1985

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The Performance and Chemical State
of a Sulfur Poisoned Fischer-Tropsch Catalyst

by

Chester T. Barry

BS MIT (1983)

Submitted to the Department of
Chemical Engineering
in Partial Fulfillment of the
Requirements for the
Degree of

MASTER OF SCIENCE

at

Lehigh University
Bethlehem, PA 18015
May 1985

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May 15, 1985

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Abstract

The effect of prepoisoning a fused iron Fischer-Tropsch catalyst on its performance and chemical state was investigated. Following reduction at 400 °C, the catalyst was poisoned or carbided at 250 °C and 1 atm. As a result of poisoning with 1.6 mg S/g Fe, catalytic activity decreased 25% and the extent of carbide formation in the bulk after 12 hours of synthesis did not change significantly. The selectivity and chemical state of the catalyst did not change significantly. As a result of poisoning with 134 mg S/g Fe, catalytic activity decreased 95% and the extent of carbide formation in the bulk after 0.5 hours of synthesis was lowered. The selectivity was improved and the chemical state of the catalyst was different from that of an unpoisoned catalyst. The selectivity shifted toward olefin production and higher molecular weight products.

Thesis Advisor: Harvey G. Stenger, Jr.
Assistant Professor of Chemical Engineering

Dedication

I dedicate this thesis to Mommy and Daddy Chester. I couldn't have done it without your love.

Acknowledgements

Harvey, thanks so much for your guidance, enthusiasm, and support throughout my sojourn at Lehigh. It was a real horror show. Karl, you made the lab such a warm and cheery place to work. Ox, thanks for cracking the reactor each time I was too weak to do it myself.

Sincere thanks go to Dr. Gary Simmons and Dave Cole in the Chemistry Department for their very patient and helpful assistance with Mossbauer Spectroscopy.

Finally, I would like to thank the Department of Chemical Engineering and Exxon for supporting me and the project.

TABLE OF CONTENTS

LIST OF FIGURES

I. Introduction

I.A. Background

The Fischer-Tropsch reaction is the catalytic hydrogenation of carbon monoxide followed by polymerization to n-paraffins, olefins, and oxygenated species. Consequently, Fischer-Tropsch technology provides a synthetic route to liquid fuels, olefins, and other hydrocarbons. This technology is in commercial operation at SASOL in South Africa. At this time, there are no Fischer-Tropsch processes in commercial operation in the United States.

Fischer-Tropsch catalysts are usually made of iron promoted with potassium and alumina. One serious limitation of these Fischer-Tropsch catalysts is their poor selectivity. A Flory distribution of products is characteristic of the synthesis reaction. For the process to become attractive from an economic standpoint, the amount of gaseous products must be reduced and the olefinic content improved. Olefins are generally more reactive than paraffins and can more easily be upgraded to high value-added products.

I.B. Effect of Sulfur on Fischer-Tropsch Catalysts

Sulfur severely poisons iron Fischer-Tropsch catalysts. Synthesis gas from coal gasifiers contains high levels of H_2S and other sulfur-bearing compounds. As little as 0.4 mg S/g Fe reduced the activity of a fused iron catalyst ten-fold in laboratory studies (Karn, et al., 1963). Poisoning occurs as a result of adsorption of sulfur onto the surface of metallic catalysts (Bartholomew et al., 1982). Calculations indicate that at Fischer-Tropsch conditions, sulfur adsorption is essentially irreversible (Stenger, 1984). Sulfur poisoning is a serious problem in a number of commercial catalytic processes such as ammonia synthesis and steam reforming.

In small amounts, however, sulfur is a selective poison. As it decreases the activity, it reduces the rate of olefin hydrogenation and chain termination. Hence, sulfur-poisoned iron catalysts produce more olefins and higher molecular weight products per mole synthesis gas converted than fully active catalysts (Bartholomew et al., 1982). Stenger (1984) observed a decrease in methane production and enhanced olefin selectivity in his poisoning studies.

There is a need to improve the selectivity of iron catalysts for the Fischer-Tropsch reaction. If better understood, selective poisoning by sulfur might provide a route to this objective.

I.C. Activity and Chemical State of Catalyst

During the activation of reduced iron Fischer-Tropsch catalysts, it has been shown that the activity of the catalyst rises almost linearly with the extent of carbide formation in the bulk (Raupp and Delgass, 1979). Models which attempt to explain this observation consider the role of diffusion of carbon into the bulk of the catalyst (Niemantsverdriet and Van Der Kraan, 1982).

The present work proceeded with the hypothesis that the concentration of sulfur at the surface influences the rate of carbide formation in the bulk of an iron catalyst.

I.D. Objective and Experimental Approach

The objective of this research is to better understand the effect of sulfur on the performance and chemical state of a fused iron Fischer-Tropsch catalyst.

All reaction experiments were carried out using the same microreactor. After reduction to iron metal, some catalyst samples were poisoned with hydrogren sulfide for various periods of time. Poisoned and unpoisoned samples were used to catalyze a mixture of carbon monoxide and hydrogen for the Fischer-Tropsch synthesis. During the synthesis reaction, gas chromatography was employed to determine preadsorbed sulfur's effect on the activity and selectivity of the catalyst. After catalyzing the synthesis reaction for various periods of time, poisoned and unpoisoned samples were removed from the reactor and analyzed using Mossbauer spectroscopy. After analyzing the Mossbauer spectra with the aid of the SIRIUS Spectrum Evaluating Sysytem, the effect of preadsorbed sulfur on the chemical state of the catalyst was determined.

II. Experimental

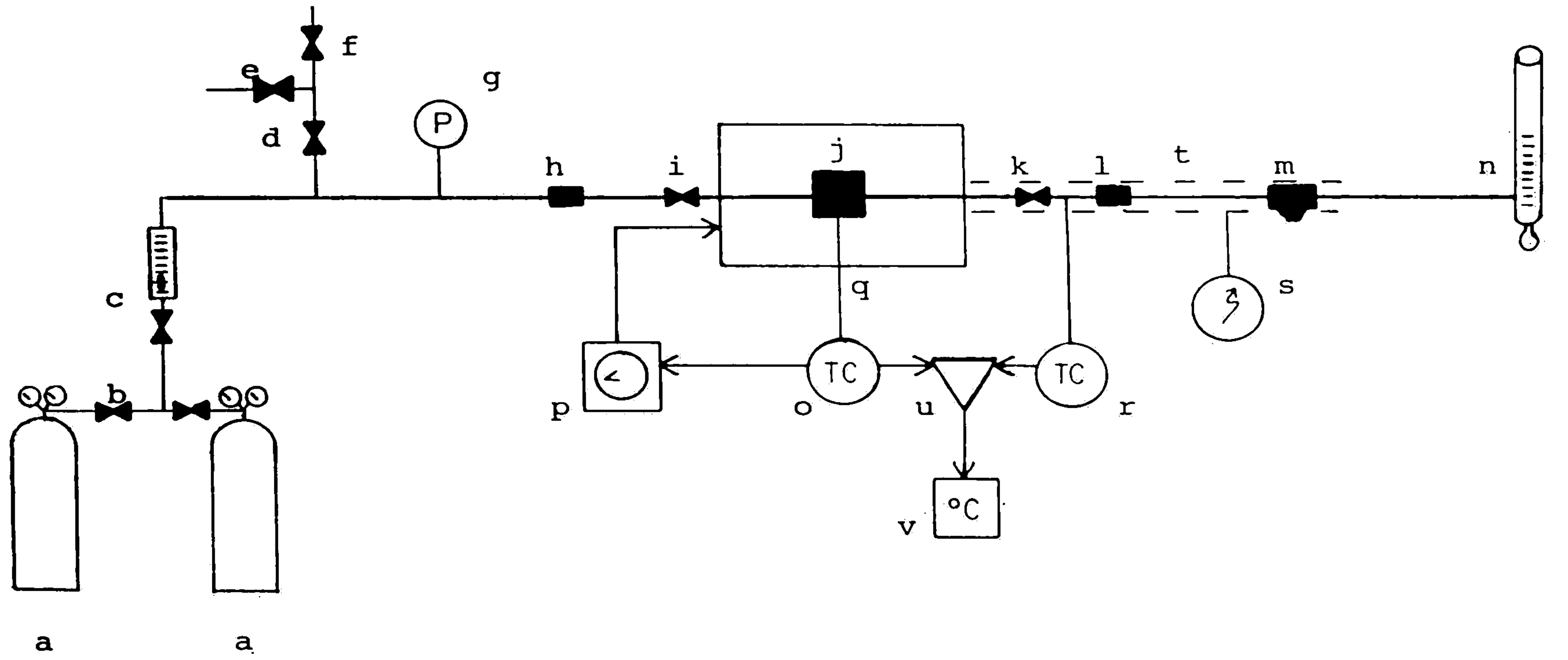
II.A. Operation of Reactor System

II.A.1. Reactor System

A single reactor system was used to carry out catalyst reduction, poisoning, and Fischer-Tropsch reactions (Figure 1). The system can be broken down into four sections: the upstream section (a-g), the microreactor module (h-l), the downstream section (m-n), and temperature control equipment (o-v). All connecting tubing was 1/4-in stainless steel.

In the upstream section, reactant flowrate was regulated using a Linde Model FM 4441-1 rotameter. It was equipped with a metering valve and two spherical floats. The glass float was useful for nitrogen flow of 5-50 ml/min. The 316 stainless steel float was useful for nitrogen flow of 15-150 ml/min. The system pressure was measured using a pressure gauge. A 10 psig pressure relief valve (f, Swagelok No. SS-4C-10) was installed in the event that high molecular weight waxes plugged the reactor, causing the reactor pressure to rise. During operation, valve d was open and valve e closed.

Since reliable information on the chemical state of the catalyst was desired, it was necessary to prevent oxidation of the catalyst as it was transferred from



<u>Upstream Section</u>:

a - reactant or inert
    gas cylinder
b - regulator valve
c - rotameter and valve
d - valve
e - valve
f - pressure relief valve
g - pressure gauge

<u>Microreactor Module</u>:

h - upstream Quick-connect
i - upstream reactor valve
j - reactor
k - downstream reactor valve
l - downstream Quick-connect

<u>Downstream Section</u>:

m - GC sampling port
n - soap bubble meter

<u>Temperature Control Section</u>:

o - microreactor thermocouple
p - temperature controller
q - microreactor furnace
r - heating tape thermocouple
s - power regulator
t - heating tape (- - - -)
u - thermocouple selector switch
v - digital temperature display

<u>Figure 1</u>: Reactor System

the microreactor to the Mossbauer sample holder. The microreactor module could quickly and conveniently be removed from the system using the upstream and downstream Quick-connects (h and l). Upstream and downstream reactor valves (i and k) were closed prior to module removal. Once the module was in the inert chamber, the reactor could be opened to recover the unoxidized catalyst.

The microreactor (j) consists of a Swagelok union flanked on both sides by a porous stainless steel frit which serves to contain the catalyst in the reactor. The dimensions of the reactor are 10.4 mm x 5.6 mm (diameter x length, volume = 0.48 cm^3. Thermocouple "o" extends through the wall of the union and is embedded in the catalyst during experiments.

In the downstream section, a sampling port from which gas chromatography samples were withdrawn was fashioned from a 1/4-in stainless steel "T" fitting. A 9 mm Supelco Thermogreen LB-2 septum was held in place by a nut at the bottom of the "T".

The temperature control equipment served two purposes. The microreactor thermocouple (o) and the temperature controller (p) regulated the power supplied to the furnace (p) to maintain the temperature inside the microreactor at 400 ^oC during reduction and at 250 ^oC during poisoning and synthesis runs. During experimental runs, temperatures differed from these desired values by no more than 1 ^oC. The Lindberg tubular furnace (Type 55035-A) heated the microreactor and 6 inches of tubing on either side of the reactor. Heating tape (t) was wrapped around the downstream section valve, Quick-connect, and sampling port to prevent condensation of heavy waxes in these fittings. Thermocouple "r" was positioned beneath the heating tape adjacent to the outside of the downstream valve. The heating tape was plugged into a Variac (s) used to maintain the temperature of the valve at approximately 70 °C. The thermocouple selector switch (u) was positioned to accept a signal from either thermocouple "o" or "r" and divert it to an Analog Devices Model AD 2050 J digital readout (v).

II.A.2. Catalyst Reduction

All catalyst samples were reduced at 1 atm under flowing hydrogen at 400 °C for 60 hours prior to any subsequent poisoning or Fischer-Tropsch reaction. The desired flowrate was 40 ml/min yielding a gas hourly space velocity (GHSV) of 5000 (ml gas at STP/hr/ml empty reactor). Following reduction, hydrogen flow to the catalyst was stopped and the temperature was reduced to 250 °C.

II.A.3. Poisoning

Catalysts that were sulfided were done so under flowing 2% hydrogen sulfide in hydrogen at 250 °C prior to Fischer-Tropsch reaction. The desired flowrate was 10 ml/min yielding a GHSV of 1250. After 5 minutes or 7 hours of poisoning, flow to the catalyst was interrupted by closing valves adjacent to the reactor.

II.A.4. Synthesis

For synthesis, catalyst samples were exposed to synthesis gas (50 vol.% carbon monoxide in hydrogen) flowing at 5 ml/min at 250 °C. Heating tape wrapped around the downstream valve, downstream Quick-connect, and GC sampling port prevented high molecular weight waxes from condensing in these fittings and plugging the apparatus. With the aid of a thermocouple positioned between the heating tape and the downstream valve, a Variac was used to maintain the temperature in these fittings above 70 °C. Periodically, 1 ml gas samples were withdrawn from the flow system through the septum of the downstream sampling port using a Hamilton Gas-Tight 1001 1 cm^3 syringe. These gas samples were then analyzed using gas chromatography.

After 0.5, 12, or 98 hours of Fischer-Tropsch reaction, flow was switched from synthesis gas to argon flowing at 40 ml/min in order to flush the catalyst of reactants. At the same time, the furnace was turned off and opened to quickly cool the reactor. Once the temperature inside the reactor reached about 100 °C, the flow of argon was turned off and the reactor sealed shut by closing both the upstream and downstream valves, V3 and V4, respectively. Once the reactor was cool enough to handle, it was removed from the apparatus using the Quick-connect fittings and clamped securely in the vise within the inert chamber.

II.B. Catalyst and Reactants

The catalyst used in this work was a fused iron ammonia synthesis catalyst purchased from United Catalyst, Inc. and designated C-73-1-101. Its analysis as determined by Galbraith Laboratories of Knoxville, TN was 64.4% Fe, 0.76% Al, 0.31% K, and 0.74% Ca on a weight basis, with oxygen and trace elements making up the balance. The catalyst was sieved to a particle size of 150 - 300 microns (48 to 100 mesh).

Gases were obtained from Union Carbide Corporation. For reduction, Extra Dry Grade hydrogen was used. Uncertified Grade 2% (v/v) hydrogen sulfide in hydrogen and 50% (v/v) carbon monoxide in hydrogen were used in poisoning and synthesis experiments, respectively.

II.C. Product Analysis by Gas Chromatography

II.C.1. Instrumentation and Materials

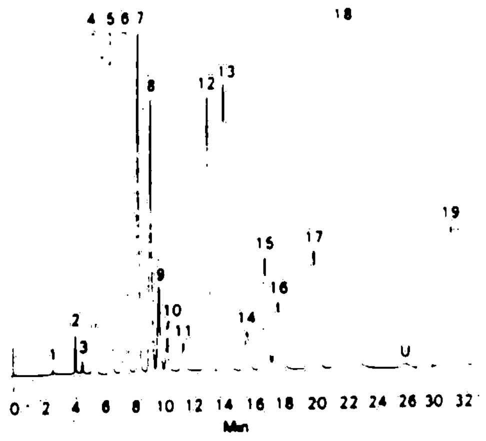
The product analysis system consisted of a Hewlett-Packard 5750 gas chromatograph, a Supelco SP-1700 packed GC column, a Hewlett-Packard 3370A integrator, and a Perkin Elmer 690 strip chart recorder.

The HP 5750 gas chromatograph consisted of an oven, a thermal conductivity (TC) detector, a strip chart recorder, and associated modules for control of the TC detector and oven temperature control. All samples were analyzed using temperature programmed separations. The injection port temperature was the same as the oven temperature. Following a four minute post injection interval at room temperature, the oven temperature was programmed to rise 4 °C per min to the upper limit of 90 °C. At this time the oven lid automatically opened and the column cooled at a rate of 40 °C per min. The thermal conductivity temperature was 120 °C. High Purity Grade helium obtained from Union Carbide Corporation was used as the carrier gas at a flowrate of approximately 25 ml/min. Supelco Thermogreen LB-2 12.5 mm injection port septa were replaced as needed.

A pre-conditioned and pre-packed 30' x 1/8" stainless steel column was obtained from Supelco, Inc. The column packing consisted of 23% SP-1700 on 80/100 Chromosorb and was designed for separation of light hydrocarbons. Information supplied by the manufacturer (Figure 2) indicates that, in general, the column elutes paraffins before olefins in order of increasing carbon number.

The HP 3370A integrator was used to integrate the area under GC peaks as components were detected by the

1 Ethene
2 Propene
3 Propylene
4 Isobutane
5 n-Butane
6 1-Butene/Isobutylene
7 trans-2-Butene
8 cis-2-Butene
9 Isopentane
10 1,3-Butadiene
11 n-Pentane
12 1-Pentene
13 2-Methyl-1-butene
trans-2-Pentene
14 cis-2-Pentene
15 2-Methyl-2-butene
16 2-Methyl-1-pentene
17 3-Methyl-1-pentene
18 n-Hexane
U Unknown
19 3-Methylhexane



23% SP-1700 on 80/100 Chromosorb P AW, 30' x 1 8" OD SS, Col. Temp. 70°C, Inj. Temp 100°C, Det. Temp 150°C, Flow Rate: 25ml/min., He, Det. FID, Sens. 32 x 10^{-10}, Sample 0 6µl ASTM Section L Blend No 6, plus C5s

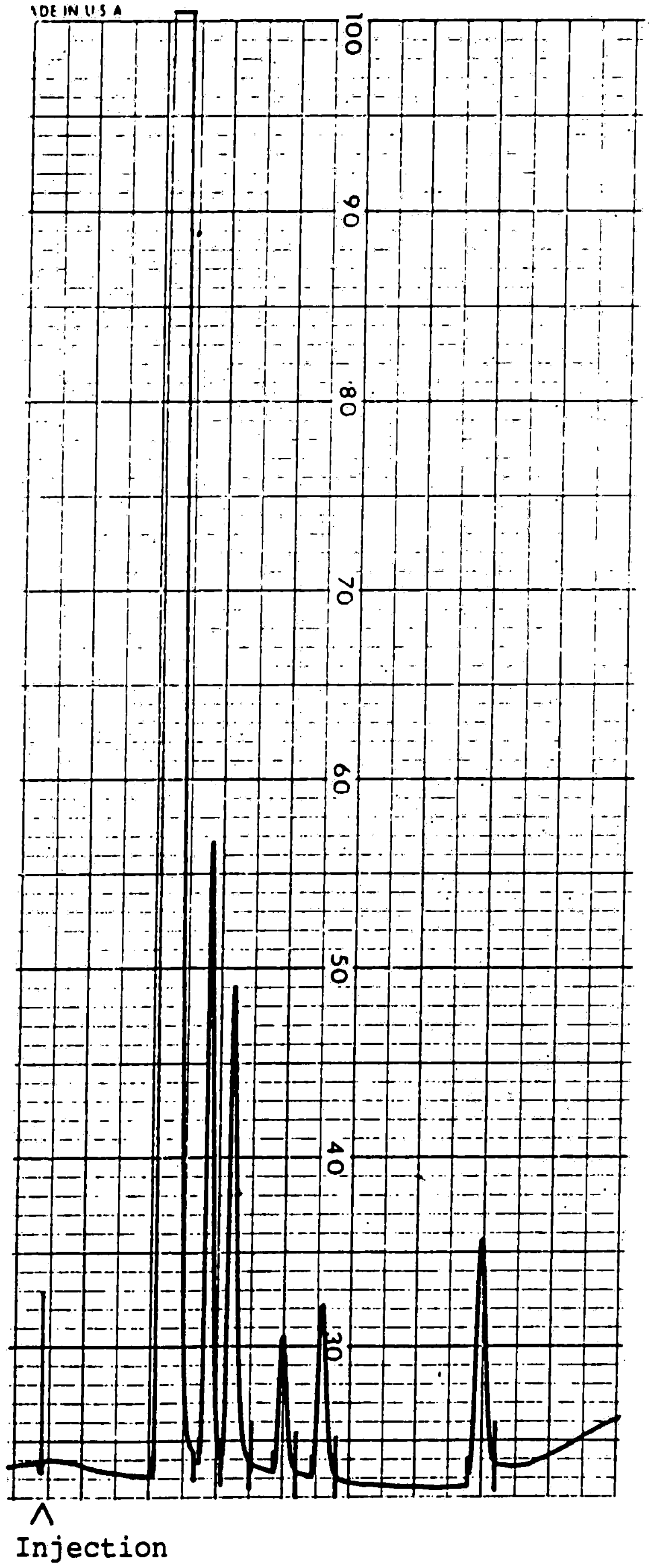
Figure 2: Separation Characteristics of Supelco SP-1700 GC Column

TC detector. The integrator operated in the automatic mode with equal up and down slope sensitivities of 0.03 micro volt/min. That is, integration of a peak began when the electrical signal from the TC detector increased by 0.03 μV per minute. Similarly, integration of that peak ended as soon as the signal decreased by less than 0.03 μV per minute. Periodically, the integrator recalculated the baseline to account for septum "bleed". The baseline reset delay was set at 0.3 min. Figure 3 shows a sample chromatogram and its corresponding peak area data as it is presented by the integrator. The lower number of each pair is the retention time of the peak in units of seconds (S). The upper number is the area of that peak in units of micro volts per second. Powers of ten appear in the right column alongside the area data.

The Perkin-Elmer 690 Strip Chart Recorder created the chromatogram based on electrical signals from the integrator. The recorder advanced paper at a rate of 5 mm/min.

II.C.2. Operation

In general, throughout the period of this research that GC samples were being analyzed, the instrument was in a ready mode with carrier gas flowing constantly. Therefore, most instrument settings did not require adjustment, with the notable exception of periodically



Integrator Data

2611 0
0791 S

1630 0
0504 S

1185 0
0433 S

4497 0
0340 S

4766 0
0298 S

6688 2
0225 S

Figure 3: Sample HP-5750 Chromatogram

checking and adjusting the helium carrier gas flowrate to 25 ml/min. The Coarse Zero and Fine Zero controls of the HP 5750 Conductivity Module were often adjusted to align the pen of the strip chart recorder on a convenient baseline.

Prior to GC sample injection, the integrator and strip chart recorder were turned on. Most of these instruments' settings did not require adjustment throughout this research.

After inserting the syringe needle through the injection port septum, the 1 ml gas sample was injected into the injection port by depressing the syringe plunger rapidly but steadily. Immediately following sample injection, the GC "Inject Start" and integrator "Start Analysis" buttons were depressed. After the temperature programmed cycle was complete, the GC automatically shut off and the integrator "Stop Analysis" switch was manually depressed.

II.C.3. Data Reduction

The following calculations are based on the GC peak area data provided by the HP 3370A integrator. An arbitrary molar area unit (herein referred to simply as "molar area", and abbreviated "M") is defined as:

$$M_X = \frac{(A_I)(F_I)}{(W_I)} ,$$

where:

A_I = area of peak I
F_I = thermal conductivity detector response factor for component I
W_I = molecular weight of component I
I = 1,2,3, or 4 which denote ethane, ethylene, propane, or propylene, respectively.

Response factors for GC analyses of hydrocarbons are available in the literature (Dietz, 1967). The values for the compounds of interest in this work are: ethane, 0.59; ethylene, 0.585; propane, 0.68; and propylene, 0.652.

a. Relative Activity Calculation

Since the activity of the catalyst was not measured directly, the activity of poisoned samples was reported relative to that of unpoisoned samples. The total molar area of C2 and C3 compounds formed by a poisoned catalyst sample at time t_0 during the synthesis reaction was determined. This value was then compared to the C2+C3 molar area formed by an unpoisoned catalyst at the same time. That is,

$$\text{relative activity} = \frac{\sum_1^4 M_I \text{ (poisoned, } t_0)}{\sum_1^4 M_I \text{ (unpoisoned, } t_0)} .$$

Poisoned catalyst activity is therefore always an experimentally determined percentage of the activity of the unpoisoned catalyst.

b. Selectivity Calculation

Selectivity to a reaction product species I, S_I, is defined as:

$$S_I = \frac{M_I}{\sum_1^4 M_I} .$$

Note that selectivity is defined as the molar area percent of ethane, ethylene, propane, or propylene relative to the total of these four reaction products only.

II.D. Catalyst Analysis by Mossbauer Spectroscopy

Mossbauer spectroscopy is an analytical technique useful in determining the chemical state of Mossbauer effect absorbers such as iron. The Mossbauer spectrometer "sees" only the recoil-free fraction of ^{57}Fe nuclei in the catalyst, not the entire catalyst. Assuming that the recoil-free fraction is the same for different iron-bearing compounds in the sample, percent spectral area is proportional to molar percent of the iron present. For example, if X-Fe_5C_2 accounts for 20% of the spectral area of a catalyst that is 50% iron, the catalyst is 10% X-Fe_5C_2 on a mole basis.

A detailed explanation of the Mossbauer effect is outside the scope of this thesis. There are a number of well-written books on this subject (May, 1971 and Wertheim, 1964). There is also at least one excellent review of Mossbauer spectroscopy and its applications to research in heterogeneous catalysis (Dumesic and Topsoe, 1977).

Mossbauer analysis of a catalyst sample involves preparing the sample, operating the spectrometer, reducing the raw data, and fitting the spectrum. The chemical state and composition of the iron in a catalyst sample can be determined after comparing the fitted Mossbauer parameters with accepted values in the literature.

II.D.1. Preparation of Mossbauer Sample

a. Mossbauer Sample Holder Fabrication

The Mossbauer sample holder (Figure 4) consisted of a front panel, a back panel, and a central "well" piece. Using a band saw, two identical 1.5-inch x 1.5-inch panels were cut from 1/16-inch thick sheet Plexiglas (Rohm and Haas Co.). The well piece was a 2-inch x 3-inch piece cut from 1/4-inch thick sheet Plexiglas with a 1-inch diameter hole drilled through it. With the back

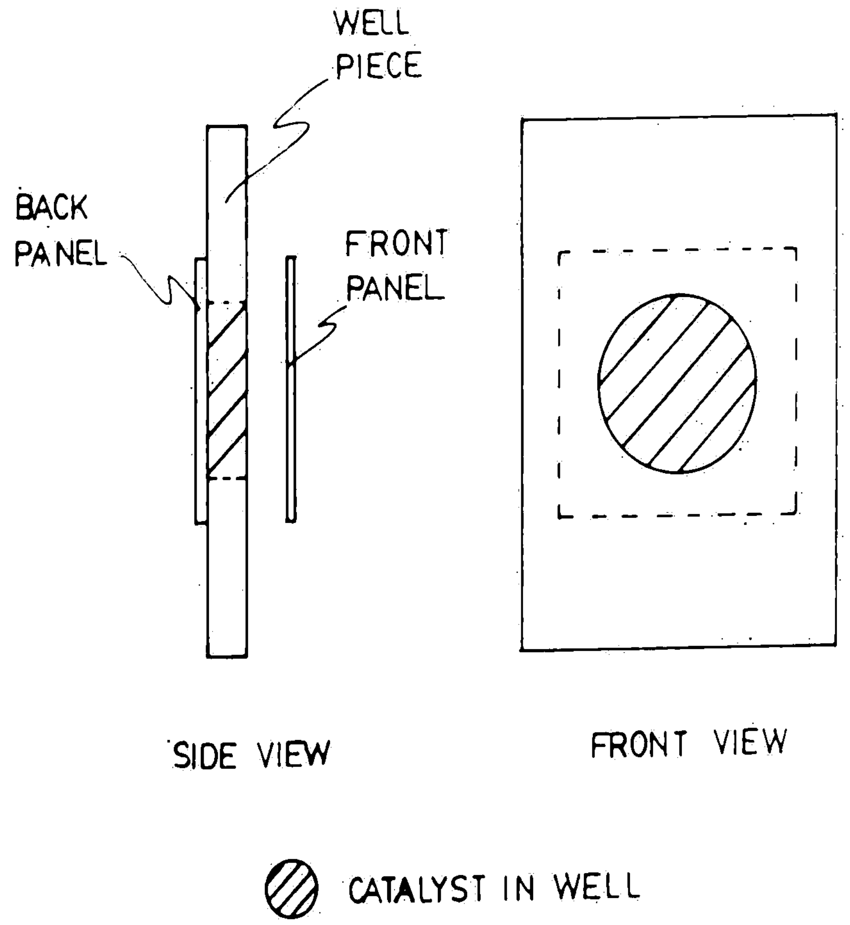


Figure 4: Mossbauer Sample Holder

panel centered securely over the hole, methylene chloride solvent was applied along the perimeter of the back panel in order to securely join the two pieces and form a well.

b. Inert Chamber Preparation

In order to prevent the oxidation of the catalyst, the reactor was opened and the catalyst placed in the Mossbauer sample holder under an inert (argon) environment. Figure 5 shows the inert chamber. With the reactor clamped firmly in the vise, the following materials were placed inside the inert chamber: Playtex gloves, 13/16-in and 7/8-in open end wrenches, Mossbauer sample holder and front panel, one 4-ml glass vial and plastic screw top, dual-chamber epoxy dispenser, and a plastic stirrer. After collapsing the glove bag (Instruments for Research and Industry, Model X-27-27) to remove as much air as possible, the chamber was sealed shut using Handy-Lok^{TM} closures (see Figure 5 inset) supplied by the glove bag manufacturer. The chamber was inflated with argon passing into the chamber through a 1/4-in Tygon tube. The chamber was then purged by breaking the recloseable seal slightly and forcing the remaining air and argon out of the chamber. This procedure of purging and inflating the chamber with argon was repeated two or three times to reduce the oxygen concentration within the chamber to a very low level. The reactor was opened under flowing argon.

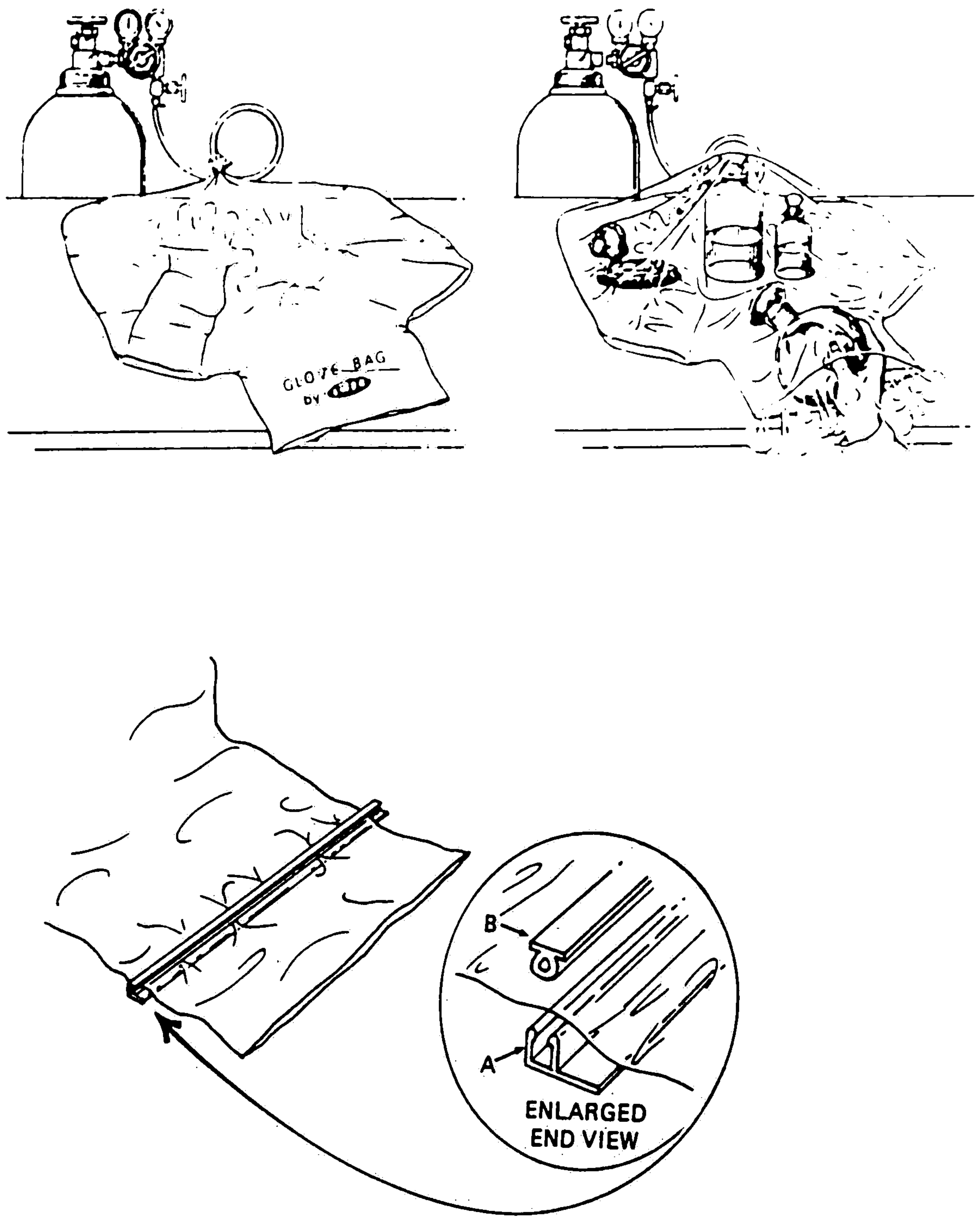


Figure 5: Inert Chamber

c. Opening the Reactor

After donning a pair of absorbent gloves to ward against sweaty palms, the experimenter inserted his hands and arms into the glove portion of the glove bag. To reduce the risk of puncturing the bag on sharp objects within the bag, Playtex gloves were worn inside the glove bag. Using the wrenches, the reactor was opened by loosening the upstream 7/8-in nut. The reactor was tilted to deposit the catalyst into the well of the Mossbauer sample holder. Just enough epoxy was added to the catalyst as to fill the "well" portion of the sample holder. The plastic stirrer was used to throughly mix the epoxy resin, hardener, and catalyst. After mixing, the sample holder front panel was centered over the well. The epoxy served not only to seal the catalyst in an airtight environment, but also to firmly attach the front panel to the rest of the holder. Once the epoxy had hardened, the argon flow was shut off, the glove bag opened, and the sample labeled.

II.D.2 Spectrometer System and Materials

The "experiment" taking place in Mossbauer spectroscopy requires a radioactive source, a velocity drive, the absorber (iron-containing catalyst sample), a detector, and associated instrumentation (see Figure 6).

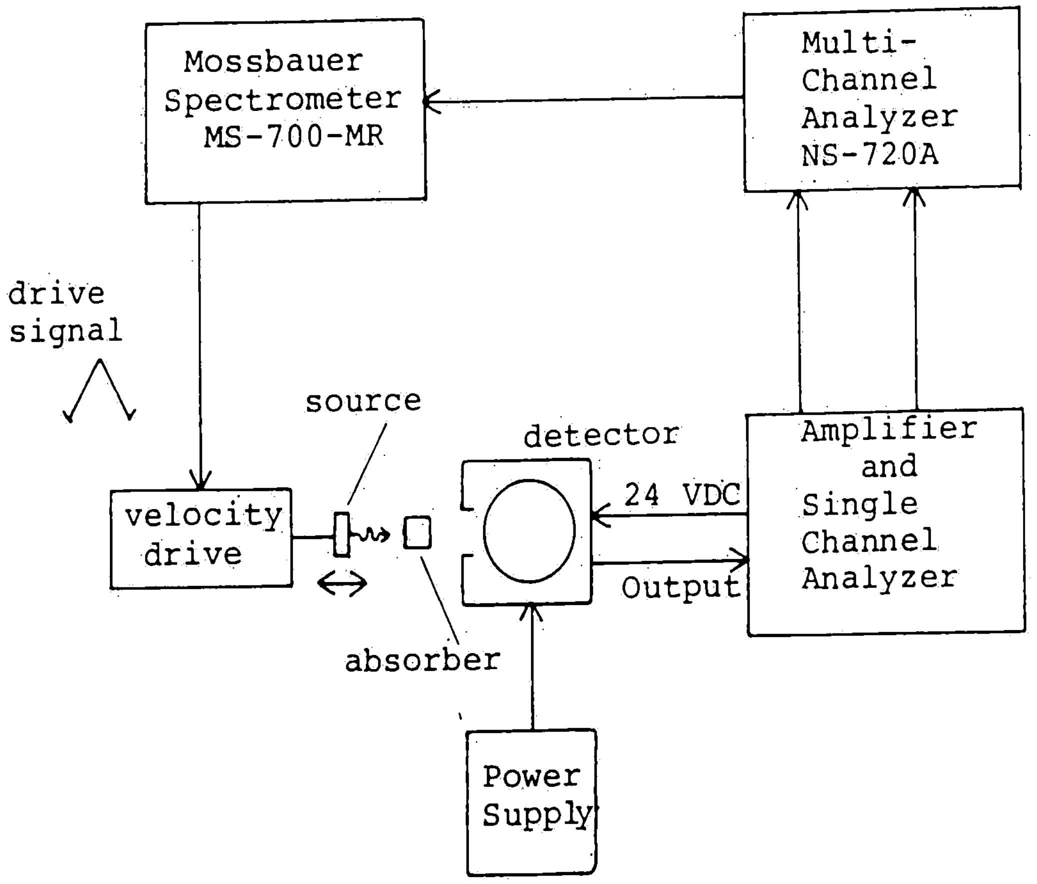


Figure 6: Mossbauer Spectrometer System

The ^{57}Co source (New England Nuclear, NER-072) emits energetic gamma radiation as a result of the 14.4 keV nuclear transition. The purpose of the velocity drive (Ranger Electronics, VT-700) is to accelerate the source over a specified range of positive and negative velocities. Acceleration of the source Doppler shifts the energy of the emitted gamma radiation over a range of energies. A Kr/CO_2-filled proportional counter (Ranger Electronics, PA-700) placed behind the absorber detects gamma radiation passing through the sample.

The electrical impulses from the proportional counter are amplified in the single channel analyzer (AMP/SCA, Ranger Electronics, DA-600). The analog-to-digital converter of the multichannel analyzer (MCA, Tracor Northern, NS-720A) converts the AMP/SCA signals to radiation "counts". At regular time intervals corresponding to different source velocities and radiation energies, the count data are stored in 1024 channels of the MCA.

The spectrometer (Ranger Electronics, MS-700MR) sets the velocity range of the velocity drive (Ranger Electronics, VT-700). Samples were typically analyzed using the -10 to +10 or -15 to +15 mm/sec range. The velocity drive oscillates the source along a rectilinear path. In Figure 7, the letters refer to source position relative to the absorber. The channel number containing transmission data (counts) corresponding to that source position is in parentheses. The arrows indicate the direction of motion of

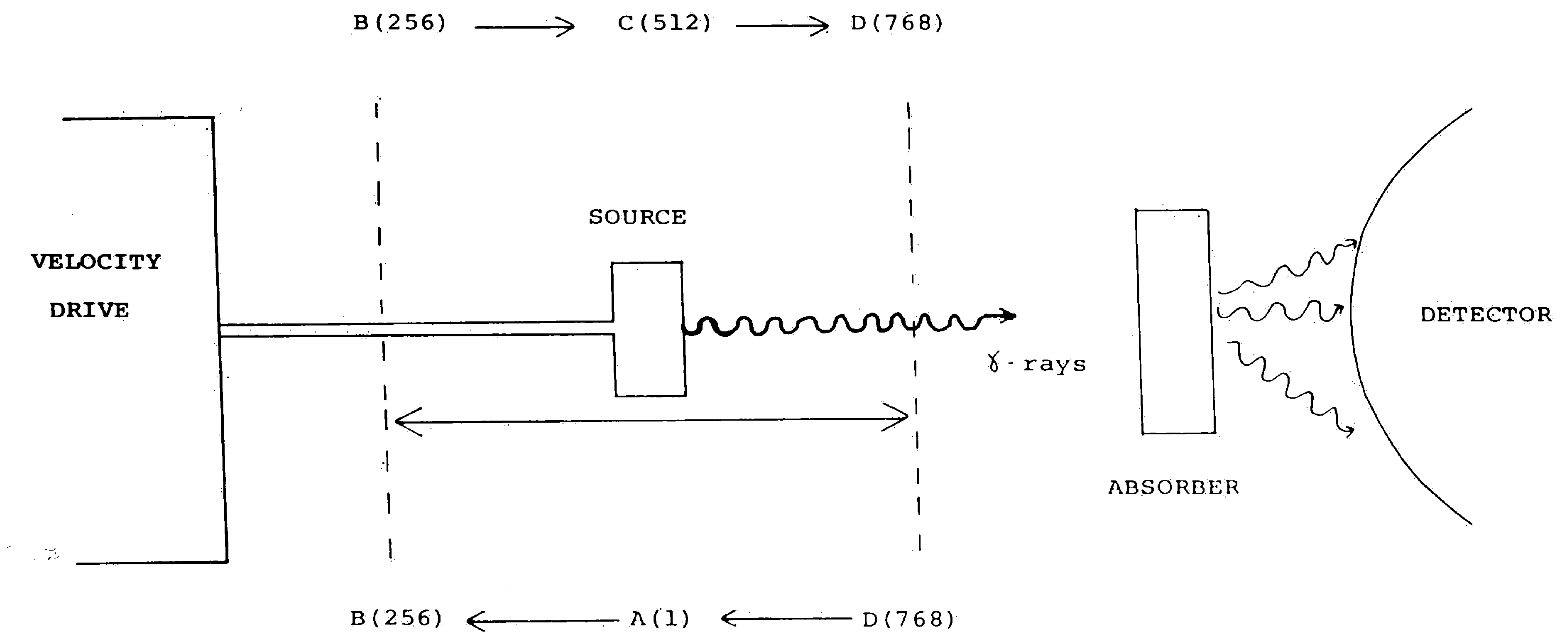


Figure 7: Channel Number and Velocity Correspondence

the source. Motion toward the absorber is the positive velocity direction (B -> C -> D). Gamma radiation emitted during this phase of motion are more energetic than those emitted while the source is at rest. Motion away from the absorber is the negative velocity direction (B <- A <- D). Radiation emitted during this phase is less energetic than that emitted at rest.

The source is accelerating from channel 1 to 512 and at rest at about channel 256. From channel 513 to 1024, the source is decelerating and at rest at about channel 769. Figure 8 is a plot of counts versus channel number. Since the same velocity range is covered twice across the 1024 channels, there are two sextets in the spectrum. Corresponding peaks are numbered accordingly. The peak positions are reversed since the velocity scale is reflection-symmetric about channel 512. Continuous change in the solid angle between the source and detector is responsible for the sinusoidal curve of the spectral baseline. This experimental artifact may distort the shape and line width of peaks. By "folding" the raw spectrum (see section II.D.6.d, JOBFOLD), these distortions are minimized. After the raw spectroscopic data is reduced, corrected, and folded as described below, the "true" Mossbauer spectrum appears as it does in Figure 9.

Once the correct correspondence between channel number and source velocity has been determined (see Section II.D.6, Velocity Calibration), the SIRIUS Spectrum

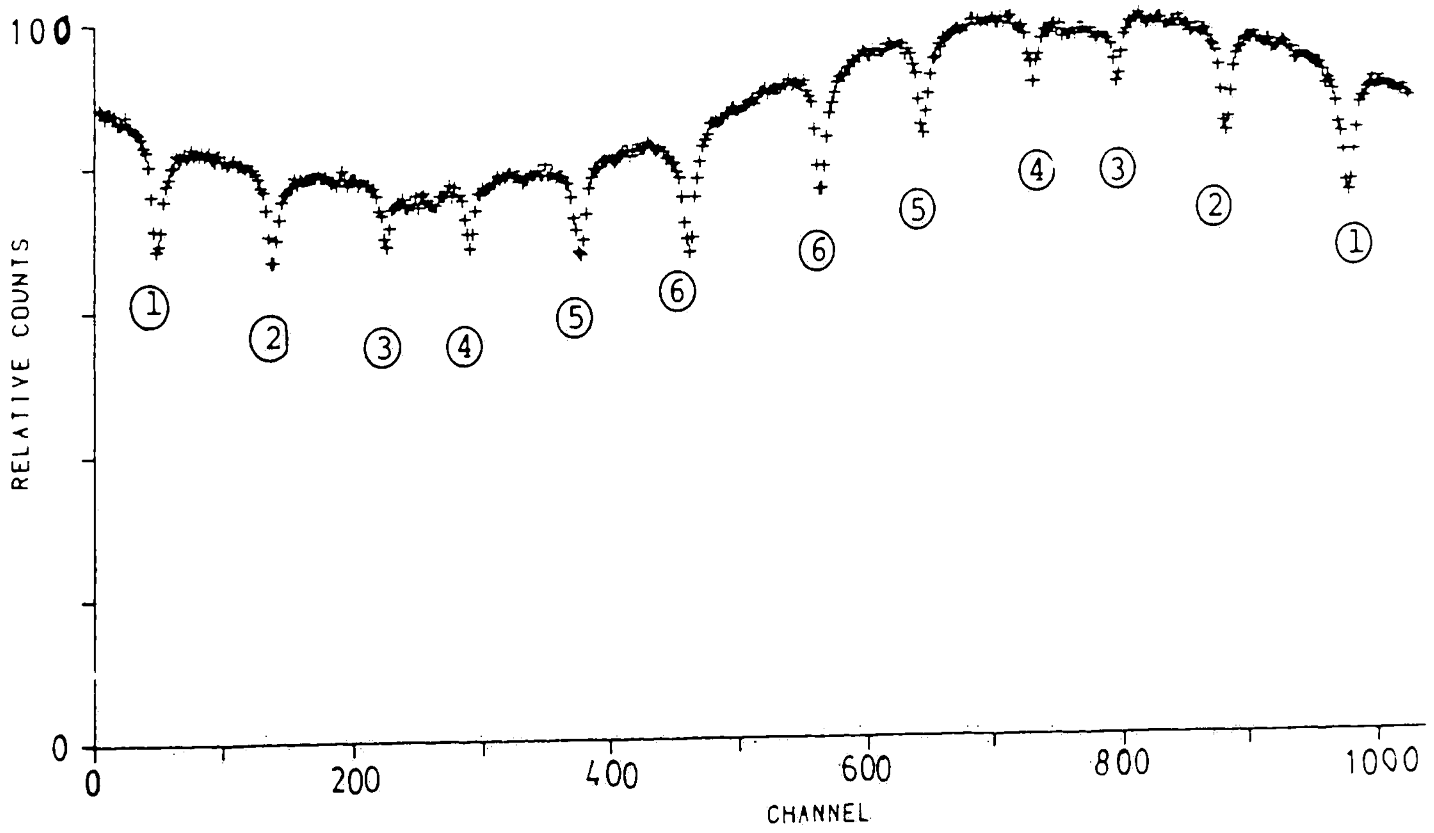


Figure 8: Raw, Unfolded Spectrum

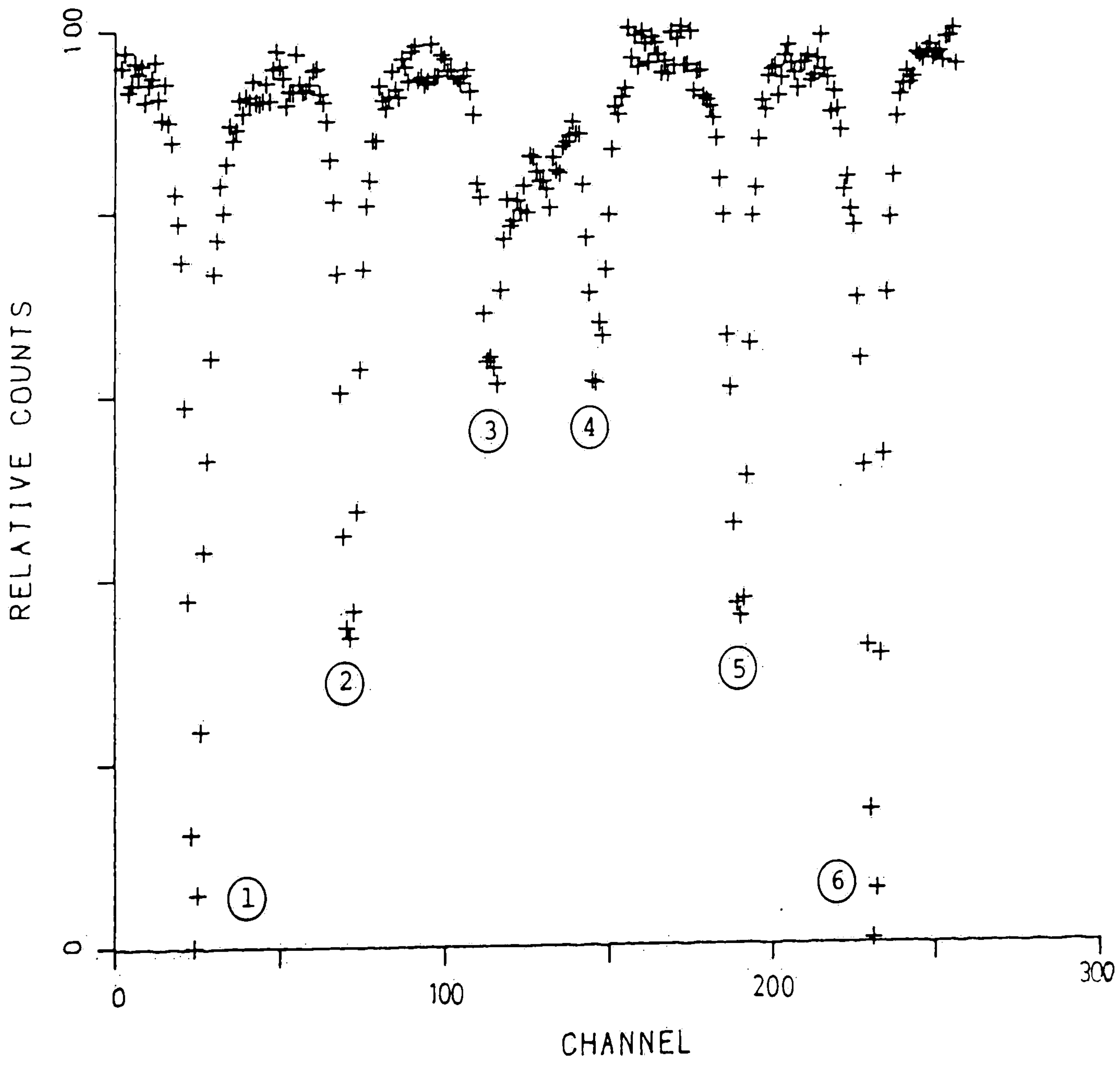


Figure 9: "True" Mossbauer Spectrum

Evaluating System is used to curve-fit the Mossbauer spectra. SIRIUS fits the spectra to a series of Lorentzian lines by varying five spectral parameters until a convergence criterion is satisfied. The parameters are the line amplitude, width at half-height, isomer shift (IS), quadrupole splitting (QS), and hyperfine field (HF). The last three parameters are the Mossbauer parameters used to identify the absorber. Accepted values for these parameters are available in the literature (Muir, Ando, and Coogan, 1966 and Le Caer, et al., 1982). These three parameters have units of velocity (mm/sec). The isomer shift is the displacement of the center of the spectrum from zero-velocity. The quadrupole splitting is a measure of the asymmetry of the positioning of peaks within a sextet. It is also the width of a doublet. The hyperfine field is the width of a sextet.

Iron metal was chosen as the arbitrary zero in defining the velocity scale. That is, the center of the iron metal spectrum locates the zero-velocity position of the velocity scale.

II.D.3. Operation of Spectrometer

The catalyst absorber contained within the air-tight Mossbauer sample holder was centered and secured in place over the proportional counter window. The source and velocity drive were positioned approximately 1.5 inch from the absorber along an adjustable length track. Lead sheets were positioned around the source and counter to shield researchers nearby from exposure to excessive radiation.

The desired memory group was selected by positioning the Memory Group dial of the multichannel analyzer (MCA) to either 1/4, 2/4, 3/4, or 4/4. Each memory group contains 1024 channels. The spectral data contained therein were erased by first setting the Read Mode to "CRTx4", depressing the Start Readout button, and then simultaneously depressing the two red Erase buttons.

The range of the velocity drive was set at 10 or 15 mm/sec by adjusting dials on the Ranger Electronics MS-700MR Mossbauer Spectrometer. All analyses employed the constant acceleration mode.

Mossbauer analysis began after simultaneously depressing the Mossbauer Spectrometer "Power" switch and the MCA "Start Analysis" switch. By adjusting the Intensity, Focus, Horizontal, Vertical, and Display Scale settings on the MCA, the spectrum of an absorber being analyzed could be observed while the spectrometer was operating. Samples wree on the spectrometer for a period from several hours to over two weeks until the spectral signal to noise ratio reached an acceptable level. Analysis was stopped by simultaneously depressing the Mossbauer Spectrometer "Power" and MCA "Stop" switches.

Data stored in the MCA was transfered to a computer data file. The procedure required two transfers, one from the MCA to a cassette tape and another from the tape to a data file. Details of this procedure are described in Appendix I.

II.D.4. Data Reduction

Copies of the files described below are listed in Appendix II. Each of the jobs is run using the GET and SUBMIT commands.

a. JOBRED

JOBRED is the job that runs the program REDUCE in batch mode. The purpose of REDUCE is to reduce the number of data from 1024 to 512. REDUCE does this by reading every other raw data point from the file RAWDAT and writing them into the file WDRIFT ("With DRIFT").

The raw data is reduced by issuing the following commands:

```
/GET,JOBRED
/SUBMIT,JOBRED,TO
```

If there are any unacceptable data in the file RAWDAT (e.g., letters instead of numbers), JOBRED automatically runs a post mortum dump to locate the error in the data field. If this occurs, the file RAWDAT must be edited. Once JOBRED runs successfully, the file WDRIFT will consist of 52 lines of data. It is helpful and necessary to add a label line at the beginning of the file in order to identify the sample to which the data belongs. This label line will later be used by the job JOBDRFT. At this point in the procedure, the file WDRIFT should appear as it does in Appendix II.

b. JOBDRFT

JOBDRFT (sic) is the job that runs the program DRIFT in batch mode. The purpose of the program DRIFT is to correct the data in the file WDRIFT for drift in the spectral baseline. The file NDRIFT ("No DRIFT") is created and contains the data corrected for baseline drift.

II.D.5. SIRIUS Spectrum Evaluating System

a. General

The SIRIUS Spectrum Evaluating System is designed for storing, handling, evaluating, and plotting Mossbauer spectra collected by multichannel analyzers. A complete explanation of the structure, use, and application of the system is available elsewhere (Nagy and Weir).

SIRIUS consists of three principle components: the program, spectrum library volume 1, and spectrum library volume 2. SIRIUS is stored on three magnetic tapes located in the Lehigh University Computing Center Tape Library. When SIRIUS is to be used, the program tape and the two spectrum library tapes are loaded off tape and onto disk. Any changes to the program or the spectrum library are done to the disk copy. The tapes are updated by writing the disk versions onto tape.

Volume 1 of the spectrum library contains the spectra that have been reduced from 1024 to 512 data points and corrected for baseline drift. Volume 2 spectra are volume 1 spectra that have been "folded". The SIRIUS curvefitting macro SEXT fits spectra from volume 2 since these are true Mossbauer spectra, not mirror-image spectra.

The files described below are created by the user and are not a part of SIRIUS, per se. They activate SIRIUS and instruct it to perform specified functions in a batch mode. Copies of these files appear in Appendix III.

b. MORN

MORN is the batch job that loads the program, volume 1, and volume 2 tapes onto disk. It creates the indirect access files PR, V1, V2, and ST (STorage file).

c. JOBTAPE

JOBTAPE is the batch job that activates SIRIUS and calls the file TAPLST. TAPLST prints a list of the spectrum numbers and labels from volumes 1 and 2 of the spectrum library. This information is necessary when telling SIRIUS which spectrum to fit and when new spectra are added to the library.

d. JOBFOLD

JOBFOLD is the batch job that activates SIRIUS and calls the file FOLD. FOLD reads the 512 data corrected for baseline drift into volume 1 of the spectrum library, "folds" this mirror-image spectrum, and reads the 256 folded data into volume 2 of the spectrum library. The spectra in volume 2 are true Mossbauer spectra, being the end result of all the data collection, reduction, correction, and folding.

e. JOBFIT

JOBFIT is the batch job that activates SIRIUS and calls one of several SEXTet files. The SEXTet file specifies the number of sextets and doublets (components) SIRIUS should use in fitting a particular spectrum in the library. It is possible to have SIRIUS fit a spectrum by varying the five spectral parameters of any number of components. The user may constrain any of the five parameters while SIRIUS varies the others.

Once the convergence criterion is met, SIRIUS lists the values and tolerances of the five spectral parameters for each component specified by the user. The "goodness of fit" can be determined from the calculated relative chi-square value. SIRIUS also calculates the area each component contributed to the total area. Assuming the same recoil-free fraction for each component percent composition and percent area are equivalent.

f. EVE

EVE is the batch job that writes the disk version of SIRIUS back onto tape.

II.D.6. Velocity Calibration

The SIRIUS curvefitting routine requires information concerning the correspondence between velocity and MCA channel numbers. The CALIbration command specifies the velocity calibration in units of mm/sec/channel and the channel number corresponding to zero velocity. This information must be determined iteratively by assuming calibration values, fitting the spectrum of a calibration standard, and comparing the "fitted" parameters with the accepted Mossbauer parameters of the standard material. The assumed calibration values are then adjusted to the correct value.

A National Bureau of Standards foil of reduced iron enriched in ^{57}Fe was analyzed using Mossbauer spectroscopy. The velocity drive was set to 15 mm/sec or 10 mm/sec to cover the velocity range -15 mm/sec to 15 mm/sec or -10 mm/sec to 10 mm/sec, respectively. The data was transferred from the MCA, reduced, corrected for drift, folded, and added to volume 2 of the spectrum library, as described above.

For purposes of illustration, the procedure used to calibrate the 15 mm/sec scale is outlined below. The spectrum was fit using the UNIVersal macro. The code of the fitting file SPEC62 is listed in Appendix IV. Table 1 lists the seed and intermediate values of the velocity calibration, zero-velocity channel, and the resulting fitted Mossbauer parameters.

Table 1: Calibration of 15 mm/sec Velocity Scale

		HF (mm/sec)	IS (mm/sec)
Run	Accepted Value:	10.657	0.00
1	CALI(0.08,125)	10.5436725	-0.0517380
2	CALI(0.08085987,124.3532750)	10.6569903	-0.0000007
3	CALI(0.08085994,124.3532749)	10.6569995	-0.0000007

The seed values for the CALI command in Run 1 were good guesses. However, the assumed value of 0.08 mm/sec/channel resulted in SIRIUS underestimating the hyperfine field (width) of the iron sextet. Therefore, the velocity calibration value was increased by a factor of 1.01074839 (10.657/10.5436725).

By setting the zero velocity position at channel 125, SIRIUS calculated a negative isomer shift value for reduced iron. Since reduced iron is the zero reference, its isomer shift is defined to be zero. Therefore, the zero-velocity channel was shifted to the left (in the negative energy direction) by 0.6467250 channels ((0.0517380 mm/sec)/(0.08 mm/sec/channel)) to 124.3532750.

The process was repeated to fine-tune the velocity calibration, although Run 3 was not absolutely necessary. Most Mossbauer parameters are accurate to only two significant figures. Figure 10 is a plot of the velocity-calibrated and fit spectrum.

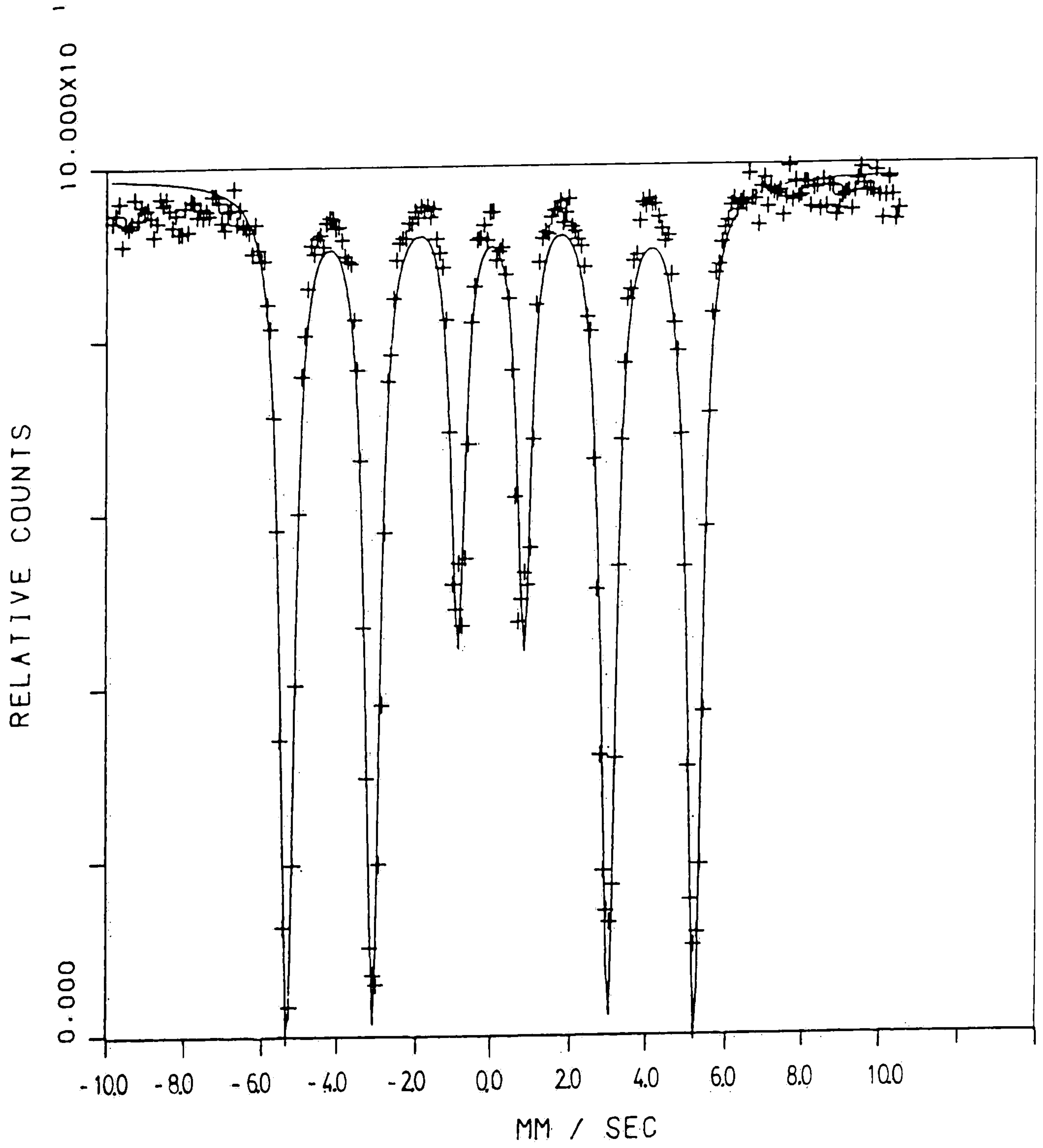


Figure 10: Fit spectrum of NBS calibation standard, ^{57}Fe-enriched alpha-iron.

III. Results

III.A. Extent of Reduction

The Mossbauer spectra of two catalyst samples appear in Figure 11. One sample (a) was not reduced, poisoned, or carbided. The other sample (b) was reduced for 10 hours. Three sextets were used to fit each spectrum. The fitted Mossbauer parameters appear in Table 2.

Table 2: Mossbauer Parameters of Untreated and Partially Reduced Catalyst

	This Study		Literature Data			
	IS (mm/sec) (0.01)	HF (kOe) (10)	IS (mm/sec) (0.01)	HF (kOe) (10)	Ref.	Area (%)
Untreated Catalyst (a):						
Fe304 I	0.30	491	0.36	500	1	91.8
II	0.63	455	0.61	450	1	
Fe	0.00	335	0.00	330	1	8.2
Reduced 10 hr (b):						
Fe304 I	0.30	488	0.36	500	1	51.6
II	0.64	453	0.61	450	1	
Fe	0.00	332	0.00	330	1	48.4

1 - (Muir, Ando, and Coogan, 1966)

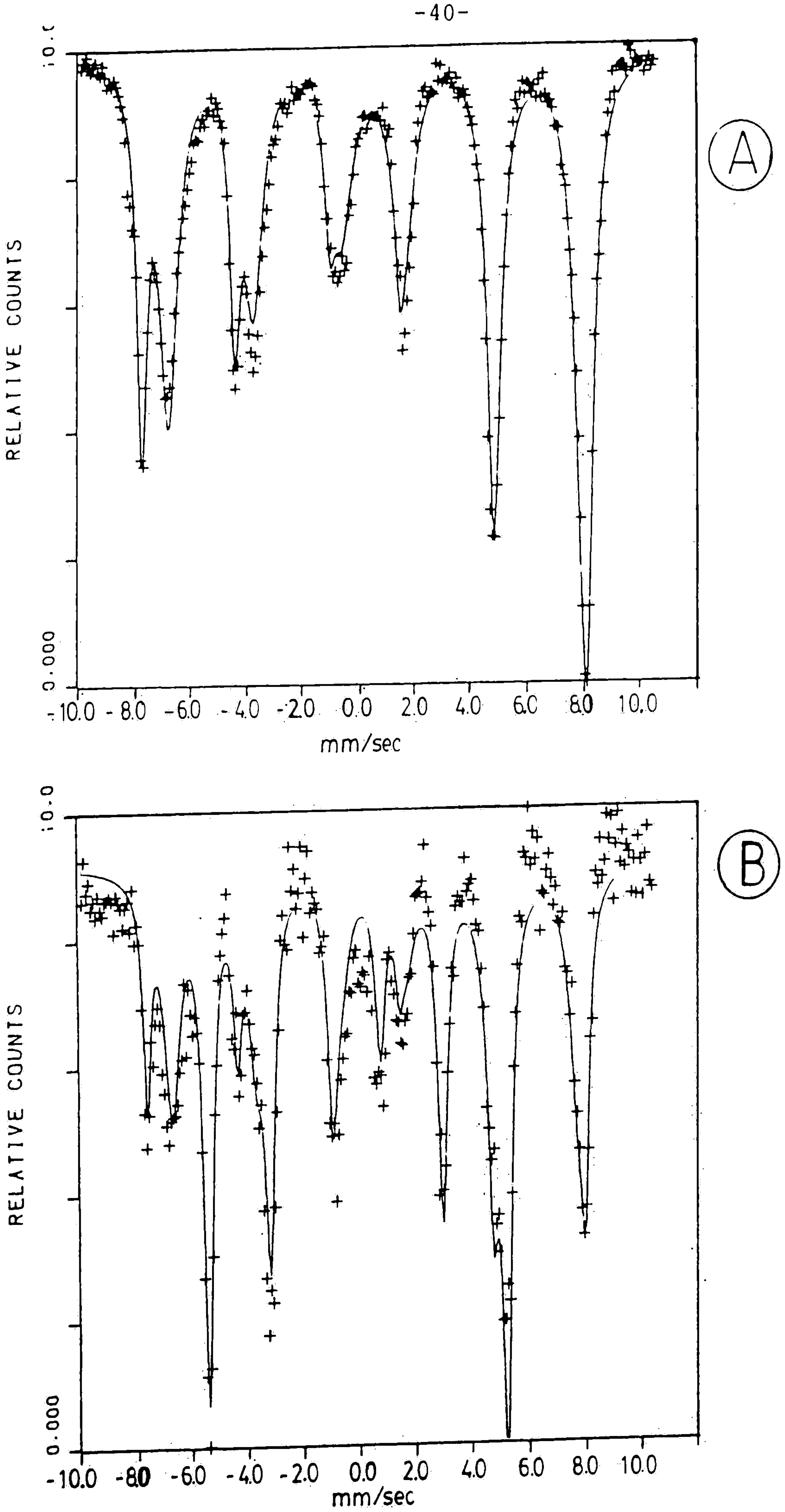


Figure 11: (a) Untreated catalyst
(b) Reduced for 10 hr

The Mossbauer parameters of these spectra agree well with those of magnetite, Fe_3O_4, and iron metal, Fe. Ten hours of reduction decreased the area of the iron oxide sextets from 91.8% to 51.6% of the total spectral area. That is, after ten hours, 48.4% of the iron was reduced.

III.B. Identification of GC Peaks

A mixture of light hydrocarbons prepared by Air Products and Chemicals, Inc. was analyzed on the packed column and gas chromatograph used throughout this study. The mixture contained CO, CO_2, methane, ethane, ethylene, propane, propylene, and n-butane. The chromatogram of the mixture appearing in Figure 12 has six numbered peaks. According to information supplied by the column manufacturer (see Section II.C.1.), light hydrocarbon components elute in order of increasing carbon number and degree of saturation. Therefore, the following assignments were made:

Component(s)	Peak
CO, CO_2, CH_4	1
ethane	2
ethylene	3
propane	4
propylene	5
n-butane	6

III.C. Relative Activity of Poisoned Catalyst

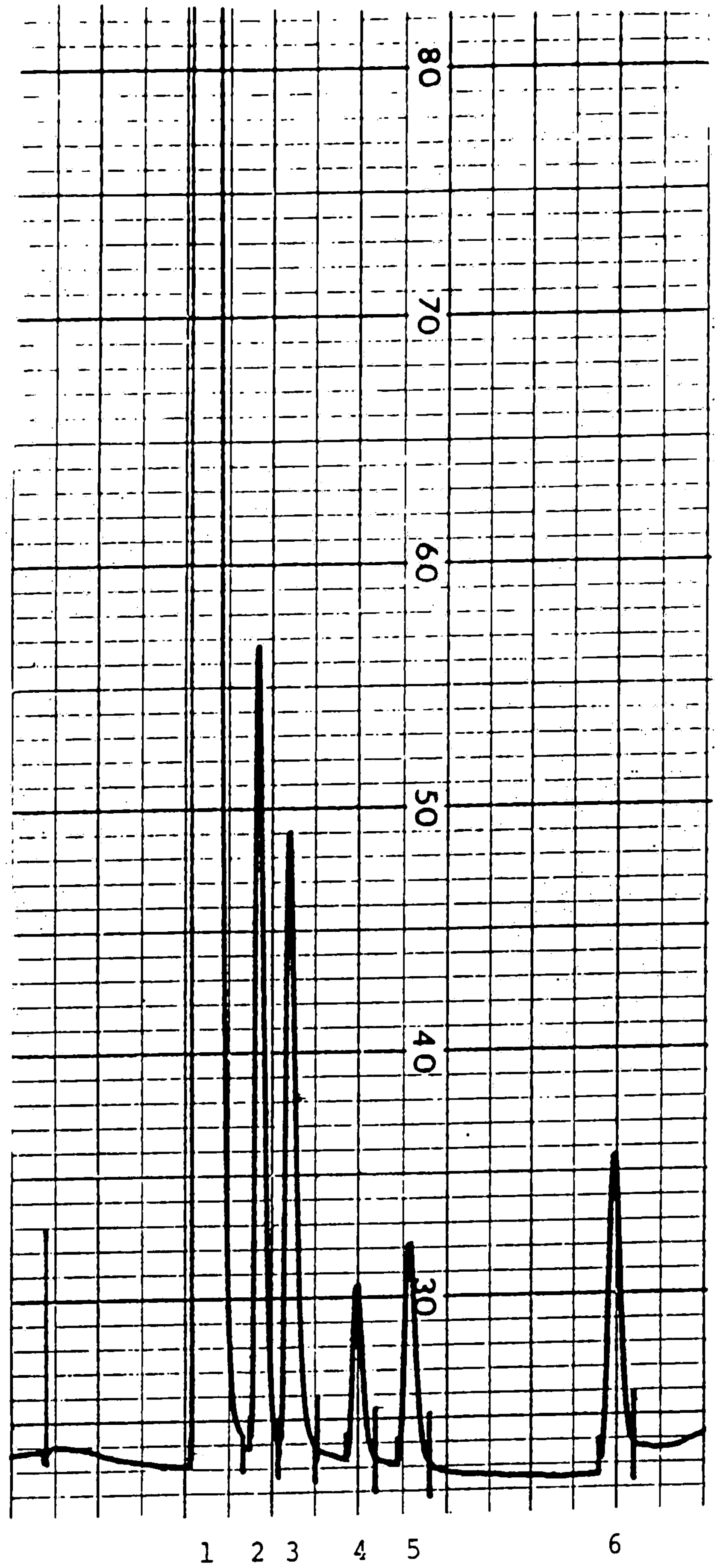


Figure 12: Chromatogram of a mixture of light hydrocarbons.

Column: SP-1700

The effect of preadsorbed sulfur on the activity of the catalyst for the Fischer-Tropsch reaction was investigated. Samples were poisoned for 5 minutes or 7 hours. The activity data are listed in Table 3 and plotted in Figure 13. The average activity of the catalyst sulfided for 5 minutes was 75.9% that of the unpoisoned catalyst. The average activity of the catalyst sulfided for 7 hours was 4.3% that of the unpoisoned catalyst.

Table 3: Effect of Sulfiding on Catalyst Activity

Sulfide time	Synthesis time (hr)	Total Molar Area: reduced catalyst	Total Molar Area: sulfided catalyst	Relative activity (%)	Average relative activity,%
5 min	2.7- 4.9	3477	2611	75.1	75.9
	4.9- 8.4	3103	2756	88.8	
	8.4-11.5	2685	1716	63.9	
7 hr	0.25	1388	55	4.0	4.3
	0.50	1764	82	4.6	

III.D. Unpoisoned 98 hour Synthesis Run

III.D.1 Selectivity

An unpoisoned catalyst sample was used to catalyze the synthesis reaction for 98 hours. The gas chromatography data of the C2 and C3 peaks are reported in Table 4. The selectivity of the catalyst to ethane, ethylene, propane, and propylene are reported in Table 5.

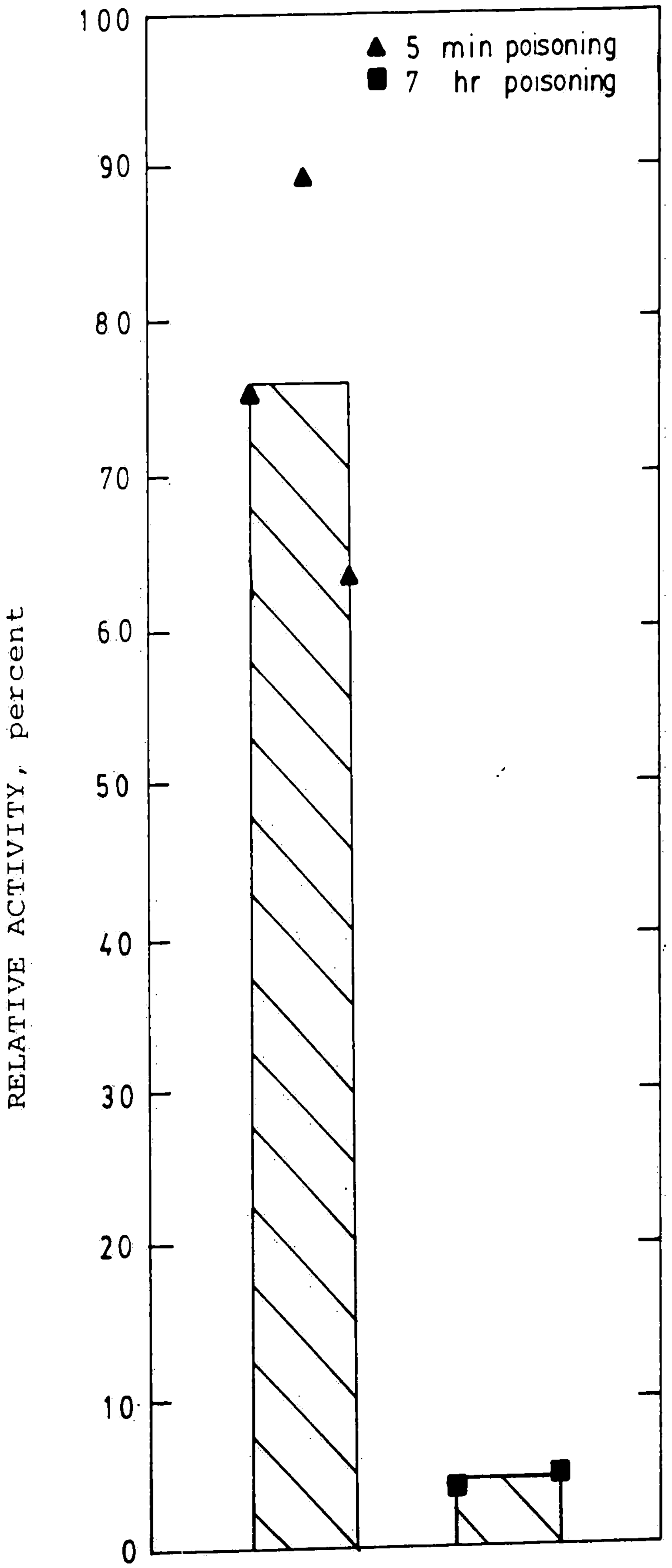


Figure 13: Relative Activity of Poisoned Catalysts

Table 4: Integrator Data for 98 hr Synthesis Run, Freshly Reduced Catalyst

Time	Peak Area (uV-sec) (*)				Molar Area (*)				Total Molar Area
(hr)	A1	A2	A3	A4	M1	M2	M3	M4	
1.50	1988	70510	475	1606	39	1473	7	25	1545
2.45	2378	80280	542	2106	47	1677	8	33	1765
4.70	5157	131400	1013	4557	101	2745	16	71	2933
6.27	5256	124500	861	4568	103	2601	13	71	2789
9.83	6237	129300	1033	5296	123	2701	16	82	2922
13.53	2423	49450	171	2202	48	1033	3	34	1118
24.87	3638	52590	113	2758	72	1099	2	43	1215
32.03	2547	33360	91	1856	50	697	1	29	777
33.50	3019	39030	200	2122	59	815	3	33	911
49.65	709	7710	10	373	14	161	<1	6	181
54.78	470	5360	1	251	9	112	<1	4	125
60.52	2376	24540	321	1296	47	513	5	20	585
81.20	1927	21420	36	1134	38	448	1	18	504
82.90	2322	20810	389	1590	46	435	6	25	511
97.52	1626	16980	37	905	32	355	1	14	401

(*) 1 [=] Ethane
2 [=] Ethylene
3 [=] Propane
4 [=] Propylene

Table 5: Selectivity of 98 hr Synthesis Run, Freshly Reduced Catalyst

Time	Selectivity (%)				Molar Ratios (*)		
(hr)	Ethane	Ethylene	Propane	Propylene	C2-O/P	C3-O/P	C2/C3
1.50	2.5	95.4	0.5	1.6	37.7	3.4	46.9
2.45	2.6	95.0	0.5	1.9	35.9	3.9	42.0
4.70	3.5	93.6	0.5	2.4	27.1	4.5	32.9
6.27	3.7	93.3	0.5	2.5	25.2	5.3	32.1
9.83	4.2	92.4	0.5	2.8	22.0	5.1	28.8
13.53	4.3	92.4	0.2	3.1	21.7	12.9	29.3
24.87	5.9	90.4	0.1	3.5	15.4	-	26.3
32.03	6.4	89.7	0.2	3.7	13.9	20.5	24.7
33.50	6.5	89.5	0.3	3.6	13.7	10.7	24.3
49.65	7.7	89.0	0.1	3.2	11.6	-	29.4
54.78	7.4	89.5	0.1	3.1	12.1	-	31.0
60.52	8.0	87.7	0.8	3.4	11.0	4.1	22.3
81.20	7.5	88.9	0.1	3.5	11.8	-	26.7
82.90	8.9	85.1	1.2	4.8	9.5	4.1	15.7
97.52	8.0	88.4	0.1	3.5	11.1	-	26.5

(*) C2-O/P [=] Ethylene/Ethane
C3-O/P [=] Propylene/Propane
C2/C3 [=] (Ethane+Ethylene)/(Propane+Propylene)

(-) These data are inaccurate since the propane concentration is 0.1 + 50%.

The molar ratios of ethylene to ethane, propylene to propane, and C2s to C3s are also reported.

Ethylene was the major product, accounting for over 88% of the products throughout the run. Ethane and propylene were the second and third most concentrated products, respectively. Propane was a minor product, seldom accounting for more than 1% of the product mix. After the first 10 hours, the concentration of propane was at or below the limits of detectability.

The ethylene to ethane mole ratio is plotted with respect to time on stream up to 98 hours in Figure 14. The ratio initially decreases rapidly then levels off after about 50 hours on stream. At steady state, about 11 moles of ethylene are synthesized for every mole of ethane.

The ethylene to ethane, propylene to propane, and C2s to C3s mole ratios of the first 12 hours of the 98 hours synthesis run are plotted in Figure 15. Far more moles of olefins are produced than moles of paraffins. During this period, however, there is a shift in selectivity toward the paraffins and the C2 species.

III.D.2. Chemical State of Catalyst

The Mossbauer spectrum of the unpoisoned catalyst from the 98 hour synthesis run appears in Figure 16. Six sextets and one doublet were used to fit the

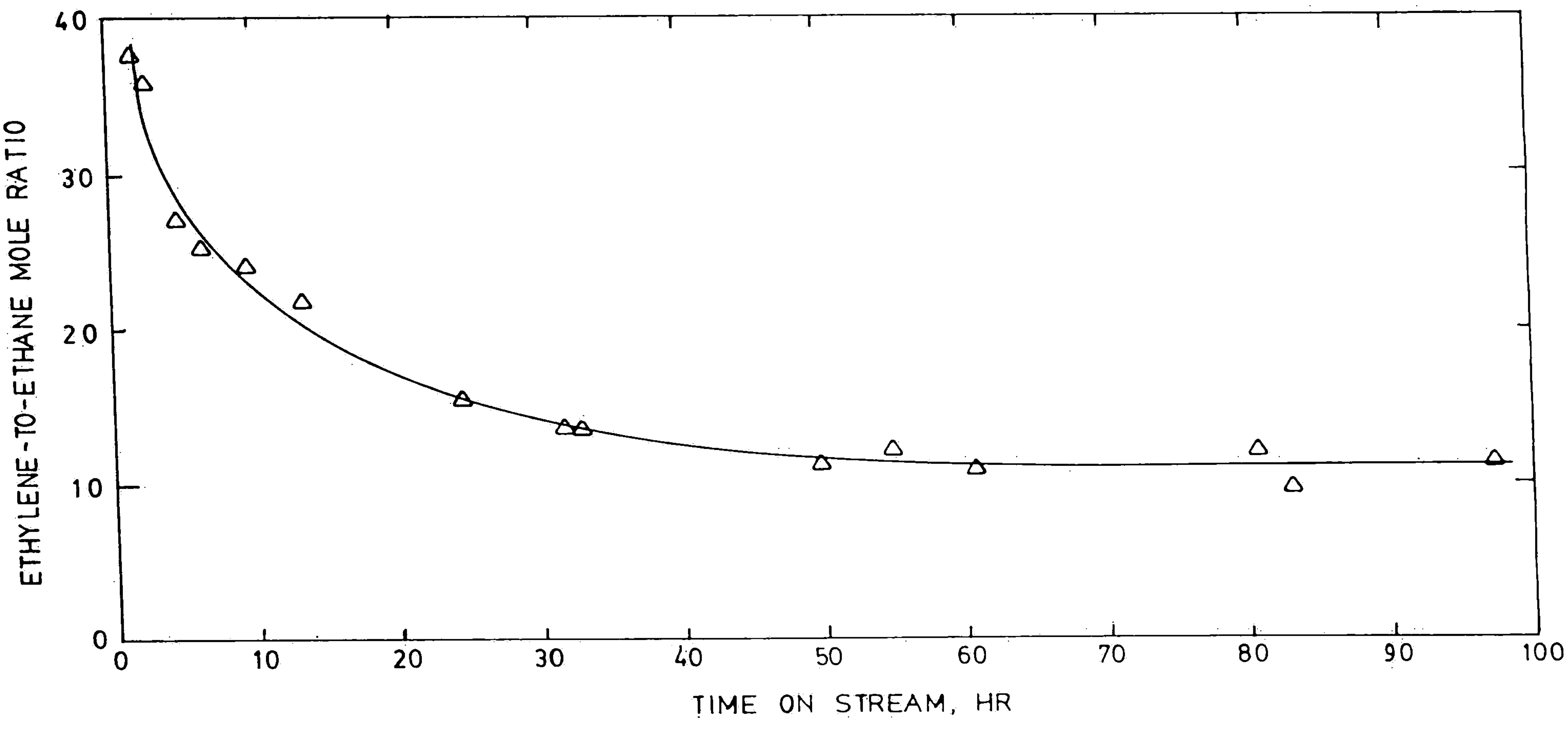


Figure 14: C2 olefin-to-paraffin ratio of unpoisoned catalyst, 98 hr run

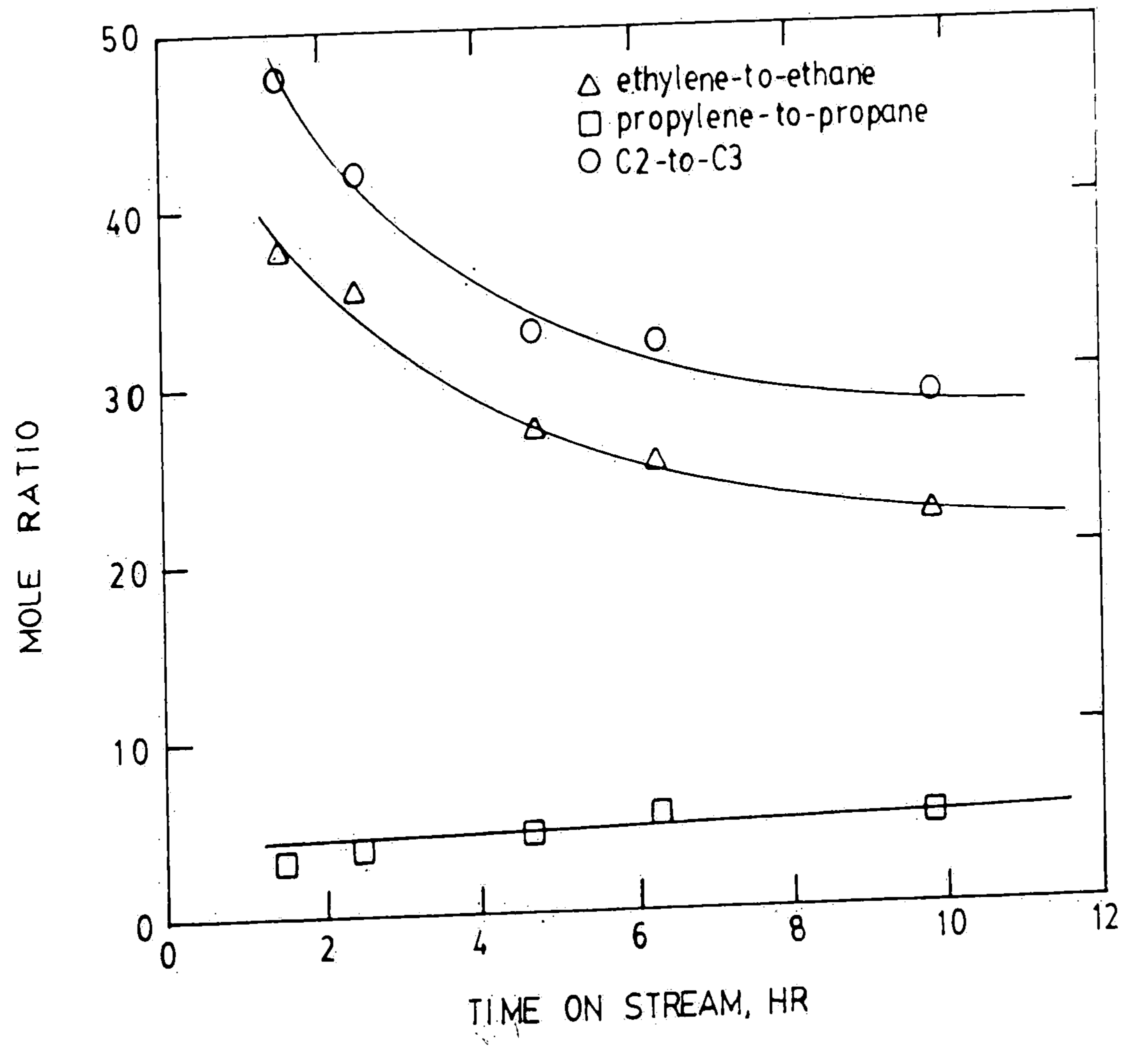


Figure 15: Selectivity of unpoisoned catalyst, 98 hr run

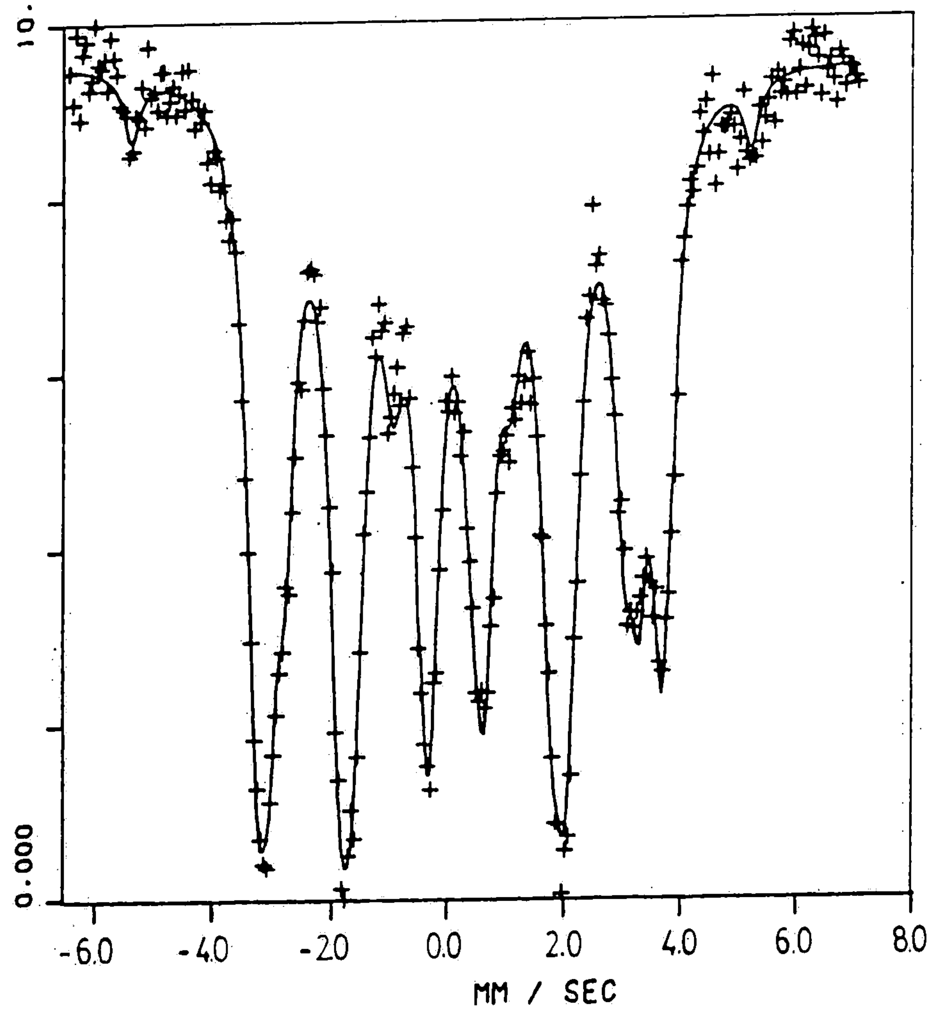


Figure 16: Mossbauer spectrum of unpoisoned, 98 hr run catalyst.

spectrum. The results of the curve-fitting procedure are reported in Table 6. The fitting parameters of the sextets

Table 6: Mossbauer Parameters of Unpoisoned 98 hr Fischer-Tropsch Catalyst

	This Study		Literature Data			Distribution, %	
	IS (mm/s)	HF (kOe)	IS (mm/s)	HF (kOe)	Ref.	Total Area	Carbide Area
FexC (*)	0.15	239	0.18	241	1	0.1	0.1
X-Fe5C2 I	0.23	198	0.22	183			
II	0.24	216	0.26	219	1	69.7	78.2
III	0.12	110	0.17	106			
e'-Fe2.2C	0.23	182	0.24	171	1	19.3	21.7
Total Carbide:						89.1	100.0
Fe	-0.06	330	0.00	330	1	3.4	
		QS (mm/s)		QS (mm/s)			
Doublet (*)	0.15	0.41	0.25	0.8	2	7.5	
Total Area:						100.0	

1 - (Tau, et al., 1984) * - See Discussion
2 - (Raupp and Delgass, 1979)

agree with those of iron metal and three iron carbides, Fe_xC, $X-Fe_5C_2$, and $e'-Fe_{2.2}C$. Fe_xC is an unknown carbide observed by Tau, et. al., (1984). Their nomenclature for this carbide has been used throughout this study. The doublet is thought to be that of superparamagnetic iron.

The area of the carbide sextets account for 89.1% of the total spectral area. $X-Fe_5C_2$ (78.2%) and e'-

$Fe_{2.2}C$ (21.7%) account for nearly all the carbide area. Fe_xC accounts for only 0.1% of the carbide.

Reduced iron accounts for 3.4% of the total spectral area. The doublet accounts for 7.5% of the total area.

III.E. Unpoisoned and poisoned 12 hour Synthesis Run

III.E.1. Selectivity

An unpoisoned catalyst and one poisoned for 5 minutes were used to catalyze the synthesis reaction for 12 hours. The gas chromatography data of the C2 and C3 peaks for both catalysts are reported in Table 7. The selectivity of each catalyst to ethane, ethylene, propane, and propylene is reported in Table 8. The molar ratios of ethylene to ethane, propylene to propane, and C2s to C3s are also reported.

The molar ratios of the unpoisoned and poisoned 12 hour synthesis samples are plotted versus time on stream in Figure 17. The poisoned catalyst data are not significantly different from the unpoisoned catalyst data. The 12 hour synthesis data are very similar to the data of the first 12 hours of the 98 hour synthesis run (Figure 15). That is, the ethylene to ethane and propylene to propane ratios decrease while the C2s to C3s ratio increases with time on stream.

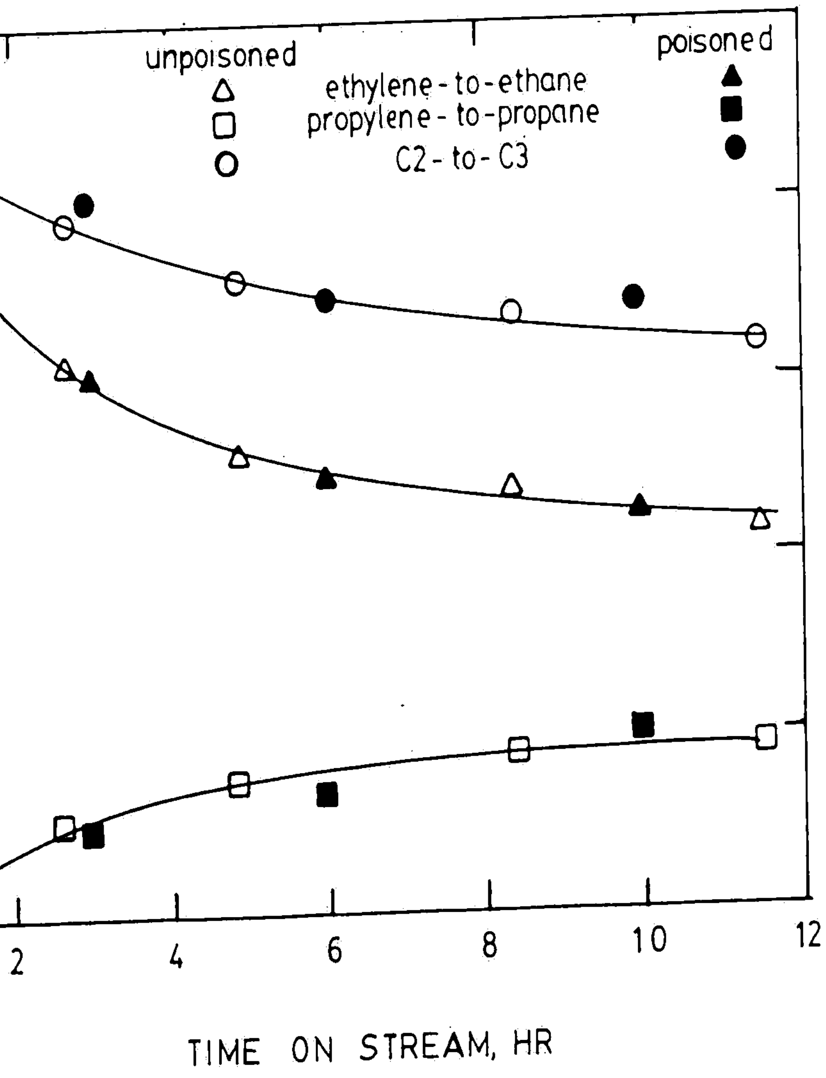


Figure 17: Selectivity of unpoisoned and 5 minute poisoned catalysts, 12 hr run

Table 7: Integrator Data for Unpoisoned and Poisoned 12 hr Synthesis Run

Time (hr)	Peak Area (uV-sec) (*) A1	A2	A3	A4	Molar Area (*) M1	M2	M3	M4	Total Molar Area
Unpoisoned:									
1.37	1401	52010	600	1108	28	1087	9	17	1141
2.67	5340	155500	950	4907	105	3249	15	76	3445
4.87	6380	157000	819	5871	125	3280	13	91	3509
8.40	5504	119800	567	4880	108	2503	9	76	2696
11.53	6035	118100	572	5083	119	2467	9	79	2674
Poisoned 5 min.:									
3.00	4108	38340	752	3549	81	2463	12	55	2611
6.00	5267	117900	723	4621	104	2570	11	72	2756
9.00	3578	123000	248	3100	70	1594	4	48	1716

(*) 1 [=] Ethane
2 [=] Ethylene
3 [=] Propane
4 [=] Propylene

Table 8: Selectivity of Unpoisoned and Poisoned 12 hr Synthesis Run

Time (hr)	Selectivity (%) Ethane	Ethylene	Propane	Propylene	Molar Ratios (*) C2-O/P	C3-O/P	C2/C3
Unpoisoned:							
1.37	2.4	95.3	0.8	1.5	39.4	1.9	42.1
2.67	3.0	94.3	0.4	2.2	30.9	5.2	36.9
4.87	3.6	93.5	0.4	2.6	26.1	7.2	32.8
8.40	4.0	92.8	0.3	2.8	23.1	8.6	30.9
11.53	4.4	92.3	0.3	3.0	20.8	8.9	29.5
Poisoned 5 min.:							
3.00	3.1	94.4	0.4	2.1	30.5	4.7	38.1
6.00	3.8	93.2	0.4	2.6	24.8	6.4	32.2
9.00	4.1	92.9	0.2	2.8	22.7	12.6	32.0

(*) C2-O/P [=] Ethylene/Ethane
C3-O/P [=] Propylene/Propane
C2/C3 [=] (Ethane+Ethylene)/(Propane+Propylene)

III.E.2 Chemical State of Catalyst

The Mossbauer spectra of the unpoisoned catalyst (a) and the catalyst poisoned for 5 minutes (b) from the 12 hour synthesis run appear in Figure 18. The two spectra were fit using six sextets and one doublet. The results of the curve-fitting procedure are reported in Table 9. The fitting parameters of the sextets agree with those of iron metal and three iron carbides, Fe_xC, X-Fe_5C_2, and e'-$Fe_{2.2}C$. The doublet is thought to be that of superparamagnetic iron.

Carbides accounted for a slightly smaller proportion of the total spectral area in the 5 minute poisoned catalyst (81.4%) than in the unpoisoned catalyst (85.6%). X-Fe_5C_2 accounted for a slightly larger proportion of the carbides in the poisoned catalyst (83.8%) than in the unpoisoned catalyst (82.5%). e'-$Fe_{2.2}C$ accounted for a slightly smaller proportion of the carbides in the poisoned catalyst (14.6%) than in the unpoisoned catalyst (15.5%). Fe_xC accounted for no more than 2% of the carbides in either the 5 minute poisoned or unpoisoned catalyst.

Reduced iron accounted for a slightly larger proportion of the total spectral area in the 5 minute poisoned catalyst (17.0%) than in the unpoisoned catalyst (11.4%). The doublet accounted for a slightly smaller proportion of the total area in the poisoned catalyst (1.6%) than in the unpoisoned catalyst (3.0%).

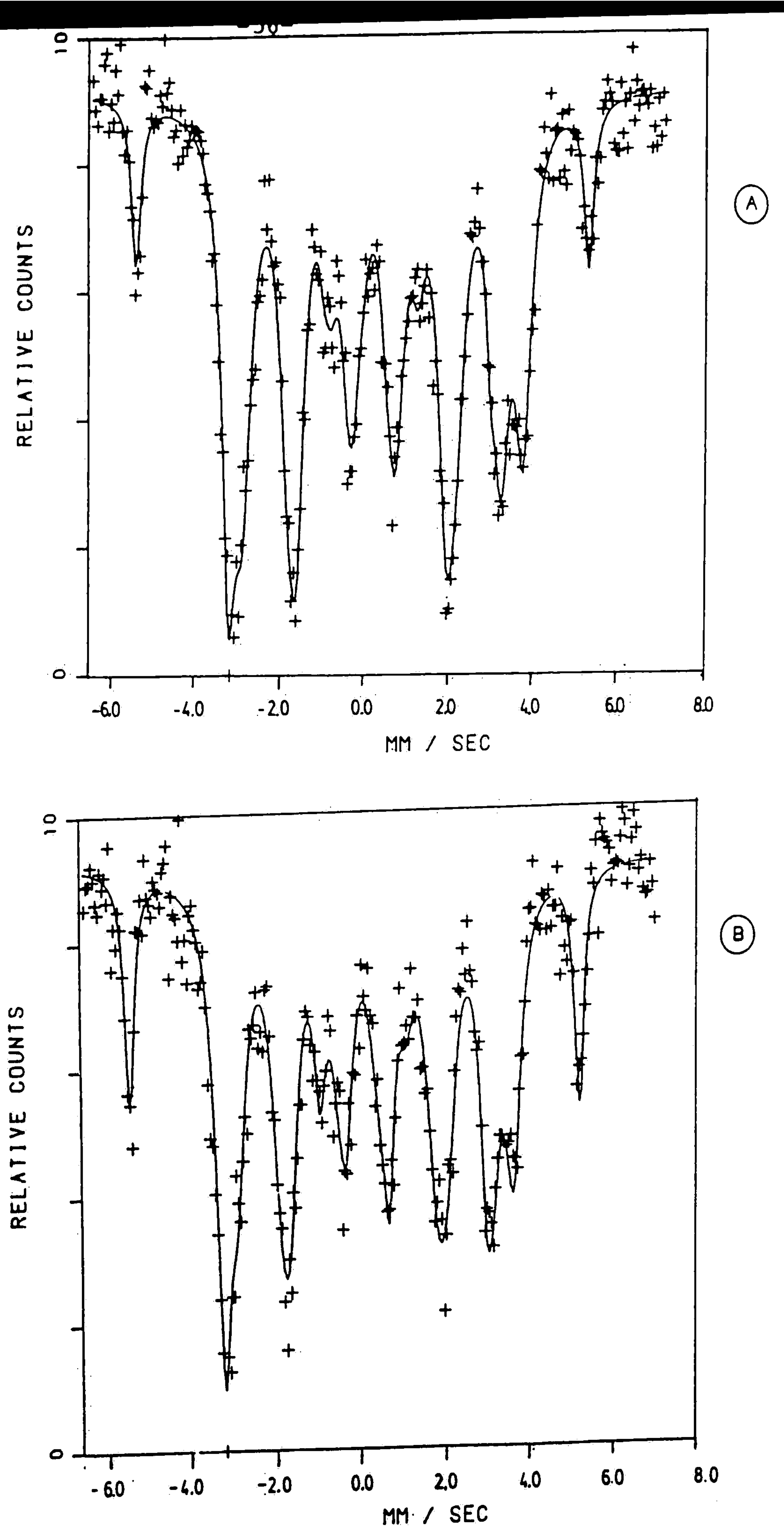


Figure 18: Mossbauer spectra of unpoisoned (a) and 5 min poisoned (b) 12 hour synthesis run catalysts.

Table 9: Mossbauer Parameters of Unpoisoned and Poisoned 12 hr Fischer-Tropsch Catalyst

	This Study		Literature Data			Distribution, %	
	IS (mm/s)	HF (kOe)	IS (mm/s)	HF (kOe)	Ref.	Total Area	Carbide Area
Unpoisoned (a):							
FexC (*)	0.18	252	0.18	241	1	1.7	2.0
X-Fe5C2 I	0.18	194	0.22	183	1	70.6	82.5
II	0.24	215	0.26	219			
III	0.15	106	0.17	106			
e'-Fe2.2C	0.24	182	0.24	171	1	13.3	15.5
Total Carbide:						85.6	100.0
Fe	-0.05	331	0.00	330	1	11.4	
		QS (mm/s)		QS (mm/s)			
Doublet (*)	0.14	0.40	0.25	0.8	2	3.0	
Total Area:						100.0	
Poisoned for 5 min (b):							
FexC (*)	0.10	239	0.18	241	1	1.3	1.6
X-Fe5C2 I	0.20	194	0.22	183	1	68.2	83.8
II	0.22	215	0.26	219			
III	0.02	102	0.17	106			
e'-Fe2.2C	0.19	177	0.24	171	1	11.9	14.6
Total Carbide:						81.4	100.0
Fe	0.00	331	0.00	330	1	17.0	
		QS (mm/s)		QS (mm/s)			
Doublet (*)	0.21	0.33	0.25	0.8	2	1.6	
Total Area:						100.0	

1 - (Tau, et al., 1984)
2 - (Raupp and Delgass, 1979)

* - See Discussion

III.F. Unpoisoned and poisoned 0.5 hr Synthesis Run

III.F.1. Selectivity

An unpoisoned catalyst and a catalyst poisoned for 7 hours were used to catalyze the synthesis reaction for 0.5 hours. The gas chromatography data of the C2 and C3 peaks for both catalysts are reported in Table 10. The selectivity of each catalyst to ethane, ethylene, propane, and propylene is reported in Table 11. The molar ratios of ethylene to ethane, propylene to propane, and C2s to C3s are also reported. The major product of the unpoisoned catalyst was ethylene. No other product accounted for more than 2% of the product mix. The major products of the poisoned catalyst were ethylene and propylene. No paraffins were detected by the gas chromatograph.

The molar ratios of the unpoisoned and poisoned 0.5 hour synthesis samples are plotted versus time on stream in Figure 19. The poisoned catalyst data are significantly different from the unpoisoned catalyst data. During the 0.5 hr period of synthesis, the ethylene to ethane ratio of the poisoned catalyst was one and one-half orders of magnitude higher than that of the unpoisoned catalyst. As the synthesis run proceeded, the poisoned catalyst shifted the selectivity toward propylene at the

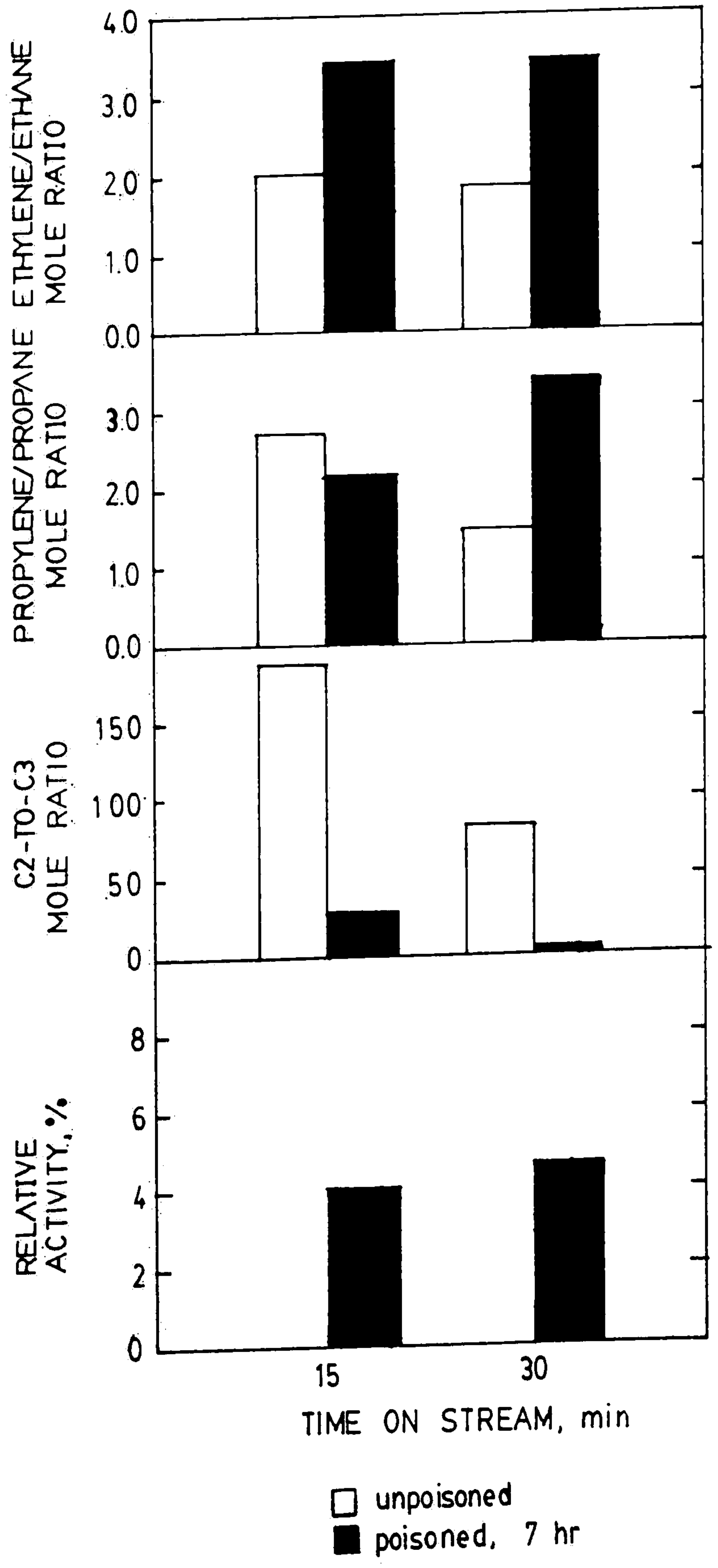


Figure 19: Selectivity of unpoisoned and 7 hour poisoned catalysts, 0.5 hr run

Table 10: Integrator Data of Unpoisoned and Poisoned 0.5 hr Synthesis Run

Time	Peak Area (uV-sec) (*)				Calculated Moles (*)				Total
(hr)	A1	A2	A3	A4	M1	M2	M3	M4	Moles
Unpoisoned:									
0.25	684	65430	<1	476	13	1367	<1	7	1388
0.50	1486	82010	47	1308	29	1713	1	20	1764
Poisoned for 7 hr:									
0.25	<1	2553	<1	121	<1	53	<1	2	55
0.50	<1	2528	<1	1901	<1	53	<1	30	82

(*) 1 [=] Ethane
2 [=] Ethylene
3 [=] Propane
4 [=] Propylene

Table 11: Selectivity of Unpoisoned and Poisoned 0.5 hr Synthesis Run

Time	Selectivity (%)				Molar Ratios (*)		
(hr)	Ethane	Ethylene	Propane	Propylene	C2-O/P	C3-O/P	C2/C3
Unpoisoned:							
0.25	1.0	98.5	<0.1	0.5	101.6	478.1	186.4
0.50	1.7	97.2	<0.1	1.2	58.6	28.0	82.9
Poisoned for 7 hr:							
0.25	<0.1	96.5	<0.1	3.4	2712.2	121.5	28.2
0.50	<0.1	64.1	<0.1	35.8	2685.6	1909.5	1.8

(*) C2-O/P [=] Ethylene/Ethane
C3-O/P [=] Propylene/Propane
C2/C3 [=] (Ethane+Ethylene)/(Propane+Propylene)

expense of propane. Poisoning reduced the selectivity to C2 products and enhanced C3 production.

Figure 19 also plots the relative activity of the poisoned catalyst as the run proceeded. The activity of the poisoned sample was less than 5% the activity of the unpoisoned catalyst.

III.F.2. Chemical State of Catalyst

Two sextets and one doublet were used to fit the Mossbauer spectrum of the unpoisoned catalyst from the 0.5 hour synthesis run. The results of the fitting procedure are reported in Table 12. In Figure 20, the doublet component of the spectrum appears as a broad singlet

Table 12: Mossbauer Parameters of Unpoisoned 0.5 hr Fischer-Tropsch Catalyst, Peak 2 Included

	This Study		Literature Data			Area (%)
	IS (mm/sec)	HF (kOe)	IS (mm/sec)	HF (kOe)	Ref.	
Fe	0.05	335	0.00	330	1	60.0
Sextet	0.64	297	-	-		31.4
		QS (mm/s)				
Doublet	0.36	0.10	-	-		8.6
Total Area:						100.0

1 - (Muir, Ando, and Coogan, 1966)

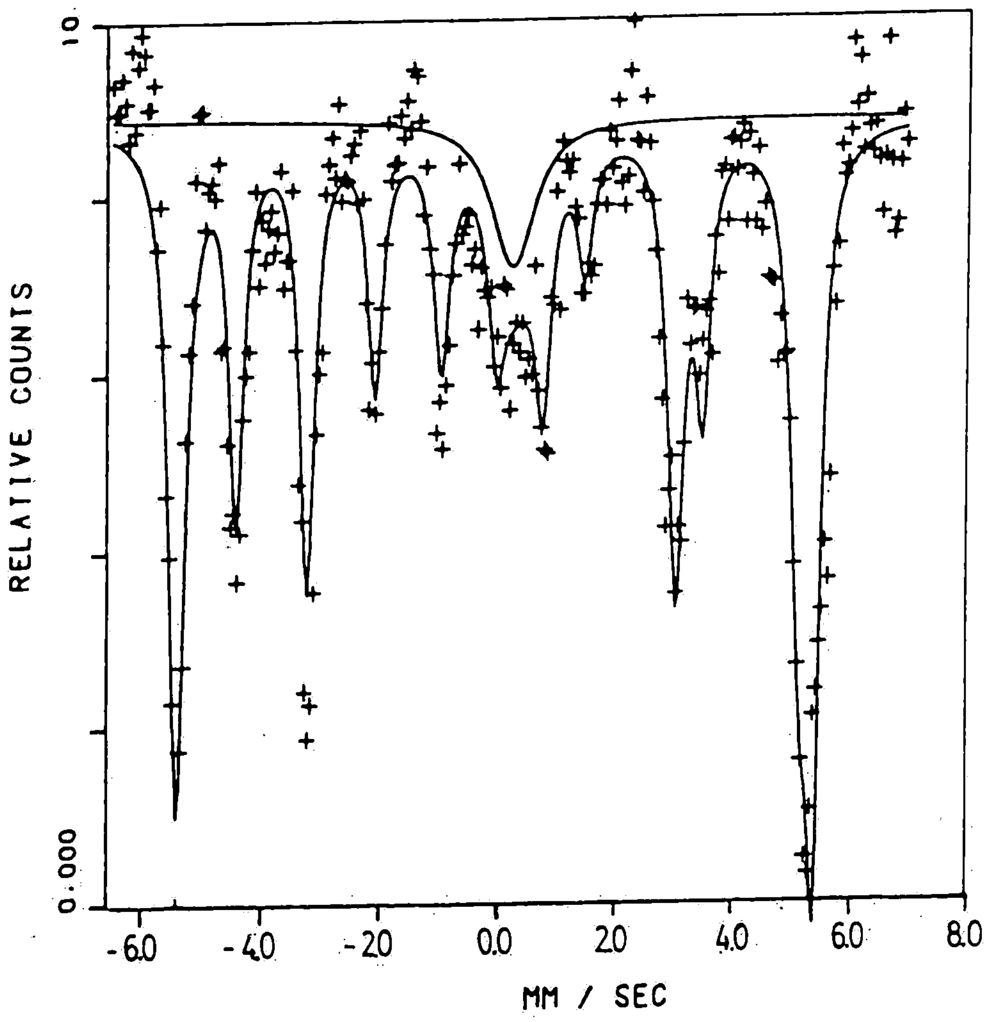


Figure 20: Mossbauer spectrum of 7 hour poisoned, 0.5 hour synthesis run catalyst. Fit with two sextets and one doublet.

since the value of the quadrupole interaction (0.10 mm/s) was small. The Mossbauer parameters of one sextet agree within experimental error with those of iron metal, Fe. The other sextet has not been identified. The doublet is thought to be that of superparamagnetic iron.

The area of the unknown sextet accounts for 31.4% of the total spectral area. Reduced iron accounts for 60.0% of the total area. The doublet accounts for 8.6% of the area.

Another attempt was made to fit the spectrum of the unpoisoned catalyst from the 0.5 hour synthesis run. Peak number 2 of the unpoisoned catalyst spectrum (Figure 20) was ignored in the fitting procedure. The results of this fit are reported below.

The Mossbauer spectra of the unpoisoned catalyst (a) and the catalyst poisoned for 7 hours (b) from the 0.5 hour synthesis run appear in Figure 21. The two spectra were fit using six sextets and one doublet. The results of the curve-fitting procedure are reported in Table 13. The fitting parameters of the sextets agree with those of iron metal and three iron carbides, Fe_xC, X-Fe_5C_2, and e'-$Fe_{2.2}C$. The doublet is thought to be that of superparamagnetic iron.

Carbides accounted for a smaller proportion of the total spectral area in the 7 hour poisoned catalyst (7.0%) than in the unpoisoned catalyst (29.2%). X-Fe_5C_2 accounted for a larger proportion of the carbides in the

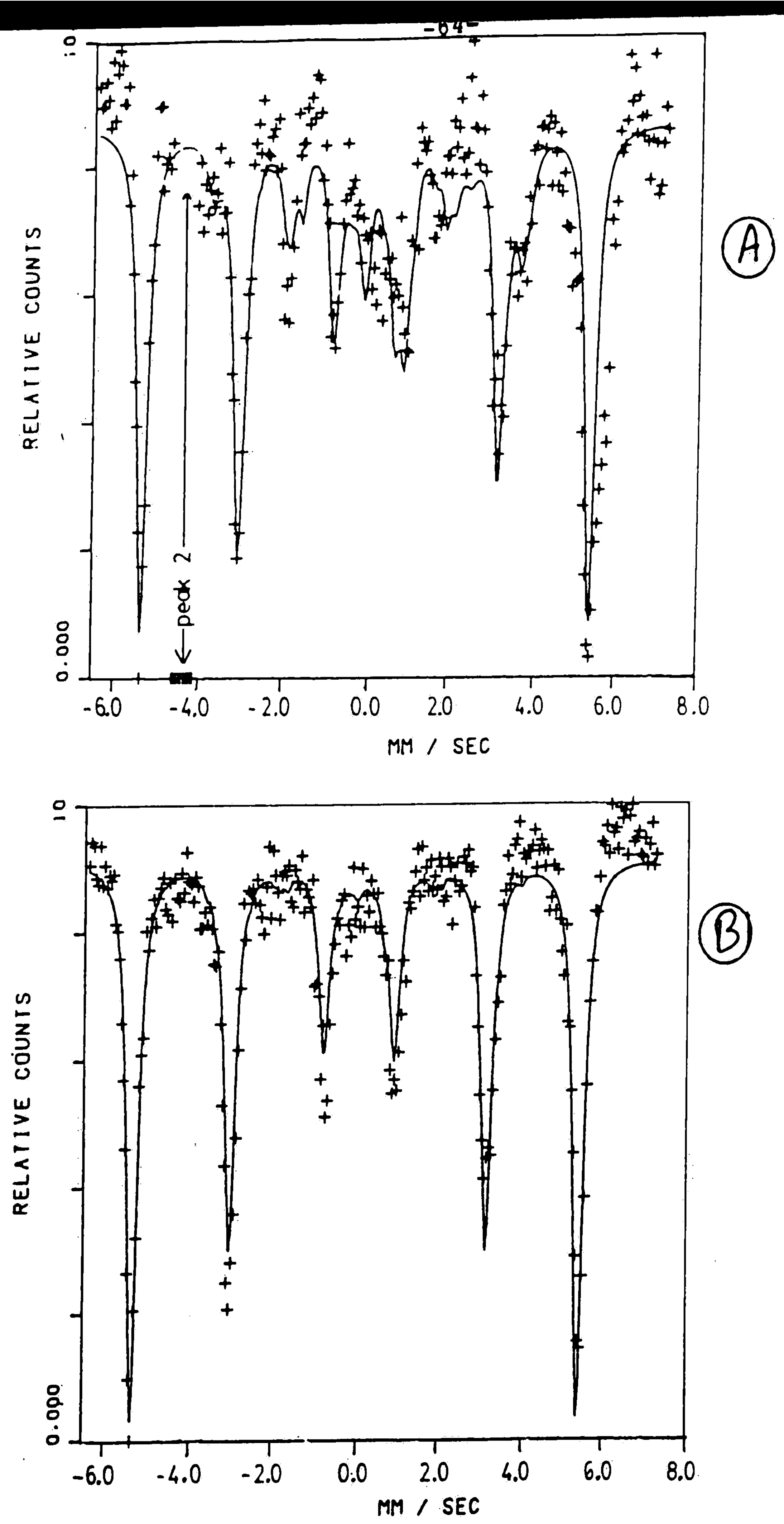


Figure 21: Mossbauer spectra of unpoisoned (a) and 7 hour poisoned (b) 0.5 hour synthesis run catalysts (peak 2 ignored).

Table 13: Mossbauer Parameters of Unpoisoned and Poisoned 0.5 hr Fischer-Tropsch Catalyst

	This Study		Literature Data			Distribution, %	
	IS (mm/s)	HF (kOe)	IS (mm/s)	HF (kOe)	Ref.	Total Area	Carbide Area
Unpoisoned (a):							
FexC (*)	0.13	233	0.18	241	1	7.4	25.3
X-Fe5C2 I	-0.01	194	0.22	183	1	20.7	70.9
II	0.16	211	0.26	219			
III	0.10	107	0.17	106			
e'-Fe2.2C	0.15	173	0.24	171	1	1.1	3.8
Total Carbide:						29.2	100.0
Fe	-0.01	331	0.00	330	1	62.6	
		QS (mm/s)		QS (mm/s)			
Doublet (*)	0.25	0.35	0.25	0.8	2	8.1	
Total Area:						99.9 (#)	
Poisoned for 7 hr (b):							
FexC (*)	0.13	234	0.18	241	1	0.4	5.7
X-Fe5C2 I	-0.03	195	0.22	183	1	6.3	90.0
II	0.00	211	0.26	219			
III	0.01	110	0.17	106			
e'-Fe2.2C	0.19	177	0.24	171	1	0.3	4.3
Total Carbide:						7.0	100.0
Fe	0.00	330	0.00	330	1	91.0	
		QS (mm/s)		QS (mm/s)			
Doublet (*)	0.26	0.33	0.25	0.8	2	2.0	
Total Area:						100.0	

1 - (Tau, et al., 1984)
2 - (Raupp and Delgass, 1979)

* - See Discussion
\# - Round-off error

poisoned catalyst (90.0%) than in the unpoisoned catalyst (70.9%). Fe_xC accounted for a smaller proportion of the carbides in the poisoned catalyst (5.7%) than in the unpoisoned catalyst (25.3%). e'-$Fe_{2.2}C$ accounted for a slightly larger proportion of the carbides in the poisoned catalyst (4.3%) than in the unpoisoned catalyst (3.8%).

Reduced iron accounted for a larger proportion of the total spectral area in the 7 hour poisoned catalyst (91.0%) than in the unpoisoned catalyst (62.6%). The doublet accounted for a smaller proportion of the total area in the poisoned catalyst (2.0%) than in the unpoisoned catalyst (8.0%).

IV. Discussion

IV.A. Extent of Reduction

The porosity and surface area of fused magnetite catalysts are improved by reducing the magnetite, Fe_3O_4, to iron metal, Fe, prior to synthesis reaction (Anderson, 1956). The extent of reduction after the full 60 hour period was estimated using the data from the 10 hour reduction reported in section III.A.

The reduction rate was assumed to be first-order in the iron oxide concentration. Calculations indicate that after 60 hours, the catalyst was 98.4% iron metal (see calculation in Appendix V). It was sufficiently reduced to actively catalyze the synthesis reaction.

IV.B. Activity of the Unpoisoned Catalyst

The gas chromatograph and packed column did not resolve the CO, CO_2, H_2, and CH_4 peaks. Therefore the conversion of $CO+H_2$ could not be measured experimentally. The activity of the unpoisoned catalyst for the synthesis reaction was estimated using the steady state Langmuir-Hinshelwood rate model derived by Huff (1982). In his Fischer-Tropsch studies, Huff (1982) used the same catalyst reduced at the same conditions that was used in this work. The rate expression he obtained was:

$$-R_{H2+CO} = \frac{k\ K\ P_{CO}\ (P_{H2})^2}{P_{H2O} + K\ P_{CO}\ P_{H2}}\ .$$

Where:

$-R_{H2+CO}$ = reaction rate, (umoles of H_2+CO converted per gram unreduced catalyst-min)

k = kinetic constant, (umoles H_2+CO converted per gram unreduced catalyst-min-atm)

K = adsorption equilibrium constant, (atm^{-1})

P_X = partial pressure of component X, (atm).

According to Huff, at conversion less than about 70%, the formation of water is low, so the rate expression reduces to:

$$-R_{H2+CO} = k\ P_{H2}.$$

In order to apply Huff's model, it was necessary to determine the period of time required for this system to reach steady state. Huff (1982) observed that the ethylene-to-ethane ratio stabilized shortly after activity had reached its steady value. The ethylene-to-ethane molar ratio of the 98 hour synthesis run shown in Figure 14. Steady state was reached after about 50 hours on stream.

Steady state conversion was estimated using a plug flow reactor model and Huff's kinetic constant data. At the reaction conditions used in this work, the conversion of hydrogen and carbon monoxide to Fischer-Tropsch products was calculated to be 33% (see calculation in Appendix V). The average activity of the unpoisoned catalyst on a reactor basis was 53.4 umole H_2+CO converted per gram unreduced catalyst-min.

IV.C. Selectivity of Unpoisoned Catalyst

The total molar area of the C2 and C3 GC peaks is plotted versus time on stream in Figure 22. The data are from the 0.5, 12 and 98 hour unpoisoned synthesis runs reported in Tables 4,7, and 10, respectively. The syringe sampling technique was probably a source of experimental error and may explain the scatter in the data. In general, only one syringe sample was taken for each datum. The percent iron as iron carbide of the catalysts from the 0.5, 12, and 98 hour synthesis runs is also plotted in Figure 22.

During the first 12 hours, the amount of C2 and C3 products increased, reached a maximum, and decreased as the catalyst carbided. By the end of the 98 hour run, the steady state amount of C2 and C3 products had decreased to about 16% its level at 12 hours. During this period, the iron carbide concentration in the catalyst increased slightly.

Raupp and Delgass (1979) showed that the extent of iron carbide formation tracts the increase in activity of a supported iron Fischer-Tropsch catalyst. Furthermore, the catalyst becomes more selective to higher hydrocarbons as

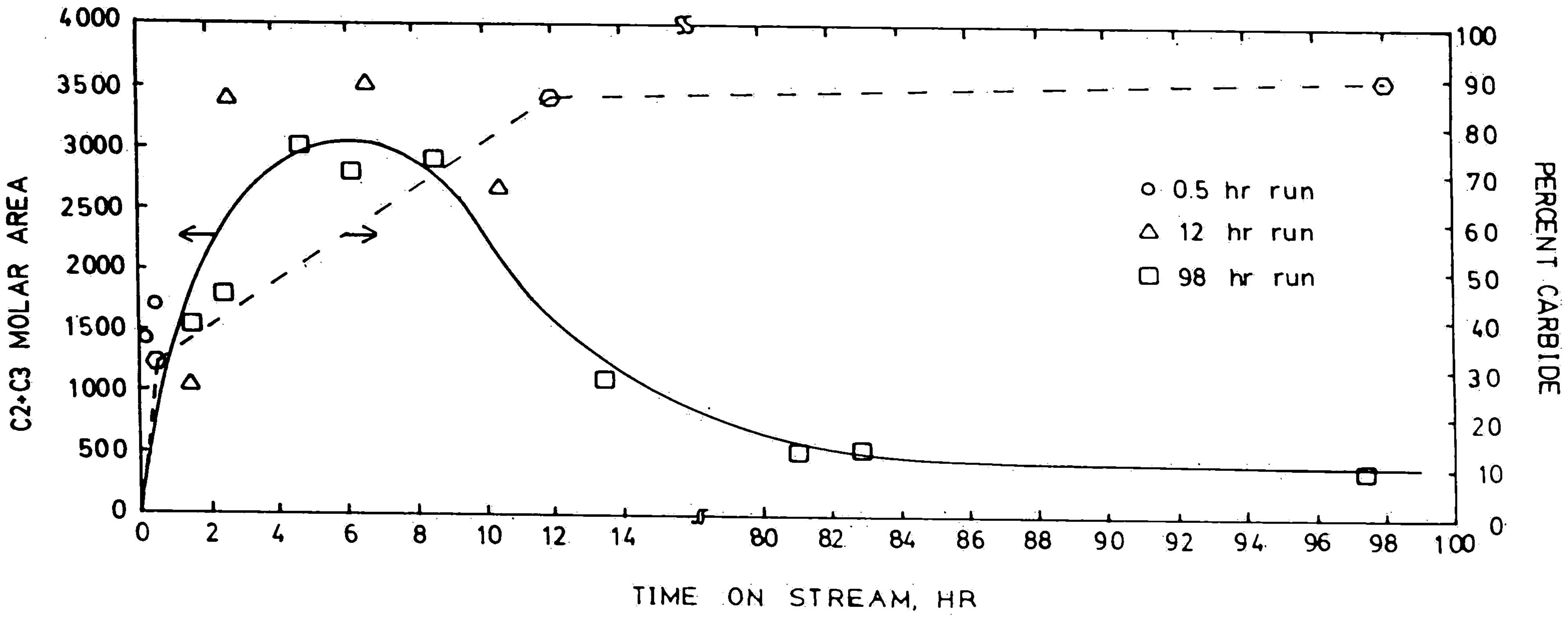


Figure 22: C2+C3 production and percent carbide of unpoisoned catalysts.

the iron carbides. Assuming that methane formation did not increase, the decrease in C2 and C3 production during the 98 hour synthesis run is consistent with the selectivity findings of Raupp and Delgass (1979). Since production of C2 and C3 products is not a measure of activity, these data cannot support or challenge the activity and carbide formation finding.

IV.D. Relative Activity of Poisoned Catalysts

As described in section II.C.3.a., relative activity of the poisoned catalyst was determined by comparing the GC molar area data of the poisoned catalyst with that of the unpoisoned catalyst. This method of calculating relative activities assumes that there is a linear relationship between unsteady-state conversion and the total molar area of C2 and C3 products. Steady-state data from Huff (1982) plotted in Figure 23 show a non-linear relationship between conversion and total molar area of C2 and C3 products. The problem can best be described by example. Suppose sulfur had no effect on the activity of the catalyst, but shifted the selectivity toward higher molecular weight hydrocarbons. The molar area of the C2 and C3 peaks would decrease in proportion to the reduction in their respective products' concentration. A calculation of relative activity would suggest that the catalyst had been poisoned. In fact, the C2 and C3 concentration had simply

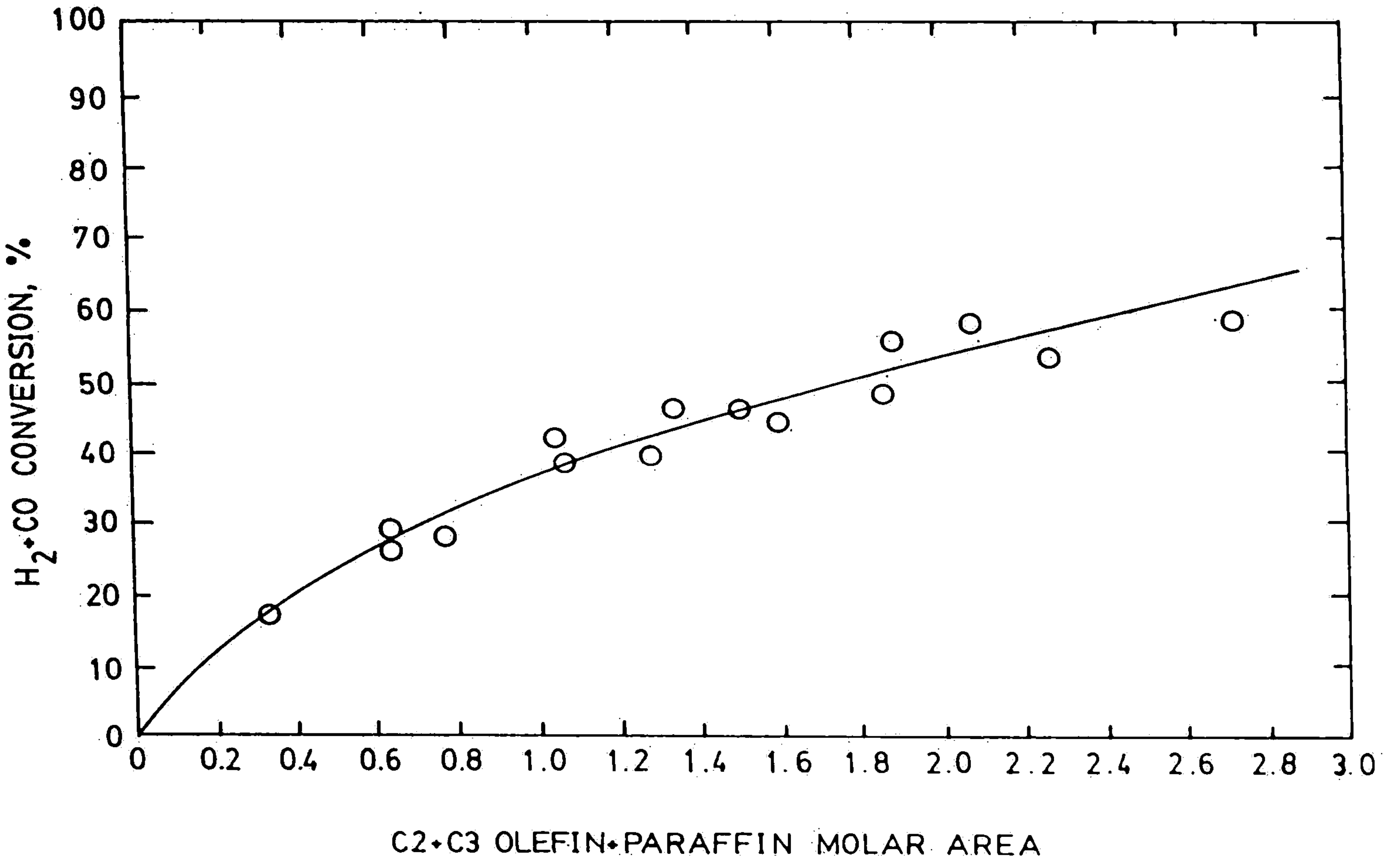


Figure 23: Conversion as a function of C2+C3 olefins and paraffins molar area (Data from Huff, 1982)

decreased and not the overall conversion. On the basis of these arguments, the relative activity as defined above reflects changes in both the activity and selectivity to C2 and C3 products.

In section III.C., the effect of poisoning on the relative activity of the catalyst was discussed. Calculations were made to determine the amount of sulfur fed to the catalyst in both poisoning experiments (see calculation in Appendix V).

Poisoning for 5 minutes introduced 1.6 mg S/g Fe to the catalyst. The relative activity decreased 24.1%. This result is consistent with other findings. Shultz et al. (1962) observed a 25% loss of activity after poisoning a reduced catalyst with 1.2 mg S/g Fe as H_2S dissolved in heptane. The work of Karn et al. (1963) and Shultz et al. (1962) showed that the activity loss of a reduced catalyst and a used (i.e., carbided) catalyst are similar. Stenger (1984) poisoned a used catalyst with 3.8 mg S/g Fe as H_2S and observed a 50% loss of activity.

Poisoning for 7 hours introduced 134 mg S/g Fe to the catalyst. The relative activity decreased 95.7% to 0.043. This result is consistant with other findings. Anderson Karn, and Shultz (1965) observed that the activity of reduced iron oxide and reduced steel turnings decreased linearly to 0.60 after 0.2-0.3 mg S/g Fe had been introduced in situ. The activity of the turnings decreased steadily to zero after 1-2 mg S/g Fe was introduced. However, the activity of the fused iron oxide catalyst approached a constant value of 0.05-0.10 after 2-4 mg S/g Fe had been introduced. Despite prolonged exposure to sulfur, the catalyst in this study maintained a low but detectable activity.

IV.E. Selectivity of Poisoned Catalyst

In section III.E., the effect of prepoisoning for 5 minutes on the unsteady-state selectivity of the catalyst was discussed. Figure 17 clearly shows that the selectivity of the catalyst poisoned with 1.6 mg S/g Fe was nearly identical to that of the unpoisoned catalyst.

Karn et al. (1964) found that in situ poisoning had little influence on the selectivity of a fused catalyst until the relative activity decreased to 20%. Stenger (1984) observed slight changes in the selectivity of a used fused iron catalyst poisoned in situ with 3.8 mg S/g Fe. The relative activity was 50%.

In section III.F., the effect of poisoning for 7 hours on the selectivity of the catalyst was discussed. Poisoning the catalyst with 134 mg S/g Fe improved the selectivity of the catalyst dramatically. The olefinic content of the C2 fraction increased one and one-half orders of magnitude. The olefinic content of the C3 fraction also improved, but this result may be due to uncertainty in the propane and propylene molar area data. There was also a shift in selectivity to C3 formation.

The improved selectivity to olefins is the result of electronic effects of sulfur poisoning and not conversion effects. At lower conversion, one would expect to find a higher concentration of paraffins in the product stream due to the higher hydrogen partial pressure.

Stenger (1984) also observed a significant improvement in the selectivity of the same reduced iron catalyst after prepoisoning with an organic sulfide, dibenzothiophene. The prepoisoned catalyst formed more olefins and less methane.

IV.F. Chemical State of Unpoisoned Catalyst

The results of the Mossbauer analysis are summarized in Figures 24-26. Figure 24 shows the change in composition of iron as iron carbide. It appears that the iron phases progress as carbidization proceeds (from left to right):

$$Fe^0 \rightarrow Fe_xC \rightarrow X\text{-}Fe_5C_2 \rightarrow e'\text{-}Fe_{2.2}C.$$

Tau et al. (1984) made a similar observation using a supported iron catalyst. Perhaps it is not surprising that the progression should tend toward the phases higher in carbon content. However, the stability of these carbides

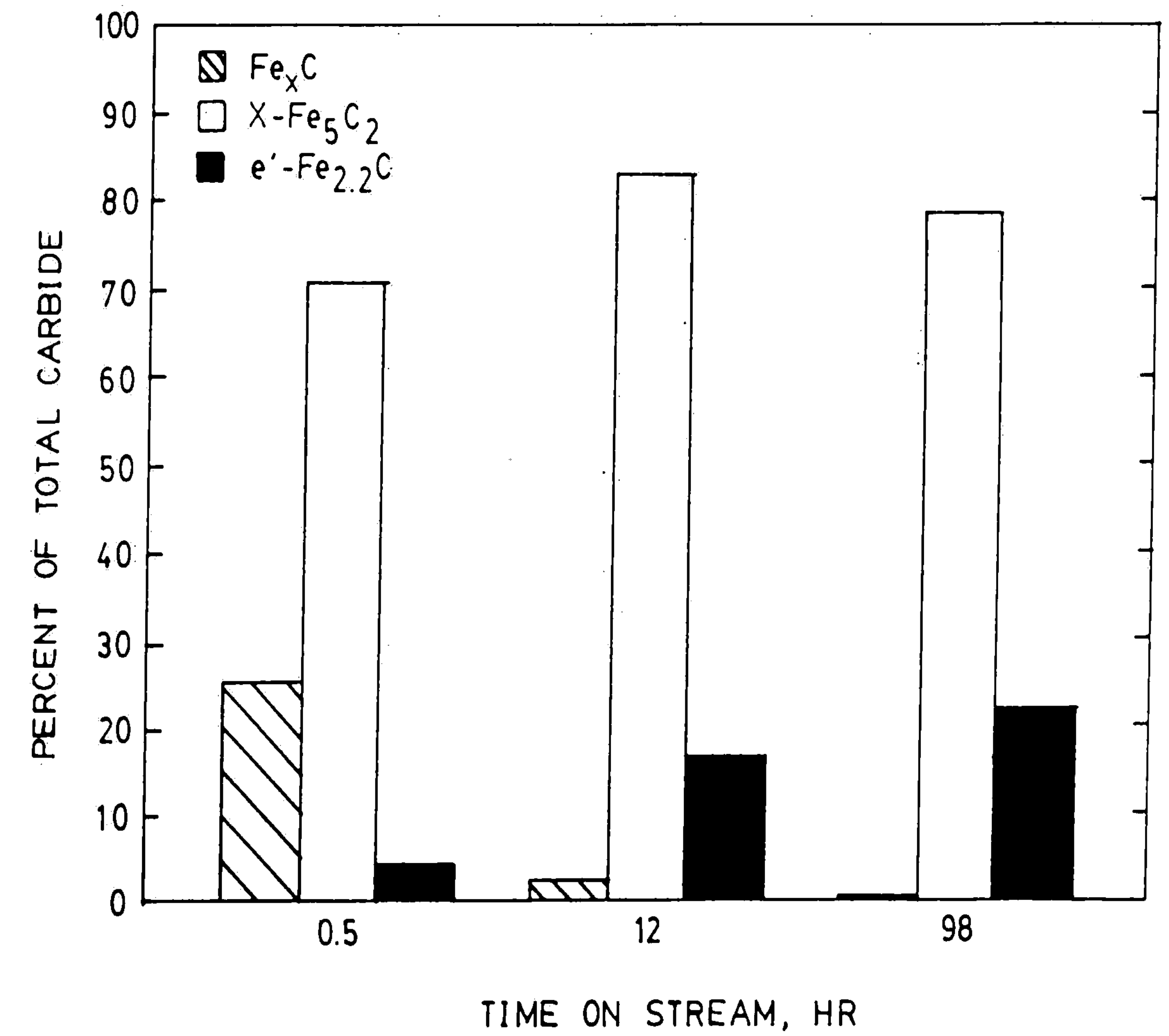


Figure 24: Carbide distribution of unpoisoned catalyst as carbidization progresses.

increases as the carbon content decreases (Le Caer et al., 1982):

$$Fe_2C < e'\text{-}Fe_{2.2}C < \chi\text{-}Fe_5C_2 < Fe_{\chi}C < \theta\text{-}Fe_3C$$

The carbides formed during the Fischer-Tropsch reaction will result from competing effects between the tendency to have a high carbon content (i.e., the relative rates of surface reaction and diffusion of free carbon) and a decreasing stability as the carbon content increases (Le Caer, et al., 1982). Since we observe a progression in the order of decreasing stability, the conclusion is that surface reaction and diffusion of free carbon is very fast.

The doublet observed in the Mossbauer spectra of the carbided samples indicated the presence of superparamagnetic iron. Superparamagnetisn is observed in absorbers with very small particles (Dumesic and Topsoe, 1977). Raupp and Delgass (1979) also observed the appearance of a superparamagnetic component as their iron Fischer-Tropsch catalyst carbided. When calculated on a doublet-free basis, the percent iron as iron carbide data were very similar to the results reported in section III.

IV.G. Effect of Sulfur on the Catalyst Chemical State

In this study, the role of sulfur as a selective poison of the Fischer-Tropsch synthesis reaction has been demonstrated. As a poison, sulfur reduced the activity of a catalyst sample to 5% of its unpoisoned activity. Sulfur is a selective poison since the loss in activity was accompanied by a significant improvement in the olefinic content and a shift toward higher molecular weight products. We turn our attention now to a discussion of sulfur's effect on the chemical state of the synthesis catalyst hoping to explain these activity and selectivity effects.

Figures 25 and 26 summarize the effect of sulfur poisoning on the extent of carbide formation and the carbide composition, respectively. After 12 hours of carbidization, the extent of carbide formation was 95% that of the unpoisoned catalyst. Hence, the prepoisoning did not alter the rate of carbide formation significantly. In Figure 26, it is clear that poisoning for 5 minutes had no significant effect on the relative rates of formation of individual carbide phases. The composition of the carbides was essentially that of the unpoisoned catalyst.

Seven hours of prepoisoning had a significant effect on the rate of carbide formation. After 0.5 hours of carbidization, the amount of iron as iron carbide in the 7 hour poisoned catalyst was 24% that of the unpoisoned catalyst. There was also a significant change in the iron carbide distribution. Much less Fe_XC was formed in the

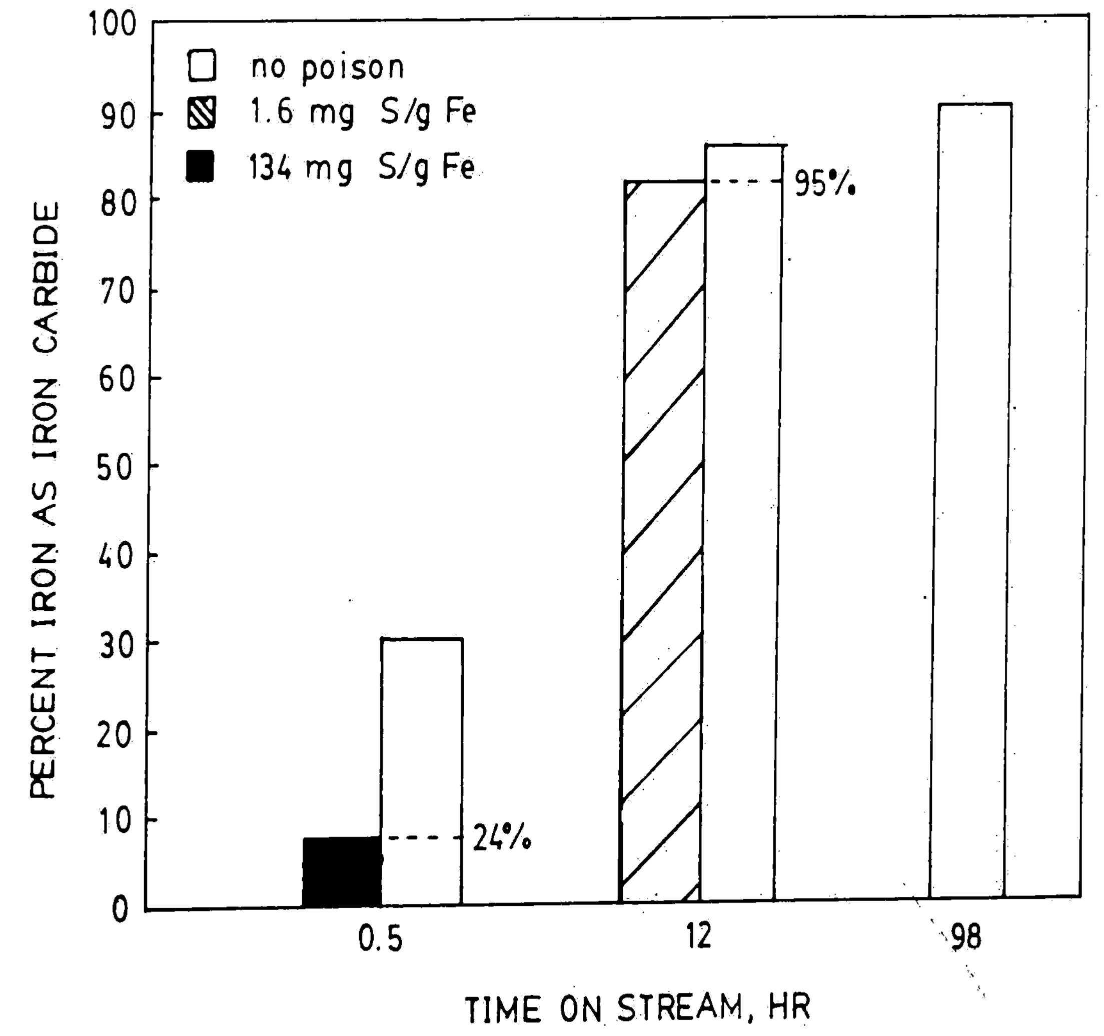


Figure 25: Effect of sulfur on the rate of carbidization.

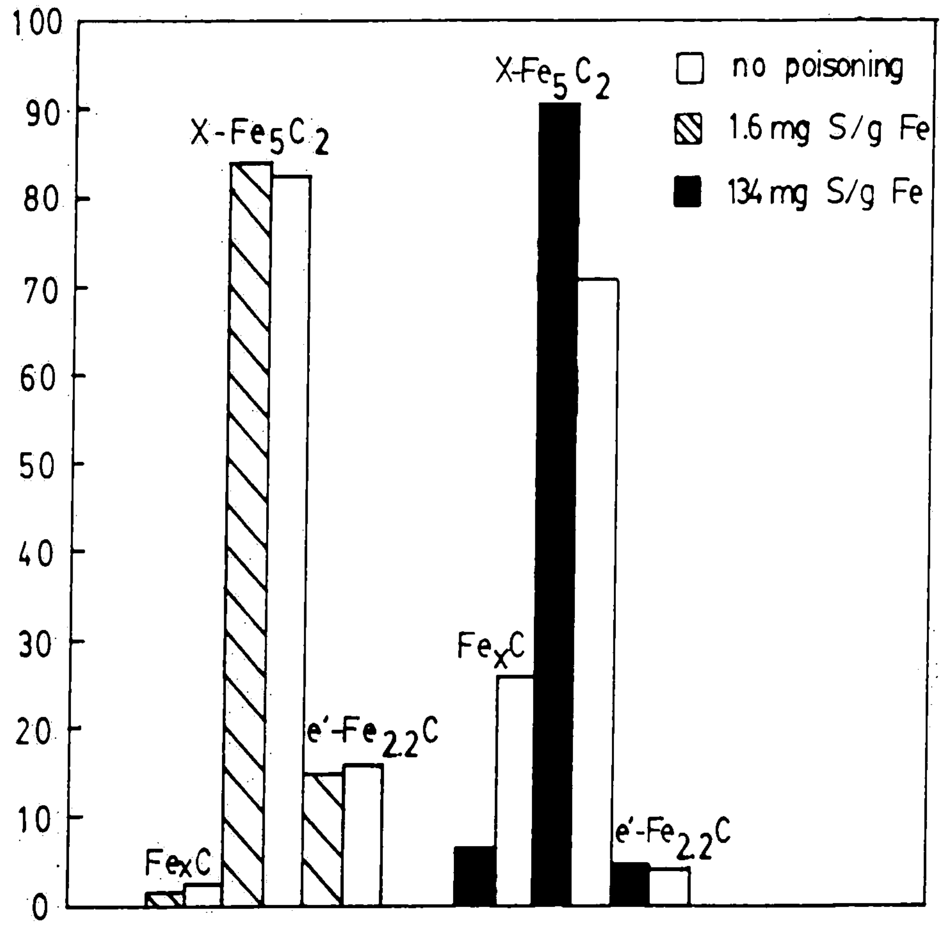


Figure 26: Effect of sulfur on carbide distribution

prepoisoned catalyst than in the unpoisoned catalyst. The proportion as X-Fe_5C_2 increased considerably.

IV.H. Models of Iron's Catalytic Behavior

At least two models have been proposed to explain the behavior of iron in the Fischer-Tropsch synthesis. They are the "carbide model "and the "competition model". These models will be described briefly.

In an elegant in situ Mossbauer experiment, Raupp and Delgass (1979) showed that the activity of a Fischer-Tropsch catalyst increased almost linearly with the extent of iron carbide formation in the bulk. They developed what has come to be known as the "carbide model". The carbide model suggests that the relationship is causal in that the bulk iron controls the concentration of active surface sites.

The competition model (Niemantsverdriet and Van Der Kraan, 1982) views iron atoms at the surface as the active sites. Following adsorption and dissociation of CO, the surface carbidic species, C^*, has three possible fates. It may react to form Fischer-Tropsch products, diffuse into the bulk of the catalyst and form iron carbide, or it may polymerize and form inactive carbon on the surface. This model can also explain the results of Raupp and Delgass (1979). Initially, the catalyst is reduced iron. In the early stages of synthesis, carbon diffuses into the bulk where it forms iron carbide. As the bulk becomes more and more carbided, more surface species are available for hydrocarbon synthesis or deactivation. The three reactions compete provided CO dissociation is slower than carbidization.

There are several possible mechanisms by which sulfur can decrease the rate of iron carbide formation. One possibliity is that sulfur on the surface has an electronic effect which hinders the chemisorption and dissociation of CO and/or H_2. Or it may be a geometric effect having the same effect on chemisorption and dissociation. Another possibility is that a layer of sulfur at the catalyst surface restricts the diffusion of carbon into the bulk. The results of this study do not indicate which effect is responsible for the lower rates of carbidization in sulfur poisoned catalysts. But a combination of both effects is probably responsible.

V. Conclusions

Several conclusions can be drawn from the results of this investigation:

- Sulfur on the surface of a reduced fused iron catalyst lowers the rate of carbidization of the catalyst. Moreover, poisoned catalysts that carbided slowly were far less active than unpoisoned catalysts.

- It is not clear what effect the relative amounts of different iron carbides in the bulk of the catalyst have on the product selectivity. The carbide distribution may determine the selectivity, or it may be a consequence of other effects.

- Prepoisoning with 1.6 mg S/g Fe reduced the activity of the iron catalyst 25%. The rate of carbidization decreased slightly. The selectivity did not change significantly, nor did the chemical state of the catalyst.

- Prepoisoning with 134 mg S/g Fe reduced the activity of the catalyst 95%. The rate of carbidization decreased significantly. The selectivity was shifted toward production of olefins and higher molecular weight products.

The carbide distribution of the catalyst was changed significantly.

The mechanism by which sulfur decreases the rate of carbidization is not known. Sulfur may reduce the rate of dissociation of the reactants. Sulfur may also reduce the rate of carbon diffusion in the catalyst bulk. An experiment to determine the effect of preadsorbed sulfur on the rates of carbidization and decarbidization would indicate which mechanism is more likely.

VI. References

Anderson, R. B., in Catalysis, vol. 4 (P. H. Emmett, ed.,), Rheinhold, New York, 1956.

Anderson, R. B., Karn, F. S., and Shultz, J. F., Journal of Catalysis, vol. 4, 1965.

Bartholomew, C. H., Agrawal, P. K., and Katzer, J. R., Advances in Catalysis, vol. 31, Academic Press, 1982.

Dietz, W. A., Journal of Gas Chromatography, Feb., 1967.

Dumesic, J. A., and Topsoe., H., Advances in Catalysis, vol. 26, Academic Press, 1977.

Huff, G. A., Fischer Tropsch Synthesis in a Slurry Reactor, ScD Thesis, Massachusetts Institute of Technology, April, 1982.

Karn, F. S., et al., Industrial and Engineering Chemistry Product Research and Development, vol. 2, 1963.

Karn, F. S., et al., Industrial and Engineering Chemistry Product Research and Development, vol. 3, 1964.

Le Caer, G., et al., Journal of Physical Chemistry, vol. 86, 1982.

May, L., ed., "An Introduction to Mossbauer Spectroscopy." Plenum, New York, 1971.

Muir, A. H., Jr., Ando, K. J., and Coogan, H. M., "Mossbauer Effect Data Index 1958-1965." Interscience, New York, 1966.

Nagy, S. I., and Weir, T. W., "The SIRIUS Spectrum Evaluating System." (unpublished) Copies available from Dr. Gary Simmons, Department of Chemistry, Lehigh University, Bethlehem, PA 18015

Niemantsverdriet, J. W., and Van Der Kraan, A. M., Journal of Catalysis, vol. 72, 1981.

Raupp, G. B., and Delgass, W. N., Journal of Catalysis, vol. 58, 1979.

Shultz, J. F., et al., Journal of Physical Chemistry, vol. 66, 1962.

Stenger, H. G., Jr., Studies of the Fischer-Tropsch Synthesis in a Slurry Reactor, ScD Thesis, Massachusetts Institute of Technology, February, 1984.

Tau, et. al., Journal of Catalysis, vol. 87, 1984.

Wertheim, G. K., "Mossbauer Effect, Principles, and Applications." Academic Press, New York, 1964.

VII. Appendices

VII.A. Appendix I - Mossbauer Data Transfers

Transfer from MCA to Computer Data File

1. Turn on the modem and computer terminal.

2. Insert cassette into the Techtran 817 data cassette deck. Turn power on. Set the Line Mode to "Off" and Binary to "Off".

3. Dial the Interface selector switch to "Term/Modem" in order to control the Techtran 817 data cassette from the terminal.

4. At the terminal, depress CTRL Z (by depressing CTRL and Z simultaneously) to rewind the tape. CTRL R puts the cassette deck in the Write mode. The Write light should now be on. Type in at the terminal any desired spectrum label followed by Return and Line Feed.

5. At the Techtran 817, switch Binary to "on-line".

6. Dial the Interface selector switch to "MCA". This action links the MCA to the Techtran 817.

7. Set the MCA Read Mode to "Type". Set the Memory Group selector switch to the position (1/4, 2/4, 3/4, or 4/4) corresponding to the group from which the data is to be transfered. Depress "Start Readout".

8. The tape will advance intermittently as data is transfered from the MCA. Transfer to the tape is complete when the MCA automatically resets to the Stop Mode.

9. Change the Binary switch to "Off" on the Techtran 817 unit.

10. Position the Interface selector switch to "Term/Modem".

11. At the terminal, depress CTRL T to terminate the Write mode. The Write light will turn off. CTRL Z rewinds the tape.

12. Turn the Techtran 817, computer terminal, and modem off.

Data Transfer from Tape to Computer Data File

1. Turn on the modem, Techtran 8410 datacassette deck, and terminal/printer in Room 315 of Sinclair Lab. Logon to the CYBER via telephone lines.

2. Issue the following commands to create the datafile RAWDAT:

```
/SENATOR

*NEW,RAWDAT

*INPUT
```

3. Insert the cassette into the Techtran 8410. Depress the Read button. Data is printed at the terminal as it is read into RAWDAT.

4. Once all 1024 data have been properly read into RAWDAT, turn the Techtran off momentarily to discontinue reading from tape. Enter ";" and hit RETURN. Re-enter ";" and hit "RETURN" again. Once back in SENATOR, enter "REPLACE" to save the file RAWDAT.

5. Transmission errors may result in the appearance of letters where there should be numbers. Hence, the file RAWDAT may need to be edited. The numerical equivalents of some letters are listed below.

A=1 B=2 C=3 D=4 E=5

F, G, I, Q, and U also appear occassionally

The SENATOR commands "FIND" and "CHANGE" are helpful in editing these transmission errors.

VII.B. Appendix II - Data Reduction Jobs

JOBRED -

```
/JOB
JOB,T20.
/USER
GET,REDUCE.
GET,RAWDAT.
REWIND,*.
FTN,I=REDUCE,L=0,GO,PMD.
REWIND,PMDUMP.
COPYSBF,PMDUMP,OUTPUT.
SAVE,WDRIFT.
```

REDUCE -

```
      PROGRAM REDUCE(RAWDAT,WDRIFT,TAPE5=RAWDAT,TAPE6=WDRIFT)
      DIMENSION A(205,5),Y(1025),X(256)
      INTEGER Y,A
C READ DATA
      DO 50 I=1,205
      READ(5,10)(A(I,K),K=1,5)
   10 FORMAT(5X,4(I6,1X)I6)
   50 CONTINUE
C CHANGE TWO DIMENSIONAL ARRAY TO A ONE DIMENSIONAL ARRAY
      J=0
      DO 205 I=1,205
      DO 5 K=1,5
      J=J+1
      Y(J)=A(I,K)
    5 CONTINUE
  205 CONTINUE
C REDUCE THE NUMBER OF DATA POINTS
      I=0
      DO 20 K=1,1023,2
      I=I+1
      Y(I)=(Y(K)+Y(K+1))/2
   20 CONTINUE
C PUNCH DATA

      WRITE(6,100)(Y(J),J=1,512)
  100 FORMAT(10(I6,1X))
      END
        26 LINES COPIED.
```

RAWDAT -

```
3072 914021 376000 376000 376571 371334
3077 361100 362078 359606 356315 365520
3082 363045 345828 351862 347811 357086
3087 343562 335657 339803 346505 336873
3092 336058 335046 320678 330851 321879
3097 315553 311272 309300 312677 312724
3102 295438 297652 299793 286752 288284
3107 285153 274903 271053 264553 256222
3112 251142 238017 227290 210573 210780
3117 219188 216277 212329 243393 229706
3122 237933 237909 238603 229687 242299
3127 251202 254188 244848 240883 249059
3132 229540 223161 231349 226248 214255
3137 225770 223691 214713 235023 201746
3142 200279 201420 190735 198174 188843
3147 182428 168364 174565 172520 177874
3152 165774 165303 163099 161681 168506
3157 166392 175777 162547 164852 164956
3162 173195 162238 177376 166197 163256
3167 158323 161025 157463 162662 145416
3172 146626 161950 150114 150404 147725
3177 143046 144301 154097 145587 150666
3182 135446 134969 130655 129422 136240


3187 131320 142870 126935 118236 116678
3192 106087 103732 097128 099141 081446
3197 080934 077865 079438 078063 098044
3202 096319 097854 097830 104151 099718
3207 095083 104784 104362 112320 104126
3212 099610 114156 104996 103397 101256
3217 108608 114861 097117 096688 092096
3222 083635 088150 086197 098176 092435
3227 090546 090806 087912 083023 071139
3232 089001 082427 086759 069775 073423
3237 058462 048739 054158 068394 055014
3242 060576 071663 071958 067546 066333
3247 068495 070250 076609 067113 071657
3252 066001 068378 072031 070804 064414
3257 059885 066767 063345 063503 061204
3262 061636 062302 062968 064489 066010
3267 064573 068040 060021 057484 056610
3272 054980 055160 053288 043814 043336
3277 032408 038273 030365 018852 024262
3282 041261 028347 030132 030133 031920
3287 041158 030585 052510 040961 042419
3292 038835 046017 053199 042288 042690
3297 031114 044138 037962 041763 043000
```

RAWDAT (continued) -

```
3302 037840 032513 030895 033525 029954
3307 028184 040528 021433 026462 029642
3312 025696 028917 029897 024297 032988
3317 028431 027249 027380 025759 031937
3322 034223 037929 031329 037668 022000
3327 024295 030042 020822 033717 024054
3332 031355 035268 037509 027044 035004
3337 039536 024335 029355 023018 027822
3342 026145 010058 014310 020100 022551
3347 026868 032001 036666 035576 037832
3352 047175 043633 041078 050841 054717
3357 041385 049557 038397 049435 052889
3362 057498 049847 047688 062881 054624
3367 058498 042815 054722 051173 051177
3372 033595 049810 041421 042880 049924
3377 054855 047906 058507 057519 061206
3382 072876 058548 069552 074653 072694
3387 058953 066674 066917 073779 077116
3392 074480 072616 068462 077130 081571
3397 083542 066819 079182 072050 072213
3402 079207 079984 083071 086674 089780
3407 095050 094700 077000 074863 089691
3412 078057 087552 087698 088829 096133


3417 087298 088971 092022 085034 094650
3422 075033 080947 071263 058175 056067
3427 057153 062475 075640 080770 079924
3432 096377 095608 104101 106485 103792
3437 103518 102654 109639 119433 111836
3442 107862 107512 110659 112170 109879
3447 115461 108879 104619 121532 119887
3452 135435 133856 133287 140570 126507
3457 141395 141900 144885 146715 153289
3462 153883 159784 159177 154058 157280
3467 147111 163755 166597 170872 162164
3472 169232 176926 176161 176930 178918
3477 179497 172275 178740 186444 195436
3482 188580 179500 170083 181295 181169
3487 191821 190656 187512 198271 195560
3492 197841 180988 193256 193945 204851
3497 198119 195298 213627 204718 214271
3502 200635 210808 211320 216359 208814
3507 204198 184756 203346 194833 192519
3512 177881 190677 181246 195863 204661
3517 215812 215998 219318 224429 226988
3522 229248 229209 237099 233185 236876
3527 249431 248998 251716 258064 263774
```

RAWDAT (continued) -

```
3532 261036 273053 293118 287518 290398
3537 288566 295306 306882 308645 314385
3542 313016 308520 310408 323834 319685
3547 325282 328235 341326 337541 336022
3552 343277 344345 330252 338645 343310
3557 359367 358399 343450 359918 356326
3562 359810 371769 367093 370631 370030
3567 375733 375784 381719 386886 395443
3572 382985 394465 386577 394202 400798
3577 403239 416371 415242 427314 416377
3582 425255 426353 428678 418761 426502
3587 436732 426430 434052 437319 433222
3592 447626 442114 453232 459482 470198
3597 471514 467760 464748 469264 458421
3602 479759 470268 478350 487309 477499
3607 494781 505717 487612 508579 491665
3612 514193 504041 515367 509531 517085
3617 507829 524048 522516 516085 528546
3622 521429 523559 523633 530377 528563
3627 531606 529038 523614 533620 524701
3632 534887 531008 518708 535216 514088
3637 522234 530708 536471 526448 535288
3642 531606 535943 539126 526206 535978


3647 528436 532295 520932 531204 518144
3652 540011 556488 561378 570431 559656
3657 579712 577945 588442 595713 585599
3662 591076 594032 602368 597211 597557
3667 604821 589504 609274 608420 618323
3672 616560 625644 618259 632281 626489
3677 629048 629374 633718 644791 645981
3682 646489 644394 647615 638908 638333
3687 645424 641299 647685 655462 652900
3692 649085 658869 655339 651070 649952
3697 677990 663328 666044 666573 664985
3702 666428 671264 667442 667255 662131
3707 656831 667187 674828 661150 666028
3712 669150 666448 668077 668580 677146
3717 678372 681589 691420 692036 687606
3722 694097 686708 688019 689533 689141
3727 684518 683913 667701 661784 666519
3732 667635 660965 661205 666403 692463
3737 704278 698906 710256 717283 705731
3742 717511 724504 713528 718239 714282
3747 717571 716933 726714 723510 733542
3752 739386 737170 730021 729723 742176
3757 731943 741724 725158 734569 752409
```

RAWDAT (continued) -

```
3762 750062 737108 729361 737874 737813
3767 735243 738826 738311 744870 735734
3772 736680 751248 736480 741506 737131
3777 746926 734805 744942 738736 749493
3782 737990 736655 745048 735067 740766
3787 734016 736638 746803 750277 737705
3792 750260 748788 754431 745033 750623
3797 750327 749311 758905 752310 752848
3802 753663 749831 759949 749447 761719
3807 757619 740305 745201 749264 760669
3812 743065 738381 737139 746851 728430
3817 728790 727370 734947 744146 742840
3822 744791 739189 754498 766152 752532
3827 745664 751596 747539 739622 732817
3832 750145 746794 741715 744316 756732
3837 745571 755567 747016 746759 741234
3842 749760 748712 749441 746381 748522
3847 732189 742128 755276 734491 747077
3852 760144 750031 756573 749787 760711
3857 745269 756869 749148 750004 741720
3862 756079 751251 753487 742885 743542
3867 751744 742463 751502 749388 749946
3872 751203 745613 742291 741943 743222


3877 732931 727662 728523 723372 730939
3882 724245 724202 727803 723888 738716
3887 729968 742469 744548 746047 740260
3892 743040 744298 727632 732348 744278
3897 737602 744544 735639 727464 751336
3902 733427 730858 744602 730501 734924
3907 728104 726021 737337 719102 735769
3912 722031 713109 714948 723436 728600
3917 721152 705512 701241 697834 702180
3922 692125 690490 686233 685594 695059
3927 699211 702938 698004 699785 701116
3932 708530 696310 708867 699957 703702
3937 700983 698691 697564 692920 695195
3942 691473 687015 687104 704082 683823
3947 683378 688639 682248 673890 677406
3952 684324 679253 683490 666370 673970
3957 664310 651783 648509 661848 646005
3962 643745 639286 623822 621583 623331
3967 607683 619563 619669 623848 623098
3972 630271 630555 631485 625328 633127
3977 635671 638239 639825 629176 630959
3982 633217 633324 627625 620065 631363
3987 622993 624325 609692 619339 616267
```

RAWDAT (continued) -

```
3992 618969 617780 609537 613297 605497
3997 607698 611143 602833 591903 599729
4002 599964 595707 598792 587812 580697
4007 582344 573810 573192 569189 568316
4012 560631 554036 547913 545961 544254
4017 549293 541109 555242 537422 553222
4022 547736 551893 548546 536378 553877
4027 548115 542517 547065 548250 543387
4032 526561 544374 536002 528577 531532
4037 528262 520416 528857 526276 509035
4042 514731 510560 505836 497275 502781
4047 477822 484117 476681 474755 460073
4052 441920 440759 444921 442792 446452
4057 450316 442552 445780 446633 455803
4062 461985 465189 448405 459488 456355
4067 465343 458618 460260 454894 446191
4072 455694 446283 452358 434844 424937
4077 440215 426829 427087 426944 424341
4082 415164 410079 422544 403930 413115
4087 406661 409352 400126 400999 396625
4092 390703 394279 383223 391942
```

WDRIFT -

```
CTB030
645010 376285 366217 360842 360917 354436 349836 350324 337730 341689
335552 325764 318716 310286 312700 296545 293272 286718 272978 260387
244579 218931 214984 214303 236549 237921 234145 246750 249518 244971
226350 228798 220012 219202 218384 200849 194454 185635 171464 175197
165538 162390 167449 169162 164904 167716 171786 160789 159244 154039
154288 150259 145385 149199 148126 135207 130038 133780 134902 117457
104909  98134  81190  78651  88053  97086 100990  97400 104573 108223
106883 104196 104932 105989  94392  85892  92186  91490  89359  77081
 85714  78267  65942  51448  61704  66119  69752  67414  73429  69385
 67189  71417  62149  65056  62353  61969  63728  65291  64030  57047
 55070  48551  37872  34319  21557  34804  30132  36539  41547  41690
 42426  47743  36902  41050  42381  35176  32210  29069  30980  28052
 27306  27097  30709  27314  28848  36076  34498  23147  25432  28885
 33311  32276  37270  26845  25420  18101  17205  24709  34333  36704
 45404  45959  48051  43977  51162  53672  55284  56561  48768  51175
 41702  42150  52389  53206  59362  65712  72102  65823  66795  75447
 73548  72796  82556  73000  72131  79595  84872  92415  85850  82277
 82804  88263  91715  90496  89842  77990  64719  56610  69057  80347
 95992 105293 103655 106146 115634 107687 111414 112670 106749 120709
134645 136928 133951 143392 150002 156833 156617 152195 165176 166518
173079 176545 179207 175507 190940 184040 175689 186495 189084 196915
189414 193600 201485 204462 209494 205721 213839 206506 194051 193676


184279 188554 210236 217658 225708 229228 235142 243153 250357 260919
267044 290318 289482 301094 311515 310768 317121 322483 334780 336781
343811 334448 351338 350924 358122 365789 368862 372881 378751 391164
388725 390389 402018 415806 421845 425804 423719 431617 430241 435270
444870 456357 470856 466254 463842 475013 482829 486140 496664 500122
509117 512449 512457 523282 522315 522494 527005 530084 526326 522150
532947 526962 518161 533589 530868 533774 532666 532207 526613 524674
548249 565904 569684 583193 590656 592554 599789 601189 599389 613371
621102 625270 627768 631546 645386 645441 643261 641878 644492 654181
653977 653204 663971 664686 665779 668846 667348 659481 671007 663589
667799 668328 677759 686504 689821 690402 688776 686829 675807 664151
664300 663804 698370 704581 711507 721007 715883 715926 721823 728526
738278 729872 737059 733441 743489 743585 733617 736528 738568 740302
743964 738993 742028 739873 744114 737322 740057 737391 741720 743991
749524 749732 750475 754108 752579 751747 754698 759669 742753 754966
740723 741995 728610 731158 743493 741990 760325 749098 749567 736219
748469 743015 751151 751291 743996 749236 747911 740355 748702 740784
755087 753180 752990 753008 745862 753665 748186 747643 746982 749667
748408 742117 738076 728092 727155 724223 725845 734342 743508 743153
743669 729990 740940 740091 739400 732142 737551 731514 731679 727435
717570 719192 724876 703376 700007 691307 685913 697135 700471 700450
702420 704412 702342 698127 694057 689244 695593 683600 685443 675648
681788 674930 669140 650146 653926 641515 622702 615507 619616 623473
```

WDRIFT (continued) -

```
630413 628406 634399 639032 630067 633270 623845 627178 617008 617803
618374 611417 606597 606988 595816 597835 593302 581520 573501 568752
557333 546937 546773 548175 545322 549814 542462 550996 544791 545818
535467 532289 529897 524636 517655 512645 501555 490301 480399 467414
441339 443856 448384 444166 451218 463587 453946 460849 459439 450542
450988 443601 432576 426958 425642 412621 413237 409888 404739 398812
392491 387582
       53 LINES COPIED.
```

<u>JOBDRFT</u> -

```
/JOB
JOB,T20.
/USER
GET,DRIFT.
GET,WDRIFT.
REWIND,*.
FTN,I=DRIFT,L=0,GO,PMD.
REWIND,PMDUMP.
COPYSBF,PMDUMP,OUTPUT.
SAVE,NDRIFT.
```

DRIFT -

```
      PROGRAM DRIFT(WDRIFT,NDRIFT,OUTPUT,TAPE5=WDRIFT,TAPE6=NDRIFT)
      DIMENSION X(52,10),Y(512)
      INTEGER X,Y,A,H,B L,S
C
C READ LABEL
      READ(5,10)LABEL
   10 FORMAT(A10)
C
C READ SLOPING DATA
      DO 30 I=1,52
      READ(5,20)(X(I,K),K=1,10)
   20 FORMAT(10(I6,1X))
   30 CONTINUE
C
C CHANGE TWO DIMENSIONAL ARRAY INTO A ONE DIMENSIONAL ARRAY
      J=0
      DO 50 I=1,52
      DO 40 K=1,10
      J=J+1
      Y(J)=X(I,K)
   40 CONTINUE
   50 CONTINUE
C


C CALCULATE SLOPE
      A=Y(2)+Y(3)
      H=((Y(255)+Y(256)+Y(257)+Y(258))/4)
      B=Y(511)+Y(512)
      L=((A+B)/4)
      S=((H-L)/256)
      WRITE(6,55)A,H,B,L,S
   55 FORMAT(4(I7,1X),I6)
C
C CORRECT DATA FOR SLOPE
      DO 60 J=1,256
      Y(J)=Y(J)-(S*J)
   60 CONTINUE
      DO 70 J=257,512
      Y(J)=Y(J)-(S*(513-J))
   70 CONTINUE
C
C STORE CORRECTED DATA IN FILE NDRIFT
      WRITE(6,80)S
   80 FORMAT("DATA CORRECTED FOR A SLOPE OF",I4,"COUNTS PER CHANNEL")
      WRITE(6,90)LABEL
   90 FORMAT(A10)
      WRITE(6,100)(Y(J),J=1,512)



  100 FORMAT(9(I6,1X),I6)
      STOP
      END
        49 LINES COPIED.
```

NDRIFT -

```
100 644834;375933;365689;360138;360037;353380;348604;348916;336146;339929
110 333616;323652;316428;307822;310060;293729;290280;283550;269634;256867
120 240883;215059;210936;210079;232149;233345;229393;241822;244414;239691
130 220894;223166;214204;213218;212224;194513;187942;178947;164600;168157
140 158322;154998;159881;161418;156984;159620;163514;152341;150620;145239
150 145312;141107;136057;139695;138446;125351;120006;123572;124518;106897
160 ;94173;;87222;;70102;;67387;;76613;;85470;;89198;;85432;;92429;;95903
170 ;94387;;91524;;92084;;92965;;81192;;72516;;78634;;77762;;75455;;63001
180 ;71458;;63835;;51334;;36664;;46744;;50983;;54440;;51926;;57765;;53545
190 ;51173;;55225;;45781;;48512;;45633;;45073;;46656;;48043;;46606;;39447
200 ;37294;;30599;;19744;;16015;;;3077;;16148;;11300;;17531;;22363;;22330
210 ;22890;;28031;;17014;;20986;;22141;;14760;;11618;;;8301;;10036;;;6932
220 ;;6010;;;5625;;;9061;;;5490;;;6848;;13900;;12146;;;;619;;;2728;;;6005
230 ;10255;;;9044;;13862;;;3261;;;1660;;'5835;;'6907;;;;421;;;9869;;12064
240 ;20588;;20967;;22883;;18633;;25642;;27976;;29412;;30513;;22544;;24775
250 ;15126;;15398;;25461;;26102;;32082;;38256;;44470;;38015;;38811;;47287
260 ;45212;;44284;;53868;;44136;;43091;;50379;;55480;;62847;;56106;;52357
270 ;52708;;57991;;61267;;59872;;59042;;47014;;33567;;25282;;37553;;48667
280 ;64136;;73261;;71447;;73762;;83074;;74951;;78502;;79582;;73485;;87265
290 101029;103136;;99983;109248;115682;122337;121945;117347;130152;131318
300 137703;140993;143479;139603;154860;147784;139257;149887;152300;159955
310 152278;156288;163997;166798;171654;167705;175647;168138;155507;154956
320 145383;149482;170988;178234;186108;189452;195190;203025;210053;220439
330 226388;249486;248474;259910;270155;269232;275409;280595;292716;294541
340 301395;291856;308570;307980;315002;322493;325390;329233;334927;347164
350 344549;346037;357490;371102;376965;380748;378663;386737;385537;390742
360 400518;412181;426856;422430;420194;431541;439533;443020;453720;457354
370 466525;470033;470217;481218;480427;480782;485469;488724;485142;488152
380 492115;486306;477681;493285;490740;493822;492890;492607;487189;485426
390 509177;527008;530964;544649;552288;554362;561773;563349;561725;575883
400 583790;588134;590808;594762;608778;609009;607005;605798;608588;618453
410 618425;617828;628771;629662;630931;634174;632852;625161;636863;629621
420 634007;634712;644319;653240;656733;657490;656040;654269;643423;631943
430 632268;631948;666690;673077;680179;689855;684907;685126;691199;698078
440 708006;699776;707139;703697;713921;714193;704401;707488;709704;711614
450 715452;710657;713868;711889;716306;709690;712601;710111;714616;717063
460 722772;723156;724075;727884;726531;725875;729002;734149;717409;729798
470 715731;717179;703970;706694;719205;717878;736389;725338;725983;712811
480 725237;719959;728271;728587;721468;726884;725735;718355;726878;719136
490 733615;731884;731870;732064;725094;733073;727770;727403;726918;729779
500 728696;722581;718716;708908;708147;705391;707189;715862;725204;725025
510 725717;712214;723340;722667;722152;715070;720655;714794;715135;711067
520 701378;703176;709036;687712;684519;675995;670777;682175;685687;685842
530 687988;690156;688262;684223;680329;675692;682217;670400;672419;662800
540 669116;662434;656820;638002;641958;629723;611086;604067;608352;612385
550 619501;617670;623839;628648;619859;623238;613989;617498;607504;608475
560 609222;602441;597797;598364;587368;589563;585206;573600;565757;561184
570 549941;539721;539733;541311;538634;543302;536126;544836;538807;540010
580 529835;526833;524617;519532;512727;507893;496979;485901;476175;463366
590 437467;440160;444864;440822;448050;460595;451130;458209;456975;448254
600 448876;441665;430816;425374;424234;411389;412181;409008;404035;398284
610 392139;387406;
```

VII.C. Appendix III - SIRIUS Jobs

MORN -

```
/JOB
JOB,T20.
/USER
BEGIN,MORN.
```

(See PROCFIL for MORN code)

JOBTAPE -

```
/JOB
JOB,T20.
/USER
PAGES,N,100.
PLOTS,20000.
BEGIN,NOON,,TAPLST.
REWIND,*.
ROUTE,PLOT,DC=PT.
```

(See PROCFIL for NOON code)

TAPLST -

```
=LIBR
IVOL(*DATA-2*)
TLIS(50=70)
BACK
=STOP
```

JOBFOLD -

```
/JOB
JOB,T20.
/USER
PAGES,N,100.
PLOTS,20000.
BEGIN,NOON,,FOLD.
REWIND,*.
ROUTE,PLOT,DC=PT.
```

(See PROCFIL for NOON code)

FOLD -

```
100 =SAVE
110 OVOL(*DATA-1*)
120 NEWS(
130 * 6630 CTB030: RED, 7 HR H2S, FT 0.5 HR*
140 644834;375933;365689;360138;360037;353380;348604;348916;336146;3399
150 333616;323652;316428;307822;310060;293729;290280;283550;269634;25686
160 240883;215059;210936;210079;232149;233345;229393;241822;244414;23969
170 220894;223166;214204;213218;212224;194513;187942;178947;164600;16815
180 158322;154998;159881;161418;156984;159620;163514;152341;150620;1452
190 145312;141107;136057;139695;138446;125351;120006;123572;124518;10689
200 ;94173;;87222;;70102;;67387;;76613;;85470;;89198;;85432;;92429;;9590
210 ;94387;;91524;;92084;;92965;;81192;;72516;;78634;;77762;;75455;;6300
220 ;71458;;63835;;51334;;36664;;46744;;50983;;54440;;51926;;57765;;5354
230 ;51173;;55225;;45781;;48512;;45633;;45073;;46656;;48043;;46606;;3944
240 ;37294;;30599;;19744;;16015;;;3077;;16148;;11300;;17531;;22363;;2233
250 ;22890;;28031;;17014;;20986;;22141;;14760;;11618;;;8301;;10036;;;693
260 ;;6010;;;5625;;;9061;;;5490;;;6848;;13900;;12146;;;;619;;;2728;;;600
270 ;10255;;;9044;;13862;;;3261;;;1660;;'5835;;'6907;;;;421;;;9869;;1206
280 ;20588;;20967;;22883;;18633;;25642;;27976;;29412;;30513;;22544;;2477
290 ;15126;;15398;;25461;;26102;;32082;;38256;;44470;;38015;;38811;;4728
300 ;45212;;44284;;53868;;44136;;43091;;50379;;55480;;62847;;56106;;5235
310 ;52708;;57991;;61267;;59872;;59042;;47014;;33567;;25282;;37553;;4866




320 ;64136;;73261;;71447;;73762;;83074;;74951;;78502;;79582;;73485;;8726
330 101029;103136;;99983;109248;115682;122337;121945;117347;130152;131318
340 137703;140993;143479;139603;154860;147784;139257;149887;152300;159955
350 152278;156288;163997;166798;171654;167705;175647;168138;155507;154956
360 145383;149482;170988;178234;186108;189452;195190;203025;210053;220439
370 226388;249486;248474;259910;270155;269232;275409;280595;292716;294541
380 301395;291856;308570;307980;315002;322493;325390;329233;334927;347164
390 344549;346037;357490;371102;376965;380748;378663;386737;385537;390742
400 400518;412181;426856;422430;420194;431541;439533;443020;453720;457354
410 466525;470033;470217;481218;480427;480782;485469;488724;485142;488152
420 492115;486306;477681;493285;490740;493822;492890;492607;487189;485426
430 509177;527008;530964;544649;552288;554362;561773;563349;561725;575883
440 583790;588134;590808;594762;608778;609009;607005;605798;608588;618453
450 618425;617828;628771;629662;630931;634174;632852;625161;636863;629621
460 634007;634712;644319;653240;656733;657490;656040;654269;643423;631943
470 632268;631948;666690;673077;680179;689855;684907;685126;691199;698078
480 708006;699776;707139;703697;713921;714193;704401;707488;709704;711614
490 715452;710657;713868;711889;716306;709690;712601;710111;714616;717063
500 722772;723156;724075;727884;726531;725875;729002;734149;717409;729798
510 715731;717179;703970;706694;719205;717878;736389;725338;725983;712811
520 725237;719959;728271;728587;721468;726884;725735;718355;726878;719136
530 733615;731884;731870;732064;725094;733073;727770;727403;726918;729779
540 728696;722581;718716;708908;708147;705391;707189;715862;725204;725025
```

FOLD -

```
100 =SAVE
110 OVOL(*DATA-1*)
120 NEWS(
130 * 6630 CTB030: RED, 7 HR H2S, FT 0.5 HR*
140 644834;375933;365689;360138;360037;353380;348604;348916;336146;33992
150 333616;323652;316428;307822;310060;293729;290280;283550;269634;25686
160 240883;215059;210936;210079;232149;233345;229393;241822;244414;23969
170 220894;223166;214204;213218;212224;194513;187942;178947;164600;16815
180 158322;154998;159881;161418;156984;159620;163514;152341;150620;14523
190 145312;141107;136057;139695;138446;125351;120006;123572;124518;10689
200 ;94173;;87222;;70102;;67387;;76613;;85470;;89198;;85432;;92429;;9590
210 ;94387;;91524;;92084;;92965;;81192;;72516;;78634;;77762;;75455;;6300
220 ;71458;;63835;;51334;;36664;;46744;;50983;;54440;;51926;;57765;;5354
230 ;51173;;55225;;45781;;48512;;45633;;45073;;46656;;48043;;46606;;3944
240 ;37294;;30599;;19744;;16015;;;3077;;16148;;11300;;17531;;22363;;2233
250 ;22890;;28031;;17014;;20986;;22141;;14760;;11618;;;8301;;10036;;;693
260 ;;6010;;;5625;;;9061;;;5490;;;6848;;13900;;12146;;;;619;;;2728;;;600
270 ;10255;;;9044;;13862;;;3261;;;1660;;'5835;;'6907;;;;421;;;9869;;1206
280 ;20588;;20967;;22883;;18633;;25642;;27976;;29412;;30513;;22544;;2477
290 ;15126;;15398;;25461;;26102;;32082;;38256;;44470;;38015;;38811;;4728
300 ;45212;;44284;;53868;;44136;;43091;;50379;;55480;;62847;;56106;;5235
310 ;52708;;57991;;61267;;59872;;59042;;47014;;33567;;25282;;37553;;4866
```

```
320 ;64136;;73261;;71447;;73762;;83074;;74951;;78502;;79582;;73485;;87269
330 101029;103136;;99983;109248;115682;122337;121945;117347;130152;131318
340 137703;140993;143479;139603;154860;147784;139257;149887;152300;159955
350 152278;156288;163997;166798;171654;167705;175647;168138;155507;154956
360 145383;149482;170988;178234;186108;189452;195190;203025;210053;220439
370 226388;249486;248474;259910;270155;269232;275409;280595;292716;294541
380 301395;291856;308570;307980;315002;322493;325390;329233;334927;347164
390 344549;346037;357490;371102;376965;380748;378663;386737;385537;390742
400 400518;412181;426856;422430;420194;431541;439533;443020;453720;457354
410 466525;470033;470217;481218;480427;480782;485469;488724;485142;488152
420 492115;486306;477681;493285;490740;493822;492890;492607;487189;485426
430 509177;527008;530964;544649;552288;554362;561773;563349;561725;575883
440 583790;588134;590808;594762;608778;609009;607005;605798;608588;618453
450 618425;617828;628771;629662;630931;634174;632852;625161;636863;629621
460 634007;634712;644319;653240;656733;657490;656040;654269;643423;631943
470 632268;631948;666690;673077;680179;689855;684907;685126;691199;698078
480 708006;699776;707139;703697;713921;714193;704401;707488;709704;711614
490 715452;710657;713868;711889;716306;709690;712601;710111;714616;717063
500 722772;723156;724075;727884;726531;725875;729002;734149;717409;729798
510 715731;717179;703970;706694;719205;717878;736389;725338;725983;712811
520 725237;719959;728271;728587;721468;726884;725735;718355;726878;719136
530 733615;731884;731870;732064;725094;733073;727770;727403;726918;729779
540 728696;722581;718716;708908;708147;705391;707189;715862;725204;725025
```

FOLD (continued) -

```
550 725717;712214;723340;722667;722152;715070;720655;714794;715135;711067
560 701378;703176;709036;687712;684519;675995;670777;682175;685687;685842
570 687988;690156;688262;684223;680329;675692;682217;670400;672419;662800
580 669116;662434;656820;638002;641958;629723;611086;604067:608352;612385
590 619501;617670;623839;628648;619859;623238;613989;617498;607504;608475
600 609222;602441;597797;598364;587368;589563;585206;573600;565757;561184
610 549941;539721;539733;541311;538634;543302;536126;544836;538807;540010
620 529835;526833;524617;519532;512727;507893;496979;485901;476175;463366
630 437467;440160;444864;440822;448050;460595;451130;458209;456975:448254
640 448876;441665;430816;425374;424234;411389;412181;409008;404035:398284
650 392139;387406;
660 @
670 )
680 BACK
690 =LIBR
700 IVOL(*DATA-1*)
710 OVOL(*DATA-2*)
720 FOLD(256,257,66)
730 BACK
740 =DISP
750 SIZE(,,,,1)
760 IVOL(*DATA-1*)
770 MEAS(66)

780 IVOL(*DATA-2*)
790 MEAS(66)
800 BACK
810 =STOP
```

JOBFIT -

```
/JOB
JOB,T100.
/USER
PAGES,50.
PLOTS,20000.
BEGIN,NOON,,SEXT55.
REWIND,*.
```

(See PROCFIL for NOON code)

EVE -

```
/JOB
JOB,T20.
/USER
BEGIN,DUSK.
```

(See PROCFIL for DUSK code)

PROCFIL -

DAWN -

```
100 .PROC,DAWN.
110 DEFINE,PR.
120 DEFINE,V1.
130 DEFINE,V2.
140 DEFINE,ST.
150 LABEL,TAPE,VSN=CTB004,L=CTB004,R,PO=R.
160 REWIND,*.
170 COPYEI,TAPE,PR.
180 UNLOAD,TAPE.
190 LABEL,MT1,L=$SPEC.LIB.V$,VSN=CTB002,R,PO=R.
200 REWIND,*.
210 COPYEI,MT1,V1.
220 UNLOAD,MT1.
230 LABEL,MT2,L=$SPEC.LIB.V$,VSN=CTB003,R,PO=R.
240 COPYEI,MT2,V2.
250 REVERT,NOLIST.
260 *EOR
270 .PROC,NOON,DIRECS.
280 ATTACH,PR.
290 ATTACH,V1.
300 ATTACH,V2.
310 ATTACH,ST.
```

DUSK -

```
500 .PROC,DUSK.
510 ATTACH,V1.
520 ATTACH,V2.
530 LABEL,MT1,W,L=$SPEC.LIB.V$,VSN=CTB002,PO=W.
540 REWIND,*.
550 COPYEI,V1,MT1.
560 UNLOAD,MT1.
570 LABEL,MT2,W,L=$SPEC.LIB.V$,VSN=CTB003,PO=W.
580 REWIND,*.
590 COPYEI,V2,MT2.
600 RETURN,MT2.
610 PURGE,V1.
620 PURGE,V2.
630 PURGE,PR.
640 PURGE,ST.
650 REVERT,NOLIST.
```

PROCFIL (continued) -

NOON -

```
270 .PROC,NOON,DIRECS.
280 ATTACH,PR.
290 ATTACH,V1.
300 ATTACH,V2.
310 ATTACH,ST.
320 GET,DIRECS.
330 REWIND,*.
340 DEFINE,V1NEW.
350 DEFINE,V2NEW.
360 DEFINE,STNEW.
370 COPYBF,V1,V1NEW.
380 COPYBF,V2,V2NEW.
390 COPYBF,ST,STNEW.
400 REWIND,*.
410 PR,V1NEW,V2NEW,STNEW,DIRECS.
420 PURGE,V1.
430 PURGE,V2.
440 PURGE,ST.
450 CHANGE,V1=V1NEW.
460 CHANGE,V2=V2NEW.
470 CHANGE,ST=STNEW.
480 REVERT,NOLIST.
```

```
290 ATTACH,V1.
300 ATTACH,V2.
310 ATTACH,ST.
320 GET,DIRECS.
330 REWIND,*.
340 DEFINE,V1NEW.
350 DEFINE,V2NEW.
360 DEFINE,STNEW.
370 COPYBF,V1,V1NEW.
380 COPYBF,V2,V2NEW.
390 COPYBF,ST,STNEW.
400 REWIND,*.
410 PR,V1NEW,V2NEW,STNEW,DIRECS.
420 PURGE,V1.
430 PURGE,V2.
440 PURGE,ST.
450 CHANGE,V1=V1NEW.
460 CHANGE,V2=V2NEW.
470 CHANGE,ST=STNEW.
480 REVERT,NOLIST.

490 *EOR
```

VII.D. Appendix IV - Sample SEXT File

<u>SEXT55</u> -

```
100 =SEXT
110 ITER(1,30)
120 SETA(3,2,1)
130 SETW(1,1,1)
140 CALI(0.053223,122.20866)
150 NEGL(1)
160 BASE(586000/1,0/0,0/0)
170 SEXT(38330/1,190/1,.15/1,0/1,0.5/1)
180 SEXT(38281/1,214/1,.23/1,0/1,0.5/1)
190 SEXT(10532/1,110/1,0.2/1,0/1,0.15/1)
200 SEXT(2000/1,330/1,0/1,0/1,0.2/1)
210 SEXT(6209/1,0/0,0.25/1,0.47/1,0.5/1)
220 IVOL(*DATA-2*)
230 EVAL(55)
240 BACK
250 =DISP
260 SIZE(,,,,1)
270 FITT(1,-1)
280 BACK
290 =STOP
```

VII.E. Appendix V - Calculations

Extent of Reduction:

$$[Fe_3O_4]_t = [Fe_3O_4]_0 \exp(-kt)$$

$$k = -\frac{1}{t} \ln \frac{[Fe_3O_4]_{10}}{[Fe_3O_4]_0}$$

$$k = \frac{1}{10 \text{ hr}} \ln \frac{0.516}{0.918}$$

$$k = -0.0576 \text{ hr}^{-1}$$

$$[Fe_3O_4]_{60} = 0.516 \exp[(-0.0576 \text{ hr}^{-1})(60 \text{ hr})]$$

$$[Fe_3O_4]_{60} = 1.6\%$$

Therefore, 98.4% of iron reduced after 60 hours

Conversion:

Data from Huff (1982):

at $T = 250\ ^{o}C$,

$$k = 130 \frac{\text{umoles } H_2\text{+CO converted}}{\text{g unreduced cat.-min-atm}}$$

Plug Flow Reactor Model:

$$x = 1 - \exp\left(-\frac{Vdk}{2F}\right)$$

where x = fractional conversion

V = reactor volume $0.48\ \text{cm}^3$

d = catalyst density = $2.9\ \text{g/cm}^3$

k = kinetic constant,

$$\frac{\text{umoles } H_2\text{+CO converted}}{\text{g unreduced cat.-min-atm}}$$

F = molar flowrate = 223 umole/min

Substituting:

$$x = 1 - \exp\left(- \frac{(0.48)(130)(2.9)}{(2)(223)} \right)$$

$$x = 0.33$$

Activity (Reactor Basis):

$$r = xF$$

$$r = 74.4\ \frac{\text{umole } H_2\text{+CO converted}}{\text{min}}$$

$$r = 53.4\ \frac{\text{umole } H_2\text{+CO converted}}{\text{g cat.-min}}$$

Sulfur Loading:

Seven hour Poisoning Run:

$$7\ \text{hr}\left(\frac{10\ \text{cm}^3}{\text{min}}\right)\left(\frac{60\ \text{min}}{\text{hr}}\right)\left(\frac{0.02\ \text{mole H2S}}{22400\ \text{cm}^3}\right)\left(\frac{32.06\ \text{g S}}{\text{mole } H_2S}\right)$$

$$= 0.1202\ \text{g S}/0.48\ \text{cm}^3$$

$$= \left(\frac{120.2\ \text{mg S}}{0.48\ \text{cm}^3\ \text{cat}}\right)\left(\frac{\text{cm}^3\ \text{cat}}{2.9\ \text{g cat}}\right)\left(\frac{\text{g cat}}{0.644\ \text{g Fe}}\right)$$

$$= 134 \text{ mg S/g Fe}$$

Five minute Poisoning Run:

$$= (134 \text{ mg s/g Fe})\left(\frac{5 \text{ min}}{7 \text{ hr}}\right)\left(\frac{1 \text{ hr}}{60 \text{ min}}\right)$$

$$= 1.6 \text{ mg S/g Fe}$$