DEVELOPMENT OF AN EVOLVED GAS ANALYSIS INSTRUMENT AND THE INVESTIGATION OF A STEPPED ISOTHERMAL METHOD FOR THE STUDY OF WATER DESORPTION FROM ZEOLITES

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Abstract:

A stepped isothermal pressure change method for the investigation of water desorption from zeolites has been developed. Stepped isothermal evolved gas analysis (SI-EGA) utilizes static methods, in a unique way, to determine kinetic data. This method produces isothermal kinetic data. The problems associated with dynamic methods are reduced by the use of an isothermal method. Zeolites NaY, NaX, and CaX have been investigated to determine if the SI-EGA method yields reliable kinetic data. This method consists of multiple expansions into vacuum carried out through a temperature range. The results of the SI-EGA experiments show water desorbing from zeolites NaY, NaX, and CaX with apparent energies of desorption ($E_a$) of $34 \pm 3$ kJ/mol, $16.9 \pm 0.4$ kJ/mol, and $40 \pm 1$ kJ/mol respectively. The results also give preexponential factors ($A_a$) of $156 \pm 121$ sec$^{-1}$, $0.5 \pm 0.1$ sec$^{-1}$, and $744 \pm 295$ sec$^{-1}$ for zeolites NaY, NaX, and CaX, respectively. The results confirm that the SI-EGA method produces reliable kinetic data for water desorption from zeolites. A refinement of the SI-EGA method could be useful for the investigation of desorption from microporous solids.
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List of Abbreviations:

ICTA  International Conference on Thermal Analysis
TA    Thermal Analysis
DTA   Differential Thermal Analysis
EGD   Evolved Gas Detection
EGA   Evolved Gas Analysis
SI-EGA Stepped Isothermal Evolved Gas Analysis
TG    Thermogravimetry
SIA(TG) Stepped Isothermal Analysis Thermogravimetry
CRTA(TG) Controlled Rate Thermal Analysis Thermogravimetry
TPD   Temperature programmed desorption
PDK   Pulsed Desorption Kinetics
MS    Mass Spectroscopy
GC    Gas Chromatography
H     Enthalpy
T     Temperature
T_e   Expansion temperature
P     Pressure
V     Volume
R     Gas constant
n     Number of moles
S     Entropy
t     Time
t_e   Time exposed to vacuum chamber
k     Rate constant
E     Energy
E_a   Apparent energy of activation for diffusion
E_d   Energy of diffusion
A_0   Total area of desorption curves
A_n   Area under nth desorption curve
A_a   Preexponential factor
D_e   Effective diffusivity
D     Diffusivity
D_o   Preexponential factor
R_e   Crystal radius
mA    Milliamp
VAC   Volts Alternating Current
VDC   Volts Direct Current
A/D   Analog to Digital
PC    Personal Computer
IBM   International Business Machines
psi   Pounds per square inch
CF    Conflat Flange
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<td>CaX</td>
<td>Cation exchanged 13X</td>
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<td>Pn. V.</td>
<td>Pneumatic Valve</td>
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<tr>
<td>Mn. V.</td>
<td>Manual Valve</td>
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<tr>
<td>UHV</td>
<td>Ultra High Vacuum</td>
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<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
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Chapter 1. Introduction

I was shown a plot of the temperature dependence of water desorption from zeolite NaX by Prof. George Andermann. The plot showed a large quantity of water desorbing from NaX powder at 110 °C. The plot was made by allowing the desorbing water to expand into a glass vacuum rack at a series of increasing temperatures. Attempts were made to reproduce the data but they were not successful. Upon further investigation of the original experiment and the raw data, it was determined that the experiment had not been carried out in a reproducible manner and this was the reason for my inability to reproduce the results.

The original idea of multiple expansions of the desorbing gas into vacuum seemed worthy of investigation so the project was continued. I searched for a desorption system that was simple, and easy to obtain. I began to construct an instrument specifically designed for a Stepped Isothermal Evolved Gas Analysis (SI-EGA) method to study water desorption from solids.

The aim of the project was to develop an experimental technique that would provide improvement over current non-isothermal Thermal Analysis (TA) kinetic data. The technique would be fast and simple. The question to be answered in this thesis is: can this Evolved Gas Analysis (EGA) method, using pressure changes at constant volume, be used to calculate reliable kinetic data for the desorption of water from zeolites?

The motivation behind investigating desorption thermal analysis was twofold. The first was that a project that was related to physical chemistry was of interest to me. Physical chemistry was interesting, and a project related to this discipline would
be challenging. Second was my desire to work with water. I started with the notion of studying hydrated salts, and moved to water desorption from microporous solids as a result of the difficulties associated with water desorption from hydrated salts. The reason for building the EGA instrument was to prevent water condensation as well as my desire to build an instrument. The challenge of taking an idea and implementing the idea in the form of a new technique and instrument to test the technique was exactly what I had envisioned when thinking about what to do for a masters thesis project. The project started with the idea of a thesis related to physical chemistry, and evolved into an analytical chemistry technique for studying water desorption from solids.
Chapter 2. Definition of Terms

Description and Comparison of Thermal Analytical Techniques

The method of thermal analysis discussed in this paper is unique and has not been previously carried out in the manner described in this paper. The justification for studying this method is that current methods do not yield reliable, reproducible results, therefore an investigation of a new method could yield new information not provided by current thermal analysis techniques.

Thermal analysis is a general term covering a group of related techniques whereby the dependence of the parameters of any physical property of a substance on temperature is measured (1). The principle techniques reviewed here will be limited to Differential Thermal Analysis (DTA), Thermogravimetry (TG), and Evolved Gas Analysis (EGA). TG, DTA and EGA represent the three most important and most commonly used thermo-analytical methods (2,3).

The method of EGA proposed, in this paper, required the construction of a specialized EGA instrument. The instrument is used to study water desorption from commercial zeolite powders. Zeolites were chosen because of their unique structure, and because of their wide commercial and industrial applications. It will be shown that the EGA method used to study zeolite powders will provide reliable information and is a simple tool for the determination of thermodynamic data on zeolites.

The basic parameter important to the methods of thermal analysis is the change in heat content \( (H) \). Every closed system can be characterized by its free energy \( (G) \), given by the expression

\[
G = H - TS
\]  

(1)
where $H$ is the enthalpy, $T$ is the absolute temperature and $S$ is entropy. At a given
temperature, every system has the tendency to attain a state in which the free energy
is at a minimum. An example is the desorption of water from a sorbent. At a given
temperature, the sorbate will have lower free energy in its gaseous state than the
adsorbed state, and is more stable in its gaseous state. The formation of a more stable
sorbent-sorbate system, with lower free energy, may take place on gradually heating
of the sample or via intermediate steps. The transformation of water from the
adsorbed state to a gaseous state is characterized by, the temperature at which it
occurs and by a change in heat content, manifested by an increase or decrease in
temperature, depending on whether the reaction is exo or endothermic. This is the
basis of Differential Thermal Analysis (DTA). The change in heat content may also
be accompanied by a change in weight. Observation of such a change is the basis for
the thermogravimetric method. (TG). (2,3). Methods associated with weight change
are of two classes: static and dynamic (1,2).

Static methods include isobaric and isothermal weight change determination.
Isobaric weight change determination analysis is the technique of obtaining the record
of the equilibrium weight of a substance as a function of temperature ($T$) at a constant
partial pressure of the volatile product or products (1,2). Isothermal weight change
determination is a technique of obtaining a record of the dependence of the weight of
a substance on time ($t$) at constant temperature (1,2).

Dynamic methods include Thermogravimetry (TG), a technique whereby the
weight of a substance in an environment heated or cooled at a controlled rate is
recorded as a function of time or temperature (1,2). Thermogravimetry has also been described by the method of heating or cooling. These include:

**Constant Rate Thermal Analysis (CRTA) Thermogravimetry**

The sample is heated at a constant rate and the change in weight is recorded as a function of time or temperature, which is the same as the definition given to TG by the Second International Conference on Thermal Analysis, and the International Confederation for Thermal Analysis (1). CRTA can also be used with DTA and EGA instruments, since it describes a method of heating the sample and not the method of analysis.

**Quasi-isothermal (QI) Thermogravimetry**

A technique in which a sample is heated at a constant rate, so long as the weight of the sample remains constant, but as soon as the weight of the sample begins to change, the temperature increase is stopped automatically. Thereafter the regulator system switches out the heating current whenever the rate of the weight change exceeds a small value and switches it on again when, owing to the small temperature drop, the rate of weight change decreases below a pre-selected value. The alternating process is repeated continuously until the end of the thermal decomposition. (4,5,42).

**Stepped Isothermal Analysis (SIA) Thermogravimetry**

The sample is heated at a constant rate until the reaction rate, i.e. the slope weight versus time curve, exceeds a preset limit, at which point the temperature is
held constant. The reaction thereafter proceeds isothermally until the rate becomes smaller than the limit where the heating is resumed. By this technique the reactions thus characteristically take place under isothermal conditions (6).

**Pulsed Desorption**

Pulsed desorption is a Ultra High Vacuum (UHV) technique, that uses micro-channel hot plates to apply square temperature pulses to a solid sample that has been previously allowed to adsorb a gas. The micro-channel hot plates provide temperature pulses with rise times of the order of a few milliseconds. The desorbing gas is fed into a mass spectrometer or detector, where the amount of desorbing gas is recorded. The technique allows for both activation energy and the rate constant to be calculated (7).

**Temperature Programmed Desorption**

Temperature Programmed Desorption (TPD) is a technique in which a sample is dosed with a gas, and then heated. The heating rate is usually linear and the desorbing species is fed to a detector with a carrier gas. The detector may be a thermal conductivity detector or any detector that can quantify and/or identify the gas desorbing from a sample (17). The data output is in the form of a TPD curve. TPD allows for the determination of both the activation energy and the preexponential factor. TPD is a method of Evolved Gas Analysis (EGA) but had been described as a method of Evolved Gas Detection (43).
Evolved Gas Analysis

Evolved Gas Analysis is a term that covers any technique of determining the nature and amount of volatile product or products formed during thermal analysis (1). If only the presence of a gas is detected the apparatus may be designated as Evolved Gas Detection (EGD). On the other hand if the amount or quantity of the gas evolved is measured quantitatively then the apparatus is EGA (8). The most commonly used method of EGA is Temperature Programmed Desorption.

The EGA method under investigation uses a variation SIA, to study desorption of water form commercial zeolites. The SI-EGA method consists of a number of isothermal expansions into a vacuum chamber at a series of increasing temperatures. The main difference between SI-EGA and SIA-TG is, that SI-EGA uses pressure change to quantify the amount of gas desorbing, while SIA-TG uses weight change.

SI-EGA incorporates multiple isothermal desorption expansions into a vacuum chamber at each temperature. The rate of decrease in the area under a series of desorption curves allows for the calculation of the activation energy and preexponential data with a single experiment. The method of using the change in area under a series of desorption curves is similar to Pulsed Desorption Kinetics (PDK) data analysis techniques (7).

The SI-EGA method is a static technique that attempts to characterize sorbent-sorbate interactions by doing a series of isothermal pressure change experiments within a single experiment. The instrument used in the experiments presented in this paper is a constant volume EGA instrument. The instrument measures the extent of
reaction by monitoring the change in pressure associated with desorption of water from a microporous solid at a given temperature. The technique is similar to classical pressure change chemical kinetic experiments.

**Isothermal Weight and Pressure Change Determination**

Isothermal weight and pressure change determination is an example of a method that combines EGA and TG. This method follows the change in pressure in conjunction with the change in weight to be measured simultaneously. The simultaneous measurement of the weight loss and the gas pressure of the test sample under isothermal conditions can be performed by commercially available TG instruments (9). EGA can also be combined with DTA and mass spectrometry (MS). There are many more multiple techniques that employ EGA or EGD (8,10), that will not be discussed in this paper.

**Classical Methods of Chemical Kinetics**

The classical method in chemical kinetics is the isothermal measurement of the change of concentration of reactants and/or products with time, after a sudden disturbance, which makes the starting condition unstable. The reaction order can be derived from the rate law obtained; measurements at different temperatures yield the activation energy and preexponential factor (11). The classical method yields more accepted kinetic values than dynamic methods, but dynamic techniques are faster and are more often utilized. The SI-EGA method under investigation incorporates elements of both classical and dynamic thermal analysis methods.
Comparative Techniques (TG & EGA)

The thermal analysis technique that most closely relates to the EGA method under investigation is TG. TG, like EGA, measures the extent of reaction by measuring the amount of product produced by the reaction. TG measures the change in weight of the sample as the reaction proceeds. EGA measures the change in pressure as the reaction proceeds. TG measures the change in weight as a function of time, and is often performed in conjunction with DTA as a way to double-check the data. The major problem with TG/DTA is the variation in results from one researcher to another. Agreement of the results obtained from various methods, and often by the same method performed by different people, is poor. This is due primarily to the great difficulty in obtaining identical experimental conditions (2).

One of the reasons that TG data varies from one researcher to another are the factors that effect the shape of the TG curve. These factors include (2): a) reactions of the sample with the crucible or with parts of the apparatus, b) sublimation and condensation of the reaction products, c) Shape, size, and material of the crucible, d) heat rate and heat transfer, e) composition of the atmosphere in the reaction chamber, f) sensitivity of the balance and recording system, g) method of temperature measurement, h) amount of sample and particle size, i) heat of reaction, and thermal conductivity of the sample, and j) nature of the sample and types of changes taking place.
TG uses a carrier gas to carry the evolved components of the reaction into an analyzer, such as a mass spectrometer (MS) or gas chromatograph (GC). The use of a carrier gas enables TG experiments to be conducted under isobaric conditions.

The EGA method under investigation is a constant volume technique that uses pressure change to monitor the extent of reaction. It will be shown the EGA instrument also has design and experimental factors that affect the outcome of an experiment. These factors include: a) condensation of reaction products, c) design of the sample holder and baffle assembly, d) heating step size, e) sensitivity of the pressure transducer, f) method of temperature measurement, g) amount of sample, and h) nature of the sample and types of changes taking place.

The major problem to overcome with the SI-EGA method discussed in this paper is sample movement. The sample has a tendency to be sucked into the vacuum chamber during the experiment. The experimental method requires a sample port valve that will isolate, then expose the sample to the vacuum chamber. The actuation of the sample port valve leads to pressure gradients, which transport the powder sample to the lower pressure side of the pressure gradient. The experiments discussed in this paper deal exclusively with powder samples with an average size of 4 μm. The powder is very light and the slightest pressure gradient may cause the sample to be disturbed. A large pressure gradient can cause the entire sample to be transported into the vacuum chamber. If the powder sample is sucked into the vacuum chamber, the instrument must be disassembled and cleaned. Afterwards, the experiment must be repeated. A baffle assembly was designed to minimize sample movement due to pressure gradients.
The data obtained from a TG instrument is a thermogravimetric curve, or TG curve. The information derived from a TG curve gives information on sample composition, thermal stability, thermal decomposition, and on the products formed during heating (1).

The SI-EGA method produces a series of desorption curves for a series of different temperatures. The information derived from these desorption curves include information on sample composition, thermal stability, and product formation during heating.

**Isothermal versus Dynamic Analysis**

Isothermal thermal analysis is a classical method, measuring the change in concentration of reactants and or products with time. It allows for more precise determination of kinetic values. The experiments take longer to perform, and several experiments are often necessary to characterize a sample over a temperature range.

Dynamic thermal analysis is a rapid method of determining the change in concentration of reactants and or product with time. It allows for a picture of different adsorption states to be obtained rapidly. Approximate kinetic values ($k$ and $E$) can be obtained in a few experiments.

**Isobaric versus Constant Volume**

Isobaric methods differ from constant volume methods in the nature of their environment during an experiment. The difference is that isobaric methods use a carrier gas to sweep the desorbing molecules to a detector. With isobaric methods the
sample is often in contact with the carrier gas, unless special arrangements are taken to prevent this. Constant volume methods do not use a carrier gas and the sample is instead exposed only to the species that are desorbing.

Stepped Isothermal Evolved Gas Analysis Method

The reason for investigating the desorption process by the SI-EGA method is that dynamic methods do not yield reliable kinetic data. Arnold (12) showed that TG curves are strongly influenced by the experimental conditions, and hence the kinetic parameters calculated from these curves are fictitious and their determination is uncertain. In dynamic methods, a series of experiments must be performed at different heating rates to calculate kinetic values. Therefore it was hypothesized that an experimental method (SI-EGA) could be developed to produce reliable kinetic data over a broad temperature range within a single experiment.

The EGA method that has been developed has four advantages over current TG, DTA, and classical isothermal experimental methods: a) all data can be collected with a single experiment, b) the method can supply reliable information, c) the experimental apparatus is inexpensive and simple to build, and d) it is faster than classical methods but more precise than dynamic TG and DTA experiments.

Since the current data obtained from dynamic TG and DTA are of dubious nature (13), the SI-EGA method can match, if not surpass, the validity of current non-isothermal data.

The benefit of the new experimental method will be a simpler and easier way to obtain kinetic information on temperature dependent reactions between sorbent-
sorbate systems. This method can also produce reliable kinetic information in a reasonable amount of time.

Validity of Non-Isothermal Data

"It is well-known that the physical meaning of kinetic data obtained by thermo-analytical techniques is open to discussion" (13). This statement forms the basis for investigating the SI-EGA method. It was indicated by many speakers at the 1985 ICTA conference and workshop, on the reliability of kinetic data, that 75%-100% of dynamic thermal analysis kinetic information is meaningless. The unreliability of current kinetic data derived from non-isothermal methods lends itself to the development of a method that could yield more reliable kinetic data.

Dynamic thermal analysis uses standard kinetic equations as a basis for the equations used to calculate kinetic data. The major problems in non-isothermal kinetics are three (14) (Appendix 4). First, the mathematics are cumbersome, and second, the mathematical functions used to describe the non-isothermal curves are not sensitive to changes in $E$, $n$, and $A$. Third, the assumptions used to derive the equations are not always true. The only solution to these problems is to do more experiments. One should conduct four or five isothermal experiments at different temperatures. After doing the isothermal experiments, there is no need for additional non-isothermal experiments. This fundamental problem with non-isothermal methods was the reason for investigating the SI-EGA method.

The only argument in favor of non-isothermal kinetic measurements is their rapidity compared with isothermal kinetic studies. Thus, if kinetic information for a
technological purpose is needed, the rapidity of dynamic thermal analysis techniques may be sufficient to compensate for the absence of a physical meaning of the kinetic data (13).

Dynamic methods of thermal analysis are good when they are used for practical purposes. For example, if technology requires non-isothermal conditions, then non-isothermal kinetic methods can be used to characterize the process. Dynamic methods of thermal analysis are very fruitful for the direct studies of mechanisms of solid state reactions, but only if the methods themselves and not the non-isothermal kinetic analyses based on these techniques are used. Finally, non-isothermal kinetic studies are useless for understanding the physics and chemistry of solid state reactions, as the meaning of kinetic data obtained is vague (13).
Chapter 3. Theory

Intracrystalline Diffusion

Three models have been proposed to describe desorption of ammonia from zeolite systems, desorption with no readsorption, desorption with free readsorption, and intracrystalline diffusion through the zeolite framework (15). These models have been used as the basis for determining the mechanism controlling water desorption from zeolites. The results of the three models have been analyzed on the basis of a comparison between what is expected from the calculations, based on the model assumed and what has been obtained experimentally from TPD data (16).

The analysis of TPD spectra show that the models proposed for desorption with no readsorption and desorption with free readsorption do not fit the experimental data. As a consequence, both models must be discarded as incapable of representing the phenomena analyzed (16,17). Only the model considering intracrystalline diffusion seems to interpret the data correctly (Appendix 14). Therefore, intracrystalline diffusion should be considered as the most probable rate determining step for all zeolites in which the framework structure of low-diameter channels is present, irrespective of the Si/Al ratio of the zeolite and of the degree of ion exchange of the original Na\(^+\) with H\(^+\) ions (17). The process may be represented as a surface diffusion further slowed down by reversible acid-base chemical reactions (15). Desorption of water from zeolites is assumed to follow the same process as ammonia.
Stepped Isothermal Evolved Gas Analysis

The methods of data analysis for the SI-EGA method are derived from Pulsed Desorption Kinetics (PDK), data analysis methods and diffusion equations (15,17,18). Intracrystalline diffusion of desorbed water is adopted as the rate determining step for desorption of water from zeolites NaX, CaX, and NaY powder. The parameters that can be calculated using diffusion related equations are the parameter $D/R$ (effective diffusion/crystal radius squared), the preexponential factor ($A_a$), and the apparent activation energy ($E_a$) (Appendix 5).

The raw data obtained from a SI-EGA experiment consists of a series of desorption curves taken at a series of increasing temperatures. The area under desorption curves is proportional to the amount of water desorbing from the zeolite powder. The change of the area under successive desorption curves is exponential in nature. A plot of the change in area under desorption curves versus the time that the sample is desorbing into the vacuum chamber can be used to calculate the effective diffusivity divided by the radius of the zeolite crystal, $D/R$ with units of sec$^{-1}$. Dividing by the crystal radius allows for the effect of crystal size on the diffusivity to be determined. When investigating a bed of different sized particles or unknown sized particles the term $D/R$ is used to describe the rate of the diffusion process.

Plotting the change in area under desorption curves versus time is similar to the method used by pulsed desorption kinetics, to calculate the rate constant for desorption of gases from metal surfaces (7). An Arrhenius plot of $D/R$ versus reciprocal temperatures allows for $A_a$ and $E_a$ to be evaluated by the following equation (17,18,19).
\[ \frac{D_e}{R_c^2} = A_a \exp \left(-\frac{E_a}{RT}\right) \] (2)

This equation is used to describe the temperature dependence of intracrystalline diffusion. The equation is a modified version of the Eyring expression for the temperature dependence of the diffusion process (18).

\[ D = D_\infty \exp \left(-\frac{E}{RT}\right) \] (3)

Intracrystalline diffusion is an activated process so that the diffusivity varies with temperature according to Equations 2 and 3. The diffusional activation energy is comparable to the activation energy for a chemical reaction (18).
Chapter 4. Instrumentation

Initial SI-EGA experiments were performed on a glass vacuum rack (Appendix 11). The glass vacuum rack had a number of drawbacks associated with desorption of water and the SI-EGA technique. The main drawback that could not be overcome was the condensation of water inside the glass rack. To overcome the condensation of water vapor, a stainless steel vacuum chamber was constructed.

The instrument designed and built by the author consists of a stainless steel vacuum chamber, with a series of valves and pressure transducers interfaced to a personal computer. The design of the EGA instrument was chosen for its simplicity and cost. A diagram of the vacuum chamber and instrument is shown in Figure 1. The purpose of the instrument is to investigate pressure rise experiments using a unique SI-EGA experimental method.

Vacuum Manifold

The vacuum chamber was constructed from manufactured stainless steel parts. The main body of the instrument consists of a 4-way cross and a nipple. The 4-way cross consists of two, 2.75 CF flanges, and two, 1.33 CF flanges. One end of the cross is attached to an adapter flange that attaches the pneumatic valve. To the other 2.75 CF flange end a 2.75 CF nipple is attached. The two, 1.33 CF flanges are used to attach a 0-10 Torr and a 0-1000 Torr MKS pressure transducer. An adapter flange attaches a tee to the nipple to which valves #2 and #3 are attached. The main body of
Figure 1. EGA vacuum chamber schematic (not to scale).
the vacuum chamber is attached to an aluminum bracket, which is secured with bolts to the metal housing of the instrument cabinet. The design of the vacuum chamber part of the instrument is illustrated in Figures 1. The total volume of the vacuum chamber was designed to be approximately 0.75 liter. A volume of 0.75 liter was chosen because a 0.75 liter volume is large enough to allow the expansion of water into the chamber and have a pressure reading that was large enough to overcome the error associated with each measurement. This allows for sample sizes down to 50.0 mg to be investigated. If the chamber volume is larger, a larger sample must be used to provide enough water to produce an expansion pressure that is large enough to overcome the error associated with each pressure measurement. The opposite is true for a smaller volume; less sample would be used to obtain similar expansion pressures.

The vacuum chamber has four valves. Three are manual valves and the fourth is a pneumatic valve. Valve #1 is the vacuum pump valve. It isolates the vacuum pump from the rest of the system. Valve #2 is the main shut-off valve. Its function is to isolate the vacuum chamber from the vapor traps. This valve is closed during an expansion experiment and opened when the chamber needs to be evacuated. Valve #3 is the vapor port valve and is used to introduce water vapor into the vacuum chamber. The last valve, #4, is a pneumatic valve that isolates the sample from the vacuum chamber. This valve actuates using compressed air of approximately 60 psi and a 120 VAC solenoid.

There are two 'ports' on the vacuum chamber, a sample port and vapor port (Figure 2). The sample holder is attached to the sample port. The vapor port is used to
introduce water vapor and other gasses into the vacuum chamber. The sample port is one end of a pneumatic valve that is attached to the main chamber via a CF to QF flange adapter. The temperature of the pneumatic valve is kept at the same temperature as the main chamber (above 100° C) to insure no condensation of water vapor. A pneumatic valve is necessary to insure repeatable results. To obtain repeatable results, the size of the opening allowing water vapor to expand into the vacuum chamber must be the same upon each opening. The only way to fulfill this requirement is to use a pneumatic or butterfly valve. The pneumatic valve was chosen because the valve opens to the same aperture with the same speed each time it is actuated. Manual operation of a butterfly valve could not insure both speed and opening equality upon each actuation.

The vapor port is the end of a manual valve attached to the vacuum chamber (Figures 1, 2). The vapor port serves as a means to introduce water into the vacuum chamber, which can then be adsorbed into a zeolite sample. Liquid water is placed into the vapor port, then the port is sealed, and the water is heated to above 100° C. The heated water vapor is then allowed to expand into the chamber along with some air at a ratio of 1300:1. The air does not adsorb into the sample in significant amounts.

The vacuum is supplied by a rotary vacuum pump. The vacuum pump is a Welch duo-seal 1400: rotary vacuum pump. The pump can easily pump the vacuum chamber down to 5 X 10⁻³ Torr.

The vacuum pump is attached to two vapor traps. The first vapor trap is a
Figure 2. 3-D view of EGA instrument (not to scale).
stainless steel molecular sieve vapor trap. The trap is connected on each side with 2.75 CF flanges. The second trap is a liquid N\textsubscript{2} cold trap. The trap is made of glass and is attached by vacuum hose to valve #1 on one side and the molecular sieve trap on the other.

\textbf{Detection System}

Two, MKS baratron, pressure transducers are attached to the main body of the vacuum chamber (Figures 1,2). One is a model 2221000A, which monitors the pressure from 0 to 1000 Torr. The other is a model 2220010A, which monitors the pressure from 0 to 10 Torr. The transducer housings are cooled with small fans.

The transducers were placed so as to make the vacuum chamber as symmetrical and linear as possible. The reasoning behind making the chamber linear and symmetrical was to insure that the path of the expanding water vapor was a short and straight as possible so as to minimize any effects of turbulence that might distort the pressure rise curves. A system with one transducer would be ideal but could not be realized. The pressure changes that are obtained during an expansion experiment are usually less that 1 Torr, but pressures during a normal adsorption experiment are usually in the range of 30 – 100 Torr. Therefore, an accurate pressure transducer in the range of 1 Torr was required as well as a pressure transducer to measure higher pressures. The low pressure, transducer is a 0 – 10 Torr transducer with accuracy of 0.5 % of reading, and the high pressure, transducer is a 0-1000 Torr transducer also with an accuracy of 0.5 % of reading. Having a low and a high pressure, transducer
enables the instrument to be more flexible. The instrument can be used for adsorption as well as desorption experiments. Small fans were attached to each transducer to keep the temperature of the transducer electronics below 50° C.

Sample Holder and Baffle Assembly

The sample holder and baffle assembly were designed by the author and manufactured by department machinist. The sample holder and baffle assembly are illustrated in Figures 3 and 3a. The sample holder is a modified QF16 unbored stub. The stub has been hollowed out to serve as a crucible. A thermocouple hole has been drilled through the bottom portion of the stub. A thermocouple temperature sensor fits into the hole. The baffle assembly sits inside the sample holder. The assembly consists of a set of screens, held in place by pinch rings. Above the first pinch ring two screens are sandwiched together. A second pinch ring holds a single screen with a third pinch ring securing the top screen. Above the screens is a series of three baffle plates. The baffle plates are held in position with a centering ring. The centering ring also holds a viton o-ring that seals the sample holder to the sample port.

Due to the nature of expanding into vacuum, it is necessary to minimize pressure fronts within the sample holder. This is accomplished with the aid of baffle plates and a series of 72 mesh screens. The three baffle plates and three screens help break up the pressure front and minimize sample movement. When the pneumatic valve is opened, a pressure front forms as the region of higher pressure attempts to
FIGURE 3. Sample holder and baffle assembly drawing (not to scale). See appendix.
Figure 3a. 3-D view of sample holder and baffle assembly (not to scale).

Legend:
1. 4-Hole Baffle Plate
2. 1-Hole Baffle Plate
3. Centering Ring
4. Viton O-ring
5. Pinch Ring
6. 10 mesh Screen
7. Sample Holder
8. Thermocouple Hole
equalize with the region of lower pressure. As the pressures move toward equilibrium, the turbulence they create causes the powder sample to be blown/sucked into the vacuum chamber. As the water vapor escapes from the zeolite powder it is swept up through the screens, then through the baffle plates on its way to the vacuum chamber. The first two screens are placed directly on top of one another and sandwiched between two pinch rings. The double screen serves to isolate the sample as much as possible from the vacuum chamber. If any pressure fronts disturb the sample, the double screen keeps the powder from escaping into the vacuum chamber. Above the second pinch ring is a single screen that serves to distribute any pressure front that travels through it. As the water vapor continues toward the chamber, the vapor is forced to take a S shaped path as it travels through the three baffle plates. The arrangement of holes in the baffle plates force the stream of water vapor to collide with the baffle plates. Because the zeolite powder has more mass than water vapor, the powder is slower to change direction and slams into the plates. Once the powder has hit the plate it either sticks to the plate or falls back down on the top screen. After a SI-EGA experiment has been completed the, first and second baffle plate have small amounts of zeolite powder attached to the side facing the sample. The third plate normally has no visible zeolite powder attached to it. The baffle plates function as they were designed and prevent zeolite powder from contaminating the interior of the vacuum chamber.
Electronics

The EGA instrument consists of a vacuum chamber and an instrument cabinet (Figure 2). The cabinet houses the electronic components of the instrument and serves as a mounting stand for the vacuum chamber. It also serves as a grounding point for all of the electronics associated with the EGA instrument. A voltage regulator supplies constant voltage to the variable auto transformers (variacs). The cabinet houses a temperature display and a temperature controller. Separate AC to DC voltage converters provide power to the pressure transducers and the cooling fans. Finally the terminal board and associated electronics are mounted to the cabinet. Figure 4 shows how the electrical components of the vacuum chamber are connected.

Thermal Regulation

The temperature of the vacuum chamber is maintained above 100° C with two 6’x1” heating tapes connected to two 120 V AC variacs. A Sorensen ACR1000 AC voltage regulator supplies a constant voltage of 120 VAC to the variacs that power the heating tapes. The voltage regulator keeps the voltage supply to the auto-transformers stable throughout an experiment and minimizes variations in voltage from day to day. The heating tape is wrapped in blanket material in order to insulate the chamber from the ambient temperature of the room.
Figure 4. Electrical schematic for EGA instrument.
The temperature is monitored by a type T thermocouple attached to an Omega model 199 temperature display. The temperature sensor for the display is located on the top-middle of the CF cross. The readout also has a 0-10 V DC output, which is proportional to the temperature displayed on the readout. The temperature sensor is a type T thermocouple and has a temperature range of -200°C and 400°C. The temperature range of the vacuum chamber is room temperature to 150°C. The temperature readout was calibrated with the aid of a fluke DMM thermocouple probe. The calibration range was 0°C to 150°C. This range produced a very small DC voltage output by the temperature display output. In order to get a stronger signal the output of the readout was attenuated with a LM 324 operational amplifier. The amplifier has a gain of 100. The signal from the readout is amplified, and then sent to the data acquisition card where it is converted to a digital word.

The sample holder temperature is controlled by an Omega CN76000 temperature controller. The controller uses a type T thermocouple probe for temperature measurements. The thermocouple is inserted into the thermocouple hole located at the bottom of the sample holder. The solid state relay output of the temperature controller is fed to a 12 x ¼ inch heating tape. The heating tape is wrapped around an aluminum heat sink cylinder (Figure 5). The controller heats the heat sink, which then transfers its heat energy to the sample holder. The top of the cylinder has been bored out to allow for the sample holder to fit into the aluminum heat sink. Heat sink silicon compound is placed between the aluminum heat sink and the sample holder to ensure maximum heat exchange. The cylinder is kept in place...
with a lab jack. And a bent washer is placed between the lab jack and heat sink to prevent heat exchange between the heat sink and lab jack. A heat sink was used for two reasons. The first is to insure that there is enough heat capacity in the heat sink to counter any endothermic effect from the water desorbing from the zeolite powder. Secondly the heat sink can be easily moved for easy access to the sample holder. Wrapping the sample holder with heating tape would not be an easy task, due to the small size of the sample holder.

The pressure transducers are kept near room temperature with small fans (40 mm x 40 mm). The fans are mounted on the pressure transducers, and blow a constant stream of air over the housing of the transducer. A third fan is used to keep the sample holder at room temperature during adsorption experiments. A 9 VDC 200 mA, AC to DC converter supplies power to the cooling fans. A Sorensen DC power supply provides the ±15 VDC for the pressure transducers. Both power supplies are powered from the 120 V AC wall receptacle. The power source for all the electronic components comes from the wall receptacle. The main power cord to the instrument is not grounded, and all instrument electronics are grounded to the instrument cabinet frame.
Figure 5. Aluminum heat sink drawing (not to scale). Heating tape provides heat. Units are in inches.
Data Acquisition

The output of all the components are interfaced to the data acquisition card via a terminal screw board (Figure 6). The board is mounted and grounded to the cabinet frame. The two pressure transducers and the temperature readout are interfaced with the computer though the terminal board, which is attached to a DAS-8 data acquisition card located inside the PC computer. The temperature readout signal is attenuated with a LM324 operational amplifier. The DAS-8 data acquisition card supplies the DC voltage to run the LM324 operational amplifier.

Computer Interfacing

In order to obtain pressure measurements in conjunction with accurate timing, the pressure transducers and temperature readout were interfaced with an IBM compatible computer (Figure 6). The analog outputs from the sensors are converted to digital signals with a DAS-8 data acquisition card. Software controls the acquisition and manipulation of data (Appendix 1).

The computer has a 300 MHz Pentium II CPU and a bus speed of 66 MHz. The speed of the CPU and bus play an important role in the data acquisition performance. A slow CPU takes longer to run the program, longer to store and retrieve the data, and takes longer to communicate with the data acquisition board. The same holds true for a slower bus speed. A bus speed of more than 66MHz will also cause the data acquisition card to perform at a slower pace. At bus speeds above 66MHz the timer chips on the data acquisition card cannot keep pace with the computer.
Figure 6. Terminal board wiring diagram (not to scale).

- **Temperature Display**
- **Signal Out**
- **Signal Return**
- **37-Pin Connector**
- **Analog In Connectors**
- **LL Ground Connectors**
- **Digital I/O Connectors**
- **Terminal Board**
- **Chassis Ground**
- **Shielded Cable**
- **PC Computer**

- **MKS 0-1000 Baratron**
- **MKS 0-10 Baratron**

(Refer to diagram for detailed connections and labels.)
The data acquisition card is a DAS-8 ISA card from Cyberresearch. The card has eight single ended inputs with a common low-level ground. The sensors are wired to the terminal board as shown in Figure 6. The output from a sensor is attached to the terminal board and the ground is grounded with the low-level ground. The terminal board is attached to the data acquisition card by a shielded 6-ft cable. The data acquisition card converts the analog signal from the sensor to a 12-bit digital word. The data acquisition card does not have any buffers or memory storage on the card. Therefore, after a signal is converted from DC voltage to a digital word, a software program controls how the digital word is stored and retrieved, and converted to a pressure or temperature value.
Chapter 5. Materials

Water

Water for ion exchange as well as adsorption/desorption experiments was deionized and distilled water. The water was stored in a 4-liter Nalgene jug.

Ion Exchange

The chemicals used to make the ion exchange solution were purchased from Fisher. The chemicals include: Ca(NO₃)₂ (Fisher cat#:AC42355000), and KOH (Fisher cat#:AC42355000).

Zeolites

The zeolite powders, NaX and NaY, were donated by the Molecular Sieve Division of UOP Inc. The zeolites were received in plastic bags sealed inside metal cans. The zeolites were kept in the original containers or placed in weighing bottles, which were stored in a desiccator. Further details on zeolite structure and chemistry can be found in Appendix 3.

Instrument Components

The temperature readout is an Omega Engineering Inc. model 199 type T readout. The readout has a linear DC output that is proportional to the temperature displayed on the readout. The temperature controller is an Omega Engineering Inc. model CN7600 type T thermocouple temperature controller.
The voltage regulator is a Sorenson model ACR 1000. The variable auto transformers operate on 120 VAC and can produce variable outputs of 120 or 140 VAC. All heating tapes (Fisher cat#:11-463-51C (2) and cat#:11463-48A (1)) were purchased from Fisher Scientific.

All stainless steel parts with the exception of two QF16 to 2.75 CF adapter flanges were purchased from LDS Vacuum, Inc. Huntington Laboratories, Inc. and MDC Vacuum, Inc. Two, adapter flanges were manufactured by David Kempton. Drawings are located in Appendix 2.

The pneumatic valve (PV-0620-SF) was purchased from Huntington Laboratories, Inc. Valve #2 (KAV-100) was purchased from MDC Vacuum Inc. The other two valves, as well as both vapor traps were donated by Prof. George Andermann.

The pressure transducers (122AA-00010 and 122AA-01000) were purchased from MKS Instruments, Inc.
Chapter 6. Calibration of EGA Instrument

The EGA instrument was calibrated and checked for leaks. The pressure transducers were zeroed. The range and output of the temperature display were verified. Finally the vacuum chamber was checked for leaks.

Pressure Transducers

The pressure transducers were zeroed to establish the pressure at which the pressure transducer reads 0.000 Torr for the 0-10 Torr transducer, and 0.0 Torr for the 0-1000 Torr transducer. This was accomplished by attaching the Chemistry Department's leak detector to one of the ports on the vacuum chamber. This detector was able to pump down the chamber to $1 \times 10^{-4}$ Torr. This was the base pressure used to zero both pressure transducers. After the transducers were zeroed, a calibration plot of pressure vs. digital word was constructed (Figure 7). The equation of the line of this plot is used in the data acquisition program to convert digital word to the appropriate pressure value. Both plots verify that the outputs of the pressure transducers are linear from 0-10 volts DC. The linearity of the plots shows that for a given change in pressure the difference between the two values should be within the specified accuracy range of the pressure transducer.

Temperature Sensors

To insure that the temperature of the vacuum chamber was correctly displayed, the temperature display was calibrated. The calibration was not a full-scale
Figure 7. Calibration plots for pressure transducers and temperature readout (1000 Torr transducer equation to be divided by 1000).
calibration, but instead the display was calibrated for the temperature range in which the chamber would operate. A Fluke DMM with a type K thermocouple was used to adjust and verify the temperature displayed. The DC output of the display was adjusted to reflect the temperature displayed. Figure 7 shows the calibration plot for the temperature display. The equation of the best-fit line is used to convert the digital word into a temperature value. The linearity of the plot confirms the output of the readout is functioning properly.

The integrity of the vacuum chamber was verified by checking the chamber for leaks. The longest expansion time for the experiments used to determine kinetic parameters, was 1 minute. The tests for leaks were carried out for 10 minutes. The empty sample holder was attached to the port and the system was pumped down. Upon reaching the base pressure, the isolation valve was closed and the pressure was monitored for 10 minutes. No detectable pressure change was observed during the 10 minutes. The test was repeated and the results were the same. From the leak tests, it was concluded that there were no leaks affecting the SI-EGA experiments with expansion times less than 10 minutes.

**Volume Determination**

The volume determination of the EGA instrument and its various parts was accomplished by expanding a known pressure from a known volume into an unknown volume. The resultant pressure was used to calculate the new volume by

\[ P_1V_1 = P_2V_2 \]  \hspace{1cm} (4)
The glass vacuum rack was used to first determine the volume of a small flask that was fitted with an adapter that allowed the flask to be attached to both the glass vacuum rack and the EGA vacuum chamber. Air was expanded from the flask into the EGA vacuum chamber in order to determine the volume of the main chamber. The main chamber was then used to expand air into the sample holder and vapor port, in order to determine their respective volumes. Figure 2 lists the volumes of the various sections of the EGA vacuum chamber.
Chapter 7. Experimental Method

Preparation of Calcium Hydroxide

Calcium hydroxide, \( \text{Ca(OH)}_2(s) \) was prepared with calcium nitrate, \( \text{Ca(NO}_3)_2(s) \) and potassium hydroxide, \( \text{KOH} \) by the following chemical reaction,

\[
\text{Ca(NO}_3)_2(aq) + 2 \text{KOH} \rightarrow \text{Ca(OH)}_2(s) + 2 \text{K(NO}_3)_2(aq)
\]

A 0.013 M \( \text{Ca(NO}_3)_2 \) solution and a 0.268 M solution of \( \text{KOH(aq)} \) solution were both chilled and then mixed together in an ice bath. The mixture was covered allowed to sit overnight. The next day the \( \text{Ca(OH)}_2(s) \) crystals were washed with 1.0 L of chilled water, suction filtered and washed again with 1.0 L of chilled water. The \( \text{Ca(OH)}_2(s) \) crystals were placed in a drying oven at 100° C until upon subsequent weighing, no change in weight was detected. The dried crystals were allowed to cool to room temperature in a desiccator and were then weighed and transferred to a volumetric flask for preparation of the 0.001M \( \text{Ca(OH)}_2 \) solution.

Sorbents

Zeolite CaX was prepared from UOP NaX powder using 0.05M \( \text{Ca(NO}_3)_2 \) in 0.001M \( \text{Ca(OH)}_2 \) exchange solution. Ion exchange was accomplished by bathing 2 grams of powder in the exchange solution for 5 days at 22° C. The powder-exchange solution was agitated regularly and the exchange solution was changed daily. After 5 days the powder was suction filtered, rinsed with 1 liter of 0.001 M \( \text{Ca(OH)}_2 \) solution and finally with 25 ml of \( \text{H}_2\text{O} \). The powder was then oven dried at 120° C for
3 days, then placed in a desiccator for storage. Two gram portions of both zeolite NaX and NaY were also dried in the oven for at least three days before being stored in the desiccator.

Sample Holder Setup

The sample holder (SH) is tared and the sample is then weighed into the SH. After the correct amount had been weighed into the SH, the SH is tapped gently on the counter top. Tapping the sample holder flattens the powder into a bed of uniform thickness and also flattens out any clumps that may have formed. The screen portion of the baffle assembly is then inserted into the sample holder (Figure 3a). Then upper portion of the baffle assembly is placed on top of the sample holder and the entire sample holder/baffle assembly is attached to the sample port with a hinged clamp. The sample port is kept open with the vacuum chamber at atmospheric pressure.

Dehydration of Sample at 150 °C

After the sample holder is attached to the sample port, the sample port valve (#4) is left open (Figure 1,2). It will be left open until the beginning of the SI-EGA portion of the experiment. The system is pumped down by slowly opening the main valve (#2). When the base pressure of $5 \times 10^{-3}$ Torr is reached the sample temperature is increased to 150 °C and the sample is dehydrated under vacuum for 23 hrs. The dehydration temperature of 150 °C was chosen because of the temperature limitations of the o-rings used in the instrument.
Adsorption of Water

The manufacturer specified equilibrium water capacity of zeolite NaX (13X) is 26% wt. To saturate a 50.0-mg sample of NaX powder, approximately 15 mg of water, measured to 0.1 mg, is allowed to adsorb onto the powder. A 15.0-mg aliquot of room temperature water is placed on the vapor port cap flange (Figure 1,3). The flange is then attached to the vapor port and the temperature is raised to the temperature of the vacuum chamber. With the vacuum pump on, the main valve (#2) is closed and the vapor port valve (#3) is opened. The water vapor/air mixture expands into the vacuum chamber and is allowed to adsorb onto the zeolite for 30.0 minutes with the sample at room temperature. After 30.0 minutes the main valve is slowly opened the room temperature pumping on the sample begins.

Removal of Initial Water by Room Temperature Pumping

The initial removal of water is accomplished by pumping on a sample at room temperature from 20 – 30 minutes. Pumping on a sample at room temperature means the sample is exposed to the vacuum chamber with the main valve open and the vacuum pump on. After the 20-30 minutes of room temperature pumping the sample chamber valve and vapor port valve are closed and the SI-EGA experiment begins.

Stepped Isothermal Evolved Gas Analysis Experimental Method

The sample temperature is raised to 30 °C with the temperature controller, heating mode, set to normal. The sample is given five minutes to heat up and equalize with the temperature of the sample holder and heat sink. At the end of five minutes,
the main valve is closed, the sample port valve is opened and the sample is exposed to
the evacuated vacuum chamber for one minute. Pressure readings record the
desorption process. The sample port valve is then closed, the main valve is opened,
and the vacuum chamber is pumped down to its base pressure. When the vacuum
chamber reaches its base pressure (<5 seconds) the main valve is closed and the
sample port valve is opened for one minute. At the end of the nth exposure to
vacuum, the sample is heated 10 °C to the next temperature step. The sample is
allowed five minutes for the temperature to equalize with the sample holder and heat
sink. The exposure to vacuum routine is then repeated. The entire routine is repeated
until 160 °C is reached or no more water is observed desorbing from the sample.

**Variation in Number of Expansions**

Variation in the number of expansions was examined to see what effect the
number of expansions had on the results of an SIA-EGA experiment. The variation in
number of expansions was done for NaX. Experiments were conducted using 2, 4 and
6, 1-minute expansions into the vacuum chamber. All other experimental conditions
were identical.

**Variation in Duration of Expansion**

The time that the sample is exposed to vacuum determines how much water
will desorb from the sample. It was necessary to decide on an expansion time that
would allow the maximum water desorption in the minimal amount of time. The
variation in duration of expansions was done for NaX. Experiments were conducted
using 10 and 60 second expansions into the vacuum chamber. All other experimental conditions were identical.

**Temperature Steps**

The change in temperature between temperature steps was chosen to expedite the experiment. The sample temperature controller is only accurate to ±1 °C. So 10 °C temperature steps were chosen. Smaller steps would be acceptable but would make the experiment longer. Larger temperature steps would make the experiment shorter.

**Temperature Range**

The temperature range of room temperature to 160 °C was chosen because of the limitations of the instrument. The viton o-rings are rated at a maximum sustained temperature of 150 °C. The sample is heated 10 °C past the sustained max temperature when water was observed desorbing at 150 °C. Higher temperature o-rings are available, if needed.

**Determining the Amount of Water in the Zeolite Sample**

The amount of water initially present after pumping at room temperature can be determined from the pressure measurements made at constant T and V. The ideal gas equation

\[
n(18.015 \text{g/mol}) = \frac{PV}{RT}, \quad (5)
\]

was used to calculate the number of milligrams of water desorbing from the zeolite powder. The pressure rise curves are converted to weight loss curves with Equation 5.
The total amount of water in the sample at the beginning of a SI-EGA experiment serves as the starting point of the weight loss curves.

The area under the weight loss curves is calculated using the trapezoid rule for integration (20).

\[ \int_a^b f(x) \, dx \approx \sum_{i=1}^{n} \left( \frac{f(x_i) + f(x_{i-1})}{2} \right) \Delta x \]  

Data and Calculations

If intracrystalline diffusion is taken as the rate determining step, the temperature dependence of the effective diffusivity \( D_e \) can be evaluated with Equation 2 (17,18). The effective diffusivity refers to the average diffusivity value that is a result of diffusion from a number of different sized particles. \( A_a \) and \( E_a \) are the preexponential factor and the apparent activation energy, respectively, for the diffusion process (17). See Appendix 5 for explanation of the equations. The parameter \( D_e / R_c^2 \) is the effective diffusivity divided by the zeolite crystal radius. Since the powder can be thought of as an aggregate of microcrystals the sizes of which are not easily measurable and therefore the value of the crystal radius is unknown. Thus the effective diffusivity is not calculated but instead the values of the parameter \( D_e / R_c^2 \) are reported (17).

For a series of expansions total area under the weight loss curves obtained on the \( n \)th expansion is given by

\[ A_n = A_0 \exp \left( n t_e (D_e / R_c^2) \right). \]
Where \( A_n \) is the area under the \( nth \) desorption curve, and \( t_e \) is the time that the sample is exposed to the vacuum chamber. This equation requires that the decrease in area under a series of isothermal desorption curves will be exponential in nature. The exponential behavior of the change in area under a series of desorption curves is illustrated in Figure 13b. A plot of \( \ln(A_n) \) versus \( nt_e \), the total time the sample has been exposed to vacuum chamber at temperature \( T_e \), will give the parameter \( \frac{De}{Rc^2} \) which is similar to the rate constant \( k \) and has the units sec\(^{-1}\). An Arrhenius plot of Equation 2 will give a line with a slope equal to \(-\frac{E_a}{R}\), where \( R \) is the gas constant.

**Experiments**

The experiments conducted on each of the three zeolites consisted of three experimental routines. One, four, 10-second expansion routine at each temperature was performed on each zeolite. The zeolites were then investigated with three, four, 1-minute expansion into the vacuum chamber at each temperature. The last method of investigation was a five hour expansion into the vacuum chamber at 80° C.
Chapter 8. Results

Adsorption

The amount of water necessary to saturate a 50-mg zeolite powder sample was calculated from the manufacture’s data sheet that was provided with the zeolite samples (21). A calculation was carried out for zeolite 13X, which holds the most water of all the zeolites under investigation. The amount of water calculated for 13X was used for all zeolite adsorption experiments to insure saturation of the zeolite powder with water vapor.

Water was introduced through the vapor port. After the water had been heated to the vacuum chamber temperature, the water was allowed to expand into the evacuated vacuum chamber and adsorb onto the zeolite sample. All zeolite samples were given 30.0 minutes to adsorb water. The weight gain curves, for water adsorption, are illustrated in Figure 8. The time allowed, for adsorption was determined by the shape of the adsorption curves. The adsorption curves show that the uptake of water is rapid for the first few minutes and gradually slows down. By 30 minutes the uptake of water is negligible.

Desorption

Desorption experiments were conducted in the temperature range from room temperature to 150°C. When necessary the temperature was raised to 160°C. The size of each temperature step is variable and selected to suit the experiment and
sample under investigation. For the experiments in this thesis the change in
temperature between temperature steps was chosen to be 10° C. A temperature
change of 10° C was large enough to enable the experiments to proceed at an
acceptable pace. A smaller temperature change could be used to achieve similar
results.

The time to heat a sample from one temperature step to the next higher
temperature step was five minutes. The sample heater required approximately three
minutes to increase the sample holder temperature to the next higher temperature
step. The remaining two minutes allowed the sample temperature to equalize with the
sample holder/heat sink temperature.
Removal of Initial Water by Room Temperature Pumping

The removal of initial water was accomplished by pumping on the zeolite powder sample at room temperature (22-23°C). The initial water is water that can desorb easily without having to pass through many unit cells. This water may be from or near the surface of the crystallite or from cracks in the crystallite. For a given zeolite, the time necessary to remove the initial water had to be estimated by trial and error. Removal of all 30°C and 40°C water was the criteria used to decide the length of time to pump on the sample at room temperature. The effect of pumping on a sample at room temperature, for differing lengths of time is shown in Figure 9.

Graph 9a shows a SI-EGA experiment that was not pumped on at room temperature. The graph shows a large amount of water desorbing from the sample at room temperature. A large amount of water also desorbs at 30°C and 40°C. It is not until 50°C that the amount of water desorbing reaches a minimum and the amount of water desorbing begins to increase. This graph was made with two, 1-minute expansions at each temperature.

Graph 9b shows a room temperature pump time of 30 minutes. The 30°C and 40°C water has been removed. This pump time was used for both NaX and NaY. CaX was pumped on at room temperature for 20 minutes to remove the 30°C and 40°C water. The plot also shows that a substantial amount of water is left in the zeolite after the room temperature pumping has been completed. The maximum desorption temperature for this plot is 160°C. This increase in temperature over 150°C was necessary to remove the remaining water that did not desorb at 150°C.
Figure 9. Effect of pumping on a sample at room temperature. Graphs show pressure changes associated with each expansion into the vacuum chamber. Total pressure is proportional to amount of water desorbing.
Graph 9c is the result of pumping on a zeolite sample for 60 minutes at room temperature. Doubling the pump time has removed the 50°C and 60°C water completely. It also shows that the overall amount of water desorbing at each temperature has decreased compared to the 30-minute room temperature pumping plot. The result is a graph that is smaller in magnitude at each temperature and shows the sample has lost all of its water by 140°C.

Variation in the Number of Expansions

The experimental method under investigation consists of a number of expansions into vacuum, at a series of increasing temperatures. The number of expansions and time of each expansion is variable and must be decided upon before the experiment.

A series of experiments were conducted to determine the effect of changing the number of expansions. A two, 1-minute, a four, 1-minute, and a six, 1-minute expansion experiment was performed for each zeolite. Except for the number of expansions at each temperature the experimental conditions were identical.

Figure 10a is a bar graph of the total pressure change at each temperature. It was constructed by summing the pressures of each series of expansions at each temperature. Two trends appear in Figure 10a. First, with an increasing number of expansions at each temperature, the temperature at which the maximum desorption occurs moves to lower values. The six, 1-minute expansion routine has the lowest
Figure 10a. 2, 4, and 6, 1-minute expansions at each temperature. Each bar represents the total pressure change at each temperature.

Figure 10b. Arrhenius plots of 4 and 6, 1-minute expansions at each temperature.

The temperature of maximum desorption at 70° C. The four, 1-minute expansion routine has moved the maximum desorption temperature to 80° C, and finally the two, 1-
temperature of maximum desorption at 70° C. The four, 1-minute expansion routine has moved the maximum desorption temperature to 80° C, and finally the two, 1-minute expansion routine has increased the maximum desorption temperature to 90° C. The second trend in the bar graph is in the decreasing amount of water remaining at higher temperatures with increasing number of expansions at each temperature. The two, 1-minute expansion routine shows water desorbing at 160° C. As the number of expansions are increased the amount of water remaining at higher temperatures decreases. The four, 1-minute expansion routine shows no more water desorbing at 150° C, and with a six, 1-minute expansion routine no water is observed desorbing above 120° C.

The effect of varying the number of expansions on the final result is illustrated in Figure 10b. The graph shows the Arrhenius plot used to calculate the apparent activation energy for desorption from a zeolite powder. The two, 1-minute data was not included because two expansions at each temperature does not produce enough points to accurately determine the values of $D_e/R_e^2$, of which the Arrhenius plot is constructed.

Figure 10b shows that the four, 1-minute plot is spread over a wider temperature range and has a s-shape, where as the six, 1-minute plot has a more narrow temperature range and is almost linear. The shape of the Arrhenius plot determines the apparent activation energy. This plot shows that with six, 1-minute expansions at each temperature the calculated value for the apparent activation energy will be larger than for a four, 1-minute expansion routine.
Variation in the Duration of Expansions

The duration of expansion into vacuum has also been investigated. A four, 10-second and a four, 1-minute, expansion routine experiment was performed. Except for the duration of expansion time the experiments were identical. Figure 11a shows the total pressure change at each temperature, for the two different expansion times, with the same number of expansions at each temperature. The temperature of maximum desorption changes with the duration of the expansion. The four, 10-second expansion routine has a maximum desorption temperature of 90° C. And also shows water desorbing at 160° C. The 50° C bar is missing from the four, 10-second graph due to computer problems encountered during the experiment. The portion of the bar graph corresponding to the four, 1-minute expansion routine has a maximum desorption temperature of 80° C, and shows no more water desorbing above 150° C. The magnitude of desorption at each temperature is larger for the four, 1-minute plots, than that of the four, 10-second plot.

Figure 11b illustrates the end result of different expansion times with the same number of expansions at each temperature. The Arrhenius plot has a s-shape for both the four, 10-second and four, 1-minute expansion routines. The plot shows that the duration of expansion into the vacuum chamber is not as important as the number of evacuations. The shape and slope of the plots are similar and suggest that a four, 10-second expansion routine may be sufficient to determine the parameters of desorption.
Figure 11a. 4, 10-second and 4, 1-minute expansions at each temperature. Each bar represents the total pressure change at each temperature.

Figure 11b. Arrhenius plots of 4, 10-second and 4, 1-minute expansions at each temperature.
Visual Condition of Powder Sample at each stage of Experiment

The zeolite powder shows transformation from a finely divided powder to a clumped powder during a typical SI-EGA experiment. When a sample of zeolite powder is placed in the sample holder it has a fine powder appearance. The powder is distributed on the bottom of the sample holder by tapping the sample holder on the desktop. The tapping of the sample flattens the powder out into a uniform thickness and spreads the powder evenly over the bottom of the sample holder. After a SI-EGA experiment has been completed the powder has a clumped appearance. Appendix 13 shows the condition of the zeolite powder at each stage of a SI-EGA experiment. It is apparent that after the initial pumping on the sample at 23 hours at 150° C, the powder has become clumped in appearance. The zeolite powder retains this clumped appearance for the remainder of the adsorption and SI-EGA desorption experiment.

Shape of Weight Loss Curves, $D_e/R_e^2$ Plots, and Arrhenius Plots

The shape of the weight loss curves is not consistent with first order desorption kinetics. Figure 12 shows a typical experimental weight loss curve and a calculated, first order desorption curve. The two curves begin to deviate significantly within a few seconds. The reason the initial part of the experimental weight loss curve appears to be first order can be explained by viewing a pressure rise curve for the expansion of water vapor out of the sample holder and into the vacuum chamber (Appendix 10). The pressure rise curve in Appendix 10 shows that a short period of
time is necessary for the water vapor to expand into the vacuum chamber and cause a response by the pressure transducer. The nature of the expansion is exponential. The expansion in itself produces desorption curves that appears to exhibit exponential desorption behavior initially, but the shape of the initial part of the desorption curve is a direct result of the instrumental design and method. As desorption proceeds the desorption curve becomes linear. For this reason the area under a series of desorption curves is used to determine desorption parameters, and not the individual desorption curves.

To calculate the parameter $D_e/R_e^2$, the area under a series of weight loss curves are plotted against the time that the sample is exposed to the evacuated vacuum chamber. Figure 13a shows a typical plot of $\ln(\text{Area})$ versus $t_e$ for the zeolites.
studied. The slope of the plot is equal to the parameter, $D_e/R_e^2$, at that temperature. A least squares best-fit line through all the points was used to estimate the value of $D_e/R_e^2$.

The change in area under a series of desorption curves in illustrated in Figure 13b. The change in area under a series of desorption curves taken at temperatures where substantial desorption is occurring is exponential in nature. Figure 13b shows that with each subsequent expansion the amount of water desorbing from a zeolite sample becomes less and less. This is the basis for determination of the parameter $D_e/R_e^2$ and the curvature of the plots suggest that modeling the decrease in area as exponential is valid. This plot was made from an experimental routine of 16, 30-second expansions at each temperature.

The values of $D_e/R_e^2$, are used to construct an Arrhenius plot of the parameter $D_e/R_e^2$ versus reciprocal temperature. Figure 14 is a typical Arrhenius plot. All Arrhenius plots with the exception of the plot for the six, 1-minute expansion routine have a s-shape. The plot has three distinct regions. A low temperature, middle temperature and high temperature region. The low temperature region (region 1) consists of desorption temperatures of 50 °C to 70 °C. In this region the water is beginning to desorb but has not reached a steady rate of desorption. The slope is larger than the middle temperature region, but does not have any physical meaning. The middle temperature region (region 2) corresponds to water desorbing in the range of 80 °C to 110 °C. This region of the graph represents a constant rate of desorption and is used to calculate the apparent activation energy, using Equation 2.
Figure 13a. Typical zeolite plot of \( \ln(\text{Area}) \) versus time. Slope of plot is equal to \( D_e/R_c^2 \).

Figure 13b. A Plot of area under successive desorption curves. Plot shows that the decrease in area under successive desorption curves is exponential in nature.
Figure 14. Idealized Arrhenius plot of $D_e / R_c^2$ versus inverse temperature

1 - *(Low Temperature)* Change of rate of desorption changing at each temperature step. Low temperature water has been removed by room temperature pumping. The plot is not linear and does not obey the diffusion equation (Equation 2). As the temperature is increased the plot becomes linear.

2 - *(Constant Desorption)* The water desorbing is from interior zeolitic cavities. The change in rate of desorption constant and the plot has become linear. Water desorption is diffusion controlled and the plot obeys the diffusion equation.

3 - *(High Temperature)* Decrease in rate of desorption as water available for desorption becomes less and less. The amount of water desorbing is small and does not obey the diffusion equation.
A least squares best-fit line, through the points in region 2, is used to calculate the slope of the region. The slope divided by the gas constant R, gives the apparent activation energy $E_a$ for the desorption process. The last region (region 3) is has a similar slope to that of region 1. The large slope is due to a rapid change in the amount of water remaining in the zeolite powder. The last points represent the removal of the remaining water, and the slope is a product of the water available for desorption becoming less and less. The slope of region 3 does not have any physical meaning.

Appendix 13 contains all the Arrhenius plots for the values listed in tables 1 and 2. All of the plots have a similar shape. The middle region of each plot was used to determine the apparent activation energy, $E_a$ and preexponential factor $A_a$ for the three zeolites investigated.

**Experiments**

Each zeolite (NaX, NaY, and CaX) was studied with three different expansion routines. First a four, 10-second expansion experiment was conducted. Then a series of three experiments with a four, 1-minute expansion were performed on each zeolite. Finally a 5 hour expansion at 80 °C was done for each zeolite.

**Four, 10-second Expansions**

A four, 10-second expansion routine was performed on each zeolite. Figure 15a shows a typical series of weight loss curves for a four, 10-second expansion routine. The pressure rise curves were converted to water loss curves with Equation 5.
Figure 15a. Weight loss curves corresponding to 4, 10-second expansions.

Figure 15b. A plot of area under weight loss curves versus time, corresponding to 4, 10-second expansions. Slope of plot is equal to $D_o/R_e^2$. 
Figure 16a. Weight loss curves corresponding to 4, 1-minute expansions.

Figure 16b. A plot of area under weight loss curves versus time, corresponding to 4, 1-minute expansions. Slope of plot is equal to $Dv/R_e^2$. 
The area under each weight loss curve was calculated with Equation 6. Figure 15b is a graph of the area under the desorption curve versus time that the sample is exposed to the evacuated vacuum chamber. The slope of the ln(Area) versus \( t_e \) plot is equal to the parameter \( D_e/R_e^2 \). The slope of the plot was calculated by a least squares, best fit analysis. The plot exhibits a concave up shape.

**Four, 1-minute Expansions**

Four, 1-minute expansions were performed on each zeolite. Figure 16a shows a typical series of weight loss curves for a four, 1-minute expansion routine. The original pressure rise curves were converted to weight loss curves using Equation 5. The area under each weight loss curve was calculated with Equation 6. Figure 16b is a graph of the area under the desorption curve versus time that the sample is exposed to the evacuated vacuum chamber. The slope of the ln(Area) versus \( t_e \) plot is equal to the parameter \( D_e/R_e^2 \). The slope of the plot was calculated by a least squares, best fit analysis. The plot exhibits a concave up shape.

**Desorption Parameters**

The desorption parameters calculated from the experiments conducted on the EGA instrument, using a SI-EGA method are listed in Tables 1 and 2. Table one lists the apparent activation energy for a four, 10-second, a four, 1-minute, and a six, 1-minute expansion routine and two related dynamic techniques. The energy values calculated from the four, 10-second and the four, 1-minute expansion routines are in agreement. The energy value calculated for a 6, 1-minute expansion routine is more than 2 times
as large as those calculated with four expansions at each temperature for NaX. The
reason for the large value is due to the shape of the Arrhenius plot (Figure 10b). With
6 expansions at each temperature the middle temperature region of the Arrhenius plot
becomes compressed into one or two data points on the plot. This creates a plot that is
linear with a large slope and produces an abnormally high, energy value. The energy
values calculated from the SI-EGA method show the same trends as the values
derived by other non-isothermal methods. CaX has the largest apparent activation
energy of all the Zeolites studied. The apparent activation energy for NaY is in
between those of CaX and NaX.

Table 2 lists the values calculated for the preexponential factor using the SI-
EGA method. The values vary for each expansion routine but do exhibit the same
trend as the energy values with CaX having the largest values and NaX having the
smallest values. Again the value for the 6, 1-minute expansion routine is abnormally
high.

Table 1. Apparent activation energy for diffusion, $E_a$ for Zeolites NaY, NaX, and CaX from
SI-EGA and other thermal analysis techniques.

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>4/10-second kJ/mole</th>
<th>4/1-min kJ/mole</th>
<th>6/1-min kJ/mole</th>
<th>DTA kJ/mole</th>
<th>TG (22) kJ/mole</th>
<th>NMR (24) kJ/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaY</td>
<td>33 ± 3</td>
<td>34 ± 3</td>
<td></td>
<td>18.7(23)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaX</td>
<td>18 ± 4</td>
<td>16.9 ± 0.4</td>
<td>51 ± 3</td>
<td>15.5(22)</td>
<td>18.0</td>
<td>28.9</td>
</tr>
<tr>
<td>CaX</td>
<td>42 ± 3</td>
<td>40 ± 1</td>
<td></td>
<td>21.3(22)</td>
<td>28.5</td>
<td>28.5</td>
</tr>
</tbody>
</table>

Table 2. Comparison of preexponential factor $A_a$ (sec$^{-1}$) values for Zeolites NaY, NaX, and
CaX.

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>4/10 second</th>
<th>4/1 minute</th>
<th>6/1 minute</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaY</td>
<td>33 ± 3</td>
<td>156 ± 121</td>
<td></td>
</tr>
<tr>
<td>NaX</td>
<td>3 ± 3</td>
<td>0.5 ± 0.1</td>
<td>6000 ± 3</td>
</tr>
<tr>
<td>CaX</td>
<td>966 ± 3</td>
<td>744 ± 295</td>
<td></td>
</tr>
</tbody>
</table>

**explanation of $A_a$ in Appendix 15**
One, 5-hour Expansion

Figure 17 shows the long term desorption behavior for each zeolite. The graph represents a five hour desorption of water from a zeolite powder at 80 °C. The plot shows that for each zeolite the long term desorption is constant. The constant desorption suggests that the controlling mechanism for desorption of water from these three zeolites is diffusion. The equations next to each desorption plot were calculated from a least squares, best-fit analysis of each plot. Each desorption plot has a different slope, which is consistent with the different energy values of desorption of each zeolite studied.

Figure 17. Long term desorption behavior of zeolites. Plot shows different slope for each zeolite.
Chapter 9. Error analysis

Error in Pressure

The accuracy of the pressure gauge is ±0.5% of reading. The error associated with the computer taking a pressure reading is ±5 \times 10^{-3} \text{Torr}. The pressure reading is an average of the sum of 1000 digital words acquired by the data acquisition card. The data acquisition card has an accuracy of ±1 bit or ±0.01% of reading. The maximum error associated with a given pressure measurement is ±5 \times 10^{-3} \text{Torr} (Appendix 5).

Error in Volume

The error in volume was determined by calculating the standard deviation of the mean. The error in the volume of the main chamber is ±1.2 \times 10^{-3} \text{ml}.

Error in Temperature

The temperature readout has an accuracy of ±1 °C. The temperature readout records the temperature of the vacuum chamber by way of the data acquisition card, which has an accuracy of ±0.01% of reading. The maximum error associated with a given temperature measurement is ±1 °C. The CN7600 temperature controller has an accuracy of ±0.25% of temperature span and of ±1 °C of displayed temperature.
Error in Water Amount

The amount of water desorbing from a zeolite sample is calculated using Equation 5. The determination of the maximum error associated with the calculation of the weight was determined by taking the total differential of Equation 5 (Appendix 7). The maximum error is $\pm 2.5 \times 10^{-3} \text{ mg}$. 

Error in Area under Weight Loss Curve

The error associated with the calculation of the error is estimated by the error in the trapezoidal rule (20). The estimation was based upon $f(x) = e^x$. Although the desorption curves do not exhibit 1st order behavior, this equation gives an estimate of the error. An example error calculation is given in Appendix 8. The error is less than $\pm 1\%$ of total area under a desorption curve.

Error in $A_a$ and $E_a$

The error associated with the determination of $A_a$ and $E_a$ is calculated from the least squares determination of the best-fit line and the error associated with the slope and y-intercept (Appendix 9).

Error in Time

The error in the timing is the error associated with the PC timer. The time is kept track of by subtracting the time the computer reads (in ms) at the start of desorption and subtracting it from the computer time at the end of the desorption event. Therefore the accuracy is the same as the accuracy of the onboard PC clock.
Chapter 10. Discussion

The aim of this project was to develop a method of thermal analysis based on desorption of water into a vacuum chamber, and to build an instrument that would allow the method to be investigated. It was proposed that the new method would provide more meaningful results than other dynamic thermal analysis methods.

The results of the final experiments have been compared to results made with other dynamic techniques. Many interesting aspects of thermal analysis and zeolites were discovered while reviewing the literature.

The data collected from a SI-EGA experiment can be analyzed on the basis of the shape and nature of the desorption curves, the $D_e/R_c^2$ plots and the Arrhenius plots. Desorption experiments were designed to optimize the curves and plots of the SI-EGA method. The experiments included one, four, 10-second routine, three, four, 1-minute routines, and a single 5 hour expansion. During the review of the literature in preparation for the investigation of the EGA and SI-EGA much information was learned concerning instrumentation and electronics.

Comparison of Results

The results obtained with the SI-EGA method may not be as precise as some dynamic methods. However, the problems associated with using a dynamic method have been overcome by employing a SI-EGA method. The trend in the SI-EGA results agree with those obtained from both TG and DTA methods.

Due to the limitations of the EGA instrument, the results presented in this paper may not be as precise as the results from other methods such as TPD or TG.
This is primarily due to the error associated with the pressure measurements used to calculate the SI-EGA results. The precision of the instrument could be improved with both more accurate pressure transducers and temperature measurement devices. However it remains true that dynamic techniques are not as reliable as isothermal techniques.

The validity of the kinetic parameters obtained with dynamic techniques have been questioned as to their value at an International Conference for Thermal Analysis (13). The suggestion by most authors is to perform isothermal experiments to verify the results of the non-isothermal experiments. It is generally accepted that isothermal techniques provide the most reliable information (41). Therefore the results obtained from the SI-EGA method should be an improvement over dynamic results.

The trend in the SI-EGA results as well as the values are in agreement with those obtained from dynamic techniques (Table 1). NaX show the best agreement, with the results of the TG and DTA methods. The value for the apparent activation energy, $E_a$ for diffusion of water through zeolite NaX is said to be like that through liquid water (29). The diffusion of water through water has an energy barrier of 19 kJ/mol which is very close to the $16.9 \pm 0.4$ kJ/mol calculated with the SI-EGA method.

Examination of the Literature

Before the investigation of thermal analysis and zeolites, in preparation for the development of the SI-EGA method, a large amount of information was gathered. With respect to thermal analysis the information dealt with the problems that effect
the different thermal analysis techniques and the difference between the techniques. The information relating to zeolites included the structure of the zeolites and the reactions taking place on the surface of the zeolite.

In order to determine whether the SI-EGA method had been attempted before, a number of thermal analysis books were read (2, 8, 10, 14, 22). These books dealt mainly with TG and DTA, but included less common techniques as well. The main problems with TG are heating effects and sample holder design. Thermogravimetry uses a microbalance to record the change in weight. This creates a situation were the sample holder is not in contact with the heater. The heat energy must travel through the carrier gas to the sample. This makes it harder to heat a sample evenly and to not have the balance disturbed by buoyancy effects. The recognition of drawbacks related to other thermal techniques such as TG, gave me confidence that the drawbacks of the SI-EGA method could be overcome.

Initially the desorption of water was assumed to be simple first order process. When it was apparent that desorption was not following first order reaction kinetics, a number of books on zeolites were read to further investigate desorption processes in zeolites, particularly NaX and NaY (17, 18, 24, 25, 26, 27, 29, 30). The investigation of desorption of water from zeolites uncovered the many industrial processes that use zeolites. These range from drying air streams, to chemical separations, to catalytic cracking of hydrocarbons. There are a wide variety of zeolites, varying in structure, Si/Al ratio and exchangeable cations.
Shape of Weight Loss Curves

The shape of the weight loss curves is influenced by both the vacuum chamber design and the nature of the sample under investigation. The area under a series of curves is used to plot \( \ln(\text{Area}) \) versus time of the sample is exposed the evacuated vacuum chamber, \( t_e \). The shape of the weight loss curves was examined to see if the desorption curve follows first order kinetics. Figure 12 shows an actual weight loss curve and a theoretical first order weight loss curve. The actual curve deviates from the theoretical curve almost immediately. There are two reasons for the deviation from first order behavior. First, the desorption process is diffusion controlled and does not follow first order reaction kinetics. The second reason for the immediate deviation from first order behavior is due to the design of the vacuum chamber. When the sample port valve is actuated the pressure that has built up in the sample holder during the heating of the sample must equalize the evacuated vacuum chamber. The pressure equalizes with a time constant that is unique to the shape of the vacuum chamber and the placement of the pressure transducers. An expansion with no sample present in the sample holder creates a pressure rise curve and calculated weight loss curve that looks exponential in shape. When a sample is present in the sample holder, the constant diffusion of water vapor out of the sample creates a curve that begins with an exponential-like loss of water, but becomes linear and diffusion controlled within a few seconds. Appendix 10 shows a pressure rise curve made with an empty sample holder. It illustrates how the shape of the initial portion of a pressure rise or a weight loss curve is primarily due to the action of opening the sample port valve and shows the time that it takes for the pressure
transducer to respond to a change in pressure. Upon opening the valve, the
equalization of the initial pressure within the sample holder with that of the evacuated
vacuum chamber causes the initial portion of the curve to be exponential. Therefore,
the initial portion of a weight loss curve is a product of the expanding water vapor
diffusing out of the sample and the equalization of the pressures between the sample
holder and the evacuated vacuum chamber. It has been determined that modeling the
weight loss curves would not provide the information needed to calculate the kinetic
parameters for the desorption process.

It has been suggested that water desorption from zeolites is first order (22,25). This may be the case for the actual breaking of the chemical attraction that the water molecule experiences within the zeolite framework, but is not the case for escape of the water molecule from the zeolitic crystallite. After the water molecule attains sufficient energy to break free of its attraction to the zeolite framework, the water molecule must then find a path out of the zeolite crystallite. It may lose its energy and be resorbed at another site. The molecule is not free to escape directly to vacuum and must diffuse out. The diffusion is assumed to be intracrystalline diffusion (15,16,17,18,26,27). Diffusion within the micropores of zeolites X and Y is temperature dependent and follows the Eyring expression for surface diffusion, Equations 2 and 3 (18).

The diffusion of water was confirmed with a five hour expansion for each zeolite. Figure 17 shows the five hour desorption behavior of the three zeolites investigated with the SI-EGA method. All three plots are linear over the 5-hour expansion, which is consistent with diffusion. If readsorption was occurring one
would expect to see some curvature to the weight loss curve, resulting from water vapor being readsorbed into the zeolite. No curvature was observed in the three five hour weight loss curves.

\( \frac{D_e}{R_e^2} \) Plots

The plots of \( \frac{D_e}{R_e^2} \) versus time exposed to the evacuated vacuum chamber are linear and confirm that the change in area under a set of weight loss curves is exponentially decreasing. Low and high temperature values of \( \frac{D_e}{R_e^2} \) are not reliable. In the low temperature region the amount of water desorbing is very small and the error associated with the measurement is large. The amount of water desorbing is not representative of significant desorption. In the high temperature range, the area, under a set of weight loss curves, decreases more rapidly than it does at lower temperatures. The rapid decrease in area is due to little or no desorption upon the 3\textsuperscript{rd} and 4\textsuperscript{th} expansion into the vacuum chamber. The small amount of water desorbing also has a large error associated with each measurement.

Arrhenius Plots

The values of \( \frac{D_e}{R_e^2} \) are used to construct an Arrhenius plot of parameter \( \frac{D_e}{R_e^2} \) versus reciprocal temperature (Figure 14). The shape of the plot is a result of the nature of the sample under investigation and the experimental method.

The middle region of the plot is used to calculate the apparent activation energy for diffusion, \( E_a \) and the preexponential factor, \( A_0 \). This region represents the temperatures at which a significant amount of water is desorbing from the sample.
Desorption in this region is assumed to be diffusion controlled. The temperature range of the flat region on the Arrhenius plots could be made larger by shortening the expansion times and decreasing the size of the temperature steps.

The apparent activation energy $E_a$ takes into account the physical restriction due to narrowness of the zeolitic pores and crystal size. And the slowing down of the desorption process due to the interaction of the diffusing water molecules with the acid sites and/or the cationic sites present on the walls of the pores (17).

The SI-EGA method was able to produce nearly equivalent apparent activation energy $E_a$ values with different expansion routines. Different samples and differently pretreated samples of the same zeolite often show large differences in diffusivity, but generally show little variation in diffusional activation energies. The most reasonable explanation of this behavior is that differences in sample pretreatment lead to somewhat different cation distributions and/or degrees of window blocking resulting from cation hydration effects. If a certain fraction of the windows are blocked, while those windows that remain open retain their original dimensions, one can expect to see a reduction in diffusivity with very little change in activation energy (18). The sample pretreatment in the SI-EGA experiment consists of dehydrating the zeolite sample under vacuum, allowing the zeolite to absorb water vapor at room temperature, then pumping on the sample at room temperature for 20 to 30 minutes.
Experiments

The SI-EGA methods used for the final experiments consisted of a four, 10-second expansion routine, a series of four, 1-minute expansions, and a 5 hour expansion.

Four, 10-second Expansions

The reason a single, four, 10-second expansion routine was performed on each zeolite was twofold. The primary reason was to determine if a 10-second expansion routine was long enough, to obtain reliable desorption data. The second reason was to investigate the initial desorption behavior of the zeolite.

The values calculated for the four, 10-second expansion routine are in agreement with the values derived from the four, 1-minute expansion routine. For all three zeolites studied with the four, 10-second expansion routine, the values of the apparent activation energy $E_a$ are within the calculated error of the four, 1-minute expansion routines.

This routine was also used to investigate the beginning of the desorption process. The four, 10-second expansion shows that the beginning of the desorption curve is controlled by both the instrument design and the sample under investigation.

Four, 1-minute Expansions

Three, four, 1-minute expansion routine experiments were performed for each zeolite. This routine was chosen because it is relatively fast and the amount of data collected during a typical run is manageable. The error associated with the kinetic
parameters is reduced with longer expansion times. The results of the experiments show good agreement between apparent activation energy $E_a$ values.

Two factors were considered when choosing an expansion routine that would characterize the desorption process. The routine had to be structured so as to make the experiment as short as possible and still provide reliable results. The four, 1-minute routine enabled an entire SI-EGA experiment to be completed within 3-4 hours. Having expansion times longer than one minute would make the experiment longer. Also, with a longer the expansion time, more data points must be collected. This creates a large volume of data points to work with and data manipulation becomes cumbersome.

An expansion time of one minute allows for the pressure change to be large enough to overcome the error associated with pressure measurements. The one minute expansion also maximizes the area under the desorption curve thus reducing the error associated with the calculation of the area under the curve.

The results of SI-EGA experiments conducted with a four, 1-minute expansion routine show good agreement between apparent activation energy, $E_a$ values. NaY, NaX and CaX have a apparent activation energies of $34 \pm 3$ kJ/mol, $16.9 \pm 0.4$ kJ/mol, $40 \pm 1$ kJ/mol respectively. The error was calculated by the standard deviation of the mean of three values. The relative error associated with the $E_a$ values has been reduced for both NaX and CaX. The error associated with NaY has not changed from that of the four, 10-second expansion routine. The energy values for all three zeolites agree with the results from the four, 10-second expansion
routines. The preexponential factor value for NaY, NaX, and CaX is $156 \pm 121$ sec$^{-1}$, $0.5 \pm 0.1$ sec$^{-1}$, and $744 \pm 295$ sec$^{-1}$ respectively.

The apparent activation energy is larger for zeolites NaY and CaX than for NaX (Table 1). The trend in energy values can be explained on the basis of the interaction of the water molecules with the ions in the zeolitic crystallite. The pore sizes of all three zeolites are equal and do not influence the apparent activation energy of diffusion.

The sodium ion in NaX is has a charge of +1 and the calcium ion in CaX has a charge of +2. The presence of the calcium ions creates a more polar environment for the coordination of the water molecules. The increased attraction of the water molecule to the cation increases the energy needed for a molecule to escape from a zeolitic crystallite. The time that a water molecule spends coordinated with an ion as it desorbs from the zeolite can be thought of as a multi step adsorption desorption reaction that the water molecule must undergo as it travels out of the zeolite framework (17). The interaction of the water molecules with the cations plays an important role in the intracrystalline diffusion of water from zeolites.

The number of cations present in the zeolite has a large effect on the apparent activation energy for the diffusion of water. Zeolite NaX has approximately 86 sodium ions in each unit cell. NaY has approximately 56 sodium ions in each unit cell, yet the apparent activation energy for diffusion, $E_a$, is more than twice as large than that of NaX. The difference in energy values may be due to the ability of a water molecule to move from one cation to the next as it diffuses out of the zeolitic crystallite. In zeolite NaX, the abundance of sodium ions at relatively mobile sites
may allow a water molecule to migrate through the zeolite without having to
dissociate from sodium ions until it escapes from the crystallite. Zeolite NaY has
fewer sodium ions in each unit cell. Thus, a water molecule diffusing out of a NaY
crystallite would have to overcome the attractive forces of the water molecule to the
sodium ion, as it moved from one sodium ion to the next on its path out of the
crystallite. Repeated breaking of the attractive force of the water molecule to the
sodium ion would require more energy and is reflected in the larger energy value for
NaY. The apparent activation energy of diffusion for CaX can also be explained on
the basis of the cation population in the zeolite. CaX has approximately 45 cations in
each unit cell, which is less than both NaY and NaX. The apparent activation energy
for diffusion is larger for CaX than for NaY and NaX.

The Si/Al ratio plays a role in the polarity of the zeolite framework and
determines the number of ionic sites present in the zeolite. The Si/Al ratio is higher
for NaY than for NaX. The higher Si/Al ratio in NaY creates fewer ionic sites and
NaY has fewer cations per unit cell. As mentioned before the number of cations
present has a large effect on the apparent activation energy for diffusion, \( E_a \). This
model fits with the results obtained from the four, 1-minute expansion routine as well
as the four, 10-second expansion routines for zeolites NaY and NaX. This is also
consistent with results of ammonia desorption from zeolites obtained by Forni (17).

One, 5-hour Expansion

A five hour expansion at 80° C for 5 hours was carried out in order to verify
that the desorption from zeolite NaY, NaX, and CaX was diffusion controlled (Figure
17). The long term desorption plots of the three zeolites are linear. The linear nature of the plots suggest that diffusion is controlling the desorption process. It also suggests that no significant readsorption is taking place.

Instrumentation Findings

Visual Basic was studied as well as interfacing computers with measurement devices. Vacuum chambers and vacuum pumps were studied. Simple electronics and typical problems related to wiring and grounding electronic devices was also studied.

When the SI-EGA project was first proposed, the method of data collection was manual. From experiments conducted on the glass vacuum rack, before the EGA instrument was built, it was obvious that a computerized collection of data was necessary. Fortunately, a data acquisition card was discovered in the laboratory, and was used to interface the computer to the pressure gauge on the glass vacuum rack. When the EGA instrument was built, the pressure transducers as well as the temperature sensors were interfaced to a data acquisition card. The acquisition card was controlled with a software program written in visual basic. The programming language was learned from a programming book titled “Learn Visual basic in 21 days”. The book provided the foundation for the program. Many small programming tricks such as using API functions were discovered from searching visual basic web sites on the world wide web.

Vacuum chamber design and construction was learned by talking to engineers and reading books and manuals on vacuum component design and construction (31,32). Leak detection was self taught by reading the department leak detector
manual. The repair of vacuum pumps was also self taught by reading vacuum pump manuals and repair guides found on the world wide web.

The knowledge of electronics and instrumentation was obtained from reading and studying a number of electronics text books (33,34,35). The use and wiring of electronic devices was learned. The minimization of ground loops, and the extensive use of AC to DC converters were important in the construction of the EGA instrument.
Chapter 11. Conclusions

The goal of designing a new experimental method and building an instrument to test the new method was accomplished. An EGA instrument was designed and built. A method of SI-EGA was developed and investigated. The EGA instrument produced repeatable results on three different zeolites. The SI-EGA method proved to be a valid method for determining the kinetic parameters for desorption of water from zeolites. The SI-EGA provides reasonable agreement with non-isothermal kinetic data derived from TD and DTA techniques. The error associated with the SI-EGA method could be improved with modifications to the EGA instrument. The investigation did not provide any conclusive evidence that the method is more accurate than current non-isothermal methods, but because the SI-EGA method is an isothermal method the results should be an improvement over non-isothermal results. The SI-EGA method is a fast and simple tool for analyzing desorption from zeolites. The method could also prove valuable in the investigation of other sorbent sorbate systems.

Many lessons were learned from the design and construction of the instrument. Important lessons were also learned from the investigation of the method. During the design phase of the method and instrument it was determined that a planning was very important. Obstacles such as sample movements and back streaming of pump oil illustrated the problems one may encounter if proper planning is not carried out. The investigation of the method also proved to be a learning experience. Determining the best way to test the method helped to better understand what was occurring and why. The most important lesson learned was that it is vital to know the background information on the material that is under investigation. If it had
been known that desorption from zeolites is diffusion controlled at the beginning of the planning process, a lot of time could have been saved by not investigating the first order behavior of the desorption of water form zeolites.

Suggestions for Future Work

The SI-EGA instrument can be improved. The addition of more accurate pressure transducers would allow for better determination of weight loss curves. The automation of the manual valves would also make the instrument easier to use and allow less opportunity for user mistakes. Also, allowing the computer to actuate the pneumatic valve would allow for the more precise time keeping. The addition of a temperature controller for the vacuum chamber would allow for more control over the temperature of the vacuum chamber. A more accurate temperature measurement device would also improve the EGA instrument and allow for more precise determination of kinetic parameters.

Modifications to the software would also improve the EGA instrument. Currently the software does not manage the windows global memory and the program may crash if care is not taken. Controlling the memory and writing the data values directly to a file may help to eliminate memory allocation problems.
Appendices

Appendix 1. Data Acquisition Software Programs

The software program that controls the data acquisition card was written with Visual Basic 5 for windows. The main points considered in writing the program were timing of the data acquisition and memory allocation. The program consists of 2 main sections (Appendix 1). The first section consists of routines that provide for the user interface windows when the program is started. The second section consists of two parts that contain all the variables and functions that are necessary to run the data acquisition card and to use the computer operating system components.

The program was written with Visual Basic because the author was familiar with the programming language and because the data acquisition card came with drivers for Visual Basic. The software can be written in other languages as well, such as C++ and Delphi. The data acquisition program copies the digital word from the DAS-8 card to a Windows memory buffer. When correct amount of samples have been collected the program averages the samples, converts the average to a pressure or temperature value and records the value on a Microsoft excel spreadsheet. The data acquisition program also keeps track of the time and the number of expansions. The program allows the user to view real-time pressure and temperature measurements.

The main points considered when writing the data acquisition programs are the timing of the computer, the sampling speed of the data acquisition card, and the management of windows global memory. An accurate clock is needed to time the length of each expansion. There are several ways to keep time. Visual Basic provides a function called *Timer* that initiates a routine on a millisecond time scale. The *Timer* function does not initiate the routine at the exact time that the *Timer* was set to but is controlled by the speed of the computer and size of the program. This function was used only in sub-routines were it was necessary to check on a background operations. To check on background operations the *Timer* function only needs to be near the correct timescale. For example, when the data is being collected during a typical scan, the *Timer* function checks about 3-4 times a second to see if the scan has been completed.

Microsoft Windows API functions are used to keep track of time. The Windows API includes functions to control the smallest aspects of the operating system. API stands for application programming interface. An API is a set of functions you can use to work with a component, application, or operating system. The data acquisition program uses the API functions to get the time from the motherboard timer. This timer smallest increment is a millisecond. The program reads the time at the beginning of a scan and at the end then calculates the time elapsed. This in conjunction with the sample rate was used to make the program take samples at a specific rate.

The DAS-8 card is rated at a maximum sample rate of 40,000 A/D samples/second. The actual rate is dependent on both the speed of the computer CPU and data bus. Through trial and error, the maximum sample rate was determined to be approximately 32,000 samples/second. The reason so many samples each second were needed is each sensor is sampled 1000 times each second. The average of the
1000 digital words is then used to compute the appropriate pressure or temperature value. If the data acquisition program is set to one sample (A/D conversion) each second, the data acquisition card actually takes 3,000 samples each second (1000 samples for each sensor). If a sample rate of 10 samples each second is required then the data acquisition card actually takes 30,000 samples a second, which is near the limit of the data acquisition card.

The most critical aspect of the data acquisition program in the management of windows global memory. The diver files that control the data acquisition card contain a function to set aside a specified amount of windows global memory to store the digital words during an A/D scan. The specified size of the memory must be large enough to hold the entire scan. After the scan the digital words are averaged, changed to the appropriate value and written to an Excel spread sheet. The program works fine until the spreadsheet fills up the remaining global memory. Once the memory is full the next A/D scan causes a memory error (blue screen of death) and data acquisition program crashes and closes. The Excel spreadsheet is not effected and the data recorded before the crash is not lost. The number of samples converted to a value and written in the spreadsheet are limited to about 2,000 samples. Memory problems are only encountered during a continuous data acquisition. During a normal SI-EGA experiment the data is saved at each temperature step, and memory allocation problems are not encountered.

A typical EGA-SIA experiment has expansion times in the order of 1 minute, and it not effected by memory problems. The only experiments affected by the memory allocation problems were the long-term expansion experiments.

The first section of the program consists of two routines. The first routine is called **parameters**. It consists of a user interface window that allows the user to adjust how many samples are taken each second, the total length of each expansion and the length of time to heat the sample between temperature steps. After all the parameters are set the program brings up a second user interface window. This window is controlled by the second routine. It allows the user to collect data or to view the real time pressure and temperature measurements. If the user presses the collect data button the program loads an excel spreadsheet as an object (opens excel in separate window) and prompts the user to press start when ready. This section of code also has subroutines that keep track of the number of expansion at a particular temperature, the time elapsed during an expansion, and the time elapsed during the heating step.

The second section of the program contains two parts. The first part contains the variables and call functions necessary to run the data acquisition card. This part was supplied with the manufacturer driver files. The second part is similar to the first. It contains all the variables used in the first section of the program, and initializes the API call function used to take advantage of some of the operating system functions.

**Application of computers to pressure change techniques.**

Before the widespread availability of the Personal Computer (PC), many thermal analysis instruments recorded the experimental data with a plotter or by hand. This made the analysis of the TA curves tedious and laborious. Computers allow the data to be recorded directly, and software programs allow for manipulation of the data
in order to derive all of the necessary information. Computers also allow for a precise measurement of time and the recording of data from multiple devices simultaneously. This greatly increases the ease in which experimental data can be recorded and analyzed. The computer has also made it easier to design an instrument to perform a specific function and record data that would have normally been too laborious, for example the recording and manipulation of multiple desorption curves.

Data Acquisition Software

**Parameters Section**

Private Form_Load()
  frm pressure. Visible = True
  frm pressure. Enabled = False
End Sub
Public Sub cmdSetVariable_Click()
Dim Message As String
  'Message = "Invalid entry please input numbers"
  'ButtonsAndIcons = vbOKOnly + vbExclamation
  'Title = "Caution, invalid entry!"
  L = Val(txt Timer. Text)
  frm pressure. Enabled = True
  MemHandle& = cb WinBuf Alloc(6000 * 5) 'set aside memory to hold data
End Sub

**Pressure Section**

' Analog to Digital plus temp.
' Scan A/D channel 0 & 1 at specified rate
' Ground LL Ground pins 12-18 (for stability)
Option Explicit
Dim ADData%(0 To 6000) , array to hold the form values timer
Dim EXData%(0 To 6001) , array to hold the form values timer3
Dim ChanTags%(0 To 6001) 'channel tag for converted digital word
Dim Message As String 'message box text
Dim ButtonsAndIcons As Integer 'Buttons and Icons
Dim Title As String 'message box title
Dim Response As Integer 'yes or no
Private Sub Form_Load()
  tbl Time Remain = "Time Elapsed(s):"
  cmd Start Record. Enabled = True
  cmd Start Record. Visible = True
  Set xlsApp = Excel. Application 'open Excel
  m = 5 'starts excel at row 5
  d = 0 'time multiplier (calc)
f = 0 'time
  e = 0 'time multiplier (act)
  If xlsApp. Visible = False Then
    With xlsApp
      .Visible = True 'Show Excel
      .Workbooks. Add 'Create a new workbook
      g = 0
      End With
    End If
    Message = "Press Yes to Start Data Scan"
    ButtonsAndIcons = vbYesNo + vbQuestion
    Title = "SID Absorb Data Program"
    Response = MsgBox(Message, ButtonsAndIcons, Title)
    If Response = vbYes Then
      tbl Status. Caption = "Running"
      If g = 0 Then
        xlsApp. Cells(m, 1). Value = "Time (s)"
        xlsApp. Cells(m, 2). Value = "0-100 Torr"
        xlsApp. Cells(m, 3). Value = "Temp (C)"
        xlsApp. Cells(m, 4). Value = "0-10 Torr"
        g = 1
      End If
      lng Start Time = timeGetTime
      tmr Timerr. Enabled = True 'enable time timer
    End If
  End Sub
  Private Sub cmdStop_Click()
    tmr Timerr. Enabled = False
Private Sub cmdStopRecord_Click()
    ULStat% = cbStopBackground(BoardNum%) 'Stop A/D scan
    cmdStart.Enabled = True: cmdStart.Visible = True
    cmdStopRecord.Enabled = False: cmdStopRecord.Visible = False
    cmdQuit.Enabled = True
    cmdStartRecord.Enabled = True: cmdStartRecord.Visible = True
    cmdStopRecord.Enabled = False: cmdStopRecord.Visible = False
    cmdStartRecord.Enabled = True: cmdStartRecord.Visible = True
    cmdStopRecord.Enabled = False: cmdStopRecord.Visible = False
    ULStat% = cbGetStatus(BoardNum%, Status%, CurCount&, CurIndex&)
    If Status% = 0 Then lblStatus.Caption = "Idle"
    f = f + 1
    End Sub

Private Sub tmrTimer1_Timer()
    If f = L + e Then DataScan
    f = f + 1
    End Sub

Public Sub DataScan()
    CBRate = 10000 'number of samples to collect/chan/sec
    CBCount% = 3000 '# samples to collect
    Options = BACKGROUND + SINGLEIO 'collect data in BACKGROUND
    lngFinishTime = timeGetTime
    c = (lngFinishTime - lngStartTime) / 1000
    txtTime.Text = Str(c)
    ULStat% = cbAInScan(BoardNum%, LowChan%, HighChan%, CBCount&, CBRate&,
        Gain, MemHandle&, Options)
    tmrTimer3.Interval = 2000 'expt to fmd max
    tmrTimer3.Enabled = True
    lblStatus.Caption = "Running"
    lblTimerSet = L
    txtTime.Text = ""
    ULStat% = cbWinButToArray(MemHandle&, ADData%(0), 0, 3000)
    ULStat% = cbAConvertData(BoardNum%, 3000, ADData%(0), ChanTags%(0))
    if CurCount >= 3000 Then
        ULStat% = cbWinButToArray(MemHandle&, EXData%(0), 0, 3000)
        ULStat% = cbAConvertData(BoardNum%, 3000, EXData%(0), ChanTags%(0))
        tmrTimer3.Enabled = False
        UpdateData
    End If
    End Sub

Public Sub UpdateData()
    For Ex = 0 To 2999 Step 3
        ppdata = ppdata + EXData%(Ex)
        tdata = tdata + EXData%(Ex + 1)
        edata = edata + EXData%(Ex + 2)
    Next Ex
    m = m + 1 'remember row number m
    End Sub
d = d + 1  'd is counter during each run
ppdata = 0.22291 * (ppdata / 1000) - 0.43264
tdata = 0.05187 * (tdata / 1000) - 3.49604
tdata = 0.00243256 * (tdata / 1000) + 0.00479181
temperature.Text = Format$(tdata, "0.0")
temperature.Text = Format$(tdata, "0.0")
temperature.Text = Format$(tdata, "0.0")
xlsApp.Cells(m, 1).Value = c  'time sec in col 1
xlsApp.Cells(m, 2).Value = Format$(ppdata, "0.0")  'pressure in col 2
xlsApp.Cells(m, 3).Value = Format$(tdata, "0.0")  'temperature in col 3
xlsApp.Cells(m, 4).Value = Format$(tdata, "0.00")  'tc pressure in col 4
ppdata = 0
tdata = 0
tdata = 0
a = 0
End Sub

Section 2. Variables and Function

Part 1
'Startup.bas - Global constants, functions and variables

Option Explicit
Declare Function timeGetTime Lib "winmm.dll" () As Long
Global lngStartTime As Long
Global lngFinishTime As Long
Global g% 'keeps track of excel header
Global f%/o  'time summation variable
Global e% 'datascan interval multiplier
Global L% 'timer interval multiplier
Global data! 'digital word array tc pressure
Global pdata! 'digital word array pressure
Global tdata! 'digital word array
Global temperature 'variable for summation
loop
Global LowChan%  'first channel to acquire
Global HighChan%  'last channel to acquire
Global Options 'collect data in BACKGROUND continuously
Global Gain 'set the gain
Global FirstPoint& 'first point to transfer to array
Global m% 'timer interval variable
Global tdata! 'digital word array pressure
Global ppdata! 'digital word array pressure
Global tdata! 'digital word array
Global temperature 'loop variable
Global c% 'timer variable
Global g% 'write to excel variable
Global a& 'count to 10 variable
Global CBRate& '# samples per sec
Global CurCount& 'the total number of A/D samples to collect
Global CurIndex& 'pointer to first point in last scan
Global CBCount& 'total number of data points to collect
Global Status% 'status of background function in cbAInScan
Global ULStat% 'error message variable

Global MemHandle&  'handle for memory allocated
by cbWinBufAlloc()
Public Const BoardNum% = 0  'Board number
Global xlsApp As Excel.Application 'enable excel application
Public Sub Main()
frmPressure.Show
frmParameters.Show

Part 2

'Current Revision Number
Global Const CURRENTREVNUM = 5.04
'Error Codes
Global Const NOERRORS = 0
Global Const BADBOARD = 1
Global Const DEADDIGITALDEV = 2
Global Const DEADCOUNTERDEV = 3
Global Const DEADDADEV = 4
Global Const DEADDASHDEV = 5
Global Const NOTDIGITALCONF = 6
Global Const NOTCOUNTERCONF = 7
Global Const NOTDACONF = 8
Global Const NOTMUXCONF = 9
Global Const BADPORTNUM = 10
Global Const BADBOARDTYPE = 11
THIS SECTION HAS BEEN TRUNCATED
Appendix 2. Miscellaneous Parts Drawings (drawings are not to scale and all units are in inches)

STAINLESS STEEL ADAPTER FLANGE 2.75 CF x QF16

STAINLESS STEEL BAFFLE PLATES

STAINLESS STEEL SAMPLE HOLDER

STAINLESS STEEL PINCH RING (TYP)
Appendix 3. Zeolites

History
Naturally occurring zeolites that release water when heated and reabsorb it when cooled were first reported two and a half centuries ago. By the early 1930's, x-ray diffraction studies were revealing the zeolites as crystalline materials having within each crystal a system of precisely arrayed cavities and pores. In 1948, Union Carbide Corporation’s researchers became interested in the possible use of adsorption for the separation of atmospheric gases and other industrial uses. Recognizing both the limitations of the natural minerals and the potential of zeolite-type materials, Union Carbide set out to synthesize the pure zeolites and to develop economical methods of producing them. By 1953, more than 30 distinct pure zeolite species had been prepared (21).

Structure
Zeolites are a well-defined class of crystalline, naturally occurring, aluminosilicate materials. They have three-dimensional structures arising from a framework of \([\text{SiO}_4]^{4-}\) and \([\text{AlO}_4]^{3-}\) coordination polyhedra linked together. The frameworks are generally open and contain channels and cavities in which the cations and water molecules are located. The cations often have a high degree of mobility giving rise to facile ion exchange and the water molecules are readily lost and regained; this accounts for the well known desiccant properties of zeolites (29).

Zeolites \(X\) and \(Y\) both have similar aluminosilicate framework structures. The unit cells are cubic with a large cell dimension of nearly 25 A and contain 192 (Si,Al)O₄ tetrahedra. These tetrahedra are assembled such that the oxygen at each tetrahedral corner is shared with that of an identical tetrahedron (Si or Al). This corner sharing creates infinite lattices comprised of identical building blocks in a manner common to all crystalline materials (29). The framework structure contains the largest void space of any known zeolite and amounts to about 50 vol% of the dehydrated crystal (36). The Al ions (\(N_{Al}\)) in the unit cell of zeolite \(X\) vary from 96 to about 77. In zeolite \(Y\) (\(N_{Al}\)) is about 76 to 48 (36). The molecular composition of zeolite \(X\) and \(Y\) used in this EGA method are \(\text{Na}_86[\text{AlO}_2]_{86}[\text{SiO}_2]_{106}\) • x H₂O and \(\text{Na}_{56}[\text{AlO}_2]_{56}[\text{SiO}_2]_{136}\) • y H₂O respectively. The two zeolites are similar and differ only in their Si/Al ratio.

Dehydration and Adsorption
Molecular sieves retain adsorbates by strong physical forces rather than by chemisorption. When an absorbed molecule is desorbed by the application of heat or displacement by another material, it leaves the zeolite crystal in the same chemical state as when it entered (36). When water is removed from zeolite \(X\) or \(Y\) there is no change in the basic framework structure (29,36). The water molecules do affect the specific positions of the exchangeable cations, but they do not appear to have any primary structural function and can be removed reversibly without disrupting the framework structure. The desorption of water is continuous and no steps are seen in the pressure-temperature plots (36).
The crystalline solid remaining after dehydration is a highly selective adsorbent for gases and vapors. When exposed to gas or vapor, the zeolite cavities fill rapidly with the gas or vapor, and when the filling is complete no more adsorption occurs. Due to the interaction between the dipole of the water molecule with the charge on the zeolite structure, zeolitic cavities are essentially filled with water (36).

**Hydrated NaX, NaY, and CaX**

Faujasite, when fully hydrated contains about 235 water molecules per unit cell, distributed in the large supercages and small β-cages. Nuclear magnetic resonance (nmr) provides information on the state of water in hydrated zeolites. Water molecules in the larger zeolite cavities exhibit the same pattern as the isolated liquid, thus indicating that molecules in the centers of the large cavities do not occupy definite lattice sites or are exchanging faster than the NMR time scale. For hydrated zeolites with small and narrow cavities, the positions of the water molecules are better defined and coordination occurs with cations in the cavity. The cations in hydrated zeolites seem to be surrounded by as many water molecules as is spatially possible (25).

**Dehydrated NaX, NaY, and CaX**

In dehydrated zeolite NaX, a total of up to 96 monovalent cations occupy site I, II and III corresponding to a Si/Al ratio of one. The Na⁺ ions in dehydrated NaY occupy three sites. On average, 7.5 Na⁺ ions were found at site I, 30 Na⁺ ions in site II and 20 Na⁺ ions in site I’ (25). In dehydrated CaX all Ca²⁺ ions are located with high occupancy at two crystallographic sites. There are 16 cations at site I and 30 cations at site II (37).

**Cation Exchange**

The most important technique used to modify zeolites is ion exchange. The cations in zeolites exchange with other cations in aqueous solutions under reasonable conditions (36). Complete ion exchange of Na⁺ by Ca²⁺ in zeolite NaX can be achieved at 25° C (30). Cation exchange is accomplished by placing the zeolite in a solution of the cation to be exchanged in.

**Uses**

When water is removed from a zeolite the voids created within the framework can take in other molecules. This process is called sorption and zeolites are said to ‘sorb’ molecules into their void volume. Often sorbing molecules are called ‘guests’ within their zeolite ‘host’ (29). In both natural and synthetic zeolites a wide variety of internal channel and cavity assemblages can be accessed through the oxygen windows. The geometry of zeolites give them the ability to separate mixtures of molecules, on the basis of their effective sizes, hence their description as ‘molecular sieves’ (29,36).

Zeolites X and Y are used in industry to separate C₈ aromatics. They are also used to dry gas streams and in fluid purification (29,36). Drying by absorption is used in industry because it produces a drier liquid or gas than can be obtained by other methods. Molecular sieves are the ideal adsorbent to use whenever extremely dry streams are
required. Molecular sieves are the only adsorbents that can effectively dry streams at high temperatures (21).

Zeolites as a Simple Desorption System

A simple desorption system is a molecule desorbing from the surface of a solid. This EGA method is not sensitive enough to study monolayer coverage so gas desorption from a metal surface was not studied. Instead, desorption of water from a microporous solid was investigated. The investigation of microporous solids is directly related to the industry and technology. I consulted with Prof. Karl Seff of the University of Hawaii about which zeolite might have two differently adsorbed waters. A system with only two different waters would be a simple system to investigate. Dr. Seff proposed zeolite CaX which according to crystallographic data (37,38,39) has only 2 differently adsorbed, coordinated water molecules. I chose this zeolite as my simplest system and also investigated the closely related zeolites NaY and NaX. Zeolites NaX and CaX are identical except for their cations. NaX and NaY differ only in their Si/Al ratio, and therefore the number of sodium ions per unit cell, but are otherwise identical. These three systems were investigated using the SI-EGA method. The interaction of water molecules with the ionic sites and coordination of water molecules to ions in the zeolite framework play an important role in controlling desorption of water.
Appendix 4. Non-isothermal Kinetics (14)

The non-isothermal reaction kinetics equation is derived as follows:

The following chemical equation represents the desorption of water from zeolite NaX (13X):

\[ \text{Na-X} \cdot n\text{H}_2\text{O}(s) + \text{heat} \rightarrow \text{Na-X}(s) + n\text{H}_2\text{O}(g) \]

Rate of water desorption is given by:

\[ \frac{-d[A]}{dt} = k[A]^n \]  

(1a)

\( k = \text{specific rate constant} \)

Starting with the Arrhenius equation

\[ k = Ae^\left(\frac{-E_a}{RT}\right) \]  

(2a)

\( E_a = \text{activation energy} \)
\( A = \text{pre-exponential factor} \)

Inserting equation 2a into equation 1a gives

\[ \frac{-d[A]}{dt} = Ae^\left(\frac{-E_a}{RT}\right) [A]^n \]  

(3a)

which is an expression for non-isothermal kinetics.

The experimental parameters for equation 3a: [H\(_2\)O], \(-d[H\(_2\)O]/dt\), \(T\), \(t\)

For analysis one may take the logarithm on both sides of the equation to make the exponential disappear. In addition, one may differentiate both sides with respect to \(\ln[H\(_2\)O]\) to get an explicit equation for the reaction order \(n\).

\[ \frac{d \ln(- \frac{d[H\(_2\)O]}{dt})}{d \ln[H\(_2\)O]} = - \frac{E_a}{R} \frac{d\left(\frac{1}{T}\right)}{d \ln[H\(_2\)O]} + n \]  

(4a)
The constant to be calculated: $E_a$, n, $A$.

Problems of non-isothermal kinetics
1. Cumbersome mathematics.
2. Little sensitivity to changes in $E_a$, n, $A$
3. Cannot be sure of assumptions of equation 2, as a solution, check with isothermal experiments.
Appendix 5. Derivation of Kinetic Equations for the SI-EGA Method

The process of dehydration of zeolites belongs to the reaction type:

$$A_{(s)} \rightarrow B_{(s)} + H_2O_{(g)}$$

The desorption of water from zeolites is diffusion controlled (17,18,22). Intercrystalline diffusion is an activated process so that the diffusivity varies with temperature according to an equation of the Arrhenius form (18):

$$D = D_0 \exp \left(\frac{-E_d}{RT}\right)$$  \hspace{1cm} (5a)

where $D$ is equal to the diffusivity and $E_d$ is equal to the energy of diffusion. Another form of the equation proposed to describe the diffusion out of a bed of zeolite particles is (17,19):

$$\frac{D_e}{R_c^2} = A_a \exp \left(\frac{-E}{RT}\right)$$  \hspace{1cm} (6a)

Where $D_e$ is the effective diffusivity, and $R_c$ is the crystal radius. The zeolite powder is an aggregate of microcrystals and the crystal radius is not known. Therefore, the only parameters that can be calculated are $D_e/R_c^2$, $E_a$ and $A_a$ (17). $E_a$ is the apparent activation energy and $A_a$ is the preexponential factor for the diffusion process (19).

For a series of expansions, the area under the $n$th weight loss curve $A_n$ is given by

$$A_n = A_0 \exp \left(-\frac{nt_e}{\tau}\right)$$  \hspace{1cm} (7a)

Taking the natural logarithm of both sides gives

$$\ln(A_n) = \ln(A_0) - \frac{nt_e}{\tau}$$  \hspace{1cm} (8a)

A plot of $\ln(A_n)$ vs. $nt_e$ gives a line with a slope equal to $D_e/R_c^2$.

Taking the natural logarithm of both sides of Equation 6a, gives

$$\ln\left(\frac{D_e}{R_c^2}\right) = \ln(A_a) - \frac{E_a}{RT}$$  \hspace{1cm} (9a)

And a plot of $\ln(D_e/R_c^2)$ vs. $1/T$ will give a line with a slope equal to $E_a/R$ and intercept equal to $\ln(A_a)$.
Appendix 6. Error Associated with Pressure Measurements

**Precision**: used to describe the reproducibility of results.
**Accuracy**: the nearness of a measurement to its accepted value and is expressed in terms of error.

All errors are assumed to be random.

Accuracy of pressure transducer = \( \pm 0.5\% \) of reading.

Accuracy of Analog to Digital conversion = \( \pm 0.01\% \) of reading.

The standard deviation of the mean of 1000 A/D conversions is \( \pm 5 \times 10^{-3} \) Torr.

The standard deviation of the mean was calculated by taking 1000 samples with the pressure constant. The 1000 readings were then averaged and the standard deviation of the mean was calculated using

\[
s = \sqrt{\frac{\sum x_i^2 - n(x)^2}{n-1}}
\]

\[
sm = \frac{s}{\sqrt{n}}
\]

\( s_m \) is the standard deviation of the mean.

And

\[
x = \frac{\sum_{i=1}^{n} x_i}{n}
\]
Appendix 7. Maximum Error in Weight of Water by Derivation

The maximum error associated with the calculation of the weight of water is determined by partial derivatives. The calculation is first made for the number of grams of water using the ideal gas equation:

\[ n = \frac{PV}{MRT} \quad \text{(10a)} \]

Taking the partial derivative with respect to \( g \) of Equation 10a gives,

\[ dn = \left( \frac{\partial n}{\partial P} \right)_V dP + \left( \frac{\partial n}{\partial V} \right)_{P,T} dV + \left( \frac{\partial n}{\partial T} \right)_{P,V} dT \]

\[ dg = \left( \frac{MV}{RT} \right) dP + \left( \frac{MP}{RT} \right) dV + \left( \frac{MPV}{RT^2} \right) dT \]

\[ dg = \frac{M}{RT} \left( V dP + P dV + \frac{PV}{T} dT \right) \quad \text{(11a)} \]

To determine the maximum error, actual values were substituted into Equation 11a.

For a typical expansion in the range of temperatures used to calculate the Energy of Desorption (\( E_d \)) the variables in Equation 10a and 11a are:

\( P = 0.100 \text{ Torr (0.005)} \)
\( V = 0.0218 \text{ L + 0.695.7 L = 0.7175 L (0.0012)} \)
\( T = 90^\circ \text{ C or 363.15 K (1)} \)
\( R = 63.364 \text{ L Torr mol}^{-1} \text{ K}^{-1} \)
\( M = 18.015 \text{ g mol}^{-1} \)

\[ dg = \frac{1}{63.364 (363.15)} \left( 0.7175 (0.005) + 0.100 (0.0012) + \frac{0.7175(0.100)}{363.15} (1) \right) = 1.7 \times 10^{-6} \]

The maximum error in the calculation of the weight, \( dg = 1.70 \times 10^{-6} \text{ g or 1.70 x 10}^{-3} \text{ mg} \).
Appendix 8. Error Associated with the Calculation of Area under Weight Loss Curves (20)

The maximum error associated with the calculation of area under the desorption curves is estimated by

\[
\text{Error} \leq \frac{(b-a)^3}{12n^2} \left[ f'(x) \right]
\]

(12a)

The equation for the desorption curve is estimated with a first order Arrhenius equation

\[
f = A \exp^{-x}
\]

\[
f'(x) = -A \exp^{-x}
\]

\[
f''(x) = A \exp^{-x}
\]

The interval for the function is [0.5, 59], and the maximum of \( f''(x) \) is at \( x = 0.5 \). Equation 12a becomes

\[
\text{Error} \leq \frac{(59.5-0.5)^3}{12(118^2)} \left[ e^{-0.5} \right] = 0.75
\]

The area under a desorption curve typically has a value greater than 100. Therefore the error is less than \( \pm 1\% \).
Appendix 9. Error Associated with the Calculation of $A_a$ and $E_a$

The results of the Four, 10-second expansion routine were reported with the error in $E_a$ and $A_a$ having been estimated using the ANOVA (analysis of variance) statistical program that is provided with Microsoft Excel. The program provides the standard error with both the slope and intercept of the least-squares regression line.

The equation used for the standard error of the slope of the least-squares regression line is

$$SE_m = \frac{s}{\sqrt{\sum (x_i - \bar{x})^2}}$$

The standard error of the intercept $b$ is

$$SE_b = s \sqrt{\frac{1}{n} + \frac{x^2}{\sum (x_i - \bar{x})^2}}$$

$n$ is the number of samples
$s$ in both equations is the standard deviation given by

$$s = \sqrt{\frac{\sum x_i^2 - n(x)^2}{n-1}}$$

The four, 1-minute expansion routine was repeated three times for each zeolite. The standard deviation of the mean value was calculated using

$$s_m = \frac{s}{\sqrt{n}}$$

The standard deviation of the mean was calculated for both the $E_a$ and $A_a$ values.
Appendix 10. Pressure Rise Time

The time it takes for a water molecule to travel from a zeolite to the vacuum chamber and pressure transducer, is affected by the hindrance of the vapor as it travels through the baffle assembly and the geometry of the vacuum chamber. The pressure rise plot shows that ~0.4 seconds is necessary for the sample holder gas pressure to equalize with the vacuum chamber pressure. This plot below was made by allowing water vapor to expand out of the sample holder with the baffle assembly in place.

The plot also illustrates why the desorption curves exhibit first order behavior. The initial pressure rise upon opening of the pneumatic valve creates a curve that appears to be exponential in nature. But for an actual pressure rise curve the initial rise is an artifact of the experimental method and the vacuum chamber design.
Appendix 11. Initial Experiments on a Glass Vacuum Manifold

Preliminary experiments on glass vacuum rack

I was shown a desorption experiment that showed a large quantity of water desorbing from NaX powder at 110 °C. Attempts were made to reproduce the data but they were all unsuccessful.

The idea of multiple expansions into vacuum seemed worthy of investigation so the project was continued. I searched for a desorption system that was simple, and decided to investigate CuSO₄ • 5H₂O. The desorption sequence had been extensively studied and seemed to be a simple system to use, to develop a new thermal analysis technique.

Pressure vs. time for CuSO₄ • 5H₂O

The dehydration of CuSO₄ • 5H₂O proved to be more complicated than originally thought. The experiments were not showing the sequential desorption of waters molecules. Instead the waters were coming off in groups. Through further investigation, the desorption process was determined to proceed in such a way that an entire mole of H₂O does not desorb, but instead mole fractions desorb in such a way that is dependent on the experimental procedure. After 10 attempts to figure out CuSO₄ • 5H₂O, it was determined that a simpler system was needed. The results of the 10 experiments were not consistent and the waters of hydration were not desorbing at the same temperature from one experiment to the next. At this time I also wrapped the vacuum rack in aluminum foil and heating tape to minimize condensation. Condensation was still visible in areas not totally covered by heating tape and foil.

Pressure vs. time for CaX

After some discussion with Prof. Karl Seff, I selected zeolite CaX as a simple system, having only 2 different types of coordinated waters. A small amount of zeolite NaX was cation exchanged to produce CaX. The CaX was then studied, hoping to see some distinct differences in the water desorbing from the zeolite at different temperatures. Eleven experiments were conducted on CaX before it was decided that the experimental method was not suitable for the glass vacuum rack. Condensation was visible on the glass vacuum rack. Attempts were made to insulate and heat the glass to prevent any condensation but due to the poor conduction of the glass, any area not sufficiently heated and insulated would cause condensation to occur. The sample isolation valve was also a problem. The valve was a manual valve and opening and closing the valve had to be done slowly and carefully. Since the information that I was trying to discern was time dependent, it was necessary to have an isolation valve that would allow for fast opening and closing and for the valve to open to the same aperture upon each opening. Then the t = a could be established with certainty. Finally the pressure transducer that was attached to the glass vacuum rack was 0-1000 Torr ±0.5%. This means that any reading below 5 Torr was below the lowest suggested reading of the pressure transducer. Most of the pressure changes were less than 1 Torr, so the measurements were subject to large errors.
Writing VB programs

When I first started the experiments on the glass vacuum rack, the data was recorded by hand with the aid of a timer. I was attempting to perform time dependent experiments and I needed accurate time keeping as well as pressure measurements. Therefore, I interfaced the pressure transducers and temperature readout with a computer and A/D data acquisition card. The card was programmed with Visual basic, and manufacturer driver files.

The first method of acquiring data was accomplished by having the card read the signal coming from the transducers and readout over and over as fast as possible and averaging the results to get a value every couple of seconds. The data was written to a MS flex grid that was part of the VB program. At the end of an expansion the data would be copied from the flex grid and pasted to an MS excel spreadsheet. This did not work very well and the computer would often crash due to the memory becoming full, and the speed of the data acquisition was dependent on the computer program. I overcame this obstacle when by accident I shorted out the A/D data acquisition card and computer. Both became inoperable and had to be replaced. I built a PC from spare parts I had and purchased a new data acquisition card. The new card had more versatile driver files that allowed me to scan the A/D channels at a specified rate. This enabled me to determine the maximum sample speed of the data acquisition card and to acquire data at a more precise rate. The scan function also enabled the VB program to be more complex and user friendly.

With the new data acquisition card and new scan functions, the data is collected and written to a memory buffer. At the end of an expansion, the data is written directly to an MS excel spreadsheet. This way of recording the data separates the data from the VB program, so if the program crashes, the data on the excel spreadsheet can be saved.

I decided that in order to investigate this SI-EGA method properly, a vacuum chamber had to be designed specifically for the SI-EGA method. It took two years to build an EGA instrument that would function in a manner that would allow me to study the SI-EGA method.
Appendix 12. Visual Condition of Zeolite Powder during a Typical SI-EGA Experiment

Picture 1. View of 50.0 mg of zeolite powder in sample holder. Sample has been dried in oven at 150° C for 3 days.

Picture 2. View of 50.0 mg of zeolite powder after gentle tapping on the desktop.

Picture 3. View of zeolite powder after initial dehydration, the powder retains this appearance throughout remainder of experiment. The powder returns to the appearance of Picture 2 by gentle tapping on the desktop.
Appendix 13. All Arrhenius Plots for each Zeolite Powder

**Arrhenius Curves for Zeolite NaX Powder**

![Arrhenius Curves for Zeolite NaX Powder](image1)

**Arrhenius Curves for Zeolite NaY Powder**

![Arrhenius Curves for Zeolite NaY Powder](image2)

**Arrhenius Curves for Zeolite CaX Powder**

![Arrhenius Curves for Zeolite CaX Powder](image3)
Appendix 14. Forni Models for Desorption from Zeolites (15,16,17)

Forni proposed three models to explain the desorption of ammonia gas from zeolites.

1. Desorption controlling with no readsorption.
2. Desorption controlling with free readsorption.
3. Intracrystalline diffusion controlling

Each model was compared to experimental TPD experiments.

In the case of desorption controlling with no readsorption, a series of experiments were conducted using different TPD starting temperatures. By increasing the starting temperature, only stronger and stronger sites on the zeolite should hold ammonia. The weaker sites should become progressively free. As a consequence higher and higher values of $E_a$ should be expected with increasing TPD starting temperatures. The experiments resulted in constant values of $E_a$ regardless of the starting temperature.

The desorption controlling with free readsorption model was tested by doing a series of experiments with small changes in the TPD starting temperatures. TPD Curves with small differences in their starting temperatures are representative of energetically homogeneous sites. If the difference between two starting temperatures is small then the difference curve should lead to the same value of $\Delta H_d$. The experiments resulted in values of $\Delta H_d$ that decreased with increasing temperature along the same difference curve.

The intracrystalline diffusion model describes a physical rather than chemical phenomena. If desorption is following the diffusion model then values of $E_a$ and $A_a$ should be constant regardless of the TPD starting temperature. The TPD results showed that the values of $E_a$ and $A_a$ were practically constant regardless of starting temperature. Based on these results, Forni concluded that intracrystalline diffusion was the rate determining step for the desorption of ammonia from zeolites. He also concluded that the diffusion was slowed down by reversible acid base reactions of the ammonia with the ions in the zeolite as well as the with the polar zeolite framework.

The assumption of diffusion controlled desorption of water from zeolites was made based on Forni’s models.
Appendix 15. Interpretation of the Preexponential Factor $A_a$

In 1889 Savante Arrhenius proposed

$$\frac{d \ln k}{dT} = \frac{E_a}{RT}$$  \hspace{1cm} (13a)

If $E_a$ is regarded as constant, then equation 13a can be integrated to give

$$\ln k = \ln A - \left( \frac{E_a}{RT} \right)$$

$$k = A_a \exp\left( -\frac{E_a}{RT} \right)$$

To obtain the probability of having a successful reaction (the rate constant $k$), the exponential factor must be multiplied by a preexponential factor that accounts for the collision frequency and steric effects. The steric effects include the effective collision orientation needed for a reaction to occur. The preexponential is often qualitatively correlated with the entropic component of the activation barrier. The $A_a$ factor is also equivalent to the high temperature-limiting rate constant for a reaction.
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