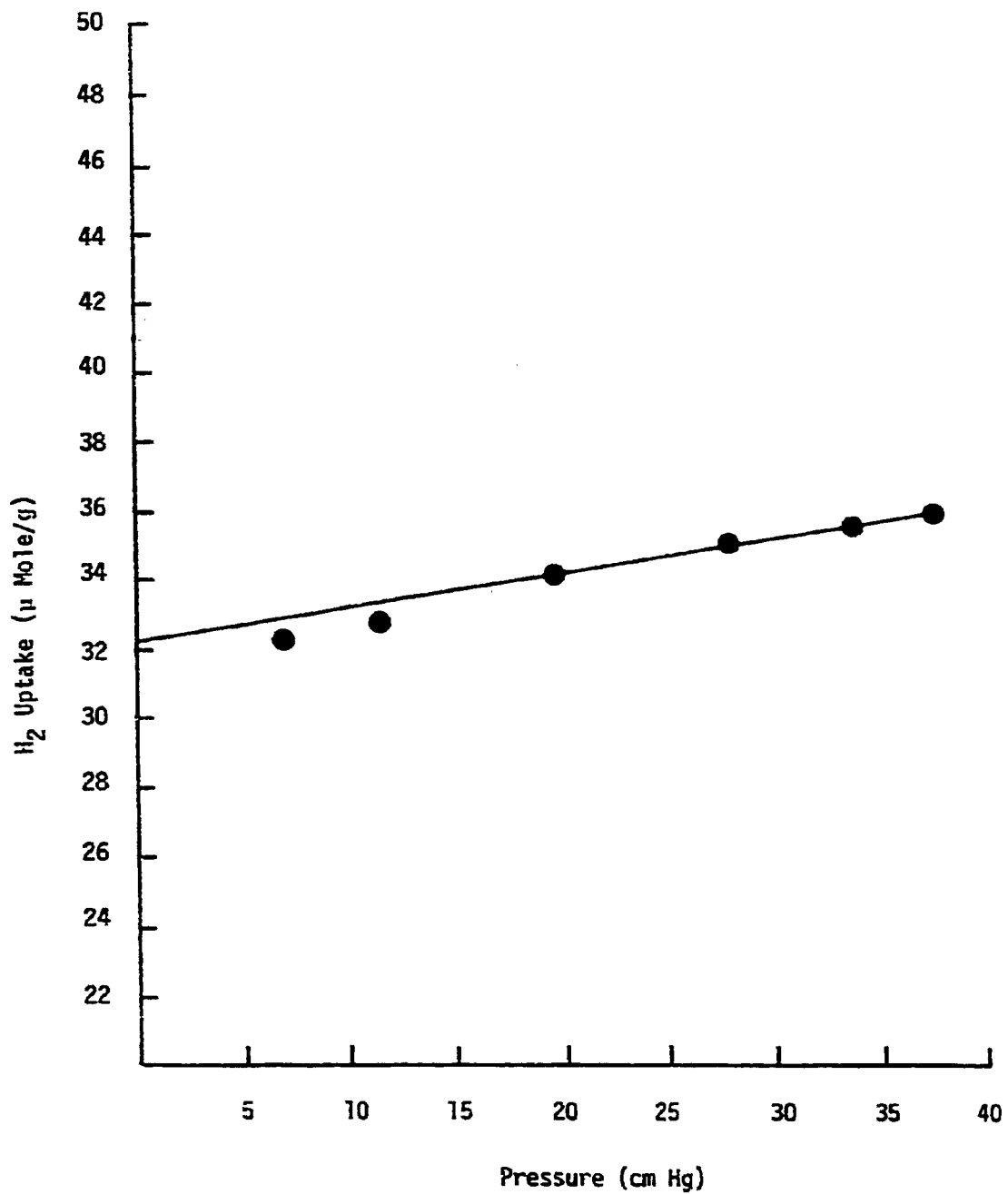


Figure 8. H₂ Chemisorption on Ni-MoO₃-A-101 at 25°C.

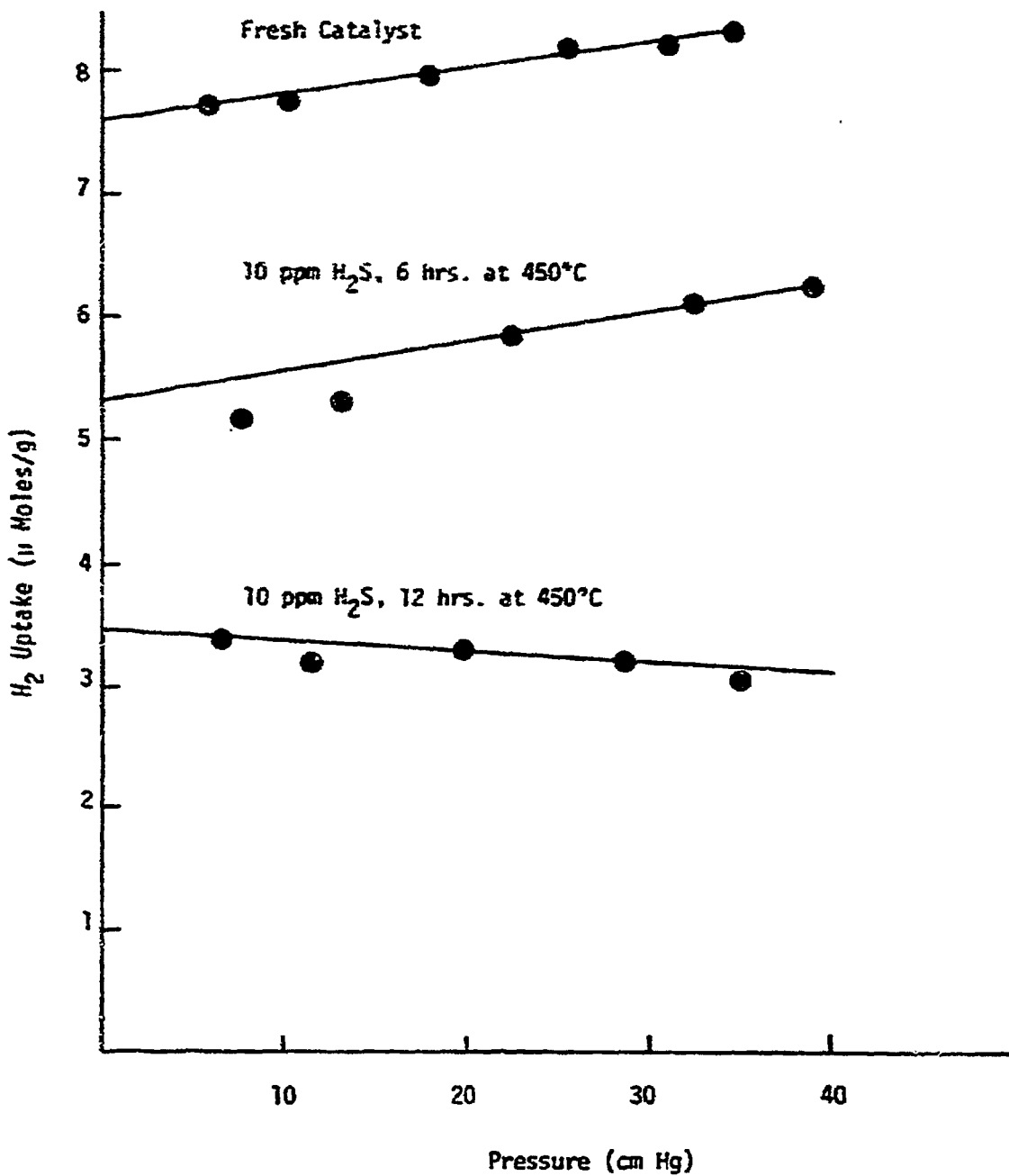


Figure 9. H₂ Chemisorption on 0.5% Ru/Al₂O₃ (Engelhard) at 25°C.

During the past five months we have devoted considerable effort to the preparation and characterization of alumina-supported nickel-ruthenium catalysts in order to find a preparation that would maximize catalyst dispersion (%D) and surface area for a 90/10 atm.% Ni/Ru alloy (2.5 wt.% Ni and 0.5 wt.% Ru). Eight different catalysts were prepared by various techniques; each was reduced in a flowing hydrogen stream at 450°C for 12-16 hours following which the dispersions were measured by hydrogen chemisorption. The results are shown in Table 6. Total dispersions for alloy catalysts were calculated assuming a stoichiometric ratio of hydrogen-to-surface metal atoms of one. Surface areas were calculated assuming the catalysts have the same metal surface composition as bulk composition. The results suggest that a basic impregnation technique gives a slightly better dispersion than the acidic impregnation. The ion exchange preparation was not successful in achieving a high surface area catalyst.

Carbon monoxide adsorption at room temperature on nickel catalysts has been studied under a variety of conditions by several groups of workers.¹⁹⁻²¹ Hughes et al.¹⁹ reported a flow technique for measuring CO chemisorption on nickel and platinum and observed significant formation of Ni(CO)₄ at room temperature and above. Based on a gravimetric study, Germain et al. suggested that CO adsorption to determine surface area is unsatisfactory because of Ni(CO)₄ formation above 0°C and because of variations in irreversibly adsorbed CO and poorly defined monolayer capacity from -78 to 0°C. Christopher and Brooks used a conventional volumetric adsorption apparatus to study H₂ and CO adsorption on nickel catalysts. They argued that adsorption studies in the upper temperature range (above 0°C) have the advantage of minimizing physical adsorption. However, they too observe formation of nickel carbonyl upon heating their catalyst in the presence of CO. Indeed carbonyl formation from nickel catalysts has been reported at temperatures as low as 0°C.²²

Carbon monoxide adsorption data for Ni-A-111 at 25 and -85°C are presented in Table 7 and Figure 10. The uptake values show considerable variation according to changes in equilibration pressure and isotherm temperature. CO/H ratios vary from 0.5 to about 4.7. The amount of CO adsorbed is especially sensitive to the equilibration pressure, i.e., the pressure at which the adsorption is allowed to reach equilibrium. Faster equilibration and better repeatability were obtained at equilibration pressures above 400 mm Hg. After equilibration for 1 hour at lower pressures the amount adsorbed was observed to change significantly over a period of a few minutes. Thus, equilibration at pressures above 400 mm Hg will be used in future experiments.

Observations in this study show two-fold evidence for nickel carbonyl formation at room temperature. First a nickel mirror was formed in both the glass sample cell and in a vacuum trap used for evacuation of the sample as they were later heated [Ni(CO)₄ is a gas which decomposes to nickel at 80-100°C]. Second, a significant decrease in hydrogen uptake from 16 μmoles/g to 11 μmoles/g was observed for a sample of Ni-A-111 exposed twice to CO at room temperature as shown in Figure 11. This observation was repeated for another sample of the same catalyst. A decrease in CO uptake from 75 to 49 μmoles/g was also ob-

TABLE 6

H₂ CHEMISORPTION DATA FOR ALUMINA-SUPPORTED Ni-Ru CATALYSTS

Catalyst	Code	Preparation	H ₂ Uptake ^a (μmoles/g)	Percent Dispersion	Surface Area (m ² /g)
2.5 wt.% Ni- 0.5 wt.% Ru/Al ₂ O ₃	Ni-Ru-A-100	Acidic Impregnation	20.5	8.62	1.71
2.5 wt.% Ni- 0.5 wt.% Ru/Al ₂ O ₃	Ni-Ru-A-101	Ion Exchange	17.1	7.2	1.42
2.5 wt.% Ni- 0.5 wt.% Ru/Al ₂ O ₃	Ni-Ru-A-102	Basic Impregnation	30.4	12.79	2.53
2.5 wt.% Ni- 0.5 wt.% Ru/Al ₂ O ₃	Ni-Ru-A-103	Acidic Impregnation	27.0	11.36	2.25
2.4 wt.% Ni- 0.48 wt.% Ru- 2.9 wt.% La/Al ₂ O ₃	Ni-Ru-La-A-100	Basic Impregnation	28.2 ^b	11.87	2.35
2.5 wt.% Ni- 0.50 wt.% Ru- 2.8 wt.% La/Al ₂ O ₃	Ni-Ru-La-A-101	Acidic Impregnation	24.3 ^b	10.24	2.02
2.5 wt.% Ni- 0.5 wt.% Ru/Al ₂ O ₃	Ni-Ru-A-104	Acidic Impregnation (doubly impregnated)	24.0 ^b	10.10	2.00
2.5 wt.% Ni- 0.5 wt.% Ru/Al ₂ O ₃	Ni-Ru-A-105	Basic Impregnation (doubly impregnated)	27.9 ^b	11.74	2.32

a. Data interpolated or extrapolated to 225 minutes following initial exposure to H₂. About 200 minutes is required to reach equilibrium adsorption for ruthenium catalysts.

b. Date extrapolated to 180 minutes.

TABLE 7

CO Chemisorption Data for Ni-A-111

Run No.	Equilibration Condition			Evacuation Between Two Isotherms		CO Uptake* ($\mu\text{mole/gr}$)	CO/H	Evaluation and Comments
	Temperature	Pressure	Time	Time	Pressure			
1	$-83 \pm 1^\circ\text{C}$	Low ^a	30 min.	30 min.	2×10^{-4} Torr	11.4	-0.5	The two isotherms have different slopes because the pressure range of isotherms was too low. It was found in later runs that it is difficult to evacuate to 2×10^{-4} within 30 min. Data are assumed to be invalid.
2	Room Temp. $25 \pm 2^\circ\text{C}$	Low	1 hr.	20 min.	3.7×10^{-4}	15.5	-0.5	H ₂ uptake before CO chemisorption of this sample showed very low uptake (2 $\mu\text{mole/gr}$). Sample was probably exposed to the air. After H ₂ chemisorption, sample was evacuated at 400°C to run CO chemisorption. Evacuation pressure (3.7×10^{-4}) within 20 min. is also questionable. Data are invalid.
3	$-83 \pm 1^\circ\text{C}$	High ^b	30 min.	30 min.	1×10^{-3}	73.7	3.80	Dead volume correction uncertain, but that effect is small according to calculations. Valid data. (H ₂ uptake = 9.7 $\mu\text{moles/g}$)

TABLE 7 Continued

Run No.	Equilibration Condition			Evacuation Between Two Isotherms		CO Uptake* ($\mu\text{mole/gr}$)	CO/H	Evaluation and Comments
	Temperature	Pressure	Time	Time	Pressure			
4	25 \pm 0.5°C	High	30 min.	30 min.	1 \times 10 ⁻³ Torr	75	--	Sample (400°C) was cooled for 20 min. before CO chemisorption. Possible nickel carbonyl formation--small effect. Valid data.
5	25 \pm 2°C	High	30 min.	30 min.	1 \times 10 ⁻³ Torr	49	3.22	Sample was same as Run #4. After Run #4 sample was reduced once again. CO uptake decrease may be due to nickel atom loss by nickel carbonyl formation of Run #4. Questionable data.
6	25 + 4°C	High	30 min.	30 min.	2 \times 10 ⁻³ Torr	55	4.74	Sample was poisoned with 10 ppm H ₂ S 6 hrs. before CO chemisorption. Color change of the sample was observed when CO was admitted and evacuated sample. Most unusual result. Must be checked.

TABLE 7 Continued

Run No.	Equilibration Condition			Evacuation Between Two Isotherms		CO Uptake* ($\mu\text{mole/gr}$)	CO/H	Evaluation and Comments
	Temperature	Pressure	Time	Time	Pressure			
7	$25 \pm 2^\circ\text{C}$	Low	1 hr.	5.5 hr.	5×10^{-5} Torr	30	0.96	Equilibration pressure was low and evacuation was over a long period of time compared to other runs. Questionable. H_2 uptake = $15.6 \mu\text{moles/g}$
8	$-83 \pm 1^\circ\text{C}$	High	1 hr.	30 min.	1×10^{-3} Torr	73.7	1.72	H_2 uptake = $21.4 \mu\text{moles/g}$ Dead volume correction OK. Valid data.

*CO uptake was taken as the difference between two isotherms extrapolated to zero pressure. The first isotherm was corrected for chemisorption on the support in Runs 3-8. Each sample was evacuated at 400°C to 5×10^{-5} Torr (about 2 hrs.) immediately following H_2 chemisorption except for Runs 5 and 6. Run 5 was a repeat of Run 4 using the same sample. Run 6 was carried out after H_2S poisoning of the sample.

a. 50-200 mm Hg

b. 400-500 mm Hg

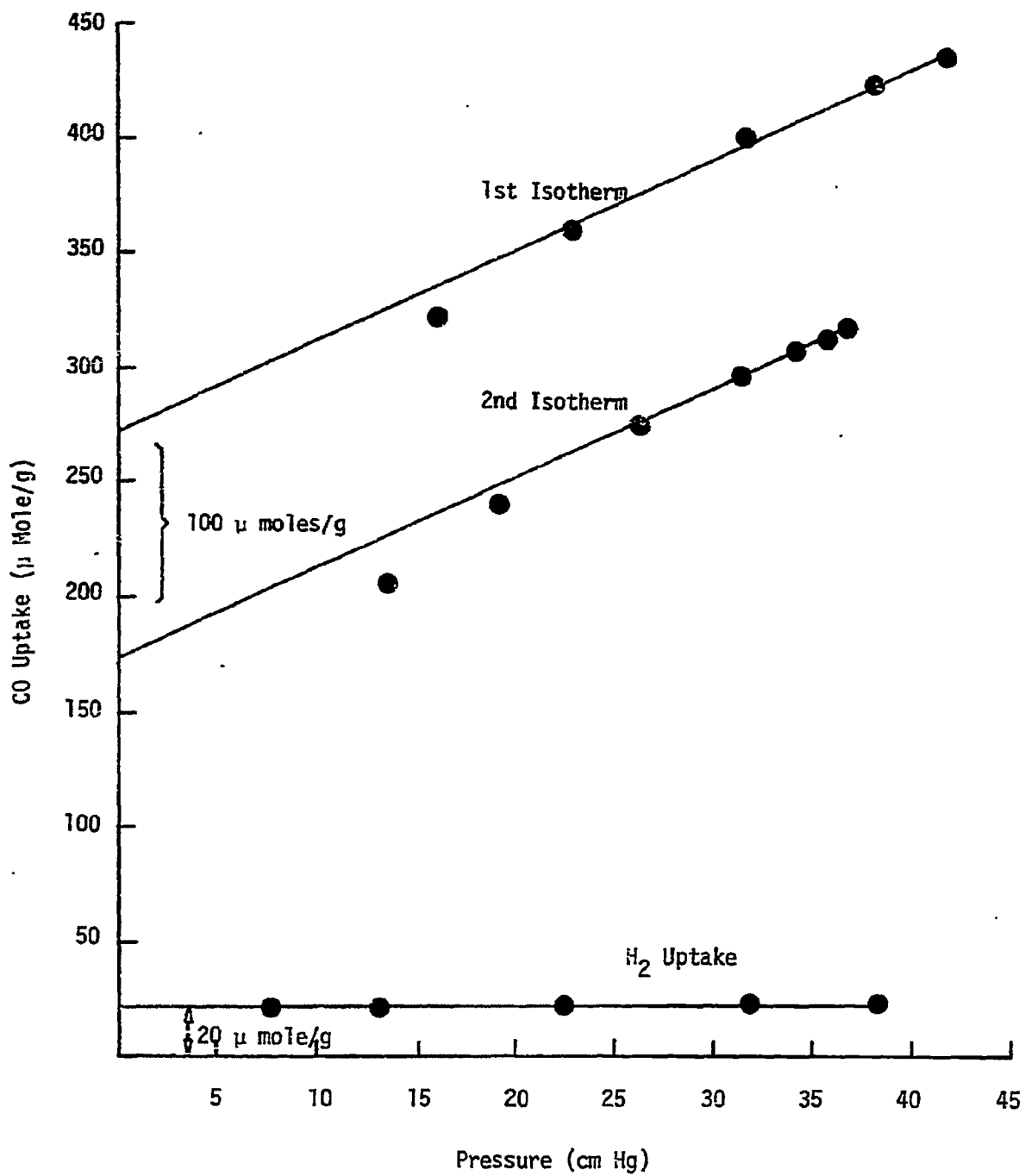


Figure 10. CO Chemisorption on Ni-A-111 at -83°C (Run #8 in Table 7).

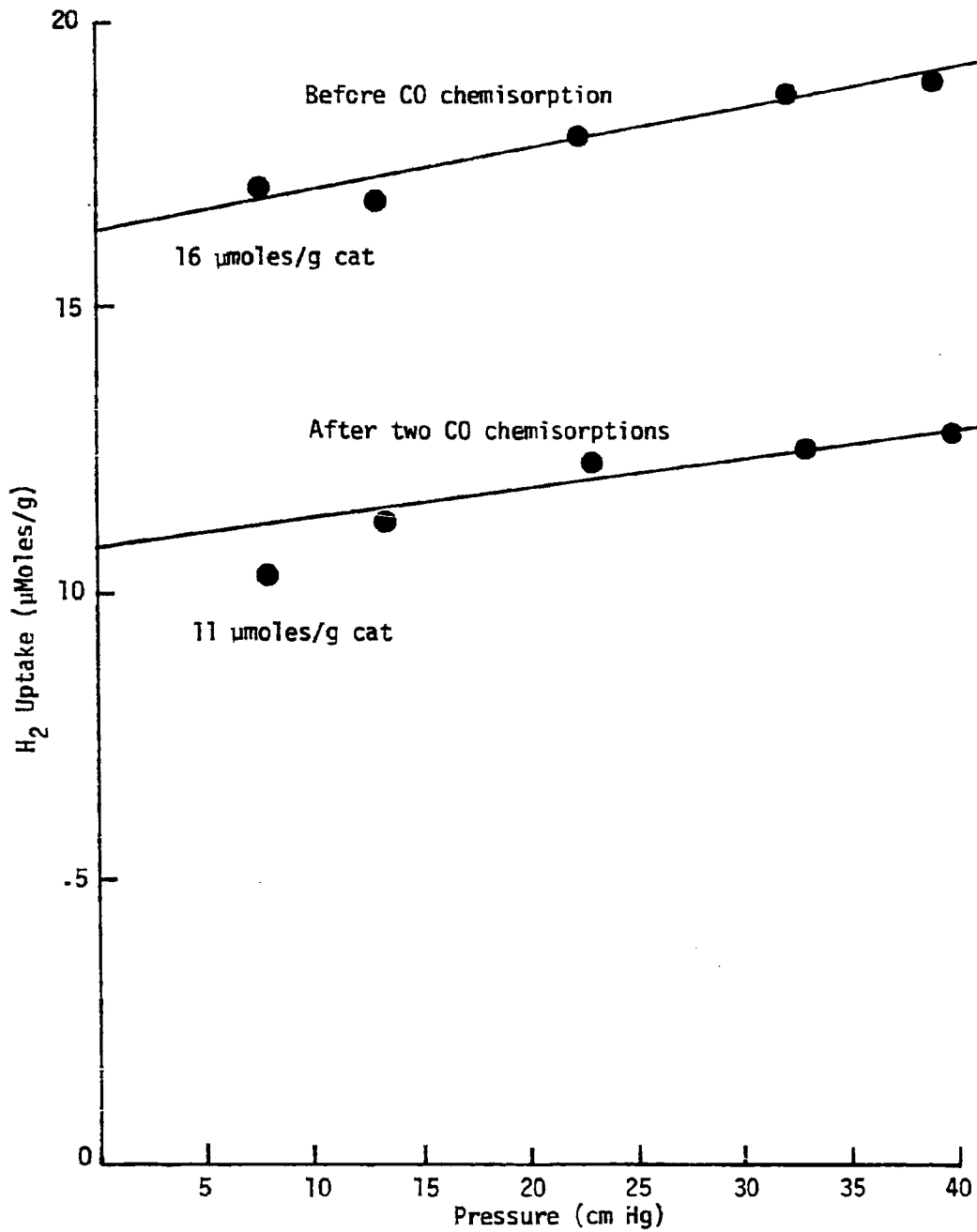


Figure 11. Effect of CO Exposure (25°C) on H₂ Chemisorption for Ni-A-111.

served between Runs 4 and 5 (see Table 7). In future experiments formation of nickel carbonyl will be avoided by (1) measuring CO chemisorption at -85°C and (2) evacuating, then heating CO-treated samples in flowing hydrogen to form CH_4 .

In order to determine accurately the amount of carbon monoxide chemisorbed on nickel it is necessary to correct for the carbon monoxide chemisorbed on the alumina support, since the initial isotherm in the adsorption procedure described in Table 4 is a combination of chemisorption on the metal and support and of physical adsorption on the support. The second isotherm corresponds to the amount of CO removed by evacuation, i.e. weakly or physically adsorbed CO. Hence the amount of chemisorption on the support should be determined by repeating the same procedure (Table 4) for the support alone, treated under identical conditions of drying, reduction, and evacuation. Hydrogen and CO adsorption uptakes are shown in Table 8 (CO isotherms are shown in Figures 12 and 13) for the Kaiser SAS Alumina support treated under conditions identical to those for Ni-A-111. The values agree reasonably well with data reported in the literature,^{19,23} also shown in Table 8. The uptake of CO by the support at either -85 or 25°C is clearly quite significant. Accordingly the CO chemisorption uptakes in Table 7 were corrected by subtracting from the initial isotherm the CO chemisorbed on the support (Table 8). Since the adsorption of hydrogen on alumina is negligibly small, no support corrections were necessary in calculating the hydrogen uptake values shown in Table 5.

Investigation of the effect of H_2S poisoning on H_2 and CO chemisorption was initiated during April. Our initial experiments using 10 ppm H_2S in a H_2/N_2 mixture at 440°C were invalid because we discovered that most of the H_2S was adsorbed in our zeolite trap used routinely to purify the hydrogen gas. In general, exposure of catalysts to trace amounts of H_2S poses some difficult experimental problems because H_2S is corrosive to most metals and adsorbs on zeolites, aluminas, and stainless steel. We have solved this problem with an all-glass poisoning apparatus (see Fig. 4).

Our measurements of the effects of H_2S exposure on H_2 adsorption for nickel and nickel alloy catalysts are shown in Table 9. The results indicate that the catalyst surface is almost completely blocked for hydrogen chemisorption on both nickel and nickel-ruthenium catalysts after exposure to 50 ppm H_2S at 385°C for 12 hours. Apparently, exposure to 50 ppm H_2S for 12 hours is adequate to almost completely cover the surface with adsorbed sulfur.²⁴ Exposure to 10 ppm H_2S for 12 hours does not completely block the surface for hydrogen chemisorption thus enabling comparison of the resistance to H_2S poisoning for different catalysts. For example, it is interesting to compare the percent decrease in H_2 uptake for various catalysts after 12 hours exposure to 10 ppm H_2S . Ni-Rh-A-100 has the smallest decrease in H_2 uptake and 0.5% Ru/ Al_2O_3 the largest. Ni-A-111 (reduced in a large batch and initially 21.4 moles/g) has very nearly the same loss in hydrogen uptake capacity as Ni-Ru-A-105. Ni-MoO₃-A-101, however, has the largest decrease in H_2 uptake for the alloy catalysts, but most of this decrease occurs in the first six hours (see Fig. 14). In other words, it appears that the molybdate catalyst initially adsorbs about 40-45% of a monolayer of sulfur and is then saturated. This is probably not unusual behavior for a hydrodesulphurization catalyst, normally activated by sulfiding.²⁵

TABLE 8

CO and H₂ Chemisorption Data for Alumina

Gas Adsorbed	Run No.	Equilibration Condition			Evacuation Between Two Isotherms		CO Uptake (μmole/gr)	Footnotes and Comments
		Temp.	Pressure	Time	Time	Pressure		
CO	1	25±2°C	Low	3 hr. ^a 45 min. ^b	1.5 hr.	5×10 ⁻⁵ Torr	22.9	a. For 1st isotherm b. For 2nd isotherm Kaiser SAS Med. Beads
CO	2	-84±1°C	High	1 hr.	45 min.	9×10 ⁻⁴	26.3	Kaiser SAS Med. Beads
CO	--	-25°C	Very Low	Very Short	--	--	5-10	Ref. 19, Flow Technique
CO	--	25°C	100 mm Hg	30 min.	--	--	25-30	Ref. 23, 100 Torr
H ₂	1	25±2°C	Med.	45 min.	--	--	0.5	Kaiser SAS Med. Beads
H ₂	--	25°C	?	30 min.	--	--	0.5	Ref. 23

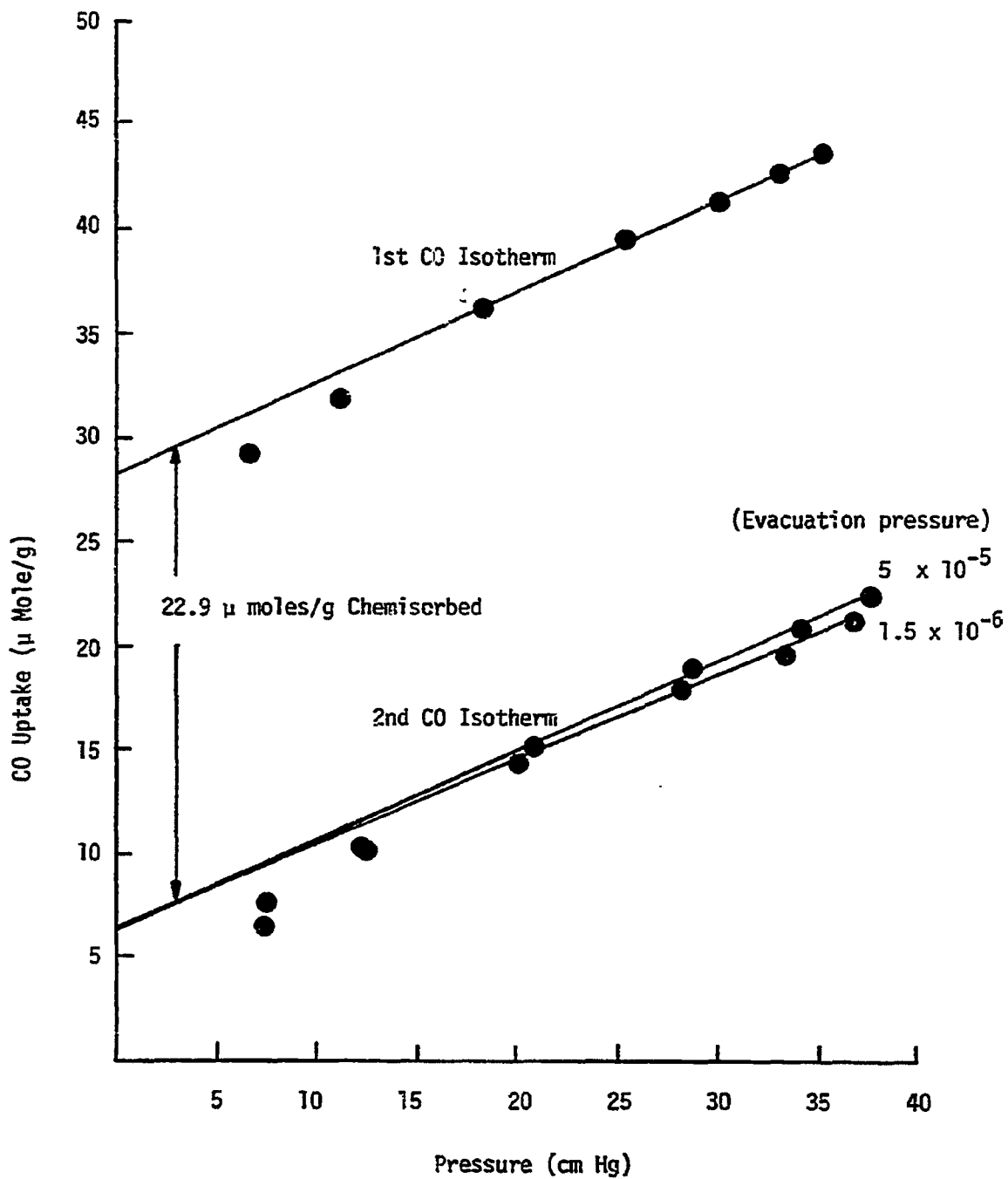


Figure 12. CO Adsorption on Kaiser SAS, Al_2O_3 Beads at 25°C.

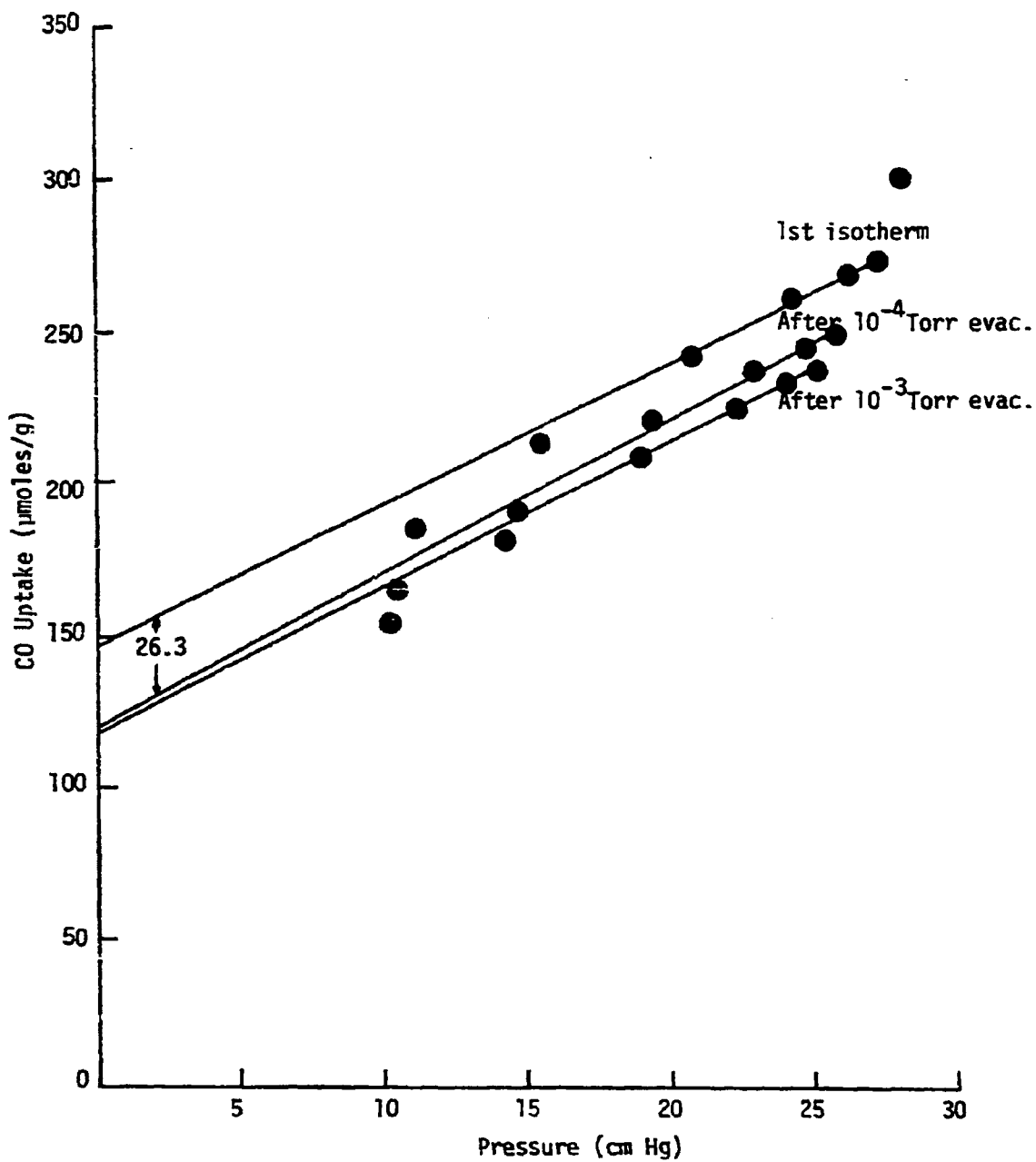


Figure 13. CO Chemisorption on Kaiser SAS Al₂O₃ Beads at -84°C.

TABLE 9

The Effect of H₂S Poisoning (450°C) on H₂ Uptake (25°C)

Catalyst Code	H ₂ S Concentration	H ₂ Uptake (μmole/g)			Footnotes
		Before	After 6 Hrs.	After 12 Hrs.	
Ni-A-111	50 ppm	8.5		0.65 ^a	a: data was taken at 385°C b: data was taken after CO chemisorption c: After 13 hr. poisoning d: After 14 hr. poisoning (): % decrease in H ₂ uptake.
	10	7.55	5.75 (23.8)	2.9 ^b (61.5)	
	10	21.4	16.8 (21.5)	14.0 (34.6)	
Ni-Ru-A-104	50	24.0		1.1 ^c	
Ni-Ru-A-105	50	33.36		2.23 ^d	
	10	39.4	32.0 (18.8)	25.8 (34.5)	
Ni-Rh-A-100	10	38.3	33.5 (12.5)	28.25 (26.2)	
Ni-MoO ₃ -A-101	10	32.3	18.18 (43.0)	17.4 (46.1)	
0.5% Ru/Al ₂ O ₃	10	7.62	5.33 (30.1)	3.45 (54.7)	

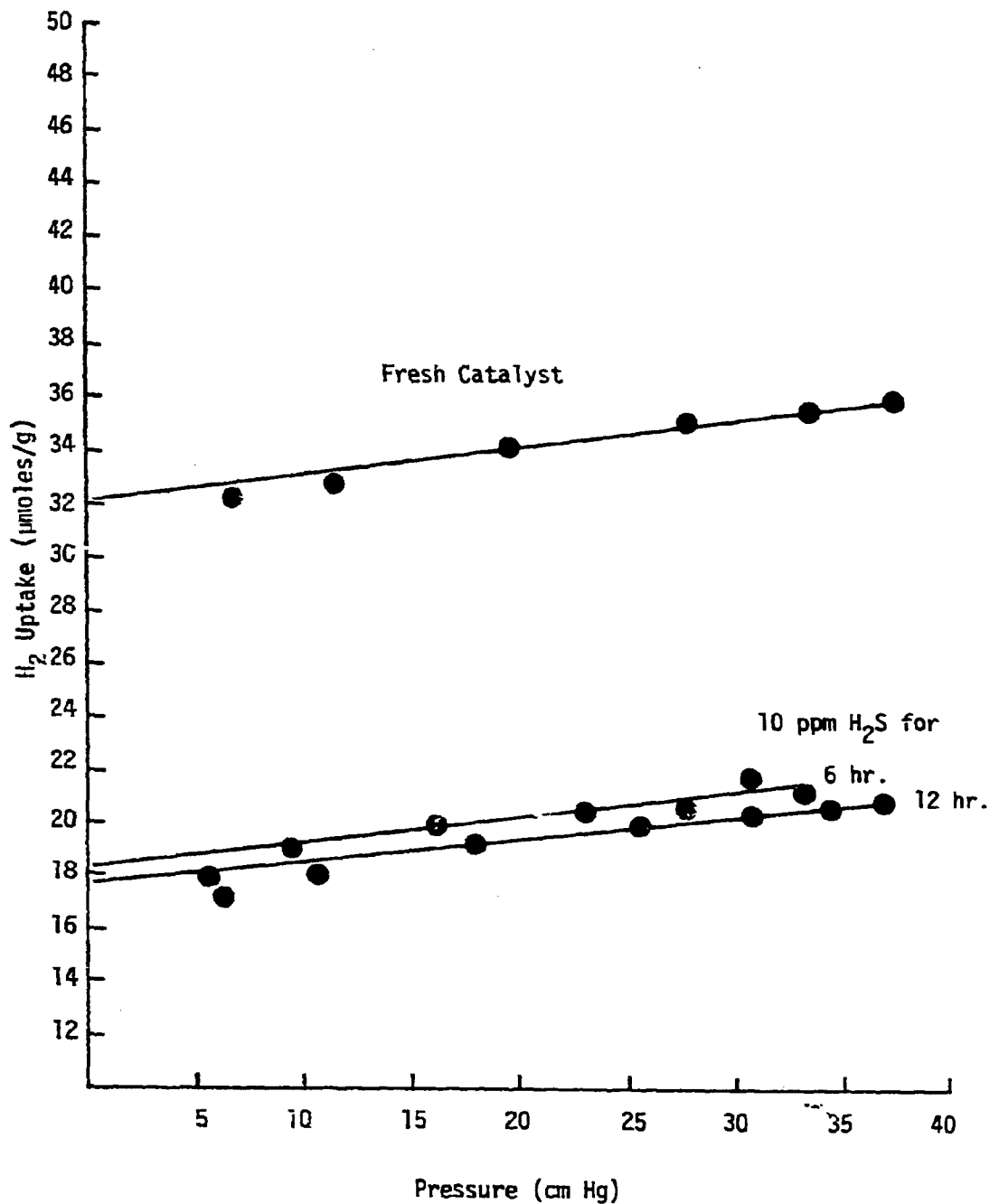


Figure 14. Poisoning of Ni-MoO₃-A-101 with 10 ppm H₂S- Effect on H₂ Chemisorption.

Thus far we have only one measurement of CO adsorption after exposure to H₂S. The CO uptake shown in Table 7 (Run 6) for a sample of Ni-A-111 following a 6-hour exposure to 10 ppm H₂S is very nearly the same as for the freshly-prepared catalyst! This is a most surprising result and must be double-checked.

The data in Table 9 suggest the interesting possibility of correlating the hydrogen uptake for a poisoned catalyst with its catalytic activity. This will be done as soon as methanation activity data have been determined for the catalysts and conditions shown in Table 9.

3. Construction of a Reduction Apparatus.

a. Purpose. As part of this study, it is necessary to prepare by reduction in flowing hydrogen fairly large, uniform batches of pelletized catalysts (100-500g) and monolithic catalysts (each 1 inch diameter by 3 inches long) for surface area studies, x-ray studies, chemical analysis, and reactor testing. A dedicated reduction system has been constructed for this purpose and has since found continuous use. This system is designed for reduction and passivation (carefully controlled exposure to air) of large catalyst samples under uniform, reproducible conditions over long periods of time. Thereby reactor and chemisorption systems are used less for long preparative reductions and more for actual measurements. Moreover, the vacuum system is spared contamination and the reactor system severe corrosion from catalyst decomposition products such as nitric acid and ammonia produced during reduction of nitrate salts in hydrogen.³

b. Description of the Apparatus. The reduction system shown in Figure 15 consists of a pyrex or ceramic combustion tube (51 mm in diameter) placed vertically in a tubular 3-zone furnace. The upper end of the combustion tube features a ground glass joint for charging and removing the sample. The furnace maintains about a 50 cm constant temperature zone controlled to $\pm 1^\circ\text{C}$ and reproducible from run to run to about $\pm 5^\circ\text{C}$. Hydrogen and nitrogen gases are purified with a Deoxo purifier followed by a molecular sieve trap; gases are metered to the combustion tube by means of regulators, valves, and flowmeters as illustrated in Figure 15.

c. Procedure. After the combustion tube is charged with a catalyst sample and placed in the furnace, the sample is purged 1/2 hour with a stream of nitrogen gas. Hydrogen is then passed through the sample at space velocities of 700-1800 hr⁻¹ while the sample is heated at 1-2°C/min to 500°C interrupted by a 1 hour hold at 230°C.³ The sample is cooled slowly in flowing hydrogen to room temperature, purged one half hour with nitrogen gas, and passivated by exposure to ppm quantities of air in nitrogen. The concentration of air is gradually increased to 1% air over a period of 15 minutes and then gradually increased to 100% air. This careful exposure to air prevents the catalyst from overheating and sintering upon exposure to the atmosphere. This is especially important for nickel and iron catalysts which are pyrophoric.

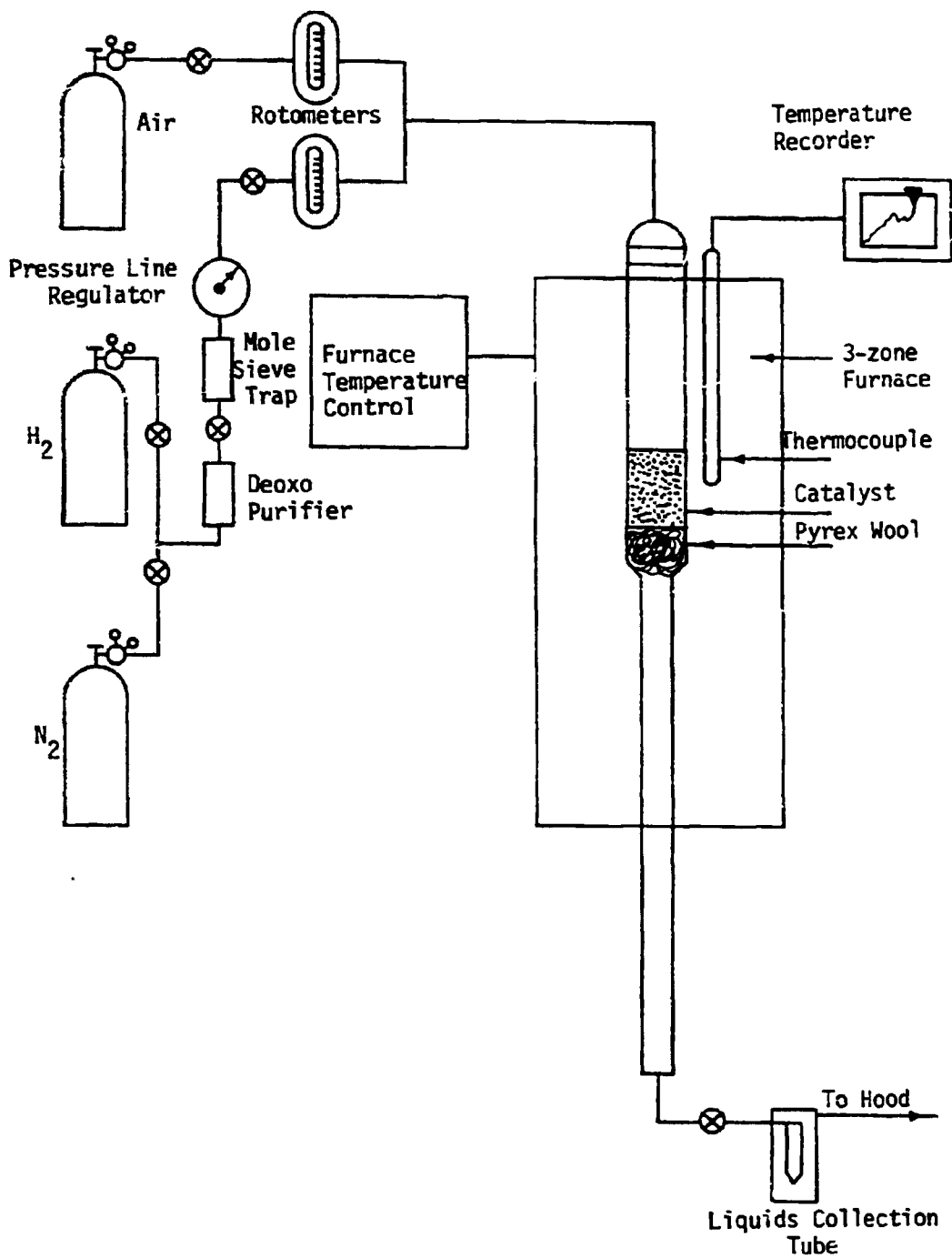


Figure 15. Reduction and Passivation System.

4. Construction of a Vacuum-Adsorption Apparatus.

a. Purpose. Vacuum adsorption measurements comprise a significant portion of effort in this study and in a companion study supported by NSF. It became very clear at the onset of this study that it would be impossible to accomplish both the goals of this and the NSF study with a single vacuum-adsorption apparatus, and thus plans were immediately formulated for construction of a new apparatus. Construction of the apparatus was completed July 15th, and the system is presently undergoing preliminary testing and calibration.

b. Apparatus and Procedure. The adsorption system (see Figures 16 and 17) is designed so that two samples may be reduced or evacuated simultaneously or independently. Using this system, it is also possible to evacuate or reduce one sample while conducting adsorption measurements on another sample simultaneously. Samples are treated in controlled atmospheres or vacuum from -196 to 500°C. The system has a vacuum capability of 1×10^{-6} Torr using an oil diffusion pump backed by a reciprocating mechanical pump (Precision Scientific). System pressure is monitored with a thermocouple gauge and a Bayer-Alpert ion gauge (Varian).

Sample cells similar to that shown in Figure 3 are suitable for evacuation, for reduction, or as the sample-containing portion of a chemisorption or BET measurement system. The sample-containing portion of each sample cell may be fitted with a furnace or a dewar flask to enable elevated or subambient temperatures to be obtained. Chemisorption or BET uptakes are measured by use of an absolute pressure Bourdon tube (Texas Instruments) with a pressure range of 0-500 Torr connected to a standard calibrated volume. The accuracy of the Bourdon tube is greater than 0.1 Torr.

Catalyst samples are reduced in flowing hydrogen at 300-500°C on either the "chemisorption" side (Fig. 16) or the "vacuum" side (Fig. 17) of the system. Hydrogen gas enters the vacuum side of the system through an oxygen removal catalyst and then passes through a zeolite adsorbent in a liquid nitrogen trap. This gas stream is then available for reductions on either side of the system. After reduction, the sample is evacuated at the reduction temperature to 10^{-5} to 10^{-6} Torr.

Following reduction and evacuation, chemisorption (or BET) measurements may be carried out. A given amount of hydrogen (or other suitable gas) is introduced into the calibrated gas bulb and then to the sample. The gas uptake is measured after equilibrium is obtained (usually 1-2 hrs.); the isotherm is generated by dosing the calibrated bulb and sample with additional amounts of H_2 (or other gas).

5. Work Forecast. During the next quarter we will continue our preparation and characterization of pelleted catalysts and initiate preparation of monolithic-supported nickel catalysts. Alumina-supported Ru-Pd and Ru-Fe will be prepared in pellet form. Hydrogen adsorption will be measured for ruthenium containing catalysts and alumina-supported Ni-Fe, Ni-Co, Ni-Pd, and Ni-Pt before and after exposure to 10 ppm H_2S . Adsorption of CO will also be measured for pelleted Ni-Ru, Ni-Rh, and

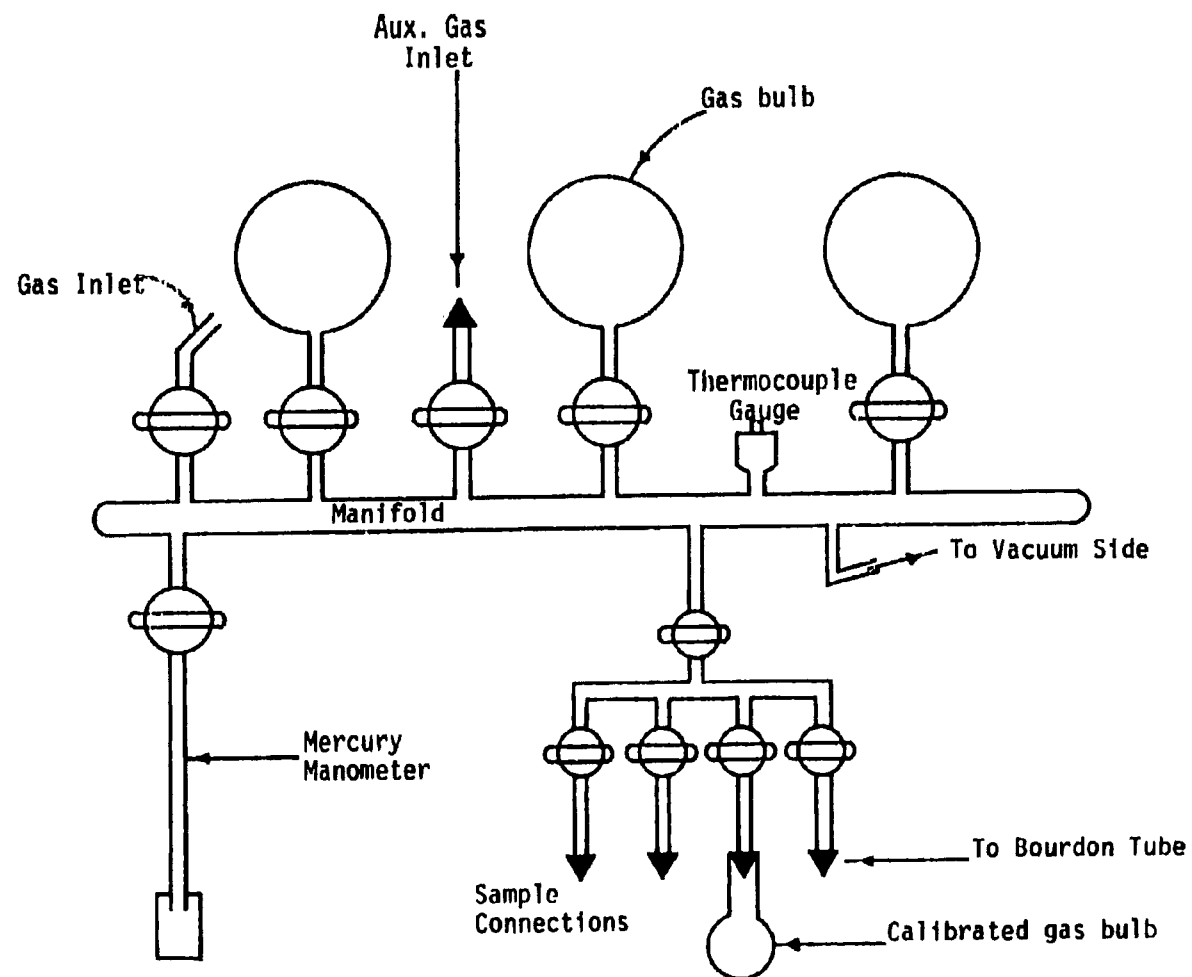


Figure 16. New Chemisorption-Vacuum System--Chemisorption Side

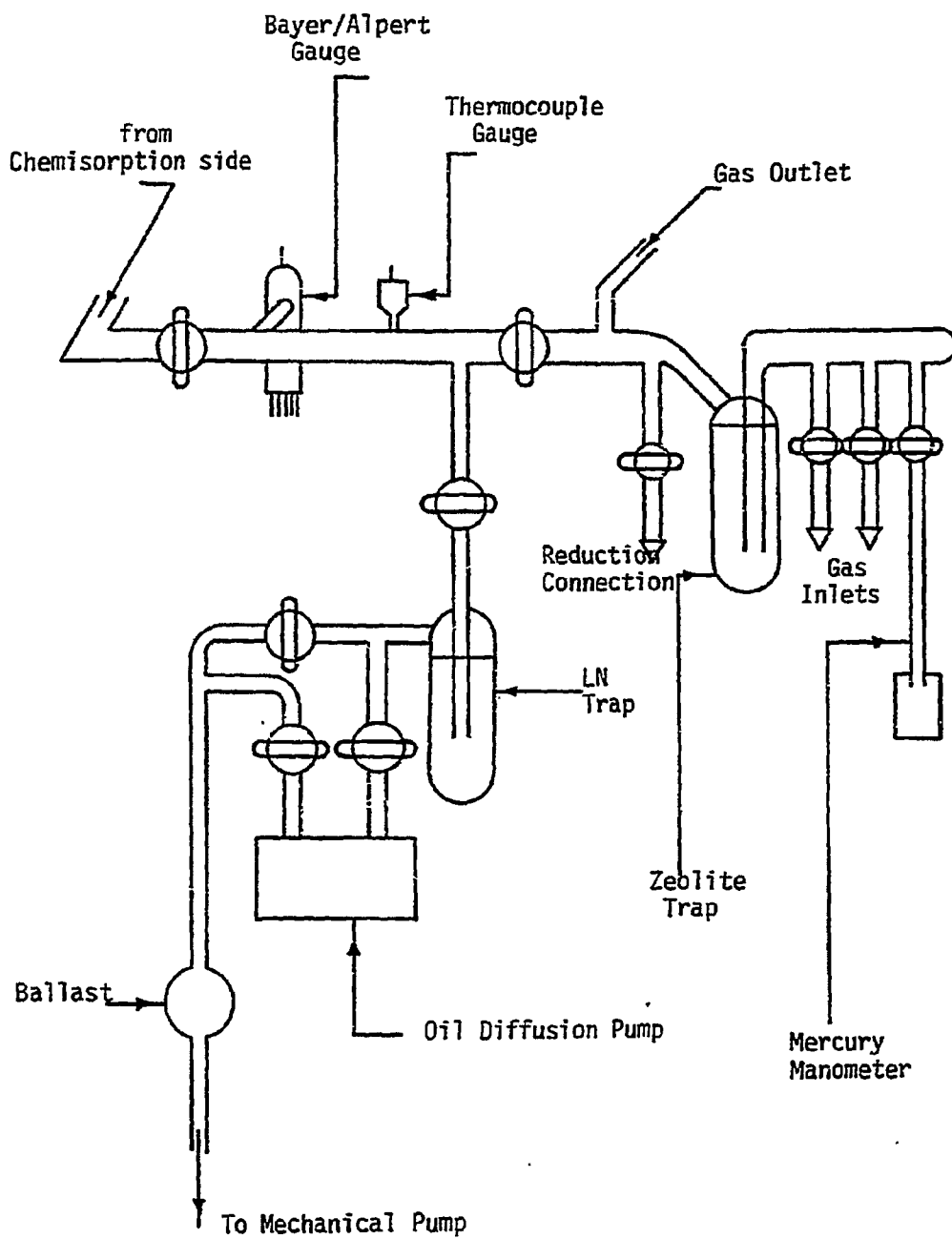


Figure 17. New Chemisorption-Vacuum System--Vacuum Side

Ni-MoO₃ catalysts before and after treatment with H₂S. In addition, x-ray diffraction and fluorescence measurements will be carried out for Ni/Al₂O₃ and Ni-Ru/Al₂O₃ catalysts to determine phase and chemical composition.

B. Task 2: Laboratory Reactor Construction

1. Design and selection of equipment and materials. At the beginning of the contract period we had operational in our laboratory a continuous flow reactor system for catalyst screening and measurement of methanation catalyst activity at either high (integral) or low (differential) conversions over a pressure range of 0-60 psig (see Figure 18). As part of this study the system has been redesigned to (1) allow for operation to 400 psig, (2) significantly upgrade the system with the addition of mass flow meters, a new furnace with temperature programming, and a continuous temperature recorder, and (3) improve the analysis of gaseous products with the addition of a continuous CO-detector, a gas concentration calibration system, and chromatographic accessories to allow accurate measurement of all reactants and products. A schematic of the proposed reactor system is presented in Figure 19. Purchase orders have already been placed for additional equipment and supplies to be used in the construction of this new system. Table 10 lists prices, dates ordered, and dates received for new equipment and materials.

The reactor system is designed such that various concentrations of desired reactant gases can be mixed with or without steam in the pressure range of 0-400 psig and at any temperature from 25-1000°C. The catalyst sample may be of either pellet or monolithic form, of any sample size from 2 ml to 100 ml. Small sample sizes will be used in differential testing and large sizes will be used for integral testing.

Reaction conditions will be monitored in the following ways. Pressure will be controlled by high pressure cylinder regulators and a high pressure line regulator. Temperature will be sensed by a type K (chromel-alumel) thermocouple inserted in the reactor bed. The signal will be continuously recorded by means of a Hewlett-Packard #7132 2-pen laboratory strip chart recorder. Flow rates will be read with a Matheson mass flowmeter system incorporating five stainless steel transducers with digital readout. The reactor furnace temperature will be programmed and controlled using electronics designed and constructed by the BYU Chemistry Instrument Shop. This instrument coupled with a Lindberg 24-inch zone furnace will allow ±2% control of catalyst sample temperature from 25°C to 1000°C, incorporating programmable temperature-time ramps and constant temperature holds.

The reactant and/or product streams will be continuously analyzed for CO using a Beckman model 864-12 NDIR analyzer and then routed to a Hewlett-Packard gas chromatograph model #5830 for periodic sampling and analysis for H₂, CO, CH₄, CO₂, H₂S, and hydrocarbons. The chromatograph with the addition of new accessories features digital control for automatic operation, sub-ambient temperature programming, column switching, and internal or external standard methods of normalization.

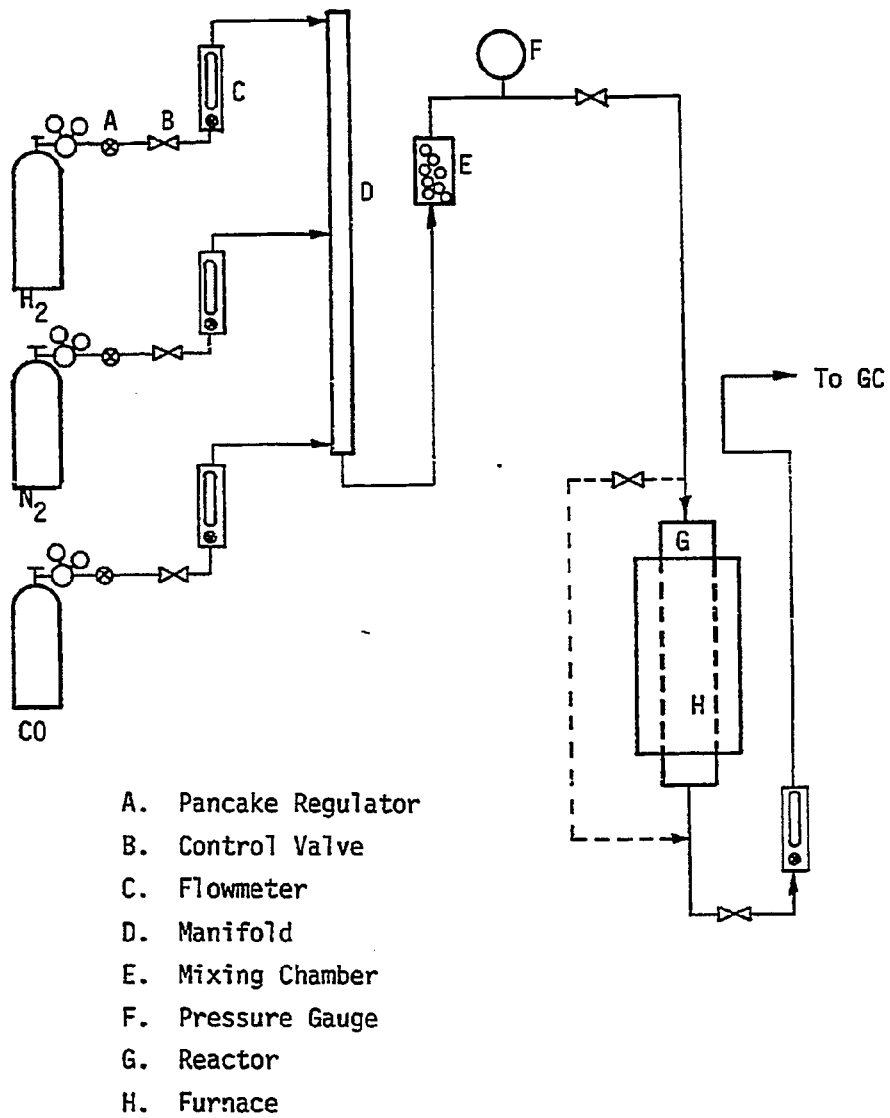
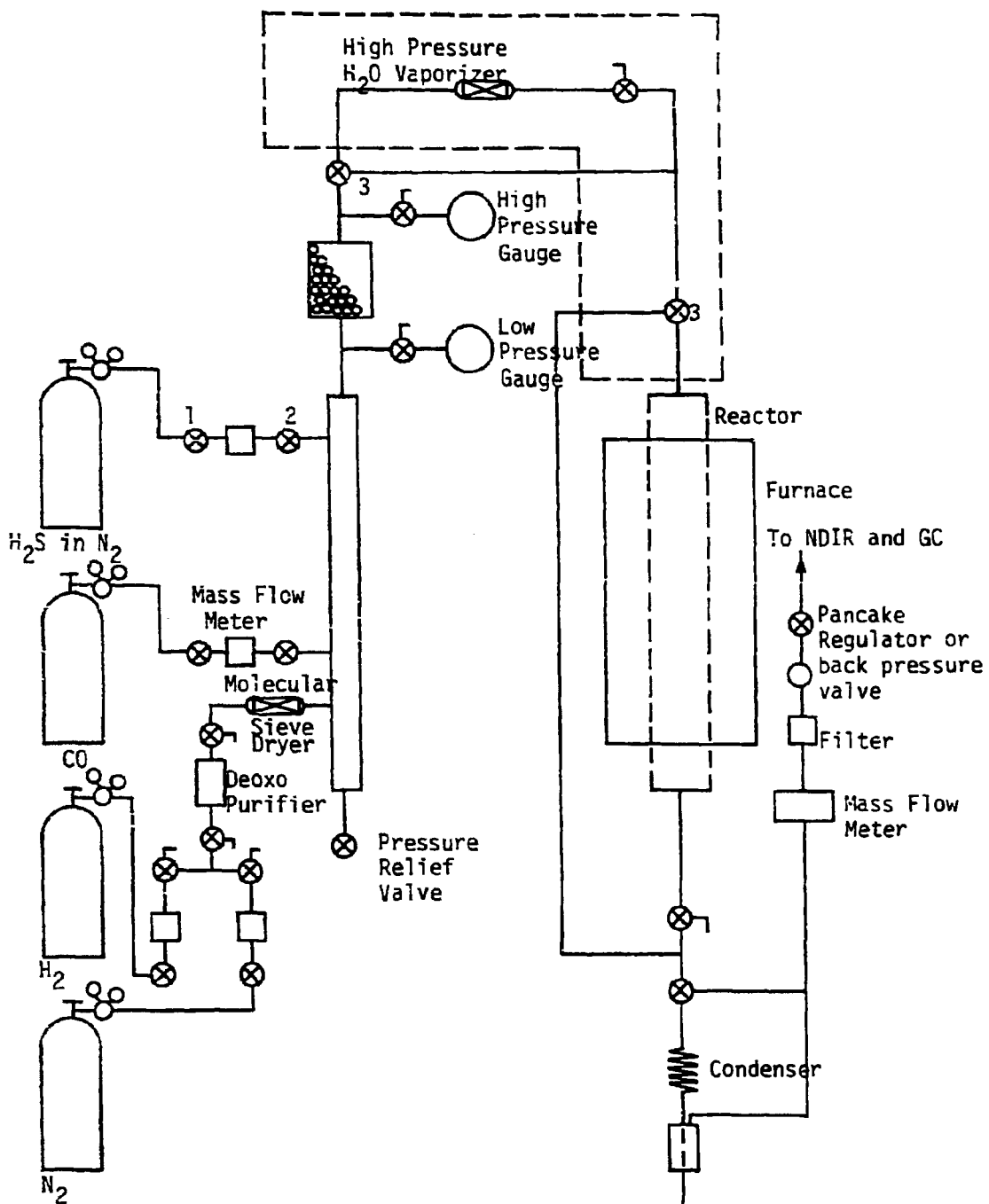


Figure 18. Low Pressure Continuous Flow Reactor System for Methanation Studies



- 1 S.S. Micro Valve
- 2 Toggle Valves
- 3 3-way Valves

The area enclosed in dotted lines will be wrapped with heating tape and asbestos cloth.

Figure 19. Proposed High Pressure Laboratory Reactor

TABLE 10

Equipment and Materials on Order for Reactor System

Name	Cost	Order Date	Date Received
1. Beckman Model 864-12 NDIR for CO ranges 0-1% and 0-5% with linearizer board, gas-free calibration	\$2825	5/12	6/30
2. Lindberg #54241 Tube furnace single zone	\$650	5/21	
3. High Pressure gas cylinders 300 ml & 150 ml, 2 each	\$101	5/21	6/10
4. H.P. #7132A 2 Pen Lab. Strip Chart Recorder w/ left hand event marker, spare pens & chart paper	\$2218.15	5/12	7/10
5. Mass Flowmeter system w/ 5 S.S. transducers, 1 digital readout box, special calibrations	\$2690	5/20	
6. Mass Flow controller S.S.	\$1295	5/20	
7. Accessories for Gas Chromatograph H.P. #5830A including Methods board, Cryogenic Kit, automatic gas sampling valve, valve driver, auxiliary heater, column switching valve	\$3838.30	5/21	
8. Rotometer S.S. with 600 tube & bench stand	\$172	5/12	6/9
9. Deoxo purification unit	\$58	5/12	5/30
10. L & N. Millivolt Potentiometer	\$552	5/21	6/10
11. S.S. Line regulator	\$206	5/12	7/10
12. 3 Low-Pressure outlet regulators	\$216	5/12	5/23
13. S.S. Check valve	\$10	5/12	5/23
14. Milton Roy minipump #396-31	\$594	5/16	6/17
15. Back Pressure valve S.S. set to 50 psi	\$120	5/13	7/15
16. 3 High Pressure regulators	\$225	6/4	6/17

TABLE 10 Continued

Fabricated on Campus:

1. Reactor chamber of 316 S.S. designed for 1000 psig
2. Water vaporizer chamber of 316 S.S. designed for 1000 psig
3. Temperature programmer-controller for tube furnace

* * * *

Supplies for Reactor System:

Name	Cost	Order Date	Date Received
CO-Matheson Purity Size 1A	\$280	5/19	7/1
Moisture Indicator	\$14	5/12	5/30
Filters & rebuild kit	\$63	5/12	
Green cast 97 castable refractory 100#	\$44.80	5/8	5/12
Analytical Columns for Chromatograph	\$247	4/29	6/10

To facilitate investigation of the effects of steam on catalyst activity and surface area a water vaporizer has been designed and is presently under construction. The vaporizer sketched in Figure 20 consists of an eight-inch length of three-quarter inch schedule 40 stainless steel pipe into which has been inserted a six-inch length of perforated 1/4" stainless steel tubing which is stuffed with a glass wool wick. Reactant gases will enter at the wick end of the pipe and leave after picking up water vapor. The vaporizer and all downstream components to the reactor will be wrapped with heating tape and insulation. The vaporizer will be maintained at a temperature of 400°C and the downstream components and tubing at 100°C. The water will be metered by a Milton-Roy mini pump into the perforated tube where it will be carried the length of the tube by capillary action, vaporized, and mixed with other reactant gases before entering the reactor.

The reactor is a stainless steel tube (see Figure 21) with an inside diameter of one-inch and a length of 26 inches. Centered at the outlet end of the reactor is a thermocouple well through which a thermocouple may be extended up into the sample zone of the reactor. This thermocouple may be placed at any desired position along the central axis of the bed. The reactor inlet is flanged so the reactor may be opened for changing or removal of samples. To insure a uniform gas temperature entering the catalyst bed, the reactor will be filled on both ends of the sample with uncatalyzed monoliths.

2. Design and Construction of a Dilution Calibration Apparatus.

a. Purpose. The design and construction of a dilution apparatus was necessary for the calibration of the gas chromatograph (G.C.). The dilution technique (explanation below) allows calibration gas mixtures to be prepared in various concentrations by dilution with a high degree of accuracy. By injecting known dilutions into the G.C. for analysis, the chromatographic areas of reactant and product mixtures can be related to concentration on a daily basis. Using this technique, very low concentrations can be accurately achieved.

b. Technique. This technique has been successfully used in other chromatographic studies.²⁶ The procedure is based upon the dilution equation of a specific volume with a constant flow of a carrier gas;

$$C = C_0 \exp (-qt/V) \quad (1)$$

where:

C = concentration at any time t (vol%)
 C₀ = initial concentration (vol%)
 q = flow rate of carrier gas (ml/min)
 t = time (min)
 V = volume (ml)

At time t = 0, a known amount of gas is injected into a calibrated volume and is immediately mixed thoroughly with the carrier gas by use of a stirrer. The concentration decreases exponentially with time,

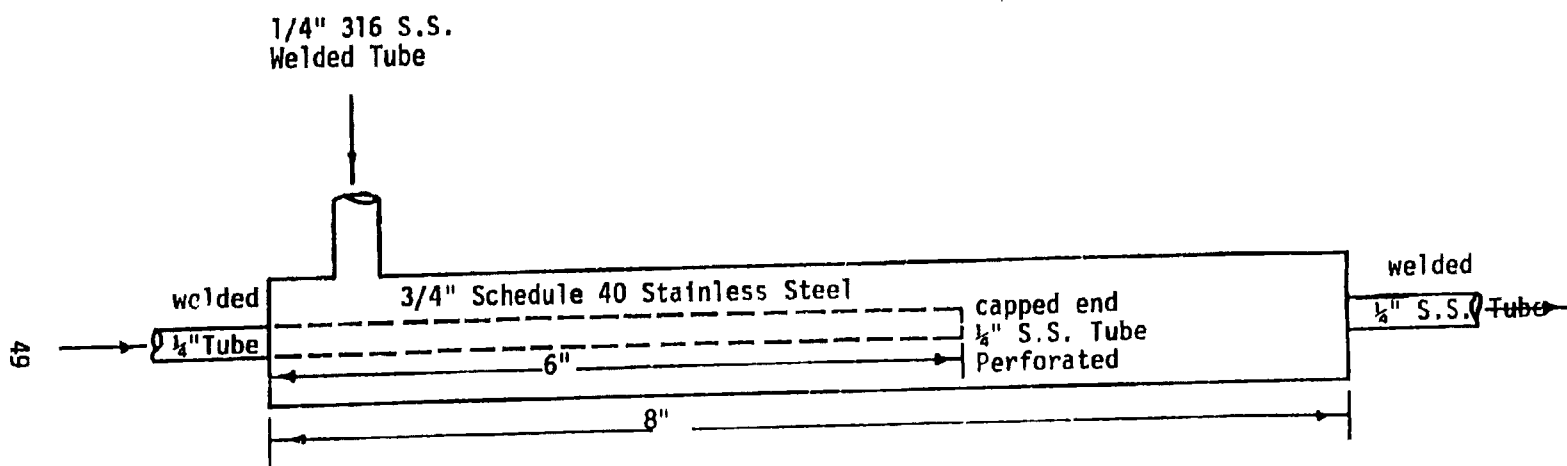


Figure 20. High Pressure H₂O Vaporizer

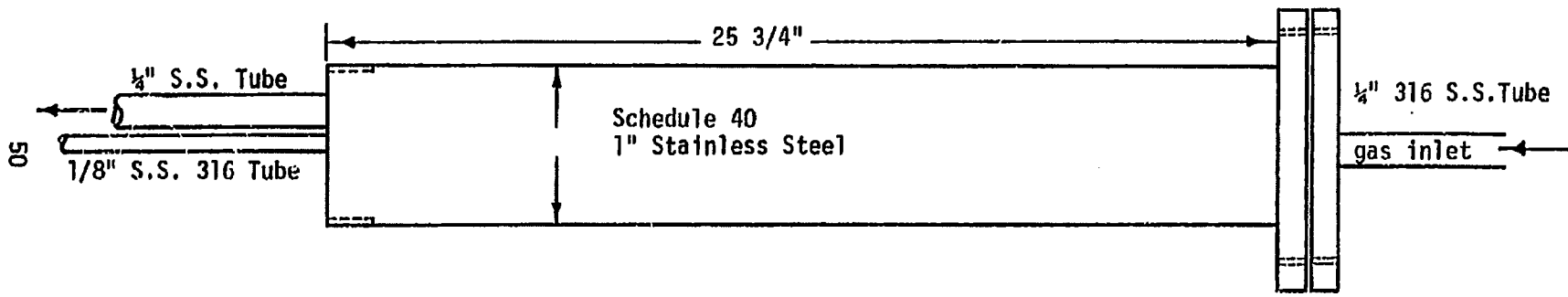


Figure 21. High Pressure Stainless Steel Reactor for Catalyst Testing.

according to Equation 1. As can be seen from the equation, the dilution rate may be increased by increasing the flow of the carrier gas (q). When the desired concentration range is reached, a sample is injected into the G.C. The chromatographic areas are plotted (see Figure 22) and compared with the theoretical slope q/v .

c. Apparatus.

(1) Dilution chamber. The dilution chamber (see Figure 23) consists of a cubical box made of Plexiglas because of its inert characteristics. The lid of the box is sealed with a rubber o-ring. The specific volume (3.980 l) was determined by filling the chamber with a measured amount of water. The stirrer was found to have a volume of 0.097 liters, making the effective volume 3.883 liters. The volume calibration will be checked using a vacuum system and a very accurate Bourdon gauge.

(2) Stirrer. The instantaneous mixing of the injected gas with the carrier gas is obtained using a mechanical magnetic stirrer. Use of a magnetic stirring bar attached to a plastic paddle (see Figure 24) eliminates rotating shafts and sealing problems. Tests with smoke and fume tracers have verified that the flow patterns set up by the stirrer itself dominate over those produced by the carrier gas flow, thereby insuring complete mixing.

(3) Ports. Quarter-inch diameter, stainless tubes were used for both the inlet and the outlet ports. These were cemented in place with Torr-seal Epoxy and fitted with Swagelok fittings. An "O" rubber stopper was used for the injection port.

The knowledge that the stirrer's flow patterns would prevail influenced considerably the placement of the inlet, outlet, and injection ports. As can be seen from Figure 23, both height difference and flow direction of the inlet and outlet streams were used to augment complete mixing. Also, the injection port was placed directly in front of the inlet port so that dispersion would be immediate. Injection of a sample into the apparatus is made using a syringe adapted with lurelok fittings and valves. The system may be modified to use a gas sample valve if desired.

(4) Flow. The flow rate will be accurately monitored and controlled by use of an electronic mass-flow controller.

3. Work forecast. During the next quarter, it is expected that most of the equipment and supplies necessary for building the new high pressure reactor system will have arrived. Construction of this system is expected to be 75 to 90% complete by the end of the next quarter, which is 2-3 months ahead of schedule.

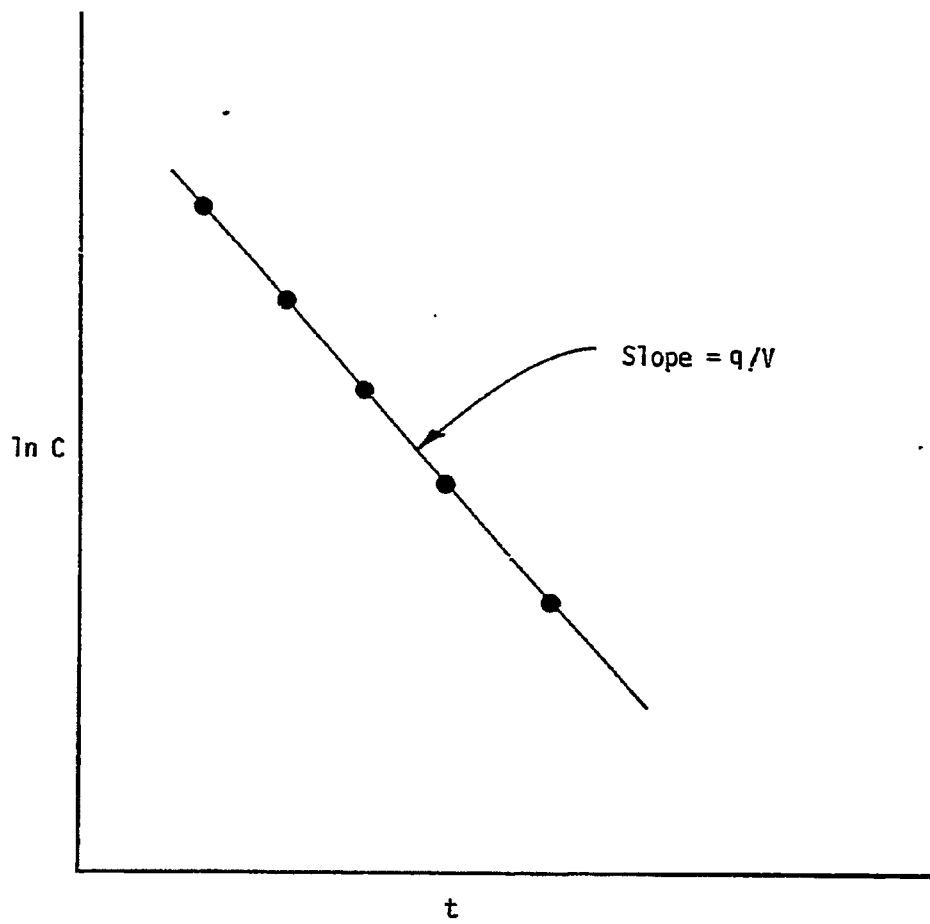
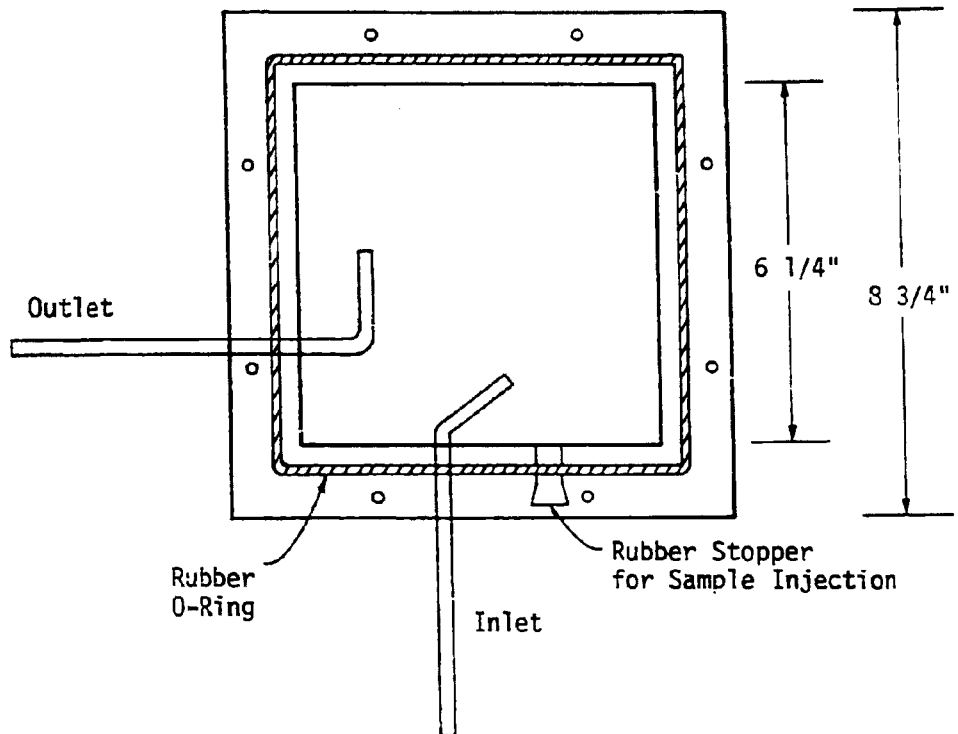


Figure 22. Concentration - Time Relation for the Gas Concentration Dilution Technique

TOP VIEW



SIDE VIEW

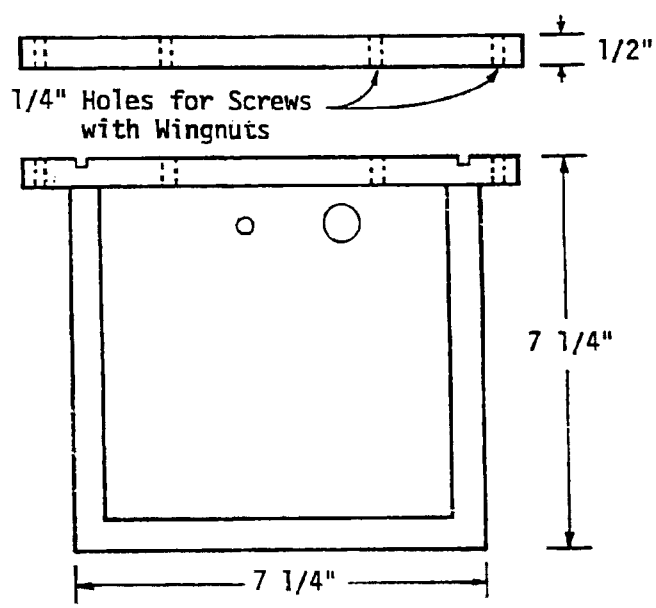
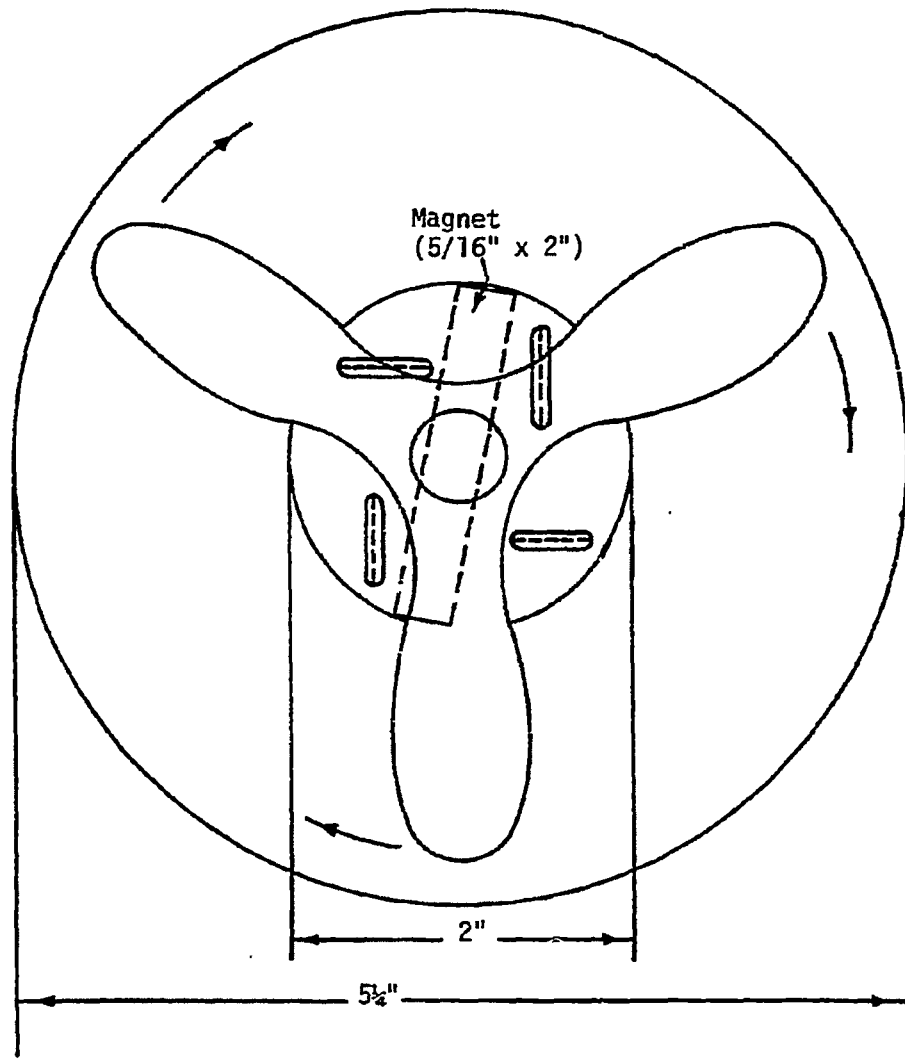


Figure 23. Dilution Calibration Apparatus

TOP
VIEW



SIDE
VIEW

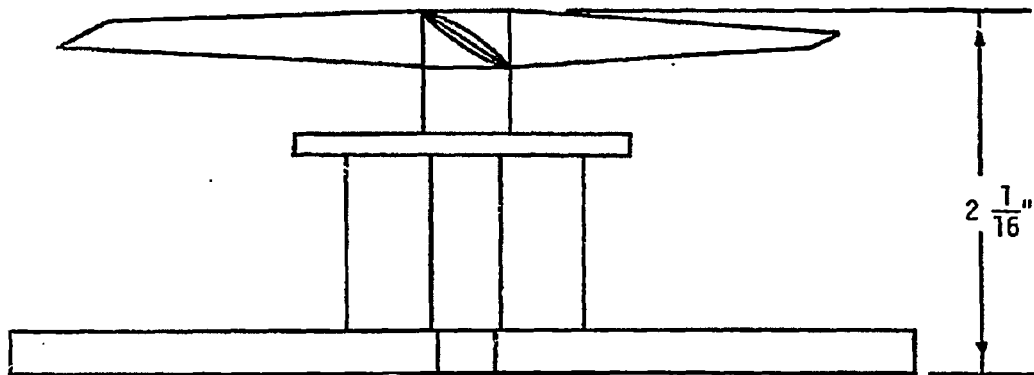


Figure 24. Stirrer for Dilution Calibration Apparatus

C. Task 3: Reactor Screening of Alloy Catalysts

1. Design of Screening and Activity Tests

a. Introduction. During this first quarter considerable effort has been directed toward designing and refining tests for catalyst screening and measurement of methanation activity. A screening test has been designed to give a quick, but useful comparison of catalyst methanation activity under steady-state, reaction-limited conditions using a continuous flow system at atmospheric pressure. The pulse technique was abandoned because (1) earlier experiments in this laboratory showed that pulse broadening in our reactor was a serious problem and (2) pulse reactor data cannot be used for calculating steady-state reaction rates for comparison with data by other workers. A procedure for measuring conversion versus temperature was also tested with the purpose of obtaining useful design data for selected catalysts in an integral plug flow system. Both the screening (differential) and integral tests are discussed below followed by a brief discussion of data collection and reduction procedure.

b. Differential test (low conversion screening test). Most catalysts are initially reduced and passivated in our catalyst reduction system (see Section III-A-3 and Figure 15). A previously reduced sample of catalyst (usually one to four grams) is loaded into the stainless steel reactor. The sample is heated in flowing H_2 (approximately $500\text{ cm}^3/\text{min}$) to 450°C and held for two hours at that temperature. The sample is then allowed to cool in flowing H_2 to about 250°C . Reactant gases (1% CO , 4% H_2 and 95% N_2) are next allowed to flow through the reactor at a space velocity of $30,000\text{ hr}^{-1}$ for 30 minutes during which time the reactor temperature is stabilized at 275°C . Three chromatographic samples are taken after which the reactants are routed through the reactor bypass while three additional chromatographic samples are taken to determine unconverted reactant gas concentrations. All important experimental conditions such as temperature and pressure are recorded at the time each chromatographic sample is taken.

The data are next reduced and the following quantities are calculated: a) conversion of CO to products, b) production of CH_4 , c) production of other species such as CO_2 and other hydrocarbons, d) selectivity, the ratio of b to a, e) rate of CH_4 production per unit weight and per unit surface area of catalyst, f) turnover number, the number of product molecules produced per atomic catalytic site per second.

c. Integral test (high conversion test). The reactor is loaded with a $20\text{-}35\text{ cm}^3$ sample of previously reduced and passivated catalyst. The sample is heated under flowing H_2 to 450°C , held constant at this temperature for two hours and then cooled to 100°C . A reactant gas mixture (1% CO , 4% H_2 and 95% N_2) next enters the reactor at a space velocity of $15,000\text{ hr}^{-1}$ and the reactor is heated at a slow rate ($3\text{-}5^\circ\text{C}$ per minute). Gas chromatographic samples are taken every 25°C over the temperature range $150^\circ\text{C}\text{-}475^\circ\text{C}$. After the run is complete the reactor is bypassed and three chromatographic samples of the unconverted reactant gas are analyzed. The resulting data are plotted as conversion vs. temperature.

d. Testing of poisoned catalysts. The catalysts are reduced in H_2 and exposed to a stream containing various H_2S concentrations from 1-50 ppm in a special pyrex system (see Figure 4) for a period of 6-24 hours. A sample of the poisoned catalyst is charged to the stainless steel reactor and tests are carried out under either differential or integral conditions as previously outlined.

e. Data collection and reduction. Reactor test data for each run are recorded on a reactor test data sheet identical to that shown in Table 11. Similar data sheets are used for recording adsorption data and summary data (composition, physical properties, and test results) for each catalyst.

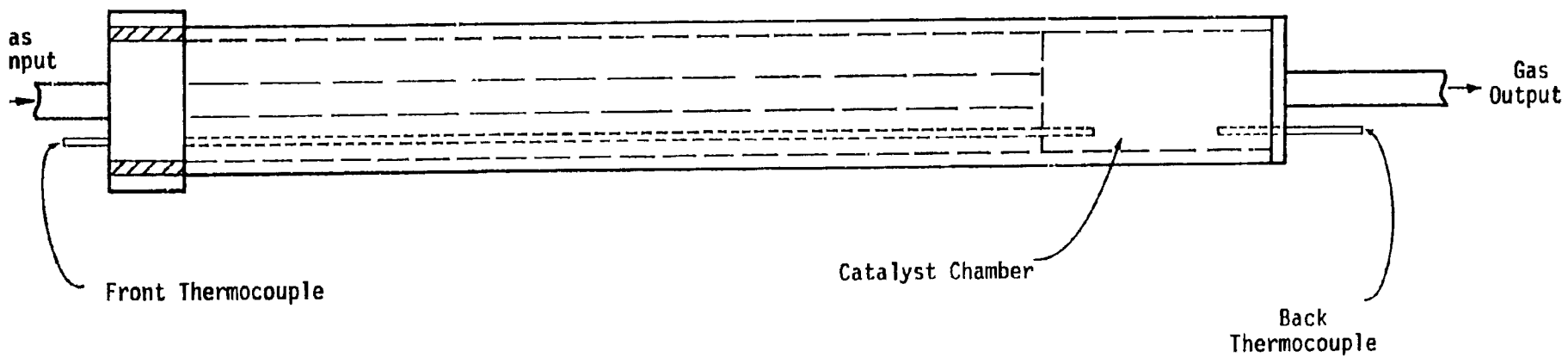
In order to calculate reactor flow rates and basic kinetic data (conversion, rate, and turnover number) with greater speed and accuracy, interacting calculator programs have been written for use on a Hewlett-Packard 9810 calculator equipped with a Plotter Block/Alpha ROM and a printer option. These programs recorded on magnetic cards are designed to request specific data input from the user and to provide a hard copy output of all input and output, significantly reducing the possibility of error in calculation. Similar programs have also been written for calculation of gas uptakes from absorption data.

2. Results.

a. Differential screening tests. Initial activity studies were conducted on selected catalysts using the atmospheric pressure reactor system shown in Figure 18. A detailed drawing of the low pressure stainless steel reactor with thermocouples to measure sample temperatures is shown in Figure 25.

Specific rates at 275°C and atmospheric pressure for nickel, nickel-ruthenium and nickel-rhodium catalysts supported on 1/8-inch alumina beads are shown in Table 12. The entering reaction mixture contained 1% CO, 4% H_2 , and the remainder was N_2 . The rates were determined at low conversions, low temperatures, and high space velocity (275°C, 15-30% conversions, GHSV = 30,000 hr^{-1}) with 2 to 4 grams of catalyst in the reactor (the remainder of the bed was filled with pure Al_2O_3 pellets) in order to minimize the influence of heat and mass transfer. Catalyst samples were initially reduced at 450-500°C for 6-12 hours before activity measurements were carried out.

The turnover numbers (N_{CO} and N_{CH_4}) shown in Table 12 indicate approximately the same order of magnitude activity for Ni, Ni-Ru, and Ni-Rh catalysts. Our turnover numbers agree well with the initial rates reported by Dalla Betta et al.²⁷ and Vannice²⁸ for 0.5% Ru/ Al_2O_3 and 5% Ni/ Al_2O_3 . After analyzing the data, it appears that a small uncertainty (1-5%)²⁹ in our results may be attributed to small variations in gas concentrations, pressure and flow rates over the test period of a given catalyst. The measurement of both activity and selectivity also includes uncertainties of 1-5% in calibration and measurement of gas concentrations. Thus, it may be possible that selectivities for CH_4 are slightly higher than indicated, although there is undoubtedly significant hydrocarbon



57

Figure 25. Stainless Steel Catalyst Reactor
(0-60 psig operation)

TABLE 11

REACTOR TEST DATA SHEET

CATALYST _____ RUN # _____ DATE: _____ PAGE: _____
 Run Mode: Differential _____ Integral _____

REACTOR LOADED BY

Weight of Catalyst _____ grams
 Nominal Composition _____
 Surface Area (if available) _____ m²/g

REDUCTION SCHEDULE

1st Ramp Rate _____ °C/min. Hold at _____ °C for _____ hrs.
 2nd Ramp Rate _____ °C/min. Hold at _____ °C for _____ hrs.
 H₂ Flow Rate _____ ml/min.

RUN CONDITIONS

CONDUCTED BY _____

Time at which mixed reactants began flow over catalyst _____
 Barometric Pressure _____ torr

Gas Sample #							
Flow Rates H ₂							
CO							
N ₂							
H ₂ S in N ₂							
Other							
Reactor Temperature							
Time							
System Pressure							
Chromatograph Page							

GAS CHROMATOGRAPH CONDITIONS

Carrier Gas: _____ Columns: _____

CALCULATIONS

DONE BY _____

Temperature							
Conversion CO							
Conversion CH ₄							
Conversion CO ₂							
Rate							
Turnover #							

Show Calculations on Back.

UPSET CONDITIONS AND OTHER OBSERVATIONS

TABLE 12

Steady-State Activity Data for Nickel and Nickel Alloy Catalysts
 275°C, 1 atm., H₂/CO = 3.5-5, GHSV = 30,000 hr⁻¹

Code	Rate		N _{CO} - Turnover # - N _{CH₄}		% Conv.		Select.
	(moles CO Conv.) ^a g - cat - sec.	(moles CH ₄ Prod.) ^a g - cat - sec.	(moles CO Conv.) ^b site - sec.	(moles CH ₄ Prod.) ^b site - sec.	CO	CH ₄	(N _{CH₄} /N _{CO})
Ni-A-111	7.56	6.3	29.8	24.8	22.0	18.2	0.83
Ni-A-114 ^c	45.2	37.1	10.7	8.8	36.2	29.7	0.82
Ni-Ru-A-101	5.1	4.7	18.3	17.2	14.8	13.9	0.94
Ni-Ru-A-102	15.3	13.5	33.5	29.6	33.1	28.9	0.87
Ni-Ru-A-103	11.5	8.9	21.2	16.5	20.8	16.2	0.78
Ni-Ru-A-104	7.3	6.8	15.5	14.4	21.6	20.0	0.93
Ni-Ru-A-105#1	8.2	7.8	14.7	14.1	23.9	22.9	0.96
Ni-Ru-A-105#2	12.0	10.1	21.6	18.1	18.1	15.2	0.84
Ni-Rh-A1-100#1	11.6	10.6	15.1	13.9	14.4	13.3	0.92
Ni-Rh-A1-100#2 ^c	23.1	21.6	30.2	28.2	14.5	13.5	0.93
0.5% Ru/Al ₂ O ₃ Englhard Catalyst Tested by Dalla Betta et al. (Ford Motor Co.) - Ref. 26			20 ^d	<u>Footnotes</u> a. x 10 ⁷ b. x 10 ³ c. GHSV = 60,000 hr ⁻¹ d. Initial Rates			
5% Ni/ZrO ₂ Dalla Betta et al. - Ref. 26			180 ^d				
5% Ni/Al ₂ O ₃ M.A. Vanñice (Exxon) - Ref. 27			38 ^d				
5% Ru/Al ₂ O ₃ M.A. Vanñice - Ref. 27			325 ^d				

and CO₂ production.^{27,28} Efforts are presently in progress to refine our methods of measurement, calibration, and analysis of the data through the addition of precision mass flow meters, analysis for CO₂ and hydrocarbons and a dilution apparatus for calibration of gas concentrations.

Dalla Betta et al.²⁹ have indicated that their steady-state rates for methanation (after a 24-hour exposure to a reaction mixture) are 25 times lower than their initial rates²⁷ shown in Table 12. Thus, exposure to a reaction mixture over a period of hours or even minutes may significantly reduce the activity of the catalyst. This may explain why the turnover numbers reported in this study which were measured after exposure for 1/2 to 4 hours under reaction conditions are significantly lower than initial rates reported in the literature for 5% Ni/ZrO₂²⁷ and 5% Ru/Al₂O₃.²⁸ The discrepancy between initial rates measured by Dalla Betta²⁷ and Vannice²⁸ for nickel and ruthenium catalysts might be similarly explained by differences in their pretreatment of the catalyst.

The conversions shown in Table 12 ranging from 14 to 30% are admittedly too large for differential conditions to exist. As a check for heat and mass transfer effects, two tests were performed using four, then two grams of Ni-Ru-Al-105 and two tests at different space velocities for Ni-Rh-A-100. Data for these tests in Table 12 show a significant increase in the turnover number for the smaller sample and higher space velocity. These results suggest that the measured rates may indeed be limited by heat and/or mass transfer. Future tests will be conducted at lower conversions (<10%) and perhaps at a lower temperature (250°C) to minimize such effects.

b. Effects of passivation on activity and integral tests for Ni-A-114. A test was conducted to determine the effects of passivation on a nickel catalyst which was prepared in our NSF Study. A 20-gram sample of Ni-A-114, 15% nickel on alumina was used. The catalyst was reduced and pretreated in the usual manner, after which an integral test was carried out. The catalyst was then passivated with a 1% air in N₂ stream at a space velocity of about 15,000 hr.⁻¹ The leading edge of the bed experienced a 12°C temperature rise which lasted about 5 minutes. The trailing edge experienced a rise of 25°C over about 10 minutes. The catalyst was again reduced followed by another integral test. The catalyst was again passivated in the same manner as previously and very similar temperature effects were noted.

Conversion versus temperature data are plotted in Figure 26 for the two integral tests described above. Conversion versus temperature curves are very similar for both runs and reach a maximum between 275°C and 300°C. Approximately 90% of the CO usage is accounted for by CH₄ production. The remainder may be assumed to have been converted to CO₂ and other hydrocarbons.

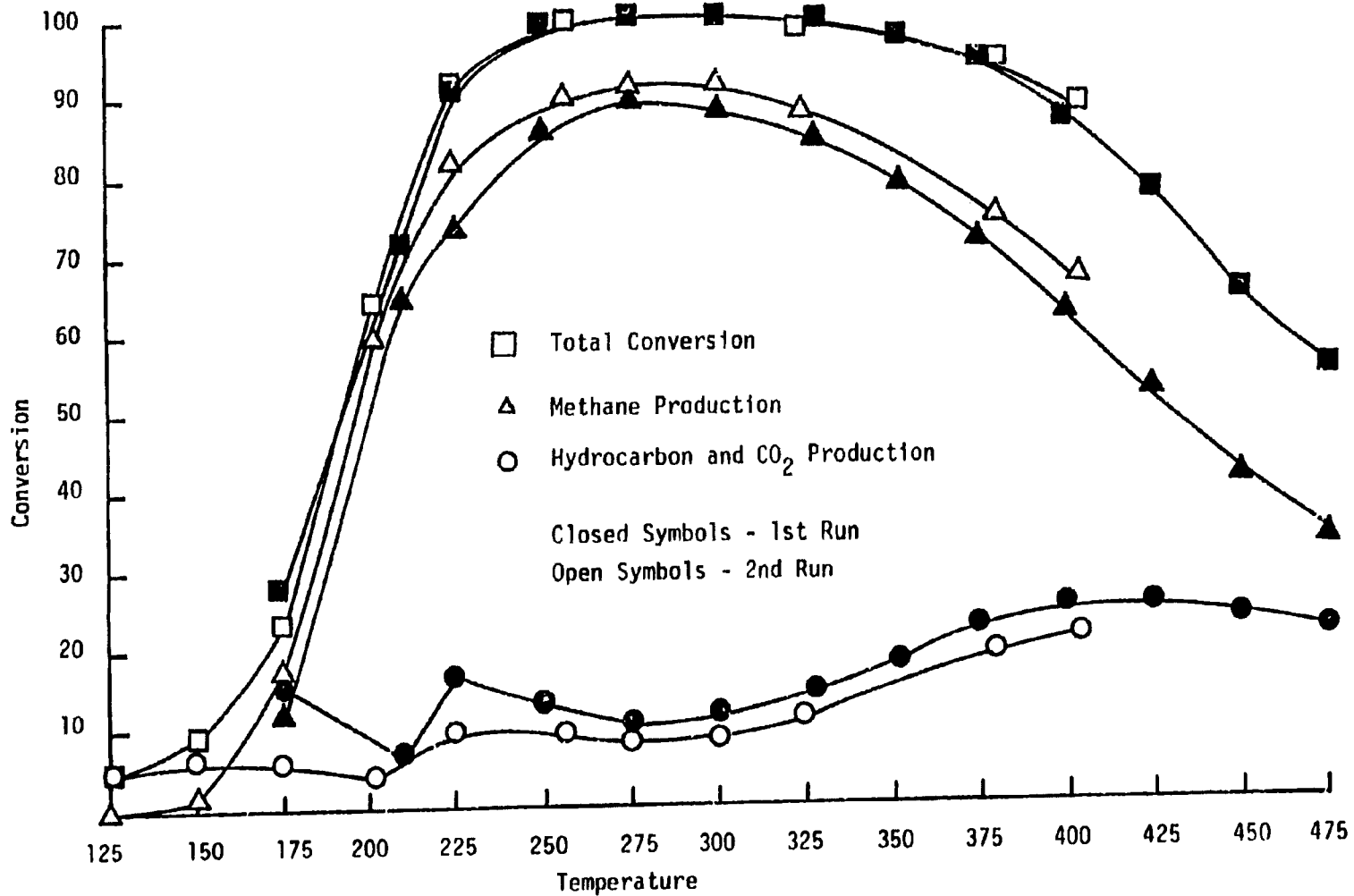


Figure 26. Integral Activity Test For Ni-A-114 (15% Ni/Al₂O₃)

3. Work forecast. During the next quarter screening tests for alumina-supported Ni, Ni-Ru, Ni-Rh, and Ru will be repeated at a lower temperature (probably 250°C) to achieve low conversions (<10%) and minimize heat and mass transfer effects. Alumina-supported Ni-MoO₃, Ni-Fe, Ni-Co, Ni-Pt, Ni-Pd and selected industrial methanation catalysts will also be screened according to the same procedure. The activities of both fresh and poisoned Ni and Ni-Ru catalysts and their conversion versus temperature behavior will be measured and compared with corresponding results for selected commercial catalysts.

D. Task 4: Catalyst Geometry Testing and Design

This task is scheduled to begin 18 months after initiation of the project or in other words October 22, 1976. No experimental work was completed during the past quarter nor is any work scheduled for the next quarter in connection with this task. Arrangements have been made with technical and sales representatives of Corning Glass Works in which they will send us monolithic supports of various geometries. In fact, some of these samples have already been received by our laboratory. The possibility of testing one or two samples of sprayed-Raney-nickel catalyst of the parallel plate configuration has also been discussed with technical representatives at the Bureau of Mines in Pittsburgh.

E. Task 5: Technical Visits and Communication

1. Accomplishments. During the past several months the principal investigator has established technical communications with other workers active in methanation catalysis, many of whom are listed on the Report Distribution List in Appendix B. Private communications in the form of letters, phone calls, exchange of preprints, and informal discussions at meetings have been very helpful in keeping up-to-date and comparing important results while avoiding unnecessary duplication of other's research.

The principal investigator is presently Secretary-Treasurer of the California Catalysis Society and the Task Force Leader for Metal Surface Areas on the ASTM D-32 Committee. These professional duties bring the principal investigator directly in contact with others working in catalyst characterization, surface area measurement, and methanation catalysis, all pertinent to this present investigation.

A particularly profitable learning experience at the beginning of this last quarter involved attendance by the principal investigator at the Symposium on Catalytic Conversion of Coal held April 21-23 in Pittsburgh. The experience was valuable both in terms of direct private contacts and communications with other workers in methanation catalysis and in very informative presentations dealing directly with methanation catalysis and other catalytic aspects of coal conversion.

2. Work forecast. During the next quarter the principal investigator will present a lecture on "Catalysis and Adsorption" at a short course "Catalysis in Industry" to be given September 8-12 at Park City, Utah and will attend the Fall meeting of the California Catalysis Society. A visit to the Bureau of Mines in connection with attendance at the Fall ASTM meeting is being planned. The principal investigator is also scheduled to present a paper on "Chemistry of Ni/Al₂O₃ Catalysts" at the 68th Annual AIChE meeting in Los Angeles in November. Attendance at these meetings will provide additional opportunities for the principal investigator to build and continue communications with other workers in methanation catalysis.

V. CONCLUSIONS

A. Hydrogen adsorption data indicate that, in general, surface areas for large catalyst samples prepared by hydrogen decomposition of alumina-supported nitrate salts with a slow, uniform increase in temperature are larger than for small catalyst samples reduced with a faster, less uniform increase in temperature.

B. Preparation of nickel-ruthenium catalysts from a basic impregnating solution results in a more uniform distribution of catalyst throughout the pellet and a slightly higher surface area compared to catalysts prepared from an acidic impregnating solution.

C. Surface areas determined by hydrogen adsorption are larger for 3 wt.% Ni-Ru/Al₂O₃ catalysts compared to 3% Ni/Al₂O₃. The dispersion of 3 wt.% (0.5 wt.% Ru) Ni-Ru/Al₂O₃ is intermediate between 3 wt.% Ni/Al₂O₃ and 0.5 wt.% Ru/Al₂O₃.

D. Carbon monoxide adsorption on nickel is an unreliable technique for measuring nickel surface area in view of (1) considerable variation in adsorption uptakes resulting from modest variations in equilibration pressure and temperature, (2) formation of Ni(CO)₄ causing significant loss of nickel from the catalyst, and (3) extensive physical and chemical adsorption of carbon monoxide on the alumina support requiring large corrections to the data with corresponding losses in accuracy.

E. Significant quantities of carbon monoxide are chem- and physisorbed on Al₂O₃ at both 25 and -85°C. Hydrogen adsorption (chemical or physical) on Al₂O₃ is negligibly small at 25°C.

F. The observed decrease in hydrogen adsorption for a catalyst after exposure to 10 ppm H₂S for 12 hours is a measure of its resistance to sulfur poisoning. The order of decreasing resistance to poisoning for catalysts studied thus far is: Ni-Rh > Ni-Ru ~ Ni > Ni-MoO₃ > Ru. However, Ni-MoO₃/Al₂O₃ shows unusual behavior by adsorbing within 3-6 hours enough H₂S to block 40-45% of the hydrogen adsorption sites after which there is no further significant adsorption of H₂S within the next 6-12 hours.

G. Steady-state conversions of carbon monoxide at 275°C, 1 atm. (inlet composition of 1% CO, 4% H₂, 95% N₂) range from 14-35% for alumina-supported Ni-Rh, Ni-Ru and Ni. Percent selectivities to methane range from 78-94%. Turnover numbers are not significantly different within experimental error for these catalysts and compare favorably with initial rates reported for 5% Ni/Al₂O₃ and 0.5% Ru/Al₂O₃.^{27,28} Methanation rate data determined in this study at 275°C are clearly influenced by heat and mass transfer; thus, a lower temperature (250°C) will be used henceforth.

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APPENDICES

- A. CALCULATION OF SURFACE AREA AND DISPERSION FOR ALLOYS
- B. REPORT DISTRIBUTION LIST
- C. BIBLIOGRAPHIC DATA SHEET

APPENDIX A

CALCULATION OF SURFACE AREA AND DISPERSION FOR ALLOYS[†]

1. Dispersion and Surface Composition of Alloys

Let x = overall mole fraction of A in alloy $A_x B_{1-x}$

x^S = surface mole fraction of A

N = total number of atoms = $N_A + N_B$

N_A^S or N_B^S = number of atoms at surface

x_{H_2} = μ moles of H_2 uptake per gram catalyst

(S.A.)_{A or B} = inverse planar density or surface area per atom of A or B

d = average crystallite diameter in \AA

D = dispersion; the ratio of surface to total number of atoms of a given kind

$M_{A or B}$ = molecular wt. of A or B

$W_{A or B}$ = weight per cent of A or B in catalyst

a. Definition of Dispersion, D

$$D_A = \frac{N_A^S}{N_A} \quad , \quad D_B = \frac{N_B^S}{N_B}$$

b. Surface Composition

$$x^S = \frac{N_A^S}{N_A^S + N_B^S} = \frac{x N D_A}{x N D_A + (1-x) N D_B}$$

$$x^S = \frac{x D_A}{x D_A + (1-x) D_B}$$

To determine surface composition we need independent measurements of D_A and of D_B

[†]Reference: C. Bartholomew, Ph.D. Dissertation, Stanford U., 1972.

c. Total Dispersion \equiv number ratio of total metal surface atoms to total metal atoms in sample

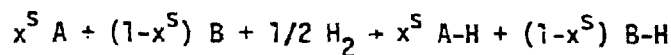
$$D_T = \frac{N_A^S + N_B^S}{N} = \frac{N_A^S}{N} + \frac{N_B^S}{N}$$

But $N_A = x N$ and $N_B = (1-x)N$

$$\begin{aligned} D_T &= \frac{x N_A^S}{N_A} + (1-x) \frac{N_B^S}{N_B} \\ &= x D_A + (1-x) D_B \end{aligned}$$

2. Calculation of Dispersion from Hydrogen Uptake

Consider the stoichiometric reaction:



1/2 mole of H_2 is taken up for every x^S moles of A

$$D_A = \frac{(\mu\text{moles A}) \text{ surface}}{(\mu\text{moles A}) \text{ total}}$$

$$\frac{(\mu\text{moles A})}{\text{g cat}} \text{ total} = W_A (\text{wt.}\% A \times 10^{-2}) \cdot \frac{1 \text{ mole A}}{M_A \text{ g A}} \cdot \frac{10^6 \mu\text{moles A}}{\text{mole A}}$$

$$D_A = \frac{x_{H_2} (\mu\text{moles } H_2) \cdot \frac{x^S \mu\text{moles Surface A}}{1/2 \mu\text{moles } H_2}}{\frac{W_A 10^{-2} 10^6}{M_A}}$$

$$= \frac{2 x_{H_2} \cdot x^S \cdot M_A}{W_A (10^4)}$$

Similarly

$$D_B = \frac{2 x_{H_2} \cdot (1-x^S) \cdot M_B}{W_B (10^4)}$$

$$D_T = x D_A + (1-x) D_B$$

$$= x \left[\frac{2x_{H_2} \cdot M_A \cdot x^S}{W_A \cdot 10^4} \right] + (1-x) \left[\frac{2x_{H_2} \cdot M_B \cdot (1-x)^S}{W_B \cdot (10^4)} \right]$$

Assume $x \cong x^S$ and $1-x \cong 1-x^S$

$$D_T = \left(\frac{2x_{H_2}}{10^4} \right) \left[\frac{M_A x^2}{W_A} + \frac{M_B (1-x)^2}{W_B} \right]$$

Example 1: For a 90/10 (at.%) Ni-Ru/ Al_2O_3 catalyst
2.5 wt.% Ni, 0.5 wt.% Ru

$$x = .9 \quad (1-x) = 0.1$$

$$W_A = 2.5\% \quad W_B = 0.5\%$$

$$M_A = 58.71 \quad M_B = 101.07$$

$$D_T = \frac{2x_{H_2}}{10^4} \left[\frac{58.71 (.9)^2}{2.5} + \frac{101.07 (.1)^2}{0.5} \right]$$

$$\% D_T = 0.421 x_{H_2}$$

3. Calculation of Surface Area For Alloys

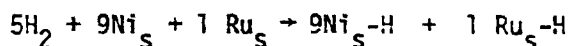
Assuming a planar density for each atom A and B which is a simple average of the planar densities for the possible surface planes for each metal, we can calculate the average surface area of each atom. Then total surface area is simply:

$$\begin{aligned} \text{Surface area} &= (\# \text{ atoms A at surface}) \left(\frac{\text{surface area}}{\text{atom A}} \right) \\ &\quad + (\# \text{ atoms B at surface}) \left(\frac{\text{surface area}}{\text{atom B}} \right) \\ &= N_A^S (\text{S.A.})_A + N_B^S (\text{S.A.})_B \end{aligned}$$

Example 2: 90/10 alloy of Ni-Ru/ Al_2O_3
(90/10 refers to relative atomic mole% of metals)

<u>Properties</u>	<u>Ni</u>	<u>Ru</u>
Surface area/atom	6.77 Å ² /atom [†]	8.17 Å ² /atom*
M. W.	58.71	101.07
density	8.98/cm ³	12.2 g/cm ³

Stoichiometric Surface Reaction Assumed:



We assume the surface and bulk compositions are the same--not necessarily true!

$$\begin{aligned} \text{S.A.} &= [0.9(6.77) + 0.1(8.17)] \frac{10^{-16} \text{ cm}^2}{\text{met. atom}} \cdot \left(x \frac{\mu\text{moles H}_2 \text{ uptake}}{\text{gm catalyst}} \right) \\ &\quad \cdot \left(10^{-6} \frac{\text{moles}}{\mu\text{mole}} \right) \cdot \left(6.02 \times 10^{23} \frac{\text{met. atoms}}{\text{mole met.}} \right) \left(\frac{2 \text{ moles met.}}{1 \text{ mole H}_2} \right) \\ &= 831.96 \text{ cm}^2/\text{g cat} \quad (x) \end{aligned}$$

$$\text{S.A.} = 0.0832 \text{ m}^2/\text{g cat} \quad (x)$$

4. Calculation of Particle Size for Alloys

Example 3: 90/10 Ni-Ru/Al₂O₃

Calculate average crystallite size, d (Å)

N_s = # surface atoms/crystallite

$$\frac{4\pi r^2}{[0.9(6.77) + 0.1(8.17)] (\text{Å}^2/\text{atom})} = \frac{\pi d^2}{6.91} \frac{\text{atoms}}{\text{crystallite}}$$

N_p = total number of metal atoms/crystallite

$$= \text{volume of particle (cm}^3) \cdot \frac{N_{\text{Avog}} (\text{atoms/mole})}{(\text{M.W.})_{\text{ave}} \text{ s/mole}} \cdot \frac{(\text{density})_{\text{ave}} (\text{g/cm}^3)}$$

[†]Based on lowest 3 index planes for nickel.

*R. A. Dalla Betta, J. Catal. 34, 57 (1974).

$$= \frac{\pi d^3}{6} \cdot \frac{6.02 \times 10^{23}}{0.9 (58.71) + 0.1 (101.07)} \cdot [0.9(8.9) + 0.1 (12.2)] \text{ atoms}$$

$$\cdot \frac{1 \text{ cm}^3}{10^{24} \text{ \AA}^3} = 0.0462 d^3$$

$$\%D = \frac{N_s}{N_p} \cdot 10^2 = \frac{\pi d^2 / 6.91 \cdot 10^2}{0.0462 d^3} = \frac{984}{d}$$

$$\%D = \frac{984}{d}$$

$$\text{or } d = \frac{984}{\%D}$$

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7. Author(s) Calvin H. Bartholomew	8. Performing Organization Rept. No.		6.
9. Performing Organization Name and Address Catalysis Laboratory Chemical Engineering Science Brigham Young University Provo, Utah 84602		10. Project/Task/Work Unit No.	11. Contract/Grant No. E(49-18)-1790
12. Sponsoring Organization Name and Address Energy Research and Development Administration Fossil Energy 2100 M Street Washington, D.C. 20037		13. Type of Report & Period Covered ATTENTION: Dr. Paul Scott Technical Representative	14.
15. Supplementary Notes			
16. Abstracts This report presents work accomplished during the first quarter of investigation of new pellet- and monolithic-supported alloy catalysts for methanation of coal synthesis gas. Alumina-supported nickel and nickel alloys were prepared, characterized by surface area measurements, and tested for methanation catalyst activity. To determine effects of sulfur poisoning on surface area, the adsorption of hydrogen on these catalysts was measured before and after exposure to hydrogen sulfide. A procedure for measuring adsorption of carbon monoxide on nickel underwent extensive testing and evaluation. In addition, screening and testing procedures to measure methanation catalyst activity were designed and tested. Preparation, adsorption, poisoning and analytical calibration systems were designed, constructed, and tested. Design of a high pressure laboratory reactor was completed and the associated equipment and supplies ordered.			
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