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CHEMISTRY AND MORPHOLOGY OF COAL LIQUE- FACTION QUARTERLY REPORT-OCTOBER 1, 1980 TO DECEMBER 31, 1980

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QUARTERLY REPORT

October 1, 1980 to December 31, 1980

CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION

Contract ET-78-G-01-3425

Principal Investigator: Heinz Heinemann

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Berkeley, CA. 94720

Introduction and Summary

During the first quarter of fiscal 1981 all tasks of this project had reached the experimental stage. Discussions between the Task Managers were continued and provided mutual stimulation. Three members of the project team attended the conference of Fossil Energy Contractors in Pittsburgh, Pa., on coal science and coal liquefaction on October 21 and 22, 1980, and discussed phases of Tasks 1, 2, and 5. The present quarterly report discusses:

- 1) Experiments on the effect of CO conversion on product distribution of hydrocarbons in a Fischer-Tropsch system.
- 2) The installation and testing of a mass spectrometer connected to the electron microscope's environmental cell. This will enable us to monitor primary products evolved during the visual observation of pyrolysis and hydro pyrolysis.
- 3) First observations of surface structural changes during the hydrogenation of graphite in the absence and presence of Ni catalysts. These should lead to a better understanding of catalyst activity, poisoning and redistribution during reaction.
- 4) The potential for hydrogen shifts in aromatic rings liganded to transition metals.
- 5) Organo metallic hydrogen transfer catalysts. It has been demonstrated that $\text{Mn}(\text{CO})_{10}$ will catalyze the water-gas shift reaction and transfer hydrogen from the water to an acceptor molecule.
- 6) Initial operation of a unit designed to observe under controlled conditions the deposition of metals from coal or petroleum liquids on hydrotreating catalysts. Kinetics of demetallation and place and depth of deposition are being investigated.

TASK 1 - Selective Synthesis of Gasoline Range Components from CO and H₂.

Task Manager: A. T. Bell

The two pieces of equipment described in the September 30 report are now in operation.

Experiments were initiated to determine the effects of CO conversion on the distribution of hydrocarbons formed over an iron catalyst promoted with both potassium and alumina (synthetic ammonia catalyst). Fifteen grams (6.3 cm³) of the catalyst were placed in 1/4" O.D. stainless-steel tube reactor and reduced with H₂ for 48h in flowing H₂ at 300°C and 1 atm. The temperature was then reduced to 250°C, and a feed composed of a 2:1 H₂/CO mixture was introduced, also at 1 atm.

Using a feed flow rate of 600 cm³/min, it was observed that the activity of the freshly reduced catalyst slowly declined with time. The conversion was about 2% initially, dropped to 0.6% after 24 hrs and remained reasonably constant thereafter. The distribution of reaction products observed during this period is shown in Table 1. The distribution of C₁ through C₅ hydrocarbons roughly obeys a Schultz-Flory distribution, characterized by an α of 0.35. It is of interest to note that a stable product distribution is achieved after 6h, even though a stable catalyst activity is not yet achieved at this point. Table 1 also shows that the product is principally olefinic and that the olefin to paraffin ratio appears to decline as the catalyst deactivates. This trend, which is seen most clearly for the C₂ and C₃ products, suggests that the sites for the synthesis of olefins deactivate more rapidly than do those which participate in olefin hydrogenation to paraffins.

After a steady-state activity had been obtained at 600 cm³/min, the flow rate was gradually decreased in a stepwise fashion. At each new flow rate the catalyst was allowed to approach a new steady state. Effects of flow rate on the distribution of products formed is shown in Table 2. It is apparent that as the flow rate decreases the conversion of CO increases, but the degree of change is a good deal smaller than would be expected on the basis of the changes in space velocity. The reason for these changes is not known at present and may be associated with further catalyst deactivation between runs. The second effect of increasing flow rate apparent from Table 2 is a decrease in the ratios C_n/C₁. The origin of this trend is not understood, but it is possible that paraffin hydrolysis may be responsible for an increase in the relative yield of methane at lower feed flow rates.

The present results must be regarded as highly preliminary and demonstrate more than anything else the proper performance of the apparatus. Work to be conducted during the next quarter will more fully explore the effects of flow rate on product distribution. In particular efforts will be made to obtain data at significantly higher CO conversions than those presented here. For such cases it is expected that secondary reactions of the olefins will be much more pronounced and will influence the product distribution to a greater degree. In pursuing these studies data will be taken at 1 atm as well as at higher pressures.

Table 1
Effects of Reaction Time on the Distribution of
Hydrocarbon Products

Time(h)	1.5	6	9	24	27
C_2/C_1	0.55	0.39	0.39	0.38	0.34
C_3/C_1	0.38	0.32	0.34	0.32	0.39
C_4/C_1	0.20	0.15	0.13	0.14	0.09
C_5/C_1	0.10	0.07	0.07	-	0.06
CO conv (%)	1.73	1.13	1.01	0.55	0.51

Table 2
Effects of Flow Rate on the Distribution of
Hydrocarbon Products

Flow rate (cm ³ /min)	600	400	100	50
$c_2^{\bar{=}}/c_1$	0.20	0.18	0.10	0.11
$c_2^{\bar{-}}/c_1$	0.14	0.17	0.12	0.15
$c_3^{\bar{=}}/c_1$	0.28	0.12	0.12	0.13
$c_3^{\bar{-}}/c_1$	0.11	0.10	0.04	0.05
$c_4^{\bar{=}}/c_1$	0.07	-	0.03	0.04
$c_4^{\bar{-}}/c_1$	0.02	-	0.03	0.02
$c_5^{\bar{=}}/c_1$	0.04	-	0.02	0.02
$c_5^{\bar{-}}/c_1$	0.02	-	0.01	0.01
CO conv. (%)	0.51	0.60	0.71	1.20

TASK 2 - Electron Microscope Studies of Coal During Hydrogenation

Task Manager: J. W. Evans

A mass spectrometer has been acquired for use in connection with the electron microscope studies of coal which have been discussed in previous reports. In such studies, an environmental cell within the electron microscope is being used to contact carbonaceous samples with gasifying atmospheres. The mass spectrometer is to be used to analyze the products of such gasification and simultaneously provide information on the rate of reaction (by auxilliary measurements of gas flow rates through the cell). The mass spectrometer arrived last quarter, was assembled this quarter and some preliminary tests were carried out to check that it was working.

Figure 1 shows the spectrometer response when air was bled into the instrument. The peaks for the expected air constituents are clearly discernible. Figure 2 shows the response of the instrument to air bled into the system through a water saturator. The enhanced water vapor peak is as expected.

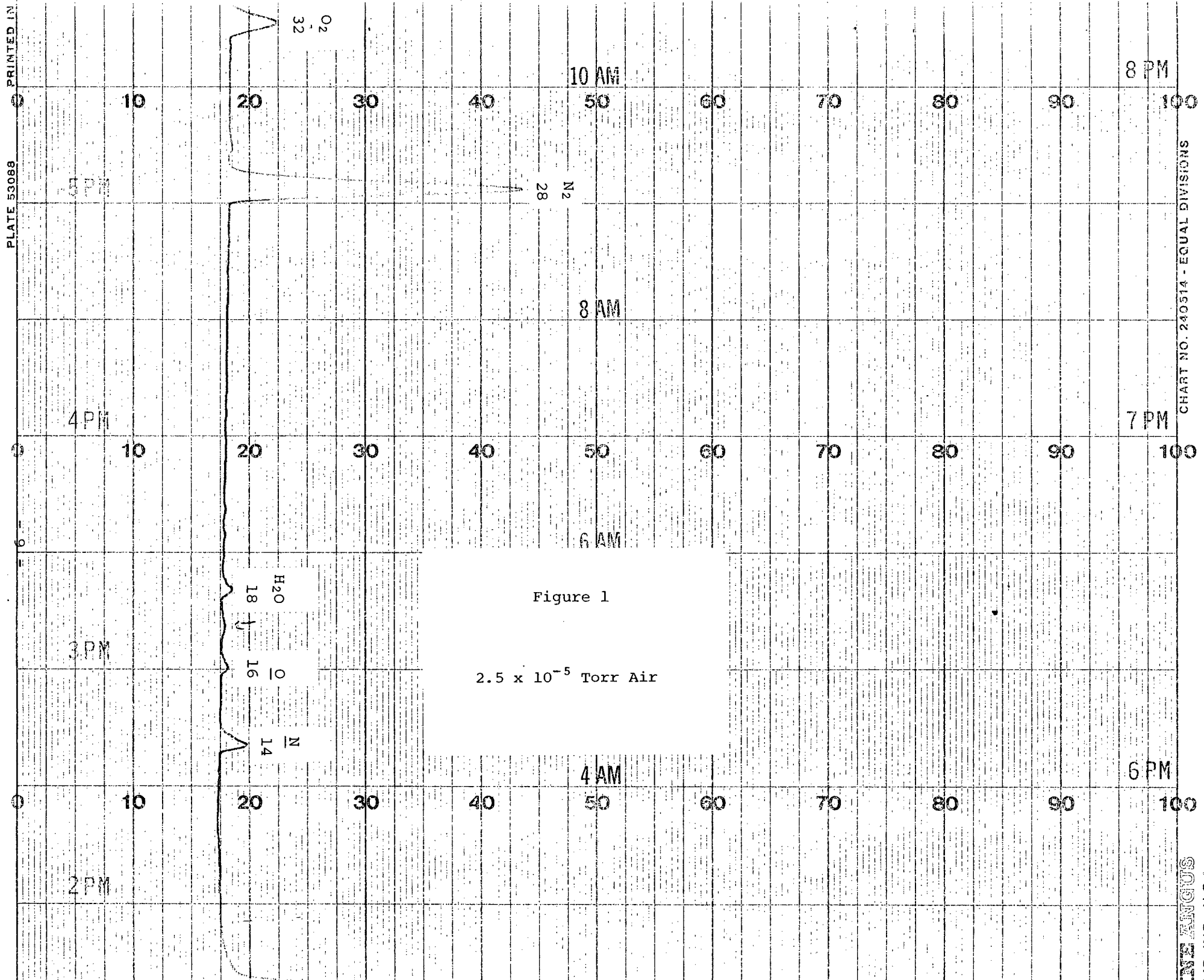
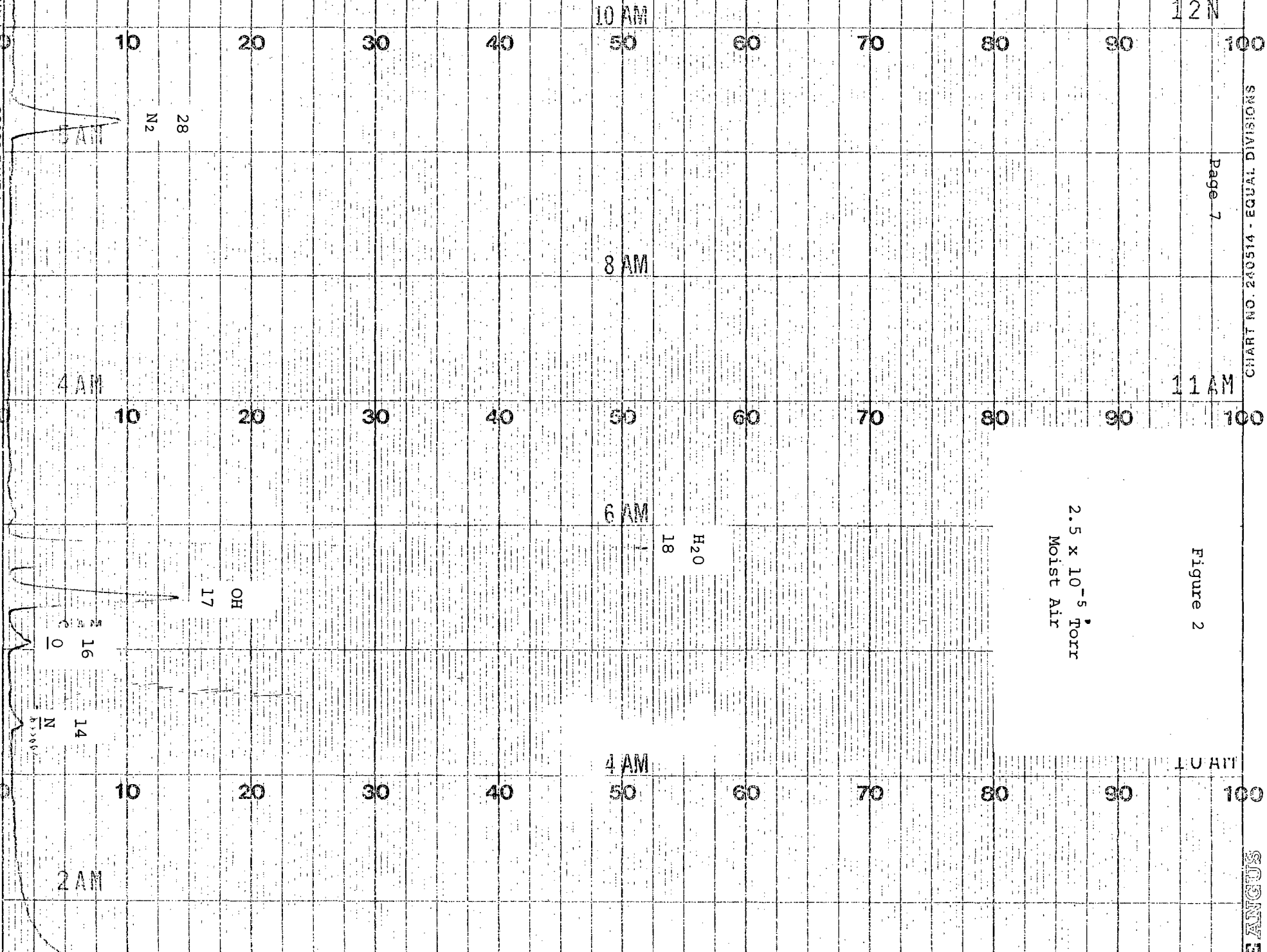


Figure 1

2.5×10^{-5} Torr Air

32
02



12 N

11 AM

Figure 2

2.5×10^{-5} Torr
Moist Air

10 AM

Task 3 - Catalyzed Low Temperature Hydrogenation of Coal.

Task Manager: G. A. Somorjai; work with A. Cabrera

Using the apparatus and spectrographic techniques described in the annual report (October 1, 1980) the surface of a piece of pyrolytic graphite was characterized and an attempt made to hydrogenate the graphite to establish a standard for future comparisons of reactions of carbons with hydrogen in the presence of catalysts. Experiments were also carried out reacting graphite-containing nickel with hydrogen and with CO. It was found that the nickel containing graphite was an excellent CO methanation catalyst.

A piece of pyrolytic graphite was hydrogenated 745°C and 5 atm of H_2 . This is the lowest temperature at which some methane is detected. There is an induction period of 49 min. before any methane is produced. After two minutes the production stopped due to a possible poisoning. The same piece of graphite with some Ni deposited on its surface was again hydrogenated. In this case, the production of methane was 2.3 times higher than that of pure graphite. There is a shorter induction period than in the case of pure graphite (only 5 min), but nevertheless the sample is poisoned after two minutes of methane production.

Experimental Details

A. Pure Graphite - A piece of graphite with dimensions of 0.75 x 0.60 x 0.05 cm was mounted on the manipulator. Two pieces of Pt wire (0.020") served as support for the graphite as well as contacts to provide heating to the sample by means of an electrical current. The contact was made just by pressing the wire against the graphite. This allowed heating the sample from room temperature to $1,000^{\circ}\text{C}$ in vacuum. The temperature of the sample was monitored by means of a chromel-alumel thermocouple that was in direct contact with the graphite. When the manipulator was positioned inside the high pressure system the sample was accessible to LEED, AES, ion sputtering and mass spectrometry. On the other hand, the reactions at high pressures were monitored with an HP 5880A gas chromatograph and the concentration of the gases was measured by means of a TC detector which has a sensitivity of detecting 1 ppm. All the gases used in the experiments were research grade purity. The sample was flashed up to $1,000^{\circ}\text{C}$ and when it cooled down to room temperature an Auger spectrum was taken from the graphite. The Auger spectrum revealed that the graphite surface was free of sulfur or other contaminants as it is shown in Figure 1. Inspection of the graphite with LEED did not show a diffraction pattern which meant that the basal planes of the graphite were disoriented.

The high pressure studies were carried out with the isolation cell closed. After the reactor was filled up with 5 atm of H_2 , the temperature of the sample was raised until some CH_4 was detected. At 745°C , after an induction period of 49 min, a concentration of $7.2 \cdot 10^{-5}$ mole of CH_4 ($4.3 \cdot 10^{19}$ molecules of CH_4) was obtained. This concentration remained constant during the 2 hours that the reaction was monitored with the G.C. This piece of graphite was then subjected to Ar sputtering during 15 min at 2.5 kv. The idea was to produce defects on the graphite surface to make it more reactive towards methanation. Argon sputtering

was ineffective and the production of CH_4 was comparable to that measured before this treatment. Experiments on thermal desorption were performed with this piece of graphite; the sample was exposed to H_2 or CO and the respective thermal desorption patterns were registered for different exposures. The heating rate was $20^\circ\text{C}/\text{sec}$ and the sample was heated between room temperature and $1,000^\circ\text{C}$. The adsorption of these gases was very weak; we can observe two peaks in the CO desorption, at 200°C and at 700°C while there is only one peak at 270°C for the H_2 desorption, as one can see in Figure 2. Since this adsorption was so weak, it was suspected that the gases detected during desorption could have come from the Pt wires. Thermal desorption was then carried out substituting the graphite by a piece of Au foil. After exposure of the gold to either CO or H_2 , the gold was flashed up to $1,000^\circ\text{C}$. Neither CO nor H_2 was detected with the mass spectrometer. Figure 2 notes that the adsorption of the gases seems to be very insensitive to exposure, especially in the case of H_2 .

Graphite With Nickel

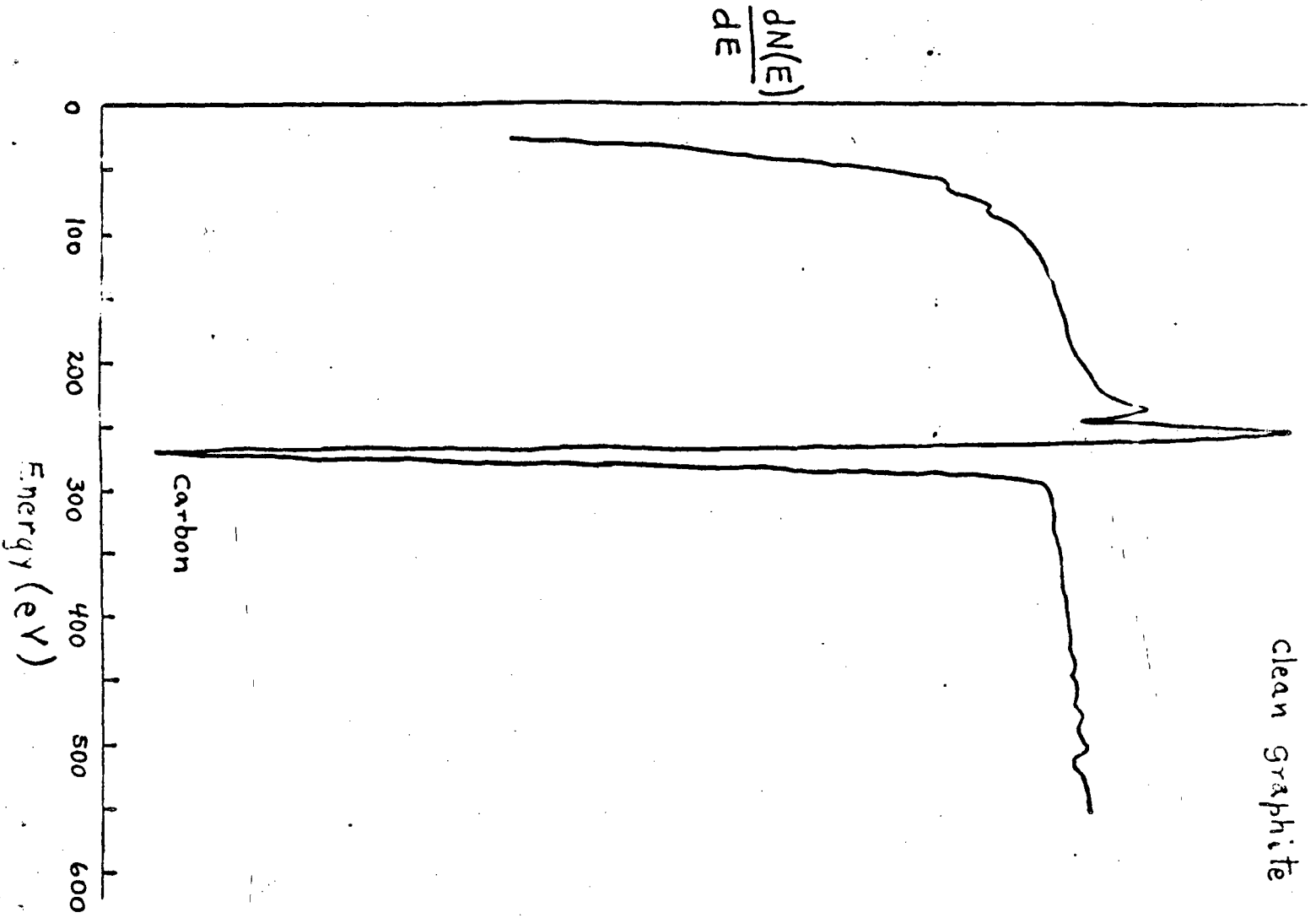
Nickel was evaporated onto both faces of the same piece of graphite used in previous experiments. In a test chamber at a pressure of 1×10^{-6} torr, 3.6 mg of Ni were evaporated from a W filament over the graphite. The sample was placed at 4 cm from the source, and from geometrical considerations it was calculated that it should have received only 3 thousandths of the total amount of Ni evaporated, which is equivalent to 1.2×10^{17} atoms of Ni on each face of the piece of graphite. This piece of graphite was then mounted in the UHV system and an Auger spectrum was taken. The spectrum showed the presence of the Ni in an oxidized state, some Cl and also a big peak corresponding to carbon, as one can see in Figure 3.

The sample was then tested in a hydrogenation reaction; with the cell closed, the reactor was charged with 5 atm of H_2 and the sample was then heated until some methane was detected. At 750°C , after a period of 5 min, a concentration of 1.68×10^{-4} mole of CH_4 (1.01×10^{20} molecules of CH_4) was obtained. This concentration remained constant for 1 hour during which the reaction was monitored by the G. C. The amount of methane did not increase when the temperature was increased to 800°C .

Thermal desorption experiments were performed with this sample; the sample was exposed to CO or H_2 for different periods of time and then flashed up to $1,000^\circ\text{C}$. The thermal desorption spectra were registered for different exposures and they are displayed in Figure 4. In this case, the high temperature peak of the CO desorption has disappeared and the low temperature peak at 250°C is ~ 4.5 times bigger than in the case of pure graphite (see Figure 2). In the case of H_2 desorption, the area of the peak is only ~ 2.8 times bigger than in the case of H_2 desorption from pure graphite (at saturation coverage).

Since the adsorption of the reactants by the substrate is an important intermediate step in the chemical reactions and due to the adsorption of CO seems to be much stronger than the adsorption of H₂ over this sample, it was considered worthwhile to try a CO - hydrogenation reaction. The reactor was then filled up to 5 atm with a mixture of 3H₂:1 CO. The sample was heated to 586°C and the H₂, CO and CH₄ concentrations were measured with the GC. The concentration of CH₄ vs. time for two temperatures (586°C and 735°C) is displayed in Fig. 5. At 735°C, after 2.5 hrs, the fractional conversion of CO to CH₄ was roughly 14%.

After these two runs were completed an Auger spectrum was taken from the sample. As one can see in Figure 6 almost all the peaks corresponding to Ni were missing with the exception of one, oxygen is still present and a peak corresponding to silicon also showed up.



clean graphite

Fig 1.

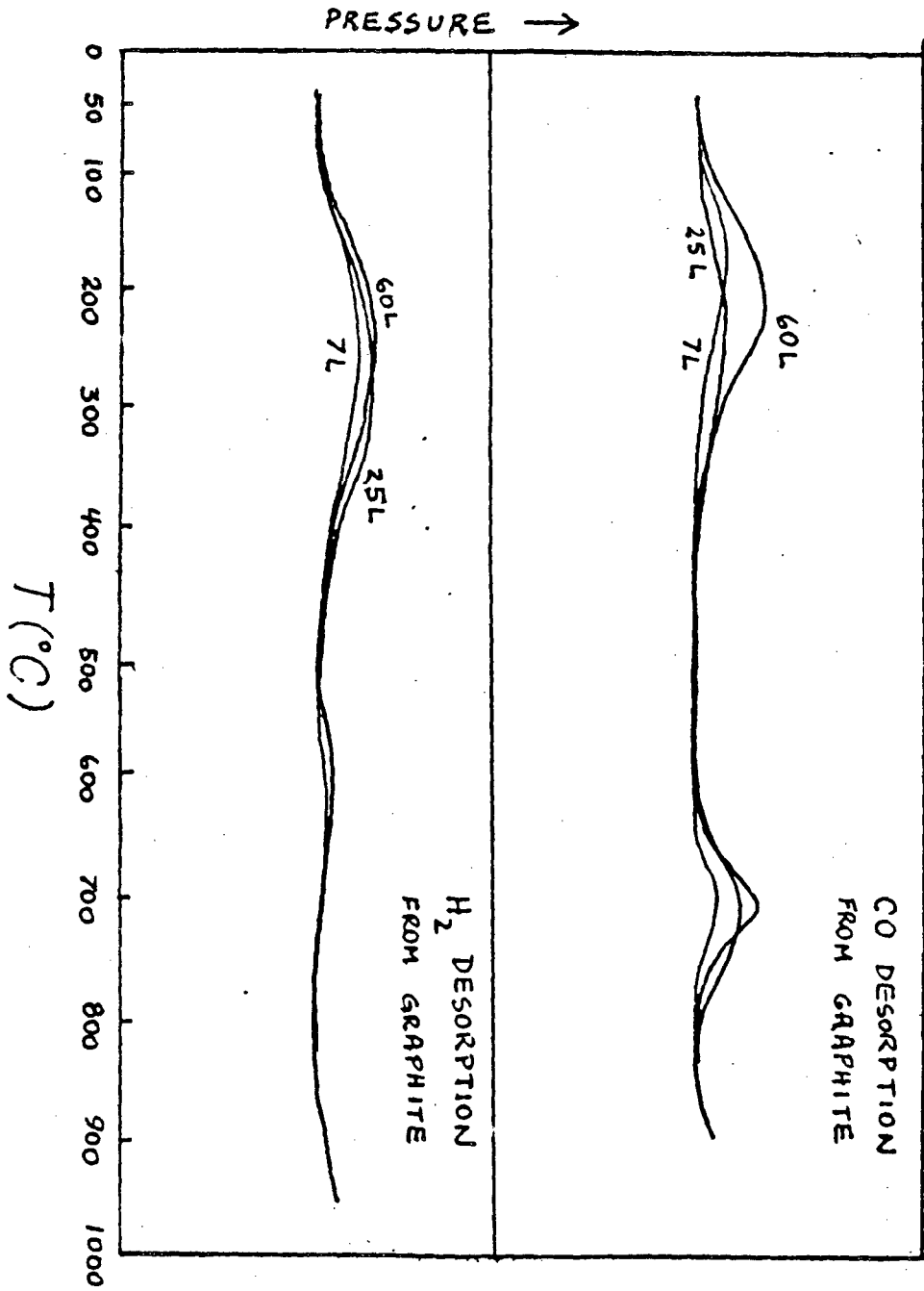


Fig 2.

graphite after Ni deposition

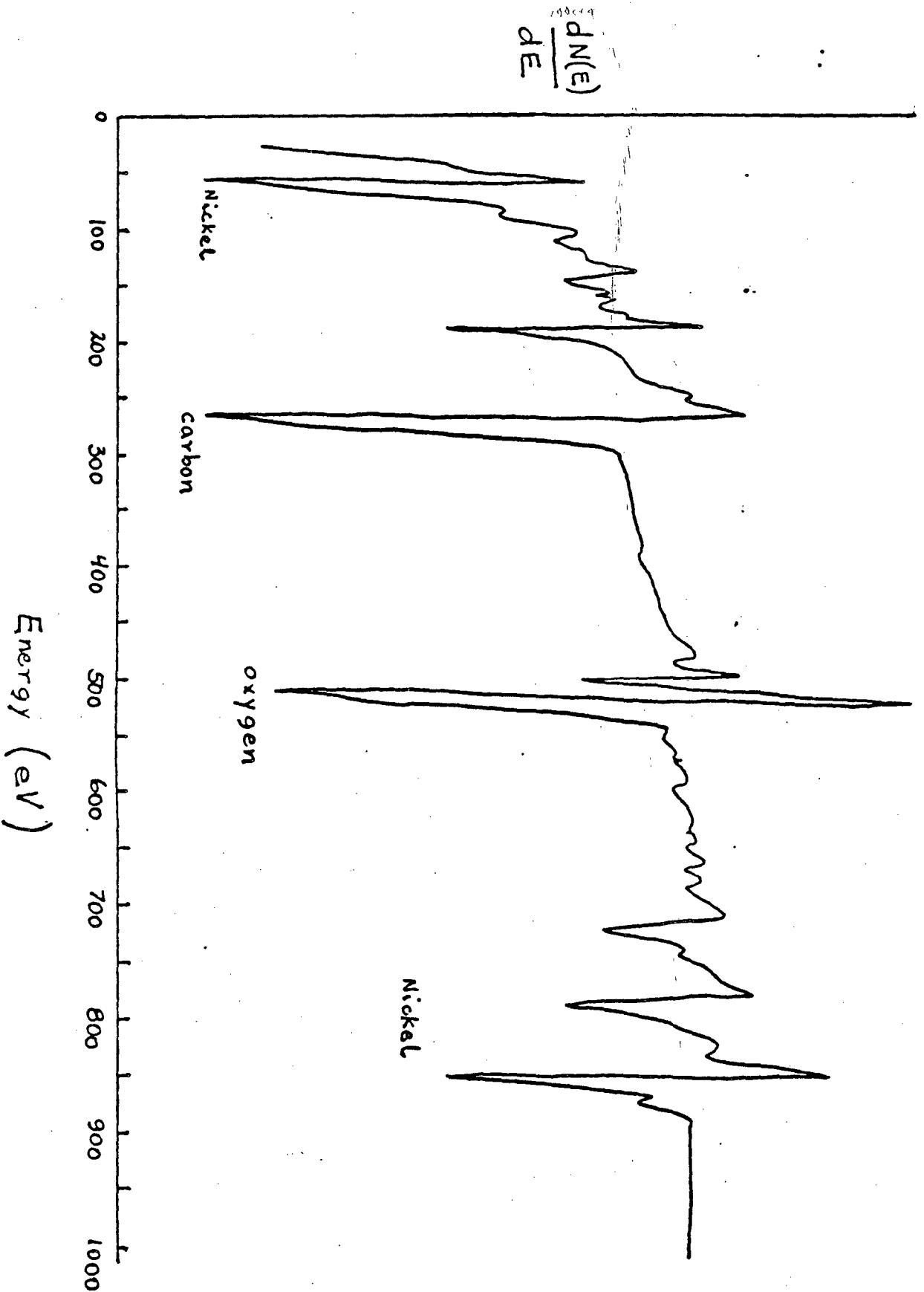


Fig 3

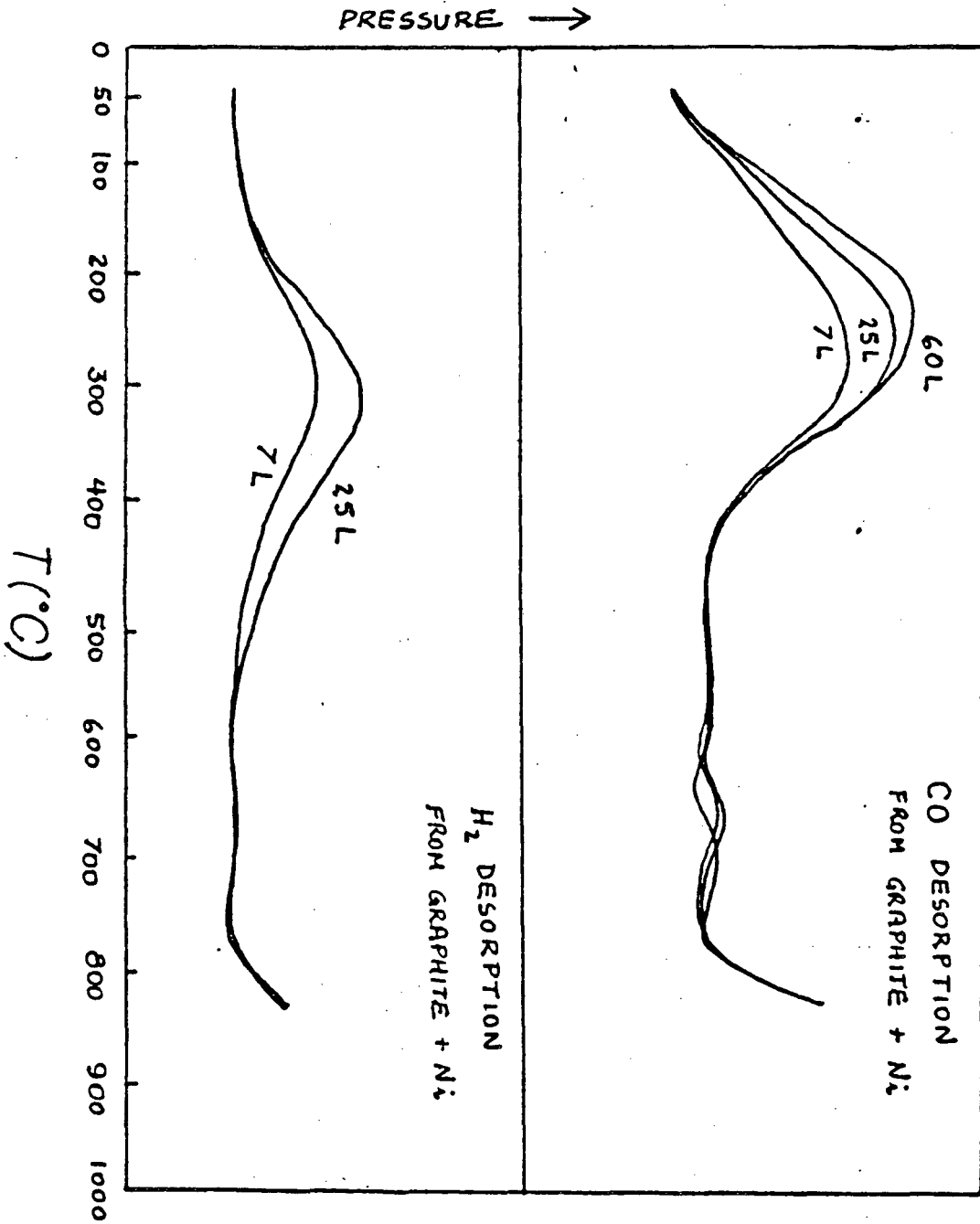


Fig 4.

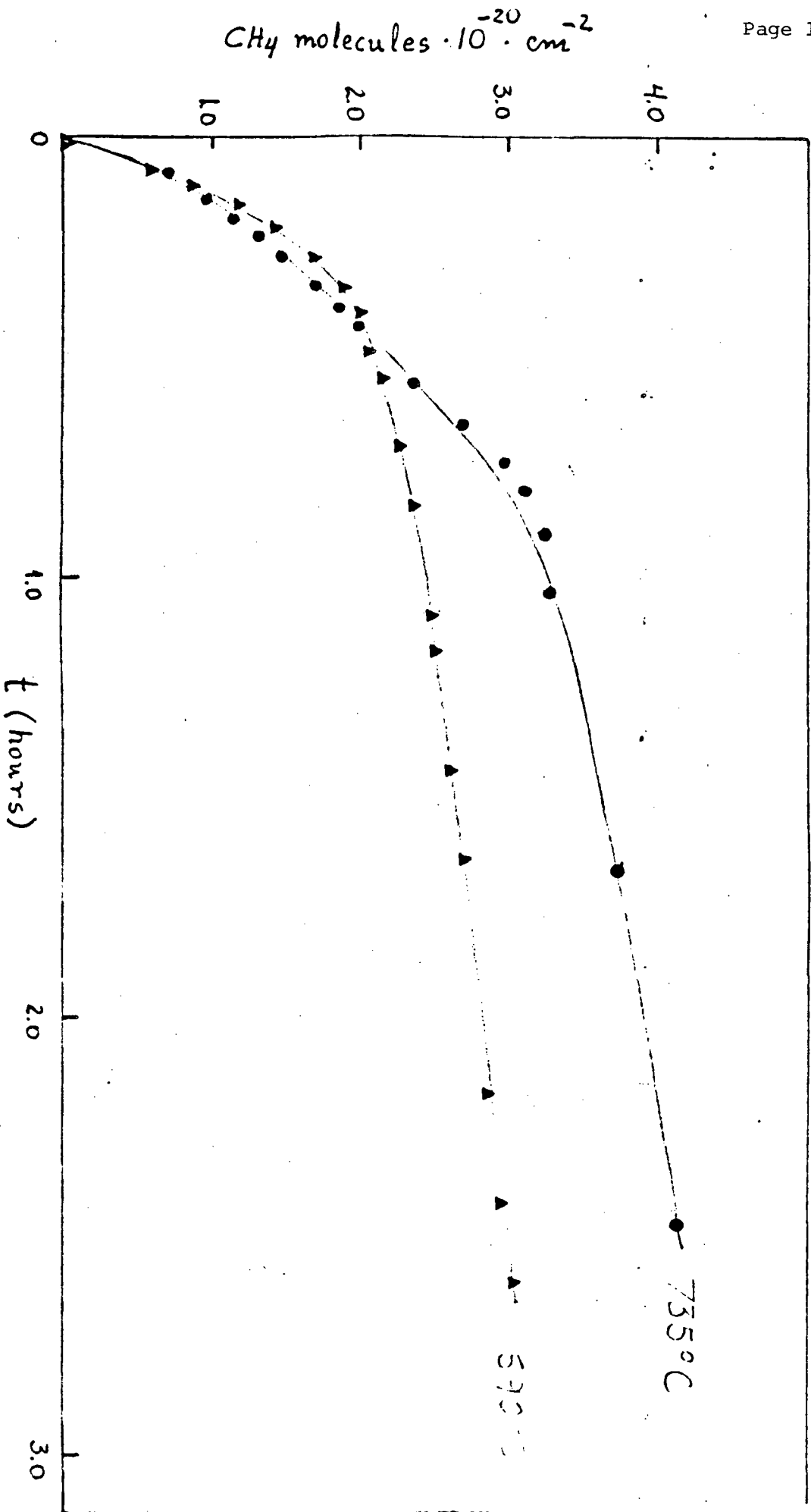
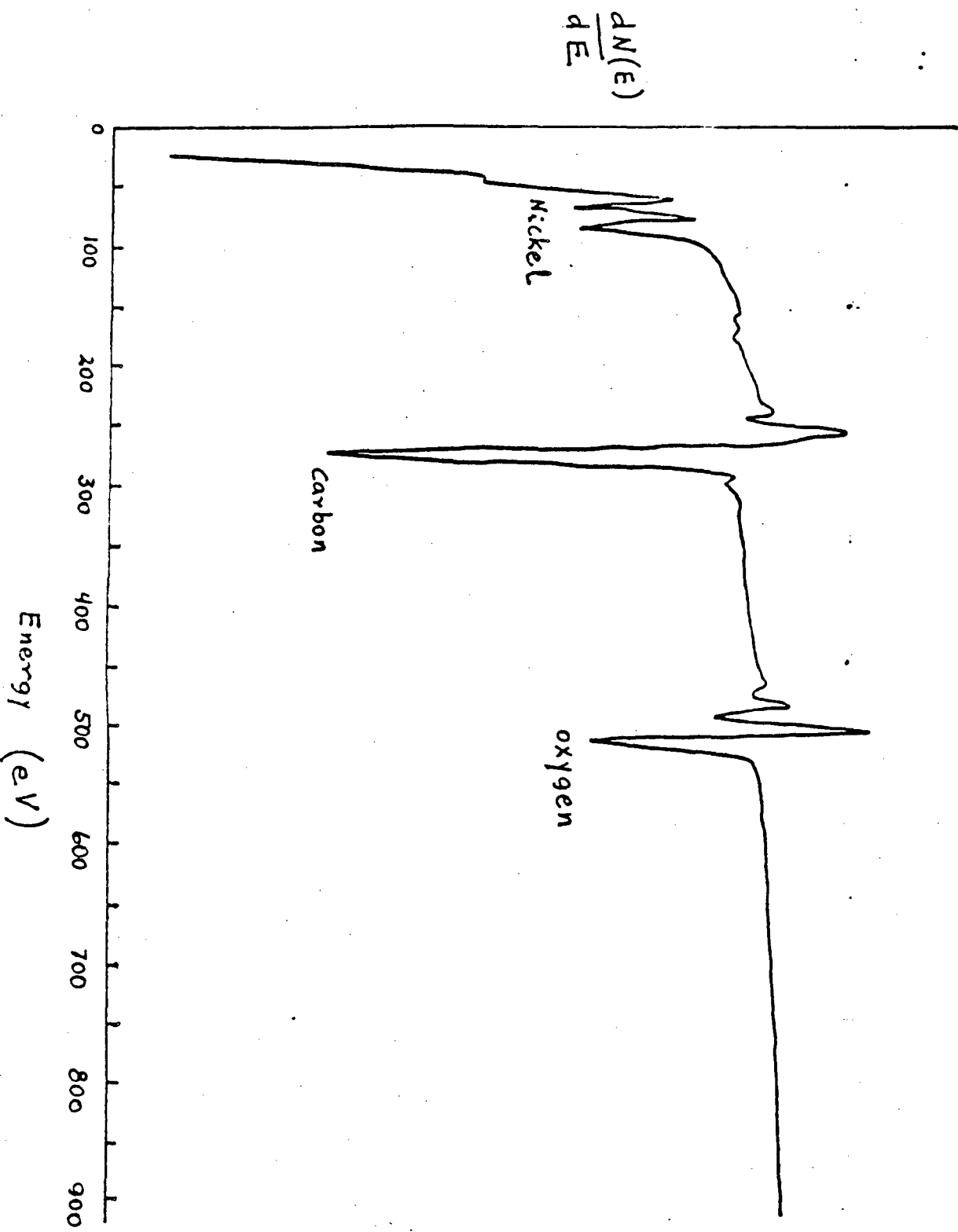


Fig 5.



graphite + Ni after
CO - hydrogenation reaction

Fig 6.

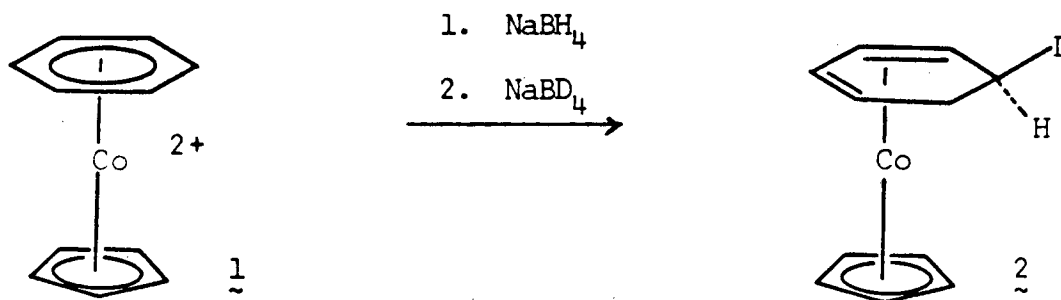
Task 4: Selective Hydrogenation, Hydrogenolysis and Alkylation of Coal and Coal Liquids by Organo Metallic Systems

Task Manager: K. P. C. Vollhardt

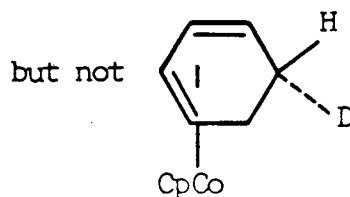
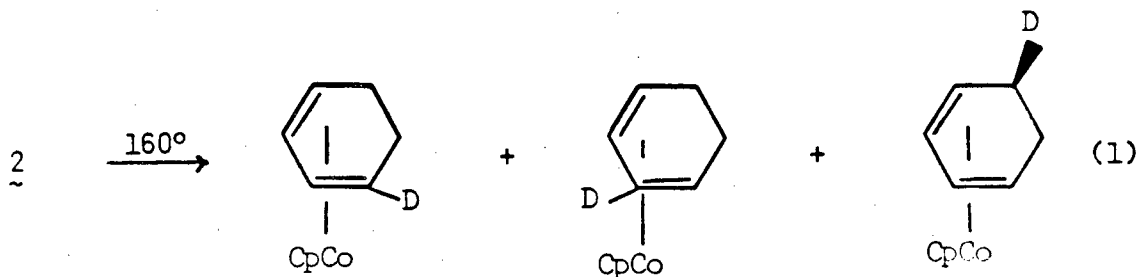
1. Models for Metal Catalyzed Thermal Hydrogen Shifts

Several transition metal complexes have been synthesized in order to establish the potential for hydrogen shifts in aromatic ring derived π -ligands to transition metals.

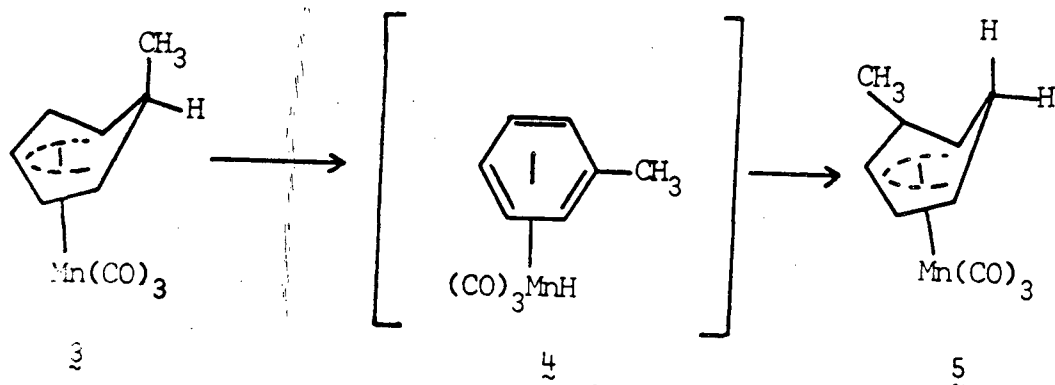
The cationic CpCo-benzene complex **1** was treated first with sodium borohydride then with the corresponding deuteride to generate **2** with the deuterium label placed stereospecifically in the exo position.



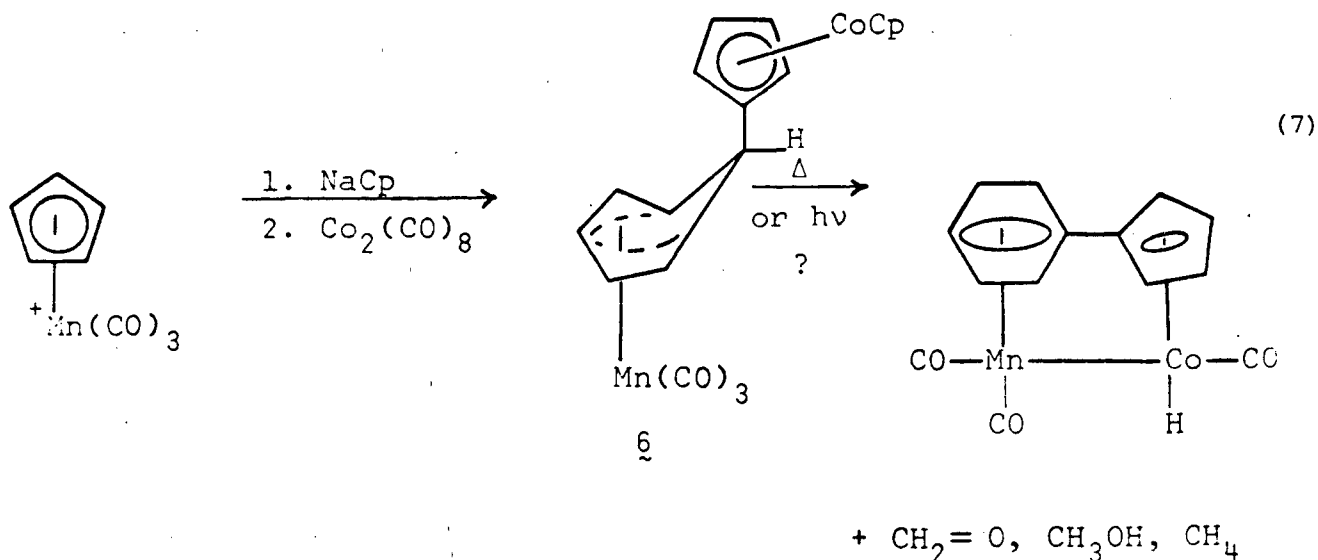
When **2** was heated to 160°C in C_6D_6 (7h) the deuterium was found to have scrambled to all non-endo positions (1). This finding is consistent with the occurrence of intramolecular metal-hydride intermediates allowing specifically migration of only endo-hydrogen atoms.



Similar metal hydrides (e.g. 4) have been postulated for the thermal rearrangement of 3 to 5.



In order to possibly intramolecularly trap an arrangement such as 4 compound 6 was synthesized. Pyrolysis or photolysis might produce 7 and/or CO reduction products (2). This is under investigation.



2. Friedel-Crafts Alkylation and Cleavage of Benzene

Further aspects of the apparent Fischer-Tropsch alkylation of benzene are being investigated, particularly variation of catalysts, use of D₂ and ¹³C₁₈O, a plot of product concentration changes with time, and conversion of C₆D₆ and C₆H₆/¹³C₆H₆ mixtures. New personnel has set up new apparatus and confirmed findings previously reported.

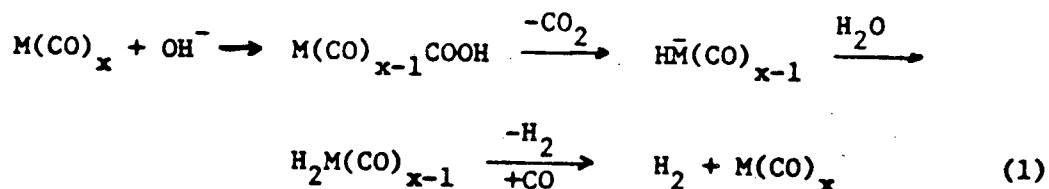
Task 5: Chemistry of Coal Solubilization and Liquefaction Pyrolysis Studies.

Task Managers: R. G. Bergman, T. Vermeulen, and R. H. Fish

1. Hydrogen Transfer Mechanism Studies

It is important to elucidate the hydrogen transfer mechanism in coal liquefaction, to define the transfer agent and the mechanism of reaction. We have initiated a series of experiments to define the role of transition metal hydrides as plausible hydrogen transfer agents from donor to acceptor molecules in the coal matrix.

Recently, work by Pettit et al.¹ has elegantly shown that the water gas shift reaction, "WGS," can be used with a wide variety of transition metal carbonyl compounds to generate transition metal hydrides catalytically. This is readily accomplished by reaction of transition metal carbonyls (e.g., Fe(CO)₅, Ru₃(CO)₁₂, Os₃(CO)₁₂, Rh₆(CO)₁₆), with a weak base, such as an aqueous solution of trimethylamine or aqueous solutions of bicarbonate or carbonate, in the presence of carbon monoxide (eq. 1).



We have performed the following reactions with coal model compounds:

"WGS" Catalyst	Solvent	Acceptor	S/C Ratio	Temp (°C)	Time (hr)	CO Base	(psi)	Product (GC)
Fe(CO) ₅	THF	Anthracene	100	110°	10	Me ₃ N/H ₂ O	350	Trace 9,10-dihydroanthracene
Fe(CO) ₅	THF	Anthracene	2	160°	24	MeN/H ₂ O	350	"
Fe(CO) ₅	THF	Phenanthrene	2	110°	20	Me ₃ N/H ₂ O	350	Trace 9, 10-dihydrophenanthrene
Ru ₃ (CO) ₁₂	THF	Phenanthrene	100	100°	10	Me ₃ N/H ₂ O	350	"
Ru ₃ (CO) ₁₂	THF	Anthracene	100	100°	10	Me ₃ N/H ₂ O	350	Trace 9, 10-dihydroanthracene
Ru ₃ (CO) ₁₂	THF	"	333	100°	5	0.1M KHCO ₃	350	"
Mn ₂ (CO) ₁₀	THF	"	20	160°	5	0.1 "	350	~1.5% 9, 10-dihydroanthracene
Mn ₂ (CO) ₁₀	THF	"	20	160°	15	H ₂ O	350	~ 10% "
Mn ₂ (CO) ₁₀	THF	"	20	160°	5	-	350	-
Mn ₂ (CO) ₁₀	THF	"	20	160°	5	D ₂ O	350	~ 5% 9,10-dideuteroanthracene

Preliminary results provide the following conclusions:

- 1) Fe(CO)₅ is a poor "WGS" catalyst and provides only trace product.
- 2) Ru₃(CO)₁₂ is an excellent "WGS" catalyst (dramatic increase in pressure due presumably to H₂), however, does not appear under the present conditions to hydrogenate aromatic coal models to any significant extent.
- 3) Mn₂(CO)₁₀ seems to give the desired product, however, in low yield. The lack of product when water is omitted tentatively indicates that THF is not acting as a hydrogen source. Presumably H₃Mn₃(CO)₁₂ or a similar complex is formed via the "WGS" reaction and is the reactive hydrogenating agent. The experiment with D₂O and the resultant product, dideuteroanthracene, clearly demonstrates that hydrogenation of the acceptor occurs with hydrogen from water, produced by the water gas shift.

References

- 1) H. Kang, C. H. Mauldin, T. Cole, W. Slegein, K. Cann and R. Pettit, J. Am. Chem. Soc., 99, 8323 (1977).
- 2) H. D. Kaesz, J. Organometal, Chem., 200, 145 (1980) and references therein.

2. Mechanism of Dehydrogenation of Tetralin

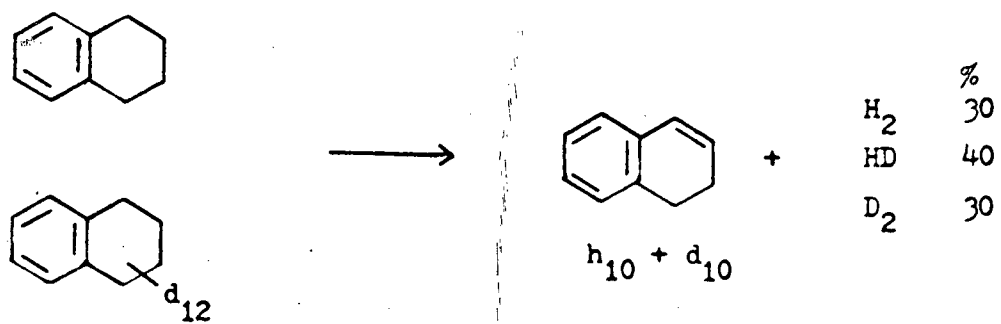
The thermal decomposition of tetralin (1) has been of interest recently in investigations of solvent hydrogen donor molecules involved in coal liquefaction. Two labelled tetralins, 1-d₁₂ and cis-1,2-dihydrotetralin-d₁₀ (1-d₁₀), were synthesized and thermalized in order to elucidate the mechanism of dehydrogenation of tetralin.

Tetralin-d₁₂ was thermalized in the presence of tetralin-h₁₂ in order to determine whether or not the hydrogen formed was isotopically scrambled. The non-condensable gases were analyzed by mass spectroscopy and found to be a mixture of H₂, HD, and D₂ in the ratio depicted in Scheme 1. The starting tetralins did not show detectable scrambling of hydrogens.

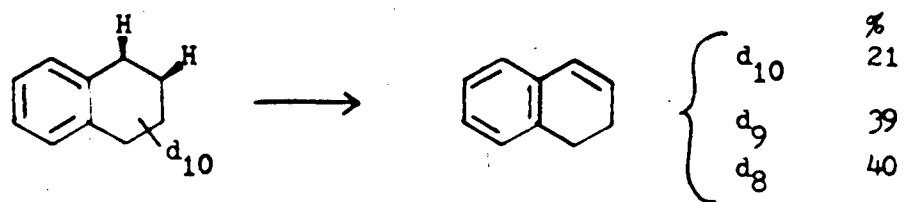
Cis-1,2-dihydrotetralin-D₁₀ was thermalized and the high-molecular weight products were analyzed by GC-mass spectroscopy. The 1,2-dihydronaphthalene formed was composed of the D₈, D₉, and D₁₀ in the ratios indicated in Scheme II. Both sets of experiments indicate that the mechanism is not a concerted cis elimination of hydrogen.

1960-1961

Scheme I



Scheme II



Task 6: Coal Conversion Catalysts-Deactivation Studies

Task Managers: A. V. Levy and E. E. Petersen

During the current quarter the apparatus described in the annual report (October 1, 1980) has been completed, pressure tested and initial runs have been made to determine the kinetics of demetallation of a metal enriched gas oil by a commercial hydrotreating catalyst. Ranges of operating variables are:

Temperature: 200-400°C
Pressure: 700-1000 psig.
Concentration of metals in feed: 100-1000 ppm
Oil/Catalyst ratio (c.c./g.): 50-100

In an initial run at relatively mild conditions (235°C, 700 psig, Oil/Cat ratio 79) the vanadium concentration in the oil was reduced from 460 ppm to 350 ppm (~ 25%) after 5 hours, using a Trilobe HDS-20A catalyst (CoMo₃ 1/8" cylindrical.) Other runs have been made but not yet fully analyzed. Catalyst samples have been removed and will be studied by SEM and other methods to determine the metal deposition and distribution on the catalyst.

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