1968

A spectrophotometric study of the system: cobalt--2,2,8,8-tetrakis (hydroxymethyl)-3,7-diaza-1,5,9-nonanetriol

Pauline Frances Fones

Recommended Citation

Fones, Pauline Frances, "A spectrophotometric study of the system: cobalt--2,2,8,8-tetrakis (hydroxymethyl)-3,7-diaza-1,5,9-nonanetriol" (1968). *Master's Theses*. 1179.
http://scholarship.richmond.edu/masters-theses/1179

A SPECTROPHOTOMETRIC STUDY OF THE SYSTEM: COBALT--2,2,8,8-TETRAKIS(HYDROXYMETHYL)-3,7-DIAZA-1,5,9-NONANETRIOL

by

Pauline Frances Fones

THESIS

Submitted to the Graduate Faculty
of the
University of Richmond
in Candidacy
for the Degree of
Master of Science - Chemistry

August 1, 1968

Approved by: Wm E. Trout, Jr.
J. Stanton Pierce
W. Allan Powell
Richard A. Mateer
R. D. Decker

ABSTRACT

Spectrophotometric studies of solutions of 2,2,8,8-tetrakis(hydroxymethyl)-3,7-diaza-1,5,9-nonanetriol, $(HOCH_2)_3CHNCH_2CH(OH)CH_2NHC(CH_2OH)_3$, with cobalt (II) gave evidence of complexes having metal-ligand ratios of 1:2 and 1:3. Complexation appeared nearly complete at pH 8 or greater. Between pH 8 and pH 11, the positions of the maxima in the absorbance spectra remained essentially constant and no precipitation was observed. The 1:2 complex formed rapidly, while the 1:3 complex formed more slowly, requiring one to two weeks to reach equilibrium, after which the solutions remained unchanged over a period of several months. Evidence of the 1:2 complex was obtained using the slope-ratio (32) within one hour of the initial mixing. At later times, precipitation in the solutions containing high relative metal concentrations inhibited measurements.

Attempts to prepare analogous cobalt (III) complexes were unsuccessful. Modification of the method of Laitinen and Burdett (44) produced solutions whose spectra changed so rapidly that the changes could be observed while the solutions were being measured. Precipitation followed within two to three hours.

The complexes of 2,2,8,8-tetramethyl-3,7-diaza-5-nonanol, $(CH_3)_3CNHCH_2CH(OH)CH_2NHC(CH_3)_3$, appeared so unstable under the experimental conditions that even at high ligand ratios precipitation of the hydroxide occurred and measurements could not be made.

ACKNOWLEDGEMENTS

I wish to express my appreciation to Dr. William E. Trout, Jr. for his suggestions, patience, encouragement and guidance throughout this project. I also wish to thank Dr. J. Stanton Pierce, Dr. W. Allan Powell, Dr. James E. Worsham and Mr. Robert H. Bell, Jr., for their interest and suggestions.

TABLE OF CONTENTS

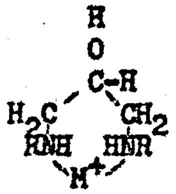
I. INTRODUCTION:

Pierce and Wotiz (65) prepared a number of polyhydroxyamines in this laboratory. Other workers have studied these and other polyhydroxyamines as chelating agents with elements of the transition series. (11,20,26,28,36,59)

The compounds prepared and studied all contained the hydroxypropylenediamine bridge structure, $RNHCH_2(CHOH)CH_2NHR$, with various R groups such as: 1) $HO{-}CH_2{-}CH_2{-}$; 2) $(CH_3)_2CH{-}$ 3) $(HO{-}CH_2)(CH_3)CH{-}$; 4) $(HO{-}CH_2)_2CH{-}$; 5) $(CH_3)_3C{-}$; 6) $(HO{-}CH_2)(CH_3)_2C{-}$; 7) $(HO{-}CH_2)_2(CH_3)C{-}$; 8) $(HO{-}CH_2)_3C{-}$.

Although the principal points of attachment of these ligands to the metal ions appeared to be at the sites of the two amino nitrogens, forming a six-membered chelate ring,

$(M^+[RNHCH_2(CHOH)CH_2NHR]) \rightarrow$



there was the possibility of the formation of additional linkages to the metal by the hydroxyl groups of the ligand, especially under conditions of high pH where the removal of the alcoholic protons might be possible. Unequivocal evidence of the role of the hydroxyl groups had not been determined; however, the stability constant data for complexes with Cu (II) and Ni (II) ions suggested either of the following:

1) The ligands were quadridentate such that two of the OH groups of the ligand would participate in chelation.
2) The chelates formed under these conditions would be polynuclear.

It was felt that a more extensive study of the complexes formed between cobalt and certain of these amines was needed. The amines chosen were 2,2,8,8,-tetrakis(hydroxymethyl)-3,7-diaza-1,5,9-nonanetriol, $(HOCH_2)_3CNHCH_2CH(OH)CH_2NHC(CH_2OH)_3$, hereafter called "Disec", and 2,2,8,8-tetramethyl-3,7-diaza-5-nonanol, $(CH_3)_3CNH\text{-}CH_2CH(OH)CH_2NH\text{-}C(CH_3)_3$, hereafter called "Symaminol". (21)

This thesis gives the results of the investigation of the coordination properties of these compounds with cobalt.

II. FUNDAMENTALS:

A. Basic Concepts:

A class of compounds known variously as coordination compounds, metal complexes, or complexes, has been recognized for many years. These compounds contain a cluster of ions or molecules attached to a central atom or ion, usually of a metal. Substances using "secondary valences" (electron donors) are said to be coordinated to the metal and are known as ligands.

Many complexes tend to retain their identities in solution, although partial dissociation may occur. They may be charged or uncharged, depending upon the sum of the charges of the central atom and the surrounding ligands, and more than one kind of ligand may be attached to the central atom. When a ligand can occupy more than one coordination position, ring formation results; the complex so formed was called a chelate by Morgan and Drew (56), and the ligands were called chelating agents. Unidentate, bidentate, terdentate, quadridentate, quinquedentate, and sexadentate, were the terms proposed by Morgan and Drew to indicate the number of donor groups from a particular molecule or ion. The general term, multidentate, was also used. Polynuclear complexes contain two or more metal atoms joined by one or more bridging ligands. (8,68) Complexes were usually divided into two broad classifications--normal complexes and penetration complexes. Normal complexes were those which rapidly dissociated reversibly in solution, while penetration complexes exhibited little dissociation (approached equilibrium slowly).

B. History

Just when the first of this group of compounds was discovered is unknown. Prussian blue, $KFe[Fe(CN)_6]$, produced at the beginning of the eighteenth century by Diesbach, is probably the earliest one on record. The date of significance usually given is that of the discovery of hexammine cobalt (III) chloride, $ClCl_3 \cdot 6NH_3$, by Tassaert—1798. (8)

1. Werner's Theory (90)

The first fruitful theory as to the nature of these compounds was enunciated almost 100 years later (1893) by Alfred Werner. Werner's ideas had been preceded by many years in which various proposals were made only to be later rejected in favor of newer ones. Werner utilized this previous work and even incorporated some of it into his own proposals.

Statements made by Claus in the 1850's and rejected by other workers appeared with slight modifications as a part of Werner's theory. (51) Blomstrand and his student, S.M. Jørgensen proposed a "chain theory" based on an analogy with organic amines, which aroused contention between Jørgensen and Werner and stimulated their research (51)

Fundamentally, Werner's theory was quite simple. In his words: "Even when, to judge by the valence number, the combining power of certain atoms is exhausted, they still possess in most cases the power of participation further in the construction of complex molecules with the formation of very definite atomic linkages. The possibility of this action is to be traced back to the fact that, besides the affinity bonds designated as principal valencies, still other bonds on the atoms, called auxiliary valences, may be called into action". (73)

The fundamental postulates of the theory are:

1. Two types of valence are exhibited by most elements: a) primary valence and b) secondary valence. Primary valences must be satisfied by negative ions, whereas, secondary valences may be satisfied by either negative ions or neutral molecules.
2. Every metal has a fixed number of secondary valences (coordination number).
3. Every element tends to satisfy both its primary and secondary valence.
4. The secondary valencies are directed toward fixed positions in space.

Two marked departures from prevailing theory were made in the development of Werner's theory and postulates. First, he discarded the "chain theory" in favor of a centralized construction similar to that proposed by Kolbe in 1860. (58) In this construction there was a central atom around which other atoms, molecules or ions arranged or coordinated themselves. Second, he deviated from the inadequate valence theory of his day.

Werner began with the concept of the valence of the central atom. He pointed out that valence varies with the nature of the elements with which the central atom is in combination— valence is not an invariant property. He pictured metals as having inner and outer coordination spheres. Those groups bound covalently he described as being held in an inner coordination sphere, while negative ions which gave the usual tests were in the outer sphere.

Coordination formulas were devised in which primary and secondary valences were distinguished. The number of groups directly attached to the central atom he called the coordination number. He proposed spatial configurations (Figure 1), explained geometric isomers and predicted optical isomers. He demonstrated <u>cis-trans</u> isomerism in both tetra-coordinated and hexa-coordinated complexes (Figure 2) as well as optical isomerism (Figure 3). (22,51,55)

The electronic theory of valency, proposed by Lewis in 1916, and extended by Langmuir in 1919, allowed chemists to express Werner's valence concepts in terms of electrons. (86)

2. Contributions of Sidgwick and Lowry (69,87)

Sidgwick and Lowry are largely responsible for putting Werner's theory on an electronic basis. They suggested that primary valences were satisfied by electron transfer and secondary valences by electron pair sharing. Sidgwick introduced the coordinate bond for the case in which both electrons in a shared pair originate on the same atom. He suggested that since all molecules and ions which can attach to metal ions seem to have at least one unshared pair of electrons, this free electron pair is partially donated to the metal ion in the formation of the bond. The resultant bond is called a dative or semipolar bond. It may be represented by an arrow, L → M, indicating that the donor group, L, has supplied both electrons to the acceptor, M.

Sidgwick also proposed the concept of effective atomic number (EAN), stating that metal ions will continue to accept electron pairs from donors until the metal in the complex has the EAN of the next noble gas. This may be illustrated with

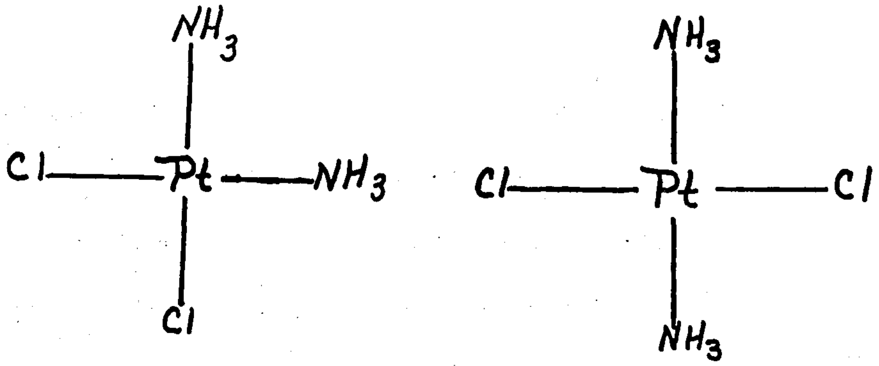


Figure 1. - Spatial Configurations

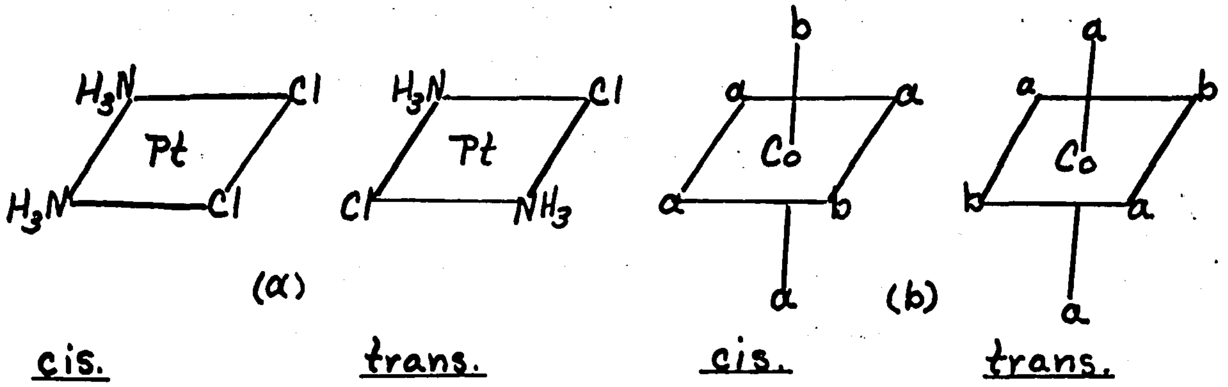


Figure 2. - Geometric Isomers

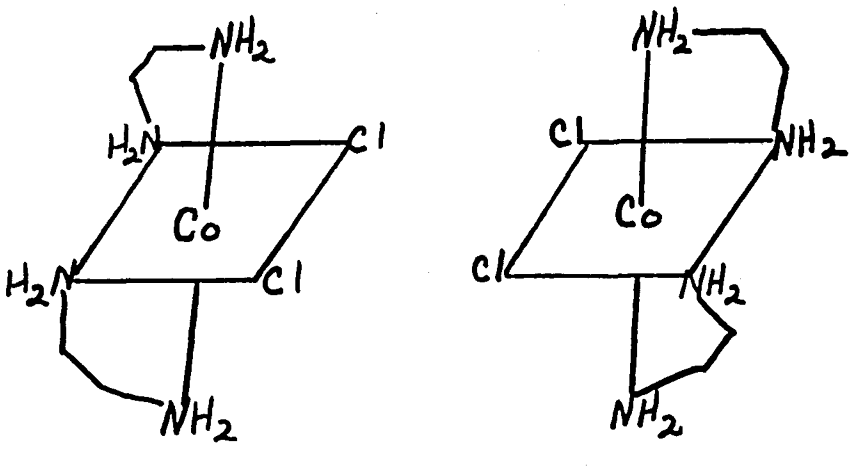


Figure 3. - Optical Isomers

$[Co(NH_3)_6]^{3+}$.

Co (III) contains 24 electrons
6 NH_3 donate 12 electrons

EAN of Co (III) 36 electrons (the AN of Kr)

This rule applies especially to the volatile metal carbonyls such as $Fe(CO)_5$.

Although many known complex ions follow this rule, there are a large number of exceptions. For example, Fe (III) which is tetra-coordinate in $[FeCl_4]^-$ and hexa-coordinate in $[Fe(CN)_6]^{3-}$ never obeys the rule. In the iron pentacarbonyl mentioned above, the oxidation state of Fe is zero.

Modifications of Sidgwick's theory were necessary to offset the serious problem of the accumulation of very high negative charge on the metal. (23)

Presently, three more or less distinct theoretical approaches to the bonding in complexes are recognized: (1) The Valence Bond Theory, (2) The Crystal Field Theory with Ligand Field modifications, and (3) The Molecular Orbital Theory. Of these approaches, only the Ligand Field Theory was designed specifically to explain complex compounds.

B. Theories of Bonding

1. Valence Bond Theory

Valence Bond Theory is attributable mainly to the efforts of Pauling (1931) to give quantum mechanical validity to the Lewis-Langmuir-Sidgwick ideas of the coordinate bond. The theory deals with the shapes, magnetic moments and structure of the electronic ground state of complexes.

The following assumptions are basic to the theory:

(a) The central metal atom makes available a number of equivalent orbitals, equal to its coordination number, for the formation of covalent bonds with ligand orbitals.

(b) Overlap of a vacant metal orbital with a filled donor orbital gives a covalent <u>sigma</u>-bond. (The bond formed, although covalent, may possess considerable polarity because of its mode of formation.)

(c) If suitable <u>d</u> electrons of the metal are present in an orbital which can overlap with a vacant donor orbital, a π-bond may be formed. A π-bond changes charge distribution such that <u>sigma</u>-bonds are strengthened.

Diagramatic representations are common in this approach. For a complex such as $[Cr(NH_3)_6]^{3+}$, the following type of diagram is used:

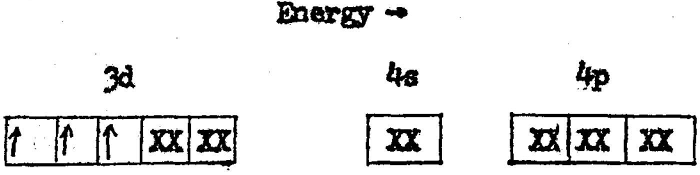


Figure 4. (19)

From this diagram, the following information may be obtained:

(1) The qualitative order of energies of orbitals is ($4p > 4s > 3d$).

(2) A d^2sp^3 hybrid is formed and occupied by six electron pairs.

(3) Three <u>d</u> orbitals remain to be occupied by three <u>d</u> electrons in accord with Hund's rule, thereby rendering the compound paramagnetic.

Although the Valence Bond Approach is a convenient model conceptually, there are several defects.

(1) Valence Bond Theory is limited to a qualitative explanation of properties.

(2) It predicts neither spectra nor detailed magnetic properties.

(3) Splitting of d energy levels is not considered.

(4) The theory doesn't account for or predict the relative energies of different structures. (22)

2. Crystal Field-Ligand Field Theory

(a) The Simple Electrostatic Theory

Around 1930, an application of a simple electrostatic theory to bonding in complexes was developed by Van Arkel and De Boer and by Garrick who applied the potential energy equations of electrostatics to their bonding model. (22)(27,88)

Using a purely electrostatic model, regular configurations may be expected for all the possible coordination numbers provided the ligands are identical, (viz. for coordination numbers 2,4 and 6, the expected configurations would be linear, tetrahedral and octahedral respectively, since these configurations would give the minimum of repulsive forces.) Metal ions and ligands are considered rigid and undistorted in this treatment.

The simple electrostatic model is not applicable in all cases. Square planar complexes cannot be justified on the basis of this model. The theory can account for neither magnetic, spectral nor kinetic properties. Ions of the second and third transition series often form complexes of greater stability than those of the first row transition elements, whereas their complexes would be predicted to be less stable due to the greater size of the heavier ions.

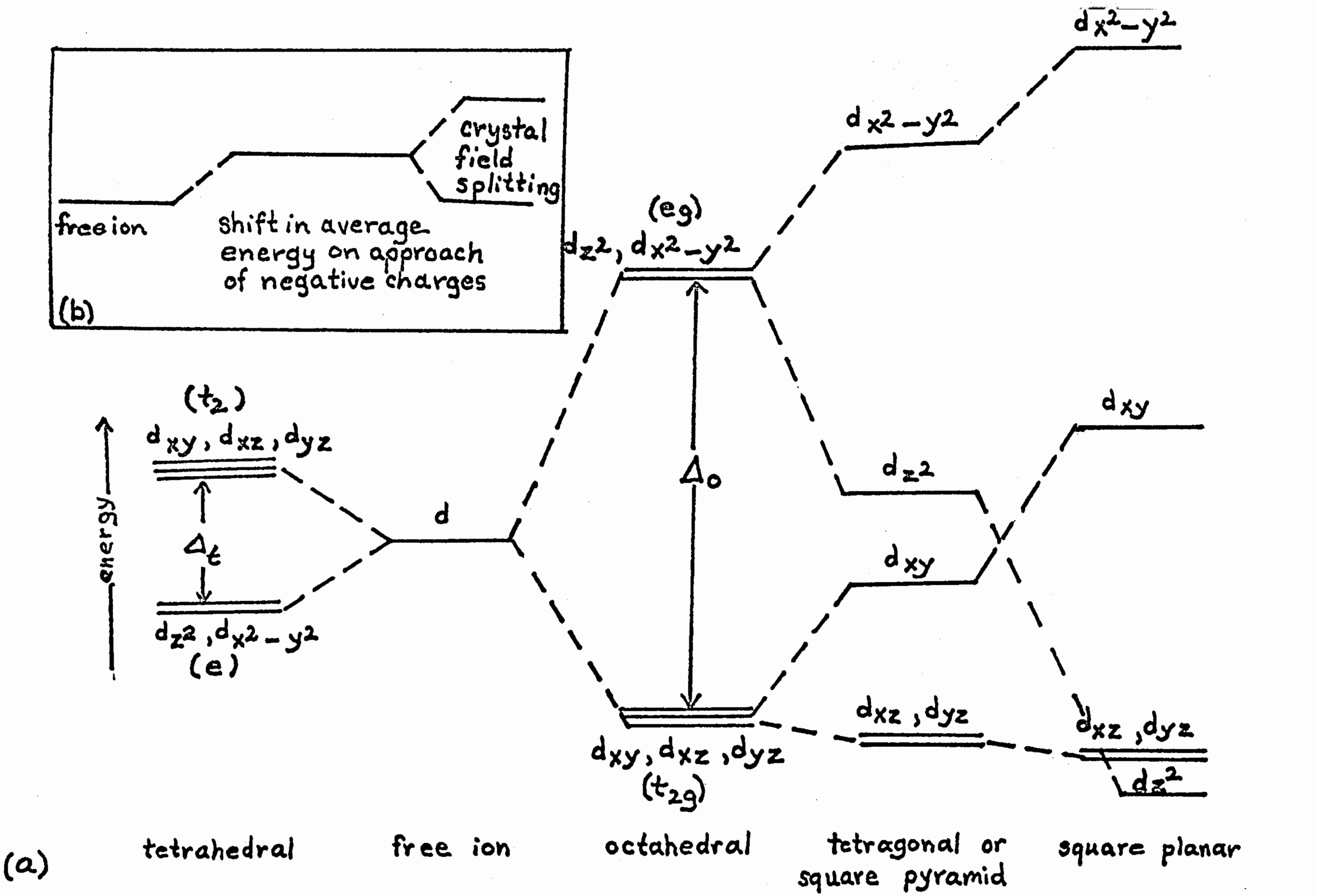
(b) The Crystal Field Theory (CFT)

Crystal field corrections are important in accounting for differences among the transition metal complexes, yet, the simple electrostatic attractions account for most of the bond energies. Although first proposed by Bethe in 1929, the application of CFT to coordination compounds is quite recent. (60)

The interaction between the central metal ion and its surrounding ligands as explained by the Crystal Field Theory is still considered an electrostatic one, in which the central ion and the surrounding ligands are regarded as "point charges" The Crystal Field Theory deals with orbitals and electrons rather than rigid entities. As a first approximation, the orbitals of the central ion are considered as separated from the ligand orbitals. The theory is primarily concerned with the effect on d orbitals caused by various electrostatic fields arising from differing geometries and strength of ligands.

In a field-free ion or atom in vacuo, the d orbitals are degenerate and of equal energy. Energy differentiation occurs in an electrostatic field created by the presence of ligands. The entire d level is displaced to some new unknown value, indicating that all d levels are repelled slightly by the ligands. Orbitals oriented toward the ligands are then raised in energy with respect to the orbitals oriented between the ligands. The similarity of the field produced by the ligands to that experienced by ions in ionic crystals accounts for the name, Crystal Field Theory. Crystal field splitting of the d orbitals of a central ion in regular complexes of various structures is indicated in Figure 5.

The energy difference between the new sublevels is called



crystal field splittings of the "d" orbitals of a central ion in regular complexes of various structures.

Figure 5 (22)

the crystal field stabilization energy (CFSE) and is measured in terms of a parameter, 10 Dq or Δ. Delta is a measure of the crystal field strength—the stronger the field, the larger Δ. The zero of energy for the crystal field effect is taken to be that for a random occupation of the split d orbitals by an electron. The CFSE is then the gain in energy due to the preferential filling of the lower lying d levels. There is no change in the energy of the system due to splitting if all five orbitals are equally occupied.

There are at least two significant opposing tendencies in determining the population distribution of d electrons under the influence of a crystal field:

1. The tendency for electrons to occupy the lowest lying orbitals as far as possible.
2. The tendency for electrons to enter different orbitals with their spins parallel.

When there are only 1,2 or 3 d electrons, both tendencies can be satisfied when the electrons occupy different t_{2g} orbitals with their spins parallel. With 4,5,6 or 7 d electrons there are two possibilities dependent upon the strength of the field produced by the ligands: a) a maximum spin state with a minimum number of unpaired electrons, or b) a minimum spin state with a maximum number of electrons requiring pairing of electrons in the t_{2g} level. For all configurations other than d^0,d^5 (high spin) and d^{10}, the splitting lowers the total energy of the system. This decrease is the crystal field stabilization energy.

If, in a d^3 case, the splitting of the d levels is small, indicating a weak field, a fourth electron would be expected to enter a destabilizing e_g orbital because the gain in CFSE from entering a t_{2g} orbital is not great enough to provide the required pairing energy.

If the splitting is large, electron pairing occurs. The CFSE is higher by $2/5\ \Delta_o$, but the gain in energy is only ($2/5\ \Delta_o$ - electron pairing energy). (22,24)

The Crystal Field Theory is advantageous for prediction of: (1) favorable coordination numbers, (2) stereochemistry, (3) reaction paths, (4) magnetic properties, and (5) absorption spectra.

Due to its emphasis on the orbitals and electrons of the central atom, CFT becomes less accurate as delocalization of ligand electrons and orbitals becomes more important. Crystal Field Theory gives little information about excited states in which there is electron or charge transfer.

(c) The Ligand Field Theory (LFT)

Ligand Field Theory is an outgrowth of the Crystal Field Theory and is often designated as the "CFT-LFT". It was found that few of the results of CFT were actually dependent upon the existence of a lattice, therefore, most of them could be carried over to the basic model of coordination chemistry--the coordination cluster. The term Ligand Field Theory has been employed to cover all aspects of the manner in which an ion or atom is influenced by its nearest neighbors. Ligand Field Theory contains CFT as a special case.

Many of the results of LFT are dependent only on the approximate symmetry of the ligand distribution around the central ion rather than on the particular ligands or the details of their locations. (24,68)

3. Molecular Orbital Theory

The Molecular Orbital approach (MO) is the most general of all the approaches to complex ion formation. First applied by Van Vleck, the method employs the same orbitals of the central ion as does the Pauling method, as well as the available orbitals of the coordinating ligands which are directed toward the central atom. (24)(19)

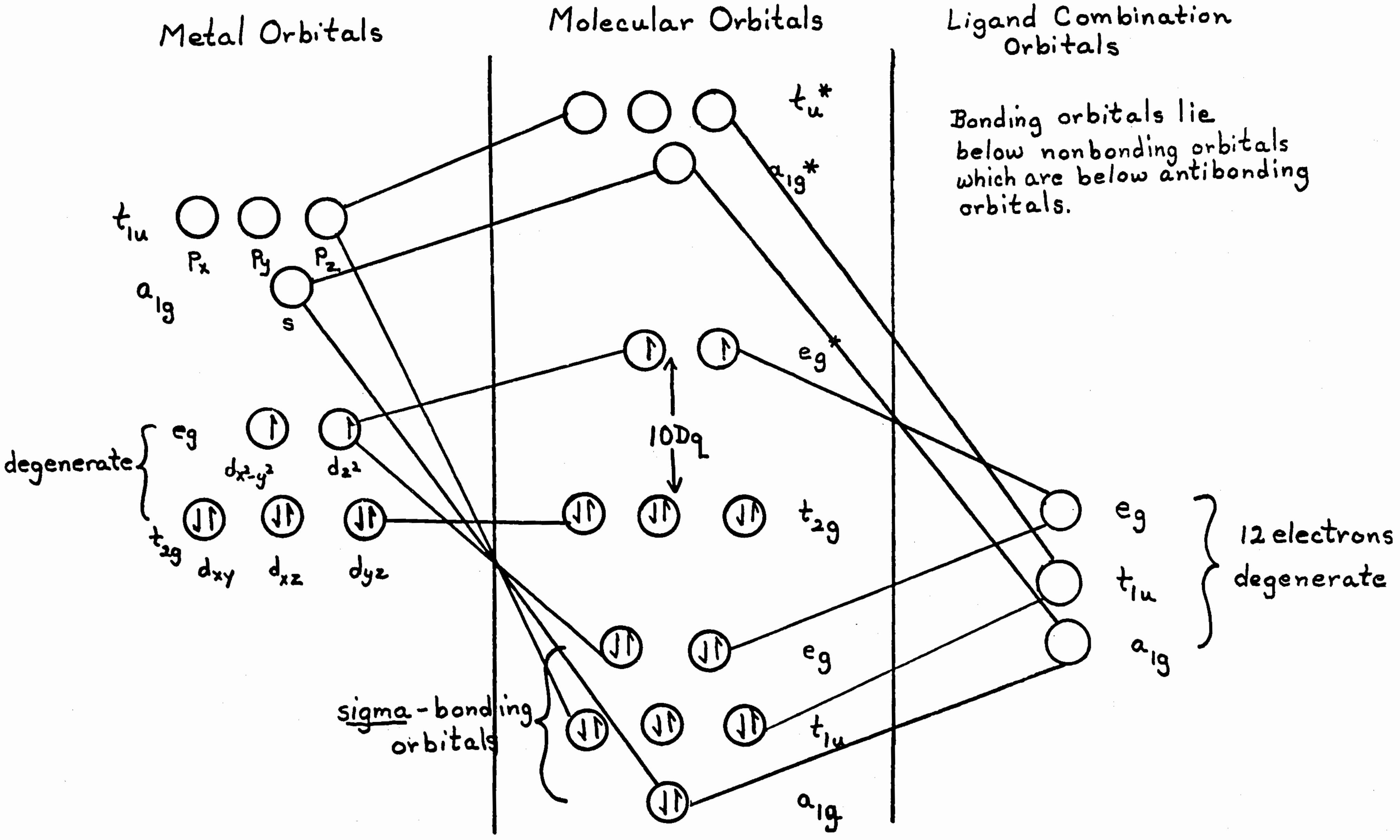
Since the Molecular Orbital approach can deal with energy levels quantitatively, molecular orbital energy level diagrams may be used very conveniently. (Figure 6) A group of composite orbitals is made for the set of ligands. Then, symmetries permitting, these are combined with the atomic orbitals of the metal ion to produce the desired bonding and antibonding molecular orbitals. The representation of the bonds utilizes a linear combination of atomic orbitals, LCAO. The orbitals are then filled successively with the available electrons, beginning with the lowest energy orbitals.

The symbolism used is based on degeneracy and symmetry of the orbitals. For an octahedral complex, the metal orbitals are indicated as shown:

Table I.

Atomic orbital	Notation
s	a_{1g}
p_x, p_y, p_z	t_{1u}
$d_{x^2-y^2}$, d_{z^2}	e_g
d_{xy}, d_{xz}, d_{yz}	t_{2g}

The notations a and b refer to non-degenerate orbitals,

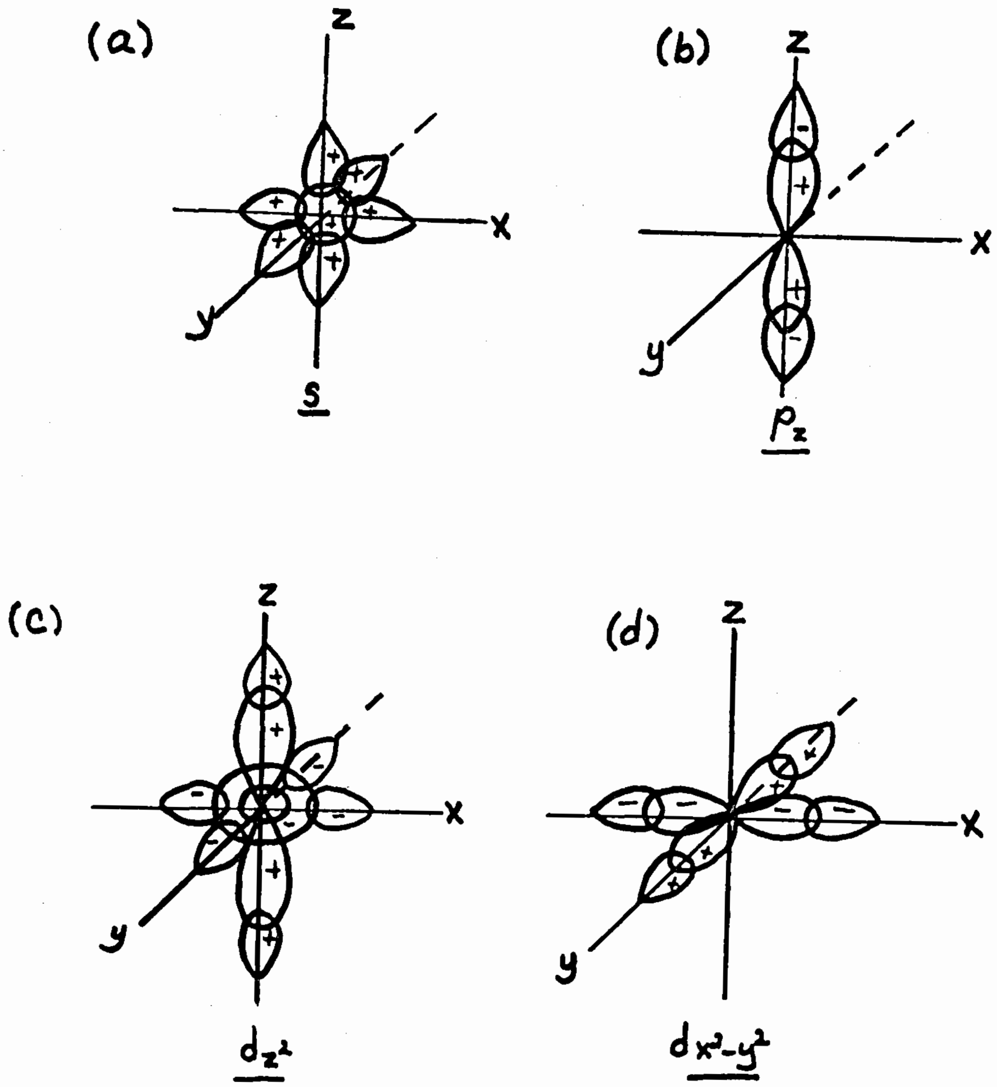


Bonding orbitals lie below nonbonding orbitals which are below antibonding orbitals.

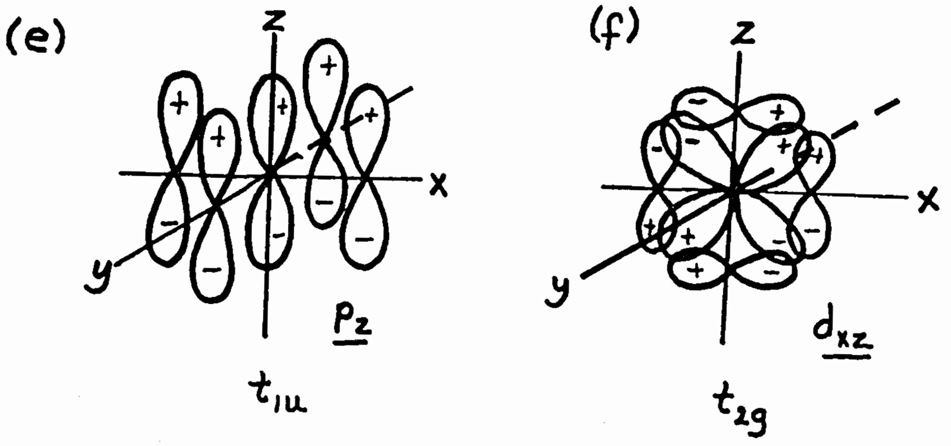
Figure 6. – Qualitative diagram for the molecular orbitals of an octahedral d^8 complex such as $[Ni(NH_3)_6]^{2+}$ (without π-bonding). (24)

e to two-fold degenerate orbitals and *t* to three-fold degenerate orbitals. The corresponding capital letters are used for the respective energy states. Numerical subscripts may differentiate among molecular orbitals of the same degeneracy or they may have a special meaning. A center of symmetry is indicated by the subscript, *g* (gerade); an orbital for which there is a change of sign on reflection through the center of symmetry is indicated by the subscript *u* (ungerade). *S* and *d* atomic orbitals are *g* and *p* orbitals are *u*.

Combination ligand orbitals can be obtained having e_g, a_{1g}, and t_{1u} symmetry. Each combination orbital plus a metal orbital having the same symmetry gives a *sigma* molecular orbital. The t_{2g} metal orbitals are non-bonding since no ligand combination orbitals with t_{2g} symmetry are available. In Figure 7a are shown the *sigma* bonds formed by atomic orbital overlap. The metal *s* orbital forms a *sigma* bond with the ligand orbital of a_{1g} symmetry. The wave functions of all six ligand orbitals have the same sign as the metal *s* orbital. The corresponding antibonding orbital would involve reversal of the sign of the wave function of the ligand orbital. The d_{z^2} and the $d_{x^2-y^2}$ orbitals combine with ligand orbitals having e_g symmetry, while each metal *p* orbital combines with a ligand combination orbital involving two ligands. The metal bonding orbitals are the same as those involved in d^2sp^3 hybridization of the Valence Bond treatment. (Figure 7 b,c and d). If the ligand composite orbitals are of lower energy than the metal orbitals with which they are combined, the electrons in the bonding molecular orbitals will be concentrated more in the region of space close to the ligand, and the electrons in antibonding



combination of atomic orbitals to form **sigma** bonds in an octahedral complex



two symmetry types of π-bonds in octahedral complexes

Figure 7. (24)

orbitals will be concentrated more in the neighborhood of the metal ion. Nonbonding electrons are located on the metal ion.

In an octahedral complex, twelve ligand electrons can enter the bonding orbitals. The metal d electrons must enter the non-sigma-bonding t_{2g} orbitals and the antibonding e_g orbitals. The antibonding orbitals are those into which electrons may be excited from the t_{2g} orbitals by absorption of energy. The greater the extent of overlap of the 3d orbitals of the metal ion with ligand orbitals, the higher will be the energy of the antibonding, e_g^*, orbital.

When π-bonding is involved, the molecular orbital treatment is the only approach giving a really satisfactory explanation of the bonding. The two types of π-bonding differ in the source of the donated π electrons, (L→M or M→L). The ligand orbitals used for π bonding are generally the p orbitals. The ligand orbitals are combined to give ligand combination orbitals of t_{1u} and t_{2g} symmetry.

In π bonding, the t_{2g} orbitals split into bonding and antibonding orbitals as shown.

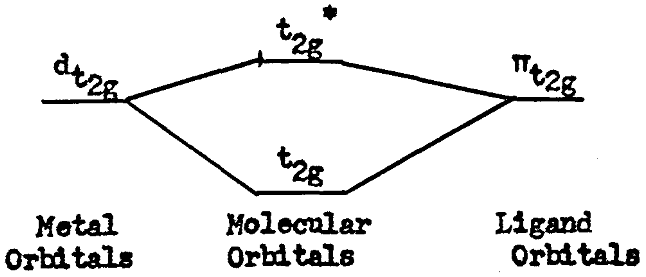


Figure 8.

The depression in energy pictured for the t_{2g} π-bonding orbitals increases the energy difference between the t_{2g} and the unaffected antibonding level, therefore, the magnitude of

Δ is increased. Hence a ligand which can form a π-bond is stronger than it would be if it could not π bond. The increased energy difference between the t_{2g} and e_g^* states due to π-bonding is responsible for electron-pairing or low-spin complexes according to the Molecular Orbital Theory.

A t_{1u} orbital is obtained from p orbitals of four ligands in the same plane (Figure 7 e) yielding three π molecular orbitals with t_{1u} symmetry on overlap with p orbitals of the metal. Each of the metal t_{2g} orbitals can interact with a ligand combination orbital obtained from the p orbitals of four ligands with all atoms and orbitals in the same plane (Figure 7f). There are a total of six possible π-bonding molecular orbitals. However, the metal t_{1u} orbitals are used for sigma bonding leaving only the antibonding t_{1u}^* level for π interaction with ligands. Pi bonding involving these high energy orbitals is not expected to be of great importance.

Without π-bonding, the results of the molecular orbital treatment are so similar to the crystal field representation that the latter is adequate for most applications. Molecular Orbital Theory includes the Crystal Field and Valence Bond approaches as special cases. Although Molecular Orbital Theory is the most general treatment, an exact treatment for complexes containing many atoms is still difficult to obtain. (24)

D. FACTORS AFFECTING THE FORMATION AND STABILITY OF COMPLEX IONS

Several physical and chemical factors influence the formation and stability of coordination compounds. Special effects are shown in chelate compounds. Some of the more important factors are:

1. Environmental Factors

Temperature and pressure exert a great influence in some cases. Elevated temperatures may shift equilibria and change absorbtion intensities. A reduction in pressure often results in the loss of volatile coordinating groups such as water in hydrates and ammonia in ammines.

2. Concentration Factors

The stabilities of complex ions in solution may be greatly influenced by concentration changes which cause equilibrium shifts in accord with Le Chatelier's principle.

3. Nature of the Metal Ion

The most stable complexes are often formed by the transition metals and the metals immediately following them. The cations which serve best as centers for coordination are those with comparatively small sizes and high nuclear or ionic charge.

The Effective Atomic Number concept has been particularly successful with metal carbonyls. (61) Instability is expected when the EAN is one or two units greater or less than the atomic number of the next noble gas. (51) Exceptions to this generalization have been previously noted. (See page 8.)

The order of stability of complexes of bivalent metal ions: Pd $>$ Cu $>$ Ni $>$ Pb $>$ Co $>$ Zn $>$ Cd $>$ Fe $>$ Mn $>$ Mg, has been noted by Mellor and Maley (53a). This order has been observed to hold for all ligands studied by them. The order for ethylenediamine and propylenediamine chelates measured by Carlson _et. al_. (14) support these data. Chaberek and Martell indicate the same order for complexes of iminodiacetic acid, iminodipropionic acid, and β- hydroxyethyliminodiacetic acid. (15a,17) However, some deviations from this series have been observed by Irving and Williams (37 a,b). The difference in stability for successive metals is sometimes small. (49)

4. Nature of the Ion Outside the Coordination Sphere

The tendencies of the external ions to enter the coordination sphere often affects the stabilities of coordination compounds. External ions may enter the coordination sphere at the expense of the material already coordinated to the metal. Ions such as CN^-, SCN^-, Cl^-, Br^-, $C_2O_4^{-2}$, and NO_2^- have a great tendency to do this. Nitrate and perchlorate ions show little tendency toward replacement.

Pfeiffer and Schmitz (63b) showed that the stability of chelates of EDTA with copper and other metals was greatly dependent on the nature of the remaining positive ions in solution. For example, the disodium salt of the chelate was stable toward NaOH, but when Ca^{+2} or Zn^{+2} replaced the sodium in the salt, $Cu(OH)_2$ precipitated.

5. Nature of the Ligand

Theoretically, almost any group containing an atom which has an unshared electron pair may act as a coordinating agent. In practice the number of donor atoms is limited. Strong coordinating groups tend to replace weak ones producing complexes of greater stability.

The relative sizes of metal and ligand are important in determining the number of ligands that can fit around the metal ion. There are several limiting radius ratios (M : L) which determine the coordination number of the metal ion. Some of these ratios are shown in the following table.

TABLE 2 (51)

Formula	M : L	Coordination Number	Arrangement
ML_2	0.00 - 0.15	2	collinear
ML_3	0.15 - 0.22	3	triangular planar
ML_4	0.22 - 0.41	4	tetrahedral
ML_4	0.41 - 0.59	4	square planar
ML_6	0.41 - 0.59	6	octahedral

Fajans and Tsuchida observed that the replacement of one ligand by another ligand often caused a shift of the spectrum to either longer or shorter wavelengths. An arrangement of ligands in order of the magnitude of the shift is known as the spectrochemical series. The more common ligands are placed in the following order: $I^- < Br^- < SCN^- < Cl^- < NO_3^- <$ $F^- <$ urea $< OH^- < ONO^- < HCOO^- < C_2O_4^{2-} < H_2O < NCS^- <$ glycine $<$ EDTA $<$ pyridine $< NH_3 <$ ethylenediamine $<$ diethylenediamine $<$ triaminoethylamine $<$ dipyridine $<$ ortho-phenanthroline $< NO_2^- \ll$ CN^-. The shifts to higher energies are associated with the ligands on the right side of the series. (59)

6. Steric Strain

Large, bulky ligands tend to form less stable complexes than do analogous smaller ligands because of steric factors. For example, ethylenediamine forms more stable complexes than $(CH_3)_2NCH_2CH_2N(CH_3)_2$. The strain is sometimes due to the geometry of the ligand coupled with the stereochemistry of the metal complex. For example, $H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$ can coordinate its four nitrogens at the corners of a square but $N(CH_2CH_2NH_2)_3$ cannot. (8,49,50,51)

E. STABILITY OF CHELATES

Steric effects, derived from both the ligand and the metal, govern to a large extent the interaction of metal ions with sequestering agents. The ability or inability of an electron donor group to approach the hydrated metal ion (steric effects) as well as the basicity of the group are the primary structural factors which must be considered when unidentate electron donors, such as amines, react with a given metal ion. Binding together a number of such groups into a single chelating agent greatly increases the importance of steric effects. The stability of the complex is also dependent upon other factors such as the size and number of chelate rings formed. The influence of ligand structure on the stabilities of metal chelate compounds is thus seen to involve properties found only in chelating agents, as well as effects which are common both to chelating and unidentate ligands.

1. Size of Chelate Rings

Since the early work of Ley (46) on the Cu (II) chelates of some simple amino acids, considerable qualitative evidence has been reported which indicates that the most important classes of sequestering agents are those which can form five- and six-membered rings. Ring systems with more than six members have generally proven unstable.

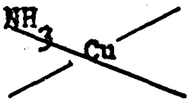
2. Number of Chelate Rings

The stabilities of metal chelates vary directly with the effective polydentate nature of the chelating agents. Good examples of this structural effect for ligands having the same kind of electron donor groups are the linear polyamine chelates of Cu (II) and Ni (II).

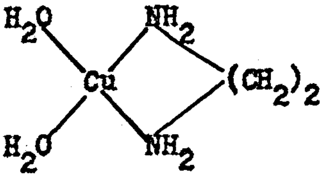
A comparison of the formation constants of the Cu (II) complexes shown in Table 3 shows that an increase in the number of chelate rings in the 1:1 complexes results in a progressive increase in log K_{MA}. The tendency to bind a second mole of ligand also decreases with an increase in polydentate nature of the chelating agent. The effect of binding the electron donor groups together into a single molecule is also shown by the table. Log K_{MA} for ethylenediamine compared to log K_{MA_1} + log K_{MA_2} for NH_3 shows approximately a thousandfold increase in stability due to formation of a five membered chelate ring. (16)

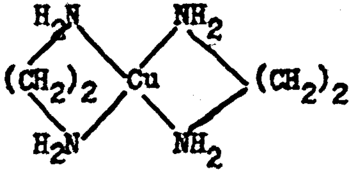
TABLE 3

Structure and successive formation constants of Cu (II)-polyamine complexes and chelates.

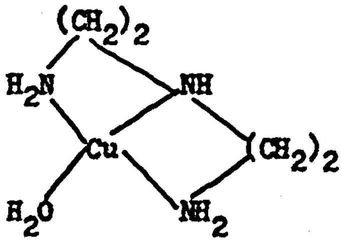


NH_3: 4.13, 3.48, 2.87, 2.11

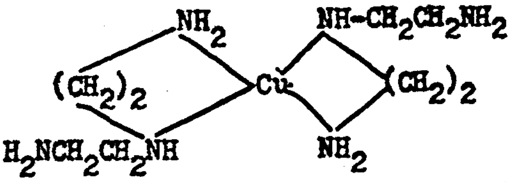


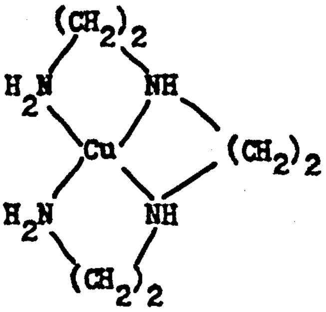


En: 10.72, 9.31



Dien: 15.9, 5.4





Trien: 20.5

---

3. Effect of Ligand Basicity

Calvin and Wilson (12) first pointed out the correlation between the basic strength of the ligand and stabilities of the Cu (II) chelates of a series of salicylaldehyde and β-diketone derivatives, showing that the stabilities vary directly with the basic strength of the ligand within each series.

4. Steric Effects

The presence of non-chelating substituents in the chelating ligand may introduce either or both of two effects: a) an inductive effect which changes the basicity of electron donors, or b) a steric interference which prevents the most favorable metal-ligand orientation. Bond strain sufficient to prevent complete coordination of the metal ion may result from steric factors. Basolo's investigation of a series of alkyl substituted ethylenediamine derivatives serves as an illustration. (7,9a,9b)

N and N,N'-alkyl substituted ethylenediamine chelates of Cu (II) and Ni (II) have basicities greater than the unsubstituted ethylenediamine chelates of these two metals. An increase in the chain length decreases the stability of the complex and an increase in the size of the substituent replacing hydrogen decreases stability. Disubstituted materials show greatest steric hindrance. Experiments using N-alkyl substituted glycines showed similar effects. (6)

F. ABSORPTION SPECTROPHOTOMETRY

Whenever a molecule is exposed to the alternating electromagnetic field of a beam of radiant energy, and the frequency of the incident radiation corresponds to one of the natural frequencies of the molecule, the radiation may be absorbed entirely or in part, increasing the energy content of the molecule, and an electronic transition to an excited state may result.

In Figure 9, is shown a schematic energy-level diagram for a simple diatomic molecule. A number of the ground state vibrational levels are populated at room temperature due to thermal motion. However, the energy differences between electronic levels are much larger, therefore, only the lower electronic levels are occupied under normal conditions.

Absorption of energy is dependent upon the molecular structure of the absorbing material. For a structure with loosely held or mobile electrons, the energy difference between the ground state and the excited state is small, and the frequency of the radiation absorbed is consequently low. In polyatomic molecules, the number of vibrational sublevels becomes large and their spacings small so that discrete peaks tend to coalesce into broad absorption bands or band envelopes. This tendency is even greater in the liquid state where physical interaction between neighbors and chemical solvation causes damping of the vibrations.

Absorbing groups, among inorganic compounds, may involve several atoms, (*i.e.* MnO_4^- and $Cr_2O_7^=$), or single atoms with incomplete outer *d*-electron shells, where closely spaced, unoccupied energy levels are available. Absorption spectra for these are thought to result from charge transfer processes in which electrons are transferred from one part of the ion to another. Changes in the complexing groups considerably alter spectra.

Incident radiation may be affected in different ways when

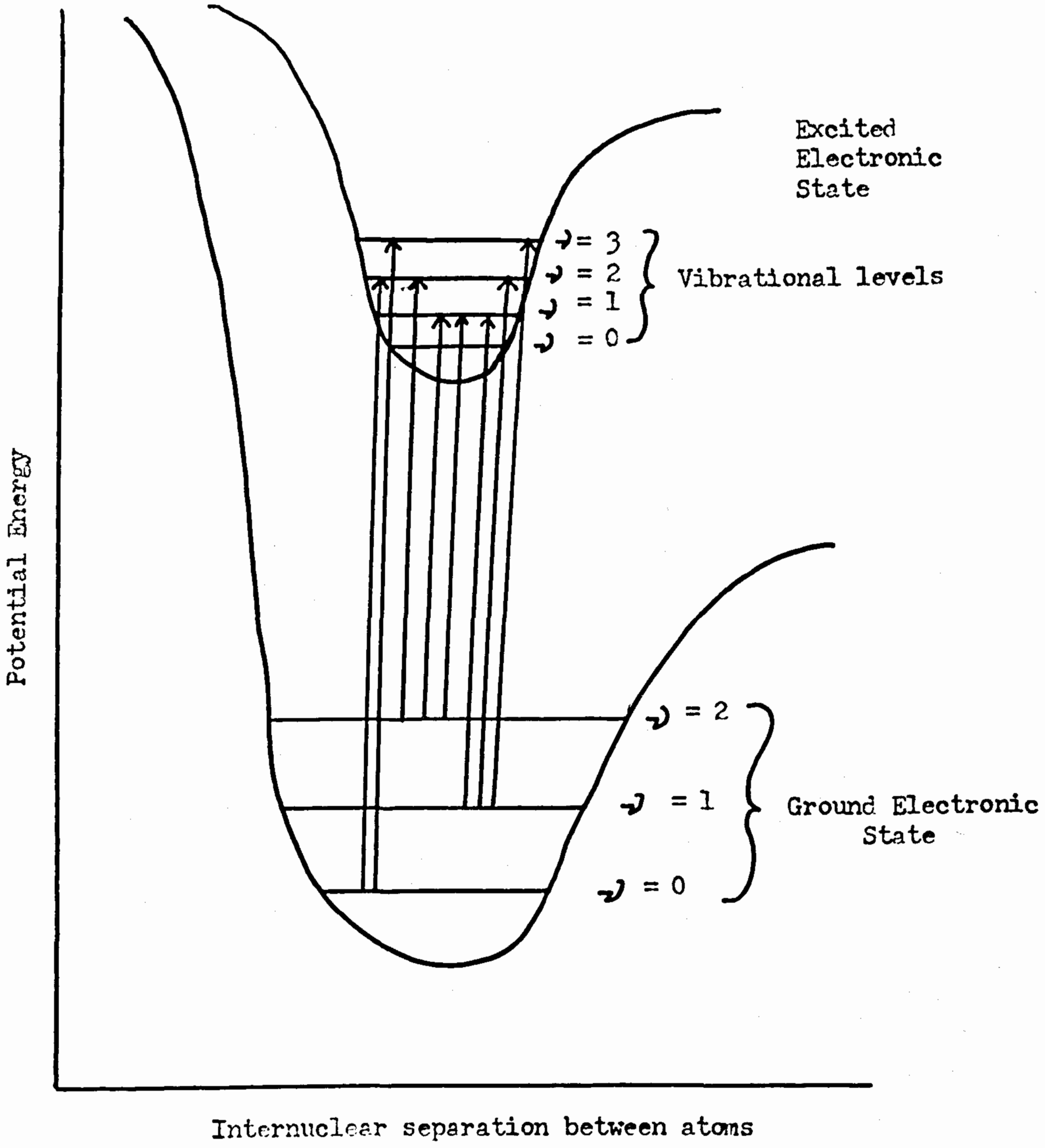


FIGURE 9: ENERGY-LEVEL DIAGRAM OF A DIATOMIC MOLECULE

it contacts a substance. It may pass through with little absorption or energy loss; the direction of the beam may be altered by diffraction, refraction, reflection or scattering from suspended particles; or the energy may be absorbed wholly or partially.

The technique of photometry is based upon two fundamental laws: 1. The Bouguer or Lambert law states that, for a plane-parallel beam of monochromatic light entering an absorbing medium at right angles to the plane-parallel surfaces of the medium, the rate of decrease in radiant power with the length of light path through the medium is proportional to the radiant power of the beam. Thus,

$$-\frac{\partial P}{P} = k\,\partial b \qquad (1)$$

where P is the radiant power of the beam and b is the length of the light path. On integrating, changing to $\log_{10}$, and putting $P = P_o$ when $b = 0$, the expression becomes

$$2.303 \log (P_o/P) = kb \qquad (2)$$

2. Beer's or Bernard's law states that the radiant power of a beam of parallel monochromatic radiation decreases in a similar manner as the concentration of the light-absorbing constituent increases. Thus,

$$2.303 \log (P_o/P) = k'C \qquad (3)$$

where C is the concentration of the light-absorbing constituent.

3. The two laws are often combined and written with a single constant as:

$$\log (P_o/P) = abC \qquad (4)$$

where a is the absorptivity and C the concentration in grams per liter. Absorbance is defined as the product of absorptivity, optical path length and concentration, $A = abC$ or $A = \epsilon bC$

where ϵ is the molar absorptivity and C is in moles per liter.

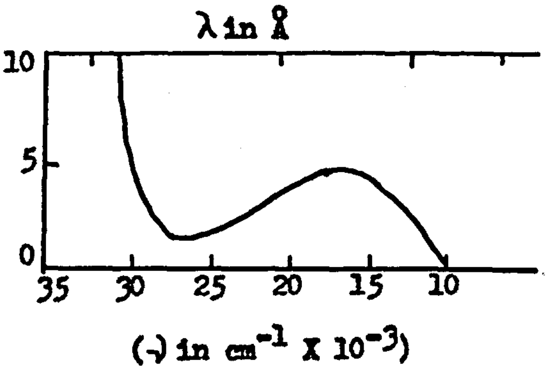
Several factors may cause deviations from the Beer-Lambert Law. Dissociation or association of the absorbing solute in solution changes the nature of the absorbing species with changes in concentration. Temperature changes shift the equilibrium. Stray light in the detector, scattered light or fluorescence will also cause a deviation from Beer's law. (49,76) Kortum and Seiler (44) indicate limitations in Beer's law which make it applicable only to solutions of low concentrations.

Ley (46) was one of the first to recognize that color was an important and distinguishing characteristic of chelate compounds. He used absorption spectra to distinguish between free metal ions and their chelates, which he called inner-complex salts. Pfeiffer (63) later used the same principles in his studies of alizarin derivatives and o,o'-dihydroxyazo compounds.

Often quantitative energy calculations and physical and chemical properties can be correlated using Crystal Field Theory. The visible absorption spectrum of a complex can be correlated with the diagram of crystal field splittings. The colors of compounds of the transition elements are due in many cases to transitions of electrons between incompletely filled d orbitals resulting in the absorption of quanta of light energy. Transitions between the ground levels of coordination clusters and the excited levels correspond to frequencies from the far infrared to the far ultraviolet. Skeletal vibrations of the coordination cluster as well as electronic transitions not essentially within the d shell of the central ion present difficulties in interpretation of spectra such that the range usually considered is restricted to the optical, near infrared, and ultraviolet regions of the spectrum. Ligand field spectra are usually in the range between 5000 and 30,000 cm^{-1}.

The spectra of coordination compounds may be classified into <u>ligand field bands</u> and <u>charge transfer bands</u>. The ligand field bands are essentially concerned with the transitions between <u>d</u> orbitals separated by the application of the ligand field while charge transfer bands are produced by transitions between levels corresponding to different electron distributions among the metal and ligand atoms in the ground and excited states. (22)

Ilse and Hartmann (36) called attention to the value of the Crystal Field Theory in the study of the absorption spectra of complexes when they applied the theory to the single weak absorption band of the d^1 system $[Ti(H_2O)_6]^{3+}$.



Absorption of $[Ti(H_2O)_6]^{3+}$ --Figure 10.

Three features of the absorption band are important--its position, intensity and width. The width of the peak is caused by the fact that the electronic excitation is accompanied by a group of vibrational excitations spread over a range of several thousand wave numbers. The intensity of the band is very weak, indicating a "forbidden" transition. The position of the band gives a Δ_o value of 20,000 cm^{-1} or approximately 57 kcal. per mole.

The number and types of components into which an octahedral field will split a state of given L is the same regardless of the d^n configuration from which it arises. The designations of the states of the ion in the crystal field are the Mulliken symbols; their origin is in group theory, but they may be regarded simply as labels.

TABLE 4 (19)

States of free ion	tates in Crystal Field
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$
G	$E + 2 T_1 + T_2$

The Co (II) ion, with d^7 electron configuration may have an octahedral ground state configuration of either $t_{2g}{}^5\ e_g{}^2$ in weak fields or $t_{2g}{}^6\ e_g$ in strong fields. Figure 11a shows a portion of the energy level diagram for Co (II) in an octahedral field. At sufficiently high octahedral field strength, a ^2E state originating in the ^2G state of the free ion will become the ground state. Rather high values of ligand field strength ($\Delta_o \geq 15{,}000$ cm^{-1}) are required to produce low spin octahedral Co (II) complexes—the high strength ligand field providing the pairing energy. High spin octahedral complexes have magnetic moments from 4.7 to 5.2 BM.

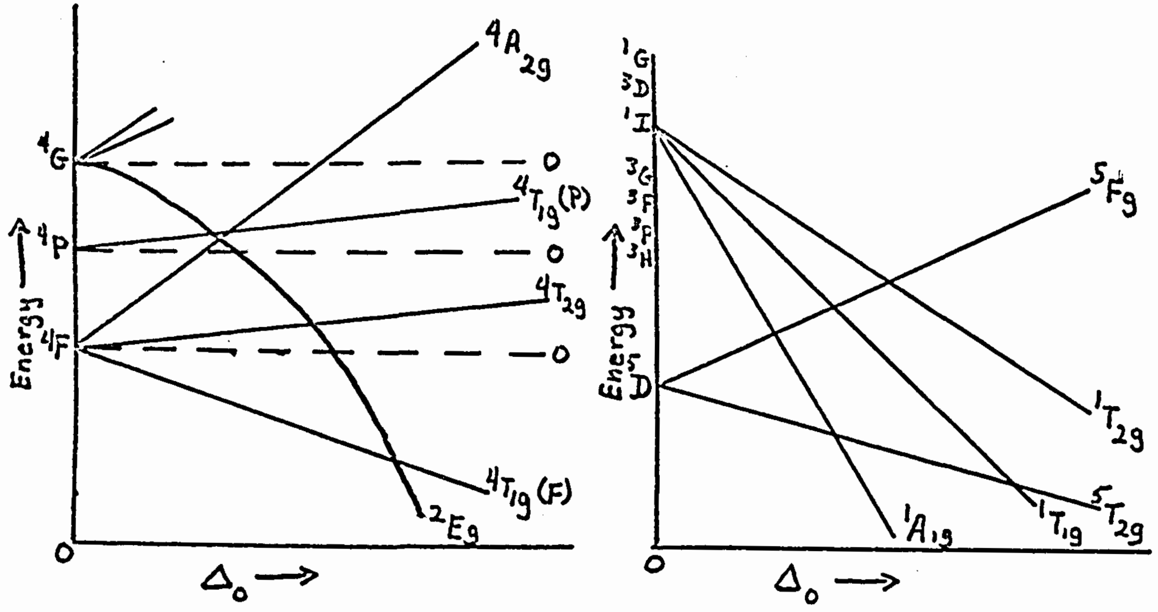
Octahedrally coordinated Co (II) should have three spin-allowed transitions: $^4T_1(F)$ to $^4T_{2g}$, $^4A_{2g}$ and $^4T_{1g}(P)$. The hexaquocobalt (II) ion, $[Co(H_2O)_6]^{++}$, has the visible absorption spectrum shown in Figure 12. The absorption is weak and in the blue region accounting for the pale pink color of the aquocobalt (II). The strong absorption band which is seen has been shown to be due to a $^4T_{1g}(F) \rightarrow {}^4A_2$ transition, the shoulder on the high frequency side being a consequence of spin-orbit coupling in the $^4T_{1g}(P)$ state. The $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ transition occurs at 1200 mμ and is not shown.

The free Co (III) ion has a $\underline{d}^6$ configuration and thus has the energy level diagram shown in Figure 11b. The $^1A_{1g}$ state originating in one of the high energy singlet states of the free Co (III) ion drops very rapidly and crosses the $^5T_{2g}$ state at a very low value of Δ_o. Nearly all Co (III) complexes known, including $[Co(H_2O)_6]^{3+}$and $[Co(NH_3)_6]^{3+}$, have diamagnetic ground states.

The visible absorption spectra of Co (III) complexes may be expected to consist of transitions from the $^1A_{1g}$ ground state to other singlet states. The two absorption bands found in the visible spectra of regular octahedral Co (III) complexes represent transitions to the upper states $^1T_{1g}$ and $^1T_{2g}$.

A table showing visible absorption maxima for selected Co (II) and Co (III) complexes may be found in Appendix D.

Several spectrophotometric methods are available for the determination of metal-ligand ratios in complexes. The method of continuous variations, introduced by Job, and its extended application, developed by Vosburg and Cooper as well as the methods of Yoe and Jones, Harvey and Manning, and Bent and French are often used.



Energy levels of Co(II) in an octahedral field

(a)

Energy levels of Co (III) in an octahedral field

(b)

Figure 11.

Visible Spectrum $[Co(H_2O)_6]^{2+}$

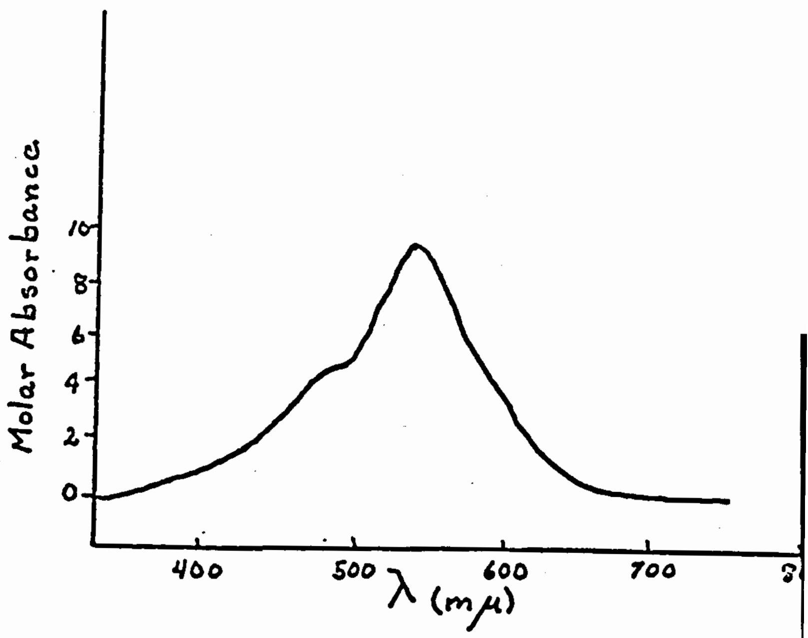


Figure 12.

1. Job's method of continuous variations (38)

The method of continuous variations is a simple, rapid method for determining the formula and relative stability of a compound provided the components in question form only a single compound. The method is readily applicable to complex ions. The procedure involves the variation of absorbance in a series of solutions containing different ratios of metal ion, [M], and chelating agent, [L], while the sum of [M] and [L] are kept constant.

When the metal ion and chelating agent are brought together in the same ratio as they exist in the chelate, the concentration of the chelate is greatest for a constant sum of the concentrations of the reacting substances. For example, let M be the metal ion and L the chelating agent; then:

$$(1) \quad M + nL \rightleftarrows ML_n$$

$$(2) \quad K_{ML_n} = \frac{[ML_n]}{[M]\,[L]^n} \qquad \text{where } K_{ML_n} \text{ is}$$

the formation constant.

If $[M] + [L] = C$, where C is a constant, then the concentration of ML_n is greatest when $[L]/[M] = n$. The absorbance of the solution is proportional to the chelate concentration in regions where the chelate compound is the only absorbing species.

If absorption due only to these species in solution is considered, the absorbance can be expressed as:

$$(3) \quad A = b(\epsilon_1[M] + \epsilon_2[L] + \epsilon_3[ML_n])$$

where b equals the path length and ϵ represents the various absorptivities.

A factor, B, can be introduced to represent the difference in the absorbance, A of equation (3) and the corresponding absorbance if no reaction occurs when M and L are mixed. This gives the expression

$$(4)\quad B = b\left\{\epsilon_1[M] + \epsilon_2[L] + \epsilon_3[ML] - (\epsilon_1[M]_t + \epsilon_2[L]_t)\right\}$$

where $[M]_t$ and $[L]_t$ are the total molarities of species containing M and L. Assuming the ligand to be optically transparent and a cell length of 1 cm., differentiation gives

$$(5)\quad dB/dL_t = (\epsilon_3 - \epsilon_1)\, d[ML_n]/d[L_t]$$

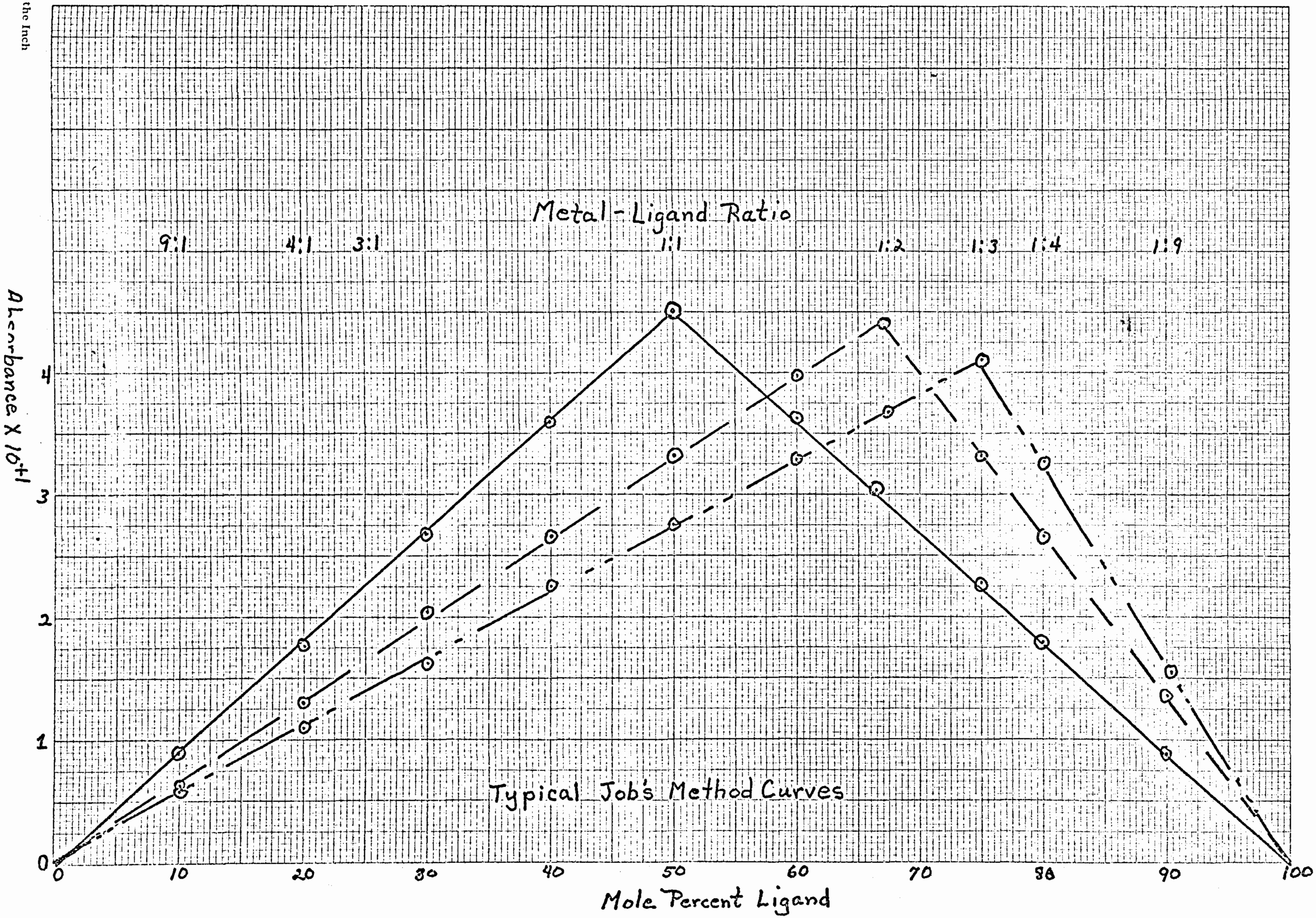
which is the basis of Job's method. It can be seen from equation (5) that a maximum in $[ML_n]$ corresponds to a maximum or minimum in B and a plot of B versus the composition of the solutions expressed in mole fractions will give a maximum or minimum value corresponding to the ratio of metal to ligand in the chelate.

To determine the metal-ligand ratio, solutions of metal ion and ligand are mixed in varying proportions and the absorbance is measured at the wavelength of maximum absorbance.

A plot of absorbance versus mole percent metal or mole percent ligand gives a straight line which reaches a maximum at the mole percent metal or ligand in the complex and then breaks sharply and decreases linearly beyond the mole ratio of the complex. The "sharpness" of the peak depends on the stability constant of the complex. For complexes of low stability, the "peak" is rounded. Figure 13 shows idealized curves for Job's method.

2. Slope Ratio Method of Harvey and Manning (34)

In the reaction, $mL + nM \rightleftharpoons L_mM_n$, if the concentration of M is constant and in sufficient excess to make dissociation


Metal-Ligand Ratio
9:1
4:1
3:1
1:1
1:2
1:3
1:4
1:9
Absorbance X 10+1
0
1
2
3
4
Typical Job's Method Curves
0
10
20
30
40
50
60
70
80
90
100
Mole Percent Ligand

negligible, the equilibrium concentration of the complex L_mM_n will be essentially proportional to the analytical concentration of L added to the reaction; therefore,

$$(1) \quad [L_mM_n] = C_L/m$$

where the brackets indicate the equilibrium concentration and C the analytical or total concentration. From Beer's law,

$$(2) \quad A = \epsilon b[L_mM_n]$$

where A is the measured absorbance, ϵ the molar absorptivity and b the thickness of the cell in centimeters. Substituting equation (1) into equation (2) gives

$$(3) \quad A = \epsilon b\, C_L/m$$

If A is plotted against different analytical concentrations of L with the concentration of M constant and in excess, over the straight line portion of the curve, equation (3) is valid and the slope, S, will equal $\epsilon b/m$. Similarly, if L is in constant excess and the concentration of M varied,

$$(4) \quad [L_mM_n] = C_M/n \; .$$

Plotting A against C_M and taking the slope of the straight line portion, $S_2 = \epsilon b/n$. The ratio of the two slopes then gives the ratio of m/n.

In the derivation for the slope-ratio method, the assumption was made that the equilibrium concentration of the colored complex is essentially proportional to the analytical concentration of the component not in excess. If the complex formed is highly dissociated, the degree of dissociation must be taken into account. Letting α represent the degree of dissociation, equations (1) and (4) are rewritten

$$(5) \quad [L_mM_n] = (1 - \alpha)\, C_L/m$$

$$(6)\quad [L_mM_n] = (1 - \alpha)\ C_M/n$$

Whenever there is no appreciable dissociation, α may be neglected. Whenever α cannot be neglected, it must still be constant over any range in which the absorbance is a linear function of the concentration of either component. If α and α' are equal, they will cancel giving the ratio of the slopes, $S_1/S_2 = n/m$. α and α' are equal if the constant concentration is the same when either L or M is in excess.

The slope ratio method is reliable as long as linearity of the curves shows that the absorbance is directly proportional to the concentration, provided that the concentration of the excess component is identical in the two series of measurements.

The slope ratio method will establish the ratio of color forming radicals to metal ions only.

3. Harvey and Manning modification of the method of Yoe and Jones (34)

Yoe and Jones found that for a very stable complex, a plot of absorbance versus molar ratio of metal to ligand, M : L, with [M] constant, rose from the origin as a straight line and broke sharply to constant absorbance at the molar ratio of the components in the complex.

In the case of a complex that undergoes appreciable dissociation in solution, a continuous curve is obtained which becomes approximately parallel to the molar ratio axis only in a large excess of the variable component. Results obtained under these conditions are uncertain.

Harvey and Manning suggest careful control of ionic strength by addition of unreacting electrolyte to make the curve break sharply at the correct molar ratio by suppression of the dissociation of the complex. This modification has been found quite effective in many cases.

4. Method of Bent and French (34)

In the method of Bent and French two sets of solutions are used. In one set the concentration of the ligand is held constant and the concentration of the metal varied; in the second set the concentration of the metal is held constant and that of the ligand varied. The ionic strength in both groups must be held constant by use of a non-complexing electrolyte.

For the following reaction $nM + mL \rightarrow M_nL_m$, the slopes of plots of log absorbance versus log concentration of M and L gives the values for n and m.

This method is only applicable to solutions in which the complex is highly dissociated.

G. DIAMINES AND POLYHYDROXYDIAMINES

Few literature references to polyhydroxydiamine chelates are available; however, a study of selected references to the chelation of ethylenediamine and substituted ethylenediamine proves helpful.

Substitution on the basic ethylenediamine molecule causes several effects:

1. The magnitude of the steric hindrance increases with the size of the alkyl group replacing the amino hydrogen in N-alkylethylenediamines, i.e., in $\overset{R}{\underset{H}{}}\!\!>NCH_2CH_2NH_2$, the more bulky the R group, the greater the steric hindrance. (9b)

2. Generally, carbon substitution in ethylenediamine has little effect on the coordinating tendencies toward copper and nickel, i.e., in $H_2NCH(R')CH_2NH_2$, the size of R' has little

effect on complex formation. Substitution of this type also causes only slight decreases in basic strength. (7)

3. Alkyl groups attached to nitrogen in ethylenediamine lower the stability of the complexes formed. (59)

   a. Keller (41) found monosubstitution of alkyl groups on nitrogen showed "no exceptional changes" in the properties of the new complex with respect to non-substituted ethylenediamine. The alkyl groups studied were: methyl, ethyl, propyl, hydroxyethyl, 3-hydroxypropyl and 2-hydroxypropyl.

   b. The stability of the chelate did decrease slowly with increasing chain length of the alkyl group except in the case of the n-butyl group studied by Basolo. (9a)

   c. Basolo and Murmann suggest that the increase in stability of the N-n-butylethylenediamine is possibly due to the ability of a four carbon chain to coil and shield the central atom. (9a)

   d. Branched alkyl substituents were also found to be less stable than straight chain substituents due to steric hindrance. (7,9b)

   e. Mono- and disubstituted amine complexes of copper (II) were found by Hall to be of lower stability than those of nickel (II). (30)

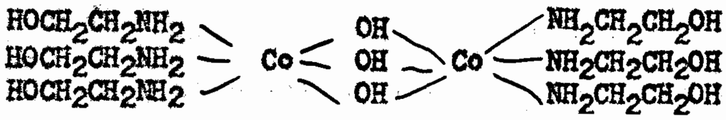
The investigation of polyhydroxyamines as chelating agents has been slow in developing. Few compounds have appeared in the literature as detailed studies. Trends noted by O'Rear (59) in his compilation of stability constant data include: 1) Chelates with 2-hydroxypropyl groups are more stable than those having 2-hydroxyethyl groups. 2) Copper complexes with one or two N-alkanol substituents are more stable than those with four. The converse is true for other metals.

Jean Harvey (35) has shown the presence of chelates of Cu (II) and Ni (II) containing hydroxyethylenediamine in the following compositions: $[\mathrm{Cu}\ \underline{\mathrm{hn}}]^{+2}$, $[\mathrm{Cu}(\underline{\mathrm{hn}})_2]^{+2}$, $[\mathrm{Cu}(\underline{\mathrm{hn}})_4]^{+2}$, $[\mathrm{Ni}(\underline{\mathrm{hn}})]^{+2}$, and $[\mathrm{Ni}(\underline{\mathrm{hn}})_2]^{+2}$.

Bertsch, Block and Fernelius (10) investigated the reaction of 1,3-diamino-2-propanol with copper (II) and found a 1:1 chelate in which the ligand was thought to be terdentate. Oxygen of the hydroxyl groups apparently take part in chelation in this instance.

The cobalt (III) complexes of several substituted ethylenediamines, including N-(hydroxyethyl)ethylenediamine, *etol-en*; N-(3-hydroxypropyl)ethylenediamine, *prol-en*; and N-(2-hydroxypropyl)ethylenediamine, *iprol-en* were prepared and studied by Keller and Edwards (41). They found that $[\mathrm{Co}(\underline{\mathrm{etol}}\text{-}\underline{\mathrm{en}})_3]\mathrm{X}_3$ was very inert toward most common reagents. The hydroxyl group was attacked only by sodium hydroxide. Possible intermolecular hydrogen bonding was proposed as the reason for this behavior. The reactivity of the $[\mathrm{Co}(\underline{\mathrm{iprol}}\text{-}\underline{\mathrm{en}})_3]\mathrm{X}_3$ was intermediate between that of $[\mathrm{Co}(\underline{\mathrm{etol}}\text{-}\underline{\mathrm{en}})_3]\mathrm{X}_3$ and the unsubstituted $[\mathrm{Co(en)}_3]\mathrm{X}_3$.

Yoneda and Kida (82, 83) studied *tris*ethanolamine cobalt (III) complexes and found evidence of the following compounds: (1) $[\mathrm{Co(NH_2CH_2CH_2O)_3}]$ (2) a 1:1 mixture of the following $[\mathrm{Co(NH_2CH_2CH_2OH)_2(NH_2CH_2CH_2O)}]\mathrm{X}_2$ and $[\mathrm{Co(NH_2CH_2CH_2OH)(NH_2CH_2CH_2O)_2}]\mathrm{X}$ and (3) a triol complex,



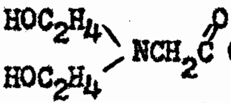
Kida (42) worked with ethanolamine and 1,2-diphenylethanolamine complexes of Cu (II), Co (II) and Ni (II). The following compounds were found: [Co eta'$(eta)_2$]ClO_4, Cu$(eta')_2$, and [Ni eta'$(eta)_2$]ClO_4, where eta is $NH_2CH_2CH_2OH$ and eta' is $(NH_2CH_2CH_2O)$. Evidence was found for two types of alcohol coordination, ROH and RO^- to metal. The type of coordination occurring was greatly influenced by the pH.

The stability of copper complexes of mono-, di-, and triethanolamine was found by Kirson (43) to increase with the number of hydroxyl groups in the ligand.

Uhlig (72) found that N-(β-hydroxyethyl)-β-alanine, 2-(β-hydroxyethylamino)-terephthalic acid and 2,5-bis(β-hydroxyamino)-terephthalic acid all behave as terdentate ligands with calcium, nickel and cobalt (II). The non-aromatic complex proved to be the least stable.

Gonick (29) worked with 1,3-diamino-2-propanol, 1,3-diaminopropane and 2,2-dimethyl-1,3-propanediamine and found that the hydroxyl group was not active in coordination with Ag (II), Co (II), Ni (II) and Zn (II).

The activity of N,N-dihydroxyethylglycinate,



$(HOC_2H_4)_2NCH_2C(=O)O^-$, with divalent copper, nickel, cobalt, iron, manganese, zinc, cadmium and magnesium as well as iron (III) was studied by Chaberek (17,18). Definite involvement of the hydroxyl group in chelation was suggested. Work was also done with substituted iminodiacetic acids, $R-N(CH_2COOH)_2$, and the following divalent metals: Ca, Mg, Mn, Pb, Cd, Zn, Co, Ni, and Cu. The stability of the chelates was found to be greatly increased by the replacement of the amino hydrogen with hydroxyethyl groups. The hydroxyl oxygen has much less affinity for the metal ion than the carboxylate oxygen.

The chelates formed between the rare earths and N-hydroxyethyliminodiacetic acid were studied by Thompson and Loraas (71). Their data indicate coordination of the hydroxyethyl group in both the 1:1 and 1:2 chelates.

Martell *et. al.* (48, 49, 50) have considered the question of alkanol hydroxyl groups in coordination and have concluded that the weight of evidence is in favor of direct coordination of the metal ion by the hydroxyl group. The ligands studied were: N-hydroxyethylethylenediamine, N,N'-dihydroxyethylethylenediamine, N-hydroxyethylaminodiacetic acid, and N-hydroxyethylaspartic acid. The more stable chelates of the above ligands with Cu (II) showed lower acidity of the proton attached to the coordinated oxygen.

Hall and his coworkers (30, 31, 33) have noted the following trends in their work with alkanol amines:

1. Quadrol, N,N,N',N'-tetrakis-(2-hydroxypropyl)-ethylenediamine, forms 1:1 and 1:2 complexes with Cu (II). The hydroxyl group shows appreciable acidic character in coordination.

2. The hydroxyl group is coordinated in the 1:1 and 1:2 complexes of Cu (II) and hydroxyethylethylenediamine. $[Cu(hn{-}O^-)]^{+1}$ undergoes slight dismutation to $[Cu(hn)]^{+2}$ and $Cu(OH)_2$. Jonassen and Dexter (39) have shown that dismutation is complete with Cu (II) and ethylenediamine. This difference in behavior is accepted as additional evidence of coordination of the hydroxyl group.

3. Greater stability was observed for 2-hydroxypropyl substituted amines than with hydroxyethyl substituted amines.

4. Copper (II) was found to form both 1:1 and 1:2 complexes with N,N'-bis-(2-hydroxyethyl)-ethylenediamine. The pH range over which the 1:2 complex was stable was found to decrease with the degree of alkanol substitution; 1:1 complexes became more stable due to the increased opportunity for ring formation involving the hydroxyl oxygen.

5. The divalent ions of copper and nickel were found to form 1:1, 1:2, and 1:3 complexes with $H_2NC(CH_2OH)_3$. The copper complexes reacted with sodium hydroxide to give coordination of the oxygen. Above pH 10, the stable species in solution was the $Cu(AO^-)_2$ ion.

Jonassen and his coworkers (39,40) have studied complexes of copper (II) and cobalt (II) with ethylenediamine and tetraethylpentamine respectively. Gradually increasing the concentration of the ligand was found to produce spectra in which the position of the maxima shift toward the shorter wavelength. A sudden change was observed in the shape of the curve after a 1:1 ratio was exceeded; no change occurred after a 1:2 ratio was exceeded.

Cobalt (II) formed two complexes with tetraethylpentamine. A green 1:2 complex was formed which exhibited maxima at 320 mμ and 350 mμ. This complex changed within 72 hours to a red 1:1 complex with maxima at 510 mμ and 460 mμ.

The bathochromic shift in the positions of absorption maxima as successive steps occur in chelation has also been observed by Roberts (66) and Basolo (4) who also indicate that the more stable of several complexes will absorb at the shorter wavelength(s), except with the Co (II) oxalate complex studied.

Wood and Higginson (77) found in their work with cobalt (III) and hydroxyethylenediaminetriacetic acid, $H_3(YOH)$, that the spectra of $Co(YOH)H_2O$ and $Co(YOH)OH^-$ were very similar to those of $Co(HY)H_2O$ and $Co(Y)OH^{2-}$. SexAdentate complexes with the oxygen of the hydroxyethyl group of the ligand coordinated to cobalt were postulated as well as quinquedentate mono-aquo complexes.

Hall and his coworkers (30,31,33) have done much work using ligands with hydroxyl groups in order to determine whether the hydroxyoxygen enters into chelation. Most of this work has been done with copper (II). With respect to spectra, the following observations have been made:

1. For solutions containing Cu (II) and hydroxyethylethylenediamine, in which the concentration of amine is two or more times greater than the concentration of metal ion, additional amine causes the right branch of the curve to increase in absorbance and causes the maximum to shift to longer wavelengths.
2. N,N'-bis-(2-hydroxyethyl)-ethylenediamine and Cu (II) show absorbance maxima of 0.53 at 630 mμ for the 1:2 complex and 0.65 at 615 mμ for the 1:3 complex. Further increase in the concentration of amine decreases the intensity of the maxima and increases the wavelength of the maximum absorbance. Addition of NaOH to produce a 1:2:0.4 mixture causes the maximum to increase. Addition of more NaOH shifts the wavelength to 640 mμ. The spectra of the 1:1:0, 1:1:1 and 1:2:0 mixtures are all different,

showing that the action of the second ligand molecule on the 1:1 complex is different from that of NaOH.

3. Copper (II) and $H_2NC(CH_2OH)_3$ give nearly identical spectra when combined in a 1:3 complex and when mixed with NaOH in the proportions, $1:2:1_{(NaOH)}$. The fact that there is little change in the spectra is taken to indicate that the colored compound in solution is identical in both cases.

Yoneda's work (81,82,84) with Co (III) complexes indicates the following trends:

1. The stability of both $[Co(en)_3]^{3+}$ and $[Co(hen)]^{3+}$, where hen is hydroxyethylethylenediamine, is high in concentrated HCl, HNO_3, acetic anhydride and aqua regia. The spectra obtained are similar before and after treatment with these concentrated reagents.

2. The position and shapes of the curves for tetrammines and pentammines, $[Co(III)(NH_3)_4X_2]X$, and $[Co(III)(NH_3)_5X]X_2$, where X represents carbonato, sulfito, chromato and maleinato groups, are almost identical. The second band for both tetraammines and pentammines appear in the same position except in the case of the maleinato compounds.

3. Hexammonia and tris-ethylenediamine complexes of cobalt and chromium with NCS^-, $SO_3^=$, $S_2O_3^=$, and $CO_3^=$ have spectra with almost the same maximum positions.

H. OBJECTIVES, METHODS AND RESULTS

The purpose of this project was to study the visible absorption spectra of various mixtures of Co (II) and Co (III) solutions with 2,2,8,8-tetrakis(hydroxymethyl)-3,7-diaza-1,5,9-nonanetriol, ("Disec"), $(HOCH_2)_3CHNCH_2CH(OH)CH_2NHC(CH_2OH)_3$, and 2,2,8,8-tetramethyl-3,7-diaza-5-nonanol, ("Symaminol"), $(CH_3)_3CNH-CH_2CH(OH)CH_2NH-C(CH_3)_3$, and to investigate the complexes formed as well as the effects of pH and time on their formation and stability.

Various methods were used to investigate the metal-ligand ratios of the complexes: 1) Job's method of continuous variations, 2) a modification of the procedure of Yoe and Jones, and 3) Harvey and Manning's slope ratio method. These and other methods were discussed in detail in Section F.

The spectra obtained indicate the presence of one or more complexes formed by Co (II) and "Disec". There were indications of rapidly formed 1:1 and 1:2 complexes as well as a slowly formed 1:3 complex.

The formation of the complexes was observed in solutions of about pH 8 or greater.

Attempts to study complexes of Co (III) were unsuccessful as were attempts to study complexes of Co (II) and "Symaminol".

The following suggestions are made for further study:

1) Further work should be done with Job's method on the solutions of Co (II) with "Disec" using mixtures which will give more data in the 1:2 - 1:3 range of metal-ligand ratios. This will help clarify the positions of the 1:2 and 1:3 peaks.

2) Attempts to obtain stability constant data should be

made.

3) Studies of the effects of the presence of CO_2 and other ions which may cause interference should also be made.

III. EXPERIMENTAL

Solutions containing cobalt ion, $[Co(H_2O)_6]^{2+}$, with the free bases (1) "Disec" and (2) "Symaminol" were studied for:

(a) The effect of pH on the absorption spectra.

(b) The metal-ligand ratios of the complexes formed.

(c) The relative rates of formation of the complexes.

(d) The relative stabilities of the complexes formed.

(e) The applicability of Beer's law.

Preparation of the Free Bases:

The samples of the hydrochlorides of the two bases used were prepared in this laboratory by Briel (11) and Davis (21).

The free base was obtained from the hydrochloride salt by means of ion exchange, using Rexyn 203 anion exchange resin in the (OH) form. An aqueous solution of the hydrochloride was passed through the column at a rate of one drop every 3 - 5 seconds. An aliquot of the eluant was titrated potentiometrically to determine the molarity of the free base. Details of the titration are given in Appendix A, page 89, with a sample titration curve.

A standardized solution of cobaltous nitrate was used as a source of metal ion. Nitric acid and sodium hydroxide solutions were used to adjust the pH. Solutions used for absorption spectra were approximately 0.01 M with respect to $NaNO_3$.

Details concerning standardization procedures and the preparation of solutions are given in Appendix A pages 83 - 89.

Measurements of pH were made using a Beckman #101900 Research pH Meter and a Sargent Model LS pH Meter.

Absorption measurements were taken with the Beckman Model DU Quartz Spectrophotometer and a set of matched silica cells having a one centimeter light path.

A. Effect of pH on the Absorption Spectra.

Spectrophotometric measurements were made on a series of solutions with metal and ligand concentrations as follows:

Set	[Co (II)] ion	[Ligand]	M:L Ratio
A	9.38×10^{-3} M	9.38×10^{-3} M	1:1
B	9.38×10^{-3} M	1.88×10^{-2} M	1:2
C	1.88×10^{-2} M	9.38×10^{-3} M	2:1

The pH was varied from 3.5 to 9.5.

In set A, M:L = 1:1, precipitation was not observed at pH 3.5 - 9.5. A special solution, in which the pH was adjusted to 11.5, showed precipitation on standing.

In set B, M:L = 1:2, precipitation was not observed in any of the solutions.

In set C, M:L = 2:1, precipitation was observed within 36 hours in all solutions in which pH was above 8.

Absorption measurmments were made over the range 400 mμ to 700 mμ. The spectra obtained are shown in Figures E-1 to B-5.

All the solutions having a pH below 6.5 show a maximum at approximately 515 mμ which is characteristic of the aquated Co (II) ion. Solutions with pH 8 or greater showed constant maxima at 550 mμ.

On standing, the maxima of solutions with intermediate pH values undergo a gradual change such that only two positions for maxima remain. All solutions having pH values below 8 have final maxima at 525 mμ and those having pH above 8 show maxima

Co(II)-"Disec" (1:1) Changes with pH

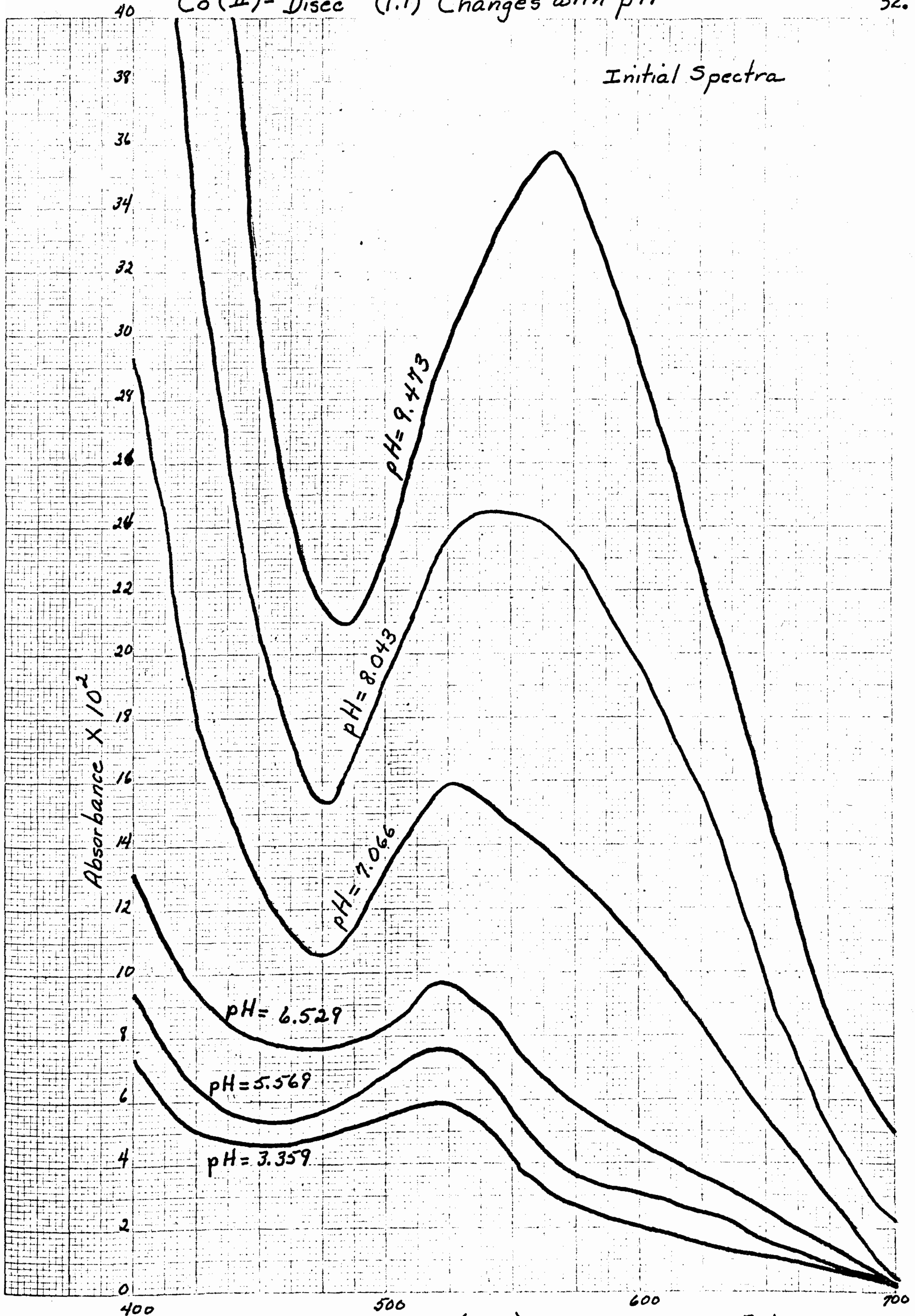


Figure E-1

Co(II)-"Disec"(1:1) Changes with pH

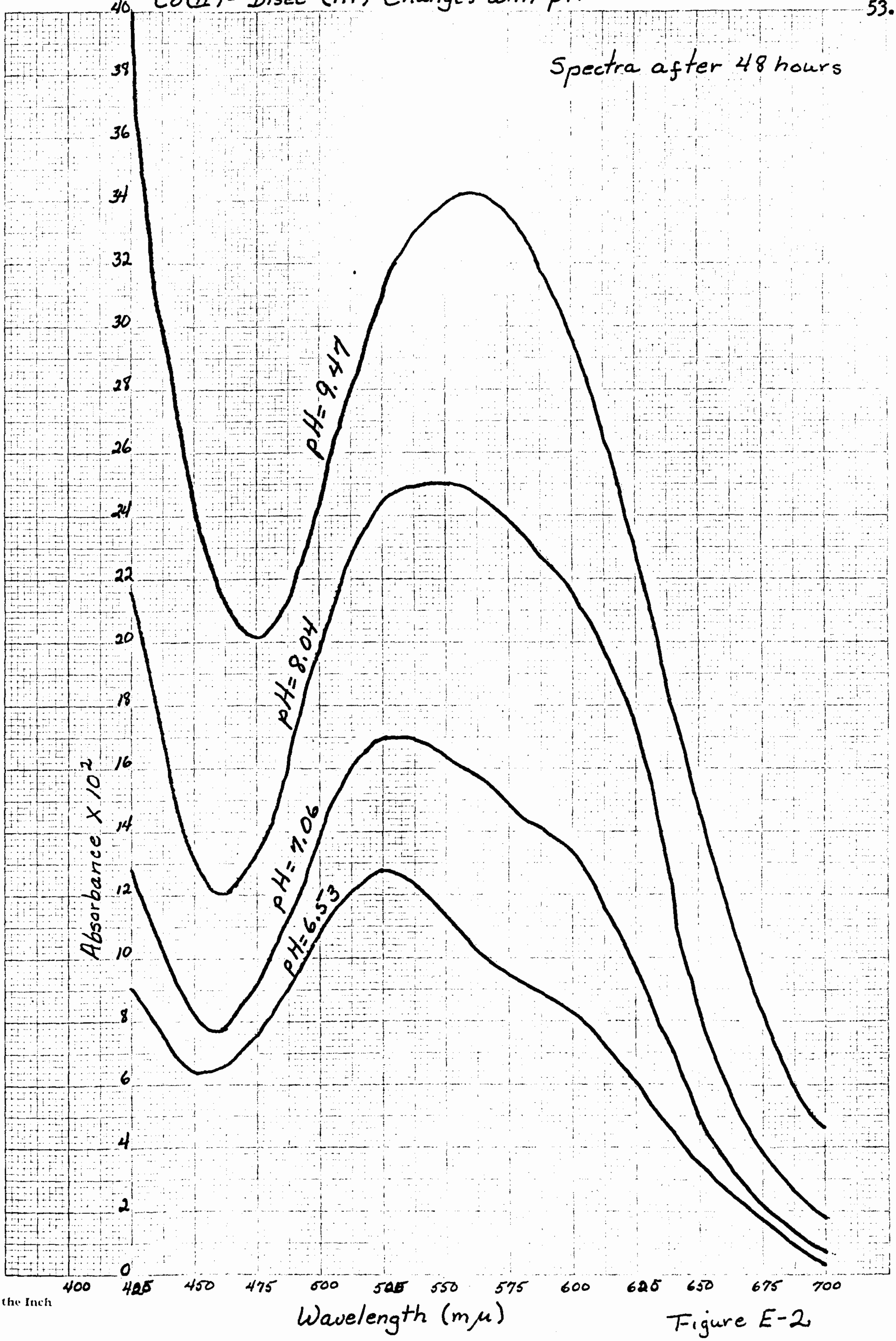


Figure E-2

Co(II)-"Disce" (1:2) Changes with pH

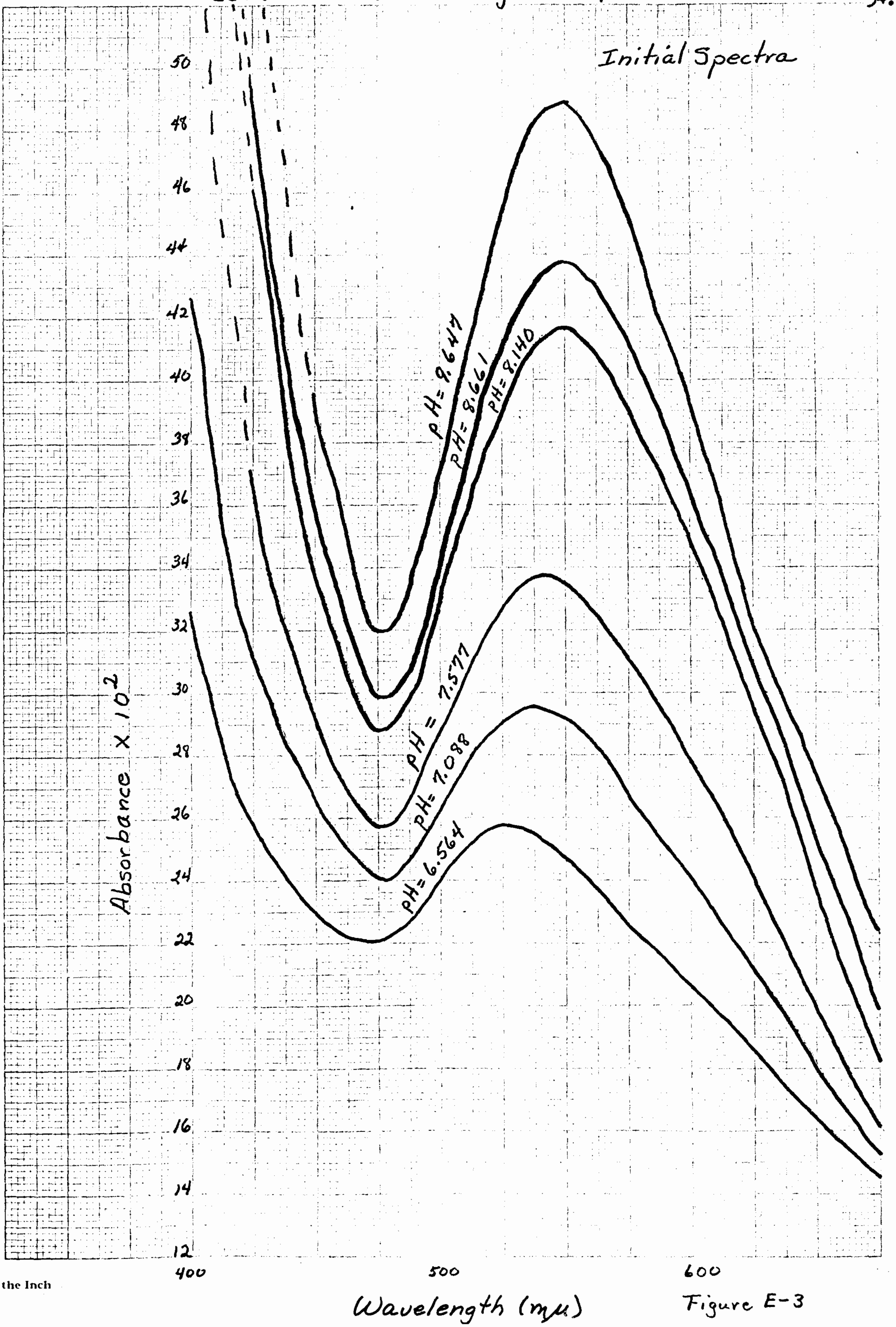


Figure E-3

Co(II)-"Disec" (1:2) Changes with pH

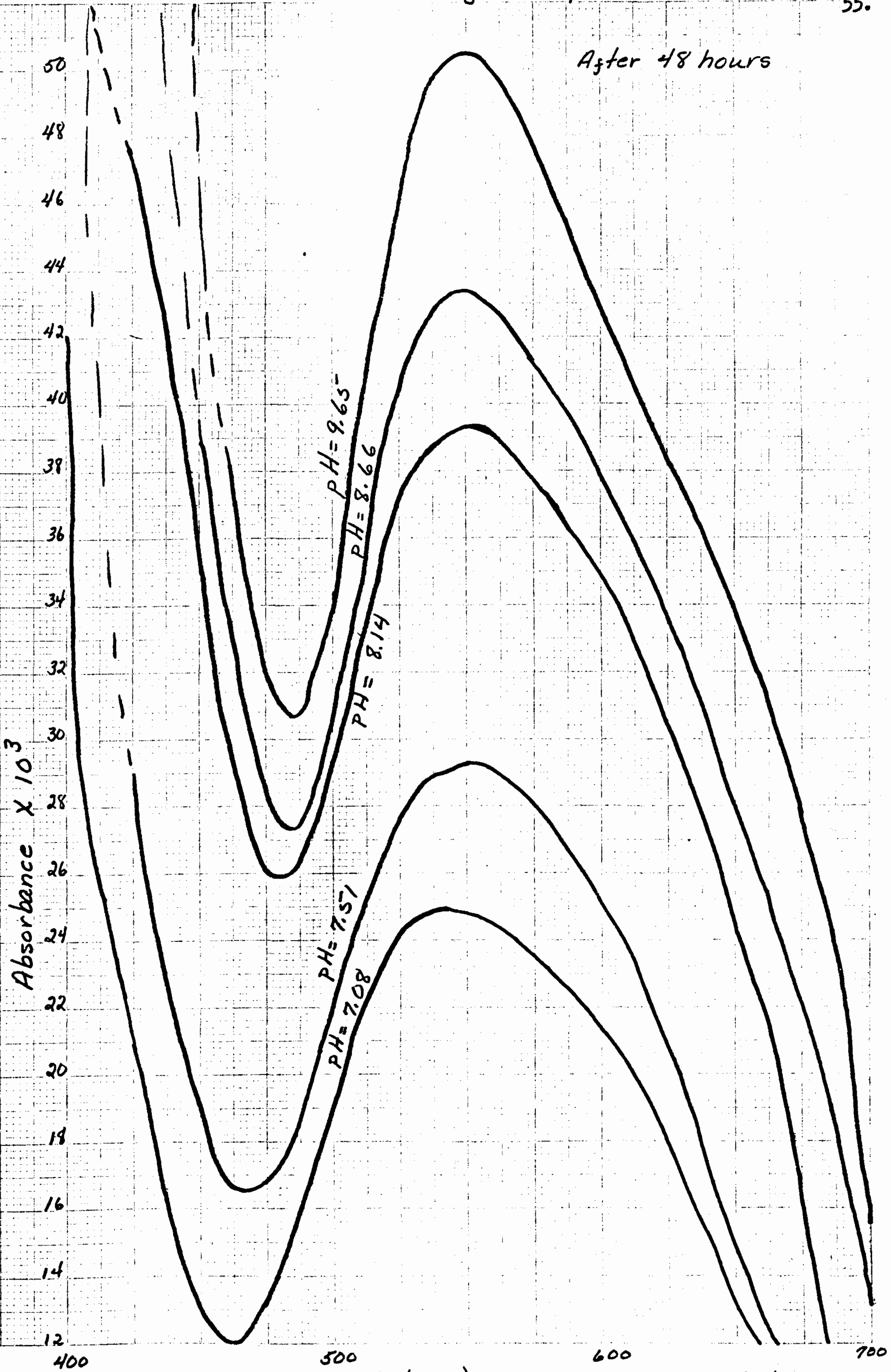


Figure E-4

Co(II)-"Disec" (2:1) Changes with pH

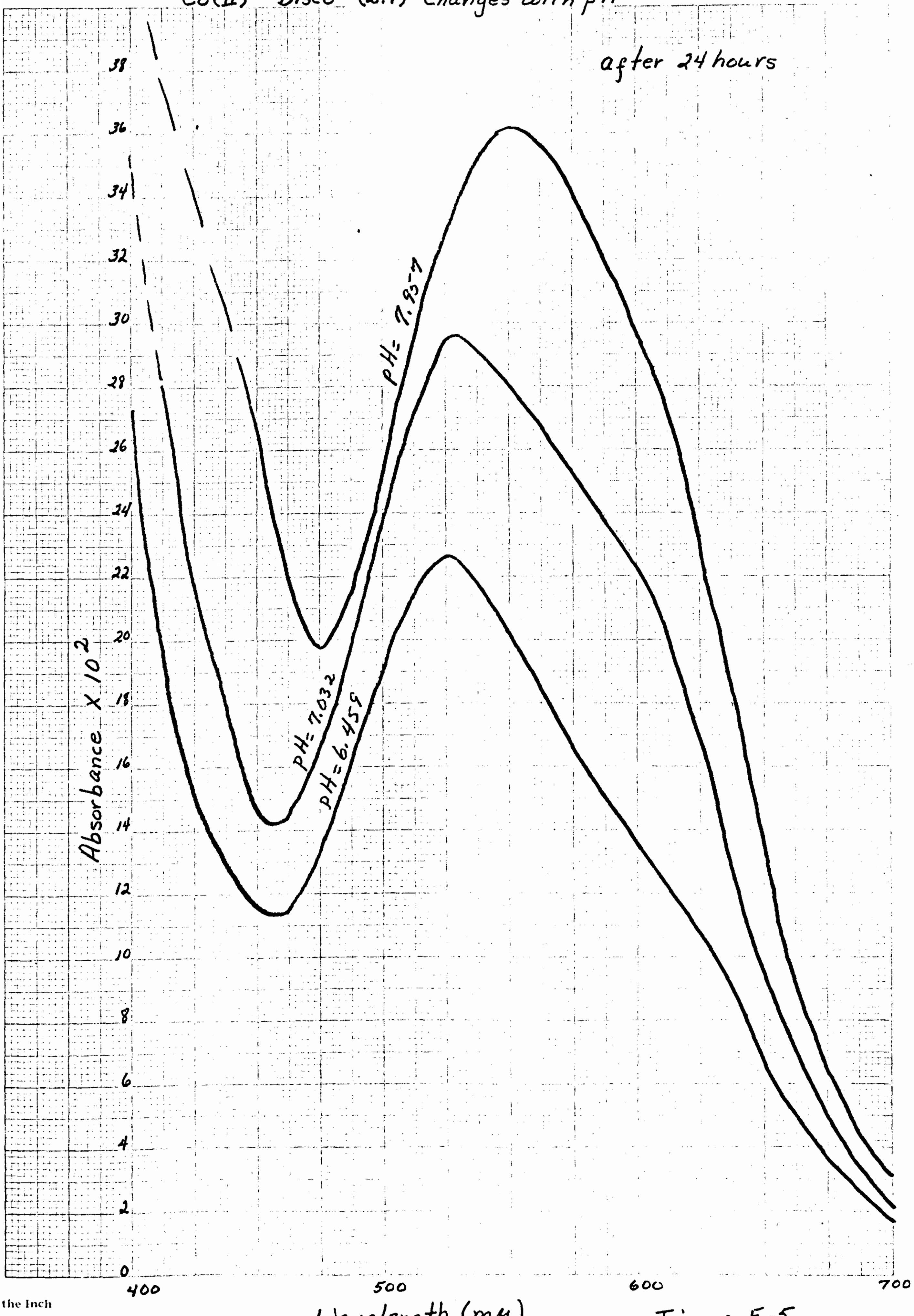


Figure E-5

at 550 mμ.

B. Metal-Ligand Ratios.

Several methods were used to study metal-ligand ratios in the complexes. These have been discussed previously. (See pages 35-40.)

1. Job's Method of Continuous Variations.

Measurements were made using solutions containing Co (II) ions, first with the ligand salt and then with the free base.

Measurements on solutions containing the hydrochlorides were erratic and inconclusive.

Solutions using the free base having a maximum cobalt concentration of 9.4×10^{-3} molar were prepared. The ionic strength was adjusted by adding a non-reacting electrolyte, $NaNO_3$, until the solutions were 0.01 molar with respect to sodium nitrate. The pH of the solutions was adjusted to approximately 8 and absorption measurements were taken at 550 mμ. Readings were made after 1 hour, 2 days, 5 days, 10 days and 53 days with the pH readjusted to between 8 and 8.5 before each spectral measurement. Adjustments of pH were made using 12 M NaOH added in very small quantities from a hypodermic syringe. The results of these measurements are shown in Figure E-6.

Initially high absorbance is observed for metal-ligand ratios of 1:1 and 1:2. With time precipitation becomes evident in the 1:1 solutions and the resultant high absorbance is due to the increasing opalescence of the solution.

The intensity of absorbance in the 1:2 solution increases slowly as the amount of ligand complexing increases. There is a possibility of a 1:3 complex also forming, but there were

Spectra for Job's Method

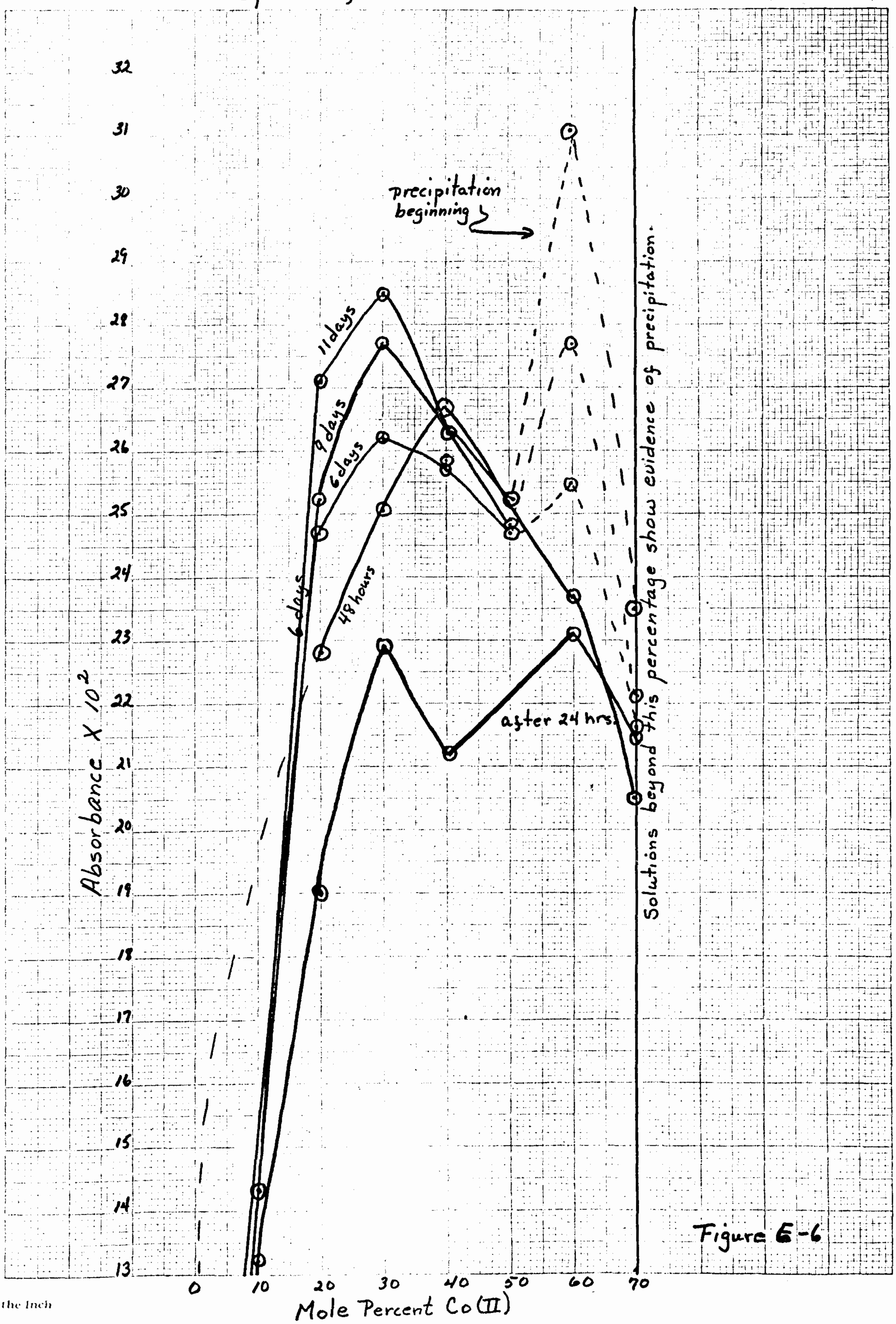


Figure E-6

insufficient points to give unequivocal evidence in this instance.

2. The Method of Yoe and Jones

Total ionic strength and pH were adjusted as for the method of continuous variations. The Co (II) ion concentration was kept at 5×10^{-3} molar. The metal-ligand ratios were varied from 1:5 to 3:1. The pH was adjusted before each spectral measurement as in the method of continuous variations. The results are shown in Figure E-7.

Note that: (a) Absorption intensity in the 1:2 solution remains essentially constant after 24 hours.

(b) Absorption intensities tend to level off in the 1:3, 1:4 and 1:5 solutions after 11 days.

These data are interpreted as indicating the presence of a 1:2 complex which forms rapidly and a slowly formed 1:3 complex occurring wherever the ligand concentration is sufficiently high. The eventual leveling of the absorbance intensities in the 1:3, 1:4 and 1:5 cases is taken as an indication of the slow formation of the 1:3 complex.

3. Method of Harvey and Manning

Two groups of solutions were prepared, Group I having excess "Disec" and Group II having excess Co (II) ion in the concentrations shown.

Solution	Group	M Conc. "Disec"	M Conc. Co (II)
a	I	2.67×10^{-2} M	5.0×10^{-3} M
b	I	2.67×10^{-2} M	1.0×10^{-3} M
c	I	2.67×10^{-2} M	1.5×10^{-3} M
d	I	2.67×10^{-2} M	2.5×10^{-3} M

Solution	Group	M Conc. "Disec"	M Conc. Co (II)
a	II	5.34×10^{-3} M	2.67×10^{-2} M
b	II	4.68×10^{-3} M	2.67×10^{-2} M
c	II	6.01×10^{-3} M	2.67×10^{-2} M
d	II	6.68×10^{-3} M	2.67×10^{-2} M

The ionic strength and pH were adjusted as for Job's method.

After one hour plots of absorbance X concentration_L versus concentration_L and absorbance X concentration_M versus concentration_M gave the following results:

$$\text{Slope}_1 = 2.33$$
$$\text{Slope}_2 = 1.11 \qquad \frac{S_1}{S_2} = \frac{L}{M} = \frac{2.33}{1.11} = \frac{2}{1}$$

This indicates the immediate formation of a 1:2 complex. The plots of the curves are shown in Figure E-8.

After a longer period of time, the evidence was inconclusive. Precipitation occurred in all of the Group II solutions within 48 hours.

4. Method of Bent and French

Two sets of solutions were prepared—Group I with [Co (II)] constant and ["Disec"] varied, and Group II with ["Disec"] constant and [Co (II)] varied as shown below.

	Group I Co (II) concentration constant at 2.5×10^{-2} M "Disec"		Group II "Disec" concentration constant at 2.5×10^{-3} M Co (II)
a	2.39×10^{-2} M	a	9.40×10^{-4} M
b	2.12×10^{-2} M	b	1.88×10^{-3} M
c	1.86×10^{-2} M	c	2.82×10^{-3} M
d	1.06×10^{-2} M	d	5.64×10^{-3} M

Yoe and Jones Method

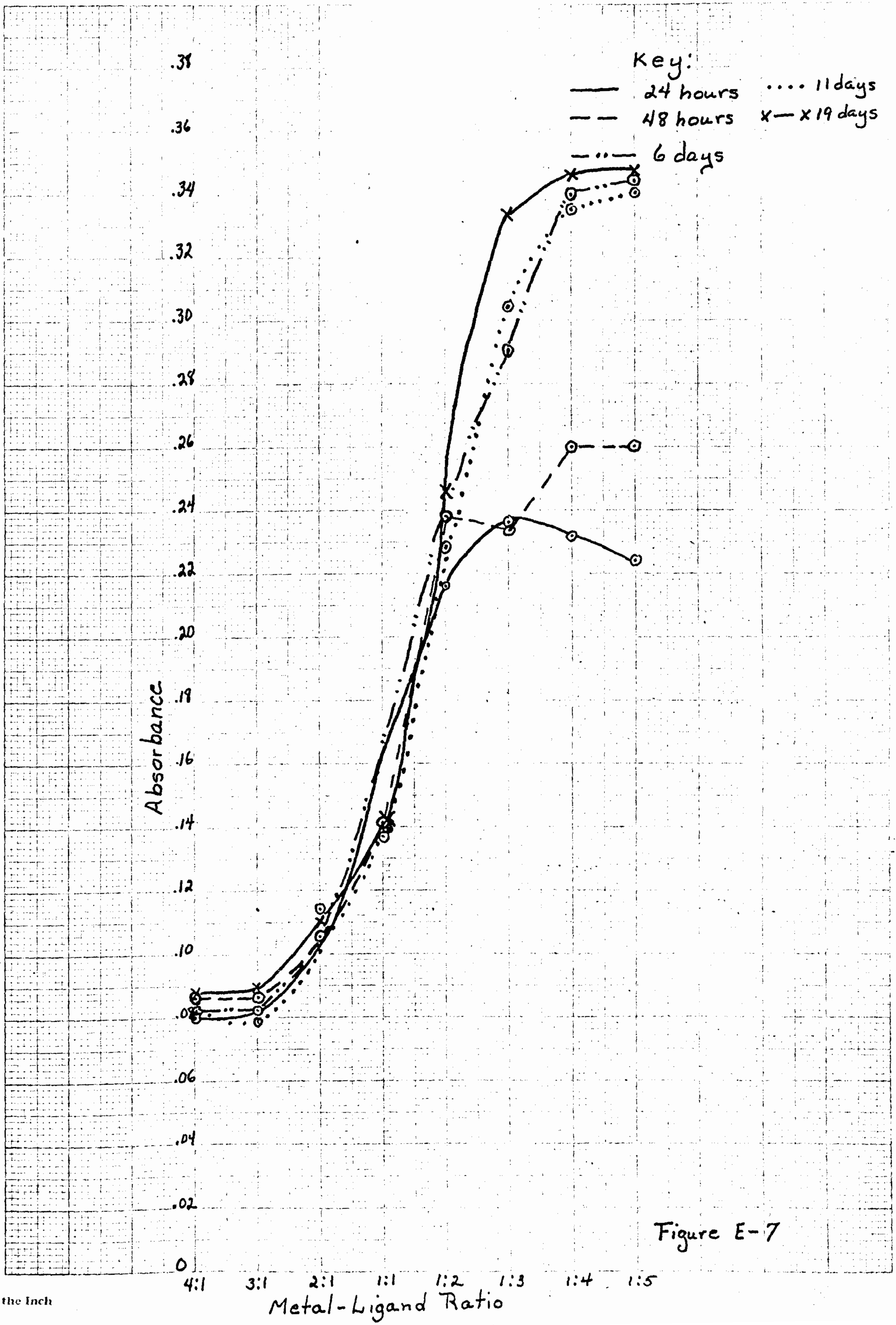


Figure E-7

Harvey and Manning Slope Ratio Method

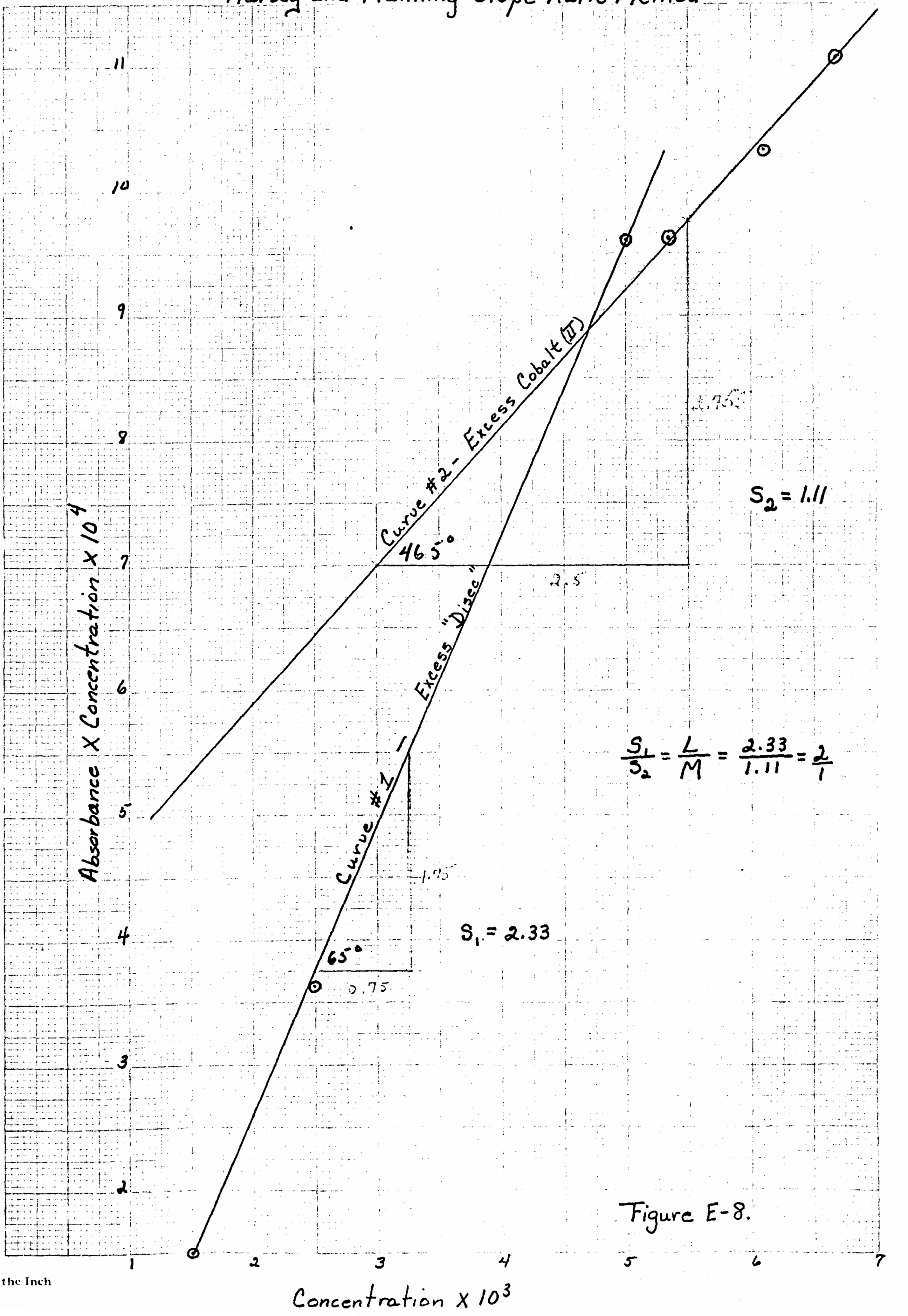


Figure E-8.

Plots of log Absorbance_L versus log Concentration_L and log Absorbance_M versus log Concentration_M did not give linear relationships; therefore, this method could not be applied.

The failure to obtain significant data is interpreted as indicating that the complexes of Co (II) and "Disec" are not highly dissociated, since the method is designed for substances which are highly dissociated.

C. Relative Rates of Formation of Complexes.

The solutions used for determining spectra were kept for several months and the absorption measurements were repeated periodically. Precautions were taken to prevent evaporation. The intensity of absorption showed an increase toward a maximum in all cases.

D. Relative Stabilities

Cobalt (II) Complexes

Stabilities of the complexes were observed relative to the time required for formation and the length of time the complex persisted.

A 1:2 complex was observed to form rapidly and was observed to remain in solution up to several months.

In solutions where the ligand concentration was sufficently high, a 1:3 complex was observed which took approximately three weeks to form.

No precipitation was observed in any of the above solutions over a six month period.

Cobalt (III) Complexes

Various mixtures of Co (II) and "Disec" (1:1, 1:2, 1:3, 2:1 and 3:1) were prepared and oxidation of the Co (II) to Co (III) was attempted by a modification of the method of

Laitinen and Burdett.

The above solutions were combined with equal volumes of approximately 0.2 N H_2SO_4. Sodium bicarbonate was added until the solutions tested neutral and an additional 5 gram excess was added to each sample. Five milliliters of 30% H_2O_2 was used to oxidize each sample. The characteristic dark green color which appears when Co (III) is in the presence of bicarbonate ion was observed. (26) When the evolution of CO_2 was complete, the pH of all solutions measured greater than 8.

Attempts to take spectra gave maxima which were observed to shift position even as measurements were being made.

Within one hour all solutions had turned yellowish and after two hours some were turbid. Precipitation occurred in almost all cases within 24 hours. The same type of difficulty was encountered with Co (II) and "Symaminol" and also with solutions of "Disec" having a very high percentage of Co (II) ions. Absorption curves for the yellow solutions are given in Figures E-9 through E-12.

Michal and Dolezal report yellow-brown solutions obtained when $[Co(en)_3]^{2+}$ was oxidized at pH 10 to $[Co(en)_3]^{3+}$. Their maxima also disappeared in a short period of time.

Two possible explanations of the yellow solutions are 1) the material which precipitated is "cobaltic hydroxide" or 2) the yellow material is a complex negative ion previously observed by Michal and Dolezal. (54)

The Hydrochlorides as Ligands

Measurements made on solutions containing the ligand hydrochlorides were inconsistent at low ligand to metal ratios. However, among the solutions having a high ligand to metal ratio, Yellow Solutions in (1:2) Co(III)-"Disec" Mixtures

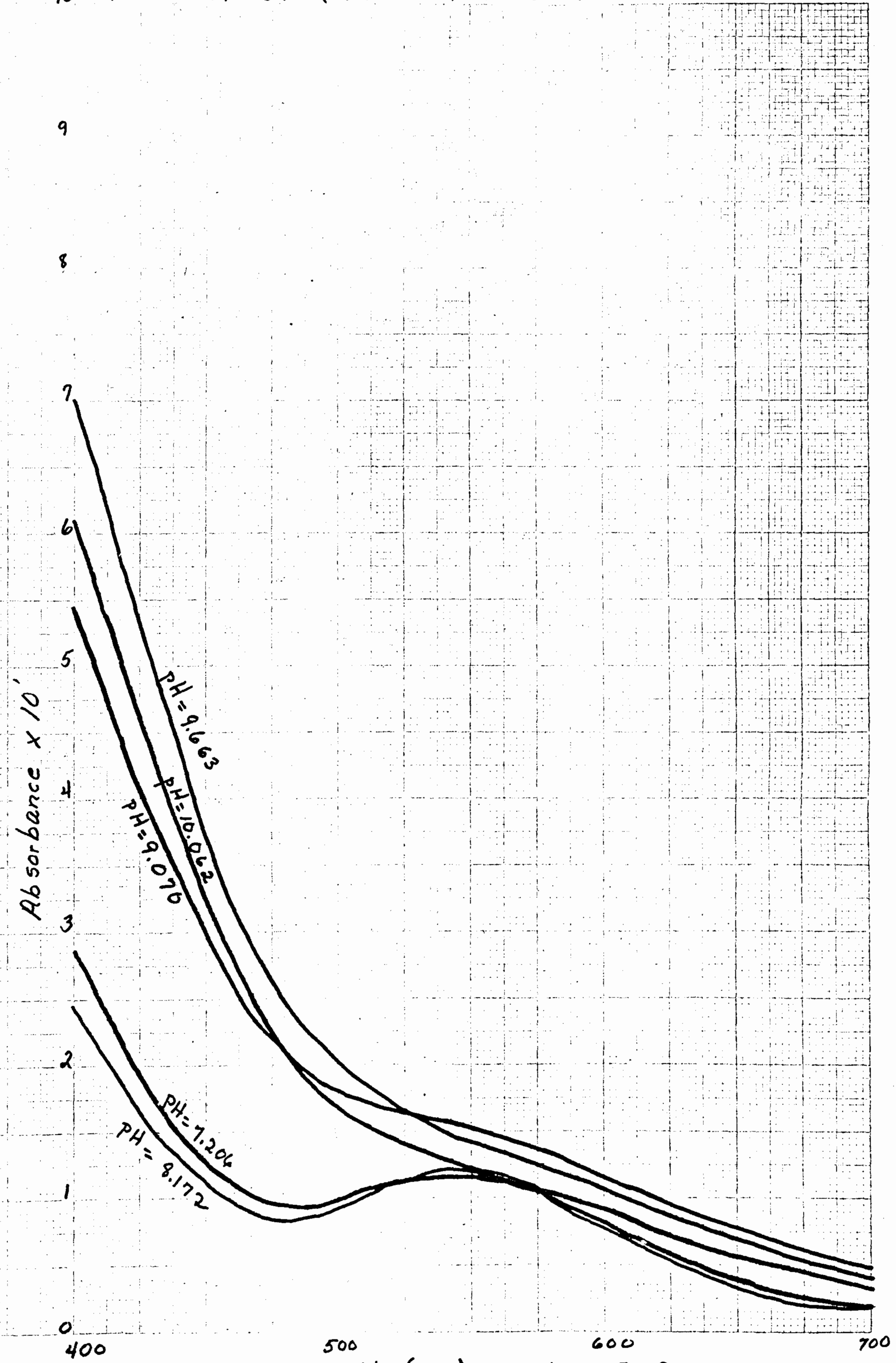


Figure E-9

Yellow Solutions from (1:3) Co(III)-"Disec" Mixtures

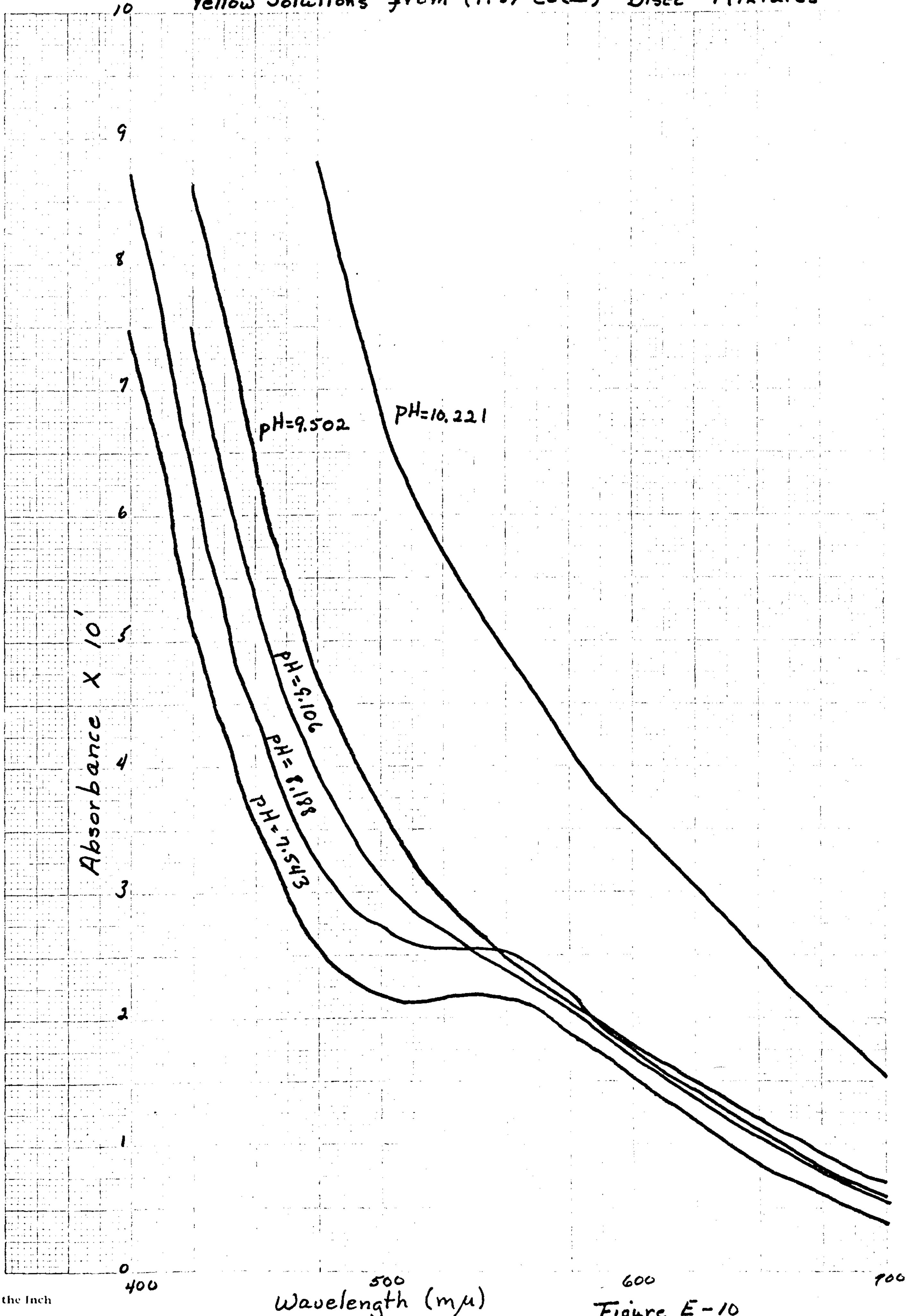
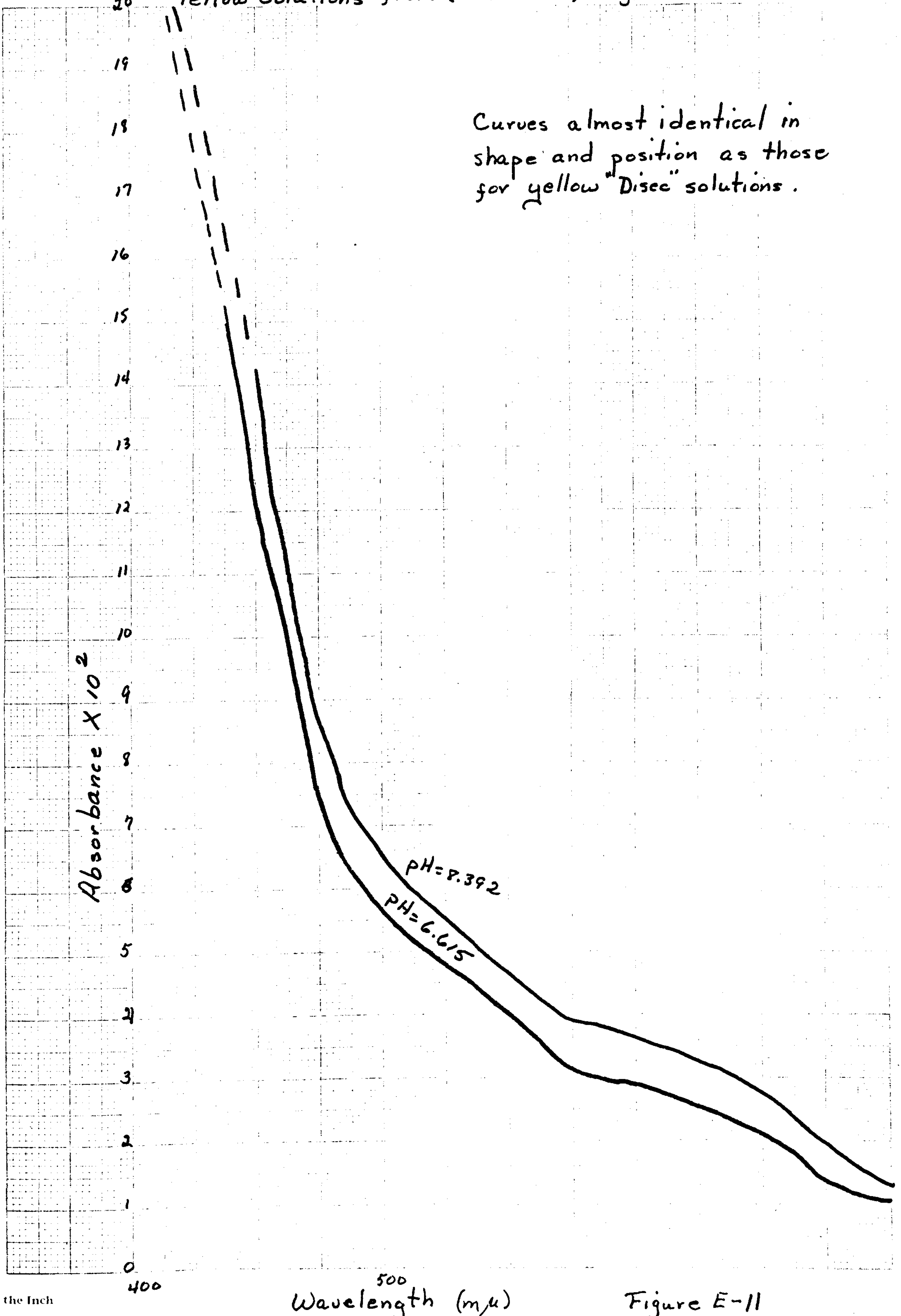


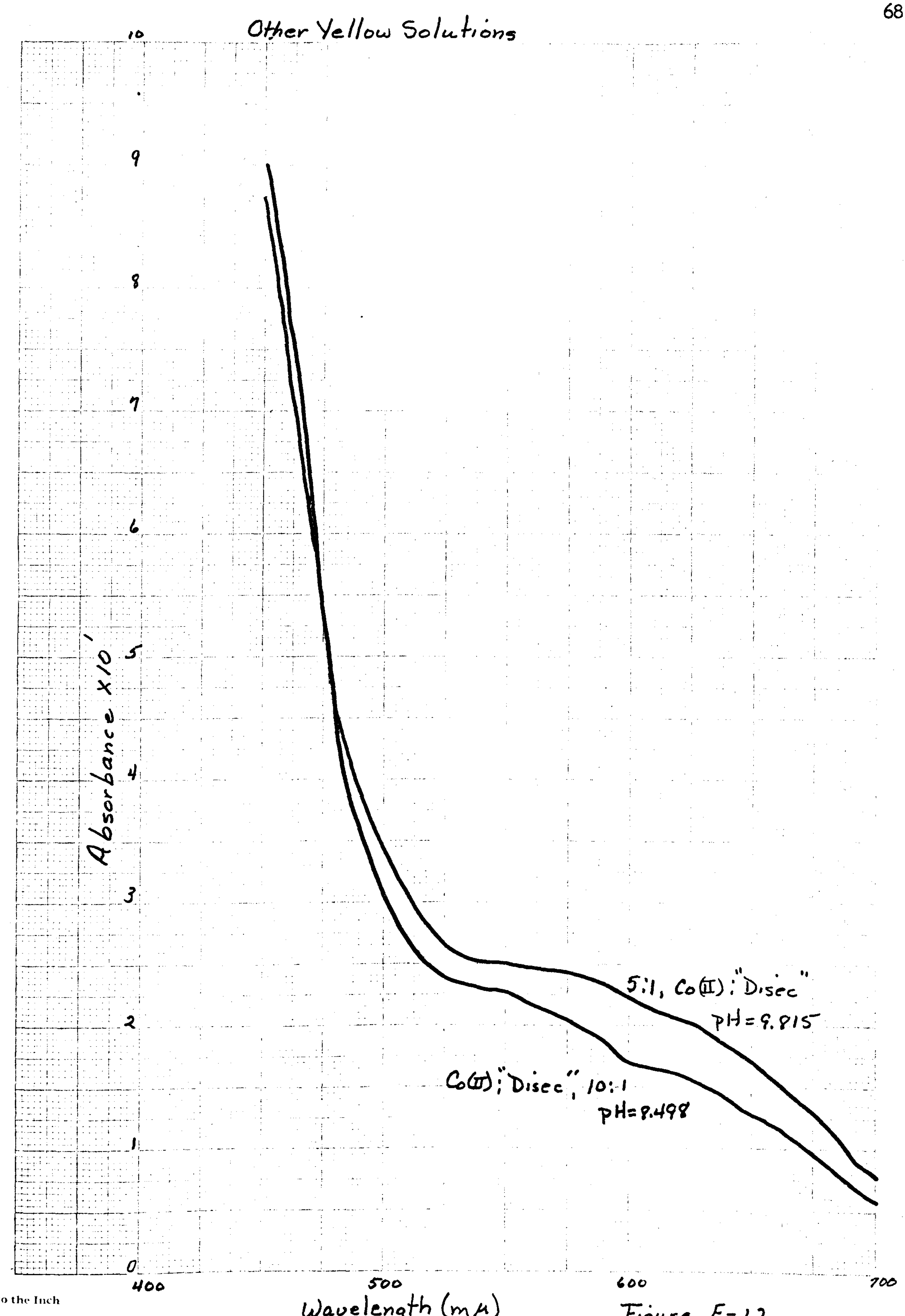
Figure E-10

Yellow Solutions from (1:3) Co(II)- "Symaminol" Solutions



Curves almost identical in shape and position as those for yellow "Disec" solutions.

Figure E-11



Other Yellow Solutions

Figure F-12

the curves were similar.

Crystal Field Splitting Energy

The position of the absorption maximum in the chelate spectrum was used to calculate a Δ_o value for the crystal field splitting in the complex. Since the complex is not symmetrical, the theory does not strictly apply; therefore, the value obtained is used for comparison only. A value of 18,182 cm^{-1} was obtained from the spectra and one of 18,430 cm^{-1} from the Orgel diagrams of Tanabe and Sugano given by Cotton and Wilkinson. (19)

E. Beer's Law

The applicability of Beer's Law over the concentration range used was checked. Fifty milliliter samples of the following compositions were used:

	I	II	III	IV
Vol. Stock Co (II)	20.00 ml	15.00 ml	10.00 ml	7.50 ml
Conc. Co (II)	0.02 M	0.015 M	0.010 M	0.0075 M
Vol. "Disec"	0 ml	2.67 ml	5.33 ml	6.66 ml
Conc. "Disec"	0	0.005 M	0.010 M	0.0125 M

	V	VI	VII	VIII
Vol. Stock Co (II)	5.00 ml	2.50 ml	1.00 ml	0.50 ml
Conc. Co (II)	0.005 M	0.0025 M	0.0010 M	0.0005 M
Vol. "Disec"	8.00 ml	9.32 ml	10.12 ml	10.39 ml
Conc. "Disec"	0.015 M	0.0175 M	0.0190 M	0.0195 M

The solutions were allowed to stand one hour after which absorbance readings were made at 550 mμ. Readings were repeated after 9 days. The intensity of absorbance continued to increase and the linear portion of the curve shifted toward lower concentrations on standing. As the intensities increased, the curve no longer passed through the origin; however, the linearity of the curve held over the concentration range used in the experimental measurements. Figure E-13 shows the initial curve.

Curves for Beer's Law

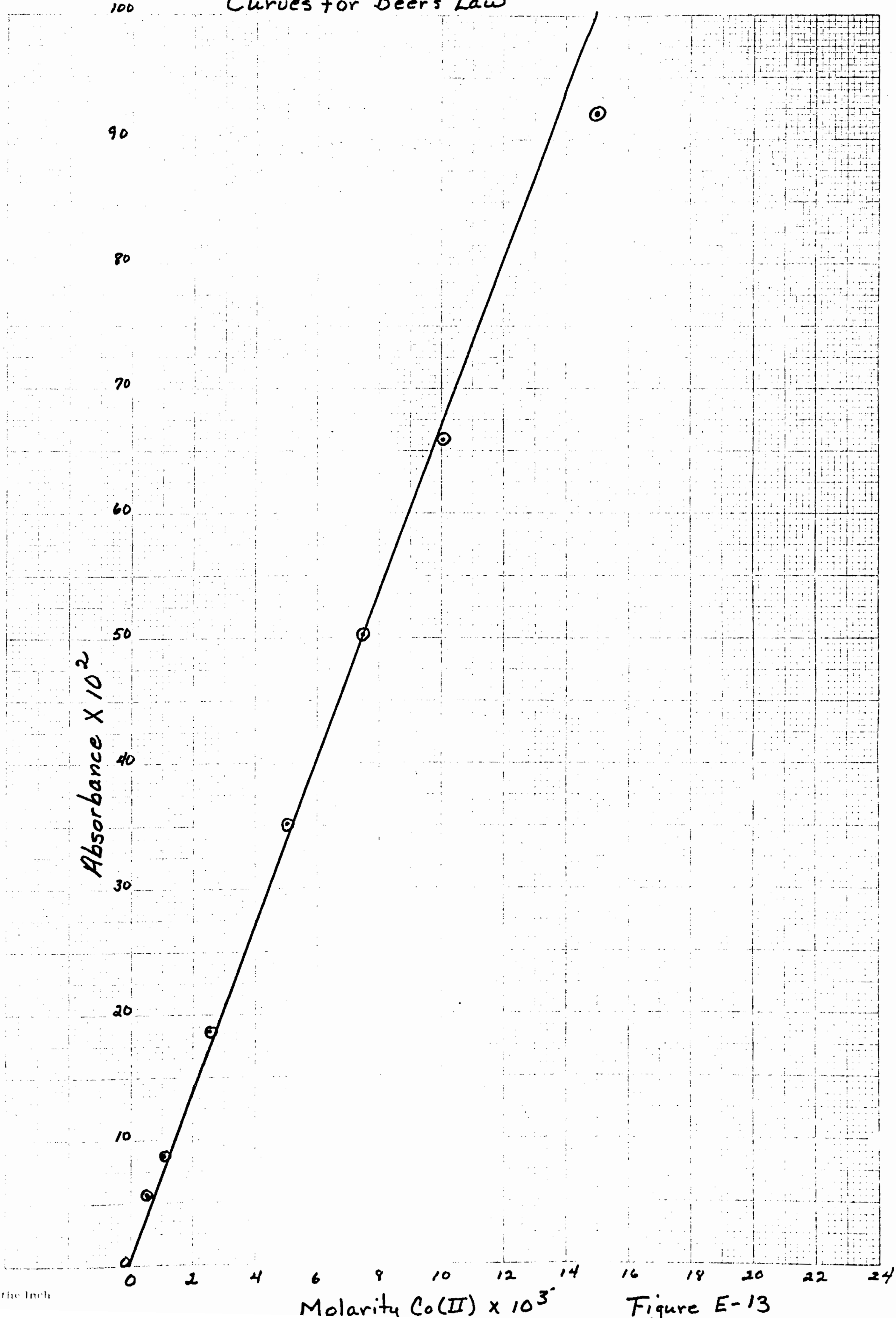


Figure E-13

IV. DISCISSION:

A. Effect of pH on Absorption Spectra

The maximum wavelength characteristic of the aqueous cobalt (II) ion, $[Co(H_2O)_6]^{2+}$, about 515 mu, shifts to a new value, about 550 mμ, that becomes steady at pH values of 8 or greater.

In the 1:1 solutions, the final maximum was at about 560 mμ.

In the 1:2 solutions, the final value of the maximum was at 550 mμ for pH above 8 and remained so on standing. This is interpreted as an indication that the complex was well formed at pH 8 and above.

B. Metal-Ligand Ratios

1. The method of continuous variations shows a peak at about 60 mole-percent ligand, which is interpreted as indicating an ML_2 complex. The gradual increase in absorbance on standing indicates that a 1:3 complex forms slowly. It is assumed that a 1:2 complex first forms, then slowly adds a third ligand, when available.

The peak at 50 mole-percent apparently indicates the beginning of precipitation.

2. The method of Yoe and Jones, modified by Harvey, might be interpreted to indicate the immediate formation of an ML_2 complex followed by the slow addition of a third ligand to form ML_3.

3. The method of Harvey and Manning indicated the immediate formation of an ML_2 complex. The precipitation occurring in most of the solutions prevented the further application of this method.

4. The method of Bent and French by its inapplicability indicates that the complexes formed are probably not highly dissociated.

C. Rate of Formation of Complexes

The changes in the absorption curves of the solutions with time appear significant.

A rapidly formed 1:2 complex was apparent; however, for those solutions in which the proportions of reagent were favorable, evidence of a 1:3 complex which formed slowly was obtained. Reference to the data taken by the method of Yoe and Jones indicates that the 1:2 complex appeared and reached maximum intensity within 24 hours. In solutions with higher proportions of ligand a leveling to constant absorbance values was observed after 19 days.

D. Beer's Law

The absorbance of the solutions varied linearly with concentration of cobalt ion over the ranges studied, even in solutions which changed on standing. The linearity remained, but of course, the method could not be used for quantitative analysis because final maxima were not readily recognized.

E. Relative Stabilities

The data appear to support the existence of two complexes, a 1:2 complex which forms rapidly and a 1:3 complex which forms more slowly. The complexes formed were stable enough to prevent precipitation over a six month period.

F. Complexes of "Symaminol"

Solutions of Co (II) and "Symaminol" in the ratios 1:1 and 1:3 were not stable enough at pH 8 to prevent precipitation. The initial green solutions changed color as their spectra were being taken. Within 24 hours the solutions were opalescent and precipitation occurred in all within 48 hours.

Since no Co (II)-"Symaminol" complex was formed which was stable enough to prevent precipitation, under the same conditions used for "Disec", this is taken as an indication that the hydroxyl groups present in "Disec" increase the stabilities of the complexes in some manner.

V. SUMMARY:

1. The effects of pH and time on the spectra produced in solution by Co (II) and "Disec", $(HOCH_2)_3CHNCH_2CH(OH)CH_2NHC(CH_2OH)_3$, were studied. In solutions containing two moles of ligand to one of Co (II) with pH of 8 or greater, the maximum absorbance occurred at 550 mμ and was relatively constant in this range. For the 1:1 solution the maximum absorbance was about 560 mμ.

On standing, with pH controlled, the absorbances gradually increased over as many as 53 days. The maxima apparently remained at 550 mμ.

2. Job's Method of continuous variations indicated the presence of a 1:2 complex of Co (II) and "Disec" at a pH of about 8.

3. The method of Yoe and Jones gave evidence of a rapidly formed 1:2 complex of Co (II) and "Disec" followed by the slow formation of a 1:3 complex whenever the ligand concentration was favorable.

4. The method of Harvey and Manning supported the evidence of a rapidly formed 1:2 complex. Precipitation occurring in most of the solutions of one group prevented the further application of this method.

5. The fact that the method of Bent and French gave no usable data is interpreted as indicating that the complexes formed between Co (II) and "Disec" are not highly dissociated.

6. Attempts to form Co (III) complexes with "Disec" by H_2O_2 oxidation gave solutions with rapidly fading maxima. Precipitation occurred within 24 hours. No complex stable enough to prevent precipitation was obtained by the above procedure.

7. Under the same experimental conditions as those used

for "Diseo", "Symaminol" appeared to form complexes too weak to remain in highly basic solutions.

8. Beer's law plots gave linear relationships over the concentration ranges studied.

VI. BIBLIOGRAPHY

1. Andreeva, M.V., Khaldin, V.G., and Andreev, S.N., Dokl. Akad. Nauk. S.S.S.R., 155(1), 115-17 (1964) ; Chem. Abs., 61: 186 f.
2. Bailar, John C., Jr., Chem. Revs., 23, 65 (1938).
3. Basolo, Fred, Chem. Revs., 52, 459 (1953).
4. Basolo, Fred, J. Am. Chem. Soc., 72, 4393 (1950).
5. Basolo, Fred, J. Am. Chem. Soc., 76, 953 (1954).
6. Basolo, F. and Chen, Y.T., J. Am. Chem. Soc., 76, 953 (1954).
7. Basolo, F., Chen, Y.T., and Murmann, R.K., J. Am. Chem. Soc., 76, 956 (1954).
8. Basolo, Fred and Johnson, Ronald C., Coordination Chemistry, W.A. Benjamin, Inc., New York, 1964.
9. (a) Basolo, F. and Murmann, R.K., J. Am. Chem. Soc., 74, 5243 (1952).
   (b) Basolo, F. and Murmann, R.K., J. Am. Chem. Soc., 76, 211 (1954).
10. Bertsch, C.R., Block, B.P. and Fernelius, W.C., J. Phys. Chem., 62, 503 (1958).
11. Briel, L.I., II, Master of Science Degree Thesis, University of Richmond, Richmond, Va., (1964).
12. Calvin, M. and Wilson, K., J. Am. Chem. Soc., 67, 2003 (1945).
13. Carassiti, V. and Martelli, R., Ann. Chim. (Rome), 47, 402-9 (1957); Chem. Abs., 51:12649 h.
14. Carlson, McReynolds and Verhoek, J. Am. Chem. Soc., 67, 1334 (1945).
15. (a) Chaberek, S., Jr. and Martell, A.E., J. Am. Chem. Soc. 74, 5053 (1952).

15. (b) Chaberek, S., Jr. and Martell, A. E., *J. Am. Chem. Soc.*, *76*, 215 (1954).

(c) Chaberek, S., Jr. and Martell, A. E., *J. Am. Chem. Soc.*, *77*, 1477 (1955).

16. Chaberek, S., Jr. and Martell, A.E., *Organic Sequestering Agents*, John Wiley and Sons, Inc., New York, 1959.

17. Chaberek, S., Jr., Courtney, R.C., and Martell, A.E., *J. Am. Chem. Soc.*, *75*,5057 (1952).

18. Chaberek, S., Jr., Courtney, R.C., and Martell, A.E., *J. Am. Chem. Soc.*, *75*, 2185 (1953).

19. Cotton, F. A. and Wilkinson, G., *Advanced Inorganic Chemistry*, Second Ed., Interscience Publishers, New York, 1966.

20. Craig, Maccoll, Nyholm, Orgel and Sutton, *J. Chem. Soc.*, 332 (1954).

21. Davis, R.W., Master of Science Degree Thesis, University of Richmond, Richmond, Va., 1964.

22. Day, M.C. and Selbin, J., *Theoretical Inorganic Chemistry*, Reinhold Publishing Corp., New York, 1962.

23. Diehl, Harvey, *Chem. Revs.*, *21*, 39 (1937).

24. Douglas, B.E. and Mc Daniel, D.H., *Concepts and Models of Inorganic Chemistry*, Blaisdell Publishing Co., New York, 1965.

25. Drago, Russell S., *Physical Methods in Inorganic Chemistry*, Reinhold Publishing Co., New York, 1965.

26. Durrant, Reginald G., *J. Chem. Soc.*, *87*, 1781 (1905).

27. Garrick, F., *Phil. Mag.*, *9*, 131 (1930); *10*, 71, 76 (1930); *11*, 741 (1931).

28. Gordon, S. and Schreyer, J.M., *J. Am. Chem. Soc.*, *74*, 3169 (1952).

29. Gonick, E., Fernelius, W.C., Douglas, B.E., J. Am. Chem. Soc., 77, 6506 (1955).

30. (a) Hall, James L. and Dean, Warren E., J. Am. Chem. Soc., 82, 3300 (1960).
    (b) Hall, J.L. and Dean, W.E., J. Am. Chem. Soc., 80, 4183 (1958).
    (c) Hall, J.L., Dean, W.E., and Pacofsky, J. Am. Chem. Soc., 82, 3303 (1960).

31. Hall, Jones, Delchamps and McWilliams, J. Am. Chem. Soc., 79, 3361 (1957).

32. Hall, J.L. and Fisher, J.F., Proc. West Va. Acad. Sci., 34, 85-8 (1962); Chem. Abs., 59:3748 d.

33. Hall, Swisher, Brannon and Liden, Inorg. Chem., 1, 409 (1962).

34. Harvey, A.E. and Manning, D.L., J. Am. Chem. Soc., 72, 4488 (1950).

35. Harvey, J.L., Tuksbury, C.I. and Haendler, H.M., J. Am. Chem. Soc., 71, 3641 (1949).

36. Ilse, F. and Hartmann, H., Z. Physik. Chem., 197, 239 (1951).

37. (a) Irving, H. and Williams, R.J.P., J. Chem. Soc., 3192 (1953).
    (b) Irving H. and Williams, R.J.P., Nature, 162, 746 (1948).

38. Job, Ann. Chim., (10) 9, 113 (1928).

39. Jonassen, H.B. and Dexter, T.H., J. Am. Chem. Soc., 71, 1553 (1949).

40. Jonassen, H.B. and Frey, F.W., J. Am. Chem. Soc., 75, 1524 (1953).

41. Keller, R.N. and Edwards, L.J., J. Am. Chem. Soc., 74, 215 (1952).

42. Kida, Shigeo, Nippon Kagaku Zasshi, 85 (7), 428-30; Chem. Abs., 61:12930 c.

43. Kirson and Barsily, Bull. Soc. Chim. France, 1959, 1926-31; Chem. Abs., 56:13785 b.

44. Kortum and Seiler, Angew. Chem., 52, 687 (1939).

45. Laitinen and Burdett, Anal. Chem., 23, 1268 (1951).

46. Ley, *Ber.*, 42, 354 (1909).

47. Liehr, A.D., *J. Chem. Ed.*, *39*, 135 (1962).

48. Martell, A.E., *J. Chem. Ed.*, *29*, 270 (1952).

49. Martell, A.E. and Calvin, M., *Chemistry of the Metal Chelate Compounds*, Prentice-Hall, Inc., New York, 1953.

50. Martell, A.E., Chaberek, Courtney, Westerback and Hyytiainen, *J. Am. Chem. Soc.*, *79*, 3036 (1957).

51. Martin, D.F. and Martin, B.B., *Coordination Compounds*, McGraw-Hill Book Co., New York, 1964.

52. Mellor, J.W., *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 14, Longmans, Green and Co., New York, 1935.

53. (a) Mellor, J.W. and Maley, *Nature*, *159*, 370 (1947).
    (b) Mellor, J.W. and Maley, *Nature*, *161*, 436 (1948).

54. Michal, Jan and Dolezal, Jan, *Chem. Listy*, *50*, 911-15 (1956); *Chem. Abs.* *50*:11162 d.

55. Moeller, Therald, *Inorganic Chemistry*, John Wiley and Sons, Inc., New York, 1952.

56. Morgan, G.T. and Drew, H.T., *J. Chem. Soc.*, 1456 (1920).

57. Murakami, M., Senoh, S., Matsusato, M., Itatani, H. and Kang, J.W., *Nippon Kagaku Zasshi*, *83*, 741-4 (1962); *Chem. Abs.*, *58*:13407 a.

58. Murmann, R.K., *Inorganic Complex Compounds*, Reinhold Publishing Co., New York, 1964.

59. O'Rear, C.E., Master of Science Degree Thesis, University of Richmond, Richmond, Va., 1961.

60. (a) Orgel, L.E., *J. Chem. Soc.*, 4756 (1952).
    (b) Orgel, L.E., *J. Chem. Phys.*, *23*, 1004, 1819, 1824 (1955).
    (c) Orgel, L.E., *An Introduction to Transition Metal Chemistry*, Methuen and Co., Ltd., London, 1960.

61. Parry, R.W. and Keller, R.N., *The Chemistry of the Coordination Compounds*, Reinhold Publishing Co., New York, 1956.

62. Pauling, Linus, *The Nature of the Chemical Bond*, Third Ed. Cornell University Press, Ithica, New York, 1960.

63. (a) Pfeiffer, Paul, *J. Chem. Educ.*, *5*,1090 (1928).
    (b) Pfeiffer and Schmitz, *Z. Anorg. Chem.*, *258*, 247 (1949).
    (c) Pfeiffer, Thielert and Glaser, *J. Prakt. Chem.*, *152*, 145 (1939).

64. Pierce, W.C., Haenisch, E.L., and Sawyer, D.T., *Quantitative Analysis*, John Wiley and Sons, Inc., New York, 1958.

65. Pierce, J.S. and Wotiz, *J. Am. Chem. Soc.*, *66*, 879 (1944).

66. Roberts, G.L. and Field, F.H., *J. Am. Chem. Soc.*, *72*, 4232 (1950).

67. Scott, W.W., *Standard Methods of Chemical Analysis*, Fifth Ed., D. Van Nostrand Co., Inc., New York, 1939.

68. Sebera, D.K., *Electronic Structure and Chemical Bonding*, Blaisdell Publishing Co., New York, 1964.

69. Sidgwick, N., *J. Chem. Soc.*, 725 (1923); *Trans. Faraday Soc.*, *19*, 469 (1923); *Electronic Theory of Valence*, Clarendon Press, Oxford, 1927.

70. Stephens, D.R. and Drickamer, H.G., *J. Chem. Phys.*, *30*, 1518 (1959).

71. (a) Thompson, L.C. and Loraas, J.A., *Inorg. Chem.* *2*, 89, 594 (1963).

72. Uhlig, E. and Linke, D., *Z. Anorg. Allgem. Chem.*, 331 (1-2), 112-20 (1964); *Chem. Abs.*, *61*:15409 c.

73. *Van Nostrand's Scientific Encyclopedia*, Third Ed., D.Van Nostrand, Co., Inc., New York, 1958.

74. Vosburg, W.C. and Cooper, G.R., *J. Am. Chem. Soc.*, *63*, 437 (1941).

75. Wentworth, R.A.D. and Piper, T.S., *Inorg. Chem.*, *4*, 202 (1965).

76. Willard, H.H., Merritt, L.L., Jr., and Dean, J.A., *Instrumental Methods of Analysis*, Fourth Ed., D. Van Nostrand Co., Inc., New York, 1965.

77. Wood, P.B. and Higginson, C.C.E., *J. Chem. Soc.*, 1484 (1964).

78. Yamatera, Kondo, Okuno and Uemura, *Proc. Symposium Chem. Coordination Compounds*, Agra, India, *1959* pt. 2, 19-34; *Chem. Abs.*, *55*:10186 a.

79. Yatsimirskii and Korableva, *Izvest. Vysshykh Ucheb. Zavedenii Khim i Khim Tekhnol*. *1958* No. 4, 19-28; *Chem. Abs.*, *53*:2775 h.

80. Yoe and Jones, *Ind. Chem. Anal. Sect.*, *16*, 111 (1944).

81. Yoneda, H., *Bull. Chem. Soc. Japan*, *28*, 125-9 (1955); *Chem. Abs.*, *52*:2531 f.

82. Yoneda, H. and Kida, S., *Bull. Liberal Arts College*, *Wakayama University (Nat. Sci.)*, *5*, 9-11 (1955); *Chem. Abs.*, *49*:10788 c.

83. Yoneda, H. and Kida, S., *J. Am. Chem. Soc.*, *82*, 2139 (1960).

84. Yoneda, H. and Kobayashi, M., *Chem. Abs.*, *49*:10055 f; *J. Chem. Soc. Japan*, *Pure Chem. Sect.*, *75*, 1192-5 (1954).

85. Bethe, H., *Ann. Physik*, *3*, No. 5, 133 (1929).

86. Lewis, J. and Wilkins, R., *Modern Coordination Chemistry*, Interscience Publisher, Inc., New York, 1960.

87. Lowry, T., *Chem & Ind.*, *42*, 316 (1923).

88. Van Arkel, A. and DeBoer, J., *Rec. Trav. Chim.*, *47*, 593 (1920).

89. Van Vleck, J., *Phys. Rev.*, 208 (1932), *J. Chem. Phys.*, *3*, 803, 807 (1935).

90. Werner, A., *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*, Fourth Ed., Friedrich Vieweg and Son, Brunswick, 1920.

VII. APPENDICES

Appendix A--Standardizations

Standardization of I_2 Solution

Reagents:

1. Arsenious oxide As_2O_3
   Code 0061 Lot 32125 Baker Analyzed Reagent
   J.T. Baker Chemical Company
   Phillipsburg, New Jersey
2. Iodine, Resublimed I_2
   Code 1800 Lot Y243 Reagent ACS
   Allied Chemical Company
   New York, New York
3. Sodium thiosulfate $Na_2S_2O_3 \cdot 5H_2O$
   Code 2307 Lot Y279 Reagent ACS
   Allied Chemical Company
   New York, New York
4. Sodium bicarbonate $NaHCO_3$
   Code 2202 Lot Y137 Reagent ACS
   Allied Chemical Company
   New York, New York
5. Sodium hydroxide NaOH
   Code 3722 Lot 22482 Baker Analyzed Reagent
   J.T. Baker Chemical Company
   Phillipsburg, N.J.
6. Hydrochloric acid HCl
   Code 9539 Lot 32065 Baker Analyzed Reagent
   J.T. Baker Chemical Company
   Phillipsburg, N.J.

Procedure:

An iodine solution was prepared by dissolving 12.7 grams of I_2 in a liter of distilled water containing 25 grams of KI. The normality of the resultant solution was determined by titrating it against primary-standard-grade arsenious oxide according to the method given by Pierce et.al. (64)

Experimental data:

Sample #	Wt. As_2O_3	Vol. I_2	Normality I_2
1	0.2411 g.	47.93 ml.	0.1017 N
2	0.3653 g.	72.05 ml.	0.1024 N
3	0.2754 g.	54.40 ml.	0.1023 N
		Average	0.1021 N

Calculations:

Sample 1 $$N_{I_2} = \frac{(241.1\text{ mg})}{(47.93\text{ ml})(49.46\text{ mg/meq})} = 0.1017\text{ N}$$

Sample 2 $$N_{I_2} = \frac{(365.3\text{ mg})}{(72.05\text{ ml})(49.46\text{ mg/meq})} = 0.1024\text{ N}$$

Sample 3 $$N_{I_2} = \frac{(275.4\text{ mg})}{(54.40\text{ ml})(49.46\text{ mg/meq})} = 0.1023\text{ N}$$

Standardization of Sodium thiosulfate

Reagents:

1. Sodium thiosulfate $Na_2S_2O_3 \cdot 5H_2O$

Code 2307 Lot Y279 Reagent ACS

Allied Chemical Company

New York, New York

Procedure:

A solution of sodium thiosulfate was prepared by dissolving

25 grams of reagent in one liter of distilled water. The normality of the resultant solution was determined by titration against a standardized iodine solution according to the method given by Pierce et.al. (64)

Experimental data:

Sample #	Vol. $Na_2S_2O_3$	Vol. I_2	Normality $Na_2S_2O_3$
1	25.00 ml.	26.32 ml.	0.1075 N
2	25.00 ml.	26.32 ml.	0.1075 N
3	25.00 ml.	26.65 ml.	0.1088 N
4	25.00 ml.	26.50 ml.	0.1082 N
		Average	0.1080 N

Calculations:

1. Normality $= \frac{(26.32 \text{ ml})(0.1021 \text{ N})}{(25.00 \text{ ml})} = 0.1075 \text{ N}$

2. (Same as above.)

3. Normality $= \frac{(26.65 \text{ ml})(0.1021 \text{ N})}{(25.00 \text{ ml.})} = 0.1088 \text{ N}$

4. Normality $= \frac{(26.50 \text{ ml})(0.1021 \text{ N})}{(25.00 \text{ ml})} - 0.1082 \text{ N}$

Standardization of cobaltous nitrate solution:

Reagents:

1. Cobaltous nitrate $Co(NO_3)_2 \cdot 6H_2O$
   Code 1597 Lot V095 Reagent ACS
   Allied Chemical Company
   New York, New York

Procedure:

A solution of cobaltous nitrate was prepared by dissolving 14.5 grams of reagent in two liters of distilled water. The solution was assayed by the method of Laitinen and Burdett. (45) Co (II) is oxidized with H_2O_2 and KI is added; I_2 liberated in the acidified solution is then titrated with standard thiosulfate.

Experimental data:

Sample #	Vol. Co(II)	Vol. $Na_2S_2O_3$	Vol. I_2 added	N Co(II)
1	35.00 ml	16.20 ml	0.00 ml	0.0499 N
2	40.00 ml	18.95 ml	0.40 ml	0.0501 N
3	45.00 ml	21.33 ml	0.45 ml	0.0501 N
			Average	0.0500 N

Calculations:

1. Meq I_2 = (15.20 ml)(0.1080 N) = 1.750 meq
   N_{Co} = 1.750 meq/35.00 ml = 0.0499 N
2. Meq I_2 = (18.95 ml)(0.1080 N) = 2.047 meq
   Meq I_2 over titrated = (0.1021 N)(0.40 ml) = 0.0408 meq
   N_{Co} = 2.006 meq/40.00 ml = 0.0501 N
3. Meq I_2 = (21.33 ml)(0.1080 N) = 2.304 meq
   Meq I_2 over titrated = (0.1021 N)(0.45 ml) = 0.0459 meq
   N_{Co} = 2.258 meq/45.00 ml = 0.0501 N

Standardization of Nitric acid

Reagents:

1. Sodium carbonate Na_2CO_3
   Lot 1.946 Baker Analyzed Reagent 99.8%
   J.T. Baker Chemical Company
   Phillipsburg, New Jersey
2. Nitric acid HNO_3
   Code 9601 Lot 30615 Baker Analyzed Reagent
   J.T. Baker Chemical Company
   Phillipsburg, N.J.

Procedure:

A solution of nitric acid was prepared by mixing 15 ml. of concentrated reagent with enough distilled water to make two liters of solution. The normality of the solution was determined by titration against primary-standard-grade sodium carbonate according to the method given by Pierce *et.al.* (64)

Experimental data:

Wt. Na_2CO_3	Wt. pure Na_2CO_3	Meq Na_2CO_3	Vol. HNO_3	N HNO_3
#1 0.1952 g	0.1948 g	3.676	33.00 ml	0.1114 N
#2 0.1992 g	0.1988 g	3.750	33.52 ml	0.1112 N
#3 0.2720 g	0.2714 g	5.122	45.75 ml	0.1118 N
#4 0.2464 g	0.2459 g	4.918	41.45 ml	0.1118 N
			Average	0.1116 N

Calculations:

1. (0.1952 g)(0.998) = g pure Na_2CO_3
   (0.1948 g)/ 53 g/meq = 3.676 meq
   3.676 meq/ 33.00 ml = 0.1114 N
2. (0.1992 g)(0.998) = 0.1988 g pure Na_2CO_3
   (0.1988 g)/(53 g/meq) = 3.750 meq
   3.750 meq/33.52 ml = 0.1112 N
3. (0.2720 g)(0.998) = 0.2714 g pure Na_2CO_3
   (0.2714 g)/(53 g/meq) = 5.122 meq
   5.122 meq/45.75 ml =0.1118 N
4. (0.2464 g)(0.998) = 0.2459 g pure Na_2CO_3
   (0.2459 g)/(53 g/meq) = 4.918 meq
   4.918 meq/41.45 ml = 0.1118 N

Standardization of free bases (Disec and Symaminol)

Reagents:

1. Rexyn 203 (OH) Anion Exchange Resin

Research Grade Cat. # R-202
Fisher Scientific Company
Fairlawn, N.J.

2. Disec dihydrochloride and Symaminol dihydrochloride
Prepared and purified in this laboratory by L.I. Briel.(11)

Procedure:

Four and one-half grams of Disec were mixed with enough distilled water to effect solution and diluted to 100 ml. The salt solution was then passed through an ion exchange column containing Rexyn 203 anion exchange resin in the OH form at a rate of a drop each 3-5 seconds. Distilled water was used to wash the free base from the column. One liter of eluant was collected and samples were assayed by potentiometric titration with nitric acid.

Two grams of Symaminol was treated in the same manner and 500 ml of eluant collected. Titration against nitric acid was again used to assay the sample.

Calculations:

1. $\frac{(10.75 \text{ ml})(0.1116 \text{ N})}{(10.00 \text{ ml})} = 0.1200\text{M}$

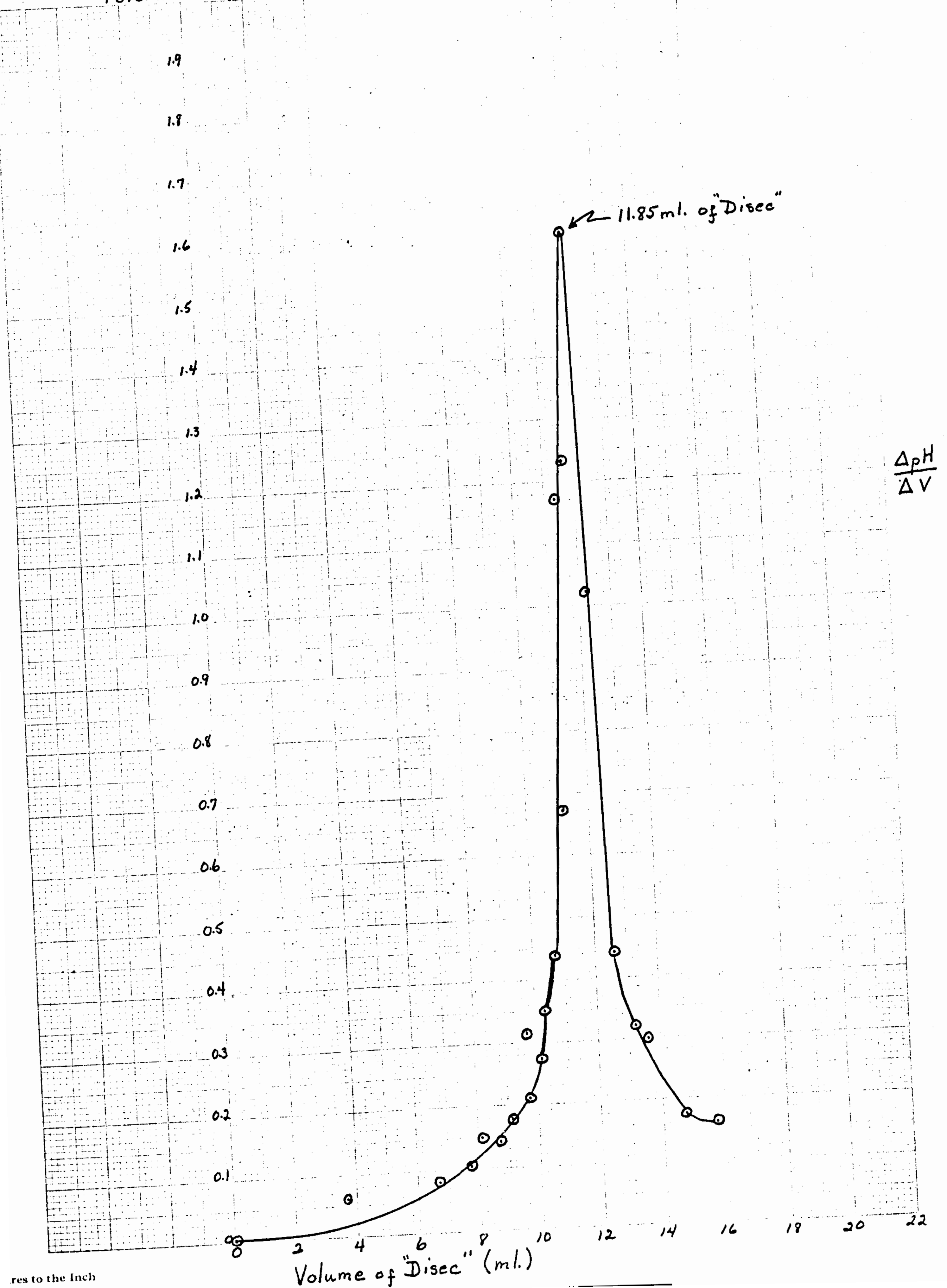
2. $\frac{(14.70 \text{ ml})(0.1116 \text{ N})}{(12.00 \text{ ml})} = 0.1358 \text{ M}$

3. $\frac{(12.92 \text{ ml})(0.1116 \text{ N})}{(10.00 \text{ ml})} = 0.1441 \text{ M}$

Average Molarity = 0.1336 M

A titration curve obtained for Disec follows.

Potentiometric Titration : Standard HNO_3 with "Disec"



Appendix B--Solutions for Spectral Study

1. Solutions for Spectra

Co (II) Final molar concentration $= 9.38 \times 10^{-3}$ M

Disec Final molar concentration $= 9.38 \times 10^{-3}$ M

Metal : Ligand = 1:1

Preparation: (Sample)

10.00 ml of 9.38×10^{-2} M stock Disec solution

18.76 ml of 5×10^{-2} M stock Co (II) solution

10.00 ml of 1×10^{-1} M stock $NaNO_3$ solution

The above solutions were mixed, the pH adjusted and the solution made up to 100 ml.

2. Solutions for Job's Method

Co (II) Final molar concentration $= 9.38 \times 10^{-3}$ M

Disec Final molar concentration $= 9.38 \times 10^{-3}$ M

Preparation: (Sample)

5.00 ml of 9.38×10^{-2} molar Disec stock solution , 5.00 ml $NaNO_3$,

9.38 ml of 5×10^{-2} molar Cobalt stock solution

The above solutions were mixed, adjusted for pH and made up to 50 ml.

3. Solutions for the Method of Yoe and Jones

Co (II) Final molar concentration $= 5.00 \times 10^{-3}$ M

Disec Final molar concentration $= 1.5 \times 10^{-2}$ M

Metal : Ligand = 1:3

Preparation: (Sample)

5.00 ml of 5.00×10^{-2} M cobalt stock solution, 5.00 ml $NaNO_3$,

8.00 ml of 9.38×10^{-2} M Disec stock solution

The above solutions were mixed, adjusted for pH and made up to 50 ml.

4. Solutions for Beer's Law

Co (II) Final molar concentration 5.0 X 10^{-3} M

Disec Final molar concentration 1.5 X 10^{-2} M

Final total concentration 2.0 X 10^{-2} M

Preparation: (Sample)

5.00 ml 5 X 10^{-2} M Co (II) stock solution

8.00 ml 9.38 X 10^{-2} M Disec stock solution

5.00 ml stock $NaNO_3$ solution

The above solutions were mixed, the pH adjusted and the solution made up to 50 ml.

5. Solutions for Method of Harvey and Manning

$$\left.\begin{array}{ll} \text{Co (II) Final molar concentration} & 5.0 \text{ X } 10^{-3} \text{ M} \\ \text{Disec Final molar concentration} & 2.67 \text{ X } 10^{-2} \text{ M} \end{array}\right\} \text{Group I}$$

Preparation: (Sample)

10.00 ml of 5 X 10^{-2} M cobalt stock solution

20.00 ml of 1.34 X 10^{-1} M Disec stock solution

10.00 ml of stock $NaNO_3$ solution

The above solutions were mixed, adjusted for pH and made to 100 ml.

$$\left.\begin{array}{ll} \text{Co (II) Final molar concentration} & 2.67 \text{ X } 10^{-2} \text{ M} \\ \text{Disec Final molar concentration} & 5.34 \text{ X } 10^{-3} \text{ M} \end{array}\right\} \text{Group II}$$

Preparation: (Sample)

53.4 ml of 5 X 10^{-2} M cobalt stock solution

4.00 ml of 1.34 X 10^{-1} M Disec stock solution

10.00 ml of stock $NaNO_3$ solution

The above solutions were mixed, adjusted for pH and made up to 100 ml.

5. Solutions for the Method of Bent and French

Co (II) Final molar concentration $= 2.5 \times 10^{-2}$ M

Disec Final molar concentration $= 2.39 \times 10^{-2}$ M

Group I, [Co] constant

Preparation: (Sample)

50.00 ml Cobalt stock solution (5×10^{-2} M)

25.43 ml 9.38×10^{-2} M Disec stock solution

The above solutions were mixed, the pH adjusted and the solution made up to 100 ml.

Co (II) Final molar concentration $= 9.4 \times 10^{-4}$ M

Disec Final molar concentration $= 2.5 \times 10^{-3}$ M

Group II, [Disec] constant

Preparation: (Sample)

2.66 ml 9.38×10^{-2} M Disec stock solution

1.88 ml 5.0×10^{-2} M Cobalt stock solution

The above solutions were mixed, the pH adjusted and the solution made up to 100 ml.

Appendix C—1. Oxidation of Co (II) to Co (III) in the presence of "Disec"

2. Spectrophotometric Measurements

Reagents:

1. Stock $Co(NO_3)_2$ solution
2. Stock "Disec" solution
3. Sodium bicarbonate $NaHCO_3$
   Code 2202 Lot Y137 Reagent
   Allied Chemical Company
   New York, New York
4. Hydrogen peroxide (30%) H_2O_2
   Code 1808 Lot Y1245 Reagent—"stabilized"
   Allied Chemical Company
   New York, New York
5. Sulfuric acid H_2SO_4
   Code 9681 Lot 31485 Reagent
   J.T. Baker Chemical Company
   Phillipsburg, N.J.

Procedure:

A 1:1 solution of Co (II) and "Disec" was prepared by combining 2.0 ml of stock $Co(NO_3)_2$ solution with 1.07 ml of stock "Disec" solution. The solution was made up to 50.0 ml. Other solutions having 1:2, 1:3, 2:1 and 3:1 metal-ligand ratios were also prepared.

The above solutions were combined with equal volumes of approximately 0.2 N H_2SO_4. Sodium bicarbonate was added until the solution tested neutral and an additional 5 grams were added. Five milliliters of 30% H_2O_2 was added and oxidation allowed to accur. The characteristic dark green known as Durrant's Bicarbonate Green (26) was observed during the oxidation process. The pH of all solutions measured greater than 8.

Within one hour, all solutions had turned yellowish and after two hours some were turbid. Precipitation occurred in almost all cases within 24 hours.

Attempts to take spectra gave maxima which were observed to shift position even as measurements were being made.

Calculations:

1. Volume of Co (II) stock solution

$$N_{Co(II)} \times V_{Co(II)} = N_{solution} \times V_{solution}$$

$$(0.0500\ N)(V) = (2.0 \times 10^{-3}\ N)(50.0\ ml)$$

$$V = 2.0\ ml$$

2. Volume of "Disec" stock solution

$$N_{Disec} \times V_{Disec} = N_{solution} \times V_{solution}$$

$$(0.0938\ N)\ (V) = (2.0 \times 10^{-3}\ N)(50.0\ ml)$$

$$V = 1.07\ ml$$

Appendix D--Table of Absorption Maxima

Compound	Solvent	Wavelength	Reference
Co (II)	3-12 M KOH	535;585,625 mµ	(28)
$Co(NO_3)_2$	Water	510 mµ	(28)
$[Co(H_2O)_6]^{2+}$	Water	513; 510 mµ	(79 (66)
$[Co(C_2O_4)_2]^{2-}$	Water	534 mµ	(79)
$[Co(NH_3)_6]^{2+}$	Water	496;609 mµ	(79)
$[Co(en)_3]^{2+}$	Water	356,480 mµ	(79)
$[Co(o\text{-}phen)_3]^{2+}$	Water	304, 313, 331, 348 mµ	(66)
Co (II) 1:1 with tetraethylenepentamine	Water	460, 510 mµ	(40)
Co (II) 1:2 with tetraethylenepentamine	Water	320, 350 mµ	(40)
Co (III) compounds			
$[Co(NH_3)_4(NO_2)_2]Cl$ (cis)	Methanol-Water	238, 327, 448 mµ	(4)
" (trans)	"	255;356,440 mµ	(4)
$[Co(en)_2(NO_2)_2]NO_3$ (cis)	"	240, 325, 438 mµ	(4)
' (trans)	"	250; 347, 433 mµ	(4)
$[Co(pn)_2(NO_2)_2]Cl$ (trans)	"	250; 340, 435 mµ	(4)
$[Co(en)_2Cl_2]Cl$ (cis)	"	240; 390; 530 mµ	(4)
" (trans)	"	252, 385, 450; 625 mµ	(4)
$[Co(pn)_2Cl_2]Cl$ (trans)	"	255, 380, 450, 610 mµ	(4)
$[Co(en)_2ClSCN]SCN$ (cis)	"	300; 510 mµ	(4)
" (trans)	"	335, 520 mµ	(4)
$[Co(en)_2ClNO_2]Cl$ (cis)	"	337; 465 mµ	(4)
$[Co(en)_2ClNO_2]NO_2$ (trans)	"	245, 340, 466 mµ	(4)
$[Co(en)_2NH_3Cl]S_2O_6$ (cis)	"	360, 512 mµ	(4)
" (trans)	"	355, 407 mµ	(4)

$[Co(en)_2(NH_3)_2]Cl_3$ (cis)	Water	338, 470 mμ	(4)
$[Co(pn)_2(NH_3)_2]Cl_3$ (trans)	"	338, 470 mμ	(4)
$[Co(NH_3)_4C_2O_4]NO_3\cdot H_2O$	"	356, 512 mμ	(66)
$[Co(NH_3)_5C_2O_4]NO_3\cdot 2H_2O$	"	500 mμ	(66)
$[Co(NH_3)_5CrO_4]NO_3$	"	385, 546 mμ	(66)
$[Co(en)_3]^{3+}$	"	320 then 360 mμ	(54)
$[Co(l\text{-}pn)_2(NO_2)_2]ClO_4\cdot H_2O$	"	440 mμ	(75)

VIII. AUTOBIOGRAPHY

I, Pauline Frances Fones, was born on March 7, 1941, in Richmond, Virginia.

I attended local elementary and junior high schools and graduated in February 1959 from John Marshall High School, where I received the Bausch and Lomb Science Medal for outstanding achievement in the area of science.

During the summer of 1959, I attended Emory and Henry College as one of 24 participants in a Science Orientation Program, sponsored by the National Science Foundation.

In September 1959, I entered Westhampton College where I was elected to πME and ΓΣE honorary Mathematics and Chemistry Fraternities. In June 1963 I received the B.S. degree in chemistry.

From September 1963 to June 1965, I was employed as a teacher in Chesterfield County.

I was awarded a National Science Foundation fellowship to attend a NSF Institute at the American University during the summer of 1965.

In September 1965 I became a full time graduate student at the University of Richmond and was awarded the Puryear Fellowship.

I returned to teaching in September 1966 and continued my graduate work in the evenings.

In 1968 I was selected to teach a special enrichment program in chemistry at the Mathematics-Science Center in Richmond where I also taught during the summer of 1968.

This thesis is submitted in partial fulfillment of the requirements for the Master of Science Degree in chemistry.