To the Graduate Council:

We are submitting herewith a dissertation written by Scott Edward Walters, entitled "Studies in Molten Chloroaluminates; A. Fischer-Tropsch Synthesis Using Metallic Dispersions; B. Infrared Spectroelectrochemistry Using Attenuated Total Reflectance." We have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

Gleb Mamantov, Major Professor

We have read this dissertation
and recommend its acceptance:

Accepted for the Council:

The Graduate School

STUDIES IN MOLTEN CHLOROALUMINATES;

A. FISCHER-TROPSCH SYNTHESIS USING METALLIC DISPERSIONS

B. INFRARED SPECTROELECTROCHEMISTRY USING ATTENUATED TOTAL REFLECTANCE

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Scott Edward Walters

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DEDICATION

The author wishes to dedicate this work to his lovely wife Carol, his daughter Amy, and his son Jason, for putting up with him and sacrificing for him during the course of this endeavor.

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ABSTRACT

The Fischer-Tropsch activity of several metallic catalysts in molten chloroaluminates has been studied at relatively low pressures. Low conversions of CO to alkanes were observed for Co, Fe, Ni, Pd, Pt, Ir, Rh and Re. No reaction was observed for W, Ta and the pure chloroaluminate melt. Methane was the major product formed using any of these heterogeneous catalysts. The most favorable product distribution for these metals was observed for Ni catalysts, since less than half of the products was CH_4.

The effect of aluminum on the Fischer-Tropsch activity of these metallic catalysts in molten chloroaluminates has also been studied. In all cases, the conversion of CO was enhanced by the presence of aluminum. The magnitude of enhancement depended on the catalyst. Large enhancements were observed for Co, Ni and Fe catalysts, while only slight enhancements were observed for Pd, Pt and Re. Aluminum behaved as a reagent, and not as a catalyst, since CO conversion varied with the amount of Al in the system. The effect of Al on product distribution was also largely dependent on the metal catalyst involved. Small amounts of Al increased the production of CH_4 relative to the other products for Co, Fe and Ni catalysts, while no clear pattern emerged for these catalysts, when larger amounts of Al were present.

The $Ir_4(CO)_{12}$ catalyst precursor was also studied in chloroaluminate melts. In batch reactions at relatively long times, a slight excess of CH_4 over C_2H_6 was found. No CH_3Cl was detected. In a recycle-flow reactor, C_2H_6 was produced in greater amounts than CH_4.

CH_3Cl was observed in the flow system. Enhancement by Al was found to be greater for small amounts of Al than for large amounts. The proportion of CH_4 in the products was observed to increase with increasing Al content.

An infrared spectroelectrochemical cell, based on attenuated total reflectance using a silicon crystal, has been developed for use in molten chloroaluminates. Spectra of chloranil and its reduction products have been obtained.

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PART A

FISCHER-TROPSCH SYNTHESIS USING METALLIC DISPERSIONS

CHAPTER I

INTRODUCTION TO THE REACTION BETWEEN CARBON MONOXIDE AND HYDROGEN

The Fischer-Tropsch reaction is the catalytic reduction of carbon monoxide by hydrogen to produce hydrocarbons.[1] Oxygen-containing products are obtained as byproducts.[2] This process is quite exothermic; the heat of formation for alkane production is -165 kJ/mole.[2] The major problem with the Fischer-Tropsch synthesis is the lack of selectivity by the catalysts. Not only is a variety of types of products formed, but the carbon chain length can vary from one to well over twenty.

Economics has played a key role in the development of Fischer-Tropsch catalysts. Coal-derived synthesis gas (carbon monoxide and hydrogen) used to produce gasoline and other products by the Fischer-Tropsch process was very important to the war effort in Germany during World War II; 600,000 tons of products were produced in 1944 alone.[3] In the early 1950's as inexpensive petroleum and natural gas became available, interest in the more costly hydrocarbon production from synthesis gas decreased. Only in South Africa, where an abundance of coal continued to make the Fischer-Tropsch process financially attractive, the interest in synthesis gas chemistry remained high in the fifties and sixties. As natural gas supplies dwindled, and as oil prices increased following the oil embargo in 1973, the cost of chemical feedstocks rose dramatically. The large increase in the prices of oil and feedstocks in the last ten years is illustrated in Table I. Prices of oil and petroleum-derived chemicals are expected to

TABLE I

PRICES OF PETROLEUM AND SOME CHEMICAL FEEDSTOCKS, TEN YEARS AGO AND TODAY

	1973 (prior to embargo)[a]	April 1983[b,c]
Crude oil ($/bbl.)	3.0	29.9
feedstocks (¢/lb.)		
benzene	4.1	21.2
butadiene	4.7	32.8
ethylene	3.0	22.5
propylene	2.9	19.5
toluene	2.4	20.3
p-xylene	4.5	25.0

[a]D. L. King, J. A. Cusumano, and R. L. Garten, Catal. Rev., 23, 233 (1981).

[b]Wall St. J., Apr. 25, 50 (1983).

[c]Chem. Market Rept., Apr. 25, 34 (1983).

rise still higher in the future, due to both the increased costs of recovering the remaining oil and the unstable political situation in the Middle East. Higher prices are reviving interest in Fischer-Tropsch chemistry, as well as related technology, to convert coal into usable chemicals and fuels.

A. A Historical Review of Fischer-Tropsch Catalysts

In 1902 Sabatier and Senderens[4] demonstrated the conversion of carbon monoxide and hydrogen into methane over nickel at atmospheric pressure and 250°C. This important discovery (the methanation reaction) was the impetus to further research which led to the development of the Fischer-Tropsch synthesis.

Badische Anilin und Soda Fabrik took out several patents[5] in 1913 and 1914 on the conversion of carbon monoxide into alcohols, ketones, aldehydes, aliphatic hydrocarbons, and fatty acids. Osmium and cobalt oxide catalysts were used at 300-400°C and 100 to 200 bar.

In the early 1920's, Franz Fischer and Hans Tropsch[1,3,5,6] produced "Synthin" from carbon monoxide and hydrogen at 400 to 450°C and 100 to 150 bar over alkali-containing iron turnings. "Synthin" consisted of mainly oxygen-containing molecules with small amounts of hydrocarbons. This "Synthol process", later called the Fischer-Tropsch synthesis, was then performed at lower pressures (7 bar). Alkanes and alkenes were the main products; a small amount of oxygen-containing products was also produced. Cobalt and nickel, prepared by the reduction of their salts or oxides, were then used by Fischer and Tropsch to produce methane and higher hydrocarbons at atmospheric

pressure and 200 to 250°C. These catalysts suffered from rapid loss of activity.

Over the next twenty years, efforts were made to improve the life and activity of Fischer-Tropsch catalysts.[1,5,6] Fischer and coworkers accomplished this aim by precipitating the catalyst, along with thoria as a promoter, onto a kieselguhr (diatomaceous earth; mainly silica and alumina) support (M:ThO_2:kieselguhr = 100:80:100; M = Ni, Co). While cobalt was a more active catalyst than was nickel, nickel was favored at that time, due to the scarcity of cobalt. Fischer's next goal was to replace thoria with less expensive promoters. As a result, a new catalyst (Ni:MnO:Al_2O_3: kieselguhr = 100:25:10:100) was developed that was sufficiently promising in the laboratory to initiate a pilot plant operation. In 1934 a 1000 ton per year pilot plant was constructed by Ruhrchemie A. G. to operate at 190 to 210°C and atmospheric pressure. Many problems were experienced during the plant's operation, such as inordinate amounts of catalyst and promoter loss, short life of the catalyst, and poor selectivity. As a result nickel was never used as a commercial Fischer-Tropsch catalyst. Cobalt catalysts were found to be more suitable than nickel, and Ruhrchemie put the first industrial Fischer-Tropsch plant into operation in 1936. A cobalt catalyst (Co:ThO_2:MgO:kieselguhr = 100:5:10:200) became the standard catalyst in commercial processes in Germany from 1938 to 1944, when bombing of the plants halted operations.

In 1936, Fischer and Pichler[1,5] increased the synthesis gas pressure from one to between five to fifteen bar for a supported cobalt catalyst. While this "medium pressure" synthesis extended the life of

the catalyst and decreased the amount of gaseous hydrocarbon products, the major significance of this discovery was that it led to the development of successful iron catalysts. A year later Fischer and Pichler demonstrated that the catalyst life for iron was increased greatly at fifteen bar; such operation also doubled the product yields. To this day iron catalysts are the catalysts of choice and are being used in the SASOL plants in South Africa.

The use of ruthenium catalysts[1,3,5,6] was studied at the Kaiser Wilhelm Institute in Germany from 1938 to 1941. High molecular weight paraffin waxes could be produced at temperatures > 130°C and at high pressures (100 to 1000 bar). Due to the high cost of ruthenium and the small demand for these waxes, little more was done with ruthenium catalysts until Pichler and Finnhalber synthesized polyethylene in 1962 from CO and H_2 at 2000 to 2000 bar and temperatures < 150°C.[3] Polyethylene produced from CO and H_2 has similar properties to that produced from ethylene, and could probably be used in its place. While any hydrocarbon source could be used for synthesis gas production, and therefore this polyethylene production, in contrast to oil-based polyethylene technology, the high pressures and low selectivities associated with its synthesis severely hamper CO-H_2 polyethylene production on a commercial scale.

Other platinum-group metals have been examined for activity as Fischer-Tropsch catalysts at high pressures.[3,5,7] Osmium and rhodium showed reasonable activity. More gaseous products were produced by osmium than by ruthenium catalysts. Rhodium produced smaller yields of

wax and significant amounts of oxygen-containing products. Iridium, palladium and platinum exhibited only slight activities.

The current trend in research on Fischer-Tropsch catalysts is in the direction of improving selectivity. As previously mentioned, Fischer-Tropsch catalysts tend to be non-selective and produce a wide range of products. Molecular sieves have been used to attempt to limit chain growth during the reactions, however results have not been very successful.[3,8] On the other hand, sieves have been quite successful in converting methanol, produced from carbon monoxide and hydrogen, into gasoline range hydrocarbons via the Mobil process,[9-11] as well as ethylene and propylene.[12]

While traditional Fischer-Tropsch catalysts have been heterogeneous or insoluble solid catalysts, homogeneous (soluble) catalysts may provide a route to better selectivity. Various transition metal complexes, primarily the carbonyls, have been shown to produce alcohols and other oxygen-containing molecules, such as ethylene glycol, from synthesis gas at pressures of 100 bar or more.[13-21] Selectivity can be tailored somewhat by changing ligands as well as solvents.[13,22]

While heterogeneous Fischer-Tropsch catalysts appear to lead to production of both hydrocarbon and oxygen-containing products, homogeneous catalysts generate oxygenated molecules only.[23] Some have suggested that formation of hydrocarbons, even if the precatalyst is soluble, is evidence of a heterogeneous process.[23,24] Apparent exceptions have been discovered by Muetterties and coworkers. Iridium and osmium carbonyl clusters ($Ir_4(CO)_{12}$ and $Os_3(CO)_{12}$) were shown to be active methanation catalysts at about two bar of synthesis gas.[25,26]

Substitution of other ligands, such as triphenyl phosphine, for some of the carbonyls, produced ethane and propane in addition to methane. Use of an aluminum chloride-rich chloroaluminate melt (mole ratio $AlCl_3$:NaCl = 2:1) as the solvent with an iridium carbonyl precatalyst gave an active Fischer-Tropsch system.[27] At 1-1/2 bar and short reaction times, ethane was the main product. Ruthenium and rhodium carbonyls were also quite active in the chloroaluminate melts.

B. Activity and Product Distribution For Heterogeneous Catalysts

The activity of most of the Group VIII metals has been determined by Vannice.[28] Supported on alumina, these metals produced the following order of activity towards methanation: Ru > Fe > Ni > Co > Rh > Pd > Pt > Ir. A slightly different order for these metals was obtained when the average molecular weight of the hydrocarbons produced was studied, that is: Ru > Fe > Co > Rh > Ni > Ir > Pt > Pd.

General trends in product distribution for cobalt, nickel, iron, and ruthenium catalysts will be discussed in this section. Effects of promoters on product distribution will be covered in later sections.

Both atmospheric and medium pressure synthesis produce very similar trends for cobalt catalysts. Methane is, by far, the major product by weight.[29] Relatively little ethane is formed, then, as the number of carbons increases, the weight of products of each carbon number increases to around C_5 and C_6. As the carbon chain increases beyond C_6, the amount of each product decreases. The ratio of alkenes to alkanes also peaks at C_5.[30] While branched isomers are formed, straight-chained isomers predominate.[5]

Fewer details are available on the product distribution for nickel catalysts than for cobalt catalysts, since sensitive analytical techniques were unavailable until after interest in nickel catalyzed Fischer-Tropsch processes had disappeared. Generally, the products tended to be more paraffinic and had a lower average molecular weight than those formed with cobalt catalysts.[5]

The product yield versus carbon number for iron catalysts differs somewhat from that for cobalt catalysts.[5,31] The C_2 fraction is generally about the same, or slightly less, than the amount of methane produced by weight. The C_3 compounds are the major products, and at C_4 and beyond the weight of products decreases as the carbon number increases. The olefin content, which is greater than that for cobalt catalysts, is small at ethylene, increases to a maximum between C_3 and C_6, then generally decreases with increasing chain length. Exceptions occur where the olefin content by weight at each carbon number remains relatively constant to about C_{12}, beyond which the amount of olefins begins to decrease. Another difference from cobalt catalysts is that a higher percentage of oxygen-containing products, primarily alcohols, is formed using iron catalysts.[5,32] While conventional iron catalysts produce about 10 % oxygenated compounds, it is possible to modify the iron catalyst, such as by nitriding it, to produce mainly oxygen-containing products. Ethanol is the major alcohol formed. The higher alcohols are mainly straight chained, and are produced in equal weight from about C_3 to C_{18}. Very little methanol is formed. Branching of hydrocarbon chains is more widespread over iron than cobalt catalysts, and increases with increasing carbon number.[31] Aromatic

hydrocarbons constitute about 6 % of the total hydrocarbons by weight.[33] Alkyl substitution is common. Aromatics can make up over 20% of some of the higher carbon number products.

Ruthenium catalysts produce very different product distributions than cobalt, iron and nickel catalysts.[3,34] Ruthenium is an excellent methanation catalyst, and is more active than nickel. While low and medium pressure syntheses (< 30 bar) yield methane as the major product, high molecular weight alkanes predominate in high pressure (1000 to 2000 bar) reactions. The products are largely free of alkenes and oxygen-containing compounds.

C. Supports and Promoters

Unsupported nickel and cobalt used as Fischer-Tropsch catalysts in the 1920's were active for only short periods. The use of kieselguhr as a support was an important discovery.[5,6,35] Increased catalyst lifetime, as well as higher conversion of carbon monoxide, resulted. Supports are not important for iron catalysts, although kieselguhr, alumina, silica gel and others have been used. Ruthenium is active in the form of a highly dispersed metal. While very active supported ruthenium catalysts have been prepared on alumina, silica gel, and activated carbon, the effects of supports on catalyst performance, found for cobalt and nickel catalysts, are absent in the synthesis of polymethylene.

Various materials used for catalyst supports can have acidic or basic sites on their surfaces.[36] This property can be useful in changing the selectivity of the catalyst, as was shown using a rhodium

catalyst.[37] Methane formation was favored on acidic supports, such as alumina or titanium oxide, whereas alcohol formation was favored on more basic supports, such as magnesia.

Enhancement in the activity of nickel and cobalt catalysts by the presence of small amounts of hard to reduce oxides, usually thoria or magnesia, has been known since the early 1930's.[5,6,38,39] While these structural promoters have very little effect on catalyst selectivity, they do increase catalyst activity by increasing the surface area of the metal. (Promoters are species added to increase the activity of a catalyst.) These structural promoters have very little effect on the activity of iron catalysts.

The most important promoter, and the only one necessary for iron catalysts, is an alkali metal oxide or salt.[40] Three key effects are produced by this promoter: a) the activity of the catalyst is enhanced; b) the average molecular weight of the products is increased; c) the fraction of alkenes in the hydrocarbon products is also increased. Promotion can occur via two routes. The alkali cations may interact with the oxygen in carbon monoxide, thereby weakening the C-O bond. The alkali oxide, as a Lewis base, may increase the electron density on the metal. The increased electron density strengthens the M-C bond between the metal and the adsorbed carbon monoxide, thereby weakening the C-O bond.[41] Potassium oxide or salts, the most usual alkali promoters, and rubidium oxide or salts were found to be the most active promoters for iron catalysts, and produced more solid hydrocarbons than with other alkali promoters.[6] Sodium-containing iron catalysts were less active than those with potassium, but produced

greater amounts of liquid hydrocarbons.[6] Lithium salts were not effective as promoters.[6] Addition of alkali oxides or salts to cobalt catalysts produced similar results as for iron catalysts, but to a much lesser degree.

D. Reaction Parameters

Varying the reaction temperature produces very significant changes in the distribution of products in Fischer-Tropsch reactions.[5] As the temperature is increased, both the average molecular weight and the yield of oxygen-containing molecules decrease. The olefin content can increase or remain the same, depending on the catalyst. Each catalytic material has its own optimum temperature range for Fischer-Tropsch processes, for example, cobalt, 170-210°C[3]; nickel, 185-210°C[6]; iron, 220-350°C[3]; ruthenium, 100-120°C[3]; $Ir_4(CO)_{12}$, 150-210°C.[42]

Changing the reaction pressure also results in significant changes in product distribution, as well as the activity of the catalysts.[5] As pressure is increased, the overall yield, the average molecular weight, and the yield of oxygen-containing molecules increase. The olefin content remains about the same. As for temperature, the optimum reaction pressure depends on the specific catalytic material, for example: cobalt, 5-20 bar;[7] nickel, 1 bar [at higher pressures, excessive loss of catalyst due to volatile carbonyl formation becomes a problem];[7] iron, 10-30 bar;[7] ruthenium, 100-200 bar.[3]

The H_2/CO ratio affects the selectivity of the catalyst.[39] High ratios (e.g. 3:1 mole ratio) tend to produce methane and

light saturated hydrocarbons. Decreasing this ratio increases the average molecular weight, the ratio of alkenes to alkanes, and the alcohol production. The "usage ratio," the ratio of H_2/CO actually consumed during a rection, depends on the catalytic material and, to a lesser extent, reaction conditions.[6] Typical usage ratios are two for both cobalt and nickel catalysts and one for iron catalysts.

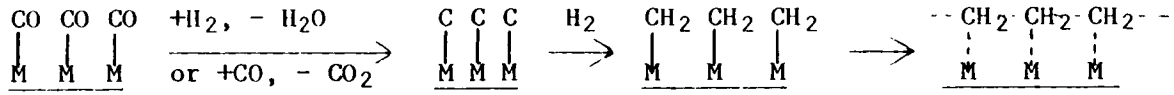
In flow reactor systems, the flow rate controls the contact time of the synthesis gas with the catalyst. The conversion of carbon monoxide decreases as the flow rate increases.[5] For an iron catalyst, the amount of gaseous hydrocarbons increased with increasing flow rates.[5]

E. Mechanisms

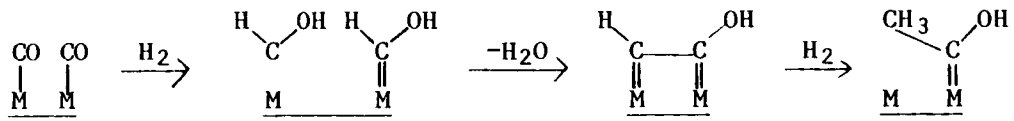
The mechanism of the heterogeneous Fischer-Tropsch reaction is not well understood; in fact, three different basic mechanisms, along with various combinations of these three mechanisms, have been proposed.

An early mechanism was the carbide theory.[43] As illustrated in Figure 1a, carbon monoxide, adsorbed on the metal surface, reacts with either hydrogen to produce water, or another carbon monoxide to produce carbon dioxide and metal carbide. Hydrogenation of the carbides gives methylene groups which can link together on the metal surface to produce higher hydrocarbons.

The hydroxypolymerization mechanism,[5,6,44] as shown in Figure 1b, involves hydrogenation of carbon monoxide adsorbed on a metal to form M=CHOH intermediates. Chain growth occurs when two of these



(a)



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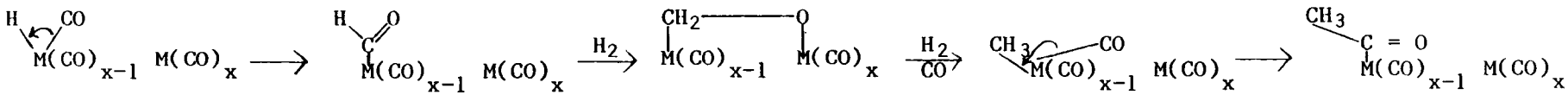

(c)

Figure 1. Possible Fischer-Tropsch Reaction Pathways: (a) the carbide theory; (b) Hydroxypolymerization; (c) Pichler-Schulz mechanism.

adjacent intermediates react, giving off water, followed by hydrogenation.

The Pichler-Schulz mechanism is illustrated in Figure 1c.[45,46] Carbon monoxide, complexed to the metal, inserts into a metal hydride bond. After hydrogenation and loss of water, another carbon monoxide is complexed and then inserts into the metal-methyl bond to lead to chain growth. An advantage of this mechanism is that it can easily be applied to explain both heterogeneous and homogeneous catalysis. A variation of this mechanism has been proposed involving formaldehyde intermediates.[47]

A hybridization of the carbide theory with a Pichler-Schulz type insertion mechanism has been proposed by Ponec.[48,49] In this mechanism, adsorbed carbon monoxide dissociates to form carbide on the metal surface, is hydrogenated, then additional carbon monoxide inserts into the $M-CH_x$ bond. Hydrogenation, followed by additional insertions, accounts for chain growth.

Rofer-DePoorter's mechanism includes the carbide, hydroxypolymerization and insertion mechanisms.[50] Each contributes to the overall synthetic pathway in varying degrees.

While the overall Fischer-Tropsch reaction appears to be a relatively simple process, the actual mechanism is complex and still the subject of disagreement today.

F. Side Reactions

The Boudouard reaction, the disproportionation of carbon monoxide, is represented by:

$$2\ CO \rightleftharpoons C + CO_2$$

All metals catalyzing the Fischer-Tropsch reaction also catalyze this disproportionation.[51-53] Temperatures used for the Fischer-Tropsch synthesis (< 300°C) are generally lower than those which favor carbon monoxide disproportionation.[39,50] The Boudouard reaction is undesirable since, in addition to consuming carbon monoxide, carbon formation can deactivate the catalyst as well as cause plugging and increased abrasion in reactions.[39]

The water-gas shift reaction:

$$H_2O + CO \rightleftharpoons H_2 + CO_2$$

is catalyzed by a number of metals, such as iron and cobalt, as well as oxides.[50] This shift reaction can result in CO_2 or H_2O as the byproducts of the Fischer-Tropsch synthesis. This is neither beneficial nor harmful on the overall synthesis.[50] This shift reaction has proven to be useful, however, in adjustment of the H_2/CO ratio of the incoming synthesis gas.

G. Molten Salts as Solvents

Molten salts possess several properties which are advantageous in their use as media for catalysis.[54-56] Since they usually have high thermal stabilities, it may be possible to work at temperatures at which the reaction products have high vapor pressures and can be removed by volatilization. Activity of the catalysts may remain high

for extended periods. Catalysts are not easily removed from the metals with the reaction products. Molten salts have high thermal conductivities, generally two to five times greater than organic media.[57] Decomposition that can occur on supports due to local overheating is avoided, since the heats of reaction are easily dissipated.

Sodium chloroaluminates, mixtures of $AlCl_3$ and NaCl, may have additional advantages over other solvents for Fischer-Tropsch synthesis. The Lewis acid ($AlCl_3$) can act as a promoter, through an M-C-O-Al association.[27,50,58-60] Sodium salts also act as promoters.[6] Chloroaluminate melts have been shown to catalyze both cracking and isomerization of saturated hydrocarbons.[61] Shorter carbon chain lengths may be favored and increased amounts of branched isomers can be expected.

Chloroaluminates were initially used for the Fischer-Tropsch synthesis by Demitras and Muetterties.[27] Various metal carbonyls and chlorides were tried as catalysts, or precatalysts, in acidic ($AlCl_3$-rich) chloroaluminate melts. Active systems were found using $Ir_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Rh_4(CO)_{12}$ and $Ru_3(CO)_{12}$. H_2PtCl_6 and $PdCl_2$ showed only slight activities, which $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Re_2(CO)_{10}$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Os_3(CO)_{12}$, $Co_2(CO)_8$, $Co_4(CO)_{12}$ and $NiCl_2$ were inactive. With $Ir_4(CO)_{12}$, methane and ethane, along with minor amounts of propane and isobutane, were obtained at 180°C and about 1.5 bar in sealed batch reactors. The relative ratio of ethane to methane varied with time; after three hours, this ratio was between 10:1 and 4:1, but fell to 1:2 after one half to three days. Quite different results were obtained by Muetterties and coworkers using a

flow reactor system in place of the batch process.[42] At short contact times, alkanes with as many as eight carbons were detected. Methane and ethane, the major products of the batch process, were produced in relatively minor amounts. On the other hand, isobutane, a minor product in the batch processes, was the major product under their flow conditions. Significant amounts of propane and pentanes were prepared. At longer contact times, the product distribution resembles the batch process results and ethane was the major product. This difference was explained by hydrocarbon cracking reactions in the acidic chloroaluminates.

Markedly different results were obtained for $Ir_4(CO)_{12}$ in acidic chloroaluminates by Collman et al. using a flow reactor at atmospheric pressure.[62] Along with ethane, the major hydrocarbon product, significant amounts of methane were formed. Relatively little propane and butanes were produced. Significant amounts of chloromethane were found, and chloromethane could became the major product at short contact times. Since chloromethane can be produced from the reaction of methanol and aluminum chloride, methanol could be an intermediate product in this reaction, as can be expected if it is a homogeneous process.[23,24] The difference in the products formed in the previous study[42] in comparison with that by Collman and coworkers,[62] especially the complete absence of chloromethane production in the former, is somewhat puzzling. It was suggested[62] that possibly a different active catalyst was formed from $Ir_4(CO)_{12}$ in the chloroaluminate melts in the studies by the two research groups.

The effects of a reducing agent, primarily aluminum metal, on Fischer-Tropsch reactions in molten haloaluminates using metal carbonyls and chlorides as catalyst precursors have been studied by Lapidus and coworkers.[63-65] Active systems studied at 150°C and one to two bar, in order of decreasing activity, were $Rh_4(CO)_{12}$, $Ir_4(CO)_{12}$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$ and $NiCl_2$. The aluminum produced an increase in the conversion of carbon monoxide as well as an increase in the amount of higher gaseous alkanes, especially isobutane. Methane was the major product in these batch processes for all systems except $Os_3(CO)_{12}$ and $NiCl_2$. Isobutane was the major product when $Os_3(CO)_{12}$ was the pre-catalyst. Isobutane and methane were produced in approximately equal amounts for the $NiCl_2$ system.

H. Production of Metallic Dispersions

A common method of producing dispersed metals has been the reduction of metal oxides and salts by hydrogen at elevated temperatures.[5,6] Dispersions have been also prepared using a variety of other reducing agents. Sodium citrate has been used to prepare aqueous dispersions of gold and platinum from their chloride salts.[66] Reducing agents have been used to prepare aqueous dispersions of cobalt, copper, silver, nickel, iron, palladium, rhodium, ruthenium and iridium.[67] Dispersions in organic solvents have been prepared by the reduction of metal salts with alkali metals.[67-69] Magnesium, zinc, indium, thallium, aluminum, lead, iron, cobalt, titanium, copper and uranium have been dispersed in this manner.

Thermal decomposition of metal salts in inert atmospheres, such as argon or nitrogen, has been used to produce platinum, palladium, gold and silver catalysts.[67]

"Raney's method" is commonly used to prepare unsupported catalysts.[67] The catalytic metal is alloyed with a base metal, such as aluminum. The base metal is then leached from the alloy, often using potassium hydroxide solutions, leaving a high surface area metal behind. Included in catalysts produced by "Raney's method" are nickel, cobalt, copper, palladium, platinum, rhodium, silver, tungsten and molybdenum.

Aqueous metallic dispersions were prepared in the 1910's by Benedicks[70] and Svedberg[71] using electric discharge. The first application of electric discharge to produce metallic dispersions in molten salts was by Piontelli and coworkers in molten NaCl.[72] Dispersions were produced by creating AC arcs between two electrodes (of the metal to be dispersed) submerged in the melt. Piontelli et al. extended these dispersions to other halide melts; aluminum, antimony, cadmium, copper, lead, platinum, silver, zinc,[73] magnesium, nickel, tellurium, a lead-tellurium alloy, lead sulfide ores,[74] brass, bronze, and monel and copper-nickel alloys[75] were dispersed in molten chloroaluminates. A wide range of particle sizes was produced, from microscopic particles (< 0.1 μm) to coarse particles (visible with the unaided eye). The dispersion process was thought to be due to vaporization and condensation of the metal, as well as ionic sputtering.

A few other methods have been applied to the preparation of dispersions in molten salt systems. Gold and silver dispersions have been prepared in nitrate melts.[76] The gold was dispersed by the reduction of $AuCl_3$ with residual nitrite; the silver dispersion was prepared by the photolysis of $AgNO_3$ in the melt. The solubility of some metals in melts has been used to produce dispersions, such as cadmium in $CdCl_2$-MCl_x (M = K, Ca, Ce, Mg, Mn and Zn) melts.[77] Titanium dispersions have been produced by the corrosion of titanium metal in molten alkali chlorides.[78]

I. Proposed Research

The main purpose of this part of the dissertation is to explore the potential catalytic utility of metallic dispersions in acidic molten chloroaluminates. The Fischer-Tropsch reaction was studied in sodium chloroaluminate melts using primarily Group VIII metal dispersions as catalysts and low pressures of synthesis gas. The dispersions were prepared by the submerged AC arc method,[72-75] since it offers several advantages, such as: a) it can be done in situ; b) no reagents have to be added which remain in the melt or reduce $AlCl_3$.

The $Ir_4(CO)_{12}$ precatalyst system was also studied, with the aim of gaining more insight into a system which has produced widely different results by other workers.[42,62] The effect of metallic aluminum on the reaction products was also explored.

CHAPTER II

EXPERIMENTAL: THE REACTION BETWEEN CARBON MONOXIDE AND HYDROGEN

A. Materials Used and Preparation of Chloroaluminate Melts

$AlCl_3$ (anhydrous, iron free) was obtained from Fluka AG (Tridom Chemical , Hauppauge, NY). It was further purified by double sublimation according to the following procedure: $AlCl_3$, a small amount of NaCl (about 1% by weight) and aluminum (m5N grade, Alfa Products, Danvers, MA) were placed in a Pyrex vessel which was sealed under vacuum ($\leq$ 1 mtorr). The vessel was placed into a furnace at 200° to 210°C for 12 to 16 hours. During this time the more noble impurities were removed via reduction with aluminum, and other impurities were extracted from the $AlCl_3$ layer into the $NaAlCl_4$ layer at the bottom of the tube.[79] The $AlCl_3$ was then sublimed through a small constriction or a coarse Pyrex frit, which acted as mechanical barriers in the event of bumping, until only 1 cm of molten $AlCl_3$ remained on top of the $NaAlCl_4$ layer. The remaining $AlCl_3$ and salt mixture were then allowed to freeze.

NaCl, certified A.C.S. reagent, was dried for four days under dynamic vacuum at 400°C prior to use.

All material transfers of chloroaluminate melts, as well as their precursors, were made in a Vacuum Atmospheres drybox containing a nitrogen atmosphere ($\leq$ 2 ppm H_2O). To prepare a melt, appropriate amounts of $AlCl_3$ and NaCl were weighed and placed into a Pyrex vessel, along with aluminum, and sealed under vacuum. The vessel was placed into a furnace at 175°C, and shaken by hand every one to five minutes

until the melting process was complete. After digesting about 20 hours in a rocking furnace, the water-clear melt was carefully poured away from the aluminum and any solid impurities, and allowed to freeze. Occasionally, fine aluminum particles were present and remained suspended in the melt. These were removed by filtration through a Pyrex frit.

B. Materials and Preparation of Metallic Dispersions and Other Catalysts

Iron (2 mm dia., m4N85 grade), cobalt (0.75 mm dia., m2n7 grade), tungsten (1 mm dia., m3N5 grade), nickel (2 mm dia., m4N75 grade), tantalum (1 mm dia., m3N grade), palladium (1 mm dia., m3N grade), rhodium (0.5 mm dia., m4N grade), rhenium (0.25 mm dia., m4N grade) and iridium (0.25 mm dia., m3N grade) wires were obtained from Alfa Products (Danvers, MA). Platinum wire was obtained from Engelhard Industries (Carteret, NJ). Wire of the metal to be dispersed was spot-welded to tungsten and sealed into a Pyrex tube so that two such electrodes were in a linear arrangement, with about 3 mm exposed wire on each side and a 1 mm gap between them. Often more than one set of electrodes was incorporated in the cell, as shown in Figure 2. The cell was cleaned in 1:1 HCl or 1:1 HNO_3, dried, and filled with the melt. The cell was sealed under vacuum, placed into a furnace at 175°C, and the chloroaluminate was allowed to melt. Using the power supply shown in Figure 3, the AC voltage output from the variable transformer was increased until arcing and dispersing occurred. The voltage varied from metal to metal; typically, 30 to 60 V (AC) has

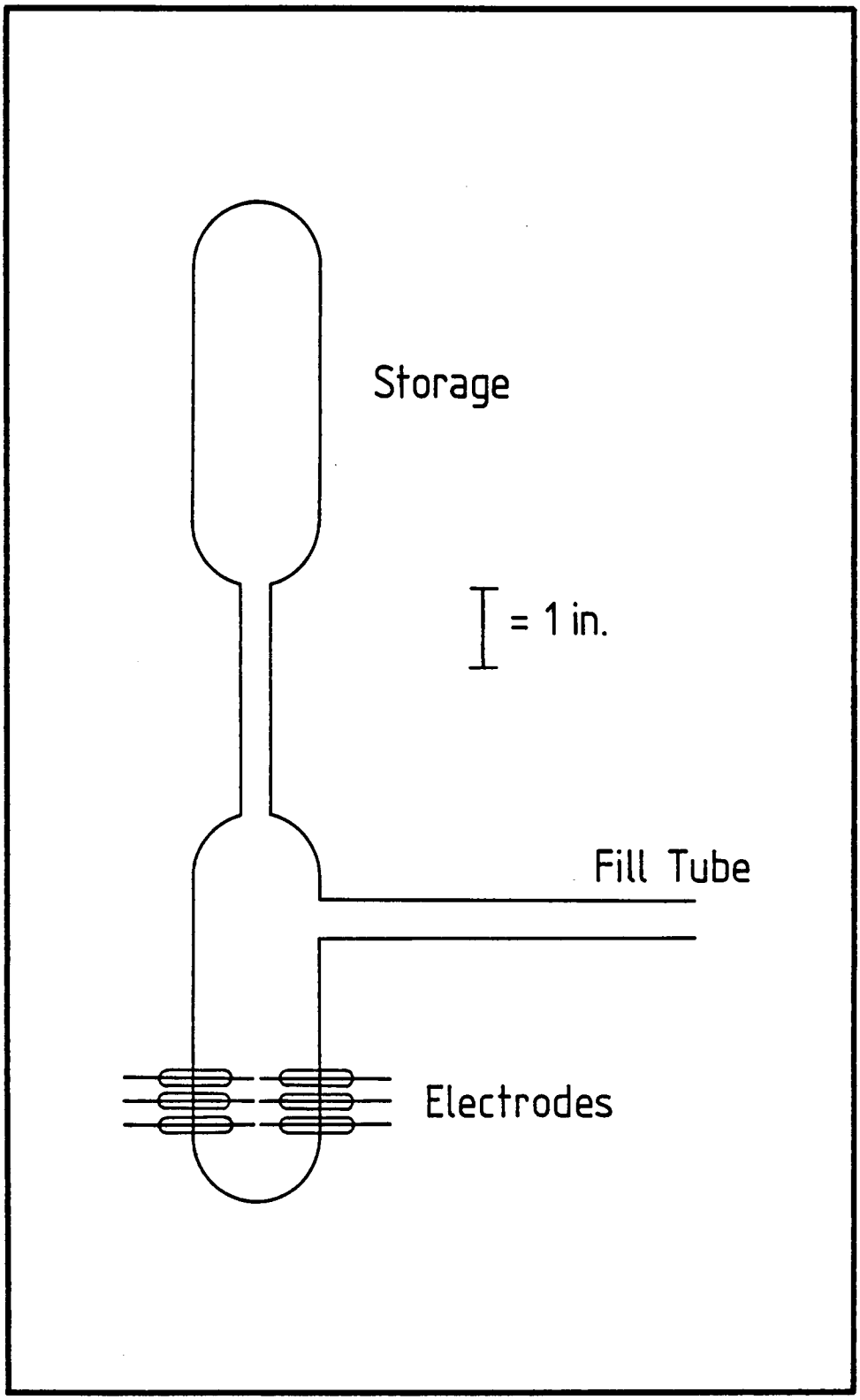

Figure 2. Multiple Electrode Dispersion Cell.

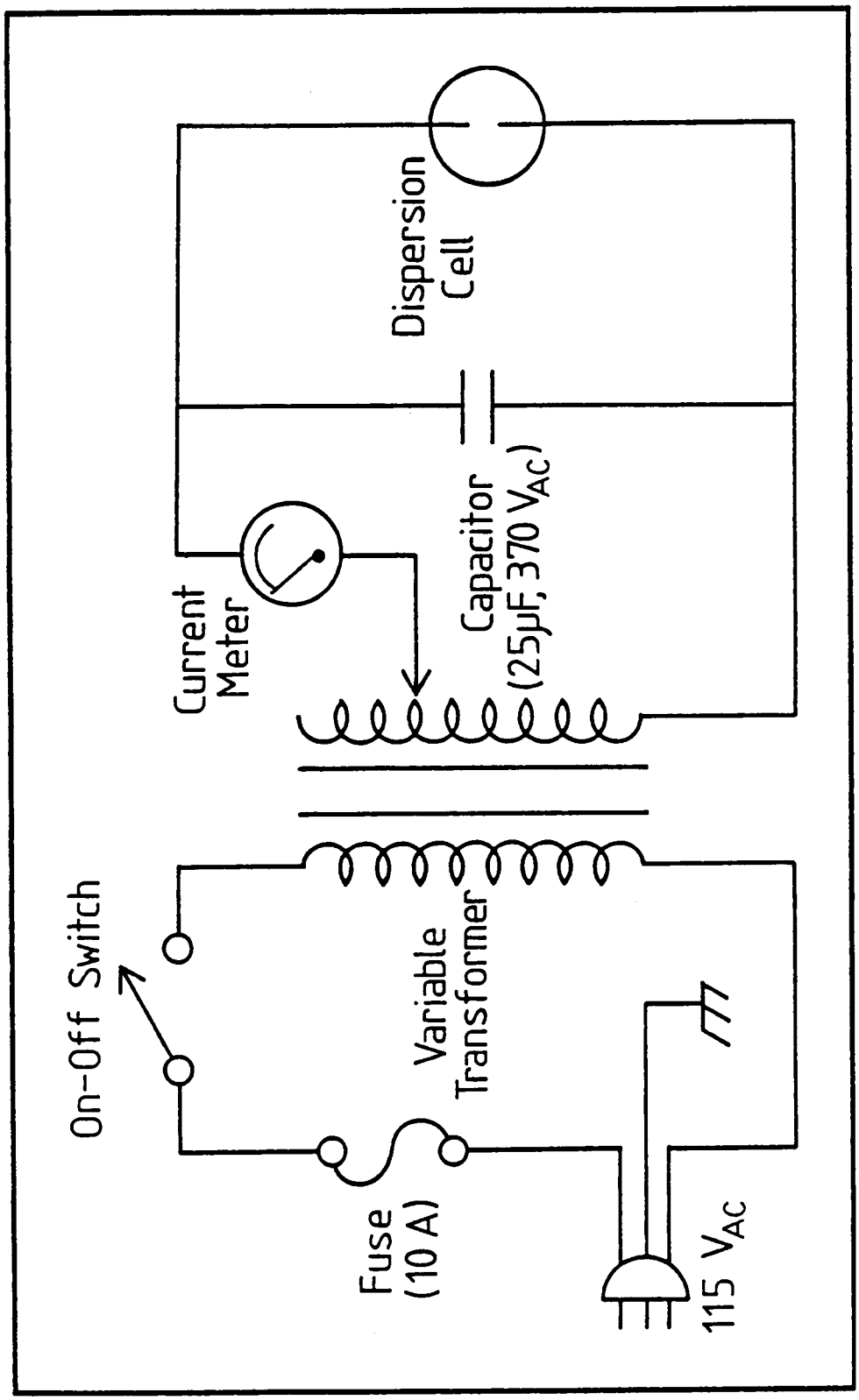

Figure 3. Supply for Producing Dispersions.

required. The high current arcs produced were usually in the range of 10 to 30 A, however, arcs in excess of 50 A were not uncommon. An arc between two electrodes is shown in Figure 4. As dispersing occurred and the electrode gap increased, the voltage required to produce arcing increased. Since a great deal of heat was generated by the arcing (the melts boiled), the voltage was not applied for more than one minute at a time. The melt was allowed to cool for several minutes before resuming the process. This procedure was repeated until all exposed wire was dispersed, the maximum output of the variable transformer would no longer produce arcing, or until the electrodes melted and fused together (only nickel and iron electrodes, which are magnetic, fused together). The dispersion-containing melt was poured away from the electrodes by inverting the cell, and then frozen.

$Ir_4(CO)_{12}$, obtained from Strem Chemicals (Newburyport, MA), was used without further purification. Iridium powder was prepared by thermally decomposing $Ir_4(CO)_{12}$ at 235°C. Ruthenium (m3N grade) and rhenium (m4N grade) powders were obtained from Spex Industries (Metuchen, NJ). Nickel on kieselguhr (55-60% Ni by weight) and aluminum powder (m5N grade) were obtained from Alfa Products (Danvers, MA). Nickel, cobalt-aluminum alloy (40% Co by weight) and iron-aluminum alloy (50% Fe by weight) were obtained from the storeroom (supplies of former researchers at the University).

C. Reaction Vessels and Procedures

Early reactions were attempted using a Parr Hydrogenator (Parr Instrument Co.) with a 500 ml Pyrex bottle, modified with an o-ring

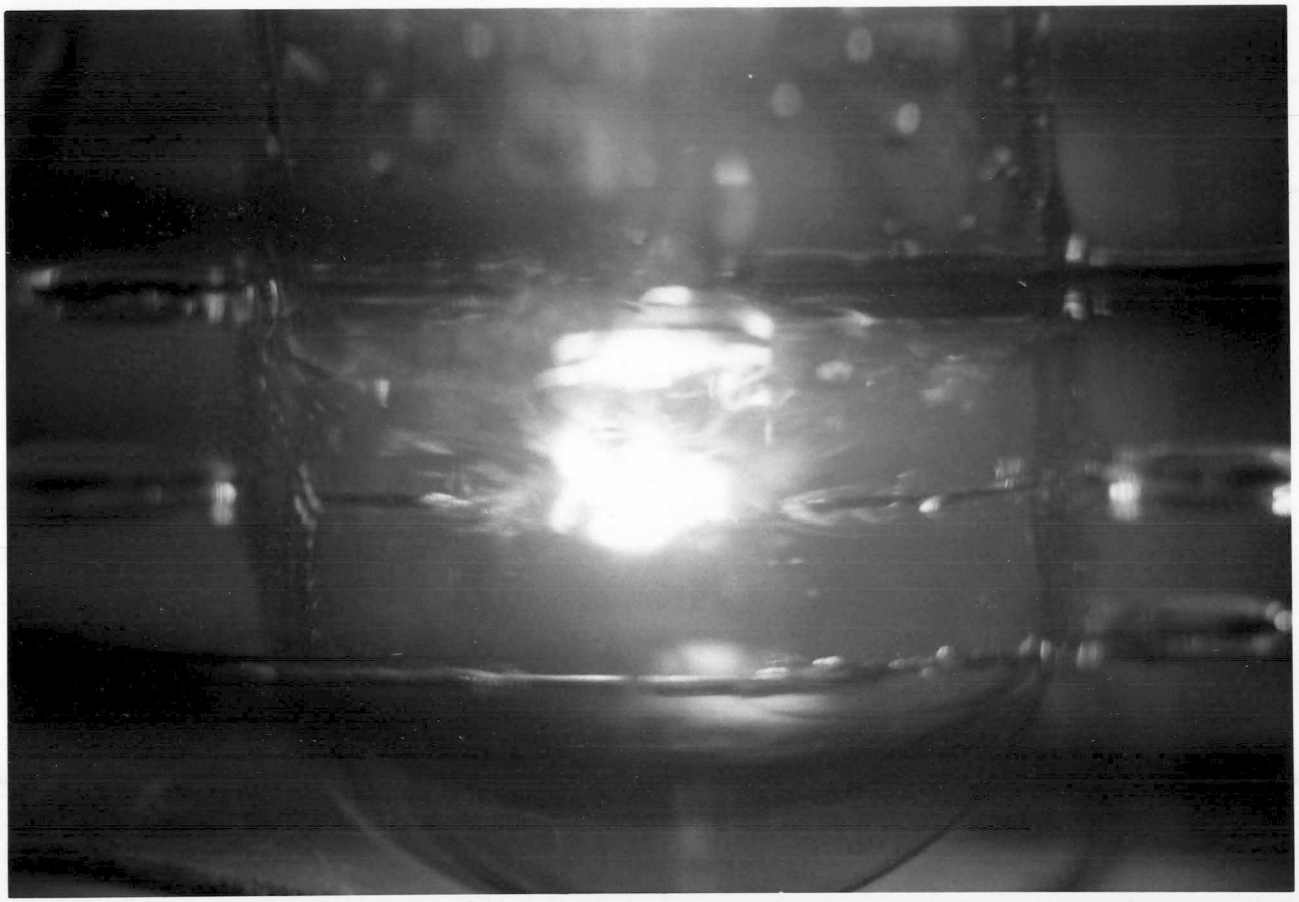

Figure 4. Photograph of an Arc During the Dispersion Process.

joint, a Teflon stopper, and two Viton o-rings. This design was abandoned due to problems with gas leakage.

The Pyrex vessel used in batch reactions is shown in Figure 5. The larger tubing on the side of the vessel was used for melt and catalyst addition. The smaller tubing with the stopcock was for synthesis gas addition. These vessels were cleaned using Micro Laboratory Cleaning Solution (Cole-Parmer, Chicago, IL). The melt, catalyst, aluminum and a 1/2 inch Teflon-covered magnetic stirring bar were placed into the vessel in the drybox. Catalysts which were not already dispersed in the melt were weighed in a capillary tube, and the entire capillary was placed into the vessel. After the larger tubing was sealed off under vacuum, the vessel was filled to 2.3 bar with synthesis gas. The synthesis gas consisted of 3:1 (mole ratio) H_2:CO (containing 2% Kr for use as an internal standard) obtained from Linde, or 1:1 mixed from H_2 and CO obtained from MG Scientific Gases. The bottom of the reaction vessel was submerged in liquid nitrogen and the small tube was sealed off at the constriction.

The reaction furnace consisted of a large Pyrex tube wrapped with a nichrome ribbon heating element, placed on a magnetic stirrer. The temperature was controlled by a variable transformer or a temperature controller (Model 22M, Omega Engineering, Stamford, CT). The reaction vessel was wired to an aluminum support rod which was used to position the reaction vessel in the center of the furnace. Upon melting, the stirring was begun to agitate the melt during reaction. To stop a reaction, the vessel was removed from the furnace and allowed to cool quickly.

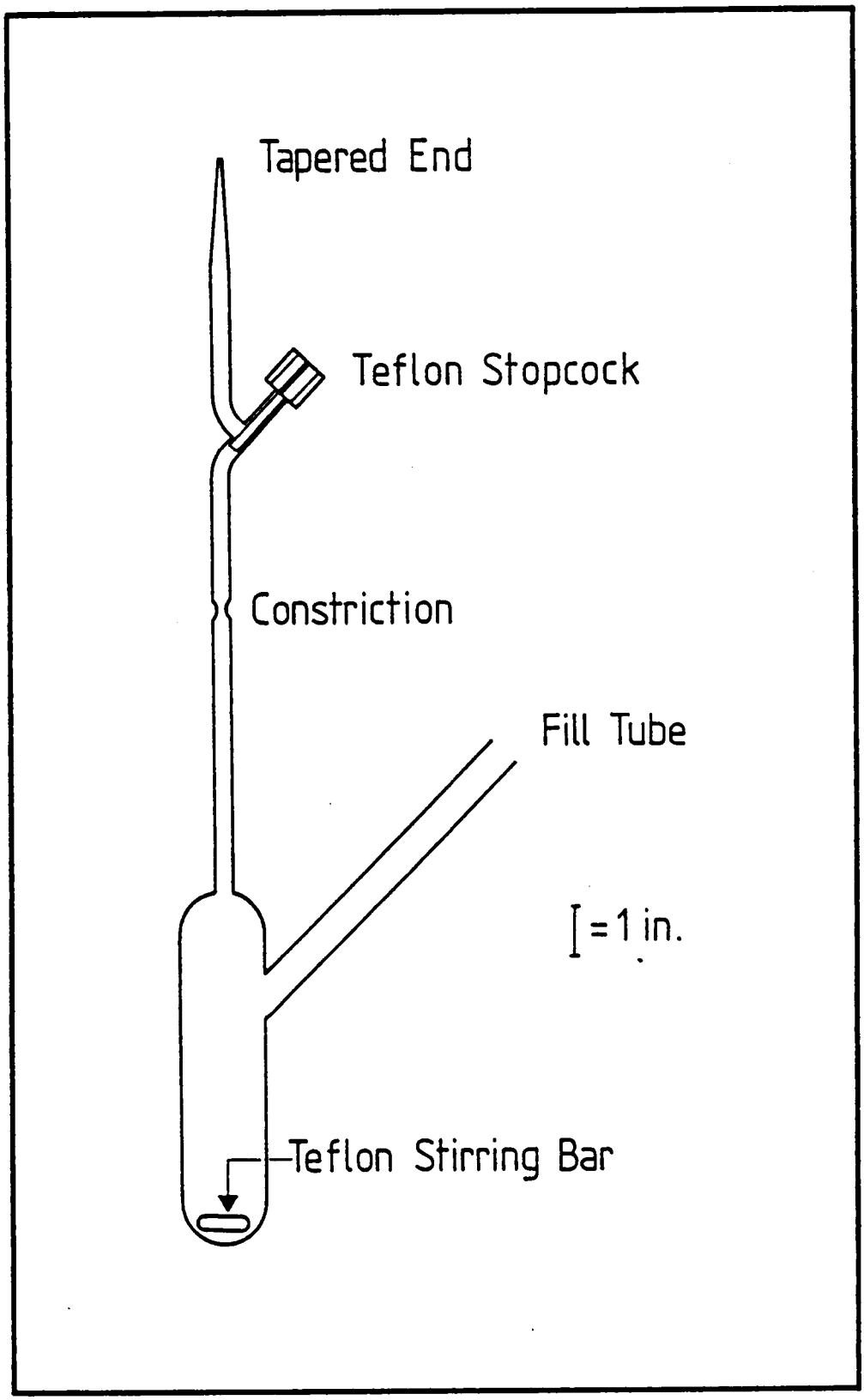

Figure 5. Batch Reactor.

The design of the recycle flow reactor is illustrated in Figure 6. This reactor consisted of a six-port automatic sampling valve (Hewlett-Packard) with a 0.5 ml sample loop (Supelco, Bellefonte, PA), a stainless steel bellows pump (Bobbins and Mayers, Gallipolis, OH) a Model B15 monel inline regulator (Matheson), a flowmeter (Matheson), a pressure/vacuum gauge (Robertshaw, Knoxville, TN), and a vacuum gauge (Sargent-Welsh, Skokie, IL). Connections were made using nickel tubing and monel Swagelok fittings, along with monel valves (Nupro and Whitey), since these materials should resist attack by HCl which could be produced as a byproduct during reactions. The melt and catalyst were held in a Pyrex vessel made from beaded process pipe (Kimax-Shott) with glass frits above and below the melt, and two bakeable stopcocks with Viton o-rings (Ace Glass, Vineland, NJ). The pipe joint was sealed using a Teflon-Viton liner (Kimax-Shott). This Pyrex vessel was attached to the rest of the reactor system using flexible stainless steel tubing (Cajon) and Swagelok unions. Various methods of attaching the Pyrex tubing through the Swagelok fittings were tried, including the use of graphite ferrules, graphite-nylon composite ferrules (Supelco, Bellefonte, PA) and o-rings. The most satisfactory seal was obtained using a reversed stainless steel back ferrule and a Viton o-ring in place of the front ferrule in the union. The flow reactor was checked for leaks by monitoring pressure over a period of time. A drop in pressure of less than 0.07 bar/10 min. at 4.5 bar was considered acceptable to proceed with the reactions. The furnace used with this reactor consisted of three pyrex tubes and two separate nichrome ribbon heating elements wrapped around the inner tube tubes.

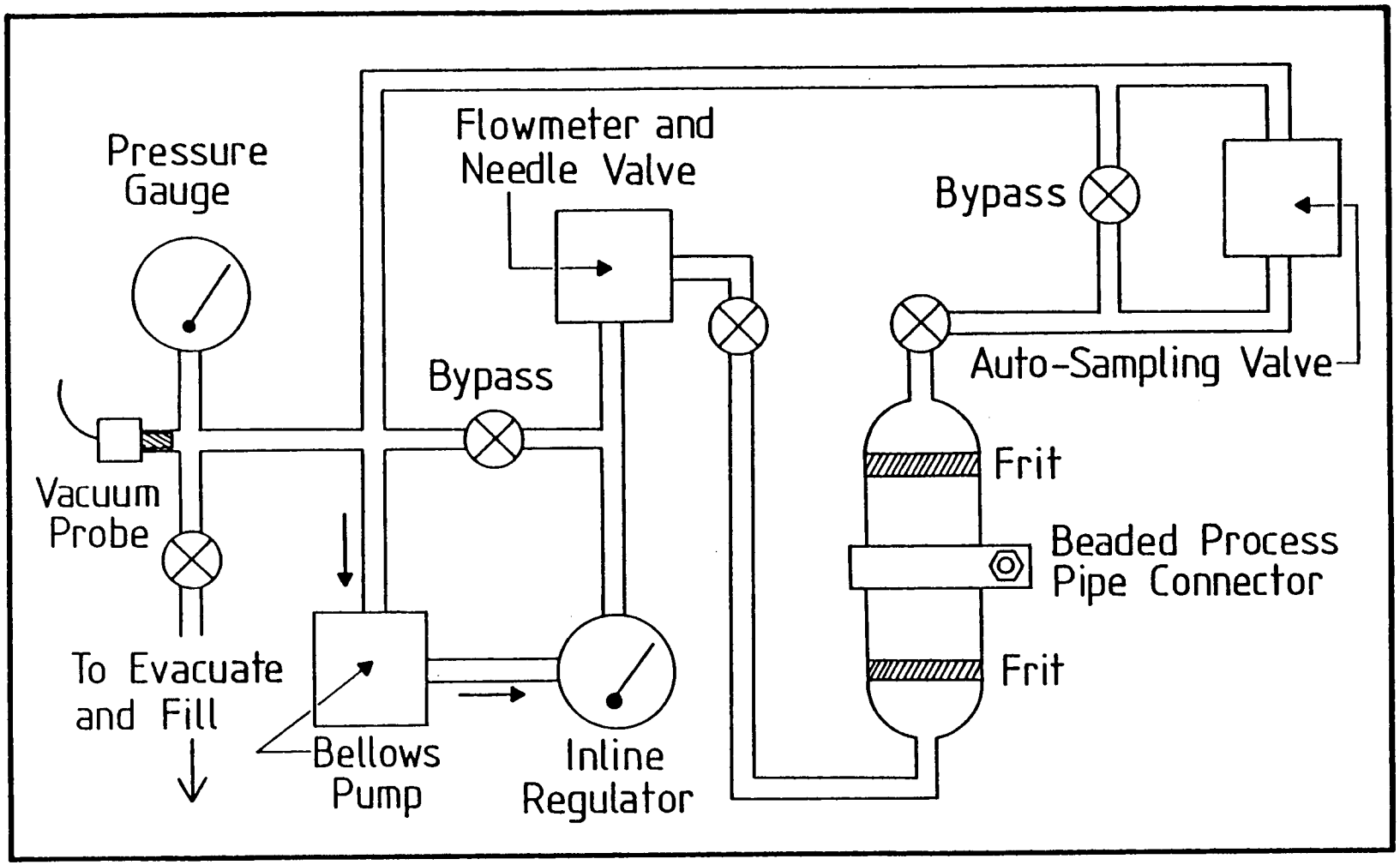

Figure 6. Recycle Flow Reactor.

The outer tube acted as insulation. The outer heating element was controlled by a variable transformer and was used to heat the furnace close to the desired temperature. A temperature controller (A Model 22M, Omega Engineering, Stamford, CT) was used to control the actual furnace temperature. A small cage-type fan was mounted in the bottom of the furnace for air circulation and produced a more uniform temperature inside the furnace.

The melt, catalyst, and aluminum were transferred into the lower section of the Pyrex reaction vessel in a drybox. The upper section was attached via the Teflon-Viton liner at the beaded process pipe joint. The vessel was attached to the remainder of the flow reactor. With the stopcocks of this Pyrex vessel closed, and all valves of the rest of the system open, the reactor was evacuated for at least seven hours to remove any gases which may have been adsorbed on the reactor tubing walls. The stopcocks were then opened and the system was evacuated for a minimum of an additional hour. The system was flushed with 3:1 H_2:CO (containing 2% Kr) and reevacuated. The system was then filled to 1 bar with the gas mixture and the pump was started to circulate the gases through the system for ten minutes before sampling the starting gases. The furnace was then turned on and the reaction was sampled at various times up to ten hours after melting occurred. The flow was maintained at 13 ml/min. through the system when the sample valve bypass was opened. Three to five minutes prior to sampling, this bypass was closed, forcing the flow to go through the auto-sampling valve. The flow dropped to approximately 5 ml/min when the bypass was closed.

D. Sampling and Analysis

Tube crackers[80,81] were used to sample the gaseous products from the batch reactions. The tube cracker used for most of reactions run consisted of a ball joint and two Ace Thred connectors (Ace Glass, Vineland, NJ). The small tube on the reaction vessel was positioned with an Ace Thred connector such that a small scratch made on the tube was in the center of the ball joint. A storage tube was connected to the other connector. The storage vessel and tube cracker were evacuated while the reaction vessel was cooled in liquid nitrogen. After closing off the storage vessel to the vacuum line using a stopcock, the reaction vessel was opened by breaking the small tube at the scratch with a sharp turn of the ball joint. The gaseous products were transferred by cooling the storage tube in liquid nitrogen while warming the reaction vessel. The gases were later sampled using a syringe through a septum-containing, Teflon Mininert valve (Pierce Chemical, Rockford, IL) built into the storage vessel.

A second type of tube cracker,[81] used towards the end of this project, consisted of flexible stainless steel tubing (Cajon) with a stainless steel insert, a pressure/vacuum gauge (Robertshaw), a thermocouple vacuum gauge (Hastings), and valves (Whitey). These were connected together using stainless steel tubing and welded to prevent any leaks. This tube cracker was attached to a six-port automatic sampling valve (Hewlett-Packard) equipped with a 0.5 ml sample loop (Supelco, Bellefonte, PA). A scratch made on the small tube of the reaction vessel was positioned in the center of the flexible stainless

steel tubing. After the cracker had been evacuated, the small tube was broken open by a sharp bending of the flexible tubing, and sampled using the automatic valve. This tube cracker design had several advantages over the other design since the automatic sampling produced more accurate "injections," was faster, less air leaked into the system, and the pressure at the end of a reaction could be determined.

The gases in the recycle flow reactor were sampled two ways, since it became necessary to perform the analysis on two different columns. The automatic sampling valve was used as previously mentioned. To sample the other column, a storage vessel from the first tube cracker design was attached to the flow reactor after the reaction was completed. After this vessel was evacuated and cooled under liquid nitrogen, a valve was opened allowing the gases in the reactor to condense in this vessel. The gases were later sampled at room temperature using a syringe.

The analyses were carried out using a Hewlett-Packard Model 5710A gas chromatograph equipped with a thermal conductivity detector and a Model 3390A integrator. Separations were performed on a 15 ft x 1/8 in. nickel tubing column packed with 50/80 mesh Porapak Q (Supelco, Bellefonte, PA). A standard gas mixture (Scott Specialty Gases, Plumsteadville, PA), consisting of 50% CO, 8.0% CO_2, 2.0% Kr, 8.0% CH_4, 8.0% C_2H_6, 8.0% C_3H_8, 8.0% i-C_4H_{10}, and 8.0% n-C_4H_{10}, was used to compare retention times and detector responses with those in the reaction products. Krypton was included as an internal standard. Good separation was obtained at a flow rate of 20 ml/min. using the following temperature program: the temperature was held at -50C for 4

minutes, then increased at 8°C/min. until 230°C was reached, where the temperature remained until the completion of the analysis. All separations in which sampling was done using the automatic sampling valve were performed using the Porapak Q column.

Separation of CH_3Cl and C_3H_8 using the Porapak Q column was very poor. Reasonable separation was obtained using a 15 ft. x 1/8 in. nickel tubing containing 50/80 mesh Porapak R (Supelco, Bellefonte, PA) at a flow rate of 20 ml/min. using the following temperature program: the temperature was held at +50°C for 4 minutes, then increased at 4°C/min. until 230°C was reached, where the temperature was held until the completion of the analysis.

Amounts of metal in cobalt, nickel and iron dispersions in $AlCl_3$-NaCl (63-37 mole percent) were determined using atomic absorption spectroscopy at Galbraith Laboratories (Knoxville, TN).

E. Analytical Problems

The analysis of reaction products proved to be considerably more complicated than it first appeared. The presence of hydrogen in the reaction gases complicated the analysis, since hydrogen has a higher thermal conductivity than the helium carrier gas and produced negative (and quite low) responses by the thermal conductivity detector. Another problem resulted from the different detector response for the product gases. The method of internal standardization was chosen to obtain accurate analysis of carbon monoxide and the products. After several possible internal standards were tested for chemical reactivity toward chloroaluminate melts and after examining their chromatographic

retention times, krypton was chosen as the most reasonable standard. Unfortunately in the course of this work, it became apparent that krypton is somewhat soluble in the melt. As a result, the values obtained (as mole percent) using this internal standard could be up to 25% too high. This should not make any difference on a normalized distribution of the resulting C_1 to C_4 hydrocarbons since their nominal mole percent values should differ from the actual values by the same factor. The use of mole percent values of carbon monoxide in a calculation of CO consumption ($\Delta CO \cdot (gfw\ metal)^{-1} \cdot hr^{-1}$) would be significantly off because of the krypton solubility problem, since the initial CO mole percent is measured prior to contact with the melt. Instead, values obtained from peak areas were used in these calculations. While the accuracy of these values would vary with the amount of air introduced by the tube cracker and syringe (typically $< 2\%$), as well as by the hydrogen amount of hydrogen in the sample, these values are undoubtedly better than those obtained by the internal standard method. To separate nitrogen and oxygen from carbon monoxide, it became necessary to begin the gas chromatographic separation at -50°C.

Another source of error in carbon monoxide consumption was due to variation in batch reaction vessel size, due to slight differences in construction, as well as differences in sealing during the loading process. These variations in size have been estimated at ± 10%. While the volume of these vessels could have been determined after each reaction, most were sealed off after sampling and saved in case analysis of the catalytic systems or of higher molecular weight products would become desirable at a later date.

The "ball-joint" tubing cracker was used for most of this work. As previously mentioned, a small amount of air was introduced during the cracking process as well as during sampling with a syringe. The "flexible tubing" tube cracker became available during the last part of this project. While the problem of air introduction during the cracking and sampling (via the automatic sampling valve) was solved, another problem was encountered. Hydrogen chloride in the sample apparently produced a broad peak (which tailed badly), in the chromatographic separation. This peak overlapped with C_3H_8 and CH_3Cl peaks, and gave rise to very unreliable values for these two compounds. This problem was also encountered with the flow reactor, which also was sampled through the automatic sampling valve. Evidently the HCl concentration was brought down to a tolerable level while using the "ball joint" tubing cracker-syringe combination. A precolumn in the gas chromatograph capable of removing HCl would have solved this problem, however time did not allow its construction and testing.

Higher hydrocarbons have not been analyzed due to the relatively small amounts which could have been produced in the small volume batch reactors used in this work. It was possible to detect C_5 and C_6 hydrocarbons while analyzing for $C \leq 4$ products; however, since they are volatile liquids at room temperature, the results were only qualitative.

CHAPTER III

RESULTS FOR THE REACTION BETWEEN CARBON MONOXIDE AND HYDROGEN

A. Chloroaluminate Melts With and Without Aluminum

No reaction was observed between CO and H_2 (1:3 mole ratio) in an $AlCl_3$-NaCl (63-37 mole percent) melt at 175°C for 24 hours. When significant amounts of aluminum powder were added ($AlCl_3$:Al = 3.2 mole ratio), a slight reaction was observed. The CO consumption was 2.7×10^{-6} (change in moles of CO per mole of Al per hour, $\Delta CO \cdot (gfw\ Al)^{-1} \cdot hr^{-1}$). Typical distribution of C_1-C_4 hydrocarbons was: CH_4, 74%; C_2H_6, 4%; C_3H_8, 11%; i-C_4H_{10}, 9%; n-C_4H_{10}, 2%. Reproducibility for product distribution was within ten percent (typically within five percent) for product distributions for this as well as the catalytic systems. Reproducibility of CO consumption was not as good, due to problems discussed in the previous chapter. Most reactions reproduced the CO value to within 20%, however a few produced discordant results and varied in excess of 50% (these were repeated, producing more reasonable values).

B. Catalysis By Cobalt

The results of batch reactions involving various cobalt catalysts in $AlCl_3$-NaCl (63-37 mole percent) melts are shown in Table 2. Very low conversion of CO at 175°C for 24 hours was observed in the absence of aluminum powder; however, the conversion of CO increased significantly in the presence of aluminum. A cobalt-aluminum alloy (2:3 by

TABLE 2

RESULTS OF CO + H_2 (1:3 MOLE RATIO) REACTIONS WITH COBALT CATALYSTS IN $AlCl_3$-NaCl (63-37 MOLE PERCENT) AFTER 24 HOURS

Cobalt Form	$AlCl_3$:CO (mole ratio)	$AlCl_3$:Al (mole ratio)	CO Conversion (ΔCO (gfw Co)$^{-1}\cdot hr^{-1}$)	CO Conversion (percent[e])	Distribution of C_1-C_4 Products Relative to Each Other				
					CH_4	C_2H_6	C_3H_8	i-C_4H_{10}	n-C_4H_{10}
dispersion[a]	408:1	[b]	2.9×10^{-4}	4	59	19	14	6	2
dispersion[a]	408:1	80:1	8.2×10^{-4}	12	73	12	5	8	1
dispersion[a]	408:1	3.1:1	4.3×10^{-3}	61	75	19	4	1	1
dispersion[c]	408:1	3.2:1	8.1×10^{-4}	12	84	9	3	2	1
Co-Al alloy[a]	[d]	[b]	5.0×10^{-5}	3	83	8	4	4	<1
Co-Al alloy[a]	160:1	73:1	9.3×10^{-4}	54	71	18	6	3	2
$CoCl_2$[a]	276:1	3.6:1	1.7×10^{-3}	39	74	17	5	3	1

[a] 175°C and 3.5 bar.

[b] Without aluminum powder.

[c] 140°C and 3.2 bar.

[d] Without $AlCl_3$-NaCl.

[e] Percent varies with amount of catalyst.

weight) produced a very low CO conversion in the absence of $AlCl_3$-NaCl; the conversion increased greatly when the alloy was dispersed in the melt.

Since some $CoCl_2$ was evidently produced during the discharge dispersion process (a slight blue color was observed), $CoCl_2$ in $AlCl_3$-NaCl (63-37 mole percent) was tested for catalytic activity towards the CO + H_2 reactions; no activity was observed. Addition of aluminum powder to this system gave an active catalytic system with conversions similar to those obtained with the cobalt dispersions under similar conditions, as shown in Table 2. This was expected, since $CoCl_2$ is reduced to cobalt metal by the aluminum powder.

The distribution of the C_1-C_4 hydrocarbons is also shown in Table 2. Small amounts of C_5 and C_6 compounds, detected for cobalt systems containing both aluminum and $AlCl_3$-NaCl (63-37 mole percent) are not included in the distribution results. Methane was the major product obtained for all cobalt systems. The presence of aluminum produced an increase in the amount of CH_4 relative to the C_2-C_4 alkanes. The product distributions for the Co-Al alloy (2:3 by weight) in the melt and $CoCl_2$ with aluminum in the melt were very similar to that observed for the dispersed cobalt with aluminum in melt. In the absence of melt, a higher percentage of CH_4 was produced using the Co-Al alloy than was in the melt.

When a lower reaction temperature (140°C) was used with the dispersed cobalt in $AlCl_3$-NaCl (63-37 mole percent) melt containing aluminum powder, a decrease in CO conversion along with an

increase in CH_4 production relative to C_2-C_4 hydrocarbon production was observed, as shown in Table 2.

Preliminary results obtained with the recycle-flow reactor for the CO + H_2 reaction using a cobalt dispersion in an $AlCl_3$-NaCl (63-37 mole percent) melt with aluminum powder are presented in Table 3 and Figure 7. Most of the products were formed in the first two hours of the reaction. The CO conversion decreases with time, showing that the system is losing activity. This could be due to loss of $AlCl_3$ from the melt by sublimation to the top of the reaction vessel or by reaction with the water formed during the CO + H_2 reaction. The amounts of C_3H_8 and CH_3Cl could not be determined during the reaction due to the presence of HCl as previously mentioned. After the reaction was terminated, 0.01 mole percent C_3H_8 was detected using a syringe for sampling. No CH_3Cl was observed. Small amounts of C_2H_4 and C_5 products were also detected. No n-C_4H_{10} was observed, which was not surprising since only minor amounts were produced during batch reactions. CH_4 made up about 75% of the C_1-C_4 alkanes, which agreed well with the results from the batch reactions.

C. Catalysis By Nickel

The results of batch reactions involving various nickel catalysts in $AlCl_3$-NaCl (63-37 mole percent) melts are shown in Table 4. Low conversion of CO at 175°C for 24 hours was observed for the nickel dispersion in the absence of aluminum powder; however, the CO conversion increased by almost a factor of 100 in the presence of large amounts of aluminum. With nickel powder in the melt, a much lower CO

TABLE 3

RESULTS OF THE RECYCLE-FLOW REACTION FOR A COBALT DISPERSION IN $AlCl_3$-NaCl (63-37 MOLE PERCENT) MELT. $AlCl_3$:Co = 410:1 (MOLE RATIO); $AlCl_3$:Al = 33:1 (MOLE RATIO) CO:H_2 = 1:3 (MOLE RATIO); 1 BAR; 175°C; 13 ML/MIN.

Reaction Time (min)	CO Conversion ($\Delta CO \cdot (gfw\ Co)^{-1} \cdot hr^{-1}$)	CO Conversion (percent[a])	Distribution of C_1-C_4 Products Relative to Each Other			
			CH_4	C_2H_6	C_3H_8	i-C_4H_{10}
66	4.7×10^{-3}	3.1	75	8	[c]	17
132	2.4×10^{-3}	0.9	72	14	[c]	14
197	4.4×10^{-4}	1.1	73	13	[c]	13
261	4.8×10^{-4}	1.2	76	12	[c]	12
480	3.0×10^{-4}	1.4	78	11	[c]	11
609	3.0×10^{-4}	1.8	75	15	[c]	10

[a]Percent varies with amount of catalyst.

[b]C_3H_8 values omitted from calculation.

[c]Unreliable values due to HCl.

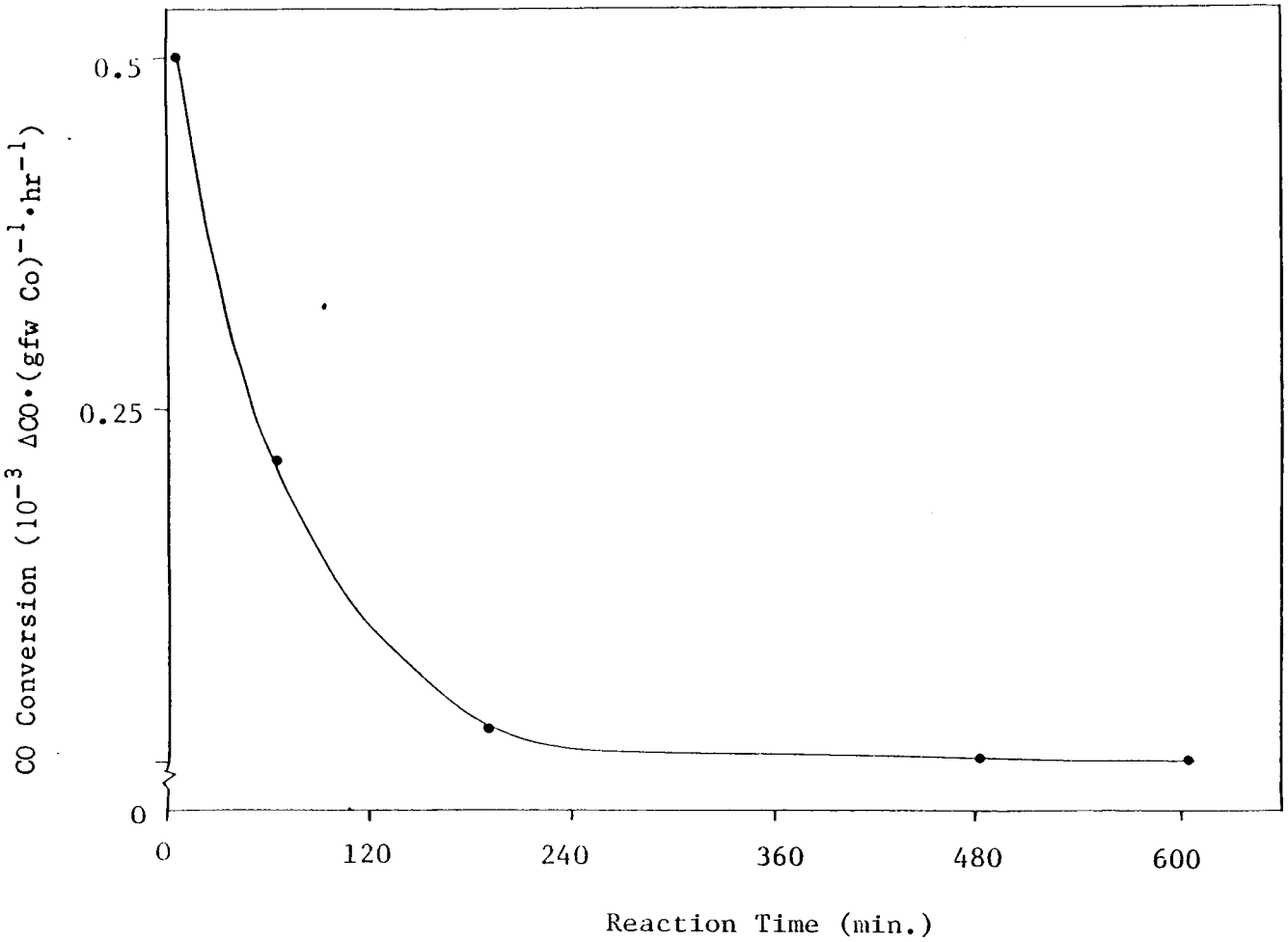

Figure 7. Variation of CO conversion with time for a cobalt catalyst in $AlCl_3$-NaCl (63-37 mole percent) melt. $AlCl_3$:Co = 410:1 (mole ratio); $AlCl_3$:Al = 3.3:1 (mole ratio); CO:H_2 = 1:3 (mole ratio) 1 bar; 175°C ; 13 ml/min.

TABLE 4

RESULTS OF CO + H_2 (1:3 MOLE RATIO) REACTIONS WITH NICKEL CATALYSTS IN $AlCl_3$-NaCl (63-37 MOLE PERCENT) MELTS

Nickel Form	$AlCl_3$:Ni (mole ratio)	$AlCl_3$:Al (mole ratio)	CO Conversion ($\Delta CO \cdot (gfw\ Ni)^{-1} \cdot hr^{-1}$)	CO Conversion (percent[g])	Distribution of C_1-C_4 Products Relative to Each Other				
					CH_4	C_2H_6	C_3H_8	i-C_4H_{10}	n-C_4H_{10}
dispersion[a]	1750:1	[f]	6.6×10^{-4}	2	41	27	20	12	
dispersion[a]	1750:1	67:1	5.6×10^{-3}	20	79	13	5	2	1
dispersion[b]	1750:1	2.9:1	3.2×10^{-2}	5	60	23	5	10	2
dispersion[c]	1750:1	3.2:1	3.2×10^{-2}	14	66	20	5	9	1
dispersion[d]	1750:1	2.8:1	2.5×10^{-2}	22	63	17	9	11	
dispersion[a]	1750:1	3.7:1	$\geq 2.8 \times 10^{-2}$	100	67	19	6	7	1
dispersion[e]	1750:1	3.6:1	3.8×10^{-5}	<1	73	13	3	11	
powder[a]	113:1	[f]	6.4×10^{-5}	3	48	26	22	4	
powder[a]	117:1	3.6:1	3.1×10^{-4}	17	56	28	9	6	<1
$NiCl_2$[a]	276:1	2.8:1	$\geq 4.5 \times 10^{-3}$	100	71	23	4	2	<1

[a] 24 hours at 175°C and 3.5 bar.

[b] 1 hour at 175°C and 3.5 bar.

[c] 3 hours at 175°C and 3.5 bar.

[d] 6 hours at 175°C and 3.5 bar.

[e] 24 hours at 140°C and 3.2 bar.

[f] Without aluminum.

[g] Percent varies with the amount of catalyst.

conversion was observed than with the dispersion, probably due to the much larger particle size (and therefore lower surface area) of the powder. The presence of aluminum in the nickel powder-melt system increased the CO conversion by less than a factor of ten. No reaction was observed for nickel powder in the absence of melt.

Nickel chloride could have been produced during the discharge dispersion process. However, no reaction was observed using $NiCl_2$ in $AlCl_3$-NaCl (63-37 mole percent). Addition of aluminum to this system reduced $NiCl_2$ to nickel metal and produced an active system, as shown in Table 4.

The distribution of the C_1-C_4 hydrocarbons is also shown in Table 4. For nickel dispersion or powder in $AlCl_3$-NaCl (63-37 mole percent) melts containing no aluminum, CH_4 made up less than 50% of the C_1-C_4 alkanes. Small amounts of aluminum powder produced large increases in the relative amount of CH_4 in the products, however the relative CH_4 amount decreased when a larger amount of aluminum was added. Similar product distribution was observed with the $NiCl_2$-aluminum-melt system as with the dispersion-aluminum-melt system under the same conditions. For nickel powder in the melt with aluminum, a lower amount of CH_4 relative to the C_2-C_4 alkanes was observed. C_5 and C_6 hydrocarbons were detected for systems containing Ni, Al and the melt.

The reaction time resulted in little difference in either the CO conversion, or the C_1-C_4 product distribution as shown in Table 4.

When a lower reaction temperature was used for the nickel dispersion in an $AlCl_3$-NaCl (63-37 mole percent) melt with aluminum powder, a significant decrease in the CO conversion and a slight increase in the

amount of CH_4 relative to C_2-C_4 alkanes were observed, as shown in Table 4.

A nickel catalyst supported on kieselguhr was used for comparison to the nickel-melt systems. Conversion of CO was observed to be 2.1×10^{-4} ($\Delta CO \cdot (gfw\ Ni)^{-1} \cdot hr^{-1}$), which is similar to that observed for nickel dispersion in melt in the absence of aluminum. The distribution of the C_1-C_4 hydrocarbons obtained is: CH_4, 79%; C_2H_6, <1%; C_3H_8, 17%; i-C_4H_{10}, 4%; n-C_4H_{10}, none. During this reaction the walls of the Pyrex vessel became coated with nickel metal. $Ni(CO)_4$ was evidently formed from Ni and CO during the reaction. Since $Ni(CO)_4$ is not stable at the reaction temperature (it decomposes at 60°C), decomposition to Ni and CO is probably responsible for the Ni on the walls of the vessel. Since Ni formation was not observed on the reaction vessel walls for Ni catalysts in melts, the chloroaluminate melts may stabilize Ni catalysts by preventing formation of $Ni(CO)_4$ or its escape from the melt.

D. Catalysis By Iron

The results of batch reactions involving various iron catalysts in $AlCl_3$-NaCl (63-37 mole percent) melts are shown in Table 5. Low conversion of CO at 175°C or 250°C for 24 hours with a 3:1 mole ratio of H_2:CO was observed for the dispersion in the absence of aluminum powder; however, the conversion at 250°C was increased by about a factor of ten in the presence of large amounts of aluminum. An Fe-Al alloy (1:1 by weight) produced similar CO conversion in the melt as did the dispersion with aluminum powder.

TABLE 5

RESULTS OF CO + H_2 REACTIONS WITH IRON CATALYSTS IN $AlCl_3$-NaCl (63-37 MOLE PERCENT) MELTS AFTER 24 HOURS

Iron Form	$AlCl_3$:Fe (mole ratio)	$AlCl_3$:Al (mole ratio)	CO Conversion ($\Delta CO \cdot (gfw\ Fe)^{-1} \cdot min^{-1}$)	CO Conversion (percent[e])	Distribution of C_1-C_4 Products Relative to Each Other				
					CH_4	C_2H_6	C_3H_8	i-C_4H_{10}	n-C_4H_{10}
dispersion[a]	305:1	[d]	2.1×10^{-4}	4	100				
dispersion[b]	305:1	[d]	6.3×10^{-4}	13	75	25			
dispersion[b]	305:1	60:1	9.2×10^{-4}	19	81	6	9	4	1
dispersion[b]	305:1	3.2:1	$\geq 5.0 \times 10^{-3}$	100	91	6	2	1	<1
dispersion[c]	305:1	[d]	5.6×10^{-5}	1	50	22	<1	17	11
dispersion[c]	305:1	3.8:1	1.6×10^{-3}	28	77	4	6	10	2
Fe-Al alloy[b]	121:1	58:1	1.2×10^{-3}	59	81	15	3	<1	<1

[a] 175°C and 3.5 bar of 3:1 H_2:CO (mole ratio).

[b] 250°C and 4.1 bar of 3:1 H_2:CO (mole ratio).

[c] 250°C and 4.1 bar of 1:1 H_2:CO (mole ratio).

[d] Without aluminum.

[e] Varies with amount of catalyst.

The distribution of the C_1-C_4 hydrocarbons is also shown in Table 5. Only CH_4 and C_2H_6 were observed for reactions in the absence of aluminum powder. With added aluminum, C_3H_8, i-C_4H_{10}, n-C_4H_{10} as well as small amounts of C_5 and C_6 hydrocarbons were produced. The amount of CH_4 relative to the C_2-C_4 hydrocarbons was observed to increase with increasing amounts of aluminum. The same relative amount of CH_4 was observed for the Fe-Al alloy (1:1 by weight) as for the dispersion-melt-aluminum system, however the C_2H_6 amount was higher at the expense of the higher hydrocarbons. C_5 and C_6 hydrocarbons were detected in reactions involving Fe, Al and $AlCl_3$-NaCl.

At a lower reaction temperature (175°C) only CH_4 production was observed for the dispersion in an $AlCl_3$-NaCl (63-37 mole percent) melt, as shown in Table 5.

Results using a more common gas mixture for iron catalysts, H_2:CO = 1:1 (mole ratio), are also given in Table 5 for the iron dispersion in $AlCl_3$-NaCl (63-37 mole percent). A decrease in CO conversion and a shift to less CH_4 produced relative to the C_2-C_4 hydrocarbons was observed both in the presence and absence of aluminum powder, when compared to reactions involving H_2:CO = 3:1 (mole ratio) under the same conditions.

E. Other Metallic Catalysts

Other metals, not traditionally associated with the Fischer-Tropsch reaction, were tested for activity for the CO + H_2 reaction at 175°C in $AlCl_3$-NaCl (63-37 mole percent) melts. Results for palladium, platinum and rhodium dispersions are found in Table 6. In the absence

TABLE 6

RESULTS OF CO + H_2 (1:3 MOLE RATIO) REACTIONS WITH VARIOUS HETEROGENEOUS CATALYSTS IN $AlCl_3$-NaCl MELTS FOR 24 HOURS AT 175°C AND 3.5 BAR

Metal and Form	$AlCl_3$:Al (mole ratio)	CO Conversion (percent[c])	Distribution of C_1-C_4 Products Relative to Each Other				
			CH_4	C_2H_6	C_3H_8	i-C_4H_{10}	n-C_4H_{10}
Pt dispersion[a]	[b]	5	94	6			
Pt dispersion[a]	3.2:1	23	90	2	[e]	2	4
Pt dispersion[d]	2.7:1	<1	100				
Pd dispersion[a]	[b]	11	97	3			
Pd dispersion[a]	3.7:1	14	86	7	3	2	1
Rh dispersion[a]	[b]	2	100				
Re powder[a]	[b]	3	~100	<1		<1	
Re powder[a]	3.3:1	5	75	13	8	4	1
Ir powder[a]	[b]	4	64	36			

[a] $AlCl_3$-NaCl (63-37 mole percent).

[b] Without aluminum.

[c] Varies with amount of catalyst.

[d] $AlCl_3$-NaCl (49-51 mole percent).

[e] Value unreliable due to presence of HCl.

of aluminum powder, CH_4 made up more than 90% of the C_1-C_4 hydrocarbons obtained using these dispersion-melt systems. While the CH_4 amount decreased relative to the C_2-C_4 hydrocarbons in the presence of aluminum for Pt and Pd, it was still much higher than those observed with Ni and Co catalysts. CH_4 was the only product observed for platinum dispersed in a NaCl-rich $AlCl_3$-NaCl melt. Since none of these catalysts was sent out for analysis, only changes in CO values could be determined. These are dependent on the amount of catalyst in each reaction. These values do indicate a significant enhancement in CO conversion occurred when aluminum was present for Pt catalysts, but very little for Pd catalysts. No reaction was observed using tantalum or tungsten dispersions in $AlCl_3$-NaCl melts.

Results for rhenium powder in $AlCl_3$-NaCl (63-37 mole percent) melts with and without aluminum are also shown in Table 6. In the absence of aluminum the products were almost entirely CH_4; the CO conversion was 1.3×10^{-4} ($\Delta CO \cdot (gfw\ Re)^{-1} \cdot hr^{-1}$). In the presence of aluminum, the amount of CH_4 dropped to 75% of the C_1-C_4 hydrocarbons. The CO conversion only increased slightly to 2.7×10^{-4} ($\Delta CO \cdot (gfw\ Re)^{-1} \cdot hr^{-1}$). These results could be due to catalysis by Al, not enhancement, since product formation and change in CO are very low.

Iridium powder in $AlCl_3$-NaCl (63-37 mole percent) melts produced a ratio of CH_4:C_2H_6 of about 2:1 with no higher hydrocarbons, as shown in Table 6. A 3.0×10^{-4} ($\Delta CO \cdot Ir^{-1} \cdot hr^{-1}$) CO conversion was observed.

F. Catalysis Using $Ir_4(CO)_{12}$ as a Catalyst Precursor

$Ir_4(CO)_{12}$ is not stable in the $AlCl_3$-NaCl (63-37 mole percent) melt and is rapidly converted to one or more other carbonyl complexes as indicated by infrared and UV-visible spectroscopy.[82] The infrared spectrum of $Ir_4(CO)_{12}$ added to the melt is shown in Figure 8 about 45 min. after melting. Bands, observed at 2157, 2141, 2133, 2124, 2117, 2108 and 2082 cm^{-1}, are quite different from a spectrum of $Ir_4(CO)_{12}$ in CH_2Cl_2, where bands at 2067 and 2017 cm^{-1} have been observed.[83] The intensity of the bands observed decreased and the bands were almost absent after 24 hours, indicating decomposition of the carbonyl(s).

The results of batch reactions involving $Ir_4(CO)_{12}$ as a precatalyst in $AlCl_3$-NaCl (63-37 mole percent) melts are shown in Table 7. The CO conversion in the absence of aluminum powder is significantly greater than was observed for heterogeneous catalysts under similar conditions. Addition of small amounts of aluminum powder increased the CO consumption somewhat more than larger amounts both at reaction temperatures of 160 and 175°C. CO conversions were similar at both temperatures.

The distribution of the C_1-C_4 hydrocarbons is also shown in Table 7. A slightly greater amount of CH_4 than C_2H_6 was observed after 24 hours at 175°C in the absence of aluminum. This result agrees with the results of Demitras and Muetterties,[27] that is, CH_4 predominates at long reaction times. At 175°C, the amount of CH_4 relative to the C_2-C_4 hydrocarbons increased with the amount of aluminum. At 160°C in the absence of aluminum, more CH_4 relative to the C_2-C_4 hydrocarbons was

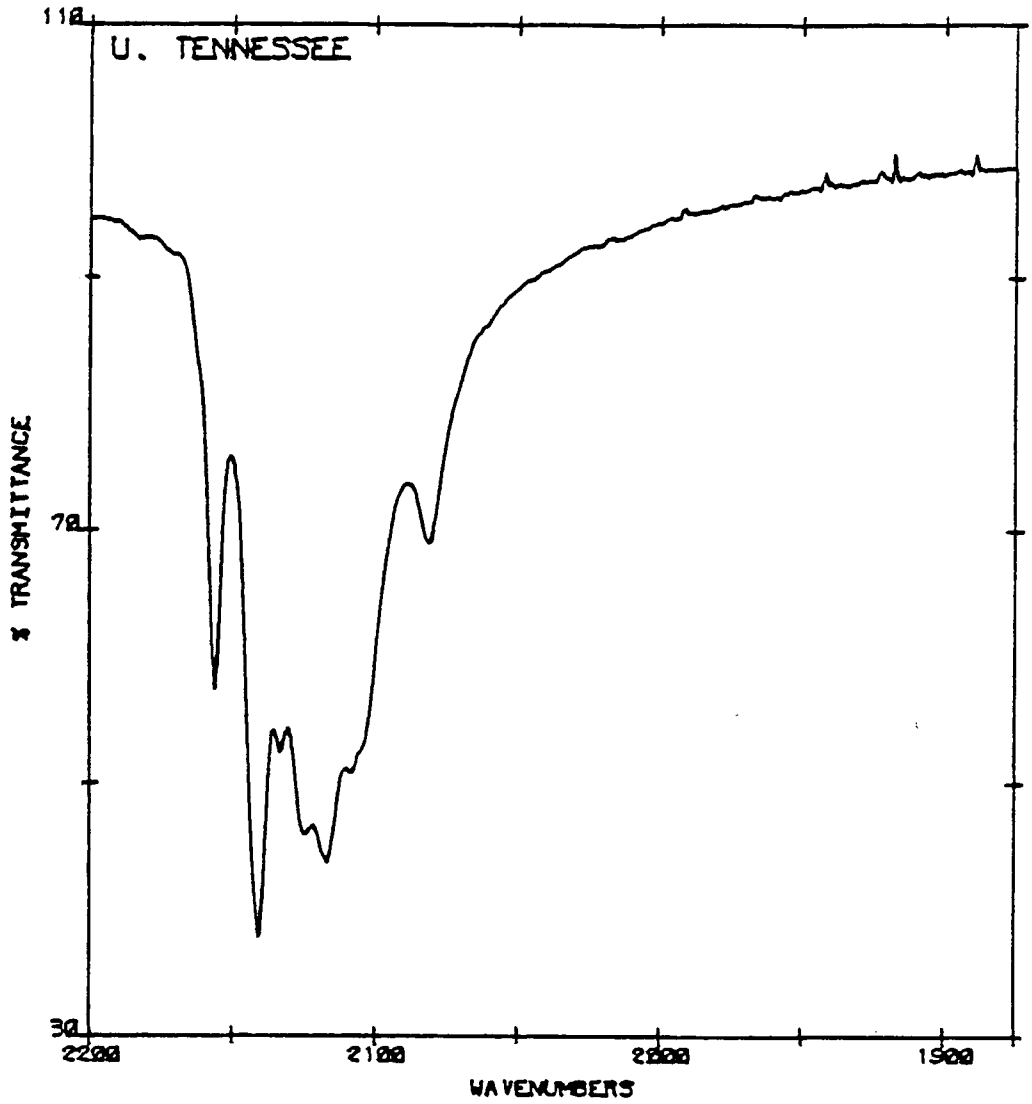

Figure 8. Infrared ATR spectrum of $Ir_4(CO)_{12}$ in $AlCl_3$-NaCl (63-37 mole percent).

TABLE 7

RESULTS OF CO + H_2 (1:3 MOLE RATIO) REACTIONS WITH $Ir_4(CO)_{12}$ CATALYST PRECURSORS IN $AlCl_3$-NaCl (63-37 MOLE PERCENT) MELTS

$AlCl_3$:Ir (mole ratio)	$AlCl_3$:Al (mole ratio)	CO Conversion ($\Delta CO \cdot (gfw\ Ir)^{-1} \cdot hr^{-1}$)	CO Conversion (percent[e])	Distribution of C_1-C_4 Products Relative to Each Other				
				CH_4	C_2H_6	C_3H_8	i-C_4H_{10}	n-C_4H_{10}
590:1[a]	[d]	3.1×10^{-3}	17	47	43	10	<1	
810:1[a]	60:1	1.7×10^{-2}	50	74	13	9	3	1
590:1[a]	3.6:1	2.5×10^{-3}	41	87	9	2	2	<1
990:1[b]	[d]	9.1×10^{-3}	14	75	20	5		
990:1[b]	62:1	2.6×10^{-2}	41	68	19	8	3	1
990:1[b]	3.0:1	1.1×10^{-2}	17	67	23	5	5	1
600:1[c]	[d]	7.0×10^{-2}	4	68	23	10		

[a] 24 hours at 175°C and 3.5 bar.

[b] 24 hours at 160°C and 3.4 bar.

[c] 30 min. at 175°C and 3.5 bar.

[d] Without aluminum.

[e] Varies with amount of catalyst.

observed than at 175°C. Added aluminum at 160°C was observed to decrease the relative amount of CH_4.

Results of a 30 min. batch reaction at 175°C are also shown in Table 7. A much higher CO conversion value was observed than for the 24 hour reaction, as well as a higher proportion of CH_4. This is in agreement with Collman and coworkers,[62] who observed a rapid initial burst of CH_4 in their flow reactions.

Preliminary results using the $Ir_4(CO)_{12}$ precatalyst in the recycle-flow reactor are shown in Table 8 and Figure 9. The initial rapid burst of CH_4 was obvious from the high value observed for the initial sample; high CO conversion value was also observed. From this point, the mole percent of CH_4 first appeared to decrease with time; this was due to incomplete mixing of the gases in the reactor at short sample times. After the initial CH_4 burst, C_2H_6 production occurred at a more rapid rate than CH_4 production. The values of C_3H_8 and CH_3Cl obtained during the reaction were unreliable due to the presence of HCl. After termination of the reaction, 0.10 and 0.11 mole percent C_3H_8 and CH_3Cl were observed. The final distribution of the C_1-C_4 products relative to each other was: CH_4, 39%; C_2H_6, 50%; C_3H_8, 5%; CH_3Cl, 5%; i-C_4H_{10}, 1%. These results are similar to those obtained by Collman and coworkers.[62]

The addition of aluminum powder to the $Ir_4(CO)_{12}$ in $AlCl_3$-NaCl (63-37 mole percent) has also been studied in the recycle-flow reactor. As shown in Table 9, and Figure 10 the initial rapid burst of CH_4 was also observed for this system, coupled with an initial high CO conversion value. A drop in the CO conversion value and the amount of

TABLE 8

RESULTS FOR THE RECYCLE-FLOW REACTION BETWEEN CO AND H_2 FOR THE $Ir_4(CO)_{12}$ CATALYST PRECURSOR $AlCl_3$-NaCl (63-37 MOLE PERCENT) MELT. $AlCl_3$:Ir = 570:1 (MOLE RATIO); CO:H_2 = 1:3 (MOLE RATIO), 1 BAR; 175°C AT 13 ML/MIN

Reaction Time (min)	CO Conversion ($\Delta CO \cdot (gfw\ Ir)^{-1} \cdot hr^{-1}$)	CO Conversion (percent)	Distribution of C_1-C_4 Products Relative to Each Other[a]				
			CH_4	C_2H_6	C_3H_8 and CH_3Cl	i-C_4H_{10}	n-C_4H_{10}
12	.50	11	89	11	b		
66	5.2×10^{-2}	6	64	36	b		
143	1.5×10^{-2}	4	58	42	b	<1	
210	9.0×10^{-3}	3	56	44	b	<1	
279	1.9×10^{-2}	9	47	51	b	2	
600	1.5×10^{-2}	17	43	55	b	2	

[a] C_3H_8 and CH_3Cl values were not included in the distribution.

[b] Unreliable values due to HCl.

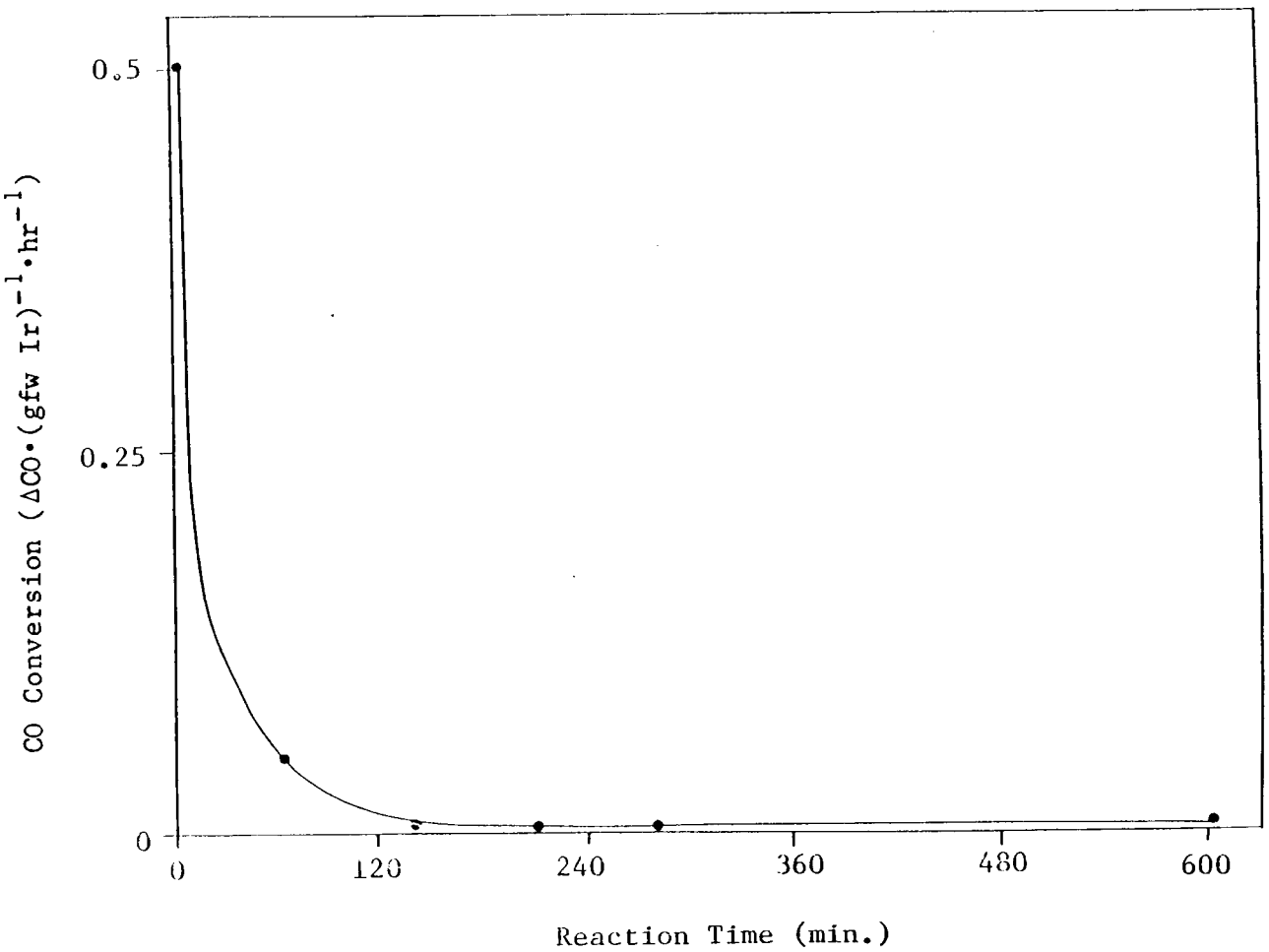

Figure 9. Variation of CO conversion with time for $Ir_4(CO)_{12}$ catalyst precursor in $AlCl_3$-NaCl (63-37 mole percent) melt. $AlCl_3$:Ir = 579:1 (mole ratio); CO:H_2 = 1:3 (mole ratio) 1 bar; 175°C; 13 ml/min.

TABLE 9

RESULTS FOR THE RECYCLE-FLOW REACTION BETWEEN CO AND H_2 FOR THE $Ir_4(CO)_{12}$ CATALYST PRECURSOR $AlCl_3$-NaCl (63-37 MOLE PERCENT) MELT. $AlCl_3$:Ir = 590:1 (MOLE RATIO); $AlCl_3$:Al = 3.1:1 (MOLE RATIO); CO:H_2 = 1:3 (MOLE RATIO), 1 BAR; 175°C; 13 ML/MIN.

Reaction Time (min)	CO Conversion ($\Delta CO \cdot (gfw\ Ir)^{-1} \cdot hr^{-1}$)	CO Conversion (percent[c])	Distribution of C_1-C_4 Products Relative to Each Other[a]					
			CH_4	C_2H_4	C_2H_6	C_3H_8 and CH_3Cl	i-C_4H_{10}	n-C_4H_{10}
10	.34	6	92		8	[b]		
60	1.6×10^{-2}	2	61		32	[b]	7	
121	7.2×10^{-2}	15	66	8	13	[b]	12	1
304	4.9×10^{-2}	26	64	11	13	[b]	11	1
370	3.9×10^{-2}	25	66	9	13	[b]	11	1
503	2.8×10^{-2}	25	67	8	13	[b]	11	1
600	2.3×10^{-2}	24	69	5	13	[b]	12	1

[a] C_3H_8 and CH_3Cl values were not included in the distribution.

[b] Unreliable values due to HCl.

[c] Varies with amount of catalyst.

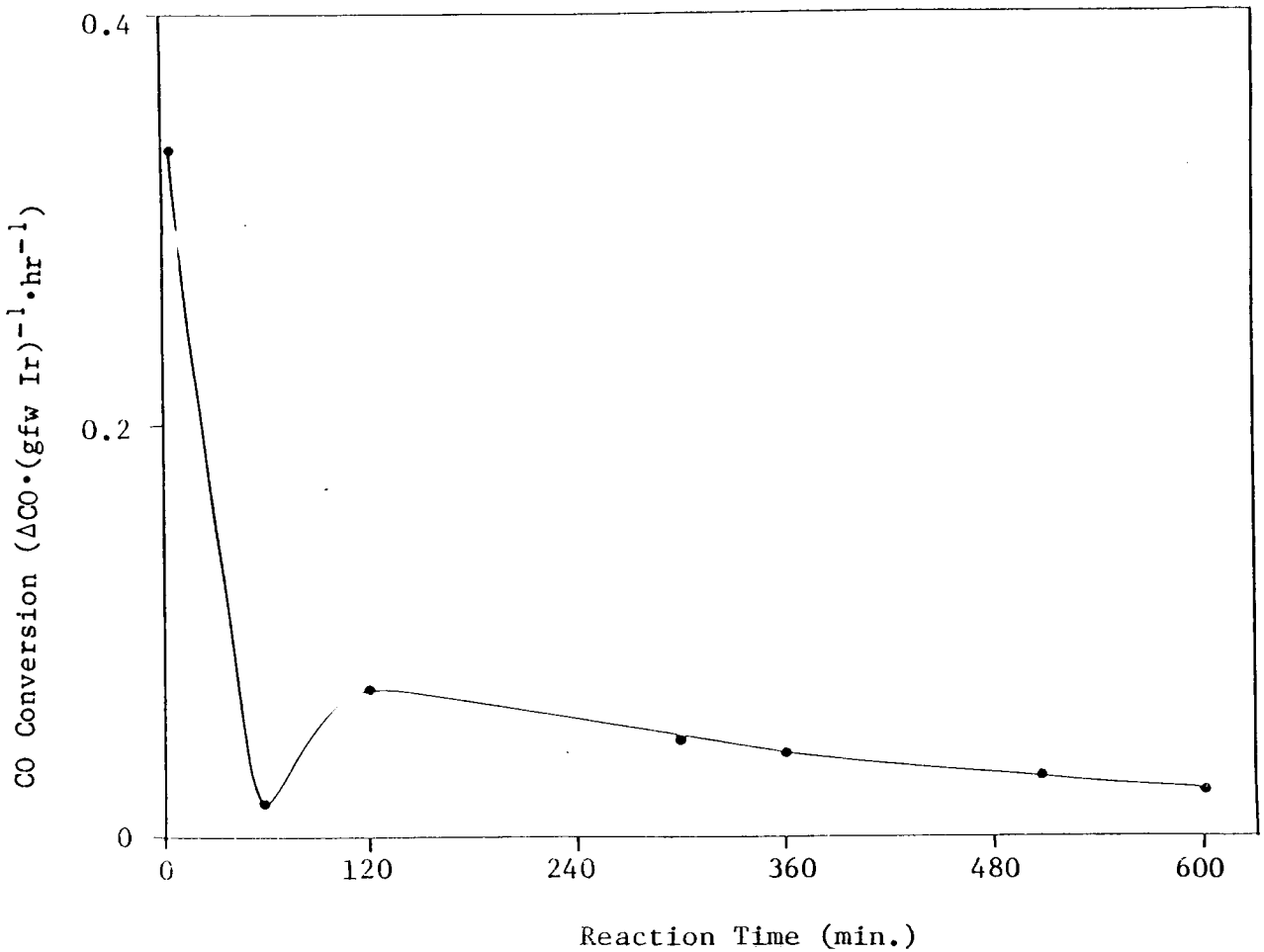

Figure 10. Variation of CO conversion with time for $Ir_4(CO)_{12}$ catalyst precursor in $AlCl_3$-NaCl (63-37 mole percent) melt. $AlCl_3$:Ir = 590:1 (mole ratio); $AlCl_3$:Al = 3.3:1; CO:H_2 = 1:3 (mole ratio) 1 bar; 175°C; 13 ml/min.

CH_4 is observed due to mixing of gases in the reactor. Their values then increase again along with these of other products. After five hours no additional C_2-C_4 products were produced, and only a slight increase in the amount of CH_4 was observed. The CO conversion value was decreasing and the system was becoming inactive. This loss of activity could be due to decomposition of the catalyst or to change in melt composition, since $AlCl_3$ was lost both through sublimation to the top of the reaction vessel and due to reaction with H_2O formed during the CO + H_2 reaction. A small amount of C_2H_4 was observed and appeared to decrease in concentration after five hours. The C_3H_8 and CH_3Cl analyses were unreliable during the reaction due to the presence of HCl, however 0.23 mole percent C_3H_8 and no CH_3Cl were detected after termination of the reaction. The final distribution of the C_1-C_4 products relative to each other was: CH_4, 64%; C_2H_4, 5%; C_2H_6, 12%; C_3H_8; C_3H_8, 7%; CH_3Cl, 0.%; i-C_4H_{10}, 10%; n-C_4H_{10}, 1%. C_5 and C_6 hydrocarbons were also detected.

CHAPTER IV

CONCLUSIONS: THE REACTION BETWEEN CARBON MONOXIDE AND HYDROGEN

The Fischer-Tropsch activity of several metallic catalysts in molten chloroaluminates has been studied at relatively low pressures. Low conversions of CO to alkanes were observed for Co, Fe, Ni, Pd, Pt, Ir, Rh and Re. No reaction was observed for W, Ta and the pure chloroaluminate melt. Methane was the major product formed using any of these heterogeneous catalysts. The most favorable product distribution for these metals was observed for Ni catalysts, since less than half of the products was CH_4.

The effect of aluminum on the Fischer-Tropsch activity of these metallic catalysts in molten chloroaluminates has also been studied. In all cases, the conversion of CO was enhanced by the presence of aluminum. The magnitude of enhancement depended on the catalyst. Large enhancements were observed for Co, Ni and Fe catalysts, while only slight enhancements were observed for Pd, Pt and Re. Aluminum behaved as a reagent, and not as a catalyst, since CO conversion varied with the amount of Al in the system. The effect of Al on product distribution was also largely dependent on the metal catalyst involved. Small amounts of Al increased the production of CH_4 relative to the other products for Co, Fe and Ni catalysts, while no clear pattern emerged for these catalysts, when larger amounts of Al were present. Almost no change in the percent of CH_4 formed was observed for Pt when Al was added, however a decrease in CH_4 was observed for Pd

and Re in its presence. The actual amounts of C_1-C_6 products increased when Al was added.

The $Ir_4(CO)_{12}$ catalyst precursor was studied in chloroaluminate melts, both in batch reactions and recycle-flow reactions. The batch reaction results were similar to those observed by Demitras and Muetterties,[27] since a slight excess of CH_4 over C_2H_6 was observed at long reaction times. No CH_3Cl was detected (however none was found in any batch reaction). Somewhat different results were observed with the recycle-flow reactor. The amount of C_2H_6 produced was greater than the amount of CH_4 (after an initial burst of CH_4). CH_3Cl was observed in the flow system. These results are quite similar to those observed by Collman and coworkers[62] for the same system.

Enhancement by Al of the $Ir_4(CO)_{12}$ catalyst precursor was also studied in chloroaluminate melts using both batch reactions and recycle-flow reactions, confirming prior work by Lapidus and coworkers.[63-67] Enhancement of CO conversion was much greater with small amounts of Al than with larger amounts. The proportion of CH_4, the major product, in the products observed at 175°C increased with increasing Al content. The initial rapid burst of CH_4 was also observed for this system using the recycle-flow reactor. The system became somewhat inactive after five hours due to either catalyst decomposition or loss of $AlCl_3$ from the melt due to reaction with H_2O, formed during the Fischer-Tropsch synthesis, or through sublimation. In the presence of Al, products from C_1 to C_6 were observed, and included C_2H_4.

The results for $Ir_4(CO)_{12}$ in chloroaluminate melts in a flow reactor reported by Muetterties and coworkers[26] remain a mystery. In that work isobutane was the major product observed; no CH_3Cl was detected. Since their results were quite different from those found in this work as well as from those by Collman and coworkers,[62] a different active catalyst must have been involved.

The results presented here represent a survey of catalysts in the chloroaluminate melts. There are many questions left unanswered, such as identification of organic products which remain in the melts and length of time that these catalysts remain active. Nickel carbonyl formation may have been inhibited in the melt. It would be interesting to determine whether there is a loss of Ni from the melt with time in a flow-through reactor (as opposed to a recycle-flow).

The utility of these catalytic systems by industry is severely hampered by lack of catalyst selectivity (a common problem with Fischer-Tropsch catalysts), the difficulties involved with handling $AlCl_3$-rich melts, and reaction of $AlCl_3$ with the H_2O formed during the Fischer-Tropsch synthesis.

PART B

INFRARED SPECTROELECTROCHEMISTRY USING ATTENUATED TOTAL REFLECTANCE

CHAPTER V

INTRODUCTION TO INFRARED SPECTROELECTROCHEMISTRY USING ATTENUATED TOTAL REFLECTANCE

Spectroelectrochemistry involves the coupling of spectroscopy to electrochemistry. The redox chemistry of an electroactive species is monitored spectroscopically in solution next to the working electrode. Although molten salts represent a large class of non-aqueous solvents, spectroelectrochemical techniques have rarely been applied to them, especially in the infrared region. The extension of spectroelectrochemical techniques in molten salts into the infrared region should provide a better understanding of redox chemistry in these solvents.

A. Review of the Literature

1. Spectroelectrochemical Techniques

Spectroelectrochemistry involves the simultaneous use of spectroscopic and electrochemical techniques for the study of redox chemistry of solutes. The electroactive species are oxidized or reduced at a working electrode while the solution adjacent to this electrode is monitored spectroscopically. These techniques are useful in obtaining both redox potentials and spectra of electrogenerated materials, as well as for studying any follow-up chemical reactions of the electrogenerated products.

The most widely used spectroelectrochemical techniques involve absorption spectroscopy. These encompass a variety of transmission and reflection methods. Other techniques, such as fluorescence and Raman spectroelectrochemistry, have not been as widely used. More detailed

treatment of theory, applications and cell design is available elsewhere.[84-91]

In transmission spectroelectrochemistry, the most common spectroelectrochemical technique, the light beam passes through an optically transparent electrode (OTE) and the adjacent solution. Many kinds of OTE's have been reported in the literature.[84,85,91] One type of OTE is prepared by depositing a very thin film of a conducting substance onto a transparent material (e.g. quartz for UV-visible, germanium for IR). Antimony-doped tin oxide (Nesa) films, tin-doped indium oxide (Nesatron) films, and vapor deposited films of platinum, gold and carbon have been used as conducting films. A major problem with this type of OTE is the trade off between resistance and transparency. The lower the resistance, the thicker the film which, in turn, results in a lower transmittance.

In another type of OTE, the electrode material contains small openings or pores which transmit the light beam. Since the openings are generally quite small, the diffusion layer thickness becomes larger than the size of the opening after electrolyzing a short time.[85] Platinum gauze and screen (45-80 wires per inch) and various wire micromeshes (100-2000 wires per inch, 20-80% transmission), made of materials such as copper, gold, nickel and silver, have been used.[91] A porous glassy carbon material, reticulated vitreous carbon (RVC, trademark of The Fluorocarbon Co., Anaheim, CA) has also been used.[92] RVC has an open-pore structure of random vitreous carbon struts, and is available with void volumes up to 97%.[93]

Conventional transmission cells with pathlengths of about 1 cm are well suited for studying chemical kinetics.[91] The preferred electrochemical method for quantitative absorbance-time measurements has been chronoamperometry.[84-86,91]

In thin-layer spectroelectrochemical cells with pathlengths between 0.05 to 0.3 mm, electrolysis of the small amount of solutions trapped adjacent to the OTE is rapid and complete usually within a few minutes. This method provides a rapid way of obtaining spectra of electroactive species and products. Electrochemical information about the redox system can also be obtained.[94] Thin layer coulometry involves measuring the charge passed vs. time while an exhaustive electrolysis is performed. The number of electrons, n, per GFW is related to the faradaic charge component, Q_F, according to Faraday's Law:

$$Q_F = n\ F\ VC, \tag{1}$$

where F is the Faraday, V is the volume of the thin layer cell in liters, and C is the molar concentration of the electroactive material.

If a reversible redox system is used in a thin-layer electrochemical cell, the potential applied to the electrode, $E_{applied}$, can be used to determine the ratio of the reduced form (R) and the oxidized form (O) of the electroactive species using the Nernst equation:

$$E_{applied} = E^{\circ\prime} + \frac{RT}{nF} \ln \frac{[O]}{[R]}, \tag{2}$$

where $E^{\circ\prime}$ is the formal potential of the redox system, R is the molar

gas constant, T is the absolute temperature; n and F have been defined previously. In a thin-layer spectroelectrochemical cell containing a reversible electrochemical system, when a potential is applied to the OTE, electrolysis occurs, quickly altering the ratio [O]/[R] to obey the Nernst equation. If the initial form of the electroactive species is a non-absorbing R ([O]/[R] < 0.001) and the oxidized form absorbs, the ratio of [O]/[R] increases as the potential of the OTE is made more positive, and an absorption band (or bands) appears. Finally as the potential becomes sufficiently positive, only the oxidized form is present ([O]/[R] > 1000). The ratio of [O]/[R] at different applied potentials can be calculated from the spectra. A plot of $E_{applied}$ vs. log [O]/[R] should be linear. $E^{\circ\prime}$ is the y-intercept and the value of n may be calculated from the slope.[84,91]

Other widely used techniques for spectroelectrochemistry are specular reflectance[84-88,91] and internal reflection.[84-86,89,91] In specular reflectance spectroelectrochemistry the electrode surface acts as a mirror, and therefore should be made from a material that is smooth, flat, conducting and capable of reflecting incident radiation. Bulk metal surfaces and thin metal films on glass or quartz plates have been used. The incident beam of radiation passes through a window and the solution to the electrode, where it is reflected back through the solution and window toward the detector optics. In a variation of this technique, specular reflectance at a glancing incidence, the incoming light is reflected off the electrode at a very small incident angle.[95-98] This technique involves relatively long pathlengths compared to more common reflection methods or transmission methods.

Absorbance is enhanced by a factor of 100-200 for this technique as compared to using an OTE.[95]

In internal reflection spectroelectrochemistry the beam of light passes through the window element at an angle greater than the critical angle of the window material, such that total reflection of the beam occurs. The electric field vector of the beam penetrates a short distance into the solution, giving spectral information on the solution at the interface.[89] The window element can either double as the electrode or a separate electrode can be positioned close to the window. In the UV-visible region, thin metal films, such as gold and platinum, deposited on glass or quartz have been used. Germanium internal reflection elements have been used in the infrared region. Doped germanium has been used as a combination window and electrode; intrinsic (undoped) germanium has been modified with a thin carbon film on its surface to serve as an electrode.[99] Another technique is to place an electrode, such as a gold minigrid, adjacent to the germanium window.[85,89,100]

Raman spectroscopy has also been applied to spectroelectrochemical studies. Both soluble products and adsorbed films produced at an electrode surface have been studied by this technique.[91,101] Resonance Raman spectroelectrochemistry at or near the surface of a metal electrode produces an enhanced Raman signal on the order of 10^2-10^6 times that for normal Raman spectroscopy.[102] Solute concentrations in the millimolar range may be studied by this resonance technique. Another promising Raman technique is surface-enhanced Raman. In this

technique, the Raman scattering is increased for some species when they are adsorbed on a metal electrode surface.[103]

Other spectroelectrochemical techniques developed use fluorescence,[104] chemiluminescence,[105] photoacoustic[106] and photothermal[107,108] spectroscopies.

2. Infrared Spectroelectrochemical Cells

Murray and coworkers developed an infrared OTE consisting of four gold minigrids (100 lines per inch) sandwiched between NaCl plates.[109] The minigrids were separated from each other by Teflon spacers. This multielectrode cell achieved a transparency of 30% transmittance. This OTE provided a longer pathlength through the solution in the vicinity of the electrodes than in a single grid design, permitting the use of lower concentrations. Drawbacks in this cell design involved the following factors: 1) alignment of the minigrids was not reproducible, therefore an identical reference cell could not be prepared; 2) light scattering by the minigrids reduced resolution; 3) strongly absorbing solvents could cause problems due to the relatively long pathlength.

An infrared specular reflectance cell was constructed by Kissinger and Reilley.[110] A platinum electrode was prepared by thermally reducing platinum paint on a glass slide. A Teflon spacer was placed between the slide and an NaCl plate. Without using focusing optics, about 50% of the incident infrared radiation passed through the NaCl plate, reflected off the electrode, and passed through the plate again. Good sensitivities and time responses were reported.

In the early infrared internal reflection spectroelectrochemical studies, semiconducting germanium served as both the optical element and the working electrode.[111-113] Major problems were encountered with the use of semiconducting germanium in this capacity. Doping increased free carrier absorption in the germanium lattice.[114] Since the transmitted radiation through undoped germanium internal reflection elements was already quite low, the free carrier absorption in semiconducting germanium elements decreased the usable infrared region significantly. The second problem was due to the high resistance of the semiconducting germanium.[112] Potential gradients across the electrode were set up by the iR drop. The potential applied where contact was made to the semiconductor electrode was not the same at other points of the electrode. For this reason attempts at improving semiconducting germanium OTE's have not been reported.

The possibility of using thin gold films as electrodes on intrinsic germanium elements for internal reflection spectroelectrochemistry has been investigated.[115] A 50Å layer of gold was vacuum deposited on a germanium internal reflection element. This OTE had major problems. It had a sizable electrical resistance which produced potential gradients similar to those observed for semiconducting germanium elements. Also, no throughput was obtained in the 2-11 μm region.

Carbon films on germanium internal reflection elements proved to be much more satisfactory than gold films.[99] Reasonable optical throughput was obtained and film conductivities were high enough for use as electrodes without potential gradient problems.

Other designs used intrinsic germanium internal reflection elements adjacent to an electrode. Laser and Ariel wrapped a gold minigrid around the germanium plate.[100] This design avoided the potential gradient problem observed for the higher resistance semiconductor or thin metal film electrodes. A disadvantage of this design was the low throughput of light. The minigrid evidently scattered or absorbed about 50% of the light. A gold film electrode placed near the germanium element was also used as an electrode.[115] Relatively long electrolysis times were necessary because of the distance from the germanium element to the electrode. This proved to be a disadvantage, since short-lived intermediates could not be observed due to the long time scale of the experiment.

An infrared spectroelectrochemical flow cell has been designed by Clark and Evans.[116] Their design used a glassy carbon porous bed working electrode and a conventional transmission cell with calcium fluoride windows. The solution flowed through the electrode and then into the infrared cell. There was no decrease in optical throughput due to the electrode, since the electrode was not in the optical path. This electrode position could also be a disadvantage, since spectra were not obtained at or adjacent to the electrode surface. Short-lived intermediates could react before reaching the spectroscopic cell.

3. Electrochemistry of Chloranil in Chloroaluminates

Mamantov and coworkers examined the electrochemical behavior of chloranil (tetrachloro-1,4-benzoquinone) in $AlCl_3$-NaCl melts.[117] Upon addition of the chloranil to the melt, a chemical reduction of the quinone to semiquinone occurred to a small extent. Reductions were

observed close to the anodic limit of the melts and showed irreversibility.

Bartak and Osteryoung studied the electrochemistry of chloranil in $AlCl_3$-NaCl melts.[118] It was found that in equimolar melts the reduction of the quinone to hydroquinone proceded through an ECEC mechanism. The following scheme was proposed:

$$Q \xrightarrow{e^-} Q^{\bullet -} \xrightarrow{e^-} Q^{2-} \xrightarrow{AlCl_3} \text{complex} \qquad (3)$$

$$Q^{\bullet -} \longrightarrow Q^{\bullet -}(AlCl_3) \qquad (4)$$

$$Q^{\bullet -}(AlCl_3) \xrightarrow{e^-} Q^{2-}(AlCl_3) \xrightarrow{AlCl_3} Q^{2-}(AlCl_3)_2 \qquad (5)$$

where Q refers to chloranil. At fast voltammetric scan rates, two waves due to the reductions in Equation (3) were observed. The chemical reaction in Equation (4) is quite slow and not important at fast scan rates. At slower scan rates this reaction in Equation (4) becomes important and the reduction in Equation (5) replaces the second reduction in Equation (3). Since the product of the chemical reaction can be reduced at the potential of the first reduction in Equation (3), only one reduction wave was observed. In $AlCl_3$-rich melts, again only a single reduction wave was observed, since the additional acid species present accelerate Equation (4).

Cheek and Osteryoung studied the electrochemistry of chloranil in $AlCl_3$-n-butylpyridinium chloride ($AlCl_3$-BuPyCl) melts.[119] Very similar results were obtained as for $AlCl_3$-NaCl melts, except the degree of complexation between chloranil and $AlCl_3$ was found to be much greater in the lower temperature melts. It was concluded that

complexation involved both the carbonyl oxygens and the chlorides attached to the ring.

4. Infrared Spectroscopy of Chloranil in Chloroaluminates

While no infrared spectra of chloranil or its reduction products have been reported in $AlCl_3$-NaCl melts, Cheek and Osteryoung have reported spectra of chloranil in $AlCl_3$-BuPyCl melts.[119] An infrared transmission cell using NaCl windows which were protected from the melts using polyethylene films was used. In a BuPyCl-rich melt, chloranil bands were observed at 1692 and 1570 cm^{-1} due to carbonyl and carbon-carbon double bond stretching modes, respectively. The intensity of the band at 1692 cm^{-1} in an $AlCl_3$-rich melt was diminished considerably compared to that observed with the BuPyCl-rich melt, due to complexation of the carbonyl bond with $AlCl_3$. The complexed carbonyl produced a new band at 1545 cm^{-1}. The band at 1570 cm^{-1} was absent from the spectrum in the $AlCl_3$-rich melt, since complexation of the chlorides on the ring shifted the frequency outside the spectral window of BuPyCl.

Spectra of chloranil and its reduction products in DMSO were reported by Clark.[115] Absorbances due to chloranil were observed around 1690 and 1575 cm^{-1}, while bands at 1525 and 1460 cm^{-1} were due to the reduction products.

B. Proposed Research

While there have been several examples of spectroelectrochemical studies in molten salts,[120-127] there are no reports of studies in the infrared region.

The purpose of these investigations is to develop infrared spectroelectrochemical techniques for use in molten salt systems. For this purpose, chloranil in $AlCl_3$-NaCl melts was used as a model system.

CHAPTER VI

EXPERIMENTAL: INFRARED SPECTROELECTROCHEMISTRY USING ATTENUATED TOTAL REFLECTANCE

A. Materials Used

Chloranil (Practical grade, Eastman, Rochester, NY) was purified by sublimation under vacuum through a glass frit at 290°C. All additions of chloranil to chloroaluminate melts and other transfers were performed in a drybox (Vacuum Atmospheres, Hawthorn, CA) with a moisture content under 2 ppm. Wires for electrodes and materials for and preparation of chloroaluminate melts were covered in Chapter II. The chloranil and melt were sealed in Pyrex tubes under vacuum ($\leq$ 1 mtorr) and were melted together in a rocking furnace for about eighteen hours at 175°C. Platinum foil was obtained from Engelhard Industries (Carteret, NJ).

B. Spectroelectrochemical Cell

The cell used for spectroelectrochemical studies is shown in Figure 11. The cell bottom consisted of a silicon crystal (Barnes Analytical, Stamford, CT or Harrick Scientific, Ossining, NY) sealed to a Pyrex cup with a flat o-ring flange. The internal angle of the beveled edges of the crystal and its back surface was 30°.

Three electrodes were sealed in the top section of the cell: a platinum wire electrode, a platinum foil counter electrode, and an aluminum wire reference electrode. The counter electrode was made by spot welding 1 cm^2 of platinum foil to a platinum wire. Both the

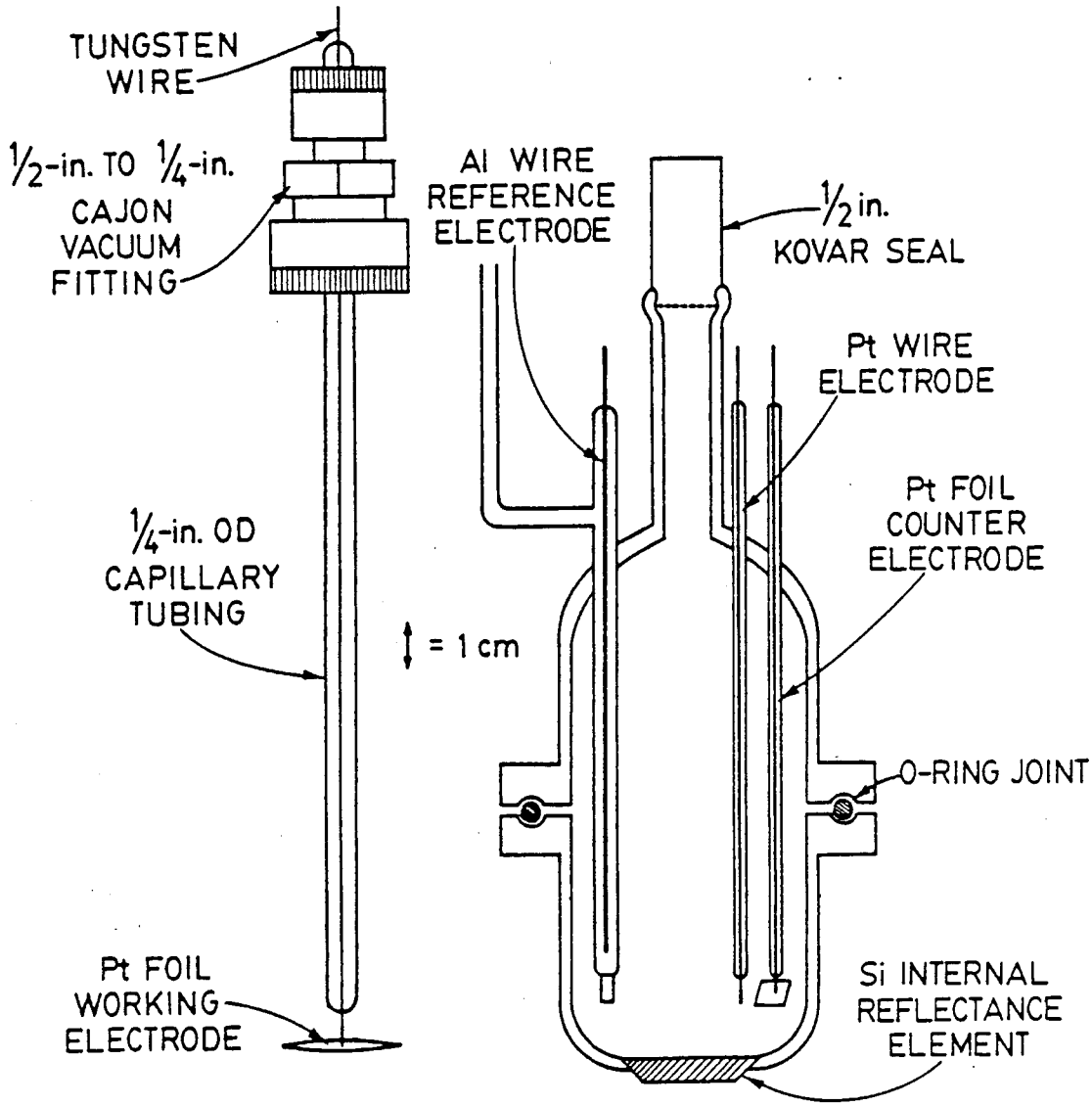

Figure 11. Silicon ATR Cell For Spectroelectrochemistry.

platinum wire for the counter electrode and the platinum wire electrode were spot-welded to tungsten wires and sealed to Pyrex, such that only platinum would be exposed to melt. The reference electrode consisted of aluminum wire in a Pyrex tube and was separated from the remainder of the cell compartment by a Radiometer frit (The London Co., Cleveland, OH). At the center of the cell top was a Kovar seal, used for positioning of the working electrode. A flat o-ring flange was used for coupling the cell top to the bottom with a Viton o-ring. A tube attached to the top of the cell, not shown in Figure 11, was used for filling and evacuating the cell.

The working electrode consisted of a 3/4 inch diameter platinum foil disk spot welded to platinum wire which was in turn spot-welded to tungsten wire. The wire was sealed into 1/4 inch O.D. Pyrex tubing. A 3/4 inch O.D. Teflon sleeve with a 1/4 inch I.D., one inch in length, was placed over the Pyrex tubing and sealed to the platinum disk with Teflon FEP at about 285°C. (This forced the electrochemical reaction to occur on the optically viewed side of the electrode.) The electrode was attached to the cell top at the Kovar seal using a bored-through Ultra-Torr reducing union (Cajon, Macedonia, OH).

C. Optical Arrangement and Cell Holder

The external optics used with the FTS-20 Fourier transform infrared spectrometer (Digilab, Cambridge, MA) consisted of two planar front surface mirrors (Edmund Scientific, Barrington, NJ) to direct and collect the infrared beam to and from the silicon crystal faces. These mirrors were mounted in Bakelite supports and attached to an aluminum

frame. The mirrors were rotated to optimize the throughput at the beginning of each experiment. The top of the frame contained a depression which fit the o-ring clamp. This was used to support and position the cell. A blackened brass strip was attached to the frame to block any stray radiation between the mirrors and silicon crystal.

Two furnaces were used to heat the cell, both constructed from nichrome ribbon wrapped around Pyrex tubing. One furnace fit over the cell, frame, and mirrors and was used to heat the lower section of the cell. Two sections of tubing were cut out, one on each side, to allow the infrared beam to pass to and from the mirrors. The other furnace fit over the top of the cell and was used to heat the upper part of the cell. Both furnaces were controlled by variable transformers.

Curved aluminum (focal length = 1.5 cm) and aluminized front surface (focal length = 7.5 cm) mirrors (Edmund Scientific, Barrington, NJ) were used in an attempt to focus the infrared beam and increase the throughput of the silicon crystal. Since no significant improvement resulted, all experiments utilized the planar gold mirrors.

D. Procedure

The cell was filled with chloroaluminate melt and chloranil in the drybox. The reference electrode compartment was filled with melt only. After the cell and the reference compartment were evacuated and sealed, copper wire leads were silver soldered to the tungsten wires of the electrodes. The cell and external optics were placed in the sample compartment of the FTS-20 spectrometer and aligned to produce the strongest signal. The cell was then heated to 160°C, and a spectrum

was obtained with the working electrode raised above the melt. Another spectrum was obtained after the working electrode was lowered into position against the silicon crystal. Potentials were applied using a PAR 173 Potentiostat/Galvanostat (Princeton Applied Research Corp., Princeton, NJ) and spectra were obtained at various applied potentials.

Prior to cooling down the cell after an experiment, it was necessary to raise the working electrode above the level of the melt, and to tilt the melt away from the fill tube and silicon crystal as much as possible. Without these precautions, the silicon crystal was likely to crack when dissolving the melt in water, since a vigorous reaction occurs, liberating a sizable quantity of HCl.

CHAPTER VII

RESULTS AND CONCLUSIONS: INFRARED SPECTROELECTROCHEMISTRY USING ATTENUATED TOTAL REFLECTANCE

A. Silicon Crystal

Silicon was chosen as the attenuated total reflectance (ATR) element primarily because of its resistance to chemical attack by molten chloroaluminates, since most common infrared window materials, such as cesium iodide and potassium bromide, are attacked. Silicon is far from an ideal choice and posed a few problems. The crystal absorbs most of the infrared radiation, forcing the Fourier transform spectrometer to be operated at the highest sensitivity. While a new silicon crystal resulted in a maximum of about seven percent transmittance in the ATR mode, the surface soon became roughened through use and handling, decreasing this value considerably. A spectrum of the silicon crystal referenced against air, shown in Figure 12, produced a maximum of 2.7 percent transmittance. A band at 1760 cm^{-1} obscured an interesting region of the spectrum of chloranil, and had to be subtracted out. Bands at 1450 cm^{-1} and below caused the crystal to be practically useless below 1450 cm^{-1}. The transmittance of the silicon crystal decreased as the temperature increased. Since spectra of the melts were obtained at 160-165°C, some decrease in signal occurred.

B. Spectrum of the Chloroaluminate Melt

The spectrum in Figure 13 is that of an $AlCl_3$-NaCl melt (63-37 mole percent) referenced against the silicon crystal. As expected, the

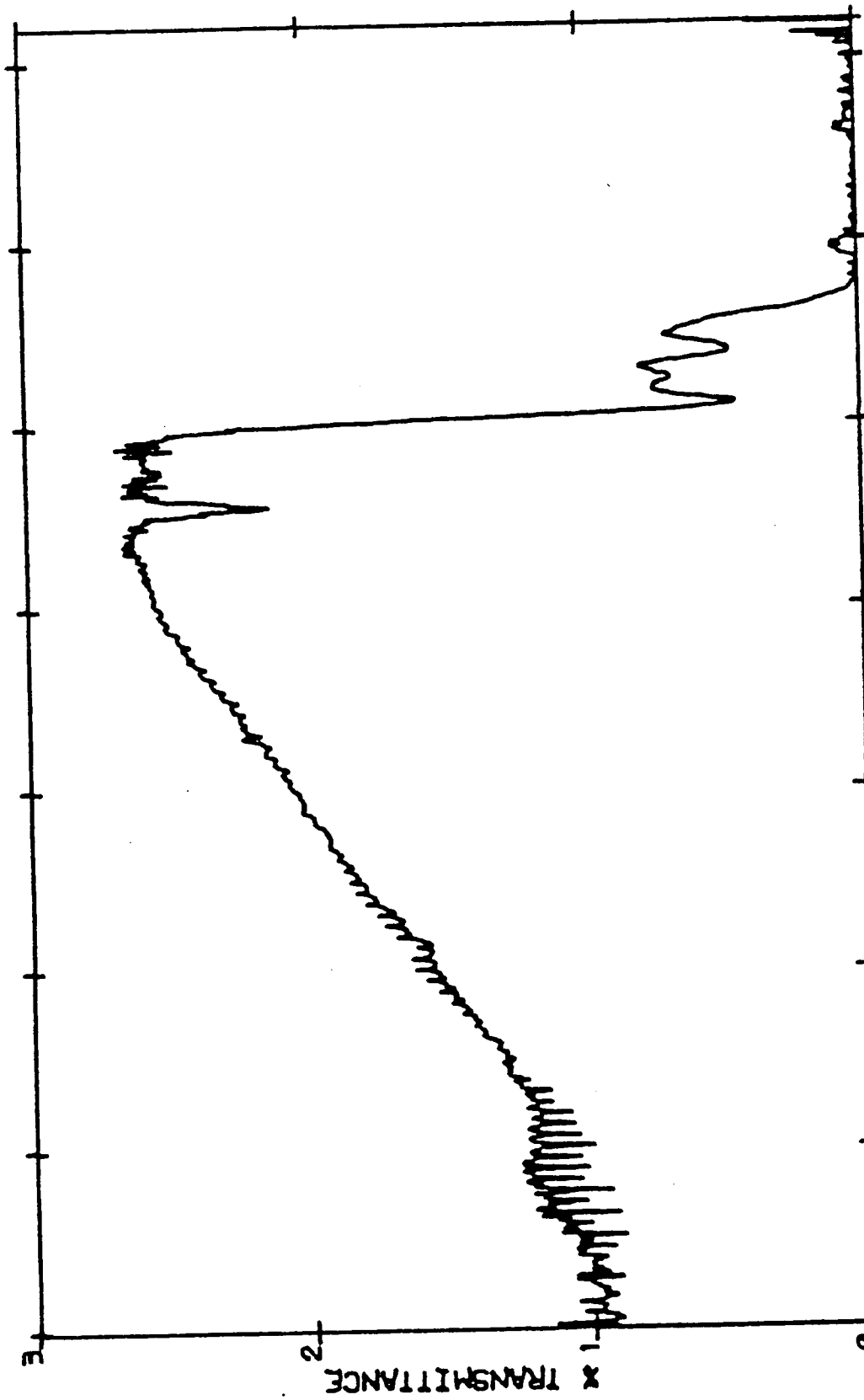

Figure 12. Infrared ATR spectrum (Smoothed) of the silicon crystal.

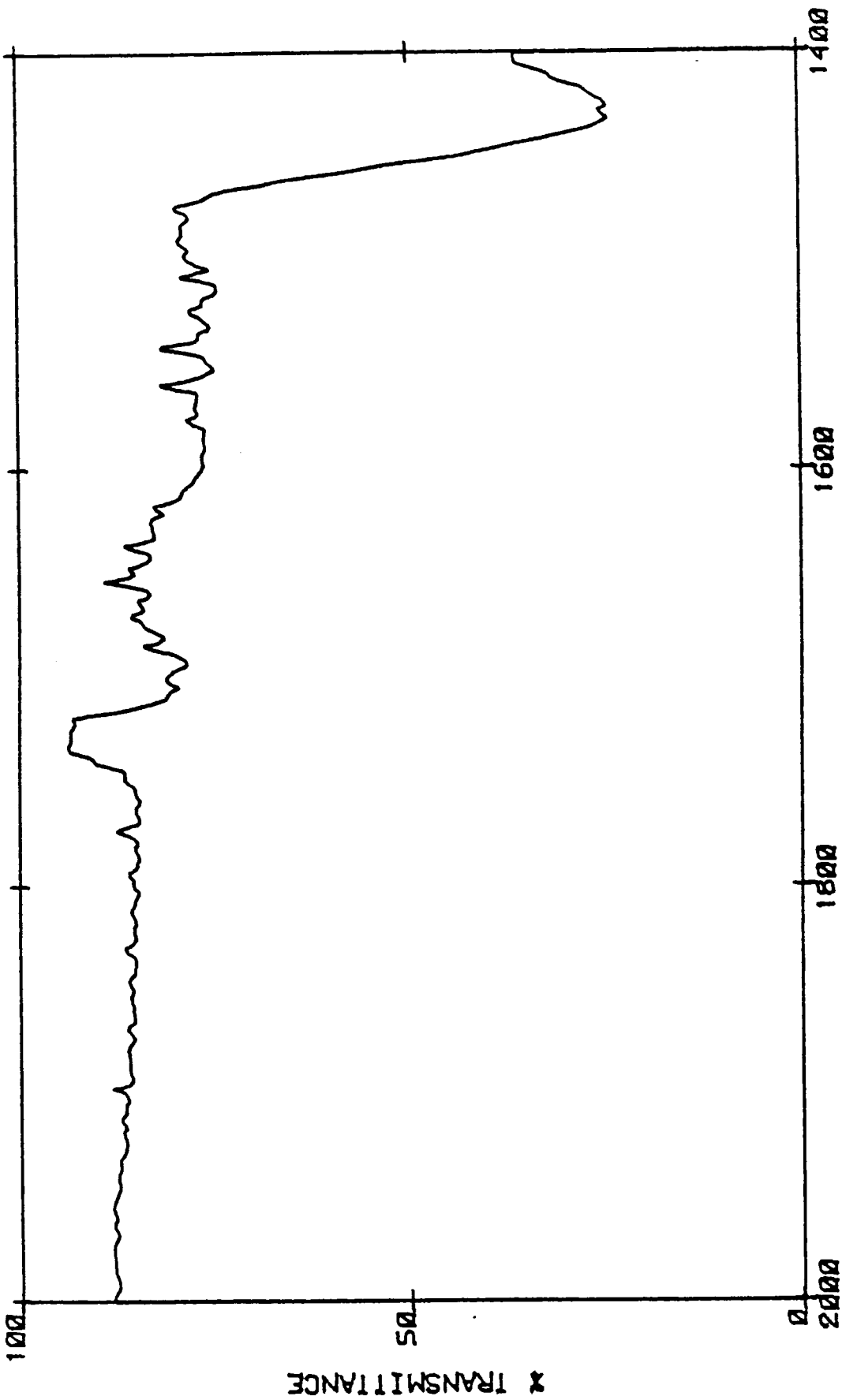

Figure 13. Infrared ATR spectrum of $AlCl_3$-NaCl (63-37 mole percent).

melt is transparent over the entire 2000-1400 cm^{-1} range. The broad inverted peak around 1725 cm^{-1} may be due to incorrect ratioing of the silicon crystal.

C. Spectrum of Chloranil in the Chloroaluminate Melt

A spectrum of 0.130 m chloranil in a $AlCl_3$-NaCl melt (63-37 mole percent) is shown in Figure 14 (referenced against the melt). Bands are present at 1697, 1630, 1578 and 1529 cm^{-1} (the working electrode was raised above the melt when the spectrum was obtained.)

The spectrum of chloranil in an $AlCl_3$-rich $AlCl_3$-BuPyCl melt, obtained by Cheek and Osteryoung,[119] differed from that shown in Figure 14. Bands assigned to chloranil were observed at 1692 and 1545 cm^{-1}, compared to those at 1697 and 1529 cm^{-1} found in this work. In the spectrum of chloranil in dimethyl sulfoxide (DMSO), Clark[125] observed bands at 1690 and 1575 cm^{-1}. These bands agree well with bands at 1697 and 1578 cm^{-1} in Figure 14. The band at 1630 cm^{-1} was probably due to the carbonyl complexed with $AlCl_3$. This band was not observed by Cheek and Osteryoung, however a strong n-butylpyridinium cation band at 1635 cm^{-1} would mask a band at 1630 cm^{-1}. Clark[115] also obtained the spectrum of the radical anion, or semiquinone ($C_6Cl_4O_2^{-\bullet}$), in DMSO, where a broad band at 1525 cm^{-1} was found. Again, good agreement was obtained between this band and a band in Figure 14, at 1529 cm^{-1}. It was found that the potential of a platinum wire versus the aluminum reference electrode (in $AlCl_3$-NaCl, 63-37 mole percent) was 1.80 V. Since the $E_{1/2}$ for chloranil in this melt was

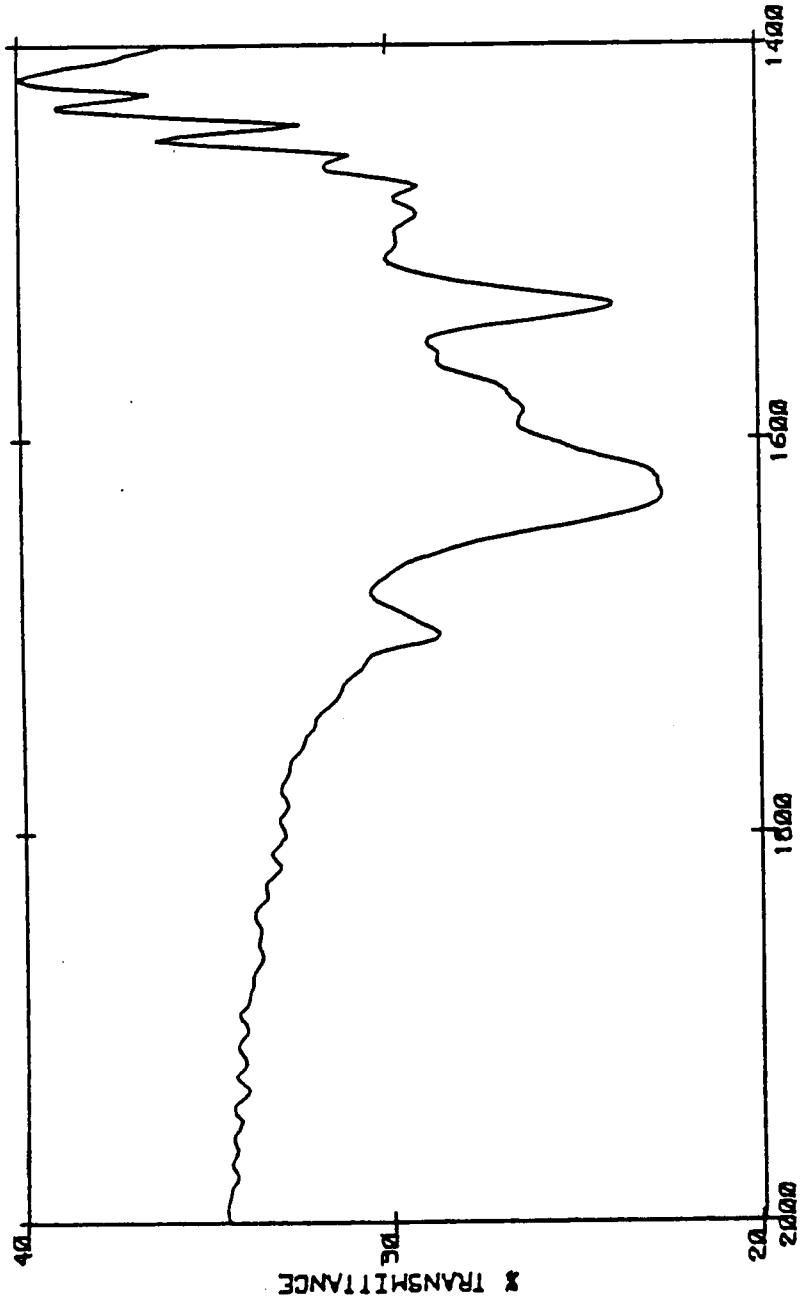

Figure 14. Infrared ATR spectrum (Smoothed) of chloranil in $AlCl_3$-NaCl (63-37 mole percent) in spectroelectrochemical cell with the working electrode raised above the level of melt.

determined by Bartak and Osteryoung[118] to be 2.0 V, some reduction of the chloranil would have already taken place.

D. Spectroelectrochemistry

Prior to applying potentials during spectroelectrochemical experiments, the spectrum of chloranil in the $AlCl_3$-NaCl (63-37 mole percent) melt in Figure 15 was obtained 30 min. after the working electrode was lowered into position against the silicon crystal. This spectrum was referenced against the melt only, as are all spectra shown in this section. With the electrode in the optical path, the transmittance of the cell decreased substantially. (Note difference in % transmittance axis between Figures 14 and 15.) The bands at 1697, 1630, 1578 and 1529 cm^{-1} decreased about 30% of their original size in Figure 14. Bands grew in at 1495, 1472 and 1463 cm^{-1}. A spectrum of tetrachlorohydroquinone in DMSO was obtained by Clark.[115] A band was observed at 1460 cm^{-1}, which agrees well with the band at 1463 cm^{-1}. Bands at 1495 and 1472 cm^{-1} seem to be produced by the same species that produces the 1463 cm^{-1} band, however they are absent in Clark's work. Chloranil appears to be a sufficiently strong oxidant to cause some oxidation of platinum.

A potential sufficiently less positive than the initial potential was chosen to attempt to obtain a spectrum of the tetrachlorohydroquinone only. After 10 min. at 0.05 V, the spectrum in Figure 16 was obtained. (Note the % transmittance axis varies from that in other spectra.) The bands due to chloranil at 1697, 1630 and 1578 cm^{-1} and the semiquinone band at 1529 cm^{-1} decreased, but didn't completely

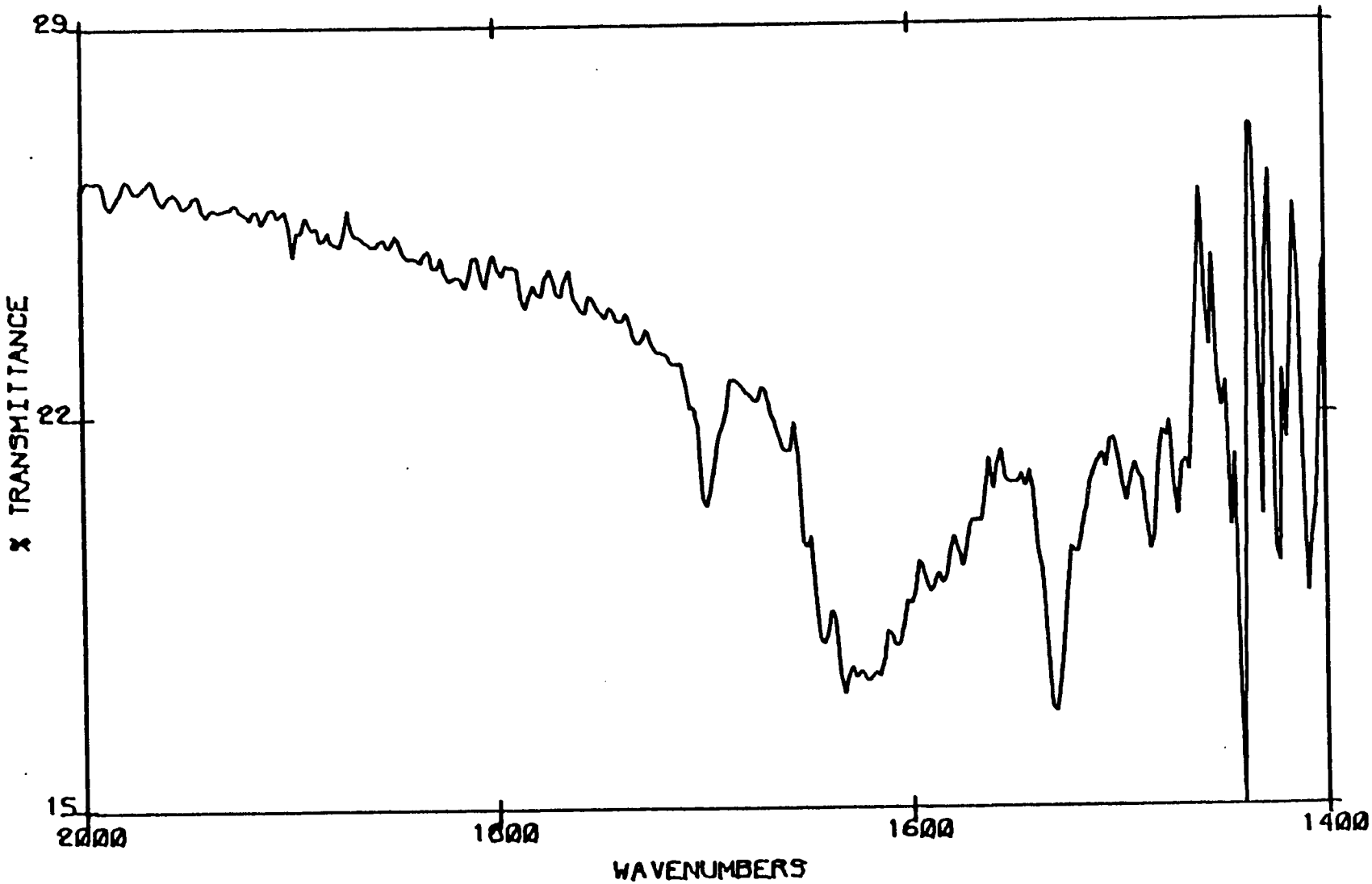

Figure 15. Infrared ATR spectrum of chloranil in $AlCl_3$-NaCl (63-37 mole percent) in spectroelectrochemical cell after electrode was lowered into position.

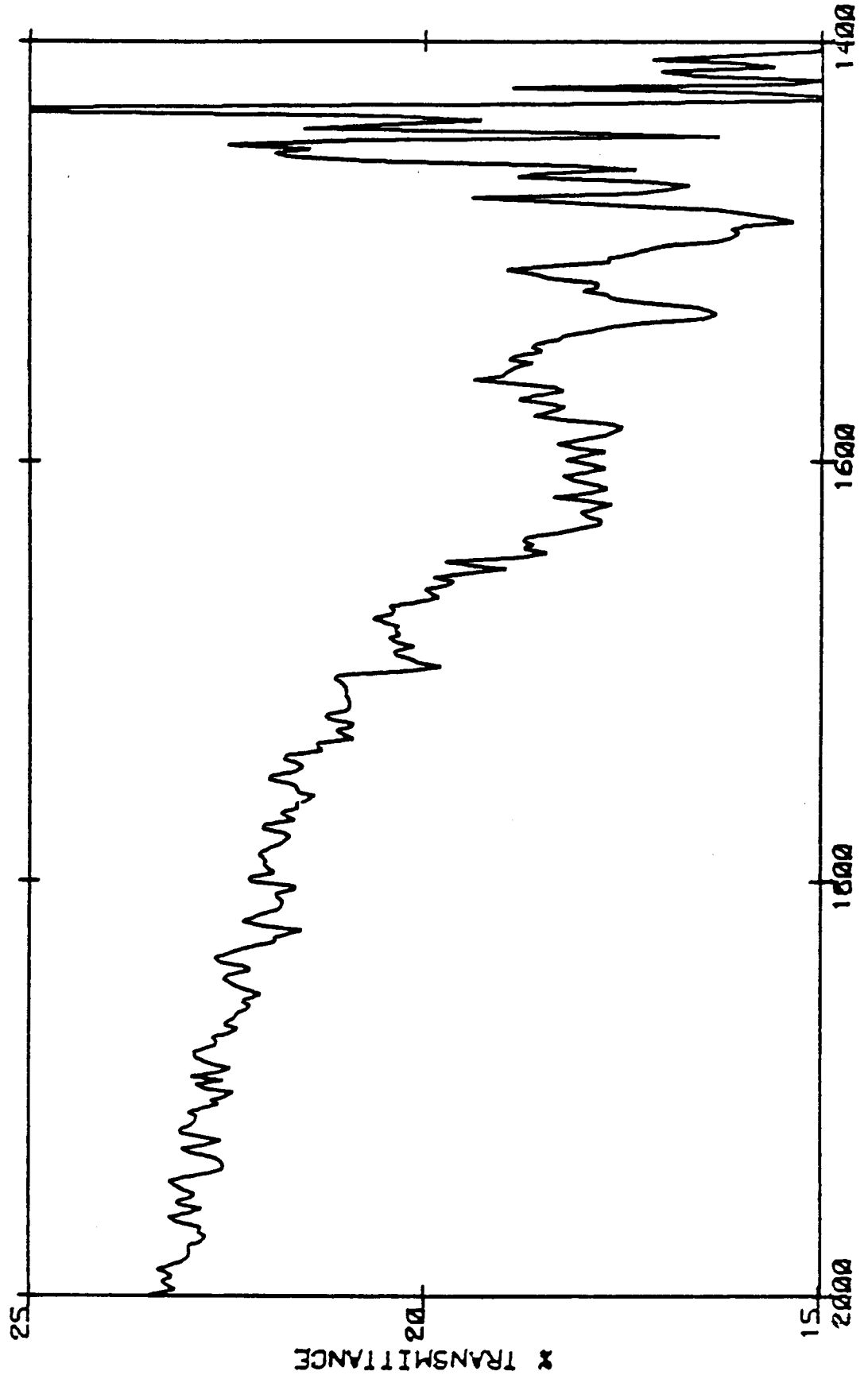

Figure 16. Infrared ATR spectrum of chloranil in $AlCl_3$-NaCl (63-37 mole percent) at 0.05 V.

disappear. The tetrachlorohydroquinone band at 1460 cm^{-1} increases in intensity, as do the bands at 1495 and 1472 cm^{-1} which may also be due to the tetrachlorohydroquinone.

When the potential was set at 2.00 V for ten minutes, the spectrum in Figure 17 was obtained. The percent transmittance for the cell has decreased drastically when compared with Figures 14-17. Increases in band intensity were observed for the chloranil bands at 1692, 1630 and 1578 cm^{-1} and the semiquinone band at 1529 cm^{-1}. A large decrease in band intensity was observed for apparent tetrachlorohydroquinone bands at 1495, 1472 and 1463 cm^{-1}.

Attempts to go to a more positive potential, 2.09 V, produced a sharp drop in the percent transmittance of the cell. Since this potential is in the vicinity of the anodic limit of the chloroaluminate melt, chlorine formation at the electrode could have been responsible for this decrease. Spectra obtained from this point on were of very poor quality and of dubious value.

E. Conclusions

An ATR cell for spectroelectrochemical measurements in chloroaluminate melts has been demonstrated as a qualitative tool for obtaining spectra at various applied potentials. Its usefulness is limited by the failure to achieve complete electrolysis of the thin layer between the silicon crystal and electrode, as well as the limited infrared region in which silicon passes enough energy to allow useful spectra to be obtained.

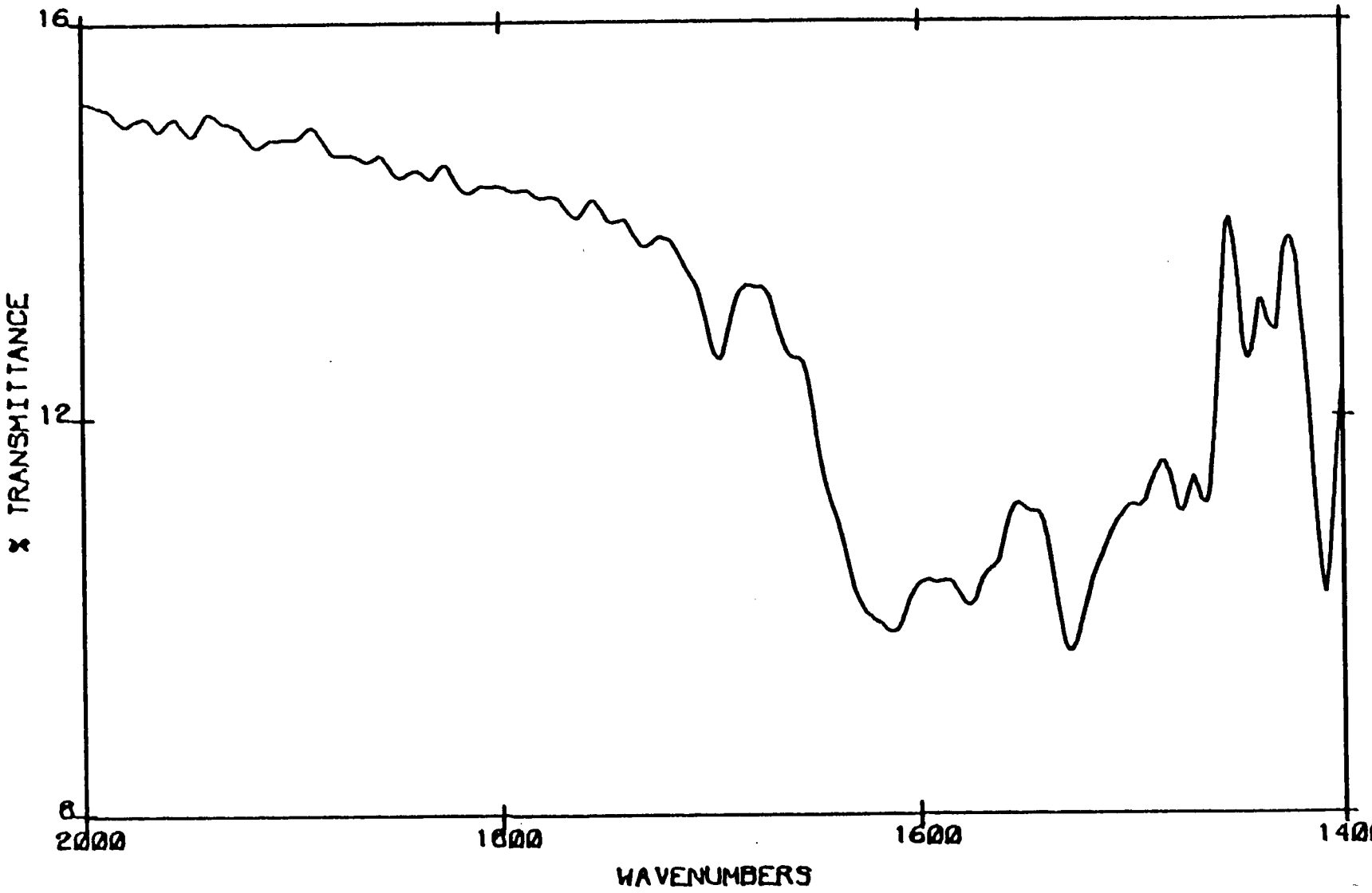

Figure 17. Infrared ATR spectrum (Smoothed) of chloranil in $AlCl_3$-NaCl (63-37 mole percent) at 2.00 V.

Recently Hvistendahl[128] has developed a technique for obtaining infrared emission spectra in chloroaluminate melts. This technique may be useful to expand infrared spectroelectrochemistry to regions below 1000 cm^{-1}, where many interesting inorganic compounds are infrared active.

LIST OF REFERENCES

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1. C. D. Kalfadelis and H. Shaw, in Encyclopedia of Chemical Technology, Vol. II, Third Edition, pp. 473-478, H. F. Mark, D. F. Othmer, C. G. Overberger, and G. T. Seaborg, Editors, Wiley-Interscience, New York (1980), and references within.

2. C. D. Frohnig, H. Kölbel, M. Ralek, W. Rottig, F. Schnur, and H. Schulz, in Chemical Feedstocks From Coal, pp. 309-432, J. Falbe, Editor, Wiley-Interscience, New York (1982), and references within.

3. C. D. Frohnig, in New Synthesis With Carbon Monoxide, pp. 309-371, J. Falbe, Editor, Springer-Verlag, Berlin (1980), and references within.

4. P. Sabatier and J. B. Senderens, J. Soc. Chem. Ind., 21, 504 (1902).

5. R. B. Anderson, in Catalysis, Vol 4, pp. 29-371, P. H. Emmett, Editor, Reinhold Publishing Corp., New York (1956), and references within.

6. H. H. Storch, N. Golumbic, and R. B. Anderson, The Fisher-Tropsch and Related Synthesis, John Wiley & Sons, Inc., New York (1951), and references within.

7. H. Pichler, in Advances in Catalysis, Vol. IV, W. G. Frankenburg, V. I. Komarewsky, and E. K. Rideal, Editors, pp. 272-341, Academic Press, Inc., New York (1952), and references within.

8. I. Abdulahad and M. Ralek, Erdöl, Kohle, Erdgas, Petrochem., 25, 187 (1972).

9. C. D. Chang and A. J. Silvestri, J. Catal., 47, 249 (1977).

10. S. L. Meisel, J. P. McCollugh, C. H. Lechthaler, and P. B. Weisz, CHEMTECH, 6, 86 (1976).

11. G. A. Mills, CHEMTECH, 7, 418 (1977).

12. W. W. Kalding and S. A. Butter, J. Catal., 61, 155 (1980).

13. W. Keim, M. Berger, and J. Schlupp, J. Catal., 61, 359 (1980).

14. R. B. King, A. D. King, Jr., and K. Tanaka, J. Mol. Catal., 10, 75 (1981).

15. R. J. Daroda, J. R. Blackboro, and G. Wilkinson, J.C.S. Chem. Commun., 1098 (1980).

16. R. J. Daroda, J. R. Blackboro, and G. Wilkinson, J.C.S. Chem. Commun., 1101 (1980).

17. J. W. Rathke and H. M. Feder, J. Am. Chem. Soc., 100, 3623 (1978).

18. Y. Kikuzono, S. Kagami, S. Naito, T. Onishi and K. Tamuru, Chem. Lett., 1249 (1981).

19. B. D. Dombek, J. Am. Chem. Soc., 102, 6855 (1980).

20. B. D. Dombek, J. Am. Chem. Soc., 103, 6508 (1981).

21. J. F. Knifton, J. Am. Chem. Soc., 103, 3959 (1981).

22. A. Deluzarche, R. Fonseca, G. Jenner, and A. Kiennemann, Erdöl, Kohle, Ergas, Petrochem., 32, 313 (1979).

23. J. S. Brady, J. Am. Chem. Soc., 101, 7419 (1979).

24. J. P. Collman and L. S. Hegedus, Principles and Applications of Organotransition Metal Chemistry, p. 450, University Science Books, Mill Valley, CA (1980).

25. M. G. Thomas, B. F. Beier, and E. L. Muetterties, J. Am. Chem. Soc., 98, 1296 (1976).

26. R. A. Schunn, G. C. Demitras, H. W. Choi, and E. L. Muetterties, Inorg. Chem., 20, 4023 (1981).

27. G. C. Demitras and E. L. Muetterties, J. Am. Chem. Soc., 99, 2796 (1977).

28. M. A. Vannice, J. Catal., 37, 449 (1975).

29. F. Martin, Chem. Fabrik, 12, 233 (1939).

30. R. A. Friedel and R. B. Anderson, J. Am. Chem. Soc., 72, 1212 (1950).

31. A. W. Weitkemp, H. S. Seelig, N. J. Bowman, and W. E. Cady, Ind. Eng. Chem., 45, 343 (1953).

32. R. B. Anderson, J. Feldman, and H. H. Storch, Ind. Eng. Chem., 44, 2418 (1952).

33. W. E. Cady, P. J. Launer, and A. W. Weitkamp, Ind. Eng. Chem., 45, 350 (1953).

34. P. H. Emmett, Catalysis Then and Now, p. 156, Franklin Publishing Co., Inc., Englewood, NJ (1965), and references within.

35. R. B. Anderson, J. T. McCartney, W. K. Hall, and L. J. E. Hofer, Ind. Eng. Chem., 39, 1618 (1947).

36. K. Tanabe, Solid Acids and Bases, pp. 1-33, Academic Press, New York (1970).

37. J. R. Katzer, A. W. Sleight, P. Gajardo, J. B. Michel, E. F. Gleason, and S. McMillan, Faraday Disc., #72, 121 (1981).

38. M. E. Dry, J. A. K. du Plessis, and G. M. Leuteritz, J. Catal., 6, 194 (1966).

39. J. A. Cusumano, R. A. Dalla Betta, and R. B. Levy, Catalysis in Coal Conversion, pp. 247-66, Academic Press, New York (1978), and references within.

40. G. Henrici-Olive' and S. Olive', J. Molec. Catal., 16, 187 (1982).

41. M. E. Dry, T. Shingles, L. J. Boshoff and G. T. Oosthuizen, J. Catal., 15, 190 (1969).

42. H. Wang, H. W. Choi, and E. L. Muetterties, Inorg. Chem., 20, 2661 (1980).

43. S. R. Craxford and E. K. Rideal, J. Chem. Soc., 1604 (1939).

44. Y. T. Eidus, Russ. Chem. Rev., 36, 338 (1967).

45. H. Schulz and A. Z. El Deen, Fuel Process. Technol., 1, 45 (1977).

46. H. Pichler and H. Schulz, Chem.-Ing.-Tech., 42, 1162 (1970).

47. G. Henrici-Olive' and S. Olive', Angew. Chem. Int. Ed. 15, 136 (1976).

48. W. A. van Barneveld and V. Ponec, J. Catal., 51, 426 (1978).

49. V. Ponec, Catal. Rev.-Sci. Eng., 18, 151 (1978).

50. C. K. Rofer-DePoorter, Chem. Rev., 81, 447 (1981).

51. G. D. Renshaw, C. Roscoe, and P. L. Walker, Jr., J. Catal., 18, 164 (1970).

52. G. D. Renshaw, C. Roscoe, and P. L. Walker, Jr., J. Catal., 22, 394 (1971).

53. K. J. Singh and H. E. Grenga, J. Catal., 47, 328 (1977).

54. W. Sundermeyer, Angew. Chem. Int. Ed., 4, 222 (1965).

55. C. N. Kenney, Catal. Rev., 11, 197 (1975).

56. B. W. Hatt and D. H. Kerridge, Chem. in Brit., 15, 78 (1979).

57. H. Bloom, The Chemistry of Molten Salts, pp. 104-7, W. A. Benjamin, Inc., New York (1967).

58. J. S. Kristoff and D. F. Shriver, Inorg. Chem., 13, 499 (1974).

59. D. F. Shriver, J. Organometal. Chem., 94, 259 (1975).

60. R. E. Stimson and D. F. Shriver, Inorg. Chem., 19, 1141 (1980).

61. Y. Ohtsuka and Y. Tamai, J. Catal., 67, 316 (1981).

62. J. P. Collman, J. I. Brauman, G. Tustin, and G. S. Wann III, J. Am. Chem. Soc., 105, 3913 (1983).

63. A. L. Lapidus and M. M. Savel'ev, Izv. Akad. Nauk SSSR, Ser. Khim., 1470 (1978).

64. A. L. Lapidus and M. M. Savel'ev, Izv. Akad. Nauk SSSR, Ser. Khim., 335 (1980).

65. A. L. Lapidus, M. M. Savel'ev, L. T. Kondrat'ev and E. V. Yastrebova, Izv. Akad. Nauk SSSR, Ser. Khim., 1564 (1981).

66. R. M. Wilenzick, D. C. Russel, R. H. Morriss, and S. W. Marshall, J. Chem. Phys., 47, 533 (1967).

67. K. Kinoshita and P. Stonehart, in Modern Aspects of Electrochemistry, No. 12, pp. 183-266, J. O'M. Bockris and B. E. Conway, Editors, Plenum Press, New York (1977), and references within.

68. R. D. Rieke, Acc. Chem. Res., 10, 301 (1977).

69. R. D. Rieke, J. Org. Chem., 44, 3445 (1979).

70. C. Benedicks, Koll. Z., 11, 263 (1912).

71. T. Svedberg, Koll. Z., 24, 1 (1919).

72. R. Piontelli, G. L. Coccia, and U. Ducati, Electrochim. Metall., III, 101 (1968).

73. R. Piontelli, G. L. Coccia, and U. Ducati, Electrochim. Metall., III, 343 (1968).

74. R. Piontelli, G. L. Coccia, and U. Ducati, Electrochim. Metall., IV, 20 (1969).

75. R. Piontelli, G. L. Coccia, U. Ducati, and C. Annouazzi, Electrochim. Metall., IV, 121 (1969).

76. H. W. Kohn and T. E. Willmarth, Science, 163, 924 (1969).

77. D. Cubicciotti, J. Am. Chem. Soc., 74, 1198 (1952).

78. C. B. Gill, M. E. Straumanis, and A. W. Selecten, J. Electrochem. Soc., 102, 42 (1955).

79. A. A. Fannin, Jr., L. A. King, and D. W. Seegmiller, J. Electrochem. Soc., 119, 801 (1972).

80. D. D. Coleman, Anal. Chem., 53, 1962 (1981).

81. D. J. DesMarais and J. M. Hayes, Anal. Chem., 46, 1651 (1976).

82. Brisco Harward, unpublished work.

83. F. Cariati, V. Valenti, and G. Zerbi, Inorg. Chim. Acta, 3, 378 (1969).

84. W. R. Heineman, Anal. Chem., 50, 390 A (1978).

85. T. Kuwana and W. R. Heineman, Acc. Chem. Res., 9, 241 (1977).

86. T. Kuwana and N. Winograd, in Electroanalytical Chemistry, Vol. 7, pp. 1-78, A. J. Bard, Editor, Marcel Dekker, New York (1974).

87. Symp. Faraday Soc., No. 4 (1970).

88. J. D. E. McIntyre, in Advances in Electrochemistry and Electrochemical Engineering, Vol. 9, pp. 61-166, R. H. Muller, Editor, Wiley-Interscience, New York (1973).

89. W. N. Hansen, in Advances in Electrochemistry and Electrochemical Engineering, Vol. 9, pp. 1-60, R. H. Muller, Editor, Wiley-Interscience, New York (1973).

90. T. M. McKinney, in Electroanalytical Chemistry, Vol. 10, pp. 97-278, A. J. Bard, Editor, Marcel Dekker, New York (1977).

91. V. E. Norvell and G. Mamantov, in Molten Salt Techniques, Vol. 1, D. G. Lovering, Editor, Plenum Press, (1983), in press.

92. V. E. Norvell and G. Mamantov, Anal. Chem., 49, 1470 (1977).

93. RVC Bulletins and Application Notes, The Fluorocarbon Company, Anaheim, CA 92803.

94. T. P. DeAngelis and W. R. Heineman, J. Chem. Ed., 53, 594 (1976).

95. R. L. McCreery, R. Pruiksma, and R. Fagan, Anal. Chem., 51, 749 (1979).

96. J. P. Skully and R. L. McCreery, Anal. Chem., 52, 1885 (1980).

97. J. F. Tyson and T. S. West, Talanta, 26, 117 (1979).

98. J. F. Tyson and T. S. West, Talanta, 27, 335 (1980).

99. J. S. Mattson and C. A. Smith, Anal. Chem., 47, 1122 (1975).

100. D. Laser and M. Ariel, J. Electroanal. Chem., 41, 381 (1973).

101. R. P. Van Duyne, in Chemical and Biochemical Applications of Lasers, Vol. 4, C. B. Moore, Editor, Academic Press, New York (1979).

102. H. H. Willard, L. L. Merritt, Jr., J. A. Dean, and F. A. Settle, Jr., Instrumental Methods of Analysis, 6th Edition, pp. 219-21, Van Nostrand, New York (1981).

103. R. P. Cooney, M. R. Mahoney and A. J. McQuillan, in Advances in Infrared and Raman Spectroscopy, Vol. 9, pp. 188-281, R. J. H. Clark and R. E. Hester, Editors, Heyden & Sons, London, (1982).

104. F. M. Hawkridge and B. Ke, Anal. Biochem., 78, 76 (1977).

105. L. R. Faulkner and A. J. Bard, in Electroanalytical Chemistry, Vol. 10, pp. 1-95, A. J. Bard, Editor, Marcel Dekker, New York (1977).

106. B. R. E. Malpas and A. J. Bard, Anal. Chem., 52, 109 (1980).

107. A. Fujishima, H. Masuda, K. Honda, and A. J. Bard, Anal. Chem., 52, 682 (1980).

108. G. H. Brilmyer and A. J. Bard, Anal. Chem., 52, 685 (1980).

109. W. R. Heineman, J. N. Burnett, and R. W. Murray, Anal. Chem., 40, 1974 (1968).

110. P. T. Kissinger and C. N. Reilley, Anal. Chem., 42, 12 (1970).

111. H. B. Mark, Jr. and B. S. Pons, Anal. Chem., 38, 119 (1966).

112. D. R. Tallent and D. H. Evans, Anal. Chem., 41, 835 (1969).

113. A. Trifonov, T. L. Popov, and B. Jordanov, J. Molec. Struct., 15, 257 (1973).

114. N. J. Harrick, private communication.

115. B. R. Clark, dissertation, University of Wisconsin (1974).

116. B. R. Clark and D. H. Evans, J. Electroanal. Chem., 69, 181 (1976).

117. G. Mamantov, R. Marassi, and J. Q. Chambers, High Energy Cathodes for Fused Salt Batteries, Final Report, Contract DAA 07-73-70060 (1974), ECOM-0060-F.

118. D. E. Bartak and R. A. Osteryoung, J. Electroanal. Chem., 74, 69 (1976).

119. G. Cheek and R. A. Osteryoung, J. Electrochem. Soc., 129, 2739 (1982).

120. J. P. Young, G. Mamantov, and F. L. Whiting, J. Phys. Chem., 71, 782 (1967).

121. F. L. Whiting, G. Mamantov, and J. P. Young, J. Inorg. Nucl. Chem., 35, 1553 (1973).

122. A. de Guibert and V. Plichon, J. Electroanal. Chem., 90, 399 (1978).

123. A. de Guibert, V. Plichon, and J. Badoz-Lambing, J. Electroanal. Chem., 105, 143 (1979).

124. G. Mamantov, V. E. Norvell, and L. N. Klatt, J. Electrochem. Soc., 127, 1768 (1980).

125. V. E. Norvell, K. Tanemoto, G. Mamantov, and L. N. Klatt, J. Electrochem. Soc., 128, 1254 (1981).

126. M. Sorlie, G. P. Smith, V. E. Norvell, G. Mamantov, and L. N. Klatt, J. Electrochem. Soc., 128, 333 (1981).

127. K. Tanemoto, G. Mamantov, R. Marassi, and G. Begun, J. Inorg. Nucl. Chem., 43, 1779 (1981).

128. J. Hvistendahl, dissertation, Universitetet I Trondheim (1982).

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