

A KINETIC STUDY OF THE ADSORPTION OF  
COBALT SPECIES FROM AMMONIA-AMMONIUM CARBONATE  
SOLUTION BY A CHELATING CATION EXCHANGE RESIN

by

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## ABSTRACT

A study of the rate of cobalt adsorption from ammonia-ammonium carbonate by a chelating cation ion exchange resin was carried out by measuring the rate of disappearance of cobalt ion from the solution. Effect of temperature, initial cobalt concentration, ammonium bicarbonate concentration, and pH were evaluated. The initial cobalt concentration was the most sensitive factor among the variables affecting the rate of adsorption of cobalt.

Kinetics of adsorption were studied in the temperature range 35-71°C. The cobalt concentration range was 50-400 ppm, and the ammonium bicarbonate concentration ranged from 25 to 246 g/l. The pH was varied from 8.0 to 10.0.

The kinetics of cobalt adsorption conforms to an ash layer diffusion model for all variables. The activation energy below 55°C was 1.4 kcal/mole, while above 55°C the activation energy was 4.4 kcal/mole, indicating that the diffusion of an ionic species through an aqueous continuous medium is the rate-controlling mechanistic step.

The kinetics exhibit a first-order dependence on initial concentration of cobalt in the ammonia-ammonium carbonate solution. A slight dependence on ammonium bicarbonate concentration and pH was observed.

## INTRODUCTION

### Statement of the Problem

Recovery of nickel from lateritic deposits is accomplished by reductive roasting of the ore followed by leaching with ammonia-ammonium carbonate solution to extract nickel and cobalt values from the reduced ore. Most often the nickel is recovered from the leach solution by solvent extraction, leaving the cobalt species in the raffinate. This raffinate contains 0.05-0.10 grams per liter cobalt.

This amount of cobalt, if not recovered, represents a sizable financial loss. Also, reportedly (Hatch, 1977), a build-up of cobalt in the ammoniacal solution from recycling of solution gradually decreases the ability of the raffinate to leach metals each time the raffinate is recycled. Hatch also states that the presence of cobalt in ammoniacal solutions, even in small quantities, can adversely affect the leaching of metallic nickel from certain ores. It is therefore necessary to develop an economically feasible technique to remove the cobalt from the raffinate before recycling of the solution to the leach circuit in the plant.

Solvent extraction at these low concentrations is probably not feasible economically; however, ion exchange recovery of cobalt may be economical. Ion exchange resins for cobalt extraction are commercially available; however, the physico-chemical interaction of such resins with the metallic species in the ammoniacal solutions is not well understood. The purpose, therefore, of this kinetic investigation was to identify

and explain the physico-chemical interactions between a cation exchange resin and cobalt species present in the  $\text{Co-NH}_3\text{-CO}_2\text{-H}_2\text{O}$  system.

### Cobalt Recovery Processes

Nickel and cobalt are extracted from low-grade nickeliferous laterite ores by the Caron process (Caron, 1950). This treatment involves a reductive roast of the ore followed by an ammonia-ammonium carbonate leaching of the calcine to solubilize nickel and cobalt. Selective removal of the nickel by solvent extraction results in a pure nickel product. The cobalt, however, remains in the solvent extraction raffinate as trivalent cobalt.

Separation of nickel and cobalt is described by Drobnick and Millsap (1964). The process uses an oxime type solvent extraction reagent to extract copper and nickel from the leach solution with cobalt remaining in the raffinate. However, satisfactory methods of removing the cobalt before recycling of the raffinate to the leach circuit are not known. Cobalt recovery from these raffinates is by precipitation of cobalt sulfide or cobalt carbonate. The former is achieved using hydrogen sulfide which produces a precipitate having poor handling qualities. The latter is produced by steam stripping of ammonia from the raffinate. This method is uneconomical because of the large quantities of ammonia which must be removed from the raffinate.

Laskorin, Logvinenko, and Ashurkova (1969) reported development of a process in which the conversion of nickel and cobalt in the ore to their chlorides was achieved in one step. The method consisted of "filtration-free sorption" of the cobalt and nickel species in the

solution or pulp onto the hydroxyl form of a weak or medium basic anion exchanger. The nickel and cobalt are then desorbed separately with hydrochloric acid to produce pure nickel and cobalt chlorides.

Logvinenko et al. (1969) contacted ammonia-ammonium carbonate leach solutions with a carboxyl cation exchanger in the presence of steam to remove the cobalt values and strip the ammonia from the raffinate for recycling.

#### Chemistry of the System

Hewedi and Engle (1973, p. 809) stated, "Unfortunately, calculations of pH-potential relationships in systems concerning metals in ammonia-ammonium carbonate solutions are scarce in the literature . . . . Accordingly, the literature does not include the solid basis for a reliable theoretical analysis of complex formation of many metals." Unfortunately, this is still the case for the system under consideration.

The Eh-pH relationships are known for the systems Ni-NH<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O (Letowski and Niemiec, 1966), Ni-NH<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O (Powers and Geiger, 1977), and Co-NH<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O (Letowski and Niemiec, 1969). Letowski (1970) has even calculated the stability constants of nickel amines at temperatures up to 180°C. The stability constants for Co-NH<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O are not reported in the literature; therefore it is not possible to construct an Eh-pH diagram for this system. Also, due to the lack of stability constant data, it is not possible to determine quantitatively the equilibrium concentrations of various ionic species under given conditions.

Hurst (1976) has, by a pressurized ion-exchange chromatographic method, separated the various nickel and cobalt species present in an

ammonia-ammonium carbonate solution. Dowex 50W-X8 (15-25 $\mu$ ) was the cation exchanger used to separate the cobalt species. Hurst (1976) was able to identify the three Cobalt (III) species as  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$ ,  $[\text{Co}(\text{NH}_3)_5\text{CO}_3]^+$ , and  $[\text{Co}(\text{NH}_3)_6]^{+3}$ . The wavelengths at which the three species absorb are in the visible region. The maximum absorbance peaks occurred at 475 nm for the yellow hexammine complex and 510 and 523 nm, respectively, for the red pentammine and the purple tetrammine complexes. Hurst also found the cobalt hexammine to be more strongly sorbed than the other two cobalt species or the nickel species, and so concluded that with Dowex-50W-X8 resin, all of the cobalt species would have to be converted to the cobalt hexammine in order to achieve a good separation of nickel and cobalt complexes.

The cobalt pentammine complex is a thermodynamically stable species in the pH range of interest (Hatch, 1977). Intermediate cobalt complexes are formed, however (Basolo and Johnson, 1964), and the conversion to the cobalt hexammine complex is exceedingly slow (Hatch, 1977). One of these intermediates may be a bridged peroxo Cobalt (III) species reported by Basolo and Johnson (1964, p. 91-92) to be the result of air oxidation of the Cobalt (II) hexammine.

A method has been described (Hatch, 1977, 1978) to convert all cobalt species in an ammonia-ammonium carbonate solution to the Cobalt (III) hexammine. The ammoniacal solution is contacted with activated carbon at a redox potential in the range +20 to -150 mV. The carbon acts as a catalyst in conversion of all the cobalt species to

$[\text{Co}(\text{NH}_3)_6]^{+3}$ . In this process, the cobalt hexammine can then be extracted using a weak carboxylic ion exchanger.

### Ion-exchange Resins

Ion-exchange resins are insoluble substances which contain fixed electrical charges. A cation-exchange resin contains fixed electronegative charges, while an anion-exchange resin contains fixed electropositive charges. These fixed charges are associated with mobile or potentially mobile ions of the opposite charge, called counterions. The mobility of the counterions is responsible for the phenomena of ion exchange. Ion exchangers are also known as polyelectrolytes because of the large number of contained fixed electrical charges.

One method of classifying ion-exchange resins is by the chemical nature of their ion exchanging, or active, groups. In a cation-exchange resin, active groups can be either strongly acidic, that is, the acid group can be assumed to be completely dissociated, or weakly acidic, in which the acid group is dissociated only to a small extent. Examples of these two types of cation-exchange groups are, respectively, the sulfonic acid group,  $-\text{C}_6\text{H}_4\text{SO}_3\text{H}$ , and the carboxylic acid group,  $-\text{COOH}$ . The anion-exchange resin can be strongly basic or weakly basic. Quaternary amine groups are strongly basic, while secondary amine groups are weakly basic.

There are also resins termed chelating resins because they show a specificity for ions of multivalent metals like nickel, cobalt, and copper. Chelation involves the binding of a charged species at more than one site, providing an extremely stable structure. Whether or not

the active group in these resins actually chelates with the counterions in the same manner as a chelate-forming species like EDTA chelates with transition metals is not known. This specificity of an ion exchanger for certain metals has been known to occur in certain acidic or basic ion exchangers (Abrams and Benezra, 1967).

An example of an active group in a chelating resin is the imino-diacetic acid group,  $-N(CH_2COOH)_2$ , which contains a weakly basic secondary amine group and the weakly acidic carboxyl groups. Resins containing both acidic and basic substituents are also known as amphoteric resins.

Resins can also be classified according to the polymer to which the active groups are attached. Styrene cross-linked with divinylbenzene is the most widely used backbone for ion-exchange resins, although polymers produced by phenol-formaldehyde condensation reactions are still used to make strong acid cation-exchange resins.

Ion-exchange resins can also be either macroreticular (beads) or microreticular (gel).

#### Kinetics of Ion-exchange Resins

The first kinetic study of ion exchange was performed by Nachod and Wood (1944). They studied the rate of exchange of a number of ion pairs with a cation exchanger in dilute solutions. They concluded that film diffusion was the rate-controlling step in the systems studied.

Kunin and Myers (1947) studied anion exchange in a number of weakly basic resins and concluded that particle diffusion was rate-controlling in all cases.

Boyd, Myers, and Adamson (1947) derived equations for three possible rate-controlling mechanisms: chemical reaction, film diffusion, and particle diffusion. These equations were derived under the assumption that the mobile counterion diffusing into the resin was present in the solution in small concentration compared with the concentration of the ion displaced in the resin. Thus, the ion exchanger was essentially unaltered by the exchange process. This method of performing ion-exchange experiments is known as the shallow bed or infinite bath method. Use of this method requires that radioactive tracers must be employed to study the rate of reaction.

Boyd et al. (1947) investigated the kinetics of exchange of several ion pairs with a phenolsulfate resin and concluded that film diffusion was the rate-controlling step in solutions of displaced ion of concentrations less than 0.003 N. At concentrations of displaced ion greater than 0.1 N, particle diffusion was determined to be rate-controlling.

Reichenberg (1953) modified the equations of Boyd, Myers, and Adamson for the ion diffusing into the resin as a macrocomponent of the system.

Kressman and Kitchener (1949) also studied the kinetics of exchange on a phenolsulfate resin. They used a limited bath technique in which there were equivalent amounts of adsorbing ion and desorbing ion. The solution concentration used in all experiments was 0.02 N of the adsorbing ion. They concluded that in some exchanges film diffusion was rate-controlling, while with exchange of different ion pairs, the



rate-controlling step was particle diffusion. They also found that the activation energy under conditions of particle diffusion was 5 kcal/mole, which is of the same magnitude as the activation energy for film diffusion (Reichenberg, 1953).

Boyd et al. (1947) and Kressman and Kitchener (1949) have noted that the activation energies for the diffusion of ions in ion-exchange resins are similar to those obtained for the diffusion of similar ions through water. They suggested that diffusion in the resin might be regarded as diffusion through an aqueous medium.

In all of the cases described above the ion-exchange process occurs by reversible electrostatic exchange of two cations or anions. The process of exchange between ions in the solution and the porous ion-exchanger occurs uniformly throughout the solid phase (Nativ, Goldstein, and Schmuckler, 1975). Although Boyd et al. (1947) and Reichenberg (1953) developed equations for the case of chemical reaction as the rate-controlling mechanism, particle diffusion or solution diffusion has been found to be the rate-controlling mechanism in a majority of the exchange processes.

Helfferich (1965) first derived rate laws for ion-exchange processes accompanied by chemical reactions, in which the exchanging ions do not retain their identity. Examples of these processes are complex-formation, neutralization, and association reactions. In these processes the exchange process is accompanied by fast chemical reactions and the interacting ions progress in shells into the resin matrix.

therefore, a sharp boundary exists between the reacted portion and the unreacted portion of the resin bead.

A mathematical model for such a shell-progressive mechanism has been developed by Nativ, Goldstein, and Schmuckler (1975). The model was shown to explain the data from their experiments with Dowex A-1, a chelating resin with an iminodiacetic acid functional group. The authors concluded that diffusion through the product layer was the rate-controlling step. They also concluded that the rate of the adsorption reaction was dependent upon particle size and also on the concentration of the solution.

Heitner-Wirguin, in conjunction with several authors (Heitner-Wirguin and Markovits, 1963; Heitner-Wirguin and Urbach, 1965; Heitner-Wirguin and Ben-Zwi, 1970, 1971, 1972), has contributed to the study of chelating ion-exchange resins. With Markovits, she has studied the kinetics of ion exchange by Bio-Chelex 100, which also contains iminodiacetic acid as the chelating group. The  $H^+$  form of the resin was used to exchange alkaline earth metals. Activation energies for the reactions were determined to be 12.8, 14.8, and 17.2 kcal/mole for  $Mg^{+2}$ ,  $Ca^{+2}$ , and  $Sr^{+2}$ , respectively. The rate-determining step was concluded to be pore diffusion through the resin particle. The authors postulated that the high-activation energies obtained may be due to the low swelling of the resin, which results in small pore size.

Heitner-Wirguin and Urbach (1965) studied the exchange of  $Ca^{+2}$ ,  $Cu^{+2}$ ,  $Th^{+4}$ , and  $UO_2^{+2}$  with the  $Na^+$  form of Bio-Rex 63, a phosphonic-type cation exchanger. In the case of calcium and copper ions, which do

not complex with the exchanger, activation energies of 21 and 15 kcal/mole, respectively, were noted. The rate of exchange increased considerably with increasing temperature, while increased solution concentration decreased the exchange rate. The authors concluded that the rate of exchange of these ions with the resin was controlled by the rate of particle diffusion.

The  $\text{Th}^{+4}$  and  $\text{UO}_2^{+2}$  ions complex with the functional group of the resin. An increase in concentration of these ions in the solution increased the ion exchange rate considerably, while an increase in temperature increased the rate of exchange, but not as dramatically as in the case of  $\text{Ca}^{+2}$  and  $\text{Cu}^{+2}$  exchange. The rate of exchange was determined to be independent of stirring speed. The activation energies for exchange of  $\text{Th}^{+4}$  and  $\text{UO}_2^{+2}$  were found to be 11 and 10 kcal/mole, respectively. The authors concluded that chemical reaction was the rate-determining step in the case of these complexing ions.

Schwarz, Marinsky, and Spiegler (1964), in their study of  $\text{Co}^{+2}$  self exchange using radioactive  $\text{Co}^{60}$ , concluded that the ion-exchange reaction with an iminodiacetic ion exchanger was controlled by particle diffusion.

Matsuzuru and Wadachi (1975) also experimented with an iminodiacetic ion exchanger. They examined the reactions of the resin with  $\text{Ag}^{+}$ ,  $\text{Zn}^{+2}$ , and  $\text{Cr}^{+3}$  at very low concentrations. It was determined that the activation energies were on the order of 4 kcal/mole for  $\text{Ag}^{+}$  and  $\text{Zn}^{+2}$ , indicating particle diffusion as the rate-determining step,

whereas the activation energy for  $\text{Cr}^{+3}$  with the resin was 15.5 kcal/mole, indicating the chelate-forming reaction as the rate-controlling step.

## EXPERIMENTAL TECHNIQUES

The experiments were designed to determine the rate of cobalt adsorption from the cobalt-ammonia-ammonium carbonate solutions by an ion-exchange resin. Tests were performed to determine the hydrogen ion ( $H^+$ ) capacity of the resin, the ratio of dry weight ammonium ion ( $NH_4^+$ ) form of the resin to dry weight  $|H^+|$  form of the resin, and the moisture content of the  $|NH_4^+|$  form of the resin. The size distribution of the wet resin was also determined. The initial kinetic tests were to determine the optimal stirring speed. Tests were also performed to determine the effects of temperature, cobalt concentration, ammonium bicarbonate concentration, and pH on the rate of cobalt adsorption. Cobalt capacity determinations were performed at various pH's and temperatures. Visible spectrophotometric measurements were performed in an effort to determine which cobalt species was adsorbed on the resin.

### Materials

All chemicals used in all experiments were analytical grade reagents, except the ammonium bicarbonate, which was food grade.

The ion-exchange resin used in this study was supplied by Rohm and Haas Company (1975) under the trade name XE-318. This resin is a cross-linked macroreticular chelating cation-exchange resin.

Distilled water with a specific conductance of  $2 \times 10^{-6}$  mhos/cm was used in all the experiments.

### Hydrogen Ion Capacity Determination

The  $H^+$  capacity of the resin was determined according to the method described by Fisher and Kunin (1955). This method is outlined below:

- 1) 0.1 N NaOH in 5% sodium chloride solution was prepared using boiled distilled water.
- 2) The NaOH solution was standardized by titrating samples of potassium biphthalate, dissolved in distilled water, with the NaOH solution using 1 weight percent phenolphthalein in ethyl alcohol as an indicator.
- 3) The 0.1 N  $H_2SO_4$  was standardized by titrating 10 ml aliquots with the standardized NaOH solution, also using phenolphthalein as an indicator for the titration endpoint.
- 4) The resin was conditioned before capacity measurements by contacting the resin alternately with 2M  $HNO_3$  and 2M NaOH. This cycle was repeated three times. This contacting of resins with solutions required that the resin be stirred. An overhead stirrer was used, as it was found that a magnetic stirring bar fractured the beads.
- 5) Approximately 5 g of resin was converted to  $|H^+|$  form by passing 1 liter of 1M  $HNO_3$  over the resin. The acid was passed through the resin slowly with the resin beads covered by solution at all times.
- 6) Approximately 1 g of the wet  $|H^+|$  form resin, weighed to the nearest 0.1 mg, was added to exactly 200 ml of the standardized

NaOH. The sample was stoppered and allowed to stand overnight. The remainder of the resin was dried at 80°C overnight.

- 7) Fifty-milliliter aliquots of the supernatant solution were titrated to the phenolphthalein endpoint with the standard 0.1N  $\text{H}_2\text{SO}_4$  to determine the total  $\text{H}^+$  consumed by the resin, and therefore determine its  $\text{H}^+$  capacity.
- 8) The dried resin was weighted to determine the percent moisture of the  $|\text{H}^+|$  form resin.

Ratio of Dry Weights  $|\text{NH}_4^+|$   
Form Resin to  $\text{H}^+$  Form Resin

This determination was necessary because it was found that the  $|\text{H}^+|$  form resin did not remove cobalt from the ammonia-ammonium carbonate solution.  $|\text{NH}_4^+|$  form resin, however, did remove cobalt from the solution.

The dry  $|\text{H}^+|$  form resin from the  $\text{H}^+$  capacity measurements was stirred in 2M  $\text{NH}_3(\text{aq})$  for 1 hour. The converted resin was dried and weighed.

Moisture Content of Wet  $\text{NH}_4^+$  Form Resin

- 1) Approximately 4 g of wet  $|\text{NH}_4^+|$  form resin was placed in each of 5 Erlenmeyer flasks.
- 2) The resin in the flasks was dried overnight in the drying oven.
- 3) The dried samples of resin were weighed.
- 4) The resin in each flask was rehydrated with dilute  $\text{NH}_4^+$  solution and then was filtered. The excess moisture was blotted from each sample of resin and the wet resin was weighed.

- 5) Each portion of resin was returned to an Erlenmeyer flask and steps 2 and 3 were repeated to minimize experimental error involved in the determination.

#### Size Distribution Determination

The resin was separated into size fractions by wet screening. The method is described by Gaudin (1939).

#### Kinetic Experiments

To minimize error due to separate weighings, a 40 gpl stock solution of cobalt was prepared using reagent grade  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ .

The apparatus used in all kinetic experiments is shown in Figure 1. The essential features are a Polyscience Corporation Model 73 Immersion Circulator clamped into the water bath, and the baffled reactor equipped with a thermometer, a sampling device, and a stirrer turned by a variable speed motor. A Pioneer stroboscope was used for setting the stirring speed. A Leeds and Northrup Model 7411 pH meter was used to determine the pH of solutions.

- 1) Two liters of cobalt-ammonia-ammonium bicarbonate solution were prepared having the desired pH, cobalt concentration, and ammonium bicarbonate concentration. The standard conditions were: temperature at  $35^\circ\text{C}$ , pH of 8.5, solution saturated in ammonium bicarbonate, and a cobalt concentration of 100 ppm.
- 2) The solution was transferred to the reactor which was clamped into the water bath. This solution was stirred and allowed to reach the desired temperature.



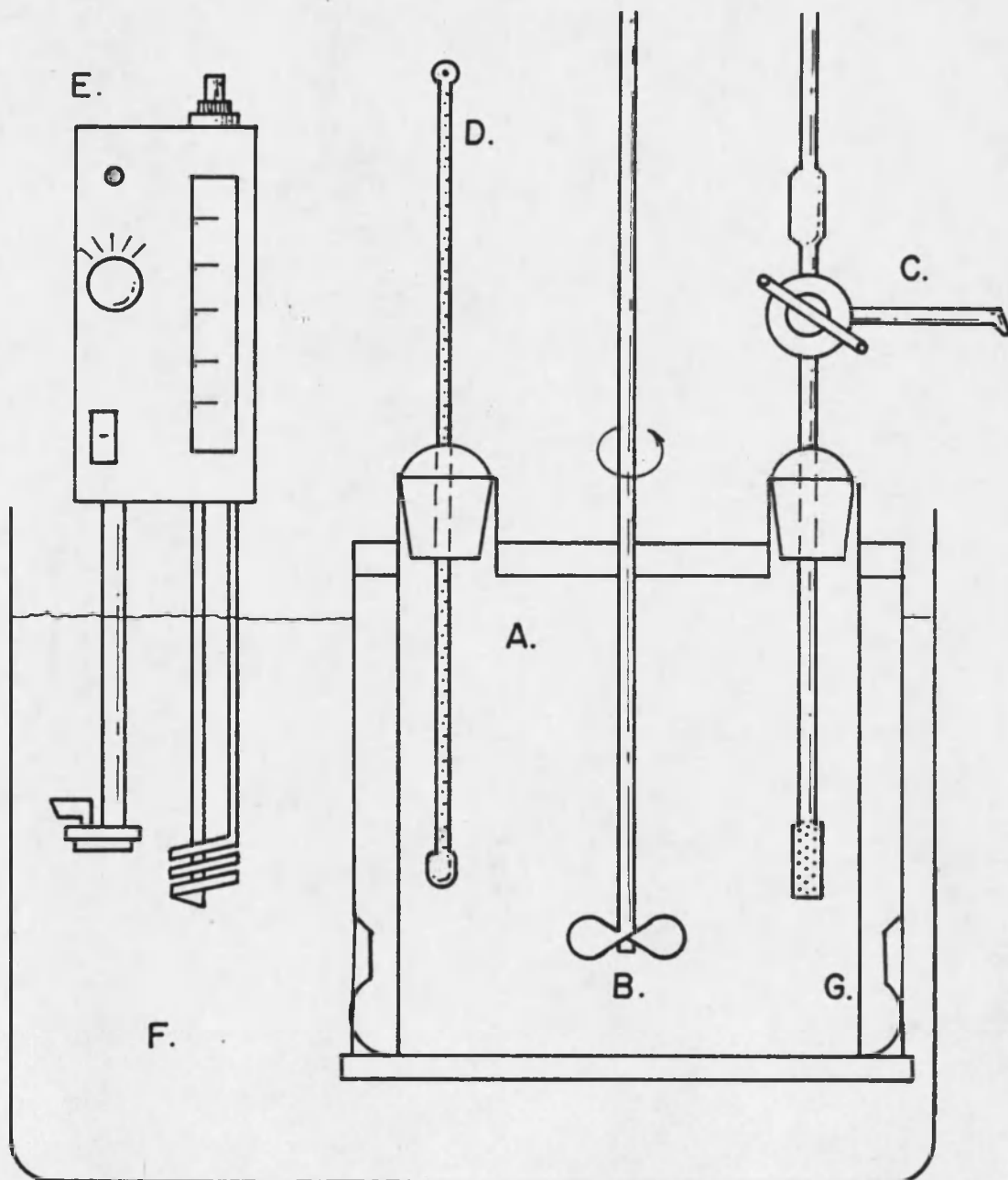


Figure 1. Apparatus for Kinetic Experiments. -- A = plexiglass reactor; B = stirrer; C = sampling device; D = thermometer; E = immersion heater-circulator; F = water bath; G = baffles.

- 3) About 6 g of the wet resin were prepared for the experiment by filtering the resin and patting the excess moisture from the resin with filter paper. The resin was weighed on a dry tared filter paper.
- 4) The stirring speed was adjusted with the stroboscope.
- 5) After the solution in the reactor reached the desired temperature, a 12 ml sample of the solution was taken for analysis.
- 6) The resin was introduced directly into the reactor from the filter paper and the timer was started.
- 7) Twelve-milliliter samples were taken using the sampling apparatus at various times up to 60 minutes after the addition of the resin.
- 8) The resin was filtered from the solution and was stripped of cobalt by stirring in 2M  $\text{HNO}_3$  for 1 hour. The resin was filtered from the nitric acid solution and rinsed with distilled water.
- 9) The resin was regenerated to  $|\text{NH}_4^+|$  form by stirring it in a 2M  $\text{NH}_3(\text{aq})$  solution for 1 hour. The resin was filtered, rinsed, and stored in a dilute  $\text{NH}_3(\text{aq})$  solution to prevent hydration of the resin.

#### Cobalt Capacity Tests

A 1000 ml graduated cylinder was used as the reaction vessel. A large stopper with a hole for the stirrer was used to cover the reactor.

- 1) Five hundred milliliters of 100 ppm cobalt solution saturated in ammonium bicarbonate, at the desired pH, was placed in the cylinder.

- 2) The cylinder was clamped into the constant temperature bath. The solution was stirred at 600 rpm and was allowed to reach the desired temperature.
- 3) Approximately 3 g of the wet resin were prepared for the experiments by filtering the resin and patting the excess moisture with filter paper. The resin was weighed on a dry tared filter paper.
- 4) At 120 minutes after the introduction of the resin, the reactor was removed from the bath.
- 5) The depleted solution was separated from the resin and analyzed.

#### Atomic Absorption Analysis

A Perkin-Elmer Model 360 atomic absorption spectrophotometer was used to determine the cobalt concentration of the ammonia-ammonium carbonate solutions.

- 1) All samples from kinetic or cobalt capacity experiments were diluted to between 5 and 25 ppm Co with distilled water. In the capacity experiments, the entire depleted solution was diluted into the desired concentration range.
- 2) The absorbance of samples was measured using the standard conditions for cobalt analysis as described in the Perkin-Elmer Manual (n.d.). Because of the downward drift of the instrument, approximate concentrations were first found by taking absorbance readings of standards and dilute samples. Each sample was aspirated into the instrument a second time and the standard solutions having higher and lower absorbance readings than the

sample, in the first determination, were also aspirated into the A.A. These second absorbance values were determined in quick succession to minimize error in the determination.

- 3) All sample bottles were washed using Alconox detergent, rinsed in tap water, and then rinsed with distilled water. The bottles were dried in the drying oven for subsequent samples for A.A. determination.

#### Visible Spectrophotometric Analysis

A Spectronic 100 visible spectrophotometer with 1 cm pyrex glass cuvettes was used to obtain the visible range spectra of the solution samples.

- 1) The spectrophotometer was calibrated according to instructions in the Bausch and Lomb Operator's Manual (n.d.).
- 2) Cuvettes were filled with solution and were wiped with wiping tissues to remove any fingerprints or dust.
- 3) The absorbance reading of the instrument was zeroed at each wavelength with distilled water and then the absorbances of the solutions were determined. The absorbance measurements were taken in the wavelength range 350-625 nm.

## EXPERIMENTAL RESULTS AND DISCUSSION

The experimental data gathered and its analysis are presented in this section. A discussion on the reproducibility of the data is presented first. The data gathered during the kinetic experiments, its analysis and interpretation are presented next.

### Reproducibility

At the onset of this investigation, it was necessary to establish the reproducibility of the experimental data. Two major sources of error that could be foreseen are: 1) error associated with analysis of solution samples, and 2) error in weight of resin used during the experiments because of the moisture content of the resin.

The error involved in solution analysis by atomic absorption is typically around  $\pm 2\%$ , although this varies according to the instrument used and the element determined (Fritz and Schenk, 1969). During the course of the investigation it was found that sometimes the reproducibility was poorer than that expected due to error associated with A.A. analysis.

The data collected for percent solids for  $|\text{H}^+|$  form of the resin indicated that the percent solids in the  $|\text{H}^+|$  form resin was  $44.0 \pm 5\%$ , or a relative error of  $\pm 3\%$ . It could then be presumed that the  $|\text{NH}_4^+|$  form of the resin would exhibit similar error. However, the percent solids in the  $|\text{NH}_4^+|$  form varied from 29.5 to 45.5%, with a mean of 37.3% solids, indicating a relative error of  $\pm 12\%$ . Thus, a fairly large

error factor was involved in the weight of the resin used during an experiment. Other investigations have used dried resin. It was felt that similar, if not greater, error in the measurement of the rate of reaction would result if dry resin were used. As a result of these errors, it was not possible to obtain good reproducibility of the data.

In addition to the above sources of error, an unforeseen source of error became apparent during the course of the investigation. There was an apparent increase in the capacity of the resin during the investigation. Table I shows the capacity of the  $|\text{NH}_4^+|$  form of the resin under various conditions and at different time periods. No explanation for this apparent increase in the capacity of the resin is possible with the data and facilities available.

#### Resin Capacity

The mean  $\text{H}^+$  capacity was determined to be 5.10 meq  $\text{H}^+$  exchanged per gram of dry  $|\text{H}^+|$  form resin. The ratio of dry weight  $|\text{H}^+|$  form resin to dry weight  $|\text{NH}_4^+|$  form resin was determined to be 1.07 g dry  $|\text{H}^+|$  form resin per gram dry  $|\text{NH}_4^+|$  resin. Thus, the  $|\text{NH}_4^+|$  form resin capacity, which is related to the number of reactive sites available in the resin, was determined to be 5.46 meq cation exchangeable per gram of dry  $|\text{NH}_4^+|$  form resin. This compares well with the value 5.3 meq cation exchangeable per gram of dry  $|\text{NH}_4^+|$  form resin claimed by the manufacturer (Rohm and Haas, Co., 1975). Sample calculations for  $\text{NH}_4^+$  capacity and  $\text{H}^+$  capacity of the resin are shown in Appendix B.

Table I. Cobalt Adsorptions Capacity of the Resin.

<u>Temperature (°C)</u>	<u>Mg Co Adsorbed/g</u> <u>Dry Resin</u>	<u>Mg Co Adsorbed/g</u> <u>Dry Resin</u>
	<u>December, 1977</u>	<u>May, 1978</u>
35	28.72	44.82
45	30.03	42.06
55	33.96	43.63
65	-	45.53
-----		
<u>pH</u>	<u>January, 1978</u>	<u>April, 1978</u>
7.0	39.70	-
8.0	38.79	-
8.5	31.01	44.82
9.0	28.60	-
10.0	23.51	26.64
-----		
<u>(NH<sub>4</sub>)HCO<sub>3</sub></u> <u>Conc. (gpl)</u>	<u>December, 1977</u>	<u>April, 1978</u>
25	-	51.77
50	-	45.92
100	-	45.05
246 (sat'd)	28.72	44.82

Size Distribution of the Resin

The size distribution of the XE-318 resin is given in Table II.

Table II. Size Distribution of XE-318 Resin.

Mesh Size, U.S. Sieve Series	Particle Size, Microns	Weight %
+20	841	3
-20+30	595	36
-30+40	420	46
-40+50	297	11
-50	-297	4

It can be seen that more than 80% of the resin is included in the size range between 841 and 420  $\mu$ .

Kinetics

The kinetic experiments were performed to determine the effects of agitation, temperature, concentration of cobalt in solution, concentration of ammonium bicarbonate in solution, and pH of the solution on the rate of absorption of cobalt on XE-318 ion exchange resin.

Effect of Agitation

In an investigation of reaction mechanisms in a solid-liquid system, it is generally important to eliminate agitation as a variable.



As the degree of agitation is increased, the stagnant boundary layer that surrounds the solid particle decreases in thickness, until at some rate of agitation, a limiting boundary layer thickness is reached. In order to determine the degree of agitation necessary to reach this limiting boundary layer thickness, experiments were performed at agitation speeds of from 200 to 800 rpm. Higher agitation rates were not investigated because of excessive shaking and bouncing of the apparatus at agitation speeds greater than 800 rpm. The data collected are presented in Figure 2. The scatter in the data is very apparent due to the reasons discussed earlier. However, it can be seen that as the agitation increased, the rate of adsorption of cobalt on the resin increased, and that between 600 and 800 rpm, there is a very small increase in the rate of cobalt adsorption. It was therefore decided to conduct all subsequent experiments at 600 rpm.

#### Effect of Temperature

The temperature of reaction was the next variable investigated. Figure 3 shows the effect of temperature on the rate of cobalt adsorption. It can be seen that as the temperature is increased, the rate of cobalt adsorption also increases. The scatter and overlap, due to the errors in experimental technique discussed earlier, are again evident. In fact, the plots for 45 and 55°C are identical and the data for 65 and 71°C are indistinguishable after 30 minutes.

In order to determine the mechanism of cobalt extraction, it is necessary to formulate a mathematical relationship that can linearize the data and explain the results.

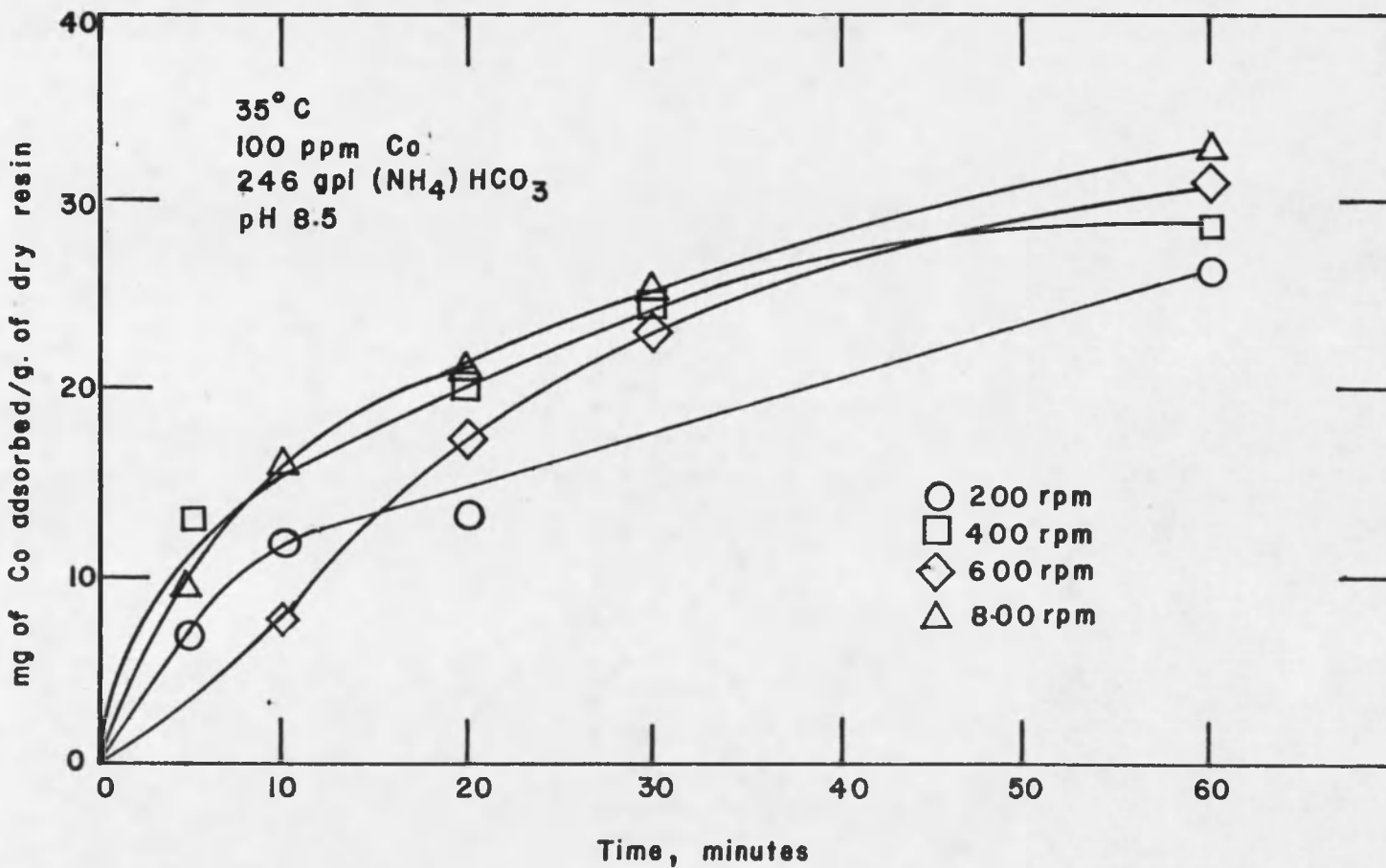


Figure 2. Effect of Agitation on Adsorption of Cobalt by Resin as a Function of Time.

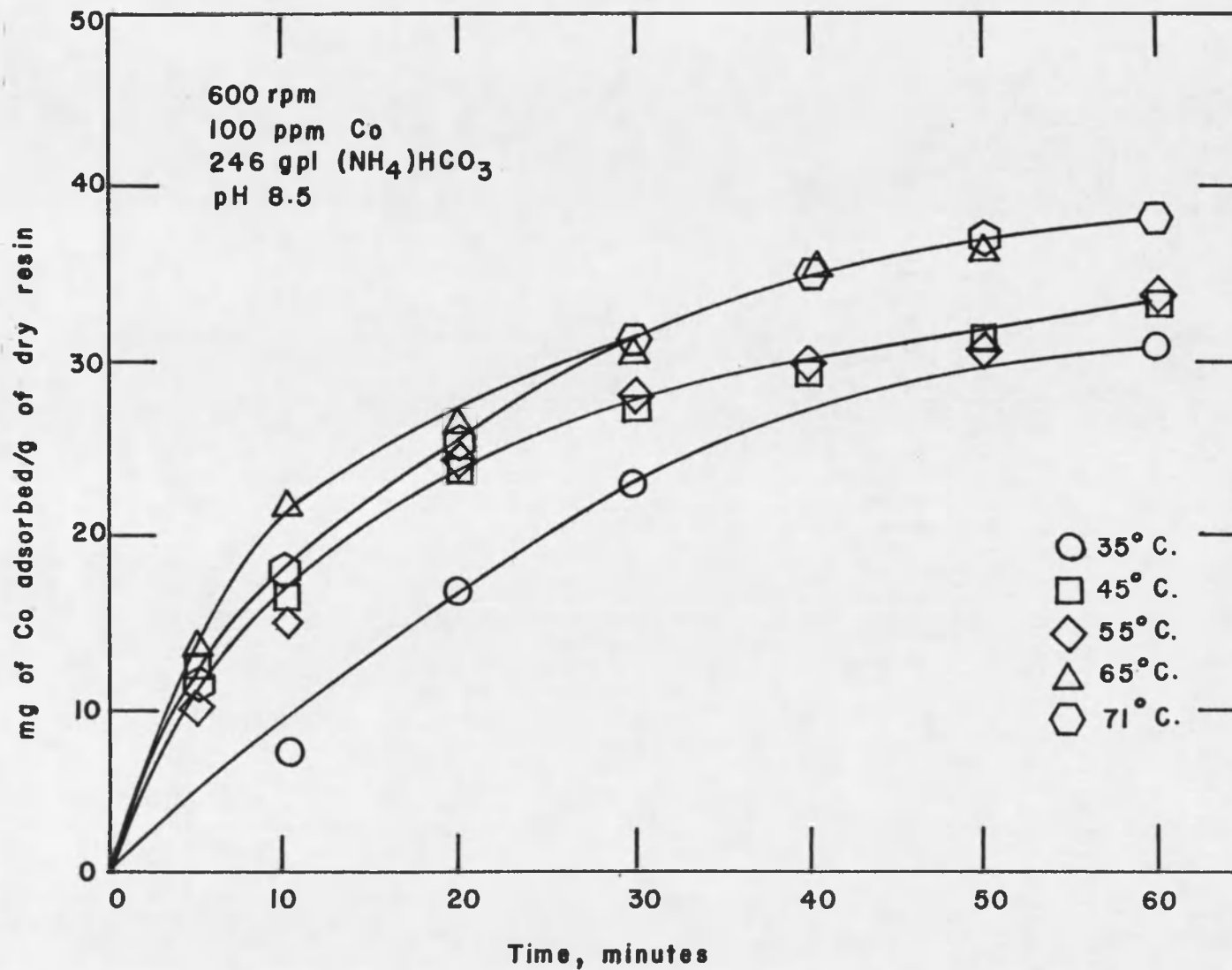


Figure 3. Effect of Temperature on Adsorption of Cobalt by Resin as a Function of Time.

In the heterogeneous reaction under consideration, the following seven mechanistic steps may be involved, any one of which could be the rate-controlling step:

- 1) diffusion of the cobalt complex through the boundary layer to the surface of the resin bead,
- 2) diffusion of the cobalt complex to the reaction site from the surface of the resin bead,
- 3) adsorption of cobalt complex at the reaction site,
- 4) chemical reaction,
- 5) desorption of the reaction product from the reaction site,
- 6) diffusion of the reaction product through the resin bead to the surface of the bead,
- 7) diffusion of the reaction product through the boundary layer surrounding the bead to the bulk solution.

The rate-controlling step is that step in the reaction sequence which occurs at the slowest rate. In the system investigated, it is believed that the rate-controlling step could be one of the following mechanistic steps:

- 1) boundary layer diffusion,
- 2) diffusion of either the cobalt ammine complex or the ammonium ion through the resin bead, or
- 3) a chemical reaction.

Mathematical expressions that describe each of these steps can be derived from first principles. These expressions can be used to linearize the data for the determination of the apparent rate constant.

In the case of boundary layer diffusion as the rate-controlling step, the appropriate equation is (Chaubal, 1978):

$$\ln|A|/|A_0| = -k_a t \quad (1)$$

where  $|A_0|$  = original concentration of the species which is diffusing through the film layer.

$|A|$  = instantaneous concentration of the diffusing species, A.

$k_a$  = apparent first-order rate constant.

$t$  = time.

The activation energy for this process is generally less than 5 kcal/mole in an aqueous system (Fisher, 1977).

In the case of diffusion of the reacting species through a product layer to the reacting site as the rate-controlling step, the following equation applies (Fisher, 1977; Chaubal, 1978):

$$1 - (1 - \alpha)^{2/3} - 2/3\alpha = k_a t \quad (2)$$

where  $\alpha$  = fraction of the particle reacted.

$k_a$  = apparent first-order rate constant

$t$  = time.

The activation energy for product layer diffusion is on the order of 10-25 kcal/mole for pore diffusion. For diffusion through bulk aqueous phase, the activation energy is less than 5 kcal/mole (Fisher, 1977).

In the case of chemical reaction with decreasing surface area and no ash layer as the rate-controlling step, the appropriate equation is (Fisher, 1977; Chaubal, 1978):

$$1-(1-\alpha)^{1/3} = k_a t \quad (3)$$

where  $\alpha$  = fraction of the particle reacted.

$k_a$  = apparent first-order rate constant.

$t$  = time.

All of these equations were tried, and it became apparent that the rate-controlling step involved diffusion and increasing diffusion path length as the reaction proceeded.

Figure 4 is a plot of equation (2) for the data presented in Figure 3. It can be seen that within experimental error, equation (2) can linearize the data. It can be concluded that the mechanistic step responsible for the rate of reaction is diffusion. The apparent rate constants determined at various temperatures are tabulated in Table III.

Table III. Effect of Temperature on Apparent Rate Constant.

Temperature (°C)	$k_a$ , minute <sup>-1</sup>
35	$6.91 \times 10^{-5}$
45	$7.74 \times 10^{-5}$
55	$7.95 \times 10^{-5}$
65	$1.07 \times 10^{-4}$
71	$1.06 \times 10^{-4}$

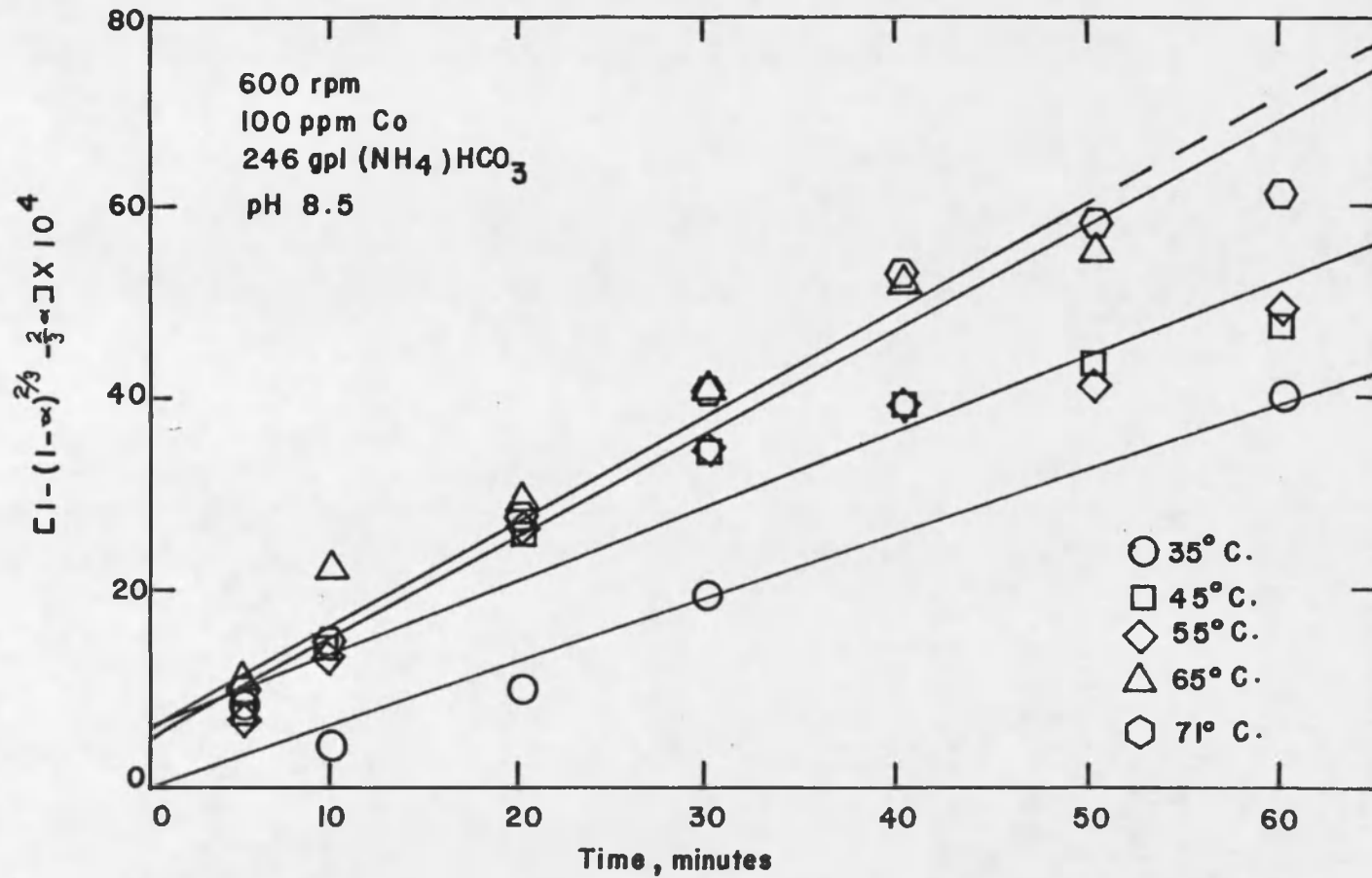


Figure 4. Plot of  $1 - (1 - \alpha)^{2/3} - 2/3\alpha$  versus Time at Varying Temperature.

In order to determine the rate-controlling step, it is necessary to determine the activation energy. The activation energy can be determined by the Arrhenius equation (Fisher, 1977):

$$k_a = Ae^{-E_a/RT} \quad (4)$$

where  $k_a$  = apparent rate constant.

A = frequency factor.

$E_a$  = activation energy.

Figure 5 is the plot of equation (4). The activation energies determined were 4.4 kcal/mole in the temperature range 55-71°C and 1.4 kcal/mole in the temperature range 35-55°C. The small activation energy rules out the possibility of pore diffusion. Diffusion through an aqueous-continuous phase is involved in the rate-controlling step.

The resin bead is extremely porous and it is reasonable to assume that an aqueous-continuous phase exists in the pores of the resin. Thus, diffusion of either the cobalt ammine complex or the ammonium ions, or both, through the porous resin is involved in the rate-controlling step. Change in activation energy at 55°C is possibly due to a change in pore size.

#### Effect of Cobalt Concentration

The effect of changing the initial concentration of cobalt present in the solution on the resin-loading characteristics is shown in Figure 6. It can be discerned that as cobalt concentration increases, the rate of cobalt adsorption increases.



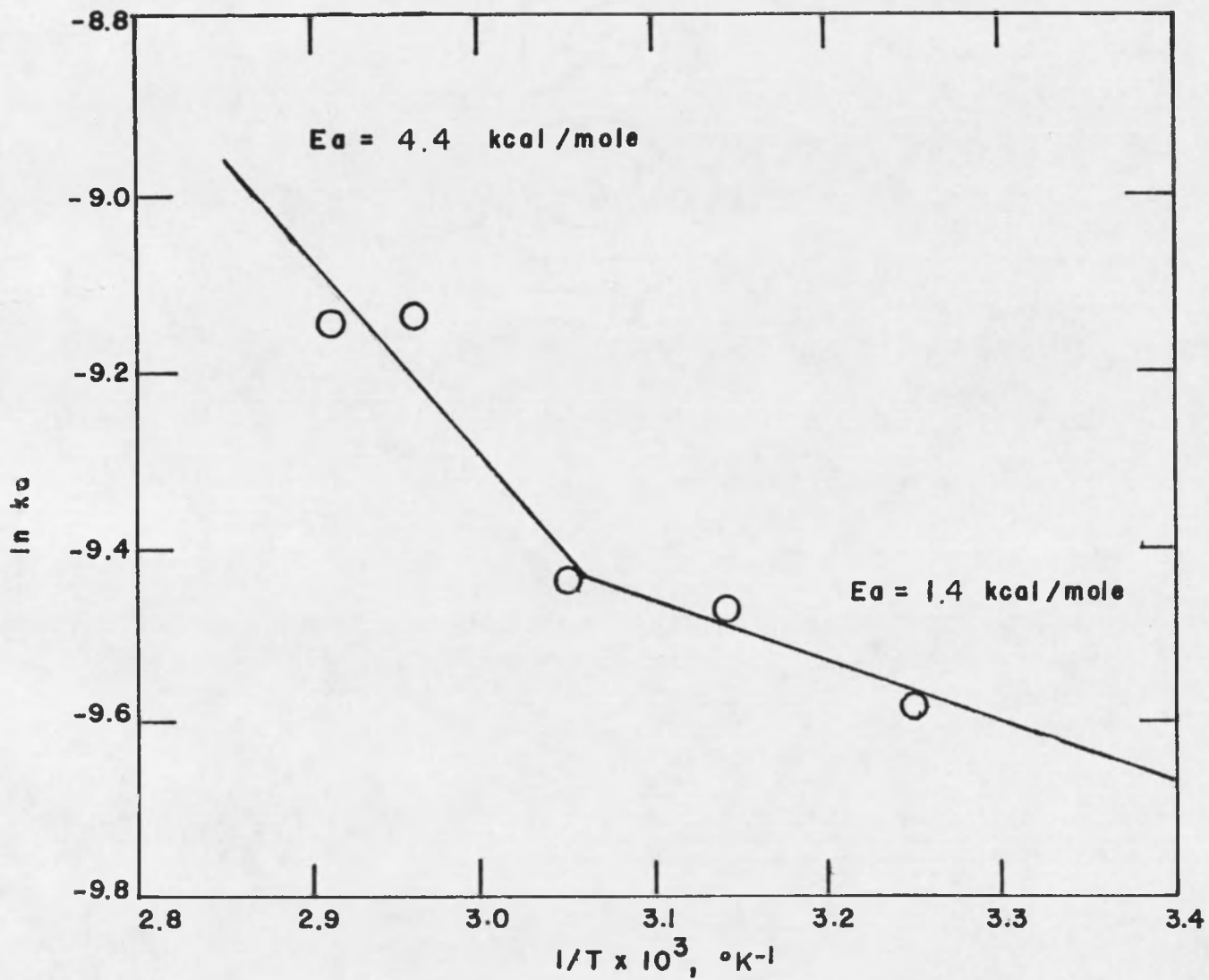


Figure 5. Effect of Temperature on the Apparent Rate of the Reaction (Arrhenius Plot).

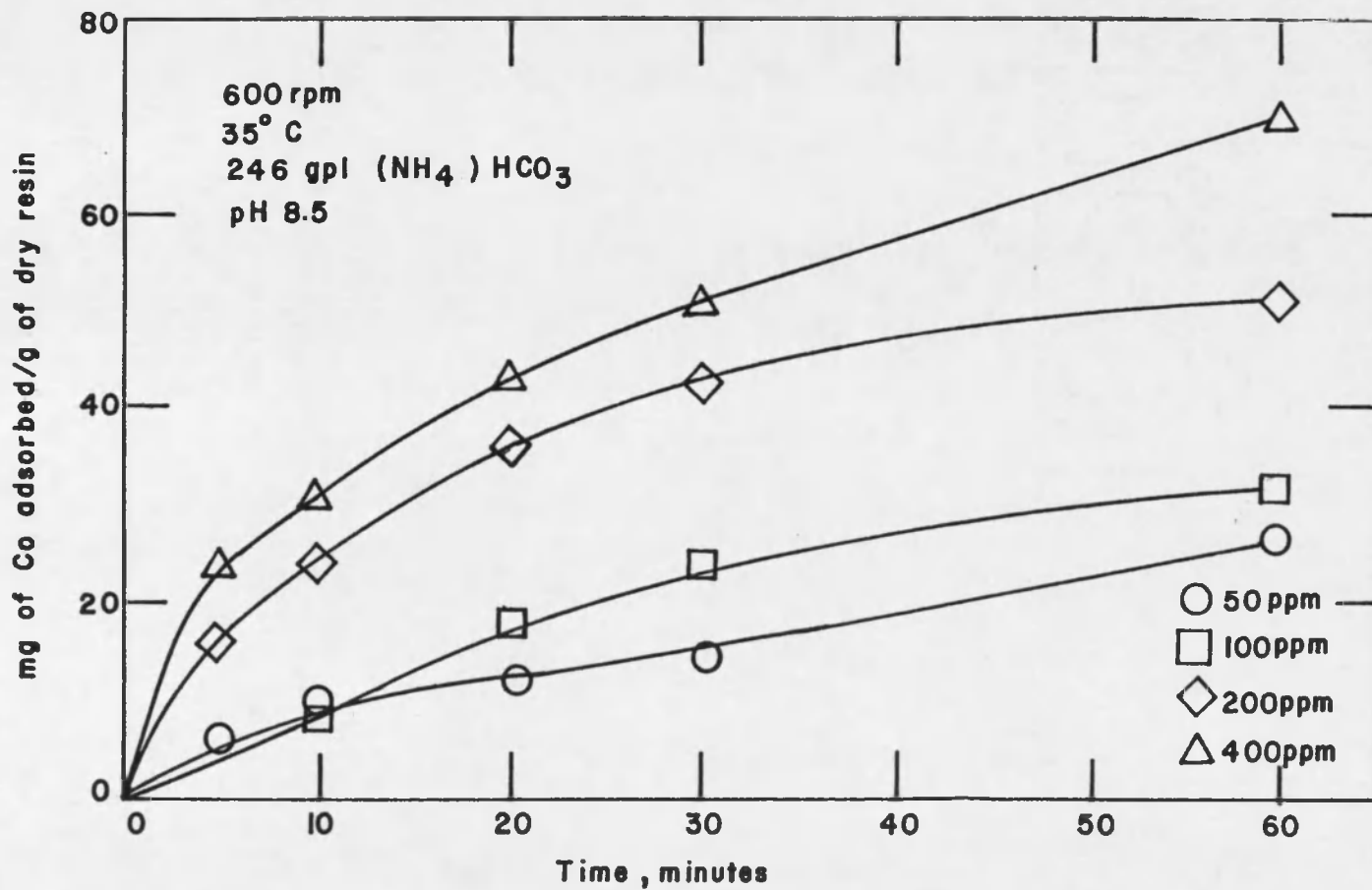


Figure 6. Effect of Cobalt Concentration on Adsorption of Cobalt by Resin as a Function of Time.

At concentrations of cobalt greater than 400 ppm a purplish-pink precipitate formed in pH 8.5, saturated ammonium bicarbonate solution. The precipitate was analyzed by x-ray diffraction and determined to be  $\text{CoCO}_3$ . The x-ray data gathered for this identification are tabulated in Appendix C. Experiments were performed at concentrations of 600, 800, and 1000 ppm in which the  $\text{CoCO}_3$  precipitate was present. Resin used in these experiments could not be regenerated using the method described earlier. The experiments at these high Co concentrations were not duplicated because of the deleterious effect of the precipitates on the resin.

The data presented in Figure 6 are plotted as the equation (2) in Figure 7. Equation (2) is valid and the apparent rate constants extracted from these plots are listed in Table IV.

Table IV. Effect of Cobalt Concentration on Apparent Rate Constant.

Cobalt Concentration (ppm)	$k_a$ , minute <sup>-1</sup>
50	$5.10 \times 10^{-5}$
100	$6.91 \times 10^{-5}$
200	$1.76 \times 10^{-4}$
400	$3.08 \times 10^{-4}$

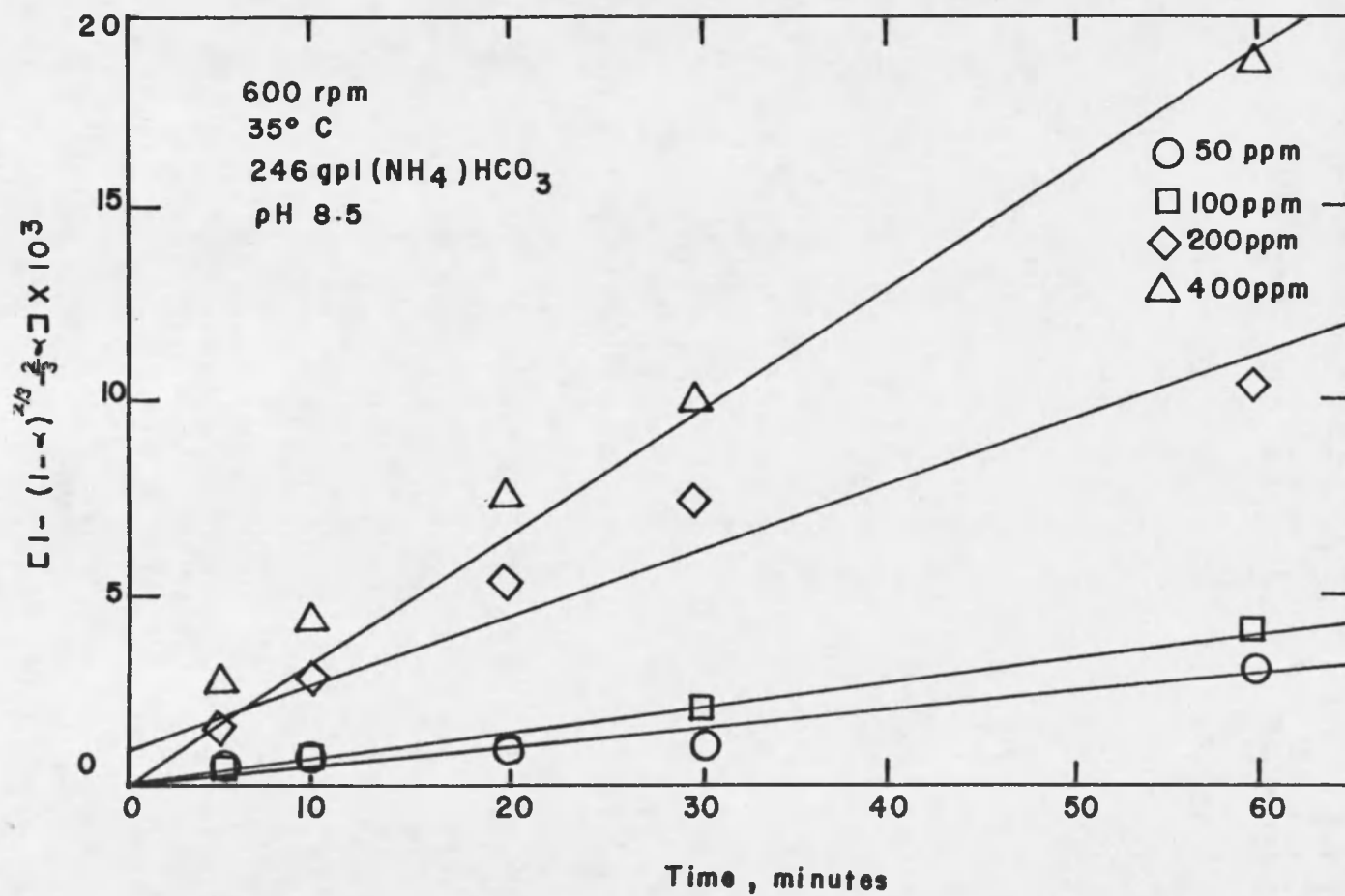


Figure 7. Plot of  $1 - (1 - \alpha)^{2/3} - \frac{2}{3}\alpha$  versus Time at Varying Cobalt Concentration.

The order of the reaction with respect to cobalt concentration in solution can be determined as follows:

$$\text{apparent rate constant} = k_a = k_s |\text{Co}|^n \quad (5)$$

where  $k_s$  = specific rate constant.

$|\text{Co}|$  = cobalt concentration in solution.

$n$  = order of the reaction with respect to cobalt concentration.

This equation can also be expressed as:

$$\ln \text{apparent rate constant} = \ln k_a = \ln k_s + n \ln |\text{Co}| \quad (6)$$

Thus, a plot of  $\ln |k_a|$  versus  $\ln \text{Co}$  will yield a slope 'n', the reaction order. Such a plot is shown in Figure 8 and yields a slope of 0.91, and therefore it can be concluded that the reaction order with respect to cobalt concentration is one. This confirms the assumption made in the derivation of equation (2) that the reaction order is one.

#### Effect of Ammonium Bicarbonate Concentration

The effect of changing the ammonium bicarbonate concentration in the solution on the rate of resin loading is shown in Figure 9. It is seen that the ammonium bicarbonate concentration has a slight effect on the rate of adsorption of cobalt. The data shown in Figure 9 are plotted as equation (2) in Figure 10. Again, the model is valid and the apparent rate constants were determined and are tabulated in Table V.

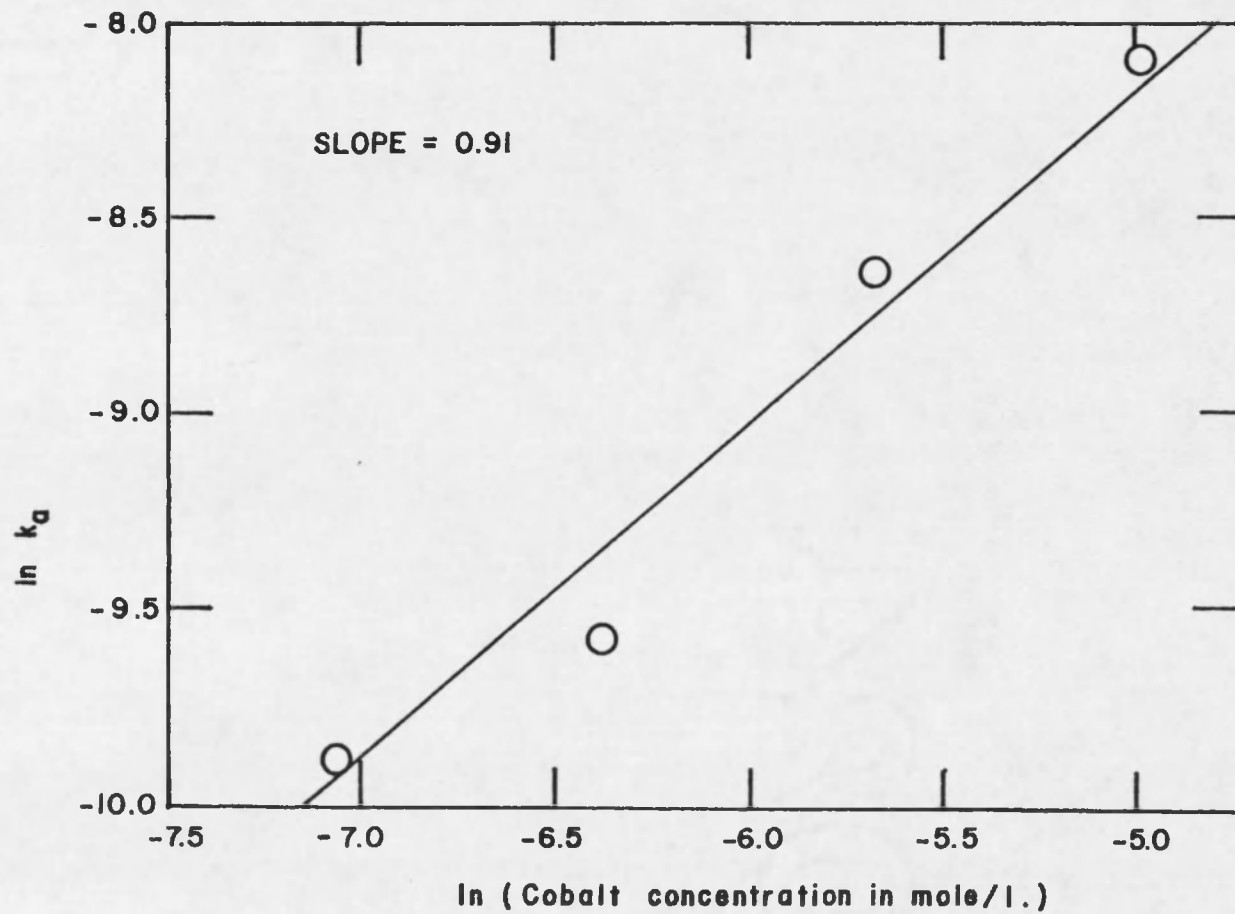


Figure 8. Effect of Cobalt Concentration on the Apparent Rate Constant.

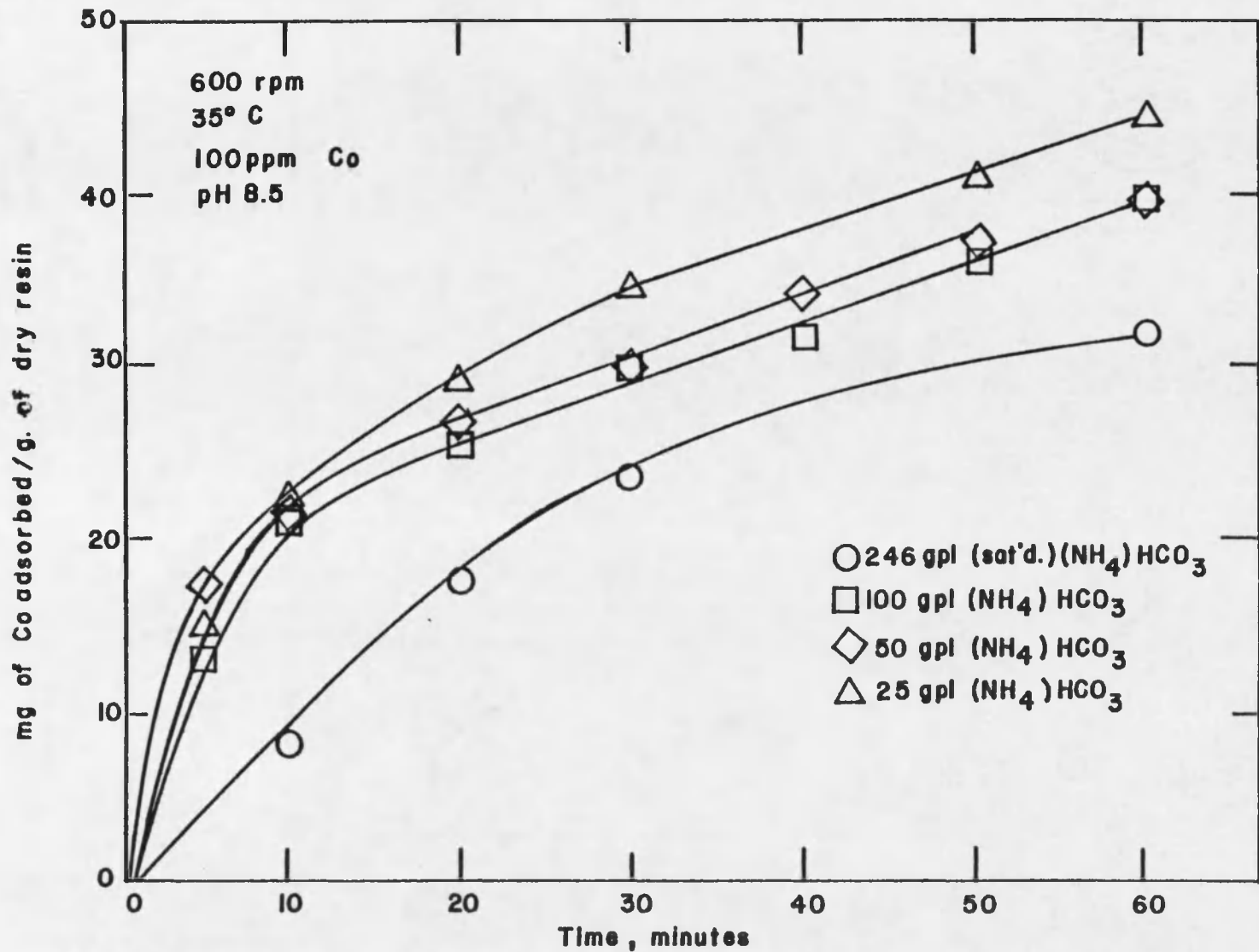


Figure 9. Effect of Ammonium Bicarbonate Concentration on the Adsorption of Cobalt by Resin as a Function of Time.

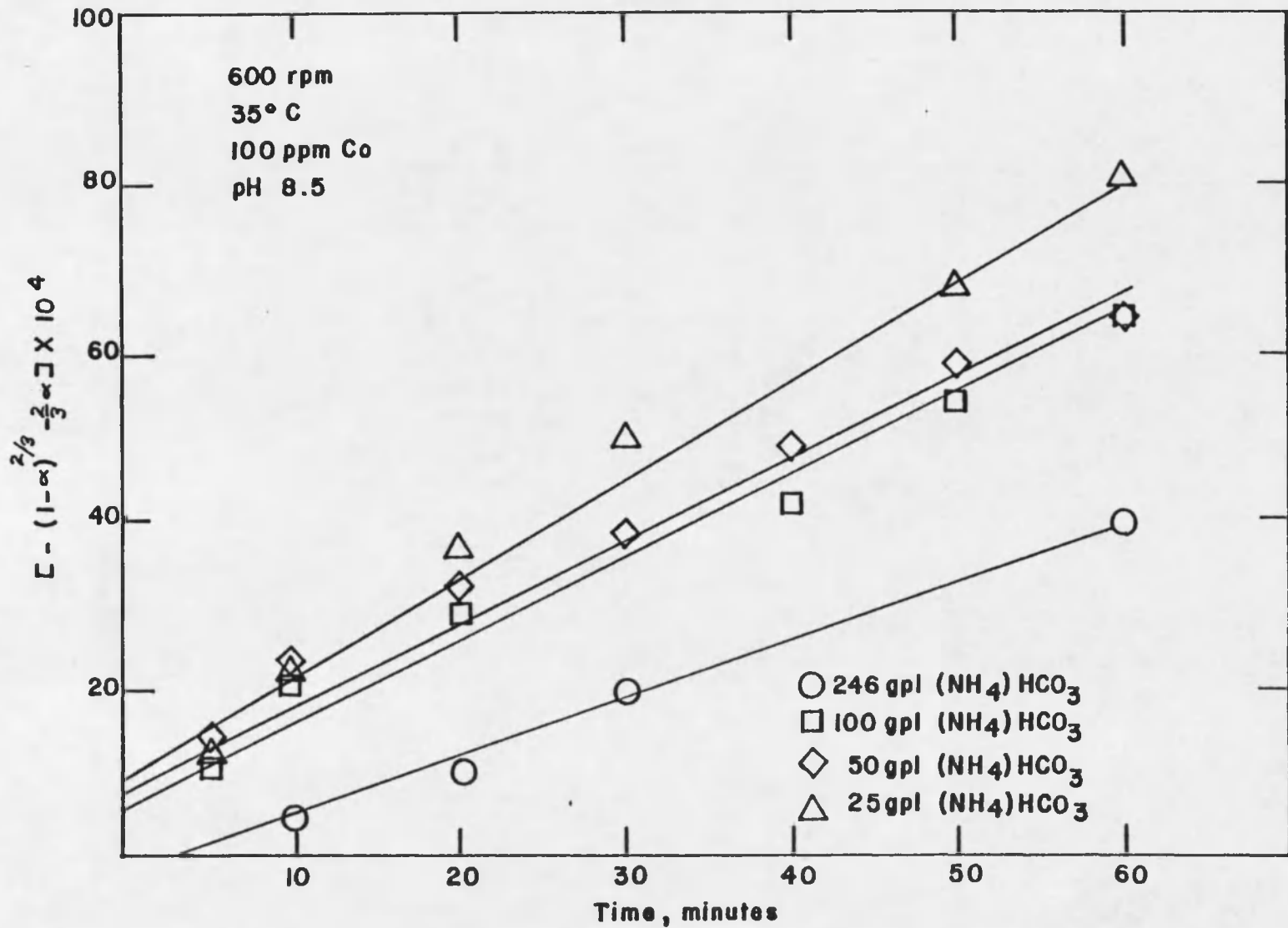


Figure 10. Plot of  $1 - (1 - \alpha)^{2/3} - 2/3\alpha$  versus Time at Varying Ammonium Bicarbonate Concentration.



Table V. Effect of Ammonium Bicarbonate Concentration.

$(\text{NH}_4)\text{HCO}_3$ Concentration (gpl)	$k_a$ , minute <sup>-1</sup>
25	$1.21 \times 10^{-4}$
50	$9.94 \times 10^{-5}$
100	$9.76 \times 10^{-5}$
246 (sat'd)	$6.91 \times 10^{-5}$

The order of the reaction with respect to ammonium bicarbonate concentration can be found from the following relation:

$$\text{apparent rate constant} = k_a = k_s |(\text{NH}_4)\text{HCO}_3|^n \quad (7)$$

which is analogous to equation (5) and can be rewritten as:

$$\text{apparent rate constant} = \ln k_a = \ln k_s + n \ln |(\text{NH}_4)\text{HCO}_3| \quad (8)$$

A plot of  $\ln k_a$  versus  $\ln |(\text{NH}_4)\text{HCO}_3|$  will thus give the reaction order with respect to ammonium bicarbonate concentration. The plot is shown in Figure 11 and the slope is -0.23.

An explanation for this behavior is that as the concentration of the ammonium bicarbonate in the solution decreases, the concentration difference between  $\text{NH}_4^+$  in the resin and bulk solution increases. If diffusion of  $\text{NH}_4^+$  from the bead were involved in the rate-controlling step, then decreased ammonium bicarbonate concentration should increase the rate of reaction. Change in the ammonium bicarbonate concentration also changes the distribution of species in the solution and indirectly affects the rate of reaction by changing the effective concentration of

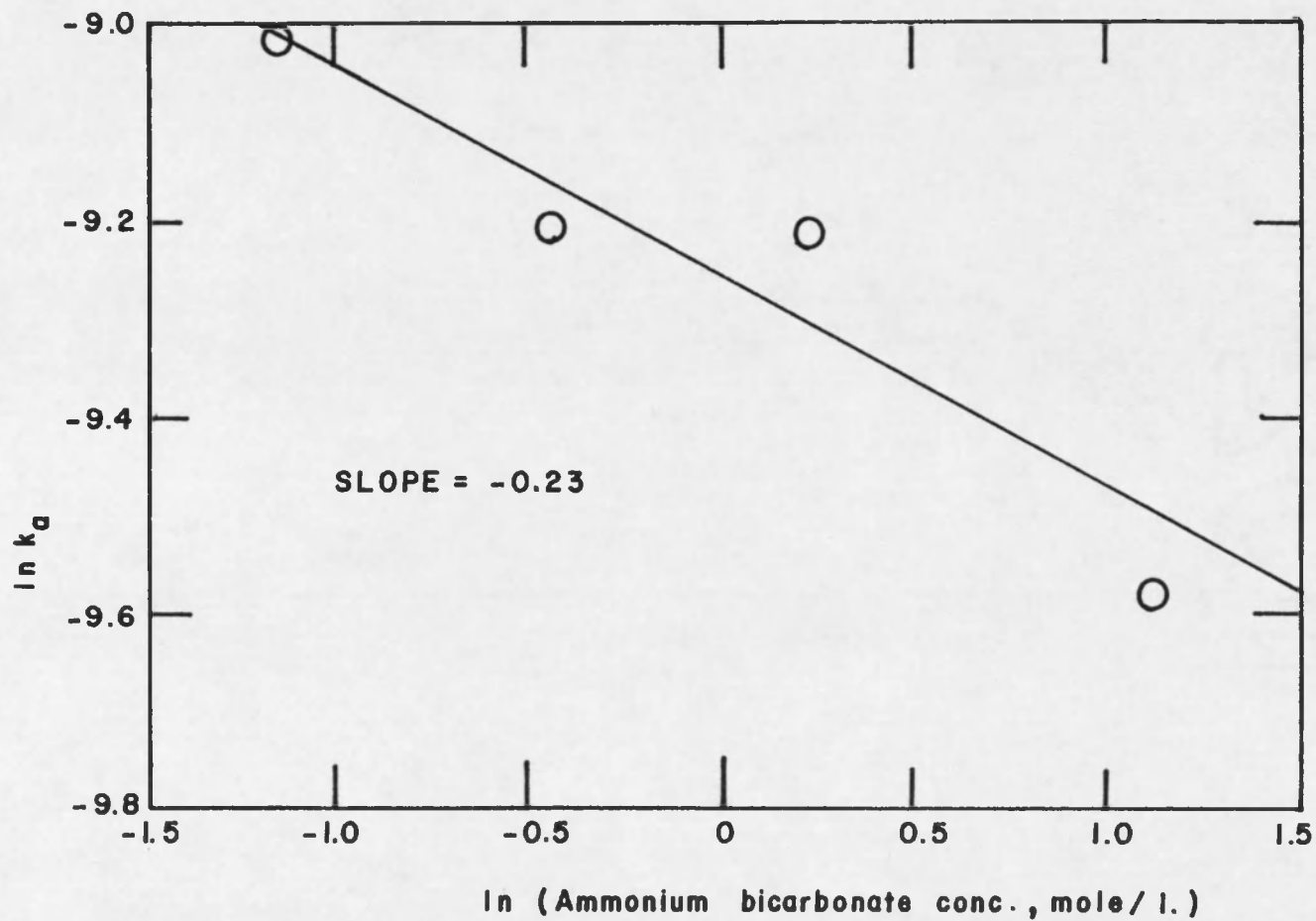


Figure 11. Effect of Ammonium Bicarbonate Concentration on the Apparent Rate Constant.

the extractable species. Since it has not been possible to determine the distribution of species because of the lack of data, it is not possible to isolate the effect.

#### Effect of pH

The pH of the solution affects the resin-loading characteristics, as shown in Figure 12. As the pH increases, the rate of cobalt adsorption decreases.

The data in Figure 12 are plotted as equation (2) in Figure 13. As in the cases of cobalt concentration and ammonium bicarbonate concentration, the equation is valid. The apparent rate constants are listed in Table VI.

Table VI. Effect of pH on Apparent Rate Constant.

pH	$k_a$ , minute <sup>-1</sup>
8.0	$6.95 \times 10^{-5}$
8.5	$6.91 \times 10^{-5}$
9.0	$4.77 \times 10^{-5}$
10.0	$3.31 \times 10^{-5}$

The order of reaction with respect to pH can be determined using the following relation:

$$\text{apparent rate constant} = k_a = k_s |H^+|^n \quad (9)$$

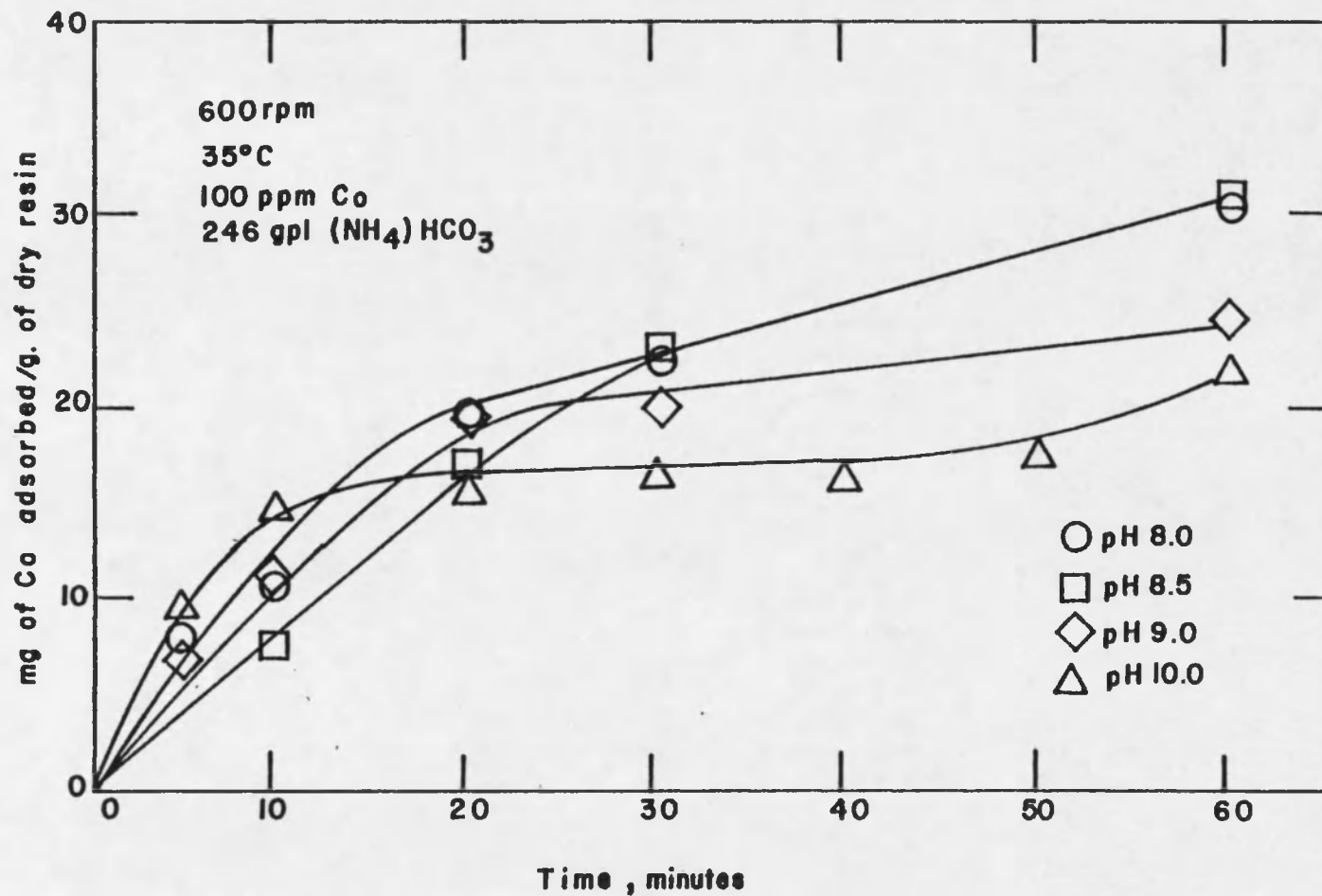


Figure 12. Effect of pH on the Adsorption of Cobalt by Resin as a Function of Time.

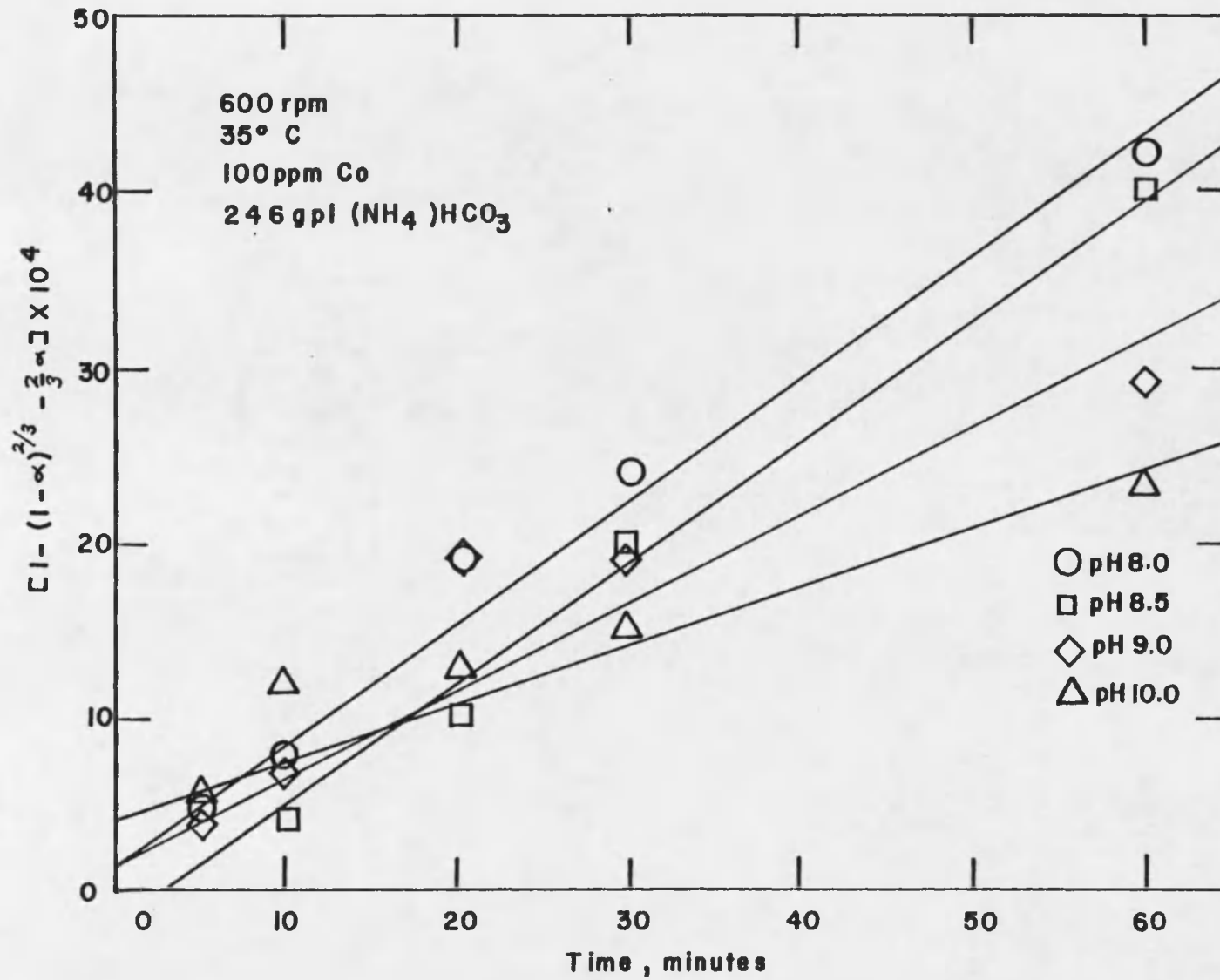


Figure 13. Plot of  $1 - (1 - \alpha)^{2/3} - \frac{2}{3}\alpha$  versus Time at Varying pH.

which can be written as

$$\log \text{ apparent rate constant} = k_a = \log k_s - n(\text{pH}) \quad (10)$$

A plot of  $\log k_a$  versus pH will yield a slope of 'n', the reaction order with respect to pH. A plot of this type is shown in Figure 14. The slope, 'n', is -0.18. Therefore, the reaction order with respect to pH is -0.18.

#### Spectrophotometric Results and Discussion

Spectrophotometrically, the species in the system cannot be determined quantitatively. As can be seen in Figures 15 and 16, the peaks of cobalt species in solution at 475, 510, and 523 nm cannot be resolved.

In Figure 15, it appears that there is no strong absorption of light by pH 7.5 solution over the range of wavelengths 430-630 nm. This indicates a low degree of complexation at this pH, which results from the small concentration of  $\text{NH}_3$  available for complexation with the cobalt ion. At higher pH's, it appears that there is absorption of light by all three species, as can be seen in Figure 15. The pH 8.5 solution was freshly prepared, while the other solutions had been prepared approximately two months earlier.

Figure 16 is a comparison of the absorbance by pH 8.5 initial and depleted solutions (solution that had been contacted with resin). It appears that all three cobalt species have been removed from the solution to some extent. This observation differs with the studies

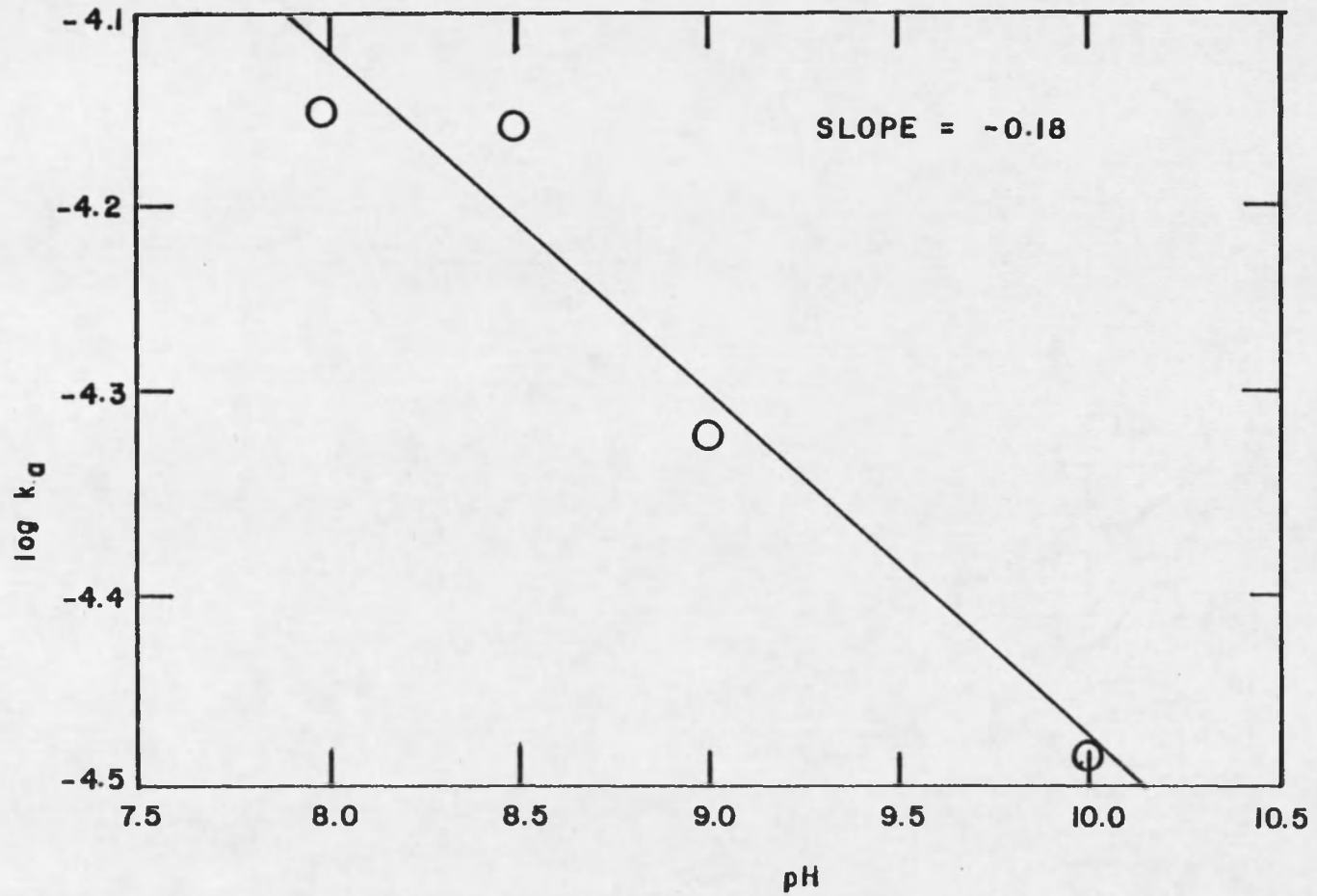


Figure 14. Effect of pH on the Apparent Rate Constant.

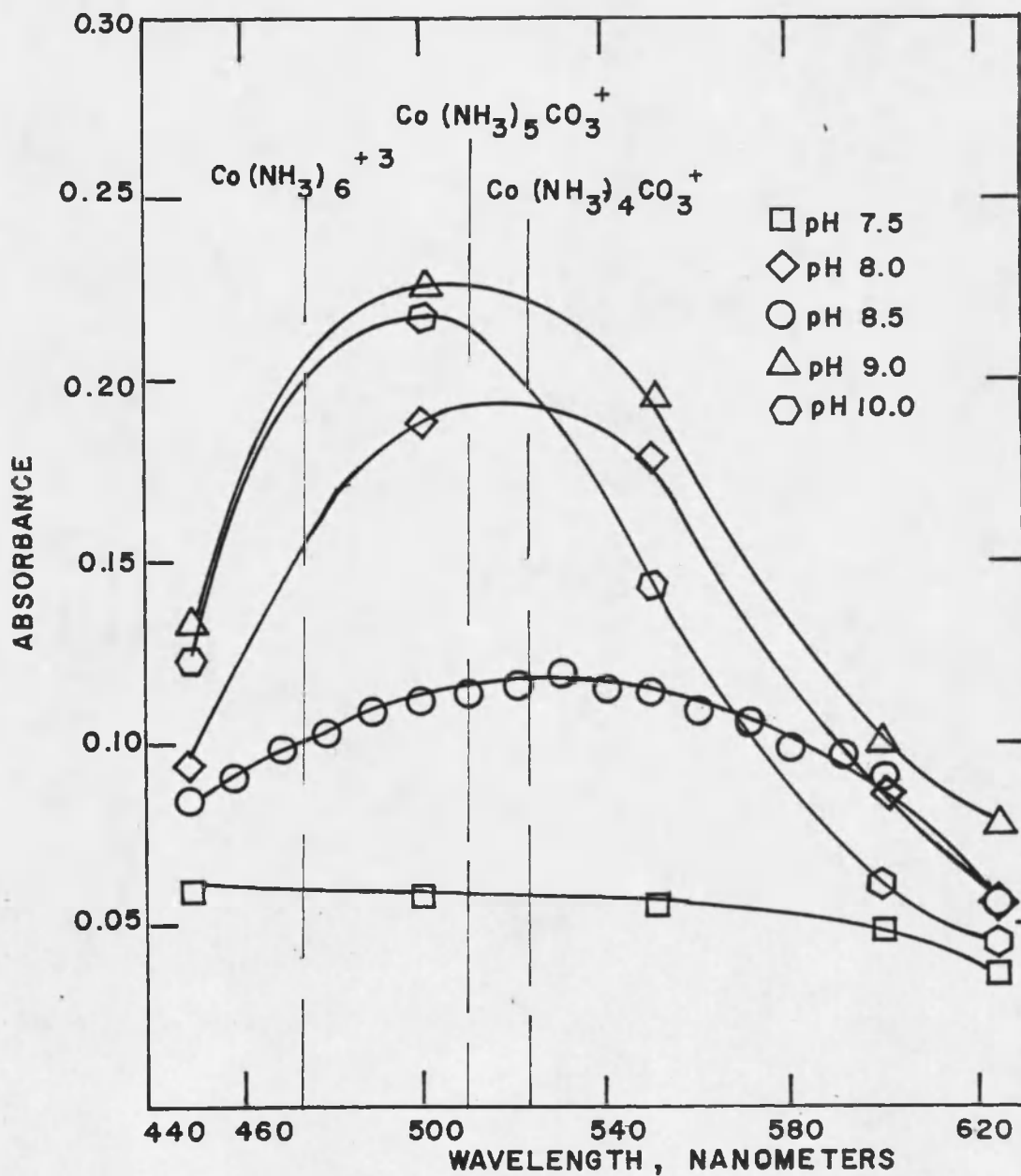


Figure 15. Absorption Spectra of 100 ppm Cobalt Solutions at Varying pH.



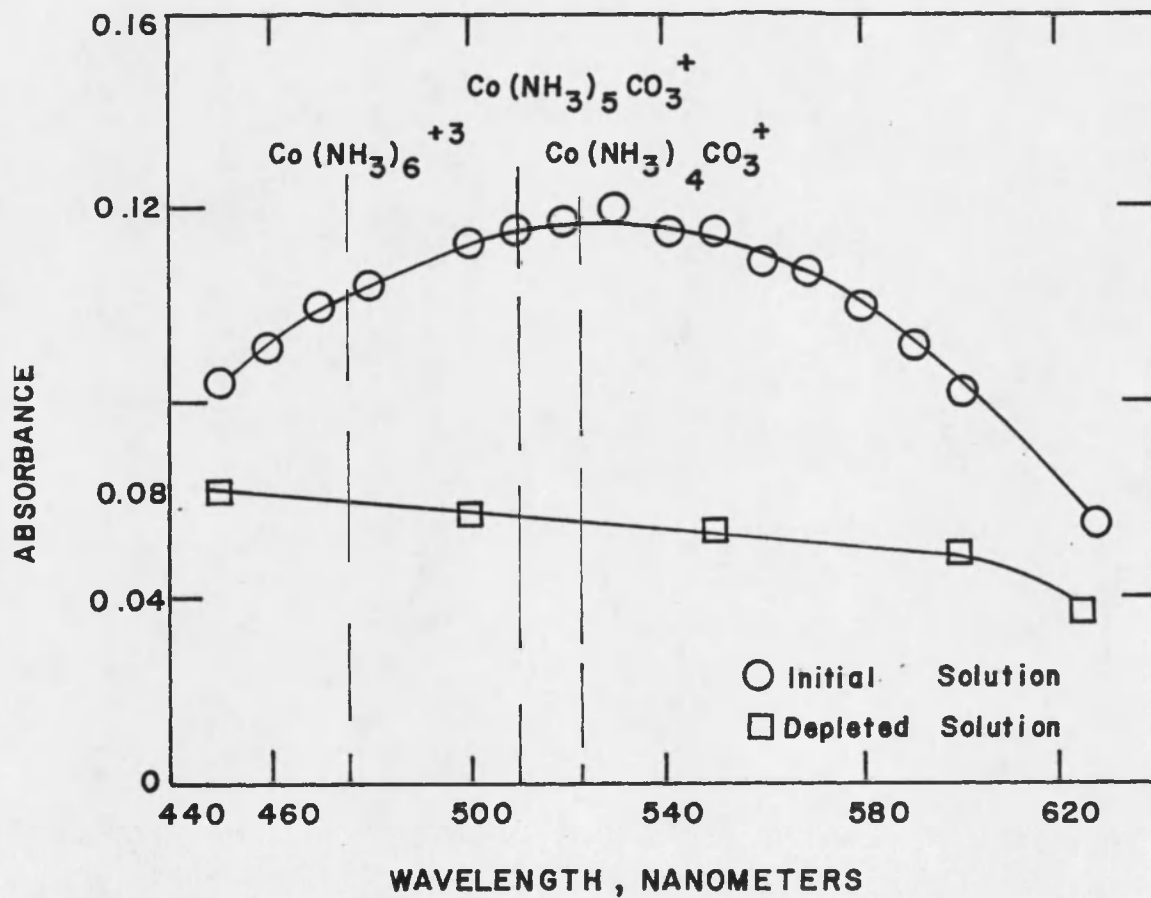


Figure 16. Absorption Spectra of Initial and Depleted Solutions.

showing only the hexammine complex to be strongly adsorbed (Hurst, 1976; Hatch, 1977).

#### Summary of Kinetic Experiments

The data can be linearized with the equation:

$$1-(1-\alpha)^{2/3}-2/3\alpha = k_a t \quad (11)$$

indicating that diffusion is involved in the rate-controlling step. The activation energy was calculated to be 1.4 kcal/mole for temperatures below 55°C and 4.4 kcal/mole above 55°C. Both of the activation energy values indicate solution diffusion as the rate-controlling step. The validity of equation (11) in combination with the low activation energies obtained indicates that solution diffusion of an ionic species in an aqueous continuous medium is involved. It also indicates an increasing diffusion path length as the reaction proceeds. In other words, the resin bead must be considered as an extremely porous structure, capable of supporting an aqueous continuous medium. The pore size must also be large. It is the diffusion of either the cobalt ammine complex or the ammonium ion which is involved in the rate-controlling step.

A possible explanation for the change in activation energy as a function of temperature is that there may be a change in resin structure as a function of temperature.

The order of reaction with respect to cobalt is 1. With respect to ammonium bicarbonate concentration, the order is -0.23. The apparent reaction order with respect to pH is -0.18.

## CONCLUSIONS

- 1) In order to extract cobalt from ammoniacal carbonate solution, it is necessary to use the ammonium ( $\text{NH}_4^+$ ) form of the XE-318 resin. The hydrogen ( $\text{H}^+$ ) form cannot be used.
- 2) The capacity of the XE-318 resin for cobalt in the system used in this investigation increases as the resin is cycled through the adsorption-desorption cycles.
- 3) At the conditions used in the study, the univalent species of cobalt ammine were present. This was indicated by the red-violet color of the cobalt solution. It was not possible to determine the concentration of species of cobalt present mathematically due to lack of stability constant data. It was also not possible to determine the amount of species present spectrophotometrically because of the overlap of the peaks of the species of interest.
- 4) The adsorption of cobalt from ammonium carbonate solution involves a reaction that is first-order with respect to cobalt concentration, and has a slight dependence on the ammonium bicarbonate and hydrogen ion concentrations. The apparent activation energy was determined to be 1.4 kcal/mole at temperatures below  $55^\circ\text{C}$  and 4.4 kcal/mole above  $55^\circ\text{C}$ . These low activation energies combined with other data presented indicate that the rate-controlling step in the mechanistic sequence is the

diffusion of an ionic species, either cobalt ammine complex or ammonium ion, through an aqueous continuous medium in the resin pore.

## SUGGESTIONS FOR FURTHER WORK

The greatest source of error in the investigation was due to the varying moisture content of the resin. The assumption that swelling of dry ammonium form resin to wet ammonium form resin was significant needs to be tested. Measurements of the mean diameters of a great number of wet and dry resin beads need to be compared to determine whether the diameter of the bead increases significantly when placed in solution.

If the increase proves to be insignificant, then the dry resin XE-318 can be used in kinetic experiments.

If the increase is found to be significant, then a possible solution to the problem of varying moisture content of wet resin could be to precisely weigh portions of the dry resin and place them in vessels such as test tubes. Solution containing the desired counterion could then be added to each tube of resin. The test tubes would be stoppered and stored until needed.

Error resulting from volume measurements of wet resin would probably be comparable to, if not greater than, the error resulting from weighing the wet resin.

Counting resin beads would not be practical unless the experiments were performed on a very small scale.

APPENDIX A

DATA

Data for Figure 2

<u>Stirring Speed (rpm)</u>	<u>Time (Minutes)</u>	<u>Mg Co Adsorbed/g Dry Resin</u>	
200	0	0	
	5	6.86	
	10	12.00	
	20	13.72	
	30	24.01	
	60	26.58	
400	0	0	
	5	12.76	
	20	20.41	
	30	24.87	
	60	28.91	
	600	0	0
10		7.80	
20		17.33	
30		23.40	
60		31.19	
800		0	0
	5	9.32	
	10	16.10	
	20	20.33	
	30	25.42	
	60	33.04	

Data for Figure 3

<u>Temperature (°C)</u>	<u>Time (Minutes)</u>	<u>Mg Co Adsorbed/g Dry Resin</u>
35	0	0
	10	7.80
	20	17.33
	30	23.40
	60	31.19
	45	0
5		12.87
10		17.17
20		24.03
30		27.47
40		30.04
50		31.76
60		33.47
55	0	0
	5	10.26
	10	15.40
	20	24.81
	30	28.23
	40	29.95
	50	30.80
	60	34.22
65	0	0
	5	14.01
	10	21.89
	20	26.27
	30	30.64
	40	35.02
	50	35.89
71	0	0
	5	11.96
	10	18.34
	20	25.52
	30	31.10
	40	35.09
	50	37.48
	60	38.28

Data for Figure 6

<u>Cobalt Conc. (ppm)</u>	<u>Time (Minutes)</u>	<u>Mg Co Adsorbed/g Dry Resin</u>
50	0	0
	5	6.00
	10	9.44
	20	12.01
	30	14.58
	60	26.59
100	0	0
	10	7.80
	20	17.33
	30	23.40
	60	31.19
	200	0
5		15.73
10		23.60
20		34.97
30		41.96
60		50.70
400	0	0
	5	23.43
	10	30.75
	20	42.46
	30	49.78
	60	68.82



Data for Figure 9

<u>(NH<sub>4</sub>)HCO<sub>3</sub> Conc. (gpl)</u>	<u>Time (Minutes)</u>	<u>Mg Co Adsorbed/g Dry Resin</u>
246	0	0
	10	7.80
	20	17.33
	30	23.40
	60	31.19
	100	0
100	5	13.00
	10	20.79
	20	25.12
	30	29.46
	40	31.19
	50	35.52
	60	38.99
	50	0
50	5	17.33
	10	21.66
	20	26.86
	30	29.46
	40	33.79
	50	37.26
	60	38.99
	25	0
25	5	14.92
	10	21.94
	20	28.95
	30	34.22
	50	40.36
	60	43.87

Data for Figure 12

<u>pH</u>	<u>Time (Minutes)</u>	<u>Mg Co Adsorbed/g Dry Resin</u>
8.0	0	0
	5	8.31
	10	11.33
	20	19.64
	30	22.66
	60	30.96
	8.5	0
10		7.80
20		17.33
30		23.40
60		31.19
9.0		0
	5	7.00
	10	11.01
	20	20.01
	30	20.01
	60	25.01
	10.0	0
5		9.78
10		15.10
20		15.98
30		16.87
40		16.87
50		17.76
60		22.20

## APPENDIX B

### SAMPLE CALCULATIONS

#### H<sup>+</sup> Capacity of XE-318

The cation-exchange capacity is calculated according to the following equation from Fisher and Kunin (1955).

$$\frac{200 \times N_{\text{NaOH}} - 4(\text{ml acid} \times N_{\text{acid}})}{\text{sample weight} \times (\% \text{ solids}/100)} = \frac{\text{meq. cation-exchange capacity}}{\text{gram of dry resin}}$$

One of the 50 ml aliquots of supernatant solution required 34.80 ml of acid to reach the phenolphthalein endpoint. The amount of resin added to the NaOH solution was 1.183 g and the percent solids was found as 44.0%. Substituting these values into the above equation gives:

$$\frac{200 \times .08029 - 4(34.80 \times .09782)}{1.183 \times .440} = 4.69 \frac{\text{meq. cation exchanged}}{\text{g of dry H}^+ \text{ form resin}}$$

The cation-exchange capacity was calculated by finding the mean value for three titrations. This value was found to be 5.10 meq H<sup>+</sup> exchanged/g of dry H<sup>+</sup> form resin.

#### NH<sub>4</sub><sup>+</sup> Capacity of XE-318

The ratio of dry weight |H<sup>+</sup>| form resin to dry |NH<sub>4</sub><sup>+</sup>| form resin was 1.07 g/g. This gives a |NH<sub>4</sub><sup>+</sup>| form resin capacity of

$$5.10 \frac{\text{meq cation exchanged}}{\text{g dry } |\text{H}^+| \text{ form resin}} \times 1.07 \frac{\text{g dry } |\text{H}^+| \text{ form resin}}{\text{g dry } |\text{NH}_4^+| \text{ form resin}} =$$

$$5.46 \frac{\text{meq cation exchanged}}{\text{g dry } |\text{NH}_4^+| \text{ form resin}}$$

#### Sample Concentrations

Absorbances of samples and standard were measured using Atomic Absorption Spectrophotometry. Because of the downward drift of the instrument, the first reading was used as a rough determination of cobalt concentration. For example, it was found that in the 65°C experiment, the 20-60 minute samples were in the range of 10-15 ppm cobalt by the first rough measurement. The absorbances of the 10 and 15 ppm cobalt standard solutions were redetermined and the five sample absorbances were found in quick succession.

The standard cobalt solution absorbances were plotted versus concentration of the standard solutions and a straight line was drawn between the two points. Concentration of diluted samples could then be determined from the plot.

In the above example, the 10 and 15 ppm cobalt standards had absorbances of 0.226 and 0.312, respectively. The dilute sample concentrations read from the graph were:

<u>Time (Minutes)</u>	<u>Absorbance</u>	<u>Diluted Sample Conc. (ppm)</u>
20	0.294	14.4
30	0.275	13.0
40	0.266	12.2
50	0.255	11.6
60	0.230	10.5

This diluted sample is multiplied by the dilution factor, which is simply the volume of diluted solution divided by the volume of concentrated solution pipetted.

For example, in the 65°C test, 5 ml of undiluted sample was diluted to 25 ml, therefore the dilution factor is 5 and the undiluted samples had concentrations of:

<u>Time (Minutes)</u>	<u>Diluted Sample Conc. x Dilution Factor</u>	<u>Undiluted Sample, Conc. (ppm)</u>
20	14.4 x 5	72
30	13.0 x 5	65
40	12.2 x 5	61
50	11.6 x 5	58
60	10.5 x 5	53

Mg Cobalt Adsorbed/g  
Dry  $|\text{NH}_4^+|$  Form Resin

Mg cobalt adsorbed/g dry  $|\text{NH}_4^+|$  form resin =

$$\frac{2 \text{ liter x (initial conc. Co, mg/l(ppm)) - conc. Co at time t, mg/l(ppm)}}{.373 \% \text{ solids wet } |\text{NH}_4^+| \text{ form resin x g wet } |\text{NH}_4^+| \text{ form resin}} =$$

$$\frac{\text{mg cobalt adsorbed}}{\text{g dry } |\text{NH}_4^+| \text{ form resin}}$$

Percent Reacted

The percent reacted,  $\alpha$ , was calculated using the  $\text{NH}_4^+$  capacity and assuming that one cobalt species was bound to one iminodiacetic group.

$$5.46 \frac{\text{meq Co}}{\text{g dry } |\text{NH}_4^+| \text{ form resin}} \times 58.9 \frac{\text{mg Co}}{\text{meq Co}} = 321.59 \frac{\text{mg Co}}{\text{g dry } |\text{NH}_4^+| \text{ form resin}}$$

Using the mg cobalt adsorbed/g dry resin value calculated above, the  $\alpha$  for 65°C at 30 minutes is:

$$\alpha = \frac{30.64 \text{ mg Co adsorbed/g dry } |\text{NH}_4^+| \text{ form resin}}{321.59 \text{ mg Co/g dry } |\text{NH}_4^+| \text{ form resin}} = 0.0953$$

#### Percent Error

The standard deviation is defined as:

$$s = \left( \frac{1}{n-1} \sum_{i=1}^n (X_i - \bar{X})^2 \right)^{1/2}$$

s is the standard deviation, n is the number of results,  $\bar{X}$  is the mean value of the set of results, and  $X_i$  is the  $i^{\text{th}}$  result of the set. This standard deviation was divided by the mean value of the set to determine the relative error.

APPENDIX C

X-RAY DATA FOR  
IDENTIFICATION OF PRECIPITATE

Relative Intensity $I/I_1 \times 100$ (measured)	d spacing $\text{\AA}$ (calculated)	Relative Intensity $I/I_1 \times 100$ (theoretical)	d spacing $\text{\AA}$ (theoretical)
43	3.52	40	3.55
100	2.75	100	2.74
21	1.95	20	1.95
25	1.68	25	1.70

This identifies the precipitate as the pink-purple Cobalt (II) carbonate.

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