



Electrochemical reduction of chlorinated nitro and nitrosobenzenes in dimethylsulfoxide [pt.I] Power series representation in the high temperature phase equilibria of several metal oxide systems [pt. II] by Harlan Jay Byker

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemistry
Montana State University
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Abstract:

This dissertation encompasses two separate and unrelated research topics.

I. Electrochemical Reduction of Chlorinated Nitro and Nitrosobenzenes in Dimethylsulfoxide The reduction potentials of nitrobenzene and all possible isomers of its chlorine derivatives have been obtained by cyclic voltammetry in dimethylsulfoxide. The first reduction wave in each case, except pentachloronitrobenzene, appears to be a one electron reversible wave. Subsequent reduction waves are irreversible and have been interpreted in terms of either loss of chloride from the benzene ring or reduction of the nitro group to nitroso. The loss of chloride is the dominant reduction process for the higher chlorinated isomers while concomitant reaction of the nitro group and chlorine is observed for the monochloronitrobenzenes. The proposed reduction processes are indicated by the observation of new electrochemical processes when a second cycle of the voltammogram is recorded. Nitrosobenzene and all possible isomers of its chlorine derivatives, except pentachloronitrosobenzene, were synthesized and cyclic voltammograms were recorded for each. The reduction potentials of nitrosobenzene and the monochloronitrosobenzenes correspond to some of the reduction potentials for the second cycle voltammograms for the polychloronitrobenzenes.

II. Power Series Representation in the High Temperature Phase Equilibria of Several Metal Oxide Systems The use of Redlich Kister power series representations of thermodynamic quantities in the study of high temperature phase equilibria is described. Literature data was used to obtain power series equations for the activity and enthalpy of the rutile phase of titanium dioxide treated as a solution of titanium metal in titanium dioxide. Mass spectrometric data for the vaporization of potassium oxides was obtained from another researcher. This data was interpreted to give new values for the heats of formation of $K_2O(s)$ and $K_2O_2(g)$. These new values and literature data were used to determine power series equations and calculate a potassium oxide phase diagram. The phase equilibria of lithium oxide and aluminum oxide was treated by power series representations and a revised phase diagram is proposed. Power series representations in the potassium oxide, calcium oxide, and silicon dioxide ternary system are presented.

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I. ELECTROCHEMICAL REDUCTION OF CHLORINATED NITRO AND NITROBENZENES
IN DIMETHYLSULFOXIDE II. POWER SERIES REPRESENTATION IN THE HIGH
TEMPERATURE PHASE EQUILIBRIA OF SEVERAL METAL OXIDE SYSTEMS

by

HARLAN JAY BYKER

A thesis submitted in partial fulfillment
of the requirements for the degree

of

DOCTOR OF PHILOSOPHY

in

Chemistry

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November, 1979

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His invisible attributes, that is to say his everlasting power and deity, have been visible, ever since the world began, to the eye of reason, in the things he has made.

Romans 1:20 (The New English Bible)

Vita

Harlan Jay Byker was born on August 31, 1954 in Grand Rapids, Michigan to Gary and Henrietta Byker. He graduated from Unity Christian High School in Hudsonville, Michigan in 1972 and attended Calvin College in Grand Rapids, Michigan for two years. Harlan attended Montana State University in Bozeman, Montana for two more years and received a B. Sc. degree in chemistry with departmental honors in 1976. In 1973, Harlan married Terri Lynn Northouse and they presently have two daughters, Erin Nichole and Cori Darleen.

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SECTION I.

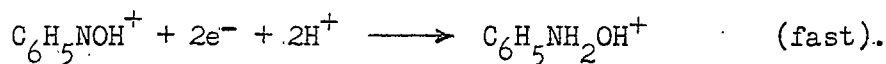
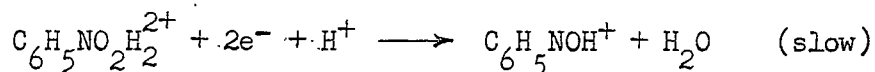
INTRODUCTION

The electrochemical reduction of nitrobenzene is one of the classical reactions of organic polarography. However nitrobenzene is rather prolific in its reduction products, and complex reduction pathways are possible. Under the proper solvent and electrode conditions one can reduce nitrobenzene to nitrosobenzene, phenylhydroxylamine, aniline, azoxybenzene, azobenzene, or hydrazobenzene. Most of these compounds can be electroactive, as well as many of their possible anions and dianions. There are indeed then, many possible intermediates and products observable electrochemically even for the reduction of unsubstituted nitrobenzene.

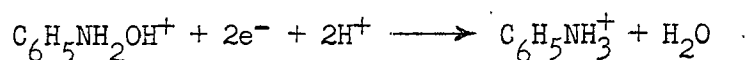
The focus of this present work is on the electrochemical reduction mechanisms of polychlorinated nitrobenzenes in the solvent dimethylsulphoxide, (DMSO). Therefore the reduction of nitrobenzene in aqueous systems will be considered only briefly and the remainder of this introductory discussion will be limited to the reactions of nitrobenzene, the halonitrobenzenes, and their decomposition products in aprotic solvent systems.

Electrochemistry of Nitrobenzene

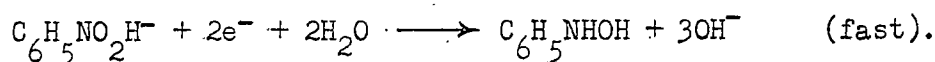
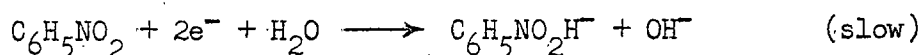
Nitrobenzene can be reduced in acidic aqueous media, pH less than 4.7, and the following mechanism has been proposed:¹



The rate determining step is the reduction of nitrobenzene to the protonated form of nitrosobenzene. Nitrosobenzene is more easily reduced than nitrobenzene and the second step leading to protonated phenylhydroxylamine is rapid. Following this four electron wave, at a more cathodic potential, a two electron reduction to the protonated form of aniline is observed:



In neutral and alkaline solution, pH greater than 4.7, the proposed mechanism is:



The second reduction wave of phenylhydroxylamine to aniline, as in the acid case, is not observed.

In the nonaqueous solvents N,N-dimethylformamide², (DMF), and acetonitrile³, (ACN), nitrobenzene is first reduced in a reversible one electron transfer to its stable anion radical. At a more cathodic potential an irreversible three electron transfer with protonation

occurs to form the major product, phenylhydroxylamine. With an added proton donor, such as phenol, the first reduction wave grows and the second decreases. At a mole ratio of acid to nitrobenzene of four to one only one irreversible four electron wave is observed as in the alkaline aqueous systems.

Reduction of nitrobenzene in the presence of a suspension of activated neutral alumina to remove every trace of electrophilic impurity, can result in the formation of the nitrobenzene dianion which is stable on the time scale of cyclic voltammetry.⁴ This observation of reversible behaviour for the dianion is successful in DMF, hexamethylphosphoramide, and pyridine, but in ACN where the solvent itself can donate protons more easily the dianion decomposes more rapidly.

In anhydrous liquid ammonia the dianion of nitrobenzene is stable with respect to protonation on the time scale of cyclic voltammetry and does not protonate even on an electrolysis time scale, although it does precipitate as the potassium salt.⁵

Electrochemistry of Halonitrobenzenes

Haloaromatics can generally be divided into two classes with respect to the mechanism of halogen loss.⁶ The first class contains aromatic compounds with only halogen substituents or if other substituents are present they are electrochemically inactive. These com-

pounds, such as the halogenated benzenes, biphenyls, benzonitriles, and naphthalenes, lose halide in a two-electron reduction with the addition of a proton to quantitatively form the dehalogenated aromatic.

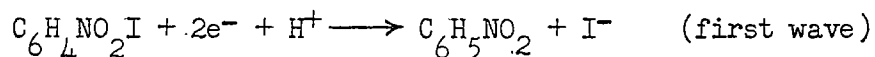
The second class of compounds, examples of which are some halogenated benzophenones, quinolines, phenzaines, and nitrobenzenes, can lose halide after less than two electrons transferred and the reductions usually result in substantially less than 100% conversion to the dehalogenated aromatic. The unhalogenated parent compounds in this class are electrochemically reducible at potentials similar to those of their halogenated derivatives and after electron transfer halide loss from these derivatives may have to compete with, or be replaced by chemical reactions of the non-halogen functional groups.

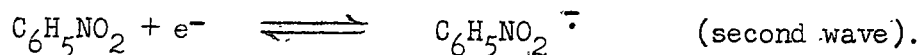
In 1962 Holleck and Becher⁷ reported the polarographic halfwave potentials for the first reduction waves of several of the isomers of iodo, bromo, and chloronitrobenzene in DMF and ACN. They observed anomalous reduction waves following the initial ones for p-bromo and p-iodonitrobenzene. Maki and Geske⁸, previous to this had not been able to observe an electron spin resonance, (ESR), signal for electrochemically generated p-iodonitrobenzene anion radical.

Adams and coworkers⁹ set about to resolve this problem. They

observed two reduction waves at a hanging mercury-drop electrode, (HMDE), for each of the six isomers of bromo and chloronitrobenzene and three reduction waves for each of the three isomers of iodonitrobenzene in DMF. By observation of its ESR spectrum during electrolysis at a potential between the second and third waves, they determined that the result of the second reduction of each of the iodonitrobenzenes was the formation of the nitrobenzene anion radical. Although they were able to show that iodide is lost by electrolysis on the first wave, no ESR signal was observed at this potential. Electrolysis of o-bromonitrobenzene in the presence of tetraethylammonium perchlorate as supporting electrolyte and of p-bromonitrobenzene in the presence of tetraethylammonium iodide at a potential more cathodic than their first reduction waves also resulted in the generation of the nitrobenzene anion radical. Loss of chloride was not observed during the time for which they electrolyzed solutions of the chloronitrobenzenes.

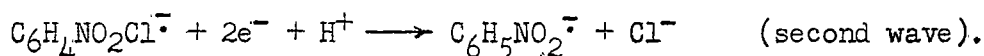
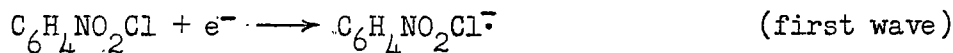
From these observations, Adams and coworkers postulated for the iodonitrobenzenes that the first wave was a two electron transfer resulting in the elimination of iodide and that the second wave was the formation of the nitrobenzene anion radical. Lawless and Hawley¹⁰ interpreted them as postulating the following mechanism:



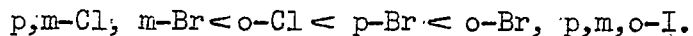


This mechanism is not consistent with the original data in that the halfwave potentials for the second waves of the iodonitrobenzenes are isomer dependent and fifty to eighty millivolts more cathodic than the first reduction of nitrobenzene.

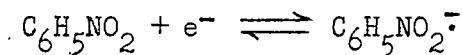
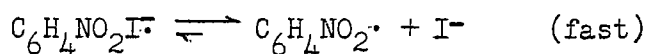
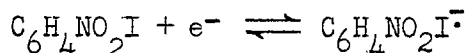
Fujinaga and coworkers¹¹ electrolyzed the three chloronitrobenzene isomers on the first wave in ACN in an ESR cavity and did not observe chloride loss. Electrolysis of the meta and para isomers in DMF, at the potential of the second wave resulted in the respective anion radical ESR spectra although at reduced intensity to that observed when the electrolysis potential was held between the two waves. In DMF electrolysis of o-chloronitrobenzene at the potential of the first wave resulted in the slow disappearance of the o-chloronitrobenzene anion radical ESR spectrum and the slow appearance of that of the nitrobenzene anion radical. When three moles of phenol were added for each mole of o-chloronitrobenzene dehalogenation was not observed at any potential. The following mechanism was proposed for o-chloronitrobenzene:



The behaviour of p-bromonitrobenzene was similar to o-chloronitrobenzene, o-bromonitrobenzene rapidly dehalogenated even when electrolyzed in ACN and dehalogenation was not observed for m-bromonitrobenzene. All of the iodo isomers showed rapid dehalogenation with formation of the nitrobenzene anion radical and the following order was deduced for the ease of dehalogenation:



Chronoamperometric techniques were used by Lawless and Hawley¹⁰ to determine that the first two reduction waves for p-iodonitrobenzene are the result of approximately two electrons being transferred. They proposed the following mechanism, where SH represents the solvent:



This mechanism, in contrast to the one they assumed to be proposed by Adams and coworkers⁹, has a total of two electrons transferred instead of three to end up with the formation of the nitrobenzene anion

radical.

Lawless and Hawley also used their chronoamperometric data and a current-reversal chronopotentiometric technique to measure pseudo first order rate constants for hydrogen abstraction by nitrophenyl radicals. The half life of the p-nitrophenyl radical, from their measurements, ranges from approximately one second in DMF to approximately nine seconds in DMSO with tetraethylammonium iodide present as supporting electrolyte. From their survey of decomposition rates these workers conclude that the stability of anion radicals in the different solvents used increases in the order $\text{DMF} < \text{ACN} < \text{DMSO}$.

In two subsequent publications Lawless, Hawley, and coworkers have described investigations into the mechanism of decomposition of dihalonitrobenzenes¹² and steric effects on reduction potential and rate of halide elimination.¹³

Electrolysis of 2,6-dichloro, 2,3-dichloro, and 2,4 dichloro-nitrobenzene at potentials just past the first reduction waves in DMF and/or ACN resulted in the formation of o-chloro, m-chloro, and p-chloronitrobenzene anion radicals respectively. Three reduction waves were observed for o-chloronitrobenzene in DMF as compared to two waves observed by Adams and coworkers⁹ under supposedly the same conditions. The second wave was attributed to the further reduction of the o-chloronitrobenzene anion radical to form the nitrobenzene.

anion radical and the third wave was considered to be the further reduction of the nitrobenzene anion radical. Controlled potential electrolysis of 2,6-dibromonitrobenzene to the point where two electrons had been transferred per mole of substrate resulted in 98% disappearance of starting material and the only product analysis they could determine was 24% conversion to nitrobenzene and 8% conversion to o-bromonitrobenzene.

Investigation of steric effects on halonitrobenzene electrochemistry led Hawley and coworkers to conclude that the twisting of the nitro group out of the plane of the ring by ortho substituents causes more loss of resonance energy for the nitro anion radical than for the neutral molecule. The higher energy product requires a more cathodic potential for anion radical formation, while the possibility for relaxation of the twisted nitro group enhances the rate of elimination of the ortho substituent. They also postulate that the cathodic reduction potential shift does not reflect the entire loss of resonance energy since part of this loss should be made up by increased solvation of the twisted nitro anion radical. Methyl substitutions on the halonitrobenzenes were observed to increase the rate of halide loss even when steric effects were not involved.

Nelson, Carpenter, and Seo¹⁴ have used cyclic voltammetry, chronoamperometry, and chronopotentiometry to investigate the reduc-

tion mechanisms of all the monohalonitrobenzenes. They have demonstrated that the first reduction wave is a one electron transfer for all of the compounds investigated except o-bromo and o-iodonitrobenzene. They concur with Lawless and Hawley¹⁰ on the one electron transfer followed by loss of halide and hydrogen atom extraction followed again by one electron transfer for the decomposition of p-iodonitrobenzene to the nitrobenzene anion radical. They observed the ESR spectrum for the nitrobenzene anion radical during electrolysis of all the monohalonitrobenzenes in ACN, although for the fluoro and chloronitrobenzenes up to several hours of electrolysis time were required. The inference is made that the p-iodonitrobenzene decomposition mechanism is general for the halonitrobenzenes. However excessive electrolysis time for generation of the nitrobenzene anion radical demonstrates that this is a very slow pathway for the fluoro and chloronitrobenzenes.

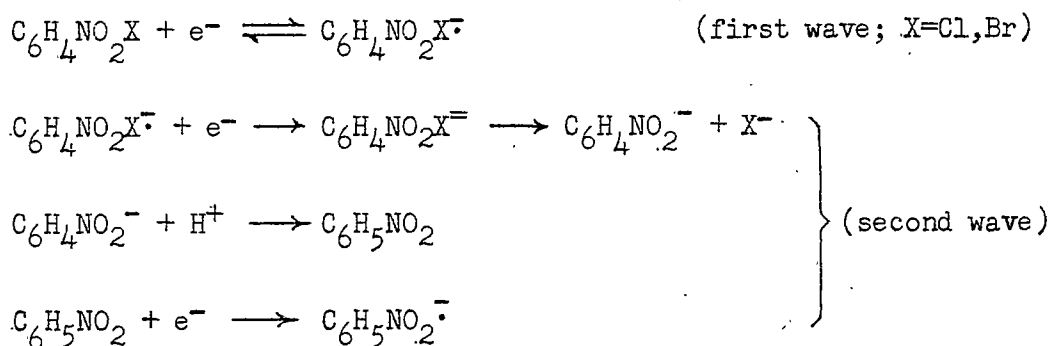
The first order rate constants measured for halonitrobenzene decomposition from chronoamperometric data show the following trends:

$$k_{\text{meta}} < k_{\text{para}} < k_{\text{ortho}} \text{ and } k_{\text{F}} < k_{\text{Cl}} < k_{\text{Br}} < k_{\text{I}}.$$

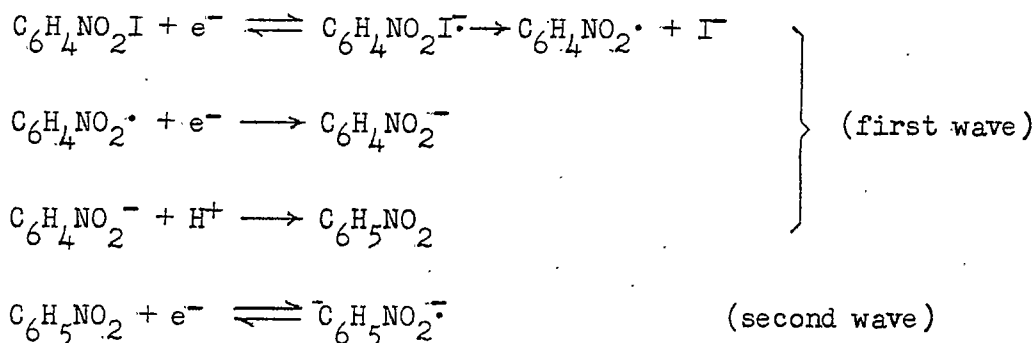
In experiments with deuterium oxide and deuterated ACN they were able to persuasively show that the solvent and not residual water is the source of hydrogen for halide replacement.

During electrochemical synthesis investigations, at high substrate concentration, 4-nitrobiphenyl was formed by electrolysis of p-iodonitrobenzene in a 50/50 mixture of ACN/benzene, also 50 - 60% yields of 4,4'-dibromoazoxybenzene were obtained by electrolysis of p-bromonitrobenzene at the potential of its second reduction wave. Notably, no dinitrobiphenyls or solvent addition products could be isolated or characterized although several unidentified products were produced.

Sosonkin and coworkers^{15,16} have used both electrochemical and chemical reduction of halonitrobenzenes to determine the mechanism of halide substitution by hydrogen. They support the mechanisms proposed for o-chloro, p-bromo, and the iodonitrobenzenes by Fujinaga and coworkers¹¹. They elaborated on these mechanisms as follows:



and

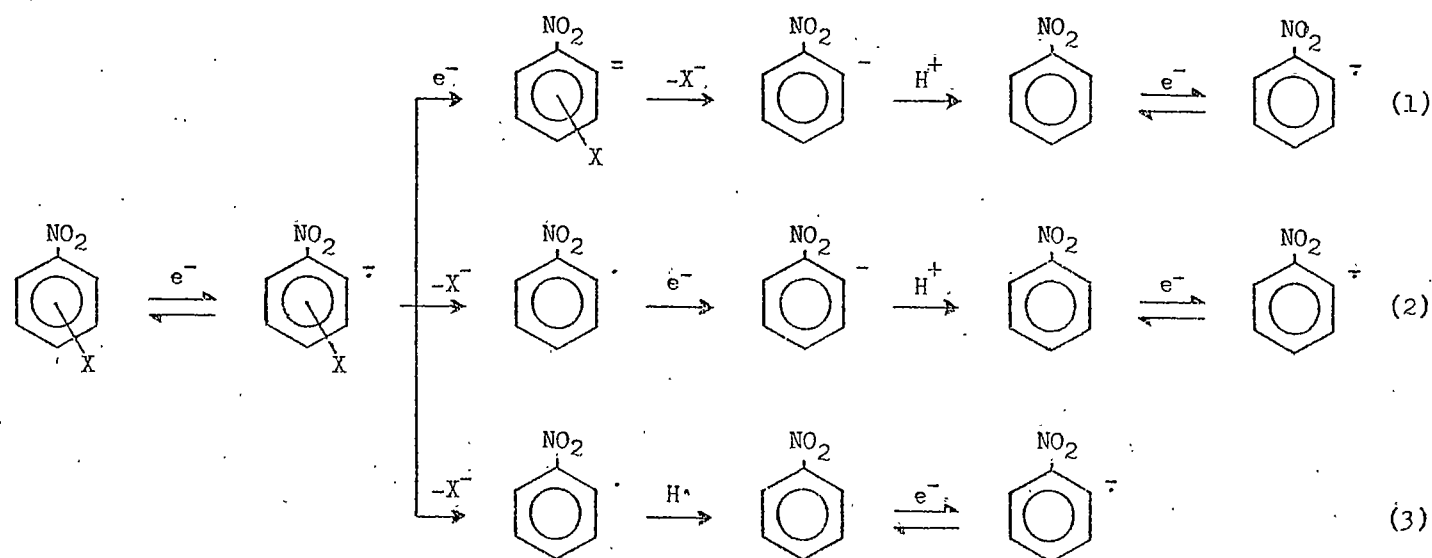


Thus far in this section, pertinent results of the electrochemical investigations of halonitrobenzenes have been presented with a minimum of personal comments. These results will now be summarized and critically analyzed.

The several proposed mechanisms are illustrated in figure 1. Pathway (1) encompasses an initial one electron reversible wave to form the stable halonitrobenzene anion radical. At a more cathodic potential, (c.a. one volt), a second electron is added, rapid dehalogenation occurs, and the resulting carbanion extracts a proton from the solvent to form nitrobenzene. Nitrobenzene is reduced more easily than the halonitrobenzene anion radical so it is rapidly reduced in a one electron transfer to make the second wave a two electron reduction. This pathway is the one originally suggested by Fujinaga and coworkers¹¹ and also supported by Sosonkin and coworkers.^{15,16}

The pathway represented by (2) begins with a two electron wave which can be broken down into an initial one electron transfer to

FIGURE 1. Halonitrobenzene Reduction Pathways



Note: Carbanions and neutral radicals will be localized on the ring position from which halide was lost.

yield an unstable halonitrobenzene anion radical. It loses halide and is rapidly reduced by a second electron to a carbanion. Protonation results in the formation of neutral nitrobenzene which is reduced at a slightly more cathodic potential, (c.a. 0.2 volts), resulting in the second wave. This pathway was inferred by the data of Adams and coworkers⁹ for the decomposition of the iodonitrobenzenes. It was also supported by the observations in references 11, 15, and 16.

Pathway (3) again begins with an initial one electron transfer to yield an unstable halonitrobenzene anion radical which loses halide. The neutral radical which results is reasonably stable and decomposes by hydrogen atom extraction from the solvent. Nitrobenzene is then reduced at the same or a slightly more cathodic potential and a total of two one electron waves are supposedly observed. The work of Hawley and coworkers^{10,11} and that of Nelson and coworkers¹⁴ support this pathway.

The following observations are made:

1. It appears obvious that any supposed conflict between the mechanisms of pathways (1) and (3) can be explained by allowing both to be valid. If an electrode is held at the potential of the first reversible wave the halonitrobenzene anion radical can lose halide at a rate characteristic of the particular halogen

and isomer involved. If as in the case of iodine, halide loss is rapid and if hydrogen atom extraction is valid, the nitrobenzene anion radical can be generated with only two electrons transferred.

When the halonitrobenzene anion radical is quite stable as for chlorine, reaction by pathway (3) will be slow. Application of an electrode potential as cathodic as the second wave can then produce the nitrobenzene anion radical with a transfer of three electrons.

2. Neither pathway (2) or (3) explain the iodonitrobenzene electrochemistry of Adams and coworkers⁹. The first reduction wave of these compounds is at least twice as large, (twice as much current), as the second wave. The halfwave potentials of the second and third waves do not correspond to those of nitrobenzene, the supposed product of the first wave. A reduction mechanism involving a solvent addition product may be able to explain these results.
3. Product analyses after controlled potential electrolysis have not resulted in the identification of the nitrobenzene radical coupling product, dinitrobiphenyl, even though the postulated lifetime of the radicals is quite long. Also the fate of the solvent radicals

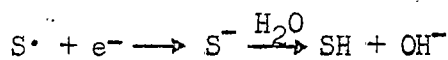
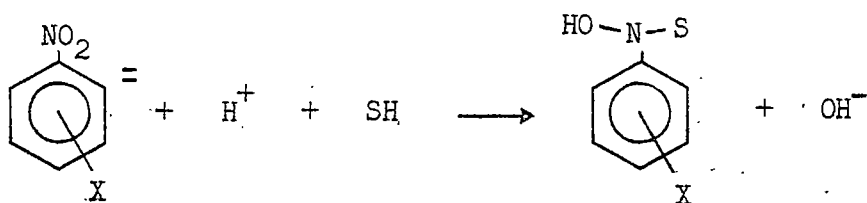
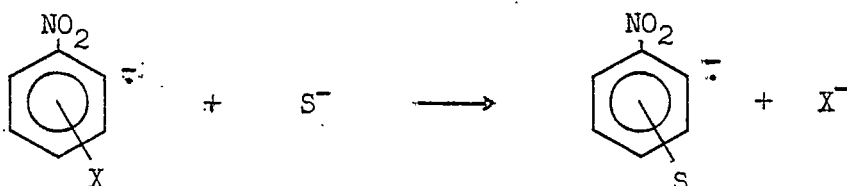
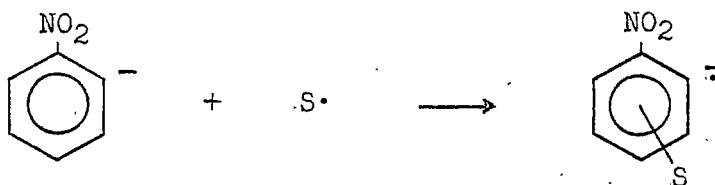
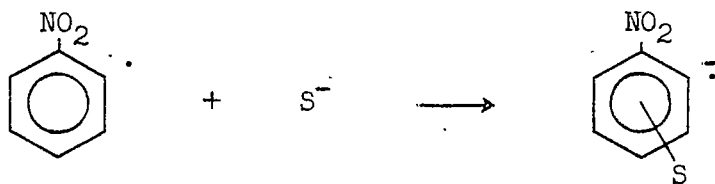
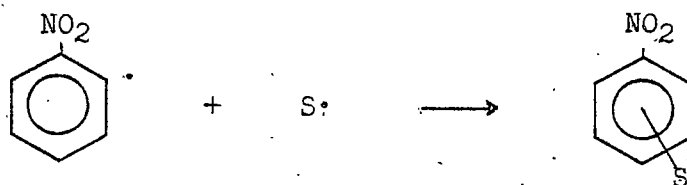
remains a mystery. A number of its addition products are possible, (figure 2), and they should be identifiable.

4. Failure to minimize residual water can have a substantial effect on the potentials and possibly the mechanisms of decomposition at the more cathodic irreversible reductions. As mentioned earlier, Adams and coworkers⁹ observed one reversible and one irreversible wave for the reduction of o-chloronitrobenzene. Lawless and Hawley¹² observed one reversible and two irreversible waves for this compound under nearly identical conditions. This author has observed that addition of traces of water to dry DMSO can cause a change from a total of three waves to a total of two for the reduction of this compound and that changes in the voltammograms of polychloronitrobenzenes by traces of water is a general feature.
5. No reactions of the nitro group concomitant to halide loss have been described previous to this investigation.

Electrochemistry of Nitrosobenzene and Azoxybenzene

Kemula and Sioda¹⁷ have investigated the electrochemical reduction of nitrosobenzene in DMF with sodium nitrate as supporting electrolyte. They observed two polarographic waves for this reduction, and the first was attributed to the formation of the nitroso-

17
FIGURE 2. Secondary Reactions With Solvent



benzene anion radical. The second wave was postulated to be a combination of the further reduction of the nitrosobenzene anion radical and the reduction of azoxybenzene formed by the reaction of two anion radicals from the first wave or anion radicals reacting with neutral nitrosobenzene molecules. Electrolysis of nitrosobenzene on the first wave resulted in the current decaying to zero before the passage of one electron per molecule of substrate. Polarography of an electrolyzed solution indicated only the formation of azoxybenzene.

Asirvathan and Hawley¹⁸ have studied the controlled potential electrolysis of nitrosobenzene in ACN and DMF. In ACN they observed unusually rapid decomposition which was complete after the passage of 0.3 moles of electrons per mole of substrate. They proposed that hydroxide ions produced during the formation of azoxybenzene also caused the decomposition of nitrosobenzene to azoxybenzene. This was supported by the fact that each 0.3 of a mole of tetraethylammonium hydroxide added to a solution of nitrosobenzene caused the disappearance of one mole of nitrosobenzene, with the formation of azoxybenzene at a 70% yield. At least nine other minor products were isolated but not identified. Similar yields of azoxybenzene were obtained from exhaustive electrolysis and again it was the only product that could be identified.

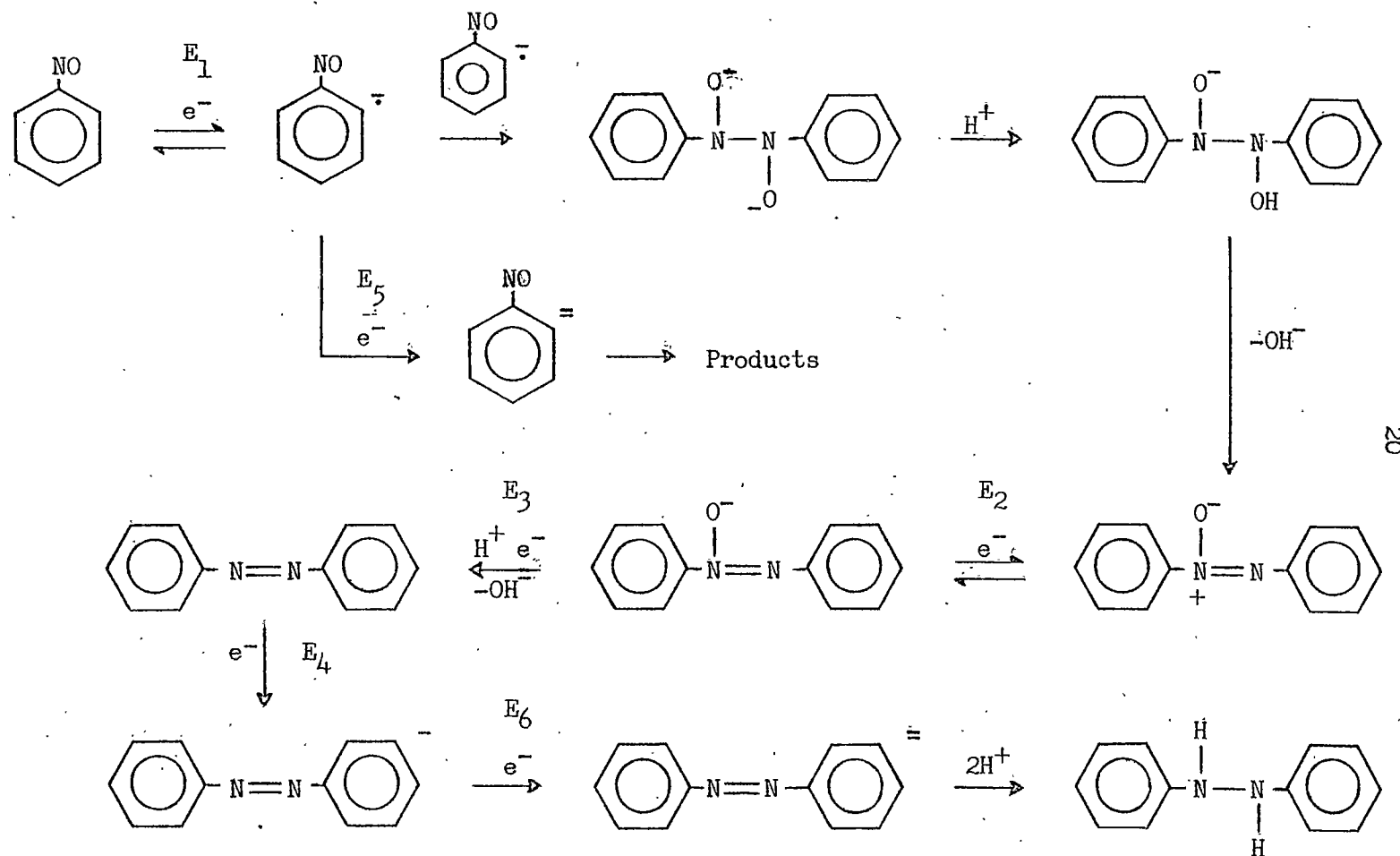
Although the nitrosobenzene anion radical was somewhat more stable

in DMF, similar results were obtained for both electrochemical and chemical decomposition in this solvent.

Lipsztajn and coworkers¹⁹ observed three polarographic waves for the reduction of nitrosobenzene in DMF with tetraethylammonium perchlorate as supporting electrolyte. However under the same conditions, four reduction waves were observed on a chrono-voltammogram taken at a hanging mercury drop electrode. They interpreted their results as shown in figure 3. Nitrosobenzene is reduced in a partially reversible one electron wave to the nitrosobenzene anion radical which can dimerize and lose hydroxide to form azoxybenzene. From the electrochemistry of authentic azoxybenzene²⁰, they were able to interpret the second wave as the reversible one electron reduction of azoxybenzene. The third wave was believed to be a combination of further reduction of nitrosobenzene anion radicals that had survived dimerization and the irreversible reduction of azoxybenzene anions to give azobenzene. The azobenzene formed is more easily reduced than the azoxybenzene anions so a second electron is instantly transferred to give azobenzene anions, whose reduction to hydrazobenzene constitute the fourth wave.

They found that changing the concentration or the cation of the supporting electrolyte could cause substantial changes in the electrochemistry of nitrosobenzene and in the presence of sodium perchlorate

FIGURE 3. Electrochemical Reduction Pathways for Nitrosobenzene

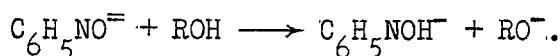
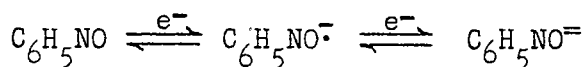
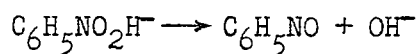
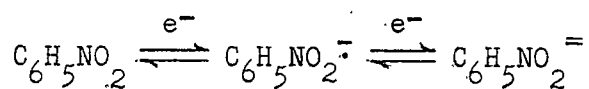


$$E_1 < E_2 < E_3 \approx E_5 < E_6$$

$$E_3 > E_4$$

their results were similar to those of Kemula and Sioda.¹⁷

In anhydrous liquid ammonia nitrosobenzene can be reduced in two reversible one electron steps to its stable dianion.⁵ Nitrosobenzene is also observed as a stable reduction product of nitrobenzene in liquid ammonia with isopropyl alcohol added as a proton donor. The proposed mechanism is as follows:



The cathodic cycle of a cyclic voltammogram shows two waves. The nitrobenzene anion radical is formed on the first wave and the protonated nitrosobenzene dianion is formed on the second wave. On the anodic scan two new waves are seen. The first is from the oxidation of the protonated nitrosobenzene dianion which after loss of an electron, rapidly deprotonated to give the nitrosobenzene anion radical. The oxidation of the nitrosobenzene anion radical makes up the second new wave. A second cathodic sweep shows the reduction

of nitrosobenzene at a potential anodic of nitrobenzene reduction.

No reports of electrochemical investigations of halogenated nitrosobenzenes in aprotic media were discovered during an extensive literature search.

STATEMENT OF PROBLEM

This work has grown out of that of S. O. Farwell²¹ and F. A. Beland.²² They investigated the electrochemical reduction of several chlorinated homologs such as the polychlorobenzenes and polychlorobiphenyls. The only electroactive functions in these compounds were the chlorine substituents and they concluded that each electrochemical reduction wave was the result of an irreversible two electron transfer with the loss of chloride and proton abstraction. They applied controlled potential electrolysis and CNDO molecular orbital calculations to the problem of determining electrochemical reduction mechanisms and product distributions for these compounds.

The electrochemical behaviour of molecules with more than one electroactive functional group, specifically the chlorinated nitro and nitrosobenzenes, are the subject of this investigation. Furthermore, both reversible and irreversible electrochemical processes are involved in the reduction of these compounds and cyclic voltammetry is needed to distinguish between the two processes. The elucidation of the mechanism of reduction in the presence of competing electrochemical and chemical reactions and the cataloging of the reduction potentials in the solvent dimethylsulfoxide for the polychloronitro and polychloronitrosobenzenes is the problem addressed in this portion of this dissertation.

EXPERIMENTAL

Electrochemical Cell and Electrodes

A small volume H-cell was constructed with a glass wool plug to divide the two compartments. A total sample volume of 8 to 10 milliliters for the two compartments was found to be convenient. Between analysis of samples the cell was rinsed repeatedly with distilled water and the cell was then dried by rinsing three or four times with acetone followed by forcing a current of air through the glass wool plug.

The working electrode was a platinum flag with a total area of approximately 60 mm^2 , coated with mercury by the procedure of Enke and coworkers.²³ An auxiliary or counter electrode was formed by a coil of 20 gauge platinum wire. The reference electrode was a silver wire which had been anodized in the presence of chloride to form a silver chloride coating. This coated wire was placed in a glass tube with a fine capillary tip and the tube was filled with a saturated aqueous solution of potassium chloride and silver chloride.

Although aqueous reference electrodes have large, unknown junction potentials when used in nonaqueous systems, these junction potentials can be made reproducible with a properly constructed reference electrode.²⁴ This Ag/AgCl reference has an equilibrium potential 0.197 volts positive of the standard hydrogen electrode. This is 0.045

volts negative of the potential of the more commonly used saturated calomel electrode and approximate comparison to potentials reported versus the saturated calomel can be obtained by subtracting 0.045 volts from the potentials reported herein.

The reference electrode was placed in contact with the solution in one compartment of the H-cell and the working and counter electrodes were placed in the other compartment. The working compartment solution was flushed with nitrogen for several minutes to remove oxygen prior to recording of a voltammogram.

Cyclic Voltammetry Instrumentation

A conventional cyclic voltammeter with a standard three electrode, operational amplifier potentiostat was constructed as shown schematically in figures 4 and 5. This design allowed for the initial potential and the cathodic and anodic limits to be independently and arbitrarily set. The anodic and cathodic sweep rates were also independently variable, but for all the work reported herein they were set equal to each other at 75 mv/sec. The uncompensated IR drop in the system was deemed negligible and was not corrected for electronically. All voltammograms were recorded on a Houston Instruments Omnigraphic 2000 X-Y recorder and peak potentials were determined graphically.

Figure 4. Cyclic Voltammeter Block Diagram.

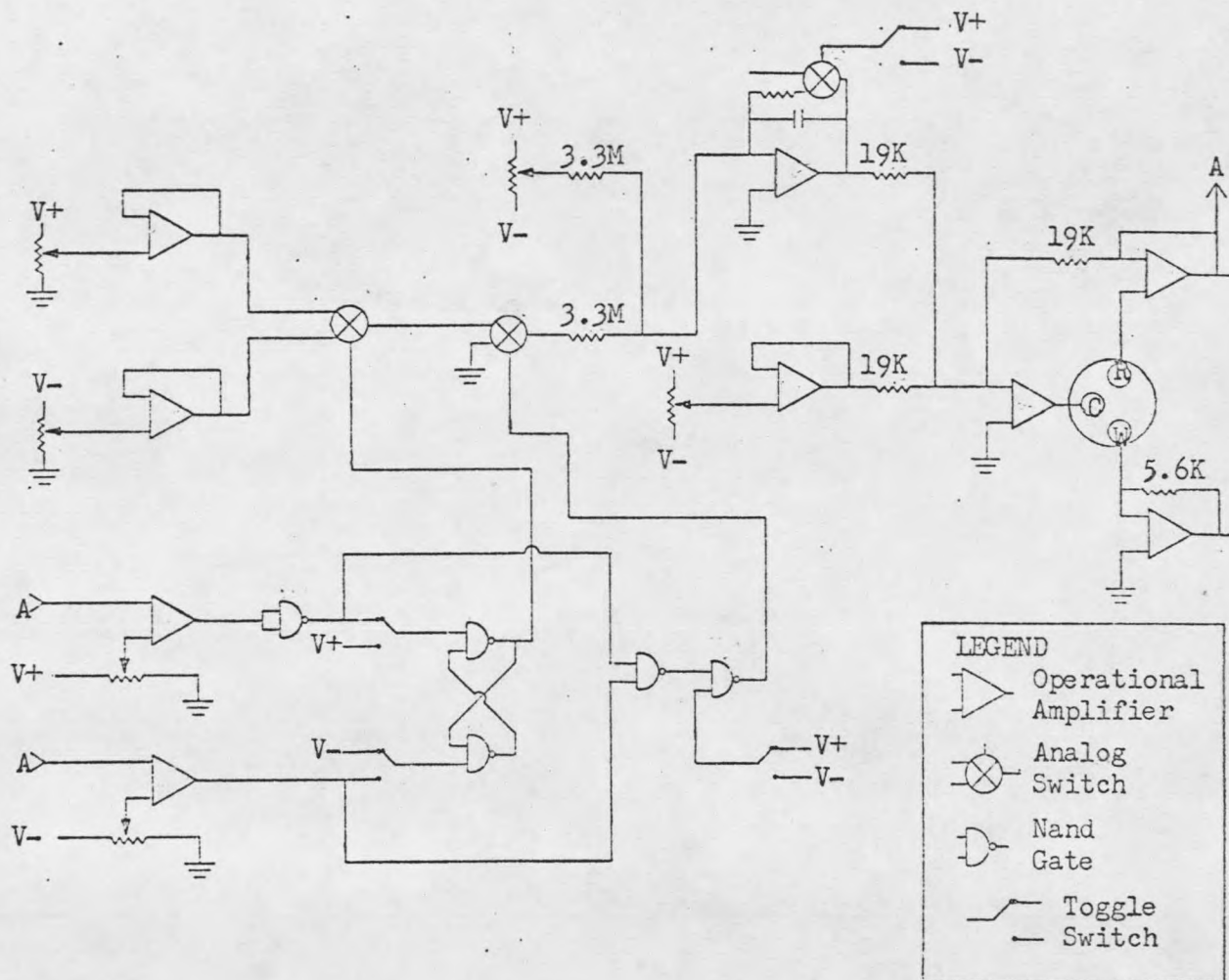
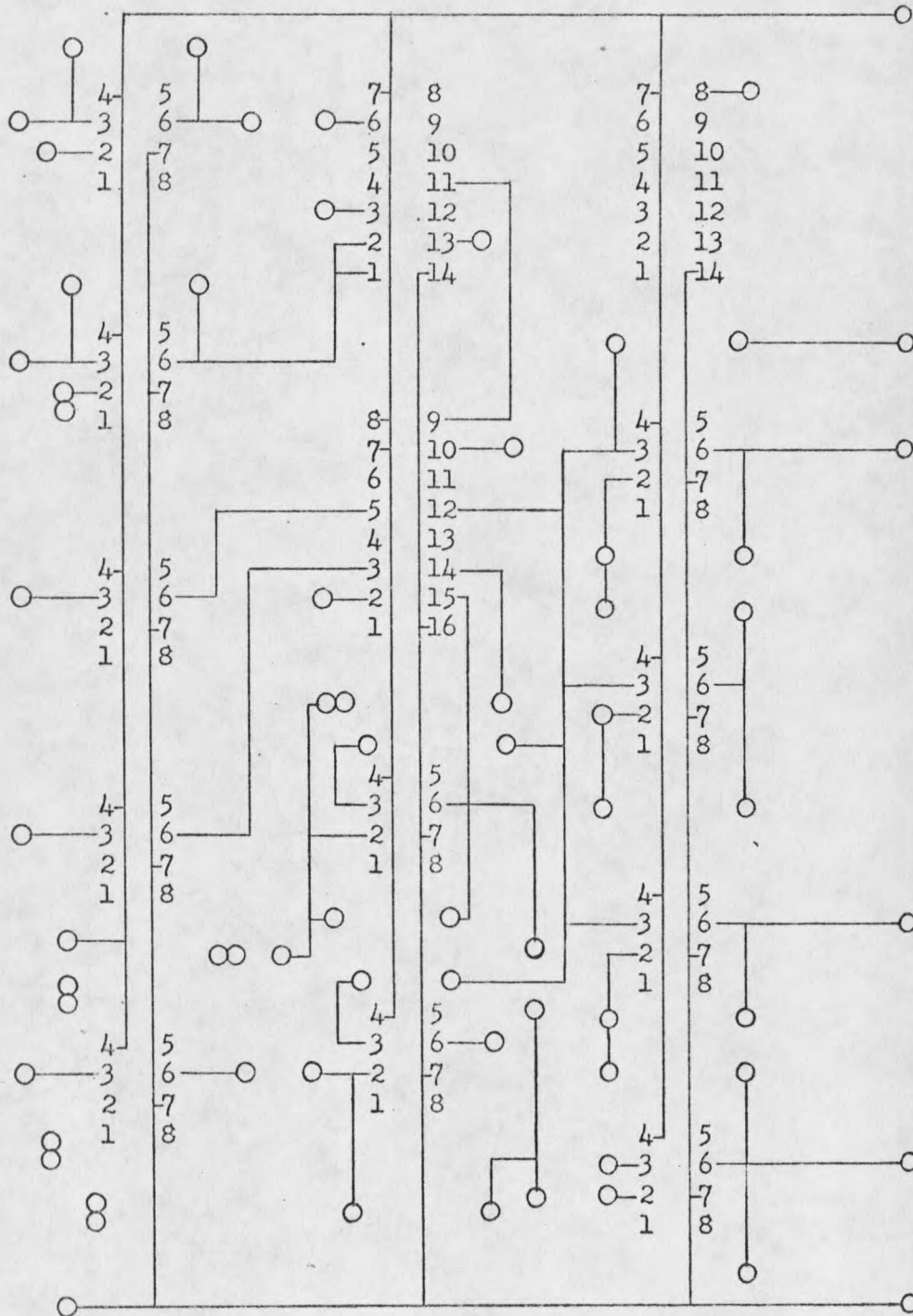


Figure 5. Cyclic Voltammeter Circuit Diagram.



Solvent Purification

Reagent grade dimethyl-sulfoxide, (DMSO), was obtained from J. T. Baker Co. and was found to contain at least one electroactive impurity which interfered with the recording of voltammograms of substrates at $5 \times 10^{-4}M$ concentrations.

The solvent was purified by refluxing 300-400 ml per batch over ten grams of sodium hydroxide at approximately 75°C for two and a half hours. The refluxing mixture was continuously stirred and maintained under an atmosphere of nitrogen at reduced pressure. The solvent was then decanted into a flask containing five grams of pulverized calcium hydride, to remove water, and the mixture was stirred for three to four hours while a nitrogen atmosphere was maintained above the liquid. The DMSO was then distilled under vacuum, with the first and last 20-30 ml being discarded. The collection flask was cooled in an ice bath and the middle fraction was obtained as a solid. All solutions for electrochemical analysis were prepared and analyzed within 48 hours after this purification and drying procedure.

Electrolyte and Organic Substrates

The supporting electrolyte used throughout this study was tetraethylammonium perchlorate from Eastman Organic Chemicals, halogens as bromide 100 ppm or less.

Polychloronitrobenzenes

Nitrobenzene was purchased from Fisher Scientific Co. Samples of 2-chloro; 4-chloro; 2,4-dichloro; 3,4-dichloro; 2,3,4-trichloro; 2,4,5-trichloro; 2,3,4,5-tetrachloro; 2,3,5,6-tetrachloro and pentachloronitrobenzene were purchased from Aldrich Chemical Co., Inc. Samples of 3-chloro; 2,3-dichloro and 2,5-dichloronitrobenzene were purchased from J. T. Baker Chemical Co.

The synthesis of the following compounds was carried out with the goal of obtaining enough pure product to carry out electrochemical analysis. Little effort was devoted to perfecting synthetic methods and yields are not reported. In the case of the polychloronitrosobenzenes, much of the crude product was sacrificed in the interest of purity. Yields were typically 1% or less, but most of these materials contained no impurities observable by voltammetry.

Samples of 2,6-dichloro; 2,3,5-trichloro; 2,3,6-trichloro; 2,4,6-trichloro and 2,3,4,6-tetrachloronitrobenzene were synthesized by Kathleen Brunke, Linda Davis, and/or Richard Geer. Samples of 2,6-dichloro and 2,4,6-trichloroaniline were oxidized with 30% H_2O_2 in a 9 to 1 mixture of acetic to formic acid at near boiling temperatures to yield 2,6-dichloronitrobenzene, m.p. 71-72°C and 2,4,6-trichloronitrobenzene, m.p. 69-70°C. A sample of 2,3,5-trichloronitrobenzene

was synthesized by chlorination of o-aminonitrobenzene in both meta positions with chlorine gas. This was followed by replacement of the amine group by chlorine with cuprous chloride via the Sandmeyer reaction, m.p. 49-50°C. A sample of 2,3,6-trichloronitrobenzene was synthesized from 2,6-dichloronitrobenzene by chlorination of one of the meta positions with antimony pentachloride, m.p. 78-83°C. A sample of 2,3,4,6-tetrachloronitrobenzene was the nitration product of 1,3,4,5-tetrachlorobenzene with nitric and sulfuric acid, m.p. 40-42°C. A sample of 3,5-dichloronitrobenzene was synthesized by deamination of 2,6-dichloro-4-nitroaniline with sodium nitrite in the presence of ethanol and sulfuric acid. The crude product was steam distilled and then recrystallized from ethanol, m.p. 58-60°C. A sample of 3,4,5-trichloronitrobenzene was synthesized by diazotization of 2,6-dichloro-4-nitroaniline with sodium nitrite in the presence of acetic and sulfuric acid. The freshly prepared diazonium salt solution was added to a solution of cuprous chloride in concentrated HCl to effect the replacement of the diazonium group by chlorine. The crude product was recrystallized from acetic acid, m.p. 67-69°C.

Polychloronitrosobenzenes

Nitrosobenzene was synthesized by the procedure of Coleman et. al.²⁵ which entailed the reduction of nitrobenzene in a vigorously stirred

aqueous suspension with zinc powder, (J. T. Baker Chemical Co.).

The reduction product, phenylhydroxylamine, was oxidized to nitrosobenzene in a cold aqueous solution of sulfuric acid and sodium dichromate. The crude product was steam distilled and recrystallized from ethanol. A sample of 4-chloronitrosobenzene was synthesized by the same procedure as nitrosobenzene except the 4-chlorophenylhydroxylamine was isolated and recrystallized from hexane and the crude product from the oxidation was used without further purification.

Samples of 2,6-dichloro; 2,3,6-trichloro; 2,4,6-trichloro; 2,3,4,6-tetrachloro and 2,3,5,6-tetrachloronitrosobenzene were synthesized by the oxidation of the respective anilines with 30% H_2O_2 by the procedure of Holmes and Bayer,²⁶ modified by the use of a 9 to 1 mixture of acetic to formic acid as solvent instead of pure acetic acid. The solutions were allowed to react for 24 to 48 hours at room temperature and the products were recrystallized from ethanol. An attempt to synthesize pentachloronitrosobenzene by this method was unsuccessful.

The remainder of the polychloronitrosobenzenes were synthesized by a procedure similar to that of Lutz and Lytton.²⁷ Typically 20 grams of the particular chlorinated nitrobenzene and 1 gram of CaCl_2 were dissolved in 150 milliliters of a 5 to 1 mixture of ethanol and water, more solvent being required for the higher chlorinated compounds. 20 grams of zinc powder, (J. T. Baker Chemical Co.), was

added and the stirred mixture was refluxed for 45 minutes. At this point the reaction pots always contained a lot of precipitated material which was filtered hot and washed with several hundred milliliters of hot ethanol. The filtered alcohol-water solution of chlorinated phenylhydroxylamine was added to 25 grams of ferric chloride hexahydrate dissolved in 400-500 ml of ice water slurry. A precipitate was obtained immediately and it was allowed to digest for several hours before it was filtered off and steam distilled. The chlorinated nitrosobenzenes distilled over as small green or green-blue droplets and collected as several large oil drop. When these oil drops solidified the product was recrystallized from ethanol. The melting points of the nitrosobenzenes are given in table 1.

Table 1. Polychloronitrosobenzene Melting Points

Chlorine Position	Observed Melting Point(C°)
-	60
2	52-56
3	68-72
4	80-84
2,3	88-90
2,4	43-45
2,5	97-98
2,6	172-173
3,4	83-85
3,5	97-100
2,3,4	58-59
2,3,5	77-78
2,3,6	170
2,4,5	88-90
2,4,6	140
3,4,5	76-86*
2,3,4,5	83-85
2,3,4,6	163-164
2,3,5,6	197-198

*Melting began at 76° to a medium green liquid and the last fine needles melted at 86°C.

RESULTS AND DISCUSSION

The peak potentials for the reduction waves of the polychloronitro and polychloronitrosobenzenes are shown in tables 2 and 3. Too few repeat measurements were recorded to determine a statistical precision for these values. However experience with measuring the peak potentials of 2-chloronitrobenzene at several different times during the period of investigation revealed that the deviation from measurement to measurement was about ± 10 millivolts. All of the reported values are believed to be precise within these limits.

The matching of peak potentials of electrochemically active intermediates with the peak potentials of authentic compounds deserves more leeway than ± 10 millivolts since the intermediates give rise to smaller current waves whose peak potential can not be measured as precisely as the peak potentials of the larger waves. Also the potentials of the intermediate waves are often close to other waves which may shift the apparent potential of the peak current.

Semi-quantitative interpretations of the voltammograms for the purpose of identifying electrochemical reduction pathways are now presented. The mechanisms presented show the electrochemical and chemical reactions to the points where the reduction product is a previously discussed compound. The electrochemistry of this compound when considered as a reduction product is taken to be the same as when this compound was considered as the substrate.

Two cyclic voltammograms of nitrobenzene are shown in figure 6. The top voltammogram shows that the first reduction process is reversible. This wave corresponds to the one electron reduction of nitrobenzene to its stable radical anion and the oxidation of the anion is observed on the anodic sweep. The current-voltage curve will track itself without any noticeable decrease in current for several hundred cycles. However if the potential of the working electrode, with respect to the reference electrode, is allowed to become more negative, a second electrochemical process takes place. On voltage scan reversal there is no corresponding oxidation and this second reduction is therefore irreversible. Also the oxidation of the nitrobenzene anion radical is observed at reduced current magnitude and a new oxidation process is observed. A second cathodic sweep shows that this new process is reversible. Figure 38 shows cyclic voltammograms for nitrosobenzene. The peak potential for the reversible wave of nitrosobenzene compares well with the peak potential for the new wave in the nitrobenzene voltammogram, -0.829 volts and -0.818 volts respectively.

A mechanism is proposed for the electrochemical reduction of nitrobenzene in figure 7. The first electron transfer corresponds to the first reversible wave of the voltammogram, peak potential -1.053. The second wave involves a second electron transfer and

yields the dianion of nitrobenzene which abstracts a proton, probably from the solvent, and loses hydroxide to form nitroso-benzene. The next two electron transfers should take place at the potential of the second wave, -2.009 volts, since their potentials from the analysis of authentic nitrosobenzene are -0.829 volts and -1.890 volts. Some of the nitrobenzene and nitrosobenzene anion radicals in the vicinity of the electrode survive further reaction since their oxidation can be seen on the anodic sweep. This is identical to the mechanism proposed by Smith and Bard⁵ for the reduction of nitrobenzene in liquid ammonia in the presence of isopropyl alcohol.

Cyclic voltammograms for 2-chloronitrobenzene are shown in figure 8. The first wave is again reversible, the second wave results in the appearance of a new electrochemical process, and the third wave results in the appearance of a second new set of waves. Figure 9 shows the proposed mechanism for the electrochemical reduction of this compound. Although the loss of chloride after the second electron transfer is not observed in terms of a wave for nitrobenzene, this process is observed for 4-chloronitrobenzene under the right conditions. The first new wave has a peak potential of -0.631 volts compared with -0.648 volts for the first reversible wave of 2-chloronitrosobenzene, figure 39. The second new wave has a peak potential

of -0.823 volts compared with -0.829 volts for the first reversible wave of nitrosobenzene. That nitrosobenzene appears to be a product of the second irreversible wave of the 2-chloronitrobenzene reduction also supports the suggestion that halide loss is one of the reactions of the dianion of 2-chloronitrobenzene.

Cyclic voltammograms of 3-chloronitrobenzene are shown in figure 10. Only one irreversible wave is observed in this case and only one new set of electrochemical waves is observed on a second voltage scan. The proposed electrochemical reduction mechanism is shown in figure 11. The peak potential of the reduction of the new wave is -0.664 compared with -0.669 for the first reversible wave of 3-chloronitrosobenzene, figure 40. On the first cathodic scan the potential sweep was interrupted at the cathodic limit and the potential was held there for ten seconds. Close examination of the original voltammogram revealed a very small set of waves just cathodic of the reversible wave for 3-chloronitrobenzene. Nitrobenzene and its anion radical are judged to be responsible for this set of waves and the loss of chloride is probably a minor pathway for the reaction of the dianion of 3-chloronitrobenzene. That the loss of halide from the meta position is slower than loss from the ortho and para positions agrees with observations in the literature.

Cyclic voltammograms of 4-chloronitrobenzenes are shown in figure

12, and the proposed electrochemical reduction mechanism is shown in figure 13. One irreversible wave with a shoulder is observed on the cathodic scan. With the information available it is impossible to distinguish the relative magnitudes of the current rising from the two irreversible processes. The middle voltammogram includes a ten second hold of the potential at the cathodic limit. The subsequent cycle shows two new electrochemical processes. The most anodic is attributed to 4-chloronitrosobenzene, figure 41, and the set of waves just cathodic of the reversible wave for 4-chloronitrobenzene are attributed to nitrobenzene. When the potential is swept out past both the irreversible waves the set of waves attributed to nitrobenzene is not observed on the second cycle, but a set of waves at the potential of nitrosobenzene is now observed.

From a qualitative analysis of the relative magnitudes of the current waves attributed to the monochloronitrosobenzene and nitrosobenzene for each of the monochloronitrobenzene voltammograms, the order of the rate of chloride loss from the dianion of the monochloronitrobenzene is ortho > para > meta.

The difficulty of observing intermediate reaction products increases with the number of substituents since the number of possible products also increases. Therefore the proposed mechanisms that follow are on a less firm footing than those that precede.

Cyclic voltammograms of 2,3-dichloronitrobenzene are shown in figure 14 and the proposed electrochemical reduction mechanism is shown in figure 16. The only possibly new electrochemical process observed after sweeping past the first irreversible wave is a very small set of waves whose potentials do not correspond to any likely reduction product and may be due to an electroactive impurity. If any 3-chloronitrobenzene was formed in the first irreversible reduction process it was not observable electrochemically since the peak potentials for the reversible reductions of the 3-chloro and 2,3-dichloro compounds differ by only one millivolt.

Surprisingly there is evidence that the loss of the meta chlorine competes with the loss of the ortho chlorine. The second irreversible wave peak potential for 2,3-dichloronitrobenzene is -1.850 compared to -1.811 and -1.870 for the first irreversible waves of 2-chloro and 3-chloronitrobenzene. Sweeping past the second wave results in one new set of waves with reduction peak potential -0.655 volts which can be compared with either -0.648 or -0.669 for the reduction waves of 2-chloro or 3-chloronitrosobenzene.

The third reduction wave peak potential is -1.977 volts compared with -2.009 for the second reduction of nitrobenzene. A second small set of waves is observed after sweeping past all the reduction waves and its reduction peak potential is -0.791 compared to -0.829 for nitrosobenzene.

Cyclic voltammograms of 2,5-dichloronitrobenzene are shown in figure 15 and the proposed electrochemical reduction mechanism is shown in figure 16. If the ortho chlorine is lost on the first irreversible wave the electrochemistry of the resulting 3-chloronitrobenzene may be obscured by that of 2,5-dichloronitrobenzene since their first reversible waves have similar potentials. The peak potential of the second irreversible reduction is -1.872 compared to -1.870 for the irreversible reduction of 3-chloronitrobenzene. The potential of the new set of waves compares very well with that of 3-chloronitrosobenzene.

Cyclic voltammograms of 2,4-dichloronitrobenzene are shown in figure 17 and the proposed electrochemical reduction mechanism is shown in figure 19. The most interesting feature is the apparent formation of nitrobenzene when the sweep was interrupted for 10 seconds at the potential of the second irreversible process. The peak potential for the new wave is -1.038 compared to -1.053 for nitrobenzene. All of the first and second sweep potentials are consistent with the dominant loss of the ortho chlorine and the formation of 4-chloro and nitrosobenzene.

Cyclic voltammograms of 2,6-dichloronitrobenzene are shown in figure 18 and the proposed electrochemical reduction mechanism is shown in figure 19. The compounds with both ortho positions chlorinated

appear to exhibit absorption phenomena at the mercury electrode. On the second cycle the reversible wave is shifted anodic if the sweep has been as cathodic as the first irreversible wave. Both 2-chloro and nitrosobenzene are postulated as reduction intermediates for this compound. Any formation of nitrobenzene may be obscured by the wave for 2,6-dichloronitrobenzene.

Cyclic voltammograms for 3,4-dichloronitrobenzene are shown in figure 20 and the proposed electrochemical reduction mechanism is shown in figure 22. The major reduction intermediate observed was 3-chloronitrosobenzene.

Cyclic voltammograms for 2,3,4-trichloronitrobenzene are shown in figure 21 and the proposed electrochemical reduction mechanism is shown in figure 22. The major reduction intermediate observed was 3-chloronitrosobenzene.

Cyclic voltammograms for 3,5-dichloronitrobenzene are shown in figure 23 and the proposed electrochemical reduction mechanism is shown in figure 25. The major reduction intermediates observed were 3-chloronitro and 3-chloronitrosobenzene.

Cyclic voltammograms for 2,3,5-trichloronitrobenzene are shown in figure 24 and the proposed electrochemical reduction mechanism is shown in figure 25. The major reduction intermediates observed were 3-chloronitro and 3-chloronitrosobenzene.

Cyclic voltammograms for 2,3,6-trichloronitrobenzene are shown in figure 26 and the proposed electrochemical reduction mechanism is shown in figure 28. The first irreversible reduction is postulated to result in the loss of an ortho chlorine to give 2,5-dichloronitrobenzene. The next two waves, irreversible waves, are similar to those of 2,5-dichloronitrobenzene, however a small trailing shoulder at the potential of the second reduction of nitrobenzene shows that like the case of 2,3-dichloronitrobenzene the ortho chlorine enhances the rate of loss of the meta chlorine.

Cyclic voltammograms for 2,4,5-trichloronitrobenzene are shown in figure 27 and the proposed electrochemical reduction mechanism is shown in figure 28. The major reduction intermediates observed were 3-chloronitro and 3-chloronitrosobenzene.

Cyclic voltammograms for 2,4,6-trichloronitrobenzene are shown in figure 29 and the proposed electrochemical reduction mechanism is shown in figure 31. The major reduction intermediate observed was nitrosobenzene, but a small amount of 4-chloronitrosobenzene also appears to have been formed.

Cyclic voltammograms for 3,4,5-trichloronitrobenzene are shown in figure 30 and the proposed electrochemical reduction mechanism is shown in figure 31. The major reduction intermediates observed were 3-chloronitro and 3-chloronitrosobenzene.

Cyclic voltammograms for 2,3,4,5-tetrachloronitrobenzene are shown in figure 32 and the proposed electrochemical reduction mechanism is shown in figure 35. The major reduction intermediates were observed on voltammograms not included here, however very small waves were observed which were attributed to 3-chloronitrosobenzene and possibly 3,5-dichloronitrosobenzene.

Cyclic voltammograms of 2,3,4,6-tetrachloronitrobenzene are shown in figure 33 and the proposed electrochemical reduction mechanism is shown in figure 35. The major reduction intermediates observed were 3-chloronitroso and nitrosobenzene.

The sweeps to more anodic potentials show an interesting electrochemical process. The anodic wave is the absorption on or reaction with the mercury electrode of electrochemically generated chloride. The cathodic waves are due to desorption or reverse reactions of the chloride mercury film. Similar observations for a "mercury iodide film pattern" have been reported by Adams *et. al.*⁹ These film patterns are a good test to see if a reduction wave results in the loss of chloride or not. That these waves are truly due to chloride reaction is supported by the observations that they occur after the reduction of hexachlorobenzene and they are also observed when tetraethylammonium chloride is added to a DMSO tetraethylammonium perchlorate solution.

Cyclic voltammograms of 2,3,5,6-tetrachloronitrobenzene are shown in figure 34 and the proposed electrochemical reduction mechanism is shown in figure 35. The major reduction products observed were 3-chloronitroso and nitrosobenzene and possibly 3,5-dichloronitrosobenzene.

Cyclic voltammograms of pentachloronitrobenzene are shown in figure 36 and the proposed electrochemical reduction mechanism is shown in figure 37. The difference in peak potentials for the reversible and first irreversible wave of the polychloronitrobenzenes has steadily decreased with increasing number of chlorines. For pentachloronitrobenzene the first wave is irreversible and chloride is lost during this process as shown by the mercury chloride film pattern. The only set of intermediate waves observed is probably due to 2,3,4,5-tetrachloronitrobenzene.

In general the electrochemistry of the polychloronitrobenzenes is greatly effected by trace amounts of water in the solvent. For example the voltammogram of 2-chloronitrobenzene only exhibits one irreversible wave when a little water is added. The new waves observed in the presence of water are larger and are poorly defined.

The observation of the formation of nitrosobenzenes as electrochemical reduction products of nitrobenzenes has not been reported and probably does not occur for work with these compounds in

acetonitrile and N,N-dimethylformamide. The fact that nitroso-benzene formation is observed in liquid ammonia with added isopropyl alcohol and in DMSO and not in ACN or DMF gives rise to the idea that the acidity of the solvent plays a major role in the likelihood of this reduction pathway.

Of the reduction pathways described in the introduction and illustrated in figure 1 the one designated as (1) is the most consistent with the observation here for the polychloronitrobenzenes. However loss of chloride from its nitrobenzene anion radical may take place if the potential is held on the first reversible wave long enough. In the case of 2,3,5,6-tetrachloronitrobenzene electrolysis on the first wave did result in the disappearance of the 2,3,5,6 compound and the appearance of 2,3,5-trichloronitrobenzene.

The cyclic voltammograms of the polychloronitrosobenzenes, except pentachloronitrosobenzene, are shown in figures 38 through 56. The electrochemical reduction mechanism proposed by Lipztajn *et. al.*¹⁹ for nitrosobenzene in DMF, figure 3, appears to be fairly general for the polychloronitrosobenzenes. However the reduction pathways are complicated by chloride loss especially for the higher chlorinated nitrosobenzenes. The first wave is somewhat reversible in all cases and is attributed to the formation of the nitrosobenzene anion radical. The loss of chloride on this first wave is observed even for

the dichloronitrobenzenes as shown by the mercury chloride film patterns.

The second major wave in each case is irreversible and is probably due to the formation of the nitrosobenzene dianion. Minor waves are observed and are attributed to the electroactivity of azoxybenzene and azobenzene. Their formation from the dimerization of the nitrosobenzene anion radicals is, in part, responsible for the partial reversibility of the first reduction of the nitrosobenzenes.

Although the ultimate reduction products of the polychloronitrobenzenes in DMSO are probably comprised mostly of phenylhydroxylamines, the formation of some azoxybenzene and azobenzene can be envisioned under the right conditions of applied potential.

The peak potentials of the first reduction waves of the polychloronitrobenzenes are shown plotted against the number of chlorines on the molecule in figure 57. Three groups can be distinguished in this figure. The compounds without an ortho chlorine are the most easily reduced for each chlorine number. The compounds with one ortho chlorine are the next most easily reduced and the compounds with both ortho positions substituted are the most difficult. The lines in figure 57 show these groupings.

Table 2. First Cathodic Sweep Reductions for Polychloronitrobenzenes. Peak Potentials in Volts vs. Ag/AgCl.

Chlorine Position	Reversible Wave	Irreversible Waves			
		First	Second	Third	Fourth
-	-1.053	-2.009			
2	-1.026	-1.811	-1.956		
3	-0.931	-1.870			
4	-0.965	-1.884	-1.999		
2,3	-0.930	-1.559	-1.850	-1.977	
2,4	-0.939	-1.664	-1.898	-2.001	
2,5	-0.898	-1.650	-1.872		
2,6	-1.094	-1.671	-1.866	-2.025	
3,4	-0.875	-1.692	-1.900		
3,5	-0.808	-1.726	-1.889		
2,3,4	-0.876	-1.481	-1.666	-1.830	
2,3,5	-0.823	-1.408	-1.723	-1.889	
2,3,6	-1.010	-1.402	-1.673	-1.885	-2.007
2,4,5	-0.838	-1.524	-1.678	-1.890	
2,4,6	-1.016	-1.480	-1.691	-1.930	-2.022
3,4,5	-0.770	-1.460	-1.732	-1.903	
2,3,4,5	-0.784	-1.253	-1.446	-1.729	-1.835
2,3,4,6	-0.942	-1.172	-1.510	-1.660	-1.856
2,3,5,6	-0.934	-1.098	-1.388	-1.727	-1.830
2,3,4,5,6	-0.892	-1.258	-1.439	-1.686	-1.797

Table 3. Peak Potentials of New Waves on the Second Cathodic Sweep for the Polychloronitrobenzenes and Peak Potentials for Reduction Waves of the Polychloronitrosobenzenes. Potentials in Volts vs. Ag/AgCl.

Chlorine Position	Polychloronitrobenzenes			Polychloronitrosobenzenes	
	New Reduction Waves Second Cathodic Sweep			Reversible Wave	Irreversible Wave
-	-0.818			-0.829	-1.890
2	-0.631	-0.823		-0.648	-1.712
3	-0.664			-0.669	-1.711
4	-0.706	-0.805	-1.032	-0.722	-1.763
2,3	-0.655	-0.791		-0.529	-1.593
2,4	-0.709	-0.792	-1.038	-0.553	-1.660
2,5	-0.671			-0.487	-1.591
2,6	-0.643	-0.827		-0.594	-1.679
3,4	-0.676			-0.588	-1.701
3,5	-0.665	-0.922		-0.524	-1.577
2,3,4	-0.675			-0.453	-1.534
2,3,5	-0.659	-0.910		-0.371	-1.399
2,3,6	-0.664	-0.693	-0.892	-0.481	-1.516
2,4,5	-0.668	-0.910		-0.413	-1.584
2,4,6	-0.723	-0.817		-0.516	-1.600
3,4,5	-0.660	-0.923		-0.473	-1.492
2,3,4,5	-0.513	-0.686*		-0.382	-1.356
2,3,4,6	-0.672*	-0.811		-0.412	-1.411
2,3,5,6	-0.522	-0.678	-0.781	-0.382	-1.396
2,3,4,5,6	-0.752				

*Estimated from anodic peak potential.

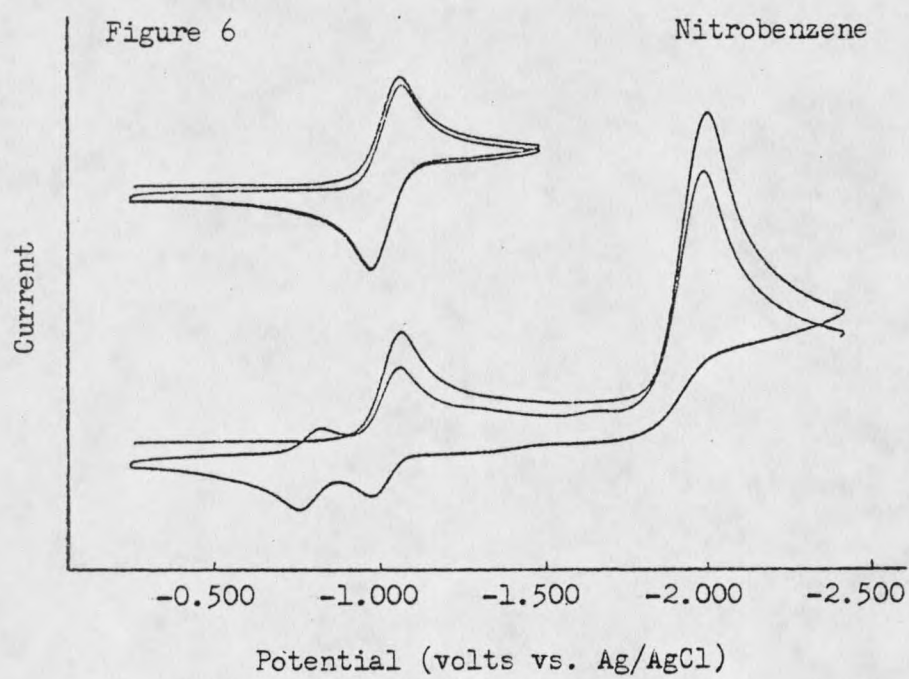
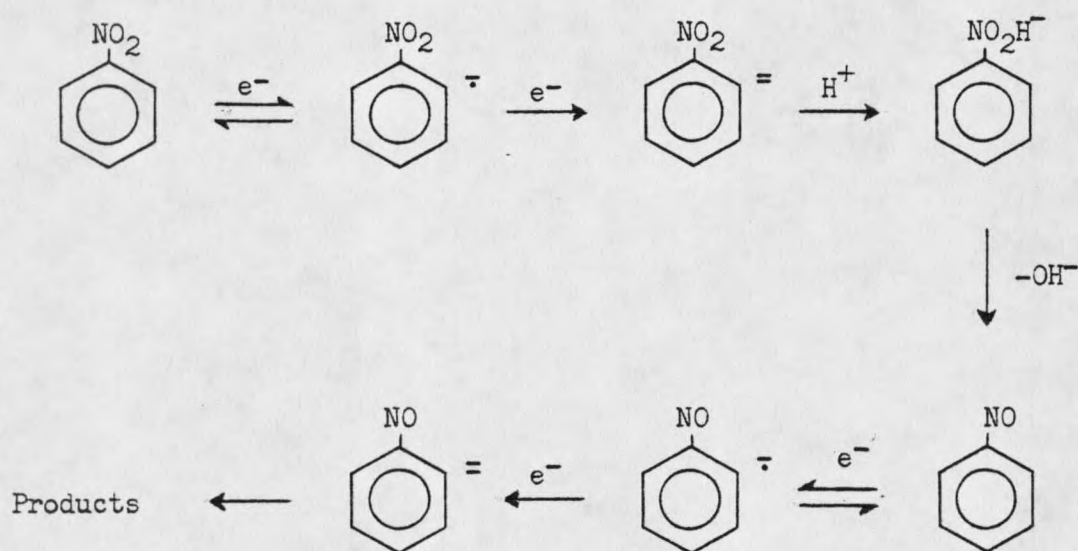


FIGURE 7. Electrochemical Reduction Pathway for Nitrobenzene



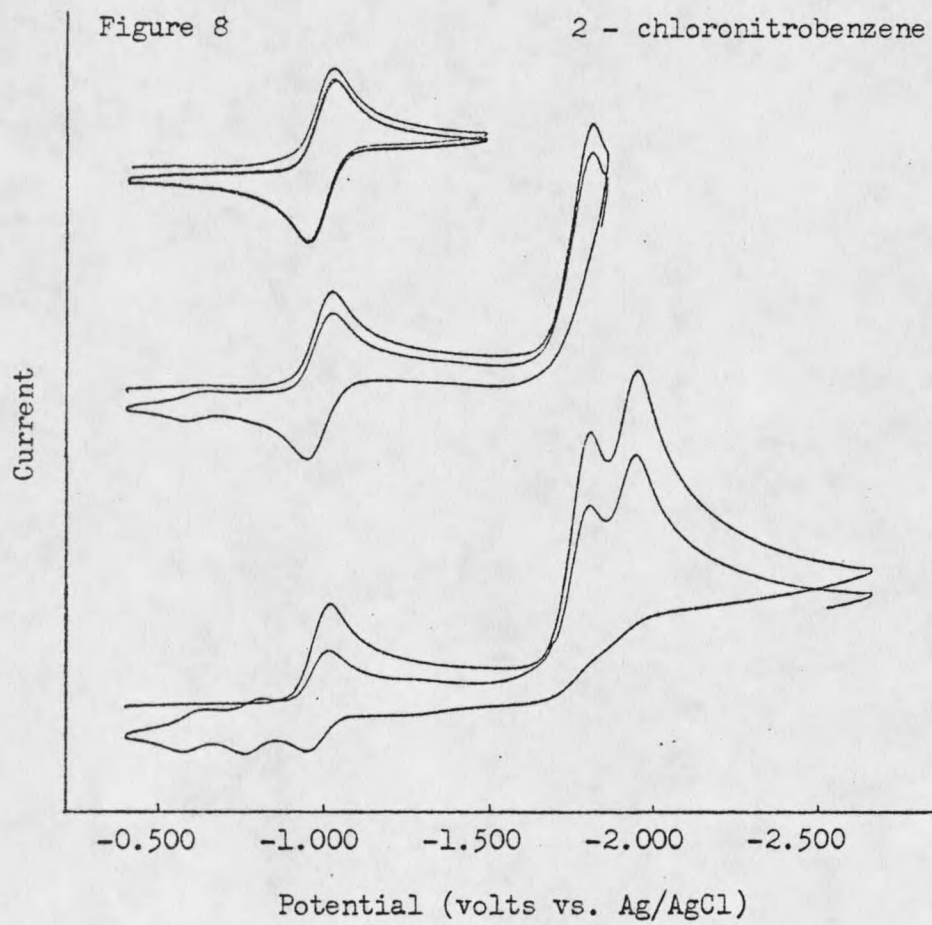
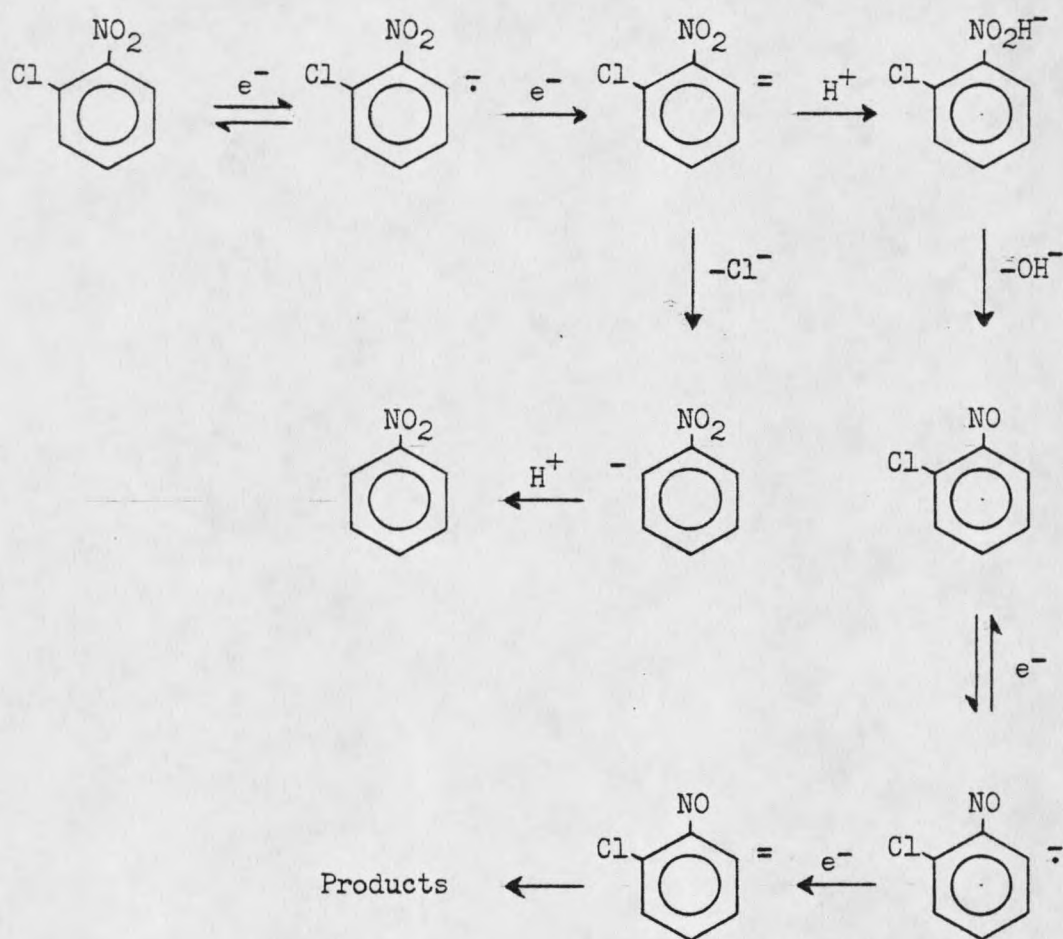


FIGURE 9. Electrochemical Reduction Pathways for 2-chloronitrobenzene



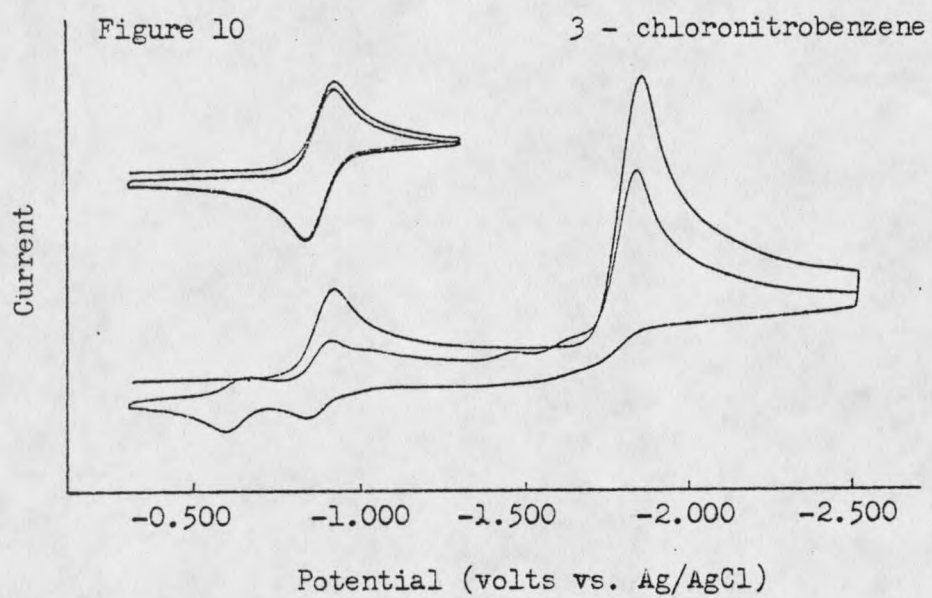
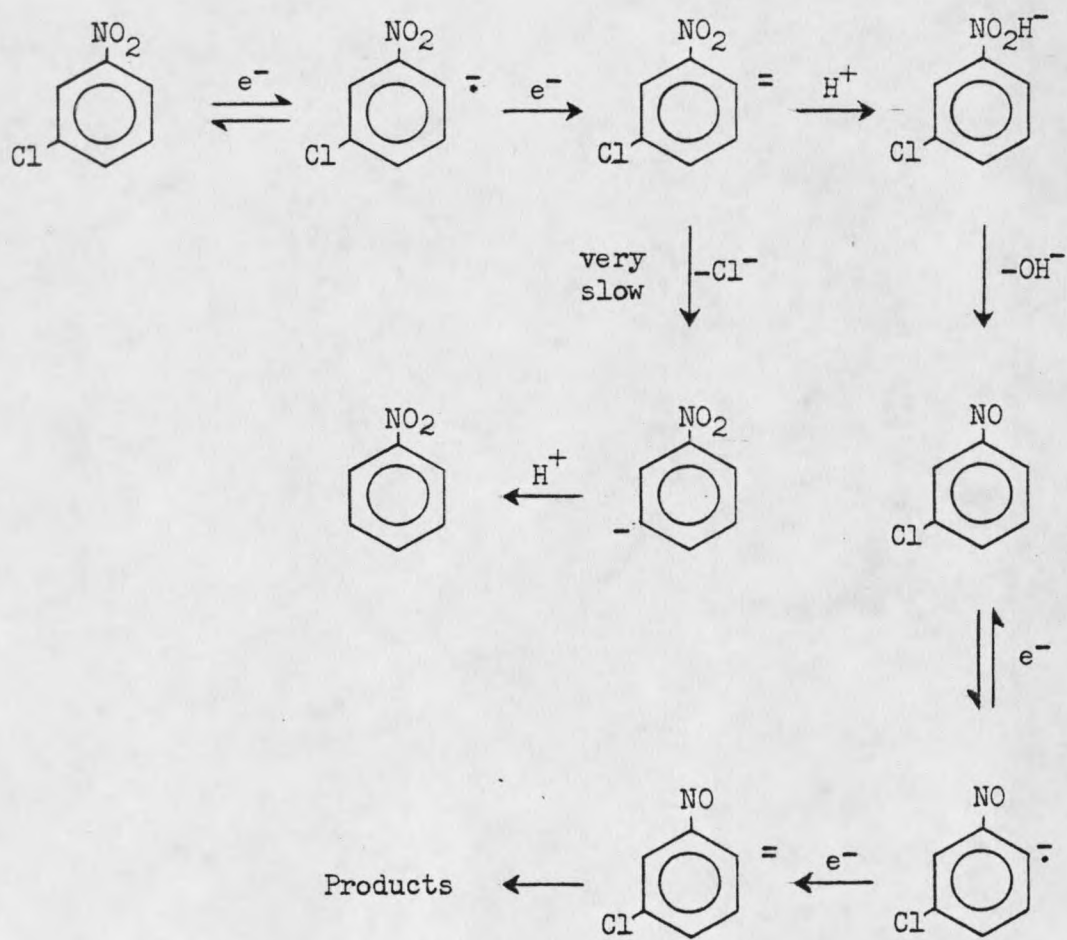


FIGURE 11. Electrochemical Reduction Pathways for 3-chloronitrobenzene



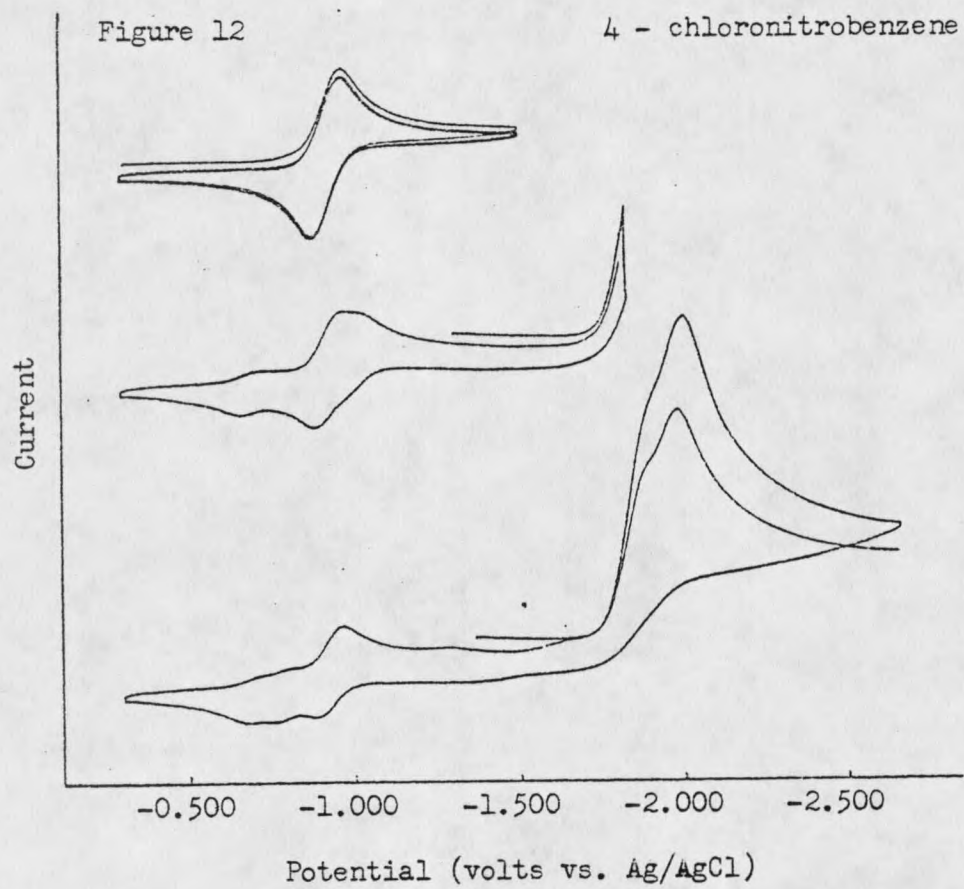
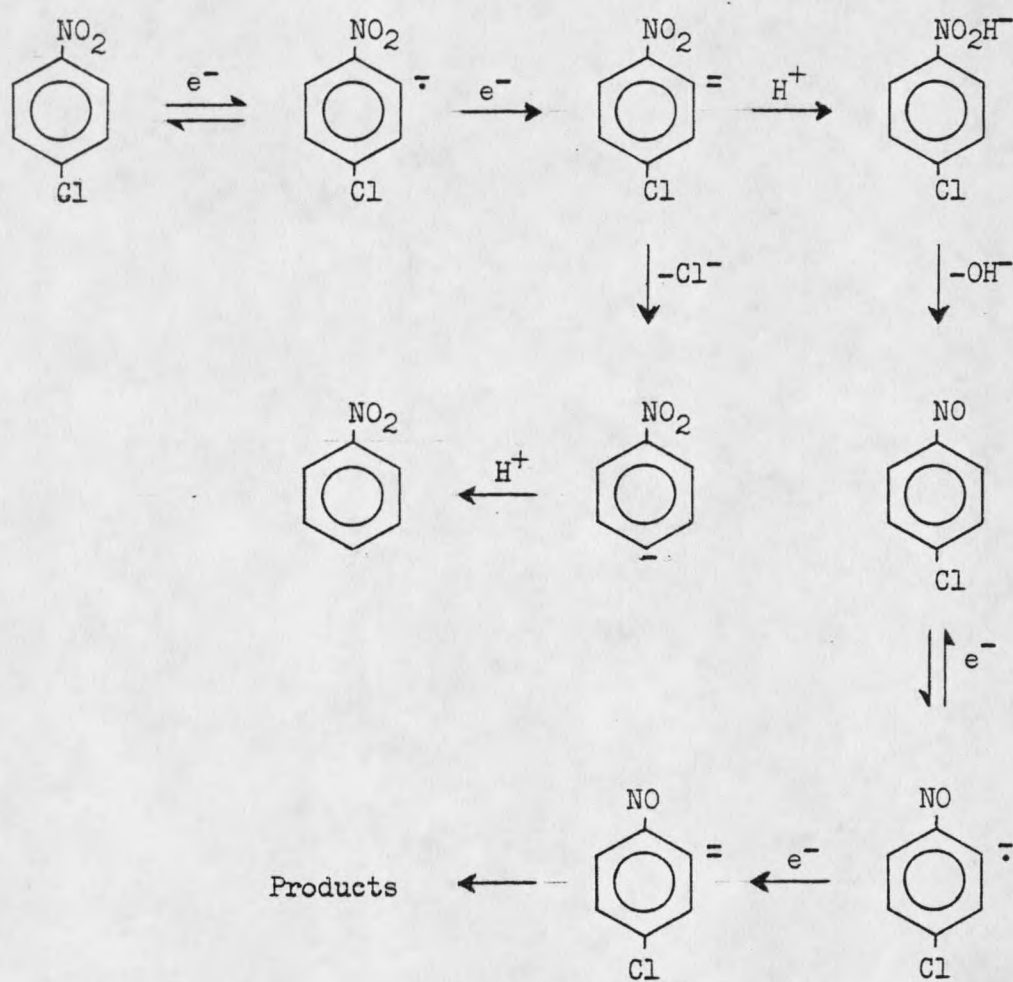
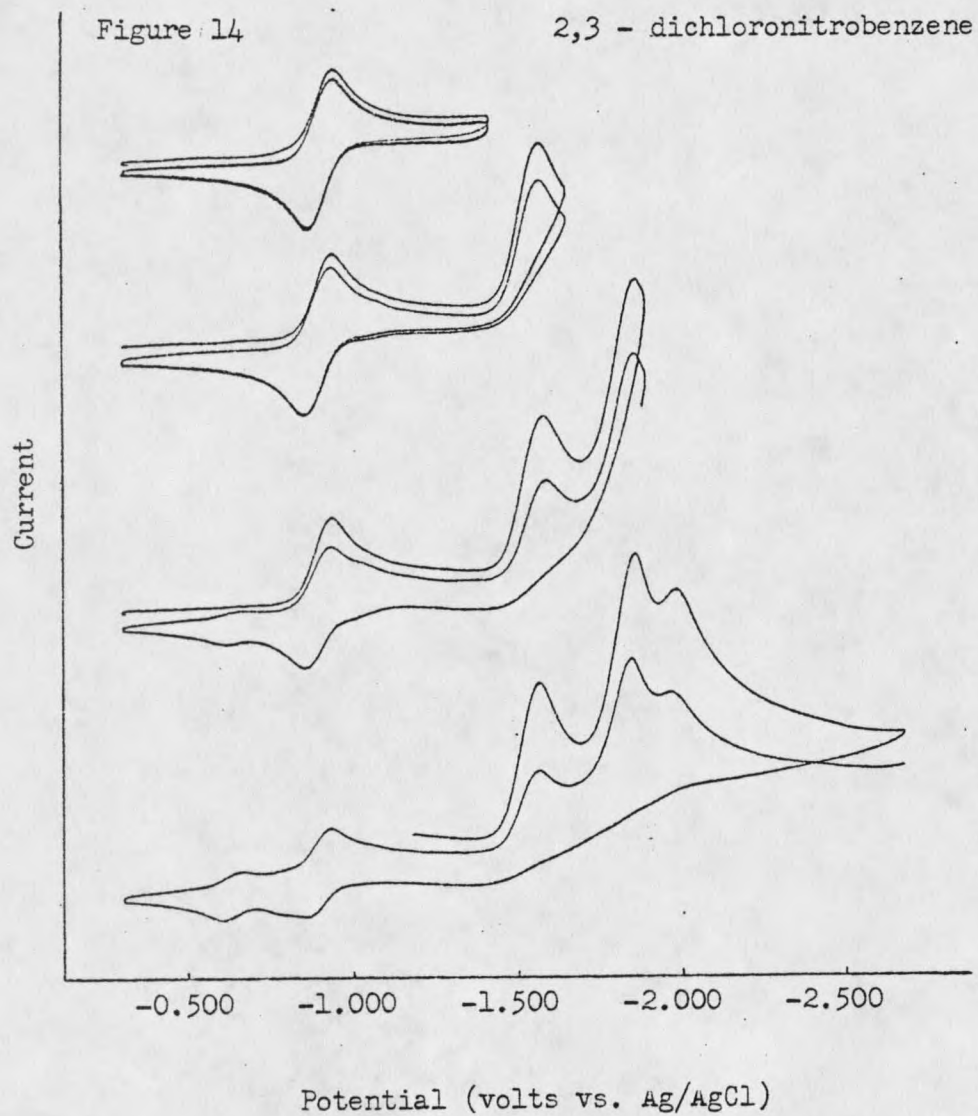


FIGURE 13. Electrochemical Reduction Pathways for 4-chloronitrobenzene





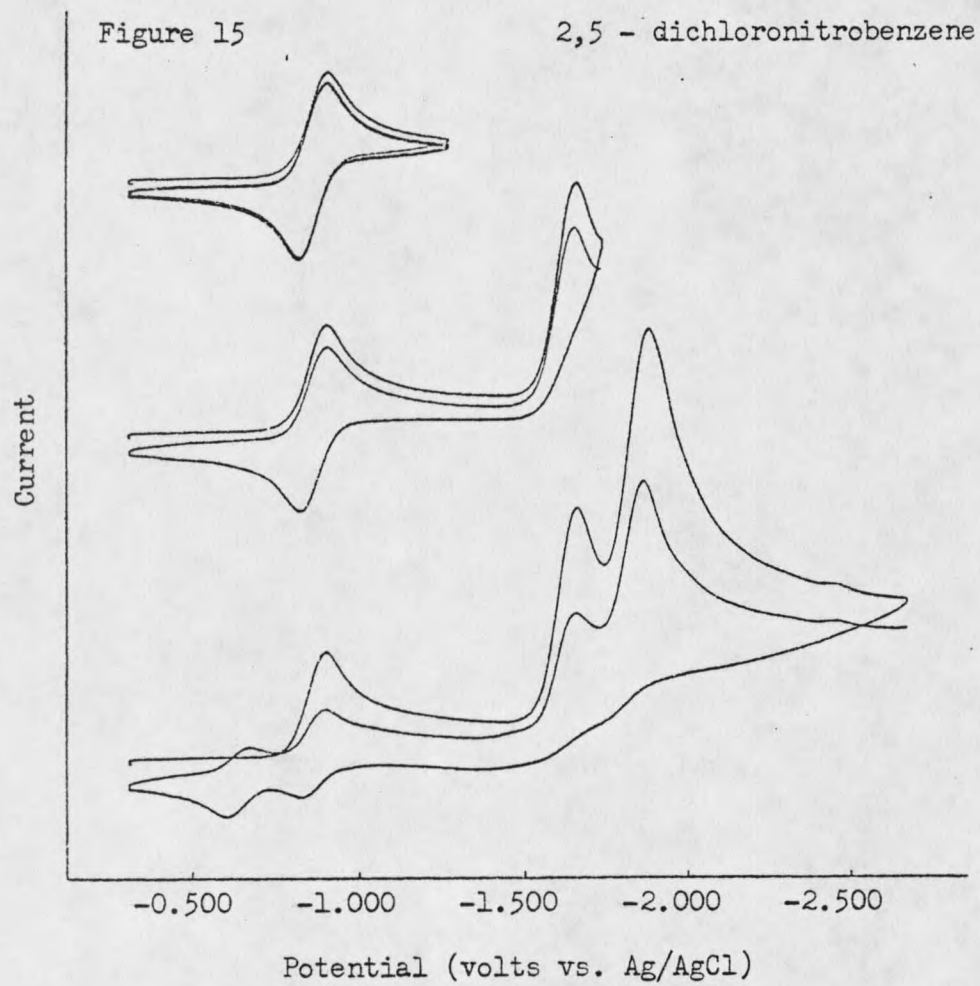


FIGURE 16. Electrochemical Reduction Pathways for 2,3 - dichloronitrobenzene and 2,5 - dichloronitrobenzene

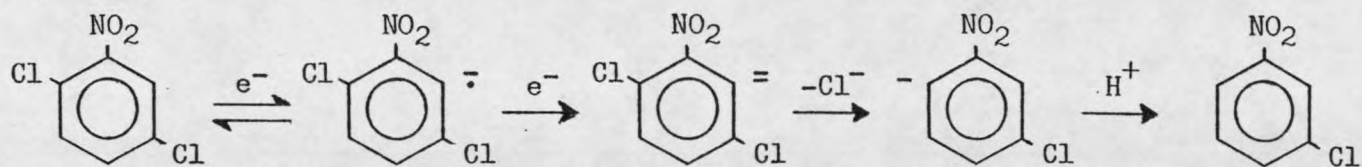
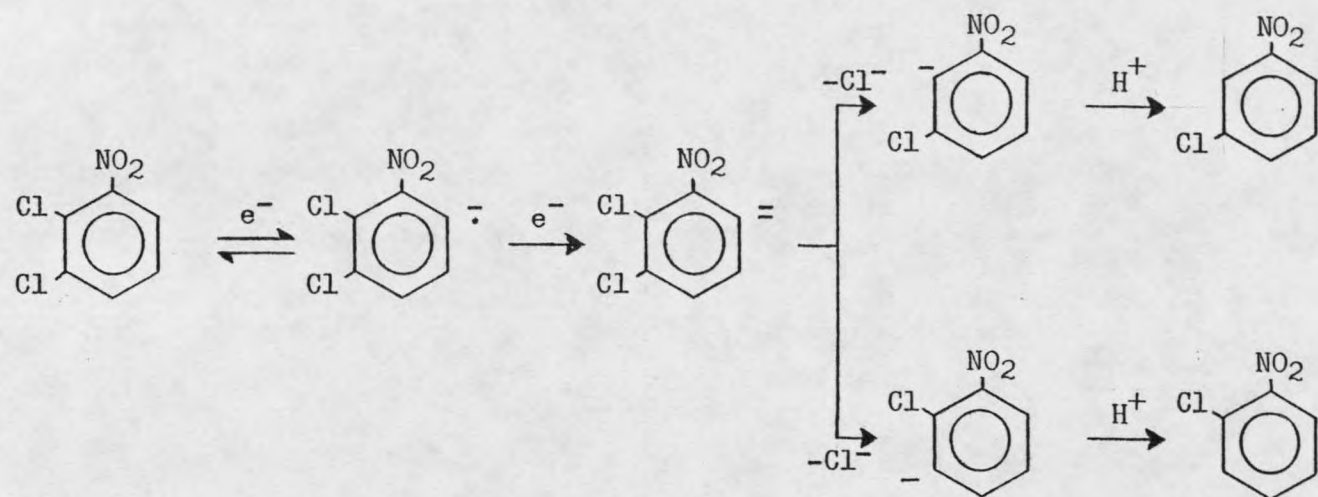
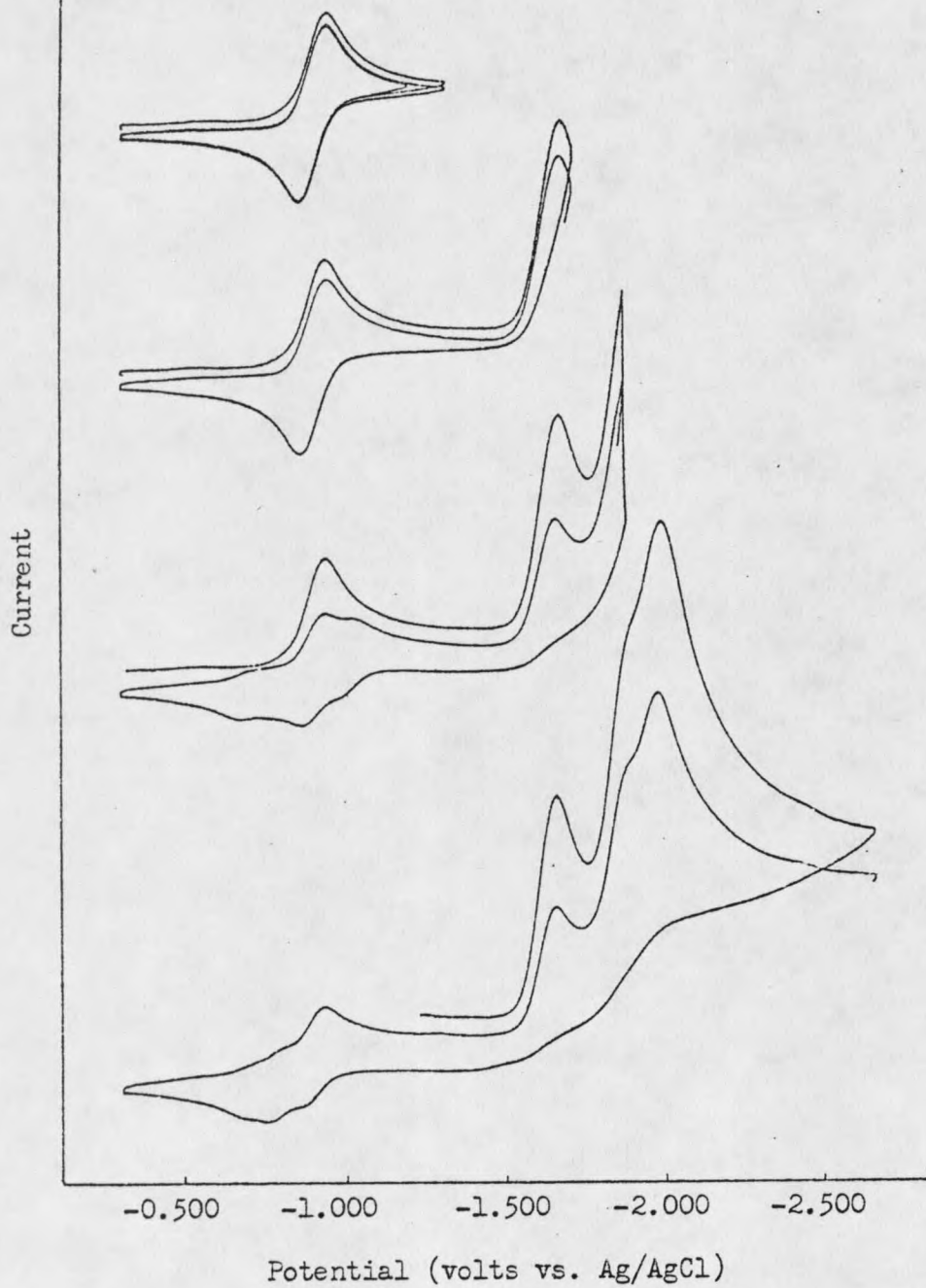


Figure 17

2,4 - dichloronitrobenzene



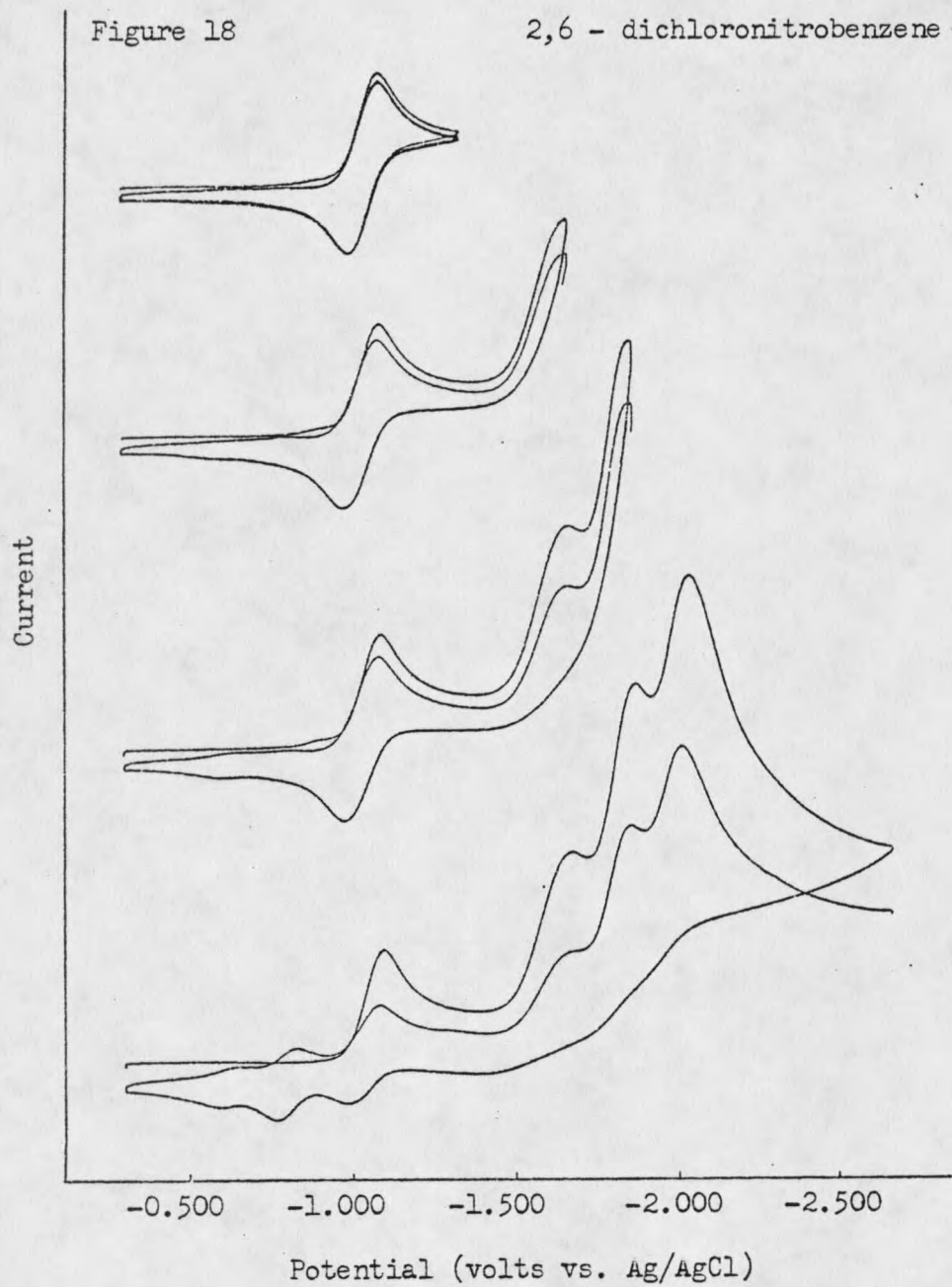
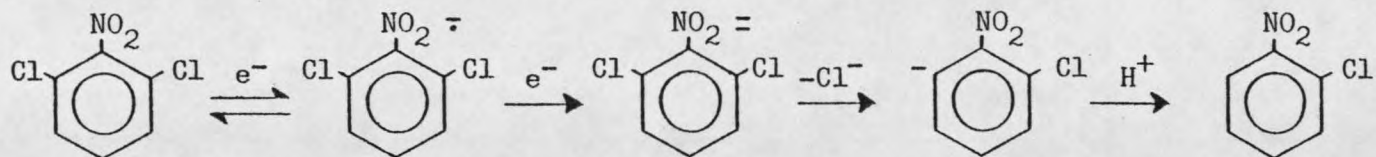
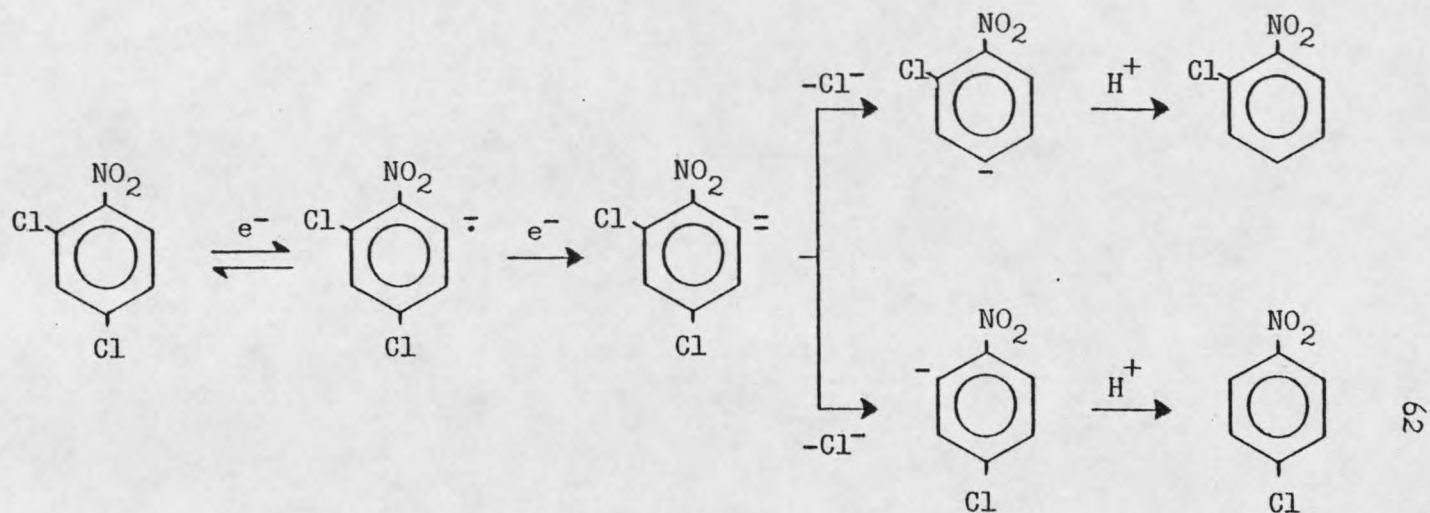
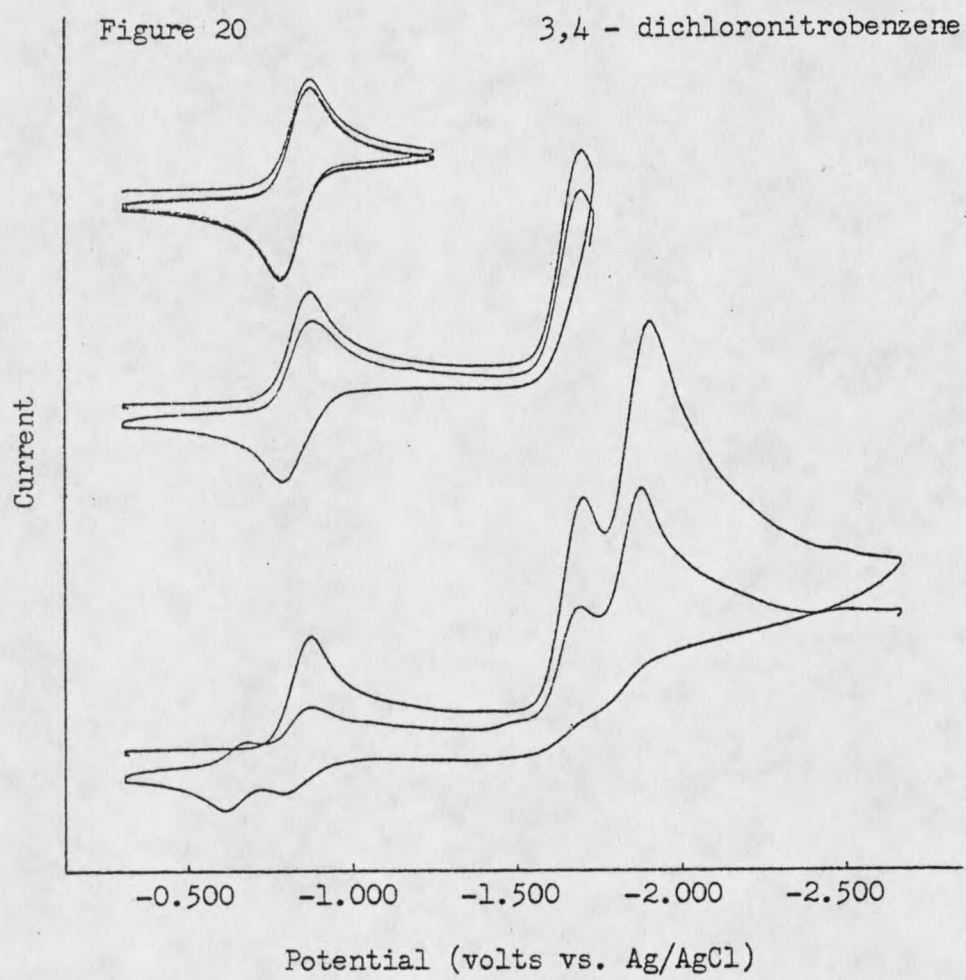


FIGURE 19. Electrochemical Reduction Pathways for 2,4 - dichloronitrobenzene and 2,6 - dichloronitrobenzene





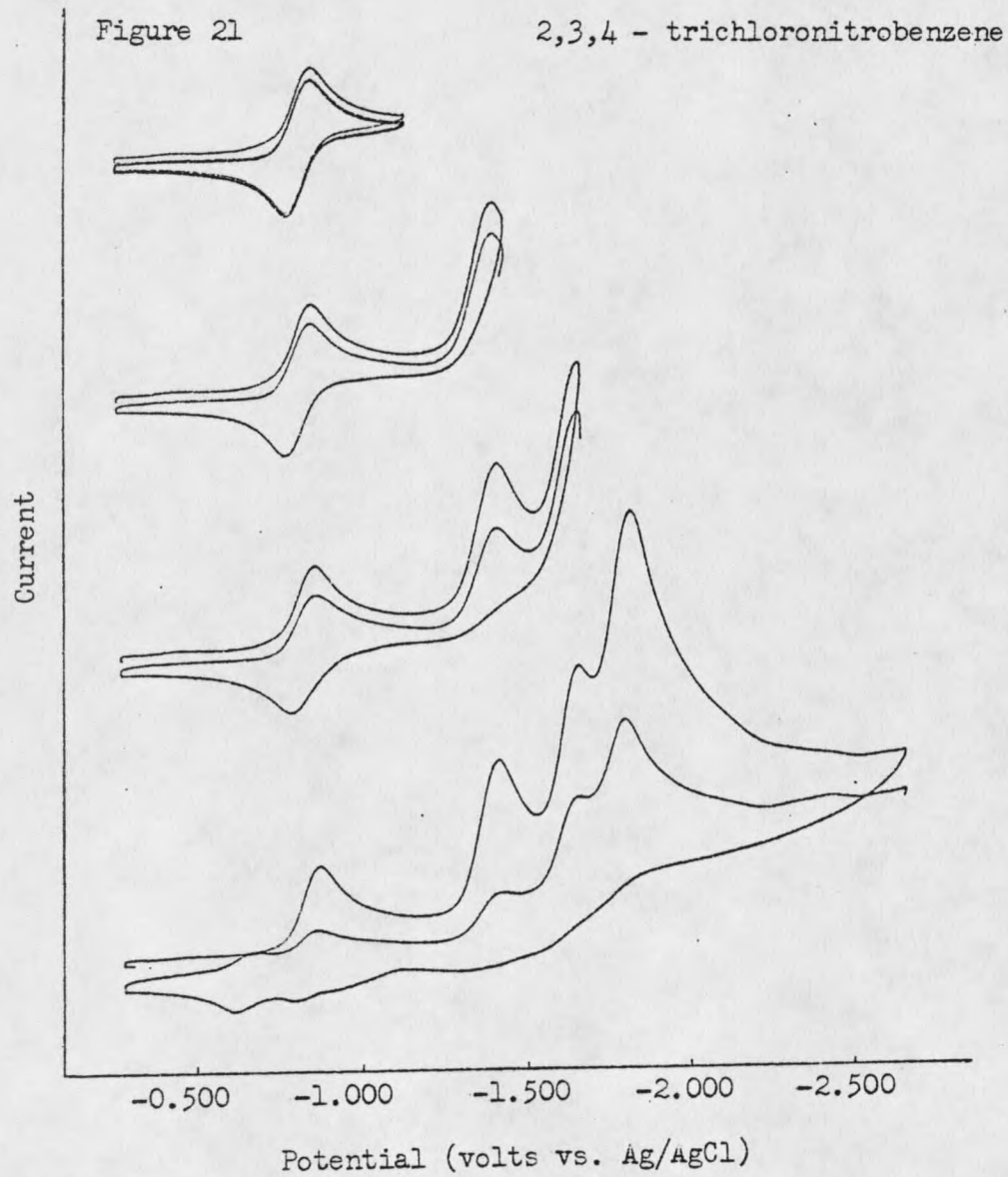
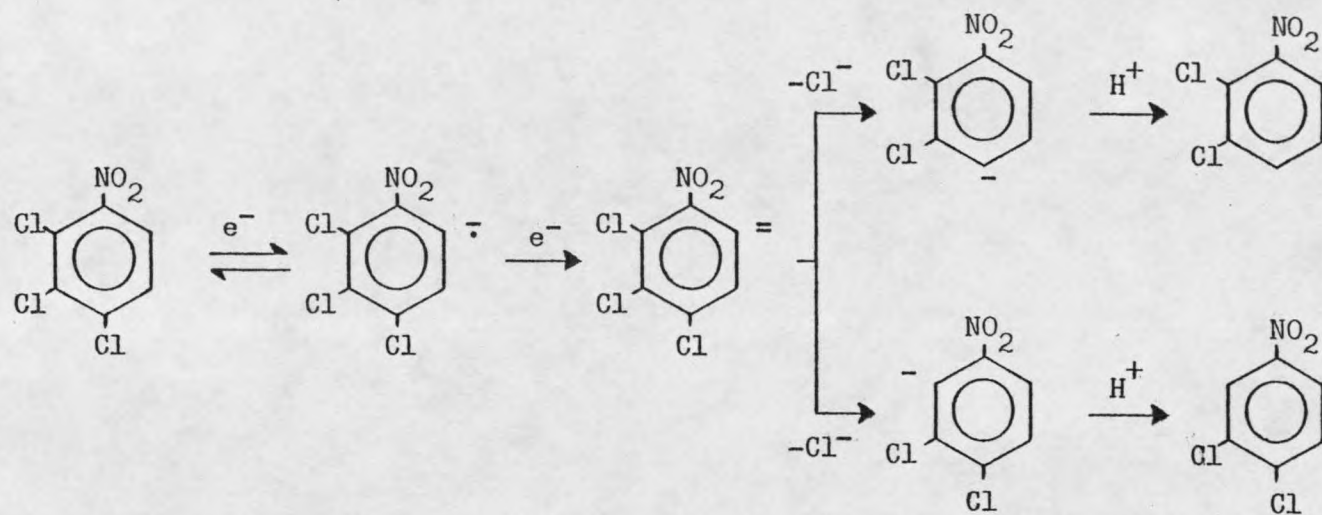
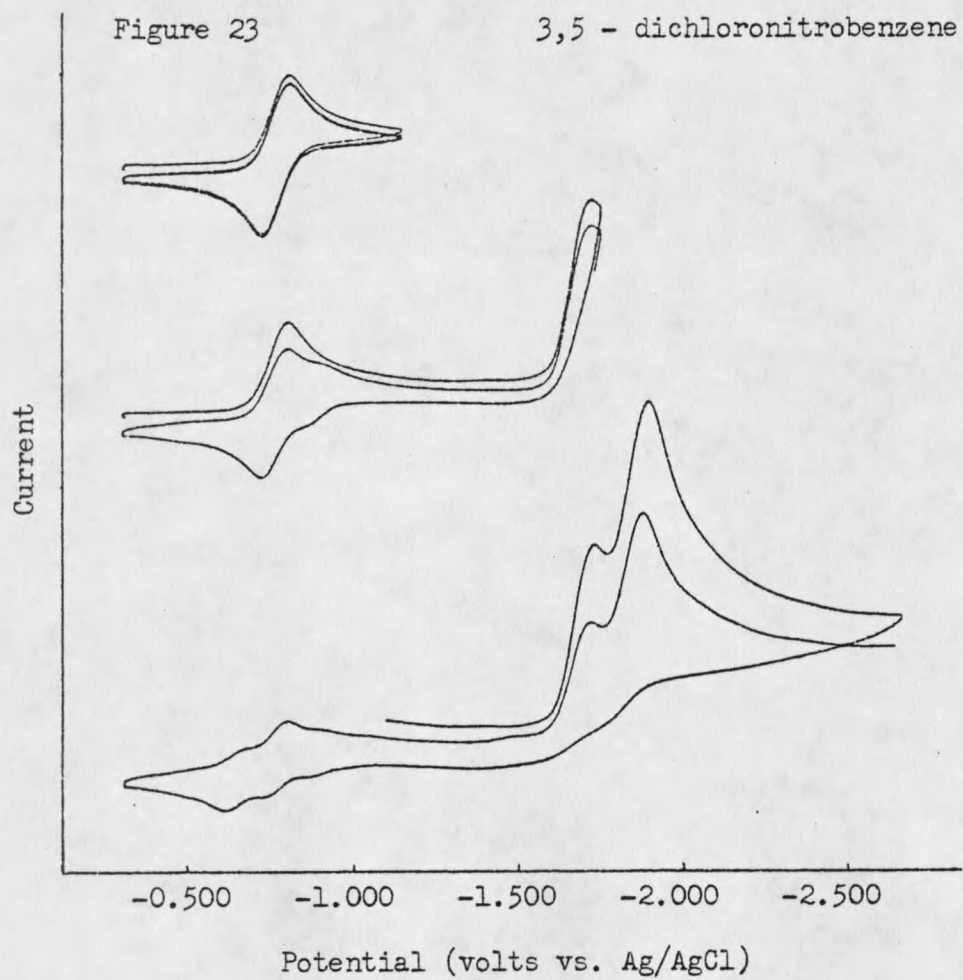


FIGURE 22. Electrochemical Reduction Pathways for 3,4 - dichloronitrobenzene and 2,3,4 - trichloronitrobenzene





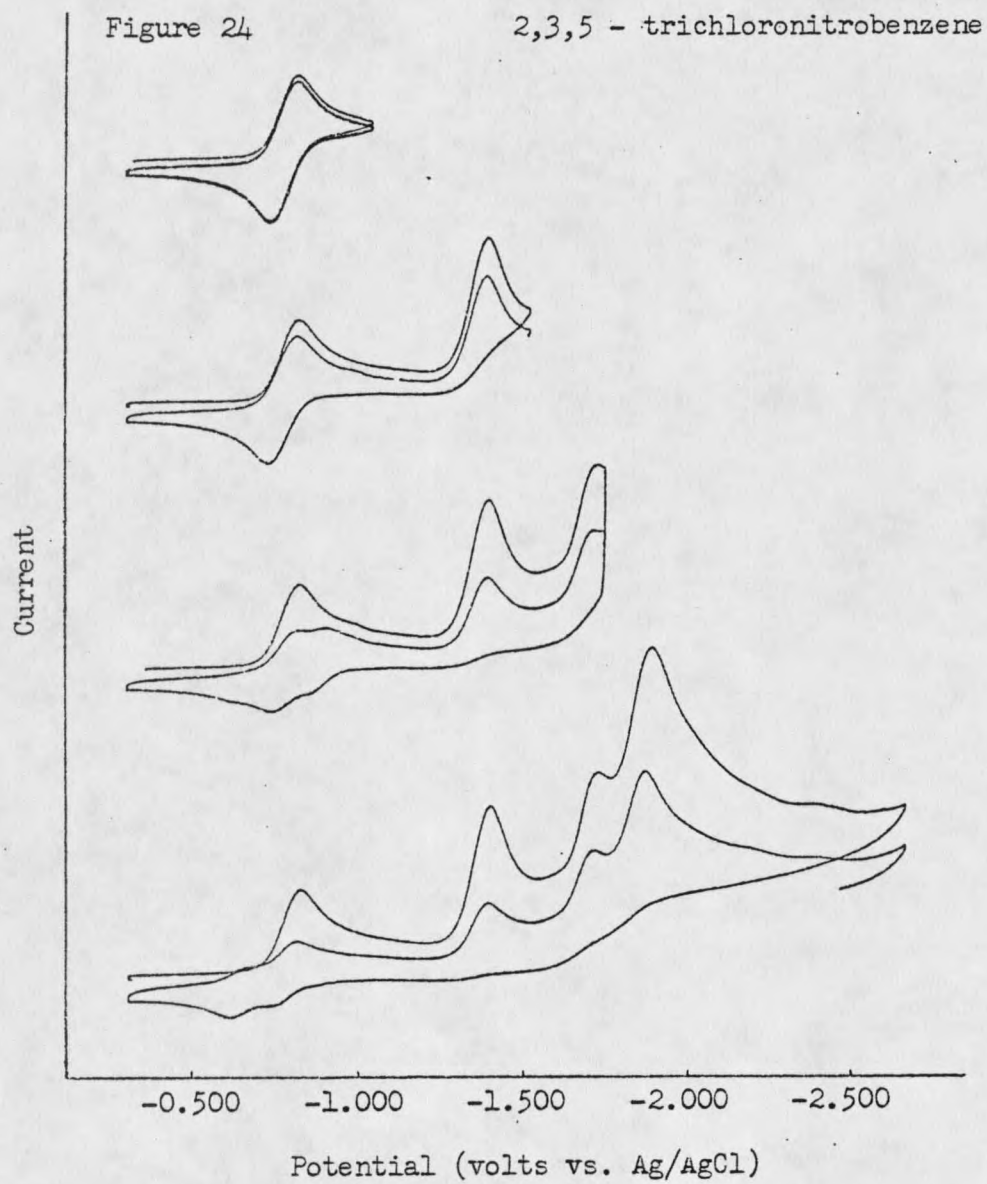
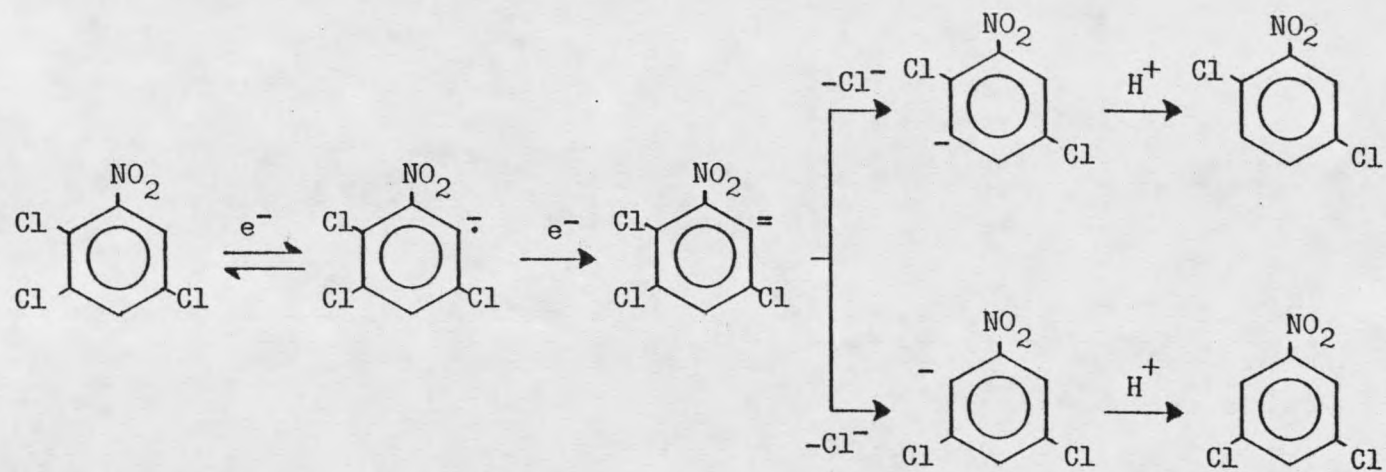
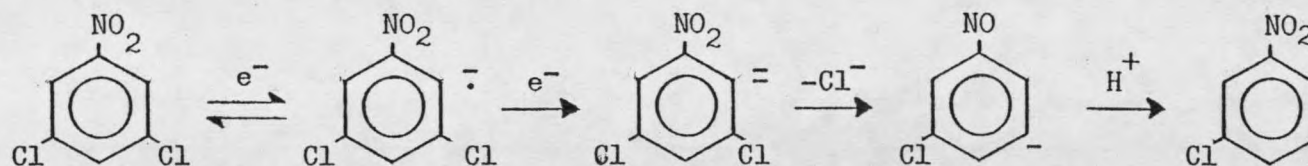
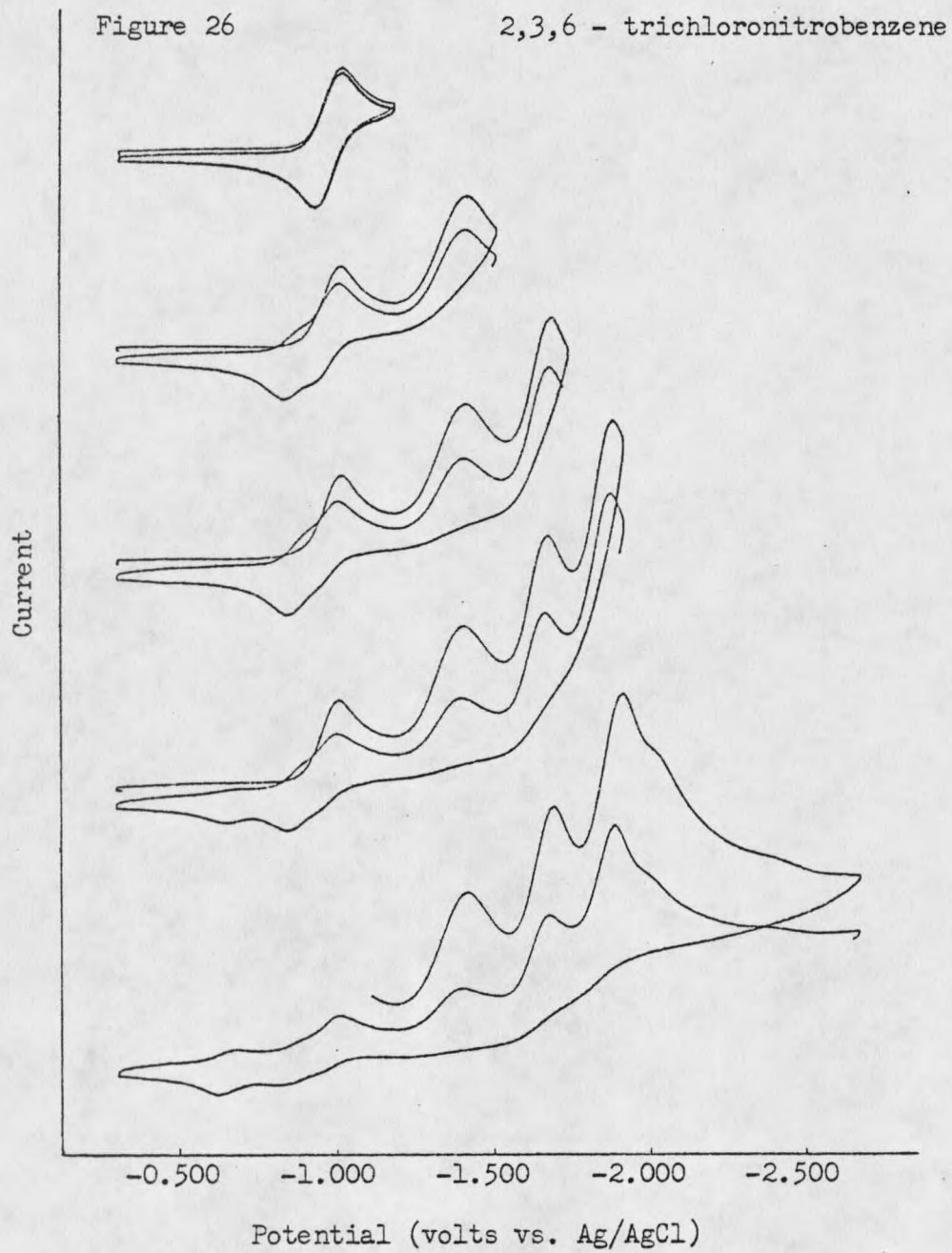


FIGURE 25. Electrochemical Reduction Pathways for 2,3,5 - trichloronitrobenzene and 3,5 - dichloronitrobenzene



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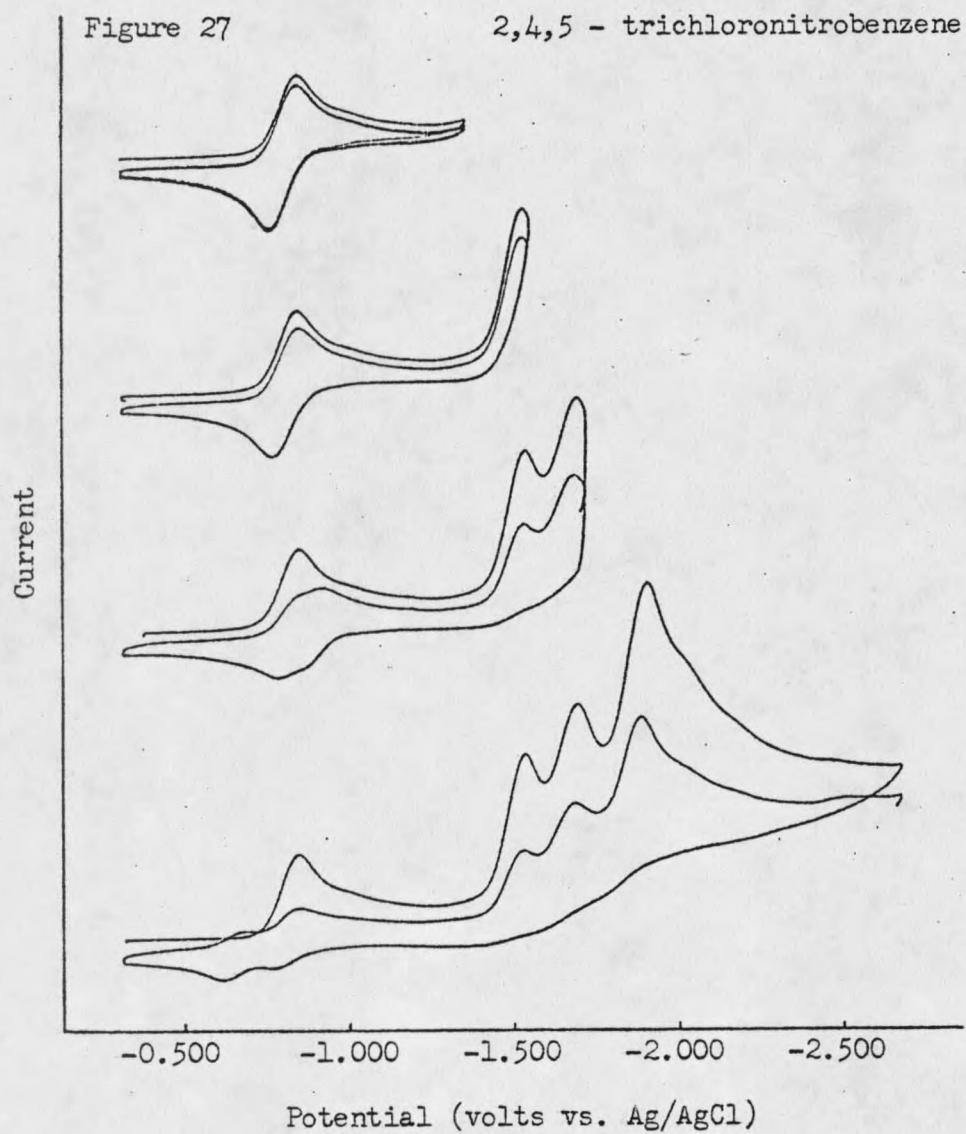
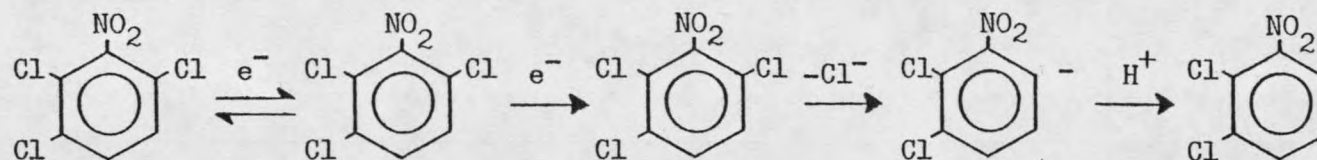
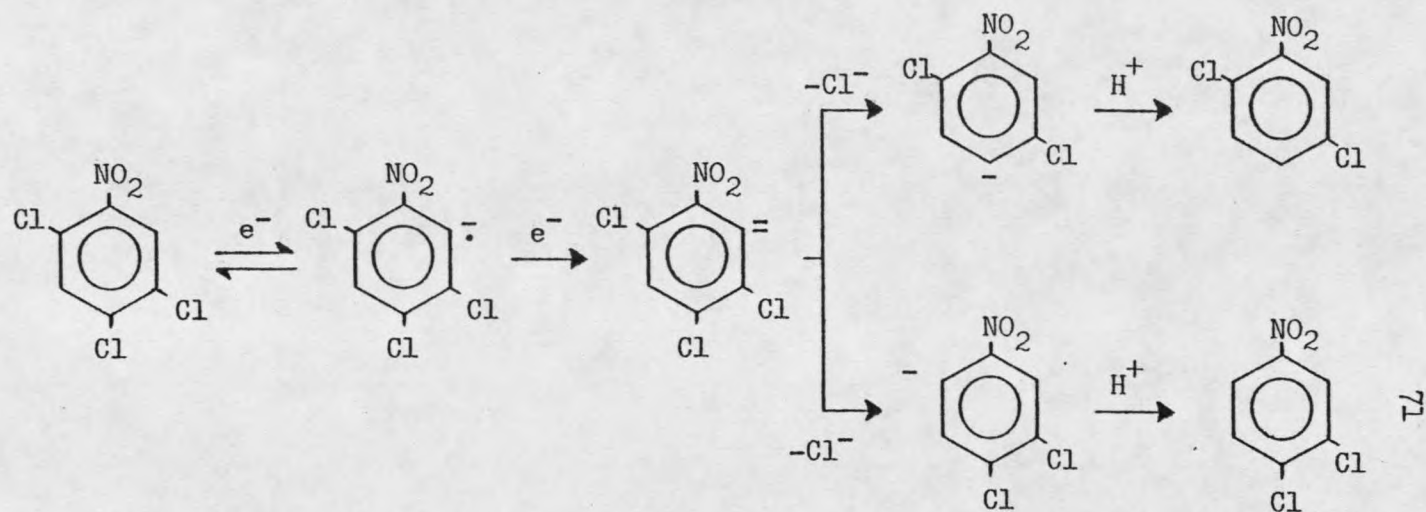
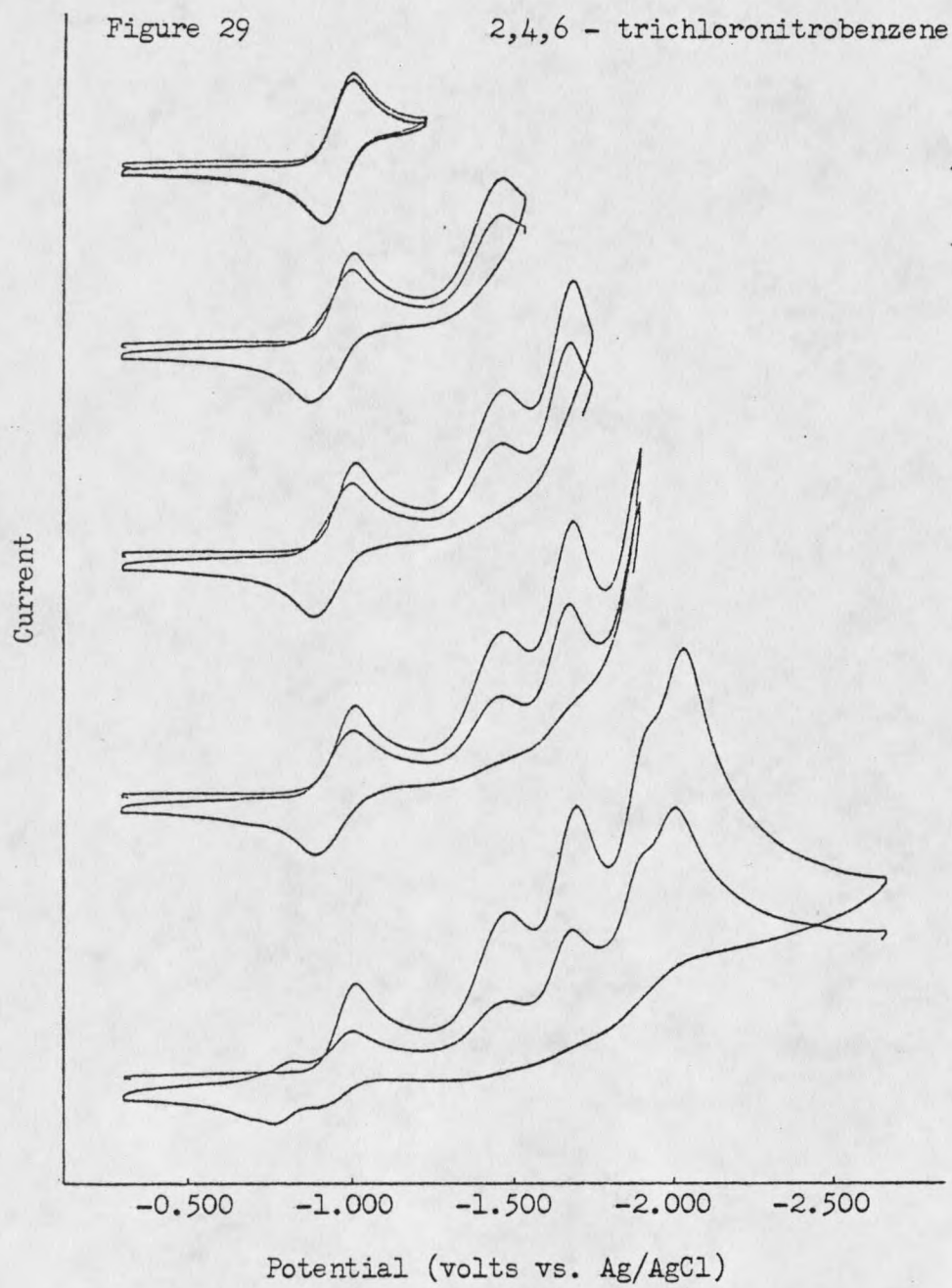


FIGURE 28. Electrochemical Reduction Pathways for 2,4,5 - trichloronitrobenzene and 2,3,6 - trichloronitrobenzene





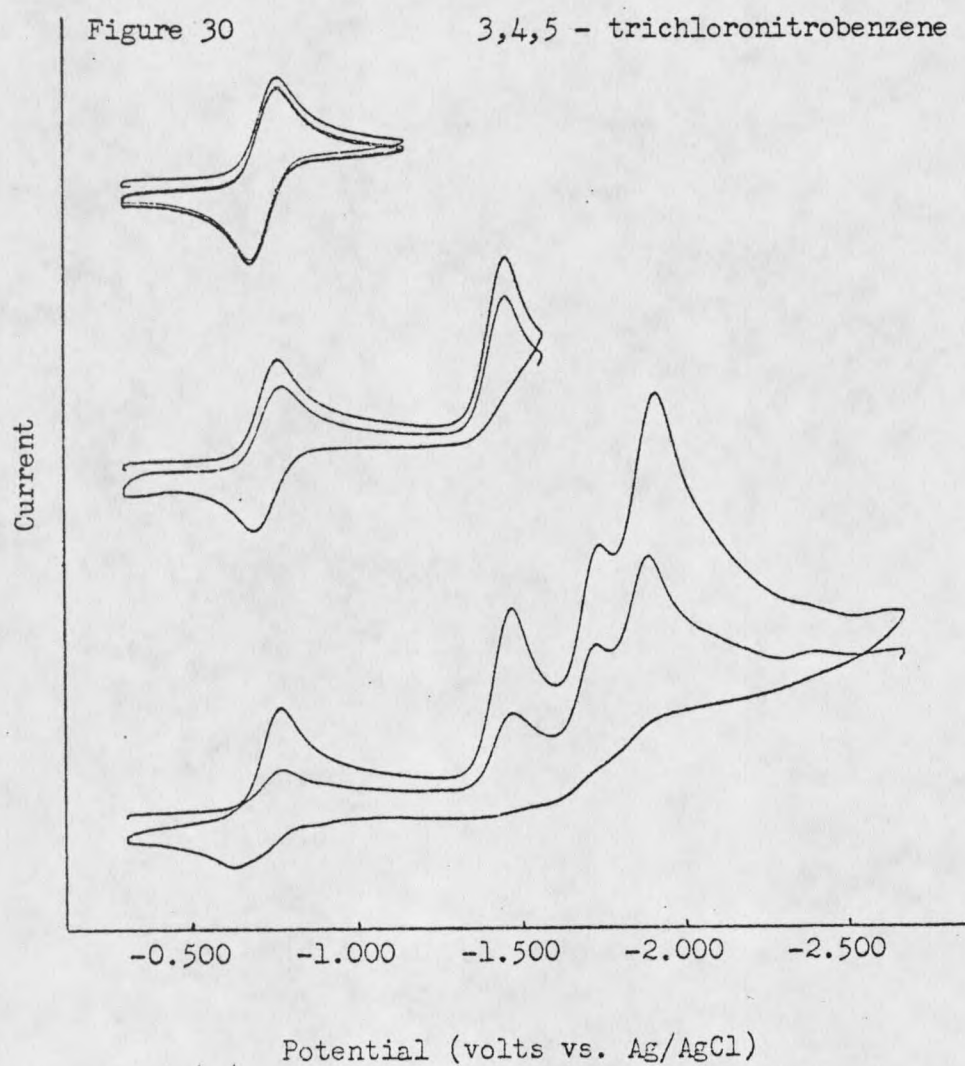
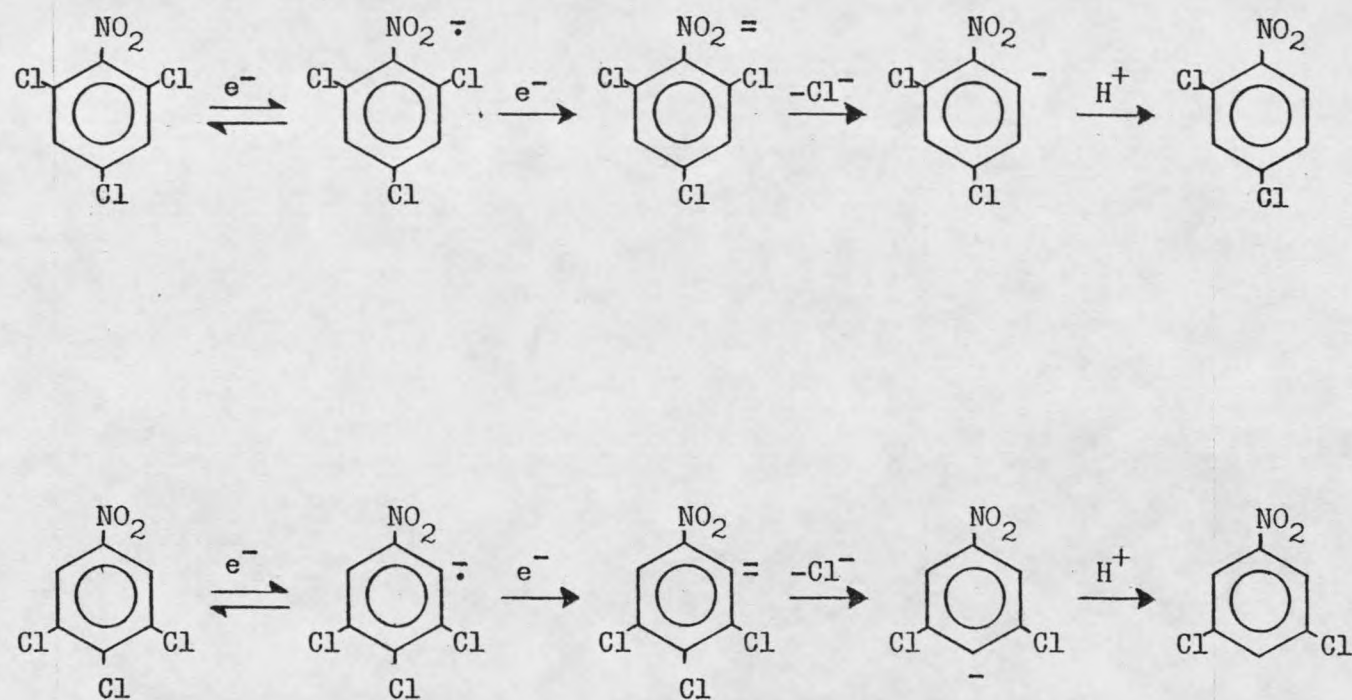
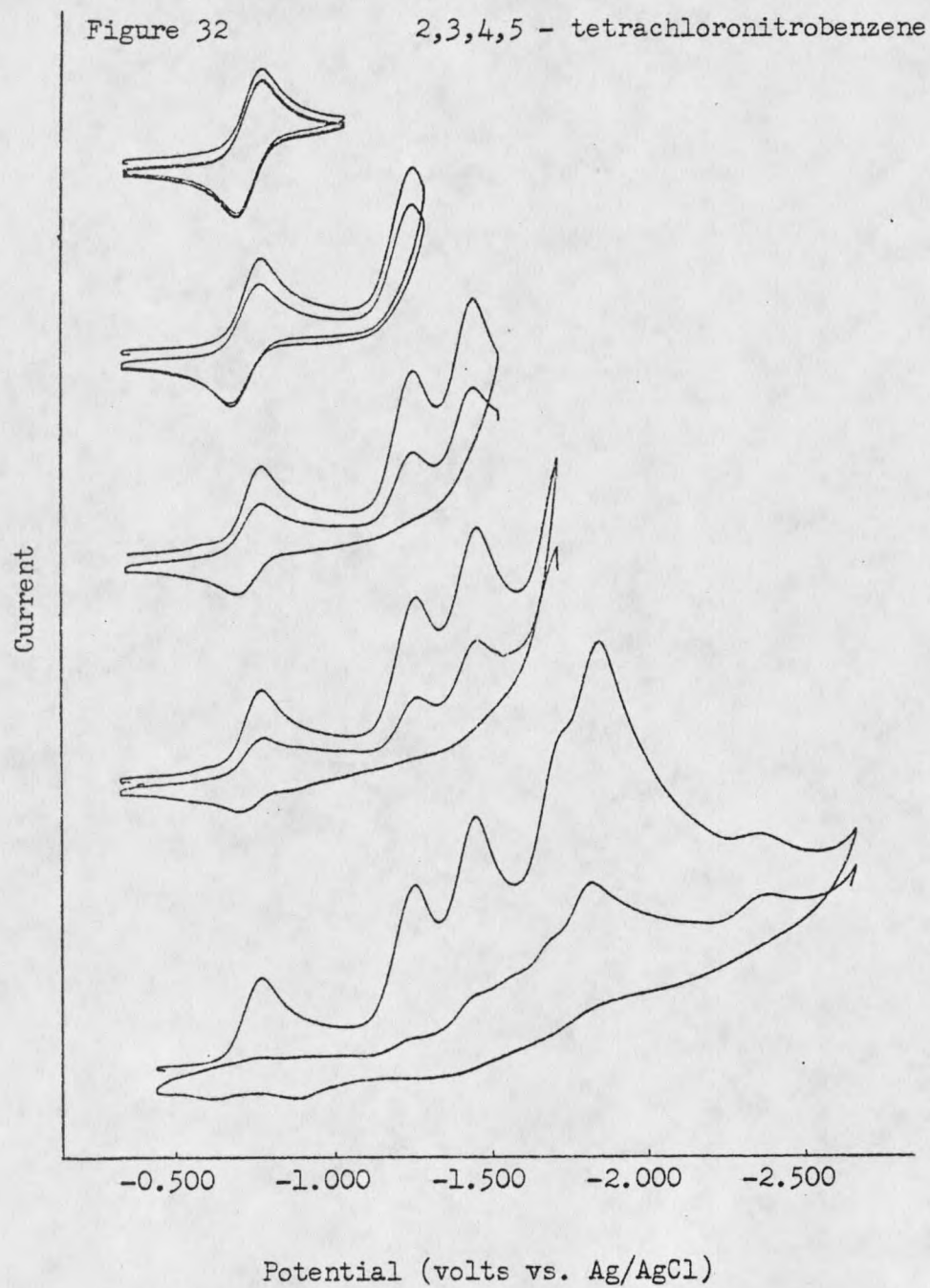


FIGURE 31. Electrochemical Reduction Pathways for 2,4,6 - trichloronitrobenzene and 3,4,5 - trichloronitrobenzene





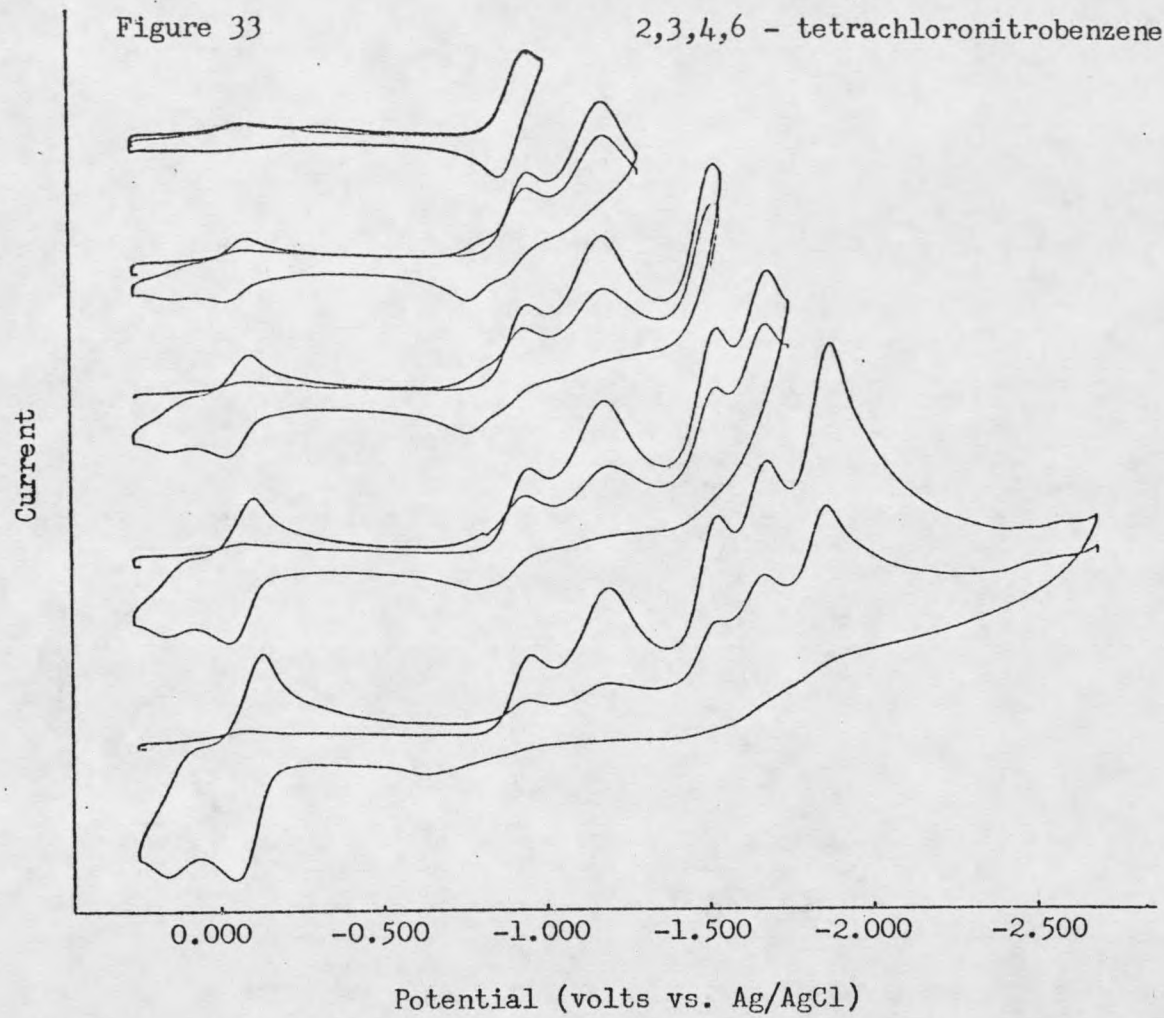


Figure 34

2,3,5,6 - tetrachloronitrobenzene

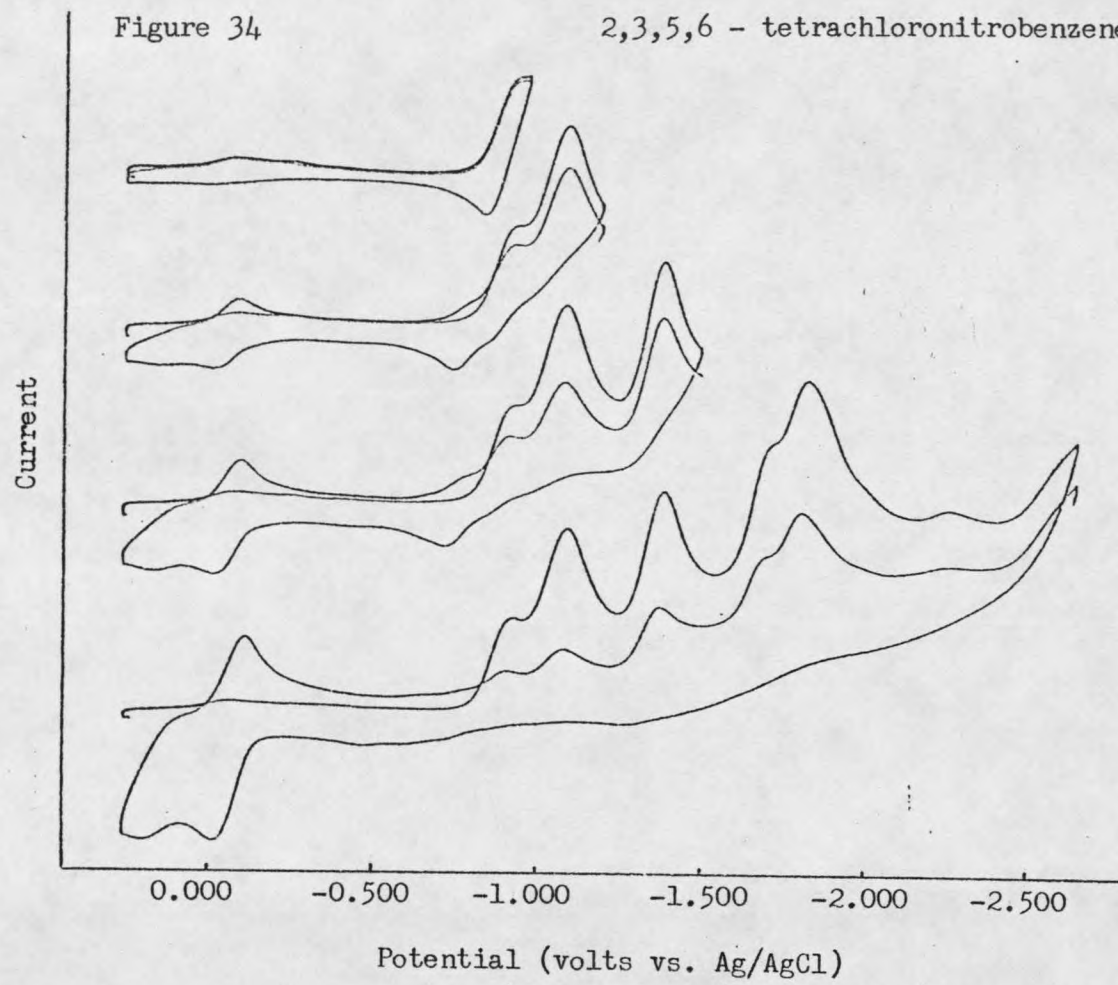


FIGURE 35. Electrochemical Reduction Pathways for 2,3,4,5 - tetrachloronitrobenzene, 2,3,4,6 - tetrachloronitrobenzene, and 2,3,5,6 - tetrachloronitrobenzene

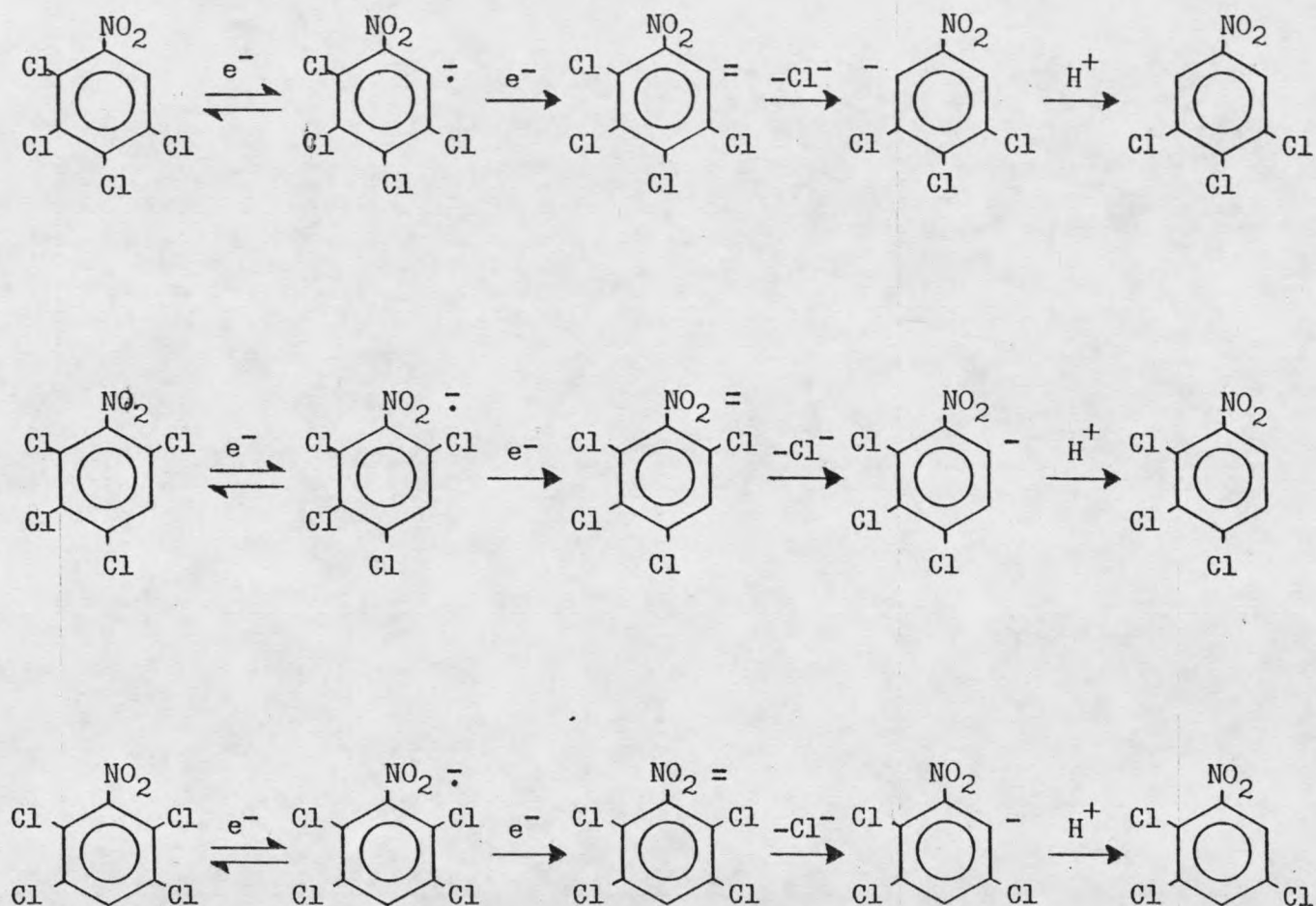


Figure 36

Pentachloronitrobenzene

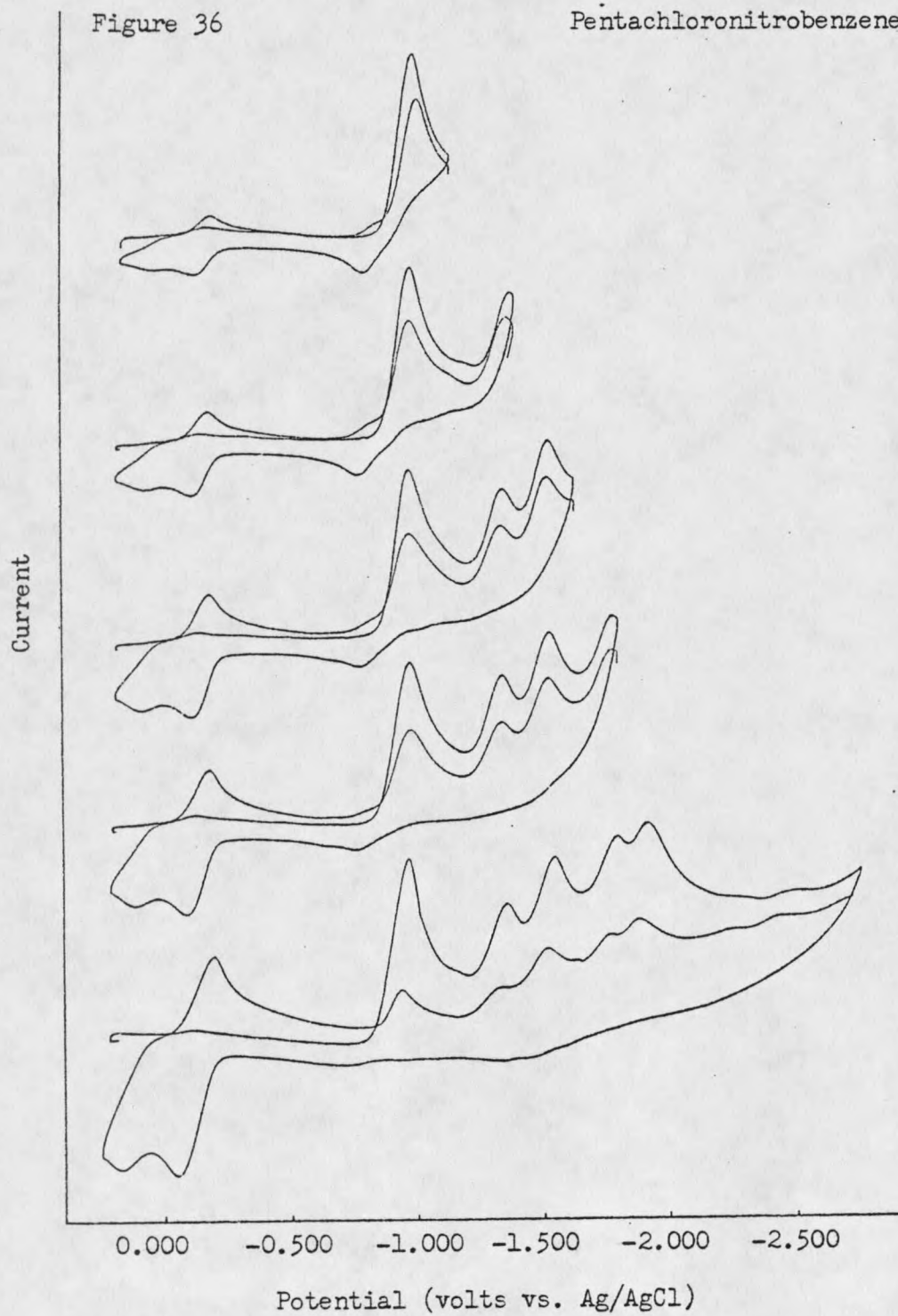
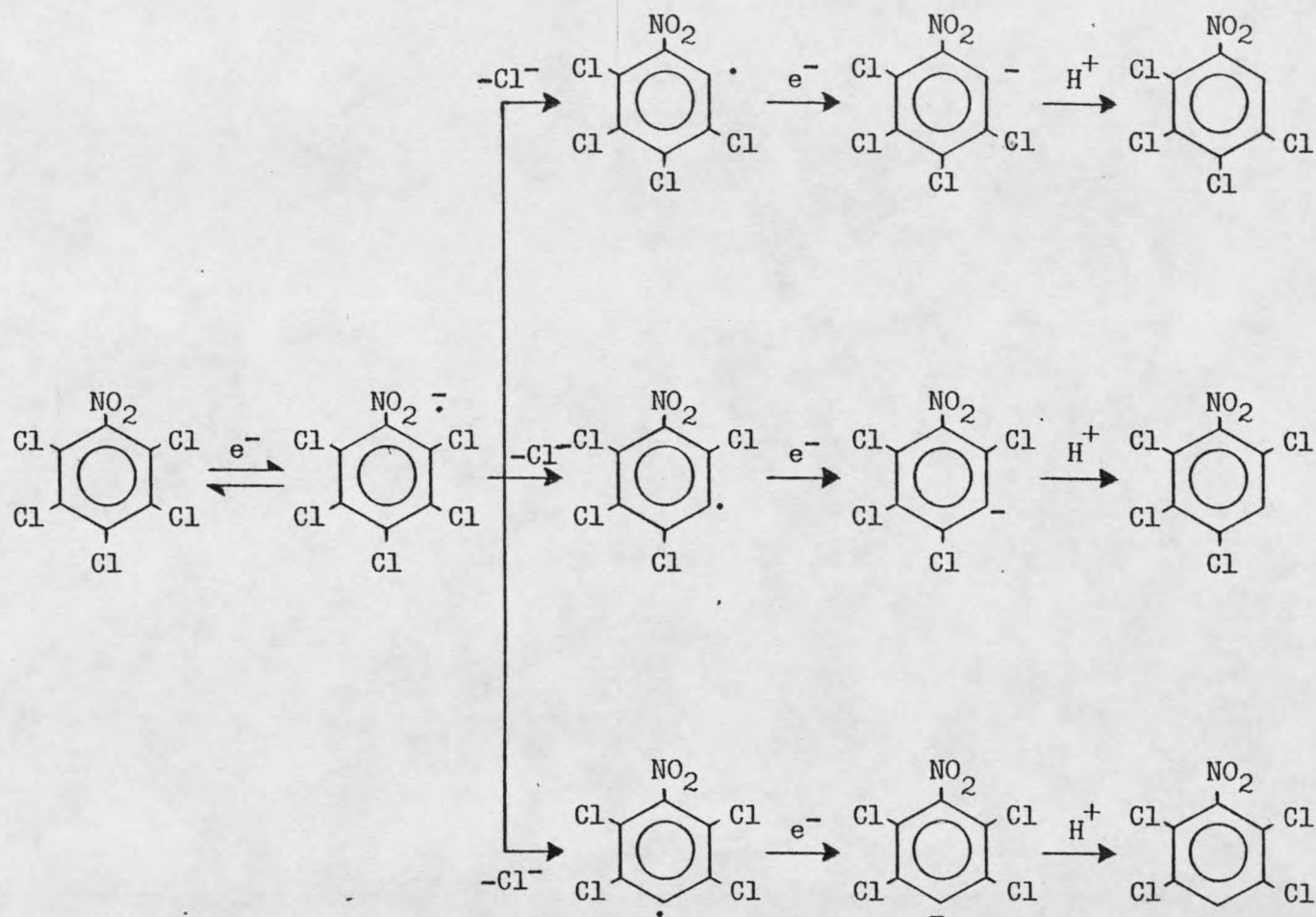
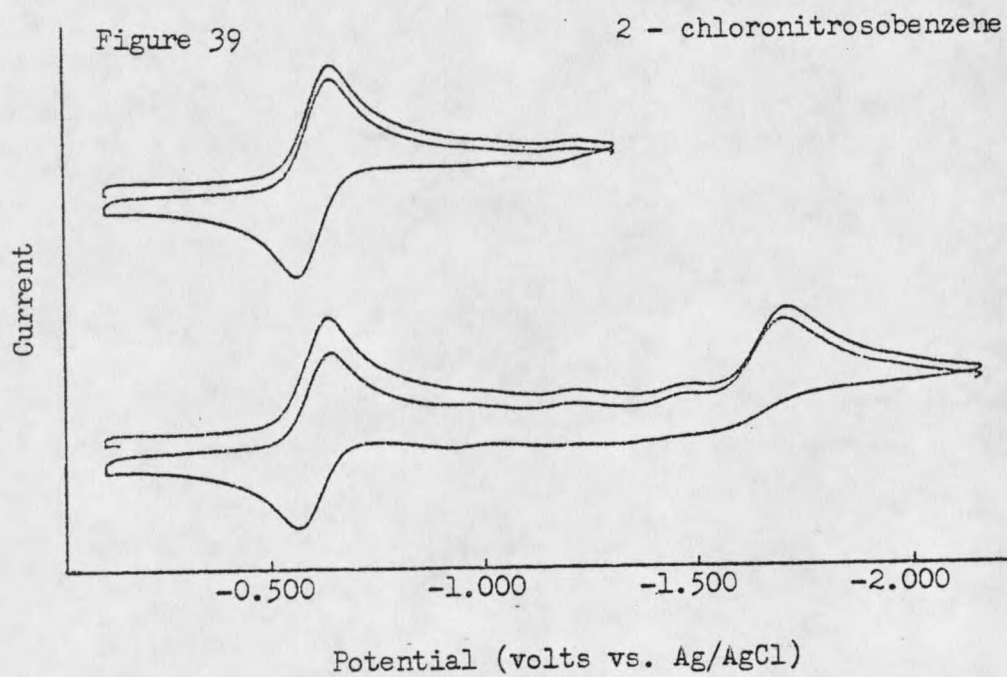
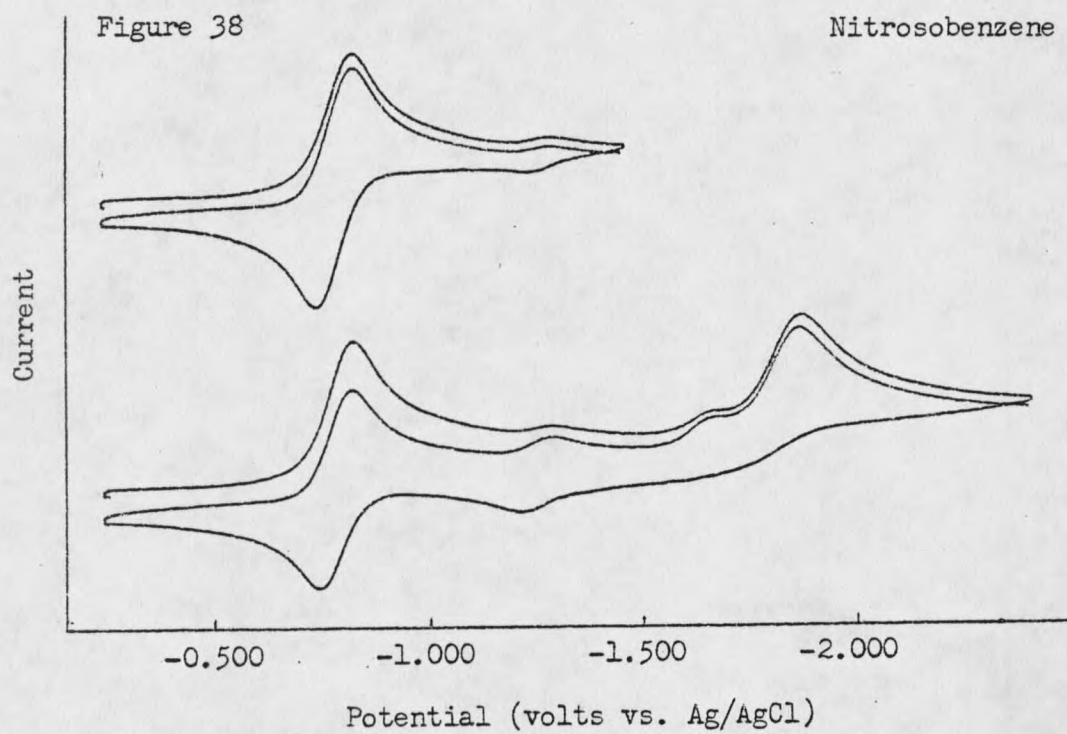


FIGURE 37. Electrochemical Reduction Pathways for 2,3,4,5,6 - pentachloronitrobenzene





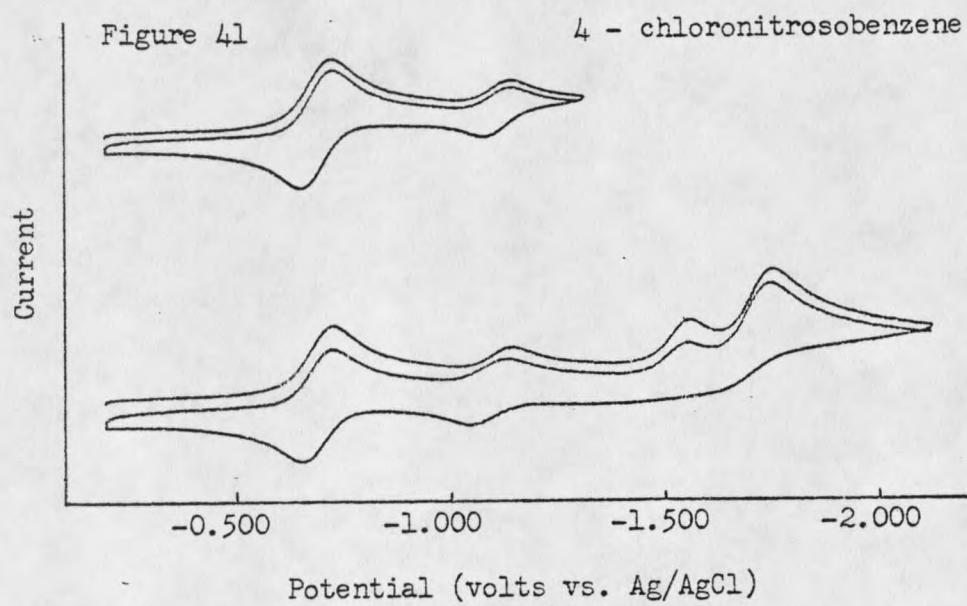
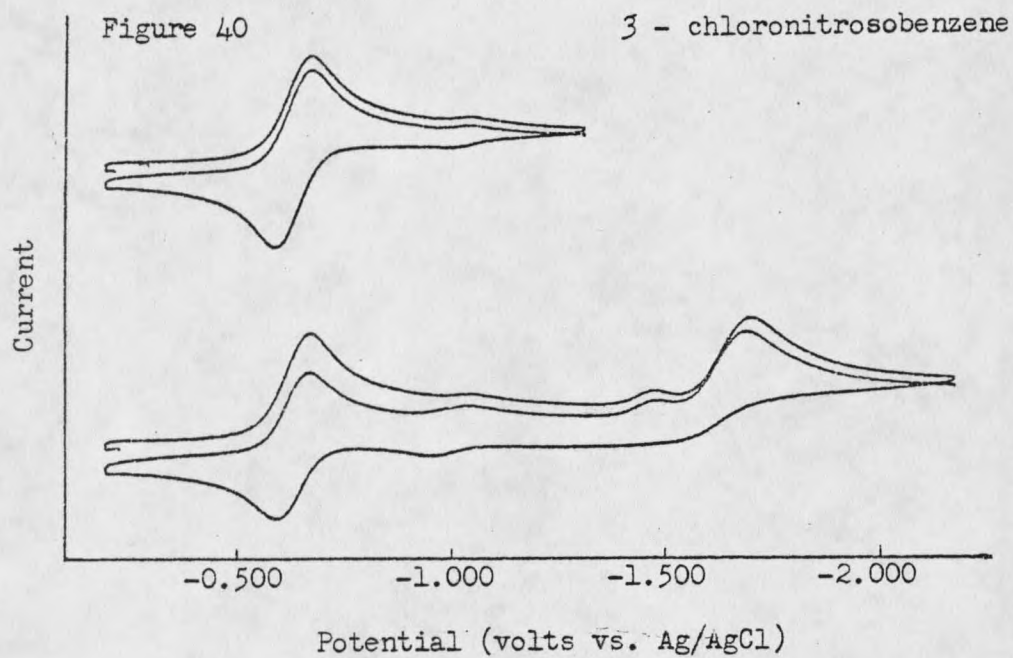
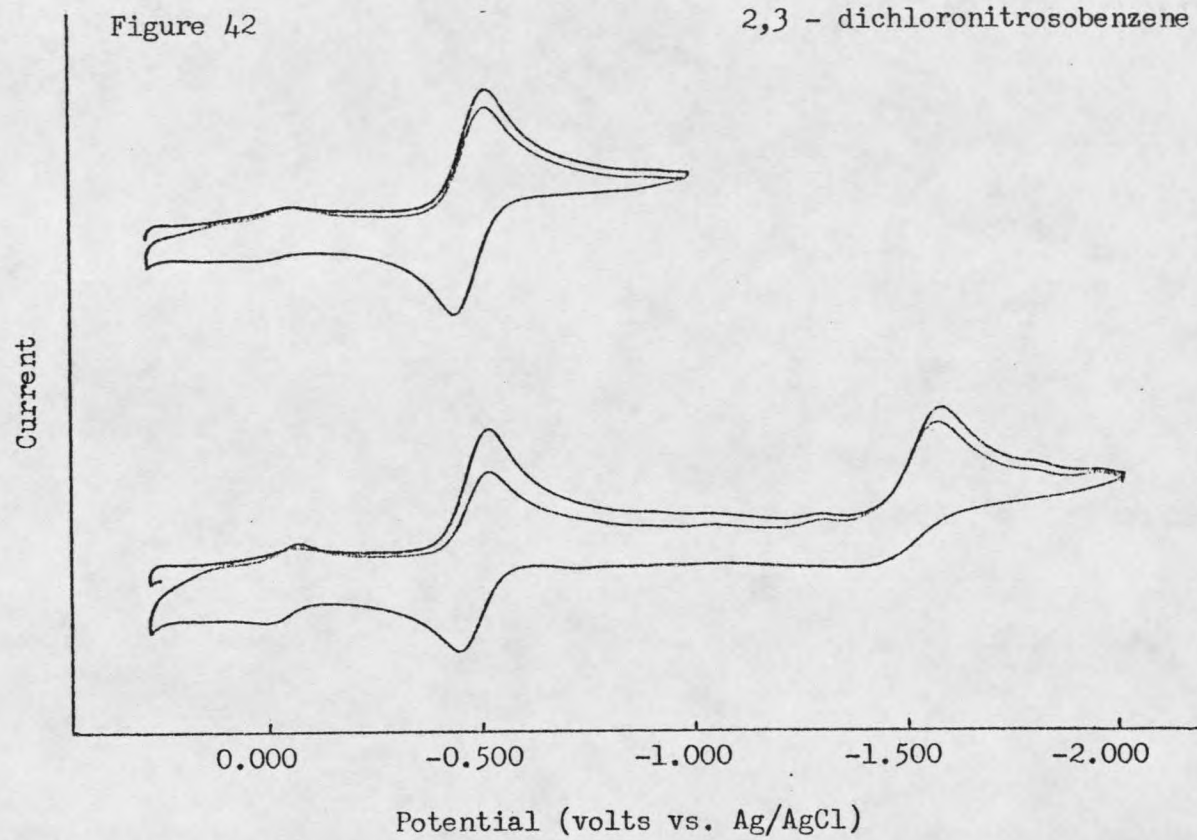
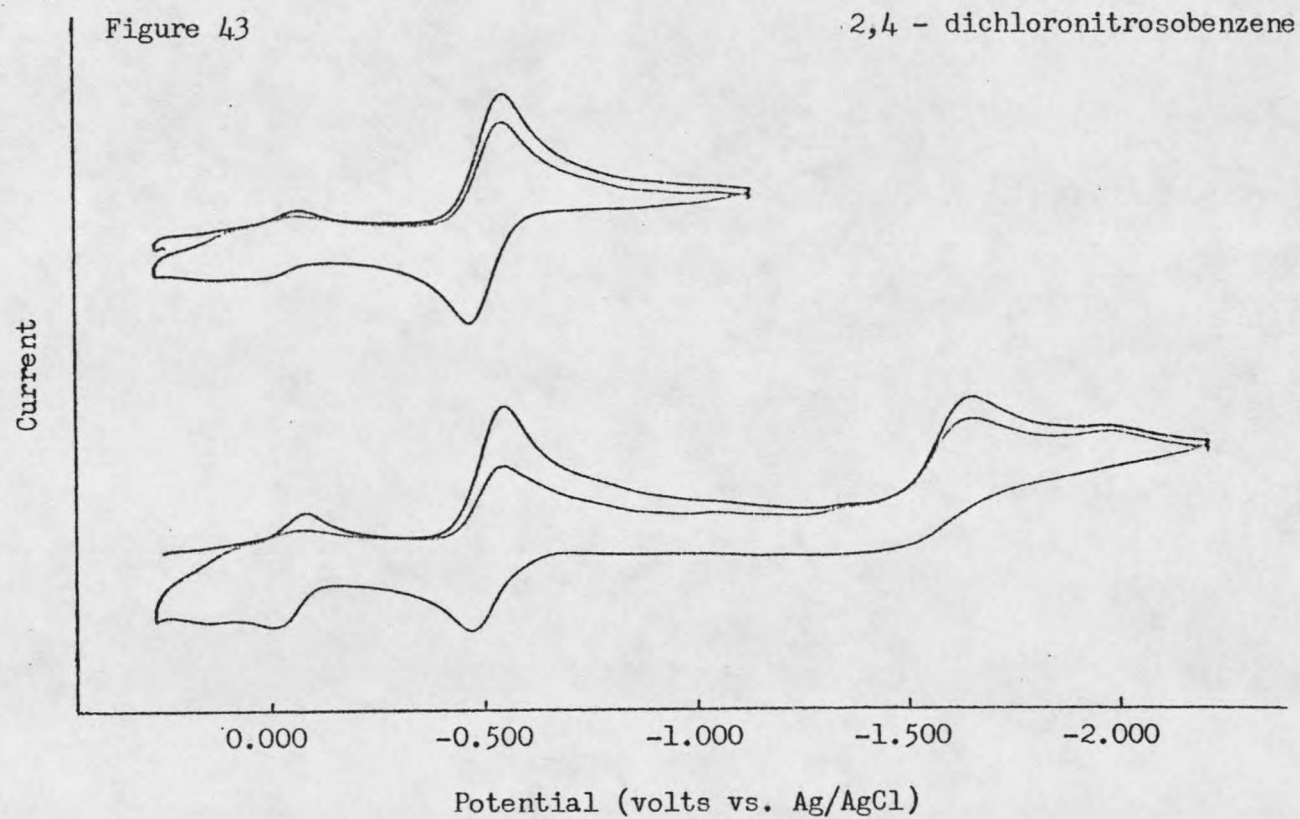
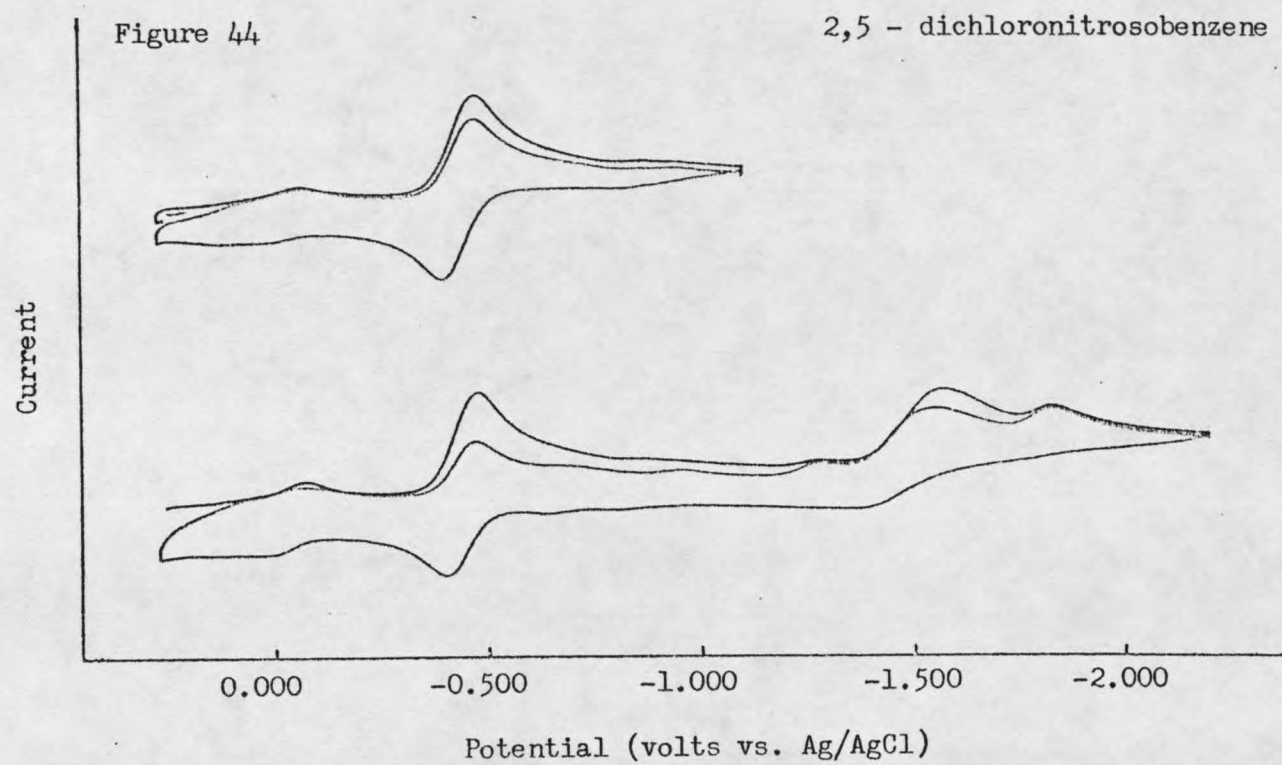


Figure 42

2,3 - dichloronitrosobenzene







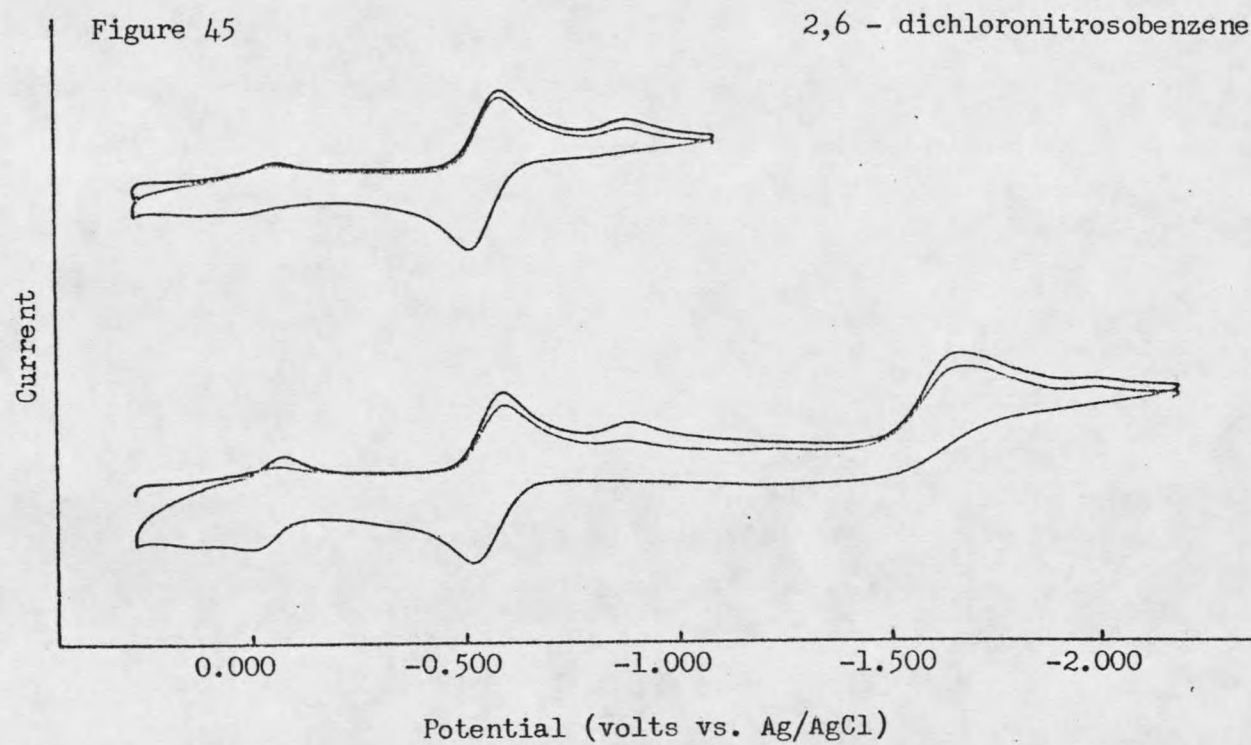
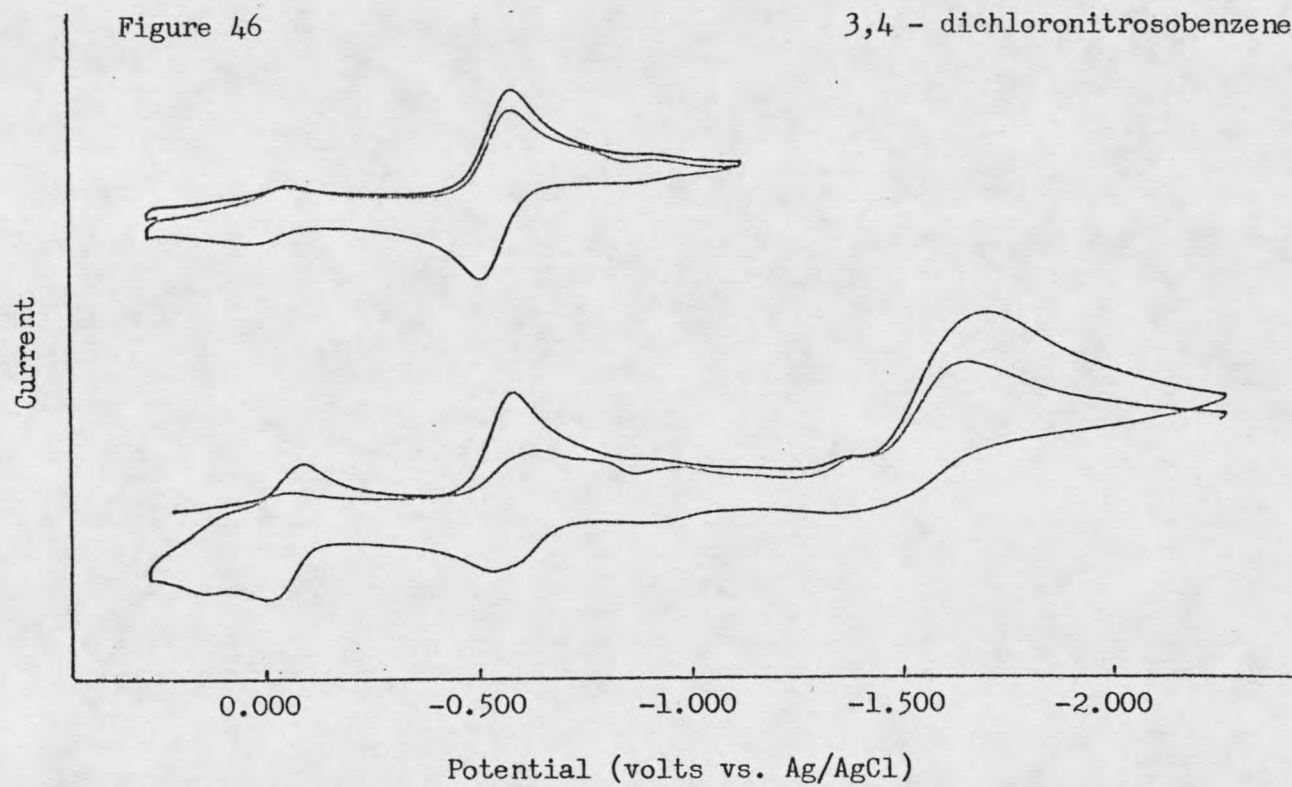


Figure 46

3,4 - dichloronitrosobenzene



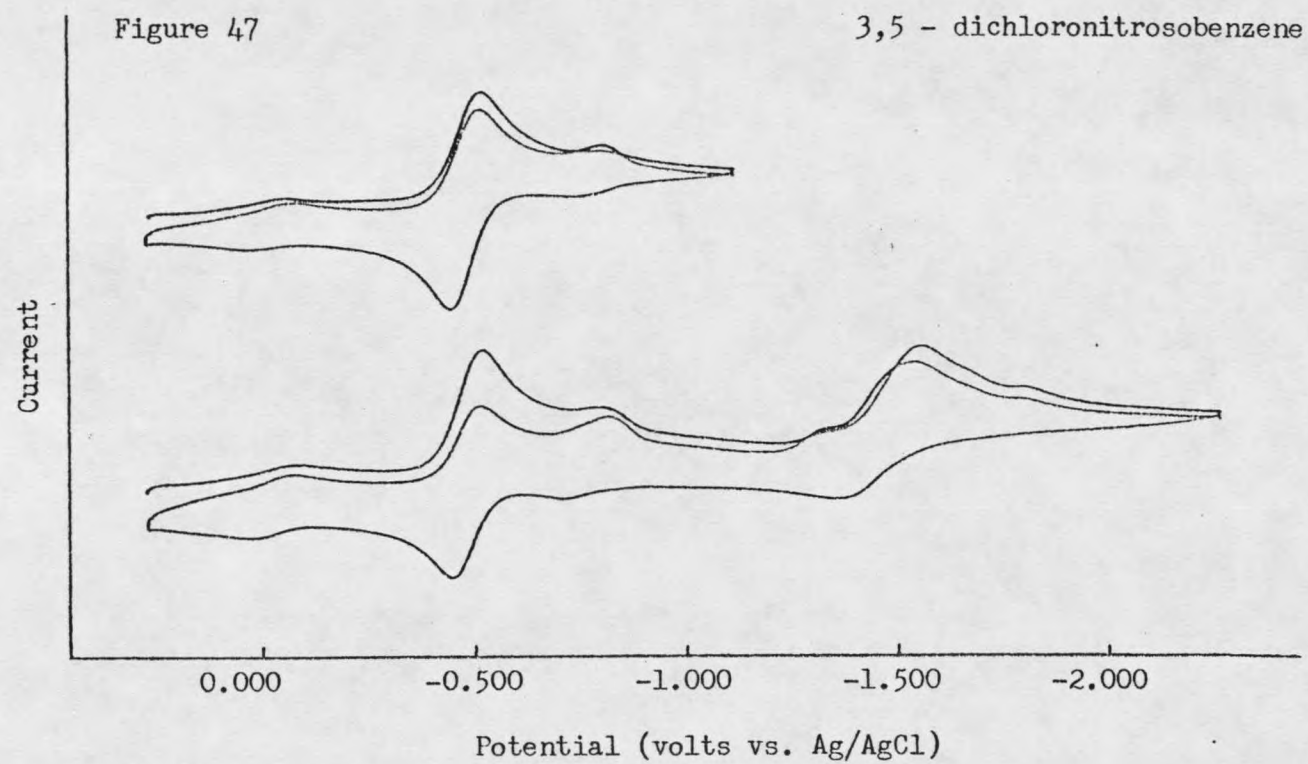
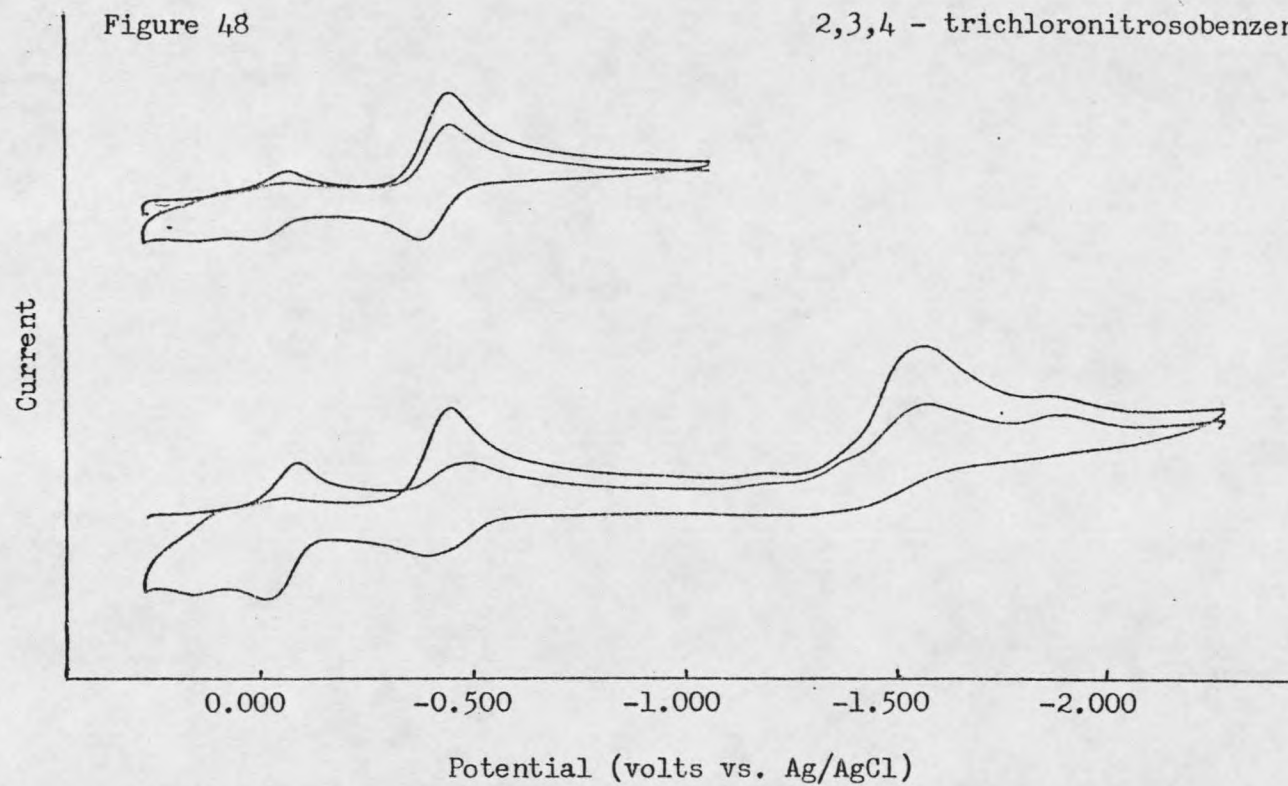
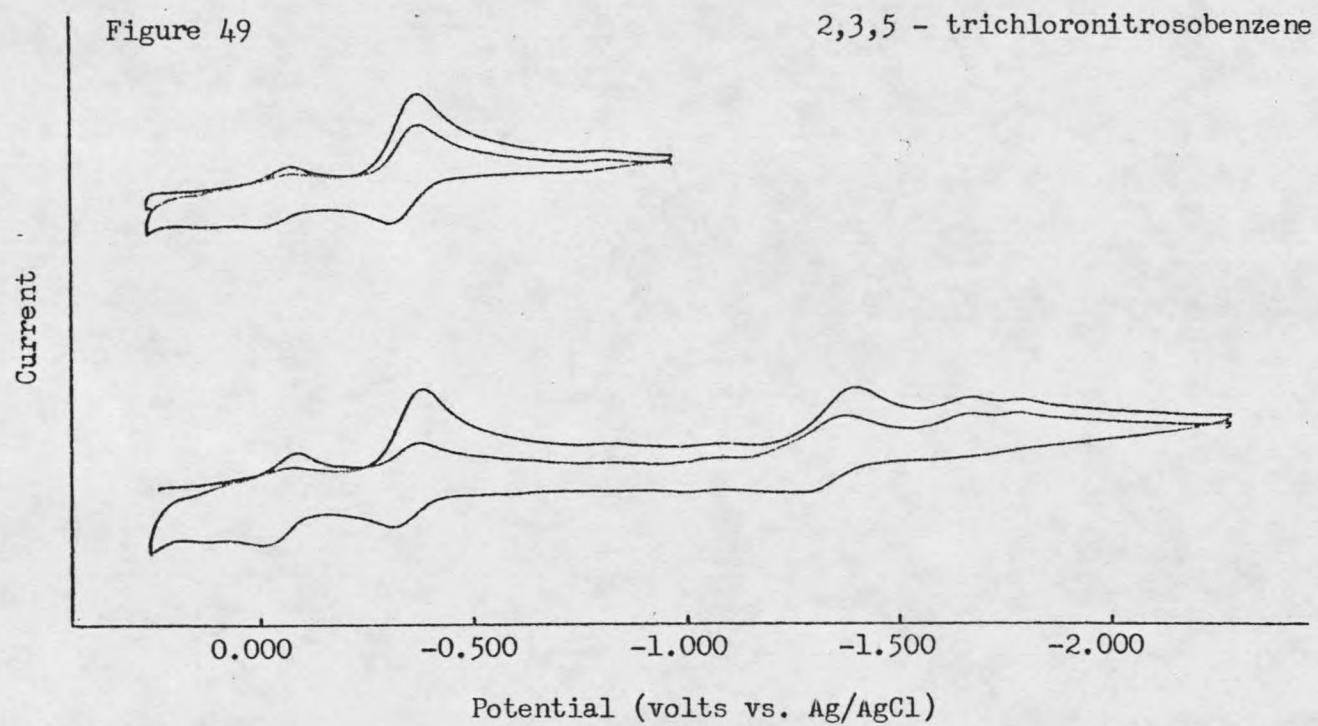


Figure 48

2,3,4 - trichloronitrosobenzene





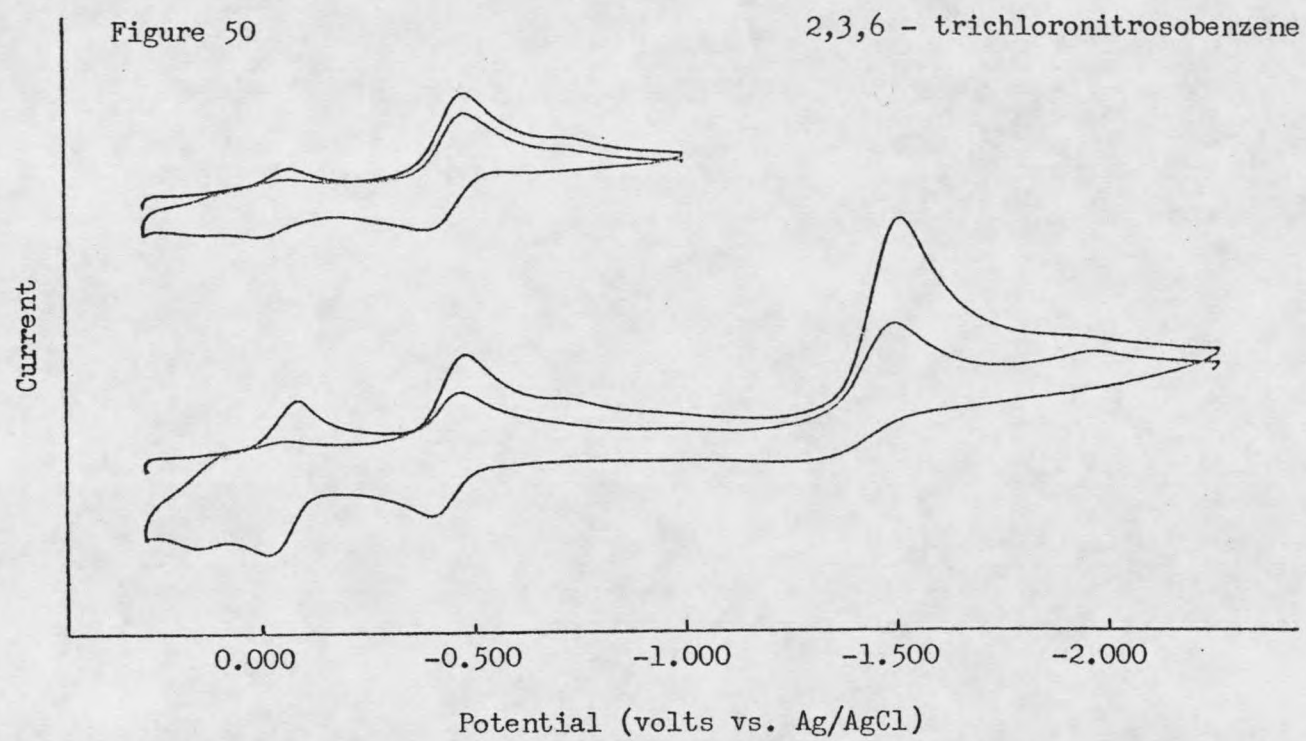
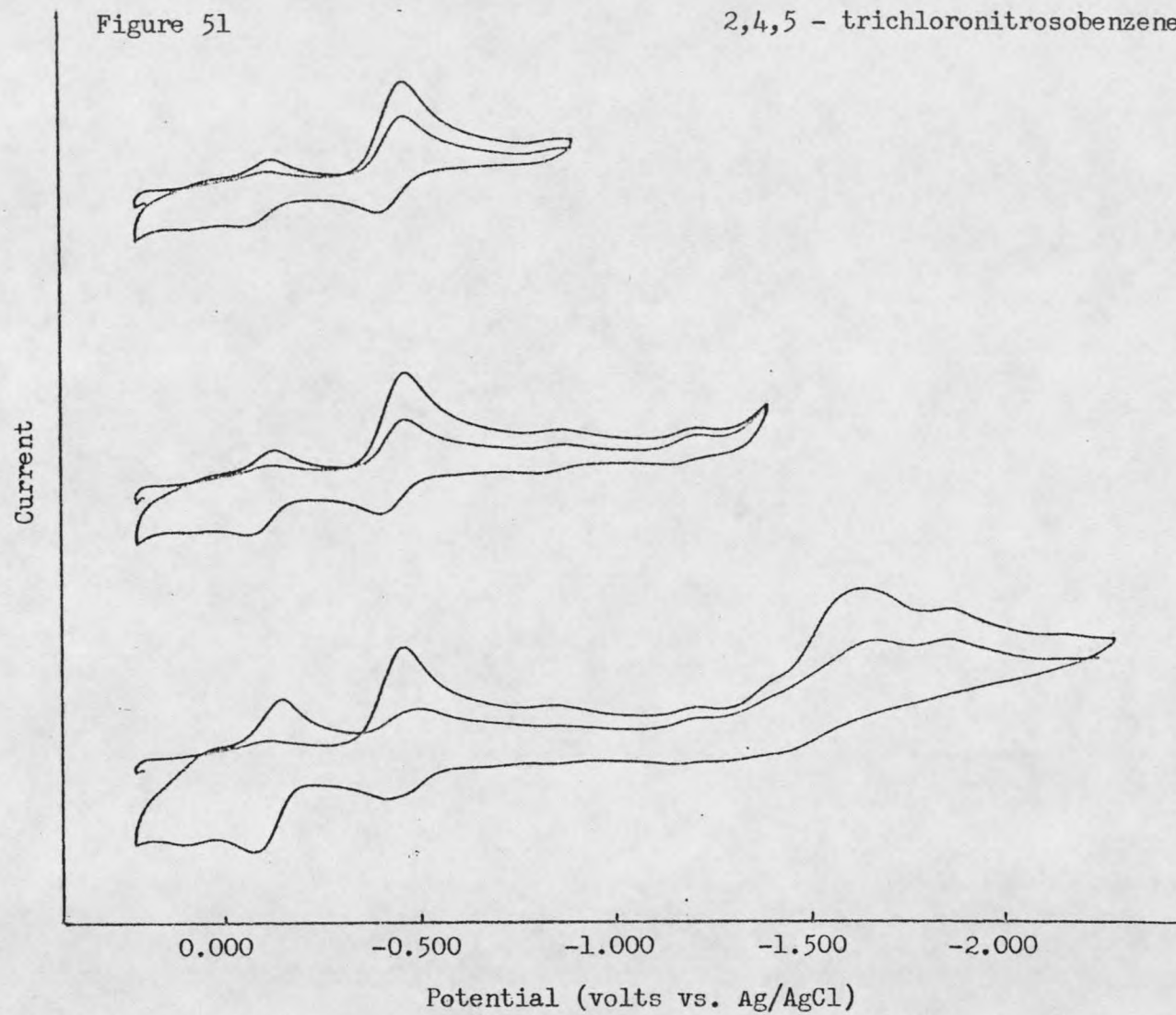


Figure 51

2,4,5 - trichloronitrosobenzene



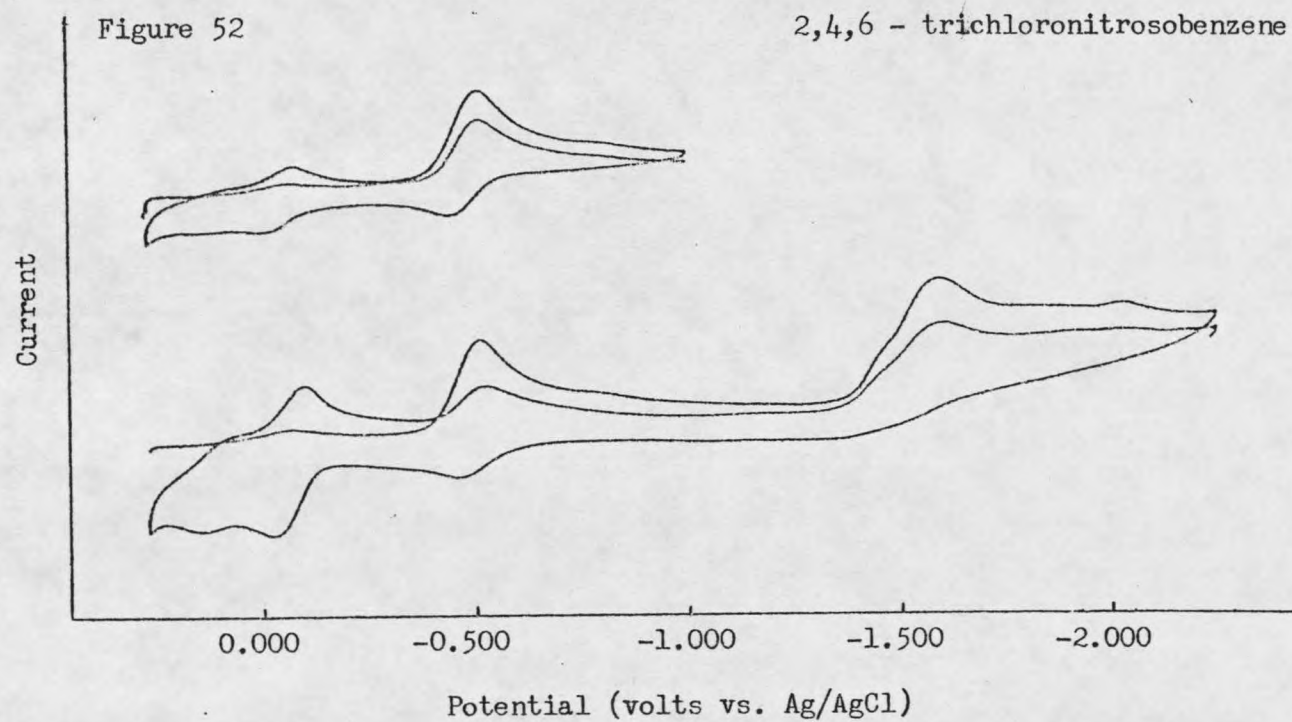
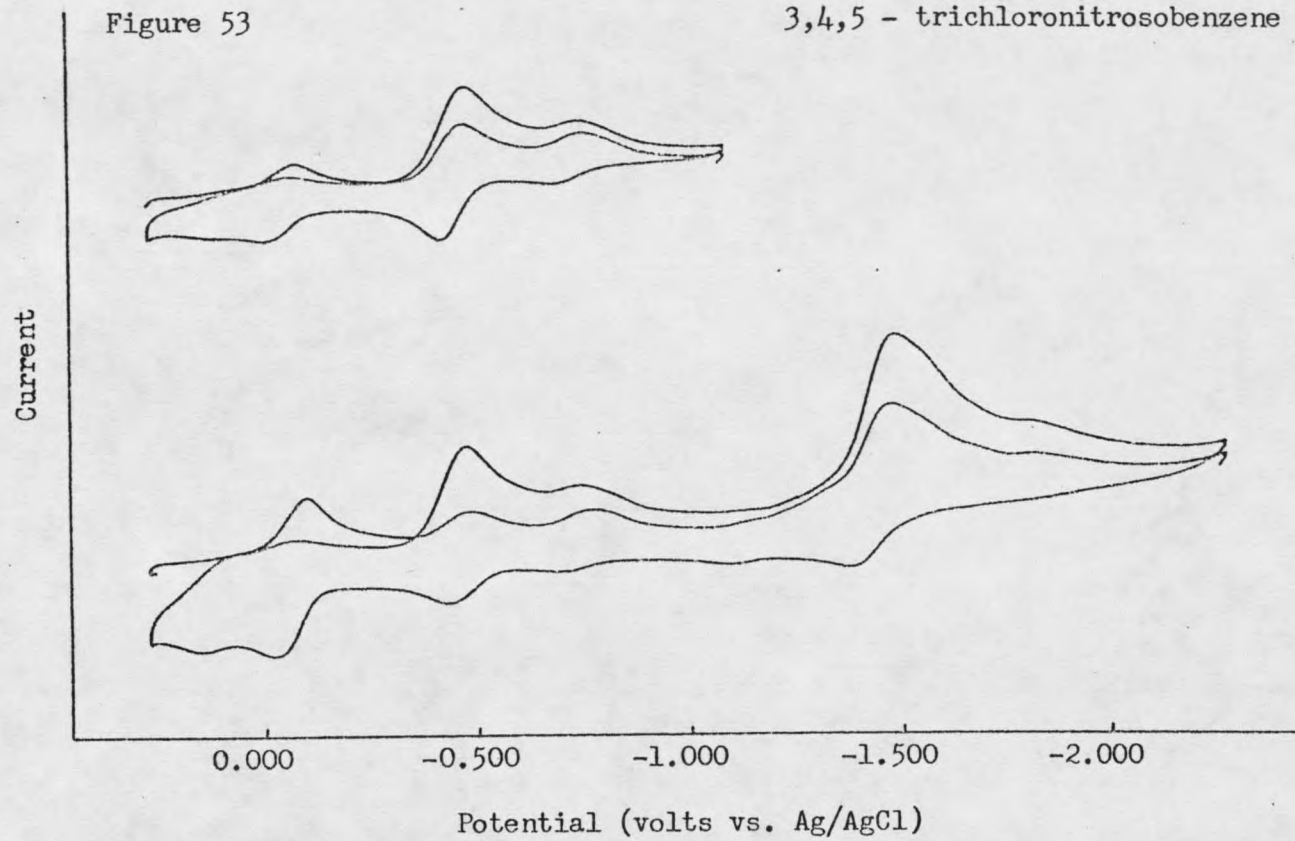


Figure 53

3,4,5 - trichloronitrosobenzene



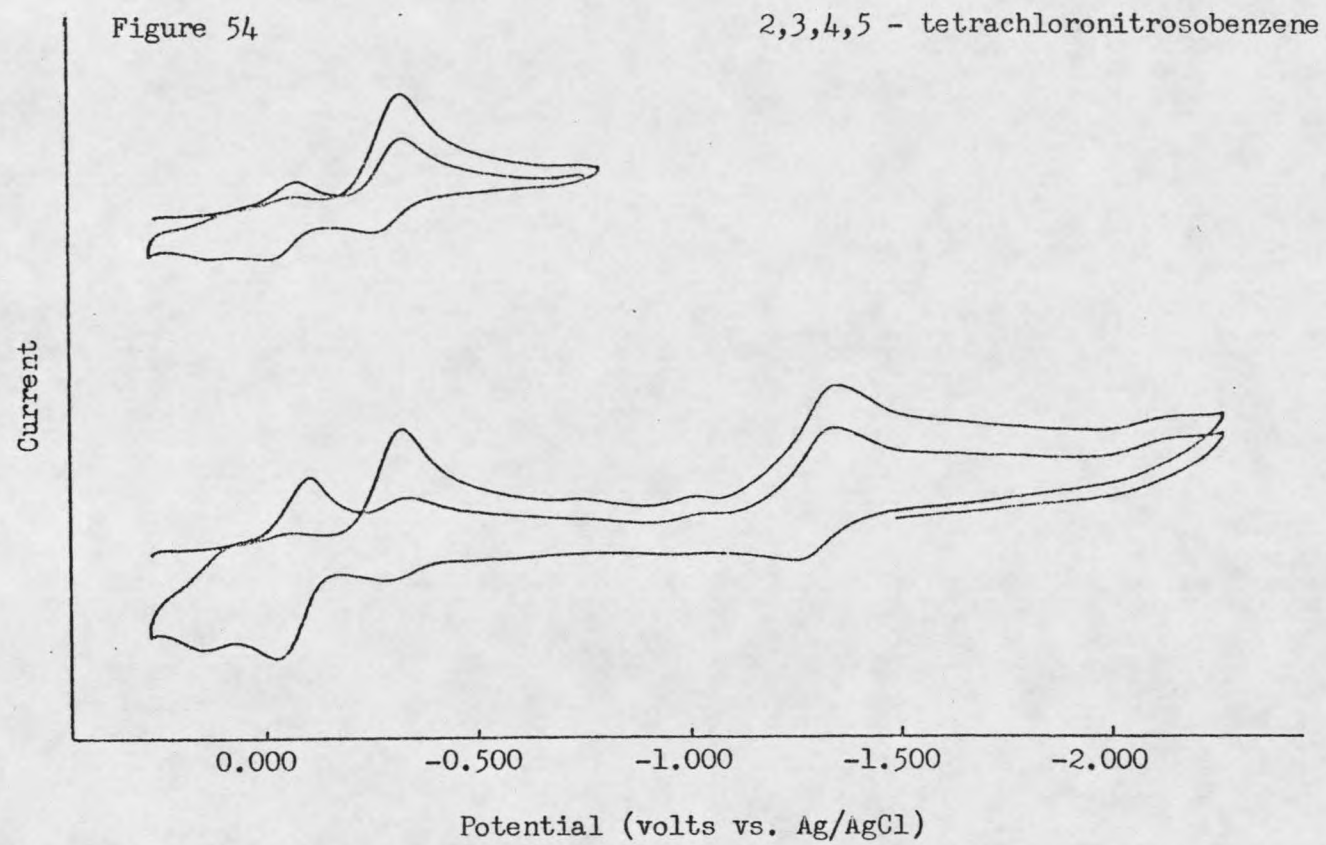
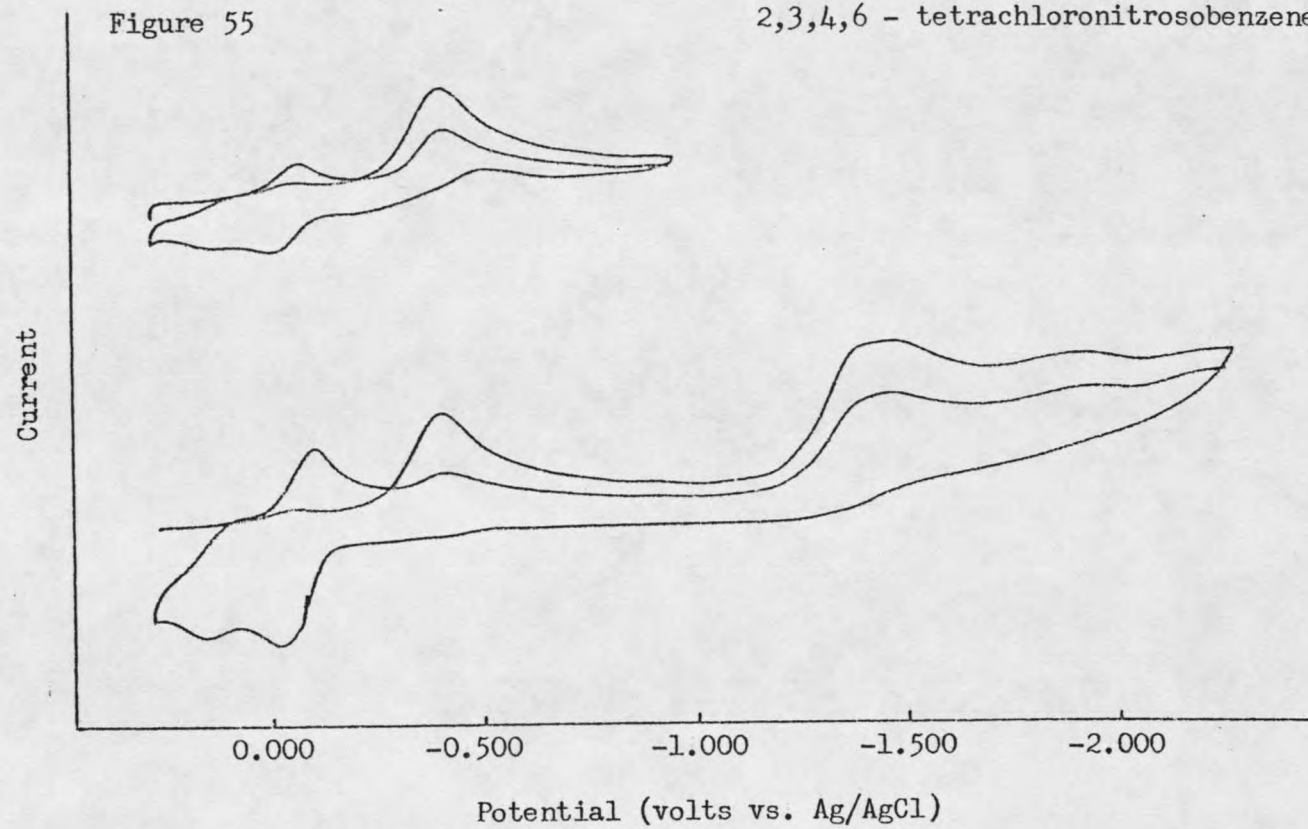


Figure 55

2,3,4,6 - tetrachloronitrosobenzene



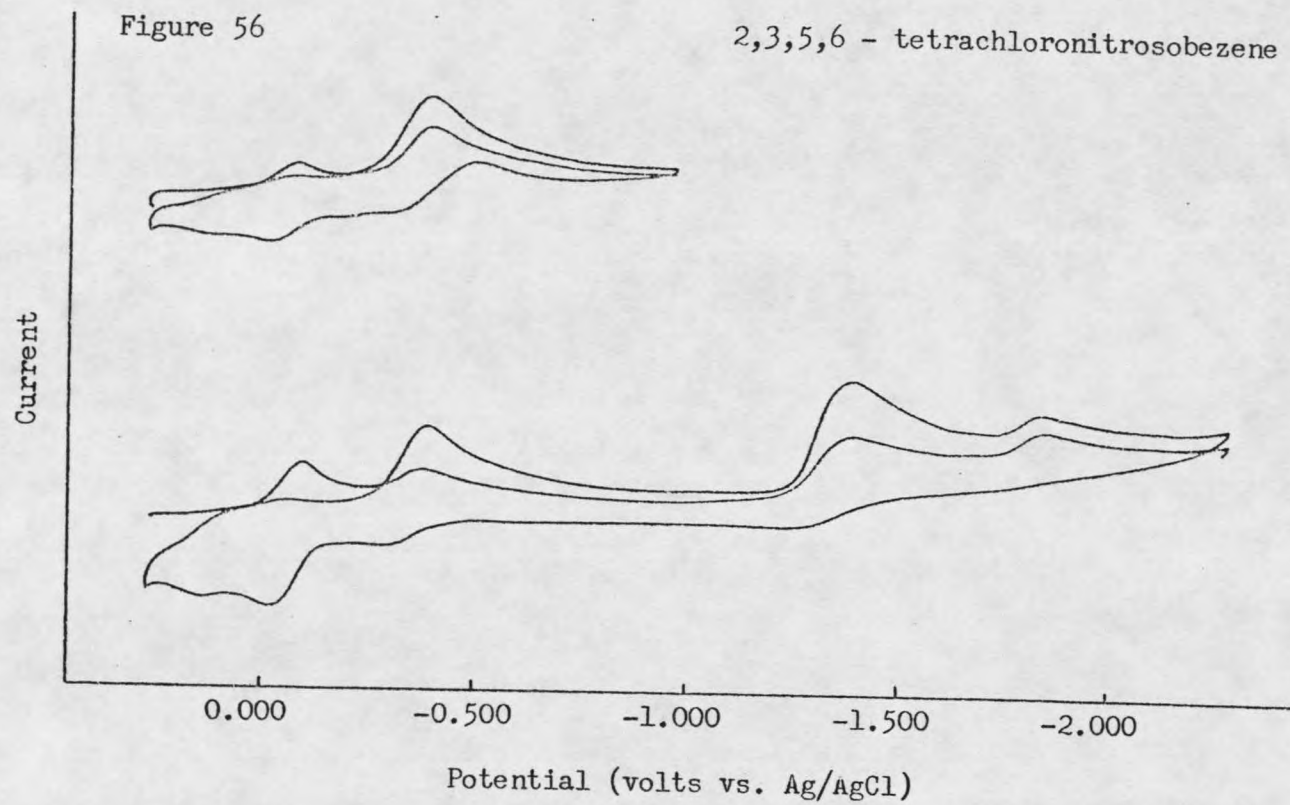
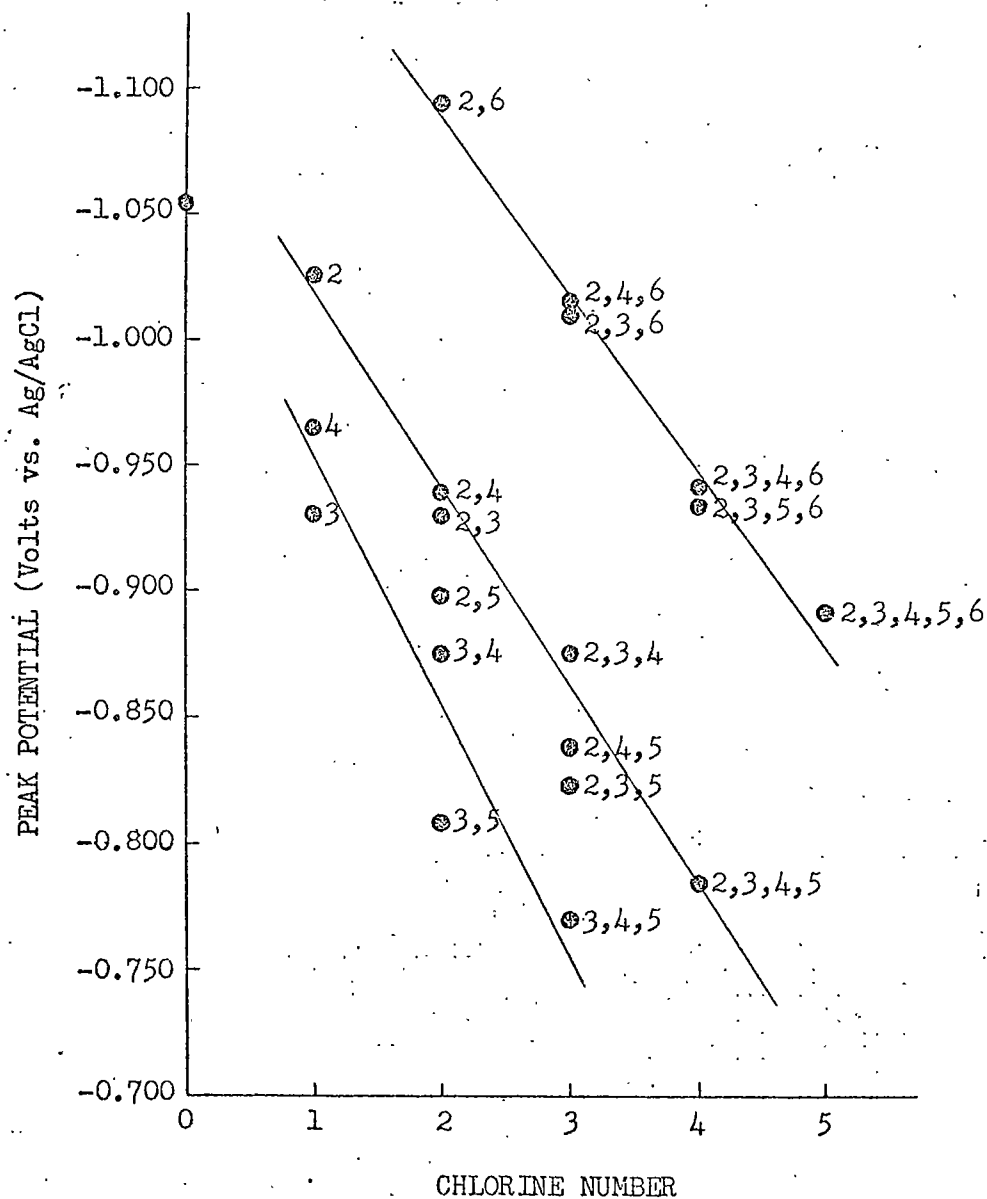


Figure 57. Peak Potentials of the First Wave Reductions of Polychloronitrobenzenes Plotted Against the Number of Chlorine Substitutions.



SUMMARY

The electrochemical reduction of the polychloronitrobenzenes was investigated by cyclic voltammetry. The first reduction in each case, except pentachloronitrobenzene is a one electron transfer to form the stable radical anion. Subsequent reduction waves correspond to electrochemical elimination of chlorine or reduction of the nitro group to nitroso. Reduction potentials, cyclic voltammograms and proposed electrochemical reduction mechanisms are given for all of the polychloronitrobenzenes. The formation of nitrosobenzene and the monochloronitrosobenzenes as electrochemical reduction products of the polychloronitrobenzenes in dimethylsulfoxide is a significant observation.

The polychloronitrosobenzenes were synthesized and their electrochemistry in dimethylsulfoxide recorded. The observed reduction processes of the chlorinated nitrosobenzenes follow the general mechanism of nitrosobenzene although loss of chlorine is a complicating factor in the mechanism determination. The reduction potentials are given and the cyclic voltammograms shown.

SECTION II.

INTRODUCTION

The study of phase equilibria involves the determination of the existence or coexistence of the three states of matter, (solid, liquid, and gas) with respect to thermodynamic stability at different temperatures and pressures. When two or more components are present the study is extended to a range of compositions as well. The thermodynamic stability of the different phases of a set of materials at different temperatures, pressures, and compositions can be determined from the thermodynamic properties of the system of materials and if the dependence of the thermodynamic properties on temperature, pressure, and composition are known, the phase equilibria of the system is determined.

Temperature and pressure dependence of thermodynamic properties are of interest apart from the study of phase equilibria. For example, the temperature dependence of the enthalpy is determined by the heat capacity and its temperature dependence and at constant temperature the pressure dependence of the Gibb's free energy is related to volume. However one new variable is of importance in the study of solution chemistry or phase equilibria and this is the composition variable.

Power series equations representing thermodynamic properties such as the enthalpy or free energy of a solution are logically chosen to

be power series in a composition variable. A number of different ways of representing the composition of a solution are commonly used, for example molarity, molality, mole percent, weight percent and mole fraction. One of the most convenient for phase equilibria work is mole fraction and power series expansions of thermodynamic properties in terms of mole fraction have been used for sometime.

One of the earliest proposed set of power series representations is that of Margules²⁸, shown here for a two component system:

$$\bar{Y}_1 - Y_1^\circ = (1-x_1)^2 (A_1 + B_1 x_1 + C_1 x_1^2 \dots)$$

$$\bar{Y}_2 - Y_2^\circ = x_1^2 (A_2 + B_2 x_1 + C_2 x_1^2 \dots)$$

$$Y^e = x_1 x_2 (A_e + B_e x_1 + C_e x_1^2 \dots)$$

Y is used to represent an arbitrary thermodynamic quantity such as enthalpy, free energy, logarithm of activity coefficient, and so forth. $\bar{Y}_1$ stands for the partial molal quantity defined as $\partial Y / \partial n_1$, Y_1° is the value of the thermodynamic property for the pure material, and Y^e is the excess quantity of mixing. As required, at the composition of either of the pure materials the excess quantity of mixing goes to zero and the partial molal quantities go to the molar values of the pure materials, i.e. $\bar{Y}_1 = Y_1^\circ$ at $x_1 = 1$.

Although the Margules equations have these essential qualities there are some disadvantages to using these simple power series. First a different set of coefficients appears in each of the equations above. Second the mole fraction terms within a given equation are nonorthogonal. If the terms were orthogonal the first three terms of a four term series would be identical to those of a three term series. However because the terms are nonorthogonal with respect to each other the coefficients would differ considerably between a three or four term fit of some thermodynamic data. The decision of how many terms to use in a power series fit of a set of thermodynamic data points is facilitated by knowing the approximate magnitude of the individual term contributions. This is possible when the terms are somewhat orthogonal.

Bale and Pelton²⁹ have proposed the following power series for thermodynamic property representation:

$$\bar{Y}_1 - Y_1^o = (1-x_1)^2 \sum_{i=0}^n a_i P_i(x_1)$$

$$\bar{Y}_2 - Y_2^o = x_1^2 \sum_{i=0}^n b_i P_i(x_1)$$

$$Y^e = x_1 x_2 \sum_{i=0}^n q_i P_i(x_1).$$

The $P_i(x_1)$ are standard Legendre polynomials which are completely orthogonal. However the relation of the partial molal quantities to

the excess quantity requires that each equation have its own set of coefficients if the Legendre polynomials are used for the mole fraction terms.

A reasonable compromise between orthogonality and convenience is provided by the Redlich Kister equations^{30,31}:

$$\bar{Y}_1 - Y_1^o = x_2^2 \left[A + B(4x_1 - 1) + C(6x_1 - 1)(2x_1 - 1) + D(8x_1 - 1)(2x_1 - 1)^2 \dots \right]$$

$$\bar{Y}_2 - Y_2^o = x_1^2 \left[A + B(4x_1 - 3) + C(6x_1 - 5)(2x_1 - 1) + D(8x_1 - 7)(2x_1 - 1)^2 \dots \right]$$

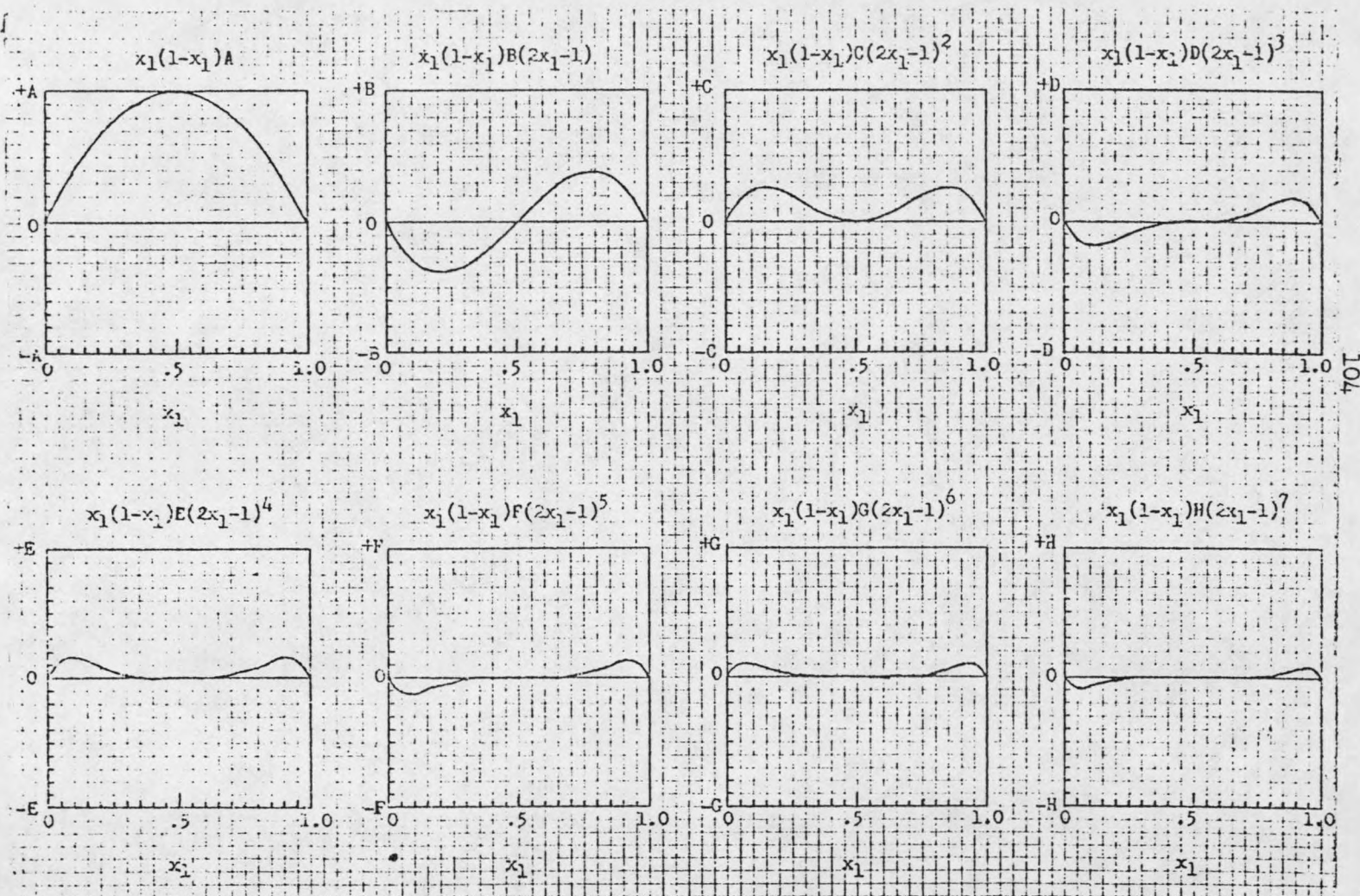
$$Y^e = x_1 x_2 \left[A + B(2x_1 - 1) + C(2x_1 - 1)^2 + D(2x_1 - 1)^3 \dots \right]$$

The coefficients are the same in each equation and although the terms in a particular equation are not exactly orthogonal with respect to each other, approximate orthogonality does exist. The individual mole fraction terms of the Y^e equation are shown in figure 58. The shapes of these terms are well suited to being added together to fit the observed behaviour of excess thermodynamic quantities.

The reason that the coefficients can be the same in each equation is that the partial molal equations are derived from their relationship to the excess quantity equation. From the definition of the partial molal quantity:

$$\bar{Y}_1 = \left. \frac{\partial Y}{\partial n_1} \right|_{n_2, T, P}$$

Figure 58. Individual Contributions to Y^e .



and the expression for the thermodynamic quantity:

$$Y = n_1 Y_1^\circ + n_2 Y_2^\circ + (n_1 + n_2) Y^e$$

the following relationship can be derived:

$$\bar{Y}_1 = Y_1^\circ + Y^e + (n_1 + n_2) \frac{\partial Y^e}{\partial n_1}$$

Since $\frac{\partial Y^e}{\partial n_1} = \left(\frac{\partial Y^e}{\partial x_1} \right) \left(\frac{\partial x_1}{\partial n_1} \right)$ and $\frac{\partial x_1}{\partial n_1} = \frac{x_2}{n_1 + n_2}$ one can write:

$$\bar{Y}_1 - Y_1^\circ = Y^e + x_2 \frac{\partial Y^e}{\partial x_1}$$

The equation for Y^e can be rewritten as:

$$Y^e = A(-x_1^2 + x_1) + B(-2x_1^3 + 3x_1^2 - x_1) + C(-4x_1^4 + 8x_1^3 - 5x_1^2 + x_1)$$

and

$$x_2 \frac{\partial Y^e}{\partial x_1} = A(-2x_1 x_2 + x_2) + B(-6x_1^2 x_2 + 6x_1 x_2 - x_2) + C(-16x_1^3 x_2 + 24x_1^2 x_2 - 10x_1 x_2 + x_2)$$

$$\begin{aligned} Y^e + x_2 \frac{\partial Y^e}{\partial x_1} &= A(-x_1^2 + x_1 - 2x_1 x_2 + x_2) \\ &+ B(-2x_1^3 + 3x_1^2 - x_1 - 6x_1^2 x_2 + 6x_1 x_2 - x_2) \\ &+ C(-4x_1^4 + 8x_1^3 - 5x_1^2 + x_1 - 16x_1^3 x_2 + 24x_1^2 x_2 - 10x_1 x_2 + x_2) \end{aligned}$$

Using $x_1 + x_2 = 1$ this equation can be rearranged to:

$$Y^e + x_2 \frac{\partial Y^e}{\partial x_1} = x_2^2 \left[A + B(4x_1 - 1) + C(6x_1 - 1)(2x_1 - 1) \dots \right] = \bar{Y}_1 - Y_1^\circ$$

The individual terms for the $\bar{Y}_1 - Y_1^\circ$ equation are shown in figure 59. The shapes of the individual terms for $\bar{Y}_2 - Y_2^\circ$ can be obtained from those for $\bar{Y}_1 - Y_1^\circ$ by reflecting the points of the graph through a plane perpendicular to the paper at $x_1 = .5$ for the terms A, C, E . . . and by rotating the points of the graph 180° about an axis through the point where $x_1 = .5$ and coefficient equals zero for the terms B, D, F . . .

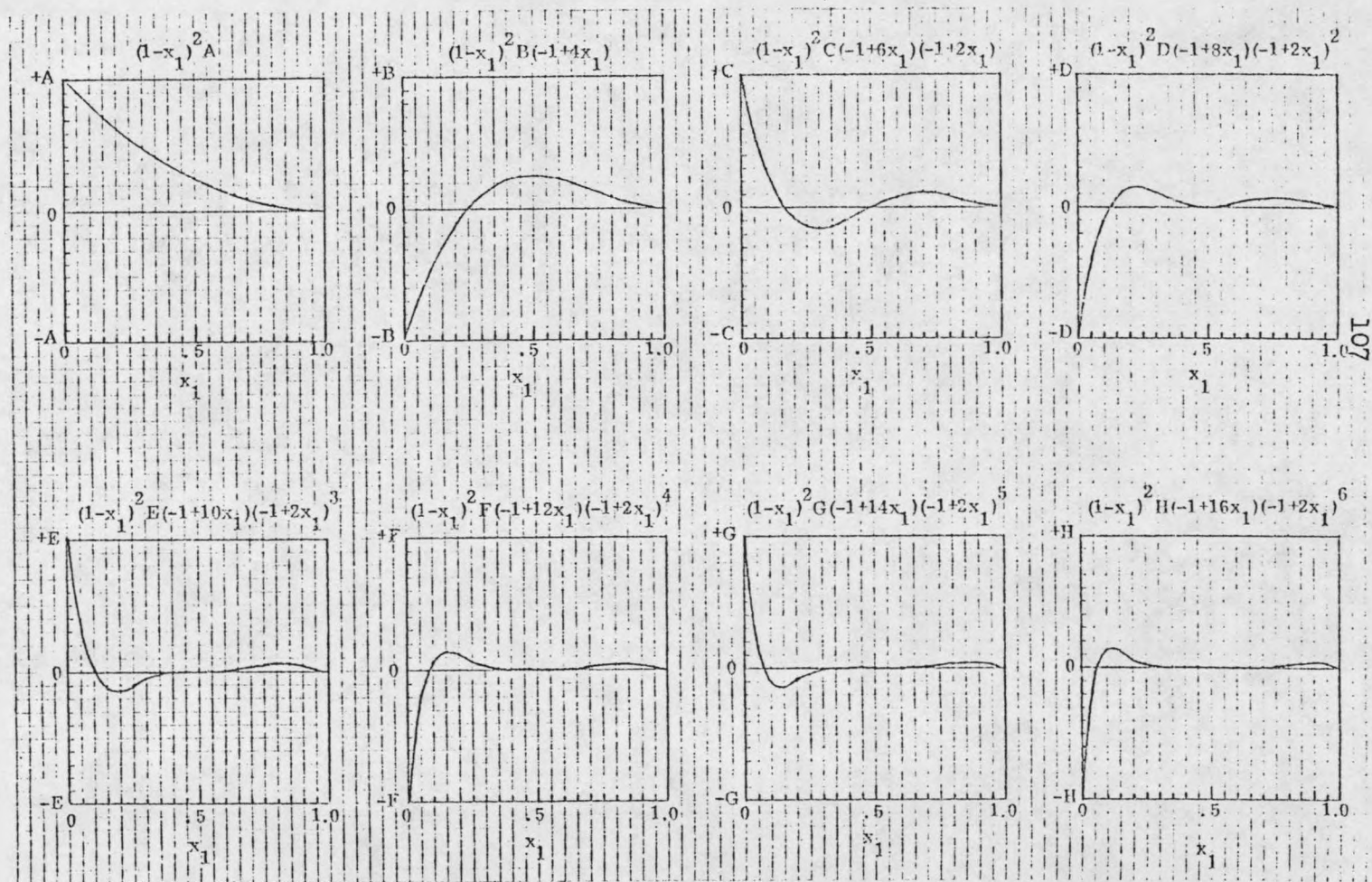
Least Square Fitting of Data

The method of least squares is based on finding the line which will minimize the sum of the squares of the differences between observed and calculated data points. If values of a dependent variable, y , are measured at a series of values of an independent variable, x , a straight line fit of the y values will have the form $y = mx + b$ where m is the slope and b is the intercept. The square of the difference between the measured value y and a calculated value $mx + b$ is $(y - mx - b)^2$. The best fit line can be determined by minimizing the sum of these differences for all the y values. This minimization can be accomplished by setting the derivatives of the sum of the differences with respect to m and b equal to zero.

$$\frac{\partial}{\partial m} \sum (y - mx - b)^2 = \sum 2(y - mx - b)(-x) = 0$$

$$\frac{\partial}{\partial b} \sum (y - mx - b)^2 = \sum 2(y - mx - b)(-1) = 0$$

Figure 59. Individual Contributions to $\bar{Y}_1 - Y_1^0$.



Rearrangement gives:

$$\sum xy = b \sum x + m \sum x^2$$

$$\sum y = bn + m \sum x$$

where n is the number of observations. These two equations in two unknowns can be easily solved for m and b .

The least squares method can be used to determine the Redlich Kister power series coefficients similar to the procedure for m and b in the linear case. For example:

$$Y^e = x_1(1-x_1)(A + B(2x_1-1) \dots)$$

$$\sum \left[Y^e - x_1(1-x_1)(A + B(2x_1-1) \dots) \right]^2$$

Taking derivatives with respect to A and B gives:

$$\sum 2 \left[Y^e - A(-x_1^2 + x_1) - B(-2x_1^3 + 3x_1^2 - x_1) \right] (-x_1^2 + x_1) = 0$$

$$\sum 2 \left[Y^e - A(-x_1^2 + x_1) - B(-2x_1^3 + 3x_1^2 - x_1) \right] (-2x_1^3 + 3x_1^2 - x_1) = 0$$

and rearrangement gives:

$$\sum Y^e (-x_1^2 + x_1) = A \sum (-x_1^2 + x_1)^2 + B \sum (-2x_1^3 + 3x_1^2 - x_1)(-x_1^2 + x_1)$$

$$\sum Y^e (-2x_1^3 + 3x_1^2 - x_1) = A \sum (-x_1^2 + x_1)(-2x_1^3 + 3x_1^2 - x_1) + B \sum (-2x_1^3 + 3x_1^2 - x_1)^2$$

The experimental values of Y^e as a function of x can thus be used to determine the power series equation.

Equilibrium Constants

Equilibrium constants are very useful in the study of phase equilibria since they indicate the relative amounts of the different components present at equilibrium. An equilibrium constant is related to the standard Gibbs free energy of the components involved in the equilibrium by the following expression:

$$G_T^\circ = -RT \ln K_T$$

The equilibrium constant can also be expressed as:

$$K_T = e^{-\Delta H_T/RT} e^{\Delta S_T/R}$$

or:

$$K_T = 10^{-\Delta H_T/2.303RT} 10^{\Delta S_T/2.303R}$$

However tabulations of thermodynamic properties often include the free energy function, Φ , which contains the temperature dependence of both ΔH and ΔS .

$$\Phi_T = \frac{H_{298.15}^\circ - G_T^\circ}{T}$$

Although several slightly different definitions of $\bar{\Phi}$ are sometimes used in the literature, this definition results in a familiar form for the equilibrium constant expression:

$$K_T = 10^{-\Delta H_{298.15}/2.303RT_{10} + \bar{\Phi}/2.303R}.$$

The free energy function is preferred in tabulations such as the JANAF tables³² since its variation with temperature is nearly linear. This allows free energy function values of reasonable accuracy to be determined at intermediate temperatures by interpolation between the tabulated values.

Computer calculation of free energy function values at different temperatures is easily accomplished if both the value of the free energy function at a particular temperature and a heat capacity equation valid for the temperature range considered are known. A convenient equation for heat capacity as a function of temperature used throughout this work is:

$$C_p = A + B(T-T_0) + C(T-T_0)^2 + D(T-T_0)^3 \dots$$

The coefficients can be determined by least squares fitting of experimental heat capacity data and the A value automatically gives the heat capacity at the standard temperature, T_0 .

A set of standard thermodynamic properties can be chosen to allow the calculation of equilibrium constants at various temperatures.

For each component the values of $\bar{\Phi}_{T_0}$, $H_{T_0}^\circ$, $H_{298.15}^\circ$, and a valid heat capacity equation are sufficient to allow equilibrium constant calculation.

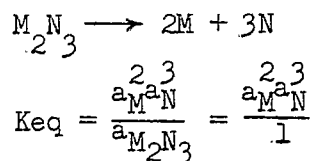
Calculation of a Phase Diagram

In order to calculate a phase diagram it is necessary to know the activity of the components as a function of temperature and composition with the pressure frequently chosen to be constant. Redlich Kister equations for $\log \gamma$ at a standard temperature and for the enthalpy of the system can provide this necessary information on activity to a reasonable approximation. If the heat capacity of the system and the temperature dependence of the heat capacity are known as a function of composition, activity values at different temperatures can be calculated with greater accuracy. The accuracy of the calculated values will of course depend on the accuracy of the experimental data used to determine the coefficients of all the power series equations, and on the quality of the fit obtained.

The lines on a two component phase diagram show the temperatures and compositions at which the different phases are in equilibrium. Therefore if one calculates the equilibrium constant at a particular temperature for the reaction of the components of the one phase going to form the components of another, one will have an expression for the activities of the product components divided by the reactant com-

ponents raised to the appropriate stoichiometry powers. The Redlich Kister equations allow the activity of each component at this temperature to be calculated at any composition. The composition or compositions at which the calculated activities in the appropriate equilibrium expression equal the equilibrium constant will be the compositions of the points of equilibrium on the phase diagram lines at that temperature.

For example a solid of stoichiometry M_2N_3 can be in equilibrium with liquid of composition $x_M M + x_N N$ below the melting point of M_2N_3 . The reaction and equilibrium constant for M_2N_3 going to liquid will be:



This equilibrium constant can be calculated from tabulated thermodynamic properties for M, N, M_2N_3 . Power series equations for $\log \gamma_M$ and $\log \gamma_N$ allow the following relationships to be written:

$$K_{eq} = (x_M 10^{\log \gamma_M})^2 (x_N 10^{\log \gamma_N})^3$$

$$K_{eq} = \left[x_M 10^{x_N^2 (A+B(4x_M-1) \dots)} \right]^2 \left[x_N 10^{x_M^2 (A+B(4x_N-3) \dots)} \right]^3$$

Since the equilibrium constant is known and the A, B, C . . . are obtained from experimental data, a computer can easily step through mole fraction values and by a minimization process arrive at the mole fraction or mole fractions that make the two sides of the equation equal. By repeating this process at different temperatures the entire line of equilibrium compositions and temperatures for solid M_2N_3 in equilibrium with liquid can be determined.

Extended Redlich Kister Notation

One of the major advantages of power series representations in the study of phase equilibria is that, in principle, all of the thermodynamic information of multicomponent systems can be represented by a relatively small number of power series coefficients. Thus far most of this discussion has been oriented toward two component systems. However a notation for extending Redlich Kister power series representations to three component systems has been presented in the literature.³³ This notation has been superseded by a slightly different notation which has been checked out for up to six component systems and will be described here.

Ideally the description of a multicomponent system will include contributions from each of the binary, ternary, quaternary, etc. subsystems plus contributions from the properties of the components when all are present at once. The coefficients through E terms for a three

component system with the newest notation are shown in Table 4. The first three columns correspond to the Redlich Kister coefficients for the three binary subsystems. The remainder of the terms must be determined from thermodynamic property measurement in the three component system.

Table 4. Three Component Extended Redlich Kister Coefficients.

A_{12}	A_{13}	A_{23}				
B_{12}	B_{13}	B_{23}	B_{321}^a			
C_{12}	C_{13}	C_{23}	C_{321}^a	C_{321}^b		
D_{12}	D_{13}	D_{23}	D_{321}^a	D_{321}^b	D_{321}^c	
E_{12}	E_{13}	E_{23}	E_{321}^a	E_{321}^b	E_{321}^c	E_{321}^d

For the excess quantity the mole fraction terms which are multiplied by these coefficients are coded for by the subscripts and superscripts.

As for the binary power series the coefficients times mole fraction products in the first three columns are $A_{12}x_1x_2$, $E_{13}x_1x_3(x_1-x_3)^4$, $C_{23}x_2x_3(x_2-x_3)^2$, . . .

The number of superscripts is always two less than the number of subscripts. The number of subscripts starts at two for each capital letter and can increase to a maximum of one more than the position of the letter in the alphabet or to the number of components considered which ever is smaller. For example the maximum number of subscripts for E is six if six or more components are being considered

but is limited to three for a three component system.

The A term is second power in mole fraction, the B term is third power and so on. The small case letters also code for powers and the following scheme is helpful:

	A	B	C	D	E	F	G	H . . .
a	b	c	d	e	f	g	h	i . . .
0	1	2	3	4	5	6	7	8 . . .

The contribution to the excess thermodynamic property of E_{321}^b is sixth power in mole fraction and the first three mole fractions are $x_3x_2x_1$ for the subscripts 3 2 1. The next mole fraction term is T^m where m is the number of the capital letter, which is 6 for E, minus the number of subscripts. In this case m is $6-3=3$. T is defined as $1-x_i$ where i is the first subscript. For E_{321}^b i is also 3 and so far this gives $E_{321}^b x_3x_2x_1(1-x_3)^3$. The superscripts are correlated with the subscripts starting from the right. Therefore for a coefficient such as E_{1234}^{ca} , a correlates with 4 and c correlates with 3. For each superscript there is a Z^n term where n is corresponding power of the superscript. Z is defined as $(x_j-x_k)/T$ where j is the second subscript from the left and k is the subscript correlated with this Z term's superscript. For E_{321}^b the only Z term corresponds to the superscript b which is correlated with the subscript 1. This gives j equal 2, k

equal 1, and $n=b=2$. The complete contribution is:

$$E_{321}^b x_3 x_2 x_1 T^3 Z^2 = E_{321}^b x_3 x_2 x_1 (1-x_3)^3 \left(\frac{x_2-x_1}{1-x_3} \right)^2 = E_{321}^b x_3 x_2 x_1 (1-x_3) (x_2-x_1)^2$$

This can be extended to terms that can appear in systems with more than three components such as G_{12345}^{aca} where i equals 1, m equals $8-5=3$ and j equals 2. For the first a on the right k is 5 and n is 0 and:

$$(Z(a))^0 = \left(\frac{x_2-x_5}{T} \right)^0 = 1$$

For the c superscript k is 4 and n is 2 and:

$$(Z(c))^2 = \left(\frac{x_2-x_4}{T} \right)^2$$

The second a superscript gives k equal 3 and n equal 0 and:

$$(Z(a))^0 = \left(\frac{x_2-x_3}{T} \right)^0 = 1$$

The total contribution of G_{12345}^{aca} to the excess quantity is:

$$G_{12345}^{aca} x_1 x_2 x_3 x_4 x_5 (1-x_1)^3 (1) \left(\frac{x_2-x_4}{1-x_1} \right)^2 (1) =$$

$$G_{12345}^{aca} x_1 x_2 x_3 x_4 x_5 (1-x_1) (x_2-x_4)^2$$

Some more examples are:

$$D_{3254}^{ba} x_3 x_2 x_5 x_4 (x_2-x_5)$$

$$F_{23564}^{aac} x_2 x_3 x_5 x_6 x_4 (x_3 - x_4)^2$$

$$C_{614}^b x_6 x_1 x_4 (x_1 - x_4)$$

$$E_{1234}^{bb} x_1 x_2 x_3 x_4 (x_2 - x_4)(x_2 - x_3)$$

$$G_{345}^c x_3 x_4 x_5 (1 - x_3)^3 (x_4 - x_5)^2$$

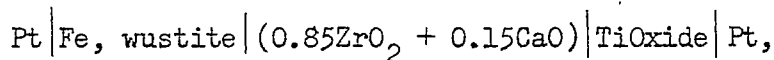
The use of the extended Redlich Kister equations in phase equilibria work is very involved and will not be explained here. However several investigations of power series use in binary systems will be described in the next sections and a short look at a ternary system will be taken in the final section.

TITANIUM DIOXIDE

The first example of the application of Redlich Kister power series to the description of phase equilibria is somewhat trivial but serves as good tutorial example of the methods used.

The rutile phase of titanium dioxide exists over the temperature range of 800°K to its melting point at 2143°K. Rutile can be reduced a moderate amount so that the composition range over which the integrity of the rutile crystal structure is maintained is from TiO_2 to $\text{TiO}_{1.992}$ ³⁴. For the sake of thermodynamic calculations the reduced rutile will be considered as a solution of titanium metal dissolved in titanium dioxide.

In order to obtain a power series that represents a thermodynamic property, the first thing that is needed is experimentally measured values of the thermodynamic quantity. Blumenthal and Whitmore³⁵ have used a solid electrolyte electrochemical cell,



to measure potentials which can be related to the equilibrium oxygen pressures over titanium oxides of different stoichiometries. The values they obtained for oxygen pressures over $\text{TiO}_{1.992}$ at several temperatures are given in Table 5.

Normally if the measured activities or pressures were those of one of the solution components, a power series equation for the logarithm of the activity coefficient could be fit directly. In this case the measured values can be related to the

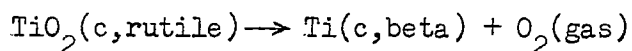
Table 5. Equilibrium Oxygen Pressures Over $\text{TiO}_{1.992}$ From EMF Data

Temperature(°K)	Partial Pressure O_2 (Atm.)
1123	2.36×10^{-23}
1173	9.95×10^{-22}
1223	3.03×10^{-20}
1273	7.16×10^{-19}
1323	1.37×10^{-17}

Table 6. Equilibrium Constants for the Reaction
 $\text{TiO}_2^{(c)} \rightarrow \text{Ti}(c) + \text{O}_2(g)$

Temperature(°K)	K_{eq}
1173	2.8507×10^{-33}
1273	5.7239×10^{-30}
1323	1.6558×10^{-28}
1735	1.0782×10^{-19}

activities of the solution components by the following reaction and equilibrium constant:



$$K_{eq} = \frac{a_{\text{Ti}} P_{\text{O}_2}}{a_{\text{TiO}_2}}$$

Equilibrium constants can be calculated at the temperatures of the experimental data from the standard thermodynamic properties in table 7. The calculated equilibrium constants appear in table 6 .

Chemists are quite used to thinking about solutions of solid solutes dissolved in liquid solvents. The solutes in these solutions normally dissolve as molecules or they dissociate into ions. In a solid solution a dissolved molecule can dissociate into atoms and each fragment of the molecule can behave as an independent solute species. When titanium dioxide dissolves in nearly pure titanium metal, the oxygen atoms will occupy interstitial positions in the titanium lattice and will no longer be associated with a particular titanium atom. The effective molecular weight of titanium dioxide which contributes one mole of independent solute species for each mole of material dissolved is half that of TiO_2 and has the formula $\text{Ti}_{.5}\text{O}$.

The effective molecular weight of titanium metal dissolved in nearly pure titanium dioxide can be determined from the Henry's Law

Table 7. Standard Thermodynamic Properties

	C _p equation							
	H ₁₀₀₀ ^o -H _{298.15} ^o	H ₁₀₀₀ ^o	Φ ₁₀₀₀	C ₁	10 ³ C ₂	10 ⁶ C ₃	10 ⁹ C ₄	10 ¹² C ₅
TiO ₂ (c, rutile)	46.940	-897.81	82.320	17.50	3.208	-0.6238	0.4187	-0.1087
TiO ₂ (liquid)	46.940	-839.56	107.10	21.0				
Ti(c, beta)	19.062	25.058	49.869	6.821	1.096	0.5772	0.3882	-0.2635
Ti(liquid)	19.062	39.924	56.605	8.5				
O ₂ (gas)	22.707	22.707	220.77	8.334	1.141	0.9701	0.7151	-0.1935

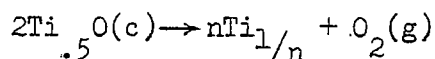
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Enthalpies in kJ/mole; Free Energy Function in J/mole°K

C_p equation is C_p = C₁ + C₂(T-1000) + C₃(T-1000)² . . .

Values taken from JANAF Tables

behaviour of the titanium metal activity. In the Henry's Law region of a solution the activity of the dilute component will be proportional to its mole fraction and the proportionality constant is the Henry's Law constant. If an arbitrary molecular weight for titanium is assumed, the following reaction can be written:



and the following equations deduced:

$$a_{\text{Ti}_{1/n}} = k x_{\text{Ti}_{1/n}} \quad (\text{Henry's Law})$$

$$a_{\text{Ti}_{1/n}}^n = k^n x_{\text{Ti}_{1/n}}^n$$

$$a_{\text{Ti}_{1/n}}^n = \frac{K_{\text{eq}} a_{\text{Ti}_{.5}\text{O}}^2}{P_{\text{O}_2}}$$

$$k^n x_{\text{Ti}_{1/n}}^n = \frac{K_{\text{eq}} a_{\text{Ti}_{.5}\text{O}}^2}{P_{\text{O}_2}}$$

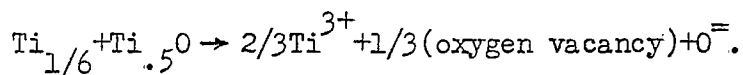
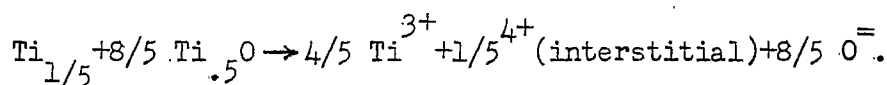
Blumenthal and Whitmore determined the equilibrium oxygen pressure at 1173°K for $\text{TiO}_{1.992}$ and $\text{TiO}_{1.998}$ and found that it increased by a factor of 1900. The value of $a_{\text{Ti}_{.5}\text{O}}$ changes very little over this range of composition and the mole fraction of $\text{Ti}_{1/n}$ changes by a factor of 4 no matter what the value of n . The value of n is calculated as follows:

$$\frac{k^n x_{\text{Ti}_{1/n}}^n (1.992)}{k^n x_{\text{Ti}_{1/n}}^n (1.998)} = \frac{\frac{\text{Keq } a_{\text{Ti}_{.5}\text{O}}^2}{\text{Po}_2 (1.992)}}{\frac{\text{Keq } a_{\text{Ti}_{.5}\text{O}}^2}{\text{Po}_2 (1.998)}}$$

$$\left(\frac{x_{\text{Ti}_{1/n}} (1.992)}{x_{\text{Ti}_{1/n}} (1.998)} \right)^n = \frac{\text{Po}_2 (1.998)}{\text{Po}_2 (1.992)}$$

$$(4)^n = 1900, n = 5.45$$

The value of n can be chosen to be either five or six corresponding to the formulas $\text{Ti}_{1/5}$ or $\text{Ti}_{1/6}$. The solution of titanium metal in $\text{Ti}_{.5}\text{O}$ is postulated to proceed by one or both of the following reactions:



Both equations result in the formation of one mole of independent solute species for each mole of dissolved titanium and both give Ti^{3+} ions which are the electron donating impurities responsible for the n -type semiconducting properties of reduced rutile.

Since Raoult's Law is obeyed by the major component, $\text{Ti}_{.5}\text{O}$ and Henry's Law is obeyed by the minor component, $\text{Ti}_{1/5}$ or $\text{Ti}_{1/6}$, the acti-

vities are varying linearly with mole fraction and there is little to be gained by fitting more than one power series coefficient for $\log \gamma$. One coefficient for $\log \gamma$ at 1173°K can be exactly determined by an equilibrium constant and one oxygen pressure value:

$$K_{eq} = \frac{P_{O_2} a_{Ti_{1/5}}^5}{a_{Ti_{.5}O}^2} = \frac{P_{O_2} \gamma_{Ti_{1/5}}^5 x_{Ti_{1/5}}^5}{\gamma_{Ti_{.5}O}^2 x_{Ti_{.5}O}^2}$$

$$5 \log \gamma_{Ti_{1/5}} - 2 \log \gamma_{Ti_{.5}O} = \log \left[\frac{K_{eq} x_{Ti_{.5}O}^2}{P_{O_2} x_{Ti_{1/5}}^5} \right]$$

The one coefficient Redlich Kister equations for $\log \gamma$ are:

$$\log \gamma_{Ti_{.5}O} = A(1 - x_{Ti_{.5}O})^2, \quad \log \gamma_{Ti_{1/5}} = A x_{Ti_{.5}O}^2.$$

Substitution of these equations into the previous one gives:

$$A \left[5 x_{Ti_{.5}O}^2 - 2(1 - x_{Ti_{.5}O})^2 \right] = \log \left[\frac{K_{eq} x_{Ti_{.5}O}^2}{P_{O_2} x_{Ti_{1/5}}^5} \right]$$

For the oxygen pressure, equilibrium constant, and mole fraction at 1173°K and $TiO_{1.992}$ the value of A is:

$$A(\log \gamma, Ti_{1/5}) = -.313164$$

By a similar procedure, the value of A at 1173°K for $Ti_{1/6}$ can be calculated:

$$A(\log \gamma, Ti_{1/6}) = -4.8732 \times 10^{-4}.$$

Although the coefficients were determined at the $TiO_{1.992}$ composition, the power series equations are valid over the entire rutile composition range. As a check the equilibrium oxygen pressure over $TiO_{1.998}$ can be calculated and compared with the experimental value. The Redlich Kister equations are:

$$\log \gamma_{Ti_{.5}O} = A(1 - x_{Ti_{.5}O})^2 \text{ and } \log \gamma_{Ti_{1/5}} = Ax_{Ti_{.5}O}$$

The mole fraction of $Ti_{.5}O$ at $TiO_{1.998}$ for the $Ti_{1/5}$ case is .997504 and the activities are $a_{Ti_{.5}O} = .997500$ and $a_{Ti_{1/5}} = 1.21811 \times 10^{-3}$. The calculated equilibrium oxygen pressure at 1173°K is:

$$P_{O_2} = \frac{K_{eq} a_{Ti_{.5}O}^2}{a_{Ti_{1/5}}^5} = 1.067 \times 10^{-18} \text{ atm.}$$

This compares well with the experimental value 1.9070×10^{-18} atmospheres at this temperature and composition³⁵.

The enthalpy of this solution can be determined from the temperature dependence of the activities. A form of the Gibbs-Helmholtz equation:

$$\frac{\partial \log \gamma}{\partial 1/T} = \frac{H^\circ}{2.303R}$$

gives the temperature dependence of the activity or activity coefficient in terms of the enthalpy of the solution. The $\log \gamma$ coefficients at 1273°K are $A(\log \gamma, \text{Ti}_{1/5}) = -.222985$ and $A(\log \gamma, \text{Ti}_{1/6}) = 7.49602 \times 10^{-2}$. By use of a modified Gibbs-Helmholtz equation:

$$\frac{\Delta A(\log \gamma)}{\Delta 1/T} = \frac{A(H)}{2.303R}$$

The value of the enthalpy coefficients are:

$$A(H, \text{Ti}_{1/5}) = -2.59 \times 10^4 \text{ J/mole and } A(H, \text{Ti}_{1/6}) = -2.16 \times 10^4 \text{ J/mole}$$

These coefficients for enthalpy can be used to calculate $\log \gamma$ coefficients at any other temperature via the following equation:

$$A(\log \gamma, T_2) = \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \frac{A(H)}{2.303R} + A(\log \gamma, T_1).$$

With these values for enthalpy and $\log \gamma$ coefficients and the calculated equilibrium constants the activities of both components and the equilibrium oxygen pressure can be calculated at any temperature and composition over which the rutile phase of titanium dioxide exists.

POTASSIUM OXIDES

The high temperature thermodynamic behaviour of potassium oxides is of particular interest in molten carbonate fuel cell chemistry where oxygen dissolved in the Li_2CO_3 - K_2CO_3 mixtures results in the formation of some potassium oxide. The phase equilibria of potassium oxides is also of interest in the operation of coal fired magnetohydrodynamic channels where potassium metal is used to increase the conductivity of the working plasma.

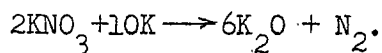
Three compounds of potassium and oxygen are known to exist: potassium monoxide, (K_2O); potassium peroxide, (K_2O_2); and potassium superoxide, (KO_2).

Potassium Monoxide is the most reactive of the oxides, it is difficult to keep pure, and is so corrosive at high temperatures that reaction with most crucible materials interferes with accurate thermodynamic measurements. The potassium oxide system will be treated as a solution of $\text{KO}_{.5}$ (l) and O (l) in equilibrium with the solid compounds. The molecular weight of $\text{KO}_{.5}$ was chosen because of the solution behaviour of K_2O with SiO_2 and Al_2O_3 and so that the power series equations from this system could be combined with those of the other systems. The selection of O (l) will be discussed later.

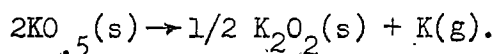
The generally accepted value for the enthalpy of formation of $\text{KO}_{.5}$, -180.75 kJ/mole, comes from a single reported heat of solution³⁶.

Attempts to obtain a phase diagram using this value indicate the possibility that this value is in error.

The original records from experiments with potassium monoxide heated in a platinum effusion cell in a mass spectrometer were obtained from Dr. Thomas Ehlert of Marquette University, Milwaukee, WI. In Dr. Ehlert's experiments, solid K_2O was formed by the reaction^{37,38}:

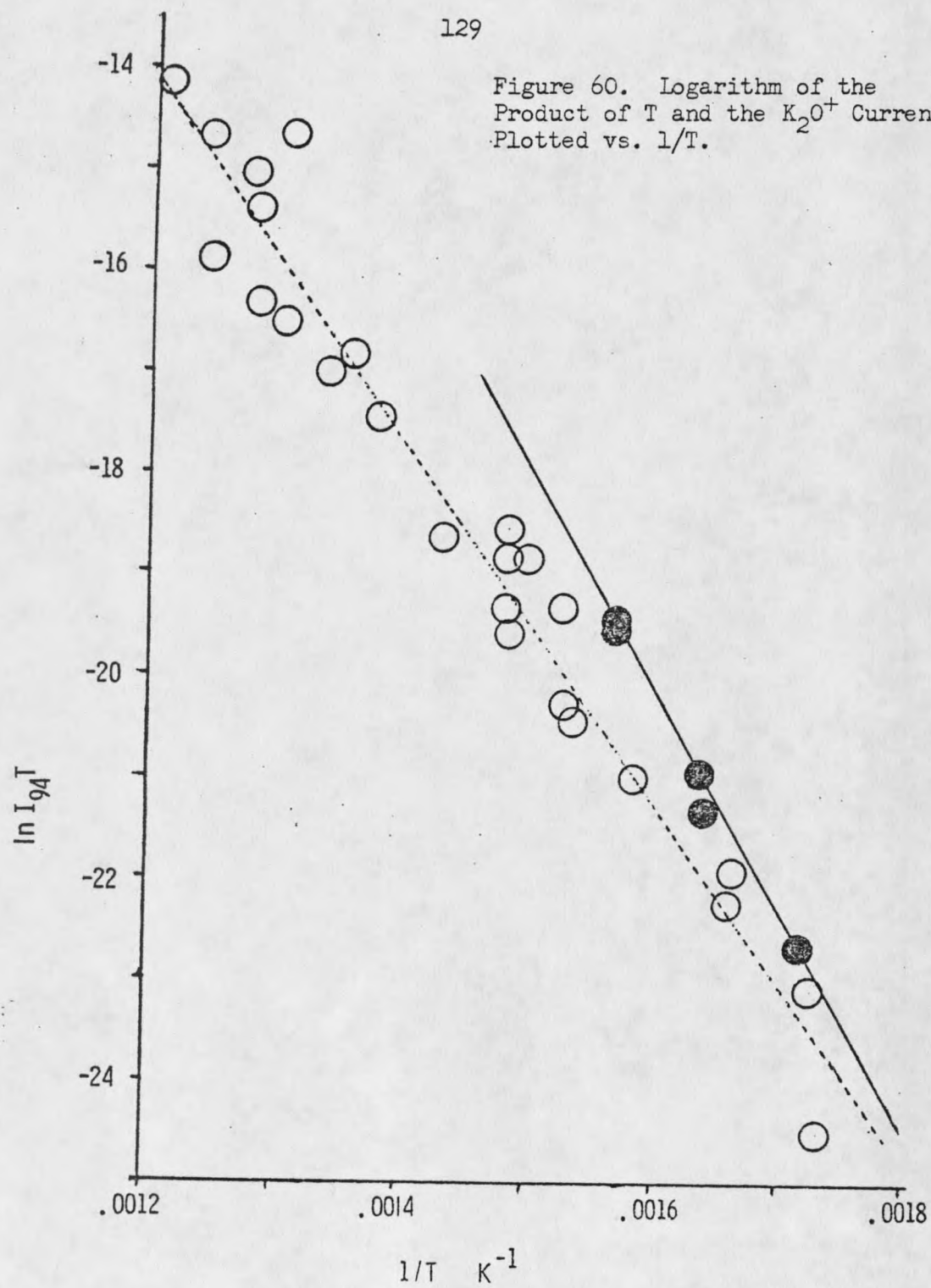


The potassium nitrate was reacted with excess potassium metal; the unreacted portion of which was distilled off at 500°K. This resulted in high potassium ion currents in the mass spectrometer and eliminated the possibility of measuring equilibrium potassium pressures. These would have been of value in determining the monoxide enthalpy from the predominant decomposition reaction:

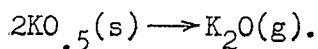


However good ion currents for K_2O^+ could be measured and the enthalpy of formation of solid potassium monoxide could be determined from its heat of sublimation and an independently determined value of the heat of formation of K_2O gas³⁹. Figure 60 shows two separate experiments for which the logarithm of K_2O^+ current times tempera-

Figure 60. Logarithm of the Product of T and the K_2O^+ Current Plotted vs. $1/T$.



ture is plotted against reciprocal temperature. Since equilibrium pressures can be related to the current by pressure = (sensitivity constant) • (current) • (temperature), the enthalpy of sublimation can be calculated from the Gibbs-Helmholtz equation and the slopes in figure 60. The sublimation reaction is:



The equilibrium constant is:

$$K_{\text{eq}} = \frac{P_{\text{K}_2\text{O}(\text{g})}}{a_{\text{K}_2\text{O}(\text{s})}^2} = P_{\text{K}_2\text{O}(\text{g})}.$$

The Gibbs-Helmholtz equation is:

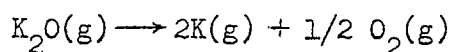
$$\Delta H_{\text{subl}} = R \frac{\Delta \log K_{\text{eq}}}{\Delta 1/T} = R \cdot (\text{slope}).$$

This is designated as a second law treatment.

The five values shown as solid circles came from what appeared to be the better experiment and the slope of the least squares line through these points was used to calculate a ΔH_{298}° of sublimation of 181 kJ/mole. In conjunction with a previously measured value of $\Delta H_{f,298}^\circ$ for $\text{K}_2\text{O}(\text{g})$ of -142 kJ/mole³⁹, the value of $\Delta H_{f,298}^\circ$ for

$\text{KO}_{.5}(\text{s})$ is determined to be -162 kJ/mole .

Another value of $\Delta H_{f,298}^\circ$ for $\text{KO}_{.5}(\text{s})$ can be obtained from a third law treatment if the value of the sensitivity constant is known. An experimental value for the sensitivity constant has been determined from a mass spectrometric study of the equilibrium³⁹:



This value has been corrected for the size of the effusion orifice and the detector gain differences⁴⁰. The resulting value is 2.975. The value of $I_{94}^+ T$ at 600°K is 3.765×10^{-10} and the corresponding pressure is 1.12×10^{-9} . This pressure is equal to the equilibrium constant for the sublimation of K_2O and is also equal to:

$$K_{\text{eq}} = \frac{P_{\text{K}_2\text{O}(\text{g})}}{(1)^2} = 10^{-\Delta H_{\text{subl},298}/2.303RT} 10^{\Delta \bar{\Phi}_{600}/2.303R}$$

The value of $\Delta \bar{\Phi}_{600}$ can be calculated from the heat capacities and $\bar{\Phi}_{1000}$ values for $\text{KO}_{.5}(\text{s})$ and $\text{K}_2\text{O}(\text{g})$ and the equation:

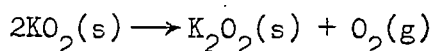
$$\bar{\Phi}_T = \bar{\Phi}_{T_0} - [H(T_0) - H(298.15)] \left(\frac{1}{T} - \frac{1}{T_0} \right) - \frac{1}{T} \int_{T_0}^T C_{p,d} T + \int_{T_0}^T \frac{c_p}{T} dT$$

to correct to 600°K . The free energy functions at 600°K are 62.00 and 278.06 J/mole $^\circ\text{K}$ for $\text{KO}_{.5}(\text{s})$ and $\text{K}_2\text{O}(\text{g})$ respectively and $\Delta \bar{\Phi}_{600}$ equals 154.06 J/mole $^\circ\text{K}$. The calculated value for $\Delta H_{\text{subl},298}$ is -195

kJ/mole and the third law value for $\Delta H_{f,298}^\circ$ is -169 kJ/mole for $\text{KO}_{2.5}(\text{s})$. For table 8 the value has been rounded off to -170 +5 kJ/mole. This value agrees reasonably well with the second law heat and has been adopted for the calculation reported here.

Potassium Peroxide The enthalpy of formation of K_2O_2 reported in the JANAF³² tables refers back to the data of Centnerszwer and Blumenthal^{41,42}, but their data for the previous thought to exist compound K_2O_3 are for the temperature range 753-912°K. These temperatures are above the KO_2 - K_2O_2 eutectic. De Forcrand⁴³ reports a heat of solution for K_2O_3 which was used by Riley⁴⁴ to calculate an enthalpy of formation of -489.53 kJ/mole for $\text{K}_2\text{O}_2(\text{s})$.

Measurements of oxygen pressures over KO_2 provide an even better means of calculating this enthalpy of formation via the reaction:



Second law calculations for the heat of this reaction from two separate experimental investigations^{44,45} yield 61.76 and 65.27 kJ/mole respectively.

These two studies are in excellent agreement on the oxygen gas pressure at 573°K. A third law treatment at this temperature using the estimated entropy for $\text{K}_2\text{O}_2(\text{s})$ given in JANAF³² gives a heat of reaction at 298°K of 75.55 kJ/mole. The heats of reaction 65.27 and 75.55 kJ/mole and the accepted heat of formation for $\text{KO}_2(\text{s})$ of

Table 8.

Thermodynamic values for the pure materials.^a

Material	$H^\circ_{298.15}$	H°_{1000}	$S^\circ_{298.15}$	Φ°_{1000}	equation ^b		
					C_p C_1	$10^3 C_2$	$10^6 C_3$
KO ₂ (s)	-284512 ± 2000	-221589	122.499 ± 4	166.067	95.502	3.066	-29.415
K ₂ O ₂ (s)	-495411 ± 3000	-408020	109.923 ± 4	167.830	147.029	60.799	-8.406
KO _{0.5} (s)	-170000 ± 5000	-140708	51.004 ± 6	75.689	38.062	4.017	
KO _{0.5} (l)	-159536 ± 9000	-123972	59.918 ± 9	87.990	47.907	7.531	
O (l)	-8397 ^c	11648	31.367 ^c	45.719	29.288	2.092	
K ₂ O (g)	-142256 ± 15000	-98480	265.805 ± 8	297.524	62.358		
KO (g)	65270 ± 12000	91575	238.112 ± 2	256.722	38.200	1.168	-0.097
K ₂ O ₂ (g)	-297669 ± 15000	-249922	271.460 ± 10	305.432	62.358 ^d		

a) All values are given in SI units, J, K, and moles. The number of figures given was selected to reproduce equilibrium constant calculations to five or six significant figures, and bears no relationship to the accuracy of the terms. Uncertainties are estimated for H°_{298} and S°_{298} .

b) The equation for heat capacities is $C_p = C_1 + C_2(T-1000) + C_3(T-1000)^2$.

c) A defined standard state is used for O (l), and there is nothing to measure the uncertainty against.

d) An additional Einstein heat capacity term at $h\nu/k = 1266$ K is added for K₂O₂ (g).

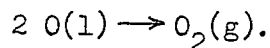
-284.51 kJ/mole yield heats of formation for $K_2O_2(s)$ of -503.75 and -493.49 kJ/mole. The average of these values and -489.53 from the heat of solution of K_2O_3 gives $\Delta H_{f,298}^\circ = -495.58$ kJ/mole for $K_2O_2(s)$. The free energy function and heat capacity in table 8 are from the JANAF tables³².

Potassium Superoxide The thermodynamic values for $KO_2(s)$ in table 8 are essentially those of the JANAF tables³². The heat capacity equation is a least squares fit of the JANAF high temperature extrapolated values.

Traces of KOH dissolved in solid KO_2 are virtually impossible to eliminate. Besides this impurity, the decomposition of $KO_2(s)$ forms some $K_2O_2(s)$ before the melting point of KO_2 is reached even in the presence of oxygen at one atmosphere. Melting points reported in the literature range from 653 to 838°K^{41,46-50}. The best values, 823 and 838°K^{47,50} are extrapolations that take account of the potassium hydroxide impurity content. Taking account of both hydroxide and potassium peroxide impurities should give a still higher melting point. For this work the temperature at which solid KO_2 is in equilibrium with liquid of the same composition is estimated to be 845°K.

Hypothetical Oxygen Liquid The use of a hypothetical material such as oxygen liquid at atmospheric pressure and temperatures near 1000°K is justified simply by the convenience its use provides and

by the fact that it can be very easily related to reality. First since potassium and oxygen form liquids with K to O ratios from 2:1 to 1:2, a simple means of treating this variable composition liquid as a solution of two materials is needed. $KO_{.5}(l)$ and $O(l)$ have been chosen to fulfill this need. Second $O(l)$ can be easily related to the equilibrium oxygen gas pressure over the liquid via an equilibrium constant for the reaction:



This equilibrium constant can be calculated from the known thermodynamic properties of oxygen gas and the arbitrarily chosen thermodynamic properties of oxygen liquid. The standard enthalpy was picked so that it would be similar to that of $O_2(g)$ at 1000°K and 500 bars pressure. The free energy function was chosen so that the activity of $O(l)$ would vary smoothly through out the entire composition range of the phase diagram. The standard state properties of $O(l)$ are given in table 8.

Activity Coefficients Leffler and Wiederhorn⁵¹ have measured equilibrium oxygen pressures over potassium oxide liquids at 773, 873, and 923°K. They measured these pressures over the composition range in mole fraction from $x_{KO_{.5}} = .877$ to $x_{KO_{.5}} = .441$. However the values from $x_{KO_{.5}} = .877$ to $x_{KO_{.5}} = .6667$, (the K_2O composition),

appear to be in error, possibly because one of the vaporization species is $K_2O_2(g)$ which may have reacted with their quartz crucible holder to release additional oxygen.



The oxygen pressure values in the region between the K_2O_2 and KO_2 compositions were used to determine activities for $O(l)$ via the equilibrium constant described above. The $\log \gamma_{O(l)}$ values calculated from these activity values and the corresponding mole fractions are shown in table 9.

Three values for $\log \gamma_{KO_{.5}(l)}$ were estimated by assuming that the solution of $K_2O_2(l)$ in $K_2O(l)$ is ideal. For the Raoult's Law region the activity of $K_2O(l)$ will be equal to its mole fraction in the $K_2O(l) - K_2O_2(l)$ system. At $x_{K_2O(l)} = .9, .8, .7$ the activity of $K_2O(l) = .9, .8, .7$ and since $a_{KO_{.5}(l)}^2 = a_{K_2O(l)}$ the activity of $KO_{.5}(l) = .949, .894, .837$. For the $K_2O(l) - K_2O_2(l)$ system the mole fractions $x_{K_2O(l)} = .9$ and $x_{K_2O_2(l)} = .1$ correspond to 1.8 + .2 moles of $KO_{.5}(l)$ for each .1 moles of $O(l)$ or $x_{KO_{.5}(l)} = .952$. For $x_{K_2O(l)} = .8, .7$ the mole fraction of $KO_{.5} = .909, .870$. The following values obtain:

Table 9. Activities and Log γ 's for O(1).

773°K			873°K			923°K		
$x_{\text{KO},5}$	$a_{\text{O}(1)}$	$\log \gamma_{\text{O}(1)}$	$x_{\text{KO},5}$	$a_{\text{O}(1)}$	$\log \gamma_{\text{O}(1)}$	$x_{\text{KO},5}$	$a_{\text{O}(1)}$	$\log \gamma_{\text{O}(1)}$
.568	2.3978×10^{-4}	-3.2557	.645	3.5764×10^{-4}	-2.9968	.645	4.4632×10^{-4}	-2.9006
.541	3.4331×10^{-4}	-3.1261	.599	4.3416×10^{-4}	-2.9655	.613	5.4052×10^{-4}	-2.8549
.524	4.4858×10^{-4}	-3.0258	.571	6.3554×10^{-4}	-2.8293	.585	6.4162×10^{-4}	-2.8108
.518	5.4940×10^{-4}	-2.9432	.556	6.9620×10^{-4}	-2.8046	.565	6.9143×10^{-4}	-2.7987
.508	6.1131×10^{-4}	-2.9057	.538	7.6088×10^{-4}	-2.7833	.552	7.9004×10^{-4}	-2.7536
.498	7.5824×10^{-4}	-2.8209	.529	8.3673×10^{-4}	-2.7504	.538	8.4683×10^{-4}	-2.7368
.488	8.4774×10^{-4}	-2.7810	.515	8.9879×10^{-4}	-2.7321	.448	2.8694×10^{-3}	-2.2841
.469	9.2865×10^{-4}	-2.7572	.503	9.4266×10^{-4}	-2.7220			
.455	1.0173×10^{-3}	-2.7290	.483	1.2711×10^{-3}	-2.6093			
.442	2.1108×10^{-3}	-2.4222	.448	2.0098×10^{-3}	-2.4388			
.441	2.9366×10^{-3}	-2.2796	.446	2.4614×10^{-3}	-2.3523			

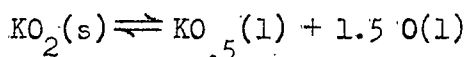
$x_{\text{KO}_{.5}}(1)$	$\log \gamma_{\text{KO}_{.5}}(1)$
.952	-1.69×10^{-3}
.909	-7.06×10^{-3}
.870	-1.68×10^{-2}

An alternative manner in which to treat the ideality of this solution is to say that oxygen reacts with $\text{KO}_{.5}$ to form $\text{K}_2\text{O}_{2.2}$ and for nearly pure $\text{KO}_{.5}$ the expected activity is:

$$a_{\text{KO}_{.5}} \approx (x_{\text{KO}_{.5}} - 2x_{\text{O}})/(1 - 2x_{\text{O}}) = (3x_{\text{KO}_{.5}} - 2)/(2x_{\text{KO}_{.5}} - 1)$$

This expression comes from the fact that two molecules of $\text{KO}_{.5}$ react with each atom of O to form $\text{K}_2\text{O}_{2.2}$. The values of $\log \gamma_{\text{KO}_{.5}}$ calculated this way are very close to those calculated by the previous method and although the first method was actually used in the phase diagram calculation, the second method was presented in the literature⁵².

Tsentsiper et. al.^{47,50} in their phase diagram studies of potassium oxides, conducted experiments which allow the estimation of the composition and temperature of a point on the curve for liquid in equilibrium with solid KO_2 . This point at $x_{\text{KO}_{.5}} = .486$ and $T = 733^\circ\text{K}$ for the equilibrium:



and the equilibrium constant:

$$K_{eq} = \frac{\gamma_{KO_{.5}} x_{KO_{.5}} \gamma_O^{1.5} x_O^{1.5}}{1}$$

allow the calculation of a value for $\log \gamma_{KO_{.5}} \gamma_O^{1.5}$.

$$\log \gamma_{KO_{.5}} \gamma_O^{1.5} = \log \frac{K_{eq}}{(.486)(.514)^{1.5}}$$

The melting point of KO_2 , estimated to be 845°K, allows the calculation of a similar value at $x_{KO_{.5}} = .4$:

$$\log \gamma_{KO_{.5}} \gamma_O^{1.5} = \log \frac{K_{eq}(845)}{(.4)(.6)^{1.5}}$$

The potassium oxygen ratio of K_2O_2 corresponds to $x_{KO_{.5}} = .6667$ and the melting point of K_2O_2 is reported to be 763°K^{41,42}. A value for $\log \gamma_{KO_{.5}}^2 \gamma_O$ can be obtained from the equilibrium constant for K_2O_2 in equilibrium with liquid at this temperature as was done for the melting point of KO_2 . However a mixed least squares fit of the $\log \gamma_{O(1)}$, $\log \gamma_{KO_{.5}(1)}$, $\log \gamma_{KO_{.5}(1)} \gamma_{O(1)}^{1.5}$ values and this value for $\log \gamma_{KO_{.5}(1)}^2 \gamma_{O(1)}$ showed that the oxygen pressure measurements⁵¹, ($\log \gamma_{O(1)}$ values), were inconsistent with this K_2O_2 melting point

value. When this point was omitted from the least squares calculation the activity coefficient equation that was obtained resulted in a calculated melting point below 650°K and the $K_2O_2 - KO_2$ eutectic temperature was well below 633°K. This is inconsistent with Riley's⁴⁴ observation of solid-solid-gas equilibrium in this composition region at 633°K. This conflict between the measured oxygen pressures and the reported melting point of $K_2O_2(s)$ was resolved by calculating the value of $\log \gamma_{KO_{1.5}}^2 \gamma_{O_2}$ for the K_2O_2 melting point at 700°K. Performing the least squares with this point at relatively low weight gave an activity coefficient power series with which the melting points of 683 and 865°K for K_2O_2 and KO_2 were calculated. The mixed least squares fit of the $\log \gamma$ values was performed after all the values had been corrected to 1000°K with the enthalpy equation described in the next section. The Redlich Kister power series equation for $\log \gamma$ is shown in table 10.

Enthalpy Equation Although the standard enthalpies of the solid compounds have been chosen, the enthalpies of the liquid components must be determined as a function of composition so that the temperature dependence of the activities can be calculated.

The heats of fusion for the potassium oxide compounds were estimated to be $16.74 \pm 8.4 \text{ kJ}$, ($4 \pm 2 \text{ kcal}$), per mole of potassium in the compound. The heat of fusion equals the difference between the enthalpy

Table 10. Redlich-Kister Coefficients for the $\text{KO}_{0.5}$ - O Liquid System.

	A	B	C	D	E	F
$\log_{10} \gamma_{1000}$	-9.213020	0.636777	-7.401393	-2.102460	29.207264	-19.554747
H (J mol ⁻¹)	-167664	-9966	-199623	-12185	1152339	941663

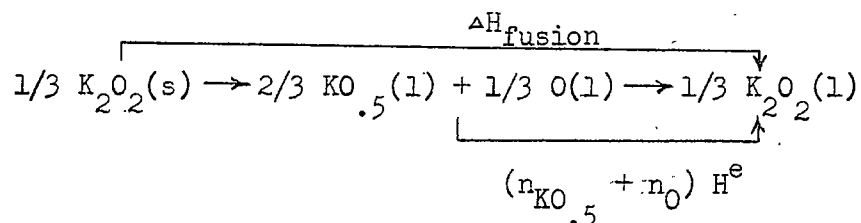
of the liquid and the enthalpy of the solid. The enthalpy of the liquid equals:

$$H_{\text{liquid}} = n_{\text{KO}.5} H_{\text{KO}.5}^{\circ} + n_{\text{O}} H_{\text{O}}^{\circ} + (n_{\text{KO}.5} + n_{\text{O}}) H^{\text{e}}$$

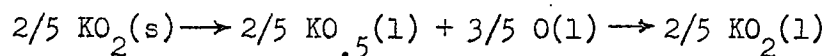
and

$$\Delta H_{\text{fusion}} = n_{\text{KO}.5} H_{\text{KO}.5}^{\circ} + n_{\text{O}} H_{\text{O}}^{\circ} + (n_{\text{KO}.5} + n_{\text{O}}) H^{\text{e}} - n_{\text{S}} H_{\text{solid}}^{\circ}$$

For the fusion reactions:

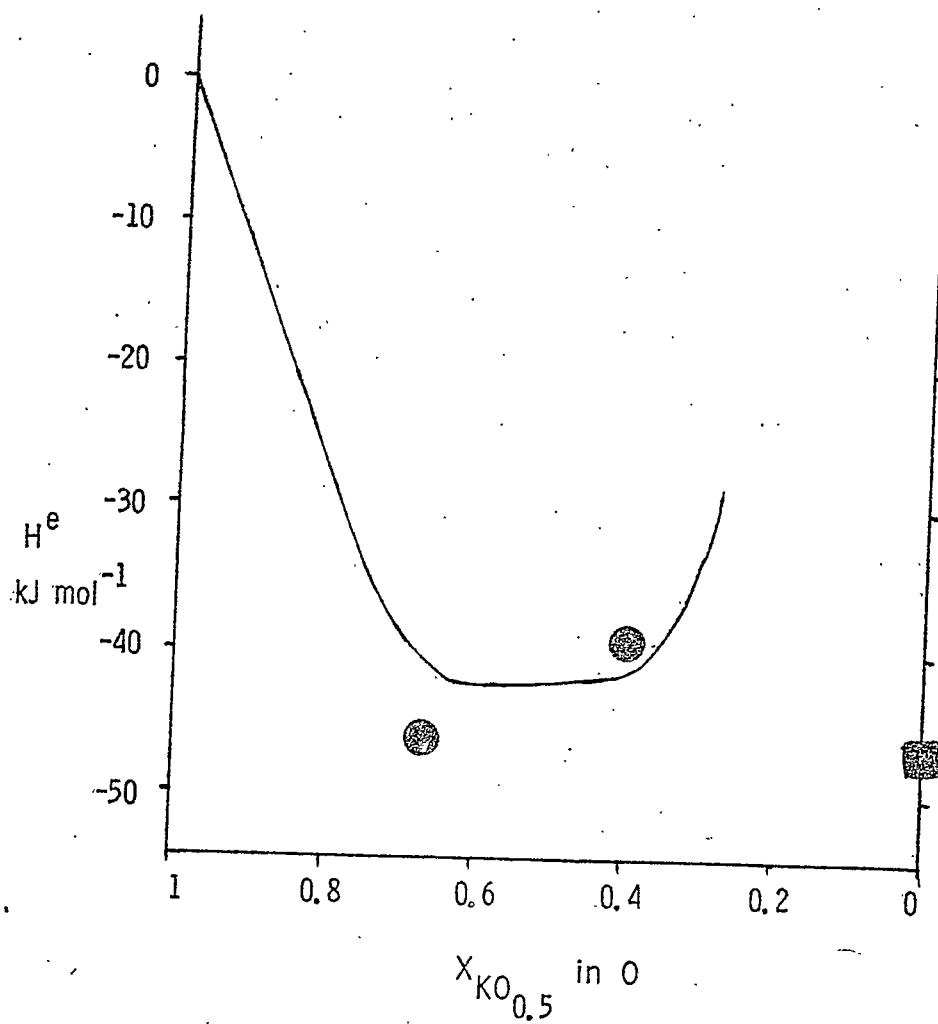


the ΔH at 1000°K for the first reaction can be calculated to be -57.24 kJ from the values in table 8. Then the excess enthalpy of mixing, H^{e} , at 1000°K equals $2/3(16.74) - 57.24 = -46.08 \text{ kJ/mole}$. For the fusion reactions:



The value of H^{e} at 1000°K is -39.34 kJ/mole. These two values for H^{e} are plotted at their appropriate compositions in figure 61.

Figure 61. Plot of Enthalpy Data for $\text{KO}_{0.5}$ - O Liquid System.



Earlier, in the discussion of the relationship of the partial molal Redlich Kister equations to the equation for the excess quantity the following equation was derived:

$$\bar{Y}_1 - Y_1^\circ = Y^e + x_2 \frac{\partial Y^e}{\partial x_1}$$

A similar equation is valid for $\bar{Y}_2 - Y_2^\circ$:

$$\bar{Y}_2 - Y_2^\circ = Y^e - x_1 \frac{\partial Y^e}{\partial x_1}$$

The intercept at $x_2=1$ of any line drawn tangent to the curve for Y^e will give a value for $\bar{Y}_2 - Y_2^\circ$ since

$$y = mx + b, m = \frac{dy}{dx}, b = y - x \frac{dy}{dx}$$

Leffler and Wiederhorn⁵¹ have measured oxygen pressures at three different temperatures near the composition $x_{\text{KO}.5} = .586$ and the value of $\bar{H}_2$ was calculated to be -46.57 kJ/mole at this composition. This means that a line tangent to the curve for H^e at $x_1 = .586$ should intercept the $x_1 = 0$ axis at -46.57 kJ.

The experiments of Leffler and Wiederhorn also indicate that $\bar{H}_2$ does not vary greatly between $x_1 = .45$ and $.60$ and this is not surprising since the mixing of $\text{KO}.5$ and KO_2 liquids is not expected to be highly exothermic.

A curve for H^e like that in figure 61 was drawn by hand by try-

ing to best fit the H^e values and the character observed for $\bar{H}_2$.

A number of points were taken off this hand drawn curve and a least squares fit was calculated. The actual curve shown in figure 61 is that determined from the least squares equation for enthalpy which is given in table 10.

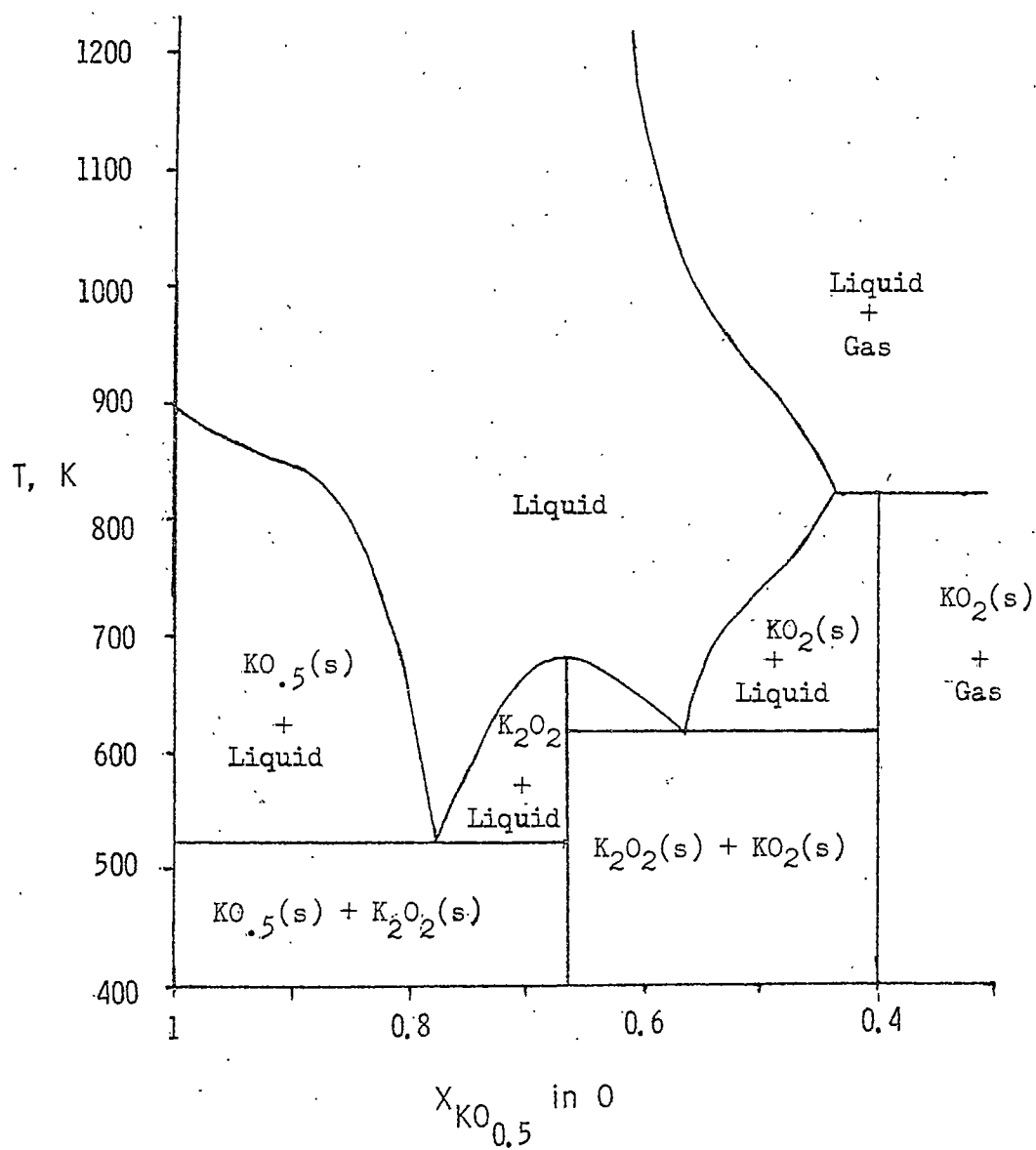
The lines of the phase diagram, figure 62, were calculated by the procedure described in the introduction. The $KO_{.5}$ liquidus line was calculated by finding the compositions for which the activity of $KO_{.5}(l)$ satisfy the equilibrium constants for $KO_{.5}(c) \rightleftharpoons KO_{.5}(l)$ at a series of temperatures. The temperatures and compositions of liquid in equilibrium with solid K_2O_2 were calculated by using the $\log \gamma$ and enthalpy Redlich Kister equations to find the activities of $KO_{.5}(l)$ and $O(l)$ that make the following equilibrium expression true:

$$K_{Temp.} = \frac{a_{KO_{.5}}^2 a_O}{a_{K_2O_2}} = a_{KO_{.5}}^2 a_O.$$

In this case a composition will be found on each side of the K_2O_2 composition for each temperature. The KO_2 liquidus curve comes from the $\log \gamma$ and enthalpy equations and the equilibrium constants for $KO_2(c) \rightleftharpoons KO_{.5}(l) + 1.5O(l)$.

The intersections of the liquidus curves correspond to the eutectic temperatures and compositions. The horizontal lines connect

Figure 62. Potassium Oxides Phase Diagram.



the three phases that are in equilibrium at these temperatures.

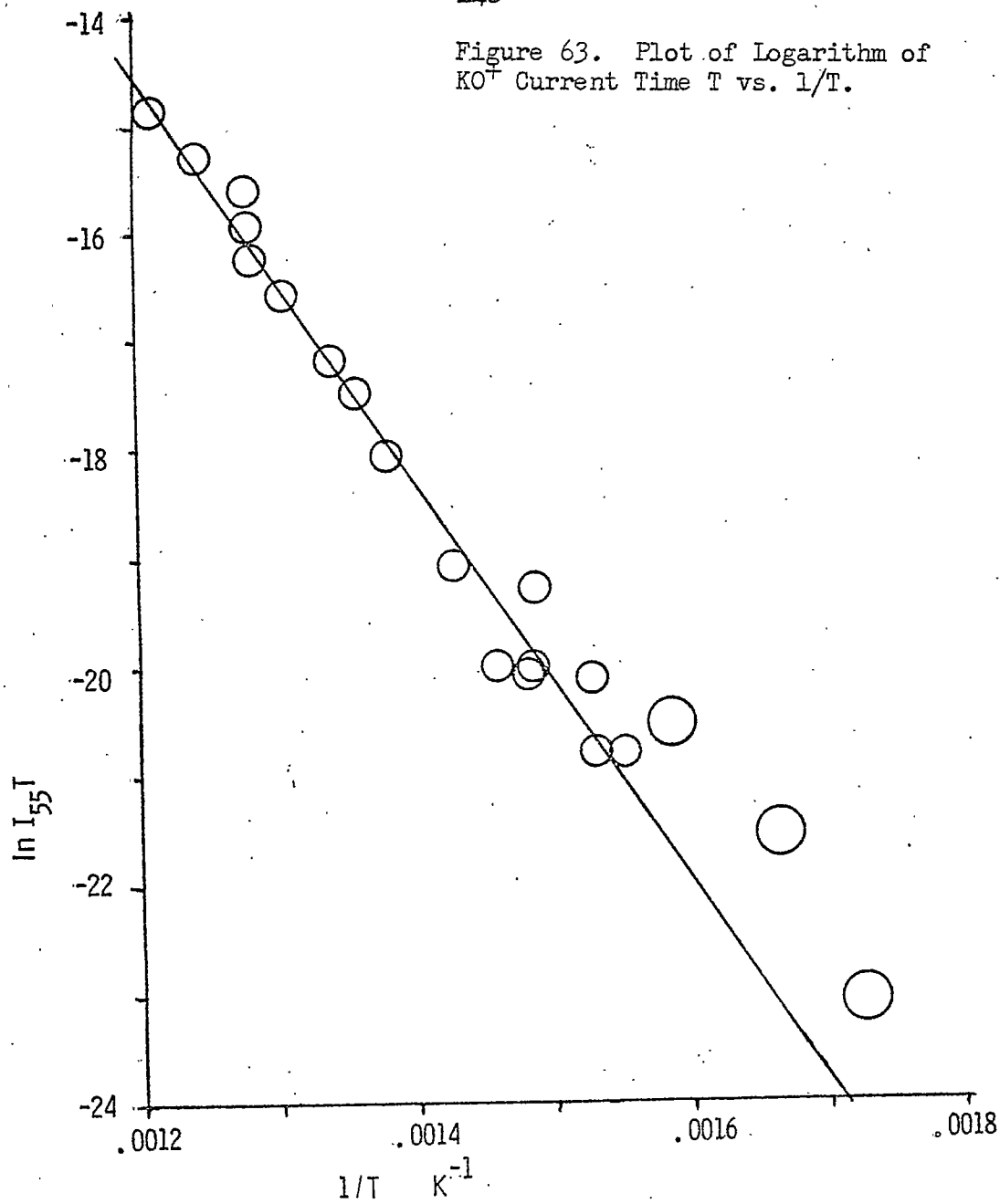
Equilibrium between liquid potassium oxide and oxygen gas at one atmosphere is obtained at the higher temperatures of the phase diagram near the composition of $\text{KO}_{2.5}$. This line was calculated by finding the temperatures and compositions at which the activities of O_2 satisfy the equilibrium expression:

$$K_{\text{Temp.}} = \frac{P_{\text{O}_2}}{a_{\text{O}}^2} = \frac{1}{a_{\text{O}}^2}.$$

The temperatures of the $\text{KO}_{1.5}$ - $\text{K}_2\text{O}_{2.5}$ and $\text{K}_2\text{O}_{2.5}$ - KO_2 eutectics from the phase diagram calculation are 525°K and 620°K respectively. The 525°K eutectic is supported by differential scanning calorimetric data which shows an endotherm at $520 \pm 10^\circ\text{K}$ for a sample of $\text{KO}_{1.5}$ in a pure gold crucible⁵³.

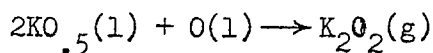
Thermodynamic Properties of $\text{K}_2\text{O}_2(\text{g})$ An additional bonus of the use of the mass spectrometric data of Dr. Ehlert was the chance to interpret the vaporization information to estimate the thermodynamic properties of $\text{K}_2\text{O}_2(\text{g})$. In addition to the K_2O^+ currents observed for the potassium oxide samples, currents of nearly equal magnitude were observed for KO^+ . This contrasts with the situation with K_2CO_3 sample where at higher temperatures the KO^+ current was an order of magnitude lower than the K_2O^+ current^{39,40}. Figure 63 shows a plot of $\ln(I_{\text{KO}^+})(T)$ vs. $1/T$ and a least squares line with a slope corre-

Figure 63. Plot of Logarithm of KO^+ Current Time T vs. $1/T$.



sponding to a heat of vaporization of 154 kJ/mole. This would correspond to a heat of formation of KO(g) of -65 kJ/mole which seriously disagrees with a previously determined value, +65 kJ/mole³⁹.

The most reasonable species that could be responsible for the KO^+ currents is $\text{K}_2\text{O}_2(\text{g})$. A second law treatment of liquid vaporization by the reaction:



gives $\Delta H_f^\circ = -310$ kJ/mole for $\text{K}_2\text{O}_2(\text{g})$. This value is supported by a third law calculation and leads to reasonable values for K_2O_2 vapor pressures. This vaporization process could also be responsible for the high oxygen pressures over heated K_2O_2 samples since it can react with glass or quartz to produce oxygen.

LITHIUM ALUMINATES

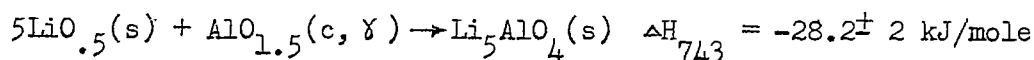
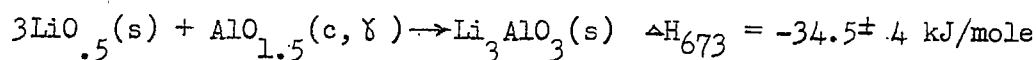
Although lithium monoxide is not as basic or corrosive as potassium monoxide, it is still reactive enough to react with aluminum oxide, a weak acid, to form a series of compounds. The best known and characterized compound is the meta-aluminate LiAlO_2 . The thermodynamics of this material is of particular interest since it is being used as a porous ceramic support for high temperature molten carbonate fuel cells. There is also a stable spinel structure on the alumina-rich side of the phase diagram^{54,55} which has the formula LiAl_5O_8 although it is stable over a substantial range of stoichiometry at high temperature^{56,57}. Two compounds have been identified and characterized on the lithium-rich side of the phase diagram. They have the formulas Li_3AlO_3 and Li_5AlO_4 ⁵⁸.

The molecular weights for lithium oxide and aluminum oxide that have been chosen for this study correspond to the formulas $\text{LiO}_{.5}$ and $\text{AlO}_{1.5}$. $\text{LiO}_{.5}$ will be designated as component one and $\text{AlO}_{1.5}$ will be designated as component two.

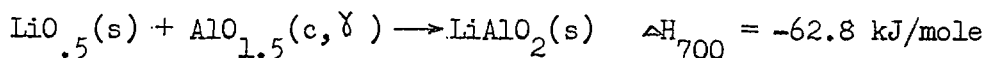
The standard thermodynamic properties of $\text{LiO}_{.5}(\text{s})$ are quite well established^{32,73,74}. The same is true for LiAlO_2 ⁵⁹ although the melting point in reference 59, 1883°K, is questionable. There is however a reasonable amount of evidence for an alternative melting temperature near 1973°K^{60,61}. The choices used for the standard thermodynamic properties of alpha, gamma, and liquid $\text{AlO}_{1.5}$ have been discussed in

the literature⁶². These selections are listed in table 11 along with heat capacity equations.

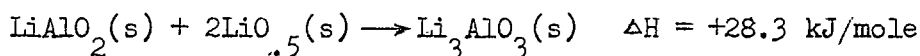
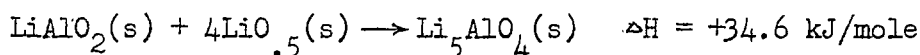
La Ginestra et. al.⁵⁸ have reported differential thermal analysis results for the heats of reaction:



From the information in table 11 the enthalpy change is calculated for the reaction:

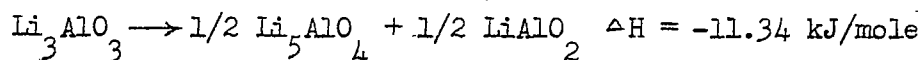


ignoring the slight variation of ΔH with temperature. The following reactions can now be written:



If ΔC_p is assumed to be zero the standard heats of formation of $\text{Li}_5\text{AlO}_4(\text{s})$ and $\text{Li}_3\text{AlO}_3(\text{s})$ can be calculated as -2350 and -1758 kJ/mole respectively.

These values can be used to calculate the heat for the disproportionation of Li_3AlO_3 to Li_5AlO_4 and LiAlO_2 .



Since this reaction occurs when Li_3AlO_3 is heated⁶³, it follows that if this reaction is exothermic Li_3AlO_3 is thermodynamically unstable at all temperatures. However the uncertainty of the ΔH reported by La Ginestra *et. al.*⁵⁸ for the formation of Li_3AlO_3 is almost enough to allow the disproportionation reaction to be endothermic and Li_3AlO_3 may be stable at 298°K. In any case, Li_3AlO_3 is not included in the high temperature phase diagram proposed here.

Li_5AlO_4 (c) is a thermodynamically stable phase even though its formation from LiAlO_2 and $\text{LiO}_{.5}$ is endothermic. It is stabilized by the entropy of mixing of the lithium and aluminum on the cationic sites rather than by its enthalpy.

There is essentially no enthalpy data for lithium aluminate liquids, however from the heats of reaction of $\text{LiO}_{.5}$ and $\text{AlO}_{1.5}$ to form solid it is reasonable to conclude that the most negative excess enthalpy of mixing for the liquid components will occur at a mole fraction near 0.5, the composition of LiAlO_2 . If LiAlO_2 melts at 1973°K the enthalpy of the solid at this temperature can be calculated to be -1020 kJ/mole from the information in table 11. JANAF⁵⁹ reports a $\Delta H_m = 88$ kJ/mole so that the enthalpy of the liquid will be -932 kJ/mole. This value is 41.5 kJ more negative than the sum

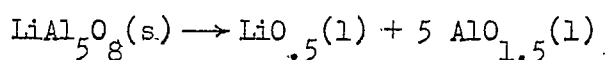
of one mole of each of the pure liquids at this temperature and corresponds to an excess enthalpy of mixing of $-41.5/2$ or -20.7 kJ/mole. An excess enthalpy curve which has a minimum of -20.7 kJ at $x = .5$ is represented by the Redlich Kister power series with the following coefficients:

$$A(H) = -82931, B(H) = 0, C(H) = +47095$$

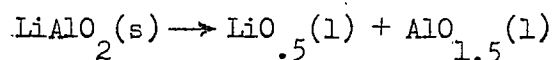
Venero and Westrum⁶⁴ have measured the heat capacity of solid LiAl_5O_8 from 7.4 to 541°K, which gives a value for $S_{298}^\circ = 149.79$ J/mole °K. The heat capacity at higher temperature can be estimated with little error by the sum $C_p(\text{LiO}_{.5}) + 5 C_p(\text{AlO}_{1.5})$. This data along with the value for the enthalpy of formation of LiAl_5O_8 at 968°K reported in reference 64 would give a usable set of thermodynamic values for the spinel, unfortunately they predict disproportionation to LiAlO_2 and corundum, $\text{AlO}_{1.5}(c, \infty)$, at all temperatures. However if the high temperature distribution of the lithium and aluminum ions is completely random in both the tetrahedral and octahedral sites of LiAl_5O_8 an additional 22.6 J/mole °K entropy of mixing can be added to the entropy and 298.15 °K and to the free energy function at 1000°K. Also there is an order-disorder transition in the LiAl_5O_8 crystal structure near 1563°K^{57,65} and if this transition is assumed to involve a ΔH of 10.7 kJ/mole and a ΔS of 4 J/mole °K, a reason-

able phase diagram can be obtained. The standard thermodynamic values chosen for the high temperature form of the spinel material are given in table 11.

Activity A eutectic is reported to occur between LiAl_5O_8 and LiAlO_2 at $x_1 = .45$ and $T = 1943^\circ\text{K}$ ⁵⁵. The equilibrium constants for the reactions:



and



yield values for $\log \gamma_1 \gamma_2^5 = -1.572$ and $\log \gamma_1 \gamma_2 = -1.376$ at this composition and temperature. These two values allow the calculation of $\log \gamma_2 = -.049$, $\gamma_2 = .893$, and $a_2 = 0.491$ for liquid alumina at $x_2 = .55$. Since the value of a_2 is only about 10% less than x_2 , it appears that the Raoult's Law region for $\text{AlO}_{1.5}$ extends out to a mole fraction of nearly .45 for $\text{LiO}_{.5}$.

The equilibrium constant for congruent melting of LiAlO_2 at 1973°K is .0117542 and the value of $\log \gamma_1 \gamma_2$ is -1.3278. By using the enthalpy equation discussed earlier this value can be corrected to $\log \gamma_1 \gamma_2 = -1.34470$ at 1943°K and $x = .50$. If the logarithms of activity coefficients with Raoult's Law behaviour for γ_2 out to

Table 11

Thermodynamic Properties of the Pure Materials in the $\text{Li}_{10.5}\text{-Al}_{10.5}$ System

Substance	S_{298}^0	S_{1000}^0	H_{298}^0	H_{1000}^0	Cp equation		$C \times 10^6$	$D \times 10^9$	$E \times 10^6$
	$\text{cal mol}^{-1} \text{K}^{-1}$	$\text{cal mol}^{-1} \text{K}^{-1}$	kcal mol^{-1}	kcal mol^{-1}	A	$B \times 10^3$			
LiAlO_2 (c, γ)	12.75	23.007	-284.1	-268.706	24.35106	4.0882	-0.83333		
$\text{AlO}_{1.5}$ (c,corundum)	6.087	12.2175	-200.25	-190.933	14.908	2.3471	-1.2717	.34615	
$\text{AlO}_{1.5}$ (c, γ)	6.25	12.668	-198.000	-188.245	15.5835	1.40191	-1.12140	0	-.53590
$\text{AlO}_{1.5}$ (l,<2000K)	9.27	16.5551	-190.358	-182.152	17.312				
$\text{AlO}_{1.5}$ (l,<2000K)	--	(19.1587)	-190.358	(-191.020)	27.66	-2.96			
$\text{Li}_{10.5}$ (c)	4.528	8.6045	-71.445	-65.222	10.3127	3.1535	-1.5276		
$\text{Li}_{10.5}$ (l)	6.58	12.5897	-64.2084	-57.9674	9.84	2.7			
LiAl_5O_8 (c,spinel,high temp form)	41.198	75.90	-1080.437	-1027.637	84.5049	9.84839	-2.1074	0	-2.5592
LiAl_5O_8 (c,ordered spinel,low T)	40.198	74.399	-1082.8	-1030.0	84.5049	9.84839	-2.1074	0	-2.5592
Li_5AlO_4 (c)	27.83	64.8742	-561.61	-521.324	65.6019	16.702	-6.9437		
Li_3AlO_3 (c)	22.	44.	-420.22	-392.60	40.9765	10.3952	-3.8885		

$x_1 = .45$ and this value for $\log \gamma_1 \gamma_2$ at $x = .50$ are fitted to a three term power series, the Redlich Kister coefficients at 1943°K are:

$$A(\log \gamma) = -2.6894, B(\log \gamma) = 0.0, C(\log \gamma) = 1.52724$$

However when this set of coefficients was tested in a phase diagram calculation the LiAl_5O_8 - LiAlO_2 eutectic was well below 1943°K. A much better phase diagram can be obtained by taking into account the stoichiometry of the spinel phase, LiAl_5O_8 , that is in equilibrium with LiAlO_2 and liquid at the eutectic temperature.

Lejus and Collongues⁵⁷ report the composition $x_2 = .85714$ at 1673°K for the saturation of LiAl_5O_8 with corundum. This gives a value of $\log \gamma_2 = -0.07287$. At 1673°K a value of $\log \gamma^e = -.314074$ at $x_2 = .83333$ can be calculated from the properties of stoichiometric LiAl_5O_8 . If four coefficients are used to fit these two values a reasonable representation of the activity of $\text{AlO}_{1.5}(c, \gamma)$ and $\text{LiO}_{.5}(c)$ in the solid spinel solution can be obtained. The Redlich Kister coefficients are shown in table 12. With these coefficients the boundary lines for the spinel phase can be calculated and an estimation of the composition of LiAl_5O_8 in equilibrium can be made. Somewhere between $x_1 = .2$ and $x_1 = .16667$ the activity of $\text{AlO}_{1.5}(c, \gamma)$ will be .64 and the corresponding activity of $\text{AlO}_{1.5}(l)$ is .4759.

Table 12. Redlich-Kister Coefficients for the Solid Spinel Phase in the $\text{LiO}_{.5} - \text{AlO}_{1.5}$ System Referred to $\text{LiO}_{.5}(\text{c})$ and $\text{AlO}_{1.5}(\text{c}, \gamma)$ as Standard States.

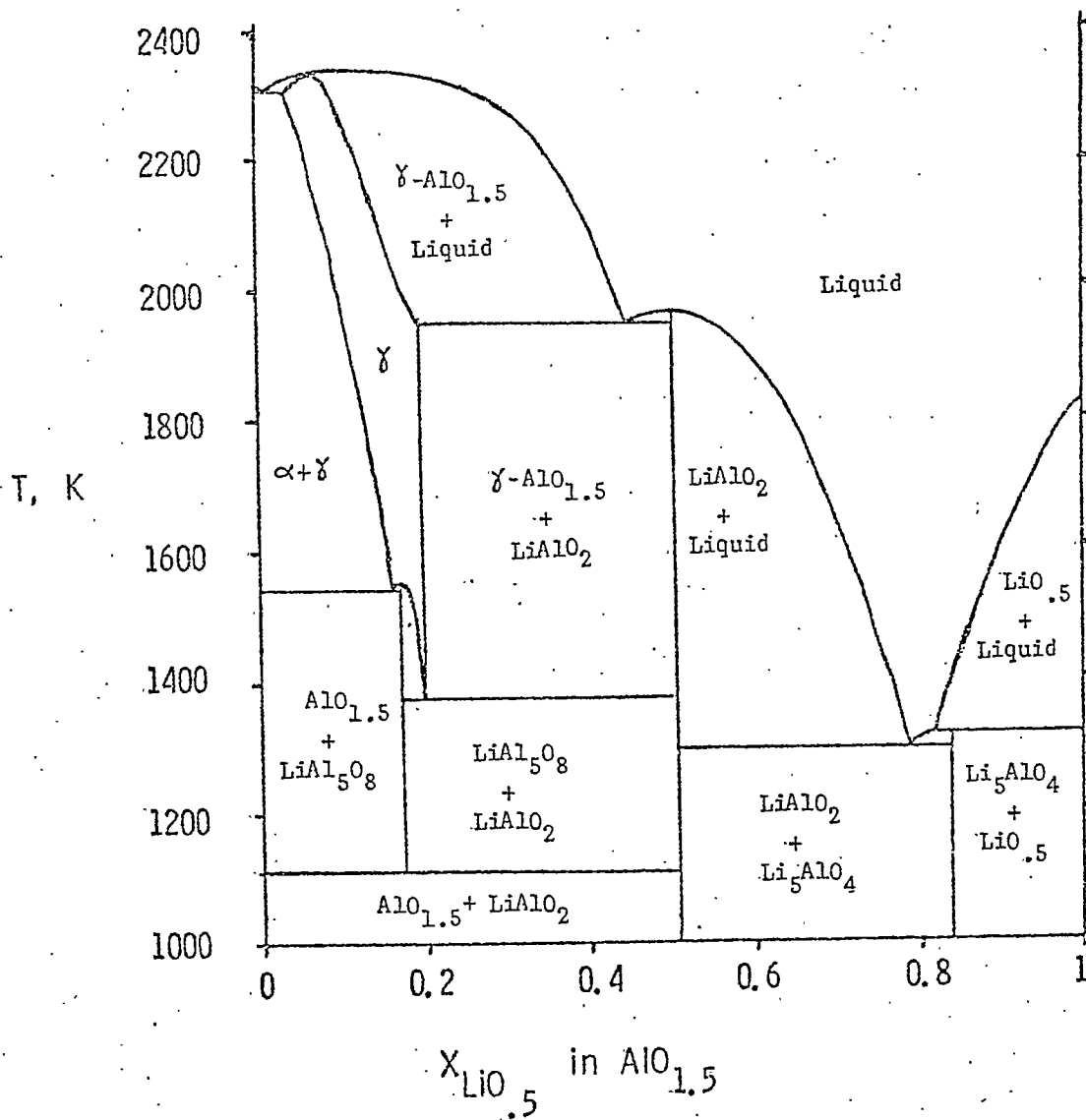
	A	B	C	D
$\log \gamma_{1000}$	-3.971271	.847024	-.578040	-.068274
enthalpy kJ/mole	-99.4210	21.2087	-14.4737	-1.7096

Table 13. Redlich-Kister Coefficients for the Liquid Phase in the $\text{LiO}_{.5} - \text{AlO}_{1.5}$ System.

	A	B	C
$\log \gamma_{1000}$	-4.7918	-1.9826	1.1939
enthalpy kJ/mole	-82.931	0.0	47.095

$\log \gamma_2$ for $\text{AlO}_{1.5}$ liquid at $x_2 = .55$ is $-.0628$ and two Redlich Kister coefficients for the liquid can be fit by requiring the B value to give this $\log \gamma_2$ value exactly. At 1943°K the coefficients are $A(\log \gamma) = -2.6894$, $B(\log \gamma) = -1.9826$, $C(\log \gamma) = 0.0$. The enthalpy coefficients were used to correct these values to 1000°K with the results shown in table 13. These coefficients have been used to calculate the liquidus curves of the phase diagram, figure 64. This lithium aluminate work has been published in reference 72.

Figure 64. Lithium Aluminate Phase Diagram.



$KO_{.5} - CaO - SiO_2$ TERNARY SYSTEM

This system is a subsystem of a larger system which also includes the oxides of sodium, aluminum, and iron. The thermodynamics of this large system is needed to accurately model the phase equilibria of a coal fired magnetohydrodynamics channel.

The binary subsystems $KO_{.5} - SiO_2$ and $CaO - SiO_2$ have been treated by the power series method^{66,67} and the $KO_{.5} - CaO$ solution will be assumed to be ideal. $KO_{.5}$, CaO , and SiO_2 are designated as components one, two, and three respectively.

Redlich Kister coefficients for enthalpy for the three binary subsystems are given in the first three columns of table 14. The ternary terms in this table were determined by interpolation between the binary terms. The general procedure for this interpolation process is described by G. W. Toop⁶⁸⁻⁷⁰. Several A terms have been determined for the heat capacity and its temperature dependence in the binary systems. Since there are no ternary corrections to the A terms, the binary coefficients can be used directly to correct the corresponding enthalpy coefficients for changes in temperature. The heat capacity coefficients are shown in table 15.

Activity data for this system comes from several sources. Potassium gas pressures were measured over samples of the three components at a number of compositions in a Woodruff Furnace by Puligandla Viswanadham. These data are shown in table 16.

Table 14. Ternary Enthalpy Coefficients.

A_{12}	A_{13}	A_{23}				
0	-8.64100	-5.96122				
B_{12}	B_{13}	B_{23}	B_{321}^a			
0	-7.76211	-6.27582	-5.67394			
C_{12}	C_{13}	C_{23}	C_{321}^a	C_{321}^b		
0	-3.22126	-4.02094	11.43433	0.775185		
D_{12}	D_{13}	D_{23}	D_{321}^a	D_{321}^b	D_{321}^c	
0	2.51210	-1.62641	-72.99906	-11.59743	-1.97295	
E_{12}	E_{13}	E_{23}	E_{321}^a	E_{321}^b	E_{321}^c	E_{321}^d
0	2.19437	0	48.00184	18.37785	3.56585	0.27430

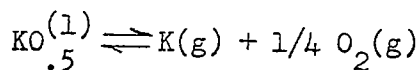
Table 15. Heat Capacity Coefficients.

C_p	$A_{12} = 0$	$A_{13} = 8$	$A_{23} = 5.6$
$\frac{\partial C_p}{\partial T}$	$A_{12} = 0$	$A_{13} = -0.0267$	$A_{23} = 0$
$\frac{\partial^2 C_p}{\partial T^2}$	$A_{12} = 0$	$A_{13} = 22.2 \times 10^{-6}$	$A_{23} = 0$

Table 16. Potassium Pressures Over $KO_{.5}$ - CaO - SiO_2 Liquid Solutions.

Sample	$x_{KO_{.5}}$	$\frac{x_{CaO}}{x_{CaO} + x_{SiO_2}}$	$\log P_K$	Temp. ($^{\circ}K$)
1	.0502	.33691	-5.16879	1701
2	.09985	.33341	-5.05297	1649
3	.15003	.32953	-4.92072	1649
4	.20015	.33760	-5.05439	1538
5	.1000	.20013	-4.8888	1649
6	.19999	.20010	-4.96717	1649
7	.09998	.40012	-4.68744	1649
8	.19998	.40012	-4.54763	1538

The potassium pressure can be converted to $KO_{.5}$ activities by the following equilibrium and equilibrium constant:



$$P_{O_2} = 1/4 P_K$$

$$K_{eq} = \frac{P_K P_{O_2}^{1/4}}{a_{KO_{.5}}}$$

The equilibrium constants were calculated from the known thermodynamic properties of the equilibrium components.

Two activity or $\log \gamma_4$ values were determined from the two points at 1553 and 1693°K where tridymite is in equilibrium with liquid on a published ternary phase diagram⁷¹. The $\log \gamma_4$'s are $\log \gamma^e$'s for the difference between the $\log \gamma$'s for CaO and SiO_2 calculated from the equilibrium constants for cristobalite and pseudowollastonite going to liquid and the $\log \gamma$'s for CaO and SiO_2 as the mole fraction of $KO_{.5}$ goes to zero, calculated from the CaO - SiO_2 binary.

The lines in the three component phase diagram defined by $x_{CaO}/(x_{CaO} + x_{SiO_2})$ are pseudobinary systems which intersect the $KO_{.5}$ apex. The pseudobinary Redlich Kister coefficients can be determined for thermodynamic quantities along these lines of composition just as if they were true binary systems. The relationship

between the pseudobinary coefficients and the extended notation, three component coefficients is complicated, but conversion between the two types of coefficients is possible.

The three component coefficients were obtained in the following manner: first an entire set of $\log \gamma$ coefficients was obtained from the coefficients for the three binary subsystems by Toop interpolation. Since a limited amount of experimental activity data was available, the extended notation coefficients from the interpolation were used to calculate pseudobinary coefficients, through F terms, for the three values of $x_{\text{CaO}}/(x_{\text{CaO}} + x_{\text{SiO}_2})$ shown in table 16. The last three terms were retained for each pseudobinary and the first three coefficients obtained by least squares fit of the $\log \gamma_1$ and $\log \gamma_4$ values, after they had been corrected to 1000°K with the enthalpy and heat capacity equations.

An additional constraint was placed on each least squares equation in the form of an initial slope for $\log \gamma_{\text{KO}.5}$ at $x_{\text{KO}.5} = 0$. For the $\text{KO}.5 - \text{SiO}_2$ binary the initial slope for $\log \gamma_{\text{KO}.5}$ is -71.319 and for the $\text{KO}.5 - \text{CaO}$ binary the initial slope for $\log \gamma_{\text{KO}.5}$ is zero since the system is assumed to be ideal. The values of $x_{\text{CaO}}/(x_{\text{CaO}} + x_{\text{SiO}_2})$ are 0.334363, 0.200115, and 0.400120 for the three pseudobinaries and these are also the values of x_{CaO} when $x_{\text{KO}.5}$ equals zero. The values of $\log \gamma^e = x_{\text{CaO}} \log \gamma_{\text{CaO}} + x_{\text{SiO}_2} \log \gamma_{\text{SiO}_2}$ for the

CaO - SiO₂ binary at the appropriate mole fractions of CaO are $x_{\text{CaO}} = 0.334363$, $\log \gamma^e = -1.00985$; $x_{\text{CaO}} = 0.200115$, $\log \gamma^e = -1.24526$ and $x_{\text{CaO}} = 0.400120$, $\log \gamma^e = -1.24526$. The initial slopes for the three pseudobinaries are calculated by interpolating between the initial slopes for $\log \gamma_{\text{K}0.5}$ in the $\text{K}0.5 - \text{SiO}_2$ and $\text{K}0.5 - \text{CaO}$ systems and then subtracting the value of $\log \gamma^e$:

x_{CaO}	Initial Slopes $-71.319(1-x_{\text{CaO}}) - \log \gamma^e$
0.334363	-46.4628
0.200115	-56.5096
0.400120	-41.5370

The first three $\log \gamma$ coefficients for each of the pseudobinaries were calculated from the $\log \gamma_1$ and $\log \gamma_4$ values under the constraints of these initial slopes. The pseudobinary coefficients are:

x_{CaO}	A	B	C	D	E	F
0.334363	-6.9600	10.0800	-22.6487	9.8186	3.7244	0.68004
0.200115	-9.7998	9.9504	-12.0849	13.8819	-8.7454	2.0472
0.400120	-8.6813	9.8013	-12.3149	7.6560	-2.7192	0.36424

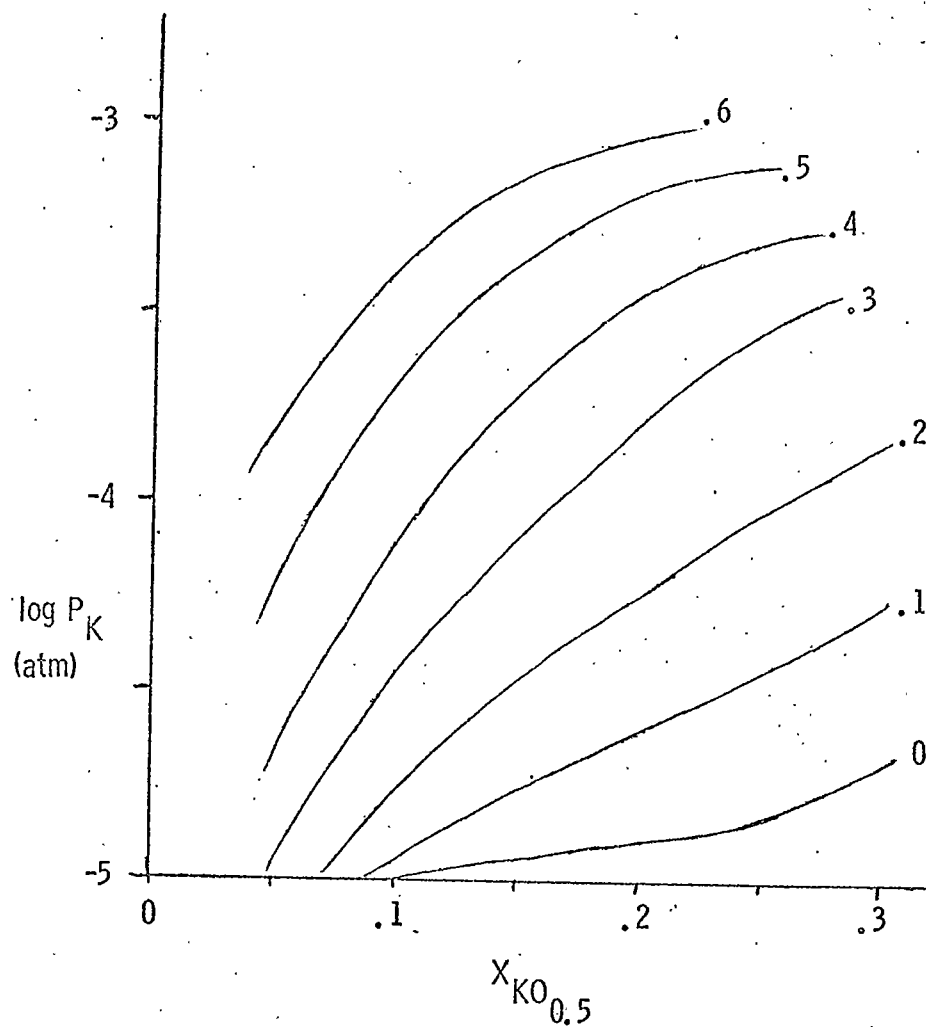
The extended notation, three component $\log \gamma$ coefficients at 1000°K were calculated from the pseudobinary coefficients and are shown in table 17.

Table 15. Ternary $\log \gamma_{1000}$ Coefficients for $\text{K}_{0.5} - \text{CaO} - \text{SiO}_2$ Liquid System.

A_{12}	A_{13}	A_{23}					
0	-18.7154	-11.3125					
B_{12}	B_{13}	B_{23}	B_{321}^a				
0	-15.7461	-11.4036	-17.8786				
C_{12}	C_{13}	C_{23}	C_{321}^a	C_{321}^b			
0	-11.3359	-5.1273	63.1499	0.51250			
D_{12}	D_{13}	D_{23}	D_{321}^a	D_{321}^b	D_{321}^c		
0	-13.9369	0.25908	-327.2701	-41.7019	-8.8452		
E_{12}	E_{13}	E_{23}	E_{321}^a	E_{321}^b	E_{321}^c	E_{321}^d	
0	-16.5173	2.4022	546.1408	168.8564	40.5704	2.5203	
F_{12}	F_{13}	F_{23}	F_{321}^a	F_{321}^b	F_{321}^c	F_{321}^d	F_{321}^e
0	-7.8163	0	-381.5330	-183.6830	-51.7836	-7.8163	-0.4885

Potassium gas pressures over $\text{K}_{0.5} - \text{CaO} - \text{SiO}_2$ solutions calculated with these coefficients are shown in figure 65.

Figure 65. Calculated Potassium Pressures Over $\text{K}_{0.5} - \text{CaO} - \text{SiO}_2$
Liquid Solutions.



Vapor pressure of potassium at 1888 K over $\text{K}_{0.5} - \text{CaO} - \text{SiO}_2$
slags as a function of $X_{\text{K}_{0.5}}$ and $X_{\text{CaO}} / (X_{\text{CaO}} + X_{\text{SiO}_2})$

SUMMARY

Power series representation of thermodynamic quantities provides a convenient method for handling the phase equilibria of multicomponent systems. The use of the Redlich-Kister power series formalism has been described and its application to several metal oxide systems has been presented.

The rutile phase of titanium dioxide can be treated as a solution of titanium metal in titanium dioxide and the activity of these two components over the composition range of the rutile phase are given in the form of a power series.

The thermodynamic data available in the literature and some mass spectrometric data for the potassium oxides were used in conjunction with Redlich-Kister equations to calculate a complete potassium oxides phase diagram. This is the first proposed diagram for the potassium monoxide to potassium peroxide region.

Literature data and power series representations were used to calculate a revised phase diagram for the lithium oxide and aluminum oxide system.

Measured potassium pressures and information from the binary subsystems were used to determine ternary Redlich-Kister coefficients for the potassium oxide, calcium oxide, and silica ternary systems.

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A large, dense, black and white image showing a close-up of a textured surface, possibly a book cover or a piece of paper with a complex pattern. The texture is highly irregular, with many small, dark, vertical and horizontal lines and speckles, giving it a grainy, almost abstract appearance. The overall effect is one of intense detail and contrast.

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Byker, Harlan J

Electrochemical reduction of chlorinated nitro and nitrosobenzenes in dimethylsulfoxide

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