1960

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Recommended Citation
LaPlante, Joseph Paul, "Complexes of nickel with 4-carboxy-1,2-cyclohexanedionedioxime in alkaline media " (1960). *Retrospective Theses and Dissertations*. 2764.
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Mic 60–4899

LaPLANTE, Joseph Paul. COMPLEXES OF NICKEL WITH 4–CARBOXY–1,2–CYCLOHEXANEDIONEDIOXIME IN ALKALINE MEDIA.

Iowa State University of Science and Technology
Ph.D., 1960
Chemistry, analytical

University Microfilms, Inc., Ann Arbor, Michigan

COMPLEXES OF NICKEL WITH 4-CARBOXY-1,2-CYCLOHEXANEDIONEDIOXIME IN ALKALINE MEDIA

by

Joseph Paul LaPlante

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Analytical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

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Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1960

TABLE OF CONTENTS

I. INTRODUCTION

The chemistry of the nickel(II) complexes of the *vic*-dioximes has been very difficult to elucidate, because of the slight solubilities of the *vic*-dioximes and the bis(*vic*-dioximato-*N*,*N*')nickel(II) complexes. Several complete investigations have been carried out since Feigl (1) studied the reaction between several oxidizing agents and bis(2,3-butanedionedioximato-*N*,*N*')nickel(II) in alkaline media, but the conclusions of these investigators have differed substantially. Even after it was realized (2, 3) that two complexes of different composition and characteristics were formed, depending on the conditions employed, controversy still existed as to the *vic*-dioxime and nickel ratio, and the oxidation state of the nickel atom in the complex. The red color obtained from the reaction has been attributed to a *vic*-dioxime complex of nickel(IV) in which the ratio of ligand to metal was 2:1 (1), 3:1 (4, 5, 6, 7, 8), and 4:1 (3, 9); to a complex of nickel(III) in which the ratio of ligand to metal was 3:1 (10, 11, 12, 13); and to complexes of an unknown oxidation product of the *vic*-dioxime with nickel(II) in which the ratio of ligand to metal was 1:1 (14), 2:1 (15, 16), 3:1 (17, 18), and 4:1 (18).

The difficulties due to limited solubility have been overcome with the preparation of 4-carboxyl-1,2-cyclohexanedionedioxime (4-carboxynioxime) (19). This investigation was undertaken in the hope that this vic-dioxime would allow higher concentrations of the complexes to be present in solution so that spectrophotometric, polarographic, and magnetic susceptibility data would resolve the problem and permit the formulation of the correct course of reaction and an estimation of the values of the stability constants involved.

In this investigation, the nickel(II) complexes of the vic-dioxime were studied in concentrated potassium hydroxide media. An attempt was also made to determine the reaction mechanism of the oxidation of the complexes with oxygen.

II. REVIEW OF LITERATURE

A. Oxidation of Nickel(II) Complexes

The application of the vic-dioximes for the detection or determination of nickel in alkaline media appeared in the literature as early as 1913. Fortini (20) reported that a mixture of dimethylglyoxime, nickel(II) chloride, ethyl alcohol, and concentrated ammonium hydroxide gave a rose color that could be used as a sensitive qualitative test for nickel.

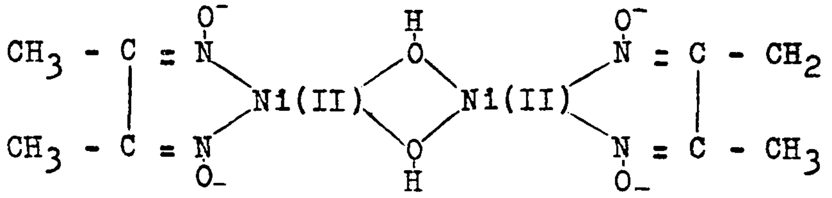
In 1924, Feigl (1) reported that oxidizing agents such as ferricyanide, peroxides, permanganate, and lead dioxide tended to prevent the formation of the typical nickel precipitate with dimethylglyoxime. An intensely red colored solution resulted from the reaction of bis(2,3-butanedionedioximato-N,N')nickel(II) and lead dioxide in basic solution. By careful neutralization of the solution, he was able to obtain a red colored precipitate. From analysis of this precipitate, he assigned the following formula $[HON{:}C(CH_3){\cdot}C(CH_3){:}NO]_2Ni{:}O$. The precipitate was unstable in acidic media and if potassium iodide was present, I_2 was liberated. Iodometric titrations indicated that there was a reduction of approximately two electrons per nickel atom. From this, Feigl postulated that the nickel was quadrivalent.

Rollet (21) reported in 1926 that quantities of nickel varying from 0.001 to 0.01 mg. could be determined in steel and organic materials. He used a slight excess of bromine to oxidize the bis(2,3-butanedionedioximato-*N*,*N'*)nickel(II) complex in an ammonical solution. Since then various procedures have been developed for the determination of nickel employing the reaction between an oxidizing agent and the bis(*vic*-dioximato-*N*,*N'*)nickel(II) complex in alkaline media. The oxidizing agents that have been used are bromine (15, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37), iodine-potassium iodide (10, 29, 38, 39, 40, 41, 42, 43, 44, 45, 46), sodium hypochlorite (15, 47), sodium hypobromite (15, 48), ammonium and potassium peroxydisulfate (15, 49, 50, 51, 52, 53, 54, 55, 56), lead dioxide (29), and atmospheric oxygen (18, 56). These procedures were based on the work of Feigl and Rollet.

Wulff and Lundberg (15) were the first to make an exhaustive study of the method using all of the common oxidizing agents. They qualitatively attempted to explain the color formation and were able to reproduce the color obtained by Rollet (21) provided they added the oxidizing agent to the *vic*-dioxime and then the nickel. The soluble red color was not produced if the *vic*-dioxime was added to nickel(III). On this evidence they proposed that it was the *vic*-dioxime, not the nickel, which was oxidized.

The color produced when bromine or other oxidizing agents are used is unstable. By maintaining rigid control of the amounts of reagents, the order of addition, and the time for the development of the color, it is possible to obtain reproducible results. In an effort to standardize the method, Furman and McDuffie (2) discovered that the red color reported in previous literature was actually one of two complexes formed depending upon the method of preparation. Bromine oxidation in the presence of ammonia yielded an unstable complex, Complex A, which decomposed in a few hours to give Complex B. This complex was stable for a few days. They found that the optimum condition for the formation of Complex B was at a pH 12 or greater with potassium peroxydisulfate as the oxidant.

Okáč and Polster (14) repeated Feigl's (1) work and obtained a solid compound which had the same appearance and oxidizing properties, but contained lead, sodium, chlorine, and only one-half of the nitrogen reported by Feigl. Attempts to isolate an oxidation product of dimethylglyoxime and a hydrolysis or reduction product of dimethylfuroxan failed. The qualitative nature of the reactions in alkaline media indicated the formation of such products. Okáč and Polster (59) also found that oxidation of the nickel-dimethylglyoxime complex took place slowly even without the addition of oxidizing agents. This reaction was accelerated by heating or by the addition of oxidizing agents. A crystalline red-brown colored substance was isolated, $DNaNiOH\cdot H_2O$, which was stable only in strongly alkaline media. These workers proposed the following structure,



Upon hydrolysis bis(2,3-butanedionedioximato-*N*,*N*')nickel(II) and nickel(II) were obtained. They concluded that the oxidation occurred on the oxime group rather than on the nickel.

Hooreman (3) assumed that the oxidation state of the nickel was plus four in the two complexes which were designated I and II. These two complexes correspond to the Complexes A and B reported by Furman and McDuffie (2). Hooreman reported the ratio of *vic*-dioxime to nickel in Complex I was 2:1 and in Complex II, 4:1. Both complexes were unstable, Complex I being completely destroyed and Complex II, 20% destroyed in 24 hours. No reaction mechanisms were given.

Edelman (58) reported the preparation of a stable bis(1,2-diphenylethanedionedioximato-*N*,*N*')nickel(III) complex by a bromine oxidation with bromine in carbon tetrachloride. From the analysis of the dark brown colored substance, Edelman concluded that the formula was $NiC_{28}H_{22}N_4O_4Br$. This material was soluble in alkaline media and upon hydrolysis gave bis(1,2-diphenylethanedionedioximato-*N*,*N*')nickel(II).

Babko (17) reported a 2:1 complex in ammonical media, presumably Complex I. If sodium hydroxide was used in place of ammonium hydroxide, a 3:1 complex was produced, presumably Complex II. The maximum color intensity of Complex II was observed at a nickel:dimethylglyoxime:oxidizing agent ratio of 1:3:3. Babko concluded that the vic-dioxime was oxidized rather than the nickel.

Okáč and Šimek (59) studied the compound prepared by Rollet (21). By oxidation-reduction titrations, they found an exchange of 1.86 electrons. In 8 N sodium hydroxide, dimethylglyoxime and nickel(II) gave a yellow solution, which could not be oxidized to yield the red color. In 4 N sodium hydroxide, oxidation of the yellow solution was slow and incomplete. They were able to isolate from these yellow solutions a compound which they considered to be $DNaNiOH \cdot H_2O$ (57).

Carlson (4) studied Complexes I and II with several different vic-dioximes. He established by Job's method that the ratio of vic-dioxime to nickel in both complexes was 3:1. In an effort to establish the oxidation state of nickel in Complex II, iodometric titrations, sodium hydrosulfite titrations, and polarographic reduction were used. The results obtained approached, but never reached, the reduction of two electrons per nickel atom. Magnetic susceptibility measurements indicated that the complex was diamagnetic, but the solutions used were too dilute to allow much confidence to be placed in these measurements. Therefore, all the evidence collected by Carlson indicated the Complex II was a 3:1 complex of nickel(IV). He proposed the following reaction

$$HNiO_2^- + 3D^{-2} + \frac{1}{2}O_2 + 2HOH = NiD_3^{-2} + 5OH^-$$

He reported K' for the reaction to be 1.1×10^9, but the range in the values used to obtain this average was 4×10^2.

Booth and Strickland (10) made an extensive study of the reaction of bis(2,3-butanedionedioximato-*N*,*N'*)nickel(II) and an oxidizing agent in alkaline media. They reported two complexes, one with a ratio of *vic*-dioxime to nickel of 2:1 and the second, 4:1. Using this information, they prepared solutions containing stoichiometric amounts of nickel and dimethylglyoxime. By adding varying amounts of bromine and following the disappearance of bromine as a function of the change in absorbance of the solution. They concluded that there was a total electron transfer of three per mole of complex formed. Migration experiments indicated that Complex II was negatively charged and monovalent. They proposed the following reaction

$$Ni^{+2} + 4DH_2 + 6OH^- = [Ni(OH)_2(DH)_4]^- + 4H_2O + 3e^-$$

and that the nickel was present as nickel(III).

In 1953, Yatsimirskiĭ and Grafova (18) reported a study of the formation of the complex in ammonical media using atmospheric oxygen as the oxidizing agent. Three methods were used to determine the ratio of *vic*-dioxime to nickel in the complex, but to explain the discrepancies in their data, they postulated a 3:1 complex and the simultaneous existence of a 1:1 colorless complex. The following reactions were proposed

$$Ni(NH_3)_6^{+2} + 3DH^\circ = Ni(DH^\circ)_3^- + 6NH_3$$

$$Ni(DH^\circ)_3^- + 2Ni(NH_3)_6^{+2} = 3Ni(DH^\circ)(NH_3)_x^+ + (12-3x)NH_3$$

They assumed that nickel was present as nickel(II) and DH° represents some unknown oxidation state of dimethylglyoxime.

Okáč (9) studied the oxidation of bis(2,3-butanedione-dioximato-*N*,*N*')-nickel(II) potentiometrically in acid and alkaline media. He concluded that dimethylglyoxime was oxidized rather than the nickel. In acid solution, the oxidation was preceded by the decomposition of dimethylglyoxime to give 2,3-butanedione and hydroxylamine. Furoxan derivatives are probably formed in alkaline media. The reaction mechanism was not given.

Nadezhina and Kovalenko (11, 12) studied the formation of the complex in both alkaline and ammonical solutions using iodine, bromine, potassium ferricyanide, ammonium peroxydisulfate, and atmospheric oxygen as oxidants. They found that the ratio of *vic*-dioxime to nickel was 3:1 and that this ratio was independent of the oxidizing agent used. They suggested that nickel was oxidized to nickel(III) in the complex.

German (5) made an extensive study of the reaction of nickel(II) chloride, 4-carboxy-1,2-cyclohexanedionedioxime and an oxidizing agent in alkaline media. German obtained a value of approximately 0.5 for the number of unpaired electrons from magnetic studies. German proposed that Complex II was actually a mixture of two complexes, one complex having a <u>vic</u>-dioxime to nickel ratio of 3:1 containing nickel(IV), and the other a 2:1 complex of nickel(II). The following reactions were proposed

$$Ni^{+2} + 2D^{-3} = NiD_2^{-4}$$

$$H_2O + \frac{1}{2}O_2 + NiD_2^{-4} + D^{-3} = NiD_3^{-5} + 2OH^-$$

The formation constants for the above reactions are

$$K_1' = (11 \pm 10) \times 10^6$$

$$K_2' = 34 \pm 20$$

From these data he attempted to explain the failure of previous workers to agree on the ratio of ligand-to-metal in the complexes and why oxidation-reduction titrations consistently yield electron changes approaching two, but due to the small amount of reagent available, he was unable to conclusively prove this hypothesis.

Babko (16) reported the preparation of a water-soluble red colored precipitate from the reaction of nickel and dimethylglyoxime in the presence of an oxidizing agent. Babko proposed that the precipitate was either (a) a compound of nickel(IV) or nickel (V) with dimethylglyoxime or (b) a compound of nickel(II) or nickel(III) with partly oxidized dimethylglyoxime. Babko supports hypothesis (b) on the basis of the following arguments: Dimethylglyoxime can be oxidized more readily than nickel. The complex is destroyed by excess unoxidized dimethylglyoxime. The intermediate oxidation product of dimethylglyoxime formed a red solution when nickel(II) hydroxide was added.

Yamasaki and Matsumoto (6) determined the ratio of _vic_-dioxime to nickel in the dimethylglyoxime complexes formed by oxidation in alkaline media by the spectrophotometric molar-ratio method. They proposed the following compounds $[\mathrm{Ni(D)_2(NH_3)_2}]$ and $[\mathrm{Ni(D)_3}]^{-2}$ in which the nickel was present as nickel(IV).

Kudo (60) used lead dioxide to oxidize the bis(2,3-butanedionedioximato-_N_,_N_')nickel(II) complex in 6 N ammonium hydroxide. A black colored powder was obtained. Iodometric titration indicated that nickel(IV) was present. The proposed structure of the powder was

$$\mathrm{H_4}\ \left[\ \mathrm{D_2}\overline{\mathrm{NiONi(D_2)O}}\ \right]$$

or a polymer.

Peshkova and Mel'chakova (13) investigated the reaction of nickel with dimethylglyoxime in the presence of bromine, iodine, ammonium peroxydisulfate, and lead dioxide in alkaline and ammonium hydroxide medium. They found that the ratio of vic-dioxime to nickel was 3:1 and assumed (III) to be present.

Okáč and Šimek (7) studied the oxidation of bis(2,3-butanedionedioximato-N,N')nickel(II) photometrically, potentiometrically, and by paper chromatography. The oxidizing agents used were hydrogen peroxide, potassium ferricyanide, lead dioxide, potassium peroxydisulfate, and atmospheric oxygen. From a carbon tetrachloride suspension of bis(2,3-butanedionedioximato-N,N')nickel(II), a black colored amorphous precipitate of $Ni(DH)_2Br_2$ was obtained using bromine as the oxidant. It was insoluble in ethanol, ether, chloroform, benzene and soluble in sodium hydroxide, ammonium hydroxide, and pyridine. A red colored precipitate of bis(2,3-butanedionedioximato-N,N')nickel(II) was obtained upon hydrolysis. They proposed that Na $[DNi(II)OH]$ was either (a) oxidized in the presence of dimethylglyoxime yielding $[Ni(IV)D_3]^{-2}$ or (b) it reacts with dimethylglyoxime to give $[Ni(II)D_3]^{-4}$, which is afterward oxidized to $[Ni(IV)D_3]^{-2}$. In a different paper (8) Okáč and Šimek studied the reduction of $[Ni(IV)D_3]^{-2}$ by the same methods as above. The reducing agents used were sodium stannate, hydrazine, hydroxylamine, and cobalt(II) salts. The reduction is represented by the following equation

$$\text{(red)}\ [\mathrm{Ni(IV)D_3}]^{-2} + 2e^- = \text{(yellow)}\ [\mathrm{Ni(II)D_3}]^{-4}$$

Dilution or neutralization of the alkaline solutions resulted in hydrolysis.

$$[\mathrm{NiD_3}]^{-4} + 3\mathrm{H_2O} = \mathrm{Ni(DH)_2} + \mathrm{DH}^- + 3\mathrm{OH}^-$$

$$[\mathrm{NiD_3}]^{-2} + 3\mathrm{H_2)} + 2e^- = \mathrm{Ni(DH)_2} + \mathrm{DH}^- + 3\mathrm{OH}^-$$

They proposed the following mechanism for the oxidation of bis(2,3-butanedionedioximato-*N*,*N'*)nickel(II)

$$2\mathrm{Ni(DH)_2} + 6\mathrm{OH}^- = [\mathrm{DNi(OH)_2NiD}]^{-2} + 2\mathrm{D}^{-2} + 4\mathrm{H_2O}$$

$$[\mathrm{DNi(OH)_2NiD}]^{-2} + 4\mathrm{D}^{-2} = 2\,[\mathrm{NiD_3}]^{-4} + 2\mathrm{OH}^-$$

then,

$$[\mathrm{NiD_3}]^{-4} = [\mathrm{NiD_3}]^{-2} + 2e^-$$

Selbin and Junkin (61) reported that bis(2,3-butanedionedioximato-*N*,*N'*)nickel(II) dissolved in alkaline media absorbs oxygen in a reversible manner. Deoxygenation may be accomplished by headting the solution, bubbling an inert gas through the solution or by reducing the pressure above the solution. Bis(2,3-butanedionedioximato-*N*,*N'*)palladium(II) does not show this behavior.

Diehl (62) reviewed the general chemistry, synthesis, and the application of the *vic*-dioximes to the gravimetric, volumetric, and colorimetric determination of nickel.

Banks and Richard (63) found that vic-dioximes could be quantitatively dehydrogenated with iodine in the presence of mercury(II) acetate to give the corresponding furoxanes in carbon tetrachloride. Fifteen different vic-dioximes were determined by this method. Several furoxanes were isolated.

A review of the chemistry of furoxanes has been prepared by Kaufman and Picard (64). A critical discussion of the various structures which have been proposed, isomers, reactions of furoxanes, preparation, and nomenclature was presented.

The following references pertain to the oxidation of nickel complexes in which the vic-dioximes have been replaced with other ligands. Malatesta and Monti (65) prepared and studied the complexes of nickel(II) and benzamide oxime. The compound, $[PhC(:NO-)NH_2]$ 3Ni(II), was diamagnetic and changed into a black colored salt, $C_{14}H_{13}O_3N_5Ni$, in methanol, ethanol, benzene, and chloroform. In potassium hydroxide the following black colored compound, $C_{14}H_{13}O_3N_5NiKOH$, was isolated. When the above compounds were treated with dimethylglyoxime, the bis(2,3-butanedionedioximato-N,N')nickel(II) precipitate was obtained indicating that nickel was present as nickel(II). In the absence of air, sodium thiosulfate titrations indicated that approximately two oxidimetric equivalents per nickel atom. The oxidizing power of $[PhC(:NO-)NH_2]$ 3Ni(II) is due to one of the benzamide oxime molecules and not to nickel(III). The compound PhC(:NOH)N(:O):NH or PhC(:NOH)N:NOH was isolated from the oxidation.

Malatesta and Pizzotti (66) prepared the blue colored salt $2H[Ni(NO)(CN)_{1.5}(OH)_{.5}]$ $[Ni(CN)_2 \cdot 3EtOA]$. The molecular susceptibility, χ_m, at 20° C. was 104×10^{-6}. In the solid state, it oxidizes slowly and then gives the reaction of nitrites. The compound $H[Ni(NO)(CN)_{1.5}(OH)_{.5}] \cdot 5 H_2O$ was prepared from the above salt. It was difficult to prevent oxidation of this compound, with the formation of nickel(II) nitrite and nickel(II) cyanide.

Jensen and Nygaard (67) prepared a red colored complex from the addition of sodium hydroxide to nickel(II) sulfate and aminoguanidine. It was readily oxidized to a black colored compound, possibly $Ni(CH_5N_4)_2(OH)_2$, which decomposes to give ammonia, nitrogen, and carbon dioxide. The complexes of diaminoguanidine and triaminoguanidine with nickel are progressively more readily oxidized. These complexes are diamagnetic.

Hieber and Bruck (68) oxidized o-aminothiophenolate-nickel(II) suspended in strong alkali with atmospheric oxygen to give the u-dioxo-nickel(IV) compound via a hydroxo complex with six coordinated nickel(II). Similar complexes are also formed in systems where nickel carbonyl is formed. Thus, if bis(2,3-butanedionedioximato-N,N')nickel(II) in 30% sodium hydroxide is treated with carbon monoxide, the nickel(IV) complex in formed, but is unstable and up to 90% of the carbonyl was formed.

Nyholm (69) reported that $[NiCl_2(C_6H_4(AsMe_2)_2)_2]$ Cl was oxidized by chlorine, cerium(IV), and concentrated nitric acid to a compound containing nickel(IV). The compound is diamagnetic and Nyholm assumed it was octahedral with $d^2s\ p^3$ binding.

Hieber and Bruck (70) prepared a yellow colored compound, $Ni\ [SC_6H_4NH_2]_2$. It can be oxidized to $ONi(SC_6H_4NH_2)_2$ in concentrated sodium hydroxide by oxygen, peroxide, chlorine, bromine, potassium permanganate, potassium ferricyanide. Cryoscopic molecular weight determinations showed that it was a dimer. They assumed that nickel was present as nickel(IV).

B. Magnetic Susceptibility

The application of magnetic measurements to the study of metal chelates was due largely to Pauling (71, 72, 73). Pauling (74) has reviewed the relative stability and directional properties of atomic orbitals. Theoretical discussions of the magnetic properties of complexes (74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84) and the applications of crystal field theory and molecular orbital theory (79, 80, 85, 86, 87, 88, 89, 90, 91, 92) are discussed in detail in the literature.

The more important tetrahedral "ionic" type compounds that have been reported to date are $Ni(N_2H_4)_2SO_3$, $Ni(N_2H_4)_2$

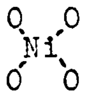
$(NO_2)_2$, $Ni(NH_3)_4SO_4$, $[Ni(C_2H_4(NH_2)_2)_2]$ $(SCN)_2 \cdot H_2O$, (93); bis(acetylacetone)nickel(II), (94, 95, 96); bis(1,2-diphenylethanedionemonoximato-N,N')nickel(II), (97); bis(ethyl-3,3',5,5'-tetramethylpyrromethene-4,4'-dicarboxylate)nickel(II), (98, 99); bis(salicylaldehydate)nickel(II), (100, 101); $Ni(OxH_2)_2Cl_2 \cdot 6H_2O$, where OxH_2 is oxalenediamidioxime, (102); bis(o-hydroxyacetophenone)nickel(II), bis(formylcamphor)-nickel(II), (103); bis(phenylphosphine)nickel(II), (104, 105, 106, 107); nickel(II) complexes of 4-methyloxybenzaldehyde, 5-bromo-2-hydroxylbenzaldehyde, 5-bromo-2-hydroxybenzal-anilinate, 2-hydroxy-1-naphthal-p-iodoanilinate, (108); $Ni(NO)(OH)_3$, $Ni(NO)(OCH_3)_2(OH)$, $Ni(NO)(OCH_2CH_3)_2(OH)$, $Ni(NO)(OCH_2CH_3)(OH)_2$, $[Ni(NO)_2(OCH_3)(CH_3OH)]_2$, $Ni(NO)(OH)(OCH_3)_2$, (109); bis(bromosalicyaldehydato)-nickel(II), benzidinesalicylaldehydatonickel(II) acetate, (110); the magnetic moments of the above complexes were 2.6 to 3.2 Bohr magnetons.

The octahedral complexes with magnetic moments of about 3.2 Bohr magnetons that have been reported are $Ni(NH_3)_6SO_4$, (99); nickel(II) complexes of nitro acetic acid and ethylenediaminetetraacetic acid (111); $NiCl_3 \cdot 2C_6H_4(As(CH_3)_2)_2$, (112); tris(1,2-bis(ethylthio)ethane)nickel(II) perchlorate, tris(1,2-bis(methylthio)ethane)nickel(II) perchlorate, (113); bis(2,3-butanedionedioximato-N,N')nickel(II) chloride, (114); dicyanamminedipyridinenickel(II), (115); nickel(II) complexes of o-$(NH_2)_2C_6H_4$, $PhCH_2NH_2$, $(H_2NCH_2)_2$, (116); tris(2-pyridinaldoxime)nickel(II) iodide, (117); Ni(ethylenediamine)$_2$(NCS)$_2$, (118); nickel(II) complexes of biacetyldihydrazone, 2-pyridinalhydrazone, 2,6-pyridindialdihydrazone, and 2-pyridinal-p-tolilimine, (119); tris(ethylenediamine)nickel(II) sulfate, (110); and a polymer bis(N-methylsalicylaldimine)-nickel(II), (120).

Some of the planar diamagnetic complexes reported are $K_2Ni(CN)_4$, $K_2Ni(CN)_4 \cdot H_2O$, nickel(II) glyoximes, potassium dithiooxalatonickel(II), bis(acetyldioxamto)nickel(II), bis(ethylxanthato)nickel(II), bis(ethyldithiocarbamato)-nickel(II), bis(phenylethylenediamine)nickel(II) nitrate, potassium succinimidonickel(II), etc., (99); bis(1,2-benzylmethylglyoximato-N,N')nickel(II), (121); $(CN)_2Ni \cdot 2NH_3 \cdot 3H_2O$, $(CN)_2Ni \cdot NH_3 \cdot C_6H_6$, (122); dimethylmesoporphyrin-nickel(II), tetramethylhematoporphyrinnickel(II), (123); bis(salicylaldiminato)nickel(II), (96, 100, 101); bis(oxalenediamidoximato-N,N')nickel(II), (102); bis(o-hydroxyacetophenoneiminato)nickel(II), bis(salicylaldehydepropylenediamine)nickel(II), bis(o-aminobenzaliminato)nickel(II), bis(o-benzaldehydephenylenediamine)nickel(II), (96, 103); bis(formylethylenediiminocamphor)nickel(II), (124); bis(1,2-vic-dioximato-N,N')nicekl(II), (125); bis(diacetylbenzoylhydrazone)nickel(II), (126); bis(N-methylsalicylaldiminato)-nickel(II), (101, 127, 128); nickel(II) complexes of o-phenanthroline and dipyridl, (129, 130); nickel(II) complexes of 4-methyl-2-hydroxybenzaliminate, 5-bromo-2-hydroxybenzaliminate, 5-bromo-2-hydroxybenzalmethyliminate, 5-bromo-2-hydroxybenzalbutyliminate, 5-bromo-2-hydroxybenzalethylenediiminate, (108); bis(bromosalicylaldehyde-o-phenylenediamine)-nickel(II), (110); NiBr$_2$·2PET$_3$ (131); 17 diamagnetic nickel(II) complexes, (132); and the nickel(II) complexes of o-carboxyformazylbenzene and o-hydroxyformazylbenzene with a coordination number of three (133).

Summaries and tables of magnetic moments of nickel(II) complexes (81, 94, 99, 129, 132, 134, 135, 136) are reported in the literature.

Mellor and Craig (99) made a study of the factors affecting the nature of the bonds between nickel and nonmetallic atoms. The electronegativeties of S, N, and O indicate that the tendency to form covalent complexes with nickel should be greatest with sulfur and least with oxygen. They divided 37 nickel(II) complexes having a coordination number of four into the following six groups.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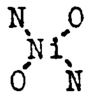
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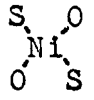
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VI

The five compounds in group I were paramagnetic; group II, five paramagnetic and eight diamagnetic; group III, five paramagnetic and seven diamagnetic; group IV, one paramagnetic and three diamagnetic; group V, one paramagnetic; group VI, two diamagnetic. They concluded that while the electronegativity of the atoms attached to the nickel was important, other factors, such as the nature of the functional group in which the atom bonded to nickel occurs, may also be significant.

Mills and Mellor (96) studied the absorption spectra of some para- and diamagnetic nickel complexes. They found that diamagnetic complexes exhibit the following features, (a) the bands of the coordinated chelate molecule are slightly displaced to longer wavelengths, and (b) a band of appreciable intensity is observed at approximately 400 mμ, which must be attributed to the nickel. Paramagnetic complexes have no bands in the range 250-650 mμ. The spectra appear to be that of the organic chelate molecule, sometimes displaced to longer wavelengths. The spectra of the paramagnetic complexes in ethanol resembles those of the chelate molecule in ethanol and sodium hydroxide. A survey (132) showed that the correlation between the color of nickel complexes and their magnetic behavior was unreliable. They suggested that a better classification would be furnished by a study of the visible and ultraviolet regions of the spectrum.

Willis and Mellor (134) found that a number of nickel complexes are diamagnetic in the solid state and had magnetic moments as large as 3.2 Bohr magnetons in solution. The solvents used were dioxane, benzene, chloroform, pyridine, ethanol, and methanol. They postulated the formation of an octahedral complex containing two molecules of pyridine in a pyridine media. When the magnetic moment was less than 3.2, they suggested that under the influence of the solvent, the complex was converted to a tetrahedral one.

Sone (137, 138, 139, 140) made a study of the absorption spectra of nickel chelates in the ultraviolet, visible, and infrared regions of the spectrum. He found that the bands in the visible and infrared obeyed the same regularity. Absorption maxima for a number of nickel complexes was given.

Basolo and Matoush (141) isolated several well-defined crystalline compounds of hexacoordinated nickel(II) from anhydrous pyridine solutions of diamagnetic nickel(II) complexes. The solids were paramagnetic and upon removal of the pyridine, yielded the original diamagnetic compound. Thus they concluded that the paramagnetism of certain pyridine solutions of diamagnetic nickel(II) complexes results from expanding the coordination sphere of nickel to form hexacoordinated compounds.

Ballhausen (142) used crystal field theory to derive formulas which can be used to calculate the spectra of simple para- and diamagnetic nickel(II) ammines. The absorption spectra of paramagnetic complexes, assumed to have a tetrahedral configuration, do not seem to fit these formulas. In a later paper (143), the calculations of d^2-systems were used for comparison with the strong and weak tetragonal fields.

The ground state of diamagnetic nickel(II) complexes was found. The magnetically anomalous complexes were discussed and peculiarities in the tetragonal splitting pointed out.

Orgel (144) considered the energy-level diagrams in terms of a function, D_q, which depends on the geometry of the ion and observed the following regularities, (a) the values of D_q for hydrated bivalent ions were close to 1000 cm^{-1}, (b) the common ligands could be arranged in a sequence such that the D_q values for their complexes with any metal ion increase in the order: iodide, bromide, chloride, floride, water, oxalate, pyridine, ammonia, ethylenediamine, nitrite, and cyanide, (c) the evidence available suggests that D_q was much smaller for tetrahedral complexes than for corresponding octahedral complexes.

Williams (145) states that in its present form the crystal field theory makes unrealistic assumptions about the strength of the electrostatic fields produced by different ligands. The molecular orbital theory does not suffer from the same disadvantages. He discussed the absorption spectra of various transition metal complexes in terms of molecular orbital theory.

George et al. (89) made the following conclusions from crystal field theory, (a) cobalt(II) is more likely than nickel(II) to give tetrahedral complexes, (b) the tendency of the transition metal ions of the second and third series to form complexes with a maximum number of paired electrons is attributed to the larger crystal field splittings and the small repulsions between d electrons because the orbitals are larger, and (c) electron promotion from 3d to 5s orbitals in octahedral complexes with d^7 or d^8 seems improbable in most instances.

Jørgensen (90) recorded the absorption spectra in the near infrared and visible regions of the spectrum for ethylenediaminetetraacetate, glycinate, acetylacetone, 2,2'-bypyridine, and 1,10-phenanthroline complexes of chromium(II), cobalt(II), nickel(II), and copper(II). The tris complexes of 2,2'-bypyridine, 1, 10-phenanthroline and nickel(II) **had** spectra predicted by crystal field theory for a cubic complex. He showed that the lowest singlet state, $'\Gamma_3(D)$, intermixes strongly with the triplet states and gives rise to double bands. The energy decrease of this state at increasing crystal field strength was ascribed to interaction with some states of other electronic configurations.

Carassiti (146) calculated with the help of group theory, the relative plane and tetrahedric tetragonal configuration of cyanide and ammine complexes of nickel(II). He found that plane tetragonal symmetry was indicated for $Ni(CN)_4^{=}$ and that $Ni(NH_3)_4^{+2}$ has tetrahedric symmetry.

Kolos (147 applied crystal field theory (strong field approximation) to the calculation of the relative stabilities of square and tetrahedral complexes of copper(II), cobalt(II), and nickel(II). The most stable state of nickel(II) was square planar, which agreed with experimental results.

Venanzi (104) discussed the formation of tetrahedral nickel(II) complexes in terms of crystal field theory. The transition from paramagnetic to diamagnetic complexes is attributed to the force of the field generated by the ligands. He suggested that tetrahedral compounds form instead of paramagnetic octahedral compounds when the ligands do not have enough perturbing power to cause "spin pairing" or if it is required by the steric requirements of the ligands.

Sacconi et al. (148, 149) studied the effects of solvents on some bis(N-alkyl-salicylaldiminato)nickel(II) complexes. Their results disagreed with the hypothesis that the complexes are tetrahedral in noncoordinating solvents and suggest an outer orbital $4s4p^24d$ planar configuration in equilibrium with the inner orbital dsp^2.

Orgel (86) applied crystal field theory to some of the problems in transition metal chemistry. He corrected the heats of hydration by subtracting the stabilization energies of the crystal fields. The stability of tetrahedral and octahedral complexes shows that the crystal field splittings from the d^1-d^{10} configurations favors octahedral complexes of nickel(II) and vanadium(II). They should be more stable than those of titanium(II) and cobalt(II). He states that the transition from ionic to covalent complexes occurs when the separation of the t_{2g} and e_g orbitals exceeds the D_q^o where D_q^o is the crystal field stabilization for the complex.

Sutton (88) reviewed the crystal field theory, application of the Jahn-Teller theorem to copper(II) complexes, and molecular orbital theory in detail. Because nickel(II) has one less electron than copper(II), it is not subject to the Jahn-Teller distortion. Its eight d-electrons can fill the four low lying orbitals of an infinitely distorted octahedron. Therefore, it should form planar complexes readily. The more polarizable the ligands are, the greater the splitting will be, so that these eight electrons will tend to reside in the lower orbitals rather than occupy all five. For the more electronegative ligands, the splitting, and therefore the stabilization, will be less. The tendency for the eight electrons to spread over all five orbitals will be greater, so the complexes may be paramagnetic. It does not follow that the complex will become tetrahedral, because for a given ligand the stabilization is much less for this arrangement than for a regular octahedral one.

Nyholm (82) has reviewed the fundamentals and determination of magnetic susceptibility, applications to valency problems, relationship of susceptibility and bond type, and determination of stereochemistry of transition metal complexes. Tables of the magnetic behavior of spin free and spin paired complexes are given. Nyholm (87, 91) has also published two other reviews pertaining to the application of crystal field theory to the interpretation of the magnetic properties of complexes and the use of magnetic susceptibility in the study of the stereochemistry of metal complexes.

Nortia (150) investigated the paramagnetic characteristics of chelate compounds of the transition groups on the basis of ionization of the element, the nature of the complex bond, and the stereochemistry of the chelate compound. He found that the paramagnetic characteristics were closely associated with the ionic character of the metal resulting from its electron-shell structure. The nature of the complexing compound has no effect on the magnetic properties, and the stereochemistry of the compound had very little effect.

Schilt (151) studied mixed complexes of nickel(II) with cyanide and 1,10-phenanthroline. He isolated three insoluble substances, $[Ni(1,10\text{-}phen)_3]$ $[Ni(CN)_4]\cdot 4H_2O$, $[Ni(1,10\text{-}phen)(CN)_2]\cdot H_2O$ (yellow), and $Ni(1,10\text{-}phen)(CN)_2(H_2O)_{0.5}$ (lavender). The magnetic moment of the substances were 2.19, 2.26, and 1.67 Bohr magnetons, respectively.

Katzin (152) suggested that paramagnetic nickel(II) compounds of normal green color or having an absorption band about 410 mμ, can be presumed to be 6-coordinate. Other nickel(II) compounds which do not show this peak (may be blue) are presumably tetrahedral or of an equivalent electronic structure.

Griffith (153) calculated the general formula for the matrix elements in octahedral complexes and applied the calculation to the spin-orbit coupling energies. Structural isomorphism was established between $(dt_{2g})^n$ and P^n configurations. Fair agreement was found between the calculated and experimental magnetic moments of the transition metals.

Ballhausen and Liehr (154) discussed the magnetic and spectral properties of tetra-coordinated nickel(II) complexes in terms of the crystal field theory. They point out that for such nickel(II) complexes there exist both strong experimental evidence and theoretical arguments against (a) the existence of dsp^2 bonding, and (b) the existence in solutions and melts of planar-tetrahedral conformational equilibria. Equations governing the magnetic susceptibility of partially paramagnetic planar nickel(II) systems were derived and used in the determination of the singlet-triplet energy separation.

C. Stability Constants

Freiser (155, 156) published the first papers on the structure and stability of chelates that are of analytical importance. Ionization and formation constants were determined in 50%dioxane-50%water mixtures for various cations and chelating agents. Anderson (157) determined the stability constants of various <u>vic</u>-dioxime complexes of nickel(II) in

75%dioxane-25%water mixtures. Potentiometric studies of the nickel(II) complexes of acetyacetone, malonates, and β-keto esters in absolute ethanol were made by Van Uitent and Fernelius (158). The stability constants for some bivalent metals and methylene-substituted β-diketones in 75%dioxane-25%water mixtures at 30° C. were reported by Martin and Fernelius (159).

Lotz <u>et</u> <u>al</u>. (160) made a thermodynamic study of some coordination compounds of metal ions with amines containing oxygen. Stability constants were reported. They also found that heats of reaction were more important than entropy changes. Hoyer (161) investigated the stability of nickel(II) and copper(II) complexes of substituted 1,2-diaminoethanes. The formation curves and stability constants are given. The composition and instability constants of nickel(II) pyridine complexes were determined polarographically by Tur'yan and Serova (162).

Bjerrum <u>et</u> <u>al</u>. (163, 164) have published two very good reviews dealing with stability constants of metal ions with organic and inorganic ligand. Freiser <u>et</u> <u>al</u>. (165) have listed stability constants for nickel(II) and zinc(II) complexes with 79 organic ligands.

Sillén (166) reviewed the problems dealing with the determination of stability constants. The review covers the various experimental methods, computations, accuracy, and the conditions necessary for obtaining good results.

Charles and Freiser (167) used titrimetric methods to determine the stability constants of nickel(II), copper(II), lead(II), cobalt(II) and zinc(II) with dimethylglyoxime and dimethylglyoxime O-monomethyl ether. The stability constants, log k_1 and log k_2, for nickel(II) are 11.16, 10.54 and 6.38, 5.69, respectively.

Bochkova and Peshkova (168) determined stability constants for the nickel(II) complexes of dimethylglyoxime, dimethylglyoxime O-monomethyl ether, diacetylmonoxime, methylglyoxime, ethylmethylglyoxime in 50%dioxane-50%water mixtures. The values for the over-all stability constant, K_2, are 22.3, 12.0, 14.5, 18.8, and 22.5, respectively.

Peshkova and Bochkova (169) investigated the complexes of nickel(II), cobalt(II), and copper (II) with PhC(:NOH) C (:NOH)H, p-MeOC$_6$H$_4$C(:NOH)C(:NOH), and 1,2-di(2-furyl)ethanedionedioxime. The stability constants (log k_1 and log k_2) for nickel(II) are 9.9, 9.4; 9.1, 8.6; and 8.4, 6.4, respectively.

Wenger et al. (170) reported the formation of three complexes of nickel(II) with 1,2-diaminoethanedionedioxime in acid medium. The stability constants for the three complexes were 2.69, 4.70, and 7.33, respectively.

Dyrssen et al. (171) studied the distribution of $^{63}Ni^{+2}$ between the aqueous phase and chloloform as a function of

H^+ and dimethylglyoxime concentration. The data could be completely explained by the equilibrium:

$$Ni(DH)_2(aqueous) = Ni(DH)_2(CHCl_3)$$

The value of K_2 from the distribution data was 17.24.

III. MATERIALS AND APPARATUS

The 4-carboxy-1,2-cyclohexanedionedioxime was prepared in this laboratory by the procedure of Banks et al. (19). 4-Carobxylcyclohexenfuroxane was prepared by J. J. Richard using the procedure of Banks and Richard (63).

Nickel(II) chloride stock solutions were prepared from special low cobalt $NiCl_2 \cdot 6H_2O$ obtained from the Baker Chemical Company. The solutions were prepared using deionized distilled water and were standardized by the heptoxime method (172).

The potassium hydroxide was of certified reagent-grade quality and was obtained from Fisher Scientific Company. All other chemicals were of reagent-grade quality.

All glassware used in this study was Class A.

The pH titrations were made using a Beckman, Model G, pH meter equipped with a Type E glass electrode.

A Cary Recording Spectrophotometer, Model 14, was used to obtain all of the spectrophotometric data. Matched silica cells were used for the measurements in the ultraviolet, visible, and infrared regions of the spectrum. When required, silica slugs were used to give cell paths of 0.005, 0.02, 0.05, and 0.2 cm.

Magnetic susceptibility measurements were carried out using an apparatus of the Gouy type. The operation and description of the apparatus are given in detail by Vander Haar (173). The samples were contained in 40-cm., two compartment, sample tubes of 5-mm. and 7.5-mm. inside diameter. The tubes were calibrated by filling with dry air and making measurements at various coil currents, and corrections were applied whenever necessary. The instrument was checked for deviations from a previous calibration by Vander Haar by measuring the susceptibility of deionized water and nickel(II) chloride solutions of known susceptibility. All measurements were made at 20.0° C.

All computations were made on a Magnetic Drum Data-Processing Machine, Type 650, manufactured by International Business Machines Corporation.

The polarographic data were obtained with a Metrohm Polarecord, Model E 261, distributed by Brinkmann Instrument Inc.

IV. EXPERIMENTAL PROCEDURES

A. Determination of the Ligand to Metal Ratio

1. Job's Method

A modification of Job's method (174) of continuous variations by Vosburgh and Cooper (175) was used to determine the ligand to metal ratio. This modification made it possible to apply the method to cases in which more than one compound was formed from the same components. The conditions stated by Job to obtain reliable results are, (a) the two simple constituents have, in solution, a well determined molecular formula, (b) there was a single complex formed, (c) the law of mass action was applicable, (d) for all equimolar mixtures, within the concentration range, the maximum composition must remain the same, (e) for non-equimolar mixtures, the value of the equilibrium constant must remain the same within the conditions as far as possible. Vosburgh and Cooper stated that if two or more compounds could be formed, the maximum should vary with wavelength. If only one compound is formed, the maximum should not vary. Therefore, it should be possible to determine if there was more than one compound formed by using several wavelengths.

Jones and Innes (176) have reported two restrictions inherent in Job's method, (a) the effect which activity coefficents can have on the molar ratio at which the concentration of the complex is a maximum, and (b) the limitation of the choice of physical measurements which can be used. When the measured property is not a linear function of the concentration of the species involved, the maximum observed may not coincide to the maximum concentration of the complex.

In this method solutions of equal concentrations of the ligand and metal are prepared. These solutions are mixed in varying proportions such that the total volume is the same in all cases. The absorbances of the solutions measured are corrected for the absorbances of the pure components. A plot is made of absorbance versus mole fraction of ligand in the final solution. A maximum will appear on this curve at the mole fraction corresponding to the ratio of ligand to metal in the complex.

2. Mole ratio method

The method of deducing the stoichiometry of complexes in solution from spectrophotometric data was introduced by Yoe and Jones (177). A mathematical treatment has been developed by Meyer and Ayres (178). The method is based on the consideration of a reaction of the type:

$$A + nB = AB_n \qquad \text{Eq. (1)}$$

If the product is very little dissociated, a plot of the ratio of B-to-A, if A is held constant or if B is held constant, A-to-B, will be a straight line passing through the orgin below the ratio of the complex and a straight line of different slope above this point. Thus producing a break in the curve at a point corresponding to the ratio of A to B in the complex. If the complex is highly dissociated, the mole ratio plot will show no sharp break, but a gradual change of slope.

The stoichiometry of all the complexes in solution can be defined by spectrophotometric measurements of solutions of mole ratios corresponding to each complex, of one solution between successive complexes, and two solutions above and below the mole ratio of the terminal complexes. The absence of a change in slope, in the mole ratio plot, over the entire spectrum is good evidence that a complex of a given mole ratio does not exist. The mole ratio method has several advantages over the method of continuous variations, (a) one of the reactants is held constant, thus simplifying the preparation of solutions, (b) conserves reagents if a limited supply is available, (c) in ideal cases, fewer than three solutions may be required for each complex in solution, and (d) the method is especially suitable for determining the composition of high ratio complexes.

B. Determination of Bond Type and Oxidation State by Magnetic Susceptibility

Magnetic susceptibility measurements have been used for the elucidation of oxidation state, bond type, and stereochemistry in the study of the coordination compounds. The detailed discussion has been cited on pages 16 to 27. Magnetic susceptibility arises from the electrical nature of the atom and the possible energy states the atom may occupy. Diamagnetism is a property all atoms possess and arises from the tendency of the electrons in closed shells to orient their planes of rotation so as to suffer the minimum interaction with the imposed magnetic field. The atomic susceptibility for a polyelectron atom can be derived either from Classical mechanics or quantum mechanics and is given by the equation

$$\chi_D = \frac{-Ne^2}{6mc^2} \sum_n \bar{r}_n^2 = -2.832 \times 10^{10} \times \sum_n \bar{r}_n^2 \qquad \text{Eq. (2)}$$

where N is Avogadro's number, e the unit of electrostatic charge, c the velocity of light, m the mass of the electron, and $\bar{r}^2$ the sum of the squares of the x projections of the orbits for all electrons on a plane. Thus diamagnetic susceptibility is virtually independent of the temperature.

Atoms or molecules that behave as though they have a permanent magnetic moment are said to be paramagnetic. This is due to the fact that unpaired electrons possess both spin and orbital angular momenta. A paramagnetic substance is subject to two opposing effects, (a) the magnetic field which tends to align the molecular moments in the same direction as that of the field and (b) the thermal agitation (kT effect) which tends to randomize the directions of the molecular moments. The susceptibility is given by the equation

$$\chi_P = \frac{N^2 \mu^2}{3R\ T} \qquad \text{Eq. (3)}$$

where N is Avogadro's number, μ the magnetic moment, R the universal constant, and T the absolute temperature.

The temperature independent (Van Vleck) paramagnetism ($\chi_{V.V.}$) is the contributions to the configuration of the molecule in which the energy states are separated from the ground state by an energy ($h\nu$), which is large compared to kT. The effect is pictured as arising from an unbalanced orbital contribution.

In practice, one determines χ_M which is the sum of $\chi_{V.V.} + \chi_D + \chi_P$. Because the value for $\chi_{V.V.}$ is usually not known, a corrected molar susceptibility (χ'_M) which equals $\chi_M - \chi_D$ is used. Solving for μ and substituting for the constants, one obtains

$$\mu_{eff} = 2.84\sqrt{\chi'_M \quad T} \qquad \text{(Curie Law)} \qquad \text{Eq. (4)}$$

If the susceptibility χ_P is proportional to 1/T, the Curie Law is obeyed. The substance is said to follow the Curie-Weiss Law if χ_P is proportional to $1/T + \alpha$, where α is a constant.

The magnetic behavior of paramagnetic compounds is dependent upon three things, (a) the number of unpaired electrons, (b) the spectroscopic ground state and upper states, and (c) the symmetry and strength of the electric field arising from the ligand. The first transition series has the "spin only type" behavior. The equation is

$$\mu = \sqrt{4S\ (S + 1)} \qquad \text{Eq. (5)}$$

where S is equal to n/2, gives the best agreement between theory and experimental data. The orbital contribution is ignored.

Therefore, if the molar susceptibility is known, the number of unpaired electrons can be calculated from equations 4 and 5.

The application of magnetic susceptibility to the determination of the configuration of nickel(II) complexes may be seen from Table I. From Table 1, it may be seen that some ambiguity exists, but much information can be gained from

Table 1. Relationships between oxidation states, coordination numbers, configurations, and magnetic moment for nickel complexes

Oxidation state	Coordination number	Unpaired electrons	B. M. (calc.)	Configuration
2	4	0	0	Sq. Planar $3d4s4p^2$
	4	2	2.83	Tetrahedral $4s4p^3$
	6	2	2.83	Octahedral $4s4p^34d^2$
	6	0	0	Octahedral $3d^24s4p^3$
3	4	1	1.73	$3d4s4p^2$
	4	3	3.86	$4s4p^3$
	6	3	3.86	$4s4p^34d^2$
	6	1	1.73	$3d^24s4p^3$
4	4	2	2.83	$3d4s4p^2$
	4	2	2.83	$4d4p^3$
	6	2	2.83	$4s4p^34d^2$
	6	0	0	$3d^24s4p^3$

magnetic susceptibility measurements, particularly if combined with independent knowledge as to the coordination number or oxidation state.

The crystal field theory has recently been applied by chemists to explain the magnetic behavior of complexes. The details of the theory can be outlined briefly as follows. The central metal atom is surrounded by anions or dipoles, which set up a strong electrostatic or crystalline field. The normally degenerate d levels are split by this field. The extent of the splitting depends upon the central cation, the symmetry and strength of the applied field. It is due to the fact that electrons tend to avoid those regions where the field due to the negative ions and dipoles is the largest. Orgel (179) has discussed the physical ideas of electron distribution according to the crystal field theory and their application to magnetism, color, configuration, and heat of hydration of the transition metals.

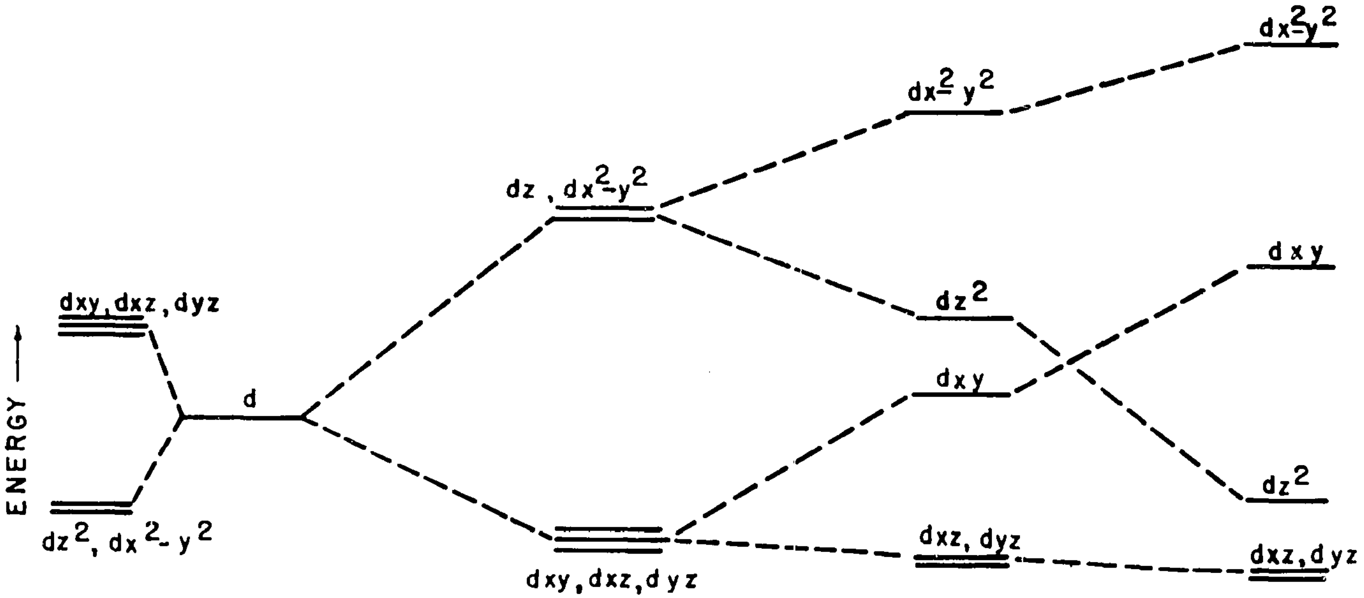
The energy levels of the d orbitals due to the crystal field splittings are shown schematically in Figure 1. From crystal field theory, the stereochemistry expected for nickel(II) with eight d electrons for the spin free case (two unpaired electrons) is a perfect octahedron or for the spin paired case (no unpaired electrons) square planar or tetragonal.

In the Gouy method of measuring magnetic susceptibility, a cylindrical sample of uniform cross section is suspended, from a balance, between the pole pieces of an electromagnet so that the sample extends from an area of large magnetic field to an area of negligible magnetic field. The change in weight is related to magnetic susceptibility by the following relationship

$$g \, \Delta W = 1/2AH^2(\kappa_1 - \kappa_2) \qquad \text{Eq. (6)}$$

where g is the acceleration of gravity, A is the cross sectional area of the sample, H is the largest magnetic

Figure 1. Crystal field splittings of the d orbitals of the central atom in regular complexes.


ENERGY
dxy, dxz, dyz
dz2, dx2-y2
d
dz , dx2-y2
dxy, dxz, dyz
dx2-y2
dz2
dxy
dxz, dyz
dx2-y2
dxy
dz2
dxz, dyz

field present, and κ_1 and κ_2 are the volume susceptibilities of the sample and the surrounding atmosphere, respectively. In this study the instrument was so calibrated that change in weight at a particular coil current could be related directly to κ_1. Division of κ_1 by the density then gives χ_g, the gram susceptibility, and multiplication of this by the molecular weight of the sample gives χ_M, the molar susceptibility, which can then be used for the calculation of n as described above.

C. Determination of Absorption Spectra and Molar Absorptivities

Solutions of known concentration were prepared by weighing 4-carboxynioxime on a balance and transfering to a 50 ml. class A volumetric flask, adding an aliquot of standard nickel(II) chloride solution, 28 g. of potassium hydroxide, and diluting to a volume of approximately 40 ml. with distilled deionized water. The flask was placed in a cold water bath and shaken until the potassium hydroxide had dissolved. The solution was allowed to come to room temperature and then diluted to volume with distilled deionized water. It was transferred to a polyethylene bottle, with provisions for passing a gas continuously into it, and placed in a constant temperature bath. The temperatures used in this study were 25° and 50°C. Three milliliter aliqants were removed at various time intervals, diluted to a volume of 25 ml. with 8.923 M potassium hydroxide and scanned immediately. The reference was air.

Spectra were scanned on an automatic recording Model 14 Cary Spectrophotometer. Matched silica cuvettes were used for all the measurements in the ultraviolet, visible, and infrared regions of the spectrum. Silica slugs were used to reduce the size of the cell paths. The cell paths obtainable with these slugs are 0.005, 0.02, 0.05, and 0.2 cm.

To obtain the absorption spectra of the nickel complexes, the observed spectra were corrected for the absorption of the *vic*-dioxime and 8.923 M potassium hydroxide.

V . RESULTS

A. Determination of Stability Constants of the Nickel(II) Complexes

1. Evidence for the existence of nickel(II) complexes

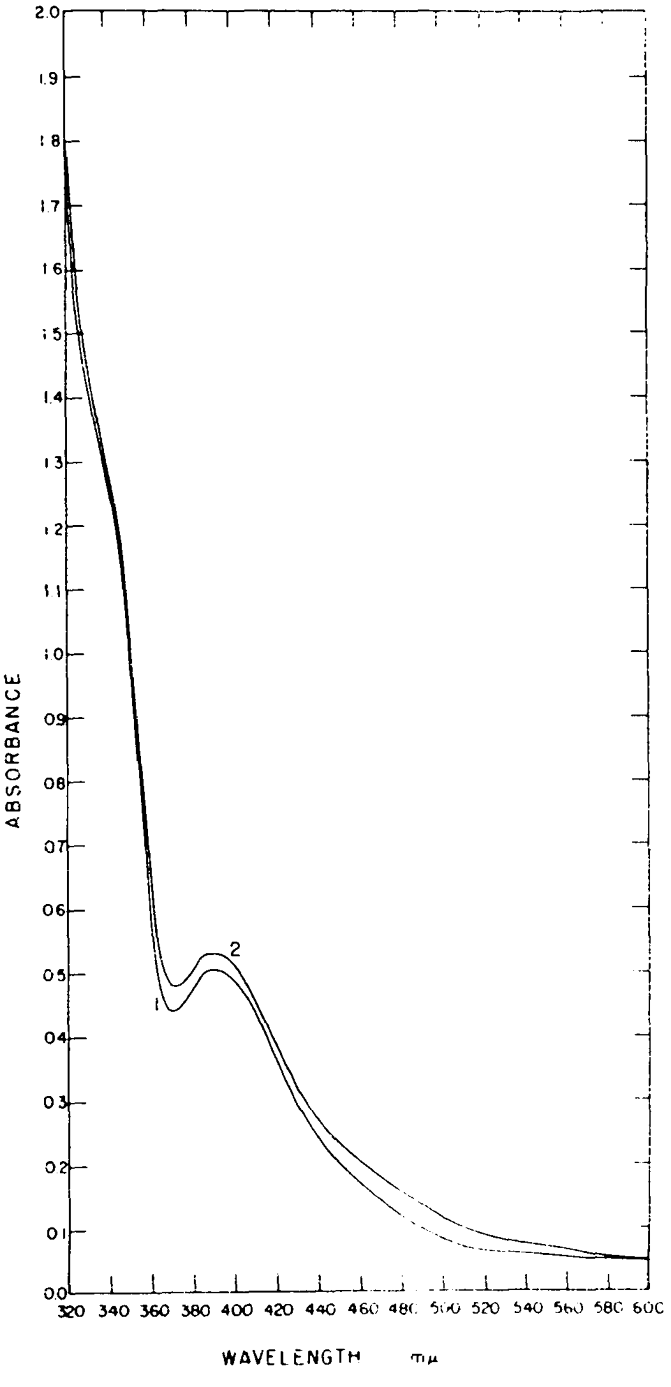
Due to the nature of the reaction, the determination of the stability constants of the nickel(II) complexes of the *vic*-dioximes is very difficult. Many chemists have used the reaction to determine nickel, but most have made no attempt to determine the reaction mechanism. Several papers (155, 156, 164, 167, 168) have been published concerning the stability constants of nickel(II) complexes of *vic*-dioximes in 50% dioxane-50% water. Wenger *et al*. (170) determined the stability constants for the three complexes of nickel(II) with 1,2-diaminoethanedionedioxime in acid medium. In the study of the oxidation of bis(2,3-butanedionedioximato-*N*,*N*')nickel(II) in alkaline media, Okáč and Šimek (7, 8, 59, 46, 57, 58) proposed the existence of Na [DNi(II)OH] and $[Ni(II)\,D_3]^{-4}$ to explain their experimental data. They did not determine stability constants for either of these species. German (5) reported a stability constant of 1.1 x 10^7 for the formation of bis(4-carboxynioximato-*N*,*N*')nickel(II).

In this investigation, an attempt has been made to show that there are three complexes, mono(4-carboxynioximato-

N,N')nickel(II), NiD^-; bis(4-carboxynioximato-N,N')nickel(II), NiD_2^{-4}; and tris(4-carboxynioximato-N,N')nickel(II), NiD_3^{-7}; present in concentrated alkaline media. To determine which absorption maxima were due to the nickel(II) complexes of 4-carboxynioxime, two studies were made. In the first study, the solution was prepared in an atmosphere of helium. The concentrations of 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide were 8.843×10^{-3}, 1.446×10^{-3}, and 8.923 M, respectively. These reactants were placed in a 50 ml. volumetric flask. Approximately 40 ml. of water was added and the flask was placed in a cold water bath and shaken until the potassium hydroxide dissolved. The solution was allowed to come to room temperature and then diluted to volume with water. A 3 ml. aliquant was removed, diluted to a volume of 25 ml. with 8.923 M potassium hydroxide. This solution was then placed in a silica cell with a cell path of 0.2 or 0.005 cm. and sealed with Scotch Electrical Tape, No. 33. The solution was scanned from 320 to 900 mu at various intervals over a period of 96 hrs. The reference was air. The spectra obtained are shown in Figure 2. No change in absorption was found in the region 600 to 900 mu.

The second study was carried out in a similar manner, except that oxygen was used instead of helium and the cell was not sealed. The concentrations of 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide were the same

Figure 2. Absorption spectra obtained from a rate study of a solution sealed in a silica cell. Curve 1, 0.0 hrs. Curve 2, 53.0 hrs.


ABSORBANCE
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
1
2
320
340
360
380
400
420
440
460
480
500
520
540
560
580
600
WAVELENGTH mμ

as in the first study. These reactants were placed in a 50 ml. volumetric flask. Approximately 40 ml. of water was added and the flask was placed in a cold water bath and shaken until the potassium hydroxide dissolved. The solution was allowed to come to room temperature and then diluted to volume with water. It was transferred to a polyethylene bottle and placed in a constant temperature bath. The temperature of the bath was 50° C. Oxygen was bubbled continuously into the solution. Three-milliliter aliquants were removed at various time intervals, diluted to a volume of 25 ml. with 8.923 M potassium hydroxide and scanned from 320 to 900 mμ. The reference was air. The spectra obtained are shown in Figures 3 and 4. By comparing the absorption spectra obtained from the two studies, the 393 mu absorption maximum may be assumed to be due to a nickel(II) complex and the 489 and 740 mμ absorption maxima are due to some oxidized complex of nickel(II) with 4-carboxynioxime. Due to the high concentration of the vic-dioxime in these studies, the absorption maximum at 335 mμ was not observed. If the 4-carboxynioxime, nickel(II) chloride, and postassium hydroxide concentrations are 1.446×10^{-3}, 1.446×10^{-3}, and 8.923 M, respectively, the 335 mμ absorption maximum can be observed as is shown in Figure 3, Curve 1. This absorption maximum is also due to a nickel(II) complex.

Figure 3. Absorption spectra obtained from a rate study of a solution treated with oxygen. Curve 1, 0.0 hrs. Curve 2, 12.0 hrs. Curve 3, 29.0 hrs.

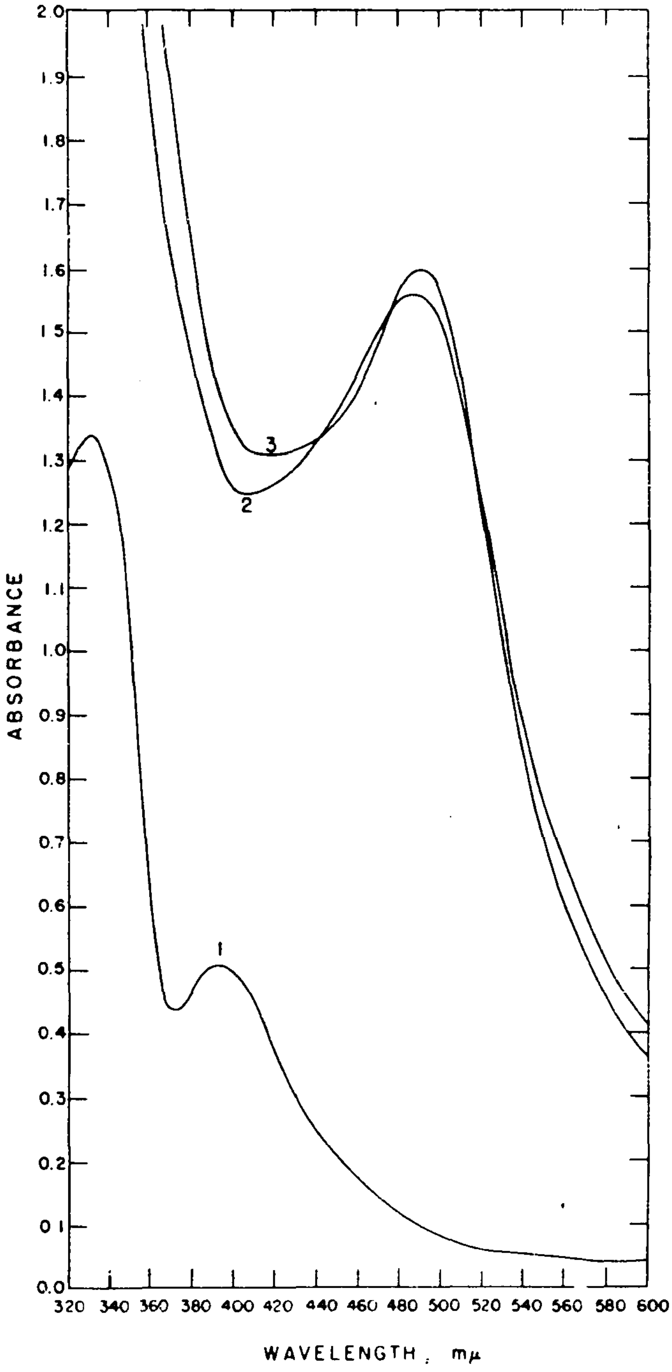
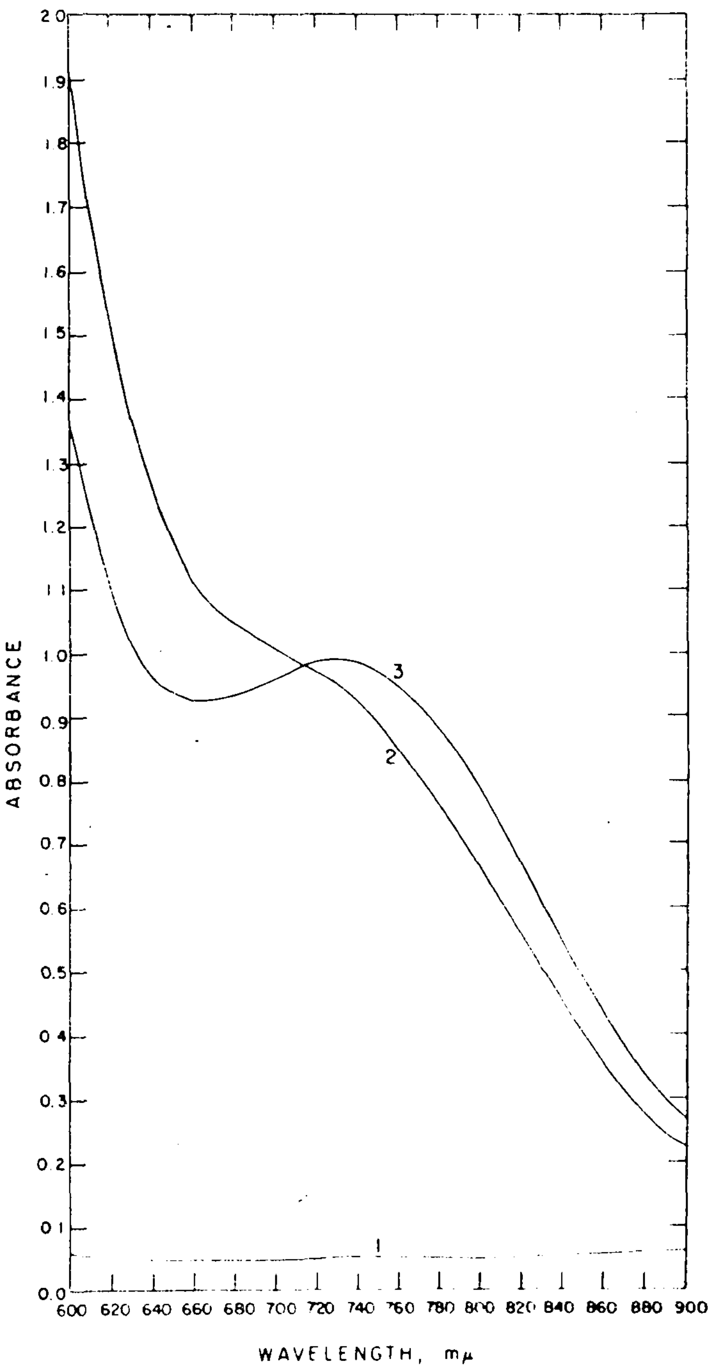

2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
ABSORBANCE
320
340
360
380
400
420
440
460
480
500
520
540
560
580
600
WAVELENGTH, mμ
1
2
3

Figure 4. Absorption spectra obtained from a rate study of a solution treated with oxygen. Curve 1, 0.0 hrs. Curve 2, 12.0 hrs. Curve 3, 29.0 hrs.

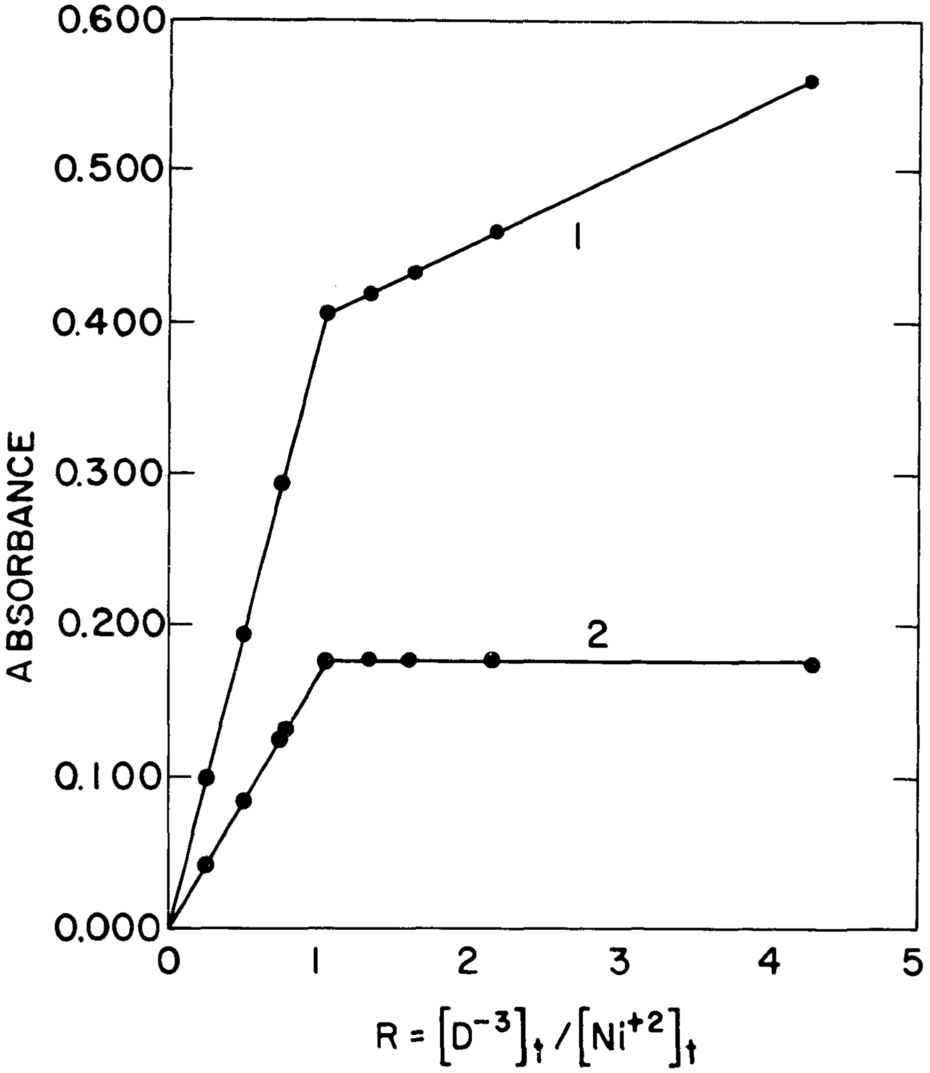

ABSORBANCE
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
600
620
640
660
680
700
720
740
760
780
800
820
840
860
880
900
WAVELENGTH, mμ
1
2
3

The study of the effect of oxygen and helium on the system has also shown that there was not a significant amount of the oxidized complex of nickel(II) and 4-carboxynioxime present immediately after the preparation of the solution.

The vic-dioxime to nickel ratio in the nickel(II) complex was determined by the mole ratio method described on page 34. The solutions are described in Table 2. The mole ratio plots are given in Figure 5. It was concluded that both the 335 and 393 mμ absorption maxima were due to the mono(4-carboxynioximato-N,N')nickel(II) complex ion. Because there were no other changes in the slope of the lines in the mole ratio plots, complexes of higher 4-carboxynioxime to nickel(II) ratios probably do not exist or they do not have any appreciable absorption in this region.

Magnetic susceptibility measurements were made on a series of solutions immediately after they were prepared. The concentration of 4-carboxynioxime was varied from 4.727 x 10^{-2} to 4.001 x 10^{-1} M, while the concentrations of nickel(II) chloride (4.634 x 10^{-2} M) and potassium hydroxide (8.923 M) were held constant. The reactants were placed in a 50-ml. volumetric flask and diluted to a volume of of approximately 40 ml. with water. The flask was placed in a cold water bath and shaken until the potassium hydroxide had dissolved. The solution was allowed to come to room temperature and then diluted to volume with water and the

Figure 5. Mole ratio plots for the determination of the ratio of 4-carboxynioxime to nickel(II). Curve 1, mole ratio plot obtained at 390 mμ. Curve 2, mole ratio plot obtained at 335 mμ.


ABSORBANCE
0.000
0.100
0.200
0.300
0.400
0.500
0.600
0
1
2
3
4
5
$R = [D^{-3}]_t / [Ni^{+2}]_t$
1
2

magnetic susceptibility measurements were made. The results are shown in Figure 6.

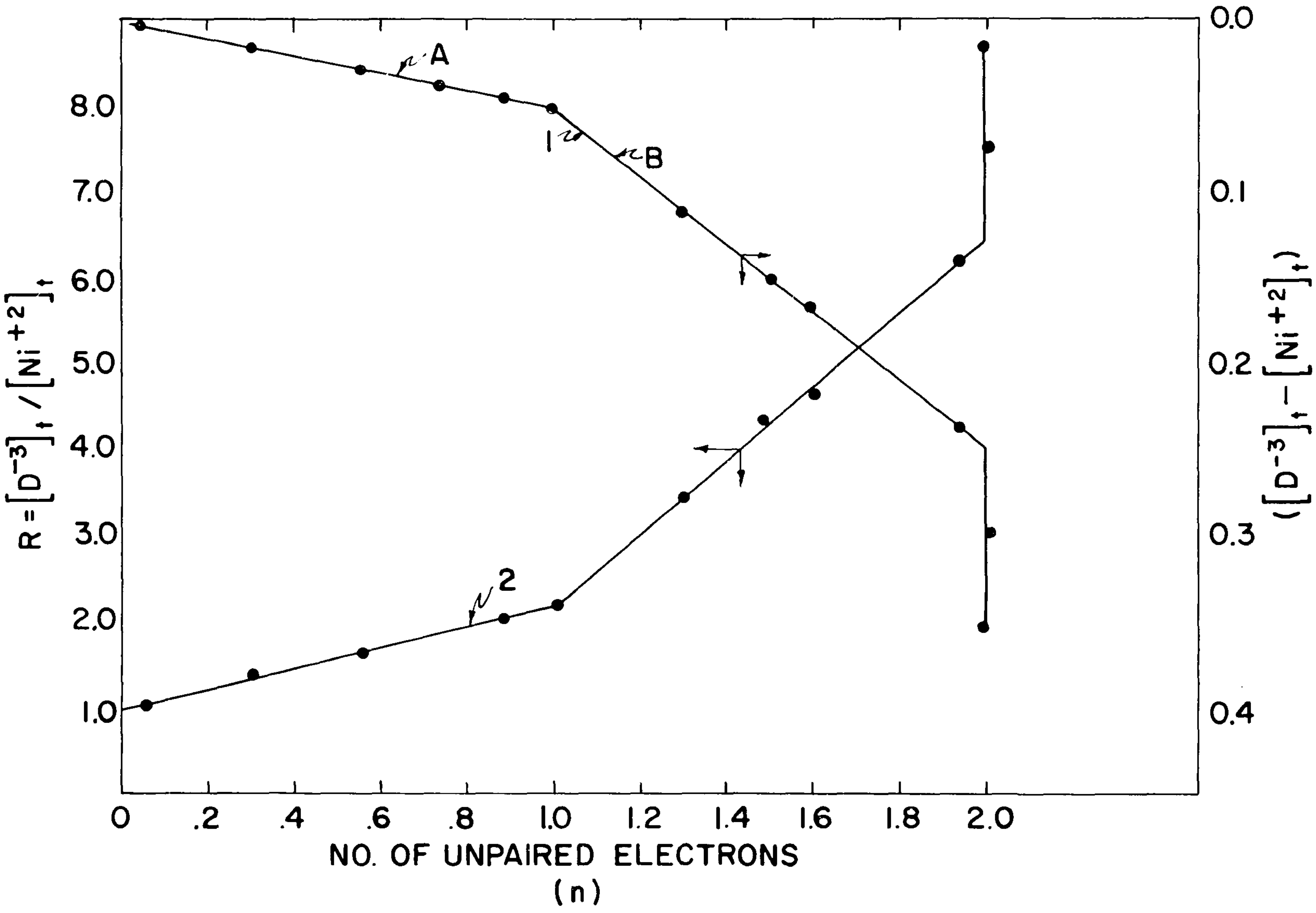
Table 2. Description of solutions used to determine the ratio of *vic*-dioxime to nickel by the mole ratio method

Solution no.	$[D^{-3}]_t \times 10^3$	$[Ni^{+2}]_t \times 10^3$	$[D^{-3}]_t /[Ni]^{+2}{}_t$
1	1.334	5.559	0.2400
2	2.668	5.559	0.4800
3	4.002	5.559	0.7200
4	5.673	5.559	1.0205
5	7.500	5.559	1.3492
6	9.000	5.559	1.6190
7	12.000	5.559	2.1587
8	24.000	5.559	4.3173

2. Determination of stability constants for the three complexes

The solution used to determine k_1 was prepared by the procedure cited on page 43. The concentrations of 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide were 1.446×10^{-3}, 1.446×10^{-3}, and 8.923 M, respectively. The spectrum is given in Figure 3, Curve 1. It was assumed that the concentrations of NiD_2^{-4}, NiD_3^{-7}, and NiO_2^{-2} were not significant in the calculation of k_1. The number of hydroxyl

Figure 6. Magnetic susceptibility measurements of 4-carboxy-nioxime-nickel(II) solutions.


A
B
1
2
R = [D⁻³]t / [Ni⁺²]t
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.1
0.2
0.3
0.4
([D⁻³]t − [Ni⁺²]t)
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
NO. OF UNPAIRED ELECTRONS
(n)

radicals associated with NiD^- and NiD_2^{-4} were not determined and were omitted in the equations below. The pK values (19) were determined for the three acidic hydrogens of 4-carboxynioxime and the results obtained were: $pK_1 = 4.85$, $pK_2 = 10.45$, $pK_3 = 12.37$. The D^{-3} ion was found to be the most important hydrogen species of the <u>vic</u>-dioxime present in concentrated base. The system may be defined in the following manner

$$Ni^{+2} + D^{-3} = NiD^- \qquad \text{Eq. (7)}$$

$$Ni^{+2} + OH^- = NiOH^+ \qquad \text{Eq. (8)}$$

$$Ni^{+2} + 2OH^- = Ni(OH)_2(s) \qquad \text{Eq. (9)}$$

$$Ni(OH)_2(s) + OH^- = HNiO_2^- + H_2O \qquad \text{Eq. (10)}$$

$$[D^{-3}]_T = [D^{-3}] + [NiD^-] \qquad \text{Eq. (11)}$$

$$[Ni^{+2}]_T = [Ni^{+2}] + [NiD^-] + [NiOH^+] + [Ni(OH)_2(s)] + [HNiO_2^-] \qquad \text{Eq. (12)}$$

$$A = \epsilon_1 l|D^{-3}| + \epsilon_2 [NiD^-] \qquad \text{Eq. (13)}$$

$$k_1 = \frac{[NiD^-]}{[Ni^{+2}]\ [D^{-3}]} \qquad \text{Eq. (14)}$$

$$K_4 = \frac{[NiOH^+]}{[Ni^{+2}]\ [OH^-]} = 2.3 \times 10^3 \qquad \text{Eq. (15)}$$

$$K5 = \frac{[Ni(OH)_2\ (s)]}{[Ni^{+2}]\ [OH^-]^2} = 1.54 \times 10^{17} \qquad \text{Eq. (16)}$$

$$K_7 = \frac{[HNiO_2^-]}{[Ni(OH)_2(s)] \quad [OH^-]} = 6.0 \times 10^{-5} \qquad \text{Eq. (17)}$$

From equations 11 and 13, an expression for (NiD^-) may be obtained

$$[NiD^-] = \frac{A - \epsilon_1 l \; [D^{-3}]_T}{\epsilon_2 l - \epsilon_1 l} \qquad \text{Eq. (18)}$$

An expression for $[Ni^{+2}]$ may be obtained by substituting equations 15, 16, and 17 into equation 12

$$[Ni^{+2}] = \frac{[Ni^{+2}]_T - [NiD^-]}{L + K_4 \; [OH] + K_5 \; [OH]^2 + K_5K_6 \; (OH)^3} \qquad \text{Eq. (19)}$$

Substituting equations 11 and 19 into equation 14, we obtain for k_1

$$k_1 = \frac{[NiD^-] \; (1 + K_4[OH] + K_5[OH]^2 + K_5K_6 \; [OH]^3)}{([Ni^{+2}]_T - [NiD^-]) \; ([D^{-3}]_T - [NiD^-])} \qquad \text{Eq. (20)}$$

The values for K_4, K_5 and K_6 were determined by Gayer and Gattett (180, 181). Due to the slight solubility of nickel(II) hydroxide, the $(NiO_2^{=})$ term was neglected in equation 8. The data for A, ϵ_1 and ϵ_2 from 320 to 600 mμ, and the computed values of k_1 are listed in Table 2. The molar extinction coefficient (ϵ_1) for the <u>vic</u>-dioxime was determined from an experiment in which the nickel(II) chloride was omitted.

Table 3. Determination of k_1[a]

, mu	A	ϵ_1 for D^{-3}	ϵ_2 for NiD^-	ϵ_3 for NiD_2^{-4}[b]	ϵ_4 for NiD_3^{-7}[c]	log k_1
320	0.701	592.4	2461	4638	5902	28.73
330	0.710	205.7	2493	5106	4975	28.73
340	0.689	101.2	2419	5157	4532	28.73
350	0.584	62.39	2050	4098	3537	28.73
360	0.383	38.78	1345	2096	1956	28.73
370	0.292	21.36	1025	1433	1443	28.73
375	0.295	15.74	1036	1514	1478	28.73
380	0.308	10.12	1081	1707	1605	28.74
385	0.323	6.755	1134	1904	1687	28.74
390	0.332	3.934	1166	2055	1769	28.74
395	0.332	2.248	1166	2089	1773	28.74
400	0.330	1.686	1159	2067	1737	28.74
405	0.321	1.124	1127	1967	1668	28.74
410	0.304	1.124	1067	1791	1534	28.74

Ave. log k_1 = 28.74
Std. Dev. = 0.004

[a] The absorption spectrum was obtained from a solution 1.446 x 10^{-3} <u>M</u>, 1.446 x 10^{-3} <u>M</u>, and 8.923 <u>M</u> in 4-carboxy-nioxime, nickel(II) chloride, and potassium hydroxide, respectively.

[b] ϵ_3 was calculated from an absorption spectrum of a solution in which the vic-dixoime to nickel ratio was 2:1, using the values obtained previously for ϵ_1, ϵ_2, and ϵ_4.

[c] ϵ_4 was calculated from an absorption spectrum of a solution in which the vic-dioxime to nickel ratio was 6:1. The NiD_2^{-4} was assumed to be negligible.

Table 3. (Continued)

λ, mμ	A	ϵ_1 for D-3	ϵ_2 for NiD^-	ϵ_3 for $NiD_2$4b	ϵ_4 for NiD_3^-7c	log k_1
420	0.264	1.124	927.0	1405	1211	28.74
430	0.226	1.124	793.5	1055	948.2	28.74
440	0.197	1.124	691.7	799.9	763.2	28.74
450	0.180	2.482	632.0	681.1	615.5	28.74
460	0.161	2.248	566.3	415.8	478.7	28.74
470	0.148	2.248	519.7	263.0	372.8	28.74
480	0.138	2.248	484.5	103.3	272.2	28.74
485	0.133	2.248	467.0	70.66	236.0	28.74
490	0.128	2.248	449.4	62.98	181.0	28.74
495	0.123	2.248	431.9	49.68	159.0	28.74
500	0.116	2.248	407.3	89.13	130.2	28.74
510	0.103	2.248	361.7	133.1	90.27	28.74
520	0.089	2.248	312.5	117.7	75.29	28.74
530	0.077	2.288	270.4	103.5	71.94	28.74
540	0.067	2.248	235.3	74.48	61.21	28.73
550	0.061	2.248	214.2	71.24	54.79	28.73
560	0.054	2.810	189.6	72.14	45.27	28.73
570	0.045	2.810	158.0	71.22	42.74	28.73
580	0.038	2.810	133.4	71.37	18.68	28.73
590	0.036	2.810	126.4	70.29	21.27	28.73
600	0.036	2.810	126.4	70.29	21.27	28.73

The concentration of 4-carboxynioxime and potassium hydroxide were 8.896 x 10^{-3} and 8.923 M, respectively. These reactants were placed in a 50-ml. volumetric flask and diluted to a volumetric flask and diluted to a volume of approximately 40 ml. with water. The flask was placed in a cold water bath and shaken until the potassium hydroxide had dissolved. The solution was allowed to come to room temperature and then diluted to volume with water. A 3-ml. aliquant was diluted to a volume of 25 ml. with 8.923 M potassium hydroxide. The solution was scanned in a silica cell with a cell path of 0.02 cm. from 320 to 900 mµ. The solution did not have any absorption from 370 to 900 mµ. The reference was air. The absorbancies were corrected for the absorption of the potassium hydroxide.

For the determination of ϵ_2, a solution was prepared in which the concentrations of 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide were 1.446 x 10^{-3}, 1.446 x 10^{-3}, and 8.923 M, respectively. The procedure cited above was used. The absorbancies obtained were corrected for the absorption of the vic-dioxime and potassium hydroxide. The value found for k_1 was $(5.4 \pm 0.03) \times 10^{28}$. The standard deviation was 0.04×10^{28}.

On the basis of the conclusions that were made on page 60 to explain the magnetic susceptibility determinations, the following equations were used to calculate k_2 and k_3

$$NiD^{-} + D^{-3} = NiD_2^{-4} \qquad \text{Eq. (21)}$$

$$NiD_2^{-4} + D^{-3} = NiD_3^{-7} \qquad \text{Eq. (22)}$$

$$[D^{-3}]_T - [Ni^{+2}]_T = [D^{-3}] + [NiD_2^{-4}] + 2[NiD_3^{-7}] - [Ni^{+2}] \qquad \text{Eq. (23)}$$

$$k_2 = \frac{[NiD_2^{-4}]}{[NiD^{-}]\ [D^{-3}]} \qquad \text{Eq. (24)}$$

$$k_3 = \frac{[NiD_3^{-7}]}{[NiD_2^{-4}]\ [D^{-3}]} \qquad \text{Eq. (25)}$$

The equations for the straight lines, A and B, in Figure 6, Curve 1 are

$$n = 18.27\ ([D^{-3}]_T - [Ni^{+2}]_T) + 0.0423 \qquad \text{Eq. (26)}$$

$$n = 4.966\ ([D^{-3}]_T - [Ni^{+2}]_T) + 0.757 \qquad \text{Eq. (27)}$$

If we assume $[Ni^{+2}] < [D^{-3}]$, then substituting equations 24 and 25 into equation 23, we obtain

$$[D^{-3}]_T - [Ni^{+2}]_T = [D^{-3}] + k_2[D^{-3}][NiD^{-}] + 2k_2k_3 [D^{-3}]^2\ [NiD^{-}] \qquad \text{Eq. (28)}$$

or,

$$[D^{-3}] = \frac{-(1 + k_2[NiD^{-}]) + ((1 + k_2[NiD^{-}])^2 + 8k_2k_3[NiD^{-}]\,([D^{-3}]_T - [Ni^{2}]_T))^{\frac{1}{2}}}{4k_2k_3\ [NiD^{-}]} \qquad \text{Eq. (29)}$$

$$[D^{-3}]_T = [D^{-3}] + [NiD^-] + 2[NiD_2^{-4}] + 3[NiD_3^{-7}] \quad \text{Eq. (30)}$$

The number of unpaired electrons is a measure of the amount of $[NiD_2^{-4}]$ and $[NiD_3^{-7}]$ present in solution. The concentration of $[NiD^-]$ is the difference between $[Ni^{+2}]_T$ and the sum of $[NiD_2^{-4}]$ and $[NiD_3^{-7}]$. A typical example of calculating $[NiD^-]$ is

For $n = 1.0$

$$[NiD_2^{-4}] + [NiD_3^{-7}] = 50\% \ [Ni^{+2}]_T \quad \text{Eq. (31)}$$

$$[NiD^-] = 50\% \ [Ni^{+2}]_T \quad \text{Eq. (32)}$$

The quantity, $[D^{-3}]_T - [Ni^{+2}]_T$, was computed from either equation 26 or 27. Using the data calculated from equation 26 and the corresponding values for n, $[NiD^-]$, and the trial values for k_2 and k_3, the best value for k_2 was computed by holding k_3 constant and varying k_2. The k_2 was adjusted so that the computed $[D^{-3}]_T$ in equation 30 was within 1% of the experimental value. The quantities $[NiD_2^{-4}]$ and $[NiD_3^{-7}]$ in equation 30 were calculated from equations 24 and 25. Then using the same procedure and equation 27, the new k_2 was held constant and k_3 was adjusted. Three iterations were required. The values for k_2 and k_3 are 5.8 and 4.7 x 10^3, respectively.

In order to obtain a check on the accuracy of the computation, the computed values of k_1, k_2, and k_3 were used to calculate an absorption spectrum, which was then compared with an experimentally obtained spectrum. The results are shown in Figure 7. It may be seen that the spectra are almost identical. Therefore, the assumptions made concerning the bis(4-carboxynioximato-N,N')nickel(II) and tris(4-carboxynioximato-N,N')nickel(II) complex ions were justified.

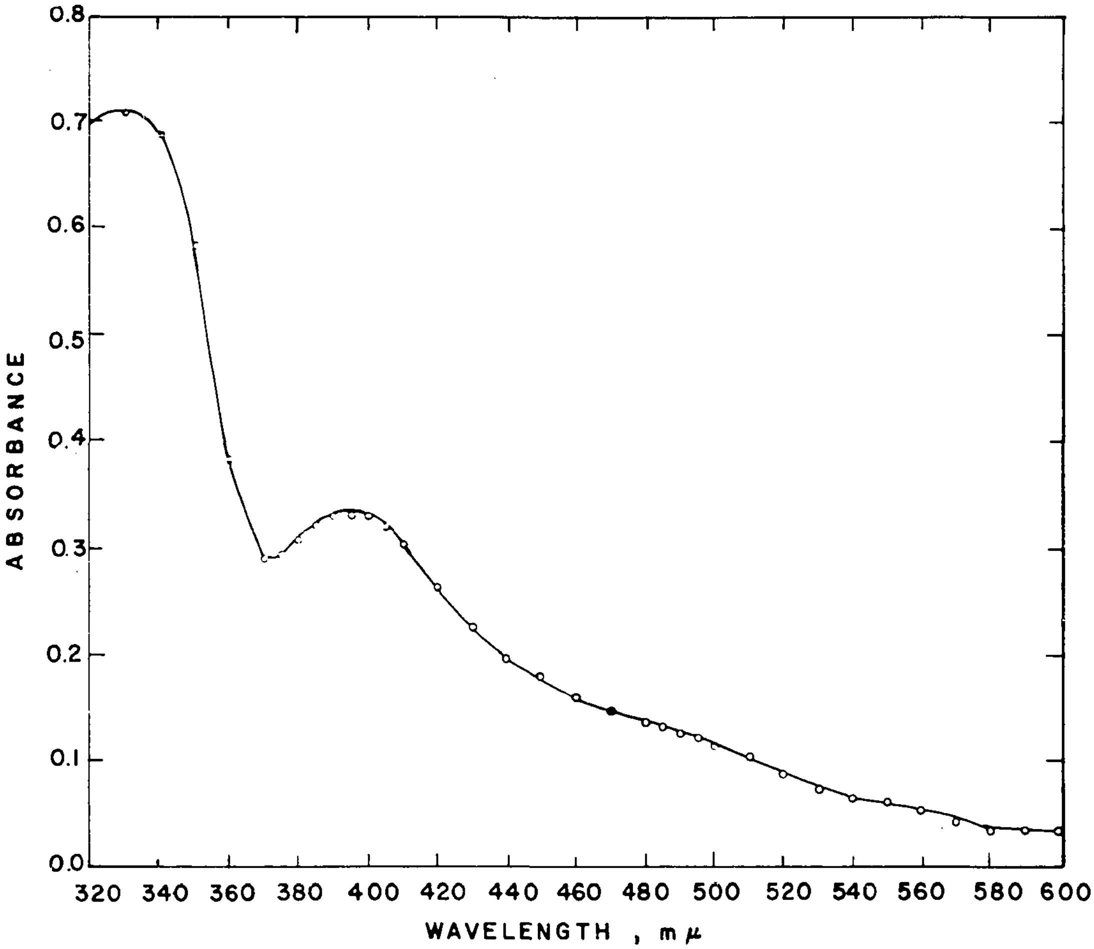
3. Discussion

Stability constants have been reported for the nickel(II) complexes of *vic*-dioximes in various solvents, but not in alkaline medium. There seems to be no correlation between the stability constants obtained in concentrated potassium hydroxide and other media. No experiments were preformed to determine the dependence of NiD^- or NiD_2^{-4} on the concentration of base. It has been substantiated by previous workers (2, 5, 7, 57, 59) that the oxidation of the nickel(II) complexes is very slight at 25° C. in 8 to 10 *M* soldium or potassium hydroxide.

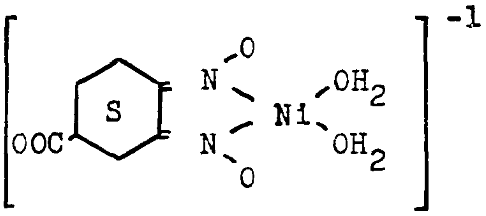
The order of the magnitudes of k_1, k_2, and k_3 are in agreement with the theoretical stabilities of the nickel(II) complexes predicted from energy level diagrams (144) and crystal field theory (82, 88, 89, 104, 147).

The magnetic susceptibility studies shown in Figure 6 explain why the odd magnetic susceptibility values were obtained by Carlson (4) and German (5), when the *vic*-dioxime to nickel(II) ratios were between 1:1 and 4:1.

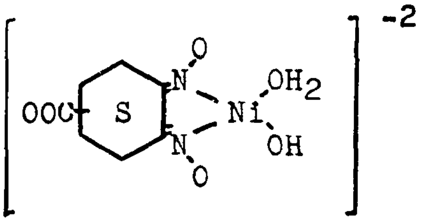
Figure 7. Comparison of calculated and experimental absorption spectra; o-o-o- are the calculated values plotted on the experimentally recorded curve.


0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
ABSORBANCE
320
340
360
380
400
420
440
460
480
500
520
540
560
580
600
WAVELENGTH , mμ

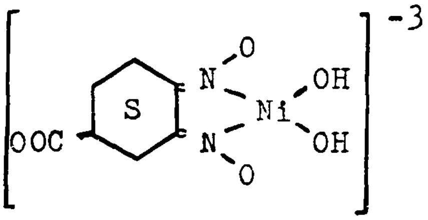
From Figure 6, Curve 2, it may be seen that the 1:1, 4-carboxynioxime-nickel(II), complex ion is diamagnetic. If we assume that the geometrical configuration of the 1:1 complex in solution may be predicted from the valence bond theory, then the 1:1 complex ion is planar. This complex ion may have one of the following structures



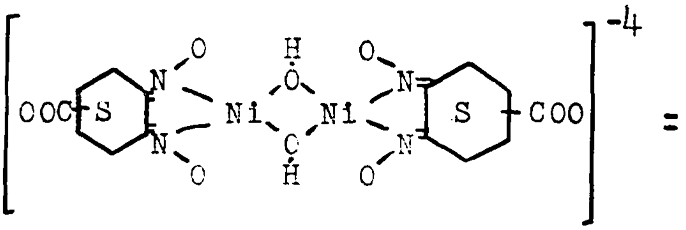
I



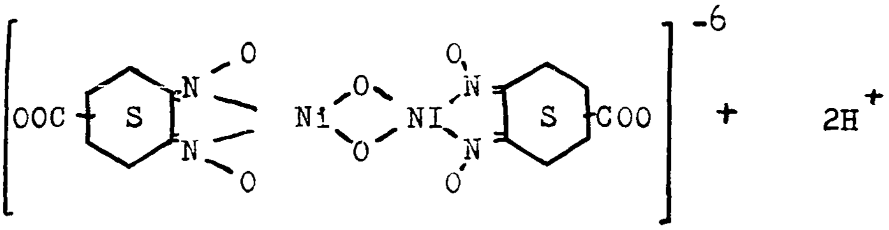
II



III



IV



IV (Cont.)

Structure I can be eliminated from consideration, because the stability constant for the 1:1 complex ion indicates that it would compete with the observed red colored bis(4-carboxynioximato-N,N')nickel(II) precipitate. The 1:1 complex ion has not been observed in aqueous solution between pH = 4.5 and pH = 12.0. It is difficult to conclusively show that structure II is not present, but in 8.923 M potassium hydroxide solution, we may assume that structures III and IV predominate. Various authors (7, 25, 38, 52, 65, 99, 122, 151) have proposed complexes which have structures similar to III while others (7, 66) have proposed complexes which have structures similar to IV.

From Table 1, three complexes could be formed that are paramagnetic, a tetrahedral, NiD_2^{-4}, an octahedral, $NiD_2(OH)_2^{-6}$, or an octahedral, NiD_3^{-7}. Because the 1:1 complex ion is diamagnetic, the change in slope at a ratio of approximately 2:1, and one unpaired electron may be the transition from the tetrahedral, NiD_2^{-4}, or octahedral, $NiD_2(OH)_2^{-6}$, to the octahedral, NiD_3^{-7}.

The initial absorption spectra obtained from the studies in which the nickel(II) concentration was held constant and the vic-dioxime concentration was varied were the same, indicating that there was no significant amount of the oxidized complex present and there were no complexes having an appreciable absorption spectra in this region. The number of unpaired electrons found from the magnetic susceptibility studies of the same solutions increased with increasing *vic*-dioxime concentration. These results have been shown in Figure 6. Therefore, nickel(II) complexes of 4-carboxy-nioxime having two unpaired electrons were present in solution, but they did not alter the absorption spectra. Mills and Mellor (96), Katzin (182) and Sone (137, 138, 139, 140) have also found that paramagnetic complexes of nickel(II) do not have an absorption maxima in this region.

Consideration of all the evidence concerning the *vic*-dioxime complexes of nickel(II) leads to the following probable courses of reaction

$$\text{(a)}\quad Ni(OH)_2 + D^{-3} = NiD(OH)_2^{-3} \qquad \text{Eq. (33)}$$

$$NiD(OH)_2^{-3} + D^{-3} = NiD_2(OH)_2^{-6} \qquad \text{Eq. (34)}$$

$$NiD_2(OH)_2^{-6} + D^{-3} = NiD_3^{-7} + 2OH^- \qquad \text{Eq. (35)}$$

$$\text{or}\quad \text{(b)}\quad Ni(OH)_2 + D^{-3} = NiD(OH)_2^{-3} \qquad \text{Eq. (36)}$$

$$NiD(OH)_2^{-3} + D^{-3} = NiD_2^{-4} + 2OH^- \qquad \text{Eq. (37)}$$

$$NiD_2^{-4} + D^{-3} = NiD_3^{-7} \qquad \text{Eq. (38)}$$

$$\text{or}\quad \text{(c)}\quad Ni(OH)_2 + D^{-3} = NiD(OH)_2^{-3} \qquad \text{Eq. (39)}$$

$$2NiD(OH)_2^{-3} = [DNi(O)_2NiD]^{-6} + 2H_2O \qquad \text{Eq. (40)}$$

$$[DNi(O)_2NiD]^{-6} + D^{-3} + 2H_2O = NiD_2(OH)_2^{-6} + NiD(OH)_2^{-3} \qquad \text{Eq. (41)}$$

$NiD_2(OH)_2^{-6} + D^{-3} = NiD_3^{-7} + 2OH^-$ Eq. (42)

or (d) $Ni(OH)_2 + D^{-3} = NiD(OH)_2^{-3}$ Eq. (43)

$2NiD(OH)_2^{-3} = [DNi(OH)_2NiD]^{-4} + 2OH^-$ Eq. (44)

$[DNi(OH)_2NiD]^{-4} + 2D^{-3} = [D_2Ni(OH)_2NiD_2]^{-10}$ Eq. (45)

$[D_2Ni(OH)_2NiD_2]^{-10} + 2OH^- = 2NiD_2(OH)_2^{-6}$ Eq. (46)

$NiD_2(OH)_2^{-6} + D^{-3} = NiD_3^{-7} + 2OH^-$ Eq. (47)

or (e) $Ni(OH)_2 + D^{-3} = NiD(OH)_2^{-3}$ Eq. (48)

$2NiD(OH)_2^{-3} = [DNi(O)_2NiD]^{-6} + 2H_2O$ Eq. (49)

$[DNi(O)_2NiD]^{-6} + 2D^{-3} = [D_2Ni(O)_2NiD_2]^{-12}$ Eq. (50)

$[D_2Ni(O)_2NiD_2]^{-12} + 2H_2O = 2NiD_2(OH)_2^{-6}$ Eq. (51)

$NiD_2(OH)_2^{-6} + D^{-3} = NiD_3^{-7} + 2OH^-$ Eq. (52)

The highly charged species, NiD_3^{-7}, $[DNi(OH)_2NiD]^{-4}$, $[DNi(O)_2NiD]^{-6}$, $[D_2Ni(OH)_2NiD_2]^{-10}$, and $[D_2Ni(O)_2NiD]^{-12}$ probably exist in solution associated with potassium ions. Feigl and Suter (183) and Chatterjee (102) have isolated the metal salts of similar vic-dioxime complexes of nickel(II).

The mechanism of the formation of NiD_3^{-7} will be discussed again after the rate data have been presented.

B. Study of the Oxidized Complex

1. Determination of the ratio of ligand to metal

Job's method was used to establish the ratio of 4-carboxynioxime to nickel in the oxidized complex at 25° C. A series of solutions was prepared by the procedure cited on page 43. Oxygen was bubbled continuously through the stock solutions. The description of the solutions used in given in Table 4. The absorption spectra obtained after 48 hrs. are shown in Figures 8 and 9. The corresponding Job's plots are shown in Figure 10. Similar absorption spectra and Job's plots were obtained for the time intervals of 24, 72, and 96 hrs. It will be seen that the maximum of these plots falls at a mole fraction corresponding to a ratio of 4-carboxynioxime to nickel of approximately 3:1. Similar results were obtained from mole ratio studies.

The mole ratio method was used to determine the ratio of 4-carboxynioxime to nickel at 50° C. The solutions were prepared by the procedure cited above. The description of the solutions used is given in Table 5. The mole ratio plot obtained after 53 hrs. is shown in Figure 11. It will be seen that there is one break, corresponding to a ratio of 4-carboxynioxime to nickel of 3:1. Similar mole ratio plots were obtained for the various other time intervals.

Figure 8. Absorption spectrum obtained after 48 hrs. from a rate study of a solution treated with oxygen.

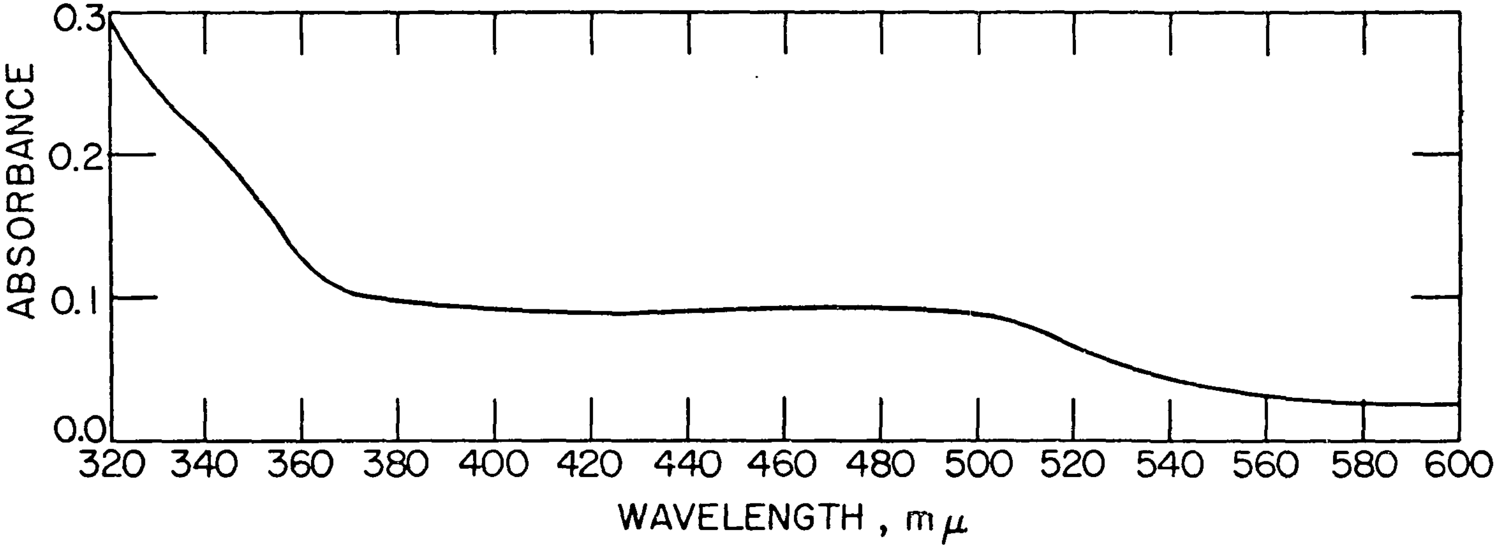

ABSORBANCE
0.3
0.2
0.1
0.0
320
340
360
380
400
420
440
460
480
500
520
540
560
580
600
WAVELENGTH , mμ

Figure 9. Absorption spectrum obtained after 48 hrs. from a rate study of a solution treated with oxygen.

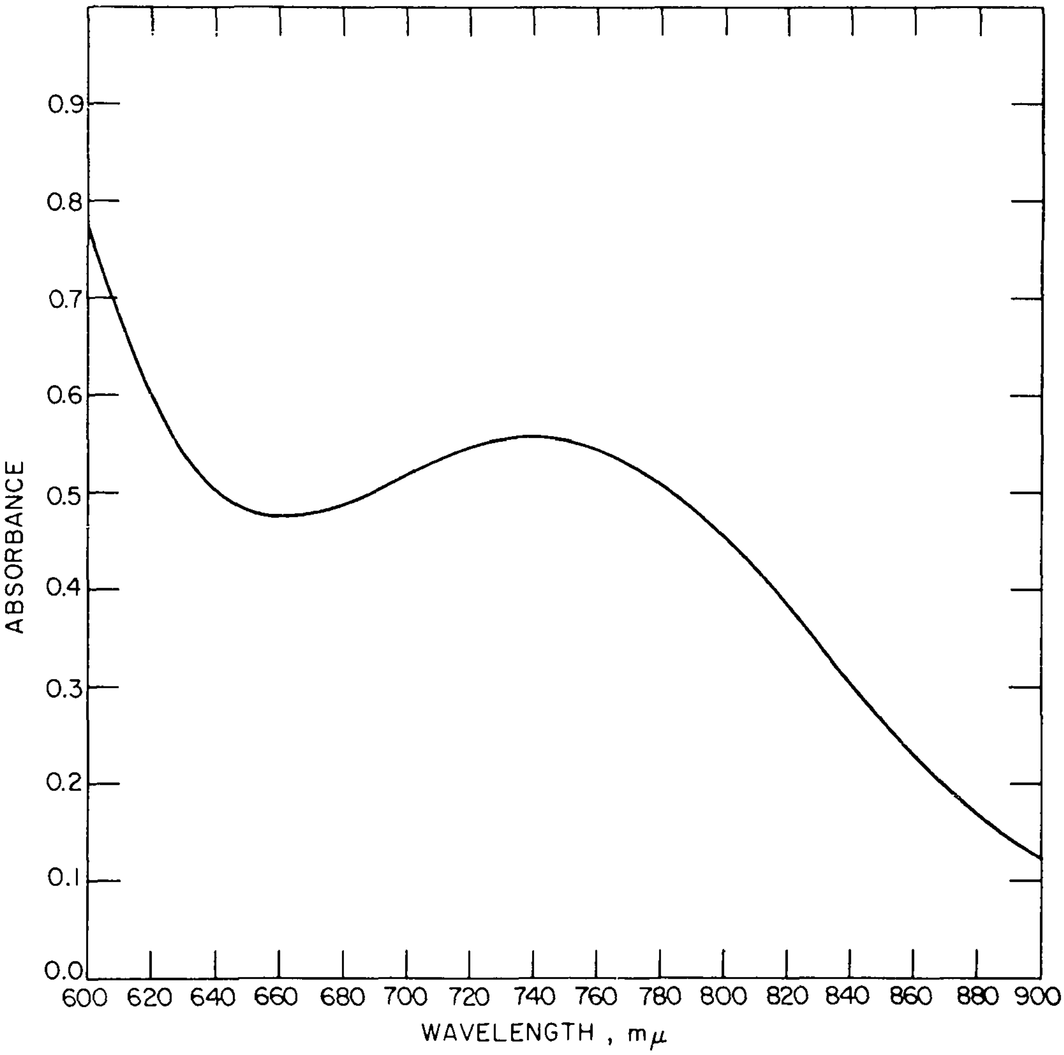

ABSORBANCE
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
600
620
640
660
680
700
720
740
760
780
800
820
840
860
880
900
WAVELENGTH , mμ

Figure 10. Job's plots for the determination of the ratio of 4-carboxynioxime to nickel in the oxidized complex .

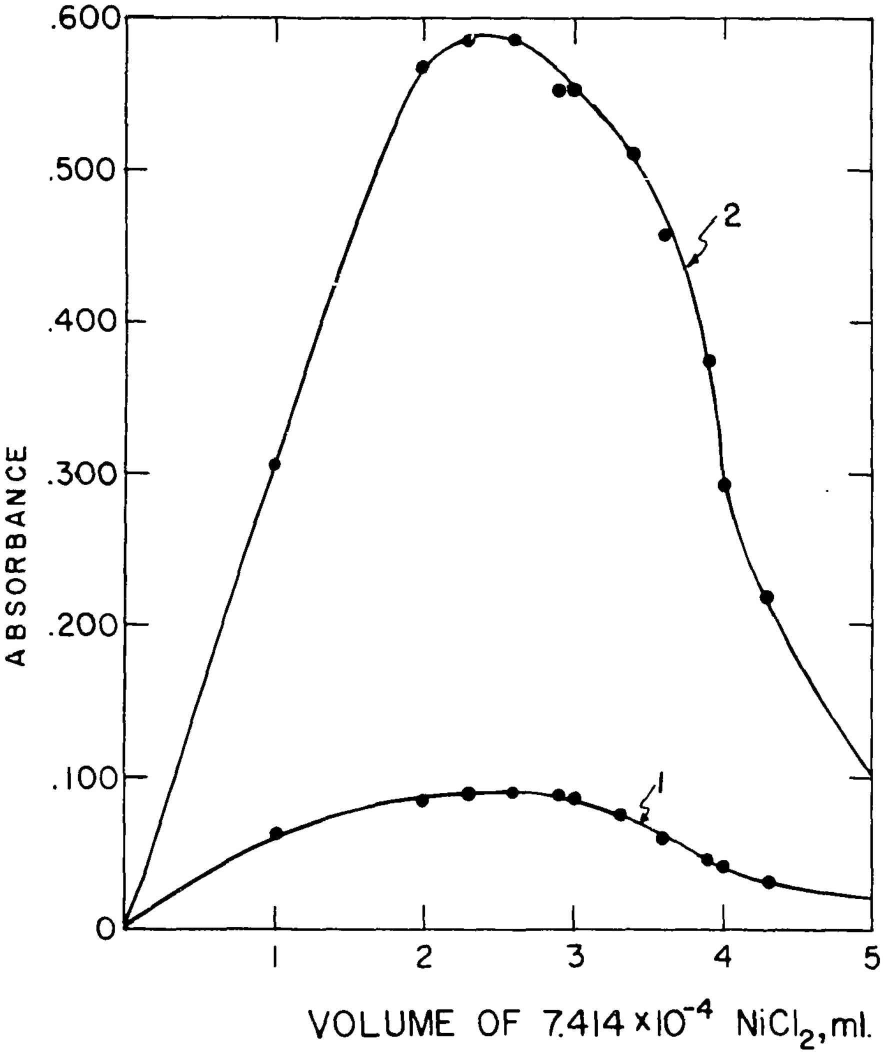

ABSORBANCE
.600
.500
.400
.300
.200
.100
0
1
2
3
4
5
2
1
VOLUME OF 7.414 × 10^{-4} NiCl$_2$, ml.

Figure 11. Mole ratio plot for the determination of the ratio of 4-carboxynioxime to nickel in the oxidized complex.

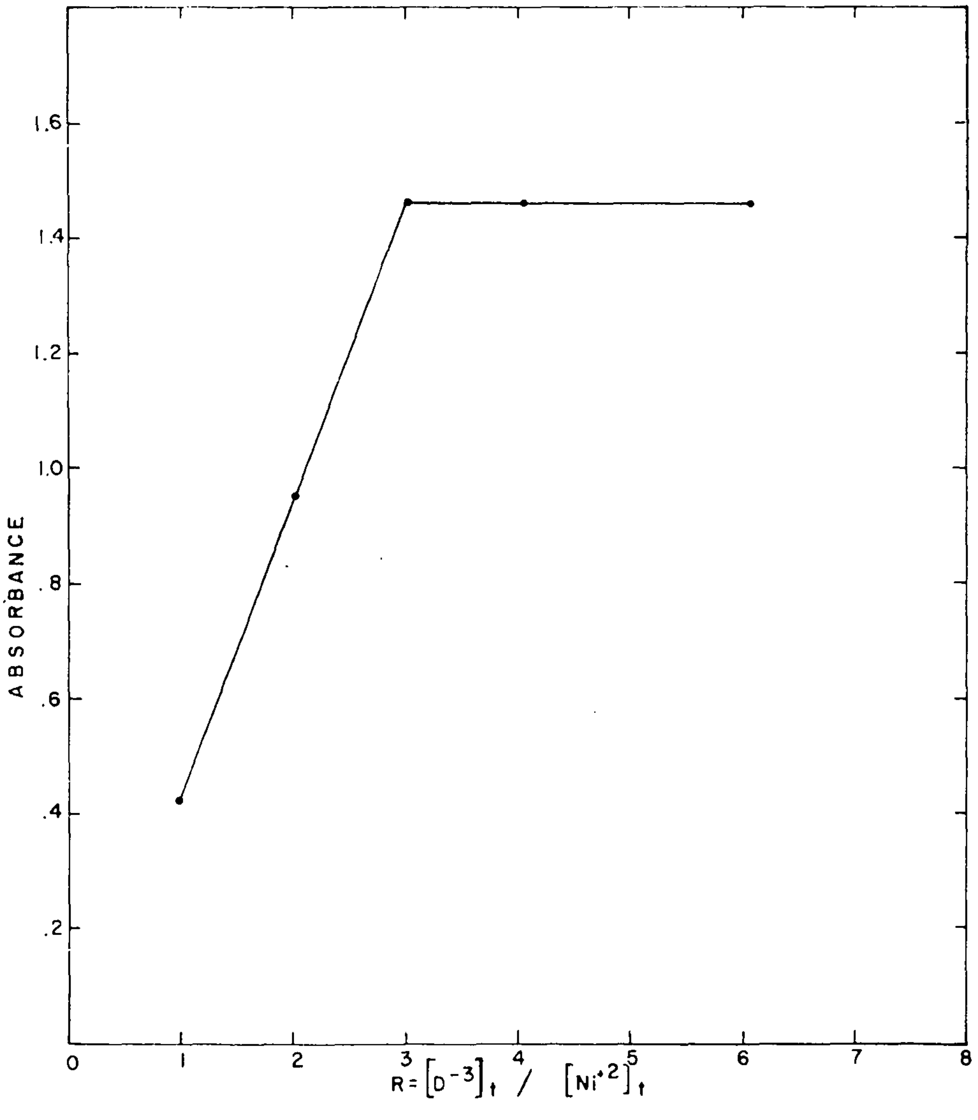

ABSORBANCE
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
1
2
3
4
5
6
7
8
$R = [D^{-3}]_t / [Ni^{+2}]_t$

Table 4. Description of solutions used to determine the ratio of *vic*-dioxime to nickel by Job's method

Solution no.	$[D^{-3}]_t \times 10^3$	$[Ni^{+2}]_t \times 10^3$
1	7.414	0.0
2	6.673	0.741
3	5.931	1.483
4	5.709	1.706
5	5.486	1.928
6	5.264	2.150
7	5.190	2.224
8	4.968	2.446
9	4.746	2.669
10	4.522	2.892
11	4.449	2.966
12	4.226	3.188
13	3.707	3.707

2. Magnetic susceptibility studies

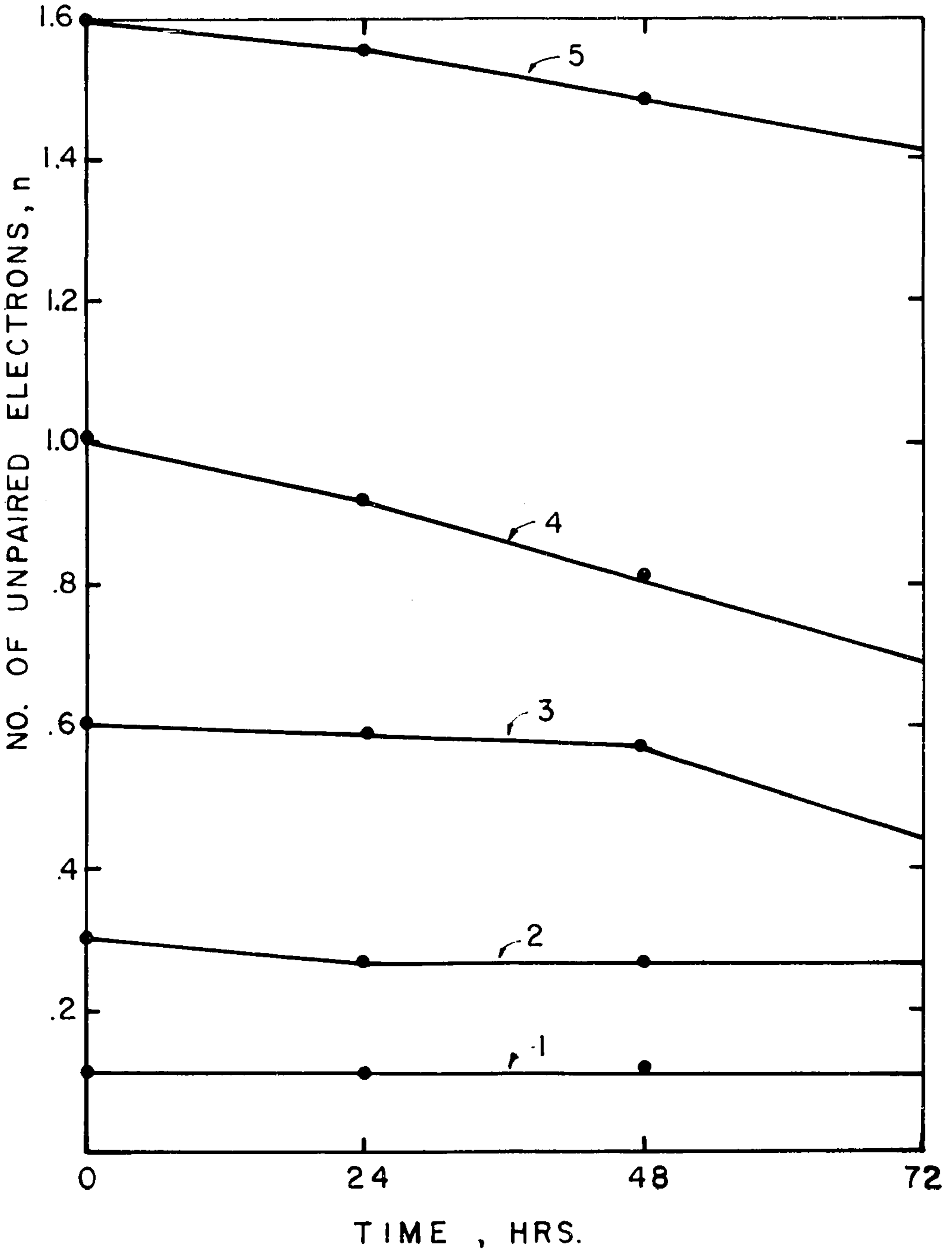
The magnetic susceptibility determinations were made at 20° C. only because of the rapid attack of potassium hydroxide on the sample tube and instrumental limitations. The solutions were prepared by the procedure cited on page 43. The concentration of 4-carboxynioxime was varied from 4.727×10^{-2} *M* to 2.0×10^{-1} *M*, while the concentrations of nickel(II)

Table 5. Description of solutions used to determine the ratio of vic-dioxime to nickel by the mole ratio method

Solution no.	$[D^{-3}]_t \times 10^3$	$[Ni^{+2}]_t \times 10^3$	$[D^{-3}]_t/[Ni^{+2}]_t$
1	1.446	1.446	1.00
2	2.892	1.446	2.00
3	4.338	1.446	3.00
4	5.856	1.446	4.05
5	8.821	1.446	6.10

chloride (4.634×10^{-2} M) and potassium hydroxide (8.923 M) were held constant. Measurements were made at 24 hr. intervals. The results are shown in Figure 12. It will be seen that the number of unpaired electrons found decreases with increasing time. This decrease in the number of unpaired electrons may be due to the oxidation of nickel(II) to the nickel(IV) state in which the nickel in the complex, tris(4-carboxynioximato-N,N'nickel(IV) may have $3d^24s4p^3$ bonding or to the oxidation of the tris(4-carboxynioximato-N,N')-nickel(II) to some oxidized state, followed by the decomposition of this complex to give NiD^- and oxidized 4-carboxynioxime.

Figure 12. The change in the number of unpaired electrons obtained from a rate study of a solution treated with oxygen at 25° C. Curve 1, 4.727×10^{-2} M, 4.634×10^{-2} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively. Curve 2, 6.250×10^{-2} M, 4.634×10^{-2} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively. Curve 3, 7.499×10^{-2} M, 4.634×10^{-2} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively. Curve 4, 1.000×10^{-1} M, 4.634×10^{-2} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively. Curve 5, 2.000×10^{-1} M, 4.634×10^{-2} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively.


NO. OF UNPAIRED ELECTRONS, n
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
24
48
72
TIME , HRS.
5
4
3
2
1

3. Rate studies

The solutions used were prepared by the procedure cited on page 43. The temperatures used in the rate studies were 25° and 50° C. The samples were removed from the stock solutions at various time intervals and the measurements were made.

The rate of formation of the oxidized complex at 25° C. was determined spectrophotometrically at 490 mμ. Rate data for the experiments in which the concentrations of 4-carboxynioxime and nickel(II) were varied are given in Table 6. These data are plotted in Figure 13. Similar results were obtained at 740 mμ.

The rate of formation of the oxidized complex at 50° C. was determined spectrophotometrically, polarographically, and by the reduction of the oxidized complex with tin(II) chloride. Rate data for the spectrophotometric studies at 490 mμ in which the concentration of 4-carboxynioxime and nickel(II) chloride were varied are given in Table 7. These data are plotted in Figure 14. Similar results were obtained at 740 mμ.

Rate data was obtained from the polarographic wave with a half-wave potential of -1.06 volts vs. the saturated calomel electrode by measuring the increase of the diffusion current. The 4-carboxynioxime-nickel(II) complex exhibits a polarographic wave with a half-wave potential of -1.51 volts

Figure 13. A plot of the rate data obtained from solutions treated with oxygen at 25° C. Curve 1, 5.632×10^{-2} M, 3.615×10^{-2} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively. Curve 2, 7.136×10^{-2} M, 2.132×10^{-2} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively.

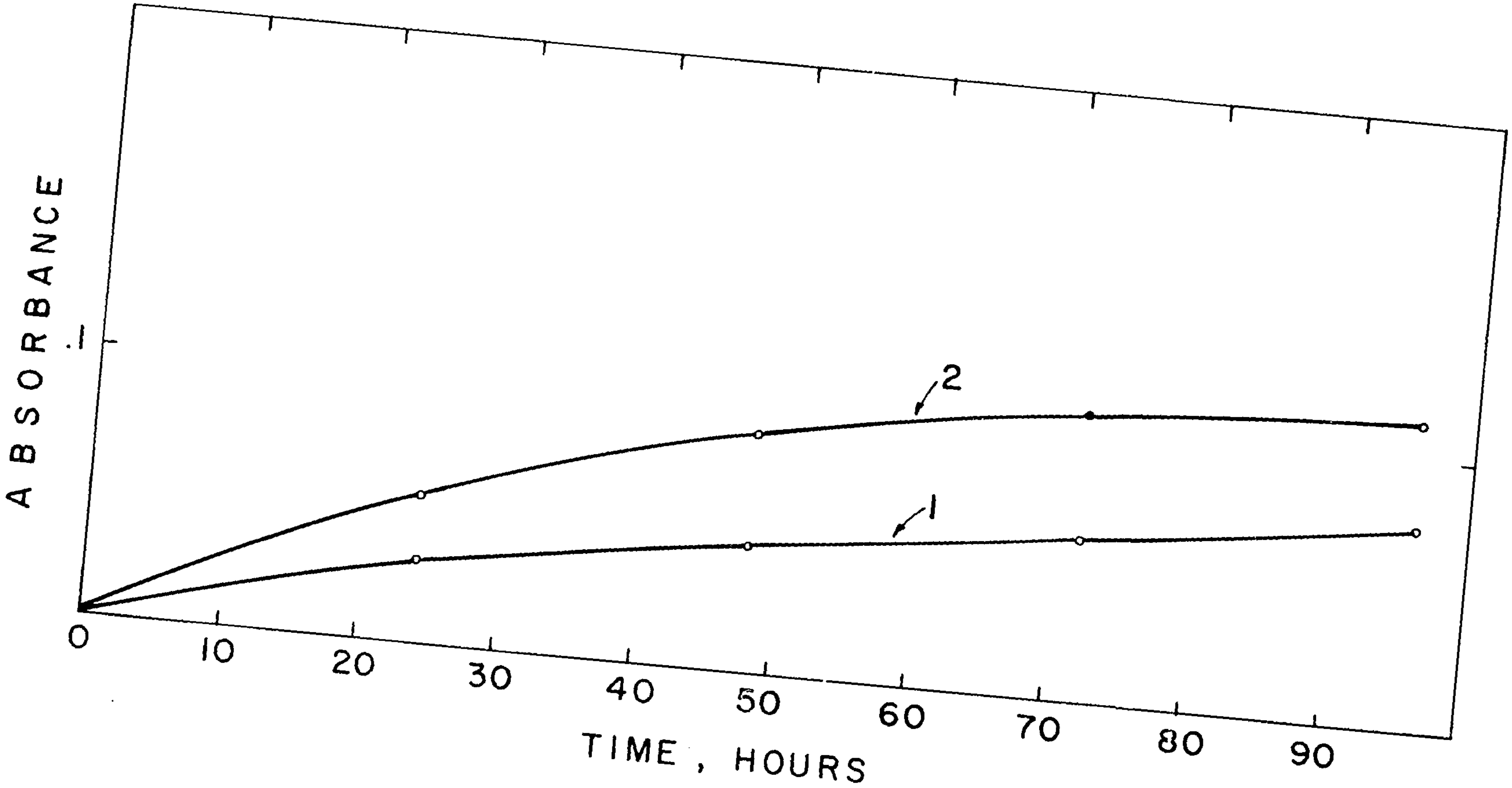

ABSORBANCE
.1
2
1
0
10
20
30
40
50
60
70
80
90
TIME , HOURS

Figure 14. A plot of the rate date obtained from solutions treated with oxygen at 50° C. Curve 1, 1.446 x 10^{-3} M, 1.446 x 10^{-3} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively. Curve 2, 2.924 x 10^{-3} M, 1.446 x 10^{-3} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively. Curve 3, 5.862 x 10^{-3} M, 1.446 x 10^{-3} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively. Curve 4, 8.794 x 10^{-3} M, 1.446 x 10^{-3} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively.

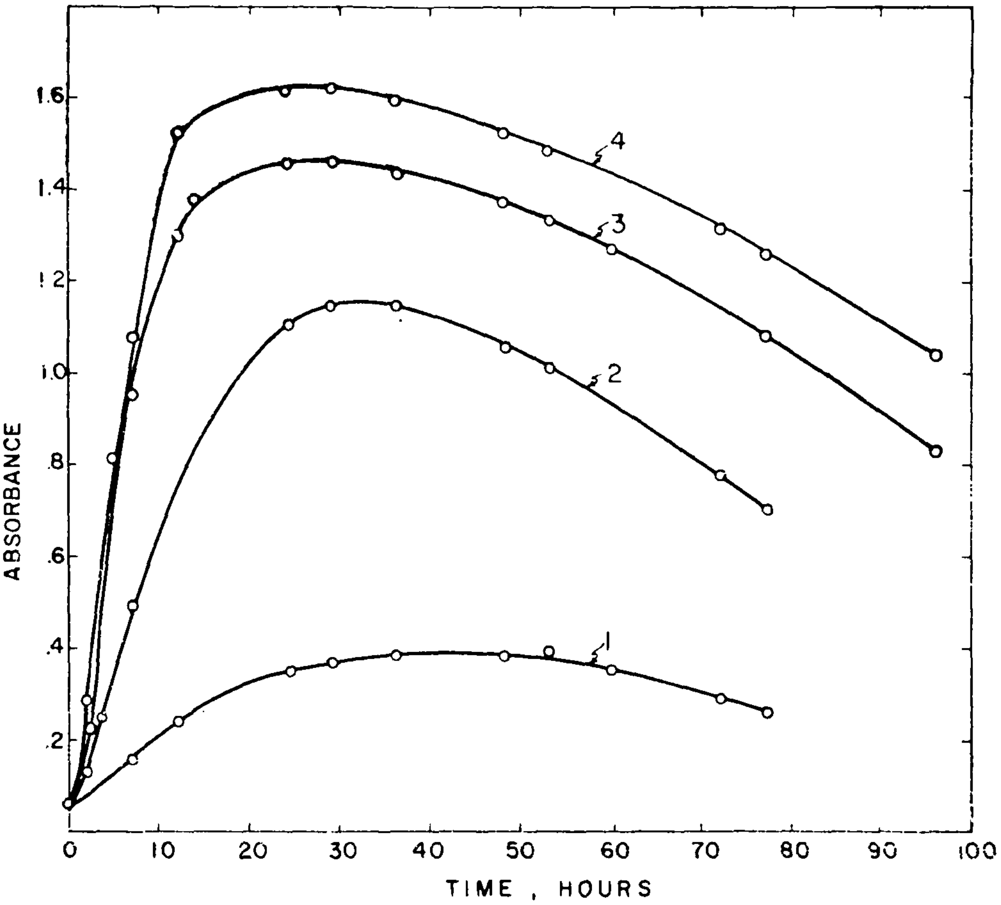

ABSORBANCE
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
10
20
30
40
50
60
70
80
90
100
TIME , HOURS
4
3
2
1

Table 6. Rate data for the formation of the oxidized complex of 4-carboxynioxime and nickel(II) at 25° C.

Time, hrs.	A^a	$k_1'^a \times 10^2$ (hrs.$^{-1}$)	A^b	$k_1'^b \times 10^2$ (hrs.$^{-1}$)
0.0	0.000		0.000	
5.0	0.007	1.99	0.015	2.85
12.0	0.017	2.17	0.032	2.77
24.0	0.031	2.26	0.053	2.64
36.0	0.040	2.16	0.074	2.96
48.0	0.046	2.03	0.087	3.06
60.0	0.053	2.10	0.098	3.37
72.0	0.060	2.31	0.105	3.68
84.0	0.066	2.65	0.110	4.32
96.0	0.074		0.113	
Average		2.21 ± 0.22		3.21 ± 0.43

[a] The rate data were obtained from a solution 5.632 x 10^{-2} M, 3.615 x 10^{-2} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively.

[b] The rate data were obtained from a solution 7.136 x 10^{-2} M, 2.132 x 10^{-2} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively.

vs. the saturated calomel electrode. Rate data for the experiments at various concentration of 4-carboxynioxime and nickel(II) chloride are given in Table 8. These data are plotted in Figure 15.

Figure 15. A plot of the rate date obtained from solutions treated with oxygen at 50° C. Curve 1, 1.954 x 10^{-3} M, 4.820 x 10^{-4} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively. Curve 2, 3.908 x 10^{-3} M, 4.820 x 10^{-4} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively.

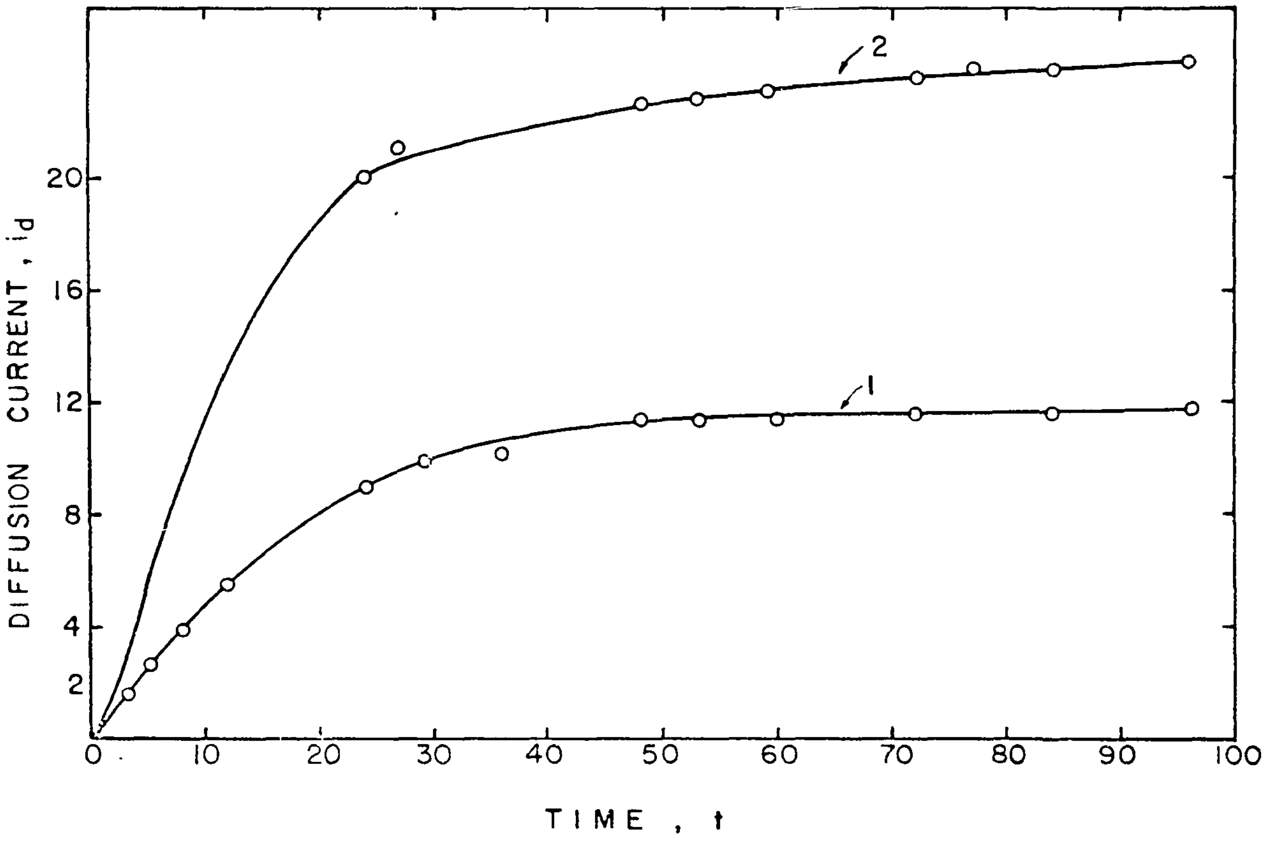

DIFFUSION CURRENT, i_d
2
4
8
12
16
20
TIME, t
0
10
20
30
40
50
60
70
80
90
100
1
2

Table 7. Rate data for the formation of the oxidized complex of 4-carboxynioxime and nickel(II) at 50° C.

Time, hrs.	A[a]	A[b]	A[c]	A[d]
0.0	0.000	0.073	0.073	0.062
2.0		0.128	0.225	0.285
5.0	0.128	0.355	0.721	0.812
7.0	0.154	0.498	0.951	1.078
12.0	0.240		1.300	1.522
14.0			1.380	
24.0	0.345	1.104	1.457	1.615
29.0	0.376	1.147	1.459	1.612
36.0	0.381	1.141	1.431	1.594
48.0	0.381	1.058	1.372	1.524
53.0	0.396	1.006	1.344	1.489
60.0	0.355	0.938	1.271	
72.0	0.291	0.776		1.316

[a] The rate data were obtained from a solution 1.446 x 10^{-3} M, 1.446 x 10^{-3} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively.

[b] The rate data were obtained from a solution 2.924 x 10^{-3} M, 1.446 x 10^{-3} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively.

[c] The rate data were obtained from a solution 5.862 x 10^{-3} M, 1.446 x 10^{-3} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively.

[d] The rate data were obtained from a solution 8.794 x 10^{-3} M, 1.446 x 10^{-3} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively.

Table 7. (Continued)

Time, hrs.	A^a	A^b	A^c	A^d
77.0	0.262	0.703	1.075	1.259
96.0			0.839	1.042

Table 8. Rate data for the formation of the oxidized complex of 4-carboxynioxime and nickel(II) at 50° C.

Time, hrs.	i_d^a	$k_1'^a \times 10^2$ (hrs.$^{-1}$)	i_d^b	$k_1'^b \times 10^2$ (hrs.$^{-1}$)
0.0	0.0		0.0	
2.0			0.6	2.66
3.0	3.9	5.89		
5.0	6.0	5.73	2.6	5.07
8.0	9.4	6.18	3.9	5.12
12.0			5.5	5.35
24.0	19.9	7.28	8.9	6.07
27.0	21.0	7.60		
29.0	21.1	7.19	9.9	6.62

---

[a] The rate data were obtained from a solution 1.954 x 10^{-3} $\underline{M}$, 4.820 x 10^{-4} $\underline{M}$, and 8.923 $\underline{M}$ in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively.

[b] The rate data were obtained from a solution 3.908 x 10^{-3} $\underline{M}$, 4.820 x 10^{-4} $\underline{M}$, and 8.923 $\underline{M}$ in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively.

Table 8. (Continued)

Time, hrs.	i_d^a	$k_1'^a \times 10^2$ (hrs.$^{-1}$)	i_d^b	$k_1'^b \times 10^2$ (hrs.$^{-1}$)
32.0	21.2	6.61		
36.0	21.6	6.29	10.5	6.54
48.0	22.5	5.65	11.2	7.01
53.0	22.8	5.51	11.3	6.90
60.0	23.1	5.30	11.4	6.77
72.0	23.5	5.13	11.5	6.60
84.0	23.7	4.88	11.6	
96.0	24.1		11.6	
Average		6.10 ± 1.11		5.89 ± 0.82

The rate of formation of the oxidized complex was followed by spectrophotometric titrations with tin(II) chloride. The wavelength used was 490 mμ. Rate data for the experiments are given in Table 9. These data are plotted in Figure 16.

The general rate equation is

$$\frac{d\,[NiD_3^{-5}]}{dt} = k_1' \,[D^{-3}]^{\,m}\,[NiD^{2-3x}]^{\,n} - k_2'\,[NiD_3^{-5}]^{p} \qquad \text{Eq. (53)}$$

where x may equal 0, 1, 2, or 3, and the sum of m and n is the order of the formation and p, the order of the decomposition of NiD_5^{-3}. The partial pressure of oxygen was assumed

Figure 16. A plot of the rate date obtained from solutions treated with oxygen at 50° C. Curve 1, 1.954×10^{-3} M, 4.820×10^{-4} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively. Curve 2, 9.770×10^{-4} M, 4.820×10^{-4} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively.

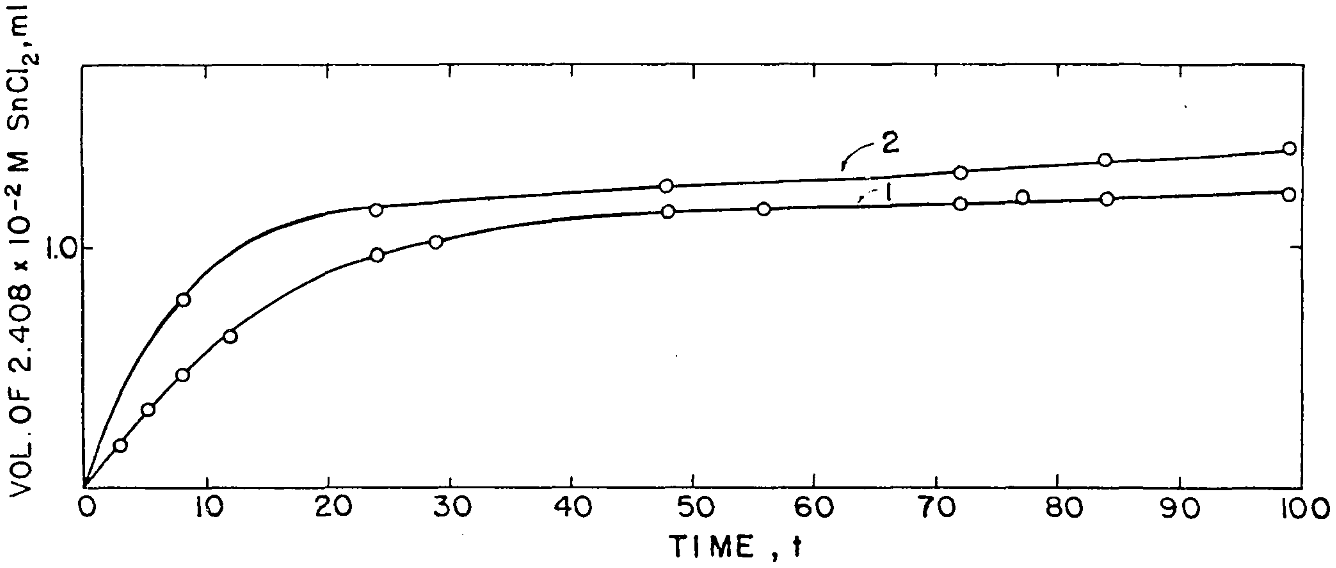

VOL. OF 2.408 x 10⁻² M SnCl₂, ml
1.0
0
10
20
30
40
50
60
70
80
90
100
TIME, t
1
2

Table 9. Rate data for the formation of the oxidized complex of 4-carboxynioxime and nickel(II) at 50° C.

Time, hrs.	Vol. of $Sn(II)Cl_2$,[a] ml. (2.408×10^{-2} M)	$k_1'^{a} \times 10^2$ (hrs.$^{-1}$)	Vol. of $Sn(II)Cl_2$,[b] ml. (2.408×10^{-2} M)	$k_1'^{b} \times 10^2$ (hrs.$^{-1}$)
0.0	0.00		0.00	
3.0	0.40	5.48	0.12	3.39
5.0	0.55	4.36	0.32	5.97
8.0	0.80	5.12	0.48	6.12
12.0	1.02	5.10	0.64	6.05
24.0	1.16	6.95	0.98	6.20
29.0	1.20	6.30	1.01	5.81
48.0	1.24	4.21	1.16	5.71
53.0	1.25	3.91	1.17	5.42
72.0	1.30	3.33	1.18	4.20
77.0	1.33	3.45	1.20	4.46
84.0	1.36	3.59	1.21	4.43
96.0	1.43		1.24	
Average		4.75 ± 1.00		5.25 ± 0.95

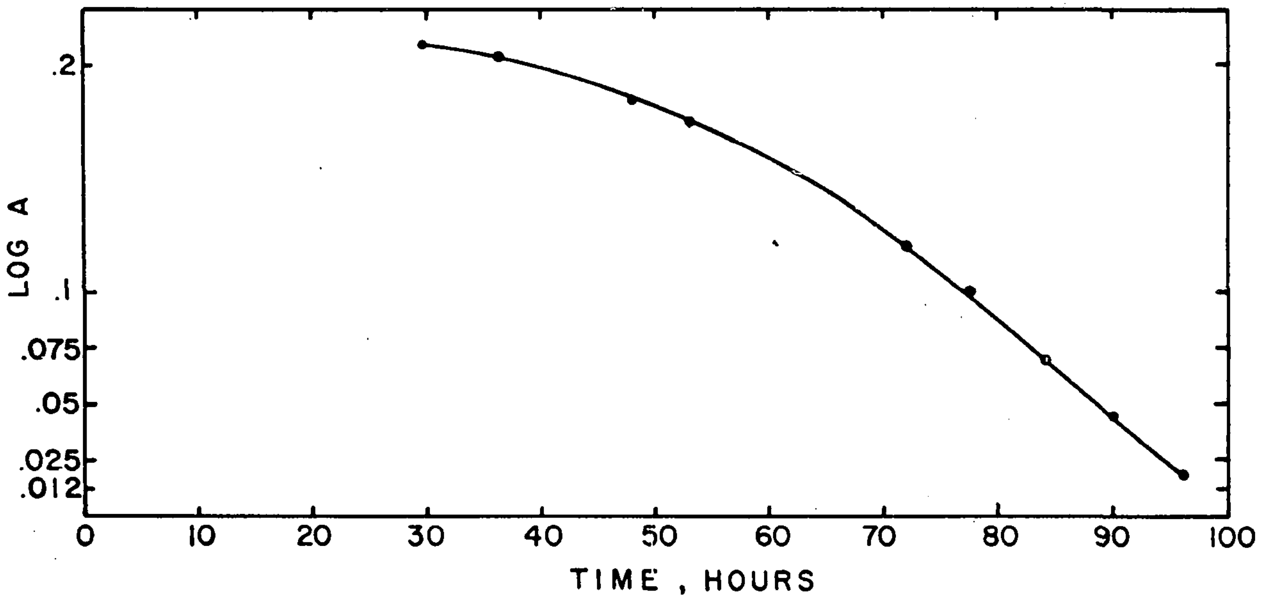
[a] The rate data were obtained from a solution 1.954×10^{-3} M, 4.820×10^{-4} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively.

[b] The rate data were obtained from a solution 9.770×10^{-4} M, 4.820×10^{-4} M, and 8.923 M in 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide, respectively.

to be constant and was included in k_1' and k_2'. To determine m and n, the ratio of the reactants was varied. The concentrations of nickel(II) chloride and potassium hydroxide were held constant and the concentration of 4-carboxynioxime was doubled. The curves are shown in Figure 14. The ratio of the slopes of Curves 1 to 2 and 2 to 3 for short intervals is equal to 2^m. It was found that m is equal to one. To determine n, a study was made varying the concentration of nickel while holding the concentrations of 4-carboxynioxime and potassium hydroxide constant. The ratio of the slopes for short intervals of the Curves 2 and 5 is equal to the ratio of the concentrations of nickel. Therefore, the value of n is one. The same values for m and n were obtained from Figure 13. To determine p, a plot of log A verse t of the data reported, c, Table 7 was prepared. The graph is shown in Figure 17. A straight line was obtained for the last portion of the curve, indicating that the decomposition of NiD_3^{-5} is first order with respect to the starting material. Therefore, p is equal to one.

There seems to be no direct way to determine the value of x. But the magnetic susceptibility measurements indicate that either NiD_2^{-4}, NiD_3^{-7}, or both are present in solution and only seven per cent of the total nickel is present as NiD^- at the beginning of the study of Curve 1, Figure 14. Thus the rate determining step is

Figure 17. A log plot of the rate date, c, Table 7.


LOG A
.2
.1
.075
.05
.025
.012
0
10
20
30
40
50
60
70
80
90
100
TIME , HOURS

$$NiD_2^{-4} + D^{-3} = NiD_3^{-7} \qquad \text{Eq. (54)}$$

Therefore, equation 28 may be written

$$\frac{d\,[NiD_3^{-5}]}{dt} = k_1'\,[D^{-3}]\,[NiD_2^{-4}] - k_2'\,[NiD_3^{-5}] \qquad \text{Eq. (55)}$$

The values of k_1' and k_2' are 2.87×10^{-2} hrs.$^{-1}$ and 1.59×10^{-2} hrs.$^{-1}$, respectively. These values were obtained from the data reported in Table 7 by a curve fitting procedure. The values of k_1' reported in Tables 6, 8, and 9 were calculated from the following equation

$$k_1' = \frac{2.303 \log}{t} \; \frac{a}{a-x} \qquad \text{Eq. (56)}$$

where a is the initial concentration of reactant, and x is the amount of reaction at time t. The rate studies indicate that there was an exchange of two electrons in the reduction of the oxidized complex.

Several attempts were made to isolate and identify the products of the oxidation. A small amount of an acidic substance was obtained from ether extractions of the neutralized solution. The substance decomposed very rapidly upon contact with air. No reaction was observed with nickel(II) chloride at any pH. After reducing a small quanity with zinc in acetic acid, a red color was obtained when a drop of nickel(II) chloride (0.2317 M) was added and the solution made slightly alkaline. This indicates that the compound obtained upon reduction may be the <u>vic</u>-dioxime. Two nitro tests were performed. Positive results were obtained with the ferrous hydroxide test reported by Hearon and Gustavson (184) and the lithium aluminum hydride test reported by Nystrom and Brown (185) and Krynitzky <u>et</u> <u>al</u>. (186). 4-Carboxycyclohexesfuroxane gave a negative nitro test. These results indicate that the oxidation product was a nitro compound and not a furoxane.

A study of the decomposition of 4-carboxynioxime in the presence of oxygen at 25° and 50° C. was made. The solutions were prepared by the procedure cited on page 43 and the concentrations of 4-carboxynioxime and potassium hydroxide were 1.00×10^{-4}, 8.896×10^{-3}, and 8.923 <u>M</u>, respectively. The spectra obtained are shown in Figures 18 and 19. There was no change in the absorption spectrum from 400 to 900 mμ at 25° C. and 600 to 900 mμ at 50° C. It is seen that there is a slight decrease in the absorption maximum at 273 mμ.

4. <u>Reduction of the oxidized complex</u>

The reduction of the oxidized species was studied spectrophotometrically. The reducing agents used were tin(II) chloride, hydrazine sulfate, and hydroxylammonium chloride. An excess of the reducing agents were added to a solution that oxygen had been bubbled through for 72 hrs. at 50° C. The concentrations of 4-carboxynioxime, nickel(II) chloride,

Figure 18. Absorption spectra obtained from a rate study of a solution treated with oxygen at 25° C. Curve 1, 0.0 hrs. Curve 2, 12.0 hrs. Curve 3, 60 hrs. Curve 4, 84 hrs. Curve 5, 96 hrs.

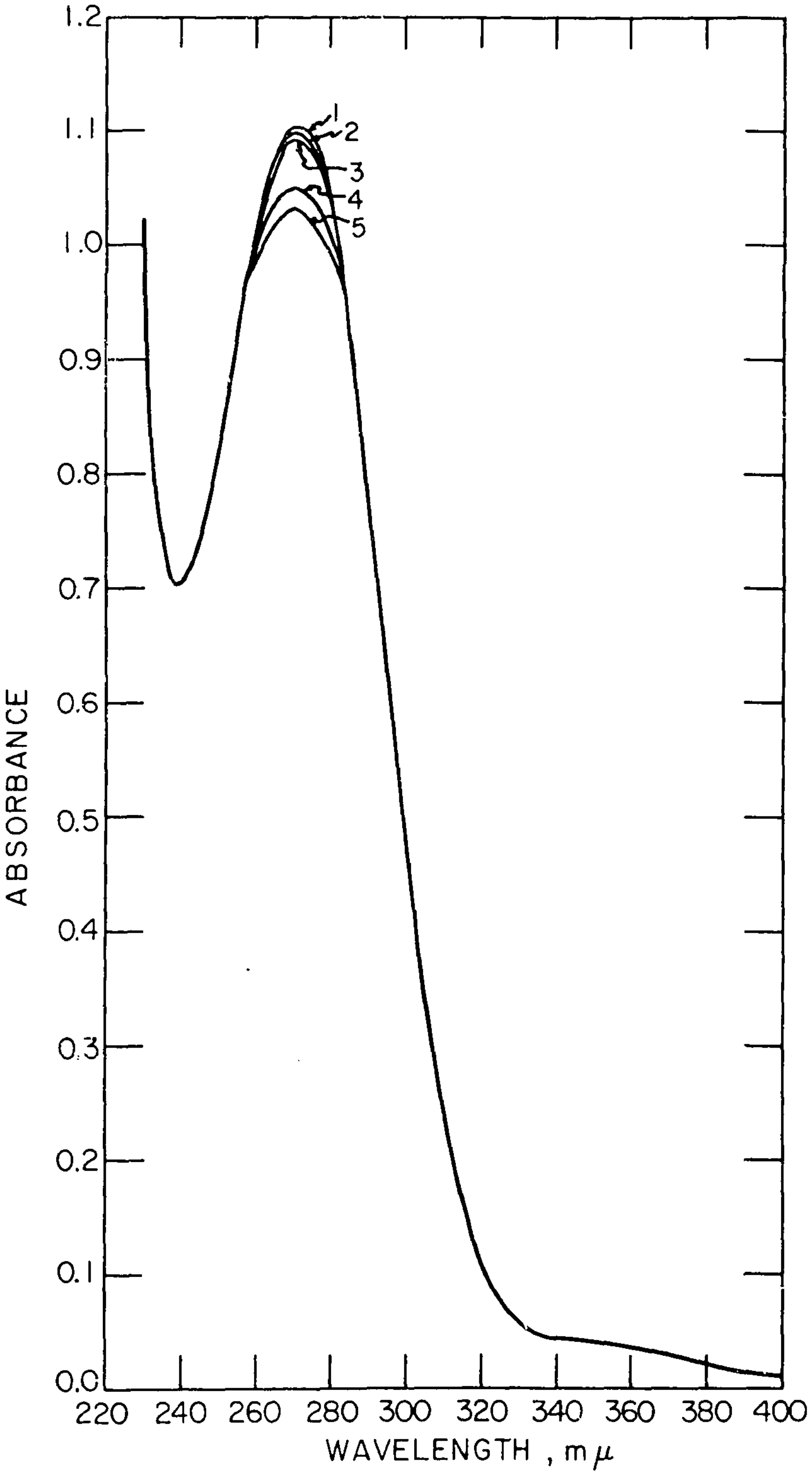
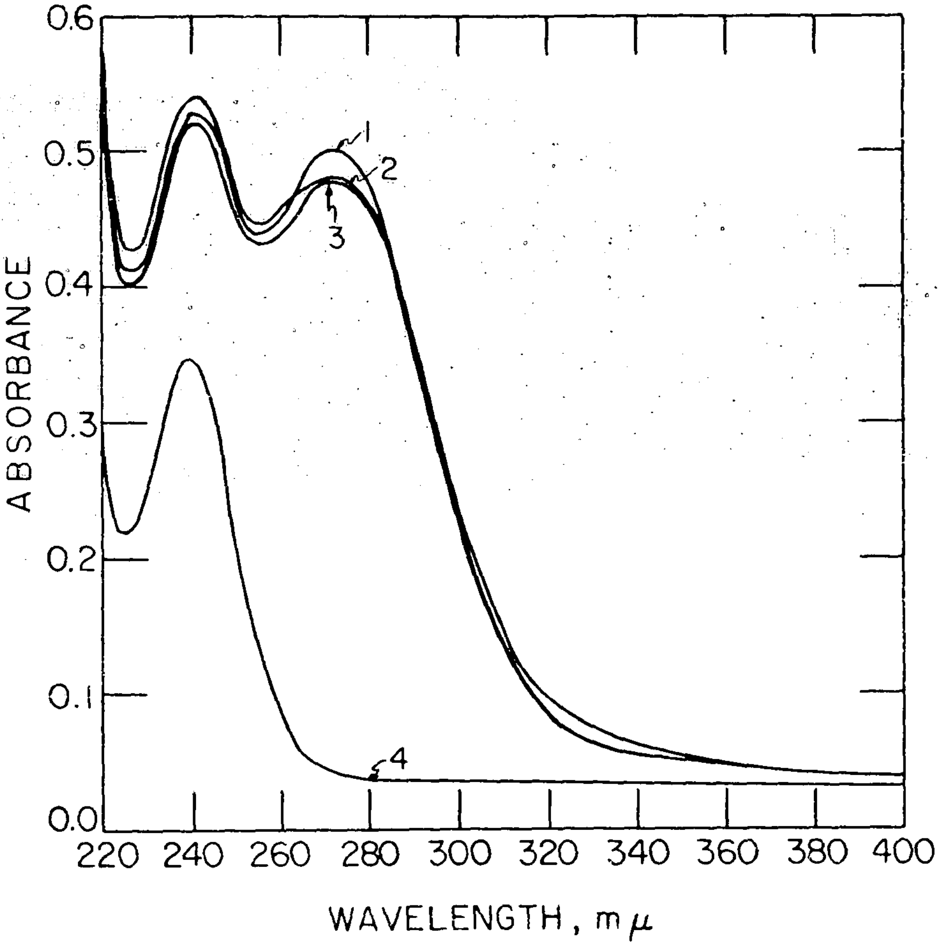

1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
ABSORBANCE
220
240
260
280
300
320
340
360
380
400
WAVELENGTH , mμ
1
2
3
4
5

Figure 19. Absorption spectra obtained from a rate study of a solution treated with oxygen at 50° D. Curve 1, 96.0 hrs. Curve 2, 29.0 hrs. Curve 3, 0.0 hrs. Curve 4, 8.923 M potassium hydroxide.


0.6
0.5
0.4
0.3
0.2
0.1
0.0
ABSORBANCE
220
240
260
280
300
320
340
360
380
400
WAVELENGTH, mμ
1
2
3
4

and potassium hydroxide were 5.863×10^{-3}, 2.169×10^{-3}, and 8.923 M, respectively. The results are shown in Figures 20 and 21. The absorption maxima at 490 and 740 mμ disappeared and no maximum was observed at 393 mμ. The solutions became turbid after 20 minutes. If a slight excess of the vic-dioxime was added, the precipitate disappeared and the original yellow color of the nickel(II) complex was obtained with an absorption maximum at 393 mμ. This indicates that no vic-dioxime-nickel complexes were present after the addition of the reducing agents.

The effect of tin(II) and tin(IV) on the nickel(II) complexes of 4-carboxynioxime was studied. They were added 15 minutes after the preparation of the solutions in which the concentrations of 4-carboxynioxime, nickel(II) chloride, and potassium hydroxide were 1.603×10^{-3}, 1.446×10^{-3}, and 8.923 M, respectively. There was no change in the absorption spectrum, indicating that the nickel(II) complexes were not destroyed. From a similar study, it was also found that hydroxylammonium chloride and hydrazine sulfate do not destroy the nickel(II) complexes.

5. Discussion

The rate data indicate that the rate determining step in the formation of the oxidized complex is either

$$NiD_2^{-4} + D^{-3} = NiD_3^{-7} \qquad \text{Eq. (57)}$$

Figure 20. Absorption spectra obtained from a solution treated with oxygen for 72 hrs. before and after the addition of $SnCl_2$. Curve 1, no $SnCl_2$. Curve 2, an excess of $SnCl_2$.

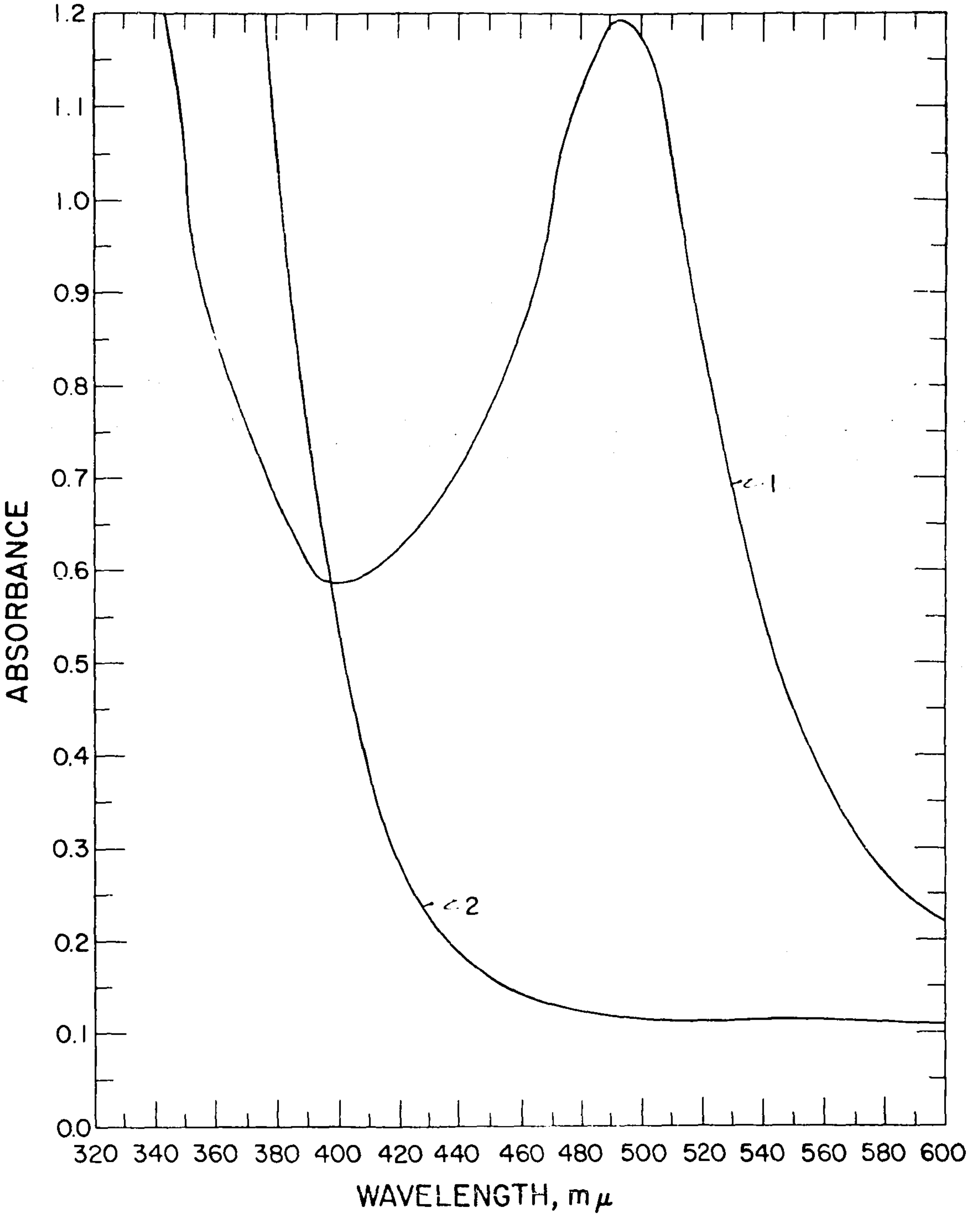
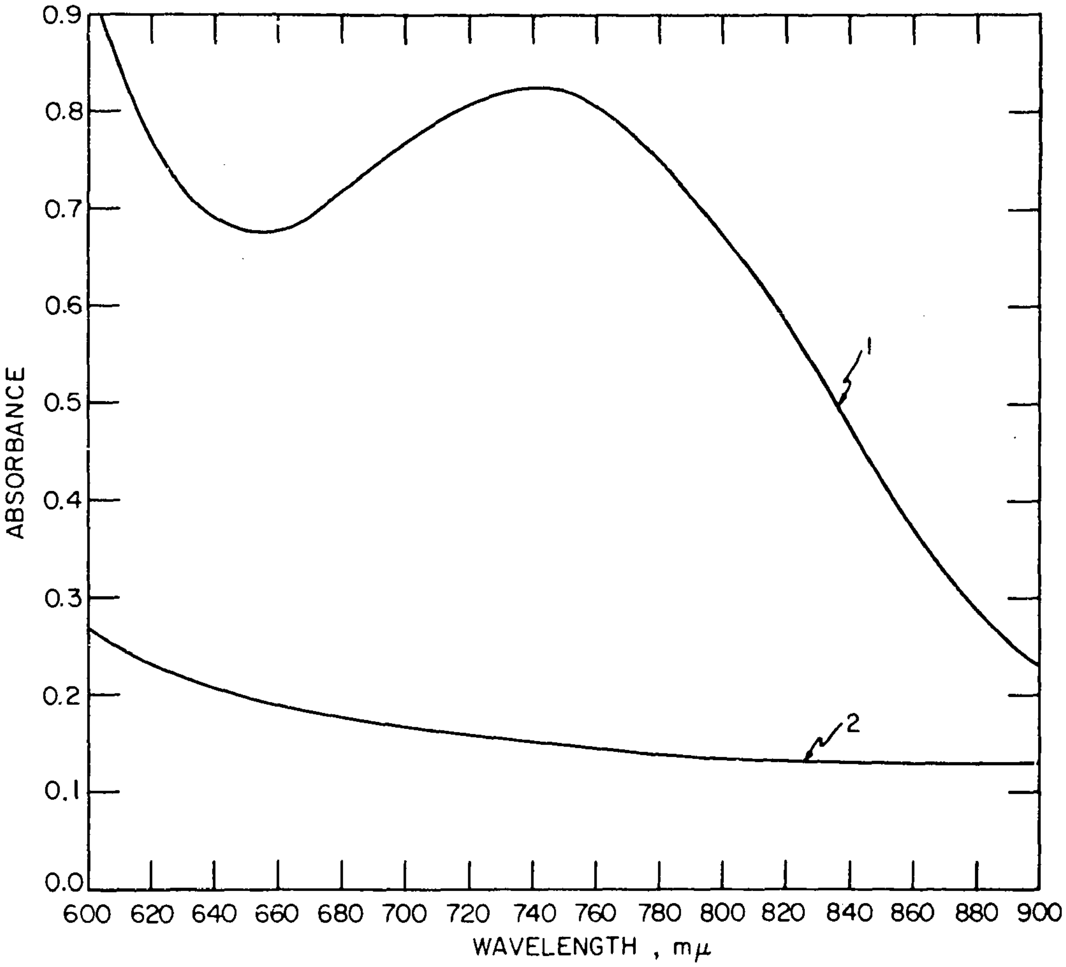

ABSORBANCE
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
WAVELENGTH, mμ
320
340
360
380
400
420
440
460
480
500
520
540
560
580
600
c-1
c-2

Figure 21. Absorption spectra obtained from a solution treated with oxygen for 72 hrs. before and after the addition of $SnCl_2$. Curve 1, no $SnCl_2$ present. Curve 2, an excess of $SnCl_2$ present


0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
ABSORBANCE
600
620
640
660
680
700
720
740
760
780
800
820
840
860
880
900
WAVELENGTH , mμ
1
2

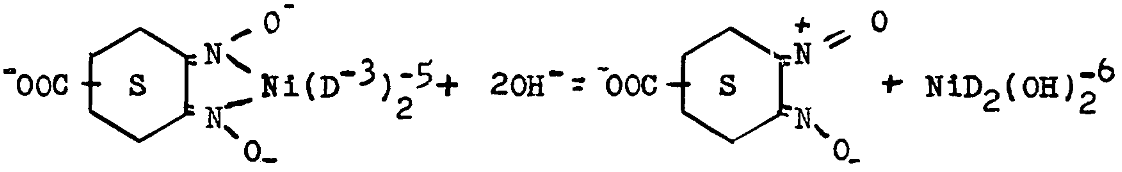
or, $NiD_2(OH)_2^{-6} + D^{-3} = NiD_3^{-7} + 2OH^-$ Eq. (58)

Therefore, mechanism a or c discussed on page 71 may describe the formation of NiD_3^{-7}.

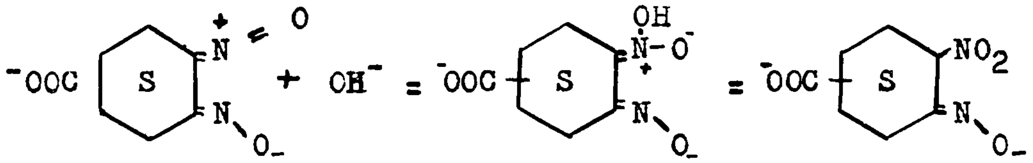
The oxidation of NiD_3^{-7} and the decomposition of NiD_3^{-5} may be described in the following manner

$NiD_3^{-7} + \frac{1}{2}O_2 + H_2O = NiD_3^{-5} + 2OH^-$ Eq. (59)

If we assume that nickel(IV) is present in NiD_3^{-5}, then the decomposition of NiD_3^{-5} may occur by the following mechanism



Eq. (60)



Eq. (61)

Consideration of all the evidence concerning the complexes of 4-carboxynioxime and nickel, leads to the following probable course of reaction

$$Ni(OH)_2 + D^{-3} = NiD(OH)_2^{-3} \qquad \text{Eq. (62)}$$

$$NiD(OH)_2^{-3} + D^{-3} = NiD_2(OH)_2^{-6} \qquad \text{Eq. (63)}$$

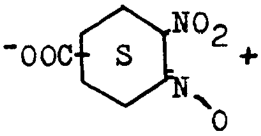
or, $$2NiD(OH)_2^{-3} = [DNi(O)_2NiD]^{-6} + 2H_2O \qquad \text{Eq. (64)}$$

$$[DNi(O)_2NiD]^{-6} + D^{-3} + 2H_2O = NiD_2(OH)_2^{-6} + NiD(OH)_2^{-3}$$

Eq. (65)

then, $$NiD_2(OH)_2^{-6} + D^{-3} \overset{k_1'}{=} NiD_3^{-7} + 2OH^- \qquad \text{Eq. (66)}$$

$$NiD_3^{-7} + \tfrac{1}{2}O_2 + H_2O = NiD_3^{-5} + 2OH^- \qquad \text{Eq. (67)}$$

$NiD_3^{-5} + 3OH^- \overset{k_2}{=}$  $+ NiD_2(OH)_2^{-6}$ Eq. (68)

The proposed mechanism is consistent with the following evidence:

(a) The 1:1 complex ion is dependent on the hydroxide concentration.

(b) The magnetic susceptibility data reported in this work and by previous workers (4, 5, 97, 99, 114, 117, 121, 125).

(c) The information obtained from the spectrophotometric and polarographic rate studies.

(d) The formation of substance containing a nitro group.

(e) Why previous workers (9, 14, 16, 17, 64) have not isolated furoxanes or their derivatives from the oxidation of the complexes of the *vic*-dioximes and nickel(II).

(f) The hypothesis by various workers (14, 15, 16, 17, 18, 65, 67, 68, 69, 70) that the ligand is oxidized.

The following interpretation of the magnetic susceptibility data by the valency bond theory is proposed. The diamagnetic NiD^-, $NiD(OH)_2^{-3}$ or $[DNi(O)_2NiD]^{-6}$ is a square planar complex ion with $3d4s4p^2$ hybrid bonding orbitals. The paramagnetic NiD_2^{-4} is a tetrahedral complex ion with $4s4p^3$ hybrid bonding orbitals. The paramagnetic $NiD_2(OH)_2^{-6}$ and NiD_3^{-7} are octahedral complex ions with $4s4p^34d^2$ hybrid bonding orbitals. The diamagnetic NiD_3^{-5} is an octahedral complex ion with $3d^24s4p^3$ hybrid bonding orbitals. The configurations predicted by molecular orbital theory and crystal field theory were similar to the configurations predicted by valency bond theory and are not discussed.

VI. SUMMARY

1. The literature concerning the oxidation, magnetic susceptibility, and stability constants of the complexes of *vic*-dioximes and nickel has been reviewed.
2. The presence of three complexes of 4-carboxynioxime and nickel(II) was established from spectrophotometric and magnetic susceptibility data. The step-wise stability constants were found to have the following values:

   $\log k_1 = 28.74$

   $\log k_2 = 0.76$

   $\log k_3 = 3.67$
3. The rate of formation of the oxidized complex was followed spectrophotometrically, polarographically, and by spectrophotometric titrations with tin(II) chloride. The following rate equation was obtained from the spectrophotometric data at 50° C.:

$$\frac{d\,[NiD_3^{-5}]}{dt} = 2.87 \times 10^{-2}\,[NiD_2(OH)_2^{-6}]\,[D^{-3}] - 1.59 \times 10^{-2}\,[NiD_3^{-5}] \qquad \text{Eq. (1)}$$

The rate of formation of the oxidized complex was found to be first-order at 25° C. The rate constant was found to have the following value:

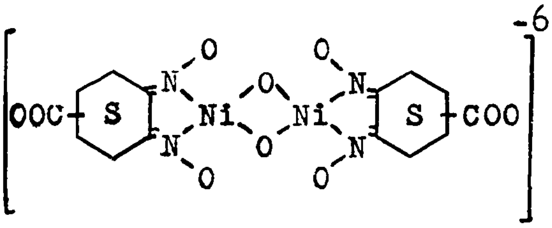
$$k_1' = 2.71 \times 10^{-2} \text{ hrs.}^{-1} \quad (25^{\circ} \text{ C.})$$

The polarographic and spectrophotometric titration data obtained indicate that the reaction is first-order at 50° C. The rate constant was found to have the following value:

$$k_1' = 5.35 \times 10^{-2} \text{ hrs.}^{-1} \quad (50^{\circ} \text{ C.})$$

4. The effect of reducing agents on the formation of the oxidized complex was studied. It was found that tin(II) chloride, hydrazine sulfate, and hydroxylammonium chloride prevented the formation of the oxidized complex.
5. The magnetic susceptibility data of the complexes of 4-carboxynioxime and nickel(II) were interpreted with the valency bond theory. The configuration of the 1:1 complex of 4-carboxynioxime and nickel(II) was discussed. The probable structures are:

or



6. The following mechanism for the formation of the oxidized complex of 4-carboxynioxime and nickel(II) is proposed:

$$Ni(OH)_2 + D^{-3} = NiD(OH)_2^{-3} \qquad \text{Eq. (2)}$$

$$NiD(OH)_2^{-3} + D^{-3} = NiD_2(OH)_2^{-6} \qquad \text{Eq. (3)}$$

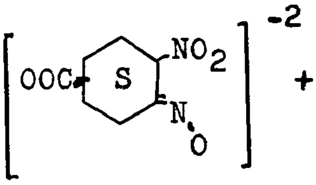
$$\text{or, } 2NiD(OH)_2^{-3} = [DNi(O)_2NiD]^{-6} + 2H_2O \qquad \text{Eq. (4)}$$

$$[DNi(O)_2NiD]^{-6} + D^{-3} + 2H_2O = NiD_2(OH)_2^{-6} + NiD(OH)_2^{-3} \qquad \text{Eq. (5)}$$

$$\text{then, } NiD_2(OH)_6^{-6} + D^{-3} \overset{k_1'}{=} NiD_3^{-7} + 2OH^- \qquad \text{Eq. (6)}$$

$$NiD_3^{-7} + \tfrac{1}{2}O_2 + H_2O = NiD_3^{-5} + 2OH^- \qquad \text{Eq. (7)}$$

$$NiD_3^{-5} + 3OH^- \overset{k_1'}{=}$$



$$+ \; NiD_2(OH)_2^{-6} \qquad \text{Eq. (8)}$$

VII. SUGGESTIONS FOR FURTHER WORK

1. The analytical application of 4-carboxynioxime should be investigated. The evidence obtained indicates that 4-carboxynioxime could be used to determine nickel spectrophotometrically and polarographically in 8.923 M potassium hydroxide.
2. Similar experiments should be performed in various concentrations of potassium hydroxide to determine the effect of hydroxyl ion on the formation of the complexes of 4-carboxynioxime and nickel(II), the rate of oxidation of NiD_3^{-7}, and the magnetic susceptibility of the complexes.
3. Rate studies should be performed with various oxidizing agents to substantiate the rate data obtained from the study with oxygen as the oxidant.
4. An attempt should be made to prepare, isolate, and identify the products of the oxidation of NiD_3^{-7}.
5. Similar experiments should be performed in 8.923 M potassium hydroxide with various *vic*-dioximes to determine the step-wise stability constants, the magnetic susceptibility, and the rate of formation of the oxidized complexes. This data would be useful in correlating the physical properties of the complexes with the structures of the *vic*-dioximes.

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IX. ACKNOWLEDGMENTS

The author is greatly indebted to Dr. Charles V. Banks for his interest, suggestions, and cooperation throughout the course of this work.

The author also wishes to thank Mr. J. J. Richard for his assistance in the synthesis of 4-carboxynioxime and for the preparation of 4-carboxycyclohexenfuroxane.