# DISTRIBUTION STUDIES OF COBALT THIOCYANATE COMPLEXES

By

Carl E. Johnson

A THESIS

Submitted to the School for Advanced Graduate Studies of Michigan State University of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

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#### ABSTRACT

The distribution of cobalt (II) thiocyanate complexes between aqueous thiocyanate-perchlorate solutions and methyl isobutyl ketone was studied by equilibrating aqueous solutions of cobalt (II) thiocyanate under different initial conditions and determining the concentration of cobalt in each phase. This examination was done in an effort to determine the formulae of the organic phase complexes and also to obtain some information on the relative stabilities of the complexes present in each phase.

The distribution coefficient (concentration of cobalt in the organic phase divided by the concentration of cobalt in the aqueous phase) was found to be dependent upon the cobalt concentration, the thiocyanate concentration and the acidity in the following manner. The distribution coefficient (1) decreases with increasing cobalt concentration, (2) increases with increasing thiocyanate concentration, and (3) decreases with increasing acidity. These variations are discussed in detail, and it is suggested that these observations are evidence that higher cobalt (II) thiocyanate complexes extract well and that dissociation of the complex acids (e.g.  $HCO(CNS)_3 \longrightarrow H^{+} + (CO(CNS)_3)$  is important in the organic phase.

Spectrophotometric examination of both the aqueous and organic phases indicate that the aqueous phase contains mainly hexacoordinated aquo and thiocyanato-aquo complexes and that the organic phase contains the tetracoordinated thiocyanato complexes.

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#### I. INTRODUCTION

When a metal M is distributed between an aqueous and an organic phase in the presence of an acid HX, composite complexes of the general composition  $M_{mn}^{\chi}(OH)_{p}(HX)_{r}(Org.)_{s}(H_{2}O)_{t}$  may be formed. Values of the subscripts and also constants for the formation of some of these complexes may be obtained from measurements of the distribution of the metal between the organic and aqueous phase as a function of the different variables. Recently, emphasis has been placed on solvent extraction as a tool in elucidating the composition of important species existing in solution. As a consequence of this much knowledge has been gained about the separation of metals from other elements.

There are drawbacks, certainly, for when the distribution of a metal between an organic and an aqueous phase is studied, generally only the gross effects are obtained. Similarly when the composition of the solution is varied by changing the concentration of the metal, acid, ligand or added salts, it is again the gross effect on the distribution which is measured. In many instances, however, these overall effects reveal much about the species present in each phase and their respective formation constants.

In view of the somewhat contradictory evidence concerning the chemistry of the cobalt complexes, it was decided to study the cobalt (II) thiocyanate system. Cobalt has a unique property in that some of its complexes are red in aqueous solution, but are blue in organic

solutions. This duality in color might lend itself well to spectrophotometric interpretation in the same samples in which the distribution studies are being carried out. Thiocyanate was chosen as the ligand in order to obtain data on its relative strength as a complexing agent and also on how it compares with the halogens in its pseudo-halogen properties.

An equation describing the distribution process was treated and the results interpreted on the basis of existing theories and of properties of the species occurring in solution. Thus, this distribution study was undertaken to discern something of the nature of the various species existing in the cobalt (II) thiocyanate organic solvent system.

#### II. HISTORICAL

Although the reaction of cobalt with thiocyanate ions has long been used for the detection and determination of cobalt, the cause of the resulting change in color from pink to a blue solution has remained in doubt and, a point of speculation. This test, named the Vogel reaction after its originator (1), consists of adding thiocyanate ions to the solution containing cobalt and then adding a suitable organic solvent. The formation of a blue color indicates the presence of cobalt ions. Many modifications of Vogel's original method of analyzing for cobalt have been made, including the choice of solvents for color developer (2-5) and of ions for complexing addenda (6).

According to Mellor (7), the reaction between a concentrated solution of ammonium thiocyanate and a solution of a cobalt (II) salt first forms cobalt (II) thiocyanate:  $CoCl_2 + 2NH_4CNS \longrightarrow 2NH_4Cl + Co(CNS)_2$ . This blue salt is converted to ammonium cobalt (II) thiocyanate in the presence of excess ammonium thiocyanate?  $Co(CNS)_2 + 2NH_4CNS \longrightarrow (NH_4)_2Co(CNS)_4$ . If water is added the color changes to pink; but if shaken with amyl alcohol and ether the blue salt passes into the ethereal layer.

A number of theories have been postulated to account for the blue color which is also found with halide ions. Hill and Howell (8) proposed that the color change in cobaltous solutions is due to the dehydration of a cobaltous-hexa aquo complex ion. In a strongly mineral acid medium they suggest that the color of the solution is transformed to blue according to the reaction:

$$\begin{bmatrix} CoCl_4(H_20)_2 \end{bmatrix}^{=} \xrightarrow{} \begin{bmatrix} CoCl_4 \end{bmatrix}^{=} + 2H_20$$
  
pink blue

This dehydration theory was not accepted by Bassett and Croucher (9). They claim that the reasoning of Hill and Howell which was based on comparison of magnesium and cobalt oxides is unjustified and also that cobalt need not have a coordination number of six. Rossi (10) bubbled dry hydrogen chloride through a 0.1 <u>M</u> aqueous cobaltous chloride solution. The solution color changed from pink to blue. He suggested that the color change is caused by formation of a compound of the type  $HCoCl_3 \cdot nH_2O$ .

Heavy metals have a general tendency to form complex anions with halogens or pseudohalogens. This tendency may also be operative in the simple halides of the metals themselves (autocomplexes) as is indicated in some cases by anomalous colors. Emeleus and Anderson (11) suggest that cobalt (II) chloride is a notable case in which this probably occurs. In the anhydrous state the salt is blue, as also happens in solution in the presence of high concentrations of chloride ions. The blue color of the solution is associated with the presence of a complex  $CoCl_4^{=}$  anion as is shown by its migration towards the anode on electrolysis. This suggests that dehydration of the pink hydrated cobalt chloride brings about the change

$$2 \left[ Co(H_2O)_3 \right] Cl_2 \xrightarrow{} Co(CoCl_4) + 12H_2C$$
  
pink blue

Feigel (12) has suggested that the blue color is probably due to solvation of complex cobalt thiocyanates such as  $K_2[Co(CNS)_4]$  since upon dilution the color reverts to pink.

Recently workers have become more concerned with the species existing in both aqueous and non-aqueous phases. Kiss and Csokán (13,14) were among the first to obtain absorbancy curves on solutions of cobalt (II) thiocyanate in non-aqueous solvents. In a non-aqueous solvent L, the complex  $Co(CNS)_2L_2$  is formed. They also state that the complex  $Co(CNS)^+$  is present in aqueous solutions containing an excess of cobalt while an excess of thiocyanate produces  $Co(CNS)_4^-$ .

Marcel Lehné (15) has studied the aqueous spectra of cobalt (II) thiocyanate at a cobalt concentration of 0.01 <u>M</u> cobalt, with potassium thiocyanate varying in a step-wise fashion from 0.1 to 8 molar. He suggests that the complex ions  $Co(CNS)^{+}$ ,  $Co(CNS)_{2}$ ,  $Co(CNS)_{3}^{-}$  and  $Co(CNS)_{4}^{-}$  are the species present. The first three are thought to include water molecules to fill the vacant sites in the inner sphere of the complex for coordination number of four.

A similar study of the absorption spectra of cobalt (II) thiocyanate in both aqueous and mixed aqueous non-aqueous media has been performed by Babko and Drako (16,17). Their conclusions are essentially the same as those of Lehné suggesting similar species; the blue  $Co(CNS)_4^=$ complex being confirmed by transference determination. Evidence is

given for the existence of the complex  $\operatorname{Co}_2(\operatorname{CNS})^{+++}$  with the solvent. In the mixed solvent studies a correlation is found between -log K (for complex formation) and  $1/\epsilon$  the dielectric constant. From these data a common mechanism is proposed whereby the non-aqueous component of the solvent promotes removal of water from the inner sphere of the complex and thus facilitates complex formation according to  $[\operatorname{Co}(\operatorname{H}_2\operatorname{O})_4]^{++}$  +  $4\operatorname{CNS}^- \longrightarrow [\operatorname{Co}(\operatorname{CNS})_4]^- + 4\operatorname{H}_2\operatorname{O}$ . This accounts for the absence of any marked specificity of the non-aqueous solvent.

Levashova (18) and his co-workers have examined the extraction of cobalt (II) thiocyanate complex into n-butyl acetate noticing the effects of thiocyanate concentration and temperature on the distribution coefficient. In the concentration range studied, 1-8 molar thiocyanate, only the species  $Co(CNS)^+$ ,  $Co(CNS)_3^-$ ,  $Co(CNS)_4^-$  are present. Because only one clearly marked maximum is observed in the absorption spectra of the ester phase under all conditions, they conclude that the  $Co(CNS)_3^-$  and  $Co(CNS)_4^-$  species are preferentially extracted by n-butyl acetate. Data are given showing the distribution coefficient to decrease as temperature increases and to increase as the thiocyanate concentration is increased.

Recently, a study of the absorption spectra of cobalt (II) thiocyanate complex in a number of non-aqueous solvents has been done by Katzin and Gebert (19). In dilute solution only the  $Co(CNS)_2$ ,  $Co(CNS)_3$ , and  $Co(CNS)_4$  complex ion species are identified. Very convincing evidence is given in favor of the existence of six coordinate thiocyanate aquo complexes in aqueous solution and four coordinate complexes

in various organic solvents. The latter complexes are supposed to be tetrahedral, having the composition  $Co(CNS)_{2+n}L_{2-n}$  where L represents a molecule of solvent.

It is interesting to note that West and DeVries (20) are the only workers to report a specie of the type  $Co(CNS)_6^{-4}$  existing in mixed solvent systems.

This history shows an absence of any study aimed at judging the relative stability of these complex ions when distributed between aqueous-non-aqueous mixed solvent systems. The next section should provide the background for the point of view taken in the study presented in this thesis.

#### III. THEORETICAL

R. M. Diamond (21) has presented a very general treatment on the solvent extraction of inorganic compounds, and most of the material in this section may be amplified by consulting his paper. Irving, Rossotti, and Williams (22) also have presented a general treatment of the same problem but with much different formulation and much different interpretation of results. Diamonds treatment follows that suggested by J. Saldick (23), extended to a more general system.

The gross extraction behavior of acid-metal halide systems has been separated into four processes. These are: (1) association and polymerization of the metal species in either or both phases and consequent dependence of the distribution coefficient on the metal ion concentration; (2) possible acid ionization of the complex metal species and hence dependence of the extraction on hydrogen ion and thus on all other acid species present; (3) complex formation with the halide ion, and consequent dependence of the extraction on halide ion concentration and thus on all other species present capable of dissociating into such ions; (4) solvation and hydration in the two phases and consequent dependence on the specific nature of the solvent.

First let us examine the equilibria existing between the simple ions and all of the various species which may make up the system of two relatively immiscible liquid phases. Step equilibria can be used to describe the concentrations of different species existing in the aqueous phase, and a series of distribution coefficients used to relate these concentrations to those in the organic phase.

We shall consider an ideal system consisting of an aqueous solution in equilibrium with a relatively immiscible organic solvent, a hydrohalic acid, and a minimum number of representative examples of cationic, neutral and anionic metal containing species. We shall assume that the concentration of acid and anion to be such that hydrolysis of any cationic species may be neglected. The components chosen will be the metal halide MX, the hydrogen halide HX, a non-complexing acid HZ, and an inert salt AZ. In the aqueous phase the species M<sup>+</sup>, MX, MX<sub>2</sub>, HMX<sub>2</sub>, M<sub>2</sub>X<sub>2</sub>, H<sup>+</sup>, X<sup>-</sup>, Z<sup>-</sup>, A<sup>+</sup> may be present. In the organic phase the species M<sup>+</sup>, MX, MX<sub>2</sub><sup>-</sup>, HMX<sub>2</sub>, M<sub>2</sub>X<sub>2</sub>, AMX<sub>2</sub>, H<sup>+</sup>, X<sup>-</sup>, Z<sup>-</sup>, A<sup>+</sup>, HX, HZ, AX may be present. Unipositive  $M^{\dagger}$  as the metal ion is chosen only for simplicity and is not to imply that unipositive metals extract easily. M\*, MX, MX2 represent respectively typical cationic, neutral and anionic metal containing species. HMX2 represents a species which may be a weak acid or simply an ion pairing between H<sup>t</sup> and MX<sub>2</sub> in the organic solvent.  $M_2X_2$  represents a dimeric or polymeric species, but also in the organic phase stands for ion triplets and higher ion associations. AMX2, HX, HZ, and AX in the organic phase represent neutral species, either true molecules or ion pairs.

The partition of the metal halide between the two phases is given by the distribution coefficient D:

$$D = \frac{\text{total concentration of metal in the organic phase}}{\text{total concentration of metal in the aqueous phase}}$$

$$= \frac{(M)_{0} + (MX)_{0} + (MX_{2})_{0} + (HMX_{2})_{0} + (AMX_{2})_{0} + 2(M_{2}X_{2})_{0}}{(M) + (MX) + (MX_{2}) + (HMX_{2}) + 2(M_{2}X_{2})}$$
(1)

where ( )<sub>0</sub> represents the concentration of species in the organic phase and ( ) represents that in the aqueous phase. Considerations of electroneutrality require the exclusion of the distribution of charged species and that  $(H^{\bullet})_{0} + (A^{\bullet})_{0} + (M^{\bullet})_{0} = (X^{-})_{0} + (Z^{-})_{0} + (MX_{2}^{-})_{0}$ . To facilitate solution of the distribution equation step equilibria of the following types are required:

(1) Concentration distribution constants a

$$\begin{split} \mathbf{\alpha}_{MX}(M)(X) &= (M)_{0}(X)_{0} \\ \mathbf{\alpha}_{H,MX_{2}}(H)(MX_{2}) &= (H)_{0}(MX_{2})_{0}, \text{ etc.} \\ \end{split}$$

$$(2) \text{ Association equilibria in the aqueous phase } \beta \\ \beta_{MX}(M)(X) &= (MX) \\ \beta_{MX_{2}}(M)(X)^{2} &= (MX_{2}), \text{ etc.} \end{split}$$

(3) Association equilibria in the organic phase  $\delta$ 

$$\delta_{MX}(M)_{0}(X)_{0} = (MX)_{0}$$
  
 $\delta_{H,MX_{2}}(H)_{0}(MX_{2})_{0} = (HMX_{2})_{0}$ 

By making proper substitutions in equation (1) we are able to express D in terms of species which have been determined for either or both of the phases.

$$D = \sqrt{\frac{\alpha_{MX}}{\alpha_{HX}}} (M) \sqrt{\frac{\alpha_{HX}(X) + \alpha_{HZ}(Z) + \alpha_{H,MX_{2}}\beta_{MX_{2}}(M)(X)^{2}}{\alpha_{HX}(H) + \alpha_{AX}(A) + \alpha_{MX}(M)}} + \delta_{MX}\alpha_{MX}(M)(X)}$$

$$+ \frac{\alpha_{H,MX_{2}}\beta_{MX_{2}}}{\sqrt{\alpha_{HX}}} (M)(X)^{2} \sqrt{\frac{\alpha_{HX}(H) + \alpha_{AX}(A) + \alpha_{MX}(M)}{\alpha_{HX}(X) + \alpha_{HZ}(Z) + \alpha_{H,MX_{2}}\beta_{MX_{2}}(M)(X)^{2}}}$$

$$+ \frac{\delta_{H,MX_{2}}\alpha_{H,MX_{2}}\beta_{MX_{2}}(H)(M)(X)^{2} + \delta_{A,MX_{2}}\alpha_{AMX_{2}}\beta_{MX_{2}}(A)(M)(X)^{2} + 2\delta_{M_{2}X_{2}}\alpha_{MX}^{2}(M)^{2}(X)^{2}}{(M) + \beta_{MX}(M)(X) + \beta_{MX_{2}}(M)(X)^{2} + \beta_{H,MX_{2}}(H)(M)(X)^{2} + 2\beta_{M_{2}X_{2}}(M)^{2}(X)^{2}}$$
(2)

Of primary interest to the present work is the variation of D with changes in the concentration of the various aqueous ions. This can best be seen by taking the partial derivatives of the logarithm of D with respect to the logarithms of the concentrations of the ions of interest.

Primarily we shall consider the variation of D with metal concentration. If we let the denominator in equation (2) be Q, the numerator be P, then D = P/Q.

Then 
$$\frac{\partial \log D}{\partial \log Q} = \frac{\partial \log P}{\partial \log (M)} / \frac{\partial \log Q}{\partial \log (M)} - 1 = \frac{(M)}{P} \frac{\partial P}{\partial (M)} / \frac{(M)}{Q} \frac{\partial Q}{\partial (M)} - 1$$
$$= \left( f \stackrel{\circ}{M^{+}} - f \stackrel{\circ}{M_{X_{2}}} \right) - \frac{1}{2} \left( \frac{\alpha_{H,MX_{2}}(MX_{2})}{\alpha_{HX}(X) + \alpha_{H,MX_{2}}(MX_{2})} - \frac{\alpha_{MX}(M)}{\alpha_{HX}(H) + \alpha_{AX}(A) + \alpha_{MX}(M)} \right)$$
$$1 + f \stackrel{M_{2}X_{2}}{1 + f \stackrel{M_{2}X_{2}}{M_{2}X_{2}}}$$
(3)

The f<sup>0</sup>'s are the fractions of the total metal concentration in the

organic phase represented by the species indicated by subscripts, and the f's are the fractions of the total aqueous metal concentration represented by the species similarly indicated. The  $f^{\circ}$ 's and f's are themselves functions of the concentrations of  $H^+$ ,  $M^+$ ,  $A^-$ ,  $X^-$ ,  $Z^-$  i.e.

$$f_{M^{+}}^{o} = \frac{\alpha_{MX}}{\sqrt{\alpha_{HX}}} \qquad (M) \qquad \sqrt{\frac{\alpha_{HX}(X) + \alpha_{HZ}(Z) + \alpha_{H,MX_{2}}(MX_{2})}{\alpha_{HX}(H) + \alpha_{AX}(A) + \alpha_{MX}(M)}} / P \qquad (4)$$

Equation (3) is probably best explained by referring to Figure 1 which is a plot of four possible cases. Curve (a) is for the case where there are no dimers present in either phase and no ionic metal containing species in the organic solvent, only MX and HMX<sub>2</sub> in the organic phase and  $M^+$ , MX, MX<sub>2</sub><sup>-</sup>, HMX<sub>2</sub> in the aqueous phase. Curve (b) indicates the same species as in (a) but dimers are also allowed in the organic phase. Curve (c) indicates the same species as (a) but this time dimers are in the aqueous phase. Curve (d) indicates the same species as in (a) but MX<sub>2</sub><sup>-</sup> also possible in the organic phase and  $a_{HXX_2} > a_{HX}$ .

It should be emphasized that the equations derived are for idealized systems in which no changes are assumed to occur in the nature of the organic and aqueous phases caused by variations in the concentrations of substances involved. That is, the two phases are always considered as immiscible liquids which keep their original individual properties throughout and hence the association and concentration constants are considered to be constant. Actually, of course, real



two phase systems are not so ideal and allowance must be made not only for their mutual solubility, but more importantly for the changes in mutual solubility, phase volumes, dielectric constants, etc. which may occur under concentration changes considered.

The experiments described in the next section of this thesis were devised to give the type of information needed to make the kind of analysis described. Thiocyanate was chosen as the ligand for study because it was felt that further data is required to interpret when and where similarities exist between the complex-ion chemistry of thiocyanates and halogens. Cobalt was chosen as the metal ion for this study because of two advantages. Firstly, it is a member of the transition element group which therefore enhances its complexing ability and secondly with the strong radioactivity of Co<sup>50</sup>, radiochemical counting techniques could be used advantageously in distribution studies. Methyl isobutyl ketone was chosen, after a variety of solvents were examined (see section IV), because as noted there it best satisfied the stipulated requirements. With this background we may now proceed to the experimental section.

#### IV. EXPERIMENTAL

Raw Materials: Perchloric acid was obtained from Mallinckrodt Chemical Works. All other acids used in these experiments were Bakers "Analyzed" reagent grade chemicals. Ammonium hydroxide, barium thiocyanate, sodium thiocyanate, cobalt (II) carbonate and cobalt (II) chloride hexahydrate were also obtained from the J. T. Baker Chemical Company. Ammonium chloride, sodium oxalate and sodium hydroxide came from Merck and Company. Sodium perchlorate was obtained from G. Fredrick Smith Chemical Company. Methyl isobutyl ketone, diisopropyl ketone, and n-hexanol were obtained from Eastman Organic Chemicals. Capryl alcohol (2-octanol), n-hexane, and n-butyl ether were obtained from Matheson, Coleman and Bell.  $\beta\beta$ '-dichlorodiethyl ether was purchased from Dow Chemical Company. The radioactive tracer used to follow the cobalt ion in the distribution studies was prepared by Oak Ridge National Laboratory by irradiation of  $Co_2O_3$  with neutrons  $[Co^{59}(n, 3)Co^{60}]$ . Twenty-four millicuries of  $Co^{60}$  were shipped as one gram of solid  $Co_2O_3$ . Upon arrival the Co203 was dissolved in one-hundred milliliters of 6 M hydrochloric acid and stored.

Preparation of Reagents: Cobalt perchlorate was prepared from cobalt carbonate and perchloric acid and recrystallized twice from distilled water. Hexammine cobalt (II) oxalate was prepared according to the procedure as given in <u>Inorganic Syntheses</u> (24). This solid was then used to prepare a weighable form of cobalt (II) sulfate according to the procedure given by Diehl and Butler (25). Cobalt (II) thiocyanate was prepared by a metathetical reaction of cobalt sulfate with barium thiocyanate. Prior to use the barium thiocyanate had been recrystallized from methanol.

Solutions of cobalt (II) perchlorate and cobalt sulfate were made and the cobalt concentration was checked by standard electrolytic procedures (26,27). From these solutions aliquots were taken and diluted in order so as to cover a concentration range of  $10^{-1}$  to  $10^{-4}$  M cobalt. In general cobalt (II) thiocyanate solutions were diluted no further than  $10^{-2}$  M. At this time Co<sup>60</sup> tracer was added to these various stock solutions and their respective specific activities determined by counting in a well-type NaI(TII) scintillation counter.

Sodium perchlorate was recrystallized from distilled water, separated by filtration and dried over a portion of the salt which previously had been dried in an oven at 110 to  $115^{\circ}$ C for 48 hours. A stock solution was made and its concentration determined by evaporating a known volume of solution to dryness, heating to  $160^{\circ}$  to destroy the monohydrate, and weighing. A check showed that this method gave the same result as prolonged heating at  $300^{\circ}$ C. This solution analyzed the same as one prepared by neutralizing a known amount of perchloric acid with reagent sodium hydroxide, and diluting to the required volume.

Standard sodium hydroxide solutions were prepared carbonate free and standardized against potassium acid phthalate. The perchloric acid used was standardized by comparison with sodium hydroxide. Sodium thiocyanate was recrystallized from distilled water. Stock solutions were made and analyzed by conventional gravimetric procedures (28).

All solvents used in the distribution studies were fractionated and a two degree "cut" used. Boiling points and refractive indices obtained from Weissberger (29) were used to check purity. When needed, ultraviolet spectra were compared with standard forms (30).

Distribution and Spectral Studies: The solutions used in the distribution studies were prepared by adding the appropriate amount of stock cobalt solution (either cobalt (II) perchlorate or cobalt (II) thiocyanate, depending upon the thiocyanate concentration range studied), standard perchloric acid solution to adjust the acidity to the desired value, standard sodium thiocyanate solution to adjust the thiocyanate concentration and distilled water to bring the total volume to 25 milliliters. All of the aqueous solutions were adjusted initially to an ionic strength of 1.50 with sodium perchlorate. Exceptions were made in runs 37 through 58, which had an ionic strength of 2.05. A volume of organic solvent equal to the aqueous phase was then added and extraction begun. At no time was either phase pre-saturated with the other before equilibration in the distribution studies.

Solutions were shaken in 50 milliliter Pyrex mixing cylinders equipped with ground glass stoppers. Equilibration was effected by mechanical shaking in a horizontal position in a constant temperature bath maintained at  $25.00 \pm 0.02^{\circ}$ C. The solutions were usually shaken overnight (8-10 hours) more as a matter of convenience than necessity.

It was noted in this study and others (31) that equilibrium was attained in less than one hour of shaking. The cylinders were then placed vertically in the bath and the phases allowed to separate completely. Usually satisfactory phase separation occurred immediately, but for a few difficult cases longer times (1-2 hours) were allowed. The levels of the menisci were noted and only in two instances (runs D and 53 through 58) was any volume change observed. Aliquot portions of each phase were removed for analysis, great care being taken to avoid contamination of one phase by the other.

Two milliliter samples from each phase were pipetted into one dram screw cap vials and  $\delta$  -counted using a well-type NaI (TII) scintillation counter. The ratio of the counting rates of the sample from the organic phase to that from the aqueous phase gives directly the value of the distribution coefficient of cobalt between the two phases. These counting rates were corrected for background; no coincidence correction was necessary at the rates used.

$$D = \frac{c/m \text{ of } 2 \text{ ml. organic phase}}{c/m \text{ of } 2 \text{ ml. aqueous phase}} = \frac{\text{cobalt molarity in organic phase}}{\text{cobalt molarity in aqueous phase}}$$

Duplicate trials from the same cylinder showed that pipetting and counting errors were less than 2%. However, variations between duplicate extractions were somewhat larger, though less than 5%.

Aliquots from each phase were titrated directly with standard sodium hydroxide solution using methyl red as the indicator. Preliminary experiments of back extraction of the acid from the organic phase showed that the end point was unaffected by the presence of the organic solvent. Standard gravimetric procedures for thiocyanate analysis were performed only on the aqueous phase. Attempts to perform the same analysis on the organic phase led to difficulties and were not carried out. Analytical errors for these analysis amounted to less than 2%.

Preliminary extractions were run on various organic solvents for the purpose of choosing the best solvent for the distribution studies. A satisfactory solvent for this research should fulfill the following requirements: (1) have a satisfactory distribution of cobalt (II) complexes in the concentration region to be studied, (2) have a very good immiscibility with the aqueous phase, (3) have a high enough boiling point so that evaporation problems do not become acute.

#### TABLE I

Run	Solvent	D%(x10²)	Remarks
A	n-Hexanol	15.2	Solvent pre-equilibrated with distilled water
В	Diisopropyl ketone	4.02	
C	Methyl isobutyl ketone	41.1	
D	Capryl alcohol .	4.66	Organic phase volume increased
Е	n-Hexane	0	
F	n-Butyl Ether	0	Sulfur at interface H <sub>2</sub> S gas odor
G	ββ' Dichlorodiethyl Ether	0	Sulfur at interface H <sub>2</sub> S gas odor

DISTRIBUTION OF COBALT WITH VARIOUS SOLVENTS (Initial conditions  $(Co^{++}) = 0.0811 \text{ M}_{,}$   $(H^{+}) = 0.750 \text{ M}_{,}$   $(CNS^{-})=0.487 \text{ M}$ )

Of all solvents tested (see Table I) methyl isobutyl ketone was judged most satisfactory. An interesting point which turned up in this preliminary investigation was the incompatibility of thiocyanate with the ethers tested. During the extraction chemical reactions took place which brought about decomposition of the thiocyanate, resulting in the presence of H2S and sulfur at the interface. These solvents when freshly distilled, acted somewhat better taking about eight hours for decomposition to set in. If not freshly distilled, decomposition took place almost immediately. Solvents could be stored over ferrous sulfate for about 24 hours after fractionation without adverse effects. Irving and Rossotti (32) have observed that peroxidation of  $\beta\beta$ 'dichlorodiethyl ether was so rapid that purification and distillation was necessary immediately before use. Nothing further was done to clarify this problem, since the distribution coefficients for both ethers were not suitable for the present studies. All subsequent distribution studies were made using methyl isobutyl ketone as the organic solvent.

Considering the variables of the system; cobalt concentration, thiocyanate concentration, and acidity, experiments were performed in which two of these variables were kept constant and the third varied. In this way the effect of each individual variable was measured. Data for all distribution studies have been compiled and placed in Tables VI to XI of the Appendix.

The effect of varying the acidity of the initial solution was studied by determining the distribution coefficients of cobalt (II) thiocyanate at different initial concentrations while the cobalt and

the thiocyanate concentrations were held constant. Table II presents the results of these extractions.

#### TABLE II

VARIATION OF THE DISTRIBUTION COEFFICIENT WITH ACIDITY

Run	Co <u>M</u> Initial	Acid M Initial	CNS M Initial	Co <u>M</u> Organic	Co <u>M</u> Aqueous	D
37	0.0500	1.00	1,00	0.0392	0,0103	3.82
38	0.0500	0.750	1.00	0.0406	0.00820	4.96
39	0.0500	0.650	1.00	0.0412	0,00757	5.46
40	0.0500	0.500	1.00	0.0427	0.00669	6.39
41	0.0500	0.250	1.00	0.0447	0.00507	8.83
42	0.0500	0.100	1.00	0.0459	0.00493	9.31

It may be seen from these results that the distribution coefficient decreases as the initial acidity is increased, i.e. the distribution coefficient has an inverse dependence on the initial acidity.

The effect of changing the thiocyanate concentration was studied by varying the amount of thiocyanate in solution while the concentrations of cobalt and acidity were held constant. Table III presents the results of one such series of extractions.

It may be seen from these data that the distribution coefficient increases with an increase in the initial thiocyanate concentration. It may be observed then, that the distribution of cobalt (II) thiocyanate between aqueous solution and methyl isobutyl ketone is dependent upon the concentration of thiocyanate present in the aqueous phase.

### TABLE III

			*****	****		
Run	Co M Initial	Acid M Initial	CNS M Initial	Co M Organic	Co M Aqueous	D
7	0.0500	0.100	0,100	0.00136	0.0488	0.0278
8	0.0500	0.100	0,200	0.00666	0.0442	0.151
9	0.0500	0.100	0.300	0.0131	0.0378	0.347

VARIATION OF THE DISTRIBUTION COEFFICIENT WITH THIOCYANATE

In order to learn whether there was any appreciable polymerization or association in either phase, the effect of the cobalt concentration on the distribution coefficient was studied. The resulting data are presented in Table IV.

### TABLE IV

VARIATION OF THE DISTRIBUTION COEFFICIENT WITH COBALT

man have been		and the second	the second s			
Run	Co M Initial	Acid M Initial	CNS M Initial	Co M Organic	Co <u>M</u> Aqueous	D
48	0.0500	1.00	1.00	0,0391	0.0101	3.87
49	0.0250	1,00	1.00	0,0209	0.00352	5.93
50	0.0200	1.00	1,00	0.0171	0.00259	6.60
51	0.0100	1.00	1.00	0.00870	0,00106	8,19
52	0.00500	1,00	1.00	0.00441	0.000476	9.27
54	0.200	0.750	1.00	0.0989	0.104	0.951
55	0.150	0.750	1.00	0.0895	0.0615	1.46
56	0,100	0.750	1.00	0.0723	0.0288	2.51
57	0.0500	0.750	1.00	0.0423	0.00805	5.26
58	0.0250	0.750	1.00	0.0224	0.00268	8.35

These data indicate that for equal initial acidity and thiocyanate concentration, the distribution coefficient increases with decreasing cobalt concentration. The data given in Tables II, III, and IV are presented graphically as Figures 2, 3, and 4.

To determine whether sodium thiocyanate was being extracted or whether thiocyanic acid was the main species extracted, a series of runs were made in which the thiocyanate concentration was varied while acidity was held constant, and in which the acidity was varied as the thiocyanate concentration was held constant. These data are presented in Table V and graphically as Figures 5 and 6.

#### TABLE V

Run	CNS <u>M</u> Initial	Acidity M Initial	CNS <u>M</u> Organic	D <sup>(CNS)</sup> o/(CNS)a
X	0.600	0.500	0.317	1.12
XI	0.500	0.500	0.287	1.35
XII	0.400	0.500	0.250	1.66
XIII	0.300	0.500	0.200	2.00
XIV	0,200	0.500	0.142	2.49
XV	0.100	0,500	0.0757	3.12
III	0,400	0.750	0.295	2.83
XXI	0.400	0,100	0.0740	0.234

### EXTRACTION DATA FOR SODIUM THIOCYANATE







Distribution Coefficient



Justifiaco notiudratil



(orcentration of CNS (organic)


These data show that the concentration of thiocyanate in the organic phase increases rather markedly when either the acidity or the thiocyanate concentrations are increased. This suggests that the thiocyanate which enters the organic phase may do so as either undissociated thiocyanic acid or as sodium thiocyanate. There are such small differences in the character of the data that one is hard put to choose one mechanism over the other.

It was judged important to record and study the visible spectra (400-700 mpl) of both phases as an aid in determining the nature of species in solution and also as possibly shedding some light on their respective stabilities. Samples of both phases were taken after equilibration, and their spectra recorded using a Beckman model DK-2 recording spectrophotometer. Figures 7 and 8 present a typical family of curves for the aqueous and organic phases respectively. There is no change at all in the shape of the aqueous spectra with increased thiocyanate concentration; only an increase in the optical density. Under the same conditions the organic phase spectra shift very definitely from a pink or red color, showing a 520 mp absorption peak to the blue 620 mm absorption peak. This shift has been explained by many (17, 33-36) as a change from the hexa-coordinated aquo and aquothiocyanato complexes, which absorb predominately around 520 mm, to the tetracoordinated tetrahedral thiocyanato complexes which absorb predominately around 620 mµ.

To obtain a clearer picture of the true status of the complex ion species existing in solution, the method of "continuous variation"





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Optical Density

developed by Job (37) is useful. The method is based upon the readily verified relation that on mixing two reagents which form an additive complex, at a fixed total molar concentration, the concentration of the complex is a maximum when the reagents are in the stoichiometric proportion in which they appear in the complex. Plotting a suitable property of the complex against concentration of the reagents should give a maximum at the concentration ratio corresponding to the formula of the complex.

This simple relationship is complicated if more than one complex is formed. Vosburgh and Cooper (38) have pointed out some of the properties of special cases of the system forming two complexes. Katzin and Gebert (39) have given the general relationships which allow extension of the method to the case for three complexes.

Two "continuous variation" determinations were made. The first used methyl isobutyl ketone which had been equilibrated with one molar perchloric acid in order to try and synthesize conditions which exist in the organic phase during the distribution experiments. Total concentration of cobalt perchlorate and sodium thiocyanate was 0.0500 Mfor this run. The second used anhydrous methyl isobutyl ketone and total concentrations of cobalt perchlorate and sodium thiocyanate of 0.0040 M. Raw data for these runs are contained in Tables XV and XVI of the Appendix. The more pertinent aspects of these data are presented in graphical form in Figures 9 and 10.

As noted from Figure 9,  $Co(CNS)_3$  and  $Co(CNS)_6^4$  are the species present in the "wet" methyl isobutyl ketone and from Figure 10,  $Co(CNS)_3^7$ 





concentration 0.0500 <u>M</u> in MIBK/1 <u>M</u> HClO<sub>4</sub>.



Figure 10. Excess density as a function of thiocyanate concentration 0.00400  $\underline{M}$  in MIBK.

and  $Co(CNS)_4^{=}$  are the species indicated in the anhydrous methyl isobutyl ketone. The most unusual part of this work is the existence of a hexa coordinated species in the organic phase. As stated in the historical section only West and DeVries (20) have reported a hexa coordinated cobalt complex ion in a mixed solvent system.

Figures 11 and 12 are plots of the molar extinction coefficient versus thiocyanate concentration for the "wet" and anhydrous ketones respectively. From these it may be seen that the "wet" ketone does not approach any limiting value at any wavelength, while the anhydrous ketone does. The largest molar extinction coefficient for the anhydrous ketone is that for the blue 620 mµ band, leveling off at a value of about 2100.

Figures 13 and 14 are plots of the molar extinction coefficient versus wavelength for the "wet" and anhydrous ketones respectively. These figures show the general shape of the spectra and the wavelength for the maximum absorption peak as the thiocyanate to cobalt ratio varies from 1/1 to 10/1. A noticeable change occurs in the spectra of the anhydrous ketone as the thiocyanate concentration is increased. A shoulder occurring at about 570 mp disappears completely and at higher thiocyanate to cobalt ratios the spectra for both the "wet" and anhydrous ketones are about the same except for intensity.



Figure 11. Molar extinction coefficient as a function of thiocyanate concentration  $(0.0500 \text{ M} \text{ in MIBK/l } \text{M} \text{ HClO}_4)$ .



Figure 12. Molar extinction coefficient as a function of thiocyanate concentration (0.00400  $\underline{M}$  in MIBK).





## V. DISCUSSION

Only one previous attempt (18) has been made to elucidate the species existing in the organic phase of the aqueous cobalt (II) thiocyanate-organic solvent systems. In the discussion that follows, some of the more important aspects of the water-methyl isobutyl ketone system will be pointed out and some conclusions will be made regarding the species present in each phase.

There are a large number of possible species present in each phase. Some of the species which might be considered for this system are Co<sup>++</sup>. Co(CNS)<sup>+</sup>, Co(CNS)<sub>2</sub>, HCo(CNS)<sub>3</sub>, Co(CNS)<sub>3</sub>, H<sup>+</sup>, CNS, HCNS, etc. In the interpretations that follow much must remain qualitative in nature, in that some of the important variables of the system cannot be measured. For example, the "free" metal ion concentration, as such, cannot be determined in either phase. It is only the total metal concentration of each phase which can be analytically determined. The "free" thiocyanate ion cannot be easily determined, although a method utilizing the recently developed silver-silver thiocyanate electrode (40) might possibly give a fair value for this quantity. As with the metal ion it is only the total thiocyanate concentration which can be analytically determined. Also, it was noticed that in these experiments it was not easy to maintain constant ionic strength, therefore not too much can be done with the thermodynamics of this system. With these limitations in mind the experimental results can now be discussed.

The Effect of Acidity on Distribution: When the acidity of the aqueous cobalt (II) thiocyanate solution is increased. the distribution of cobalt between the aqueous solution and methyl isobutyl ketone decreases considerably as can be seen from the data (Table II, Figure 2) in the experimental section. These data may be explained by assuming that complex acids such as  $HCo(CNS)_3$  and/or  $H_2Co(CNS)_4$  are the species extracted. One might expect that since thiocyanic acid is a relatively strong acid (41), the extraction of cobalt thiocyanate complexes would be aided by the presence of this acid. Although this is not the case, it does not of necessity preclude the possible existence of these complex acid species. Recalling the experimental results on the extraction of sodium thiocyanate as a function of acidity (Table V) it will be remembered that no conclusions could be drawn as to whether thiocyanic acid or sodium thiocyanate was the species extracted. Now, assume thiocyanic acid to be the major species extracted and consider the results of the cobalt (II) thiocyanate versus acidity extraction. It may be shown that the extraction of such complex acid species as  $HCo(CNS)_3$  and  $H_2Co(CNS)_4$ , which may ionize, will be decreased if another stronger acid is simultaneously extracted (23).

If only one acid is considered, a thermodynamic distribution coefficient  $K_{E_1}$  may be defined  $K_{E_1} = \frac{(H_2Co(CNS)_4)org}{(H_2Co(CNS)_4)aq}$ . It will be assumed, and rightly so judging from other data (42), that in methyl isobutyl ketone the complex acid can dissociate  $H_2Co(CNS)_4 \longrightarrow H^+ +$   $HCo(CNS)_4^-$ . A concentration equilibrium constant can be written for this ionization  $K_2 = (H^+)_0(HCo(CNS)_4^-)_0/(H_2Co(CNS)_4)_0$ . From this

equation it is seen that if the hydrogen ion concentration of the organic phase is decreased, the concentration of the  $HCo(CNS)_4$  ion must increase. The total concentration of all cobalt containing species for the organic phase is given by  $(Co)_0 = (HCo(CNS)_4)_0 + (H_2Co(CNS)_4)_0$ . The distribution coefficient, D, may now be defined as,

$$D = \frac{(Co)_{0}}{(Co)_{W}} = \frac{(HCo(CNS)_{4})_{0} + (H_{2}Co(CNS)_{4})_{0}}{(Co)_{W}}$$

Comparing D with the thermodynamic distribution coefficient  $K_{E_1}$ , it is noticed that due to ionization there is an additional cobalt containing species present. To satisfy  $K_{E_1}$ , the concentration of cobalt (II) must increase in the organic phase to compensate for that amount lost, as  $H_2Co(CNS)_4$ , through ionization. Therefore, the overall effect of decreasing acidity is that, by promoting ionization, the concentration of the cobalt containing species in the organic phase is increased, which in turn means an increase in the distribution coefficient D.

The effect of acidity may be explained in another way, namely by assuming that the major species extracted is the simple cobalt (II) thiocyanate complex,  $Co(CNS)_2$ . Again a thermodynamic distribution coefficient may be defined  $K_{E_2} = (Co(CNS)_2)_0 / (Co(CNS)_2)_W$ . It will be assumed that in methyl isobutyl ketone the  $Co(CNS)_2$  undergoes ionization,  $Co(CNS)_2 \longrightarrow Co(CNS)^+ + CNS^-$  for which an equilibrium constant may be written  $k = (CNS)_0(Co(CNS)^+)_0 / (Co(CNS)_2)_0$ . By an analysis similar to that given above, it may be concluded that extraction of the thiocyanate ion will in turn decrease the distribution coefficient. It has been previously shown that the extraction of thiocyanate increases with increasing acidity (Table V) and therefore the cobalt distribution will be directly affected.

Whether one chooses the acid repression effect or the common anion effect it must be remembered that one of the main results of increasing acidity is the extraction of thiocyanate ions from the aqueous phase into the organic phase. This overall decrease in the aqueous thiocyanate ion concentration will greatly reduce the amount of cobalt (II) thiocyanate which may cross the boundary and thus effectively decrease its distribution.

<u>The Effect of the Thiocyanate Ion</u>: If the extraction of cobalt (II) thiocyanate involves some type of complex between the cobalt ion and the thiocyanate ion (e.g.  $Co(CNS)_2$ ,  $H_2Co(CNS)_4$ ), changing the concentration of thiocyanate ion in the aqueous phase should have a very definite effect on the distribution coefficient. The data (Table III and Figure 3) in the experimental section indicate a marked change in the amount of cobalt extracted as the initial thiocyanate ion concentration is increased, while the concentration of cobalt is held constant.

A large number of extraction experiments were performed at low thiocyanate to cobalt ratios. In these cases one cannot employ the method of Diamond (21), but rather can draw certain qualitative conclusions from the experimental results. In this respect, that portion of the general treatment given by Irving, Rossotti and Williams (22) which applies to the present discussion, will be utilized where needed. In order to treat the extraction according to this method the free thiocyanate ion concentration after extraction is needed. It will be assumed for this discussion that the "free" thiocyanate ion concentration is equal to or proportional to the total aqueous thiocyanate ion concentration at equilibrium. The important equation needed for the present discussion is the following

log D = A +  $(\overline{m_0}\overline{h_0}-\overline{mh})\log(H) + (\overline{m_0}-\overline{m})\log(M) + (\overline{m_0}\overline{n_0}-\overline{mh})\log(L)$ where A is a constant independent of H, M, and L and can be eliminated by differentiation. H refers to the acid, M refers to the metal and L refers to the ligand. The bars signify average values of the numbers in question. The subscript "o" refers to the organic phase and h, m, and n are subscripts for any acid or polymeric species (e.g.  $H_h M L_n$ ,  $M_m L_n$ ).

At constant metal and hydrogen ion concentration we have

$$\frac{\partial \log D}{\partial \log (L)} = (\overline{m_0 n_0} - \overline{mn})$$

This states that the slope of a graph of log D versus log (CNS<sup>\*</sup>) would give the value  $(\overline{m_0n_0}-\overline{mn})$  which denotes the difference between the average number of thiocyanate ions associated with the complex in the organic phase  $(\overline{m_0n_0})$  and the average number associated with the complex in the aqueous phase  $(\overline{mn})$ . These are average values and are not indicative of the most important species present. Two plots of this type are presented as Figures 15 and 16. From the slopes of the lines the values of the quantities  $(\overline{m_0n_0}-\overline{mn})$  are found to vary from about



Figure 15. Distribution coefficient as a function of the aqueous thiocyanate concentration.

Log D



function of the aqueous thiocyanate concentration.

three at high cobalt concentration (0.050 M) to about two at lower cobalt concentrations (0.020 and 0.010 M). This means that on the average there are three (or two) more thiocyanate ions associated with the complex in the organic phase than there are in the aqueous phase. However, unless the number of thiocyanate ions associated with the complex in one phase is known nothing can be definitely stated about the average number of thiocyanate ions associated with the complex in the other phase.

In the concentration range studied it will be assumed that Co(CNS)<sup>+</sup> is the major species present in the aqueous phase. This assumption is substantiated by noting that Lehné (15) estimates the first association constant  $k_1 \simeq 10^3$  for the association  $Co^{++} + CNS^{-} \longrightarrow Co(CNS)^{+}$  in the aqueous cobalt (II) thiocyanate system while the second is only about one. Based on this assumption, the present treatment leads one to believe that  $Co(CNS)_3$  and  $Co(CNS)_4$  are the major species present in the organic phase. From this and other data, presented on page 32, it appears that the cobalt in the organic phase may be present as anything from Co(CNS)3 to Co(CNS)64. Subtracting three (or two) thiocyanates from the above species in the organic phase to give the species present in the aqueous phase, would imply that anything from Co++ to  $Co(CNS)_4$  might be present in the aqueous phase. Lehné's (15) work suggests that no complex higher than Co(CNS)2 exists in the aqueous phase under the present experimental conditions. Therefore, one must conclude that  $HCo(CNS)_3$  and  $H_2Co(CNS)_4$  are predominant in the ketone. This gives a fairly good picture of the average association of the cobalt complex after the cobalt has entered the organic phase.

The Effect of the Cobalt Ion: It is evident from the graphical presentation of the data (Table IV and Figure 4) that at constant acidity and thiocyanate ion concentration the distribution of cobalt decreases with increasing cobalt ion concentration (retrograde extraction). In order to treat this extraction by the method of Diamond, association equilibria are needed. These data are not available and therefore only qualitative conclusions may be reached. In carrying out the discussion in the light of Diamond's findings the conclusions reached seem more certain than at first anticipated.

With cobalt concentration as the only variable graphs of log D versus log Q have been constructed, where Q is the equilibrium aqueous cobalt ion concentration. These are presented as Figures 17 and 18. Looking back at Figure 1 of the theoretical section it is seen that these graphs have a close resemblance to one of the curves (curve c) and resembles part of another curve (curve d).

Considering the first curve, (c), Diamond states that when such a curve is obtained from a plot of log D versus log Q, the possible existence of the following types are suggested;  $Co(CNS)_2$ ,  $HCo(CNS)_3$ ,  $H_2Co(CNS)_4$  in the organic phase and  $Co^{++}$ ,  $Co(CNS)^+$ ,  $Co(CNS)_2$ ,  $Co(CNS)_3^-$ ,  $HCo(CNS)_3$ ,  $H_2Co(CNS)_4$  and  $Co_2(CNS)_4$  or some other dimer or higher polymer. Ionic metal containing species are not allowed in the organic phase, but as has been previously discussed, at least for this system, the acid species do appear to ionize to a certain extent in the organic phase. With the exception of excluding ionic metal containing species, the allowed species for the organic phase agree with the previous



Log D

49

-



Log D

conclusions. Although it is not of primary concern, dimerization or polymerization does appear a bit unusual for this system. Irving and Rossotti (43), in a recent study on the extraction of indium bromide into methyl isobutyl ketone, have worked out a treatment for polymerization of species in the aqueous phase. A plot of log  $Q_0$  versus log Q(where  $Q_0$  is the equilibrium organic cobalt ion concentration) indicates the extent of polymerization in the aqueous phase. Such a graph is presented as Figure 19. This graph has unit slope at low aqueous cobalt ion concentration but the slope tends towards the value of 0.5 at high cobalt concentration suggesting that dimerization does occur in the more concentrated solution.

The fact that there is only a partial fit to curve (d) is not too serious in that the data presented in this thesis probably do not cover a concentration range large enough to bring out the entire curve. The system represented by this curve allows exactly the same species as for curve (c), in addition allowing ionic metal containing species in the organic phase. At very low metal concentrations the hydrogen ion concentration in both phases is determined by the distribution and dissociation of HCNS or HClO<sub>4</sub> since they are present to the greater extent. In this region the graph approaches a horizontal straight line. As the cobalt ion concentration is increased a point will be reached at which the amount of hydrogen ion brought into the organic phase by the Co(CNS)<sub>3</sub><sup>-</sup> or HCo(CNS)<sub>4</sub><sup>-</sup> will be comparable to that extracting with the CNS<sup>-</sup> or ClO<sub>4</sub><sup>-</sup>. This increase in the organic hydrogen ion concentration common to both anions represses the dissociation of HCNS,





 $HCo(CNS)_3$  and  $H_2Co(CNS)_4$  and when this happens the distribution coefficient decreases. The experimental data fit these conclusions very well and thus add further support for the species chosen.

Brubaker (44), in a recent study on the extraction of tellurium (IV) chloride into  $\beta\beta$ <sup>1</sup>dichlorodiethyl ether presents a treatment similar to Diamond's (21) on retrograde extraction. When applied to the present work, it qualitatively explains the effect of added strong acids in terms of the dissociation of thiocyanic acid and thiocyanato complex acids in the organic phase. The equations have been transformed so that they correspond to the case of cobalt (II) thiocyanate.

If the extracted species are  $Co(CNS)_2$ ,  $HCo(CNS)_3$ , and  $H_2Co(CNS)_4$ , and if the complex acid species dissociate to form  $Co(CNS)_3$  and  $HCo(CNS)_4$ , then the distribution coefficient, D, is

$$D = \frac{(Co(CNS)_2)_0 + (HCo(CNS)_3)_0 + (H_2Co(CNS)_4)_0 + (Co(CNS)_3)_0 + (HCo(CNS)_4)_0}{(Co)_w}$$

where parentheses represent molar concentrations and the subscripts "o" and "w" refer to the organic and water phases respectively. This equation may be rewritten in the form

$$D = K_{D} \left\{ 1 + K_{1}(HCNS)_{0} + K_{4}(HCNS)_{0}^{2} + \frac{K_{1}K_{2}(HCNS)_{0}}{(H^{+})_{0}} + \frac{K_{4}K_{5}(HCNS)_{0}^{2}}{(H^{+})_{0}} \right\}$$

where

$$K_{D} = \frac{(Co(CNS)_{2})_{0}}{(Co)_{W}} \qquad K_{3} = \frac{(H^{+})_{0}(CNS_{0})_{0}}{(HCNS)_{0}}$$
$$K_{1} = \frac{(HCo(CNS)_{3})_{0}}{(HCNS)_{0}(Co(CNS)_{2})_{0}} \qquad K_{4} = \frac{(H_{2}Co(CNS)_{4})_{0}}{(HCNS)_{0}(Co(CNS)_{2})_{0}}$$
$$K_{2} = \frac{(H^{+})_{0}(Co(CNS)_{3})_{0}}{(HCo(CNS)_{3})_{0}} \qquad K_{5} = \frac{(H^{+})_{0}(HCo(CNS)_{4})_{0}}{(H_{2}Co(CNS)_{4})_{0}}$$

Using the above relationships, the organic hydrogen ion concentration is given by

$$(H^{+})_{0} = \left\{ K_{3}(HCNS)_{0} + K_{D}K_{1}K_{2}(HCNS)_{0}(Co)_{W} + K_{D}K_{4}K_{5}(HCNS)_{0}^{2}(Co)_{W} \right\}^{\frac{1}{2}}$$

For the tellurium extraction,  $K_D$  was evaluated from experimental results,  $K_1$  and  $K_4$  were determined spectrophotometrically. Choosing proper values for the K's of the acid ionization equilibria the experimental data could be fit very well to the above equation. It is not unlikely that the extractions studied in this thesis could be explained in a similar manner. Due to the complexity of the system evaluation of  $K_1$ ,  $K_2$ ,  $K_4$ ,  $K_5$  is especially difficult because the spectral properties of these species are not different enough to allow one to distinguish between them.

The ionization and dissociation treatment of Brubaker and Diamond seems to offer the best explanation for this system. It shows a better agreement between the expected behavior of the assumed species  $Co(CNS)_2$ ,  $HCo(CNS)_3$ , and  $H_2Co(CNS)_4$  and the experimental data.

Spectrophotometric Studies: The visible absorption spectra of the organic and aqueous phases were recorded and typical examples have been presented as Figures 7 and 8. The molar extinction coefficients (at 510 and 620 mp) for all solutions have been calculated and are given in Tables XVII and XVIII in the Appendix. In all cases the aqueous phases were red in color and quite typical of the spectra that have been attributed to the hexacoordinated octahedral complex by Katzin (19), Lehné (15) and others. Increases in either the thiocyanate

ion or cobalt ion concentrations caused no perceptible change in the character of the absorption peak nor a shifting of the wavelength of this absorption peak. As further support for Katzin's conclusions, Ballhausen and Jorgensen (45) have shown that, on the basis of ligand-field theory, the red spectrum is in agreement with the octahedral configuration. All the organic phases were blue in color with a maximum absorption at 620 mµ and most had a definite shoulder occurring at 585 mµ. These are in general quite similar to those that Katzin and Ballhausen and Jorgensen attribute to the tetrahedral configuration. As before, changes in either the thiocyanate ion or cobalt ion concentrations did not bring about changes in the character of the spectra, but only in the molar extinction coefficients.

There is a general feeling among previous workers that the major species contributing to this blue color is  $CoX_4^{-}$  where X may be chloride, bromide, or thiocyanate. To check on this a "continuous variation" study was made. When run in anhydrous methyl isobutyl ketone, the study gave evidence for the existence of  $Co(CNS)_3^{-}$  and  $Co(CNS)_4^{-}$ . This result is in accord with Katzin's work and suggests a maximum coordination number of four. However, when "continuous variation" runs were made in methyl isobutyl ketone which had first been equilibrated with 1 M perchloric acid, species with coordination mumber six were definitely indicated. These spectra were all blue except when the thiocyanate to cobalt ratio was less than two. This suggests that in the organic phase there probably are complexes higher than  $H_2Co(CNS)_4$ 

and certainly many of these solutions contained enough thiocyanate to give five or sixfold complexes.

Ballhausen and Jorgensen (45) attribute the 620 mu absorption peak to a ligand-field band for the tetrahedral configuration. In addition their assumptions require that there be two additional bands in the infra-red region at greater than 2.5  $\mu$ . Nujol-mulls of Ba<sub>3</sub>Co(CNS)<sub>4</sub> and Na<sub>2</sub>Co(CNS)<sub>4</sub> did not exhibit these bands. The ketone solutions exhibited an absorption band at about 1.3  $\mu$  but nothing else could be found. Also the extinction coefficient for the 620 mµ band is a little larger than is normally expected for ligand-field bands. These discrepancies do not rule out the tetrahedral configuration for it may be that either the 620 mµ band is not a ligand-field band at all, or that the transition may be different from the one assigned to this band by Ballhausen and Jorgensen (45).

## VI. SUMMARY

The distribution of cobalt (II) thiocyanate complexes between aqueous solutions and methyl isobutyl ketone was studied. It was found that the distribution coefficient decreased as the initial acidity was increased if the initial cobalt and thiocyanate concentrations were kept constant. The distribution coefficient was found to increase with increasing initial thiocyanate concentration at constant acidity and cobalt concentration. Also the distribution coefficient was increased, if the initial acidity and thiocyanate ion concentration were maintained constant.

Analysis of distribution data in terms of dissociation and acid ionization gives evidence for the existence of the species  $Co(CNS)_{2}$ ,  $HCo(CNS)_3$  and  $H_2Co(CNS)_4$  in the organic phase. In the solvent chosen for study (methyl isobutyl ketone) acid dissociation of these complex ion species is quite important, e.g.  $HCo(CNS)_3 \longrightarrow H^{+} + Co(CNS)_3^{-}$ . Extraction of thiocyanate from aqueous sodium thiocyanate solution into methyl isobutyl ketone can also be explained as a common anion phenomenon.

Organic and aqueous phases were examined spectrophotometrically in the visible region. In every case the aqueous phase was red in color and quite typical of spectra that have been associated with the hexacoordinated, octahedral aquo and thiocyanatoaquo complexes. The organic phase solutions were all of the pure blue type which have been attributed to the tetrahedral configuration. The absorption peaks of these blue solutions did not shift noticeably with changes in the cobalt concentration.

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APPENDICES

TABLE VI

ANALYSIS OF SOLUTIONS FROM DISTRIBUTION STUDIES (Initial Cobalt 0.0500 M p = 1.50)

0.678 0.700 5.01 1.99 D<sup>0</sup>/A xl0<sup>2</sup> 15.0 34.9 34.5 Final [Co<sup>++</sup>] xl0<sup>2</sup> A 5.06 ч. С 4.83 4.83 4.33 4.71 5.05 4.71 4.72 4.09 4.08 4.87 4.90 4.42 3.80 4.43 3.77 O Final [Co<sup>++</sup>] xl0<sup>3</sup> 0.496 0.498 0.343 0.354 2.42 7.70 7.80 2.41 3.65 3.69 9.87 9.82 1.35 6.76 6.66 1.37 13.2 1.1 0.0470 0.0469 0.0365 0.0366 0.0611 1190.0 Final [H<sup>+</sup>]<sub>A</sub> 0.590 0,290 0.378 0.378 0.290 0.591 0.510 0.540 0.334 0.488 0.333 0.487 0.0528 0.0586 0.0586 0.0383 0.0386 0.0531 Final [H<sup>1</sup>] 0.166 0.126 0.125 0.215 0.166 0.219 0.172 422.0 0.218 0.268 0.268 171.0 Final [CNS]<sub>A</sub> 0.0747 0.0749 0.0298 0.0219 0.0682 0.0297 0.0632 0.0635 0.0989 0.0475 0.0478 0,0997 0**.**0687 0,11,0 0.206 0111.0 0.206 Final [CNS]0 0.0318 0.0600 0.0779 0.0779 0.0313 0.0600 0.0703 0,0702 0.225 0.225 160°0 0.152 0.152 0.201 0.137 0.201 0.137 0.094 Initial [H<sup>1</sup>] 0.750 0.500 0.100 = Ħ = = ĩ = Ħ = t = = = Ħ F = [CNS] 0.300 0.200 0.300 0.300 0.100 0.200 0.100 0.100 0.200 0.100 0.200 0.300 0.100 0.300 0.100 0.200 0.200 0.300 7 38 8 9**a** Run 38 29 9 ξ Ч  $\sim$
TABLE VII

ANALYSIS OF SOLUTIONS FROM DISTRIBUTION STUDIES (Initial Cobalt 0.0250  $\underline{M}$   $\mu$  = 1.50)

D°∕A xlo² 0.435 0.425 0.845 0.834 2.49 2.49 0.305 0.263 0.818 4.24 4.18 0.801 **l.**22 4.30 **1.23** 4.36 12.4 12.4 Final [Co<sup>+</sup>] xl0<sup>2</sup> A 2.53 2.54 2.50 2.52 2.53 2.51 2.54 2.53 2.49 2.48 2.45 2.141 2.49 2.48 2.42 2.26 2.25 2.41 Final [Co<sup>1</sup>] xl0<sup>3</sup> 0.0665 0,0777 OIL.O 0.108 0.252 0.305 0.254 0.305 0.213 0.211 0.203 0.201 1.04 **1.02** 7**.0**4 1.05 2.80 2.78 0.0496 0.0499 0.0682 0.0684 0.0581 0.0585 Final [H<sup>+</sup>]<sub>A</sub> 0.616 0.616 0.398 0.398 0.343 0.3114 0.590 0.588 0.561 0.365 0.561 0.364 0.0406 0.0486 0,0409 0.0313 0.0481 Final [H<sup>1</sup>] LLEO.O 0,128 0,110 0412.0 0.102 0.102 0.129 0.154 0.154 0,168 0.166 0,195 0.194 0.00994 0.0450 Final [CNS]<sub>A</sub> 0.0103 0.0195 0.0193 0.0309 0.0306 0.0139 0.0139 Q.0293 0.0292 0.0455 0.0335 0.0337 0,0689 0.0686 0.105 401.0 Final [CNS]0 0.0165 0.0450 0.0708 0.0460 0.0163 LIEO.O 1150.0 0.0805 0.0361 0.0363 0.0707 0.0397 0.0501 0.0807 0.10J 0.105 6Tť.0 0.119 Initial [H] 0.500 0.100 0.750 = = = t = = = = t = = F Initial [CNS] 0.0500 0.0500 0.0500 0,0500 0.0500 0.0500 0.100 Ò.150 0.150 0.150 0.100 0.150 0.150 0.100 0.100 0.150 0.100 0.100 16а 17**a** 18**a** 15a 12a 13**a** Jla Run 108 lla 16 18 Ц 13 72 h ħ 5 口

TABLE VIII

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ANALYSIS OF SOLUTIONS FROM DISTRIBUTION STUDIES (Initial Cobalt 0.0200 M  $\mu = 1.50$ )

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Run	Initial [CNS]	Inițial [H <sup>†</sup> ]	Final [CNS <sup>7</sup> ] <sub>0</sub>	Final [cns] <sub>A</sub>	Final [H <sup>+</sup> ]o	Final [H <sup>+</sup> ] <sub>A</sub>	Final [Co <sup>+</sup> ]o xlo <sup>3</sup>	Final [Co <sup>±</sup> ] <sub>A</sub> x10 <sup>2</sup> A	D <sup>0</sup> /A x10 <sup>2</sup>
19	0.0400	0,750	0.0321	0.00789	0.138	0.618	0.0487	2.04	0,239
19 <b>a</b>	0,0400	E	0.0321	0.00789	0.138	0.616	0.0487	2.05	0.238
20	0.0800	Ħ	0.06111	0.0156	0.159	0.594	0.0920	2.02	0.455
20a	0.0800	E	0.0646	0.0154	0,160	0.596	0.0916	2.02	0.453
21	0.120	E	0.0957	0.0243	0.182	0.567	0.224	2.01	1.11
21a	0.120	Ħ	0.0957	0,0243	0.181	0.566	0.226	2.01	1.12
22	0,00400	0.500	0.0307	0.00934	0.0937	0.402	0.0448	2.03	0.221
22 <b>a</b>	0,00400	F	0.0306	0.00938	0,0940	0.399	0.0443	2.05	0.216
23	0.0800	ŧ	0.0593	0.0207	0.113	0.382	0.105	2.02	0.520
23 <b>a</b>	0,0800		0.0591	0.0209	<b>1</b> 11.0	0.380	0,100	2.00	0.500
24	0.120		0.0888	0.0312	0.JJ2	0.354	0.369	2.00	1.85
21µa	0.120	11	0.0886	0.0314	0.141	0.356	0.366	1.99	1.84
25	0,00400	0.100	0.0139	0.0261	0.0296	0,0707	0.0958	1.99	0.480
25 <b>a</b>	0.0000	E.	0.0137	0.0263	0.0299	0.0709	0.108	2.00	0.540
26	0.0800	11	0.0272	0.0528	0.0380	0.0622	0.500	1.97	2.53
2 <b>6a</b>	0.0800	ŧ	0.0269	0.0531	0.0378	0.0622	0.504	1.97	2.53
27	0.120	Ŧ	0.0382	0.0818	0.0451	0.0538	1.48	1.89	7.82
27 <b>a</b>	0.120	=	0.0384	0.0816	0.0449	0.0542	1.49	1.88	1.91

TABLE IX

ANALYSIS OF SOLUTIONS FROM DISTRIBUTION STUDIES (Initial Cobalt 0,0100 M  $\mu$  = 1.50)

D°/A xlo<sup>2</sup> 206 208 211 212 272 268 229 222 355 352 392 389 202 570 138 136 229 523 Final [co<sup>+</sup>] 0.998 0.992 0.995 166.0 166.0 0.988 0.986 0.984 1.02 1.01 1.03 1.03 1.02 1.01 1.01 1.01 1.00 1.00 0 Final [Co<sup>+</sup>] xl0<sup>3</sup> 0.0210 1120.0 0.0215 0,0216 0.0228 0.0222 0.0352 0.0388 0.0570 0.0349 0.0384 0.0204 0.0227 0.0553 0.271 0.275 0.136 0.134 0.0716 0.0657 0.0664 0.0775 0.0781 7170.0 0.636 0.635 Final [H<sup>+</sup>]<sub>A</sub> 0.394 0,612 0.418 0.406 0.419 0.407 0.394 0.624 0.623 0.611 0.0806 0.0215 0.0218 0.0276 0.0812 0.0899 0.0905 0.0333 0.0277 0,0331 Final [H<sup>1</sup>]0 0.146 0.102 0,102 0,120 44L.0 0.133 0.133 0.121 0.00279 0.00478 0.00702 0.00860 0,00281 0.00708 0.00476 0.00862 0,0100 0.0139 Final [CNS]<sub>A</sub> 0.0137 0.0122 0.0254 0.0252 0,0407 LOLO.0 0.0123 1010.0 0.00780 0.00780 0.0146 0.0148 0.0193 0,0196 Final [CNS]<sub>0</sub> 0.0463 0.0172 0.0329 0.0330 0.0152 0.0152 4LE0.0 0.0461 0,0172 0.0500 4LE0.0 0.0499 Initial [H<sup>+</sup>] 0.500 0.100 0:750 = = = Ħ = = = = ŧ = F = = = = [CNS] 0,0400 0.0600 0.0600 0.0200 0010.0 0.0600 0.0400 0.0200 0.0200 0.0400 0.0600 0.0200 0.0600 0.0200 0.0200 0.0400 0.0400 0.0600 36**a** 3lia Э5а 32**a** 33a 3**Ja** Run 28**a** 29**a** 30**a** 36 ы М 30 Ч 32 £ 34 28 59

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TABLE	

ANALYSIS OF SOLUTIONS FROM DISTRIBUTION STUDIES

gun	Initial [CNS <sup>-]</sup>	Initial [H <sup>+</sup> ]	Final [CNS] <sub>0</sub>	Final [CNS] <sub>A</sub>	Final [H <sup>+</sup> ]o	Final [H <sup>+</sup> ] <sub>A</sub>	Final [Co <sup>+1</sup> ]o xlo <sup>2</sup>	Final [Co <sup>++</sup> ] <sub>A</sub> xl0 <sup>2</sup> ] <sub>A</sub>	D°;/A
37	1.00	1.00	( <u>Initial</u> 0.718	Cobalt 0.05 0.282	$500 \text{ M} \mu = 2$ 0.630	<u>.05)</u> 0.366	3.92	1.03	3.82
38	1 <b>.</b> 00	0.750	0.634	0.366	0.529	0.215	4.06	0.820	4.96
39	1.00	0.650	0.588	0.412	0.471	0.164	4.12	0.757	5.46
0 <sup>t</sup> l	1.00	0.500	0.509	0.491	0.383	0.103	4.27	0.669	6.39
בלן	1.00	0.250	0.359	0.641	0,203	0.0387	4.47	0.507	8.83
<u>4</u> 2	1.00	0,100	0.262	0.738	0.0813	2440.0	4.59	0.493	9.31
43	1,00	1.00	( <u>Initial</u> 0.669	Cobalt 0.00	0.655 μ =	2.05) 0.331	0.439	4.67	9.45
$\frac{1}{1}$	1.00	0.750	0.574	0.426	0.562	0.178	0.457	2.83	16.2
45	1.00	0.500	0.427	0.573	כֿדון.0	0.0769	0.467	о†∙г	33.4
J46	1.00	0.250	0.224	0.756	0.224	0.0236	0.487	0.550	88.9
47	1 <b>.</b> 00	0.100	0,115	0.885	0.0924	0.00707	0.494	0.281	176

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TABLE XI

ANALYS IS OF SOLUTIONS FROM DISTRIBUTION STUDIES

107.0 0.951 D°/A 6.60 8.19 3.87 5.93 9.27 J.46 2.51 5.26 8.35 Final [Co<sup>+</sup>] x10<sup>2</sup> A 0.0476 0.106 0.352 0.259 0.268 0.805 1.01 2.88 6.15 74.7 10.4 Final [Co]<sub>0</sub> x10<sup>2</sup> 0.870 1441.0 2.09 1.71 3.91 9.89 8,95 7.23 4.23 2.24 10.3 <u>2.05)</u> 0.296 0.368 0.350 0.253 0.230 Final [H<sup>+</sup>] A 0.343 0.335 0.279 0.261 0.220 0.329 Ь, Ħ Final [H<sup>1</sup>] 0.669 0.654 0.1496 0.518 0,628 0.647 0.664 0.1469 0.1485 0.529 0.750 M ≥ 11 Final [CNS]<sub>A</sub> 0.310 0.300 0.305 0.312 0.322 0.330 0°599 0.388 [H<sup>+</sup>] 0.296 0.357 0.282 E Initial tial Final [CNS] o 0.670 0.690 0.612 0.688 0.678 0.701 0.700 0.643 0.695 0.718 0.704 0,00500 Initial [Co] 0010.0 0.0200 0.0250 0.0500 0.0250 0.0500 0.250 0.200 0.150 0°100 [CNS] 1.00 ۲. 8 1**.**00 1.00 1.0 1,00 1.00 9°-1 1.00 1**.**00 1.00 Run <u>.</u> Ю 56 5 л Л 53 48 49 25 ድ С С 겂

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TABLE XII

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ANALYSIS OF SODIUM THIOCYANATE-ACIDITY DISTRIBUTION (Initial [H<sup>+</sup>] = 0.750 M -  $\mu$  = 1.50)

Run	Initial [CNS <sup>-</sup> ]	Final [H <sup>+</sup> ] <sub>0</sub>	Final [H <sup>+</sup> ] <sub>A</sub>	Final [CNS] <sub>0</sub>	Final [CNS] <sub>A</sub>	[cns]d <sup>o</sup> /A
ii	0.600	0.435	0.325	0.395	0.205	1.93
La	0.600	0.429	0.323	0.397	0.203	1.96
II	0.500	0.384	0.372	0.353	7,41,0	2.40
IIa	0.500	0.384	0.370	0.350	0.150	2.33
TII	0.400	0.335	ענון•0	0,296	0.104	2.85
IIIa	0.1400	0.336	0.416	0.295	0.105	2.81
ΔI	0.300	0.285	0.469	0.232	0.0685	3.39
IVa	0.300	0.285	0.467	0.232	0.0683	. 3.40
Λ	0.200	0.230	0,523	0,161	0.0395	4.08
Va	0.200	0.231	0.523	0,161	0.0394	14 .09
TΛ	0,100	0.172	0.586	0.0826	0.017h	4.75
VIA	0,100	0.173	0.583	0.0827	6710.0	4.78
VII	0.0800	0.160	0.592	0.0684	0.0116	5,89
VILA	0.0800	0,160	0.593	- 0,0680	0.0120	5.67
, IIIV	0.0600	0.1L5	0.604	0.0512	0.00876	5.85
VIIIa	0.0600	0,1146	0.605	0.0512	0.00884	5.80
XI	0.0400	0.135	0.616	0.0346	0,00542	6.38
DX.B.	0,0400	0.135	0.616	0.0346	0.00538	6.42
		•				

TABLE XIII

[CNS]D<sup>0</sup>/A 1.10 1.39 1.70 1.14 1.30 1.62 2.49 2.49 3.60 1.97 2.01 3.17 3.07 3.68 3.96 3.88 4.06 ł Final [CNS]<sub>A</sub> 16700.0 0.0575 0.0246 0.0575 0.0240 1710.0 4710.0 0.0123 0.0121 0.280 0.286 0.209 0.100 0.748 0.101 0.153 0.217 ł ANALYSIS OF SODIUM THIOCYANATE-ACIDITY DISTRIBUTION (Initial [H<sup>+</sup>] = 0.500  $\underline{M}$   $\mu$  = 1.50) Final [CNS]o 0.0760 0.0626 0.0398 0.0754 0.0629 0.0479 0.0477 0.0321 0.320 0.252 0.742 0.142 0.283 0.199 0.200 4LE.0 0.291 0.247 = 0.500 M Final [H<sup>+</sup>] 0.268 0.171 0.170 0.268 0.195 0.193 0.228 0.225 0.317 0.315 0.371 0.369 0.379 0.379 0.392 0.391 0.405 0.104 0,0951 0.108 Final [H<sup>1</sup>] 0.332 0.118 0.231 0.180 0.130 0.132 711.0 0.107 0.183 0,328 0.270 0.232 0.303 0.305 0.273 I Initial [CNS] 0.0000 0.0800 0.0800 0.0600 0.0600 0°°0000 0.100 0,100 0.400 0.300 0.300 0.200 0.200 0.600 0.600 0.500 0.500 0.400 XVIIIA XVIIa XVa XVIa XIIIA XIVa Xa XIa XIIa XVIII XV IVX XVII XIII XI XII XIV Run ×

TABLE XIV

ANALYSIS OF SODIUM THIOCYANATE-ACIDITY DISTRIBUTION (Initial [H<sup>4</sup>] = 0.100 M  $\mu$  = 1.50)

[CNS]D<sup>0</sup>/A 0.161 0.199 0.208 0,220 0,161 0.234 0.288 0.295 0.389 0.380 0.540 0.548 0.618 0.598 0.623 0.619 0.745 0.738 Final [CNS]<sub>A</sub> 0.0650 0.0646 0.0498 0.0502 0.0370 0.0235 0.0371 0.0236 0.231 0.145 0.519 0.328 0.324 0.233 0.417 4411.0 0.517 414.0 Final [CNS]<sub>3</sub> 0.0830 0.0830 0.0760 0.0230 0.0830 0.0860 0.0720 0,0670 0.0690 0.0560 0.0550 0.0350 0.0354 0,0302 0.0298 0.0229 0.0175 4710.0 0.0186 0.0618 0.0730 0.0176 0.0215 0.0218 0.0259 0.0408 0.0412 0.0565 0.0569 0.0675 0,0255 0.0314 0.0621 1730.0 0.0313 0.0734 Final [H<sup>+</sup>]<sub>A</sub> 0.0378 0.0336 0.0274 0,0270 0.0786 0.0680 0.0428 0.0776 0.0738 0.0582 0.0391 0.0333 0.0734 0.0684 0.0584 0.0431 0.0785 0.0779 Firal [H<sup>+</sup>] Initial [CNS] 0010.0 0,0800 0.0800 0.0600 0,0600 0.0400 0.100 0.200 0.100 0.200 0.600 0.500 0.1400 0.300 0.600 0.500 0.1400 0.300 XXVIa XXIVa XXVa XXVIIa XXIIa XIXa XXa XXIa XXIIIa IVXX XXVII XXV XXII XXIII XXIV XXI XIX 双 Run

TABLE XV

DATA FOR "WET" KETONE CONTINUOUS VARIATIONS (Total Concentration 0.0500 M)

í ,	·		
v	4.80 20.4 50.2 105 234 234 264	Ŷ	0.75 3.40 20.0 20.0 12.1 20.0 415.0 415.0
0.D. 580 mpi	0.160 0.160 0.00 0.00 0.00 0.00 0.00 0.0	0.D. 680 mp.	0.025 0.085 0.250 0.250 0.250 0.250 0.250 0.250 0.250
Ψ	117.55 89.80 1119 89.80 1119 89.80 1119 89.80 1119 1119 1119 1119 1119 1119 1119 11	ų	4.50 19.6 1116 1116 1115 1116 1116 234 234 264
0.D. 560 mµ	0.175 0.390 0.650 0.650 0.650 0.850 0.850 0.850 0.850	0.D. 660 mp.	0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150 0.150000000000
ę	6.30 17.1 224.0 224.0 29.9 29.9 29.9 29.9 29.9 29.9	JU .	8.71 40.4 133 228 228 228 133 229 225 133 229 225 133 229 225 133 229 225 133 229 225 133 229 225 133 229 225 133 229 225 228 227 228 228 228 228 228 228 228 228
0.D. 540 mp	0.210 0.275 0.250 0.200 0.250 0.200 0.250 0.250	0.D. 640 mp.	0.29 2.25 2.25 2.25 2.25 2.25 2.25 2.25 2
Ψ	7.50 9.40 10.0 112.0 128.0 112.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 129.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 128.0 100.0 100.0 100.0 100.0 100.0 100.0 100	Ψ	9.15 1142 245 245 245 245 245 2605 231 2605
0.D. 520 Jap	0.235 0.150 0.150 0.150 0.150 0.100 0.100 0.100	0.D. 620 mp	2.95 2.15 2.15 2.15 2.95 2.95 2.95 2.95 2.95 2.95 2.95 2.9
		IJ	7.60 36.0 105 184 281 281 396 396
0.D. 500 mu		0.D. 600 mp.	0.255 0.900 1.75 2.30 2.35 2.35 2.35 2.10
(x1 <u>0</u> 2)	2.33 2.55 2.55 2.55 2.55 0.66 0.683 0.65 71 25 0.65 71 25 0.57 25 0.57 25 0.57 25 0.57 25 0.57 55 0.57 55 0.57 55 0.57 0.57 0.55 0.55	·	233 250 00 1555 00 1555 00 1555 00 1555 00 1555 00 1555 00 1555 00 1555 00 1555 00 1555 00 1555 00 1555 00 1555 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 15566 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1556 00 1500 15

<sup>0.</sup>D. = optical density **£** = molar extinction coefficient

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TABLE XVI

DATA FOR ANHYDROUS KETONE CONTINUOUS VARIATION RUN (Total Concentration  $l_{1}.00 \times 10^{-3} \text{ M}$ )

	0.D. 500 mu		0.D. 520 mp	Ų	0.D. 540 mp	Ψ	0.D. 560 mp	Æ	0.D. 580 mp	Ψ
			0.045 0.050 0.010 0.005 0.005 0.005 0.005	16.9 25.0 35.0 35.0 12.5 8.77 8.77	0.060 0.0140 0.1140 0.035 0.035 0.025 0.025	22.4 47.5 105 140 143.8 143.8 37.5 37.5	0.075 0.160 0.280 0.360 0.170 0.115 0.125	28.1 80.0 80.0 250 250 251 281 250 250 250	0.070 0.155 0.155 0.105 0.640 0.565 0.1400 0.380	28.1 77.5 919 962 989 989
	0.D. 600 mp.	Ą	0.D. 620 mpi	IJ	0.D. 640 mp	f	0.D. 660 mpi	V	0.D. 680 mpi	ę
Ομομο	0.570 0.280 0.540 0.875 0.970 0.875 0.970 0.570	1137 1100 1100 1100 1100 1100 1100 1100	0.145 0.370 0.755 0.755 0.755 0.755 0.755 0.755 0.755 0.750	54.4 185 768 21230 2022 2028 2022 2022 2022 2022 2022	0.160 0.1405 0.820 1.24 0.820 0.820 0.620 0.570	60.0 11240 11534 1138 11425 11425	0.120 0.315 0.610 0.400 0.175 0.175 0.175 0.175 0.175	457 157 157 157 156 1447 1413 1413	0.040 0.100 0.200 0.200 0.050 0.030 0.015 0.015	17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 17500 175000 17500 17500 175000 175000 175000 175000 175000 175000 175000 175000 175000 175000 175000 175000 175000 175000 175000 175000 175000 175000 175000 175000 1750000000000

0.D. = optical density **E** = molar extinction coefficient

## TABLE XVII

Run	Optical Density Aqueous - 515 mu	E	Optical Density Organic - 620 mm	E
l	0.430	8.50	0.310	90.
2	0.465	9.63	3.80	1570
3	0.540	12.4	15.0	1950
4	0.460	9.13	0.580	117
5	0.560	11.9	5.70	1575
6	0.640	15.7	30.	3049
7	0.560	11.5	1.90	141
8	0.700	15.8	9.20	1400
9	0.730	19.2	35.	2660
10	0.200	7.90	0.017	157
11	0,220	8.73	0.195	920
12	0.250	10.0	0.360	1440
13	0.190	7.49	0.035	522
14	0.245	9.80	0.445	1438
15	0.290	11.8	1.70	1650
16	0.240	9.67	0.185	974
17	0.330	13.7	1.60	1540
<b>.18</b>	0.380	16.9	4.45	1590

SPECTRAL DATA OF SOLUTIONS (Corrected to 1.00 cm Light Path)

E = molar extinction coefficient

## TABLE XVIII

	*****			
Run	Optical Density Aqueous - 515 <b>m</b> u	E	Optical Density Organic - 620 mµ	E
19	0.136	6.73	0.009	185
20	0.160	7.93	0.064	697
21	0.170	8.41	0.255	1130
22	0.125	6.16	0.011	247
23	0.165	8.17	0.094	940
24	0.190	9.50	0.450	1227
25	0.155	7.75	0.065	660
26	0.205	10.4	0,610	1210
27	0.240	12.8	1.90	1270
28	0.052	5.10	<b>2</b> 2.42	
29	0,060	5.88	0.003	140
30	0.063	6.20	0,011	403
31	0.070	7.00	-	
32	0.078	7.87	0.006	172
33	0,086	8.70	0.020	519
34	0.076	7.52	800.0	371
35	0.094	9.40	0.043	767
36	0.114	11,6	0.170	1260

SPECTRAL DATA OF SOLUTIONS (Corrected to 1.00 cm Light Path)

E = molar extinction coefficient