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Kinetics of NO Depletion by Reaction with Molten Sodium Carbonate

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Abstract

This study presents results of an investigation of nitric oxide (NO) depletion by reaction with molten sodium carbonate (Na_2CO_3). Experiments have been conducted in which NO in helium is bubbled through molten sodium carbonate. Preliminary results show a 10 to 75 % reduction of NO over the temperature range of 860 to 973 °C. The rate of depletion of NO is shown to follow a postulated pseudo first order rate law. Values of the rate constant range from 5.0×10^4 to $7.0 \times 10^6 \text{ sec}^{-1}$ with an activation energy of 372 kJ/mol (89.0 kcal/mol).

In order to predict NO_x emissions from a kraft recovery furnace, one must understand both the *in situ* rate of formation and rate of depletion of the NO_x species. In a previous paper, it has been suggested that the reaction of NO with sodium species could provide a depletion mechanism which is unique to kraft recovery furnaces[1].

Many reactive sodium species are present in a kraft recovery furnace. These species exist in different phases depending on location (as temperature varies with location in the furnace). In the lower furnace, molten smelt is a source for volatilization of sodium species which form fume [2]. At this point, the potential for reactions between NO_x species and the molten smelt exists. Above the smelt bed and traveling up the furnace, vapor phase alkali species (e.g. Na and Na_2O) could potentially react with NO_x before precipitating as fume. In the upper furnace, it is understood that fume particles react with SO_2 forming sodium sulfate (Na_2SO_4) as the final product[3]. It is suggested that these fume particles could also react with NO_x .

The kinetics of sulfation reactions has been the subject of many studies [3,4,5,6]. One review article concludes that the reaction of SO_2 with sodium carbonate below the melting point (850 °C) does not occur fast enough to account for the amount of SO_2 depletion that occurs in a recovery furnace[6]. The authors suggest that the reaction is most likely occurring with molten sodium carbonate.

The smelt in a recovery furnace is composed primarily of sodium carbonate (~ 78 wt %), sodium sulfide

(~18 wt %), and sodium sulfate (~4 wt %). The fraction of each species depends on the composition of the black liquor burned in the furnace and the operation of the furnace. The objective of this study is to investigate the rate of depletion of NO in contact with these smelt species. Initial work is presented here for sodium carbonate reactions. Results of NO depletion with mixtures of the different species will be presented in the future.

THEORY OF GAS ABSORPTION WITH CHEMICAL REACTION

This study investigates the heterogeneous reaction of a gas (NO) with a nonvolatile liquid (molten Na_2CO_3). In general terms the reaction can be written as: $\text{A}(\text{g}) + \text{B}(\text{l}) \rightarrow \text{products}$, or specifically, $\text{NO}(\text{g}) + \text{Na}_2\text{CO}_3(\text{l}) \rightarrow \text{products}$. The rate of depletion of NO has been assumed to follow the kinetic expression,

$$-r_{\text{NO}} = k C_{\text{NO}} C_{\text{Na}_2\text{CO}_3} \quad (1)$$

Assuming that the concentration of sodium carbonate, $C_{\text{Na}_2\text{CO}_3}$, is high and remains essentially constant, equation (1) can be written as a pseudo first order rate expression:

$$-r_{\text{NO}} = k_1 C_{\text{NO}} \quad (2)$$

Levenspiel derives a rate expression for pseudo first order reactions for gas-liquid systems which are considered to react totally within the liquid film[7]. The rate expression accounts for diffusion in both the gas and liquid films and can be written as:

$$-r_{\text{NO}} = \frac{1}{V_L} \frac{\delta N_{\text{NO}}}{\delta t} = \frac{a^p \text{NO}}{k_g + \frac{H_{\text{NO}}}{\sqrt{D_{\text{NO/Na}} k_1}}} \quad (3)$$

By substituting $\frac{P_{NO}}{H_{NO}} = \frac{N_{NO}}{V_1}$, separating variables and integrating over time, equation (3) can be reduced to:

$$-\ln\left(\frac{P_{NO_f}}{P_{NO_i}}\right) = \frac{a}{H_{NO}k_g + \sqrt{D_{NO/Na}k_1}} \quad (4)$$

Rearranging terms, equation (4) can be written as:

$$k_1 = \frac{1}{(at)^2} (D_{NO/Na})^{-1} \quad (\text{sec}^{-1}) \quad (5)$$

$$\left(-\ln\left(\frac{P_{NO_f}}{P_{NO_i}}\right) - \frac{1}{H_{NO}k_g}\right)^2$$

For this expression, time is calculated as the expanded volume of the liquid divided by the volumetric flow rate of the gas, $t = m/(V\rho(1-\epsilon))$. Other constants in equation (5) are calculated from correlations found in the literature. In short, a and t are functions of the gas flow rate. H_{NO} , k_g and $D_{NO/Na}$ are dependent on temperature. Thus, the pseudo first order rate constant can be found as a function of concentration, flow rate, and temperature. A complete list of equations and notation is included at the end of the paper.

It is possible to classify the reaction as fast or slow depending on the value of the Hatta number[8]. The Hatta number, $\sqrt{M_A}$, is a measure of the ratio of A reacting in the film to that going unreacted in the bulk B phase.

$$\sqrt{M_A} = \sqrt{\frac{2}{m+1} D_A k [A^*]^{m-1} [B_0]^n / k_L} \quad (6)$$

In general, fast reactions are those where $\sqrt{M_A} \geq 1$; the reaction of A occurs while it is diffusing in the film. For $\sqrt{M_A} \ll 1$, no A reacts in the film and the reaction is considered slow. It will be shown that for the experimental conditions considered in this study, the reaction of NO in molten Na_2CO_3 is fast and it is appropriate to use equation (3) described above.

EXPERIMENTAL APPARATUS

Experiments have been conducted in which NO is bubbled through molten sodium carbonate. The experimental apparatus is depicted in Figures 1 and 2.

Helium and a mixed gas of nitric oxide in helium are fed from pressurized gas cylinders. Flow is measured by Hastings-TeledyneTM digital mass flowmeters and is controlled manually by needle valves. The gas is fed to the reaction chamber which is described in detail below. Exit gas from the system is analyzed by a chemiluminescent NO_x analyzer.

Molten salt is contained in a 4 cm x 10 cm alumina crucible which is cemented to a stainless steel flange. A graphite gasket is placed between the flange and the lid which is held in place by eight bolts to form a gas-tight seal. The reaction vessel is heated by a tube furnace. Gases are bubbled through the salt using a 0.4 cm ID alumina tube. A type-K thermocouple, protected by an alumina well, is used to measure the temperature of the molten salt. The mass flowmeters, thermocouple, and NO_x analyzer are connected to

a personal computer for data acquisition. Data is acquired at a sampling rate of 0.5 Hz.

EXPERIMENTAL CONDITIONS

Gas flow rate, NO concentration, temperature, and mass of salt in the system have been selected as independent variables in this study. The mass of salt is either 17.5, 25.0, or 35.0 g, gas flow rate is targeted between 0.65 to 1.00 L/min (as air at STP), and temperature is varied between 860 to 975 °C. The NO inlet concentration is either 1857 ppm or 8400 ppm. The experimental conditions for each run are listed in Table 1.

Each experimental condition is run for six to nine minutes. Data for the flow rate, temperature and NO exit concentration are averaged over the last two minutes of this time interval. This allows the system to reach a pseudo steady state before averaging data. A sample of the time averaged data is shown below in Table 2 for experiment 1A.

Inspection of Table 2 indicates that the variables remain essentially constant over the time averaging period. Temperature fluctuations are on the order of 1 °C while the NO exit concentrations vary by approximately 10 to 30 ppm (1 to 2.5 %).

RESULTS

Figure 3 is a plot of the conversion of NO as a function of temperature. The percent conversion is calculated as: $X = 100\left(1 - \frac{P_{NO_f}}{P_{NO_i}}\right)$. Calculation of the conversion does not account for residence time or temperature but is presented as a means of normalizing the raw data.

Inspection of Figure 3 reveals conversion increasing as a function of temperature. The conversion varies from approximately 10 to 75 % over the temperature range 860 to 973 °C.

Equations (5) and (6) are used to calculate the rate constant, k_1 , and the Hatta number for each of the data points represented in Figure 3. The results of these calculations for experiment 2A are listed in Table 3. Inspection of the data reveals the Hatta number is much greater than one over the range of experimental conditions which supports the validity of the pseudo first order rate expression.

The interfacial area, a , is on the order of 0.25 cm^{-1} . This value is considerably lower than measured values for interfacial area in melts contained in agitated and sparged contactors. Ghorpade, *et al.* report values in the range of 2.3 to 4.5 cm^{-1} for a mechanically agitated contactor and 1.7 to 2.7 cm^{-1} for a bubble column [9]. However, it is not surprising that the calculated value is low as the reaction

vessel has only one sparging tube with a large diameter which creates large gas bubbles.

To determine the activation energy, the experimental data is plotted in Figure 4 as $\ln(k_1)$ vs $1/T$. The solid line in Figure 4 is based on linear regression of the data. Based on this analysis, the slope of the line, $-E_a/R$, is $-44,780$ K and the intercept, $\ln(k_0)$, is 51.78 . Thus, the pseudo first order rate constant for the depletion of NO may be written as:

$$k = k_0 e^{-E_a/RT} = 3.09 \times 10^{22} e^{-44,780/T} \quad (7)$$

Substituting these values into equation (1) gives the rate expression:

$$-r_{NO} = 3.09 \times 10^{22} e^{-44,780/T} C_{NO} \quad (8)$$

Table 4 lists activation energies for several different heterogeneous reaction systems. The activation energy for the depletion of NO by molten sodium carbonate is considerably higher than the other systems.

Data from experiment 1 has not been included in the regression analysis of the data. The data from experiment 1 gives a much lower activation energy than the rest of the experiments. It is suggested that the low mass of salt (17.5 g) provides mixing conditions that are significantly different than for the larger quantities of salt. The smaller mass is subject to splashing and may not behave according to the bubble flow that is assumed in the calculations of k_1 .

DISCUSSION

The experimental data has been fitted to a pseudo first order rate expression. Errors in the analysis may arise from some of the assumptions that have been made. One possible source of error is the calculation of the gas hold up. The correlation used is derived for bubble columns which typically have more than one sparger. Thus the calculated values for gas hold up and the surface to volume ratio may not be representative of the experimental conditions. Another source of error is the assumption that the rate is first order with respect to each of the reactants. This assumption will be addressed experimentally in future work.

Preliminary results show that NO does indeed react in the presence of molten sodium carbonate. A conversion of 10 to 75 % is observed over the temperature range of 860 to 973 °C. The reaction follows a postulated pseudo first order rate law for the depletion of NO.

Sodium carbonate has been chosen as the starting material for the first phase of this study. Future work will include adding sodium sulfide (Na_2S) to more closely simulate recovery furnace smelt. Work is also planned to identify the gas phase reaction products by on line gas chromatographic analysis.

ACKNOWLEDGMENTS

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EQUATIONS

$$a = \frac{6\epsilon}{d_b} \quad [10, \text{p.144}]$$

$$d_b = \left[\left(\frac{\sigma D_t}{\Delta \rho g} \right)^2 + 9.5 \left(\frac{V_g^2 D_t}{g} \right)^{0.867} \right]^{\frac{1}{6}} \quad [11, \text{p.228}]$$

$$D_{NO/He} = \frac{10^{-4} (1.084 - 0.249 \sqrt{1/M_{NO} + 1/M_{He}}) r^{1.5} \sqrt{1/M_{NO} + 1/M_{He}}}{P_t (r_{NO/He})^2 f \left(\frac{kT}{\epsilon_{AB}} \right)} \quad [10, \text{p.31}]$$

$$D_{NO/Na} = \frac{(117.3 \times 10^{-18}) (\rho M_{Na})^{0.5T}}{\mu^{0.6}} \quad [10, \text{p.35}]$$

$$\epsilon = 0.5 \left(\frac{U_{br}}{\sqrt{g R_c}} \right)^{0.4} \left(\frac{U_{gr}}{U_{br}} \right)^{0.8} \quad [11, \text{p.1199}]$$

$$H_{NO} = 1/K_H$$

$$k_g = \frac{D_{NO/He} P_t}{RT \rho_{He,m}} \quad [10, \text{p.49}]$$

$$k_L = 0.42 \left(\frac{D_{NO/Na}}{d_b} \right) \left(\frac{d_b^3 \rho^2}{\mu^2} \right)^{\frac{1}{3}} \left(\frac{\mu}{\rho D_{NO/Na}} \right)^{0.5} \quad [12, \text{p.230}]$$

$$K_H = \frac{\exp \left(\frac{-411Nt^2\gamma}{8.314T} \right)}{82.06T} \quad [13]$$

Physical properties of molten sodium carbonate can be calculated as a function of temperature according to the following:

$$\rho = 2.4797 - 0.4487 * 10^{-3} T \text{ (g/cm}^3\text{)} \quad [14]$$

$$\mu = 3.832 * 10^{-5} \exp(13215/T) \text{ (cp)} \quad [14]$$

$$\gamma = (254.8 - 0.0502 t)/1000 \text{ (N/m)}, t = \text{temperature (}^\circ\text{C)} \quad [15]$$

NOTATION

a = interfacial area per unit volume (cm^2/cm^3)

A = solute gas

$[A^*]$ = interfacial concentration of A (mol/cm^3)

B = non-volatile reactant

$[B_J]$ = concentration of B in the bulk (mol/cm^3)

$C_{\text{Na}_2\text{CO}_3}$ = concentration of molten Na_2CO_3 (mol/cm^3)

C_{NO} = concentration of NO in liquid film (mol/cm^3)

d_b = bubble diameter (cm)

$D_{NO/He}$ = diffusivity of NO in Helium (m^2/s)

$D_{NO/Na}$ = diffusivity of NO in Na_2CO_3 (m^2/s)

D_t = outside diameter of purge tube (m)

E_a = activation energy (J/mol)

$f(kT/\epsilon_{AB})$ = collision function (= 0.31) (Treybal¹⁰, p. 32)

g = gravitational constant = (9.81 m/s)

H_{NO} = phase distribution coefficient ($\text{atm cm}^3/\text{mol}$)

k = second order rate constant ($\text{mol}/\text{cm}^3 \text{ s}$)

k_0 = pre-exponential factor (1/s)

k_1 = pseudo first order rate constant (1/s)

K_H = Henry's Law constant ($\text{mol}/\text{cm}^3 \text{ atm}$)

m = order of reaction with respect to A

m_{Na} = mass of Na_2CO_3 (g)
 $\sqrt{M_A}$ = Hatta number
 M_i = molecular weight of species, i
 n = order of reaction with respect to B
 N = Avogadro's number = (6.022×10^{23})
 N_{NO} = moles of NO (mol)
 $[NO]_f$ = exit concentration of NO (ppm)
 $[NO]_i$ = inlet concentration of NO (ppm)
 $P_{He,m}$ = log mean pressure of helium (atm)
 P_{NO} = partial pressure of NO (atm)
 P_t = total pressure (atm)
 r = molecular radius (m)
 $-r_{NO}$ = rate of depletion of NO based on volume of liquid
 (mol/cm³ s)
 $r_{NO/He}$ = molecular separation at collision (nm)
 R = universal gas constant = $(8.314 \text{ m}^3 \text{ J/mol K})$
 R_c = radius of column = (0.02 m)
 t = time (s)
 T = absolute temperature (K)
 U_{tr} = bubble rise velocity (m/s)
 U_{gs} = superficial gas velocity (m/s)
 V = flow rate of gas (cm³/s)
 V_g = flow rate of gas (m³/s)
 V_1 = volume of molten salt (cm³)
 X = percent conversion of NO
 z = film thickness = (10^{-4} m) (estimated)
 α = correlation factor (assumed 30)
 ϵ = gas hold up
 ϕ = association factor for solvent = 1
 V_{NO} = solute molal volume at boiling point (= 0.0236
 m³/kmol)

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Table 1: Experimental Conditions for the Depletion of NO in Molten Sodium Carbonate.

Exp.	1A	1B	2A	2B	2C	3A	3B	3C	4A	4B	5A	5B	6A	6B
Mass (g)	17.5	17.5	25.0	25.0	25.0	25.0	25.0	25.0	35.0	35.0	35.0	35.0	35.0	35.0
V (L/min)	0.75	1.00	0.65	0.80	0.95	0.65	0.80	0.95	0.75	1.00	0.75	1.00	0.75	1.00
[NO] _i (ppm)	1,857	1,857	8,400	8,400	8,400	8,400	8,400	8,400	1,857	1,857	1,857	1,857	1,857	1,857

Table 2: Time averaged data for Experiment 1A.

V avg (L/min)	V std (L/min)	T avg (°C)	T std (°C)	[NO] _f avg (ppm)	[NO] _f std (ppm)	[NO] _f % rsd
0.76	0	871	0.9	1,559	22.9	1.5
0.76	0	889	0.9	1,346	15.4	1.1
0.76	0.01	908	1	1,260	14.9	1.2
0.75	0	919	0.9	1,179	13	1.1
0.76	0	931	1.2	1,113	8.4	0.8
0.76	0	943	0.9	967	13.1	1.4
0.77	0	955	0.9	889	20.9	2.3
0.76	0	959	1.1	861	11.7	1.4

(V = volumetric flow rate, T = temperature, [NO]_f = NO exit concentration)
(avg = average, std = standard deviation, rsd = relative standard deviation)

Table 3: Calculated values for the Hatta number and the pseudo first order rate constant, k_1 , for Experiment 2A.

Temp. (K)	a (1/cm)	t (s)	$-\ln(P_f/P_i)$	H_{NO} (cm ³ atm/mol)	k_g (mol/cm ² atm s)	$D_{NO/Na}$ (cm ² /s)	k_L (cm/s)	Hatta #	k_1 (1/s)
1138	0.251	0.247	0.161	1.37E+06	7.28E-03	3.05E-05	4.37E-02	59	2.21E+05
1162	0.253	0.245	0.299	1.30E+06	7.36E-03	3.98E-05	5.19E-02	93	5.89E+05
1180	0.255	0.241	0.504	1.26E+06	7.41E-03	4.82E-05	5.88E-02	139	13.95E+05
1199	0.257	0.238	0.788	1.21E+06	7.47E-03	5.83E-05	6.65E-02	194	28.55E+05
1199	0.257	0.237	0.854	1.21E+06	7.47E-03	5.84E-05	6.66E-02	210	33.62E+05
1217	0.259	0.235	1.047	1.17E+06	7.53E-03	6.97E-05	7.47E-02	231	42.78E+05
1218	0.258	0.236	1.142	1.17E+06	7.53E-03	7.00E-05	7.49E-02	250	50.27E+05
1218	0.258	0.236	1.125	1.17E+06	7.53E-03	7.06E-05	7.53E-02	245	48.39E+05
1241	0.260	0.233	1.321	1.12E+06	8.66E-03	8.75E-05	8.66E-02	252	54.35E+05
1242	0.260	0.233	1.333	1.12E+06	8.72E-03	8.85E-05	8.72E-02	252	54.76E+05

Table 4: Activation Energies for Heterogeneous Reaction Systems

Reaction System	Temperature (K)	Activation Energy (kJ/mol)	Reference
$\text{Na}_2\text{CO}_3 (\text{s}) + \text{SO}_2 (\text{g})$	623-973	65	[3]
$\text{NO} (\text{g}) + \text{C} (\text{s})$	923-1073	180	[16]
$\text{Na}_2\text{S} (\text{l}) + \text{C} (\text{s})$ in $\text{Na}_2\text{CO}_3 (\text{l})$	1190-1340	204	[17]
$\text{SnO}_2 (\text{l}) + \text{CO} (\text{g})$	873-1073	147	[18]

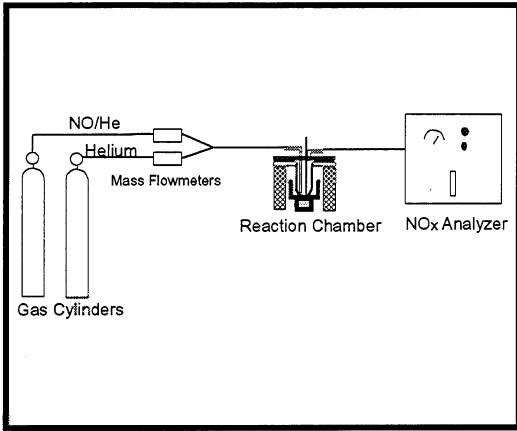


Figure 1: Experimental Apparatus

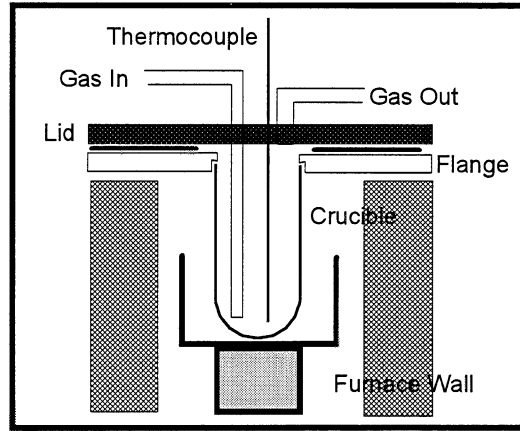


Figure 2: Reaction Chamber

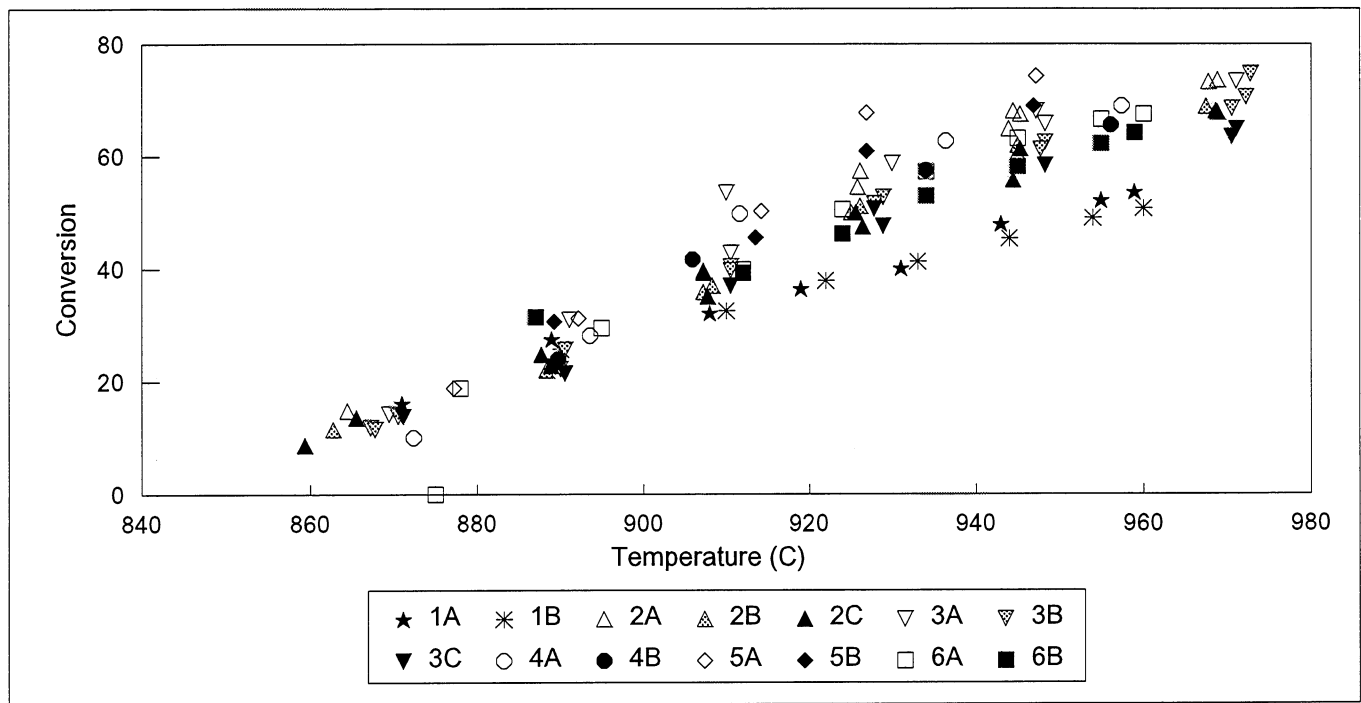


Figure 3: Conversion of Nitric Oxide as a Function of Temperature

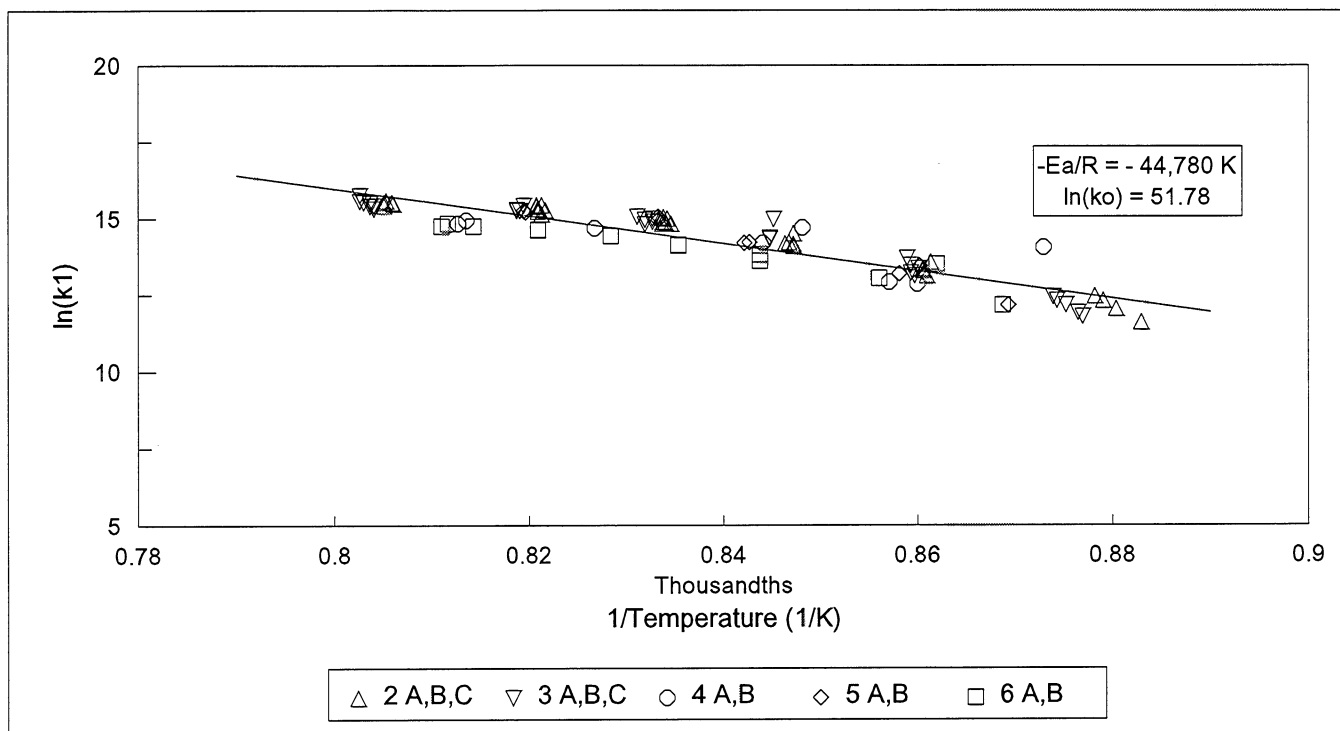


Figure 4: Determination of the Activation Energy; $\ln(k_0)$ vs $1/T$ for Experiments 2-6.

