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The Dissolution Characteristics of Chrysocolla in NH_3 $-(NH_4)_2CO_3$ Solutions

by

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Abstract

Chrysocolla samples were leached in ammonia-ammonium carbonate solutions of 0.25 to 6.00 M concentration total ammonia at a temperature range of 25°C to 55°C. The leaching curves for the fraction extracted, α, as a function of time follow the expression: $\alpha = \log_e (\beta\delta t + 1)/\beta$which is the integrated form of the exponential rate law, assuming a linear dependence of the free energy of activation with the fraction extracted. The initial kinetics follow the Langmuir-Hinshelwood relation: rate = $a(NH_4^+)/(1 + b(NH_4^+))$ which is indicative of and adsorption process preceding chemical reaction.

Introduction

Chrysocolla is a hydrous copper silicate found in the upper oxidation zones of copper deposits. It is commonly associated with malachite, azurite, and limonite. In the 1920s, Perkins and Talpin (1) patented the ammoniacal leaching of ores containing chrysocolla and other oxide minerals that have been pre-reduced at 400°C. In 1973, Frantz and McNulty (2) reported the leaching of copper silicate ores from Twin Buttes, Arizona in ammonia-ammonium carbonate solutions after a pre-reduction step at 430 °C in 2 percent carbon monoxide atmosphere. Copper recoveries of 70-85 percent were reported.

In the same year, Habashi and Dugdale (3) published a comprehensive study on the leaching of chrysocolla in ammonia-ammonium carbonate solutions. The effects of variables such as pre-reduction, solution concentration, and ammonia-ammonium ratio were presented although no reaction mechanisms were proposed. Wilmhurst (4) also reported the successful recovery of copper from dolomitic copper ores in Burra, South Australia using ammoniacal solutions in 1973.

In 1975, Bryden (5) studied the kinetics of copper extraction from malachite and chrysocolla using ammonium sulphate solutions. His results showed that the initial kinetics followed a Langmuir-type expression.

Raghavan (6) published his doctorate thesis based on the leaching of chrysocolla in ammonia-ammonium carbonate solutions in 1976. He concluded that the reaction kinetics followed mixed controlled (chemical reaction + diffusion) behavior leaning more towards chemical reaction control.

This study aims to define the leaching kinetics of chrysocolla in ammonia-ammonium carbonate solutions.

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Sample Characterization

The chrysocolla samples were obtained from Globe, Arizona. The copper content of each size fraction is shown in Table I. In order to determine the purity of the sample, the ore was allowed to undergo dehydroxilation at 650°C. The ore was then leached with aqua regia to dissolve the copper. The copper analysis was done using an IL Atomic Absorption Spectrophotometer. The residue, assumed to be pure silica, was washed, dried, then weighed. Based on the copper analysis and the weight of the residue, the ore was calculated to be 91 percent pure chrysocolla, with the remaining percent being free silica.

Table 1. Copper Content of each Size Fraction.

SIZE (mesh)	PERCENT COPPER
−100 + 150	33.75
−150 + 200	33.25
−120 + 270	33.01
−270 + 400	35.14
−400	36.16

Weak X-ray patterns were observed from the chrysocolla samples, suggesting that the samples are amorphous (8). The Infrared patterns, however, showed the characteristic 1000 cm^{-1} Si-O peak, as well as the 500 cm^{-1}, 1620 cm^{-1}, and 3400 cm^{-1} O-H peaks. The Cu-O peak was observed at 670 cm^{-1} (7). The surface area was measured at 230 m^2/gm using a 4-point BET analysis with nitrogen as adsorbate.

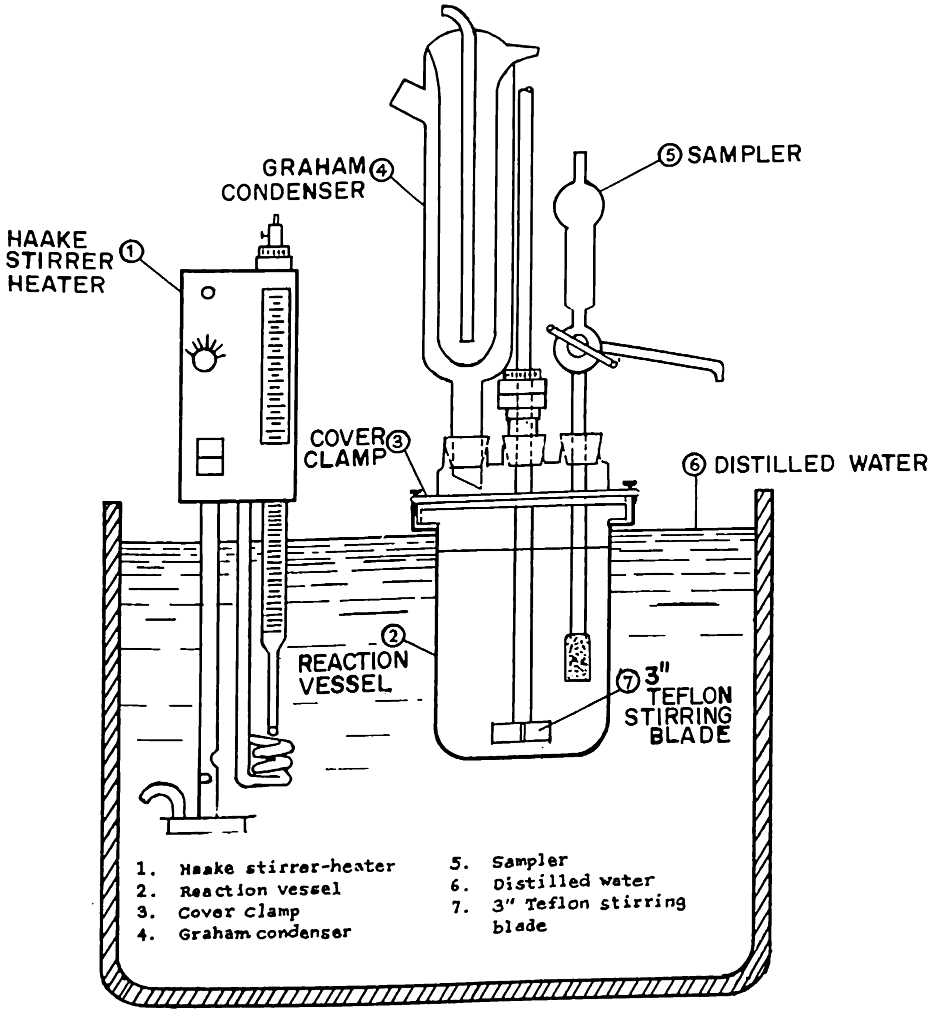

Figure 1. Experimental Set-up.

Experimental Set-Up

The leaching experiments were conducted in a one-liter reaction vessel as shown in Figure 1 The reactor cover had four 20/40 glass joint openings through which a stirrer, thermometer, condenser, and a sampler were fitted. The fritted glass end of the sampler dipping into the solution permitted the withdrawal of solid-free liquid samples. The closed-system stirrer was fitted with a three-inch flat blade impeller. The reaction vessel was immersed in a water bath equipped with a circulator/heater capable of maintaining the bath at a selected temperature within ± 0.1 °C.

Experimental Procedure

The variables studied were total ammonia concentration and temperature. The ammonia concentrations ranged from 0.25 M to 6.00 M while the temperature ranged from 25°C to 55°C. Preliminary experiments showed that the initial rate becomes independent of stirring speed after 600 RPM (see Figure 2). All experiments were therefore conducted at a stirring speed of 800 RPM. Only the results of the −100 + 150 mesh fraction are presented in this study. The ammonia-ammonium ratio of the ammoniacal solutions was kept at unity. At this ratio, the extraction rates are the fastest (3,6).

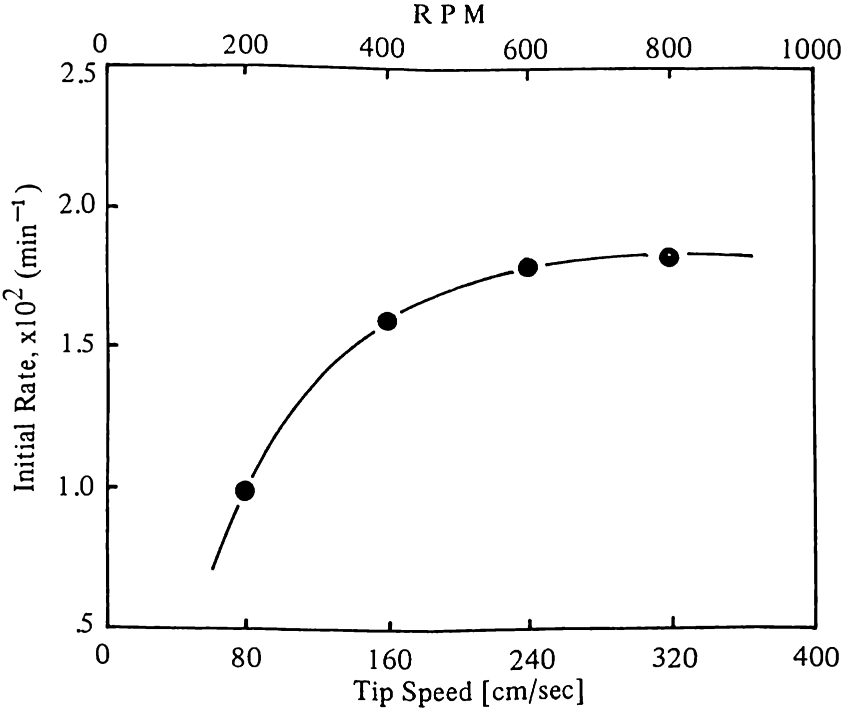

Figure 2. Effect of Stirring speed on initial rate.

When the ammoniacal solution of desired strength has equilibrated at the reaction temperature, a carefully weighed amount of sample is poured into the reactor. Liquid samples are withdrawn at pre-determined times and the copper content analyzed using an atomic adsorption spectrophotometer.

Results and Discussions

Typical leaching curves are given in Figure 3 which shows the extraction going fast initially but then levelling off after some time. In order to fit the extraction curves, the following model is being proposed.

Consider that the reaction

$$CuSiO_3\cdot nH_2O + NH_4^+ = Cu(NH_3)^{++} + OH^- + SiO_2 + nH_2O \qquad (1)$$

occurs in two steps, absorption and chemical reaction. The adsorption step is given by the reaction

$$\begin{array}{ccc} \vdots S + NH_4^+ & \overset{K}{\rightleftharpoons} & \vdots S\text{-}NH_4^+ \\ (1-\theta) & & \theta \end{array} \qquad (2)$$

where

$\vdots S$ = surface active sites

K = adsorption equilibrium constant

o = fraction of reactive sites covered.

At equilibrium,

$$\theta = \frac{K(NH_4^+)}{1 + K(NH_4^+)} \qquad (3)$$

according to the Langmuir single site relation. (NH_4^+) is the molar concentration of ammonium ion in solution.

The reaction step is

$$\begin{array}{ccc} \vdots S\text{-}NH_4^+ & \overset{k'}{=} & \text{products} \\ \theta & & \end{array} \qquad (4)$$

where

k' = intrinsic kinetic rate constant.

The first order rate expression for the chemical reaction step is given by the relation

$$\text{rate} = d\,\alpha / dt = Ak_0\theta k' \qquad (5)$$

where

α = fraction extracted
A = surface area
θ = fraction of active sites covered
k_ρ = number of active sites per unit area
k' = intrinsic kinetic rate constant.

Equation (5) integrates into

$$\alpha = Ak_0\theta k' t \qquad (6)$$

which means that the fraction extracted should plot linearly with time if equation (5) holds. Figure 4, however, shows that this is only true at very low values of α.

Structural changes in the sample and/or variations in the adsorption phenomena can cause the free energy of activation to change with the amount of copper already extracted. Similar behavior has been observed by Wadsworth (9), Cho (10), and Scheffel (11). The simplest case would be to consider a linear variation of the free energy of activation with fraction extracted. This increase in the free energy of activation as the extraction proceed means that it becomes more difficult to remove the remaining copper atoms from the chrysocolla structure.

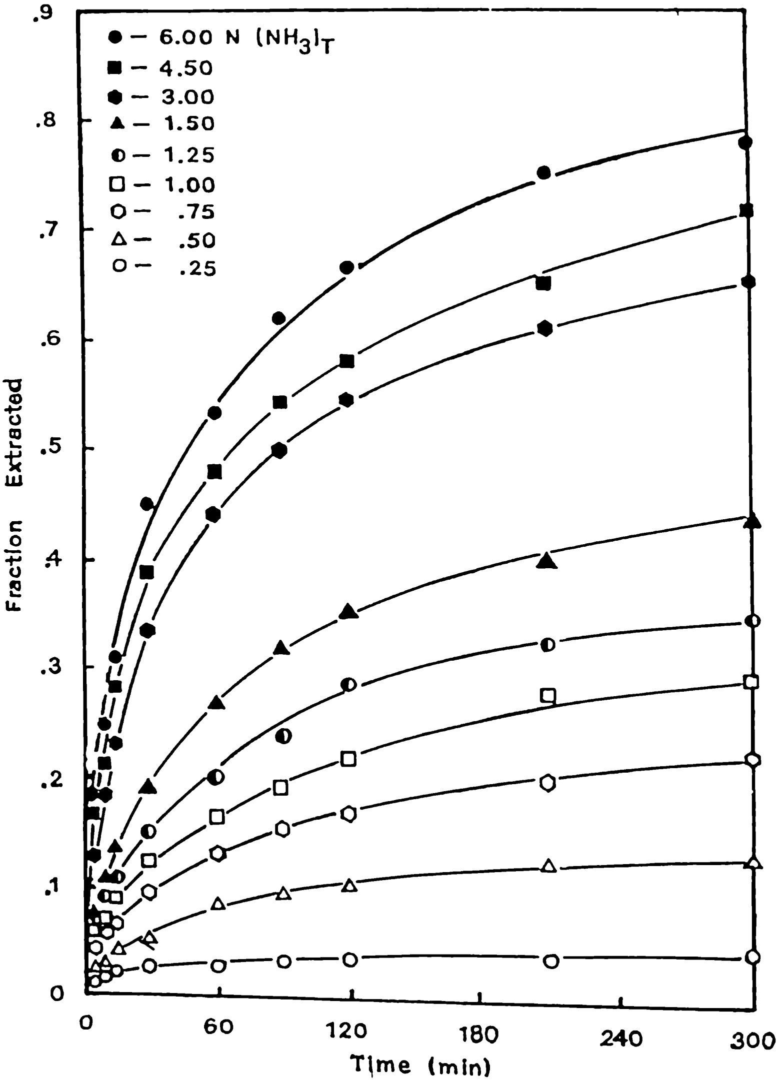

Figure 3. Typical copper extraction curves.

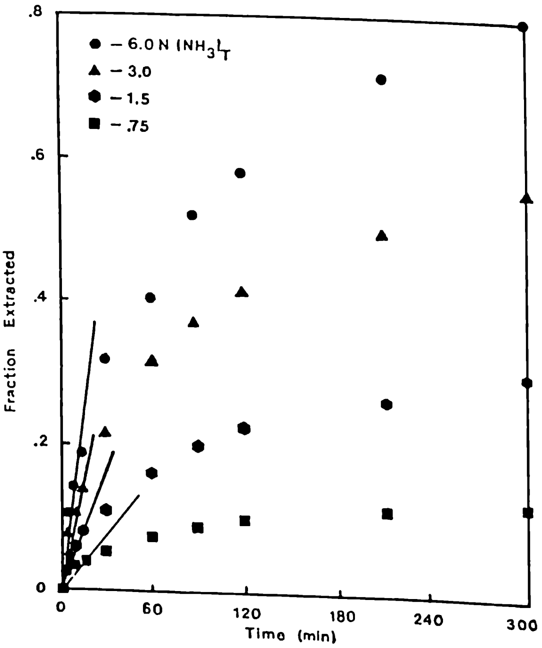

Figure 4. Plot of equation 6 for T = 25 °C.

This change in the free energy of activation may be an enthalpy effect, in which case the equation is written as

$$\Delta F^{\ddagger} + f(\alpha) = \Delta H_o^{\ddagger} + b\alpha - T\Delta S_o^{\ddagger} \tag{7}$$

or

$$\Delta F^{\ddagger} + f(\alpha) = \Delta F_o^{\ddagger} + b\alpha \tag{7'}$$

or it may be an entropy effect, in which case the equation becomes

$$\Delta F^{\ddagger} + f(\alpha) = \Delta H_o^{\ddagger} - T(\Delta S_o^{\ddagger} - b\alpha) \tag{8}$$

or

$$\Delta F^{\ddagger} + f(\alpha) = F_o^{\ddagger} + bT\alpha \tag{8'}$$

The intrinsic kinetic rate constant, k', may be written as

$$k' = (kT/h)\exp(-\Delta F^{\ddagger}/RT) \tag{9}$$

where

k = Boltzmann's constant
h = Planck's constant
T = absolute temperature
R = gas constant

$\Delta F^{\ddagger}$ = free energy of activation.

Equation (5) may thus be rewritten as

$$d\alpha/dt = Ak_0\,\theta\,(kT/h)\exp(-\Delta F^{\ddagger}/RT) \tag{10}$$

Substituting the expression for $\Delta F^{\ddagger}$ which accounts for a linear increase in the free energy of activation, the rate equation becomes

$$d\alpha/dt = Ak_0\theta(kT/h)\exp(-\Delta F_0^{\ddagger}/RT - b\alpha/RT) \tag{11}$$

where $\hat{b} = b$ if the change in the free energy is due to an enthalpy effect and $\hat{b} = bT$ if the change is an entropy effect.

Defining δ and β as

$$\delta = Ak_0\theta(kT/h)\exp(-\Delta F_0^{\ddagger}/RT) \tag{12}$$

and

$$\beta = \hat{b}/RT \tag{13}$$

equation (11) may be rewritten as

$$d\alpha/dt = \delta\exp(-\beta\alpha) \tag{14}$$

which is analogous to the exponential rate law equation for activated adsorption. Equation (14) integrates into

$$\alpha = (1/\beta)\log_e(\beta\delta t + 1) \tag{15}$$

For a given set of α and t values, n equations may be written from equation (15). Unfortunately, simple least squares regression can not be used to solve for the values of β and δ. But when $\beta\delta t >> 1$, the equation simplifies into

$$\alpha = (1/\beta)\log_e(\beta\delta t) \tag{16}$$

and the n set of equations may now be solved by least squares regression for β and δ-. Figure 5 shows the linear dependence of the fraction extracted on $\log_e t$ as suggested by equation (16). Note, however, that equation (16) is no longer valid as t approaches zero. Furthermore, it would be advantageous to know the values of β and δ that fits the whole range of experimental data because this would permit the mathematical evaluation of the experimental extraction rates using equation (14) and not rely on graphical means for estimating rates.

A Simplex Minimization Search algorithm was therefore used in order to find the best values of β and δ that will fit the experimental data points. The initial estimates for β and δ were obtained from a first order least squares estimation on the data points using equation (16). A PDP 11/34 computer was used on all these calculations. Figure 6 is a plot of the predicted α based on the values of β and δ obtained against the experimental α which shows very good agreement between the model and the experimental results.

The initial enthalpy of activation may also be obtained from δ .

Recall from equation (12) that

$$\delta = Ak_0\theta(kT/h)\exp(-\Delta F_0^{\ddagger}/RT) \tag{17}$$

where $\Delta F_0^{\ddagger}$ may be written as

$$\Delta F_0^{\ddagger} = \Delta H_0^{\ddagger} - T\Delta S_0^{\ddagger} \tag{18}$$

$\Delta H_0^{\ddagger}$ is the enthalpy of activation and $\Delta S_0^{\ddagger}$ is the entropy of activation.

At $\alpha = 0$, equation (14) becomes

$$d\alpha/dt = \delta \tag{19}$$

and

$$\delta = Ak_0\theta(kT/h)\exp(-\Delta H_0^{\ddagger}/RT + \Delta S_0^{\ddagger}/R) \tag{20}$$

which upon rearrangement yields

$$\delta/T = Ak_0\theta(k/h)\exp(--\Delta H_0^{\ddagger}/RT + \Delta S_0^{\ddagger}/R) \tag{21}$$

Taking logarithms of both sides of the equation results into

$$\log_e(\delta/T) = \log_e(Ak_0\theta k/h) - (\Delta H_0^{\ddagger}/RT) + (\Delta S_0^{\ddagger}/R) \tag{22}$$

Typical values of δ are given in Table 2 and a plot of $\log_e(\delta/T)$ against $(1/T)$ is shown in Figure 7, with a value of $\Delta H_0^{\ddagger} = 13.885$ kcal/mole being calculated.

Photomicrographs of partially leached particles show the growth of cracks as the extraction progresses. This could be indicative of an initial rapid attack of the lexivient on microcracks present on the surface of the chrysocolla. EDAX measurements on polished cross section of partially leached particles showed a non-uniform distribution of copper, indicating the absence of a moving reaction front that Polhman (7) observed in his work.

Typical values of β are given in Table 3 which shows no dependence of β on temperature. This suggests that the increase in the free energy of activation is an entropy effect. The free energy of activation can increase by as much as 7 kcal/mole at 60°C when $(NH_3)_T = 1.00M$.

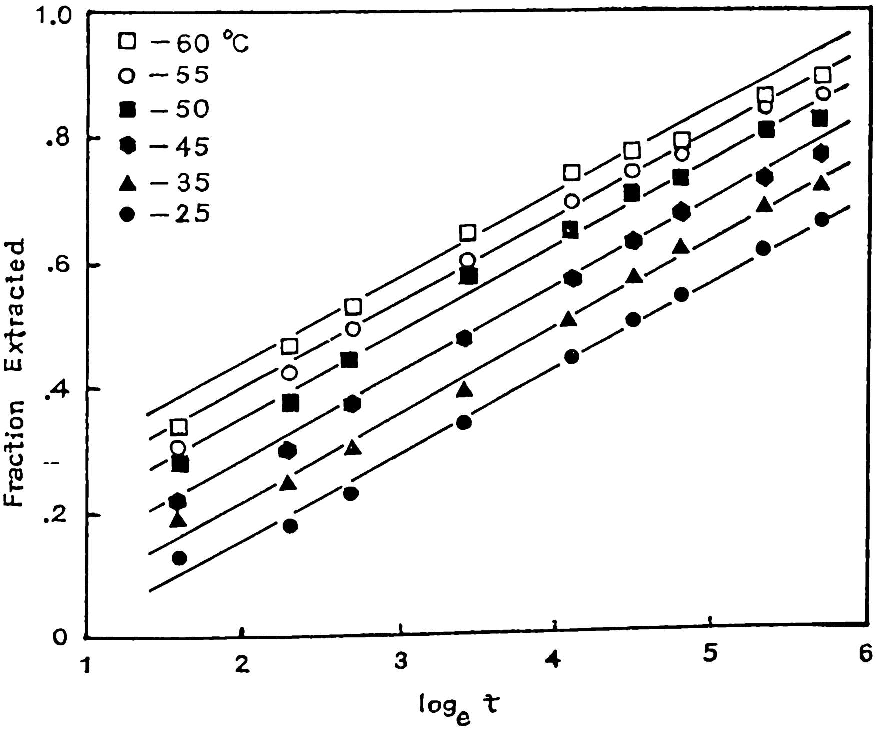

Figure 5. Linear dependence of fraction extracted on $\log_e t$.

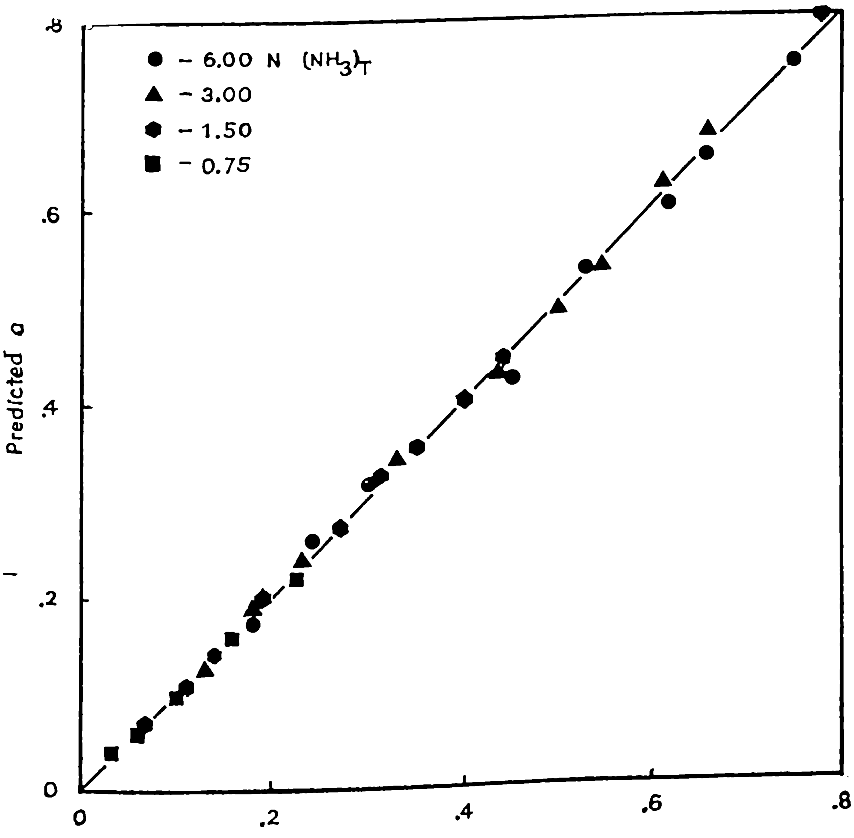

Figure 6. Comparison of model against experimental data.

Table 2. Typical Values of δ.

T (°C)	σ(min^{-1})
25	0.0337
35	0.0704
45	0.1078
55	0.3040
60	0.4523

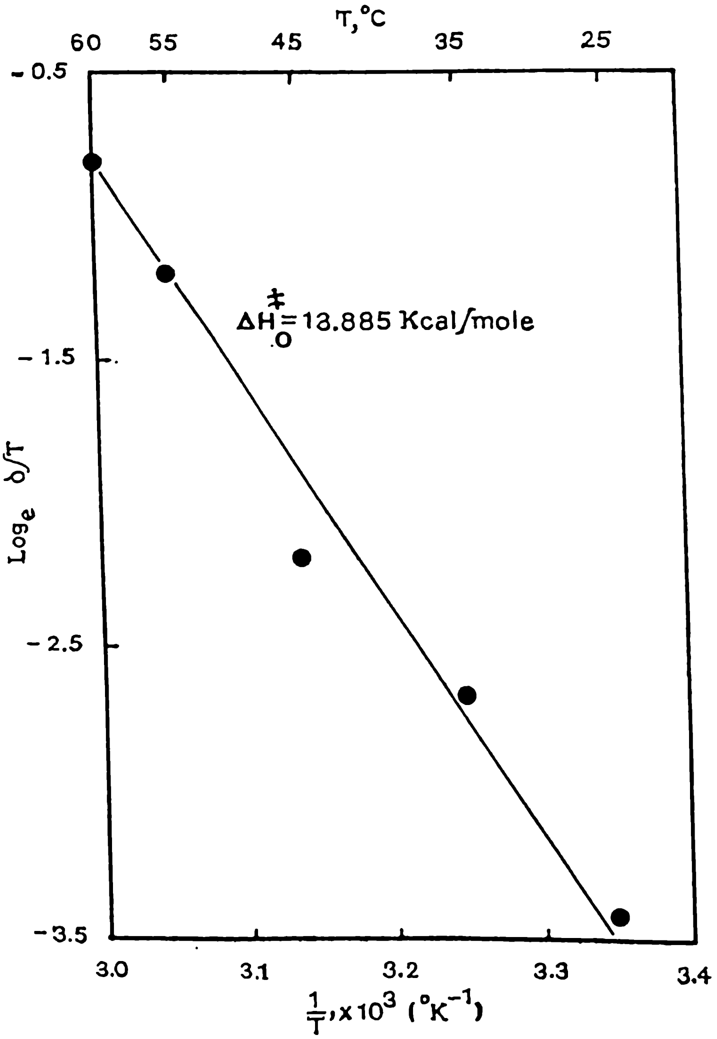

Figure 7. Arthenius-type plot of δ/T versus $1/T$.

Table 3. Typical Values of β as a function of Temperature.

T (°C)	β
25	6.3487
35	6.8932
45	6.8282
55	7.5034
60	7.8109

In order to calculate the enthalpy of adsorption and entropy of adsorption, recall equation (5), wherein,

$$r = k_o \theta k' \tag{23}$$

where r is tne initial rate per unit area and from equation (3),

$$\theta = \frac{K(NH_4^+)}{1 + K(NH_4^+)} \tag{24}$$

Combining equations (23) and (24) yields

$$r = \frac{k_o k' K(NH_4^+)}{1 + K(NH_4^+)} \tag{25}$$

Defining a and b as

$$a = k_o k' K \tag{26}$$

and

$$b = K \tag{27}$$

equation (25) may be written as

$$r = \frac{a(NH_4^+)}{1 + b(NH_4^+)} \tag{28}$$

which is known as the Langmuir-Hinshelwood rate expression. Rearrangement of equation (28) yields

$$(1/r) = (1/a)(1/NH_4^+)) + (b/a) \tag{29}$$

From equation (29), the reciprocal of the initial rate should plot linearly with the reciprocal of the ammonium concentration. This is shown in Figure 13 where the slope of the line is (1/a) and the intercept is (b/a). Table 4 shows the values of a and b obtained from Figure 8. The values of the ammonium ion concentrations used were obtained using complex equilibria calculations for the ammonia-ammonium carbonate system as outlined by Van Krevelen(12) and Kust (13).

By definition,

$$b = K = \exp(-\Delta H_{ads}/RT)\exp(\Delta S_{ads}/R) \tag{30}$$

Taking logarithms of both sides of the equation yields

$$\log_e b = (-\Delta H_{ads}/RT) + (\Delta S_{ads}/R) \tag{31}$$

where ΔH_{ads} and ΔS ads may be obtained from a plot of $\log_e b$ against (1/T), as shown in Figure 9. The values of the enthalpy and entropy of adsorption obtained were −6.741 kcal/mole and − 24.235 e.u., respectively. The value of the entropy of adsorption calculated suggests that the ammonium ion is strongly adsorbed on an active site.

The enthalpy of activation, $\Delta H_o^{\ddagger}$ may also be obtained from a and b as follows:

$$(a/b) = (k_o\ k'K)/K = k_o\ (kT/h)\exp(-\Delta H_o^{\ddagger}/RT)\exp(\Delta S_o^{\ddagger}/R) \tag{32}$$

or

$$(a/bT) = k_o\,(k/h)\exp(-\Delta H_o^{\ddagger}/RT)\exp(\Delta S_o^{\ddagger}/R) \tag{33}$$

Taking logarithms,

$$\log_e(a/bT) = \log_e(k_o k/h) - (\Delta H_o^{\ddagger}/RT) + (\Delta S_o^{\ddagger}/R) \tag{34}$$

and $\Delta H^{\ddagger}$ may be obtained from a plot of $\log_e(a/bT)$ against $(1/T)$ as shown in Figure 10.The enthalpy of activation is calculated at 12.801 Kcal per mole which agrees well with the 13.885 Kcal/mole obtained using the exponential rate law expression.

Table 4. Typical Values of a and b.

T °C	a mg m^{-2} min^{-1} mole^{-1} li	b mole^{-1} li
25	0.0598	0.2112
35	0.0704	0.1749
45	0.0983	0.0902
55	0.1675	0.0850

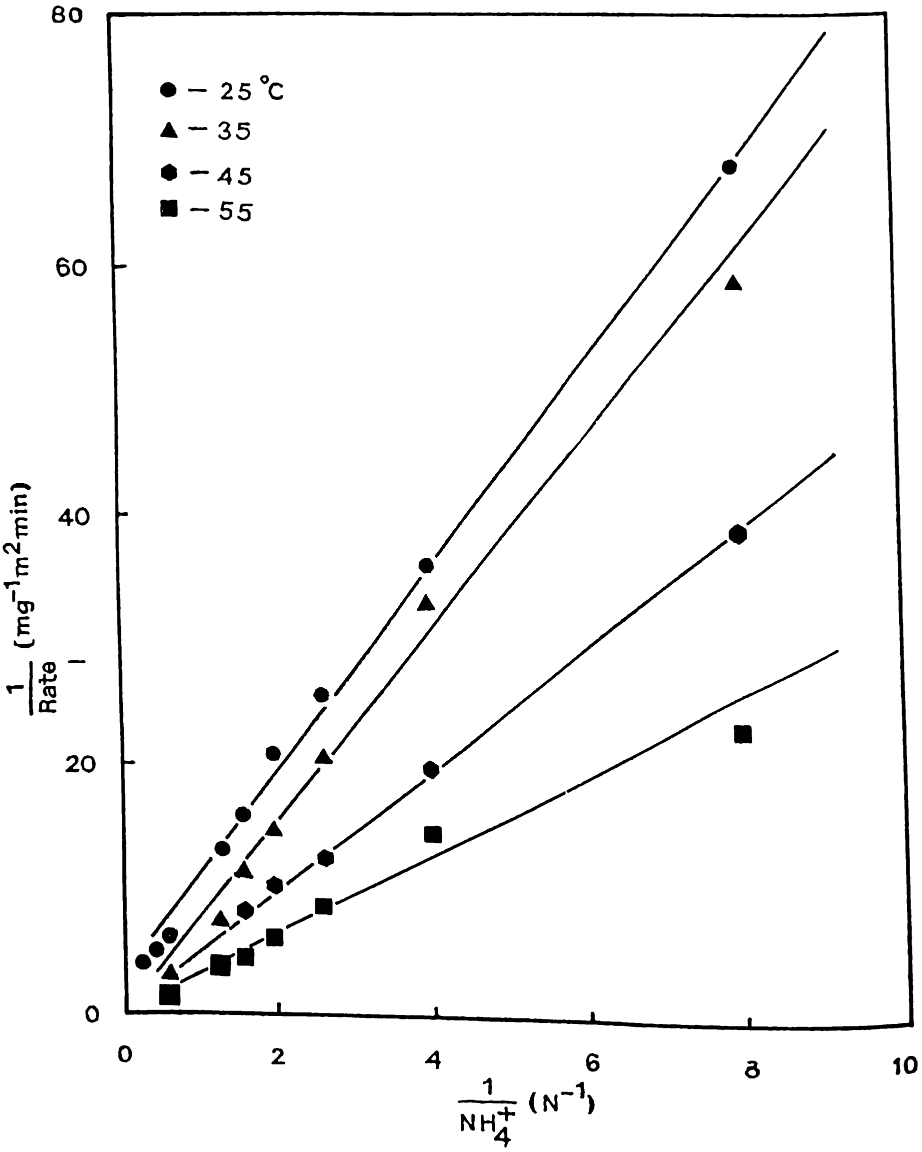

Figure 8. Plot of reciprocal rate versus reciprocal ammonium concentration.

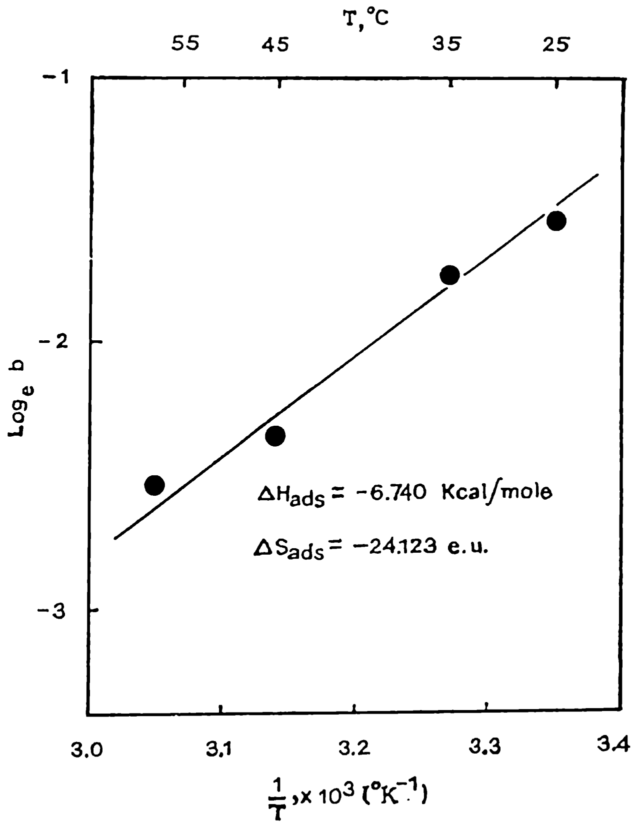

Figure 9. Arthenius-type plot of b versus 1/T.

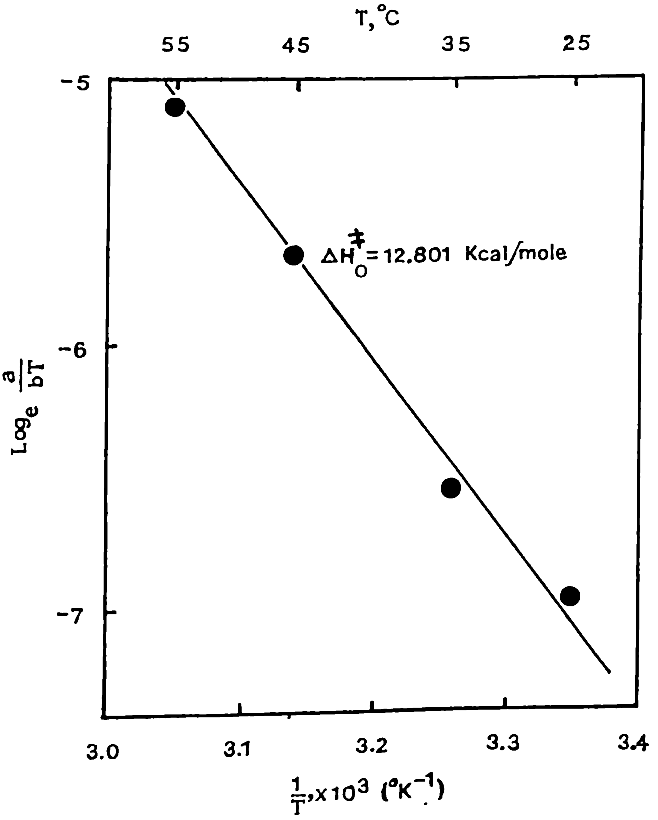

Figure 10. Arthenius-type plot of (1/bT) versus 1/T.

Summary

1. The extraction curves follow the integrated form of the exponential rate law expression from which the value of the enthalpy of activation is calculated at 13.885 kcal per mole.

2. The free energy of activation changes linearly with the fraction extracted according to the relation:

$$\Delta F^{\ddagger} = \Delta F_0^{\ddagger} + bT\alpha$$

where the free energy of activation can change by as much as 7.189 kcal per mole for (NH_3) = 1.00 N at 60°C.

3. The initial rate follows the Langmuir-Hinshelwood expression in which single site adsorption is followed by chemical reaction. The enthalpy of adsorption is calculated at −6.741 kcal per mole and the entropy of adsorption at −24.235 e.u.

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