SPACE ENVIRONMENT OPERATION OF EXPERIMENTAL HYDRAZINE REACTORS

FINAL REPORT

REPORT NO. 4715.3.68-27
CONTRACT NAS7-520

JULY 1968

Ronald A. Carlson • Jack L. Blumenthal
Robert J. Grassi

TRW
SYSTEMS GROUP

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FOREWORD

This technical report was prepared for the National Aeronautics and Space Administration, NASA Pasadena Office, Pasadena, California, by TRW Systems, Redondo Beach, California, under an extension to Contract NAS 7-520. This Final Report covers the period 29 April 1967 through 30 June 1968. The program was conducted as a part of the NASA Advanced Technology Program under the direction of Robert H. Rollins, II. The Technical Director was David D. Evans, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California. The TRW Systems Project Manager was Ronald A. Carlson.

This report contains no classified information.

This technical report has been reviewed and approved by the Technical Director.

ABSTRACT

Experimental investigations relating the low temperature high vacuum hydrazine ignition properties of Shell 405 catalyst with the concentration of adsorbed gas species (O_2, N_2, H_2, and NH_3) present on the catalyst surface are reported. The laboratory investigations revealed that: a) Shell 405 catalyst retains strongly chemisorbed oxygen which will not desorb significantly in high vacuum, even at elevated temperature. b) adsorbed hydrogen does not readily desorb in vacuum at temperatures below 600°C. c) nitrogen adsorption is extremely low, and adsorbed ammonia tends to decompose above 300°C.

Three catalyst surface conditions were investigated in high vacuum ignition tests: a surface containing chemisorbed oxygen, a "clean" surface, and a surface containing chemisorbed hydrogen. There is some indication that the presence of oxygen may enhance the ignition process, but a definite correlation between catalyst surface condition and ignition delay is not yet possible. A much larger data sample would be required to isolate the effects of surface condition. The factor exhibiting the greatest effect on ignition delay is temperature. Catalyst activity decreases greatly with temperature, and the flash vaporization and cooling of low temperature propellant upon injection into vacuum result in decreased apparent activity.

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1.0 INTRODUCTION AND SUMMARY

This report describes the experimental investigations conducted by TRW Systems under an extension of Contract NAS 7-520. The objective of this contract extension was to correlate the low temperature, high vacuum, hydrazine ignition properties of the Shell 405 catalyst with the concentration of adsorbed gas species (O_2, N_2, H_2, and NH_3) present on the catalyst surface both prior to an initial firing with the catalyst and after cool-down in vacuum.

1.1 LABORATORY EXPERIMENTS

The laboratory effort involved a systematic study of the adsorption and desorption of hydrazine decomposition products (nitrogen, hydrogen, and ammonia) and oxygen on the Shell 405 iridium based catalyst. The laboratory investigations were aimed at determining what concentrations of oxygen and hydrogen decomposition products would be present on the surface of the Shell 405 catalyst prior to initially using the catalyst in a space environment and after a vacuum firing sequence.

Hydrogen, oxygen, ammonia and nitrogen temperature (adsorption-desorption) scanning experiments were completed in the range from $0^{\circ}C$ to $700^{\circ}C$.

Hydrogen and oxygen adsorption and desorption isotherms were made with oxygen free catalysts and on catalysts initially covered with chemisorbed oxygen (as manufactured) in the temperature range from $0^{\circ}C$ to $500^{\circ}C$ and at pressures to 300 torr. Nitrogen and ammonia adsorption and desorption isotherms were made with oxygen free catalysts in the temperature range from $0^{\circ}C$ to $300^{\circ}C$ and at pressures to 300 torr.

Differential heats of adsorption were determined for hydrogen with both oxygen covered and oxygen free catalysts. Differential heats of adsorption were also determined for ammonia adsorption on the alumina support.

Oxidation rate measurements (chemisorption rate measurements) of the iridium surface of the Shell 405 catalyst were made over the temperature range of $-78^{\circ}C$ to $300^{\circ}C$ and over the pressure range from 1 torr to 100 torr.

Laboratory investigations showed that:

- Shell 405 catalyst retains strongly chemisorbed oxygen which will not desorb significantly in high vacuum, even at elevated temperatures.
- Adsorbed hydrogen does not readily desorb in vacuum at temperatures below 600°C.
- Nitrogen adsorption is extremely low, and adsorbed ammonia tends to decompose above 300°C.

Hence, the in-space operating conditions which are of interest are: 1) Adsorbed oxygen during initial operation; 2) catalyst free of adsorbed gases when cool down times are sufficient to desorb all hydrogen; and 3) adsorbed hydrogen retained from the hydrazine decomposition products during rapid cool down after operation.

1.2 VACUUM IGNITION TESTS

A series of high vacuum ignition tests were conducted simulating the catalyst surface conditions anticipated for in-space operation of a reactor. Three surface conditions were tested: A surface containing chemisorbed oxygen, a "clean" surface, and a surface containing chemisorbed hydrogen. These conditions were tested at ambient temperature (70°F) and at 40°F.

The presence of oxygen chemisorbed on the catalyst surface appears to enhance the first catalytic ignition. Formation of definite conclusions relating catalyst surface condition to ignition delay, however, is made difficult due to wide variations in the data. A much more predominant factor than surface conditions is temperature, particularly at temperatures below 70°F. An initial temperature of 40°F resulted in ignition delays in excess of 100 ms. Also, in a space environment, the local temperature at the catalyst/propellant interface is depressed due to the flash vaporization and cooling of the incoming propellant. This is an important factor which should be considered in further investigations.

2.0 LABORATORY EXPERIMENTS

The experimental apparatus and techniques are described in the following paragraphs:

2.1 APPARATUS

The all glass, constant volume, adsorption system consisted of a manifold and gas sample bulbs, a catalyst sample tube thermally isolated from the manifold, a gas analysis sampling outlet, a high vacuum pumping system, sample furnace and temperature measurement and control systems, and a very precise pressure measuring system. Figure 1 presents a schematic diagram of the apparatus and Figure 2 shows the actual equipment. The amount of gas which was adsorbed or desorbed on a sample of the catalyst was determined by measuring the pressure drop (or pressure rise) in the calibrated constant volume system as gas adsorbs (or desorbs) on the catalyst.

2.2 EXPERIMENTAL TECHNIQUE

2.2.1 Sample Pretreatment

The initially oxidized Shell 405 catalyst samples (as received)* were pretreated by simple outgassing for 16 hours at 500°C in a 10^{-5} torr vacuum. This pretreatment removed the physically adsorbed gases and the reversibly chemisorbed gases without changing the surface area or the irreversibly adsorbed oxygen concentration on the iridium surface of the catalyst. These catalyst samples are referred to as "initially oxidized" catalysts. Oxygen free iridium catalysts ("clean" catalysts) were prepared by specially pretreating to remove the oxide without changing the surface area. These catalyst samples were prepared by outgassing at 500°C for 4 hours, and then exposing the samples to hydrogen at 500°C for 8 hours at 200 torr and then outgassing for 16 hours at 600°C.

2.2.2 Temperature Scanning Technique

Both adsorption and desorption temperature scanning measurements were conducted. In desorption temperature scanning, a known amount of gas was initially chemisorbed at 0°C on the pretreated sample. Then the catalyst sample was slowly heated from 0°C to 600-700°C and the temperature and pressure were recorded as a function of time. At preselected points, the

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*The fact that the "as received" catalyst contained a significant amount of oxygen <u>irreversibly</u> adsorbed on the iridium surface was discovered shortly after the start of the program.

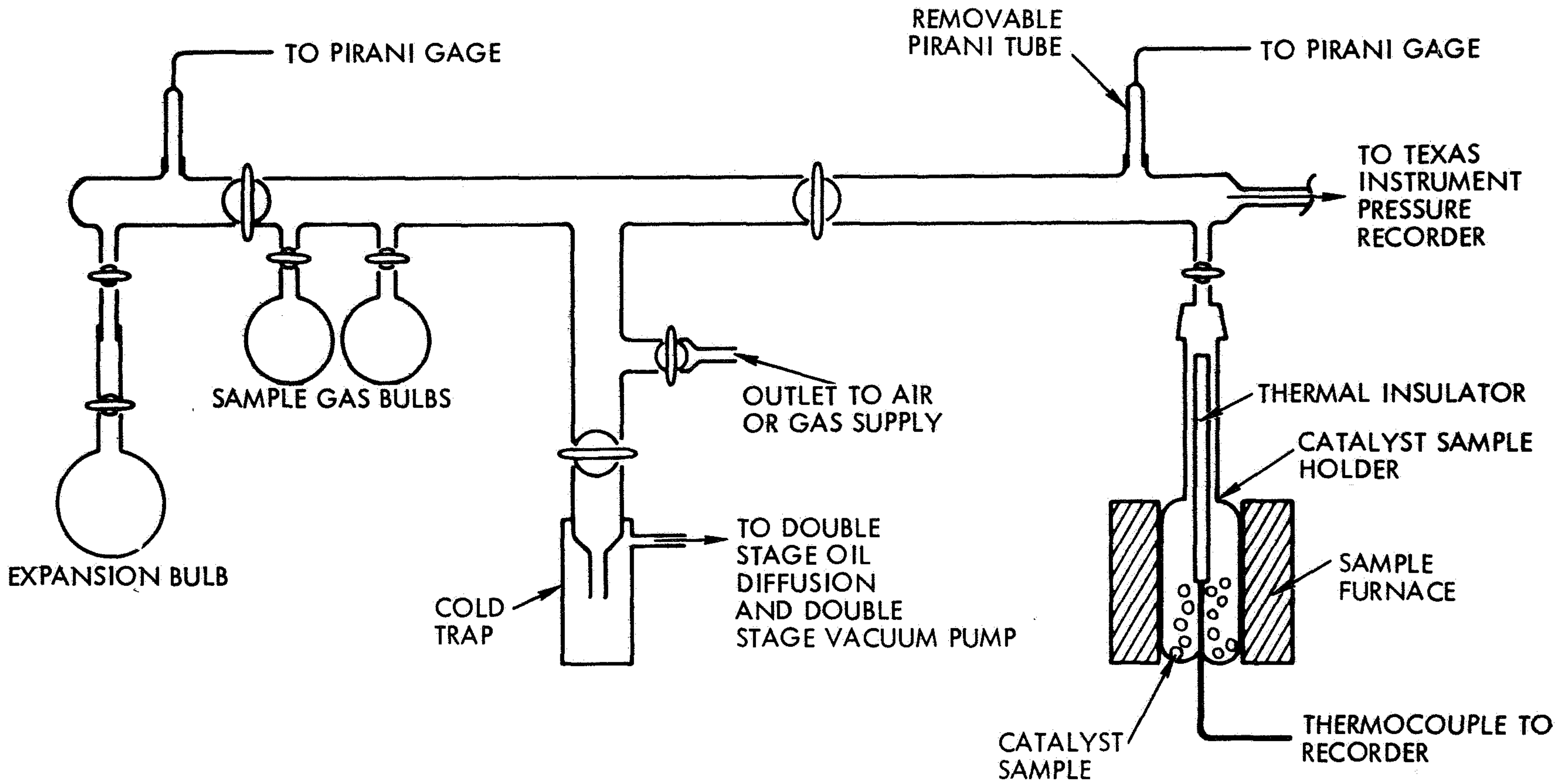

Figure 1. Schematic Diagram of the All Glass Constant Volume Adsorption System

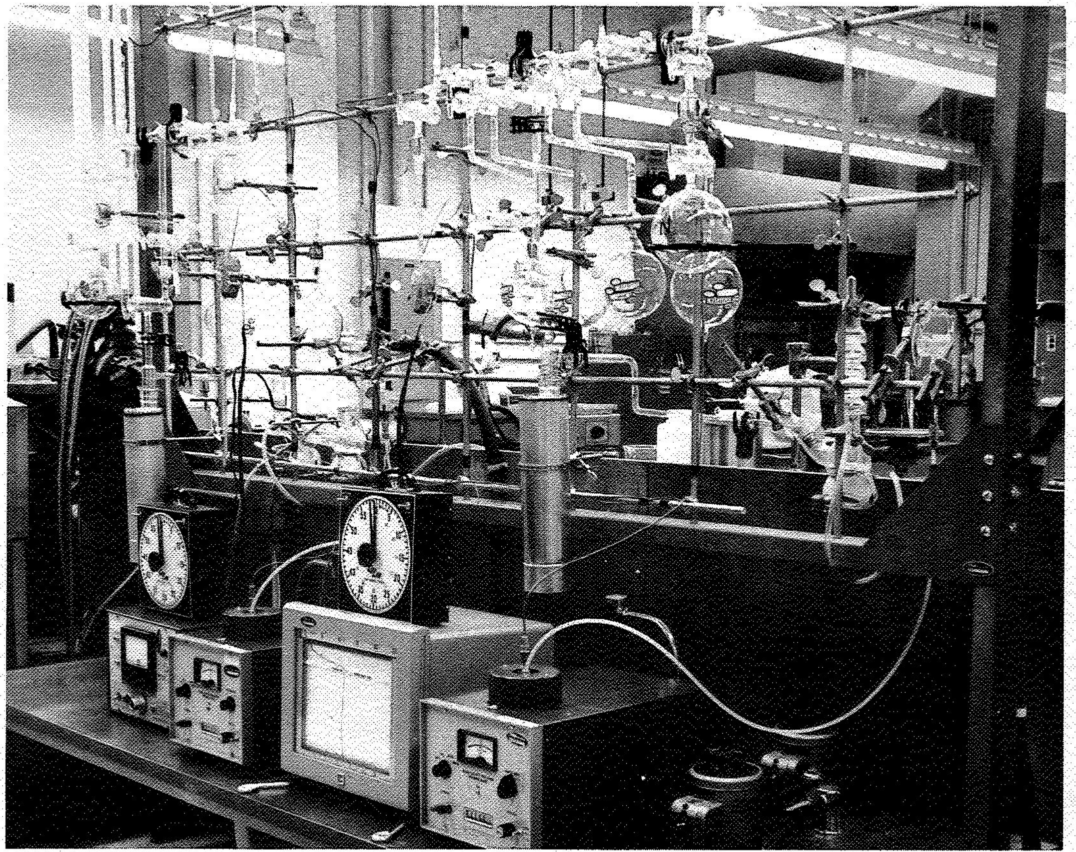

Figure 2. Photograph of the Adsorption System

catalyst was held at constant temperature for about 30 minutes while the pressure change was recorded as a function of time. The number of atoms desorbed were calculated from the pressure change data. For the ammonia studies where decomposition occurred, a known volume of gas was removed from the system by replacing the Pirani tube with a gas analysis sampling bulb. These gas samples were submitted for mass spectrographic analysis.

In adsorption temperature scan measurements, a known amount of gas was initially admitted to the system at 0°C and was allowed to adsorb when the sample was slowly heated. The pressure and temperature were recorded as a function of time, as in the desorption temperature scan measurements. When the pressure decreased to low values, an additional known volume of gas was admitted. At preselected points the pressure change with time was measured at constant temperature.

2.2.3 Adsorption and Desorption Isotherm Measurements

A known weight of catalyst was pretreated as described above (Section 2.2.1) and then allowed to come to thermal equilibrium at the isotherm temperature. A quantity of gas was initially bled into the evacuated manifold from the gas storage bulb. From the known volume of the manifold and the measured manifold pressure, the number of molecules initially in the gas phase was calculated. A stopcock connecting the evacuated sample bulb to the gas manifold was then opened and the gas introduced into the sample bulb. As the gas species (example, hydrogen) adsorbed on the catalyst sample, the pressure decreased. When there was no appreciable further change in pressure*, the system was assumed to be at equilibrium and the final gas phase pressure recorded. From the known dead space of the manifold and sample tube, the number of molecules of gas remaining in the gas phase was calculated. The difference between the original and final number of molecules in the gas phase was the number of molecules adsorbed on the sample at the isotherm temperature and the final equilibrium pressure. The amount of gas adsorbed at the final equilibrium pressure thus represents one point on the adsorption isotherm. The stopcock connecting the

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*In general, data points were taken in 1.5 hours time increments. At the higher temperatures, this was sufficient time to very nearly reach equilibrium values. However, at 0°C in some cases appreciable adsorption was observed after a 1.5 hour time increment and some data points were taken at 16 hour and 64 hour time increments.

sample tube to the gas manifold was then closed again, fresh gas admitted to the manifold and the process repeated. A new higher equilibrium pressure was obtained with a corresponding larger quantity of gas adsorbed. This process was repeated at equilibrium pressures from about 10 microns up to one atmosphere pressure.

The desorption isotherm was obtained by reversing the above described process and in each step expanding the gas present in the sample tube into the previously evacuated gas manifold.

The adsorption-desorption isotherm experiments were conducted with each of the hydrazine decomposition products (hydrogen, nitrogen and ammonia) and with oxygen.

2.2.4 Oxygen Chemisorption Rate Measurements

Oxygen chemisorption (oxidation) rates were measured at -78°C, 0°C, and 300°C at pressures of 1, 10, and 100 torr. The procedure was to take a known weight of pretreated sample and allow it to thermally equilibrate at the selected temperature. The gas was then admitted to the sample and the pressure change was recorded as a function of time. When the pressure decreased to about 10% below the preselected pressure, an additional amount of gas was rapidly admitted to the sample and the pressure was again recorded as a function of time. This sequence was repeated until the rate of the pressure change with time was very small. A final value of the pressure was recorded after 16 hours.

2.3 CALCULATIONS

The experimental data from the temperature scan measurements, adsorption and desorption measurements, and the rate measurements presented in the following sections of this report were calculated to 3 significant figures on an Olivetti desk computer using programs specially written for these measurements.

3.0 LABORATORY EXPERIMENT RESULTS

3.1 HYDROGEN STUDIES

3.1.1 Temperature Scanning Experiments

Figure 3 shows the results of a hydrogen desorption temperature scanning experiment over the range from 0°C to 700°C using an "initially oxidized"

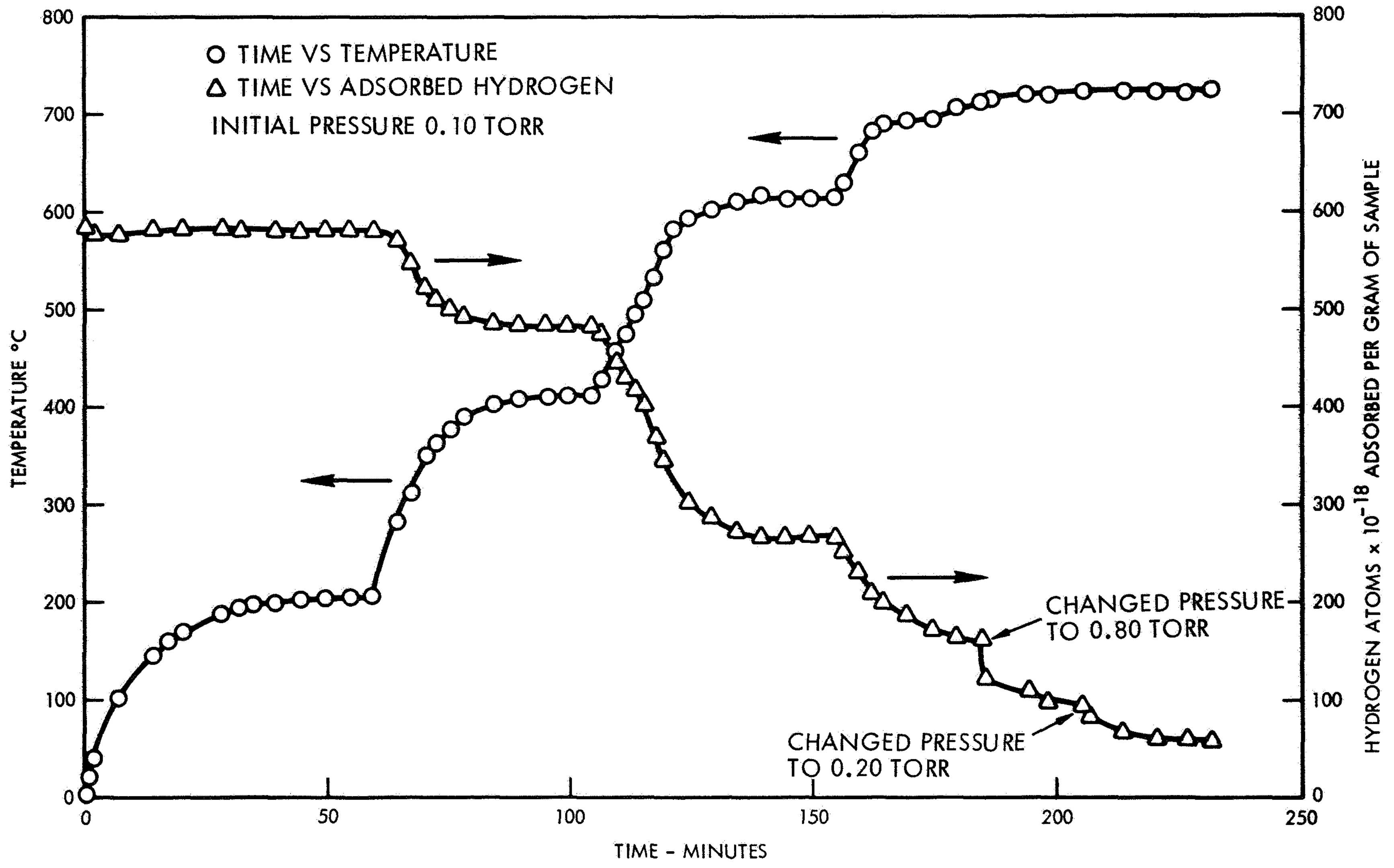

Figure 3. Hydrogen Desorption Temperature Scanning Experiment: Catalyst Shell 405 - "Initially Oxidized"

("as received catalyst" outgassed at 500°C) catalyst sample. 580×10^{18} hydrogen atoms were preadsorbed at 0°C on the catalyst. Most of the hydrogen was removed during the desorption scanning experiment, but a small residual amount of hydrogen remained adsorbed on the catalyst surface even at 700°C.

3.1.2 Adsorption and Desorption Isotherms

Figure 4 shows replicate hydrogen adsorption isotherms at 0°C for an "initially oxidized" catalyst. Final points taken after 16 and 64 hours show that equilibrium is approached rather slowly at this temperature. Figure 5 shows the 300°C and 500°C hydrogen adsorption and desorption isotherms with "initially oxidized" catalysts.

Figure 6 shows the reproducibility of two hydrogen adsorption isotherms at 300°C obtained with separate samples of the "initially oxidized" Shell 405 catalyst. Both samples were outgassed at 500°C for 16 hours prior to the experiments. The two samples were reproducible within about $\pm$ 10%.

Figure 7 shows the results of hydrogen adsorption and desorption at 500°C and 300°C with samples pretreated with hydrogen at 500°C and outgassed at 600°C for 16 hours ("clean" catalysts). At 500°C about 284×10^{18} atoms/gram of hydrogen were adsorbed and at 300°C about 348×10^{18} atoms/gram of hydrogen were adsorbed. The number of hydrogen atoms adsorbed by these samples was much lower than the amount adsorbed on samples not subjected to the hydrogen pretreatments but which were simply outgassed at 500°C for 16 hours ("oxidized catalysts")*.

3.1.3 Calculated Differential Heats of Adsorption

From the adsorption isotherms at 300 and 500°C differential heats of adsorption were calculated as a function of the surface covered by hydrogen from the Clausius-Clapeyron relationship:

$$\left(\frac{\partial \ln P}{\partial T}\right)_\Theta = \frac{\Delta \text{ Hads}}{RT^2}$$

where

P = hydrogen pressure

T = temperature °K

Δ Hads = differential heat of adsorption

Θ = fraction of the surface covered with hydrogen

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*Presumably, the strongly chemisorbed oxygen present on the iridium surface of the "as received" catalysts (oxidized catalysts) provide additional sites for adsorption of hydrogen.

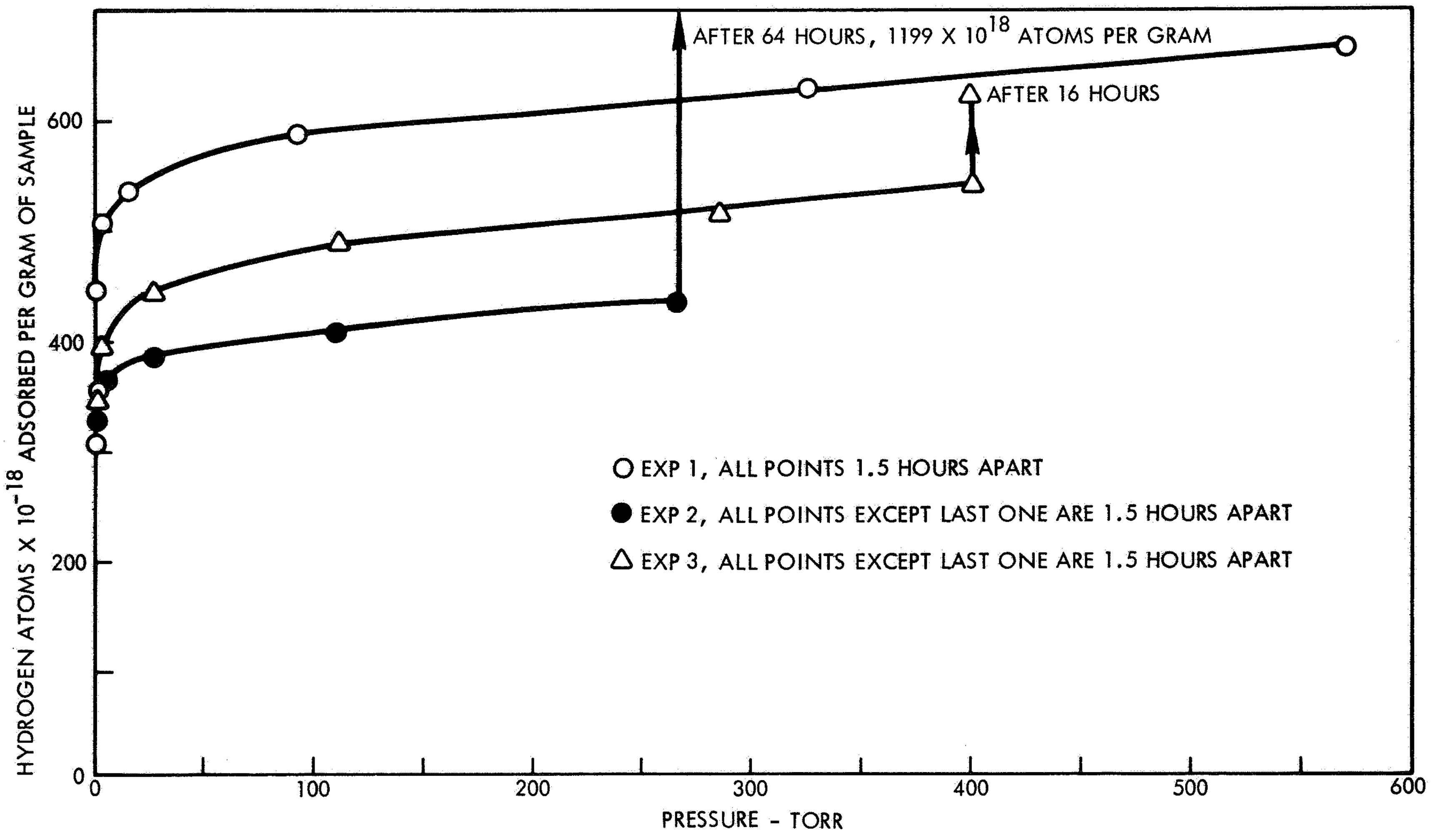

Figure 4. Hydrogen Adsorption Isotherms at 0°C
Catalyst - Shell 405 - "Initially Oxidized"

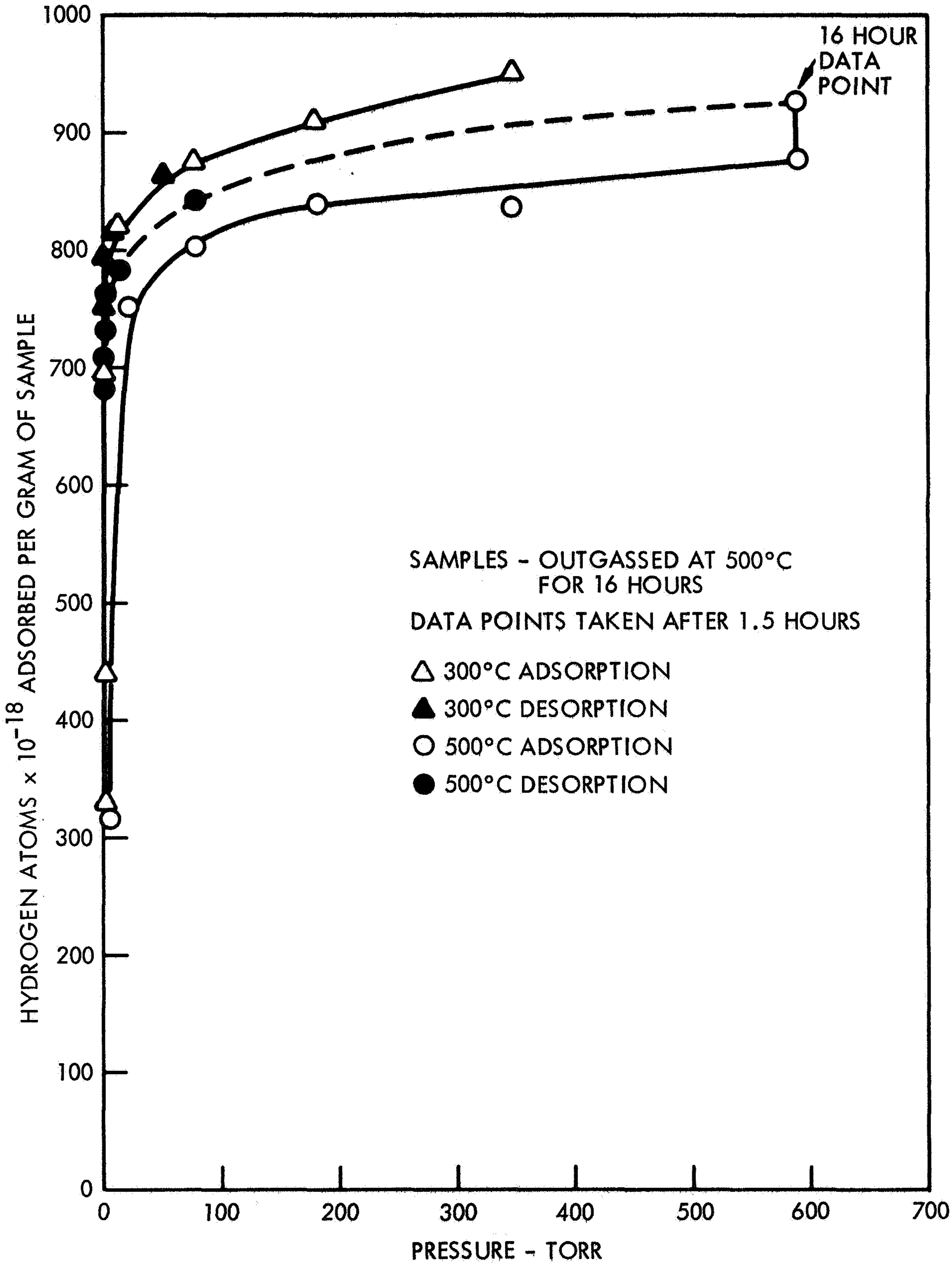

Figure 5. Hydrogen Adsorption and Desorption Isotherms at 300°C and 500°C
Catalyst - Shell 405 - "Initially Oxidized"

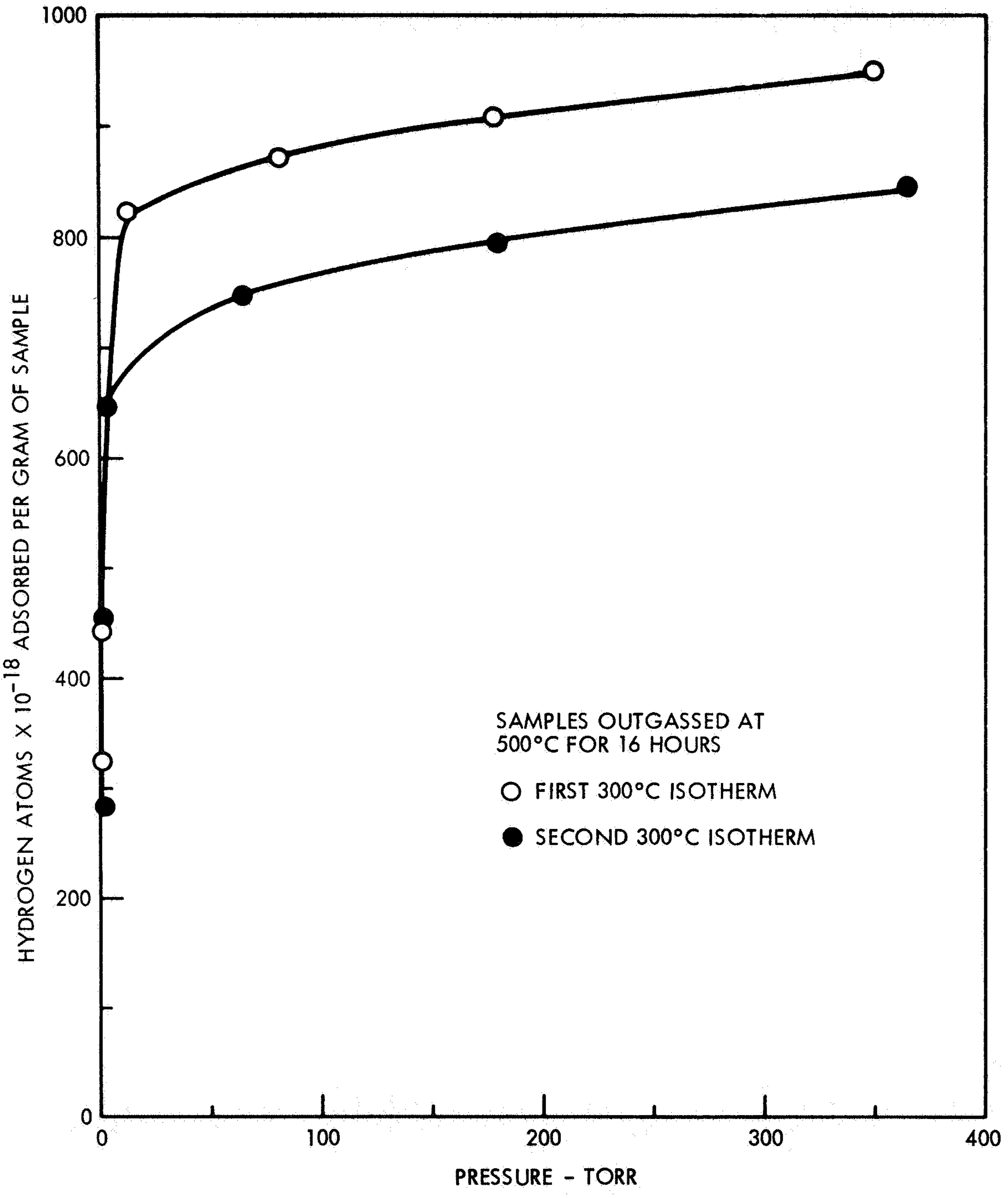

Figure 6. Hydrogen Adsorption Isotherms at 300°C
Catalyst - Shell 405 - "Initially Oxidized"

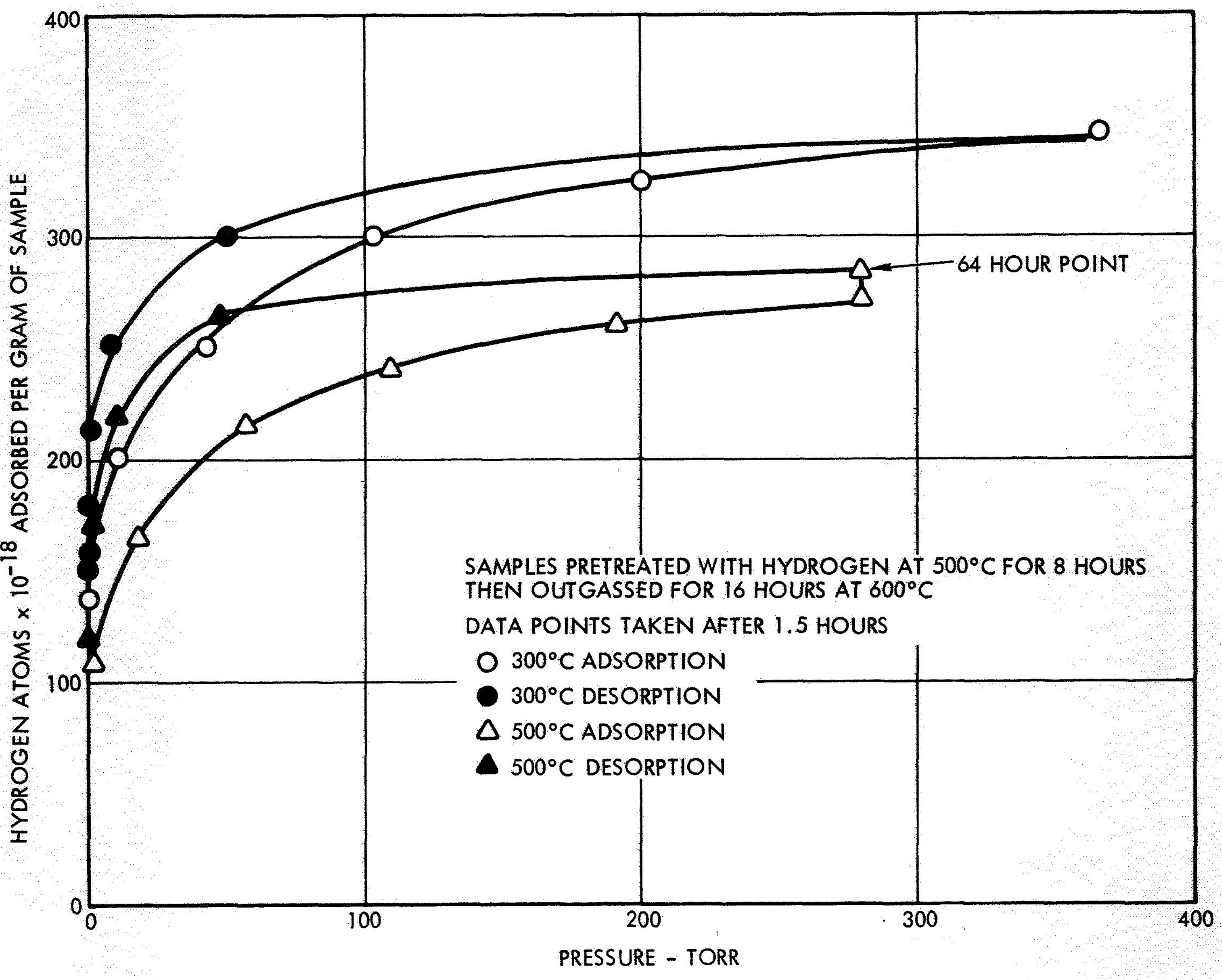

Figure 7. Hydrogen Adsorption and Desorption Isotherms
Catalyst - Shell 405 - "Clean"

Table 1 presents this data for an "initially oxidized" catalyst surface. It is apparent from Table 1 that within the limits of uncertainty of this calculation (approximately ± 4 Kcal) that the differential heat of adsorption is constant over the hydrogen adsorption range from 500 x 10^{18} atoms per gram to 850 x 10^{18} atoms per gram.

TABLE 1

CALCULATED VALUES OF DIFFERENTIAL HEATS OF ADSORPTION
FOR HYDROGEN ON SHELL 405 CATALYST

Atoms of Hydrogen Adsorbed x 10^{18}	Differential Heat of Adsorption Kcal/mole Hydrogen
500	17.2 ± 4.0
600	16.2 ± 4.0
700	17.8 ± 4.0
750	17.6 ± 4.0
800	20.0 ± 4.0
830	19.7 ± 4.0
850	18.1 ± 4.0
Δ Hads average =	18.1 ± 4.0

Note: Samples were initially outgassed for
16 hours at 500°C

The differential heats of adsorption of hydrogen for the "clean" catalysts pretreated to remove all oxygen are given in Table 2. The values show a trend to lower values as the hydrogen surface coverage increases.

3.2 OXYGEN STUDIES

The experimental results from the oxygen temperature scan, the adsorption and desorption isotherms and rate measurements are presented in the following sections:

3.2.1 Temperature Scan Experiments with Oxygen

The results of the temperature scanning experiments with oxygen are shown in Figure 8. The adsorption scanning was done over the temperature range of 0°C to 600°C. The total number of oxygen atoms adsorbed at 600°C was 1350 x 10^{18} atoms/gram at a final pressure of 93 torr.

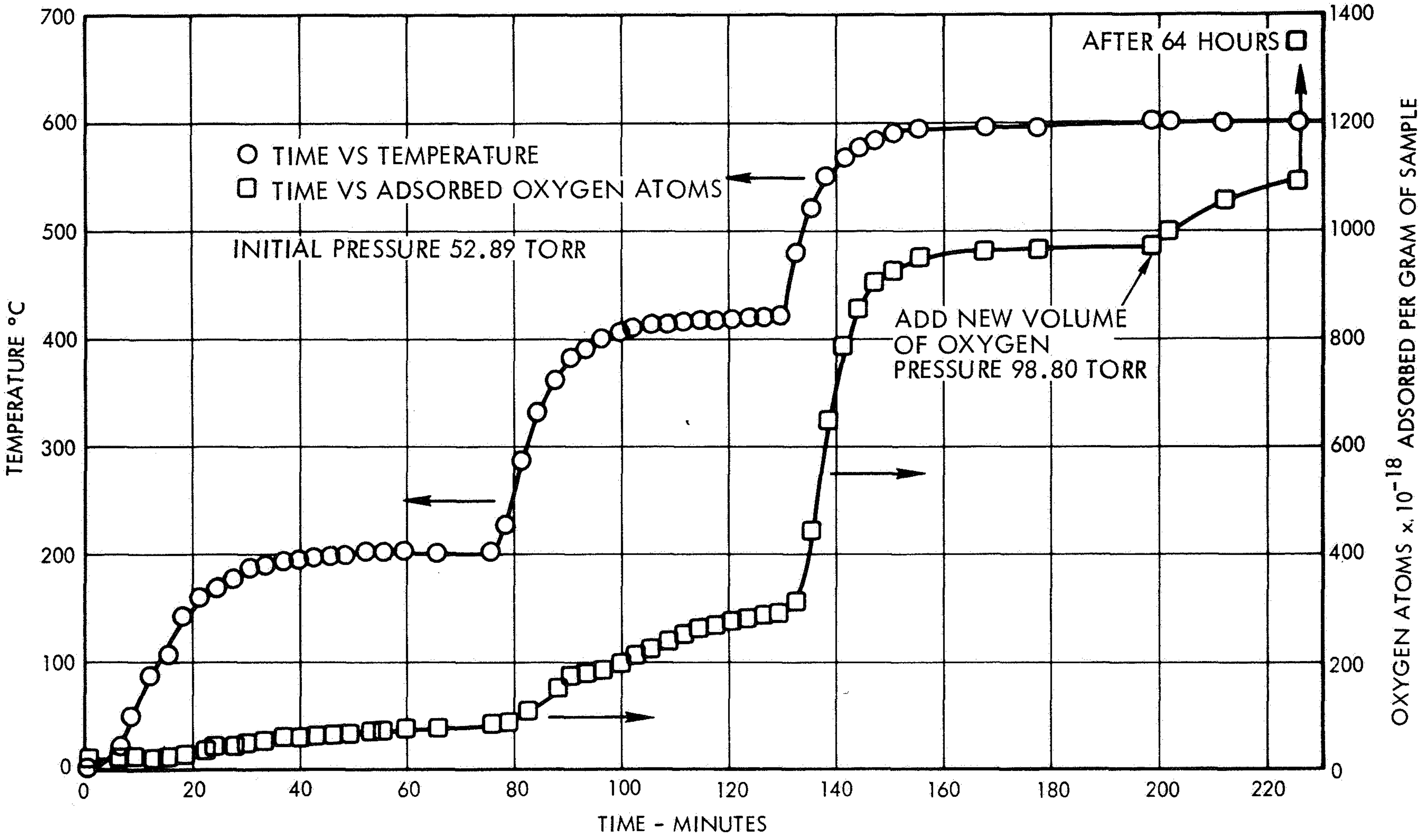

Figure 8. Oxygen Adsorption Temperature Scan
Catalyst - Shell 405 - "Initially Oxidized"

TABLE 2

CALCULATED VALUES OF THE DIFFERENTIAL HEATS OF ADSORPTION FOR HYDROGEN ON PRETREATED SHELL 405 CATALYST

Atoms of Hydrogen Adsorbed x 10^{18}	Differential Heat of Adsorption Kcal/mole Hydrogen
165	22.4 ± 2.5
175	21.1 ± 2.5
200	19.1 ± 2.5
225	15.5 ± 2.5
250	15.6 ± 2.5

In this scanning experiment, oxygen was admitted into the apparatus at 0°C until an initial pressure of 53 torr was reached*. Then the sample was heated slowly and the pressure, temperature, and time were recorded. In Figure 8, the left hand scale of the graph shows the temperature and the right hand side shows the number of oxygen atoms/gram adsorbed. From the figure, it is seen that oxygen was very slowly adsorbed up to 200°C. As the temperature approached 400°C, the rate of adsorption rapidly increased until at 600°C all of the initial 55 torr of oxygen was adsorbed. At this point, more oxygen was admitted into the system and the pressure change was monitored for two hours. The number of oxygen atoms adsorbed was 1080 x 10^{18} atoms of oxygen/gram. The sample was then kept at 600°C and at a pressure of 95 torr of oxygen for 64 hours, to give a final adsorption of 1350 x 10^{18} atoms of oxygen per gram of catalyst. In the case of oxygen, the adsorption (or oxidation) increases with increasing temperature in an irreversible manner over the temperature range from 0-600°C. The final adsorption value of 1350 x 10^{18} atoms of oxygen adsorbed per gram of catalyst corresponds to an iridium oxygen compound of stoichiometry $IrO_{1.3}$.

3.2.2 Oxygen Adsorption and Desorption Isotherms

In Figure 9 are shown the results of oxygen adsorption and desorption isotherms at 500°C for "clean" samples and "initially oxidized" ("as received") samples. Mass spectrographic analysis of the gas desorbed after a hydrogen adsorption experiment on a catalyst pretreated by a simple outgassing at 500°C for 16 hours showed that oxygen was originally present on the surface of

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*Sample initially outgassed for 16 hours at 500°C ("oxidized catalyst"). No appreciable adsorption took place at 0°C.

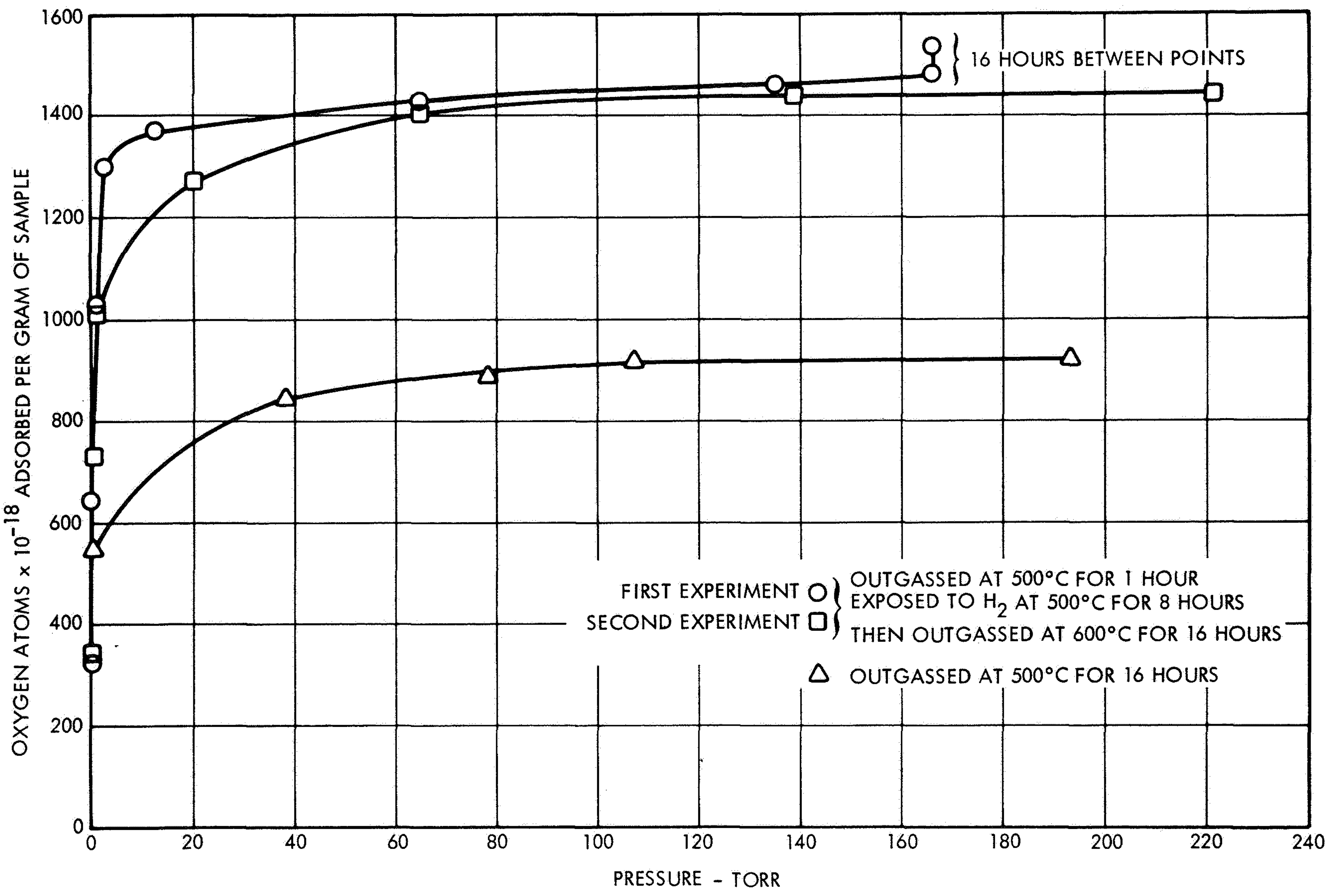

Figure 9. Effect of Pretreatment on Oxygen Adsorption at 500°C
Catalyst - Shell 405

the "as received" catalyst and was not removed by the simple outgassing procedure*. The pretreatment of initial outgassing followed by exposure to hydrogen at 500°C and then outgassing at 600°C for 16 hours did, however, produce clean catalyst surfaces free from oxygen.

As seen from Figure 9, the amount of oxygen adsorbed at 500°C for the "clean" catalysts is about 1500 x 10^{18} atoms/gram. The two experiments with "clean" catalysts showed very good reproducibility. The data points were taken after 1.5 hours except for the initial points in which the time varied, depending upon how fast the pressure dropped to essentially zero. The amount of oxygen adsorbed by the "clean" catalyst was about 600 x 10^{18} atoms/gram more than the "initially oxidized" sample which received only the simple outgassing pretreatment.

Figure 10 shows the results of adsorption and desorption of O_2 at 0°C, 300°C and 500°C on "clean" samples. From Figure 10, it is seen that the amount of oxygen adsorbed was about 1500 x 10^{18}, 950 x 10^{18}, and 200 x 10^{18} at 500, 300 and 0°C, respectively. Furthermore, it is seen that no desorption occurred, showing the irreversibility of the O_2 adsorption. All data points were taken after 1.5 hour time intervals.

3.2.3 Oxygen Chemisorption Rate Measurements

The rate of chemisorption of oxygen on "clean" catalyst surfaces were investigated at pressures of approximately 1 torr, 10 torr, and 100 torr and at temperatures of -78°C, 0°C, 100°C, and 300°C. Figure 11 shows a plot of the number of atoms of oxygen chemisorbed as a function of time and also shows the pressure change with time. When the pressure change dropped to a low value ($\sim$10% below the initial pressure), more gas was added to the system and the pressure and time measurements were continued. The chemisorption rate (r) expressed as a number of atoms of oxygen adsorbed per gram of sample per minute was obtained by graphical differentiation of the type of data shown in Figure 11.

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*The mass spectroscopic analysis of the desorption products from the hydrogen adsorption experiment showed about 27% water in addition to hydrogen. Thus, the chemisorbed hydrogen reacted with the previously adsorbed oxygen to form water.

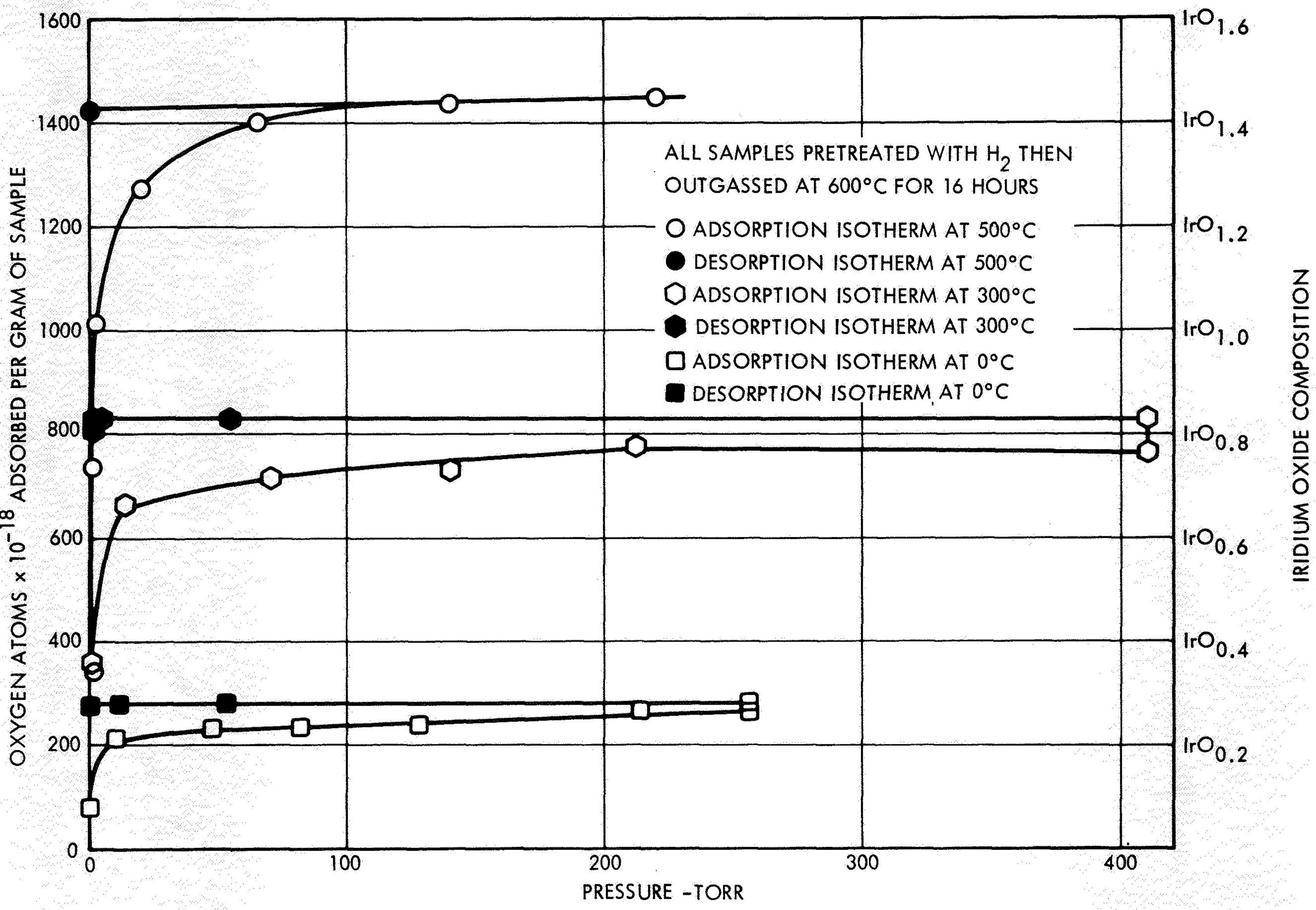

Figure 10. Oxygen Adsorption and Desorption Isotherms
Catalyst - Shell 405 - "Clean"

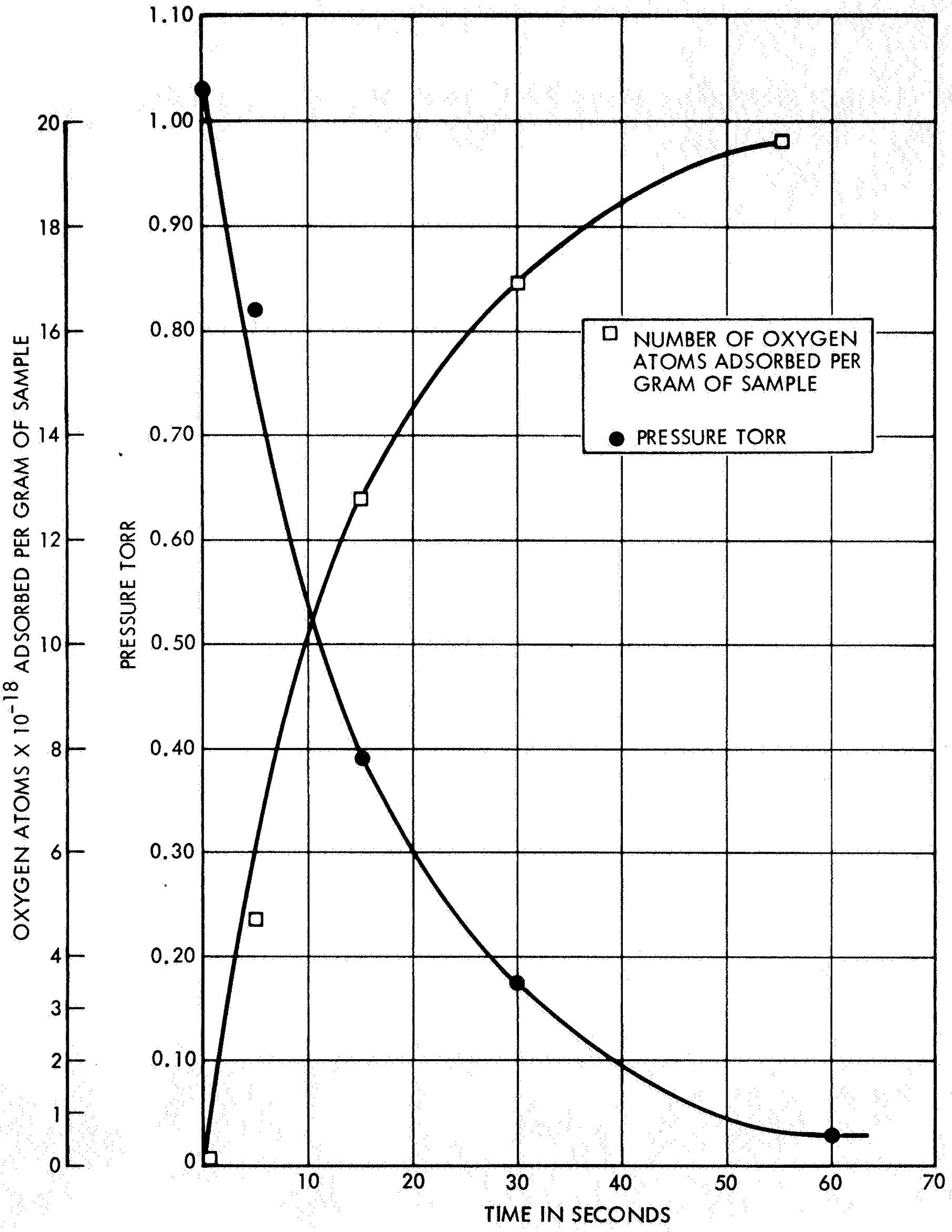

Figure 11. Chemisorption Time Curve
At -78°C, 1 torr

Figures 12 and 13 show the number of atoms of oxygen adsorbed as a function of time at average pressures of 1 torr, 10 torr and 100 torr and at temperatures of -78, 0, 100 and 300°C.

Figure 14 shows a plot of the logarithm of the adsorption rate vs. the logarithm of the number of atoms of oxygen adsorbed for an experiment at 100°C and 100 torr oxygen pressure, where the rate of chemisorption decreased rapidly with the surface coverage.

3.3 AMMONIA STUDIES

The results of the ammonia temperature scanning experiments and the adsorption and desorption isotherms are presented in the following paragraphs:

3.3.1 Ammonia Temperature Scans

In the temperature scanning experiments with ammonia, gas samples were removed at 200, 300, 400 and 600°C for mass spectrographic analysis to determine if the iridium catalyst would initiate decomposition of ammonia at these temperatures. An ammonia desorption temperature scan on the "clean" Shell 405 catalyst is shown in Figure 15 (ammonia gas was preadsorbed at 0°C prior to the scanning experiment). The amount of ammonia preadsorbed on the surface was about 500 x 10^{18} molecules/gram. As seen in Figure 15, the pressure increased with increasing temperature indicating desorption. When the temperature reached 400°C, it was held there for about 30 minutes, and then a gas sample was taken for analysis. This mass spectroscopic analysis showed that the desorbed gas sample contained only about 15% ammonia, the rest being hydrogen and nitrogen. As the temperature approached 600°C the pressure continued to rise and, at the end of the 30 minute period at 600°C, a second gas sample was taken which showed that only 1% of the gas phase was ammonia, the balance being hydrogen and nitrogen. Figure 16 shows the results of a second ammonia temperature scanning experiment performed in the same manner as the previously described temperature scanning experiment. In this experiment, a gas sample was taken for analysis after the catalyst specimen was at 150°C for 30 minutes. The analysis showed that the gas phase contained about 96.8% ammonia, the balance being nitrogen and hydrogen. The temperature was raised to 300°C and held for approximately 30

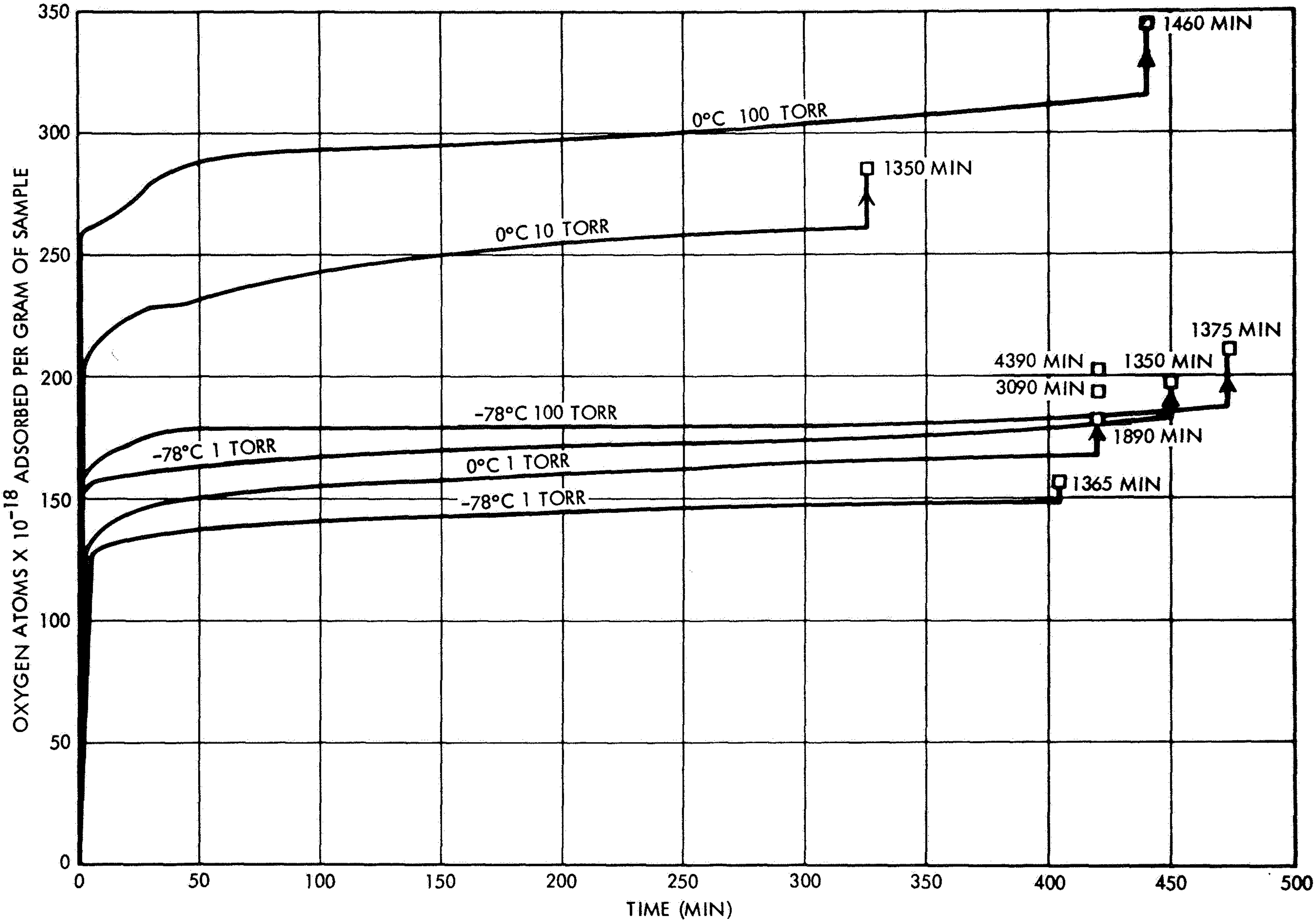

Figure 12. Chemisorption of Oxygen Versus Time
Catalyst - Shell 405 - "Clean"

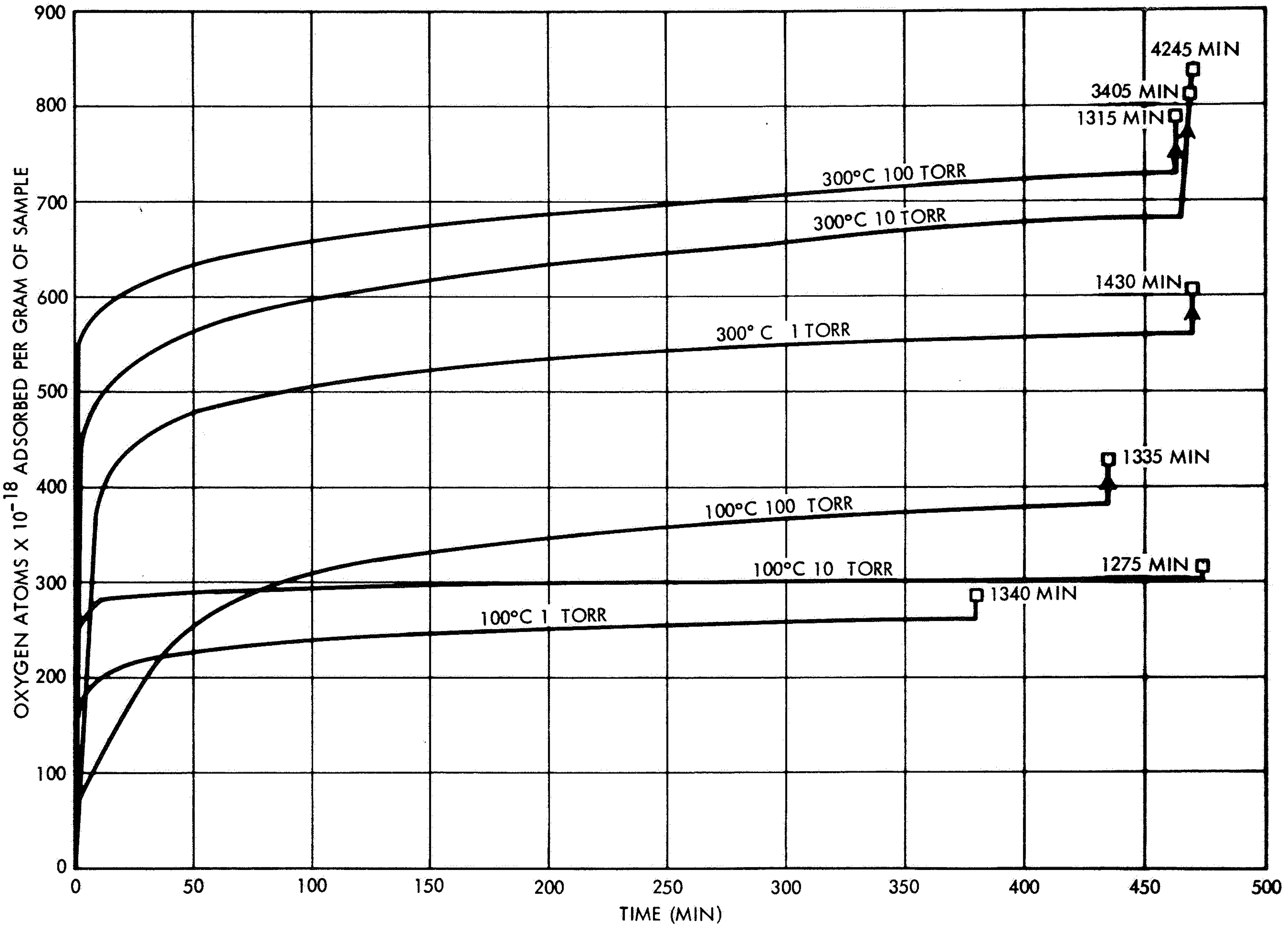

Figure 13. Chemisorption of Oxygen Versus Time
Catalyst - Shell 405 - "Clean"

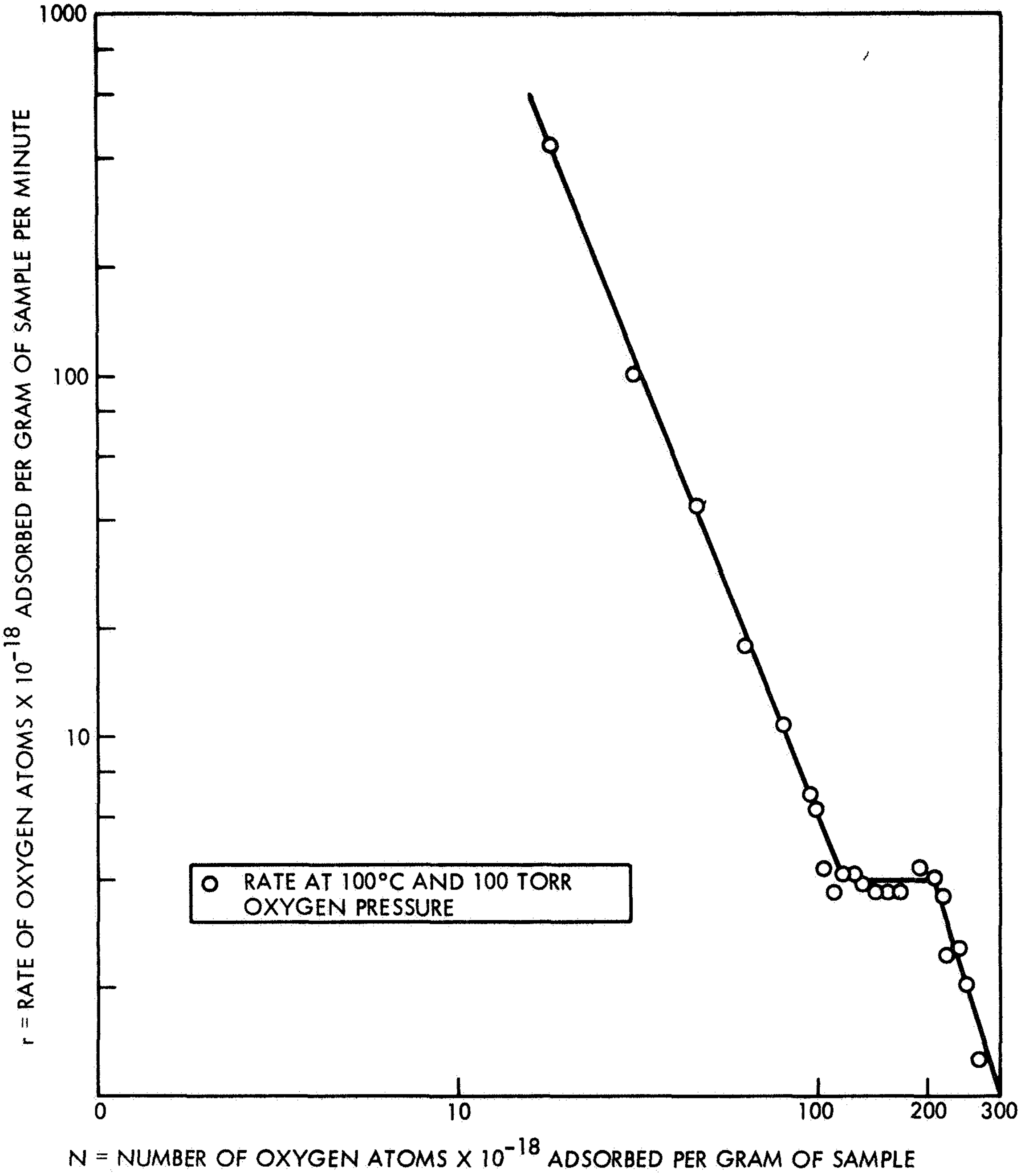

Figure 14. Rate of Oxygen Adsorbed Versus Number of Surface Atoms Adsorbed

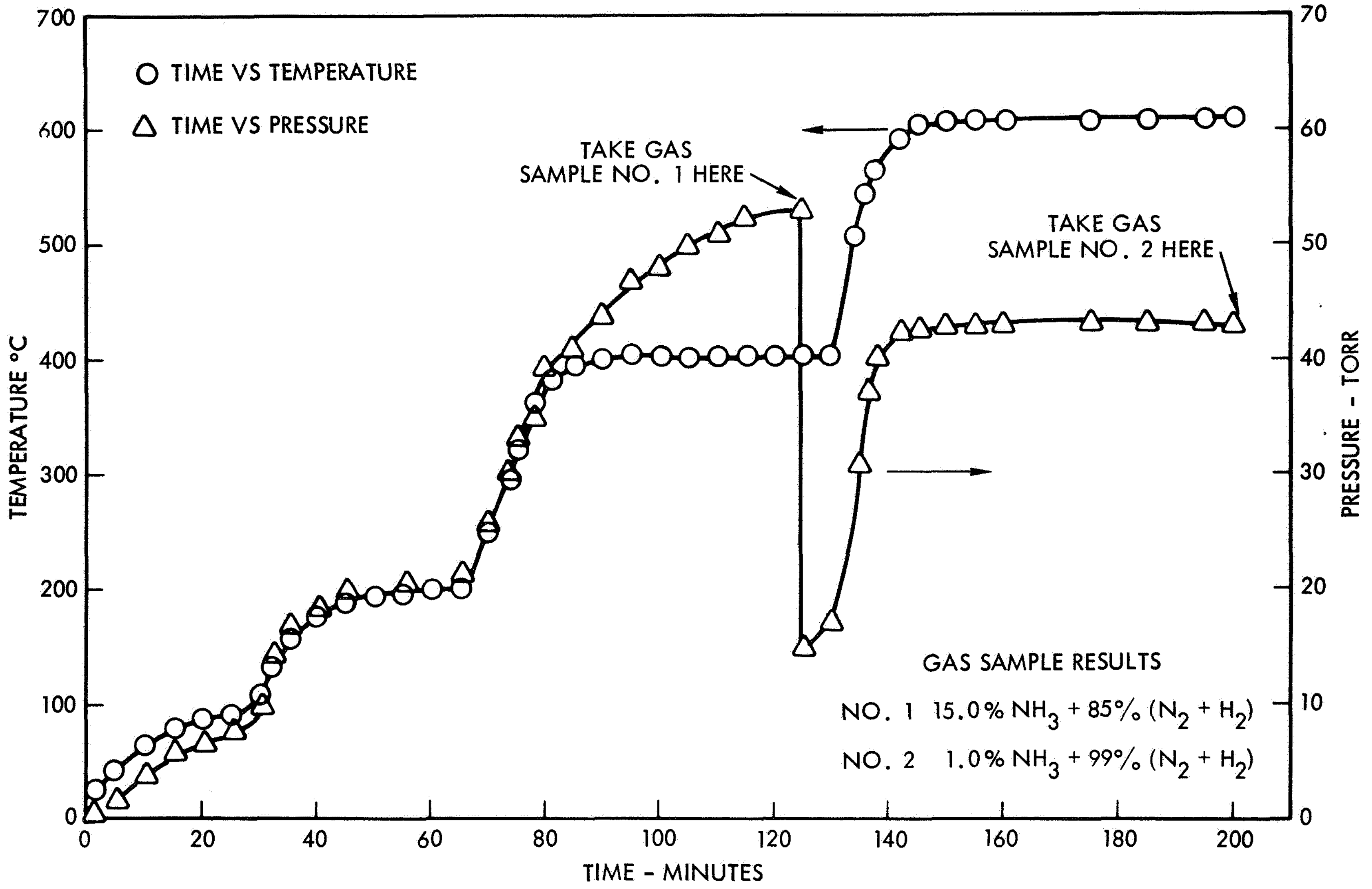

Figure 15. Ammonia Desorption Temperature Scanning Experiment
Catalyst - Shell 405 - "Clean"

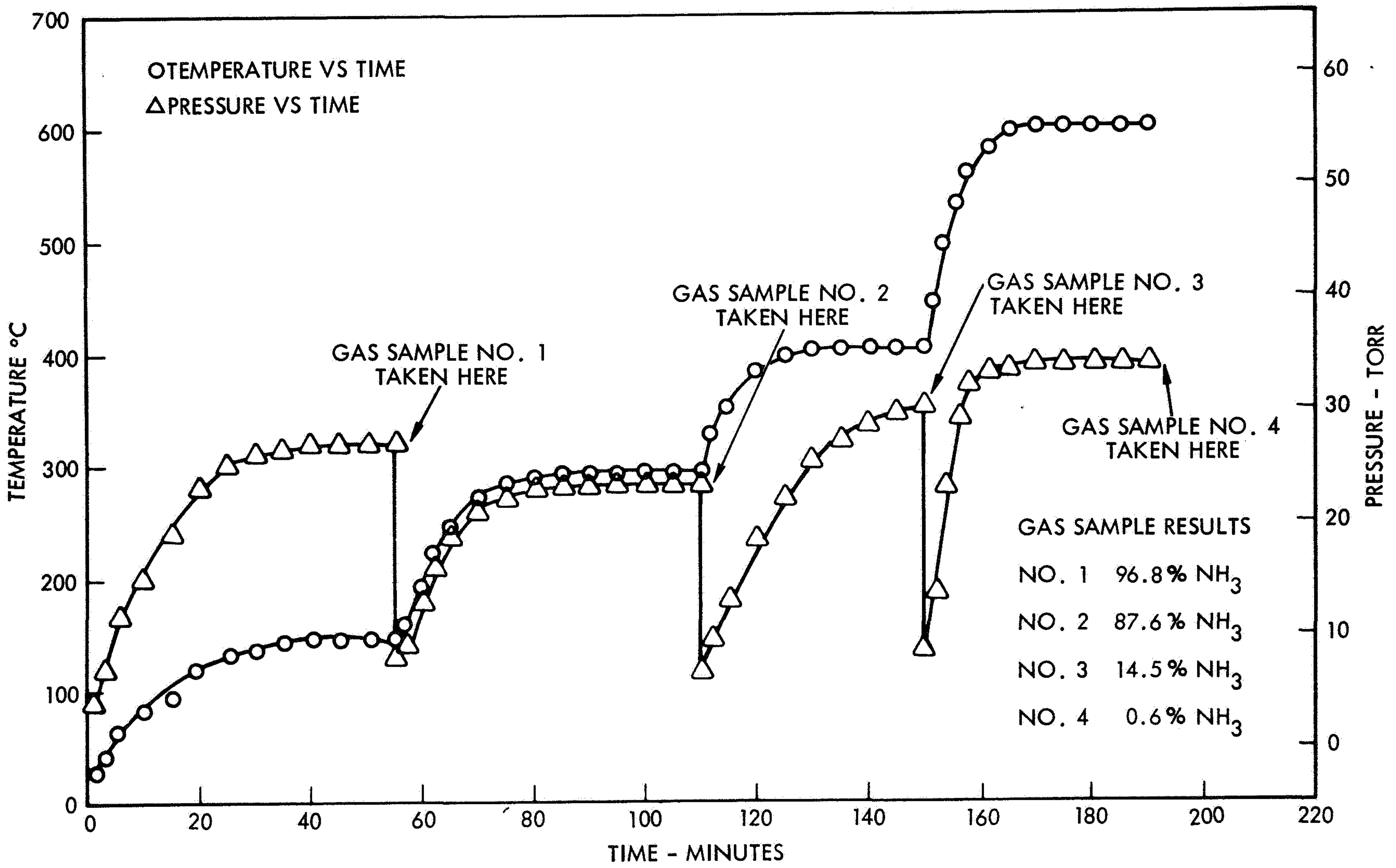

Figure 16. Repeated Ammonia Desorption Temperature Scanning Experiment Catalyst - Shell 405 - "Clean"

minutes, and then a second gas sample was taken. This sample showed 87.6% ammonia. The temperature was raised until 400°C was reached and after 30 minutes at this temperature the mass spectrographic analysis of the gas sample taken at this point showed only 14.5% ammonia in the gas phase. The system approached 600°C and remained there for 30 minutes. A fourth gas sample was then taken and its analysis indicated that only 0.6% of ammonia was present in the gas phase at this temperature.

The above procedure was also adopted for a temperature scan with the uncoated Reynolds aluminum oxide support system to determine whether the support itself was catalytically active with respect to ammonia adsorption and decomposition. The temperature scan experiment is shown in Figure 17. It is apparent from Figure 17 that significant adsorption of ammonia took place on the alumina support and at the higher temperatures the support was capable of initiating ammonia decomposition.

3.3.2 Ammonia Adsorption and Desorption Isotherms

Figure 18 shows the data for adsorption and desorption of ammonia on a "clean" Shell 405 catalyst at 0, 100, and 200°C*. At 0°C about 875 x 10^{18} molecules of ammonia were adsorbed per gram of catalyst while at 200°C only 350 x 10^{18} molecules per gram of sample were adsorbed. In Figure 19 replicate adsorption and desorption isotherms at 0°C are shown. It is seen that very good reproducibility was obtained during these experiments.

The adsorption and desorption isotherms on uncoated Reynolds RA-1 alumina support at 0, 100, and 200°C are shown in Figure 20. A comparison of Figures 18 and 20 shows that more ammonia adsorbed on the uncoated Reynolds alumina support material than on the Shell 405 catalyst itself.

3.3.3 The Differential Heats of Adsorption

The differential heats of adsorption for ammonia on the Reynolds alumina support are shown in Table 3. The average value at these surface coverages is 9.1 ± 1.5 kcal/mole.

3.4 NITROGEN STUDIES

The nitrogen adsorption and desorption isotherms at 0, 100 and 300°C with "clean" catalysts are shown in Figure 21. The amount of adsorption at

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*In this temperature region very little ammonia decomposition took place.

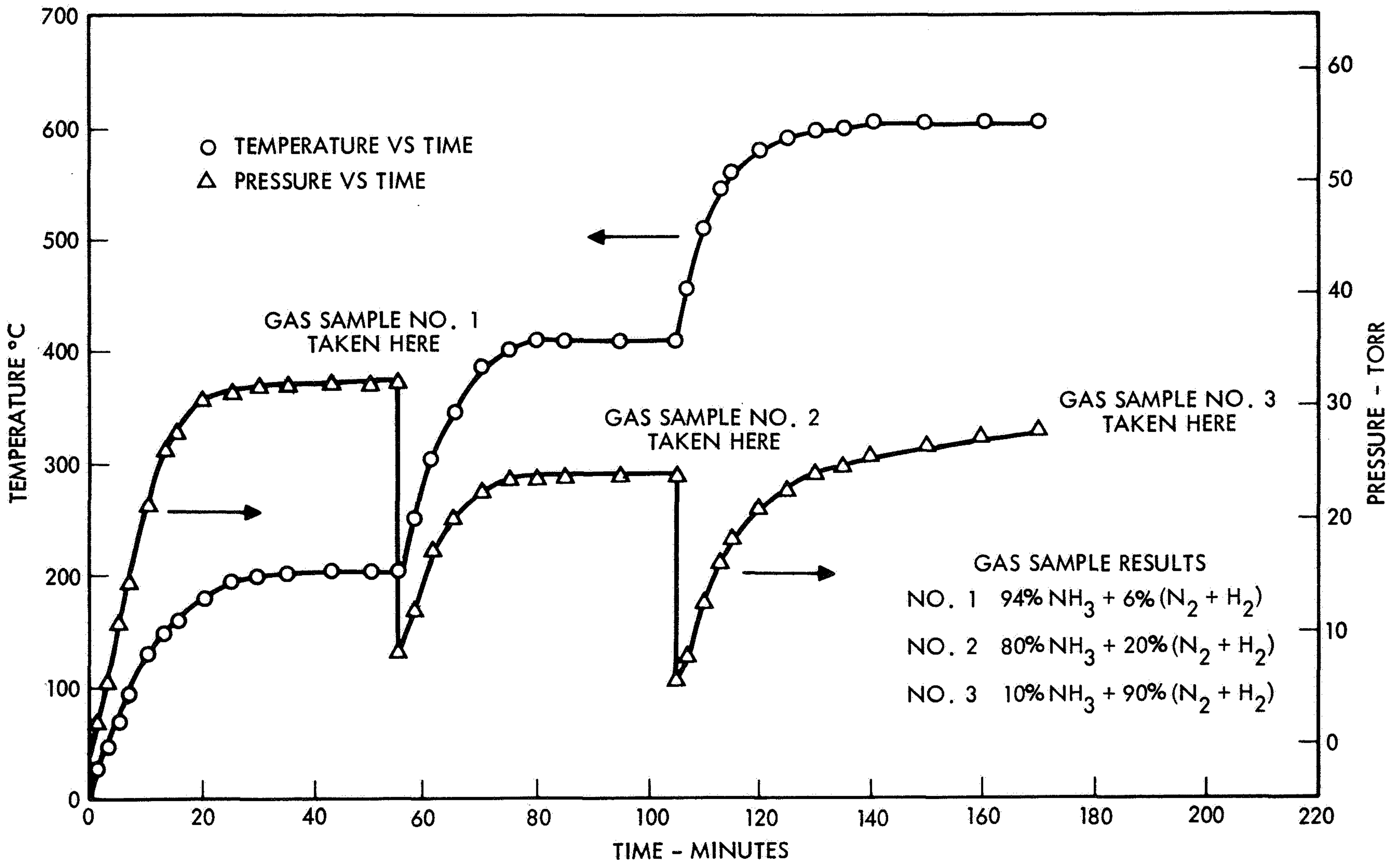

Figure 17. Ammonia Desorption Temperature Scanning Experiment on Al_2O_3 Blank

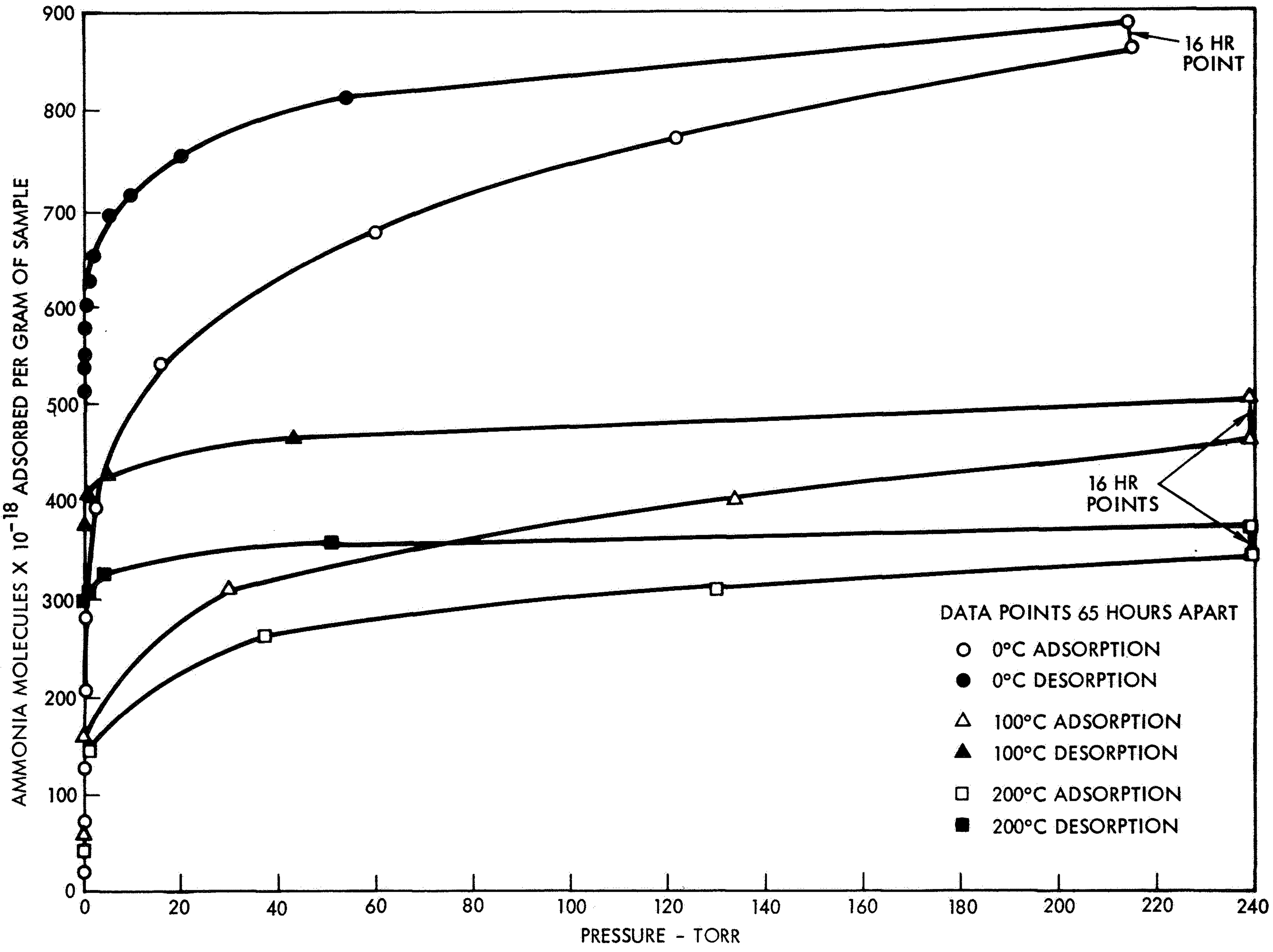

Figure 18. Ammonia Adsorption and Desorption Isotherms
Catalyst - Shell 405 - "Clean"

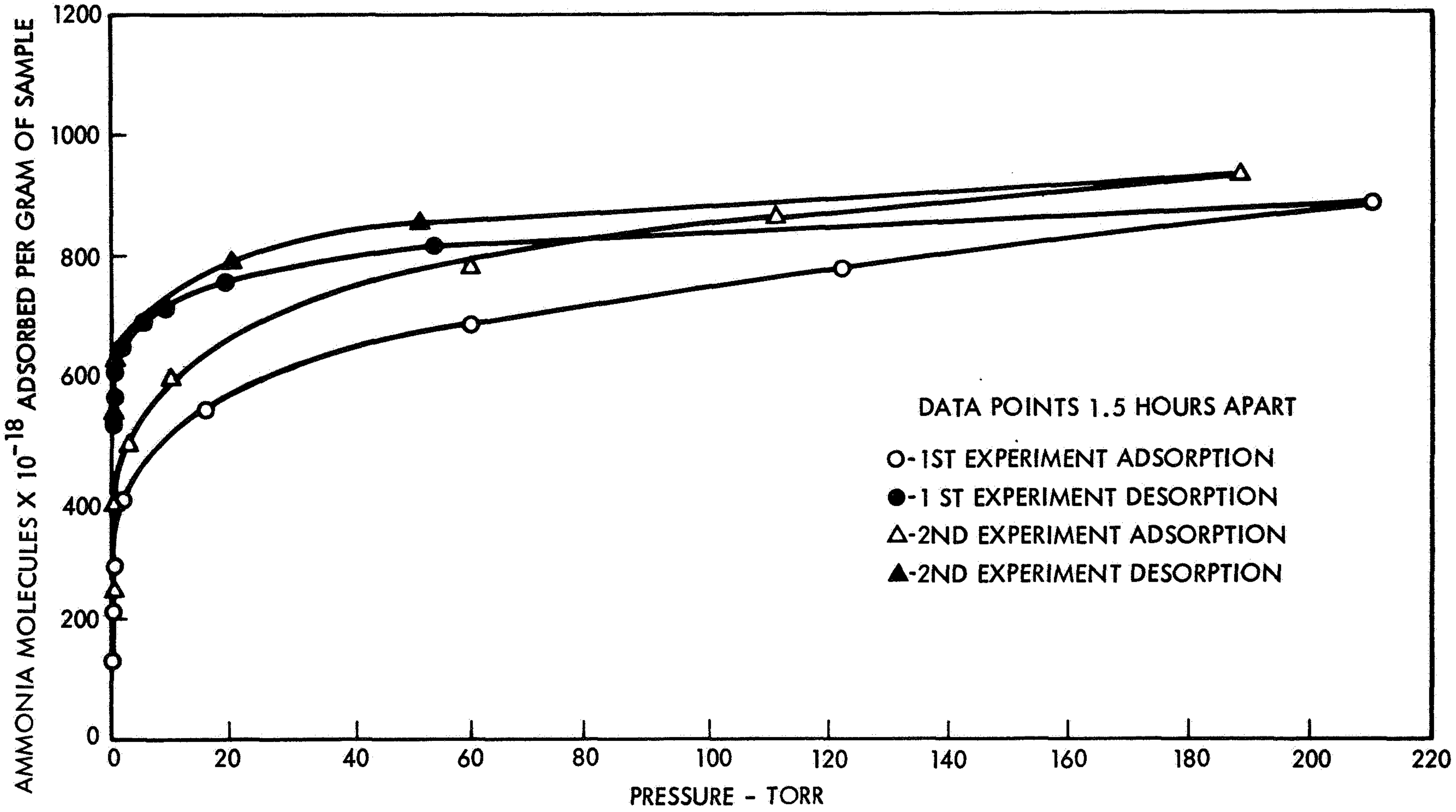

Figure 19. Repeated Ammonia Adsorption and Desorption Isotherms at 0°C Catalyst - Shell 405 - "Clean"

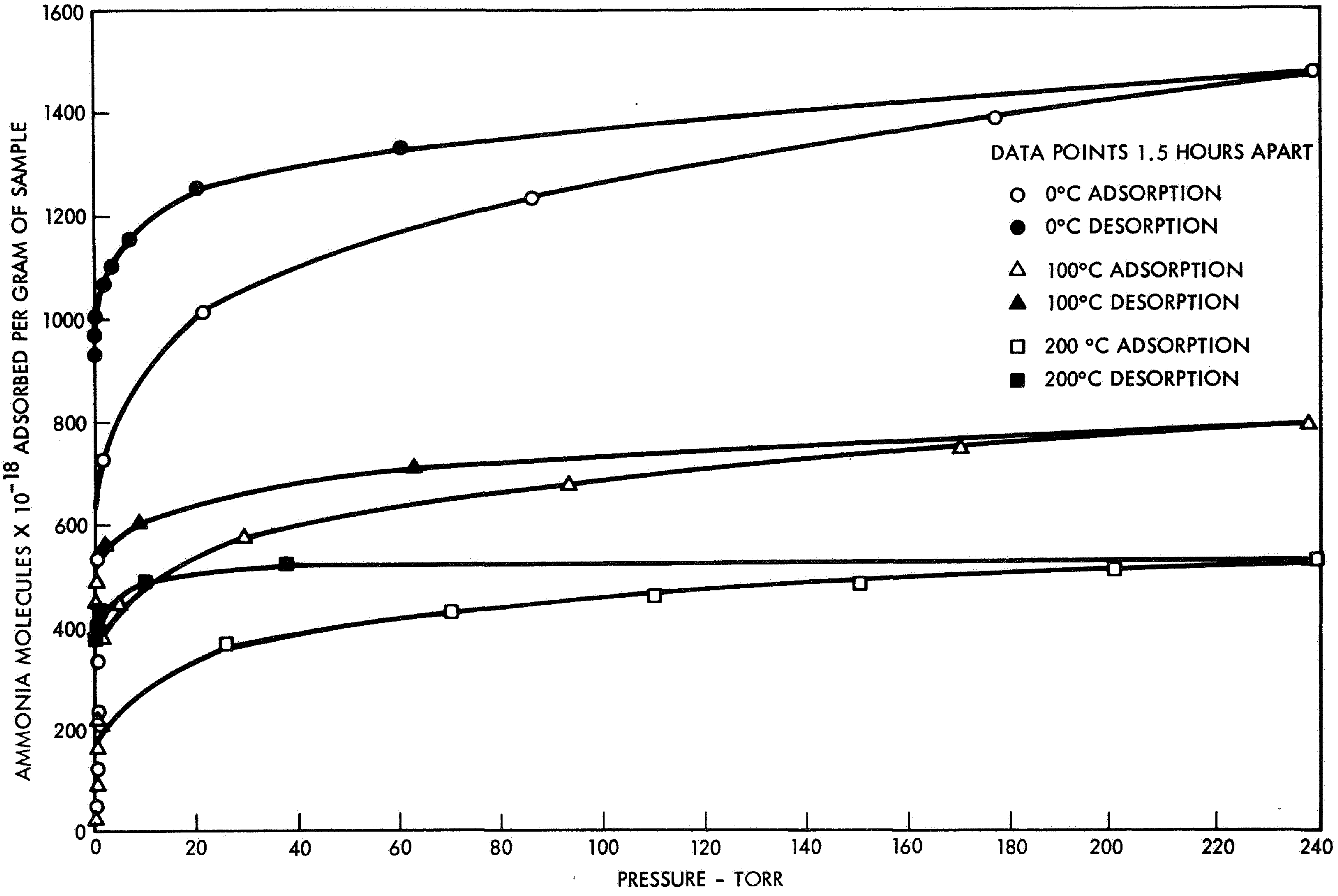

Figure 20. Ammonia Adsorption and Desorption Isotherms - Reynolds RA-1 Alumina

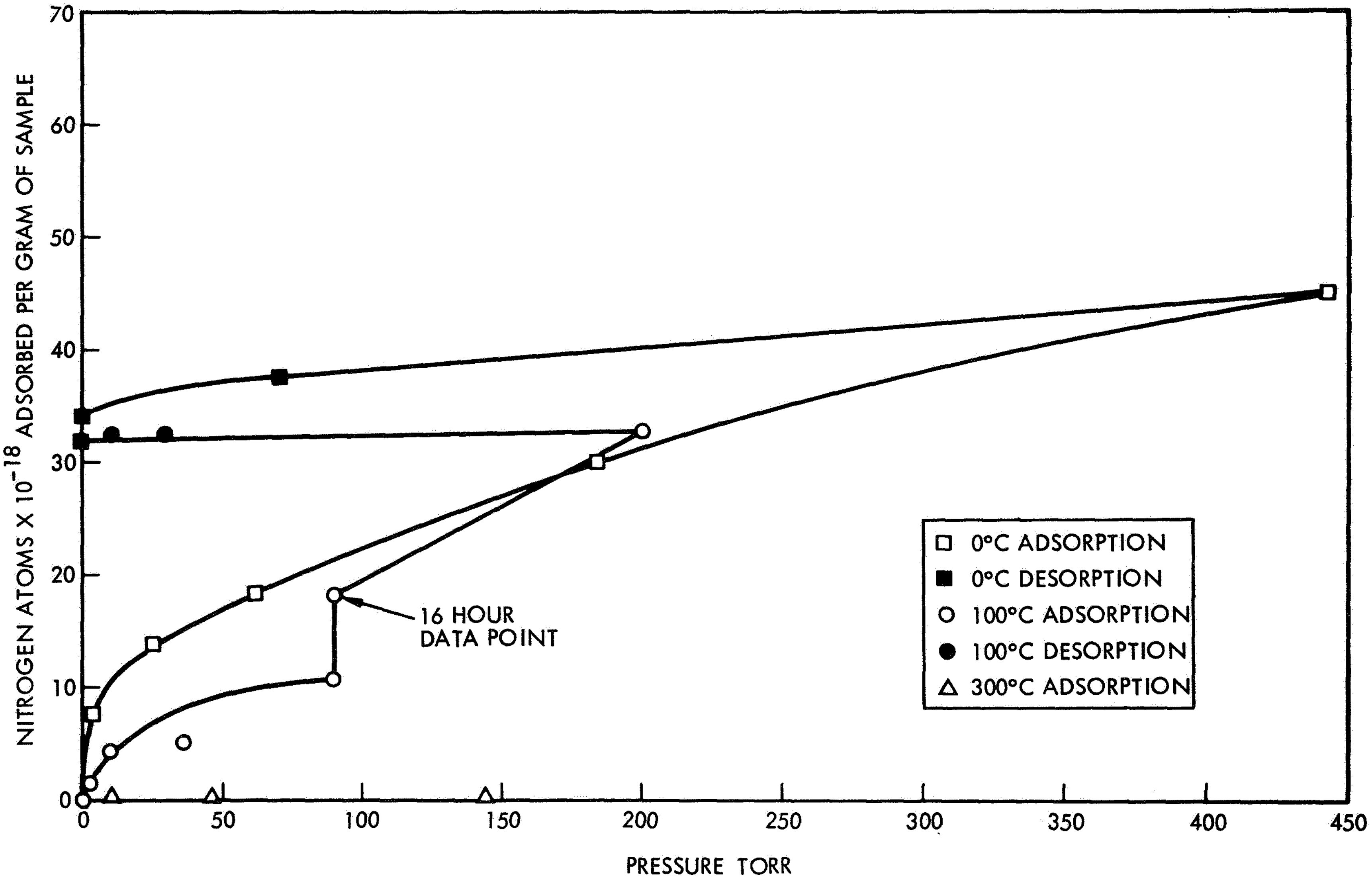

Figure 21. Nitrogen Adsorption and Desorption Isotherms
Catalyst - Shell 405 - "Clean"

0°C is very small in comparison to the previously studied adsorption of hydrogen and oxygen. The amount adsorbed at 100°C corresponds to 0.5 torr pressure change; while at 300°C the system shows essentially no adsorption.

TABLE 3

CALCULATED VALUES OF THE DIFFERENTIAL HEATS OF ADSORPTION FOR AMMONIA ON THE ALUMINA SUPPORT OF SHELL 405 CATALYST

Molecules of Ammonia Adsorbed x 10^{18}	Differential Heats of Adsorption Kcal/mole of Ammonia .
250	9.3 ± 1.5
300	8.9 ± 1.5
350	9.1 ± 1.5
400	9.3 ± 1.5
450	8.7 ± 1.5
	Average 9.1 ± 1.5

4.0 DISCUSSION OF LABORATORY EXPERIMENT RESULTS

The hydrogen adsorption data indicate that the oxygen irreversibly adsorbed on the "as received" iridium catalyst surface provides additional sites for hydrogen adsorption. This is shown in Figures 22 and 23 which compare the adsorption of hydrogen on "initially oxidized" catalysts and "clean" catalysts at 300°C and 500°C. This increased hydrogen adsorption on the oxidized surfaces is probably due to formation of bonded water. The hydrogen bonded to the "clean" catalyst surface appears to obey a Langmuir type of adsorption isotherm and the heat of adsorption (measure of the strength of the adsorption bond) is higher at low surface coverages (22.4 kcal) and decreases as the catalyst surface becomes covered with hydrogen (14.6 kcal). This is also seen in the temperature scan experiments, Figure 3, where the last traces of hydrogen (low surface coverage) are not removed even at high temperatures and low pressures.

The oxygen adsorption results for "clean" catalysts and "initially oxidized" catalysts, Figures 9 and 10, show that the initial oxide coverage

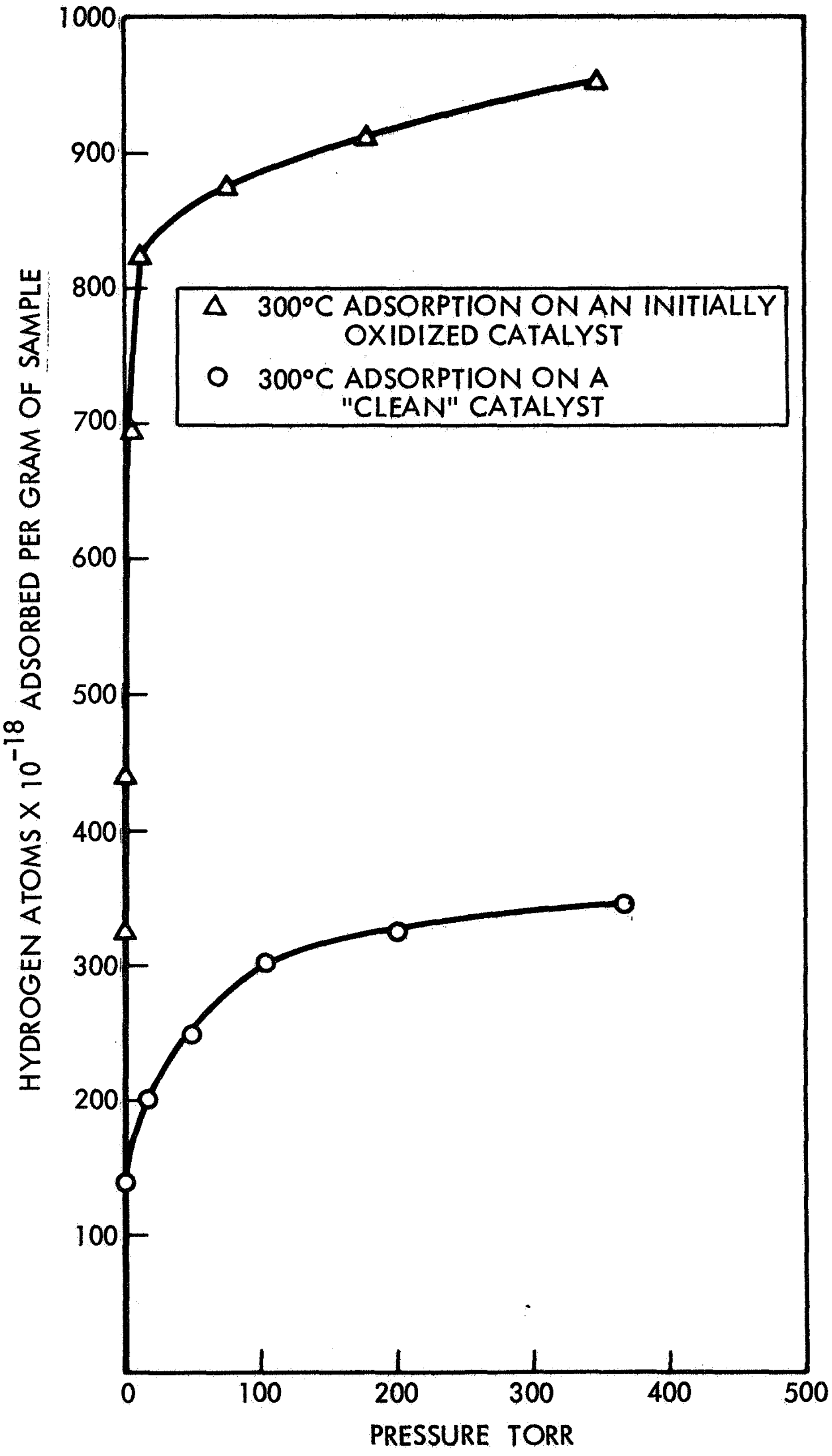

Figure 22. Hydrogen Adsorption on "Clean" and "Initially Oxidized" Shell 405 Catalysts at 300°C.

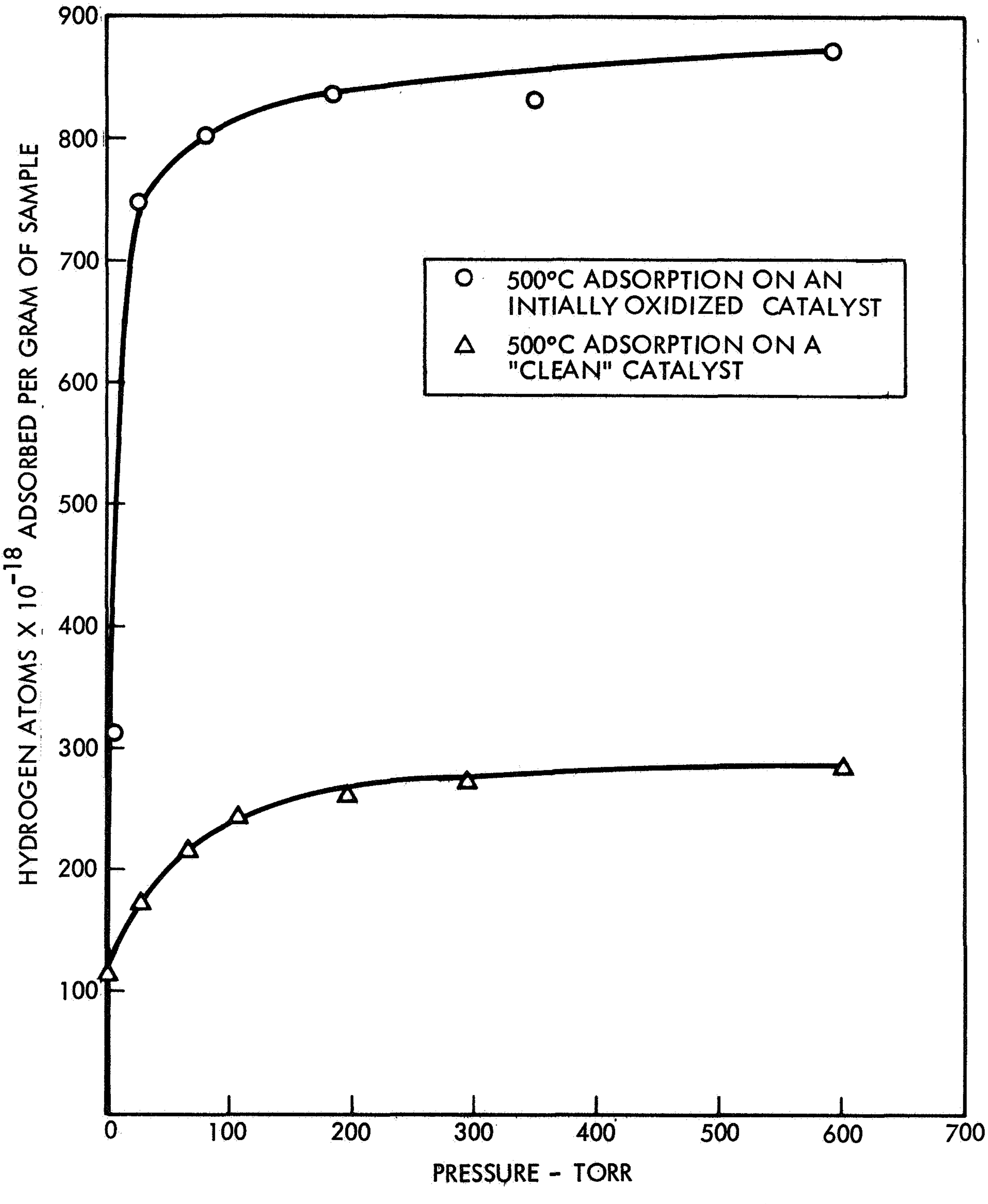

Figure 23. Hydrogen Adsorption on "Clean" and "Initially Oxidized" Shell 405 Catalysts at 500°C

formed during the manufacturing process corresponds to an iridium compound stoichiometry of $IrO_{0.3}$ to $IrO_{0.6}$. Furthermore, the oxygen adsorption is an irreversible process*, requiring elevated temperature reaction with hydrogen to remove oxygen from the surface (by formation of water).

The number of oxygen atoms adsorbed as a function of time, Figures 12 and 13, show that at low temperatures, -78°C and 0°C, the rate of adsorption is strongly dependent on both the pressure and the temperature. It is also seen that at 0°C and an oxygen pressure of 1 torr an iridium oxide with an overall stoichiometry of $IrO_{0.13}$ forms within a minute. At 300°C and 10 torr partial pressure of oxygen, an iridium oxide with an overall stoichiometry of $IrO_{0.4}$ will form in 1 minute. This shows that trace amounts of oxygen will rapidly react with a "clean" catalyst to form an oxidized surface.

The ammonia temperature scanning experiments with both the Shell 405 "clean" catalyst and the Reynolds alumina base support indicate that the iridium atoms decompose ammonia more rapidly than the base support in temperature regions above 300°C. This difference is shown in Figure 24 where the amount of ammonia present in the gas phase for both the "clean" catalyst and the alumina support is shown as a function of temperature**.

A comparison of the ammonia adsorption isotherms on the iridium catalyst and an uncoated alumina support shows that the amount of ammonia adsorbed on the support was greater than the amount adsorbed on the catalyst sample indicating that the iridium metal surface probably adsorbed much less than the alumina. This difference is clearly shown in Figures 25, 26, and 27 which compare the ammonia isotherms on the Shell 405 catalyst and the pure aluminum oxide support at 0°C, 100°C, and 200°C, respectively. It is seen that at 0°C, the amount of ammonia which was adsorbed on the blank was almost 100% greater than that which was adsorbed on the catalyst. This difference decreases somewhat so that at 100°C the amount of ammonia adsorbed on the blank is only about 60% more than that adsorbed on the catalyst and, at 200°C, the amount adsorbed on the blank corresponds to about 55% more than that adsorbed on the catalyst sample.

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*Oxygen can't be removed from the surface by evacuating the catalyst at temperatures up to 700°C.

**Exposure time for each data point approximately 30 minutes.

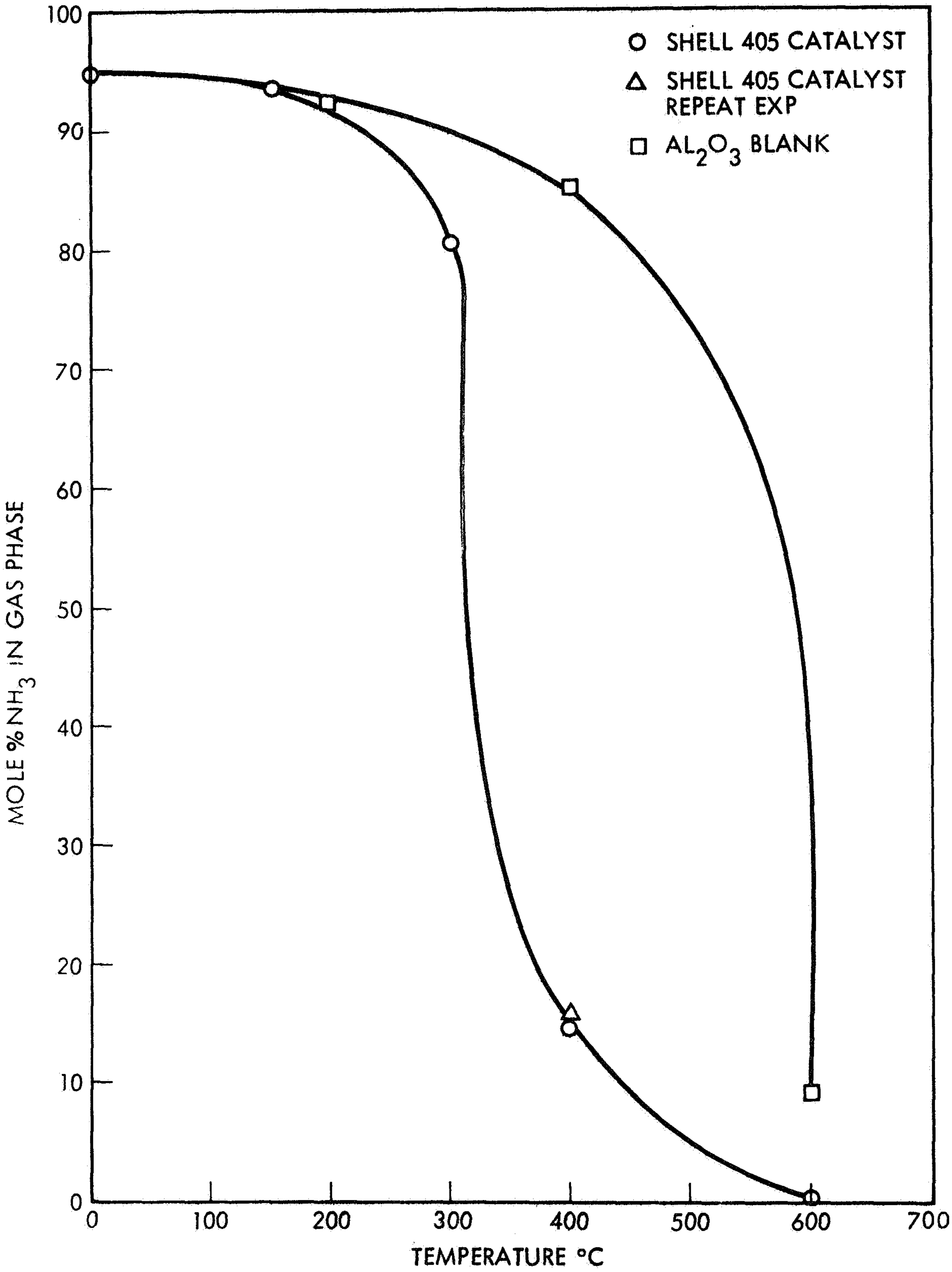

Figure 24. Mole % Ammonia in the Gas Phase as a Function of Temperature

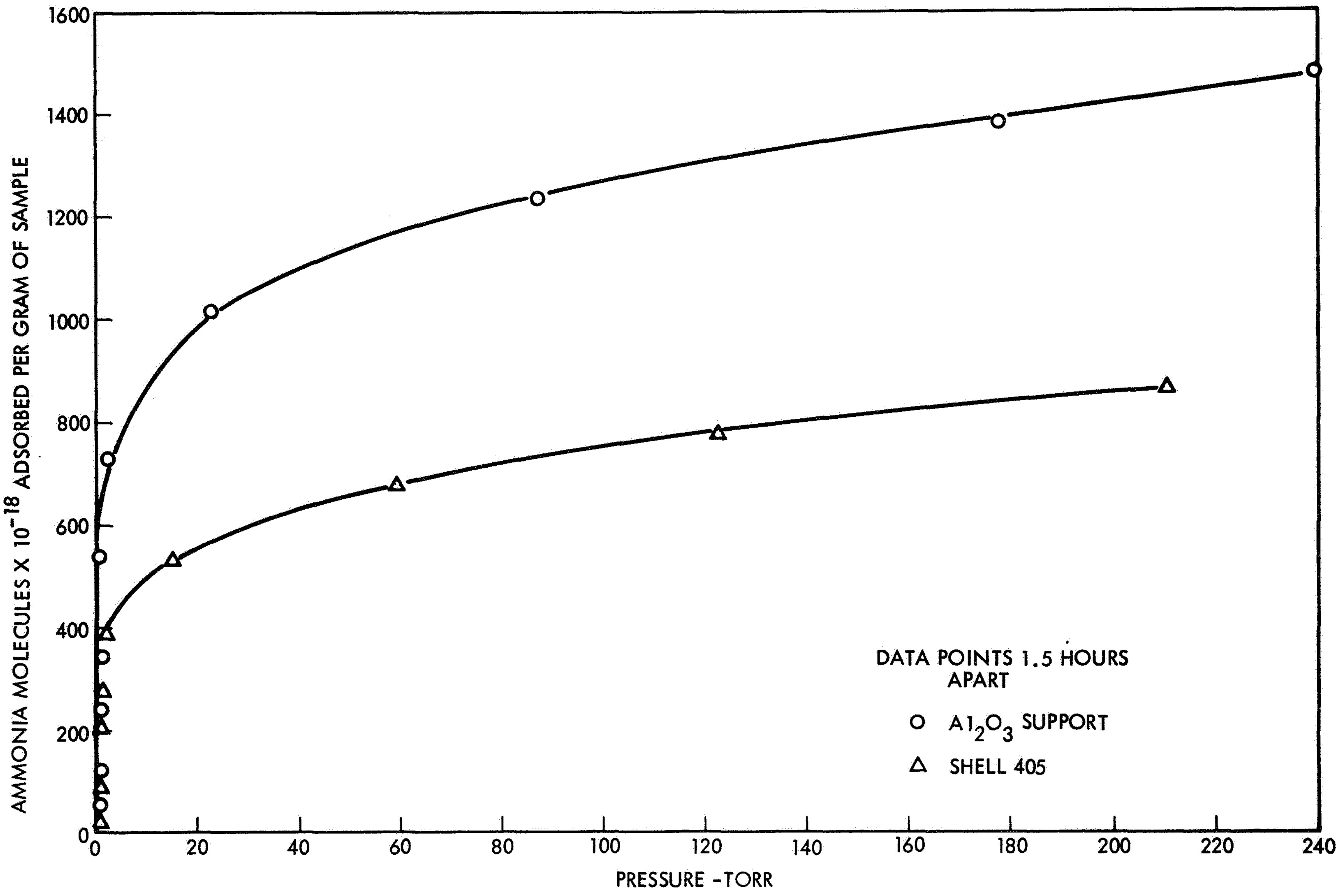

Figure 25. Ammonia Adsorption at 0°C on "Clean" Shell 405 Catalyst and Reynolds RA-1 Alumina

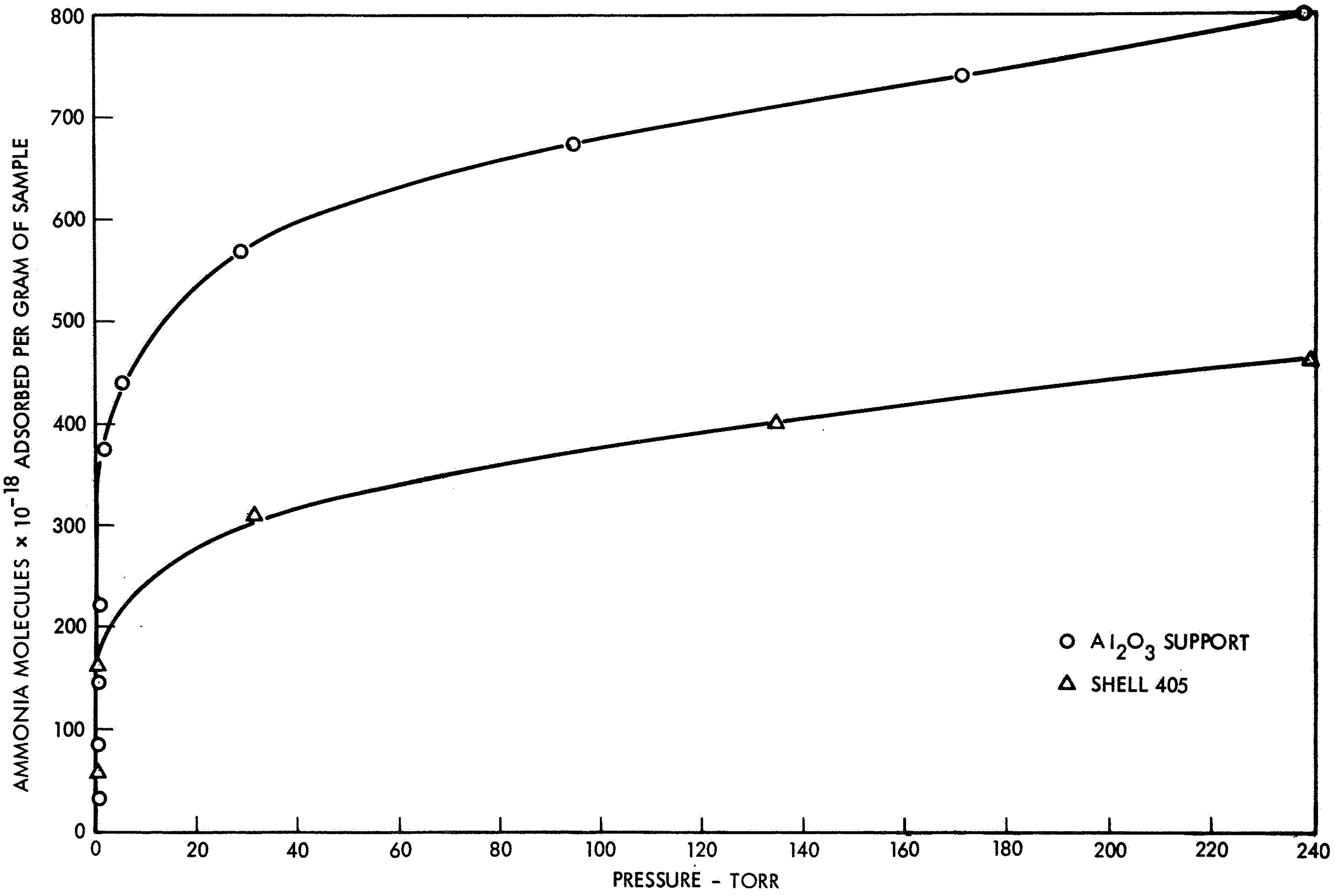

Figure 26. Ammonia Adsorption at 100°C on "Clean" Shell 405 Catalyst and Reynolds RA-1 Alumina

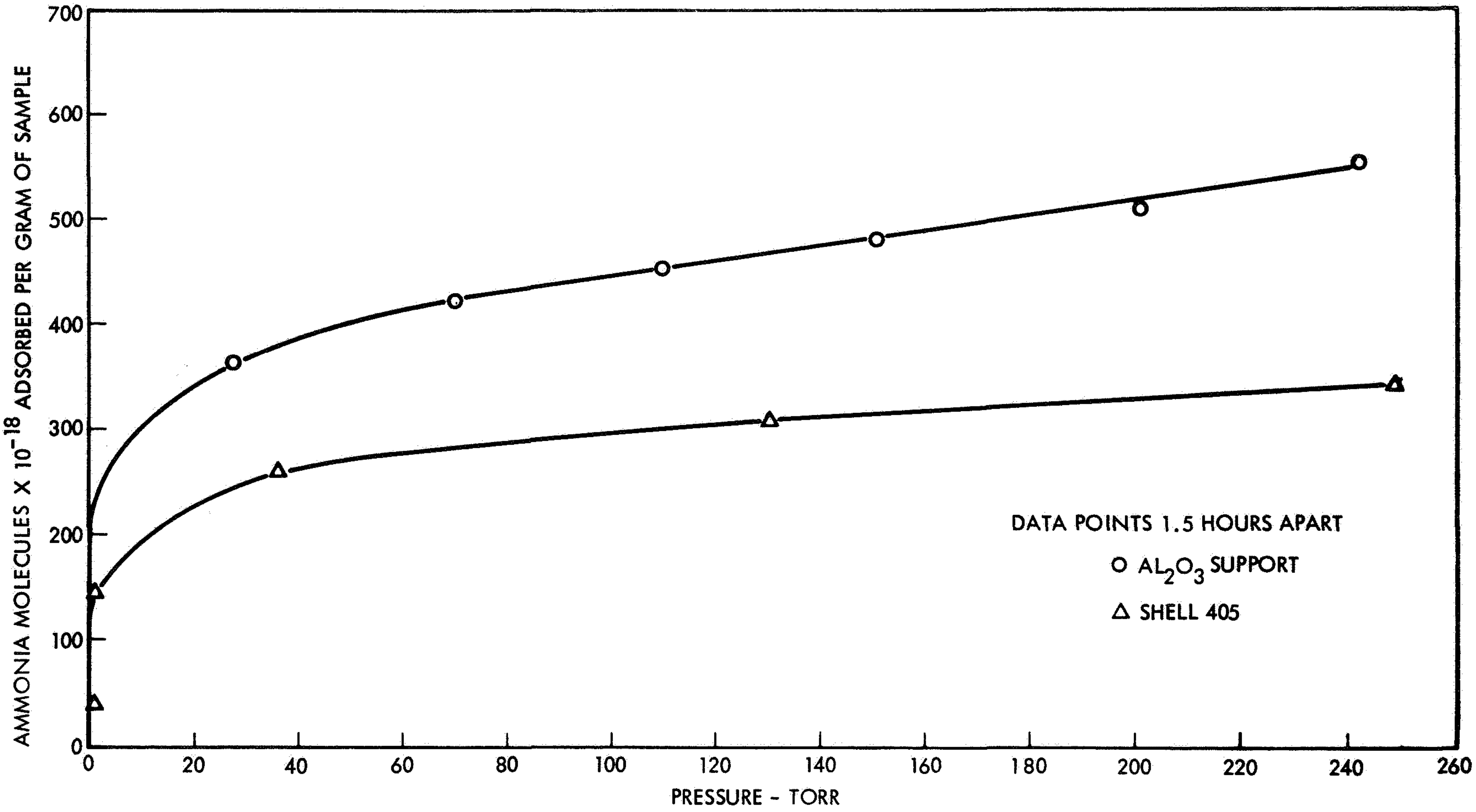

Figure 27. Ammonia Adsorption at 200°C on "Clean" Shell 405 Catalyst and Reynolds RA-1 Alumina

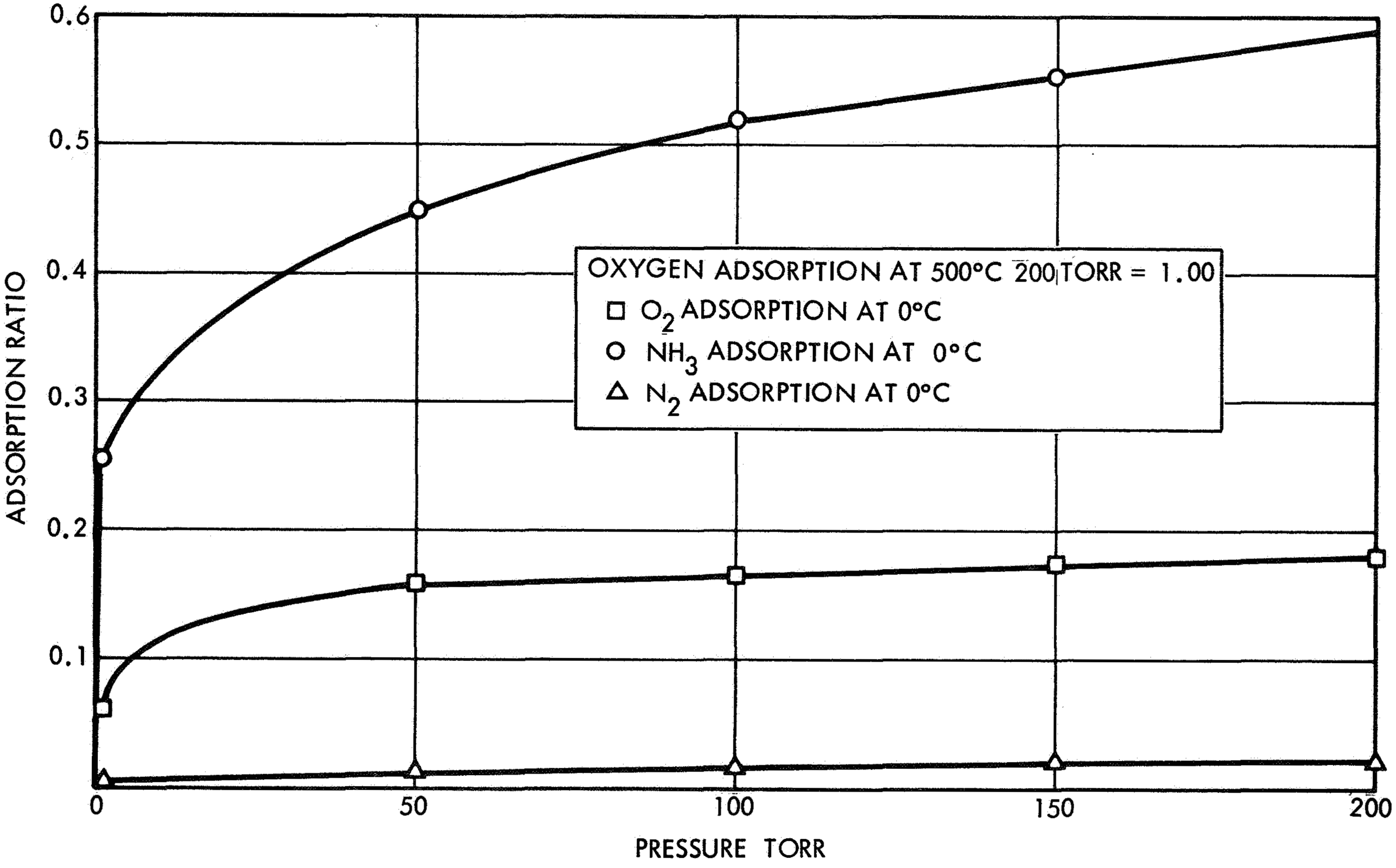

Figure 28. Relative Amount of O_2, NH_3, and N_2 Adsorbed at 0°C
Catalyst - Shell 405 - "Clean"

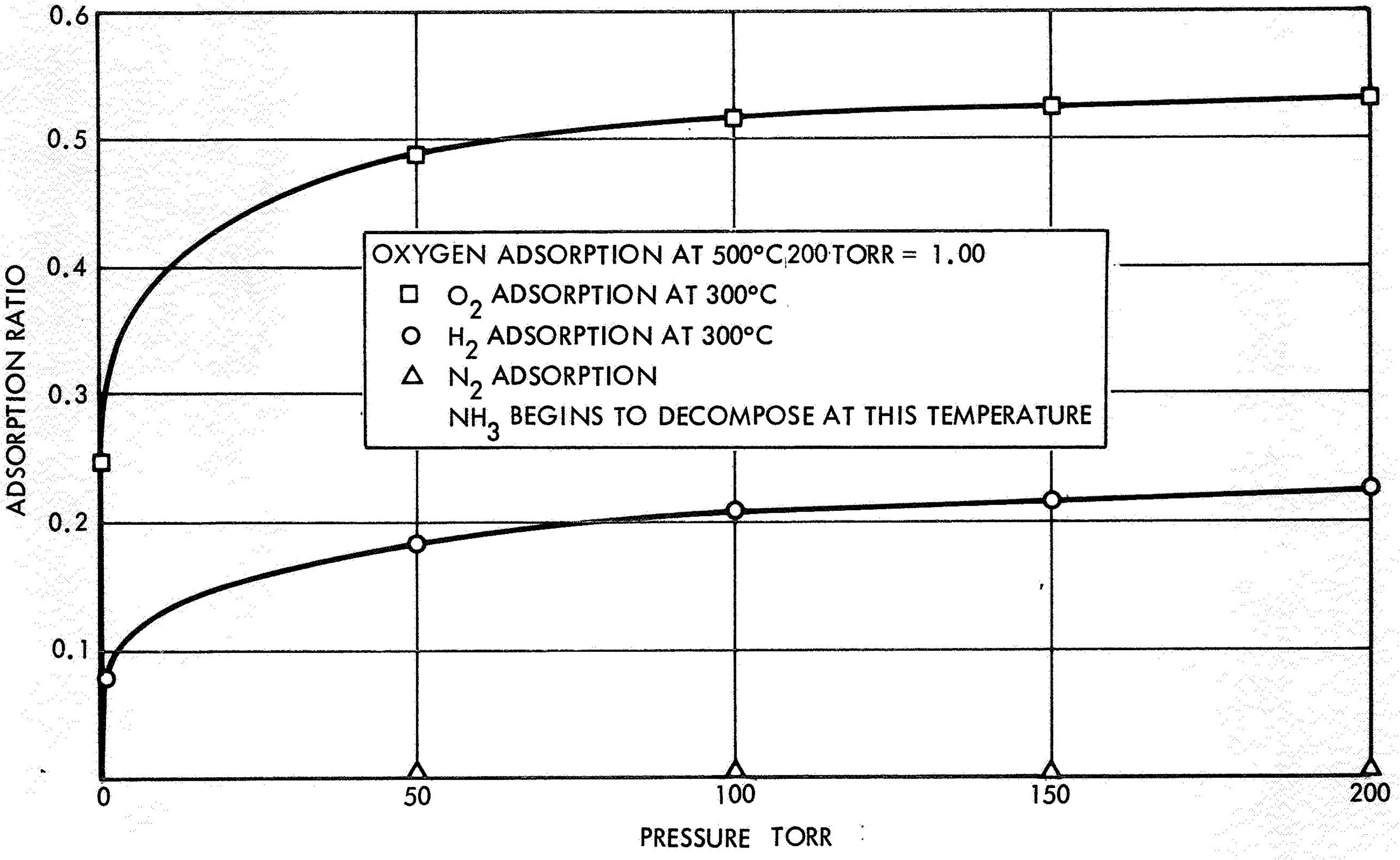

Figure 29. Relative Amounts of O_2, H_2, NH_3 and N_2 Adsorbed at 300°C
Catalyst - Shell 405 - "Clean"

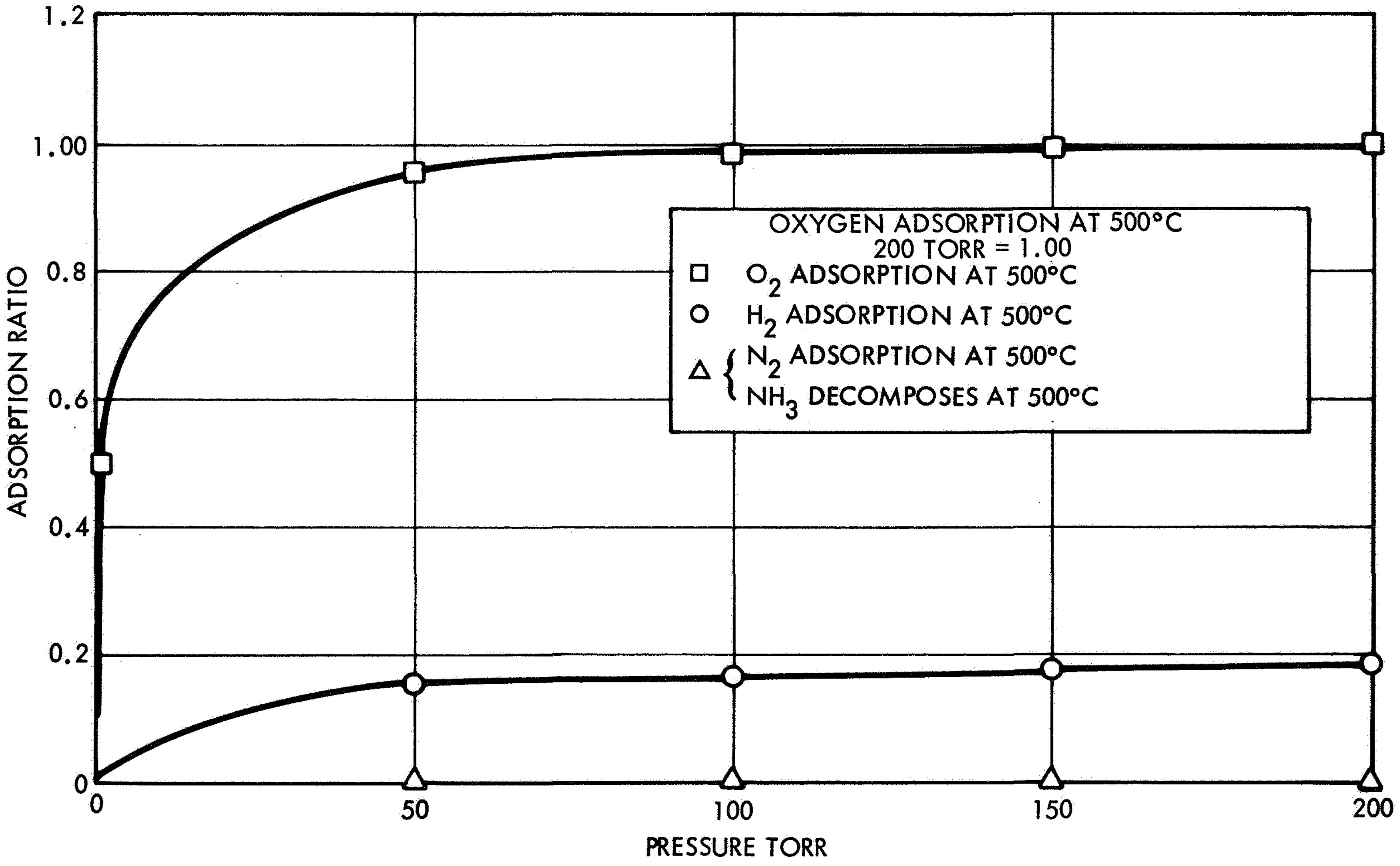

Figure 30. Relative Amounts of O_2, H_2, NH_3 and N_2 Adsorbed at 500°C. Catalyst - Shell 405 - "Clean"

The difference in affinity of the clean catalyst surface for hydrogen, nitrogen, oxygen, and ammonia are shown in Figures 28, 29, and 30 which are plots of the relative amount of gases adsorbed on the catalyst at different pressures and temperatures. The most strongly adsorbed gas species, oxygen at 500°C, 200 torr, was used as the normalizing base.

The chemical affinity of the catalyst for oxygen showed an inverse temperature dependency in the region from 0°C to 500°C. At higher temperatures (300-500°C) the catalyst adsorbs more oxygen than at the low temperatures. The only other gas specie showing an appreciable tendency to adsorb on the catalyst surface at the higher temperatures is hydrogen; it has about 20% of the affinity of oxygen at 500°C, and about 50% at 300°C. Nitrogen does not adsorb measurably at 300°C and above. Ammonia decomposes to nitrogen and hydrogen above 300°C. At lower temperatures, ammonia has a greater affinity for the catalyst than oxygen, however, this affinity is mainly due to the support. The catalyst support (Reynolds RA-1 alumina) adsorbs no measurable quantities of oxygen, hydrogen, or nitrogen over the temperature range of 0-600°C.

5.0 SUMMARY OF LABORATORY RESULTS

Based on the laboratory investigations conducted under this project, the following conclusions are presented relative to the surface chemistry of the Shell 405 catalyst prior to and subsequent to space operation in a hydrazine thruster or gas generator configuration:

- If the Shell 405 catalyst is exposed to a ground acceptance test firing and subsequent exposure to ambient air prior to space operation, then significant concentrations of very strongly chemisorbed oxygen will be present on the iridium metal surface of the catalyst at the time of the first hydrazine ignition in space. Although this chemisorbed oxygen will not desorb significantly in a high vacuum even at elevated temperatures (at least up to 600°C), the oxygen is readily removed by decomposing hydrazine (water formation). Indeed, it is possible that the chemisorbed oxygen will significantly contribute to the first hydrazine ignition (in the space environment) since the chemisorbed oxygen provides, in effect, a solid oxidizer for the hydrazine.

- Depending on the cooldown procedure used in the ground acceptance test firing of a thruster-catalyst system the final concentration of oxygen present on the iridium surface (prior to space operation) can vary over a considerable range. If the catalyst is not exposed to even low partial pressures of oxygen during cooldown from the ground qualification test firing then the final oxygen to iridium atom ratio of the catalyst after exposure to ambient air will be approximately 0.3. If, on the other hand, for example, the catalyst is exposed to air at a temperature of the order of 500°C then the oxygen to iridium atom ratio could be as high as 1.4. Even at low partial pressures (~ 1 torr), oxygen will chemisorb rapidly on the iridium surface of the catalyst at elevated temperatures.

- Depending on how fast the catalyst is cooled down after a ground acceptance hydrazine test firing there may or may not be measurable quantities of residual hydrogen chemisorbed on the surface of the catalyst. If, during the cooldown procedure, the catalyst is cooled to temperatures below 600°C in a period of seconds, then it is expected that some residual hydrogen would remain adsorbed on the iridium surface of the catalyst. However, if the catalyst remains at temperatures above 600°C for time periods in excess of a few minutes, it is expected that the great majority of the residual adsorbed hydrogen would be desorbed from the surface.

- A few seconds of thruster firing in space should be sufficient to effectively remove all chemisorbed oxygen from the iridium surface of the Shell 405 catalyst. Hence, after the first in space ignition, the Shell 405 catalyst will be effectively free of chemisorbed oxygen.

- The only gas specie likely to remain chemisorbed on the Shell 405 catalyst after cooldown from operation in space is hydrogen. As discussed above, the amount of hydrogen which remains chemisorbed on the catalyst after cooldown will depend strongly on how fast the catalyst bed temperature drops from the operational temperature (~1000°C) to below 600°C.

6.0 HIGH VACUUM IGNITION TESTS

The results of the laboratory experiments were used to derive a test plan for high vacuum ignition tests, with the objective of correlating high vacuum ignition characteristics with the surface condition of the catalyst. Three surface conditions were selected for investigation: a surface containing chemisorbed oxygen, a "clean" surface, and a surface containing chemisorbed hydrogen. A fourth test sequence was to be decided upon based on the results of the above tests and conducted at a temperature of 40°F.

The condition of oxygen chemisorbed on the catalyst surface simulates the first in-space firing of a hydrazine reactor which had previously been subjected to an acceptance test. This condition is obtained by purging clean, dry air through the reactor at ambient temperature, then attaining and maintaining high vacuum for a period of 12 hours before firing the reactor. Any nitrogen adsorbed during the air purge readily desorbs in vacuum, leaving only oxygen on the surface.

The next test series simulates the ignition of a reactor following an extended firing and cooldown in space. Any 0_2 chemisorbed on the catalyst surface is consumed during operation of the reactor, leaving only hydrazine decomposition products. Since ammonia rapidly dissociates on the catalyst above 300°C, and nitrogen readily desorbs, hydrogen is the only gas specie which may be expected to remain on the catalyst surface. Providing the cooldown rate is relatively low (as is commonly anticipated), and the reactor firing duration was sufficient to attain full operating temperature, nearly all of the hydrogen will be desorbed. Attainment of this condition involves outgassing the catalyst at 500°C in high vacuum, purging hydrogen through the catalyst bed (maintaining 500°C) to remove any chemisorbed oxygen, then outgassing the hydrogen at 600°C in vacuum. The laboratory experiments have shown that this procedure will result in a "clean" surface, free of any chemisorbed gas specie.

The next test series evaluates the effect of hydrogen chemisorbed on the catalyst surface. A procedure as described above is utilized to obtain a "clean" catalyst surface. Hydrogen is then purged through the bed for one hour while maintaining a temperature of 300°C, and the purge is utilized to accelerate the cooling of the reactor to ambient temperature.

Two end conditions are evaluated by the above sequences; a high concentration of H_2 on the catalyst surface and a very clean surface. The actual conditions encountered in in-space operation will most likely fall between the two conditions, depending upon the specific application.

6.1 TEST INSTALLATION

Existing 1 lb_f engine hardware was modified to provide the temperature conditioning circuits as shown in Figure 31. Gaseous N_2 is passed over a heating coil and through the annular passage around the reactor chamber. A wide range of catalyst bed temperature may thus be obtained by varying the power input to the heater element and the flow rate of GN_2 through the circuit. This system was also used to accelerate cooling of the reactor and to attain the $40^{\circ}F$ condition. Water coolant passages are provided to protect the propellant valve and chamber pressure transducer during the catalyst conditioning periods involving elevated temperature.

A schematic of the test system is also shown in Figure 31. A three way solenoid valve (SV-1) is utilized to isolate the propellant from the fire valve and to provide for purging of the catalyst bed as required. Another three way solenoid valve (SV-2) provides for connection to an aspirator or to the high vacuum system to eliminate residual propellant in the system prior to purging with air or H_2. Problems related to leakage through the fire valve are thus minimized by providing vacuum on both sides of the fire valve until seconds before the firing.

It is important to note that this thruster utilizes direct injection of the hydrazine into the catalyst bed. A single feed tube supplies eight .006 inch diameter orifices centrally located against the top of the catalyst. This design was selected on the basis of previous experience at TRW which showed it to be the most sensitive to changes in catalyst activity. Injection techniques used in current flight systems are designed to minimize the effects of changes in catalyst activity and to minimize the chamber pressure overshoot resulting from long ignition delays.

The test system is installed within a vacuum system capable of attaining 10^{-6} torr. The bell jar volume is such that a three second steady state firing at the 1 lb_f thrust level results in a capsule pressure increase to 0.3 psia.

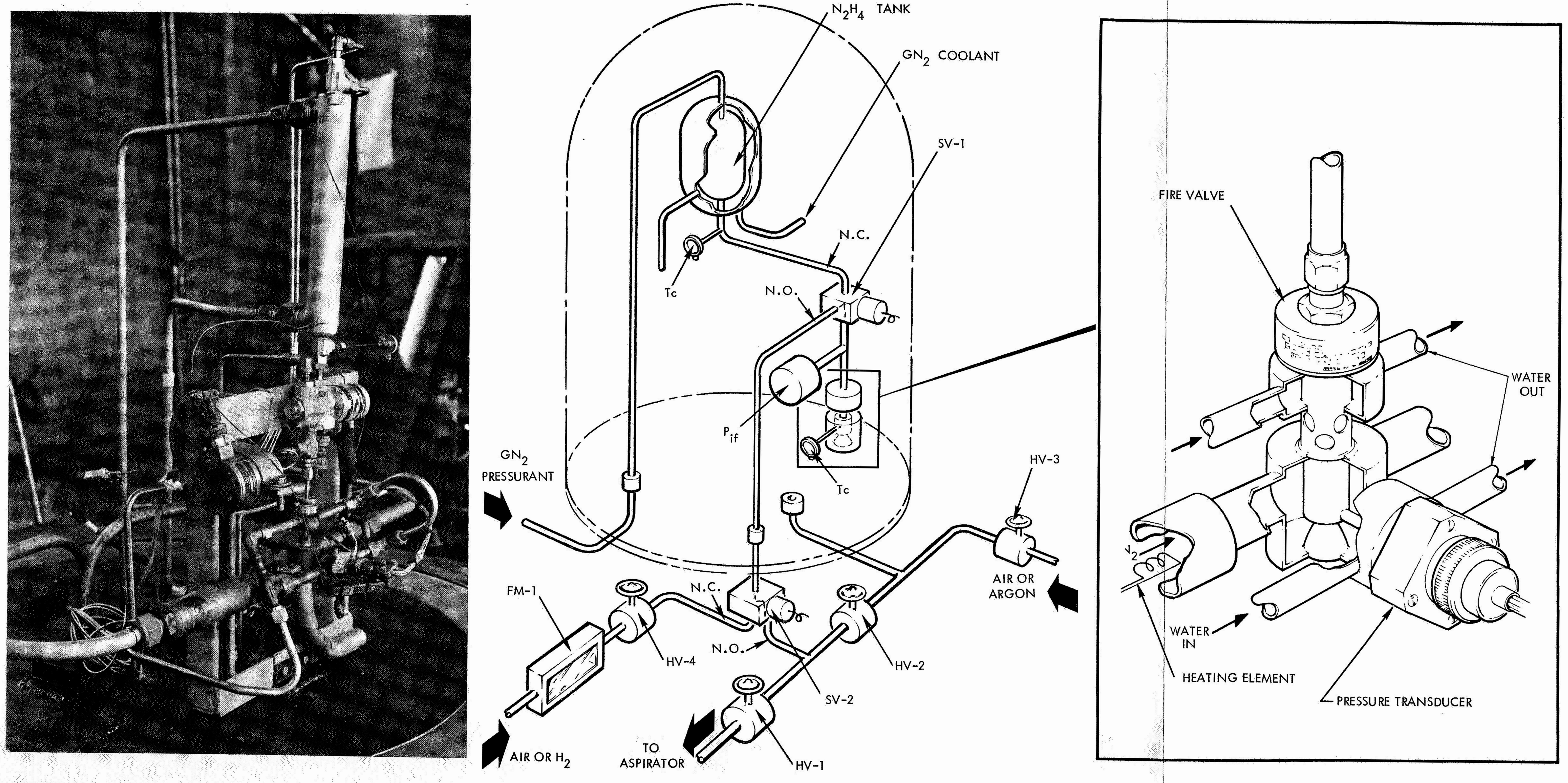

Figure 31. Test System

6.2 TEST SEQUENCE

The test sequence is detailed in Table 4 with the ignition delay data and catalyst history. The firing sequence for each test involved the propellant isolation valve (SV-1) as well as the fire valve. A pretest condition of high vacuum on both sides of the fire valve was maintained to eliminate any leakage through the fire valve. The fire valve was then opened at nominally 3 seconds after opening the isolation valve. Three seconds allows the injection pressure to stabilize after filling the volume between the two valves.

Ignition delay data is given as the times from initiation of propellant flow to a rise in chamber pressure and to a chamber pressure of 5 psia. The term "ignition delay" is used to represent the time from valve open (or initiation of propellant flow) to a rise in chamber pressure. In certain cases, however, the chamber pressure increase is quite gradual for a period of up to 20 ms. For these cases, the time to 5 psia is a more definitive parameter. Figure 32 shows the oscillograph data for Test 004 appropriately labeled to define the parameters and demonstrate the data evaluation.

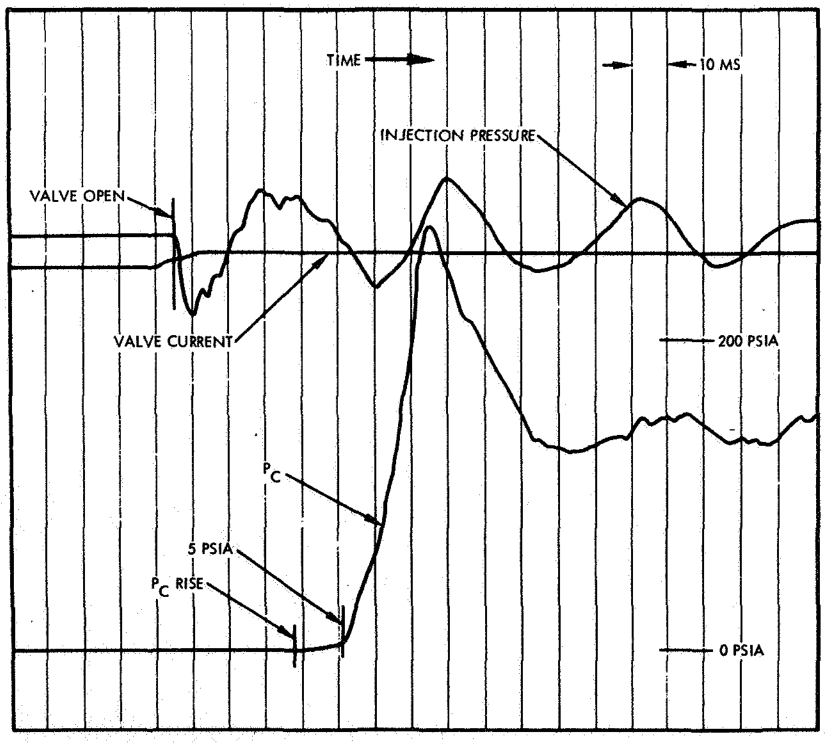

Figure 32. Data Evaluation

Table 4. Test Sequence and Results

Test Number	Time to P_c Rise*	Time to 5 psia*	Cum. Run Time (Secs.) Pre Test	Test Sequence
001 & 002				Sea level checkout tests
				Facility checkout-vacuum to 7 x 10^{-5} torr attained and catalyst heated to 1080°F.
				Vacuum broken to 1/2 atm. and air purged** through the reactor for 2 hours.
				Vacuum of 7 x 10^{-5} torr maintained for 13 hours.
				Vacuum broken for 1/2 hour (due to facility difficulties)
				Vacuum of 7 x 10^{-5} to 1 x 10^{-5} torr maintained for 11 hours.
003	16 ms	21 ms	6.50	Catalyst temperature 75°F
				Vacuum broken to 300 μ and air purged through the reactor for 2 hours.
				Vacuum of 1 x 10^{-4} to 1 x 10^{-5} torr maintained for 14 hours.
004	32 ms	45 ms	11.35	Catalyst temperature 72°F
				Vacuum broken to 3 psia and air purged through the reactor for 2 1/2 hours.
				Vacuum of 1 x 10^{-4} to 1 x 10^{-5} torr maintained for 13 hours.
005	76 ms	92 ms	15.79	Catalyst temperature verified to be 70 ± 5°F. Exact temperature not recorded.
				Vacuum of 1 x 10^{-4} torr (minimum) attained, catalyst heated to 500°C and held for 2 hours.
				Maintaining 500°C, vacuum broken to ∼ 1/2 atm. with argon and ambient temperature H_2 purged through the reactor for 4 hours.
				Vacuum of 1 x 10^{-4} torr attained, catalyst heated to 600°C and held for 4 hours.
006	54 ms	69 ms	20.09	Catalyst temperature 72°F
				Sequence between 005 and 006 repeated.
007	20 ms	32 ms	23.94	Catalyst temperature 69°F.
008				Sea level checkout of new engine.
				Sequence between 005 and 006 repeated.
009	5 ms	9 ms	4.00	Catalyst temperature 68°F.
				Vacuum of 1 x 10^{-4} torr (minimum) attained, catalyst heated to 500°C and held for 2 hours.

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*Time taken from initiation of propellant flow.

**A nominal flow rate of 80 scc/min was used for both air and H_2 purges.

Table 4. Test Sequence and Results (Cont.)

Test Number	Time to P_c Rise*	Time to 5 psia*	Cum. Run Time (Secs.) Pre Test	Test Sequence
				Maintaining 500°C, vacuum broken to ~ 1/2 atm. with argon and ambient temperature H_2 purged through the reactor for 4 hours.
				Vacuum of 1 x 10^{-4} torr attained, catalyst heated to 600°C and held for 4 hours.
				Cooled in vacuum to 300°C.
				Maintaining 300°C, vacuum broken to ~1/2 atm. with argon and ambient temperature H_2 purged through the reactor for 1 hour.
				H_2 purge maintained while cooling to ambient temperature.
				Purge stopped and vacuum of 1 x 10^{-4} torr attained.
010	29 ms	44 ms	8.28	Catalyst temperature 72°F.
				Sequence between 009 and 010 repeated.
011	17 ms	18 ms	11.45	Catalyst temperature 67°F.
				Sequence between 009 and 010 repeated.
				Test delayed following opening of the position valve (SV-1). Increase in catalyst temperature to 105°F (peak) noted.
				Hydrazine behind fire valve evacuated and vacuum re-attained.
012	9 ms	14 ms	15.28	Catalyst temperature 89°F
				Vacuum broken to ~1/2 atm. and air purged through the reactor for 2 hours.
				Vacuum of 1 x 10^{-4} torr maintained for 12 hours.
				Vacuum lost to 25 μ due to a N_2 leak in the system.
013	30 ms	33 ms	19.09	Catalyst temperature 36°F. Test at vacuum of 25 μ.
				Vacuum chamber opened and N_2 leak repaired.
				Air purged through the reactor for 2 hours.
				Vacuum of 1 x 10^{-4} torr maintained for 12 hours.
014	113 ms	117 ms	23.60	Catalyst temperature 39°F.
				Sequence between 005 and 006 repeated.
015	61 ms	63 ms	28.02	Catalyst temperature 50°F.
				Sequence between 009 and 010 repeated.
016	176 ms	198 ms	32.69	Catalyst temperature 40°F.

Tests 001 and 002 were sea level tests to functionally check the test system prior to attaining vacuum. A catalyst conditioning facility check followed in which a vacuum to better than 10^{-4} torr was maintained while raising the reactor temperature to 1080°F and cooling back to ambient. Vacuum was then broken to approximately 1/2 atmosphere and ambient air purged through the reactor for 2 hours at a nominal rate of 80 scc/min. Test 003 followed an 11 hour soak at absolute pressures ranging from 7×10^{-5} to 1×10^{-5} torr. The ignition delay on this test was 16 ms. A sequence of air purge, vacuum soak, and engine firing was also followed for tests 004 and 005 resulting in ignition delays of 32 ms and 76 ms respectively.

The inconsistent ignition delays on tests 003, 004, and 005 are attributed to the presence of small quantities of hydrazine during the last two air purges. Prior to the air purge preceding test 003, a vacuum to 10^{-4} torr was attained on the purge system to remove any hydrazine present. Following this test, a water aspirator was connected to the purge system to re remove residual hydrazine from the system. The same procedure was followed prior to test 005. A pretest condition of high vacuum on both sides of the fire valve could not be obtained on test 005, however, due to leakage through the propellant isolation valve (SV-1). During the latter air purge, a 7 to 10 psi pressure differential existed across this vllve and some hydrazine apparently leaked into the purge system. Qualitatively, if follows that the quantity of 0_2 chemisorbed on the catalyst surface was decreased due to small quantities of hydrazine present in the air purge, resulting in increased ignition delay.

Tests 006 and 007 involved a "clean" catalyst surface. The catalyst was first outgassed at 500°C, then purged with hydrogen to remove any oxygen, and finally outgassed at 600°C to obtain a catalyst surface free of any chemisorbed gases. The ignition delays on these tests were 54 and 20 ms respectively. The testing was interupted at this point due to plugging of the injector. A second reactor was then prepared and test 008 was a sea level checkout test. The sequence of outgassing, H_2 purge, and outgassing was again followed to obtain a clean catalyst surface for test 009. The ignition delay on this test was 5 ms.

The sequence of outgassing, H_2 purge, and outgassing to obtain a clean surface was again followed. After cooling to 300°C, however, hydrogen was purged through the reactor for one hour. The hydrogen purge was maintained while cooling to ambient temperature, and vacuum was then attained. A quantity of H_2 was thus chemisorbed on the catalyst surface which might simulate a condition following a very short firing duration in a reactor. Tests 010, 011, and 012 were conducted with this surface condition resulting in ignition delays of 29, 17, and 9 ms respectively.

Each of the above catalyst surface conditions were then tested at depressed catalyst bed and propellant temperatures. Test 013 followed air exposure of the catalyst and 12 hours vacuum storage. A leak in the propellant pressurization system allowed nitrogen to enter the vacuum system, however, resulting in a capsule pressure of 25 microns at the time of the test. The ignition delay on this test was 30 ms.

The air exposure and vacuum storage sequence was again followed, and test 014 conducted at high vacuum and at 40°F. An ignition delay of 113 ms resulted.

The sequence resulting in a clean catalyst surface was then followed for test 015. An error in instrumentation was made, resulting in conduction of this test with a catalyst bed temperature of 50°F and a fuel temperature of 55°F. In this case the ignition delay was 61 ms.

The final test in the sequence was conducted with a catalyst surface containing chemisorbed hydrogen and at 40°F. The ignition delay was 176 ms.

6.3 DISCUSSION OF TEST RESULTS

The test results are summarized in Table 5. A definite correlation between catalyst surface condition and ignition delay is not readily apparent, due to the scatter in the data and the small quantity of data points. Oxygen chemisorbed on the catalyst does appear to decrease the ignition delay. Temperature, however, has a much greater effect than catalyst surface condition. The work done previously on this contract,* involving low temperature catalyst bed ignition, demonstrated a discontinuous relationship between sea level ignition delay and temperature in the range of 0 to 70°F.

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*Space Environment Operation of Experimental Hydrazine Reactors Final Report, Report No. 4712.4.67-28, Contract No. NAS7-520, April 1967.

Table 5. Test Results

Catalyst Surface Condition	Catalyst Bed Temperature (^{o}F)	Ignition Delay (ms)
Air Exposed	75	16
	72	32
	70 ± 5	76
	36	30
	39	113
"Clean"	72	54
	69	20
	68	5
	50	61
Hydrogen Exposed	72	29
	67	17
	89	9
	40	176

Temperature effects become more pronounced when considering vacuum ignition, due to the flash vaporization effects on temperature. Vacuum ignition tests at TRW with less active catalyst have, in some cases, led to the freezing of hydrazine in the catalyst bed. Further definition of these effects is beyond the scope of this program. A factor which must be considered, however, is that the local temperature at the point of catalyst/propellant contact may be much lower than that which existed prior to propellant injection.

The data from the previous low temperature work is included as Figures 33 and 34, with the data from the vacuum ignition tests added. One can conclude that an effect of the vacuum is to shift the ignition delay versus temperature relationship towards a lower temperature. The data from the vacuum ignition tests thus fall within the range in which ignition delay is extremely sensitive to temperature. Definition of the relationship within this range will require a detailed analytical investigation coupled with additional carefully controlled and instrumented ignition tests.

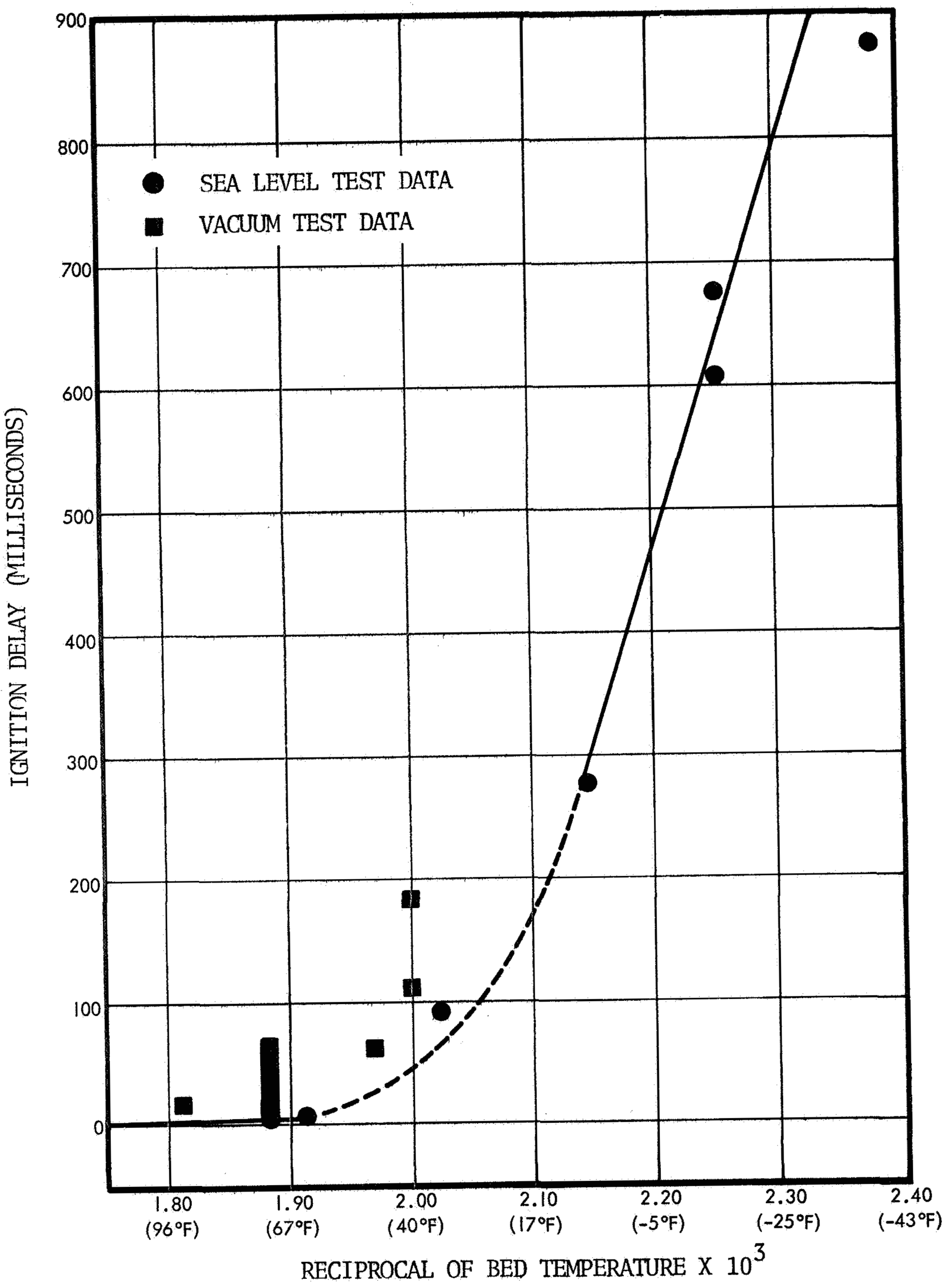

Figure 33. Ignition Delay Versus Reciprocal of Bed Temperature.

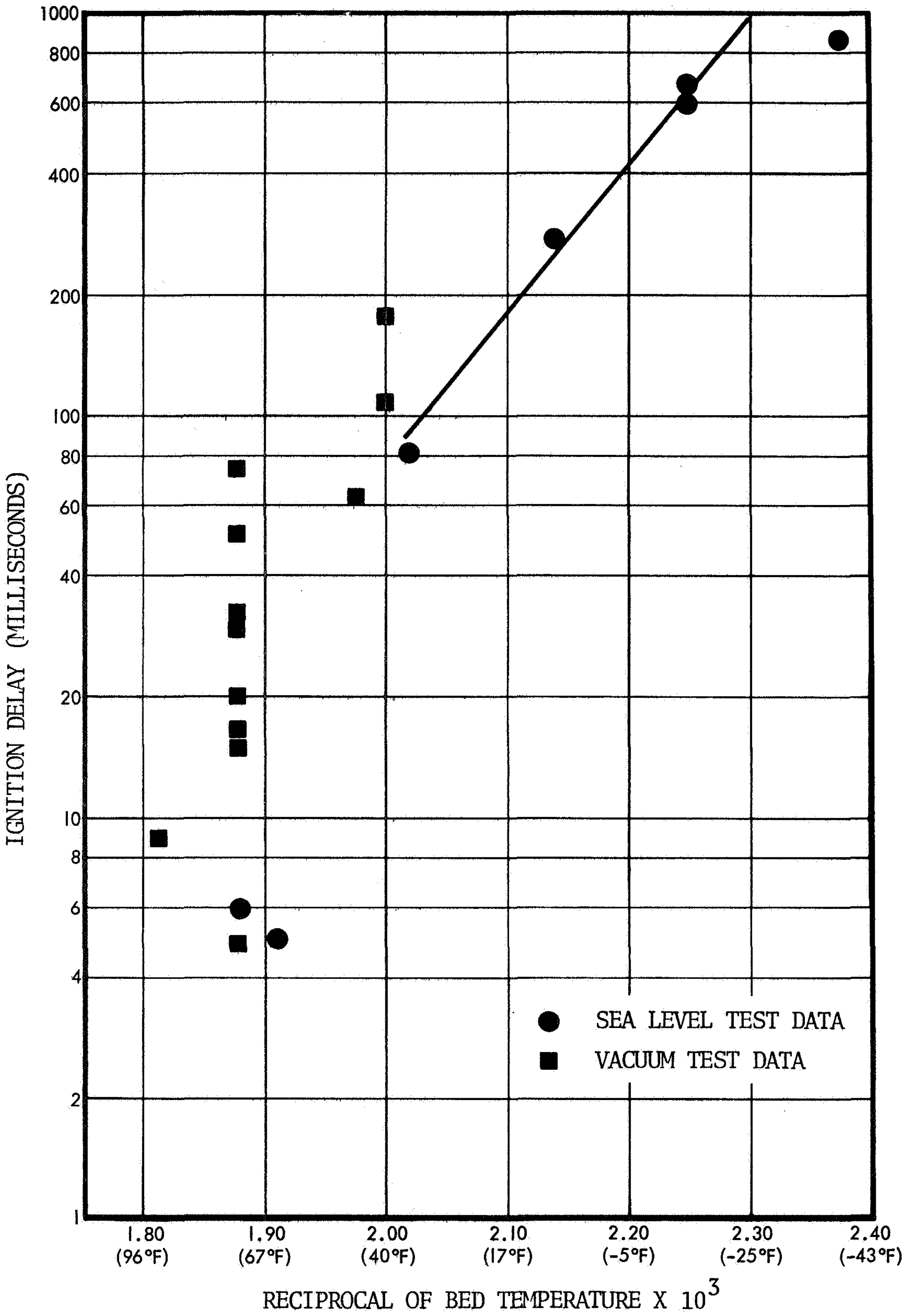

Figure 34. Ignition Delay Versus Reciprocal of Bed Temperature.

7.0 CONCLUSIONS

The laboratory experiments reveal that one of three catalyst surface conditions will exist for in-space operation of a monopropellant hydrazine reactor using Shell 405 catalyst. Oxygen or hydrogen may be chemisorbed on the catalyst surface, or the surface may be free from any adsorbed gas specie.

Oxygen chemisorbs readily on the catalyst surface, even at very low partial pressures (~ 1 torr). The quantity of oxygen chemisorbed on the surface is primarily dependent upon the temperature at the time of contact, and this oxygen will not desorb even in a vacuum of 10^{-6} torr. Any exposure of the catalyst to air will thus result in the presence of oxygen on the catalyst surface for the first in-space firing of the reactor. The oxygen is then consumed during reactor operation (forming water).

Providing that the catalyst cools relatively slowly from its operating temperature (1000°C) to below 600°C while in a vacuum environment, a catalyst surface free of any chemisorbed gas specie will result. If the cooling takes place in a matter of seconds, however, some hydrogen may remain chemisorbed on the surface. Hydrogen is thus the only gas specie which is likely to remain on the catalyst surface following operation in space. The quantity of hydrogen remaining on the surface is dependent upon the time during which the catalyst is exposed to vacuum while at a temperature of 600°C or greater.

The three catalyst surface conditions discussed above were simulated in a series of high vacuum ignition tests. There is some indication that the presence of oxygen may enhance the ignition process, but a definite correlation between catalyst surface condition and ignition delay is not yet possible. A much larger data sample would be required to define the effects of surface condition.

The factor exhibiting the largest effect on ignition delay is temperature. As was demonstrated with sea level tests previously reported under this contract*, catalyst activity decreases greatly as the temperature

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*Space Environment Operation of Experimental Hydrazine Reactors Final Report, Report No. 4712.4.67-28, Contract No. NAS7-520, April 1967.

decreases. This is complicated further under vacuum conditions due to the flash vaporization and cooling of the propellant upon injection. Any further studies into the ignition characteristics of a hydrazine reactor should include a detailed analytical investigation into the thermodynamics of the injected propellant, as well as the heat and mass transfer related to the catalyst bed.

APPENDIX A

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