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## The Kinetics of the Metal Exchange Reaction between Biseminodiacetonickelate (II) and Copper (II)

Stephen H. Erickson

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THE KINETICS OF THE METAL EXCHANGE REACTION  
BETWEEN BISIMINODIACETATONICKELATE(II) AND COPPER(II)

by

Stephen H. Erickson

A Thesis  
Submitted to the  
Faculty of The Graduate College  
in partial fulfillment  
of the  
Degree of Master of Arts

Western Michigan University  
Kalamazoo, Michigan  
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Stephen H. Erickson

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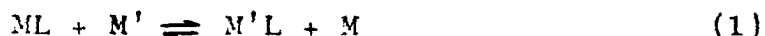


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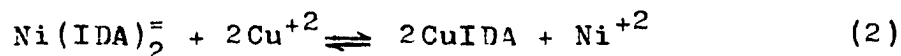
## INTRODUCTION

Multidentate ligand transfer between two metal ions, as represented by equation 1, has been the subject of extensive study for a variety of metal ion combinations and aminocarboxylate ligands (1-12).

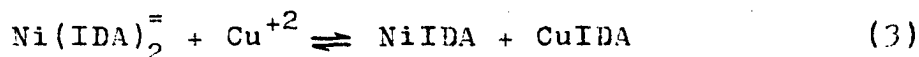


Detailed studies of these reactions have shown the mechanism to follow the successive breaking of a series of coordinate bonds from the metal-ligand complex, followed by a stepwise coordination to the attacking metal (1-3, 5-8, 11). This process leads to the formation of a dinuclear intermediate found in all cases where sterically possible (4,9,10) followed by breakup to form products. The stability of each reaction intermediate relative to the reactants can be estimated from the stability constant of the coordinated ligand segments to each metal and terms estimating electrostatic attraction or repulsion. The ratio of rate constants of two systems can be approximated by the ratio of relative stability constants for the dinuclear intermediates involved (3). The location of the rate-determining step is a function of metal ion concentration and the hydrogen ion concentration (7,11).

The present investigation was undertaken to establish what effect a coordinated ligand has upon the rate of metal attack on a second coordinated ligand. The reaction between bisiminodiacetonickelate(II),  $\text{Ni}(\text{IDA})_2$ , and copper(II), shown in equation 2,



where IDA is  $\text{HOOCCH}_2\text{NHCH}_2\text{COOH}$ , served as a model system. It was found that the reaction proceeded in two steps: a fast reaction represented by equation 3, and a slower reaction represented by equation 4.



This investigation demonstrates that the above reactions do proceed through dinuclear intermediates, that the structure of the intermediates could be estimated from the relative stability constants of the coordinated segments involved, and that the rate-determining step is dependent on the initial copper and hydrogen ion concentrations. It is interesting to note the profound influence that the second coordinated iminodiacetate group has on reaction 3 as compared to reaction 4.

## APPARATUS AND REAGENTS

### Apparatus

All spectrophotometric measurements were made in ten centimeter cells on a Cary Model 14 spectrophotometer. The spectrophotometric cells were maintained at  $25^{\circ}\text{C} \pm 0.1$  in the spectrophotometer with water jacketed cell holders.

The spectrophotometer settings for all measurements were as follows: wavelength-685 nm, dynode-2, slit control-20, slit height-20 mm, spectral slit width-programmed which varied from 0.175 to 0.325 depending on the concentration of the reagents, source-tungsten, and the chart speed was varied from 1 inch per minute to 1/3 inch per minute. The wavelength calibration was accurate to  $\pm 5 \text{ \AA}$  and the spectrophotometric accuracy was good to  $\pm 0.003$  absorbance units.

All pH measurements were made with a Beckman Research Model 110 pH meter. A glass-calomel electrode pair was used. In the reference electrode sodium chloride was substituted for potassium chloride to avoid any interference due to the precipitation of potassium perchlorate.

## Reagents

All solutions were prepared from deionized water that had been prepared by passing distilled water through a deionizing column of Amberlite MB-3 mixed bed resin.

### Primary standard copper nitrate

Baker Analyzed Reagent copper foil (99.96% pure) was cleaned and rinsed with dilute nitric acid. The foil was further rinsed with water and ethanol and then dried. A weighed portion was dissolved in a minimal amount of concentrated nitric acid and diluted to volume.

### Ethylenediaminetetraacetic acid (EDTA)

Reagent grade ethylenediaminetetraacetic acid (99.0% pure) from the Baker Co. was further purified by two successive recrystallizations from ethanol and water. The EDTA solution was standardized at pH 10 by titration against the primary standard copper nitrate solution using murexide as the indicator (13).

### Iminodiacetic acid (IDA)

Reagent grade iminodiacetic acid disodium salt monhydrate was obtained from Eastman Organic Chemicals. The IDA was further purified by two successive recrystallizations from hot water with the addition of enough sodium hydroxide to effect precipitation. The IDA

solution was standardized by titration against a carbonate free sodium hydroxide solution using bromcresol purple as the indicator, and by potentiometric titration against a carbonate free sodium hydroxide solution.

Copper perchlorate, nickel perchlorate

Copper and nickel perchlorate were obtained from the G. Frederick Smith Chemical Company as hexahydrates. Both solutions of copper perchlorate and nickel perchlorate were standardized by titration against a standard EDTA solution using murexide as the indicator (13).

$\text{Cu(IDA)}_2$ ,  $\text{Ni(IDA)}_2$

$\text{Cu(IDA)}_2$  and  $\text{Ni(IDA)}_2$  solutions were prepared by adding an aliquot of either the standard copper or nickel perchlorate solution to a standard solution of IDA. The amount of copper or nickel present in the solution is a 5% molar excess of  $1/2$  as many moles of IDA. The pH of the solutions were raised to pH 9 to allow completion of the reaction and then raised to pH 11.5 to precipitate the excess metal as its hydroxide. The excess metal hydroxide was removed by filtering the solutions through a millipore filter assembly using  $0.45\mu$  paper. For storage the pH of remaining solutions was lowered to a value where both complexes exhibit their maximum stability.

The  $\text{Ni(IDA)}_2$  solution was standardized spectrophotometrically at pH 9 by measurement of the absorbance of the complex at 578 nm. The molar absorptivity was obtained from a standard  $\text{Ni(IDA)}_2$  solution prepared from standard nickel perchlorate and an amount of standard IDA in a 5% excess of twice as many moles of nickel perchlorate.

The  $\text{Cu(IDA)}_2$  solution was also standardized spectrophotometrically at 680 nm at pH 9.0. The molar absorptivity was obtained from a standard  $\text{Cu(IDA)}_2$  solution prepared from standard copper perchlorate and an amount of IDA in a 5% excess of twice as many moles of copper perchlorate.

#### CuIDA

The CuIDA solution was prepared by adding a 5% molar excess of standard copper perchlorate to a standard iminodiacetic acid solution. The pH of the solution was raised to pH 6.0 to allow completion of reaction and then raised to pH 11.5 to precipitate the excess copper as its hydroxide. The solution was filtered through a millipore filter assembly using 0.45  $\mu$  paper to remove the excess copper. For storage the pH of the remaining solution was lowered to the pH where the complex exhibits its maximum stability.

The CuIDA solution was standardized spectrophotometrically at 720 nm at pH 9.0. The molar absorptivity was obtained from a standard CuIDA solution prepared from standard copper perchlorate and a 5% molar excess of IDA.

All other chemicals were reagent grade and used without further purification.



## EXPERIMENTAL

### Spectrophotometric Study of Reactants and Products

The absorption spectra of all reactants and products were obtained from 400 nm to 800 nm. To follow the course of the reaction, a wavelength of 685 nm was chosen. This corresponds to a maximum absorption of CuIDA with minimal contribution from the other species.

The molar absorptivities of all species were determined at 685 nm. The ionic strength of all solutions was adjusted to 1.25 with sodium perchlorate so that the rate constants in this study could be compared to those obtained in previous work. The molar absorptivities are listed in Table 1.

### Reaction Rates and Conditions

All rates of reaction of equation 2 were studied by following the increase in absorbance due to the formation of CuIDA. Since there is no net change in the number of protons in the reaction (see equation 2), no buffer was necessary. The pH of the reactants was adjusted using perchloric acid and sodium hydroxide. The pH of the solution remained constant throughout the entire course of the reaction as was demonstrated by monitoring the pH as the reaction proceeded.

TABLE 1

MOLAR ABSORPTIVITIES AT 685 nm,  $\mu = 1.25$ , 25.0°C

<u>Species</u>	<u>Concentration, M</u>	<u>Cell Length, cm</u>	<u>Molar</u>	
			<u>Abs.</u>	<u>Absorptivity</u>
Ni (II)	$1.074 \times 10^{-2}$	10	0.199	1.85
Cu(II)	$1.103 \times 10^{-2}$	10	0.572	5.19
Ni(IDA) <sub>2</sub>	$1.074 \times 10^{-2}$	10	0.198	1.84
NiIDA	$1.074 \times 10^{-2}$	10	0.193	1.80
Cu(IDA) <sub>2</sub>	$1.103 \times 10^{-2}$	1	0.442	40.1
CuIDA	$1.103 \times 10^{-2}$	1	0.806	73.1

A 20 to 250 fold excess of copper over  $\text{Ni(IDA)}_2$  was present in all cases. This corresponds to a 10 to 125 fold excess of copper since two  $\text{CuIDA}$  are formed from every  $\text{Ni(IDA)}_2$ . The experimental conditions used in all reaction rate studies are given in Table 2.

To initiate the reactions, an aliquot of stock copper perchlorate was pipetted into a 150 ml beaker. Enough stock sodium perchlorate was added to give an ionic strength of 1.25 upon dilution to the final volume. The solution was adjusted to the desired pH with perchloric acid and sodium hydroxide. The copper and stock  $\text{Ni(IDA)}_2$  solutions were placed in a constant temperature bath. At the time of the investigation, the copper solution was poured into a 250 ml beaker which was placed on a magnetic stirrer. With a syringe an aliquot of stock  $\text{Ni(IDA)}_2$  was injected into the stirred copper solution. The recorder to the spectrophotometer was turned on at the same time. The resulting solution was mixed for approximately five seconds before being transferred to a ten cm spectrophotometric cell.

The reactions were followed for at least 3 half lives or approximately 45 minutes. Some reactions were followed for 10 half lives to check for reversibility. No evidence of a reverse reaction was found in these cases.

TABLE 2

## EXPERIMENTAL CONDITIONS USED FOR ALL RATE STUDIES

Reactants:	$\text{Ni(IDA)}_2 = 2.45 \times 10^{-5} \text{ to}$ $4.21 \times 10^{-4} \underline{\text{M}}$ $\text{Cu} = 4.91 \times 10^{-4} \text{ to}$ $1.31 \times 10^{-1} \underline{\text{M}}$
Ionic Strength:	$\text{NaClO}_4, 1.25 \underline{\text{F}}$
pH Range:	3.83 to 4.49
Temperature:	$25.0 \pm 0.1^\circ\text{C}$
Wavelength:	685 nm
Cell Path Length:	10 cm

## RESULTS

### Kinetic Expression for Reaction

The rate expression tested by plotting the data was a simple first-order expression shown in equation 5.

$$\frac{-d[\text{Ni}(\text{IDA})_2]}{dt} = k_o[\text{Ni}(\text{IDA})_2] \quad (5)$$

where  $k_o = k[\text{Cu}]$ . Equation 5 integrates to

$$\ln[\text{Ni}(\text{IDA})_2]_t = \ln[\text{Ni}(\text{IDA})_2]_o - k_o t \quad (6)$$

where the subscripts  $t$  and  $o$  refer to time  $t$  and zero respectively.

An expression, equation 7, can be derived, see Appendix, which relates the concentration of  $\text{Ni}(\text{IDA})_2$  at any time to the final absorbance,  $A_\infty$ , the absorbance at any time  $t$ ,  $A_t$ , the molar absorptivities of reactants and products, and the cell path length,  $b$ .

$$[\text{Ni}(\text{IDA})_2] = \frac{A_t - A_\infty}{b(\epsilon_{\text{Ni}(\text{IDA})_2} - 2\epsilon_{\text{CuIDA}} - \epsilon_{\text{Ni}} + 2\epsilon_{\text{Cu}})} \quad (7)$$

Plots of  $-\ln(A_\infty - A_t)$  versus time showed an initial curve followed by a linear portion. An example is shown in Figure 1. The linear portion showed first-order dependence in a nickel iminodiacetate species and a slow rate constant,  $k_s$ , was calculated from the slope. To demonstrate that the curvature in Figure 1 was due to an initial faster reaction, the contribution of the slower

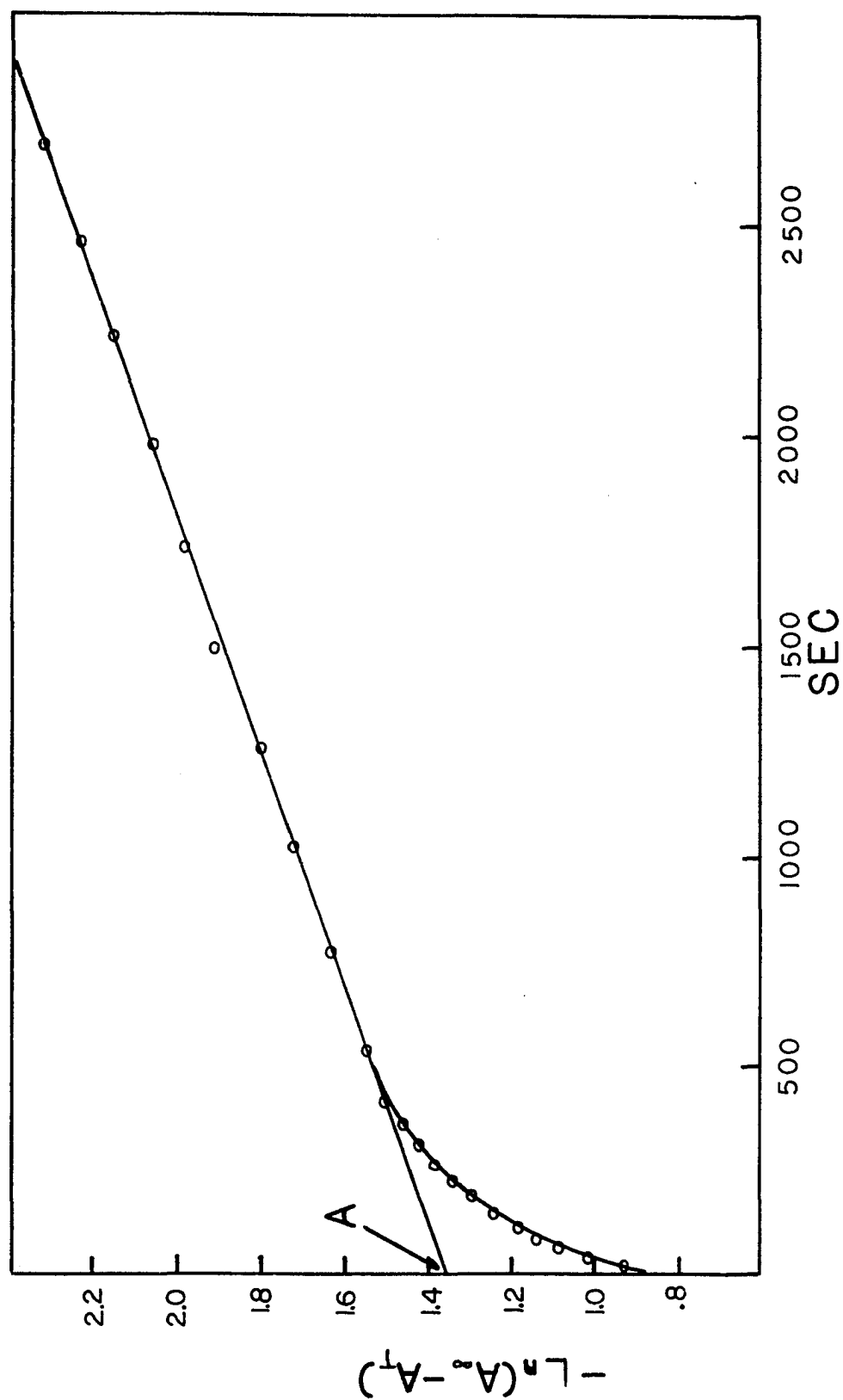


Figure 1. First-order plot of  $k_s$  also demonstrating initial curvature.

reaction was subtracted from the faster one by plotting  $-\ln(A_\infty - A_t - A_0)$  versus time (14).  $A_0$  is the y intercept of the linear portion of Figure 1. An example of this is shown in Figure 2. This also demonstrates a first-order dependence in a nickel iminodiacetate species, from which a fast rate constant,  $k_f$ , was calculated. All values of  $k_s$  and  $k_f$  are listed in Table 3 for various concentrations of copper ion and hydrogen ion. Also listed are the average values of  $k_s$  and  $k_f$  for each set of conditions. From this point on, only the average value will be used.

With the appearance of two first-order rate constants, it is believed that the reaction takes place in two steps.



where equation 8 represents the faster reaction and equation 9 represents the slower reaction. To further demonstrate this, if the initial sharper curved portion of Figure 1 is extrapolated to the point where it becomes parallel to the time axis, corresponding to an  $A_\infty$  for the fast reaction, the extrapolated absorbance agrees well with that predicted assuming NiIDA and CuIDA are the products. Also, the observed  $A_\infty$ , seen at the end of the reaction agrees well with that predicted assuming  $\text{Ni}^{+2}$

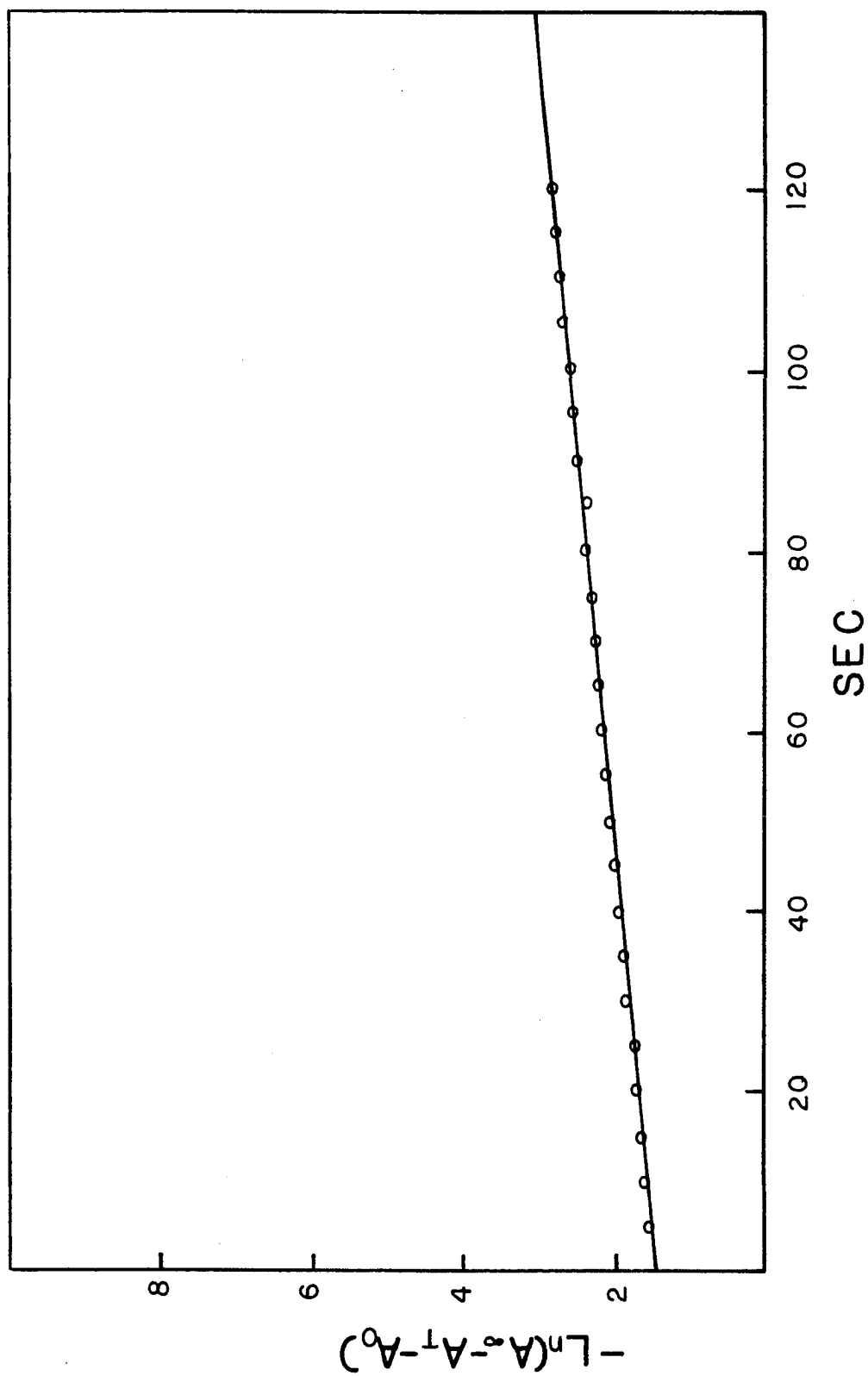


Figure 2. First-order plot of  $k_f$ .



and CuIDA are the products. Finally, equation 9 represents the work of a previous study to which the results obtained here can be compared (6). The values of  $k_s$  agree very well with values obtained in the previous work under the same conditions.

#### Resolution of Rate Constants for Slow Reaction

The values of  $k_s$  are pH dependent as can be seen by comparing the values of  $k_s$  at various pH's at a constant copper concentration. Plots of  $k_s$  versus  $H^+$  at constant copper concentrations, one of which is shown in Figure 3, were all linear. Their slopes represented a first-order term in hydrogen,  $k_H^{NiIDA}$ , and their intercepts the possibility of two terms, a copper dependent exchange and a hydrogen independent dissociation.

Table 4 lists these values. As can be seen, the values of  $k_H^{NiIDA}$  vary, but not in any regular fashion. The scatter can be attributed to lack of data, only three points being available at each constant copper concentration. The average value of  $k_H^{NiIDA}$  is  $0.95 \pm .35 \text{ M}^{-1} \text{ sec}^{-1}$  which agrees very favorably with the value of  $1.20 \text{ M}^{-1} \text{ sec}^{-1}$  obtained by Bydalek (6).

Table 4 also shows a direct dependence of the intercept on copper concentration. The values of  $k_s$  can be corrected for their hydrogen ion dependence by subtracting out the term  $k_H^{NiIDA} [H^+]$ . A plot of the corrected values

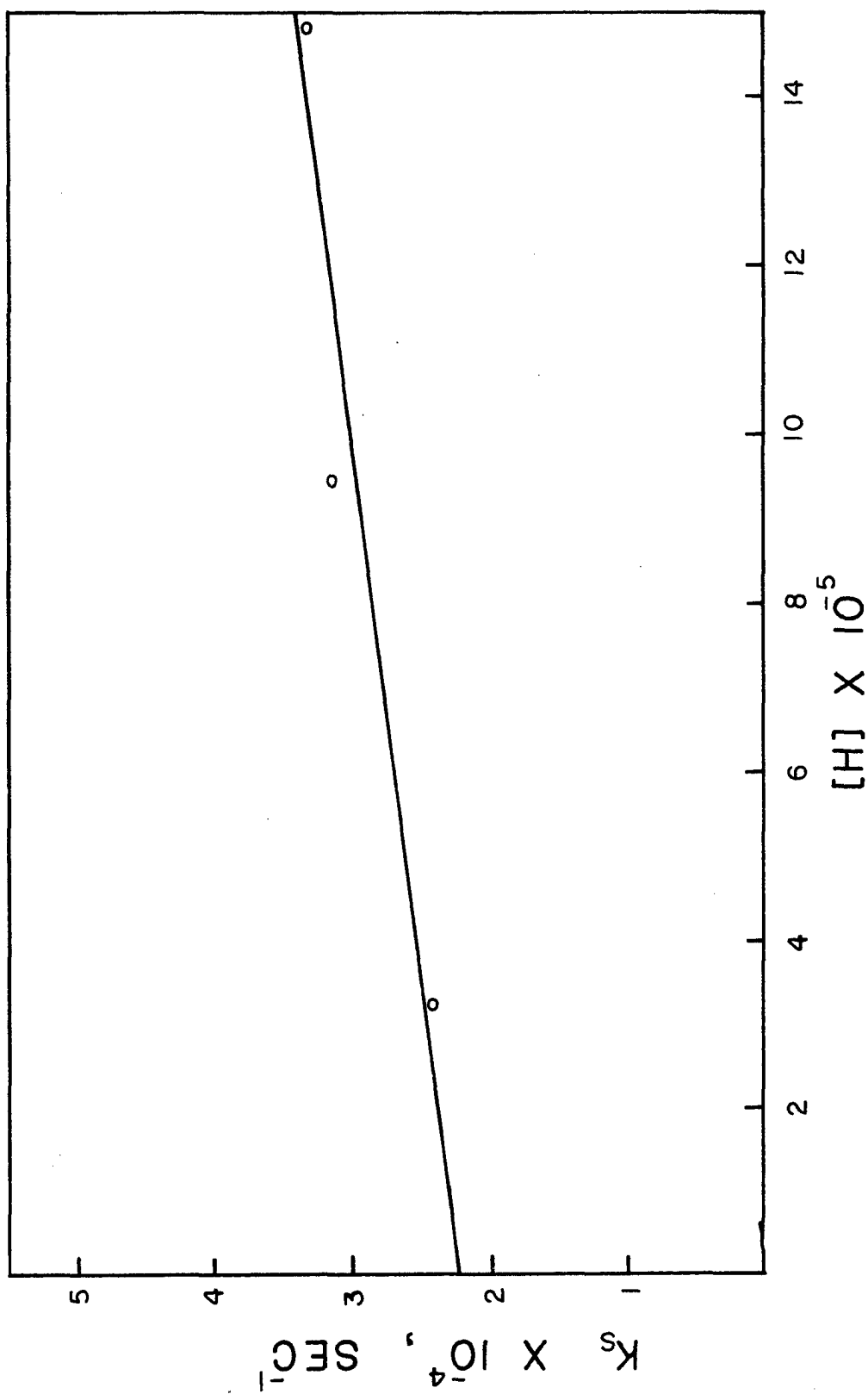


Figure 3. Resolution of the rate constant  $k_H^{\text{NiIDA}}$

TABLE 3

Observed Values of  $k_s$  and  $k_f$  for Various  
Concentrations of Copper Ion and Hydrogen Ion

pH 3.83

$[Cu] \times 10^2, M$	$[Ni(IDA)_2] \times 10^4, M$	$k_s \times 10^4, \text{sec}^{-1}$	$k_f \times 10^2, \text{sec}^{-1}$	Ave. $k_s \times 10^4, \text{sec}^{-1}$	Ave. $k_f \times 10^2, \text{sec}^{-1}$
.0491	.245	1.81	.582	2.23	.487
.0491	.245	2.43	.660		
.0491	.245	2.46	.651		
.109	.494	2.56	.710	2.60	.717
.109	.494	2.15	.682		
.109	.494	3.10	.758		
.217	.816	3.28	.997	3.34	1.03
.217	.816	3.39	1.02		
.330	1.66	3.18	.957	3.28	1.09
.330	1.66	3.37	1.23		
.421	1.98	3.80	1.23	3.79	1.25
.421	1.98	4.23	1.36		
.421	1.98	3.33	1.16		
.656	3.26	3.50	1.06	4.54	1.20
.656	3.26	3.44	1.14		
.656	3.26	3.33	1.08		
.656	3.26	4.57	1.20		
.656	3.26	3.82	1.16		
.656	3.26	5.23	1.59		

TABLE 3 (continued)

.874	4.12	5.54	1.39	5.08	1.44
.874	4.12	4.77	1.54		
.874	4.12	4.92	1.38		
1.34	4.12	3.36	1.20	4.97	1.25
1.34	4.12	4.50	1.18		
1.34	4.12	3.64	1.24		
1.34	4.12	5.44	1.38		
1.75	4.12	6.07	1.88	6.05	1.98
1.75	4.12	5.95	2.00		
1.75	4.12	6.13	2.06		
2.51	4.12	5.83	1.98	5.89	2.03
2.51	4.12	6.60	2.08		
2.51	4.12	5.23	2.03		
3.49	4.12	6.57	2.42	7.72	2.73
3.49	4.12	7.93	3.14		
3.49	4.12	7.52	2.62		
4.15	4.12	7.58		7.68	2.02
4.15	4.12	7.77	1.74		
4.15	4.12	8.47	2.30		
5.47	4.12	10.1	3.00	11.5	3.27
5.47	4.12	12.1	3.96		
5.47	4.12	12.4	2.85		
7.00	4.12	11.2	3.46	14.4	3.72
7.00	4.12	17.7	3.97		

TABLE 3 (continued)

10.1	4.12	14.0	4.10	18.3	4.45
10.1	4.12	19.3	4.82		
10.1	4.12	21.7	4.44		
pH 4.03					
.0496	.250	2.66	.505	2.40	.566
.0496	.250	2.15	.627		
.113	.494	2.50	.629	2.21	.620
.113	.494	2.50	.599		
.113	.494	2.14	.632		
.211	1.00	2.65	.775	3.12	.832
.211	1.00	3.24	.991		
.211	1.00	3.30	1.08		
.211	1.00	3.27	.890		
.325	1.75	3.12	.918	3.29	.950
.325	1.75	3.46	.981		
.420	2.00	3.05	.926	3.01	.925
.420	2.00	3.00	.916		
.420	2.00	2.99	.932		
.666	3.24	3.51	1.16	3.53	1.15
.666	3.24	3.58	1.18		
.666	3.24	3.49	1.10		

TABLE 3 (continued)

.872	4.21	3.83	1.21	3.80	1.19
.872	4.21	3.79	1.17		
.872	4.21	3.77	1.20		
1.33	4.21	4.19	1.39	4.18	1.39
1.33	4.21	4.07	1.39		
1.33	4.21	4.28	1.39		
pH 4.49					
.0496	.250	2.11	.330	1.92	.400
.0496	.250	1.73	.408		
.0496	.250	1.02	.392		
.113	.494	1.88	.392	1.98	.588
.113	.494	2.08	.581		
.113	.494	1.98	.594		
.211	1.00	2.32	.621	2.41	.638
.211	1.00	2.37	.685		
.211	1.00	2.53	.609		
.325	1.75	2.55	.715	2.53	.732
.325	1.75	2.63	.736		
.325	1.75	2.42	.746		
.420	2.00	2.20	.827	2.25	.816
.420	2.00	2.22	.809		
.420	2.00	2.08	.813		

TABLE 3 (continued)

.420	2.00	2.34	.656		
.666	3.24	3.10	.984		
.666	3.24	3.36	1.08	3.17	1.00
.666	3.24	3.06	.948		
.872	4.21	3.49	1.08	3.53	1.13
.872	4.21	3.59	1.16		
.872	4.21	3.51	1.16		
1.33	4.21	4.16	1.28	4.20	1.35
1.33	4.21	4.25	1.37		
1.33	3.21	4.19	1.39		

TABLE 4

Data for the Resolution of  $k_s$  Into  $k_H^{\text{NiIDA}}$ All Values at 25°C,  $\mu = 1.25 \text{ M}$ 

$[\text{Cu}^{+2}] \times 10^3 \text{ M}$	$[\text{H}^+] \times 10^4 \text{ M}$	$k_s \times 10^4 \text{ sec}^{-1}$	Intercept	Slope = $k_H^{\text{NiIDA}} \text{ M}^{-1} \text{ sec}^{-1}$
1.13	0.320	1.98	$1.78 \times 10^{-4}$	0.530
1.13	0.943	2.21		
1.13	1.48	2.60		
2.11	0.320	2.41	$2.22 \times 10^{-4}$	0.811
2.11	0.943	3.12		
2.11	1.48	3.34		
3.25	0.320	2.53	$2.43 \times 10^{-4}$	0.662
3.25	0.943	3.29		
3.25	1.48	3.28		
4.20	0.320	2.25	$1.80 \times 10^{-4}$	1.32
4.20	0.943	3.01		
4.20	1.48	3.79		
6.66	0.320	3.17	$2.68 \times 10^{-4}$	1.32
6.66	0.943	3.53		
6.66	1.48	4.54		
8.72	0.320	3.53	$2.94 \times 10^{-4}$	1.52
8.72	0.943	3.80		
8.72	1.48	5.08		
13.3	0.320	4.20	$3.86 \times 10^{-4}$	0.645
13.3	0.943	4.18		
13.3	1.48	4.97		

Ave. =  $0.95 \pm .35$



versus copper concentration, shown in Figure 4, was linear with all pH's fitting the same curve. Further, the linear behavior held true over an extended copper concentration range as shown in Figure 5. The slope of the line is a first-order copper dependent term,  $k_{\text{Cu}}^{\text{NiIDA}}$ , and the intercept, a copper and hydrogen independent dissociation,  $k^{\text{NiIDA}}$ . The values  $k_{\text{Cu}}^{\text{NiIDA}} = 1.81 \times 10^{-2} \pm .33 \text{ M}^{-1} \text{ sec}^{-1}$  and  $k^{\text{NiIDA}} = 1.45 \times 10^{-4} \pm .17 \text{ sec}^{-1}$  calculated from this study also agree well with those found by Bydalek (6) of  $k_{\text{Cu}}^{\text{NiIDA}} = 2.0 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$  and  $k^{\text{NiIDA}} = 1.7 \times 10^{-4} \text{ sec}^{-1}$ .

#### Resolution of Rate Constants for Fast Reaction

Table 3 shows that  $k_f$  varies directly with both hydrogen and copper ion concentrations. However, since other nickel aminocarboxylate copper exchange systems have shown an unusual copper dependence (7,11), varying from first to zero and back to first-order, and since  $k_f$  for equation 8 may also involve this dependency, treatment of the  $k_f$  data to resolve  $k_{\text{H}}^{\text{Ni(IDA)}}_2$  as was done above for  $k_s$  would not be successful because the slope would represent the sum of two hydrogen dependent terms which can not both be resolved. Nevertheless, it is most likely that the copper independent terms,  $k_{\text{H}}^{\text{Ni(IDA)}}_2$  and  $k^{\text{Ni(IDA)}}_2$  are contributing to the observed values of  $k_f$ . These terms can be calculated and the  $k_f$  values corrected for them resulting in a  $k_f$  value which depends only on copper ion.

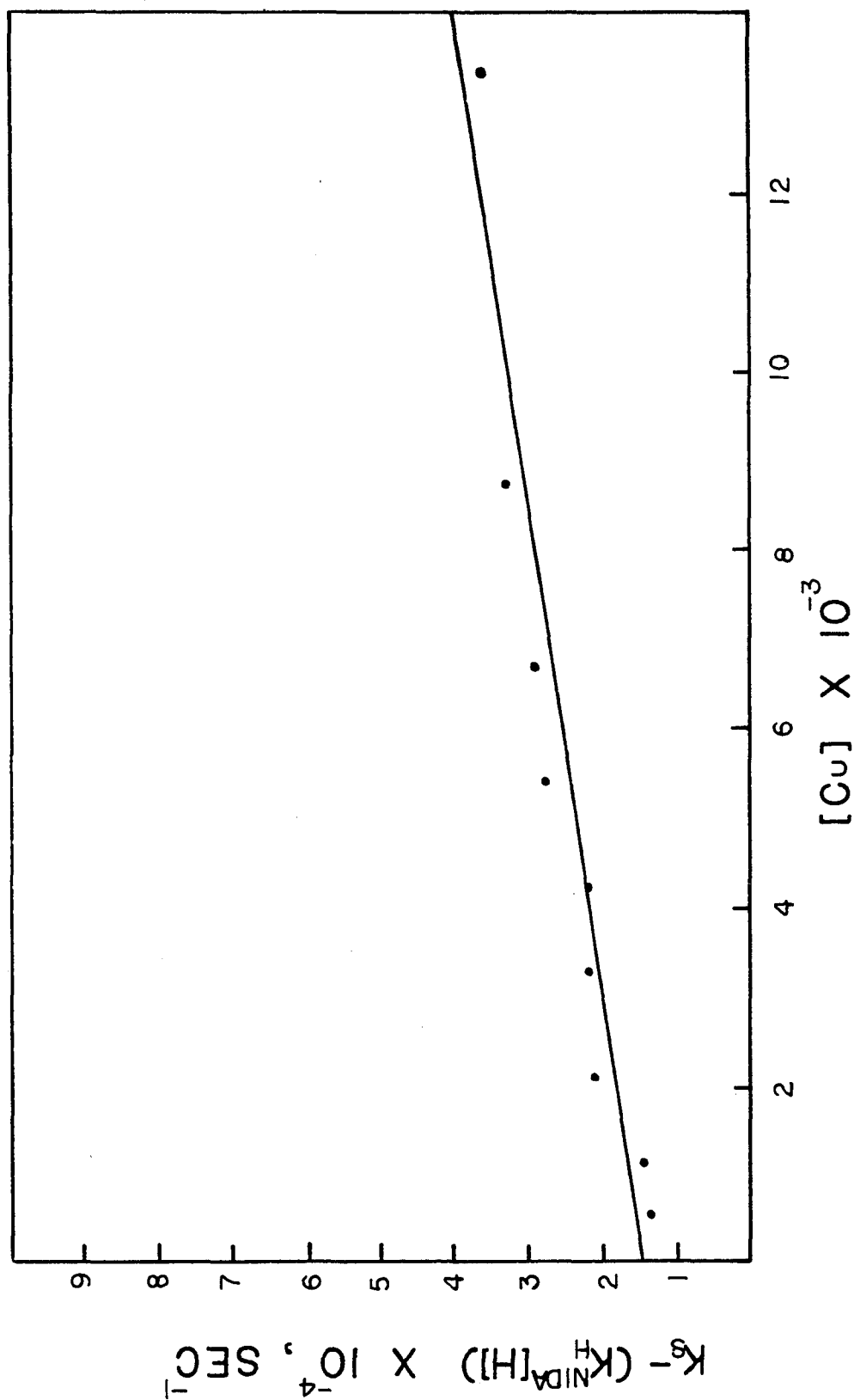


Figure 4. Resolution of  $k_{Cu}^{NiIDA}$  and  $k_{NiIDA}$

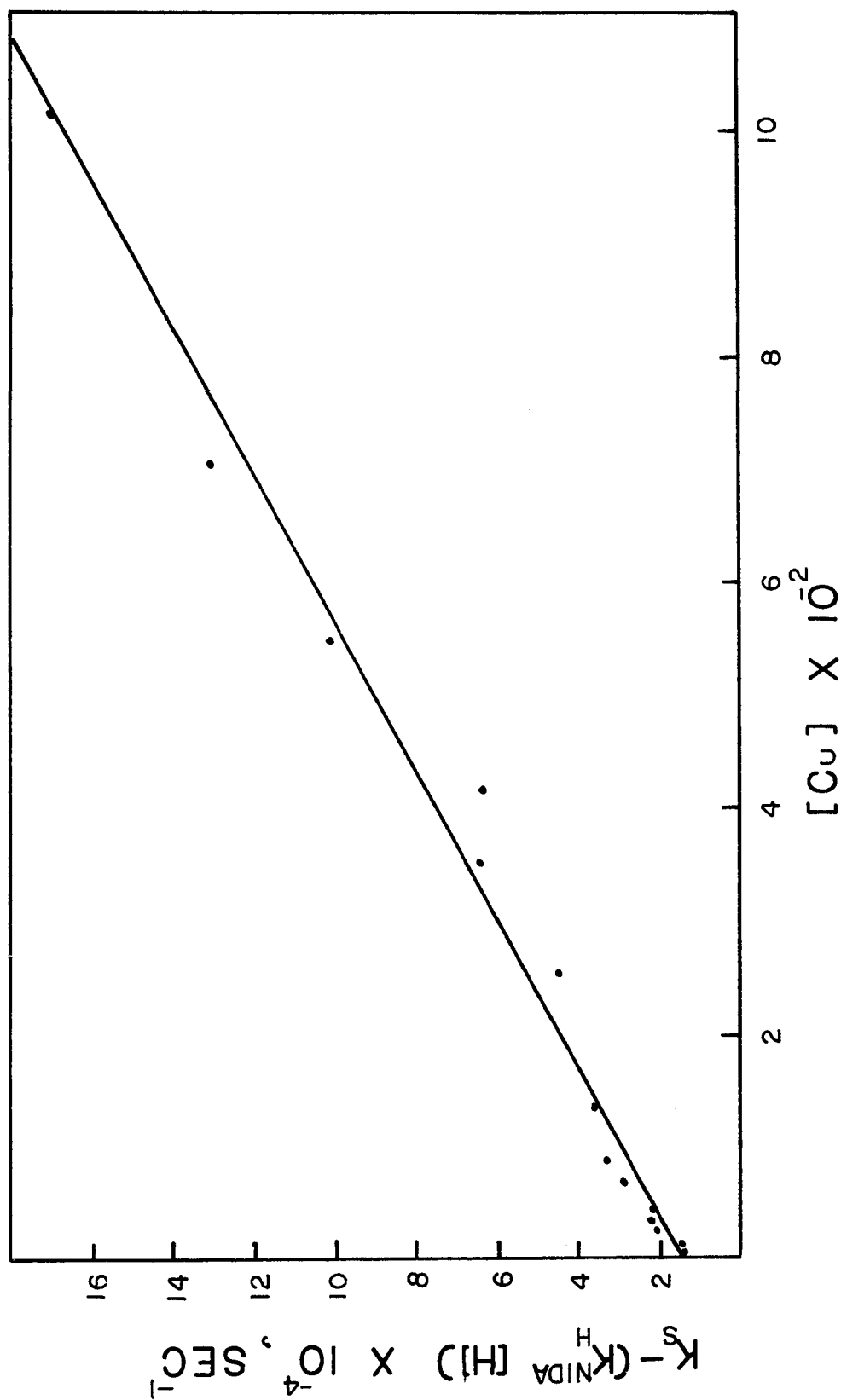
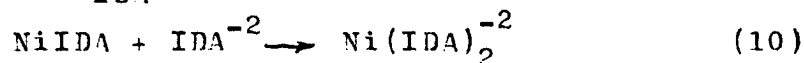


Figure 5. Corrected  $k_s$  over extended copper concentration.

The value of  $k^{\text{Ni(IDA)}_2}$  can be calculated from knowledge of  $K_{\text{Stab}}$  and  $k_{\text{IDA}}^{\text{NiIDA}}$  for equation 10.



The value of  $K_{\text{Stab}}$  is  $6.39 \times 10^6$  (15) and  $k_{\text{IDA}}^{\text{NiIDA}}$  may be calculated using a general mechanism and an equation suggested by Rorabacher (16).

$$k_{\text{IDA}}^{\text{NiIDA}} = \frac{K_{\text{os}} k^{\text{NiIDA-H}_2\text{O}} k_2^{\text{NiIDA-H}_2\text{O}}}{k^{\text{Ni-oac}}} \quad (11)$$

The value of  $K_{\text{os}}$  may be calculated using the equation for outer-sphere complex formation (17) assuming the center-to-center distance of closest approach between NiIDA and  $\text{IDA}^{-2}$  to be  $3.5 \text{ \AA}$  (3). Thus,  $K_{\text{os}}$  is  $0.16 \text{ M}^{-1}$  at  $25^\circ\text{C}$ . The value of  $k^{\text{NiIDA-H}_2\text{O}}$  has been measured to be  $5 \times 10^4 \text{ sec}^{-1}$  (18) and, although  $k_2^{\text{NiIDA-H}_2\text{O}}$  has not been experimentally measured, workers have estimated a 20-40 fold decrease for  $k_2^{\text{NiIDA-H}_2\text{O}}$  compared to  $k^{\text{NiL-H}_2\text{O}}$  due to the rotational barrier around the coordinated oxygen of a 2-amino ethanol (19,20). The situation involving IDA is quite similar with the exception of a carbonyl oxygen. The carbonyl oxygen causes about a 3 fold decrease, analogous to the difference between  $k_{\text{Ni}}^{\text{TKED}}$  and  $k_{\text{Ni}}^{\text{THPED}}$  which involves a methyl group (16). The factor of  $40 \times 3$  is therefore most appropriate, making  $k_2^{\text{NiIDA-H}_2\text{O}} = 4.1 \times 10^2$ . The value of  $k^{\text{Ni-oac}}$  has been measured to be  $5 \times 10^3$  (21). Thus,  $k_{\text{IDA}}^{\text{NiIDA}} = 6.4 \times 10^2 \text{ M}^{-1} \text{ sec}^{-1}$  and

$$k_{\text{Ni(IDA)}_2} = \frac{k_{\text{NiIDA}}}{K_{\text{Stab}} \text{Ni(IDA)}_2} = \frac{6.4 \times 10^2}{6.4 \times 10^6} = 1 \times 10^{-4} \quad (12)$$

The value of  $k_{\text{H}}^{\text{Ni(IDA)}_2}$  will differ from  $k^{\text{Ni(iDA)}_2}$  by the same factor as  $k_{\text{H}}^{\text{NiIDA}}$  and  $k^{\text{NiIDA}}$  differ (6) since the presence of hydrogen serves only to protonate the dissociated nitrogen of IDA thus preventing reformation of the chelate ring. This occurs to the same extent whether a second undissociated IDA is present or not. Thus,

$$\frac{k_{\text{H}}^{\text{Ni(IDA)}_2}}{k_{\text{H}}^{\text{Ni(IDA)}_2}} = \frac{k_{\text{H}}^{\text{NiIDA}}}{k^{\text{NiIDA}}} = 7000 \quad (13)$$

and  $k_{\text{H}}^{\text{Ni(IDA)}_2} = .7 \text{ M}^{-1} \text{ sec}^{-1}$ .

Values of  $k_f$  can now be corrected for a copper independent dissociation path by subtracting

$$k_d = (k^{\text{Ni(IDA)}_2} + k_{\text{H}}^{\text{Ni(IDA)}_2} [\text{H}^+]) = (1 \times 10^{-4} + 7 \times 10^{-1} [\text{H}^+]).$$

Plots of the corrected  $k_f$  values versus the copper concentration for a given pH, shown in Figures 6 - 8, demonstrate that as the copper concentration was increased a marked decrease in copper dependence appeared which seems to approach a zero-order behavior in copper. However, as the copper concentration was further increased, a second first-order copper dependence appears before the zero-order dependence is fully realized, as seen in Figure 9 for pH 3.8.

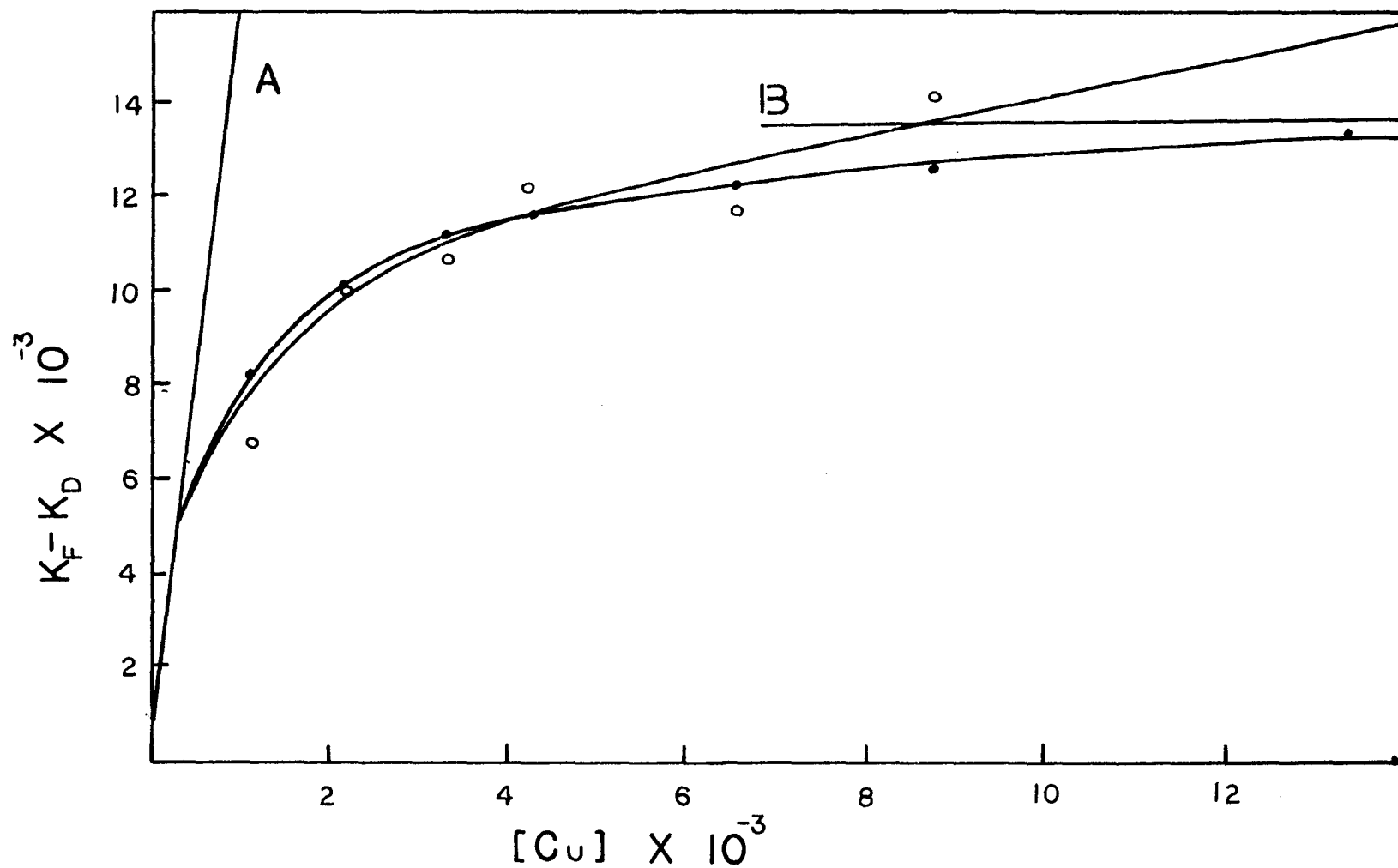


Figure 6. Effect of copper concentration on corrected  $k_f$ , pH 3.83  
Line B and curve with solid dots are theoretical values; line A and curve with circles are experimental values.

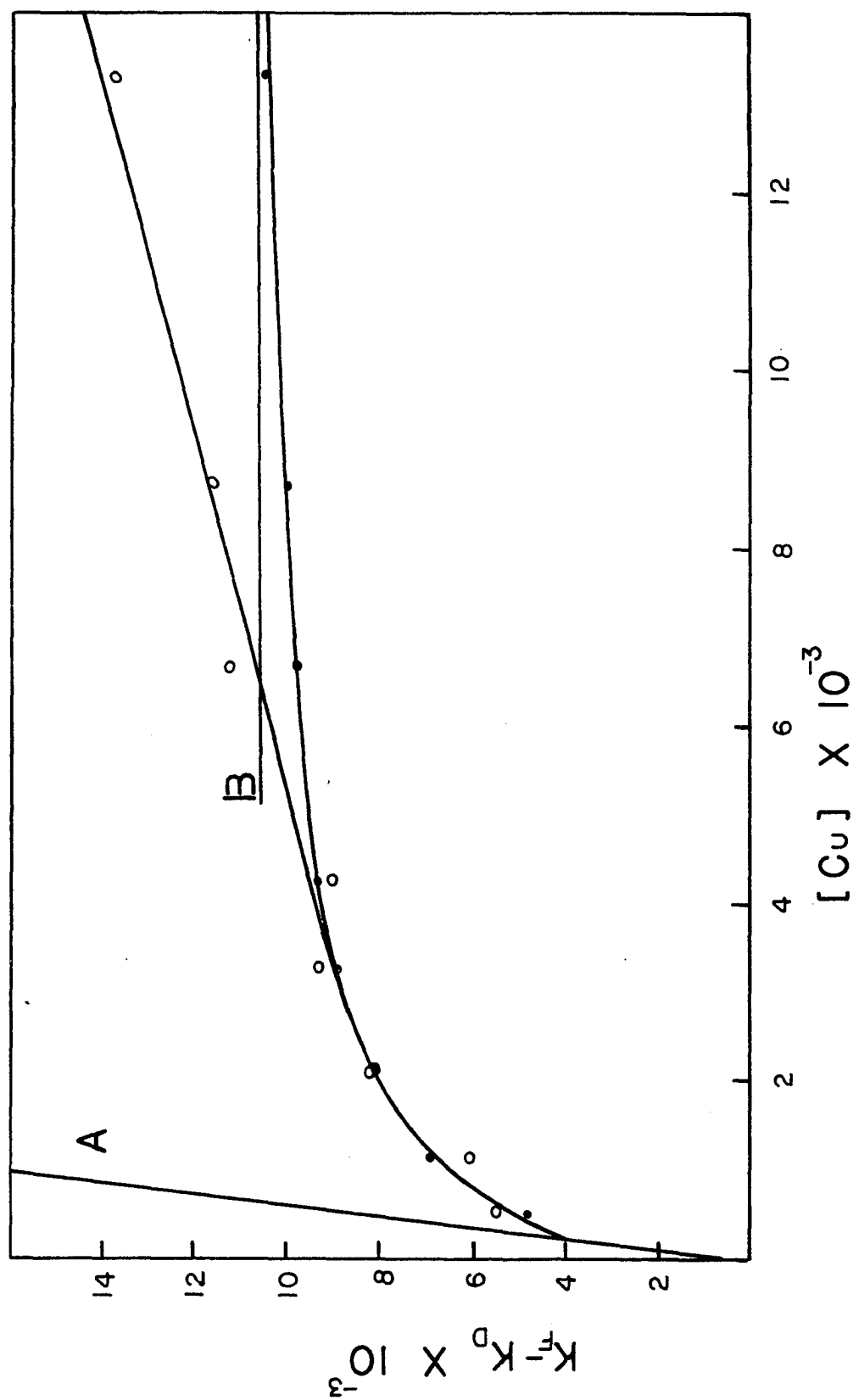


Figure 7. Effect of copper concentration on corrected  $k_f$ , pH 4.03  
Line B and curve with solid dots are theoretical values; line A and curve with circles are experimental values.

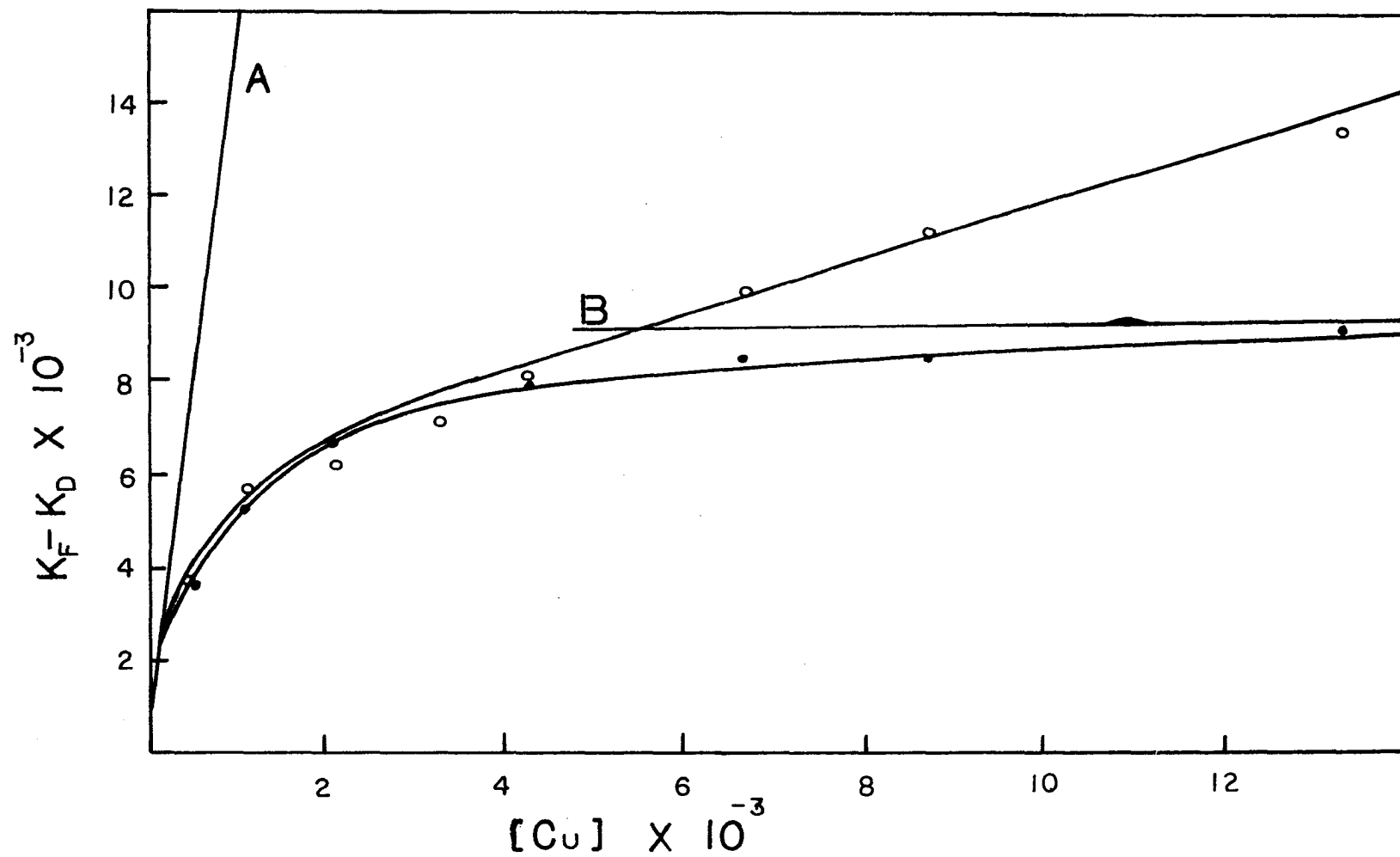


Figure 8. Effect of copper concentration on corrected  $k_f$ , pH 4.49  
Line B and curve with solid dots are theoretical values; line A and  
curve with circles are experimental values.



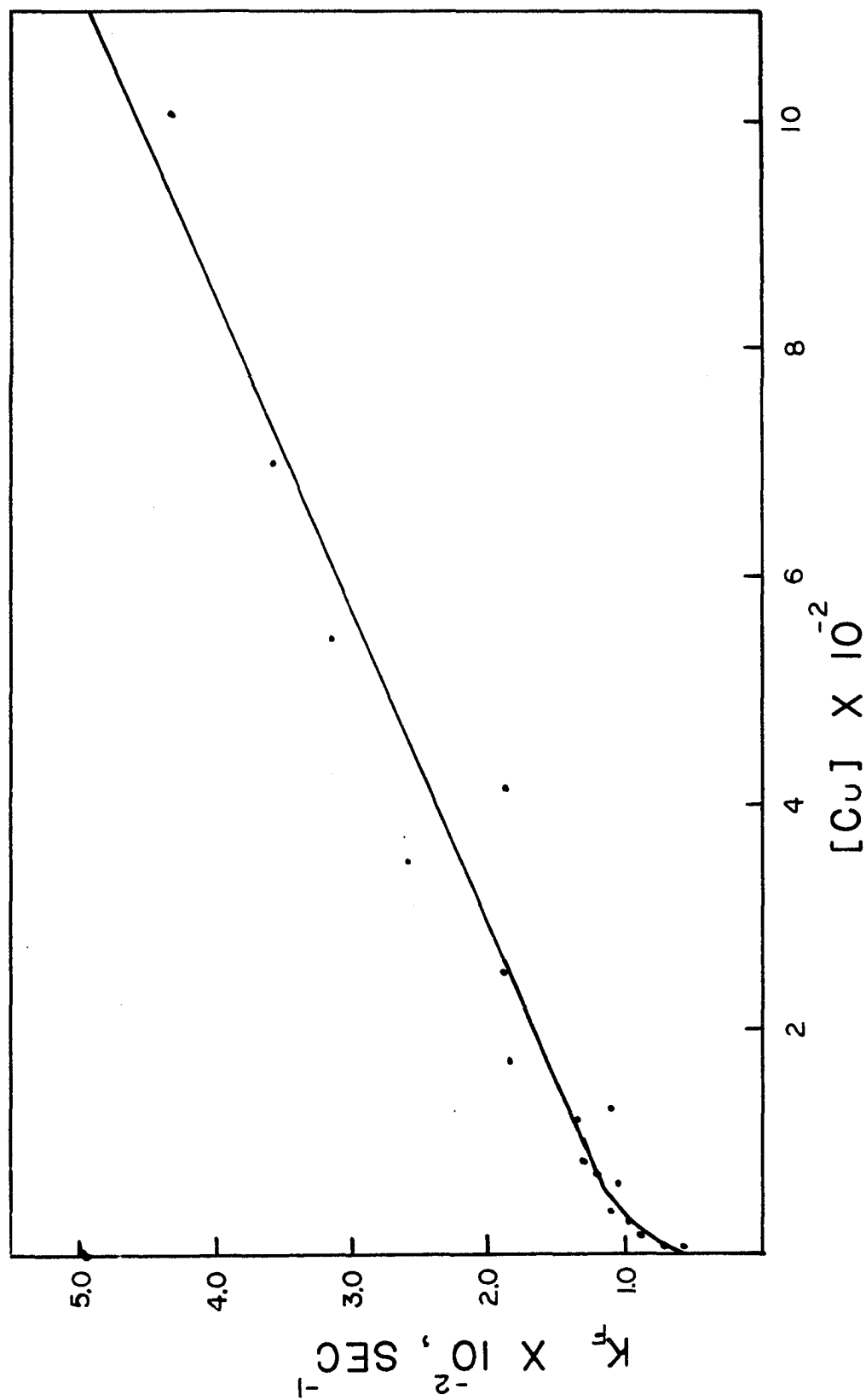


Figure 9. Appearance of a second first-order copper dependence, pH 3.83

The data in Figures 6 - 8 can be explained as a shift in the rate-determining step from one which occurs after copper attack to one which becomes rate determining before copper attack as the concentration of copper increases and confirms the necessity for the prior estimation of  $k_d$ . Similar behavior was found in previous studies of the attack of Cu on both NiEDTA (7) and NiEDDA (11). Equation 14 (7,11) can be used to resolve the two rate constants involved.

$$k_o = k [\text{Cu}] = \frac{a \times b [\text{Cu}]}{a + b [\text{Cu}]} \quad (14)$$

Here  $a$  is the rate constant for zero-order dependence and  $b$  is the rate constant for first-order dependence. At low copper concentration  $a > b [\text{Cu}]$  and at high copper concentrations  $a < b [\text{Cu}]$ . Rewriting equation 14 as

$$\frac{[\text{Cu}]}{k_o} = \frac{1}{b} + \frac{[\text{Cu}]}{a} \quad (15)$$

makes it suitable for plotting as shown in Figure 10. The recipricals of the intercepts, which are hydrogen independent, are  $k_{\text{Cu}}^{\text{Ni(IDA)}_2}$  and are listed in Table 5. Their average value is used to construct line A in Figures 6 - 8. This linear first-order behavior is approached at low copper concentrations. Further, the higher the pH, the lower the concentration of copper needed to cause deviation from the first-order copper dependency. The reciprical of the slopes, however, are hydrogen dependent

TABLE 5

Resolved Values of  $K_f$  into  
Copper Dependent and Independent Terms.  
All Values at 25°C and  $\mu = 1.25M$

<u>pH</u>	<u><math>k_{Cu}^{Ni(IDA)_2}, M^{-1} \text{ sec}^{-1}</math></u>	<u><math>k_{12} \times 10^2, \text{ sec}^{-1}</math></u>
3.83	19.5	1.35
4.03	17.2	1.06
4.49	12.1	0.915
Ave. = $16.3 \pm 3.1$		

as Figure 10 shows. Their values are listed in Table 5 and are used to construct line B in Figures 6 - 8. The linear relationship found at each pH in Figure 10 is in agreement with the transition from first-order to zero-order copper dependence.

The values of  $k_{\text{Cu}}^{\text{Ni(IDA)}_2}$  and  $k_{12}$  inserted in equation 14 allow calculation of a theoretical plot of  $k_f$  versus the copper concentration. This is shown in Figure 6 - 8 using solid dots. As can be seen, the zero-order behavior never really materialized but as the copper concentration increased to  $10^{-2}M$ , a second first-order copper dependence appeared. This is dramatically seen in Figure 8. This type of behavior is not unknown and is believed to arise from the formation of a weakly bonded species involving copper bonded to an acetate segment of the nickel ligand species. This type of intermediate has appeared in several other aminocarboxylate metal exchange studies (7, 10, 11).

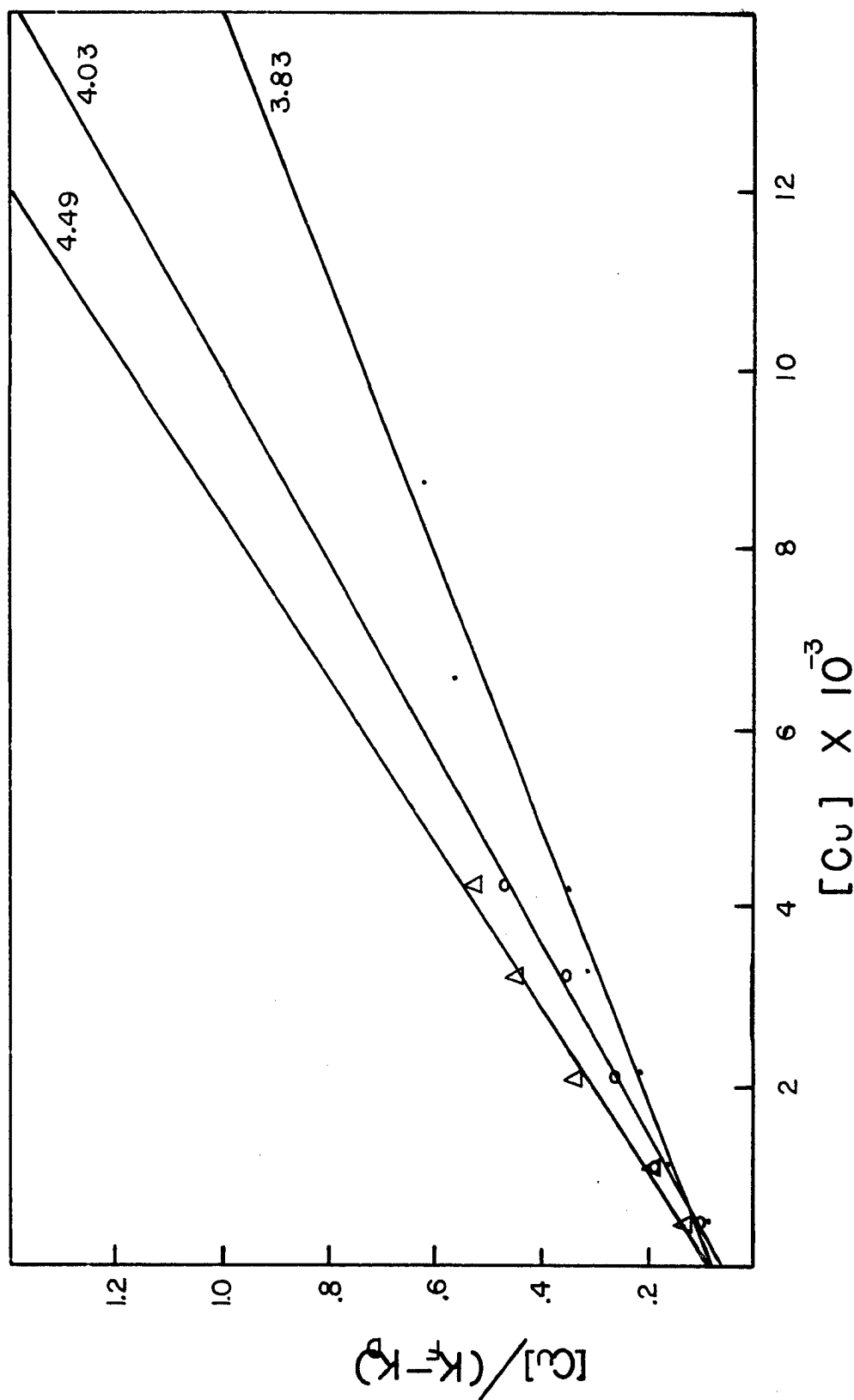


Figure 10. Resolution of  $k_{Cu}^{Ni(IDA)_2}$  and  $k_{12}$

## DISCUSSION

### Mechanisms and General Kinetic Expressions

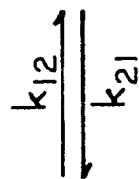
Since the overall reaction takes place in two steps, it is necessary to arrive at mechanisms that account for the continued first-order copper dependence and the pH sensitivity of the slower reaction and to account for the shifts in copper dependency and the pH sensitivity of the faster reaction.

#### Slow Reaction

Since the slow reaction, corresponding to equation 9, has already been characterized with respect to the rate-determining step and structure of the dinuclear intermediate (6), results relative to it found in this study only serve to confirm the assignment of the mechanism. However, a general kinetic expression involving the step-wise rate constants has not been derived and this will be done.

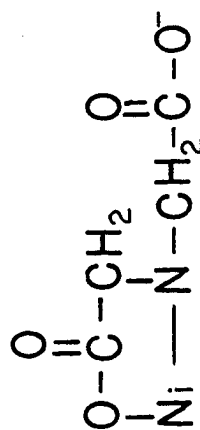
A mechanism which is consistent with the results obtained for the slow reaction, represented by equation 9, is presented in Figure 11. Protons are omitted from the mechanism for simplicity, although step 1-2 is proton dependent.

(1)

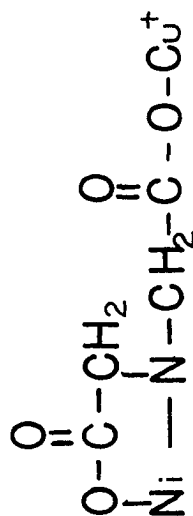
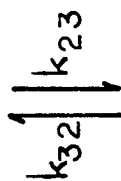


NIDA

(2)

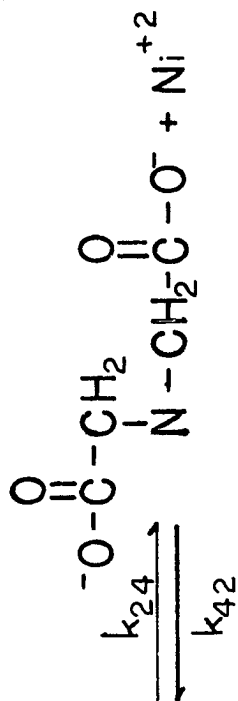


+

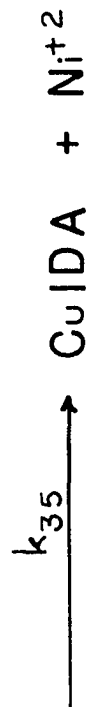
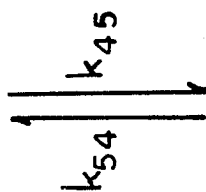
 $\text{Cu}^{+2}$ 

(3)

(4)



+

 $\text{Cu}^{+2}$ 

(5)

Figure 11. Stepwise transfer of IDA from nickel to copper

The dependence of the reaction order with respect to copper will depend on the location of the rate determining step. Because reaction steps  $2 \rightarrow 3$  and  $4 \rightarrow 5$  involve the very labile aquo copper ion, neither step should be rate limiting.

Both reaction paths  $1 \rightarrow 2 \rightarrow 4 \rightarrow 5$  and  $1 \rightarrow 2 \rightarrow 3 \rightarrow 5$  are possible and contribute to the formation of the products; however, the former reaction path would be controlled by the rate of dissociation of NiIDA and is therefore zero-order in copper.

From the results obtained in the preceding section it is possible to subtract out the contribution of reaction path  $1 \rightarrow 2 \rightarrow 4 \rightarrow 5$  from  $k_s$ . It is this corrected value that is used in obtaining rate information and in subsequent discussions.

The structure of the dinuclear intermediate, species 3, may be confirmed by comparing the ratio of relative stability constants of the various dinuclear intermediates which form prior to the rate-determining step with the ratio of experimental rate constants for metal attack upon various nickel nitrogen ligand complexes (3). Previous work (3, 5, 6, 11) has shown that the ratio of experimental rate constants is directly proportional to the ratio of intermediate stability constants if the bonding to nickel in the intermediate is the same for each set of intermediates compared. If the bonding in the rate-



determining step is the same for each intermediate compared, equation 16 could be reduced by cancellation of the last term.

$$\frac{k_{\text{Cu}}^{\text{NiIDA}}}{k_{\text{M}}^{\text{NiL}}} = \frac{K_{\text{r}}^{\text{NiIDA-Cu}}}{K_{\text{r}}^{\text{NiL-M}}} \times \frac{k^{\text{NiIDA-Cu}}}{k^{\text{NiL-M}}} \quad (16)$$

Since the ratio of the intermediate stability constants is used, it is more appropriate to use relative values for these constants. The relative stability constant,  $K_{\text{r}}$ , for each dinuclear intermediate is defined in terms of the stability constant of the CuIDA and the NiIDA segments of the intermediate structure compared to the stability constant of the initial complex.

$$K_{\text{r}} = \frac{K_{\text{Cu segment}} \times K_{\text{Ni segment}}}{K_{\text{Ni complex}}} \quad (17)$$

In some intermediate comparisons, additional stability, via an electrostatic attraction, helps to stabilize one structure relative to another.  $K_{\text{el}}$  can be estimated using the following equation (3)

$$E_{\text{el}} = RT \ln K_{\text{el}} = \frac{Z_{\text{A}} Z_{\text{B}} e^2}{D r_{\text{AB}}} \quad (18)$$

where the value of  $r_{\text{AB}}$ , the charge separation distance, has been measured using molecular models and is  $6 \text{ \AA}$  (3) and the value of  $D$ , the dielectric constant of water, is 80. In comparing the intermediate of NiIDA-Cu to NiEDTA-Cu, there is a net attraction of an unbound acetate

group for the nickel glycinate group which does not exist in the NiIDA-Cu structure. In this case,  $\log K_{e1} = 0.5$ .

In addition the formation of some intermediates are favored statistically over the formation of others. For example, the NiEDTA-Cu intermediate involves a glycine segment of EDTA bonded to nickel and an IDA segment bonded to copper which can be formed in four independent ways whereas the NiIDA-Cu intermediate involves a glycine segment of IDA bonded to nickel and an acetate segment bonded to copper which can be formed in only two independent ways.

The intermediate structures compared, the  $K_r$  values, and electrostatic and statistical factors where needed are presented in Table 6. A comparison of the ratio of relative stability constants for the dinuclear intermediates with the ratio of experimental rate constants shows that only structure I gives good agreement. Other possible intermediates give  $K_r$  values which were either very high or very low. Thus, the dinuclear intermediate which exists in the NiIDA, Cu(II) system involves a glycine segment bonded to nickel and an acetate segment bonded to copper.

Since nickel acetate bonds cleave at  $5 \times 10^3 \text{ sec}^{-1}$  (21) while nickel nitrogen bonds cleave at  $5.8 \text{ sec}^{-1}$  (19), the rate-determining step,  $k_{35}$ , for the mono IDA system is actually the breaking of the nickel nitrogen bond. If

TABLE 6

Comparison of NiIDA-Cu and NiL-Cu Reaction Intermediates  
Structures Compared to

I		II		III	
$  \begin{array}{c}  \text{O} \\  \diagup \quad \diagdown \\  \text{Ni} - \text{N} - \text{N} - \text{Cu} \\  \diagdown \quad \diagup \\  \text{O}  \end{array}  $		$  \begin{array}{c}  \text{O} \\  \diagup \quad \diagdown \\  \text{Ni} - \text{N} - \text{N} - \text{Cu} + \\  \diagdown \quad \diagup \\  \text{O}  \end{array}  $		$  \begin{array}{c}  \text{O} \\  \diagup \quad \diagdown \\  \text{Ni} - \text{N} - \text{N} - \text{Cu} \\  \diagdown \quad \diagup \\  \text{O}  \end{array}  $	
$  \begin{array}{c}  \text{NiEDTA-Cu} \\  K_r = 1.51 \times 10^{-2}  \end{array}  $		$  \begin{array}{c}  \text{NiEDDA-Cu} \\  K_r = 2.24 \times 10^{-1}  \end{array}  $		$  \begin{array}{c}  \text{NiHEEDTA-Cu} \\  K_r = 2.4 \times 10^{-1}  \end{array}  $	
Trial Structures	$K_r$	I		II	
		$\text{NiIDA-Cu} / K_r$	$\text{NiIL-Cu} / K_r$	$\text{NiIDA-Cu} / K_r$	$\text{NiIL-Cu} / K_r$
I + Ni - N-O - Cu +	$6.31 \times 10^{-2}$	.661	.282	.526	
II + Ni - N-O - Cu +	$2.04 \times 10^{-4}$	$6.75 \times 10^{-2}$	$2.88 \times 10^{-3}$	$5.37 \times 10^{-3}$	
III + Ni-O-N-O-Cu +	$1.78 \times 10^{-6}$	$1.86 \times 10^{-3}$	$7.95 \times 10^{-6}$	$1.48 \times 10^{-5}$	
IV + Ni - O-N - O	1.23	12.9	5.75	10.2	
$  \begin{array}{c}  \text{Cu} \\  \diagup \quad \diagdown \\  \text{NiIDA} / K_{\text{Cu}} + \text{NiIL} / K_{\text{Cu}}  \end{array}  $		1.13	.241	1.21	

TABLE 6 (continued)

$K_r$  values are based on the following stability constants which have been chosen from references 15, 22 to match temperature and ionic strengths as nearly as possible. The experimental ratio of rate constants are based on the following values, all at  $25.0^\circ\text{C} \pm .1$  and  $\mu = 1.25\text{M}$ .

Complex	K	M	L	$k_M^{\text{NiL}} \text{M}^{-1} \text{sec}^{-1}$	Ref.
NiEDTA <sup>=</sup>	$3.63 \times 10^{18}$	Cu	EDTA	$1.6 \times 10^{-2}$	1
NiEDDA	$3.16 \times 10^{13}$	Cu	EDDA	$7.5 \times 10^{-2}$	11
NiHEEDTA <sup>-</sup>	$1.00 \times 10^{17}$	Cu	HEEDTA	$1.5 \times 10^{-2}$	3
Ni(IDA) <sub>2</sub> <sup>=</sup>	$4.07 \times 10^{14}$	Cu	bis-IDA	16.3	this work
NiIDA	$1.62 \times 10^3$	Cu	IDA	$1.81 \times 10^{-2}$	this work
CuIDA	$1.23 \times 10^{11}$				
Ni(glycinate) <sup>+</sup>	$1.95 \times 10^5$				
Cu(glycinate) <sup>+</sup>	$3.63 \times 10^7$				
Ni(acetate)	5.5				
Cu(acetate)	$5.25 \times 10^1$				

nickel acetate bond cleavage were rate-determining, in conjunction with the  $K_r$  value of the NiIDA-Cu intermediate,  $K_r k_{35}$  greatly exceeds the experimentally observed rate constant. Therefore, nickel nitrogen bond breakage is the rate-determining step for the NiIDA system. This is consistent with previous work on the copper-NiIDA system (6) as well as the copper-NiEDTA (3) and copper-NiEDDA system (11).

The reaction sequence represented by  $k_{Cu}^{NiIDA}$  is 1→2→3→5 of Figure 11 and a general kinetic rate expression can be derived for it.

$$\frac{-d[NiIDA]}{dt} = \frac{d[CuIDA]}{dt} = k_o[NiIDA] = k_{35}[3] \quad (19)$$

Applying steady state approximations to species 2 and 3 gives the following expressions.

$$[2] = \frac{k_{12}[1] + k_{32}[3]}{k_{21} + k_{23}[Cu]} \quad (20)$$

$$[3] = \frac{k_{23}[2][Cu]}{k_{32} + k_{35}} \quad (21)$$

Substituting equation 20 into equation 21 gives the following

$$[3] = \frac{k_{12}k_{23}[1][Cu]}{k_{21}k_{35} + k_{21}k_{32} + k_{23}k_{35}[Cu]} \quad (22)$$

Substitution of this expression into the general rate expression gives

$$\frac{-d[\text{NiIDA}]}{dt} = \frac{k_{12}k_{23}k_{35}[1][\text{Cu}]}{k_{21}k_{35} + k_{21}k_{32} + k_{23}k_{35}[\text{Cu}]} \quad (23)$$

where

$$k_o = \frac{k_{12}k_{23}k_{35}[\text{Cu}]}{k_{21}k_{35} + k_{21}k_{32} + k_{23}k_{35}[\text{Cu}]} \quad (24)$$

Comparing terms in the denominator of equation 24,  $k_{23}k_{35}[\text{Cu}]$  is about a factor of 10 greater than  $k_{21}k_{35}$  because  $k_{23}$  is about  $10^4$  greater than  $k_{21}$  due to the difference in rate of water loss between Cu and Ni (23), yet  $[\text{Cu}] \sim 10^{-3}\text{M}$ . However,  $k_{32}$  is about  $10^7$  greater than  $k_{35}$ . Thus,  $k_{21}k_{32}$  becomes larger than the other two terms and equation 24 becomes

$$k_o = \frac{k_{12}k_{23}k_{35}[\text{Cu}]}{k_{21}k_{32}} \quad (25)$$

which demonstrates a first-order copper dependence.

Equation 26 gives the second-order rate constant

$$k_{\text{Cu}}^{\text{NiIDA}} = \frac{k_{12}k_{23}k_{35}}{k_{21}k_{32}} \quad (26)$$

where the rate limiting step is  $k_{35}$ .

A continued first-order copper dependence, described by equation 25, was found over the entire copper concentration range studied. This continued dependence occurred because the rate of the reaction was sufficiently slow such that the partial unwrapping of NiIDA,  $k_{12}$ , never becomes rate limiting.

## Fast Reaction

For the fast reaction the results not only indicate a shift in copper dependence from first-order to zero-order, but as the concentration of copper is increased up to  $10^{-1}M$ , a second first-order copper dependence appears. In order to suggest a mechanism for this reaction, the structure of the intermediates responsible for the three terms which are observed must be identified.

The zero-order term, which was obtained from the slope of Figure 10, is pH dependent. Equation 27, plotted in Figure 12 shows the pH dependency.

$$k_{12} = k_{dis}^{Ni(IDA)_2} + k_H^{Ni(IDA)_2} [H^+] \quad (27)$$

The slope of the line yields  $k_H^{Ni(IDA)_2} = 35.3 M^{-1} sec^{-1}$  and the intercept,  $k_{dis}^{Ni(IDA)_2} = 7.67 \times 10^{-3} sec^{-1}$ . By estimating the value of  $k_{dis}^{Ni(IDA)_2}$ , based upon the extent to which IDA has unwrapped, the structure of the partially unwrapped intermediate, can be predicted using equation 28 (7). Equation 28 relates a ratio of stabilities to a ratio of rates and has been the basis for other similar predictions.

$$k_{dis}^{Ni(IDA)_2} = k_{21} \times \frac{K_r^{Ni(IDA)(L)}}{K_{Ni(IDA)_2}} \times K_{e1} \times \frac{1}{4} \quad (28)$$

Here,  $K_{Ni(IDA)(L)}$  represents the stability of the complex with a portion, L, of the first IDA still coordinated to nickel. The value of  $k_{21}$  is the rate of water loss of

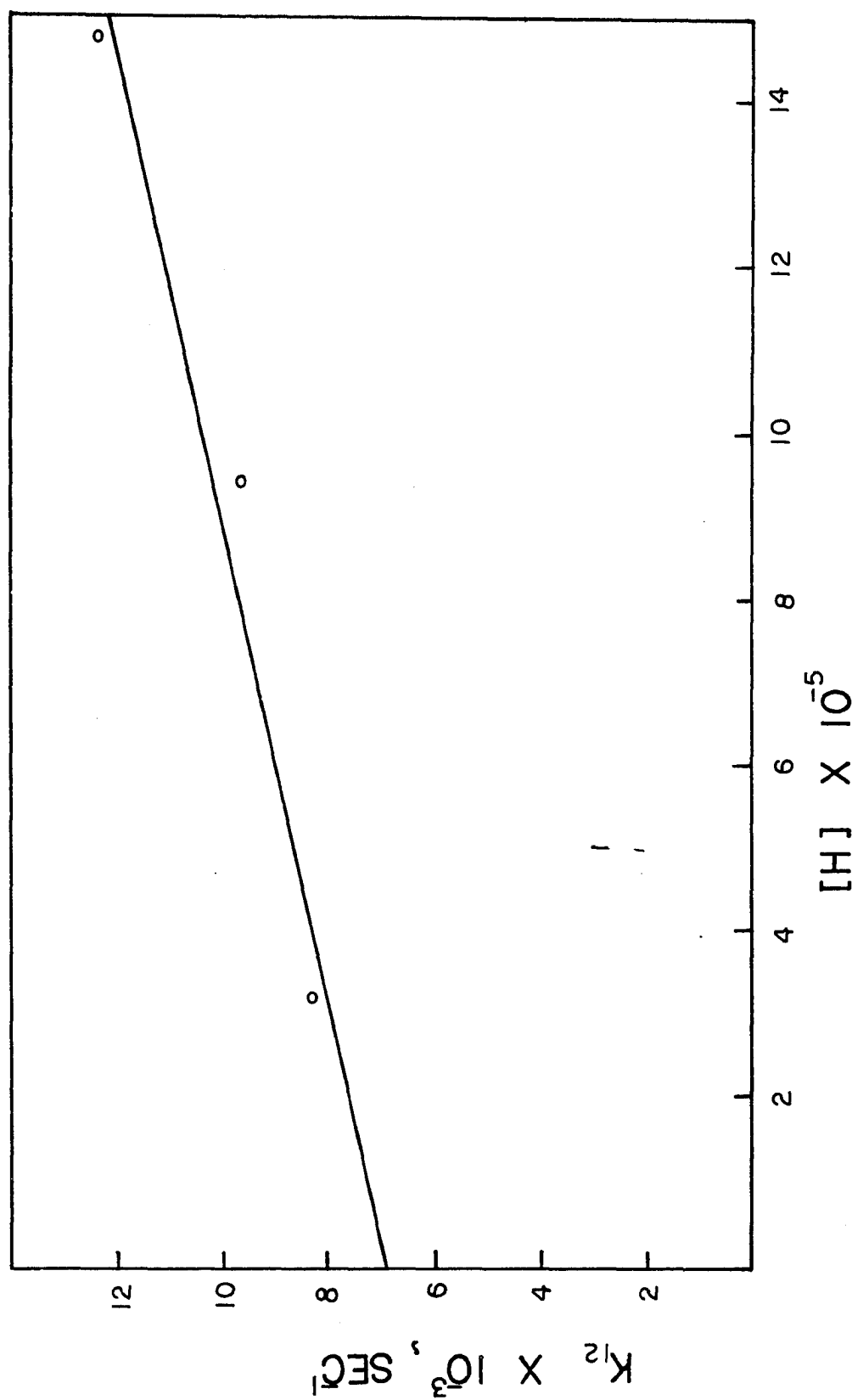


Figure 12. Resolution of  $k_{12}$  into proton dependent and proton independent terms.



nickel IDA and has been measured as  $5 \times 10^4 \text{ sec}^{-1}$  (18).

$K_{el}$  is an electrostatic term to compensate for interaction of the unwrapped segment of IDA with the negative nickel (IDA)(L), calculated using equation 18, and  $\frac{1}{4}$  is a statistical factor which favors the dissociation. From equation 28, assuming L is acetate, that is a glycine segment has unwrapped,  $k_{dis}^{Ni(IDA)_2} = 8.70 \times 10^{-3} \text{ sec}^{-1}$  which is in good agreement with the observed value of  $7.67 \times 10^{-3} \text{ sec}^{-1}$ .

Either a larger or smaller extent of unwrapping would necessitate the use of a different stability constant in equation 28 and would result in severe disagreement between the predicted and experimental values. Thus, the zero-order path involves a Ni(IDA) (acetate) intermediate with a glycine segment unwrapped.

The structure of the dinuclear intermediate for the first-order copper term at low copper concentration can be determined as discussed earlier. However, some intermediates tested does not involve nickel-nitrogen bond breakage as the rate-determining step but rather had nickel-acetate bond cleavage as rate-determining. In these cases, the ratio of rate constants is defined as in equation 16 except that  $k^{Ni(IDA)_2-Cu}$  is nickel acetate bond cleavage measured to be  $5 \times 10^3 \text{ sec}^{-1}$  (21) and  $k^{NiL-Cu}$  is nickel nitrogen bond cleavage approximated as  $5.8 \text{ sec}^{-1}$  (19) and the terms do not cancel.

The intermediate structures are shown in Table 7 along with the  $K_r$  values, the electrostatic and statistical factors and the predicted and experimental ratios. A comparison of the ratio of relative stability constants with the ratio of experimental rate constants shows that structure V gives good agreement. As before, any other possible intermediates give  $K_r$  values either very high or very low. Thus, the first order term in copper at low copper concentration has a glycine segment unwrapped from nickel and coordinated to copper.

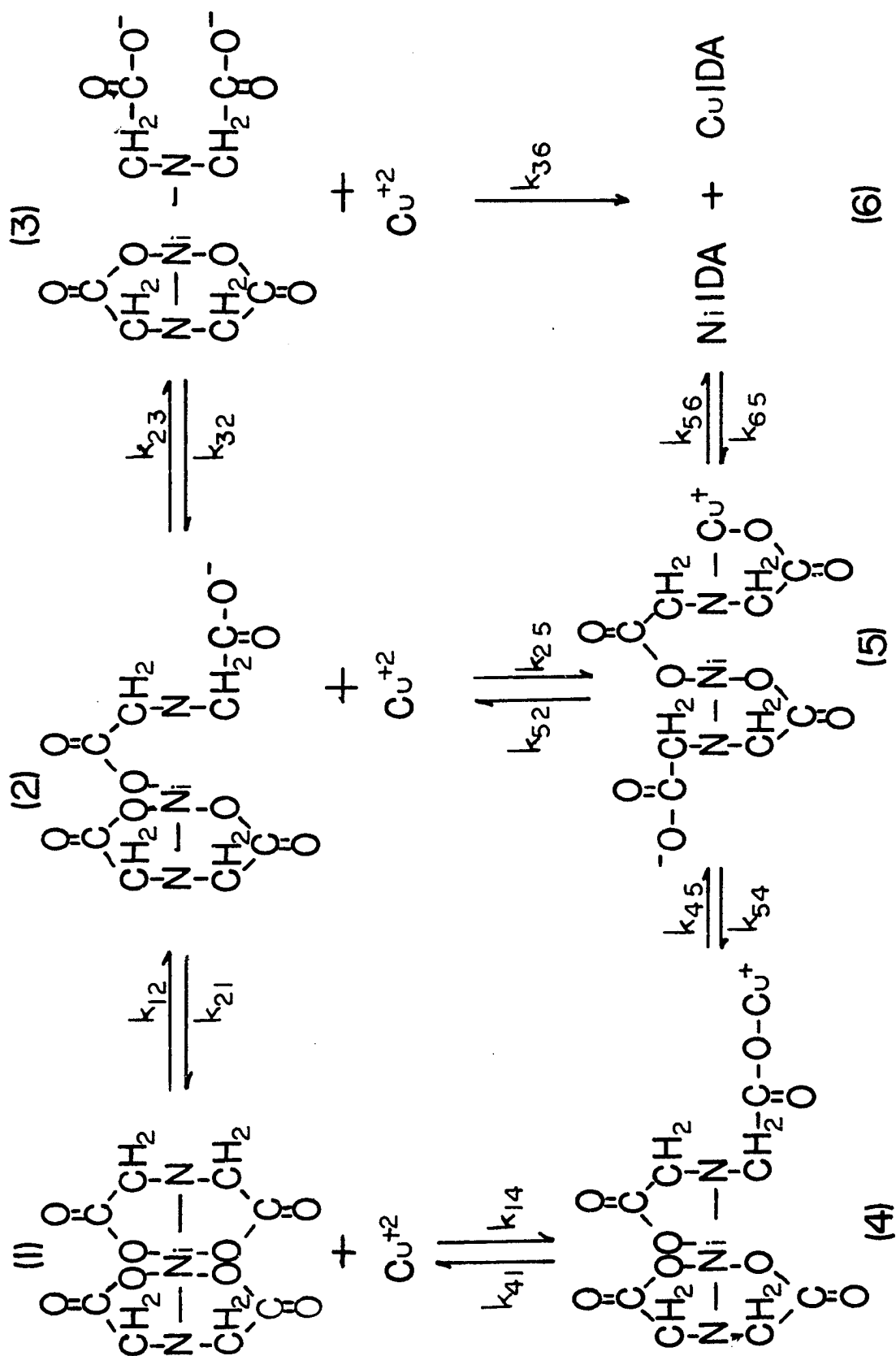
At copper concentrations greater than 0.02M a second first-order copper dependence appears rather than the expected zero-order dependence. This new dependence is attributed to a weakly coordinated  $\text{Ni}(\text{IDA})_2\text{-Cu}$  intermediate, involving a copper acetate bond, which is in rapid equilibrium with the reactants and is different from the dinuclear intermediate which occurs latter on in the mechanism. This type of complex is not unknown (7, 10, 11) and has been seen in the reaction of copper with  $\text{NiEDDA}$  (11) and  $\text{NiEDTA}$  (7) and of lead and copper with trans-1,2-diamino-cyclohexanetetraacetocadmate(II) (10). In all cases, an acetate segment of the ligand has unwrapped and is bonded to the attacking metal.

However, the structure of this dinuclear intermediate cannot be obtained directly by comparison of proposed structures to those of other systems. The difficulty



arises in estimating the values of the relative stability constants for the structures of the dinuclear intermediates of other systems and the lack of sufficient kinetic data. Nevertheless, in each previous study the only difference between the reactant and the intermediate is an unwrapped acetate segment which is subsequently bonded to the attacking metal. Therefore, it is assumed that the structure of this dinuclear intermediate has copper bonded to an unwrapped acetate segment of IDA. Thus, the structure of the dinuclear intermediate for the first-order term in copper at high copper concentration has a glycine segment bonded to nickel and the unwrapped acetate segment bonded to copper.

A mechanism can now be proposed, shown in Figure 13, which is consistent with the observed results since the structures of the intermediates are known. Protons are again omitted for the sake of clarity. The reaction order with respect to copper will dictate the location of the rate-determining step. Step 2→5, 1→4 and 3→6 involve the very labile aquo copper ion, thus none of them should be rate limiting. Further, the contribution from pathway 1→2→3→6 has been estimated and subtracted from the observed fast rate constant. Therefore, the rest of  $k_o$  must be due to pathways 1→2→5→6 and 1→4→5→6.

Figure 13. Stepwise transfer of IDA from Ni(IDA)<sub>2</sub> to copper

At low copper concentration, either step 5→6 or step 4→5 must be rate limiting corresponding to line A of Figures 6 - 8. Since 4→5 does not allow for the experimentally seen shift from first to zero and back to first-order in copper as the copper concentration increases, step 5→6 must be rate limiting. As the concentration of copper increases, the concentration of species 5 increases and  $k_{56}[5] > k_{12}[1]$ . Thus,  $k_{12}$  becomes rate limiting and the reaction shifts to zero-order in copper. However, as the concentration of copper becomes larger, the weakly bonded complex, species 4, is formed in appreciable amounts and the reaction proceeds through path 1→4→5→6.

Considering only the reaction paths 1→2→5→6 and 1→4→5→6 the general kinetic expression is

$$\frac{-d[\text{Ni}(\text{IDA})_2]}{dt} = \frac{d[\text{CuIDA}]}{dt} = k_o[\text{Ni}(\text{IDA})_2] = k_{56}[5] \quad (29)$$

Using steady state approximations for species 2 and 5 and assuming a rapid equilibrium between species 1 and 4 ( $K_{41} = k_{14}/k_{41}$ ), the following expressions can be derived.

$$[2] = \frac{k_{12}[1] + k_{52}[5]}{k_{21} + k_{25}[\text{Cu}]} \quad (30)$$

$$[5] = \frac{k_{45}K_{41}[1][\text{Cu}] + k_{25}[\text{Cu}][2]}{k_{52} + k_{54} + k_{56}} \quad (31)$$

Substitution of equation 30 into equation 31 gives

$$[5] = \frac{k_{12}k_{25}[1][\text{Cu}] + k_{45}K_{41}[1][\text{Cu}](k_{21} + k_{25}[\text{Cu}])}{k_{21}(k_{52} + k_{54} + k_{56}) + k_{25}[\text{Cu}](k_{54} + k_{56})} \quad (32)$$

Substitution of equation 32 into the general rate expression gives

$$k_0 = \frac{k_{56}[\text{Cu}][k_{12}k_{25} + k_{45}K_{41}(k_{21} + k_{25}[\text{Cu}])]}{k_{21}(k_{52} + k_{54} + k_{56}) + k_{25}[\text{Cu}](k_{54} + k_{56})} \quad (33)$$

Simplification of equation 33 is not possible since neither the absolute nor the relative values of the various stepwise rate constants or of  $K_{41}$  is known. In particular the effect that a coordinated IDA has upon nickel-ligand bond breakage is unknown but would be important in all steps except  $k_{52}$  and  $k_{54}$ .

The effect of coordinated ligands upon the rate of water loss has been studied by several workers (18, 24, 25). The results definitely indicate that coordinated ligands do affect the rate of water loss with different ligands exhibiting different effects. Coordinated IDA, for example, increases the rate of water loss of nickel by about a factor of two (18), and NTA by about five (18). However, what is needed is the effect of coordinated ligands upon the breakage of metal-ligand bonds other than water. The type of metal-dentate site being broken may well cause the effect of a coordinated ligand to be felt to a greater or lesser extent compared to water.

Another complicating factor involved in assigning values of the stepwise rate constants is the existence of two water exchange rates for nickel (25), seen under certain conditions. The ligands tren and NTA, when coordinated to nickel appear to cause enough structural difference between the remaining water molecules so as to result in two different water loss rates, the difference being about a factor of 17 in the case of tren. Both tren and NTA are branched ligands whereas IDA is not, nevertheless, the exact geometry of the various intermediates having one IDA molecule and part of another coordinated may sufficiently resemble the geometry induced by NTA or tren so as to create two nonequivalent sites.

Finally, the value of  $K_{41}$  is not known. The linear behavior of Figure 8 above 0.02 M copper indicates that the only reaction path involved is  $1 \rightarrow 4 \rightarrow 5 \rightarrow 6$ . Using a steady state treatment for species 5 and assuming  $[4] = K_{41} [Cu] [Ni(IDA)_2]$ , equation 34 results.

$$k_o [Ni(IDA)_2] = k_{56} [5] \quad (34)$$

$$k_o = \frac{k_{45} k_{56} K_{41} [Cu]}{k_{56} + k_{54}} \quad (35)$$

Thus, the slope of Figure 9 represents  $\frac{k_{45} k_{56} K_{41}}{k_{56} + k_{54}}$  but

gives no way of obtaining a value for  $K_{41}$ . Values of  $K_{41}$  in the previously cited studies ranged from 7 (7) to an estimate of 0.1 (11).



In conclusion, The reaction of  $\text{Ni}(\text{IDA})_2$  with copper is found to proceed through two steps. The first involves the stepwise unwrapping of IDA followed by coordination to copper. The portion of IDA which must be unwrapped before copper attack is a function of the copper concentration. The structure of the intermediate found at each point can be clearly identified from the experimental data. The rate at which the various nickel-IDA bonds break are seen to be affected by the presence of a coordinated IDA. The need for more study on the effect of coordinated ligands on various type of metal-dentate bond breakage is clearly shown from this study.

The second step of the reaction involves the stepwise unwrapping of the second IDA and subsequent copper attack. This reaction proceeds through an identifiable intermediate, the rate of reaction of which follows the behavior expected from comparison to other systems. The difference between the "normal" second step and the first step provide an interesting contrast and example of the effect a coordinated ligand can have on metal bond breakage.

## APPENDIX

The relationship shown in equation 7 between  $\text{Ni}(\text{IDA})_2$  and the absorbance at any time,  $A_t$ , the final absorbance,  $A_\infty$ , and the molar absorptivities of reactants and products is derived as follows. Assuming no stable intermediate to be present which was shown by spectral scans of the reaction, the absorbance at any time is equal to the absorbance of the reactants left and the products formed. Beer's law is assumed to hold and the following equations can be written.

$$A_t = \epsilon_{\text{Ni}(\text{IDA})_2} b [\text{Ni}(\text{IDA})_2] + \epsilon_{\text{CuIDA}} b [\text{CuIDA}] + \epsilon_{\text{NiIDA}} b [\text{NiIDA}] + \epsilon_{\text{Ni}} b [\text{Ni}] + \epsilon_{\text{Cu}} b [\text{Cu}] \quad (36)$$

$$[\text{Cu}] = [\text{Cu}]_f + 2[\text{Ni}(\text{IDA})_2] \quad (37)$$

$$[\text{Ni}] = [\text{Ni}]_f - [\text{Ni}(\text{IDA})_2] \quad (38)$$

$$[\text{CuIDA}] = [\text{CuIDA}]_f - 2[\text{Ni}(\text{IDA})_2] \quad (39)$$

$$[\text{NiIDA}] = [\text{Ni}]_f - [\text{Ni}(\text{IDA})_2] \quad (40)$$

Where  $f$  represents final. Substitution of these expressions into equation 36 and rearranging gives equation 41.

$$A_t = [\text{Ni}(\text{IDA})_2] b (\epsilon_{\text{Ni}(\text{IDA})_2} - 2\epsilon_{\text{CuIDA}} - \epsilon_{\text{Ni}} + 2\epsilon_{\text{Cu}} - \epsilon_{\text{NiIDA}}) + \epsilon_{\text{CuIDA}} b [\text{CuIDA}]_f + \epsilon_{\text{Ni}} b [\text{Ni}]_f + \epsilon_{\text{Cu}} b [\text{Cu}]_f \quad (41)$$

Since

$$A_{\infty} = \epsilon_{\text{CuIDA}} b [\text{CuIDA}]_f + \epsilon_{\text{Ni}} b [\text{Ni}]_f + \epsilon_{\text{Cu}} b [\text{Cu}]_f \quad (42)$$

substitution of equation 42 into equation 41 and rearranging, yields

$$[\text{Ni(IDA)}_2] = \frac{A_t - A_{\infty} - \epsilon_{\text{Ni}} b [\text{Ni}]_f}{b(\epsilon_{\text{Ni(IDA)}_2} + 2\epsilon_{\text{Cu}} - 2\epsilon_{\text{CuIDA}} - \epsilon_{\text{Ni}} - \epsilon_{\text{NiIDA}})} \quad (7)$$

The value of  $\epsilon_{\text{Ni}} b [\text{Ni}]_f$  is constant and negligible compared to  $a$  because  $\epsilon_{\text{Ni}}$  is 1.8 and  $[\text{Ni}]_f$  between  $2 \times 10^{-5}$  and  $4 \times 10^{-4}$ .

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