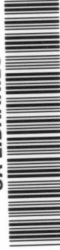# Investigation and Development of a Mathematical Model for the

Oxidation of Cyanide in the INCO SO_2/O_2 Process

By

James L. Oleson

RECOMMENDED: _____

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Advisory Committee Chair

_____
Chair, Dept. of Mining and Geological Engineering

APPROVED: _____
Dr. S. Bandopadhyay, Dean, School of Mineral Engineering

_____
Dr. S.M. Henrichs, Dean of the Graduate School

_____
December 22, 2003
Date

Investigation and Development of a Mathematical Model for the

Oxidation of Cyanide in the INCO SO$_2$/O$_2$ Process

A

THESIS

Presented to the Faculty

of the University of Alaska Fairbanks

in Partial Fulfillment of the Requirements

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MASTER OF SCIENCE

Mineral Preparation Engineering

By

James L. Oleson, M.S.

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Abstract

The purpose of this study was to develop a mathematical model to describe the oxidation of cyanide with SO_2 as proposed in the INCO process. This research employed a direct method for measuring the change in cyanide concentration with respect to time as affected by varying concentrations of SO_2 and copper and pH. This model may be applicable in determining optimum conditions in a process well known and used in the mining industry. It was determined that the reaction:

$$CN^- + SO_2 + O_2 + H_2O \xrightarrow{Cu^{+2}} CNO^- + H_2SO_4$$
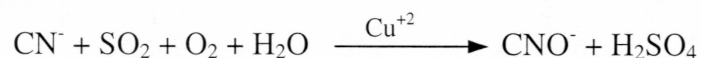
is first-order with respect to cyanide, SO_2 and $[Cu^{+2}]$. The reaction order is 0.156 or zeroth order with respect to $[H^+]$ over the pH range 8.0 to 9.5. The activation energy, E_a, is 21.1 kJ/mol and the variable D is defined as follows; $D = ([SO_2]_0 - [CN^-]_0)$. The overall rate equation, as determined through this study, is:

$$\ln \left(\frac{[CN^-]_0 \, ([CN^-]_t + D)}{[CN^-]_t \, ([CN^-]_0 + D)} \right) = 5.21 \times 10^7 e^{-21100/RT} [Cu^{+2}][H^+]^0 Dt$$

Table of Contents

List of Figures

List of Tables

Acknowledgments

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Finally I would especially like to thank my wife, Pam, and children, Nathan and Jessica, for their unending support and encouragement.

Chapter 1. Introduction

1.1 Background

While environmental concerns over the use of cyanide in mining have become more public only in the last few years, there actually is a very long history of cyanide use in metallurgical and related processes all around the world.

Dippel and Diesbach discovered "Prussian blue" (iron ferrocyanide) in 1704 [1]. The earliest well-documented work was Scheele's studies of solubility of gold in cyanide solutions dating from 1783 in Sweden. Gold-cyanide chemistry was studied actively in the mid-19th century in England (Faraday), Germany (Elsner), and Russia (Elkington and Bagration) [1]. By 1840, Elkington held a patent for the use of potassium cyanide solutions for electroplating gold and silver. Elsner led the evaluation of the role of oxygen in gold dissolution using cyanide solutions, and "Elsner's Equation" describing the extraction of gold from ores by cyanide was known by 1846 [1].

Elsner recognized that oxygen was required for the dissolution of gold [2]. The stoichiometric equation, as he proposed, for the dissolution of gold in aerated, alkaline cyanide solutions is as follows [1]:

$$4Au + 8CN^- + O_2 + 2H_2O = 4Au(CN)_2^- + 4OH^-$$

Bodlander published his theory of the hydrogen peroxide mechanism in 1896. He suggested the following equations to describe a two-step process in the dissolution of gold [2], [3]:

$$2Au + 4NaCN + O_2 + 2H_2O = 2NaAu\,(CN)_2 + 2NaOH + H_2O_2$$

$$H_2O_2 + 2Au + 4NaCN = 2NaAu\,(CN)_2 + 2NaOH$$

$$\overline{4Au + 8NaCN + O_2 + 2H_2O = 4NaAu\,(CN)_2 + 4NaOH}$$
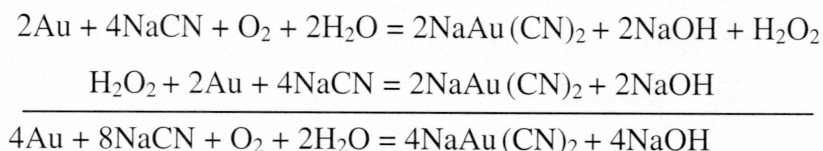
Obviously, these two equations add up to Elsner's equation. However, it is generally accepted that Bodlander's first equation is the major mechanism for the dissolution of gold, and that Elsner's is the minor mechanism [2].

Patents formalized by McArthur and the Forrest brothers in 1887 and 1888 effectively established the current cyanidation process, the use of cyanide dissolution and precipitation using zinc. Though not used, there was an earlier patent in the USA for cyanide leaching by Rae in 1869 [1]. The first commercial-scale cyanidation plant began operating at the Crown Mine in New Zealand in 1889, and by 1904 cyanidation processes were also in place in South Africa, Australia, United States, Mexico and France. Therefore, by the turn of the century, the use of cyanide to extract gold from low-grade ores was a fully established metallurgical technology [1].

The most toxic form of cyanide is HCN, hydrogen cyanide gas. The American Conference of Governmental Industrial Hygienists (ACGIH) lists the ceiling threshold limit of HCN at 4.7 ppm. At concentrations of 20 to 40 ppm of HCN in air, some respiratory distress may be observed after several hours. Death may occur within minutes when the concentrations of hydrogen cyanide are greater than about 250 ppm. The lethal dosage of free cyanide to humans, by ingestion or inhalation, ranges from 50 to 200 mg (1 to 3 mg of free cyanide per kg body mass). The lethal dosage for dermal absorption is considerably higher, at about 100 mg per kg of body weight [4].

As a rule, complexed metal cyanide is less toxic than free cyanide. In addition, the toxicity of the complexed metal is lower than an equal level of the free ionic form of the metal. The metal cyanide complexes of major and minor importance include those of mercury, cadmium, zinc, nickel, iron, copper, silver and gold [3].

Of the forms reporting as Weak Acid Dissociable (WAD) cyanide, free cyanide is the most readily degradable from a treatment viewpoint. Following treatment, an effluent often contains nondetectable and/or non-toxic levels of free cyanide (<0.01 mg/l). Therefore, the primary concerns with respect to aquatic or mammalian toxicity are the other forms of WAD cyanide.

Cyanide and metal cyanide complexes not only affect humans, but also have an ecological impact. For mining environments, three groups of ecological or environmental receptors are of concern: 1) birds (especially migratory wildfowl), 2) fish and other aquatic life, and 3) mammals, reptiles and amphibians.

The principal concern for wildfowl has always been exposure to cyanide in open ponds, especially for migratory wildfowl passing through relatively arid regions such as the western USA, where the use of cyanide in mining has become quite common. It should be noted, however, that the mortality of birds in Nevada due to exposure to cyanide solutions has been reduced dramatically from about 1,300 in 1990 to 220 in 1995, a decrease of 83% [4]. This improvement is largely due to limiting the WAD cyanide concentration of uncovered ponds to less than 50 ppm. This concentration of WAD cyanide is not acutely toxic to ducks, which are very sensitive to cyanide as compared with other wildfowl and wildlife [4]. Free cyanide (the cyanide ion and hydrogen cyanide) is well known to be the form of cyanide derivatives most toxic to mammals and aquatic life. Acute toxicity to various fish species ranges from about 20-640 micrograms per liter [5]. The more sensitive rainbow and brown trout generally exhibit acute toxicity to free cyanide in the range of 20-80 micrograms per liter. Chronic toxic effects are reported in fish when cyanide concentration range from 5-20 micrograms per liter [5].

Because of strict permitting guidelines, most, if not all, gold milling operations must consider the cost of cyanide destruction in the overall cost of operation. Regulators

typically only require the monitoring of three categories of cyanide; free cyanide, WAD cyanide, and total cyanide [5].

1.2 Research Objective

For many years, the mining industry has utilized cyanide to extract gold from ore. Environmental concerns have made the use of cyanide relatively expensive, particularly in view of the controls necessary to prevent discharge of cyanide into the environment. Consequently, extensive efforts have been carried out to control the discharge of cyanide to find feasible metallurgical alternatives to cyanide. Still, cyanide remains the dominant reagent for the extraction of gold, especially from those ores in which the gold is relatively difficult to extract using other methods.

There are several processes, which reduce the level of cyanide discharged; one such process is the INCO process. The use of sulfite in the oxidation of cyanide (INCO process) has been a very effective process in cyanide destruction. With the recent low gold prices, the need to reduce reagent consumption and associated costs is important, in order for mining companies to remain viable. It was the intent of this study to investigate the reaction kinetics and to provide a model for the destruction of cyanide through the INCO process. Such a model would aid in achieving permitted discharge requirements with efficient utilization of reagents, thus reducing costs.

Chapter 2. Literature Review

There are two major mining processes in which cyanide chemicals are used. The first is a hydrometallurgical process in which a solution of cyanide in water is used to dissolve gold and silver from their ores. This milling process uses cyanide in quantity, and typically, cyanide solutions are present in the entire mill circuit. A modification of this process is heap leaching in which a cyanide solution is sprayed over an ore pile. The solution containing the dissolved precious metals is collected in a storage pond or tank. The second major use of cyanide in mining is in the froth flotation process, where cyanide is used to alter the surface properties of mineral particles.

In addition to gold and silver, the cyanide solutions used in these processes will also dissolve and form complex ions with many other associated metals that are found in mineralized rock. These complex ions have varying degrees of toxicity and are usually disposed to a tailings impoundment.

The Environmental Protection Agency's (EPA) National Pollutant Discharge Elimination System (NPDES) program requires permits for all point source discharges to surface water. For most industries, technology based effluent limits have been established using best available technology. The standard established in 40 CFR 440 Subpart J for mills that beneficiate gold or silver by cyanidation is zero discharge: such mills may not discharge process waste water unless they are in areas where net precipitation exceeds net evaporation [6]. In such areas, mills may discharge the difference between annual precipitation and evaporation, and are subject to national effluent limitations for total suspended solids, concentration of copper, zinc, lead, mercury, cadmium, and pH. All are subject to other standards established on a case-by-case basis. Because tailing dams may leak, the point at which the zero discharge limitation is applied may be downgradient of the impoundment. In such cases, seepage from the impoundment is

collected in ponds or interceptor wells and pumped back to the impoundment during the active life of the facility.

2.1 Chemistry of Cyanide

Simple cyanide salts of sodium, potassium and calcium readily dissolve, and are readily ionized in water to form their respective metal cation and free cyanide anion. Both sodium and potassium cyanide have similar solubilities, 48 and 50-gm/100 cc respectively at 25° C. Cyanide ions in water form molecular hydrogen cyanide and hydroxide ions resulting in an increase in pH [1]. The chemical equation is as follows:

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$
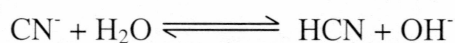
Hydrogen cyanide is a weak acid, which incompletely dissociates in water as follows [1]:

$$HCN \rightleftharpoons H^+ + CN^-$$
$$K_a (25^\circ C) = 6.2 \times 10^{-10}$$
$$pK_a = 9.36$$
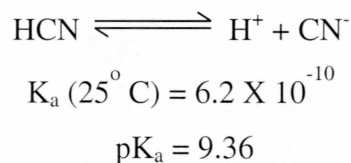
Figure 2.1 shows the extent of this dissociation reaction at equilibrium as a function of pH [1]. It can also be seen that half of the total cyanide exists as hydrogen cyanide and half as free cyanide ions at about pH 9.3. At pH 10 almost 90% of the total cyanide is present as free cyanide (CN^-). At pH 8 over 90% exists as hydrogen cyanide. Hydrogen cyanide has a relatively high vapor pressure (100 kPa at 26° C [1]) and will volatilize readily at the liquid surface under ambient conditions, resulting in loss of cyanide from the solution. This data is represented in Table 2.1.
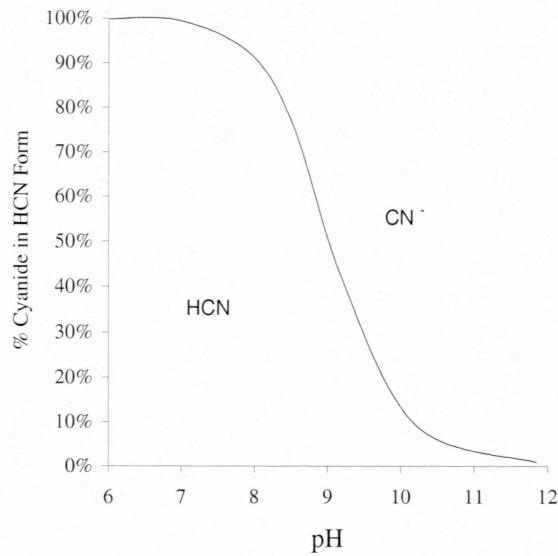
Figure 2.1 Aqueous Speciation of Cyanide and Hydrogen Cyanide as a Function of pH.

Table 2.1

Free Cyanide Speciation as a Function of pH [3]

pH	HCN (%)	CN- (%)
7	> 99	<1
8	96	4
9	70	30
9.36 (pKa)	50	50
10	12	88
11	>1	>99

Thermodynamic data relating to the chemistry of cyanide is shown in Table 2.2. As can be seen, there is considerable uncertainty in this data.

Table 2.2

Thermodynamic Data Relating to Cyanide Chemistry [7]

	kJ mole^{-1}	kcal mole^{-1}
Standard enthalpy of formation of (CN)	+ 435 (+/- 40)	+ 104 (+/- 10)
Dissociation enthalpy of (CN)	+ 745 (+/- 40)	+ 178 (+/- 10)
Standard enthalpy of formation of (CN)	+ 54 (+/- 25)	+ 13 (+/- 6)
Electron affinity of (CN)†	+ 380 (+/- 70)	+ 91 (+/- 16)
Enthalpy of hydration of (CN)	- 305 (+/- 20)	- 73 (+/- 5)

† The positive values denote a negative enthalpy of electron capture.

Hydrogen cyanide can be converted to cyanate, through oxidation, according to the following simplified reaction:

$$HCN + \frac{1}{2}O_2 \rightleftharpoons HCNO$$
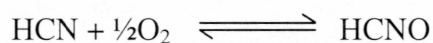
Cyanate (CNO⁻) and hydrogen cyanate (HCNO) ions are significantly less toxic than HCN. Cyanide conversion to cyanate ion in the presence of strong oxidizers such as chlorine, hypochlorite, ozone, and hydrogen peroxide has been demonstrated. In fact, the mining industry often uses several of these oxidants to decompose cyanide in wastes. When hypochlorite is combined with cyanide in an alkaline solution, an intermediate toxic compound is formed, cyanogen chloride (CNCl), which is then converted to cyanate. Various strains of microorganisms will also convert cyanide into cyanate, and then to carbon dioxide. This conversion also takes place with ultraviolet light in conjunction with a catalyst. It is theorized that the ultraviolet light causes the catalyst to convert oxygen to ozone, which promptly reacts with cyanide [3]. As shown in Figure 2.2, the thermodynamics of the cyanide-cyanate reaction should favor cyanate as the predominant species under typical leaching conditions. However, a strong oxidant is required to drive the reaction to equilibrium. Oxidation of cyanide to cyanate, under natural ambient conditions, is difficult to achieve in a timely manner.
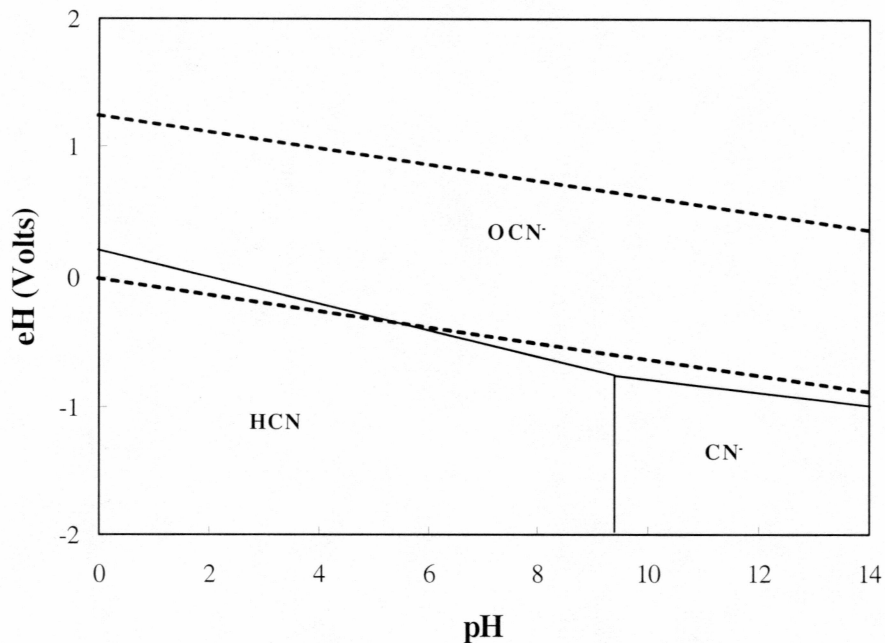
Figure 2.2 Eh-pH Diagram for the CN$^-$-H$_2$O System at 25° C [3]

Since cyanide will form strong complexes with gold, a relatively weak cyanide solution can be used. In the absence of other metal cyanide complexes, a 100-mg/l solution of NaCN (about 50-mg/l free cyanide) is sufficient to achieve the proper rate and extent of dissolution [3]. Since the silver cyanide complex is weaker than gold cyanide, a stronger cyanide solution and/or longer contact time must be employed for the dissolution of silver. With the increased concentration of cyanide, the solution concentrations of other metallic minerals present in the ore are also increased. The elevated cyanide and metal-cyanide concentrations in solution significantly increase the complexity and cost of treatment. The relative stability of metal cyanides is shown in Table 2.3.

Table 2.3

Relative Stability of Cyanide Complexes in Water [6]

Cyanide Species	Metal-Cyanide Complex
Simple Compound	CN^-, HCN
Readily Soluble	NaCN, KCN, $Ca(CN)_2$, $Hg(CN)_2$
Relatively Insoluble	CuCN, $Ni(CN)_2$, AgCN
Weak Complexes	$Zn(CN)_4^{2-}$, $Cd(CN)^{3-}$, $Cd(CN)_4^{2-}$
Moderately Strong Complexes	$Cu(CN)_3^{2-}$, $Cu(CN)^{2-}$, $Ni(CN)^{2-}$, $Ag(CN)^{2-}$
Strong Complexes	$Fe(CN)_6^{4-}$, $Co(CN)^{4-}$, $Au(CN)_6^{2-}$

In spite of the relative specificity of the gold-cyanide reaction, other metals and inorganic constituents react both with cyanide and to a certain extent with hydroxide, which must be present to maintain cyanide in its ionic form.

Nearly all of the transition elements are known to form metal cyanide complexes in aqueous solutions. Though there is reference to simple and complex transition metals cyanide complexes, both carbon and nitrogen atoms are active when cyanide acts as a donor species [7].

The most common metal-cyanide complexes found in barren solutions of gold mining operations and their dissociation constants are shown in Table 2.4. Oxidation of metal cyanides becomes increasingly difficult with the increase in stability of the complex. The metal complexes of Zn, Cd, Ni and Cu can be destroyed chemically, while the complexes of Fe, Au and Ag require ultraviolet light to complete the decomposition process [8].

Table 2.4

Dissociation Constants of Metal-Cyanide Complexes [8]

Chemical Dissociation		Ultraviolet Dissociation	
Metal	Dissociation Constant	Metal	Dissociation Constant
Zn	10^{-16}	Fe^{2+}	10^{-35}
Cd	10^{-19}	Au	10^{-38}
Ni	10^{-21}	Ag	10^{-41}
Cu	10^{-29}	Fe^{3+}	10^{-42}

The weak acid dissociable cyanide reports not only as free cyanide, but also as cyanide weakly complexed to other metals; most notably Cu, Ni, and Zn. These three metal complexes are predominantly associated with mining effluent and exhibit varying degrees of stability with greater tendencies to breakdown, when compared to iron cyanides, with the release of free cyanide. In addition, these compounds exhibit varying degrees of inherent toxicity.

2.2 Chemistry of the INCO Process

The oxidation of cyanide to cyanate with the INCO process is given as follows:

$$CN^- + SO_2 + O_2 + H_2O \xrightarrow{Cu^{+2}} CNO^- + H_2SO_4$$
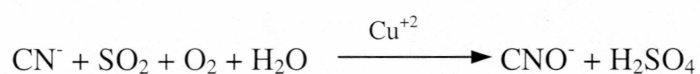
This reaction requires the presence of copper to act as a catalyst. Copper may be present in solution from normal dissolution of copper present in the ore, or may be added as copper sulfate. The copper concentration is effective in the range of 5 to 20 ppm Cu. Based on the above reaction, the theoretical requirement of SO_2 to CN^- is about 2.47 gm SO_2/gm CN^-. However, due to SO_2 consumption by other chemical reactions the SO_2 is typically greater [9].

The best pH range for the slurry treatment is 8.0 to 10.0 and is normally controlled by lime addition. However, when there is excessive undissolved lime present in the tailings, extra SO_2 is added to reduce the pH.

Only a small fraction of the oxygen from the air is actually transferred to the solution. The oxygen transfer rate required follows a straight-line relationship to the SO_2 addition rate. The oxygen transfer rate increases approximately with the square root of the airflow. Once the oxygen is in the solution, it is available to react with the SO_2 and the CN^-. If there is insufficient oxygen being transferred, the destruction performance will suffer through oxygen starvation. The oxygen transfer rate can be increased by lowering the weight percent of solids in the reactor or by the addition of more air [9].

The sulfuric acid generated during the oxidation of cyanide and other oxidation reactions is neutralized with lime to form calcium sulfate, commonly known as gypsum.

$$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 \bullet 2H_2O$$

The feed to this process commonly contains metallic cyanide complexes, which are decomposed as follows:

$$Zn(CN)_4^{2-} \longrightarrow Zn^{2+} + 4CN^-$$

$$Ni(CN)_4^{2-} \longrightarrow Ni^{2+} + 4CN^-$$

$$Cu(CN)_4^{2-} \longrightarrow Cu^{2+} + 4CN^-$$
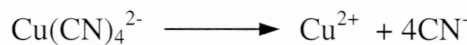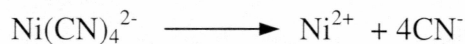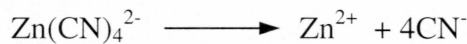
The liberated metal ions may then precipitate as metal hydroxides.

$$Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2$$

$$Ni^{2+} + 2OH^- \longrightarrow Ni(OH)_2$$

$$Cu^{2+} + 2OH^- \longrightarrow Cu(OH)_2$$

In this process, copper, if added as cuprous ion, is oxidized to the cupric ion form before it is precipitated as copper hydroxide by the following reaction:

$$2Cu^+ + SO_2 + O_2 + 2H^+ \longrightarrow 2Cu^{2+} + H_2SO_4$$
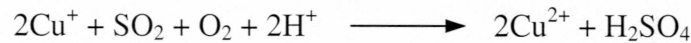
If the cuprous to cupric reaction is incomplete, thiocyanate (SCN^-) will maintain the copper in solution as $Cu(SCN)_2^-$ [9].

Typically, the iron cyanide complexes are not decomposed through this process. Ferricyanide is reduced to ferrocyanide with SO_2, which then forms a metallo-ferrocyanide complex, which is precipitated with available metal ions. The proposed reaction mechanisms are shown below:

$$2Fe(CN)_6^{3-} + SO_2 + 2OH^- \longrightarrow 2Fe(CN)_6^{4-} + H_2SO_4$$

Then:

$$2M^{2+} + Fe(CN)_6^{4-} + 7H_2O \longrightarrow M_2Fe(CN)_6 \bullet 7H_2O$$
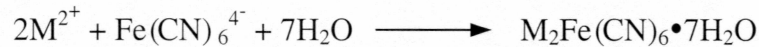
Where M^{2+} = {Zn^{2+}, Ni^{2+} or Cu^{2+}}. Other strong cyanide complexes such as silver cyanide $Ag(CN)^{2-}$, and mercury cyanide, $Hg(CN)_4^{2-}$ are not destroyed by this process. According to INCO laboratory test work, the gold cyanide $Au(CN)^{2-}$ complex is not affected by this process [9].

Sulfur compounds are partially oxidized by the SO_2/Air process when there is excess SO_2 and minimal cyanide present to be consumed in the reaction. The following mechanism is proposed:

$$2CN^- + 4SO_2 + 3O_2 + 4H_2O \longrightarrow 2CNO^- + 4H_2SO_4$$

$$2S_2O_3^{2-} + SO_2 + O_2 + 2H_2O \longrightarrow S_4O_6^{2-} + H_2SO_4 + 2OH^-$$

$$S_4O_6^{2-} + 7SO_2 + 7O2 + 12H_2O \longrightarrow 11H_2SO_4 + 2OH^-$$
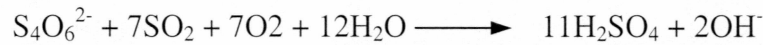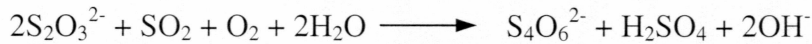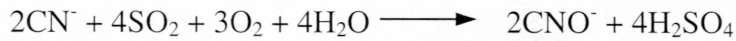
Excess SO_2, with sufficient oxygen present, will favor the decomposition of SO_2 according to the following reaction:

$$2SO_2 + O_2 + 2H_2O \longrightarrow 2H_2SO_4$$
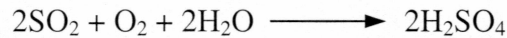
However, insufficient oxygen will favor the precipitation of SO_2 as calcium sulfite. Calcium sulfite in the tailing impoundment would then be soluble according to the following reaction:

$$Ca(OH)_2 + H_2SO_3 \longrightarrow CaSO_3 \cdot 2H_2O$$
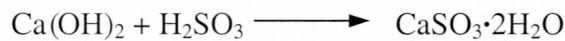
The cyanate ion, CNO^-, is not stable and will hydrolyze to carbonate and ammonium ions according to the following reaction:

$$CNO^- + 2H_2O \longrightarrow CO_3^{2-} + NH_4^+$$

The ammonium ion is stable within the pH range typically found in this system. It will exit the water system through the evolution of ammonia gas in the grinding mills, leach circuit, or tail impoundment.

2.3   Kinetics of Chemical Reactions

Kinetics, unlike thermodynamics, requires a model in order to understand and interpret the results of experimental data. Thermodynamics is concerned with the initial and final states, while kinetics is concerned with the path that is taken. Chemical kinetics then is concerned with the change in concentration of compounds over a period of time and the factors which influence this change. Differential equations can be written to describe the change in concentration with time, but solving these equations may become difficult. Consider the simple acid base reaction:

$$H_3PO_4 + 3NaOH \longrightarrow Na_3PO_4 + 3H_2O$$

The reaction rates will have the following interdependencies [10]:

$$-d[H_3PO_4]/d\,t = -1/3d[NaOH]/d\,t = d[Na_3PO_4]/d\,t = 1/3d[H_2O]/dt$$

Where: [ ] is defined as molar concentration

Several factors determine the rate of a specific reaction. These factors are expressed in the "collision theory" which states that for molecules to react; they must 1) collide, 2) have sufficient energy, and 3) have the correct geometry. To increase the rate, these factors must be made more likely to occur. This is made possible by changing other factors such as:

- Increasing the surface area (of solids), allowing for more collisions, which gives more molecules the right geometry.
- Increase the temperature, which gives more molecules sufficient energy, also called the activation energy, E_a.

Energy barrier-to-react,
molecules must have at least this
amount of energy

Increasing temperature
moves the curve to the right
allowing more molecules to
have the needed energy

# of Molecules

Kinetic Energy
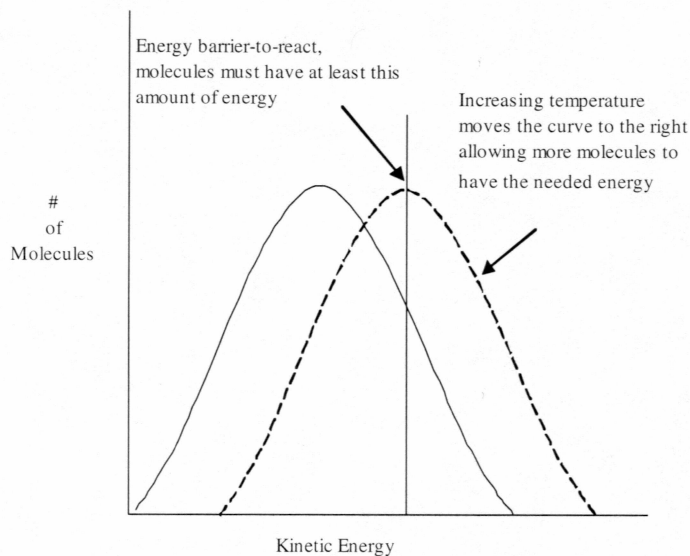
Figure 2.3 Effect of Temperature on the Reaction Rate

- Increasing the concentration of gases and solutions, allowing for more collisions and required geometry.
- Use of a catalyst, which help molecules achieve the correct geometry by providing a different way to react.

Using a catalyst moves
the energy barrier to
the left allowing more
molecules to react.

Original energy barrier

# of Molecules

Kinetic Energy
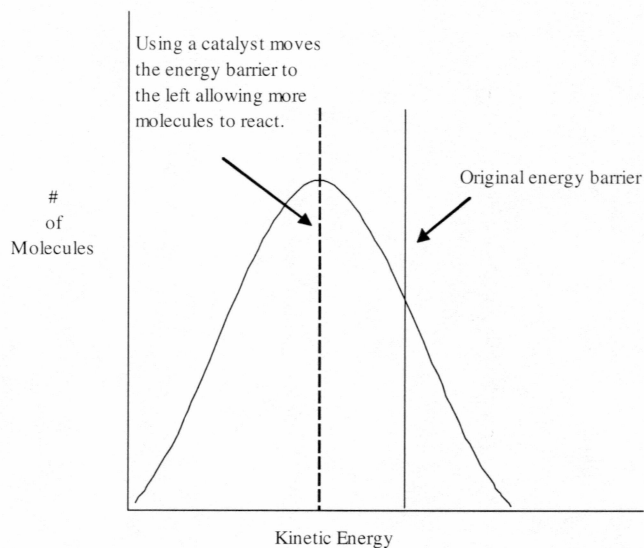
Figure 2.4 Effect of a Catalyst on the Reaction Rate

Usually, the reaction mechanism is much more complex than would be predicted from the stoichiometry of the reaction. Only through experimentation can the dependence of the rate upon the concentrations of the reactants and products be established. A generalized expression can be written as follows:

$$\text{Rate} = k\,[A]^{\alpha}\,[B]^{\beta}\,[C]^{\gamma}...$$

In the above equation, k is the rate constant, [ ] represents the molar concentration of reactants A, B and C. The α, β and γ are the powers of the respective species concentrations upon which the rate is dependent and not associated with stoichiometric ratios. These values need not always be equal to whole numbers. The overall order of the reaction (n) is given as the sum of the powers, that is:

$$n = \alpha + \beta + \gamma...$$

When a reaction is complex, an approach used to determine the dependency of the reacting species is to set up conditions in which only one species has significant changes in concentration. Determining dependency in this manner results in a reaction with a pseudo-order. Consider the reaction [10].

$$A + B \longrightarrow C$$

If the overall rate is the same as the stoichiometry given in the reaction above, the rate expression for the change in concentration of A will be:

$$d\,[A]/dt = k\,[A]\,[B]$$

Moreover, the overall reaction order is two. If experimentally the concentration of B were held constant then the above equation may be expressed as:

$$d\,[A]/dt = k'\,[A]$$

The measured rate constant, k', will be equal to:

$$k' = k\,[B]$$

This rate equation is said to be a pseudo first-order reaction. When considering the work contained in this study the overall reaction of cyanide and SO_2 is dependent on pH and the concentration of copper. If the pH and copper concentration is held constant, the order of the reaction with respect to SO_2 may be determined. The order of the reaction under these conditions would then be pseudo with some n^{th} order. It is important to note that the reaction is normally carried out in an aqueous solution with large excess of water compared to the other reactants, and, therefore no dependency on the concentration of water is usually observed [10].

Chapter 3. Methods, Materials and Instrumentation

3.1 Background

Most kinetic measurements are done using a technique first pioneered by Wilhelmy, who measured the rate at which sucrose was converted to lactose and fructose in the fermentation of wine [10]. The basic principle is to initiate a reaction and measure the concentration of an essential species as a function of time. A variety of methods may be used to determine a first order reaction.

The simplest method called the *conventional method* is to mix the reactants in a beaker, and then measure concentrations as a function of time. Generally, this is a very easy technique. However, it may take several seconds to mix the reactants and several seconds to make the concentration measurements. Consequently, this method is useful only for reactions that are slow enough, so that the reactants can be mixed and the measurements made, before there is significant conversion of reactants to products.

This conventional method is an indirect method, since it does not measure the rate as a function of concentration directly. However, the concentration is measured directly with respect to time and the data is fit to infer a rate law [10].

The oxidation of cyanide with SO_2 lends itself nicely to this method because the overall reaction is slow; approximately 60 minutes to achieve completion of the reaction. Indirect measurements are generally made in a batch system.

3.1.1 Amperometric Determination of Cyanide

The method used for determination of cyanide concentration in this study is based on measuring the potential across a silver working electrode and a silver/silver chloride reference electrode. The detector bias is set at 0.0v with a potentiometer setting of 5.0v. For each test the WAD cyanide analyzer was standardized using five standards ranging

from zero to 50 ppm cyanide. This is accomplished by performing routine analyses of standards to determine; 1) analytical time 2) coordinates of the y-axis (picoamperes), and 3) the area of under the peak, which results in the maximum peak height for concentration determination. A typical calibration curve is shown in Figure 3.1 [10].

$$y = 194265x - 2135$$
$$r^2 = 0.9999$$
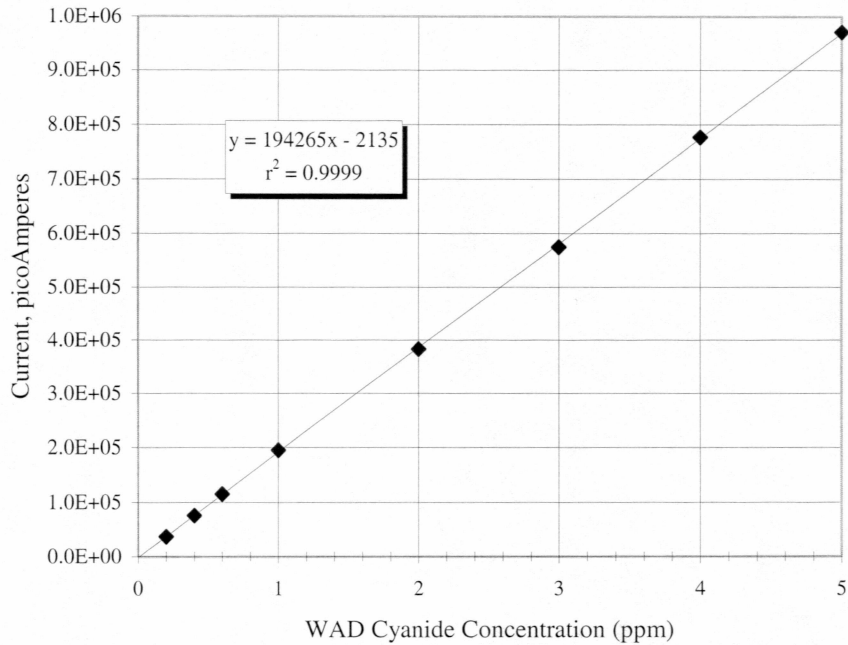
Figure 3.1 WAD Cyanide Calibration Curve (0-5 ppm) Documented [10]

Typically, this instrument is best suited for detection of low concentrations of cyanide, 0.0 to 5.0 mg/l. Testing was conducted to determine the best method for determining cyanide concentration within the parameters of the instrument. Initial tests were conducted by taking an aliquot of the batch solution and performing a 1:10 dilution in an aqueous solution of 0.1 M NaOH and 10 drops WAD reagent A and 20 drops of WAD reagent B. The aliquot was then analyzed for WAD cyanide. The cyanide concentration of the solutions tested was typically in the range of 35 to 40 mg/l CN⁻ therefore; a 1:10 dilution placed the analyses within the calibration curve of 1 to 5 mg/l CN⁻.

The preferred method, which proved to be adequate for this test, was to perform continuous WAD cyanide analyses based on a standard curve with standard concentrations in the range of 1.0 to 50 mg/l. A calibration was done prior to each test to verify proper operation of the instrument. A typical calibration curve based on these standards is shown in Figure 3.2
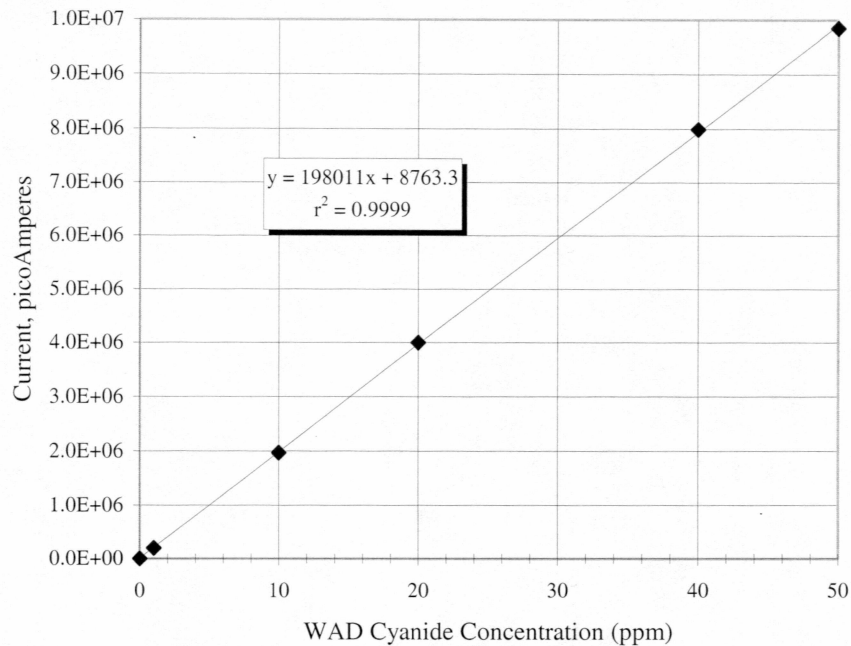
Figure 3.2 WAD Cyanide Calibration Curve (0-50 ppm) Tested

3.2 Materials

The chemicals used in this research project, unless otherwise noted, were industrial grade chemicals on hand in the laboratory of the Fort Knox gold mine. Deionized water is produced in the lab with a Barnstead/Thermolyne NanoPure deionized water system. This system is maintained to provide a consistent deionized water source with conductivity between 10 and 18 μohm^{-1}.

Stock cyanide solution was prepared from 24% CN^- solution used in the Fort Knox mill for leaching. The 24% CN^- solution is prepared from cyanide briquettes, purchased from Dupont Chemical, which are dissolved in process water taken from the fresh water impoundment. Cyanide standards were made from 1000-mg/l stock solution made from sodium cyanide pellets purchased from VWR (Van Waters and Rogers) chemical division. This stock solution was tested weekly for strength and deterioration.

The source of the SO_2 was provided from a concentrated solution of ammonium bisulfite aqueous (ABS) from the cyanide detoxification plant at the Fort Knox Mine. The concentrated (ABS) solution is purchased from Continental Nitrogen and Resources Corporation, Rosemont Minnesota, and is approximately 65% ABS by weight, and is analyzed on a lot by lot basis. By weight, the ABS is approximately 64% available SO_2. For purposes of testing, the ABS was diluted with deionized water to a concentration sufficient to give the desired SO_2 to CN^- ratio.

The source of cupric sulfate 5 hydrate, $CuSO_4 \cdot 5H_2O$ was from a stock solution used in the cyanide detoxification plant at the Fort Knox mine. This copper sulfate solution is 17% w/w copper. For purposes of testing, the copper was diluted with deionized water to a concentration sufficient to give the desired concentration. Copper analyses were done with an atomic absorption flame spectrophotometer. Copper standards were made from 1000 ppm Cu solution purchased from Perkin Elmer Scientific Instruments.

Other special chemicals are WAD reagents A and B purchased from Perstorp Analytical Inc. These are proprietary reagents used for complexing metal cyanides of copper, zinc and cadmium. All solutions were pH adjusted with 0.5 M NaOH stock solution made from Malincrodt technical grade NaOH pellets.

All tests were carried out at room temperature with the exception of the tests for determining temperature dependence.

3.3 Instrumentation

This testing required analyses to determine the concentrations of WAD cyanide and copper. The reduction of WAD cyanide concentration over time was determined with the Perstorp Analytical/ALPCHEM CNSolution Model 3200 Cyanide Analyzer, which measures cyanide concentration amperometrically. Measurements of the concentration of copper were made by classic flame AA methods with a Perkin Elmer AAnalyst 300 Atomic Absorption Spectrophotometer. A Corning model 340 pH meter with automatic temperature compensation was used to perform pH measurements. The pH meter is calibrated with pH 7 and 10 buffer solutions. The recorded temperatures are measured through the internals of the pH probe.

3.3.1 Perstorp Analytical/ALPCHEM CNSolution Model 3202 Cyanide Analyzer.

The CNSolution 3202 is a portable, automated analyzer originally designed for the measurement of cyanide in various samples found in the precious metals mining industry in the US [10]. Presently, this instrument is in use around the world in support of many industrial processes. A complete CNSolution system is comprised of the 3202 Analyzer, CNLab™ software, and an optional 120-place autosampler.

The CNSolution 3202 measures weak acid dissociable (WAD) cyanide. WAD cyanide species include free cyanide (HCN and CN⁻), the simple cyanide compounds (NaCN and KCN) and the weak metal-cyano complexes such as that bound with Zn, Cu, Cd, Hg and Ni, and to some extent Ag. These compounds are likely to break down under normal environmental conditions liberating toxic free cyanide.

The sample is first treated with specific ligand-exchange reagents to liberate cyanide from the weak metal-cyano complexes. Under acidic conditions of the system,

CN^- in the sample is converted to HCN, which diffuses across a hydrophobic membrane and is absorbed into a basic acceptor solution. The CN^- is then detected amperometrically at the flow cell. Typically, analytical time for WAD cyanide is approximately 2 minutes per sample.

As previously stated, this instrument utilizes a ligand-exchange/flow injection amperometric method of analysis. The analytical procedure employed for determination of WAD cyanide is divided into two steps: 1) sample pretreatment and 2) sample quantification finish. In the pretreatment step, ligand-exchange reagents (WAD A and B) are added to the sample at room temperature. The ligand-exchange reagents form thermodynamically stable complexes with various transition metal ions, resulting in the release of CN^- ion from the coordination sphere. The WAD A and B reagents are proprietary in chemical composition. It should be noted that these ligand-exchange reagents were not used for purposes of this test work. This was due to using a cyanide solution that did not contain the metallic cyanide complexes found in typical effluent solutions.

Cyanide ions are released from all the corresponding metal complexes with the exception of Fe $(CN)_6^{3-}$, Pd $(CN)_4^{2-}$, Pt $(CN)_6^{2-}$, Ru $(CN)_4^{4-}$, Co $(CN)_6^{3-}$, and Au $(CN)_2^-$. These species do not dissociate under commonly used methods for determination of WAD cyanide by distillation [10].

In the FIA (Flow Injection Analyses) system, a 200 μl aliquot of the pre-treated sample is injected into the flow injection manifold. The subsequent addition of HCl releases HCN, which then passes under a gas diffusion membrane. The generated HCN gas passes through a 0.5 micron membrane to an alkaline receiving solution. The cyanide in the alkaline receiving solution is monitored amperometrically with an Ag working electrode/Ag-AgCl reference electrode and stainless steel counter electrode at an applied potential of 0.0v. The current generated is proportional to the cyanide concentration

present in the original sample. A schematic diagram of the experimental setup is shown in Figure 3.3, and a schematic diagram of the flow cell is shown in Figure 3.4.

Legend:

   A. Stir Plate

   B. 600 ml Reaction Vessel with Test Solution and Reactants

   C. Positive Displacement Pump

   D. 200 μl Sample Loop Injection

   E. Injection Manifold

   F. Gas Diffusion Membrane

   G. Flow Cell Ag/AgCl Reference Electrode, Ag working Electrode (Magnified in Figure 3.4)

   H. pH Electrode with Temperature Compensation
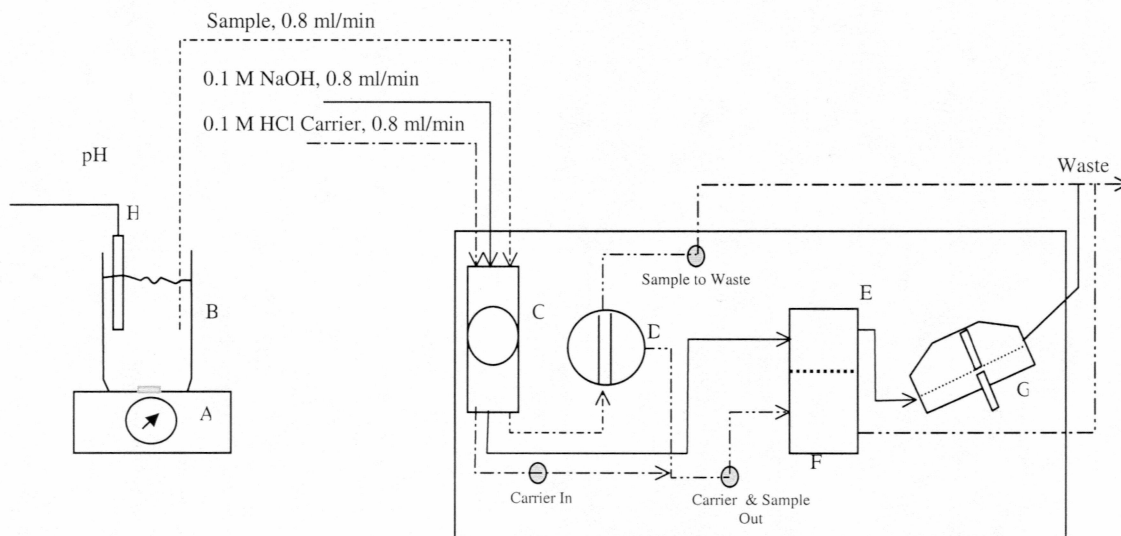
Figure 3.3 Schematic Diagram of the Perstorp WAD Cyanide Analyzer

Legend:

A.   Solution In

B.   Ag Working Electrode

C.   Ag/AgCl Reference Electrode

D.   Stainless Steel Counter Electrode

E.   Solution Out
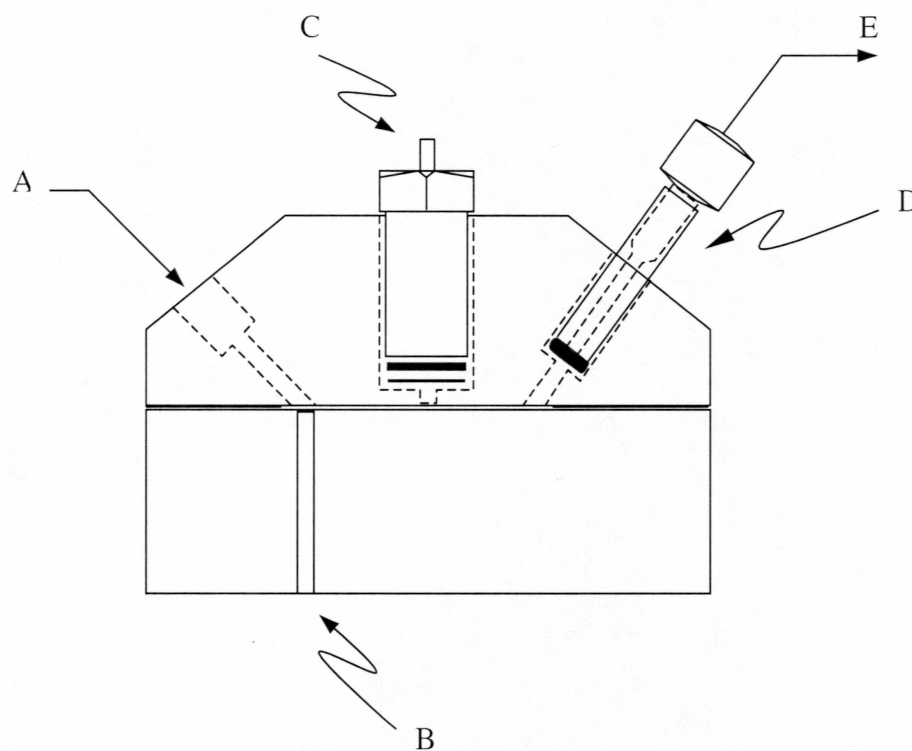
Figure 3.4 Schematic Diagram of High Performance Amperometric Flow Cell

3.3.2   Perkin Elmer AAnalyst 300 Atomic Absorption Spectrophotometer [13]

This instrument utilizes a double-beam, time-shared and space-shared optical system with deuterium background correction. The optical system is front-surface reflecting with a protective coating and sealed within a "tongue and groove" protective cover.

The monochromator is of Littrow design with a wavelength range of 185–860 nm, with a motorized drive for automatic wavelength selection and peaking. It has a diffraction grating with 1800 lines/mm blazed at 236 nm and 597 nm. The grating area is 64 x 72 mm with a reciprocal linear dispersion of 1.6 nm/mm. Its focal length is 274 mm and spectral bandwidths are 0.2, 0.7, and 2.0 nm. It also utilizes a motorized slit drive for automatic slit selection, and automatic selectable slit height settings (high or low). The detector is a wide range photomultiplier with UV-transmitting window.

The light sources may be hollow cathode lamps or electrodeless discharge lamps. Lamp elements and recommended operating currents are automatically recognized and set when using Perkin Elmer Lumina™ series AA lamps. Lamp alignment is completely automatic with a motorized 6-position lamp turret.

The AAnalyst 300 has computer-controlled oxidant selection with automatic gas sequencing and oxidant and fuel monitoring and control. There is a keyboard-actuated remote ignition system with air-acetylene. Acetylene flow is automatically incrementally adjusted prior to the oxidant change when switching to or from nitrous oxide-acetylene operation.

All gases and solution enter a high-strength inert premixing burner chamber, angled to ensure proper drainage. Separate fuel and oxidant lines to the burner chamber limit combustible gas mixtures to those areas specifically designed to accommodate them. A separate auxiliary oxidant inlet allows variation of fuel oxidant flow ratios

without varying nebulizer oxidant flow, thereby maintaining constant, optimum solution aspiration rates. The burner system also includes an adjustable high sensitivity nebulizer and an all-titanium, 10 cm, single-slot burner head for air acetylene operation. The burner mount provides horizontal, vertical and rotational adjustments to achieve optimal alignment of the flame and optical system.

The system is integrated with an AS-90, 106-position autosampler. The autosampler and AA Spectrophotometer are linked through complete PC control using AA WinLab software operating under the Microsoft Windows operating environment. The software provides complete control of the instrument and its major accessories plus data handling and storage.

Chapter 4. Mathematical Basis, Experimental Procedure and Results

4.1 Development of the Kinetic Model

As previously stated, toxic cyanide is converted to less toxic cyanate by the chemical oxidation with SO_2. The general reaction is as follows:

$$CN^- + SO_2 + O_2 + H_2O \xrightarrow{Cu^{+2}} CNO^- + H_2SO_4$$

The rate law gives the dependence of the rate upon concentrations of reactants, products, catalysts, and inhibitors. For many reactions, the rate is proportional to integer powers of the concentrations of reactant if the volume of the reaction mixture is constant and the concentrations of intermediates are negligible. Based on the above reaction, the following rate equation is proposed:

$$\text{rate} = -d[CN^-]/dt = k[CN^-]^\alpha [SO_2]^\beta [Cu^{+2}]^\gamma [H^+]^\delta \tag{4.1}$$

Where k is the rate constant, the exponents' α, β, γ, and δ are the orders of reaction with respect to each chemical constituent, and [ ] represents the molar concentration.

Copper is present to react as a catalyst, which by definition is "a substance one adds to a chemical reaction to speed up the reaction without the catalyst undergoing a chemical change itself" [10]. Holding the concentration of copper and pH constant, a new rate constant, k', can be defined as follows:

$$k' = k[Cu^{+2}]^\gamma [H^+]^\delta \tag{4.2}$$

Replacing this new constant in Eq. (4.1) would yield the following equation:

$$-d[CN^-]/dt = k' \, [CN^-]^{\alpha} \, [SO_2]^{\beta} \qquad\qquad (4.3)$$

Based on the chemical reaction, CN^- and SO_2 react on a mole per mole ratio. Therefore, the concentration of SO_2 at any time may be determined based on the measured concentration of cyanide, and expressed in the following equation:

$$[SO_2]_t = [SO_2]_0 - ([CN^-]_0 - [CN^-]_t)$$

Where, the subscripts denote concentration with respect to time. Rearranging this equation gives the following

$$[SO_2]_t = ([SO_2]_0 - [CN^-]_0) + [CN^-]_t$$

The concentrations of SO_2 and CN^- are expressed as molar concentration (moles/liter). Making the assumption of first order kinetics with respect to cyanide and SO_2 concentrations, the rate equation may be expressed as follows:

$$-d[CN^-]/dt = k' \, [CN^-]_t \, [(\, [SO_2]_0 - [CN^-]_0 \,) + [CN^-]_t]$$

and

$$-d[CN^-]/dt = k' \, ([CN^-]_t)^2 + [CN^-]_t(\, [SO_2]_0 - [CN^-]_0 \,)) \qquad\qquad (4.4)$$

At, time t = zero, the concentrations of CN^- and SO_2 are fixed. A new variable, D, is defined as follows; $D = ([SO_2]_0 - [CN^-]_0)$. Substituting this into Eq. (4.4) results in the following equation:

$$-d[CN^-]/dt = k' \, ([CN^-]_t^2 + D[CN^-]_t) \qquad\qquad (4.5)$$

Rearranging Eq. (4.5) gives the following:

$$-d[CN^-] / ([CN^-]_t^2 + D[CN^-]_t) = k'dt \qquad (4.6)$$

Integrating Eq. (4.6) gives the following:

$$\int -d[CN^-] / ([CN^-]_t^2 + D[CN^-]_t) = \int k'dt \qquad (4.7)$$

The left side of Eq. (4.7) follows the general formula $\int -dx/(ax^2 + bx)$, which has the following solution: $\int -dx/(ax^2 + bx) = -1/b \ln\{x/(ax + b)\} + C$, where C is the integration constant. The right side of Eq. (4.7) has the following solution $\int k'dt = k't + I$, where I is the integration constant [11].

With these relationships in mind, the left side of Eq. (4.7) may be written as follows:

$$\int -d[CN^-] / ([CN^-]_t^2 + D[CN^-]_t) = -1/D \ln\{[CN^-]_t /([CN^-]_t + D)\} + C$$

and:

$$-1/D \ln\{[CN^-]_t /([CN^-]_t + D)\} + C = k't + I$$

Rearranging gives the following:

$$-\ln\{[CN^-]_t /([CN^-]_t + D)\} + CD = k'D t + D I \qquad (4.8)$$

At time t = zero, the concentration of cyanide is unchanged and may be expressed as $[CN^-]_t = [CN^-]_0$, and $k'D\,t = 0$. Eq. (4.8) then may be expressed as follows:

$$-\ln\{[CN^-]_0 /([CN^-]_0 + D)\} + CD = D\,I \tag{4.9}$$

Substituting Eq. (4.9) for DI in Eq. (4.8) gives the following:

$$-\ln\{[CN^-]_t /([CN^-]_t + D)\} + CD = k'D\,t - \ln\{[CN^-]_0 /([CN^-]_0 + D)\} + CD \tag{4.10}$$

Simplifying gives the following equations:

$$-\ln\{[CN^-]_t /([CN^-]_t + D)\} = k'D\,t - \ln\{[CN^-]_0 /([CN^-]_0 + D)\}$$

and:

$$\ln\{[CN^-]_0 /([CN^-]_0 + D)\} - \ln\{[CN^-]_t /([CN^-]_t + D)\} = k'D\,t \tag{4.11}$$

Given the relationship, $\ln(A) - \ln(B) = \ln(A/B)$, Eq. (4.11) then gives the proposed rate equation for the oxidation of cyanide through the reaction with SO_2 in the INCO Process.

$$\ln\left(\frac{[CN^-]_0\,([CN^-]_t + D)}{[CN^-]_t\,([CN^-]_0 + D)}\right) = k'D\,t \tag{4.12}$$

Through experimentation, the concentration of a single reactant may be varied, while the concentration of cyanide is measured and all other reactants are held constant. A plot of the left hand side of Eq. (4.12) vs. time, with respect to the varied concentration

of the reactant of interest, should give straight lines with slopes = $k'D$, with respect to that reactant.

Reaction rates usually increase with temperature. A form commonly used to express the rate constant, as a function of temperature, is the Arrhenius equation;

$$k = Ae^{-E_a/RT} \tag{4.13}$$

where, A is the frequency factor, E_a is the activation energy, R is the gas constant (8.3 J/mole^{o}K), and T is the temperature in degrees Kelvin. Both E_a and A are usually assumed to be temperature-independent [10], which proves to be a good approximation, at least over a modest temperature range. E_a and A are determined experimentally, by maintaining constant concentration of all reactants while varying the temperature. The traditional method of fitting data to the Arrhenius equation uses a logarithmic form. From Eq. 4.13, the following form is obtained

$$\ln(k) = \ln(A) - E_a/RT$$

Thus, $\ln(k)$ will vary linearly with $1/T$, and the slope of the plot of $\ln(k)$ vs. $1/T$ will give E_a. The intercept will give the frequency factor, A.

4.2 Experimental Procedure and Results

Testing was designed to determine the reaction rates for the oxidation of cyanide in the INCO process. Three sets of tests were designed to measure cyanide concentration, while varying the concentration of the constituent of interest. For each test, one constituent's concentration was varied, while maintaining constant temperature and concentrations of the other reactants. Tests were conducted at room temperature, 22 deg C, unless otherwise noted. In order to determine E_a and A, a forth series of tests was

conducted, where the concentrations of the reactants were held constant and the temperature was varied. Descriptions of the individual tests and results are presented below.

4.2.1 Effect of [SO_2] on cyanide oxidation.

The first set of tests was performed to measure the change in cyanide concentration, with respect to SO_2 concentration, while maintaining constant copper concentration, pH and temperature. These tests were performed using a cyanide solution with a concentration of approximately 40 ppm. The SO_2 concentration was varied according to the $SO_2 : CN^-$ molar ratios of 1.35, 2.43 and 3.39. The initial pH of the test solutions ranged from 10.6 to 11.2. With the addition of SO_2 and Cu, the pH was allowed to stabilize, which was typically in the range between 6.7 and 7.2. The concentration of the copper was analyzed periodically by flame AA, and was typically 14 ppm. The results of this series of tests are shown in Figure 4.1.

4.2.2 Effect of [Cu^{+2}] on cyanide oxidation.

The second set of tests was performed to measure the change in cyanide concentration, with respect to the copper concentration, while maintaining constant SO_2 concentration, pH and temperature. All tests were done using a cyanide solution with a concentration of approximately 44 ppm. The Cu concentration was varied for each test as 10, 22, 38 and 49 ppm. The initial pH was adjusted to 10.6 with 5.0 molar NaOH. With the addition of SO_2 and Cu, the pH was adjusted to approximately 9.0 with the same 5.0 molar NaOH solution for the duration of the tests. The results of this series of tests are shown in Figure 4.2.

4.2.3 Effect of pH on cyanide oxidation.

The third set of tests was performed to measure the change in cyanide concentration, with respect to pH, while maintaining constant copper concentration, SO_2 concentration and temperature. All tests were done using a cyanide solution with a

concentration of approximately 40 ppm. The pH of the solution was varied as 8.0, 9.5 and 10.5, with the initial solution having a pH of approximately 10.7. With the addition of SO_2 and Cu, the pH was adjusted rapidly to the desired level with the addition of 5.0 molar NaOH. The concentration of the copper was analyzed periodically by flame AA and was typically 30 ppm. The results of this series of tests are shown in Figure 4.3.

4.2.4 Effect of temperature on cyanide oxidation.

A final series of tests was performed to determine the effect of temperature on the rate of cyanide oxidation. All tests were done using a cyanide solution with a concentration of approximately 40 ppm. The initial pH was about 10.7, and the pH was adjusted to approximately 9.5 after the addition of SO_2 and Cu, with the addition of 5.0 molar NaOH. The concentration of the copper was analyzed periodically by flame AA and was typically 30 ppm. The temperature was set for each test at 22°, 30° or 40° C. The results of this series of tests are shown in Figure 4.4.
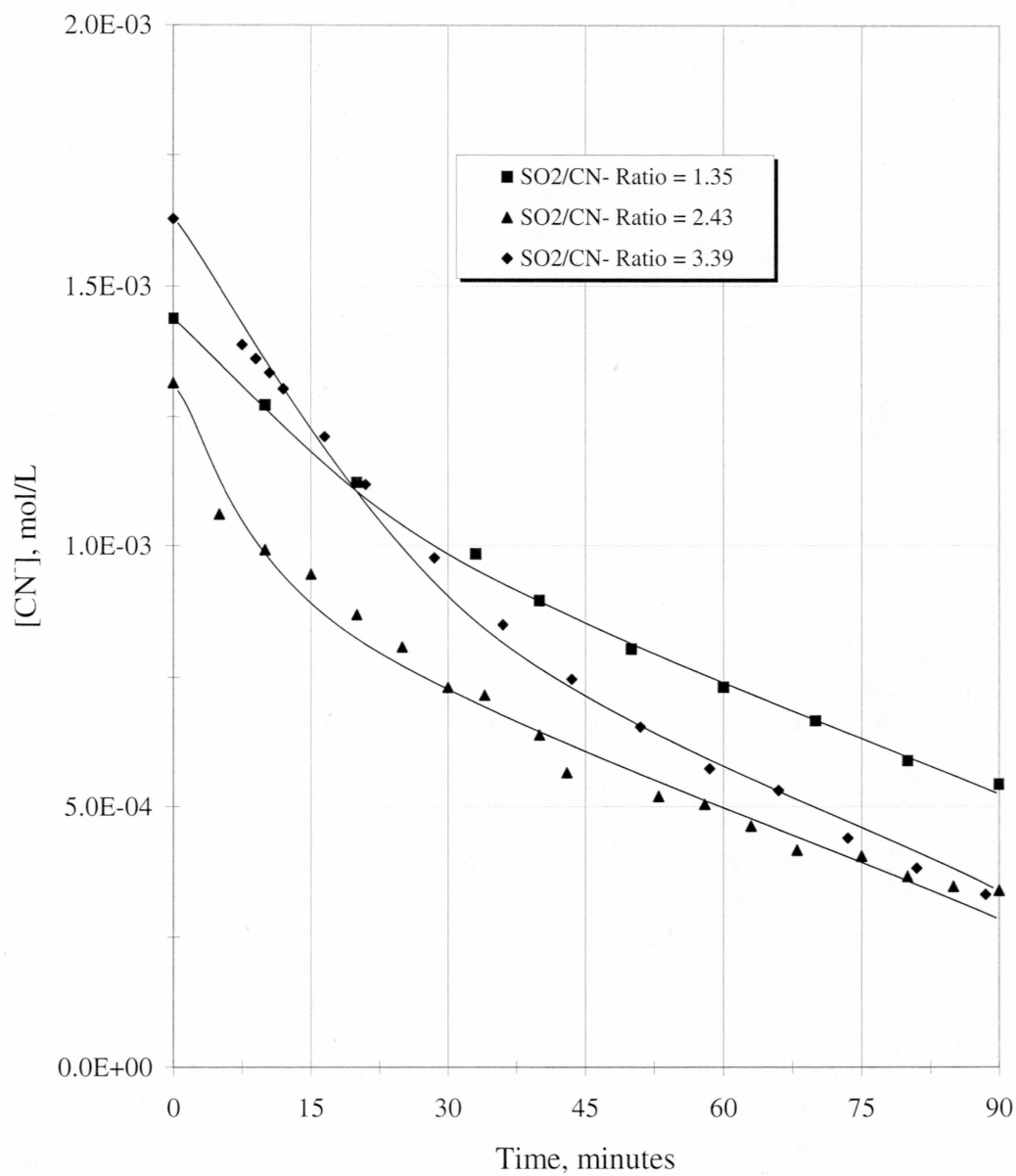
Figure 4.1 Effect of [SO$_2$] on the Oxidation of CN$^-$
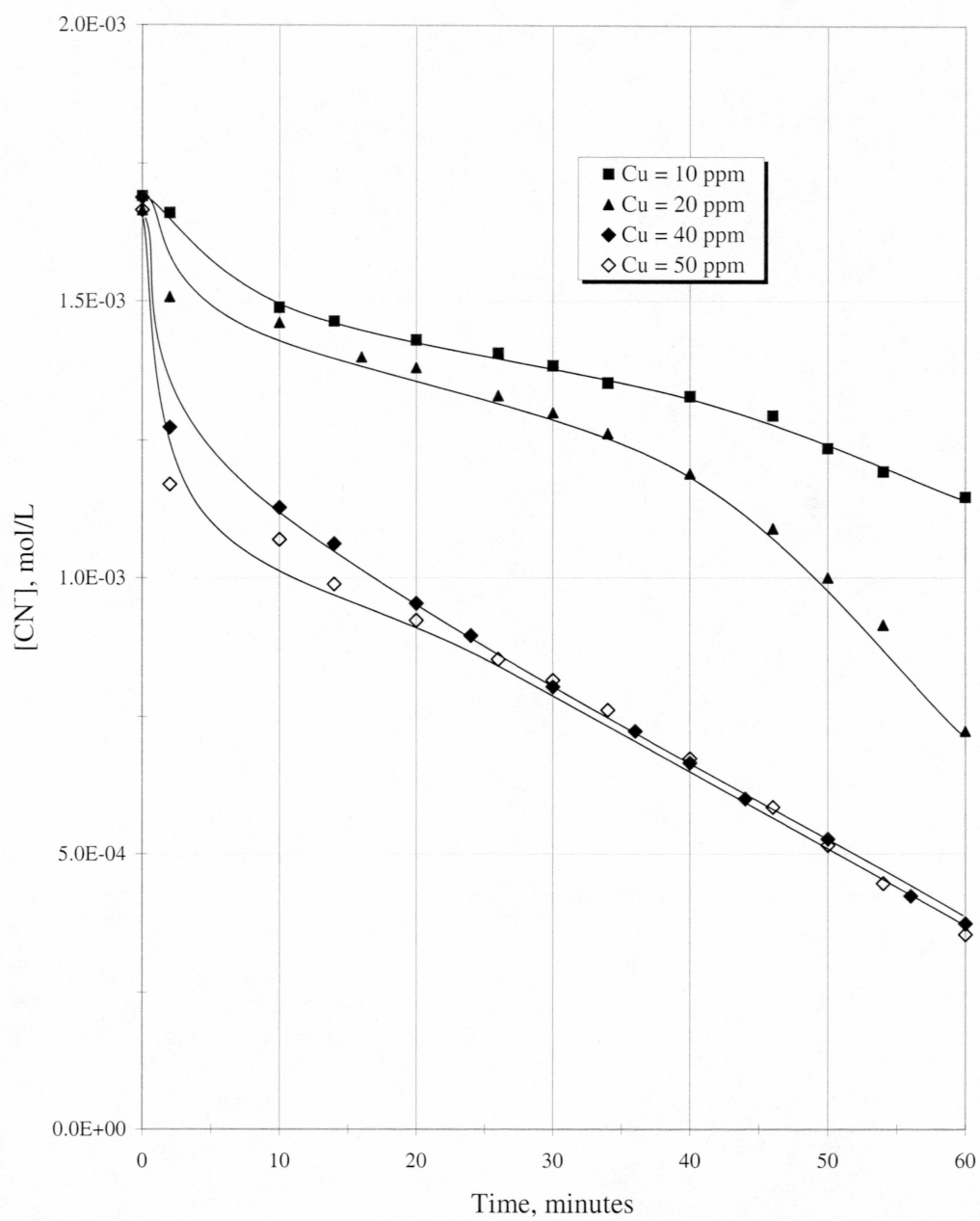
Figure 4.2 Effect of $[Cu^{+2}]$ on the Oxidation of CN^-
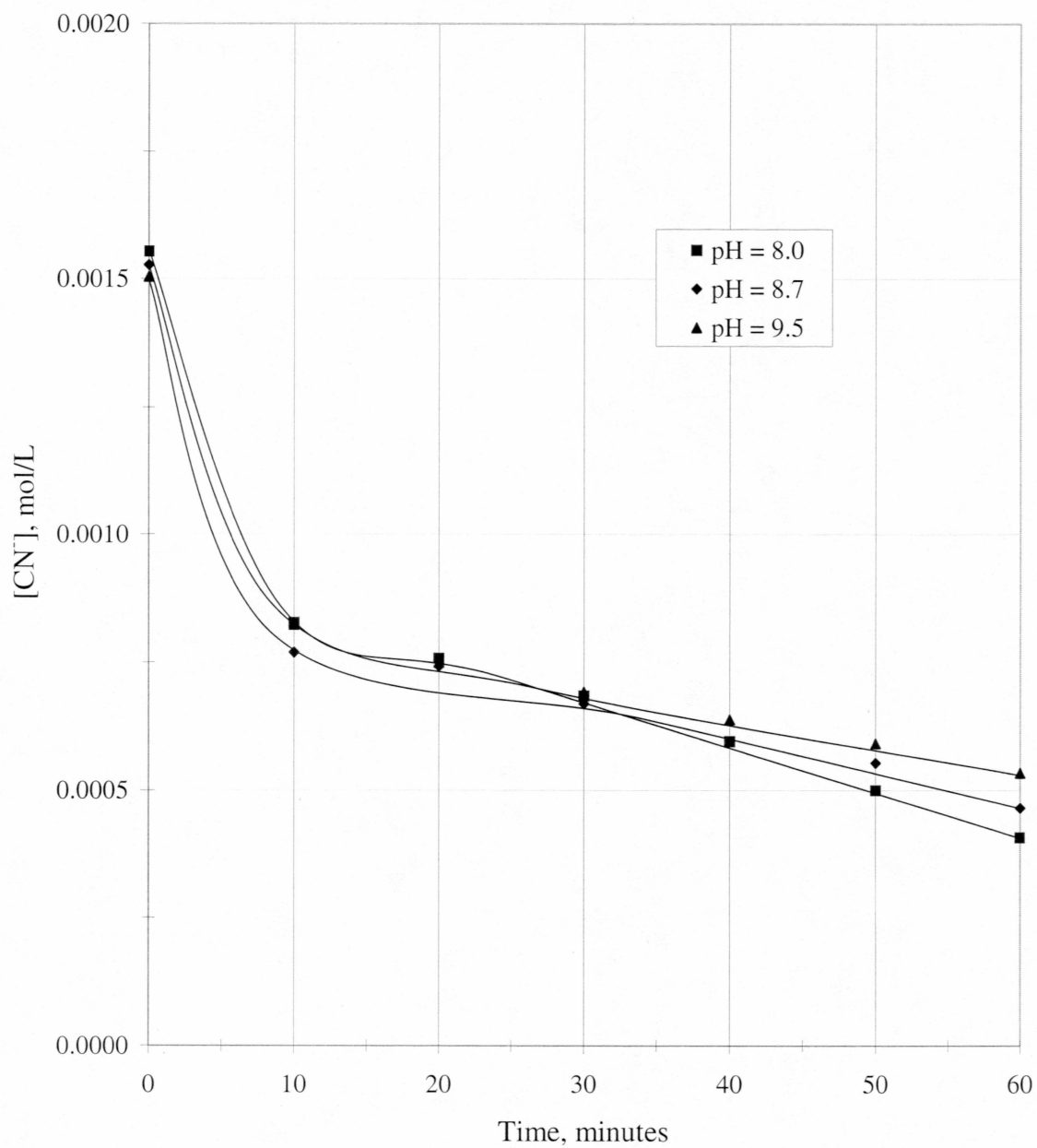
Figure 4.3 Effect of [H$^+$] on the Oxidation of CN$^-$
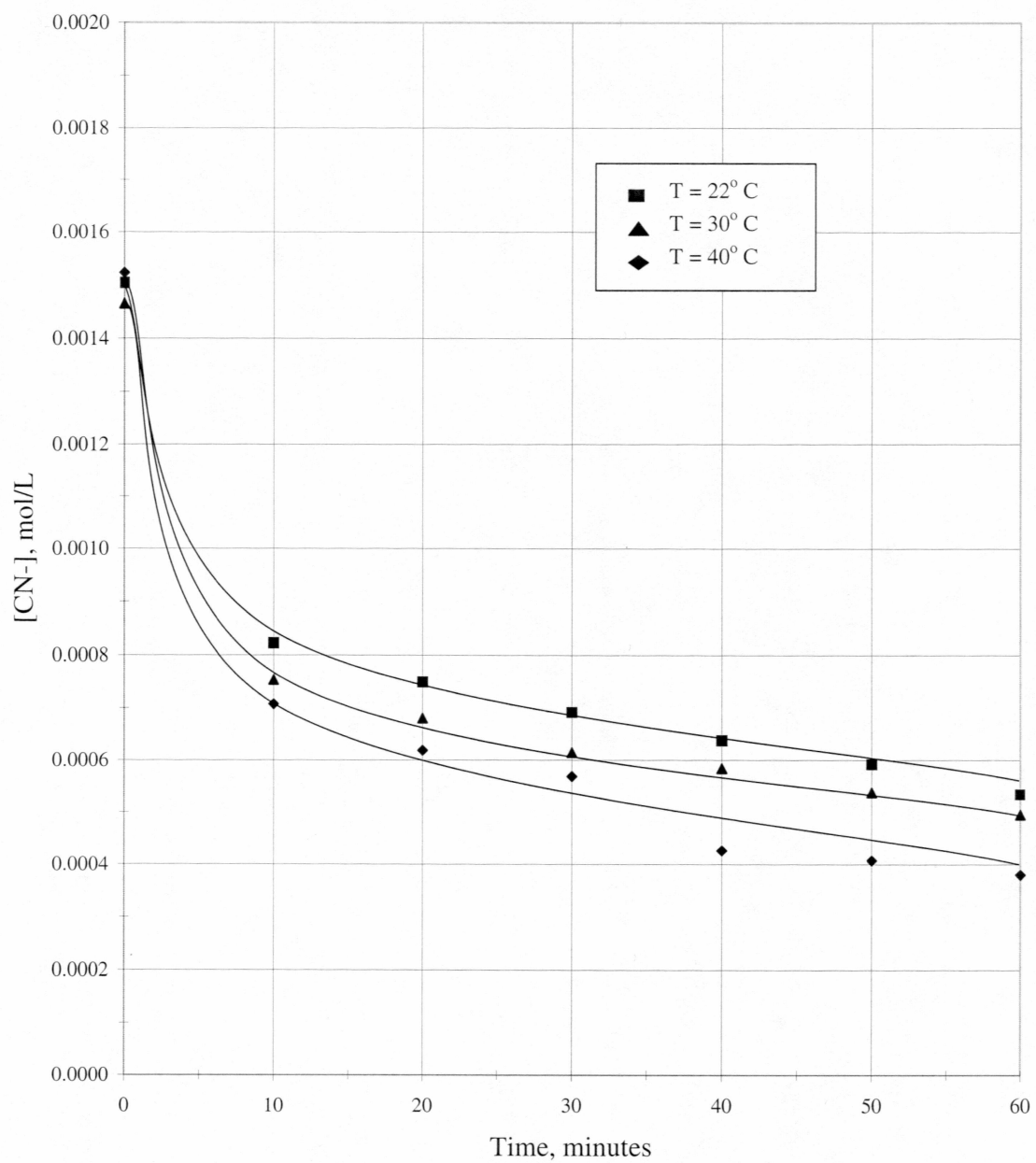
Figure 4.4 Effect of Temperature on the Oxidation of CN⁻

4.2.5 Analyses of k' data to determine reaction order for SO_2.

According to the derivation Eq. 4.12 from the kinetic model, and under conditions of constant $[Cu^{2+}]$, pH and temperature, a plot of:

$$\ln\{[CN^-]_0(\,[CN^-]_t + D)\}/\{[CN^-]_t(\,[CN^-]_0 + D)\} \text{ vs. time}$$

should be linear in a series of the tests where $[SO_2]$ is the variable. Figure 4.5 shows the above relationship is linear, indicating a first order reaction, with respect to cyanide and SO_2 concentrations, as proposed in the development of Eq. 4.12. Each line in Figure 4.5 has slope $k'D$. Figure 4.6 shows a plot of k'D vs. D,, which is also linear, and indicates that k' is approximately 3.1.
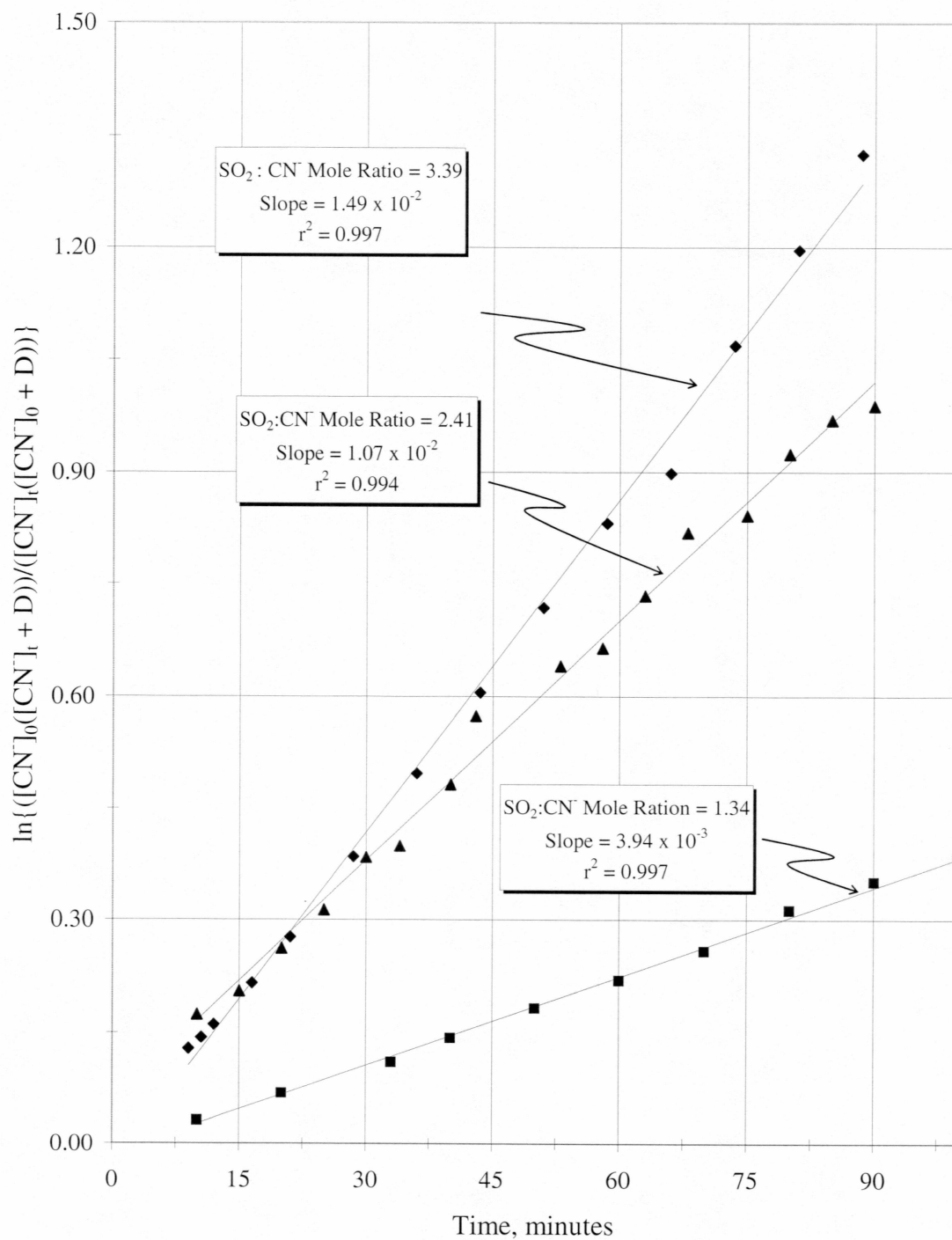
Figure 4.5 Plots to Determine the Rate Constant, $k'D$, with Respect to $[SO_2]$
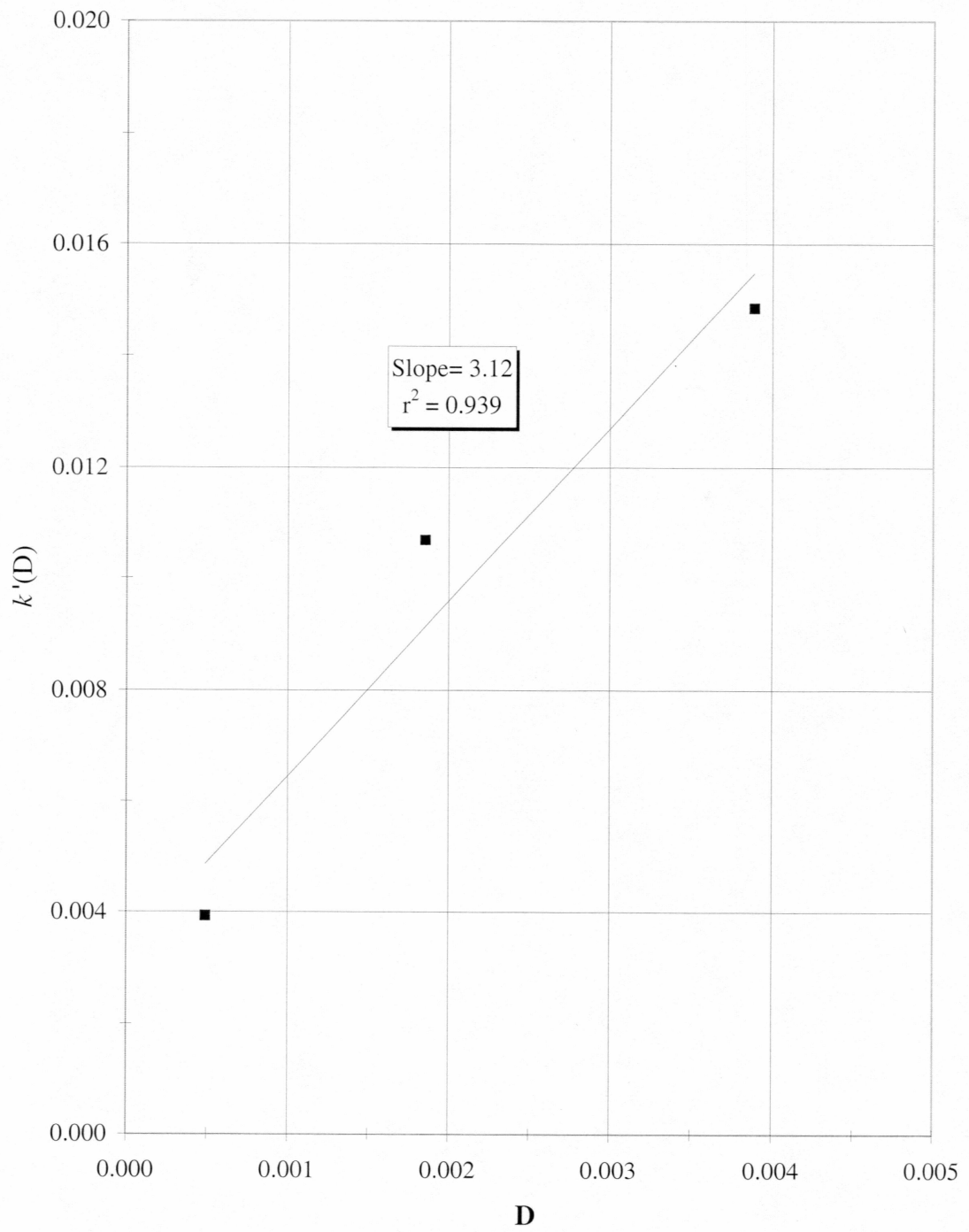
Figure 4.6 Linear Relationship of k'(D) vs. D

4.2.6 Analyses of k' data to determine reaction order for Cu^{+2}.

According to the derivation of Eq. 4.12 from the kinetic model, and under conditions of constant $[SO_2]$, pH and temperature, a plot of:

$$\ln\{[CN^-]_0(\ [CN^-]_t + D)\}/\{[CN^-]_t(\ [CN^-]_0 + D)\} \text{ vs. time}$$

should be linear line in a series of tests, where $[Cu^{2+}]$ is the variable. Figure 4.7 shows this relationship is linear, confirming a first order reaction with respect to cyanide and SO_2 concentration, as proposed in the development of the Eq. 4.12. Each line in Figure 4.7 has slope $k'(D)$, where D was held nearly constant, but k' varies with $[Cu^{+2}]^\gamma$ according to Eq. 4.2:

$$k' = k[Cu^{+2}]^\gamma [H^+]^\delta \qquad (4.2)$$

Multiplying each side of Eq. 4.2 by D and recalling that $[H^+]^\delta$ was held constant throughout the series of test gives the following:

$$k'(D) = (k(D) [H^+]^\delta)[Cu^{+2}]^\gamma \qquad (4.14)$$

Substituting a new rate constant k'', for the constant product $(k(D) [H^+]^\delta)$ yields:

$$k'(D) = k''[Cu^{+2}]^\gamma \qquad (4.15)$$

Taking the natural logarithm of both sides results in:

$$\ln(k'(D)) = \ln k'' + \gamma\ln[Cu^{+2}] \qquad (4.16)$$

Then, a plot of $\ln(k'(D))$ vs. $\ln[Cu^{+2}]$ should yield a straight line with slope γ. The plot is shown in Figure 4.8. The slope of the line, 1.06, in Figure 4.8 indicates that the reaction is a first order with respect to $[Cu^{+2}]$ at copper concentrations less than 40 ppm.

It may be seen from Figure 4.8, that increasing the copper concentration from 40 ppm to 50 ppm did not increase the rate of the reaction proportionately. This may be explained from the fact that catalytic reactions do not always form simple relationships according to the stoichiometry of the overall reaction [10]. It is common in some instance for the rate of a catalytic reaction to remain constant or even go down as the concentration of one of the reactants increases [12].
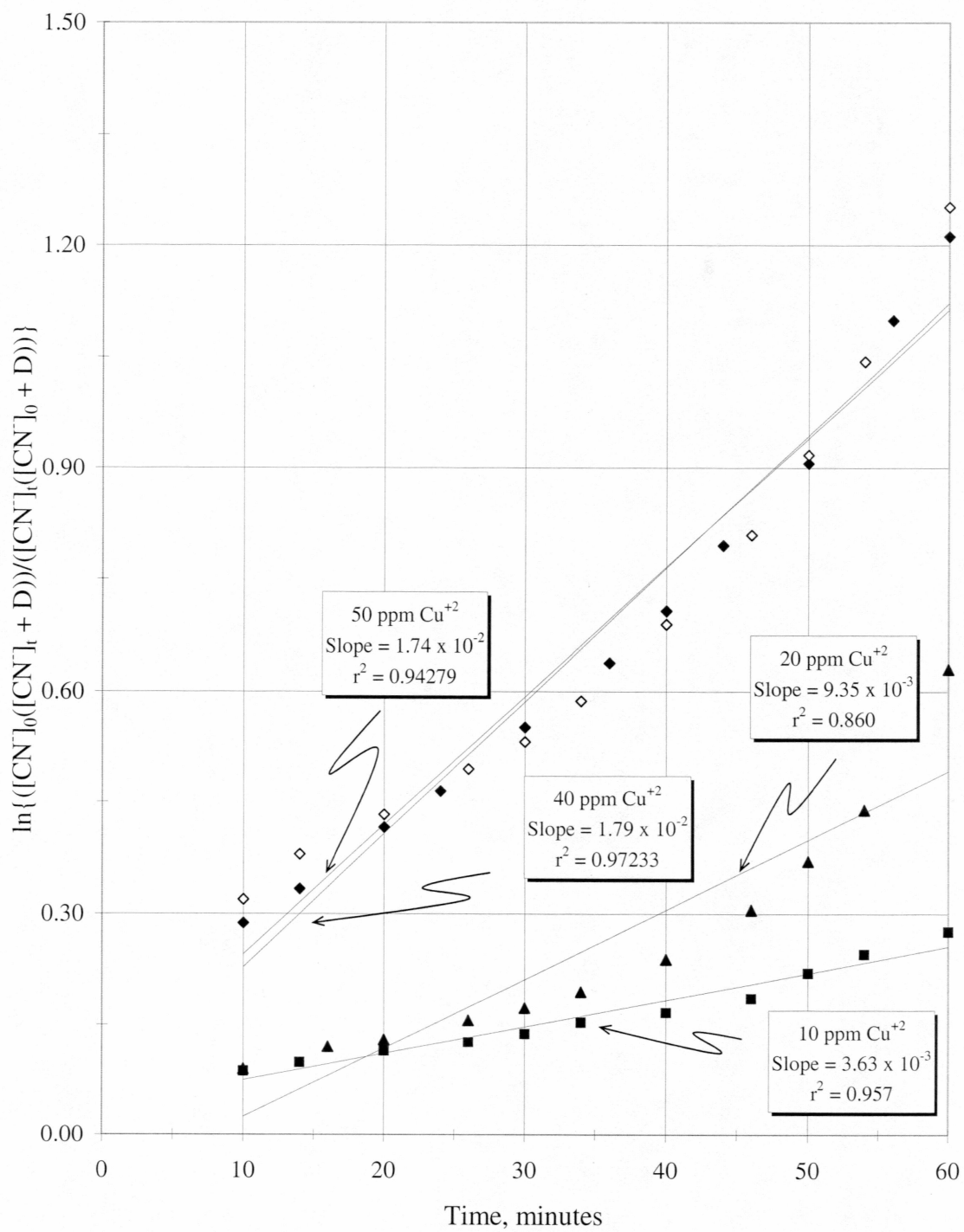
Figure 4.7 Plots to Determine the Rate Constant, k'D, with Respect to $[Cu^{+2}]$
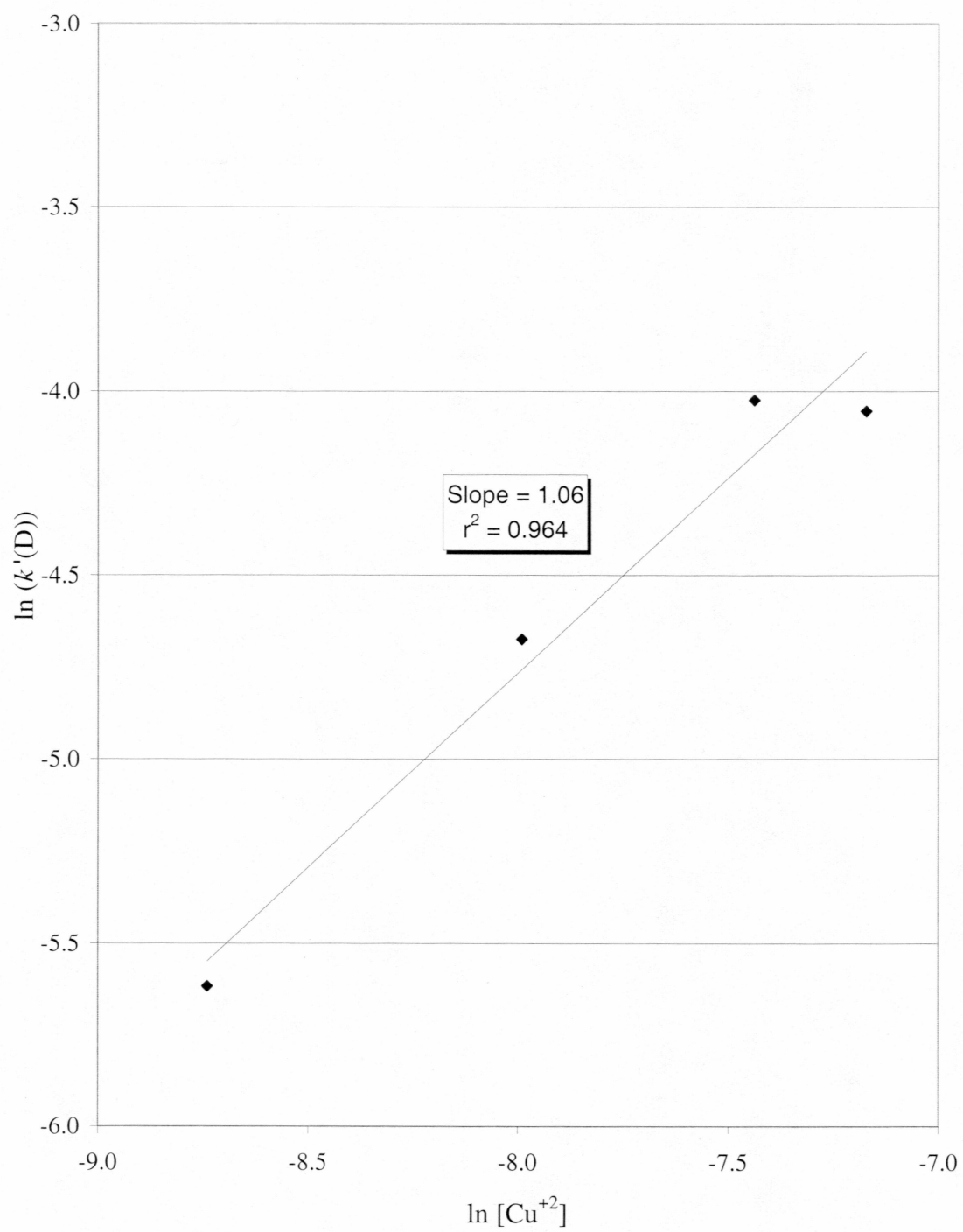
Figure 4.8 Plot to Determine Reaction Order with Respect to $[Cu^{+2}]$

4.2.7 Analyses of k' data to determine reaction order for pH.

According to the derivative of Eq. 4.12 from the kinetic model, and under conditions of constant $[SO_2]$, $[Cu^{+2}]$ and temperature, a plot of:

$$\ln\{[CN^-]_0([CN^-]_t + D)\}/\{[CN^-]_t([CN^-]_0 + D)\} \text{ vs. time}$$

should be linear in a series of tests, where the pH is the variable. Figure 4.9 shows this relationship is linear, confirming a first order reaction with respect to cyanide and SO_2, as proposed in the development of the Eq. 4.12. As previously developed in section 4.2.6, each line in Figure 4.9 has slope $k'(D)$, where D was held nearly constant, but k' varies with $[H^+]^\delta$ according to Eq. 4.2:

$$k' = k[Cu^{+2}]^\gamma [H^+]^\delta \tag{4.2}$$

Multiplying each side of Eq. 4.2 by D and recalling that $[Cu^{+2}]^\gamma$ was held constant throughout the series of test gives the following:

$$k'(D) = (k(D)[Cu^{+2}]^\gamma) [H^+]^\delta \tag{4.17}$$

Substituting a new rate constant k'', for the constant product $(k(D)[Cu^{+2}]^\gamma)$ yields:

$$k'(D) = k''[H^+]^\delta \tag{4.18}$$

Taking the natural logarithm of both sides results in:

$$\ln(k'(D)) = \ln k'' + \delta\ln[H^+] \tag{4.19}$$

Then, a plot of $\ln(k'(D))$ vs. $\ln[H^+]$ should yield a straight line with slope δ. The plot is shown in Figure 4.10. The slope of the line, 0.156, in Figure 4.10 indicates that the reaction order is essentially 0 with respect to $[H^+]$, over the tested pH range of 8 to 9.5.
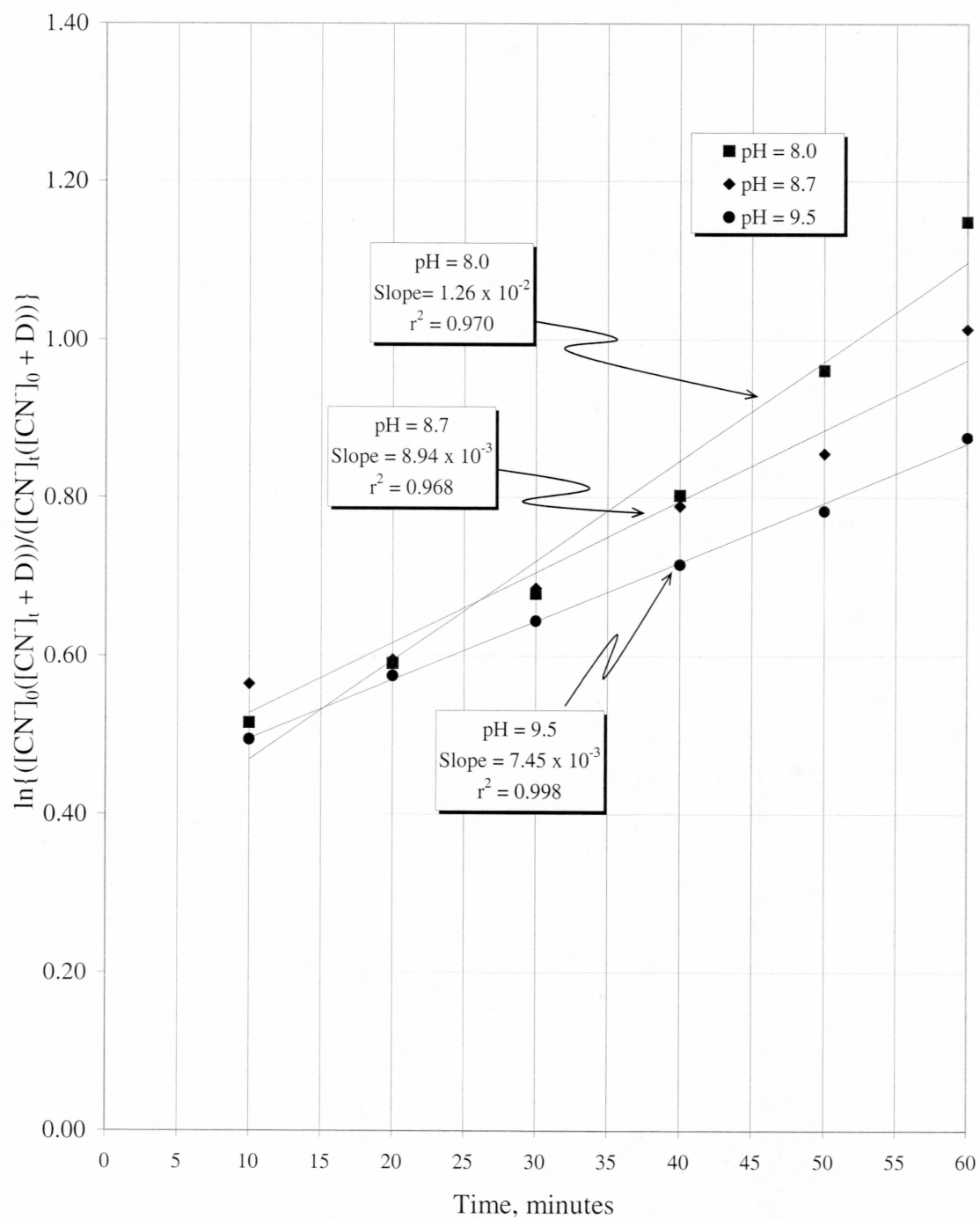
Figure 4.9 Plots to Determine the Rate Constant, k'D, with Respect to $[H^+]$
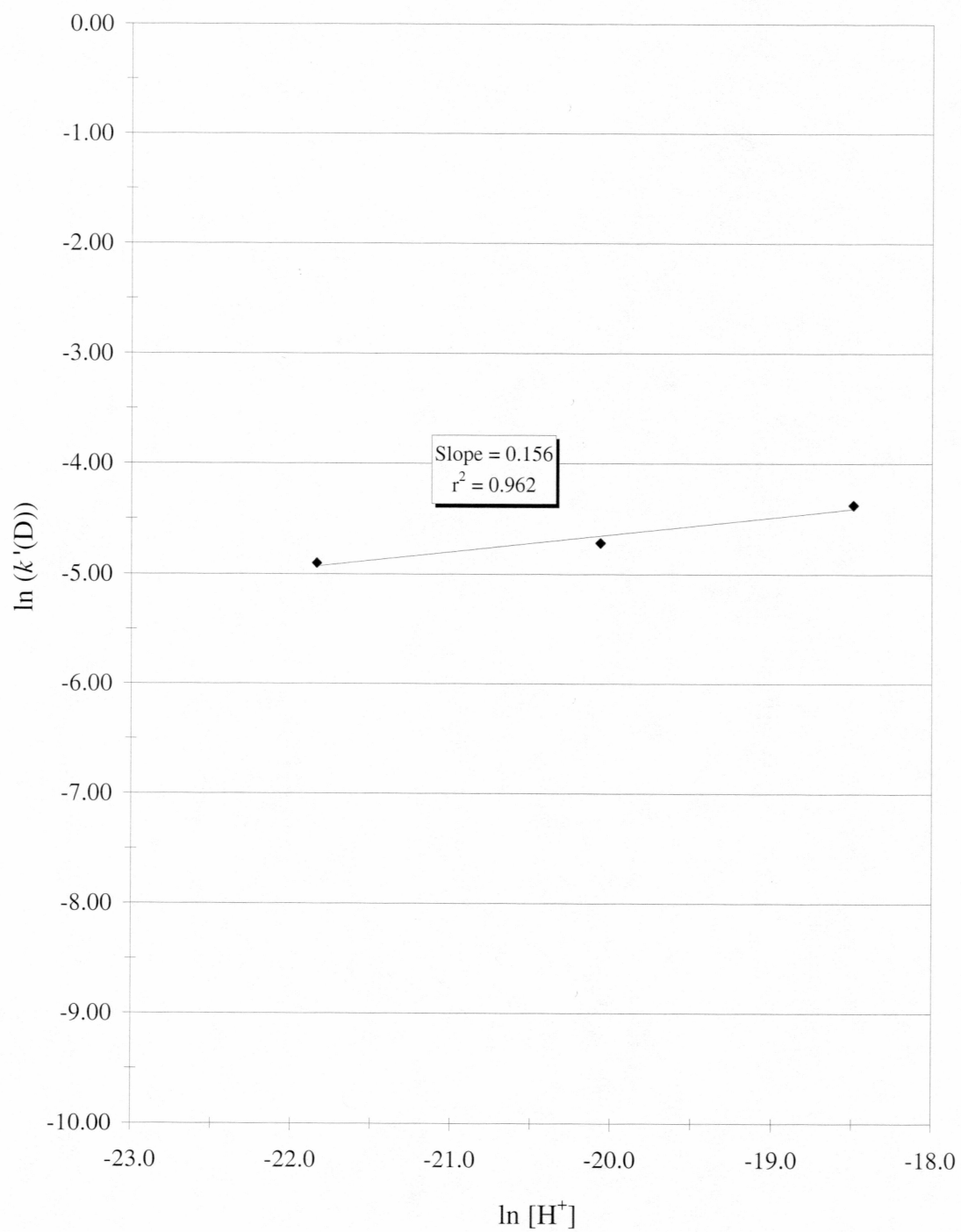
Figure 4.10 Plot to Determine Reaction Order with Respect to [H⁺]

4.2.8 Analyses of k' data to determine activation energy, E_a.

Under conditions of constant $[SO_2]$, $[Cu]$ and pH, a plot of:

$$\ln\{[CN^-]_0([CN^-]_t + D)\}/\{[CN^-]_t([CN^-]_0 + D)\} \text{ vs. time}$$

should be linear in the series of tests, where temperature is the variable. Figure 4.11 shows this relationship is linear, and each line has slope $k'(D)$. Figure 4.12 shows a plot of $\ln(k'(D))$ vs. $1/T$. The slope, -2533, for the line in Figure 4.12 yields an activation energy, E_a, of 21.1 kJ/mol. The intercept of this line yields the value for $\ln(A)$ of 3.60 or A is 36.6. This activation energy indicates that the reaction kinetics are controlled by diffusion, which is consistent with the suggestion that the reaction is limited by oxygen transfer [9].
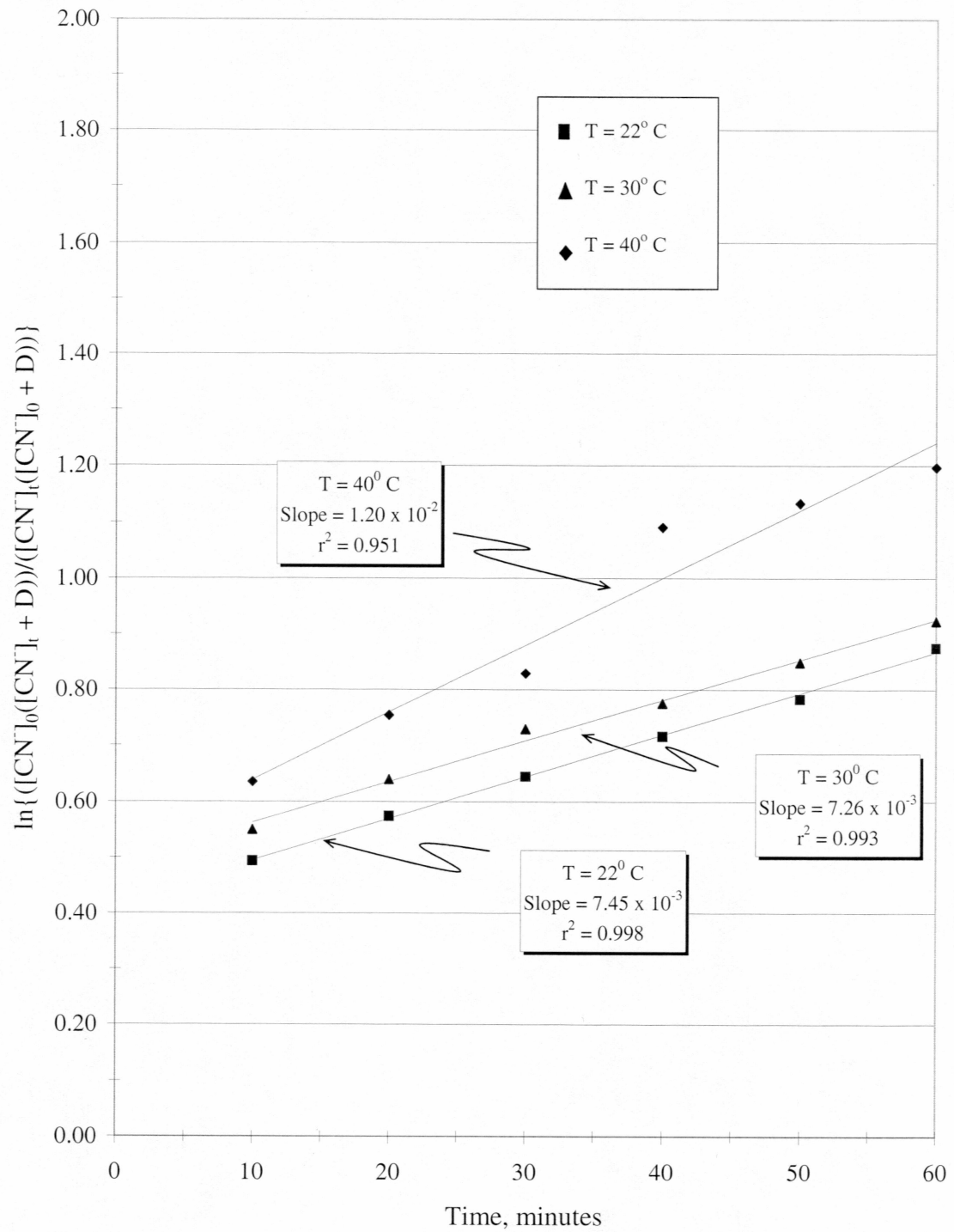
Figure 4.11 Plots to Determine k'D with Respect to Temperature
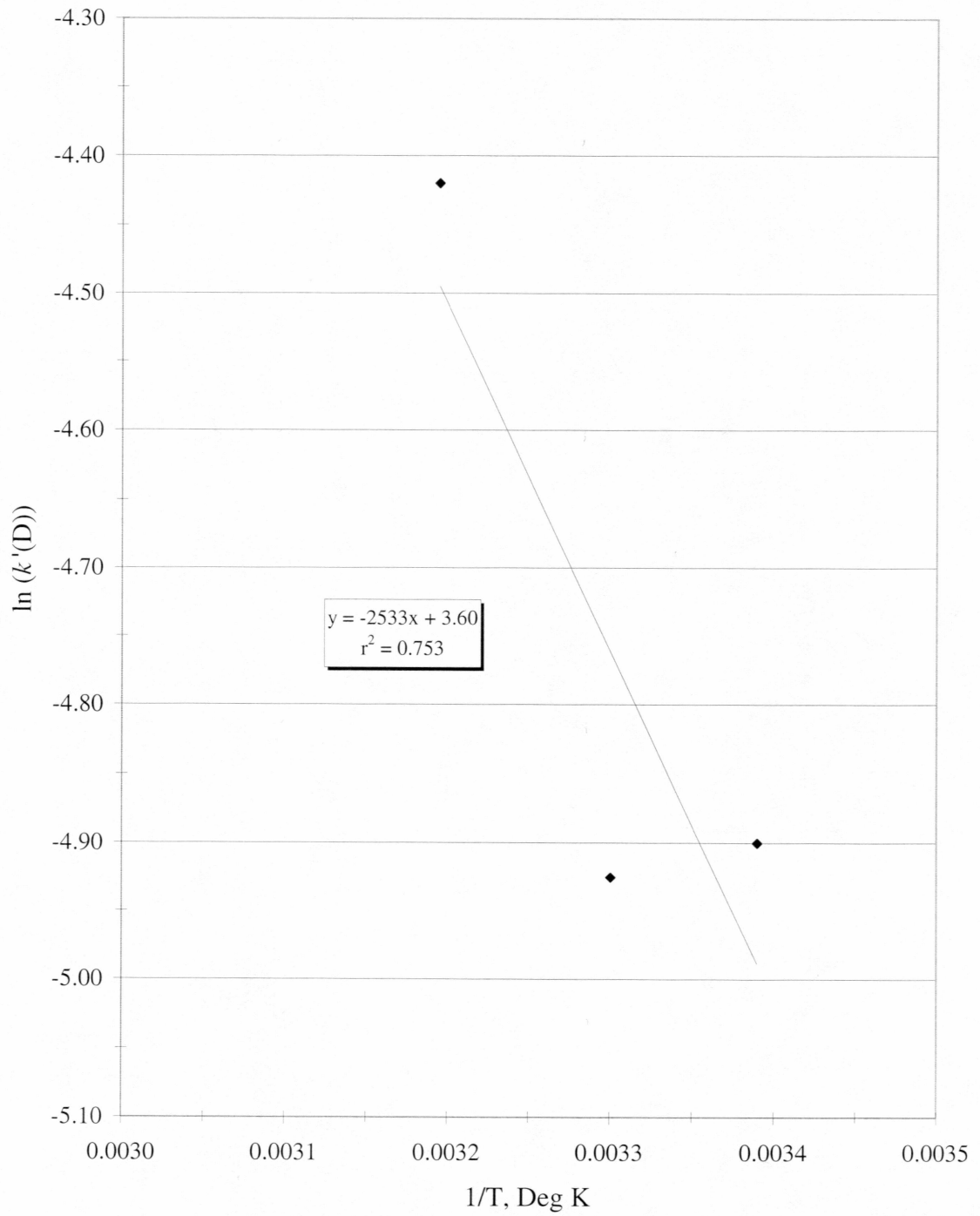
Figure 4.12 Arrhenius Plot

4.2.9 Overall rate equation

The rate equation: $\ln\{[CN^-]_0([CN^-]_t + D)/[CN^-]_t([CN^-]_0 + D)\} = k'Dt$, Eq (4.12), is developed under the conditions of constant $[Cu^{+2}]$, pH and temperature. When $[Cu^{+2}]$, pH and temperature are considered, the rate equation becomes

$$\ln\{[CN^-]_0([CN^-]_t + D)/[CN^-]_t([CN^-]_0 + D)\} = Ke^{-21100/RT} [Cu^{+2}]^1[H^+]^0Dt \qquad (4.20)$$

where K is a rate constant independent of $[SO_2]$, $[CN^-]$, D, $[Cu^{+2}]$, $[H^+]$ and temperature. Using the data from Tables IV through VII (Appendix), where the $[Cu^{+2}]$ is approximately 10, 22, 38, and 49 ppm respectively, the following respective K values are determined: 5.18×10^7, 6.83×10^7, 5.01×10^7, and 4.85×10^7. These results yield an average value for K of 5.21×10^7, with a relative standard deviation of $^+/-7\%$. Thus, the final rate equation is:

$$\ln\{[CN^-]_0([CN^-]_t + D)/[CN^-]_t([CN^-]_0 + D)\} = 5.21 \times 10^7 e^{-21100/RT} [Cu^{+2}]Dt \qquad (4.21)$$

Chapter 5. Summary and Conclusions

The development of a mathematical model to describe the oxidation of cyanide through the INCO process was investigated using a direct analytical method of measuring the concentration of cyanide over time and inferring a rate constant from the data. These measurements were made by amperometric measurements using the Perstorp/Alpchem CNSolution^{TM} model 3202 WAD Cyanide Analyzer. The summary and conclusions are as follows:

1. Based on this test work, the reaction is first order with respect to SO_2 and cyanide.

2. It is proposed that the participation of copper is as a catalyst. Based on this test work it may be concluded that the reaction is first-order with respect to copper. A catalytic reaction may be first-order with respect to the catalyst.

3. Based on literature the reaction is pH dependent, being most effective within the pH range of 9–10[8]. Results of this test work show the reaction order with respect to $[H^+]$ is determined to be 0.156, or zeroth order.

4. The effect of temperature on the rate constant is represented by Arrhenius's equation: $k = Ae^{-E_a/RT}$. It was determined from this test work that the frequency factor, A is 36.6 and the activation energy, E_a, is 21.1 KJ/mol. The solution then is:

$$k = 36.6 \, e^{-21100/RT}$$

The overall rate can be expressed as:

$$\ln\left(\frac{[CN^-]_0\,(\,[CN^-]_t + D)}{[CN^-]_t\,(\,[CN^-]_0 + D)}\right) = 5.21 \times 10^7 e^{-21100/RT}\,[Cu^{+2}][H^+]^0 Dt$$

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APPENDIX

Table I

[SO$_2$] Test 1 Data

(min)	pH	Cu ppm	CN$^-$ ppm	Moles/l x 10^{-3} [CN$^-$]$_t$	[SO$_2$]$_t$	ln(A/B)
0	10.6	13.4	37.4	1.44	1.93	0.00
10	7.2	12.9	33.1	1.27	1.77	0.03
20	7.1	13.2	29.2	1.12	1.62	0.07
33	7.0	13.7	25.6	0.98	1.48	0.11
40	7.0	13.4	23.3	0.90	1.39	0.14
50	6.9	13.5	20.9	0.80	1.30	0.18
60	6.8	13.6	19.0	0.73	1.23	0.22
70	6.8	14.2	17.3	0.67	1.16	0.26
80	6.7	13.7	15.3	0.59	1.08	0.31
90	6.7	13.6	14.1	0.54	1.04	0.35
100	6.6	13.4	13.1	0.50	1.00	0.39
110	6.6	14.1	12.5	0.48	0.98	0.41

[SO$_2$]$_0$ = 1.93 x 10^{-3} moles/liter   Mole Ratio of [SO$_2$]$_0$: [CN$^-$]$_0$ = 1.34

[CN$^-$]$_0$ = 1.44 x 10^{-3} moles/liter   D = 4.91 x 10^{-4}

k'D$_{(SO_2)}$ = 3.94 x 10^{-3} A = [CN$^-$]$_0$ ([CN$^-$]$_t$ + D)

B = [CN$^-$]$_t$ ([CN$^-$]$_0$ + D)

Table II

[SO$_2$] Test 2 Data

(min)	pH	Cu ppm	CN$^-$ ppm	[CN$^-$]$_t$	[SO$_2$]$_t$	ln(A/B)
				Moles/l x 10^{-3}		
0	11.1		34.2	1.32	3.17	0.00
5	7.3	14.6	27.6	1.06	2.92	0.13
10	5.3	14.3	25.8	0.99	2.85	0.17
15	7.2	14.7	24.6	0.95	2.81	0.21
20	7.2	14.0	22.6	0.87	2.73	0.26
25	7.1	14.8	21.0	0.81	2.67	0.31
30	7.1	14.2	19.0	0.73	2.59	0.38
34	7.1	14.5	18.6	0.72	2.58	0.40
40	7.0	14.4	16.6	0.64	2.50	0.48
43	6.9	14.3	14.7	0.57	2.43	0.57
53	6.9	14.2	13.5	0.52	2.39	0.64
58	6.9		13.1	0.50	2.37	0.66
63	6.8		12.0	0.46	2.33	0.73
68	6.8	14.0	10.8	0.42	2.29	0.82
75	6.8		10.5	0.40	2.27	0.84
80	6.7	14.4	9.5	0.37	2.24	0.92
85	6.7		9.0	0.35	2.22	0.97
90	6.7	14.3	8.8	0.34	2.21	0.99

$[SO_2]_0 = 3.17 \times 10^{-3}$ moles/liter   Mole Ratio of $[SO_2]_0 : [CN^-]_0 = 2.41$

$[CN^-]_0 = 1.32 \times 10^{-3}$ moles/liter $D = 1.85 \times 10^{-3}$

$k'D_{(SO_2)} = 1.07 \times 10^{-2}$ $A = [CN^-]_0 ([CN^-]_t + D)$

$B = [CN^-]_t ([CN^-]_0 + D)$

Table III

[SO$_2$] Test 3 Data

(min)	pH	Cu ppm	CN$^-$ ppm	Moles/l x 10^{-3} [CN$^-$]$_t$	[SO$_2$]$_t$	ln(A/B)
0.0	11.2	0.0	42.3	1.63	5.51	0.00
7.5	6.9	14.2	36.1	1.39	5.28	0.11
9.0	6.8	14.0	35.4	1.36	5.25	0.13
10.5	6.8	13.9	34.7	1.33	5.22	0.14
12.0	6.8	14.2	33.9	1.30	5.19	0.16
16.5	6.8	14.4	31.5	1.21	5.10	0.22
21.0	7.0	14.3	29.1	1.12	5.01	0.28
28.5	6.9		25.4	0.98	4.86	0.38
36.0	6.9	14.1	22.1	0.85	4.74	0.50
43.5	6.9		19.4	0.75	4.63	0.61
51.0	6.8	14.0	17.0	0.65	4.54	0.72
58.5	6.8		14.9	0.57	4.46	0.83
66.0	6.8		13.8	0.53	4.42	0.90
73.5	6.7	14.4	11.4	0.44	4.32	1.07
81.0	6.7		9.9	0.38	4.27	1.20
88.5	6.7	14.3	8.6	0.33	4.22	1.33

$[SO_2]_0 = 5.51 \times 10^{-3}$ moles/liter

$[CN^-]_0 = 1.63 \times 10^{-3}$ moles/liter

$k'D_{(SO_2)} = 1.49 \times 10^{-2}$

Mole Ratio of $[SO_2]_0 : [CN^-]_0 = 3.39$

$D = 3.88 \times 10^{-3}$

$A = [CN^-]_0 ([CN^-]_t + D)$

$B = [CN^-]_t ([CN^-]_0 + D)$

Table IV

[Cu^{+2}] Test 1 Data

(min)	pH	Cu ppm	CN$^-$ ppm	[CN$^-$]$_t$	[SO$_2$]$_t$	ln(A/B)
				Moles/l x 10^{-3}		
0	10.6	0.0	44.0	1.69	5.10	0.00
2	9.0	9.8	43.2	1.66	5.06	0.01
10	9.0	10.3	38.7	1.49	4.79	0.09
14			38.1	1.46	4.78	0.10
20	9.0	9.9	37.2	1.43	4.77	0.11
26			36.6	1.41	4.78	0.13
30	9.0	10.1	36.0	1.38	4.78	0.14
34			35.2	1.35	4.75	0.15
40	9.0	9.9	34.6	1.33	4.76	0.17
46			33.7	1.29	4.75	0.19
50	9.0	10.3	32.1	1.23	4.65	0.22
54			31.0	1.19	4.60	0.25
60	9.0	10.5	29.8	1.15	4.56	0.28

$[SO_2]_0 = 5.10 \times 10^{-3}$ moles/liter   Mole Ratio of $[SO_2]_0 : [CN^-]_0 = 3.02$

$[CN^-]_0 = 1.69 \times 10^{-3}$ moles/liter $D = 3.41 \times 10^{-3}$

$k'D_{(Cu)} = 3.63 \times 10^{-3}$ $A = [CN^-]_0 ([CN^-]_t + D)$

$B = [CN^-]_t ([CN^-]_0 + D)$

Table V

$[Cu^{+2}]$ Test 2 Data

(min)	pH	Cu ppm	CN^- ppm	$[CN^-]_t$	$[SO_2]_t$	$\ln(A/B)$
0.0	10.6		43.3	1.67	5.10	0.00
2.0	9.0	22.2	39.2	1.51	4.81	0.07
10.0	9.0	21.5	38.0	1.46	4.79	0.09
16.0			36.4	1.40	4.72	0.12
20.0	9.0	21.8	35.9	1.38	4.72	0.13
26.0			34.6	1.33	4.68	0.16
30.0	9.0	21.0	33.8	1.30	4.65	0.17
34.0			32.8	1.26	4.61	0.20
40.0	9.0	22.3	30.9	1.19	4.51	0.24
46.0			28.3	1.09	4.35	0.31
50.0	8.9	21.5	26.0	1.00	4.19	0.37
54.0			23.8	0.92	4.04	0.44
60.0	8.8	21.0	18.8	0.72	3.66	0.63

The columns under "Moles/l x 10^{-3}" are $[CN^-]_t$ and $[SO_2]_t$.

$[SO_2]_0 = 5.10 \times 10^{-3}$ moles/liter

$[CN^-]_0 = 1.67 \times 10^{-3}$ moles/liter

$k'D_{(Cu)} = 9.35 \times 10^{-3}$

Mole Ratio of $[SO_2]_0 : [CN^-]_0 = 3.06$

$D = 3.43 \times 10^{-3}$

$A = [CN^-]_0 ([CN^-]_t + D)$

$B = [CN^-]_t ([CN^-]_0 + D)$

Table VI

$[Cu^{+2}]$ Test 3 Data

(min)	pH	Cu ppm	CN^- ppm	Moles/l x 10^{-3} $[CN^-]_t$	$[SO_2]_t$	ln(A/B)
0.0	10.6	0.0	43.9	1.69	5.10	0.00
2.0	9.0	39.1	33.1	1.27	4.29	0.20
10.0	9.0	38.6	29.3	1.13	4.06	0.29
14.0			27.6	1.06	3.96	0.33
20.0	9.0	36.5	24.8	0.95	3.78	0.42
24.0			23.3	0.90	3.70	0.46
30.0	9.0	37.1	20.9	0.80	3.55	0.55
36.0			18.8	0.72	3.42	0.64
40.0	8.9	36.0	17.3	0.67	3.32	0.71
44.0			15.6	0.60	3.21	0.79
50.0	8.9	37.6	13.7	0.53	3.09	0.91
56.0			11.0	0.42	2.90	1.10
60.0	8.9	38.4	9.7	0.37	2.81	1.21

$[SO_2]_0 = 5.10$ x 10^{-3} moles/liter $\qquad$ Mole Ratio of $[SO_2]_0 : [CN^-]_0 = 3.02$

$[CN^-]_0 = 1.69$ x 10^{-3} moles/liter $\qquad$ $D = 3.41$ x 10^{-3}

$k'D_{(Cu)} = 1.79$ x 10^{-2} $\qquad$ $A = [CN^-]_0 ([CN^-]_t + D)$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $B = [CN^-]_t ([CN^-]_0 + D)$

Table VII

[Cu^{+2}] Test 4 Data

(min)	pH	Cu ppm	CN^- ppm	Moles/l x 10^{-3} $[CN^-]_t$	$[SO_2]_t$	ln(A/B)
0.0	10.6	0.0	43.3	1.67	5.10	0.00
2.0	9.0	51.0	30.4	1.17	4.13	0.25
10.0	9.0	48.0	27.8	1.07	3.99	0.32
14.0			25.7	0.99	3.86	0.38
20.0	9.0	48.0	24.0	0.92	3.77	0.43
26.0			22.2	0.85	3.67	0.49
30.0	9.0	49.3	21.2	0.82	3.62	0.53
34.0			19.8	0.76	3.54	0.59
40.0	8.9	50.2	17.5	0.67	3.39	0.69
46.0			15.2	0.58	3.24	0.81
50.0	8.9	47.6	13.4	0.52	3.11	0.92
54.0			11.6	0.45	2.99	1.04
60.0	8.9	49.4	9.2	0.35	2.82	1.25

$[SO_2]_0 = 5.10$ x 10^{-3} moles/liter   Mole Ratio of $[SO_2]_0 : [CN^-]_0 = 3.06$

$[CN^-]_0 = 1.67$ x 10^{-3} moles/liter $D = 3.43$ x 10^{-3}

$k'D_{(Cu)} = 1.74$ x 10^{-2} $A = [CN^-]_0 ([CN^-]_t + D)$

$B = [CN^-]_t ([CN^-]_0 + D)$

Table VIII

pH Test 1 Data

(min)	pH	Cu ppm	CN⁻ ppm	Moles/l x 10⁻³ $[CN^-]_t$	$[SO_2]_t$	ln(A/B)
0	10.78		40.4	1.55	6.66	0.00
10	8.05	28.7	21.5	0.83	5.20	0.52
20	8.04	28.4	19.7	0.76	5.06	0.59
30	8.03	30.6	17.8	0.68	4.92	0.68
40	8.03		15.5	0.60	4.74	0.80
50	8.02	28.4	13.0	0.50	4.55	0.96
60	8.02		10.6	0.41	4.36	1.15

$[SO_2]_0 = 6.66 \times 10^{-3}$ moles/liter   Mole Ratio of $[SO_2]_0 : [CN^-]_0 = 4.28$

$[CN^-]_0 = 1.55 \times 10^{-3}$ moles/liter $D = 5.11 \times 10^{-3}$

$k'D_{(pH)} = 1.26 \times 10^{-2}$ $A = [CN^-]_0 \, ([CN^-]_t + D)$

$B = [CN^-]_t \, ([CN^-]_0 + D)$

Table IX

pH Test 2 Data

(min)	pH	Cu ppm	CN⁻ ppm	Moles/l x 10⁻³ $[CN^-]_t$	$[SO_2]_t$	ln(A/B)
0	10.8	0.0	39.7	1.53	6.63	0.00
10	8.74	28.0	20.0	0.77	5.11	0.56
20	8.73		19.3	0.74	5.06	0.60
30	8.72		17.4	0.67	4.91	0.69
40	8.71	29.0	15.5	0.60	4.77	0.79
50	8.70		14.4	0.55	4.68	0.86
60	8.69	27.9	12.1	0.465	4.506	1.014

$[SO_2]_0 = 6.63 \times 10^{-3}$ moles/liter   Mole Ratio of $[SO_2]_0 : [CN^-]_0 = 4.34$

$[CN^-]_0 = 1.53 \times 10^{-3}$ moles/liter $D = 5.10 \times 10^{-3}$

$k'D_{(pH)} = 8.94 \times 10^{-3}$ $A = [CN^-]_0 \, ([CN^-]_t + D)$

$B = [CN^-]_t \, ([CN^-]_0 + D)$

Table X

pH Test 3 Data

(min)	pH	Cu ppm	CN⁻ ppm	Moles/l x 10⁻³		
				$[CN^-]_t$	$[SO_2]_t$	$\ln(A/B)$
0	10.8	0.0	39.1	1.50	6.61	0.00
10	9.52		21.4	0.82	5.24	0.49
20	9.51		19.5	0.75	5.10	0.57
30	9.50		18.0	0.69	4.98	0.64
40	9.47	29.1	16.6	0.64	4.88	0.72
50	9.46		15.4	0.59	4.78	0.78
60	9.45	28.6	13.9	0.53	4.67	0.88

$[SO_2]_0 = 6.61 \times 10^{-3}$ moles/liter

$[CN^-]_0 = 1.50 \times 10^{-3}$ moles/liter

$k'D_{(pH)} = 7.45 \times 10^{-3}$

Mole Ratio of $[SO_2]_0 : [CN^-]_0 = 4.39$

$D = 5.11 \times 10^{-3}$

$A = [CN^-]_0 ([CN^-]_t + D)$

$B = [CN^-]_t ([CN^-]_0 + D)$

Table XI

Temperature Test 1 Data; T = 22 Deg C

(min)	pH	Cu ppm	CN⁻ ppm	CN⁻ (Moles/l x 10⁻³)	SO₂ (Moles/l x 10⁻³)	ln(A/B)
0	10.6		39.1	1.50	6.61	0.00
10	9.52		21.4	0.82	5.24	0.49
20	9.51		19.5	0.75	5.10	0.57
30	9.50		18.0	0.69	4.98	0.64
40	9.47	29.1	16.6	0.64	4.88	0.72
50	9.46		15.4	0.59	4.78	0.78
60	9.45	28.6	13.9	0.53	4.67	0.88

$[SO_2]_0 = 6.61 \times 10^{-3}$ moles/liter

$[CN^-]_0 = 1.50 \times 10^{-3}$ moles/liter

$k'D_{(T)} = 7.45 \times 10^{-3}$

Mole Ratio of $[SO_2]_0 : [CN^-]_0 = 4.39$

$D = 5.11 \times 10^{-3}$

$A = [CN^-]_0 ([CN^-]_t + D)$

$B = [CN^-]_t ([CN^-]_0 + D)$

Table XII

Temperature Test 2 Data; T = 30 Deg C

(min)	pH	Cu ppm	CN⁻ ppm	CN⁻ (Moles/l x 10⁻³)	SO₂ (Moles/l x 10⁻³)	ln(A/B)
0	10.59	0.0	38.1	1.47	6.57	0.00
10	9.53		19.6	0.75	5.14	0.55
20			17.7	0.68	5.00	0.64
30		29.0	16.0	0.62	4.87	0.73
40	9.51		15.2	0.58	4.81	0.77
50			14.0	0.54	4.71	0.85
60	9.49	29.7	12.9	0.50	4.63	0.92

$[SO_2]_0 = 6.57 \times 10^{-3}$ moles/liter

$[CN^-]_0 = 1.47 \times 10^{-3}$ moles/liter

$k'D_{(T)} = 7.26 \times 10^{-3}$

Mole Ratio of $[SO_2]_0 : [CN^-]_0 = 4.48$

$D = 5.10 \times 10^{-3}$

$A = [CN^-]_0 ([CN^-]_t + D)$

$B = [CN^-]_t ([CN^-]_0 + D)$

Table XIII

Temperature Test 3 Data; T = 40 Deg C

(min)	pH	Cu ppm	CN⁻ ppm	Moles/l x 10^{-3} CN⁻	SO₂	ln(A/B)
0	10.75	0	39.6	1.52	6.63	0.00
10	9.47		18.4	0.71	4.99	0.64
20			16.1	0.62	4.82	0.75
30	9.43		14.8	0.57	4.72	0.83
40		29.4	11.1	0.43	4.43	1.09
50	9.41		10.6	0.41	4.39	1.13
60			9.9	0.38	4.34	1.20

$[SO_2]_0 = 6.63 \times 10^{-3}$ moles/liter   Mole Ratio of $[SO_2]_0 : [CN^-]_0 = 4.35$

$[CN^-]_0 = 1.52 \times 10^{-3}$ moles/liter $D = 5.11 \times 10^{-3}$

$k'D_{(T)} = 1.20 \times 10^{-2}$ $A = [CN^-]_0 ([CN^-]_t + D)$

$B = [CN^-]_t ([CN^-]_0 + D)$