AFIT/GEE/ENP/94S-01

USE OF INFRARED SPECTROMETRY TO DETERMINE THE EFFECT OF TEMPERATURE ON THE DESORPTION RATES OF TRICHLOROETHYLENE FROM PLASTIC CLAY 98b

THESIS

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THESIS

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Abdellatif Fares

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Abstract

This research investigated the influence of temperature on the desorption rates of trichloroethylene (TCE) from Plastic Clay 98b. It was expected that an increase in temperature will cause an increase in both the desorption rates of TCE and in the quantity of desorbed TCE. In fact, previous studies on other chemicals indicated a faster decrease in the remaining sorbed concentration with increasing temperature. To accomplish the necessary experiments, this research made use of the infrared (IR) optical absorption technique. IR spectroscopy was used to measure the concentration of the vapor TCE that desorbed from the soil. After it has been exposed to liquid TCE for a period of 48 hours, plastic clay was placed inside an enclosed glass tube and was allowed to desorb at a fixed temperature for a period of 4 hours. Similar experiments were performed with temperature as the only variable. The results were an initial and rapid desorption followed by a leveling off. This rate of this initial desorption was found to increase each time temperature was raised. The desorbed concentration was also found to increase with increasing temperature. The collected data followed the Langmuir kinetic model and the desorption rate coefficients were determined at each temperature.

I. Introduction

1.1 General Issue

The contamination of groundwater is a politically sensitive issue that may affect any city, industrial, or residential area that use local aquifers as sources for drinking water. The sensitivity of this issue increases when the cause of contamination is determined to be a hazardous waste that may cause severe environmental and health effects. If left untreated, these hazardous substances may pollute the drinking water aquifers beneath the contaminated areas. As a result of this contamination, efforts such as the Installation Restoration Program (IRP) are being conducted by the Department of Defense (DOD) to correct previous environmental problems at DOD installations throughout the nation. These remediation efforts account for several millions of dollars of the annual defense budget. Furthermore, the cost of these remediation actions may be assessed against any or all of the potentially responsible parties.[1]

Remediation projects are often directed toward groundwater. Millions of dollars are spent on treating contaminated groundwater using the "pump and treat" technique. This technique has been effective in treating groundwater; however, its efficiency tends to decline over time and reaches some limiting asymptotic value.[2] The decline of this treatment method is believed to be caused by the significant portion of the contamination that lies in the area directly between the ground surface and the water table. This area, called the unsaturated or vadose zone, has received less attention, but has the potential to pollute groundwater aquifers even after the water has been fully treated. From the unsaturated zone, the untreated contaminant can migrate downwards at a very slow rate recontaminating groundwater for years after cleanup actions were thought to have been completed.

In soils, organic contaminants can be present in one or more of five different locations. The contaminant can be in the form of free-liquid between soil particles, in the vapor state, dissolved in soil moisture, adsorbed to surface of unsaturated zone soil particles, or fully enclosed within the interior of the soil matrix.[3] During remediation processes, the portion of the contaminant adsorbed within the soil matrix causes several problems. At long-term contaminated sites, recent studies indicate that most of the contaminant in the unsaturated soil zone will adsorb to the soil particles.[3] Because of a complex slow sorption process, the longer a contaminant persists in the unsaturated zone, the larger the portion of the chemical that will be fully adsorbed within the soil matrix.[3] After a long period of time, years or decades, this adsorption is followed by a slow desorption process. As a result, the groundwater treatment will be negated by the recontamination caused by the slowly desorbing contaminant. This desorption mechanism is also thought to cause the long term evolution of contaminants from soils when remediated by incineration.[4]

During remediation of a contaminated site, additional difficulties arise because only little is known about the transport mechanisms of contaminant within both the saturated and the unsaturated zones. This migration of the volatile organic compounds depends on physical, chemical, and biological processes within the soil medium.[5] Additionally, the movement of these volatile organic compounds (VOCs) is directly affected by the physical-chemical nature of the adsorbates, soil organic matter content, nature of saturating cation, moisture content, and temperature.[6] It was also shown that the transport of VOCs within the unsaturated zone of the soil strongly depends on the sorption of these compounds within the soil.[7]

1.2 Motivation

Trichloroethylene (TCE), C_2HCl_3, is an organic chemical widely used for industrial and domestic purposes. It is a major industrial solvent (234000 metric tones produced annually worldwide) used for degreasing metal parts, electronic components, and in dry cleaning.[5] TCE has been used to a large extent by the United States Air Force to degrease and clean aircraft parts. Because of this extensive use and the poor handling of TCE, several Air Force bases are currently residing on TCE contaminated sites. This contamination extends to include both the soil and groundwater. As a result, trichloroethylene is the most frequently reported organic contaminant in groundwaters and has been identified in 35% of US Superfund sites.[8] Thus, TCE becomes a major concern as a potential health hazard in drinking waters and is considered as the most prevalent of volatile organic compound contaminants.[8] Furthermore, TCE is a suspected carcinogen and may also be converted by reductive dehalogination to more potent carcinogen, vinyl chloride.[5]

Air injection and extraction wells have been widely used to remediate VOC contaminated sites and aquifers.[9] However, the efficiency of these extraction wells decreases with time and eventually reaches some limiting asymptotic value.[2] This rate limiting step is likely due to desorption of the organic compounds from the soil matrix.[4] As stated earlier, the longer a contaminant remains in the unsaturated zone, the higher the proportion of this compound that will adsorb to the soil particle. Thus, it is now believed that this sorption process takes place over an extended period of time and slowly traps the contaminant within the soil matrix frustrating remediation techniques that rely on the rapid desorption process. That is, the slowly sorbed compounds become unaffected by the current treatment methods resulting in an incomplete treatment by the remediation projects. Specifically, this adsorbed portion of the contaminant, which may represent up to 90% of the overall contaminant, remains undetected by the current measurement techniques, therefore giving the incorrect impression of successful soil remediation.[3] This soil, which is assumed to be fully cleaned by the treatment methods, is still contaminated and is capable of polluting additional groundwater.[3]

Pump and treat is far-and-away the most prevalent technique to remediate contaminated groundwater. However, long time periods are required for the slow diffusion process to move trapped organic compounds into mobile groundwater that is being pumped by a recovery well.[16] This remediation method often causes an initial decrease in contaminant concentrations in the extracted water, followed by a leveling of concentration. In other cases, a gradual decline is seen that may be expected to continue over decades.

Several analytical models account for rate-limited desorption of an organic solute during cleanup of a contaminated site. The present research continues these studies of desorption behavior of organic compounds by examining the temperature dependence of the desorption rate of trichloroethylene.

1.3 Problem Statement

A large volume of research has been done concerning soil and groundwater contamination with TCE. However, only a little has been done to address desorption rates of the chemical in the unsaturated zone. Desorption rates are influenced by several factors. These factors include soil type, ambient temperature, moisture content of the soil, contaminant properties and its concentration in the water, the length of time the soil has been exposed to the contaminant, the amount of organic material in the soil, and the relative humidity. Furthermore, the effects of most of these factors on desorption rates are poorly understood.

In order to assist in the effective remediation of TCE contaminated sites, variables that affect the efficiency of aquifer remediation have to be determined and well understood prior to the initiation of the clean-up. How and to what extent these variables affect clean-up actions are important issues. Temperatures change dramatically from one Air Force Base to another and from one season to another. Thus, before remediation efforts commence, one must first fully understand the desorption behavior of the contaminant of concern and how this desorption depends on temperature. This will allow us to predict the optimal "pulsed pumping" periods and the length of each of these periods. This study evaluated the temperature dependence of TCE desorption rates from contaminated soils by changing temperature and keeping all other variables constant. The results of this study can be used along with the temperature profile of the contaminated site to determine the optimum clean-up time during the year, the expected length of the remediation project based on the ambient temperature of the site, and if other techniques must be used instead.

To complete this study, dry plastic clay soil was exposed to liquid TCE for a period of 2 days. This soil was then placed inside an enclosed glass tube to evaluate the desorption of TCE from the soil sample for a period of 4 hours. During this entire period, the cell was undisturbed and maintained at a fixed temperature.

1.4 Objectives

The objective of this research was to evaluate the effect of temperature on the rates of desorption of TCE from a liquid contaminated soil. It is anticipated that the higher the temperature, the faster the desorption rate, the greater the amount of TCE that will consequently desorb, and the less time it will take the chemical to completely desorb out of the soil. We also expect that a fast desorption rate, due to those molecules at the surface of the soil, will be followed by a slow desorption caused by those molecules entrained in the soil matrix (Figure 1). In addition, the following tasks had to be performed prior to beginning TCE desorption experiments:

1. Determine the infrared absorption spectrum of TCE in both the gas and liquid phase at high resolution (0.02 cm^{-1}).
2. Determine the absolute cross-section for absorption near $\lambda = 3.25\ \mu m$ as a function of temperature.
3. Measure the rates for desorption of trichloroethylene, from a particular soil, at five temperatures: 27°C, 40°C, 64°C, 70°C, and 100°C.

1.5 Scope/Overview

The remainder of this research will consist of a literature review describing the transport mechanism of TCE in the unsaturated and saturated zones, its confounding, long term effects, its physical and kinetic properties, and some spectroscopic data for this chemical.

1.6 Limitations of this study

Throughout this research, several factors may influence the results to some degree. Such factors could include:

1.6.1 Use of TCE in high concentrations

Throughout this research, high concentrations of pure TCE

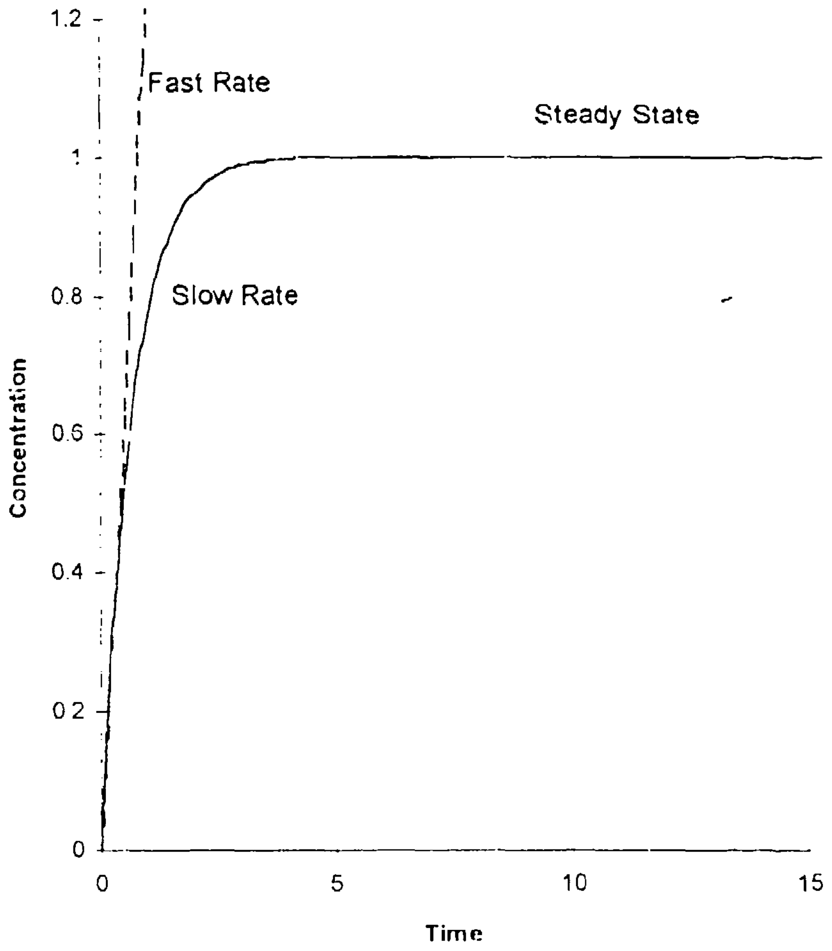


Figure 1: Expected TCE Desorption Rate Data

were used to prepare the soil to ensure larger and detectable effects. This is rarely the case in the real world where larger masses of soil are exposed to low concentrations of TCE and for longer period of times. Therefore, to offset the period of exposure, high concentrations of TCE were used. This factor must be taken into account when making conclusion about the data.

1.6.2 Type of soil

Plastic Clay 98b was used in this study. This soil is a lab-graded soil that has been dried and freed from all contaminants. Furthermore, this soil was powdered and has a uniform particle size. In the real world, a soil formation is usually composed of several types of soil with broad size distributions. These differences, which affect both adsorption and desorption of TCE to soil, must be taken into account during interpretation of the data of this study and its application to the real world.

1.6.3 Moisture content of soil

Several studies indicated that moisture content greatly influence both adsorption and desorption phenomena of TCE. In this study however, the soil was originally dried in an oven at very high temperatures and has not been exposed to water since then. In addition, the experimental cells were continuously kept under vacuum and any water in the soil should evaporate. Therefore, the effect of soil moisture on desorption of TCE is expected to be negligible and will not be evaluated in this research.

1.6.4 Leak rates in the experimental cells

The leak rates in the cells were repeatedly measured and found to be in the order of 0.01 torr every 10 minutes. This is negligible compared to the amount of TCE pressure within the cell. In addition, this leak was found to not have any influence on the experimental data because, given the pressure in the cell is much smaller than atmospheric pressure, the leak is expected to be from the room into the cell and atmospheric gases were found not to absorb the same IR frequency as TCE. However, to account for these leaks, a control experiment will be performed directly after every desorption experiment.

1.6.5 Adsorption and desorption due to apparatus

Adsorption and desorption due to glass, O-rings, and other components of the experimental apparatus were accounted for using a control experiment. The effects of the apparatus were expected to be much less than those caused by the experimental soil in the cell. If not, interpretation of the soil effects will be hard to evaluate. To lessen the effects of the apparatus, prior to every experiment, the cells were maintained under vacuum to allow off-gas of all TCE from the inside of the cell.

1.6.6 Detector float over time

The detector's response over time was expected to remain constant when the cells are empty and under vacuum. However, this was not the case, therefore, an experiment that evaluated the float of both detectors during a period equal to the period of desorption experiments was performed and corrections were made to account for this signal change not caused by TCE. This float is further explained in appendix B at the end of this thesis. However, there will always be a noise in the transmitted signal that cannot be controlled but that is expected to be rather negligible.

1.6.7 Concentration gradient in the cells

In the environment, there is enough air to disperse the TCE desorbing from the soil, allowing deeper TCE molecules to desorb from the interior of the soil particle out to the soil surface then to the atmosphere. However, in this study, the contaminated soil is maintained enclosed during the desorption process in a cell of small and constant volume. It is thus anticipated that desorption rates will be influenced by re-adsorption of TCE to the soil. In other words, the concentration of gas phase TCE in the cell will preclude more TCE from desorbing out of the soil. To evaluate this effect, the cell will be drawn down to vacuum at the end of the desorption period in order to pull out all the gas TCE and more will be allowed to desorb for another 4 hours.

1.6.8 Atmospheric interferences

Soil contamination in the environment occurs under atmospheric interferences. These interferences may affect adsorption and desorption phenomena. Therefore, it is expected that desorption rates under vacuum differ from those under atmospheric conditions. However, it is also advantageous to evaluate desorption under vacuum in order to reduce atmospheric effects on the experiment.

1.6.9 TCE decomposition and microbial activity

TCE is a chemical known to decompose to other chlorinated organic compounds. Over the time periods of these experiments, this decomposition was assumed negligible and was not evaluated. Furthermore, microbial activity in the soil was expected to be negligible because the soil was originally oven-dried. Therefore, given that the soil had very low water content and was exposed to liquid TCE for only a period of 2 days, the effects of microbial activity and chemical decomposition were considered negligible.

All the above factors may affect the quality of the data collected throughout this research, however, the ultimate goal is to evaluate and understand the desorption rate of TCE from soil and its correlation with temperature. Furthermore, some of these sources of error were corrected for and discussed in Chapter 6 and in the Appendices.

II. Background Theory

2.1 Introduction

Trichloroethylene is a colorless volatile organic compound widely used for industrial and domestic purposes. It is a major industrial solvent (234000 metric tones produced annually worldwide) used for degreasing metal parts, electronic components, and septic systems and in dry cleaning.[5] Furthermore, TCE was used as a general anesthetic in the health profession and as an extraction agent in decaffenating coffee. At numerous Air Force installations, TCE was extensively used to degrease and clean aircraft parts. All these applications of TCE illustrate the various uses industry made of this product until a study in 1976 found TCE to be a suspected carcinogen.[1] As a result of this study, TCE was added to the U.S. EPA's list of hazardous substances.[1] Because prior to the 1976 study TCE was thought to be safe, inappropriate and inexpensive methods were used to dispose of the product. Such methods included the dumping of TCE in landfills, drywells, and directly on the ground. These past poor disposal methods have contaminated much of the groundwater in the areas where TCE was dumped.[1]

TCE may appear in soils and aquifers as a result of its wide industrial use and also, possibly, as a degradation by-product of other chlorinated hydrocarbons solvents. Currently, TCE is the most reported organic contaminant in groundwaters (Table 1).[5]

Table 1
Main volatile chlorinated hydrocarbon compounds in contaminated groundwater listed in decreasing order of likely occurrence (from Folkard 1986)

1. trichloroethylene
2. tetrachloroethylene
3. 1,1,1-trichloroethane
4. dichloroethene
5. dichloroethane
6. carbon tetrachloride
7. vinyl chloride
8. dichloromethane

Currently, because of the large number of scientific studies on TCE contaminated sites and the resulting environmental and health effects, both the public and the scientific community have been aware of the danger of hazardous wastes and the contamination of groundwater.[11] Because of the regulations posed by the CERCLA, all DOD installations across the country have to deal with the problems associated with the large number of TCE contaminated sites. Remediation of these sites may cost large amounts of money.

2.2 TCE Adverse Health Effects

Until the mid 1970s, TCE was considered a safe chemical product. This was shown by its wide use during the 1970s in the medical profession and in food production.[1] It was only after a study in 1976 showed that TCE is a suspected carcinogen that the product was added to the EPA's hazardous substances list.[1] Today, trichloroethylene is the most frequently reported organic contaminant in groundwaters. Reported dissolved concentrations range from 0.01 µg/l to 5500 µg/l.[5] Therefore, it is considered a major potential health hazard.

TCE is a suspected carcinogen and may also be converted by reductive dehalogination to more a potent carcinogen, vinyl chloride.[5] TCE can be poisonous by inhalation, intravenous, and subcutaneous routes.[12] TCE is also moderately toxic by ingestion.[12] In low concentrations, TCE is a strong skin and eye irritant and can cause severe headache and drowsiness. In high concentrations, this chemical causes narcosis and anesthesia, and damages liver and other organs from chronic exposure.[12]

2.3 Transport Mechanism of TCE

Following a discharge or a leak, non-aqueous phase liquid (NAPL) TCE is expected to migrate quite rapidly in soils and other water-unsaturated conditions, leaving droplets of organic liquid in the pore spaces.[5] The amount of TCE left in pore spaces depends on the medium and on TCE properties. This amount increases when the permeability decreases. Under fully dry conditions, TCE rapidly migrates downwards. Permeability, pore size distribution of the porous medium, and size of the spill determine whether or not TCE is retained at the water table level.[5] When the TCE hydraulic head exceeds the TCE entry pressure, trichloroethylene migrates downward into the aquifer, through the water table.[5] This downwards transport of TCE away from the water table may be greatly influenced by the hydraulic characteristics of the medium.[5]

If retained at the water table (frequently), TCE may stop its downward movement and diffuse laterally, together with a slow migration downwards (TCE being denser than water). At the water table, TCE may form a NAPL reservoir providing very long lasting source of TCE for moderately slow dissolution in the moving groundwater that encounters the TCE source.[5] At this location, NAPL-TCE will slowly dissolve in groundwater. Because of natural heterogeneities, (e.g. presence of lenses of fine material), the TCE plume can spread laterally during its downward movement.[5] This feature of TCE allows the plume to expand and extend quite rapidly, contaminating several aquifers and rendering remediation actions very difficult to complete.

2.4 TCE in The Unsaturated Zone

As mentioned previously, organic compounds within the unsaturated zone may coexist in five possible states, as a free-liquid between soil particles, as a vapor, dissolved in soil moisture, adsorbed to surface of unsaturated zone soil particles, or fully enclosed within the interior of the soil matrix (Figure 2).[3] Studies show that remediation techniques can easily and effectively remove a contaminant that is present in any of the first three states. However, significant difficulties arise when trying to treat the contaminant that is adsorbed within the soil matrix.[3] Contaminants in this state appear to withstand common remediation techniques.[3] This phenomenon is caused by the slow sorption mechanism that acts on contaminants in the unsaturated zone trapping them within the soil matrix.[3]

In the unsaturated zone, the sorption process was found to take a long time to reach equilibrium.[3] To reach true equilibrium, recent studies indicate that organic compounds need "contact times that are significantly longer than is usually allowed in batch and column studies".[3] Upon initial contact

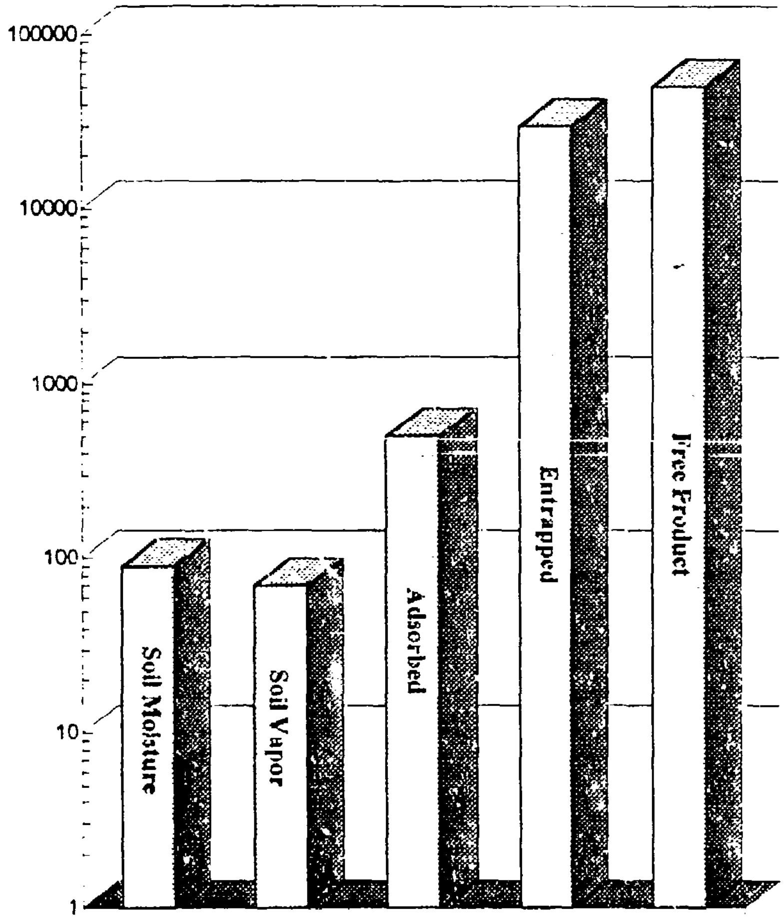


Figure 2: Distribution of 30L of TCE in One Cubic Meter of Soil[3]

between contaminant and soil, experimental data showed that there is a rapid uptake followed by a much slower adsorption toward equilibrium.[3] Results of an investigation at the Picatinny Arsenal site in New Jersey for TCE contamination indicated that "field TCE distribution between the soil and soil gas was from 1 to 3 orders of magnitude greater than the distribution predicted under normal (rapid) equilibrium conditions".[3] It was strongly suggested that this was caused by a slow TCE sorption from previously contaminated soil. In addition, it was suggested that "long-term contamination produces a fraction of the sorbed contaminant that is relatively resistant to desorption".[3] That is, the longer the contact time between contaminants and soil, the stronger the binding between the two becomes. This will allow severely contaminated sites to appear uncontaminated. Furthermore, due to desorption, these sorbed material will desorb and pollute previously treated groundwaters.

A study done by Bourg, Mouvet, and Lerner showed that TCE is weakly sorbed on soils and aquifer solids with a linear partition coefficient.[5] The study also found that gaseous TCE is more adsorbed than aqueous TCE, with the extent of uptake being greatly influenced by the moisture content of the solid. Additionally, because of its low adsorption and weak degradation under aerobic conditions, the diffuse contamination of aquifers by dissolved TCE can be very extensive.[5]

2.5 Sorption of Volatile Organic Compounds in Soil

Sorption interactions generally operate among all phases present in any subsurface system and at the interfaces between these phases. Solutes which undergo sorption are commonly termed sorbates, the sorbing phase the sorbent, and the primary phase from which sorption occurs the solution or solvent. Two broad categories of sorption phenomena, adsorption and absorption, can be differentiated by the degree to which the sorbate molecules interacts with and is free to migrate between the sorbent phase.[13] In adsorption, solute accumulation is generally restricted to a surface or interface between the solution and adsorbent. In addition, adsorption process usually yield surface to interface concentrations of solute greater than those in the bulk phase; this makes it possible for precipitation or association to occur on a surface in the absence of a solution phase reaction of the same type. In contrast absorption is a process in which solute transferred from one phase to another interpenetrates the sorbent phase by at least several nanometers.[13]

Sorption results from a variety of different types of attractive forces between solute molecules, solvent molecules and the molecules of a sorbent.[13] These forces usually act together, but one type or another may be more significant than the others in any situation. The absorption process involves exchanges of molecular environments.[13] During this process, the distribution of the solute between phases results from its relative affinity for each phase, which in turn relates to the nature of the forces which exist between molecules of the sorbate and those of the solvent and sorbent phases.[13] These forces can be similarly compared to forces in classical chemical reactions.

Adsorption also entails intermolecular forces; however, it is those molecules at the surface of the sorbent rather than bulk phase molecules which are involved and more interactions take place.[13] In addition, adsorption can be divided into three categories: physical, chemical, and electrostatic.[13] These categories can be distinguished according to the type of attractive force which predominates.[13]

Several factors control the interaction of a contaminant and the surface of soil or aquifer materials. Such factors include physical and chemical characteristics of the contaminant, composition of the surface of the solid and the fluid media encompassing both.[14] It is thus necessary to understand these factors in order to draw logical conclusions about the impact of sorption on the transport and distribution of contaminants in the subsurface. The failure to take sorption into account can lead to a significant underestimation of the amount of a contaminant at a site as well as the time required for it to move from one point to another.

In more detail, the properties of a contaminant that impact sorption include:[14]

- Water solubility
- Polar/Ionic character
- Octanol/Water partition coefficient
- Acid/Base chemistry
- Oxidation/Reduction chemistry.

Soil characteristics can also affect the process of sorption. Such characteristics include:[14]

- Mineralogy
- Permeability/Porosity
- Texture
- Homogeneity
- Organic carbon content
- Surface charge
- Surface area.

Water, the primary transporting fluid under most contamination situations, can have large impacts on sorption of a contaminant. pH, for example, dictates the chemical form and, therefore, the mobility of contaminants which can lose or gain a proton.[14] Salt content and the dissolved organic carbon content can also affect the behavior of a contaminant. For example, at high concentrations, dissolved organic matter found in lechates pose a significant influence on the movement of most nonpolar organics.[14] Following sorption is usually desorption of the contaminant from soil to groundwater. This process is explained in the next section.

2.6 Desorption Mechanism of TCE

Among the many mechanisms that influence the transport of volatile organic compounds in the subsurface zone, such as advection, dispersion, diffusion, volatilization, and sorption, desorption is one of the most important.[15] Desorption is defined as the reversible process of sorption. Desorption of contaminant from soil particles occurs in three consecutive mass-transport phases: intra particle diffusion from the interior to the outer surface of the particle, mass transfer of the contaminant from the outer surface of the particle to the gas phase, and lastly bulk transport of the contaminant in the gas phase.[16] This process, called reversibility, was found to depend on the contaminant's initial soil-phase concentration, soil organic carbon, and residence time.[15] Unfortunately, the desorption of VOCs from field contaminated soils has not been studied extensively and not enough information to fully understand the process is available. Therefore, experiments with field contaminated soils are essential to understand desorption, fate, and movement of VOCs in the subsurface zone.

Desorption of TCE from various soils was studied by Pavlostathis and Mathavan. Results indicated the presence of a fast desorption within 24 h and a slow phase beyond 24 hours.[15] The study also showed that soil type did not influence the amount of contaminant desorbed.[15] As an example, two soils with different sand contents of 12% and 82% equally resisted desorption.[15] Furthermore, the results indicated the presence of a portion of the contaminant that resisted desorption. This portion is believed to be caused by the complex pore geometry of the soil matrix.[15] However, when using different soils, the effect of pore geometry on desorption was undetectable.[15] In addition, and most importantly, it is worth noting that residence time has the largest effect on the quantity of TCE desorbed. The fraction of TCE that resisted desorption increased from 10 to 45% for the corresponding residence time of 2.5 and 15.5 months.[15]

The implications of slow and incomplete desorption are far reaching. Desorption is believed to be the rate-limiting step in most of the soil and aquifer remediation technologies currently in use.

2.7 "Pump and Treat" Remediation Method

The current and most common remediation technique to clean-up TCE contaminated sites is to "pump and treat" the groundwater. In this technique, water is pumped out of the ground, treated with air stripping to volatilize the TCE, and either injected back into the ground or disposed of. Recent studies showed that the contaminant load discharged by the "pump and treat" methods typically declines with time, asymptotically approaching a residual level.[5] Such behavior decreases the efficiency of aquifer decontamination by pumping, and is believed to be caused by the rate-limited desorption of organic contaminants from aquifer solids.[5] This implies that during contamination, a portion of TCE adsorbs into the soil and traps itself within the matrix of the soil particle. After the contaminated water is treated, it shows zero or undetectable TCE concentration. However, and unfortunately, over time, the adsorbed TCE desorbs from the soil particles into the groundwater and constitutes a continuous TCE source.

The removal of this dissolved and sorbed TCE by pumping requires the extraction of more water than is contaminated at the onset of remediation. Thus, unless injection wells are used to supply the clean water, which is rarely the case, the "pump and treat" method may require a significant volume of uncontaminated groundwater surrounding the contaminated site to flush TCE from the area.[17] However, kinetic limitations to TCE desorption from the medium can occur during the remediation period; thus, slowing the removal of TCE from the aquifer and increasing both the time required to fully clean the site and the total volume of water that must be extracted to flush the contaminated area. As a result, the long-term cost of such pumping with treatment of the extracted water is often high and the time necessary for cleanup is hard to predict due to the unknowns about the mass of NAPL at or below the water table. Furthermore, if pumping is halted before complete clean up of the site, the contaminant concentrations in the groundwater will rise as desorption continues.[17] This desorption thus decreases the efficiency of the "pump and treat" remediation technique. Due to this, it would seem imperative that a more effective and economical means of remediation be developed.

To increase the efficiency and reduce the cost of pump and treat remediation efforts, the "pulsed pumping" technique was developed. Throughout the remediation period, the pumps operate in a cycle. After the pumps have operated for a period of time, they are turned off to allow the TCE to desorb from the soil particles into the groundwater. After the TCE desorption reaches a steady state, the pumps are operated again. This method increases the efficiency of TCE decontamination and lowers the cost of the operation by reducing the functioning time of the system.

2.8 Vapor Extraction System

Another method that has recently dominated several VOC remediation techniques is the Vapor Extraction System (VES). This method involves blowing large volumes of air through the contaminated soil to first volatilize the contaminant and then trap it with collection equipment. This remediation method has been more effective than the "pump and treat" technique. However, this technique was very inefficient in recovering contaminants that are either adsorbed to the surface of the soil particle or fully entrained within the soil matrix.[9] Studies indicated that the portion of the contaminant that is entrapped in the soil matrix is impervious to the VES remediation method.[18] Under equilibrium, this portion of the contaminant can constitute up to 90% of the total amount of contaminant in the soil.[9] This fraction is expected to increase if the soil was exposed to the contaminant for a considerable period of time.[9]

2.9 VOC Measurement Techniques

To measure the effectiveness and efficiency of a remediation technique, the concentration of the contaminant is measured prior, during, and after the clean-up period. When remediating an unsaturated zone, the measurement techniques are usually poor. The current EPA's preferred method for determining VOC concentrations in soil is the "purge and trap" technique. In this technique, an inert gas is passed through the soil, driving organic contaminants from pore spaces and external soil surfaces.[19] The contaminant is then trapped and its concentrations are measured with a gas chromatograph.[19] This method of measurement underestimates and does not account for the contaminant's portion that is completely trapped within the soil matrix of a soil particle.[19] Recent studies indicate that in long-contaminated soils, approximately 90-99.9% of contamination may be trapped in the interior of the soil matrix.[19] Thus this measurement methods accounts only for a very small fraction of the soil contamination and is effective in measuring only up to 10% of the contaminant present in long-contaminated soils.[19] Additionally, this technique also ignores the portion of the contaminant that volatilizes when the contaminant is exposed to atmosphere.[20]

Several studies are underway to find more accurate and effective measurements. A potentially more effective measurement method than the "purge and trap" is called the "dynamic head space" method and is currently under investigation. This method detects the concentration of VOCs in the soil based on the strong correlation between the head space or air gap in the sample container and the amount of VOC existing in the soil sample.[16] Analysis of this method confirmed its accuracy and effectiveness in detecting VOC concentrations in soil with precision superior to that obtained with purge and trap method with most soil types.[21]

2.10 Physical Properties of TCE

As stated earlier in this chapter, volatile organic compounds in soil may occur simultaneously in five phases: as a free-liquid between soil particles, as a vapor , dissolved in soil moisture, adsorbed to surface of unsaturated zone soil particles, or fully enclosed within the interior of the soil matrix (Figure 2).[3] This partitioning is controlled by several complex factors (Figure 3).[22] Such factors include environmental conditions (humidity, hydrodynamics, surface features, temperature), VOC properties (boiling point, Henry's constant, organic carbon content, partition coefficients, solubility, vapor pressure), soil properties (bulk density, classification, conductivity, moisture content, organic carbon content, particle size, permeability), and microbiological factors (bacterial population, bacterial type).[22] Because of the effects of these factors, numerous detailed studies on the equilibrium properties of VOCs in soils have been conducted.

In general, volatile organic compounds are usually distributed between the vapor, liquid, and solid phases. This distribution is often described by the equilibrium relationship:[8]

$$C_T = aC_V\rho_b + \frac{\theta C_L}{\rho_b} + C_S \tag{2.1}$$

where

C_T = the total VOC concentration per weight of dry soil (μg/g);

C_V = the vapor phase concentration (μg/cm^3);

C_L = the solution concentration (μg/cm^3);

C_S = the sorbed concentration (μg/cm^3);

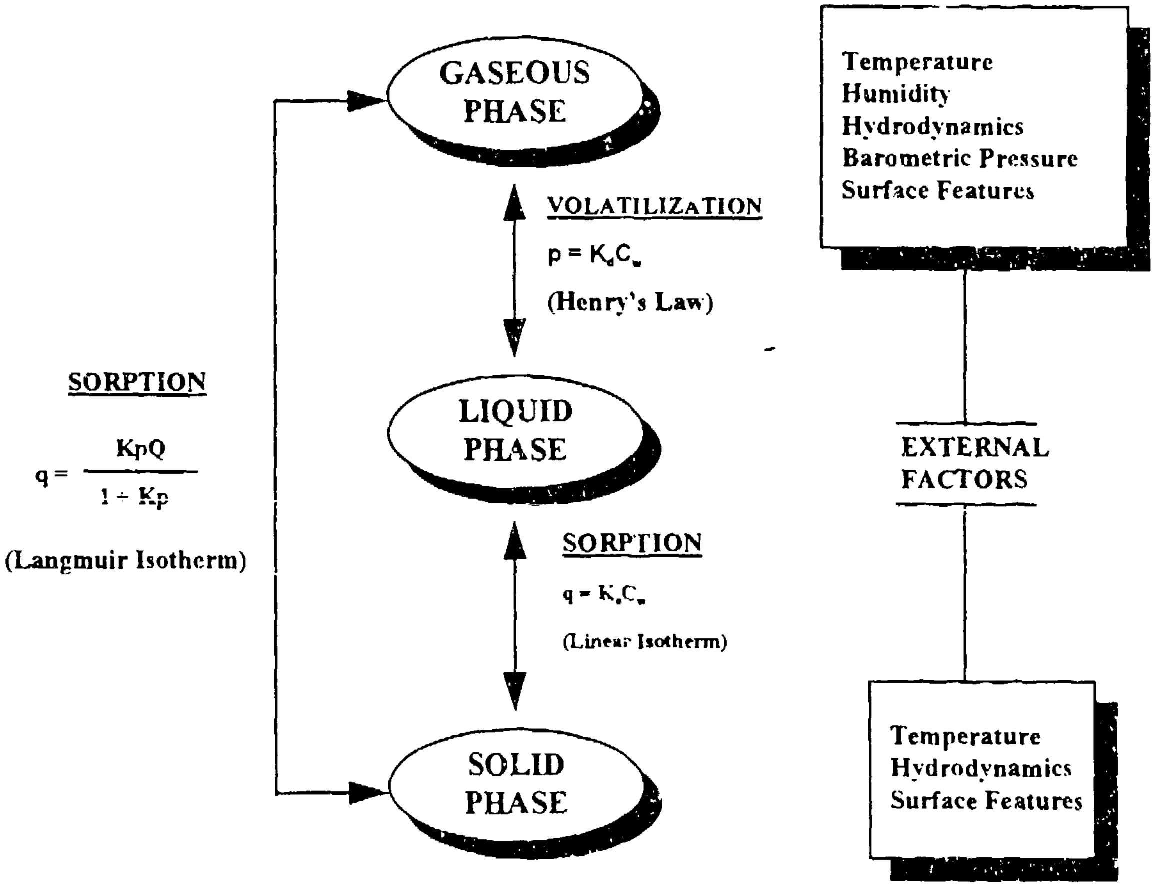


Figure 3. Equilibrium relationships for phase partitioning of VOCs in soil systems.

K_d = Henry's constant (atm-m^3)/mole
K_d = Soil/water distribution coefficient (1)
q = fraction of the surface area covered by the chemical
Q = the vapor phase concentration (g/m^3)
C_w = Solubility (mg/L)
K_p = ratio of adsorption to desorption rate coefficients
p = the vapor phase concentration (g/m^3)

a = the soil air content (cm^3/cm^3);

ρ_r = the soil density (g/cm^3); and

θ = the soil water content (cm^3/cm^3).

In this distribution, the sorbed concentration can be related to the solution concentration via the Freundlich isotherm:[8]

$$C_S = K(C_L)^{\frac{1}{n}} \tag{2.2}$$

where K is the partition coefficient of the VOC in question and n is some empirical constant, usually equal to 1. K, the partition coefficient is linearly related to the soil organic matter content and is also dependent on the water solubility.[8] Additionally, the partition of the sorbate between the water and the sorbent is linearly related to the organic carbon content of the soil and the lipophilicity of the organic content.[23] In unsaturated soils, it was found that the liquid and vapor phase concentrations are related by Henry's law:

$$C_V = K_H C_L \tag{2.3}$$

where K_H is Henry's constant.

At the same time, the sorbed concentrations and gas phase concentration are related by the Langmuir Isotherm:[24]

$$\beta = \frac{K_L C_V}{1 + K_L C_V} \tag{2.4}$$

where

β = fraction of the surface area covered by TCE; and

K_L = ratio of adsorption to desorption rate coefficients. Furthermore, the sorbed concentration of TCE can be related to the surface fraction β through the geometry of the soil particle because the Langmuir Isotherm does not account for diffusion of TCE into the interior of the soil matrix.

Some important physical properties of trichloroethylene are provided in Table 2.[8]

2.11 Kinetic Properties of TCE Desorption From Soils

Most analytical models used in aquifer cleanup efforts at contaminated sites disregarded the effects of rate-limited sorption/desorption of organic contaminant from aquifer solids. By using a retardation factor in the advection/dispersion equation to account for sorption, these models have assumed local equilibrium between the sorbed and liquid phases.[25] More recently, many advection/dispersion models were developed to also include either a physical or a chemical rate limiting process.[25] To further increase the efficiency of aquifer cleanup efforts, more analytical models that account for the large effects of rate-limited sorption/desorption are currently under development. The purpose of this thesis is to extend the experimental data base which characterizes the rates for desorption of TCE from different types of soil and to evaluate and explain the temperature dependence of these rates. The result should help construct a more efficient model which describes the non-equilibrium processes.

A recent study by Mouvet and Barberies showed that batch desorption of TCE from long-contaminated soil reached an

Table 2
Physical Properties of TCE

Property	Value	Units
Formula	$HClC=CCl_2$	Unitless
Molecular Weight	131.39	g/mol
Density (@20°C)	1.46	g/cm^3
Vapor Pressure (@ 20°C)	58.	torr
Freezing Point	-86.8	°C
Melting Point	-70.	°C
Boiling Point	86.7	°C
Flash Point	89.6	°C
Auto ignition Temperature	788	°F
Physical State (@ 15°C and 1 atm)	Liquid	
Liquid Surface tension (@20°C)	0.0293	N/m
Vapor Specific Gravity	4.5	g/cm^3
Ratio of Specific Heats of Vapor	1.116	Unitless
Latent Heat of Vaporization	$2.4X10^5$	J/kg
Viscosity	0.57	cP
Solubility (@ 20°C)	.7	g/liter
Henry's Constant	.232	Unitless
Partition Coefficient	.199	ml/g
EPA Ground Water Standard	5	µg/liter
Octanol-water coeff (log K_{ow})	2.38	Unitless
Organic carbon partition coeff (K_{oc})	126	mL/g

apparently steady state within one day (24 hours) whereas sorption reached an apparently steady state in three days (72 hours).[23] The same study indicated that the time necessary to attain equilibrium decreases with the size range.[23] During TCE desorption from contaminated soils, two distinct time scales were reported: an initial rapid (hours) rate which involved TCE near the surface of the soil followed by a slower (days) rate involving TCE diffusing from within the soil particles or from the soil matrix.[23] TCE desorption was found to depend on soil moisture content, soil type, distribution of the porous medium, temperature, and on the residence time and the initial concentration of TCE.[23] These effects and others are briefly discussed in the next section.

2.12 Factors that Affect TCE Desorption from Soil

2.12.1 Effects of Resident Time in Soil

As stated earlier, the longer a contaminant is in contact with a soil, the greater the portion of the contaminant that will become entrapped in the soil matrix, and the longer it will take this contaminant to desorb from the soil.[3] A study that evaluated the effect of resident time on desorption of TCE from soil was conducted at Clarkson University, NY. During several experiments, clean soils were exposed to diluted TCE solution for 2.5, 5.5, and 15.5 months. The results of a twelve day desorption process showed an initial fast desorption rate from soil surface followed by a slow desorption rate from the internal soil.[15] This study demonstrated that the TCE remaining in the soil was 10% for 2.5 months resident time and 45% for

15.5 months resident time. The indication of this is that the longer the period of exposure of a soil to TCE, the greater the portion of TCE that will be entrained within the soil matrix, and the longer the period of time required to desorb the same quantity of contaminant (Figure 4). A further conclusion of this study indicates that the fraction of TCE that resisted desorption was the same for different types of soils.[15]

2.12.2 Effects of Soil Moisture

Water has a very strong adsorptive behavior due to its strong polar interactions with soil minerals. Under fully dry conditions, soil matrix sorption governs over organic matter uptake.[26] In unsaturated soils, volatile organics and water vapor will competitively sorb onto a mixture of surface types.[6] In addition, in the Vadose zone, a water molecule existing in the soil minerals suppresses the uptake of non-polar organic solvents.[26] However, in a fully saturated zone, almost all soil uptake is due to organic matter in the soil and almost no uptake is due to soil minerals.[26] A study done by S.M. Steinberg and D.K. Kreamer showed that, using inverse gas chromatography, addition of a small quantity of water vapor to the carrier gas that contained some VOCs significantly decreased uptake of these VOCs by the sandy soil.[4]

In the unsaturated zone, studies confirmed that the amount of sorption in the vapor phase is strongly affected by the soil moisture content.[26] One of these studies indicated that under fully dry condition, sorption of a large amount of pesticides into the soil matrix occurred. However, as the soil moisture

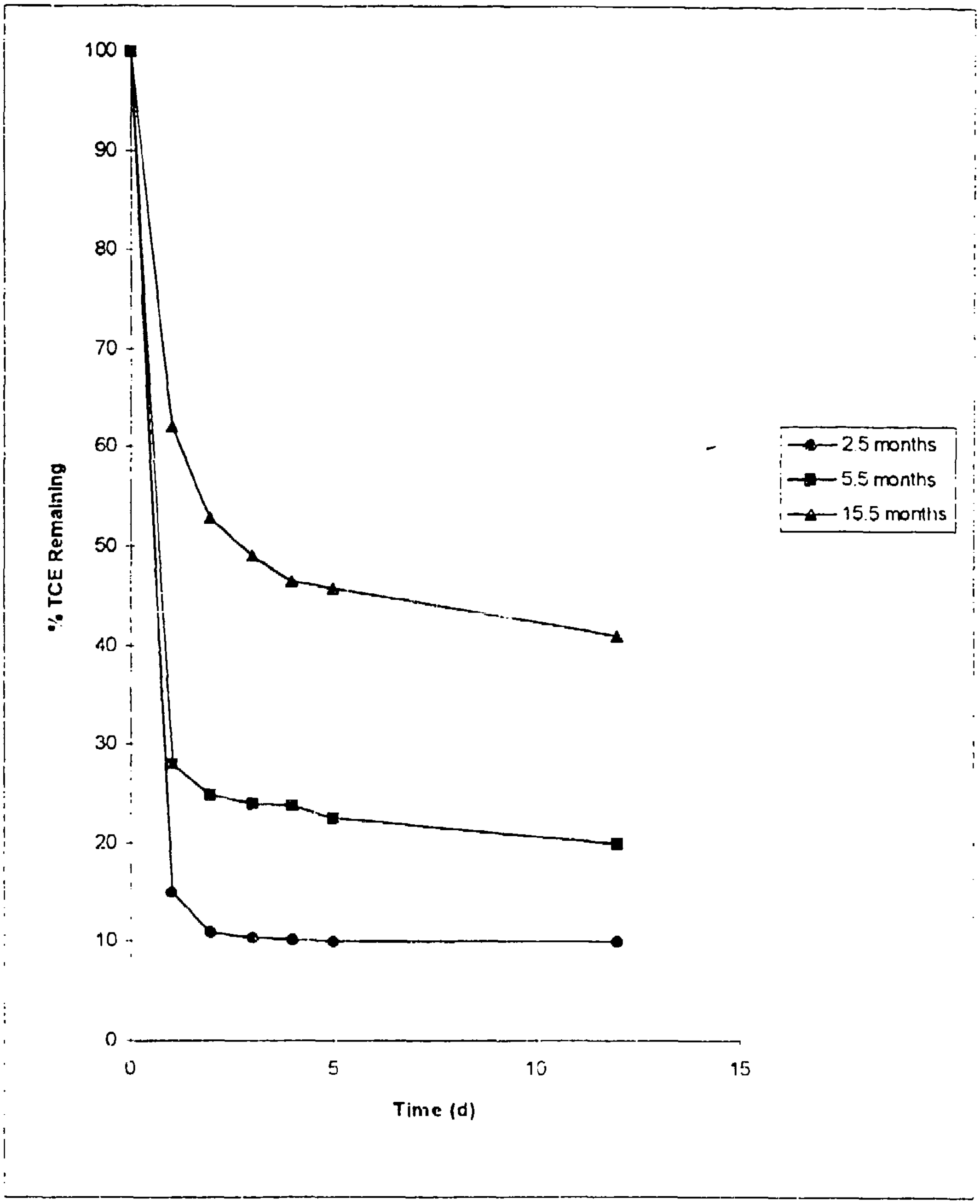


Figure 4: Effect of residence time on TCE Desorption[19]

content increased to about 90%, no pesticide sorption into the soil matrix was observed.[26] This phenomena was observed because of the competition of water molecules to sorb to the soil matrix. When in contact with a contaminated soil, water displaces the contaminant sorbed to the soil surface.[6] This occurs because soil mineral surfaces prefer polar water molecules over nonpolar organic compounds.[6] For instance, after a rainfall on a dry contaminated site, odors of the contaminant have been observed. These odors were almost unnoticeable when the soil had a moisture content.

Say Kee Ong and Leonard W. Lion investigated TCE sorption to soil as a function of soil moisture content. The results, (Figure 5), indicated a strong correlation between soil moisture content and TCE sorption.[6] Region 1 represents soil with no moisture or an oven dried surface with up to single monolayer of water. This region shows large and significant amounts of TCE sorbed to the soil surface. Region 2 represents moist soil with one to five monolayers of water on soil surface. In this region, TCE sorption to soil surface significantly decreases and reaches a minimum value. Water competitively took over and sorbed to the soil surface.[6] In region 3, where moisture content was above 5 monolayers of water to complete saturation, TCE uptake by soil slightly increased due to TCE dissolution in water.[6]

2.12.3 Effects of Temperature

Evidence strongly supports the fact that temperature enhances desorption of volatile organic compounds from

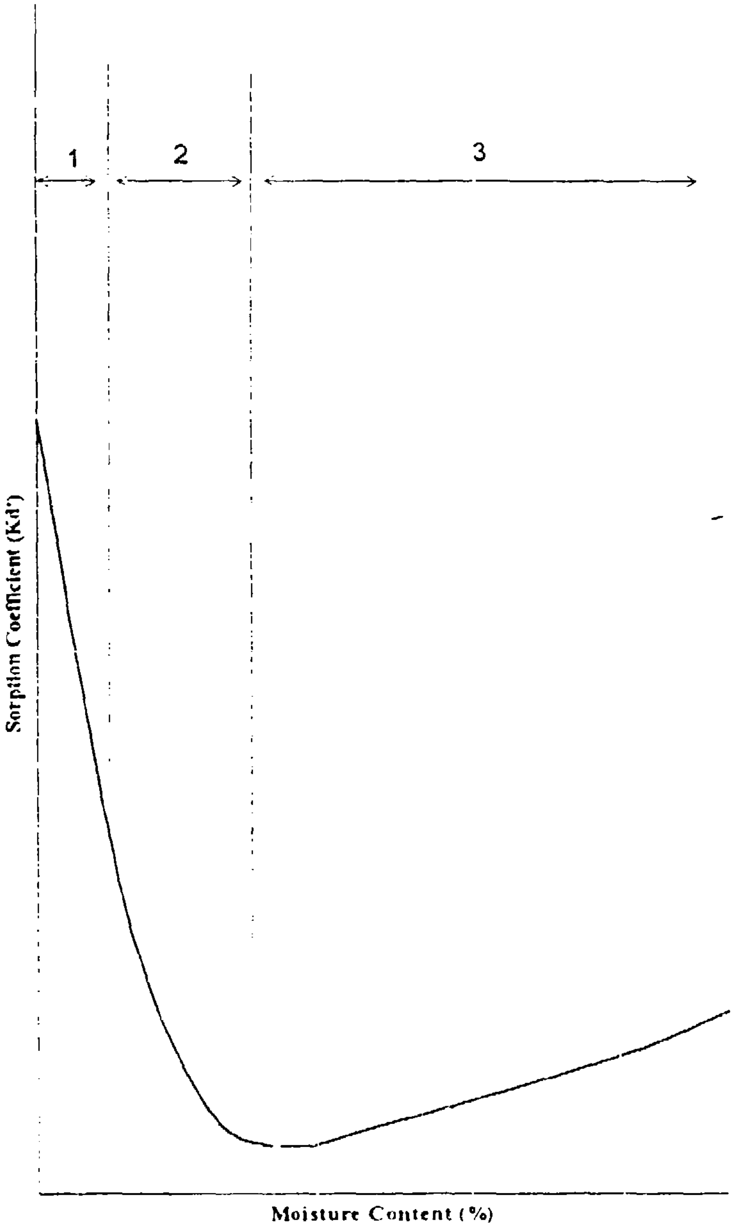


Figure 5: Designated regions and proposed sorption mechanism for vapor phase sorption as a function of moisture content of the surface[24]

contaminated soils. A kinetic treatment of the Langmuir isotherm indicated an exponential dependence of K_L upon 1/T.[24] In an experimental setting, investigators found that an increase of temperature from 10°C to 25°C enhanced the losses of four polycyclic aromatic hydrocarbons (PAHs) from two different soils.[27] Results indicated that the losses of contaminant increased from 39% at 10°C to 70% at 27°C (Figure 6).[27] This study also revealed that the rate of desorption of these PAHs from soil depends on the physicochemical properties of both the contaminant and the soil.[27] Organic matter in the soil was observed to play an important role in PAH sorption and its persistence in soil.[27]

Another study investigated thermal desorption of 1,2-dibromoethane (EDB) from two different soils. Results indicated that after being extracted at a temperature of 100°C, 79% of the initial concentration remained in the analyzed soil. However, extracted at a temperature of 200°C, the soil retained 3.6% of the initial concentration.[19] Investigators explained that this low retention was likely due to the fact that EDB could have decomposed at higher temperatures.[19]

A more detailed study performed by Mingelgrim and Gerstl in 1983 indicated that temperature can positively or negatively influence soil sorption. The two investigators explained this influence by stating that the heat of adsorption of a solute from solution can be either endothermic or exothermic.[26] In an experiment, the uptake of parathion from hexane solution by partially hydrated soils was studied. In this experiment, the

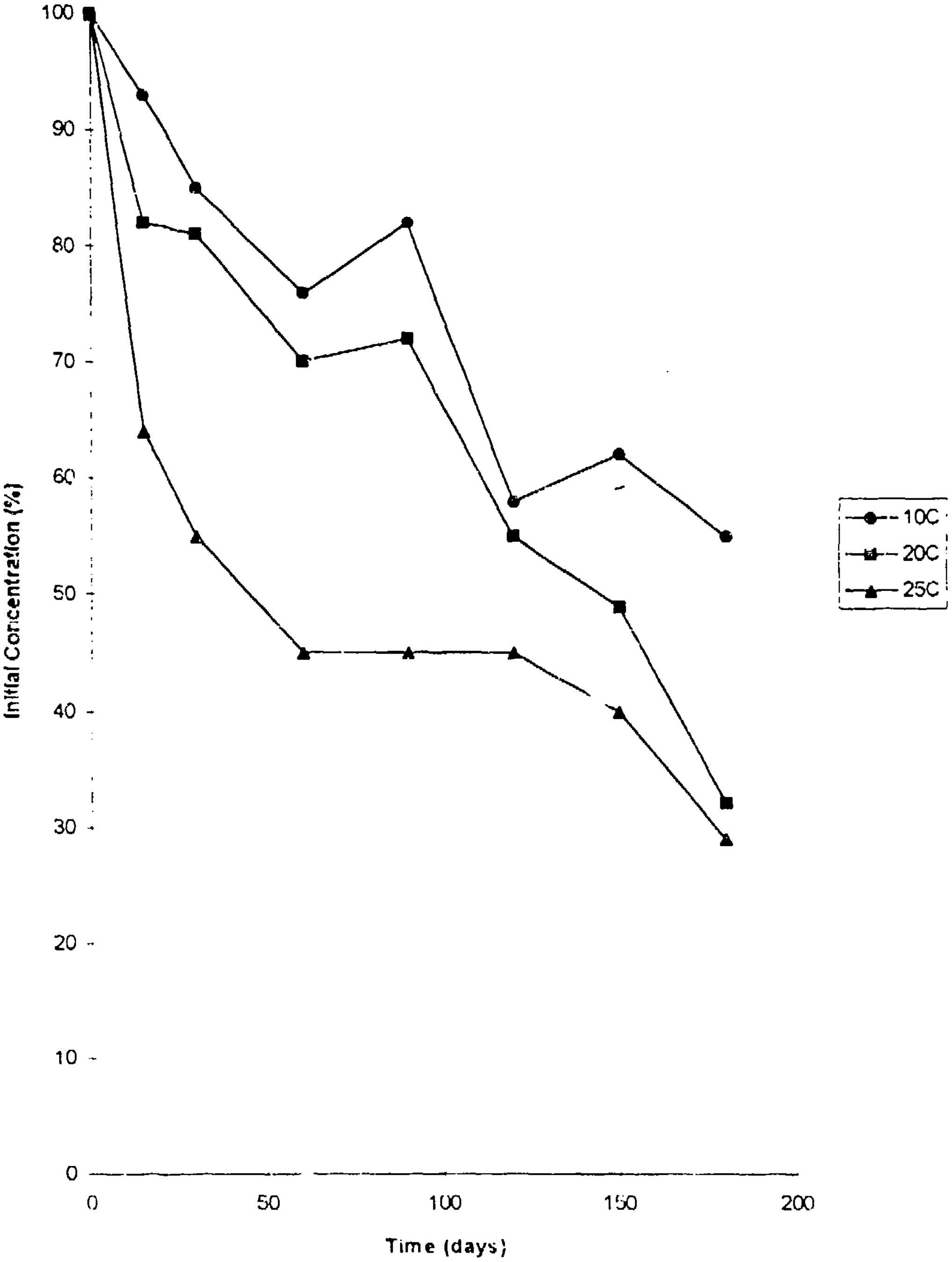


Figure 6: Disappearance of Chrysene from soil (light loam) at 3 temperatures[27]

parathion (a weaker adsorbate) was competing with water for adsorption by soil minerals. When temperature was raised, the energetic interaction of minerals with water was weakened much more than with parathion (heat of adsorption per unit area is greater for water). Thus, this increase in temperature enhances water solubility in hexane more than the solubility of parathion and allows parathion to compete more favorably for adsorption.[26]

2.12.4 Effects of pH

Several studies were performed to evaluate the effect of pH on adsorption and desorption of TCE from contaminated soil. These studies revealed conflicting results. One of these studies investigated the effects of pH on sorption of TCE in pure montmorillite clay over a 36 hour period and found that the maximum amount of TCE sorption was at a pH value equal to 4. At pH values below and above 4, TCE sorption significantly decreased.[11] However, it is of importance to indicate that the clay used in this experiment was treated with sodium citrate-bicarbonate-dithionite to remove the surface coating of amorphous metal oxides. Sorption of TCE to the same but untreated clay was not influenced by pH.[11]

The results of this study indicate that the disruption or removal of the normal surface charge of clay caused by metal oxides increases the sorption of TCE at a pH of 4.[11] However, a better understanding of the role of surface charge to the sorption process was needed to completely interpret the results. In addition, this study only investigated surface sorption and did not evaluate long-term sorption.[11]

In contract, a study that used soil contaminated with TCE for more than 18 years, indicates that changes to the pH from 3 to 13 have undetectable effects on desorption rates over a 24 hour period. The soil used in this study was composed of 56% sand, 32% silt, and 12% clay. The results established that pH has no effect on TCE desorption because TCE is a nonpolar organic compound. The investigators added that only surface soil was evaluated, however, they anticipate that long-term desorption of TCE from soil matrix is weakly affected by pH.[28]

2.12.5 Other Factors Affecting Desorption

Solubility of chemicals in water was shown to influence kinetics of both adsorption and desorption processes. In fact, organic compounds with low solubility have a strong tendency to sorb to soil. Another factor that could influence adsorption and desorption is the chemical make-up of soil. The rate of benzene sorption was three times greater in Al^{3+} saturated clay than in Ca^{2+} saturated clay.[29]

A study performed by Bourg, Mouvet, and Lerner showed that sorption and desorption are slightly influenced by ionic strength.[23] Sorption of several organic compounds was found to also be influenced by the soil particle size. The smaller the size of the soil particle, the greater the soil's available surface area, and the larger the adsorbed quantity of VOCs.[6]

2.13 Spectroscopic Data of TCE

Even thought trichloroethylene is the most frequently reported contaminant in groundwater, its spectroscopic properties have been of less concern and have received limited attention. In 1977, Stadtler Research Laboratories analyzed an infrared absorption spectrum of TCE and found that TCE absorbs light at a frequency of 3080 $\mathrm{cm^{-1}}$.[30] To confirm the above result, a part of this thesis was to determine the infrared absorption spectrum of TCE in the gas phase at high resolution (0.02 $\mathrm{cm^{-1}}$). This task was done using the Bomen spectroscopic data base. This experiment is fully described in Chapter 3 of this thesis. The results confirmed that TCE absorbs light at a frequency nearly equal to 3080 $\mathrm{cm^{-1}}$. Therefore, throughout this project, the feature at 3080 $\mathrm{cm^{-1}}$ will be used to monitor the absolute concentration of TCE in the gas phase. In addition, this feature is used to utilize sensitive indium antimonide detectors. Once the cross-section for optical absorption is determined, by measuring the ratio I_t/I_0, the absolute TCE concentration in gas phase can be determined according to Beer's Law:

$$I_t = I_0 e^{-\sigma L N} \qquad (2.5)$$

In addition to measuring desorption rates of TCE as a function of temperature, this thesis will also include an improved spectroscopic characterization of TCE absorption near 3080 $\mathrm{cm^{-1}}$ and a determination of the cross-section, σ, as a function of temperature.

III. Methodology and Description of Experiment

3.1 General Overview and Description of Experiment

To determine sorption and desorption of TCE from soil samples using infrared absorption, an optical chain that starts with an infrared glowbar source and ends with liquid nitrogen cooled InSb detectors was used. The experimental concept is shown in Figure 7 and the overall apparatus used in this experiment is diagrammed in Figure 8. To isolate the optical absorption due to TCE only, narrow band-pass filters were placed on the detectors to pass only frequencies within the range 3060-3140 cm^{-1}, because a TCE molecule very efficiently absorbs light in this frequency range. By monitoring the intensities of the incident and transmitted signals from the infrared source on the InSb detectors, the concentration of gas TCE inside the tube was measured. Furthermore, absorption due to other species present in the uncontaminated soil samples was accounted for by assessing a control sample. To improve the outcome of the experiments and to improve the minimum detectable TCE concentration, phase sensitive detection with lock-in amplifiers were used. To generate sufficient large numbers of data points with high accuracy, a computer was simultaneously collecting data from the detectors, amplifiers, and the other measurement equipment.

To eliminate atmospheric interferences, desorption directly to vacuum was studied. First, the sorption and

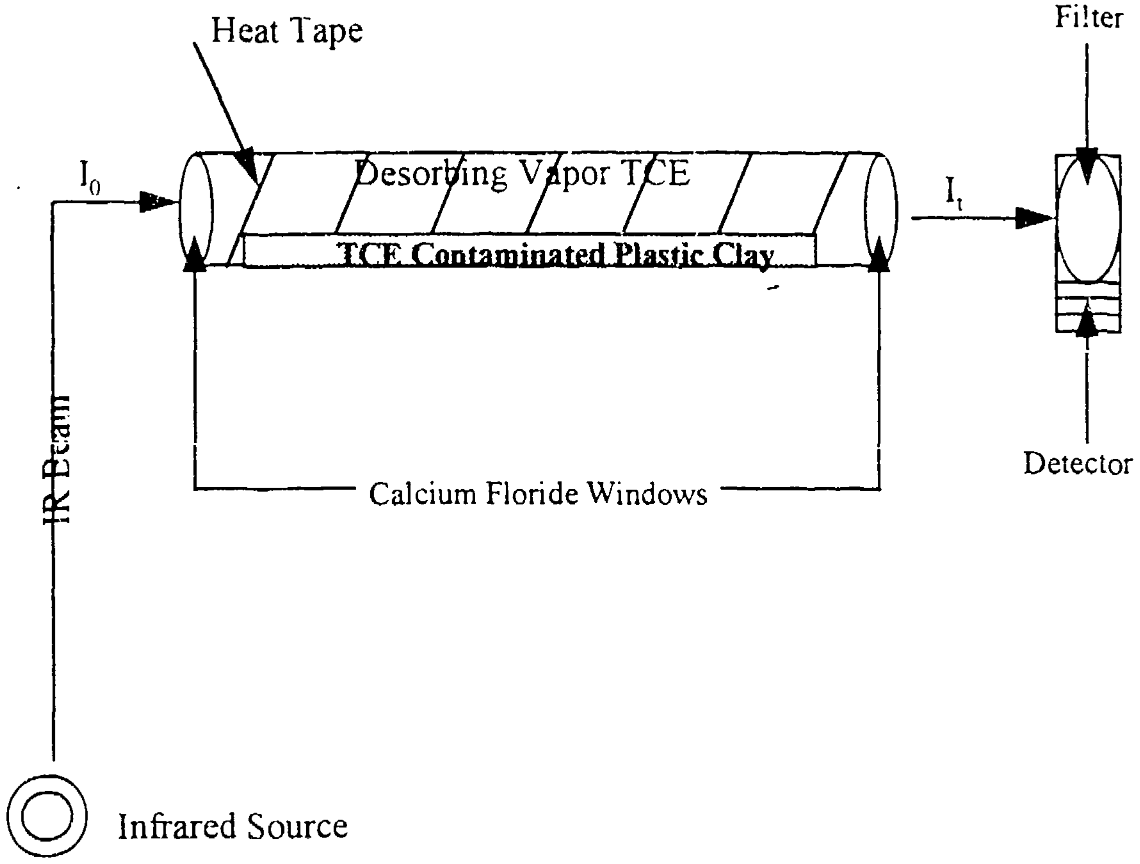


Figure 7: Concept of the desorption experiment

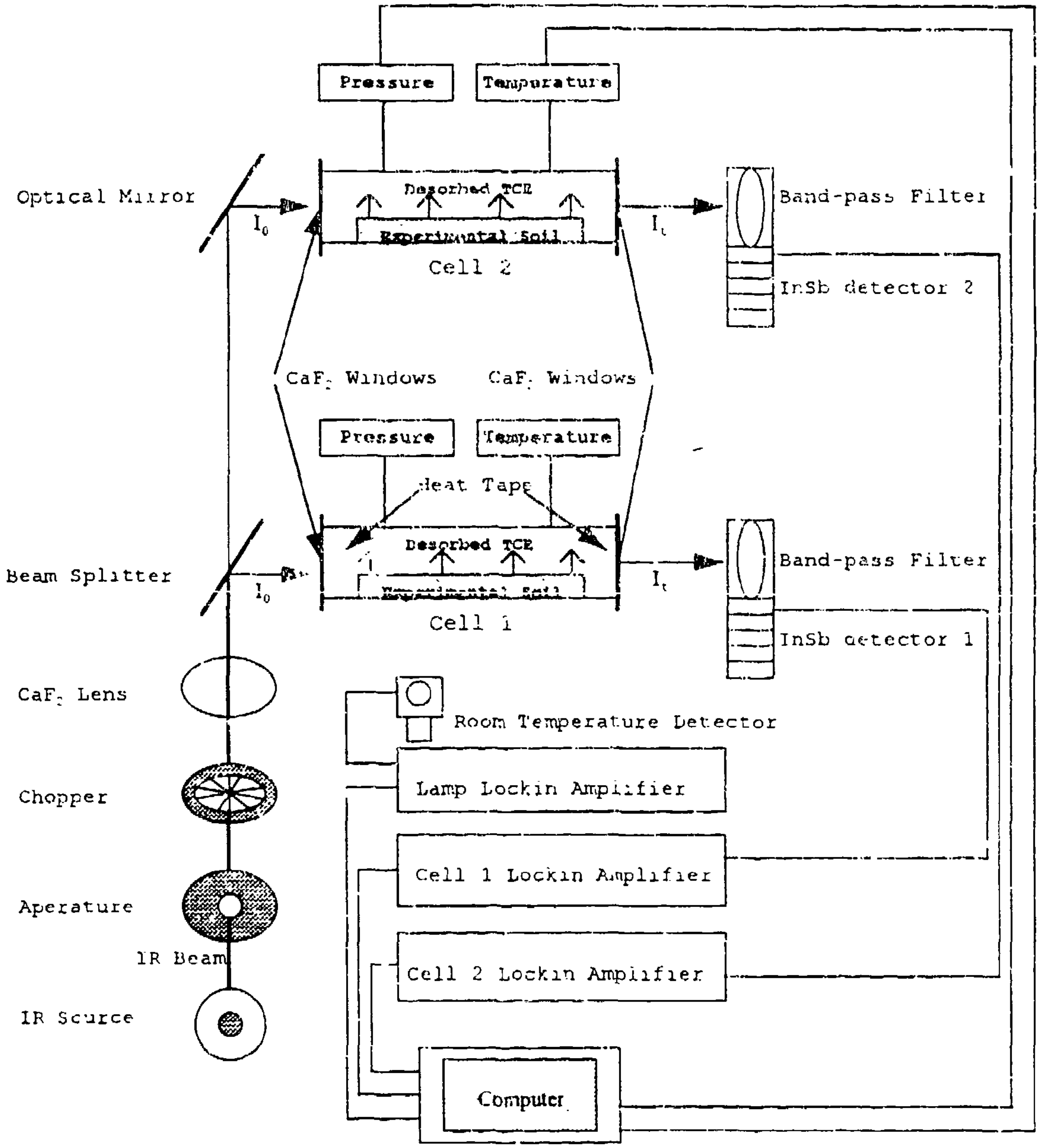


Figure 8: Experimental Apparatus

desorption by the glass and O-rings was determined by exposing both empty cells to vapor TCE and allow time for adsorption and desorption to reach equilibrium. These effects were later subtracted from the experimental data in order to obtain only those effects due to soil adsorption and desorption from the experimental soil. Second, two grams of plastic clay soil that were exposed to liquid TCE for 2 days were arranged along the tube in several particle layers. After eliminating atmospheric gases by re-evacuating the cells, sorbed TCE was then allowed to desorb from the soil into the tube for a period of 4 hours and TCE concentration over time was recorded. Capacitance manometers were used to measure the pressure in the cells. Cell temperature was also measured using gas phase thermocouples and was controlled with heat tape. A computer program was generated using Microsoft QuickC to collect sufficient data that was later analyzed.

The expected TCE vapor concentration as a function of time from these experiments is shown in Figure 1. As indicated earlier, there will be an initial rise characteristic of desorption near the surface of the soil layer and a subsequent slower rate characteristic of desorption from the soil matrix. As the period of desorption gets larger, desorption of TCE from soil is anticipated to reach a new equilibrium.

In this thesis, the temperature dependence of the initial and subsequent desorption rates will be studied very carefully. To accomplish this task, the TCE absolute absorption cross sectional area σ as a function of temperature was determined by observing the transmitted intensity from known TCE vapor concentration at different temperatures. Further, the validity of the Langmuir Isotherm will be assessed in Chapter 4 of this thesis.

In order to conduct the above described desorption rate experiments, the infrared absorption spectrum for TCE in the gas phase had to be determined and recorded at high resolution (0.02 cm^{-1}) using a Bomen DA-8 Fourier Transform Spectrometer.

3.2 Experimental Theory

3.2.1 Overview and Molecular Spectroscopy

The use and role of an infrared light source in this research is very critical. By comparing the intensities of the emitted and transmitted signals, the concentration of gas TCE in both glass tubes was determined. This was done according to Beers law:[6]

$$I_t = I_0 e^{-\sigma L N} \qquad (3.1)$$

where:

I_0 = Incident intensity;

I_t = Transmitted intensity;

σ = TCE cross section for optical absorption;

L = Path length traveled by the signal;

N = TCE concentration inside the glass tube.

Molecules absorb light at specific wavelengths. Because of its structure and its atoms, a molecule will absorb at specific electromagnetic frequencies. In addition, the amount of light absorbed by a specific molecule depends on the atoms that constitute the molecule, the structure of the molecule, and on the type of bonds that hold the atoms together.[31] Frequently, different molecules may absorb some electromagnetic frequency but with different efficiencies. For example, a TCE molecule was found to strongly absorb light at a frequency of 3080 cm^{-1} but hardly absorbed a frequency of 1500 cm^{-1}. The photons of the absorbed light can then excite the atoms and cause them to go to a higher energy level.

A molecule is a flexible structure whose atoms are bonded together by "what can be considered effective springs."[31] Therefore, the molecule can vibrate and acquire vibrational energy. This vibrational motion and corresponding vibrational energy can be altered if the molecule is exposed to infrared radiation.[31] Besides rotating, a molecule can vibrate in several different ways, with its atoms moving in various directions with respect to one another. The frequencies that are primarily absorbed by the molecule correspond to the vibrational frequencies of the atoms that form the molecule. Several molecules, TCE for example, have both vibrational and rotational resonances in the infrared (IR) and are thus considered good absorbers of light in the IR spectrum.[32]

In the photoelectric effect and in many aspects of emission and absorption, radiation behaves in a way that suggests a stream of particles called *photons*. Each photon has an amount of energy E_i related to the frequency V_i by the expression:[33]

$$E_p = hV_p \tag{3.2}$$

where *h* is Plank's constant and the subscript p stands for photon. When a photon is absorbed by a molecule, raising it from its ground state, where the molecule has energy E_0, to the excited level E_1, the relation between the energy E_p of the photon absorbed and the energy gained by the molecule is:[33]

$$E_p = E_1 - E_0 \tag{3.3}$$

These changes in energy state are called *transitions*. However, not all transitions are possible but a probability is associated with each transition.

At sufficiently low temperatures almost no molecule can acquire enough energy by collision to reach an excited state and nearly all molecules are in the ground state.[34] As temperature increases, the equilibrium numbers in excited states will increase and the amount of vibrational energy will increase.[34] The number of molecules with energy in the range E to E + *d*E is proportional to the product of the Boltzmann factor $e^{-E/kT}$ and the number of states in the range *d*E.[34] For a simple case, if we assume there are only three energy levels E_0, E_1, and E_2, the following statistical population distribution exists[34]

$$N_0 = Ae^{-\left(\frac{E_0}{kT}\right)} \tag{3.4}$$

and

$$N_1 = Ae^{-\left(\frac{E_1}{KT}\right)} \tag{3.5}$$

therefore

$$\frac{N_1}{N_0} = e^{-\left(\frac{(E_1-E_0)}{KT}\right)} \tag{3.6}$$

or

$$N_1 = N_0e^{-\left(\frac{(E_1-E_0)}{KT}\right)} \tag{3.7}$$

where A is a constant depending on the number of molecules. Therefore, it appears that temperature does in fact have an effect on the activation of TCE molecules. As temperature increases, the number of energetically activated TCE molecules increases and their movement increases as well.

3.2.2 TCE Absorption Spectrum

3.2.2.1 General Theory

Critical to this research was the use of an infrared glowbar light source and the use of few optical lenses. In order to measure the concentration of TCE in the interior of the cell, the intensity of the incident and transmitted signals on the detector had to be measured and recorded throughout the experiment. However, because TCE is the chemical that was used and because different chemicals absorb different electromagnetic frequencies (EMF), the absorption characteristics of TCE had to be determined.

As stated earlier, a study performed by Stadtler Research Laboratories indicated that TCE absorbs light very effectively, in the frequency range of 3040 to 3140 cm^{-1}. Therefore, throughout this research, this frequency range was used to determine the concentration of TCE in the gas phase within the glass tube. Using this frequency range, changes in the intensity of the transmitted signal correspond to changes in the concentration of TCE within the enclosed glass tube.

To re-evaluate the electromagnetic frequency of the light that TCE absorbs in the IR region. and to consistently define a more accurate range of TCE absorption, a new experimental analysis of the TCE low resolution spectrum was performed. To accomplish this task, a Bomen DA-8 Fourier Transform Spectrometer was used.

3.2.2.2 *Description of Experiment*

The experiment setup is shown in Figure 9. A 2 inch diameter by 1 incn long custom-made Calcium Fluoride cell was used. To eliminate atmospheric interferences, this cell was first evacuated down to vacuum, then filled with vapor TCE until the pressure within the cell reached the vapor pressure of TCE. The cell was then placed in the optical line of the Bomen spectrometer. A glowbar light source similar to the one used in the desorption experiments was used to emit a light beam that was reflected by several mirrors. Before arriving at the detector that records the wavenumbers of the transmitted light,

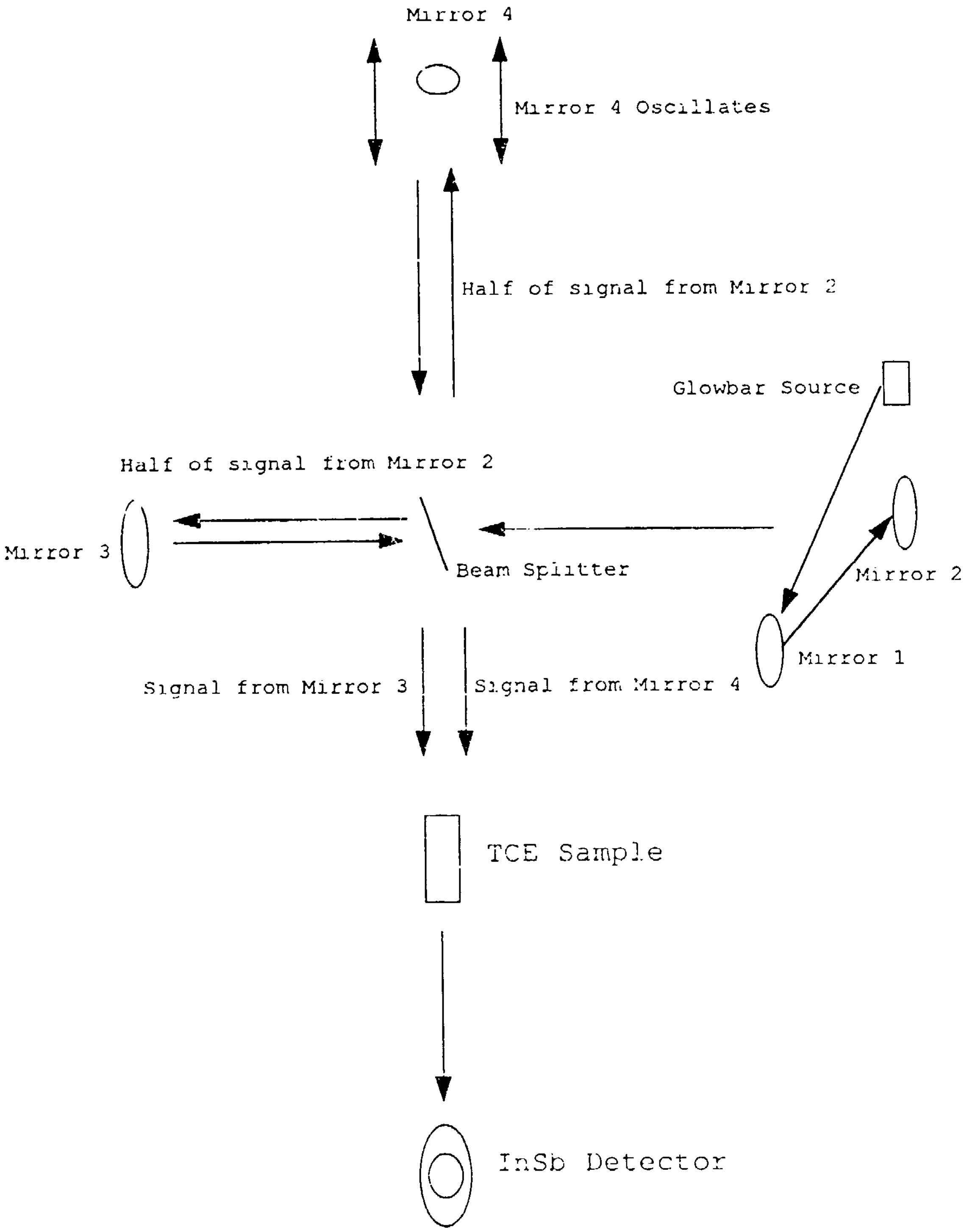


Figure 9: Bomen apparatus of the TCE IR spectrum experiment

the beam first went through the gas TCE cell. The frequency range used in this experiment was 3000 to 3200 cm^{-1} and the losses of the intensity of the signal passing through the cell was recorded and analyzed.

It is of importance to note that the windows attached to the glass tube used in the soil desorption experiment are also made of calcium fluoride material. This material, unlike glass, does not absorb wavelengths in the infrared frequency range used in this experiment. Therefore, any reduction in the signal is believed to be caused only by substances inside the cell.

To account for signal losses due to other species, a background experiment was performed using an empty cell that was first evacuated. Because the soil used in the TCE desorption experiments may be slightly moist, an experiment was performed to assess signal losses due to water by placing water in the cell. Both control experiments revealed negligible effects of water and atmosphere on the TCE optical absorption spectrum.

3.2.2.3 Results of Experiment

Figure 10 indicates that TCE absorbs light in the infrared region at a frequency near 3080 cm^{-1}. As a result, a frequency range centered at 3080 cm^{-1} was used to increase the sensitivity of the detectors and to isolate absorption due to TCE alone and not to other species in the cell. Soil desorption experiments were thus designed so that losses in signal can be used to determine concentrations of gaseous TCE desorbed from the soil samples. In addition, the nitrogen cooled indium antimonide detectors used in this research can detect intensity changes

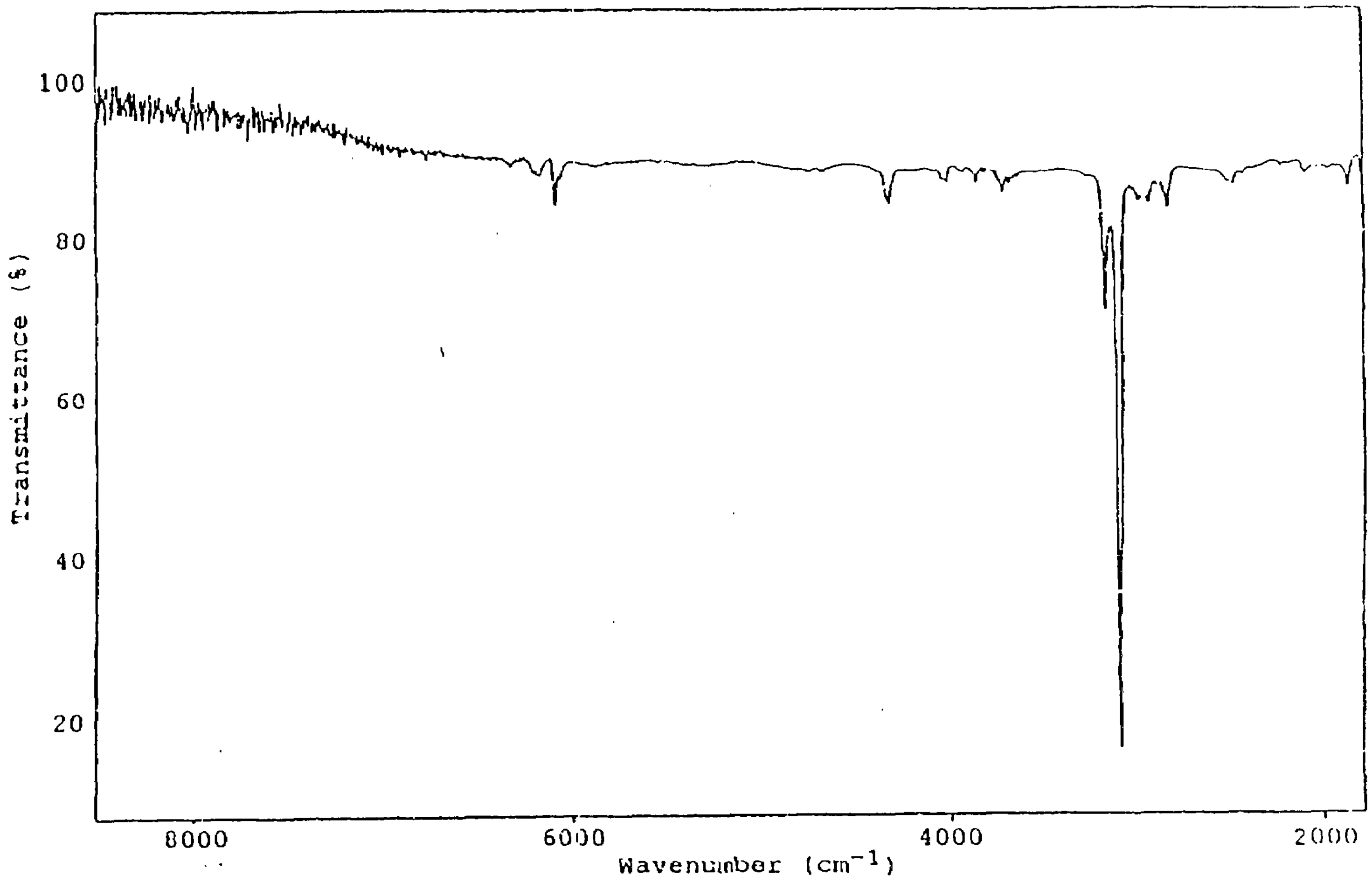


Figure 10: Low Resolution IR Absorption Spectrum of TCE

very effectively near the frequency 3080 cm^{-1}. When cooled, these detectors will detect intensity changes very effectively.

To define a smaller and more accurate frequency range for TCE absorption, a similar experiment at high resolution was performed using the same apparatus that was used for low resolution. During this experiment, TCE absorption in the gas phase was recorded near the frequency 3080 cm^{-1} with 0.02 cm^{-1} increments.

Figure 11 clearly indicates that TCE in the gas phase absorbs light very effectively (near 100 %) at a frequency near 3080 cm^{-1}. Therefore Custom-made filters centered around 3080 cm^{-1} that allow the passage of only those wavenumbers between 3060 and 3140 cm^{-1} were designed and placed on the detectors. The range 3060 to 3140 cm^{-1} was used to include those wave numbers that are not 100% absorbed by TCE but that still appear to be somewhat effectively absorbed by TCE. This will allow a minimum signal to be detected at all times. This is critical when comparing incident and transmitted signals both through high TCE concentrations. In addition, the transmitted signal will never approach zero because some frequencies within the used range will never be 100% absorbed by TCE and therefore, there will always be some signal on the detector even when the cell is completely filled with 100% pure TCE.

3.2.3 *Cross Sectional Area (σ)*

3.2.3.1 Theory

When a beam of photons is incident on a medium, its intensity decreases exponentially with increasing depth of

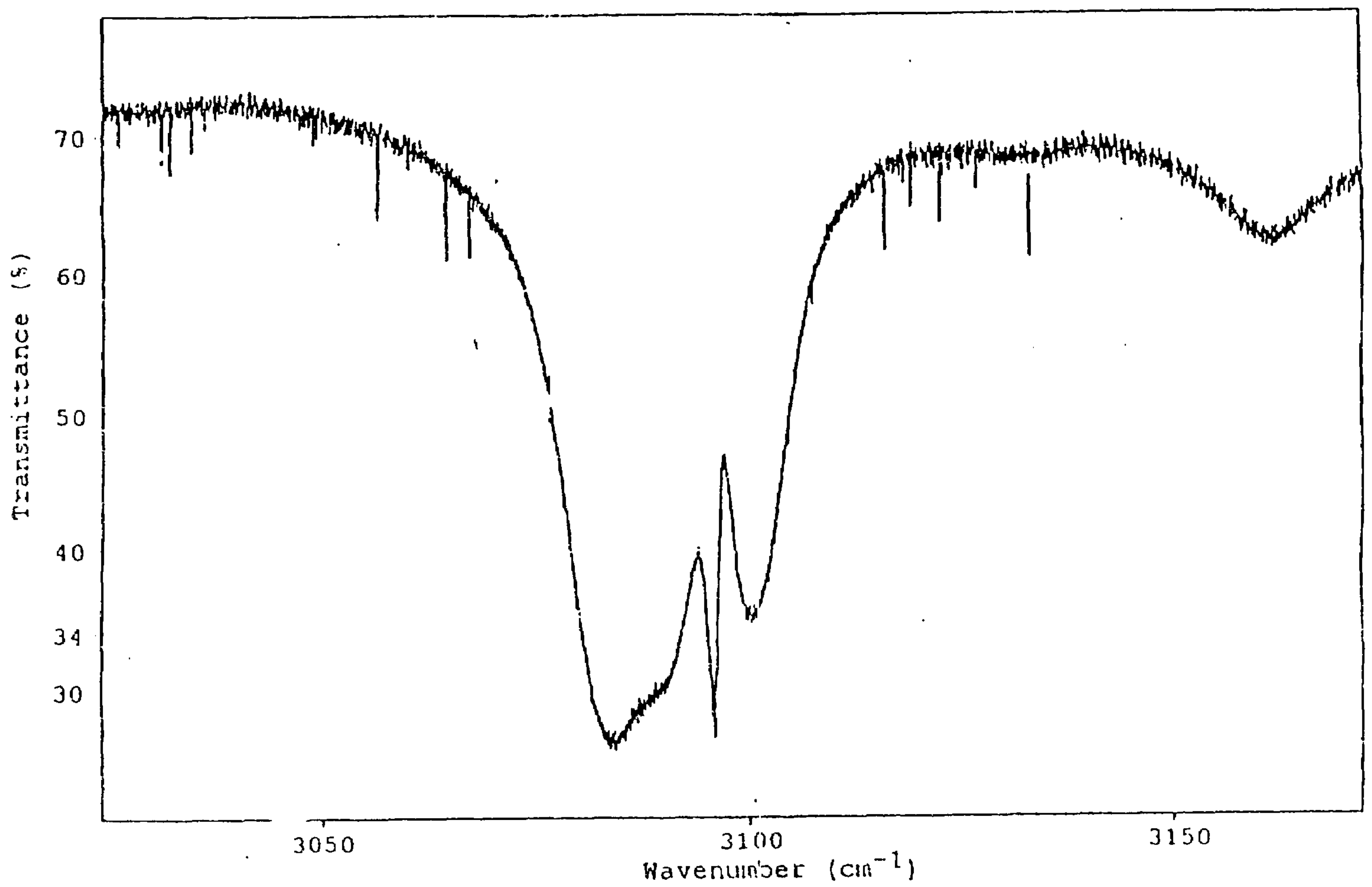


Figure 11: High Resolution IR Absorption Spectrum of TCE

penetration into the medium. This reduction in intensity is referred to as **attenuation** of the beam.[30] This attenuation of a beam can also be caused by increasing the concentration of a light absorbing chemical.

Throughout this research, the infrared beam was transmitted through the glass tube that contained gas TCE that desorbed from the contaminated soil. The photons in the beam would strike at random through the glass tube. Knowing the tube enclosed a TCE concentration, there is some chance that a TCE molecule would absorb one of the photons. Each TCE molecule has an effective area σ, called the **cross section.**[30] Cross section can be thought of as the area of the molecule that is at right angles to the direction of motion of the photons.[30] Furthermore, it is assumed that a TCE molecule will absorb a photon only if the incident photon strikes an area σ.[30] Therefore, the probability that a collision will occur is proportional to σ. That is the probability increases as the number of molecules increases. If we define:

dx = the length of the tube;

N_f = the number of incident photons;

N = the number of molecules per unit volume (particle/m),
each with cross section σ.

dN_f = the number of photons that were absorbed in the tube; and

A = the cross sectional area of the tube (πr^2),

then the ratio of the number of the absorbed photons to the number of emerging photons, dN/N, equals the ratio of the total target cross section $n\sigma A dx$ to the tube area A.[30] That is

$$-\frac{dN_p}{N_p} = \frac{NA\sigma dx}{A} = N\sigma dx \qquad (3.8)$$

The minus sign indicates that photons are being removed from the beam. Integrating this expression and letting $N_0 = N_p$ at $x = 0$ and $N_L = N_p - dN_p$ at $x = L$, the result is

$$\int_{N_0}^{N_L} \frac{dN_p}{N_p} = -N\sigma \int_0^L dx \qquad (3.9)$$

$$\ln\left(\frac{N_L}{N_0}\right) = -N\sigma L \qquad (3.10)$$

or

$$N_L = N_0 e^{-\sigma L N} = N_p e^{-\sigma L N} \qquad (3.11)$$

Equation (3.11) indicates that the number of photons that penetrates the glass tube decreases exponentially with tube length. That is, the longer the tube, the more photons get absorbed within the tube.[30]

In this study, however, the length of the tube was held constant and the variable was TCE concentration inside the tube that should increase because of desorption from the experimental soil. During the period of desorption of TCE, the concentration of TCE inside the glass tube increases and fewer photons travel through the tube without being absorbed by the TCE molecules. Therefore, by analogy, the length of the tube in the above derivation corresponds to the concentration of TCE in this research and the number of incident and emerging photons corresponds to the incident and transmitted intensities. Therefore, the intensity of the transmitted beam was expected to decrease with time. That is:

$$I_t = I_0 e^{-\sigma l N} \tag{3.12}$$

where

I_t = transmitted intensity (mVolts);

I_0 = incident intensity (mVolts);

σ = cross-section for optical absorption (cm^2/molecule);

l = path length (cm); and

N = concentration of TCE (molecules/m^3).

Equation (3.12) is known as Beers Law.[35]

Once the cross-section for optical absorption of TCE was computed, the absolute TCE concentration in gas phase could be determined simply by calculating the ratio I_t/I_0 then using equation (3.12).

3.2.3.2 Description of Experiment

To experimentally determine the optical cross section of TCE, vapor TCE was slowly introduced into each of the glass tubes in a linear form until the vapor pressure of TCE at room temperature was reached. By slowly evacuating both cells, this TCE pressure was linearly released at the same rate. During the experiment, TCE pressure, cell temperature, and the transmitted intensity of both cells were continuously recorded every second via the computer. The recorded data was later analyzed by using

Beer's law equation (3.12) to mathematically solve for the cross sectional area.

3.2.3.3 Results and Calculation of cross section

For each gas, the Ideal Gas Law states that:

$$PV = nRT \tag{3.13}$$

where

P = pressure of gas (torr);

V = volume of gas (cm^3);

n = number of moles;

R = Ideal Gas constant;

= 0.0821 (lit-atm/mol-°K);

= 1.0356×10^{-19} (cm^3-torr/molecule-°K); and

T = temperature of gas (°K).

Arranging equation (3.13) gives

$$N = \frac{n}{V} = \frac{P}{RT} \tag{3.14}$$

where

N = TCE concentration (molecules/cm).

The ratio n/V in equation (3.14) corresponds to the concentration "N" used in Beer's law (equation (3.12)). Rearranging Beer's law gives:

$$\ln\left(\frac{I_t}{I_0}\right) = -\sigma l N \tag{3.15}$$

or

$$\sigma = -\frac{\ln\left(\frac{I_t}{I_0}\right)}{LN} \tag{3.16}$$

After Substituting equation (3.14) for N, equation (3.16) thus becomes:

$$\sigma = -\frac{\ln\left(\frac{I_t}{I_0}\right)}{L} * \left(\frac{RT}{P}\right) \tag{3.17}$$

or

$$\sigma = -(RT) * \frac{\ln\left(\frac{I_t}{I_0}\right)}{PL} \tag{3.18}$$

After replacing R with its numerical value, equation (3.18) becomes:

$$\sigma = -1.0356\text{x}10^{-19} * T * \frac{\ln\left(\frac{I_t}{I_0}\right)}{PL} \tag{3.19}$$

where

σ = optical cross section of TCE (cm^2);

I_t = transmitted intensity at time t;

I_0 = incident intensity at time zero (N = 0);

L = path traveled by beam inside the tube = 43.5 cm;

P = pressure (torr); and

T = temperature (°K) = 300 K (room temperature).

To solve for σ, a graph of P versus $\ln(I_t/I_0)$ was plotted and analyzed for cell 2 (Figure 12). Because L and T were held constant in equation (3.19), if σ is assumed to be constant at a

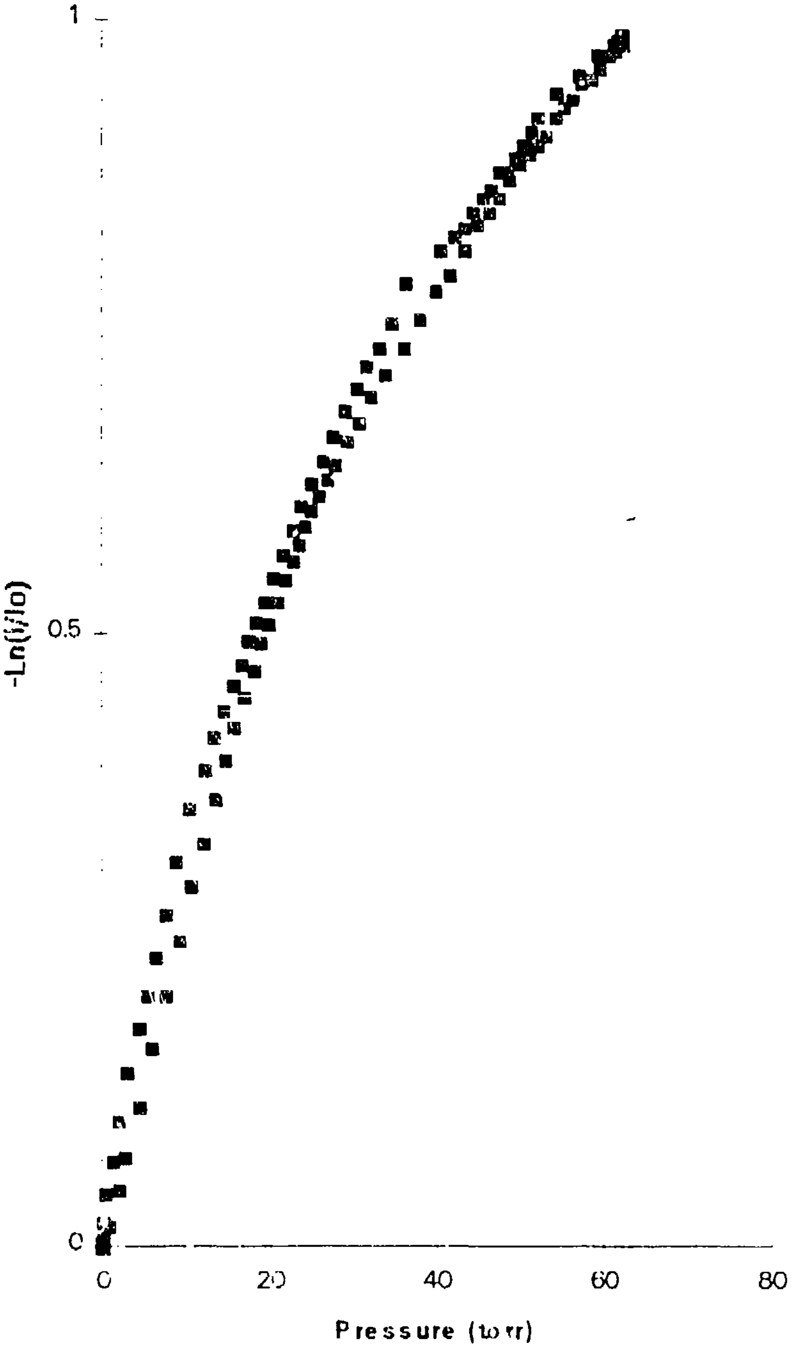


Figure 12: Uncorrected Plot of Pressure vs. LN(It/Io)

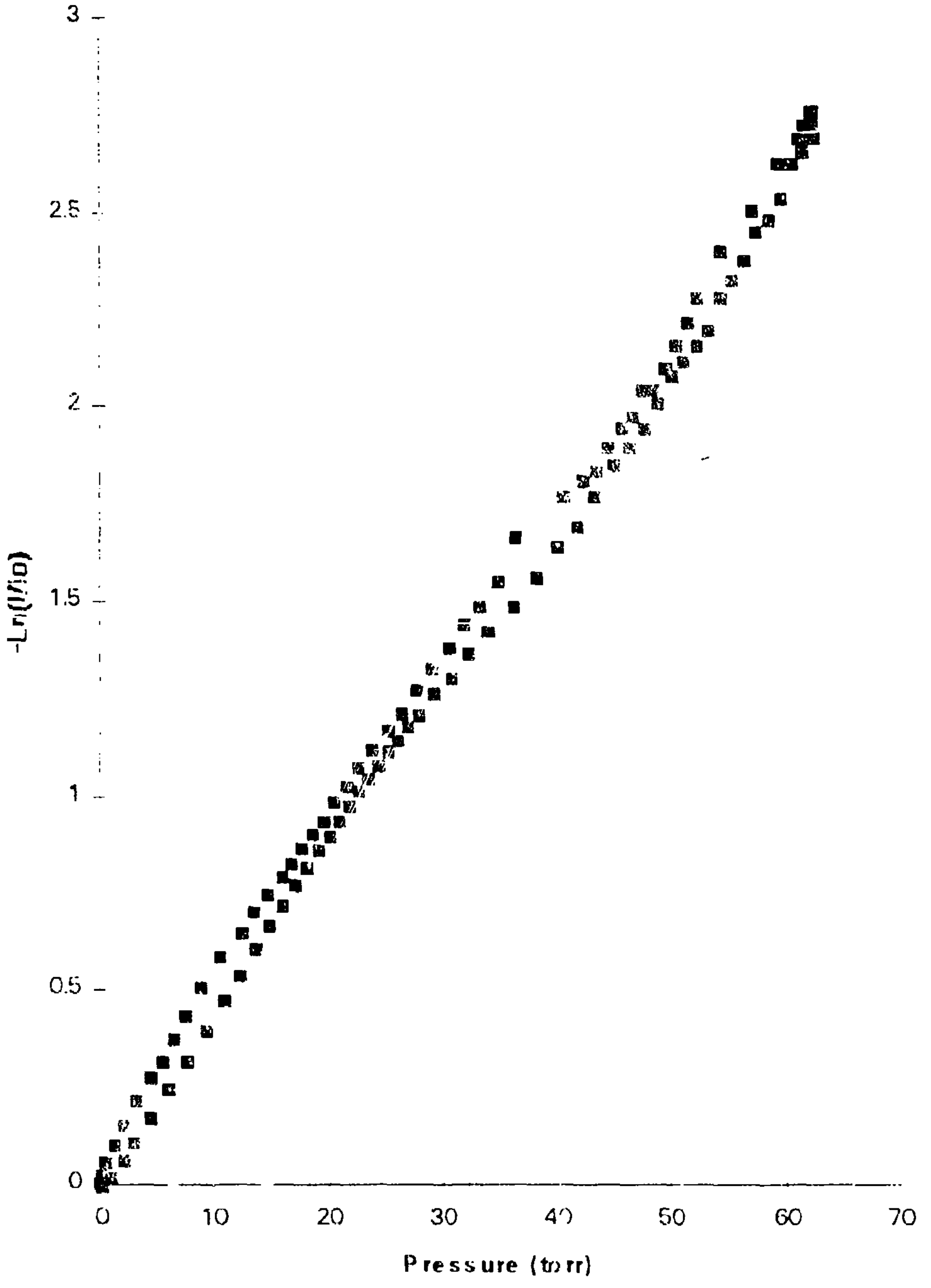


Figure 13: Corrected Plot of Pressure vs. LN(It/Io)

temperature equal to 300°K, the graph should show a linear relation between pressure and $\ln(I_o/I_t)$ with a negative slope.

Unfortunately, the graph appeared to have some curvature (Figure 12). The reason behind this curvature was that the filter placed on the detector allows frequencies that are not absorbed by TCE to pass through to the detector. As mentioned earlier, both filters allow the passage of all frequencies within the range 3060 and 3140 cm^{-1} so that a signal not affected by the presence of TCE in the cell will always be recorded by the detector. This constant intensity that was constantly being recorded by the detectors even when the cell was 100% filled with pure TCE appears to be causing the curvature on both graphs. Therefore, a correction was necessary to obtain a more accurate and representative optical cross section of TCE. A complete mathematical derivation that explains how and why the specific constants were subtracted to get a linear graph can be found in Appendix A. The results of the analysis from Appendix A indicates that the optical cross section of TCE for cell 1 was $\sigma_1 = 3.334 \times 10^{-20} cm^2/molecul$ and $\sigma_2 = 3.335 \times 10^{-20} cm^2/molecule$ for cell 2. After the necessary corrections were made, the graph was again plotted and became nearly 100% linear (Figure 13). Because both cells appeared to possess very similar characteristics, it was decided that one single cross section value would be used for both cells. This cross section was computed by taking the average of the cross sections of both cells. This value was:

$$\sigma = 3.3345 \times 10^{-20} cm^2/molecule$$

3.2.3.4 Temperature Dependence of σ

The cross sectional of TCE was experimentally determined as a function of temperature to 100°C. The experiment, which was performed in the same way previous cross sections were determined, revealed no effect of temperature on the optical cross section. Therefore, throughout this thesis, a constant optical cross section of TCE at room temperature was used.

3.3 The Experiment

3.3.1 General Overview

Kinetic rates usually exhibit strong temperature dependence in part due to activation energies. The temperature dependence of the TCE desorption rates will provide critical data for assessing the applicability of various microscopic mechanisms for the desorption process. It was expected that an increase in temperature would accompanied by an increase in desorption rates.

The experiments of this study were designed to measure temperature dependence of TCE desorption rates from Plastic Clay 98b. This dependence was evaluated within the range 27 to 100°C at a fixed sorbed liquid TCE concentration and a fixed exposure time of 2 days.

The experiments consisted of two identical glass tubes with calcium fluoride windows glued at each end. Measurement devices such as pressure detectors and thermocouples are attached to each tube to measure pressure and temperature throughout the desorption phase of the experiment. To eliminate atmospheric interferences, each glass tube was evacuated down to vacuum. To continuously maintain the experimental soil under a fixed temperature, both glass tubes had heating tape placed around them throughout the desorption period of TCE from the soil. Each of the two glass tubes was filled with 2 grams of Plastic Clay 98b that has been continuously exposed to liquid TCE for a period of 2 days. The two tubes were then closed, temperature was applied, and data collection began.

To detect and measure the concentration of desorbed TCE in the glass tube, a glowbar was used as the source of an infrared beam that would travel through the closed tubes. Before reaching the first end of the tube, this IR beam would first have to go through an optical chain discussed in the next section. Then the signal will enter and leave the experimental tube through calcium fluoride windows, pass through the filters and finally arrive at the detector where its intensity was recorded. Because data was collected via a computer, all measurements, including temperature, pressure, and signal intensity, were converted to voltage then transmitted to the computer. Via the written computer program, the computer was able to convert the recorded data back to its absolute units (°C, torr, mVolts) and stored it in a data file.

3.3.2 Components of the Optical chain

The apparatus used in these experiments consisted of several optical and electronic devices. These optical devices were placed in a chain such that the error sources were minimized and the quality of the data collected was higher. This optical chain consisted of several devices.

Throughout this research, a glowbar was used in this study as an infrared light source. Second in the optical chain, an aperture was placed next to the glowbar in order to limit the spatial extent of the IR light beam for maximum intensity on the detectors. To chop the IR signal, a chopper was placed after the aperture and was set at a constant frequency of 24Hz(not a fraction or a multiple of 60Hz). This frequency was connected to a lock-in amplifier to eliminate the IR emissions from other sources in the room and to allow only the IR signal coming out of the glowbar to be detected. To converge the chopped signal for maximum intensity, a calcium florid lens was placed after the chopper. Because of the simultaneous use of two parallel cells, and the way the experimental apparatus was designed, a beam splitter was placed after the lens to split the IR beam into two equal beams. The first half beam would go through the first cell (cell 1), and the other half, after being reflected by a mirror, would go through the second cell (cell 2). This mirror was needed because of the setup of the two cells with respect to the IR glowbar source.

In order to obtain accurate data, calcium fluoride windows were glued to the ends of each glass tube to allow the signal to pass through the glass tubes with no losses. These windows do not absorb infrared light. Therefore, any reduction in the signal's intensity would not be caused by the windows. The windows are glued on the ends of the tubes by a mix called "[illegible] Seal that is designed for applications in a vacuum environment.

In order to maintain the cells under vacuum conditions at the connections of glassware, Kelvar (Teflon) O-rings were placed between the steel connectors and the glassware. These O-rings were designed to not adsorb any organic chemicals and were found to adsorb a negligible amount of TCE. To connect the different pieces of glassware of the experimental apparatus, three types of ½ inch Cajon Tube Fittings connectors were used in the experiment. The three connectors are made of stainless steel and include T-connectors, 90 degree elbows, and straight connectors. These fittings compress O-rings to seal against the glass tubing. In addition, four valves were used in the experimental apparatus. Two of these valves were used to control vacuum conditions and the other two were used to expose the cells to vapor TCE for alignment purposes and in the TCE optical cross section experiments. Each of these two valves was placed on a glassware finger that contained liquid TCE and that was connected to the cell via a T-connector. All four valves were tested and found not to allow any leaks.

To keep the experiment enclosed and to maintain the desorbing TCE within the cell for concentration measurements, different glassware pieces were used. These glassware pieces were connected in a way to maintain the cells under vacuum and away from atmospheric interferences. Finally and most importantly, two T shaped glass tubes were used to contain the experimental soil and thus the desorbing TCE. Each of these tubes was placed in a way that allowed the incident IR beam to go through the desorbing vapor TCE and to arrive on the detector. These glass tubes were ½ inch in diameter and could hold vacuum conditions of under $5x10^{-}$ torr. After each experiment, these tubes were cleaned and maintained under vacuum to eliminate any glass adsorbed substances.

3.3.3 Data Collection System

To obtain consistent and very accurate results, several measurement devices were used in this study to continuously collect data every minute.

Gas Phase Thermocouples were used to measure temperature in the interior of the cell. These thermocouples were introduced into the cell in a way that they are in the cell's atmosphere without touching the glassware. These thermocouples were designed so that a change in the temperature in the cell would effect the resistance and thus the voltage in the thermocouples. This voltage was then recorded by the computer and converted to degree Celsius (°C) via the computer program. To measure pressure within the experimental cell, Baratron Pressure Transducers were connected to the interior of each of the two cells. These devices could measure pressure within the range 0 to 100 torr (> TCE vapor pressure). A change in pressure in the cell would cause a change in voltage that was converted to pressure in torr and was displayed by the device. These pressure transducers were connected to the computer which recorded these pressure readings every minute. A band-pass filter was placed on each detector to filter out only the frequency absorbed by TCE. These filters were designed to transmit 70% or higher of the intensity between 3060 and 3140 cm^{-1}. All other frequencies were not transmitted by these filters. This will increase the efficiency in measuring the concentration of TCE in the cell. To evaluate the accuracy of their detection, these filters were experimentally tested for transmitivity and the results are shown on Figure 14. Most importantly, 2 Photovoltaic Indium Antimonide Detectors (InSb) were used to measure the intensity of the IR signal transmitted through the experimental cell and onto the band-pass filters. These detectors were continuously cooled by liquid nitrogen to keep their temperature very low in order to increase their sensitivity. These detectors generated a voltage that corresponded to the intensity of the signal incident on the detectors. Each voltage was then transmitted to a Transimpedence Preamplifier that boosted the signal. This signal was then correlated with the frequency of the chopper by a Lock-in amplifier. Both Lock-in amplifiers were connected to the computer that recorded and stored the intensity of the transmitted signal every minute. The minimum detectable TCE concentration of these detectors was found to be in the order of 0.02 torr. Finally, a room temperature Hamamatsu Detector that did not need to be continuously cooled by liquid nitrogen was placed next to the lens facing the IR source and was used to detect changes in the intensity of the IR source. The purpose of this was to determine whether a change in the signal's intensity was due to a change in the intensity of the IR source or in the concentration of desorbed TCE in the glass tube.

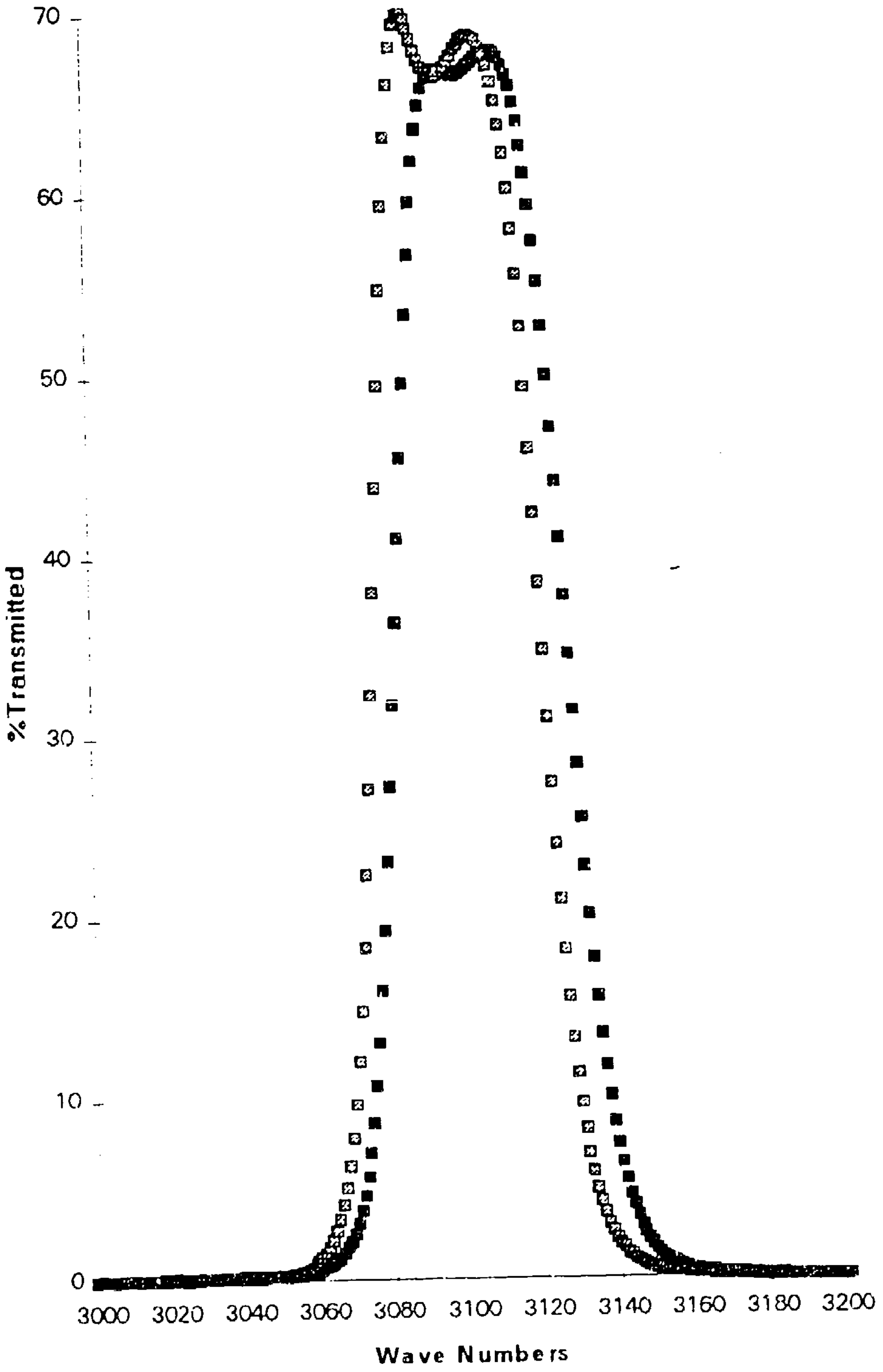


Figure 14: Transmitivity test of Filters

3.3.4 Soil Preparation

The soil used in all experiments of this study was Plastic Clay 98b that was purchased from the National Institute of Standard and Technology. This soil was initially oven-dried and freed from all contaminants. Therefore, the only contaminant in this soil was TCE. The moisture content of this soil was relatively small and its effects on adsorption and desorption were considered negligible.

The soil was placed in a glass tube and was continuously exposed to liquid TCE for a period of 2 days. Throughout this period, the soil was isolated from room atmosphere to allow longer contact with TCE. If left exposed to atmosphere, TCE would evaporate in a matter of hours. In addition, the quantity of liquid TCE (about 10 ml) was large enough to soak the 2 grams of soil, assuring full soil saturation. In addition, during the exposure period, the tube was maintained at room temperature. At the end of second day, the soil was removed from the tube and was allowed 10 to 15 minutes to slightly dry. During this period of time, the heat tape was placed around the tube and was held at a constant temperature. The 2 grams of soil were then placed in the tube in the form of several particle layers and the tubes were closed.

3.3.5 Description of the Experiment

As stated earlier, plastic clay was exposed to liquid TCE for a period of 2 days. Before beginning each experiment, the cell's walls and other components of the cell were allowed to off-gas the sorbed TCE by maintaining the cell under vacuum for a period of 24 hours. At the end of the off-gas period, the heat tape was placed around the glass tube and the soil was allowed to dry off for a period of 15 minutes (as needed). When the soil was almost dry, it was then placed inside the glass tube in the form of several particle layers. Each glass tube contained 2 ± 0.1 grams of plastic clay soil. To eliminate atmospheric interferences and to remove the desorbed gas TCE from the open cell in order to record the initial signal intensity at vacuum, the cells were evacuated down to vacuum for 10 seconds. Both glass tubes had heat tape placed around them and were maintained each at a constant temperature throughout the desorption phase of TCE from the soil. At this time, desorption test started and data was recorded.

To obtain background data, and to determine the effects of a temperature increase on the intensity of the signal, an experiment was performed while keeping the cells empty and maintained at fixed temperatures. This experiment revealed that temperature had a negligible effect on the intensity of the signal (Appendix A). Therefore, any drop in the signal's intensity was mainly caused by the presence of TCE in the cell.

Desorption was evaluated under five different temperatures: 27°C, 40°C, 64°C, 70°C, and 100°C. The variation in these temperatures was ± 2°C. Because it was found that desorption reached a steady state within a period of four hours, data for all five experiments was recorded for a period of four hours only. The detectors were cooled at the beginning of each experiment.

IV. Results and Discussion

4.1 Results

The data collected during this study was plotted against time and the results of the five experiments are as follows:

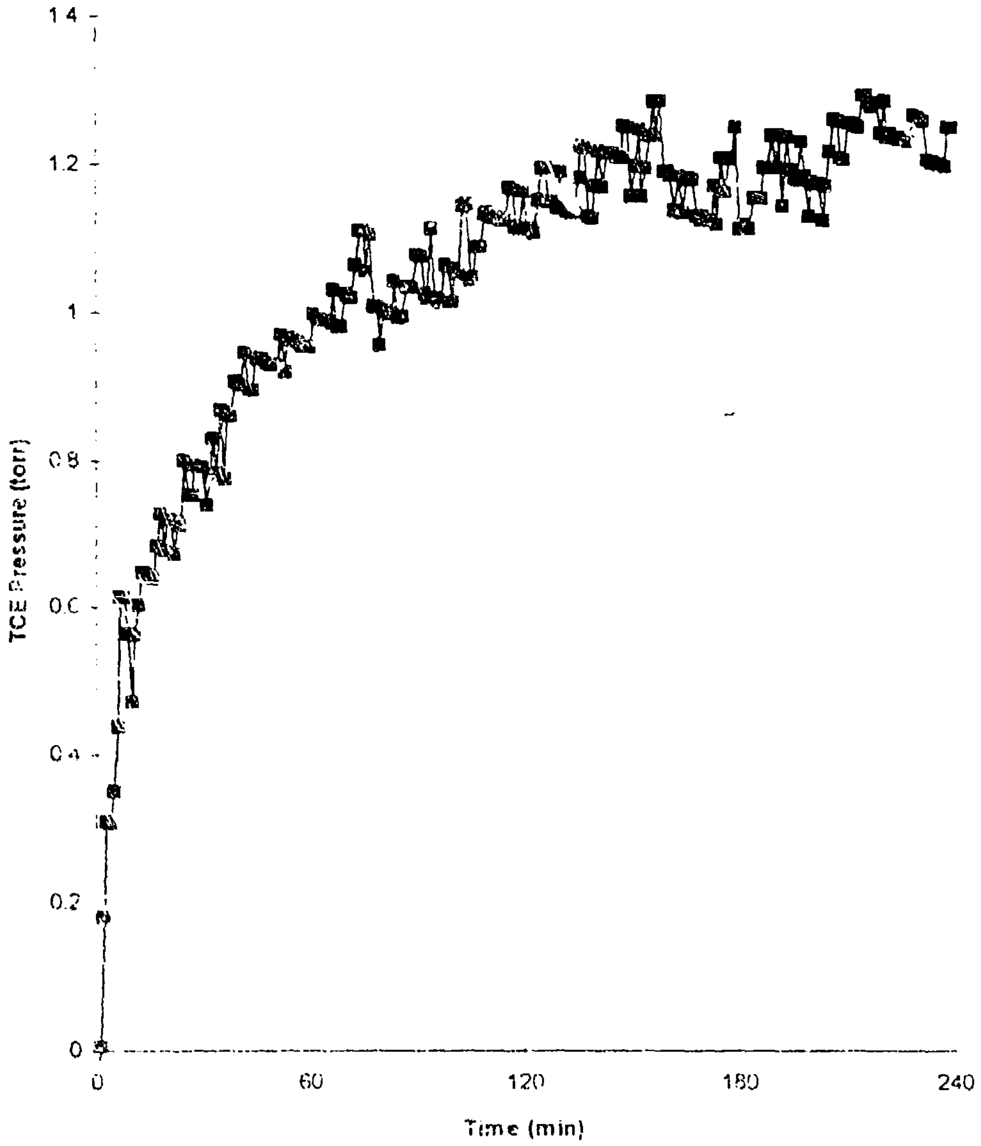


Figure 15: Actual data for TCE desorption at T = 27 C

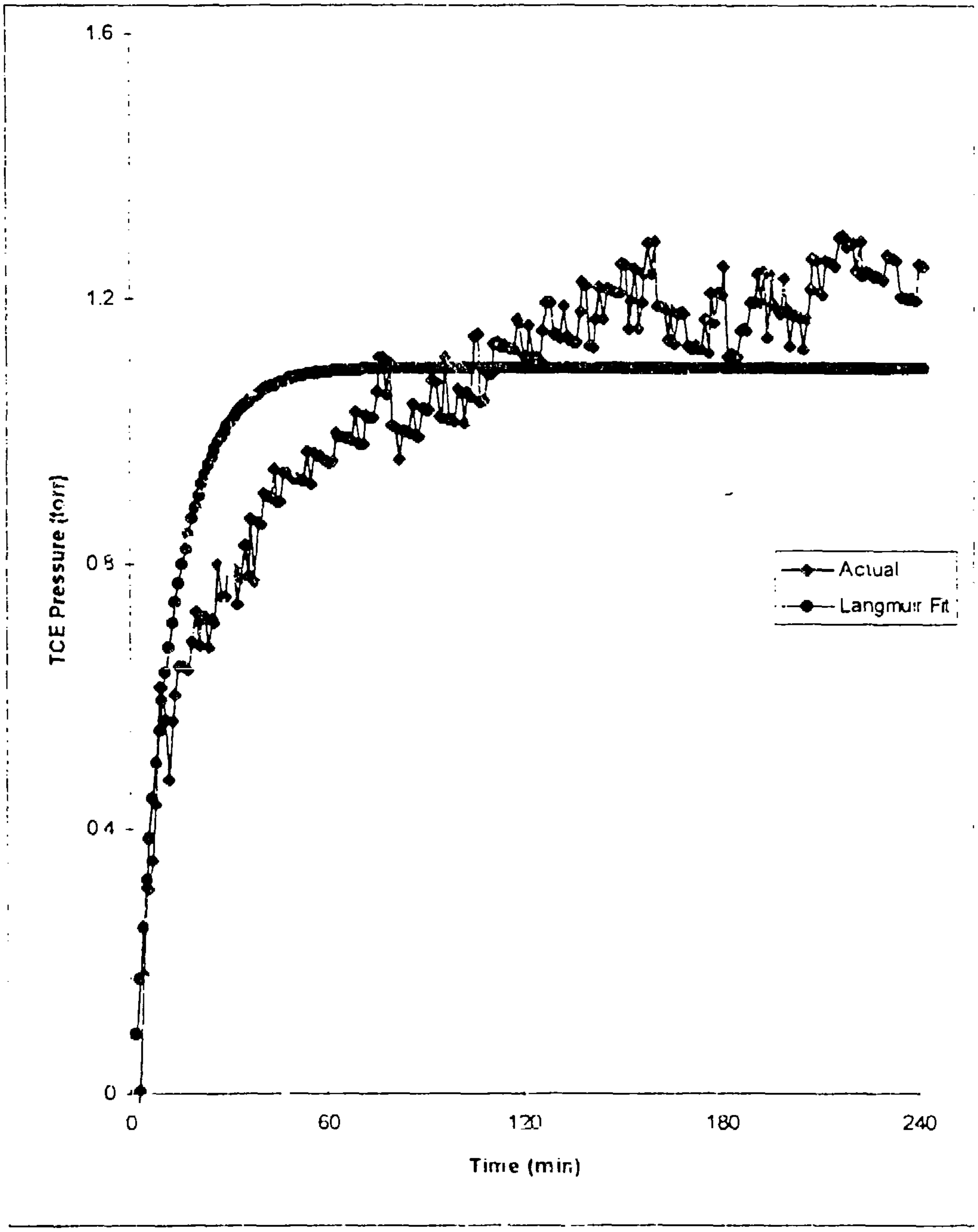


Figure 16: Langmuir Fit for TCE Desorption data at T = 27 C

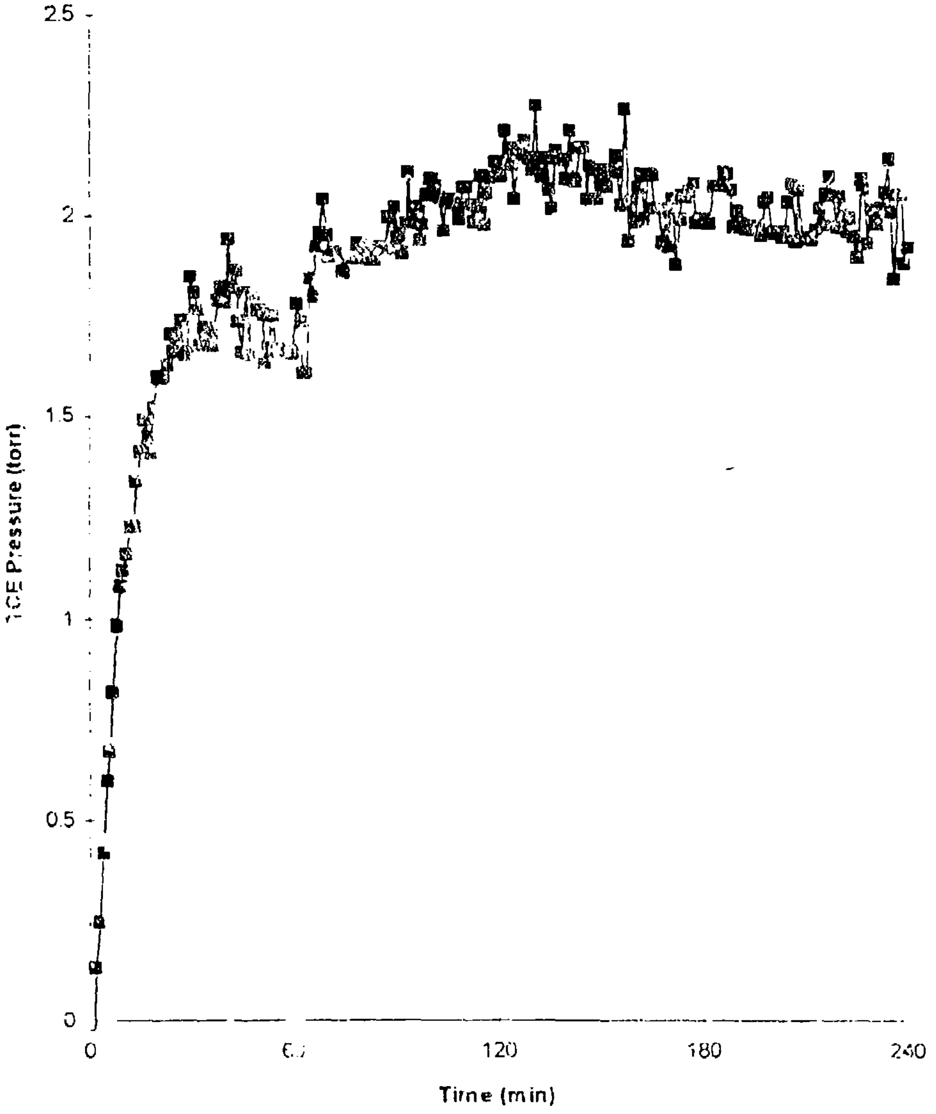


Figure 17: Actual data for TCE Desorption at T = 40 C

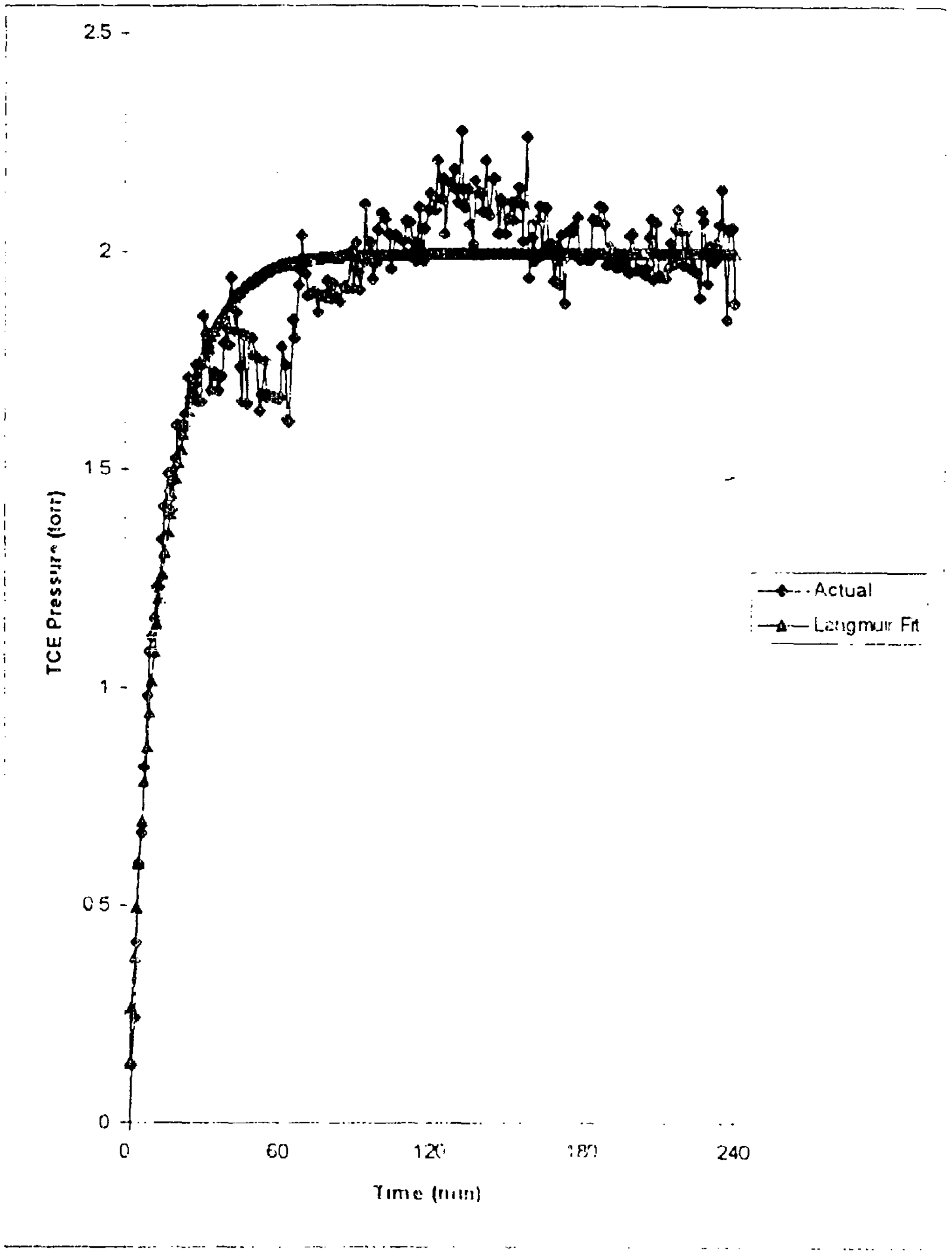


Figure 18: Langmuir Fit for TCE Desorption data at T = 40 C

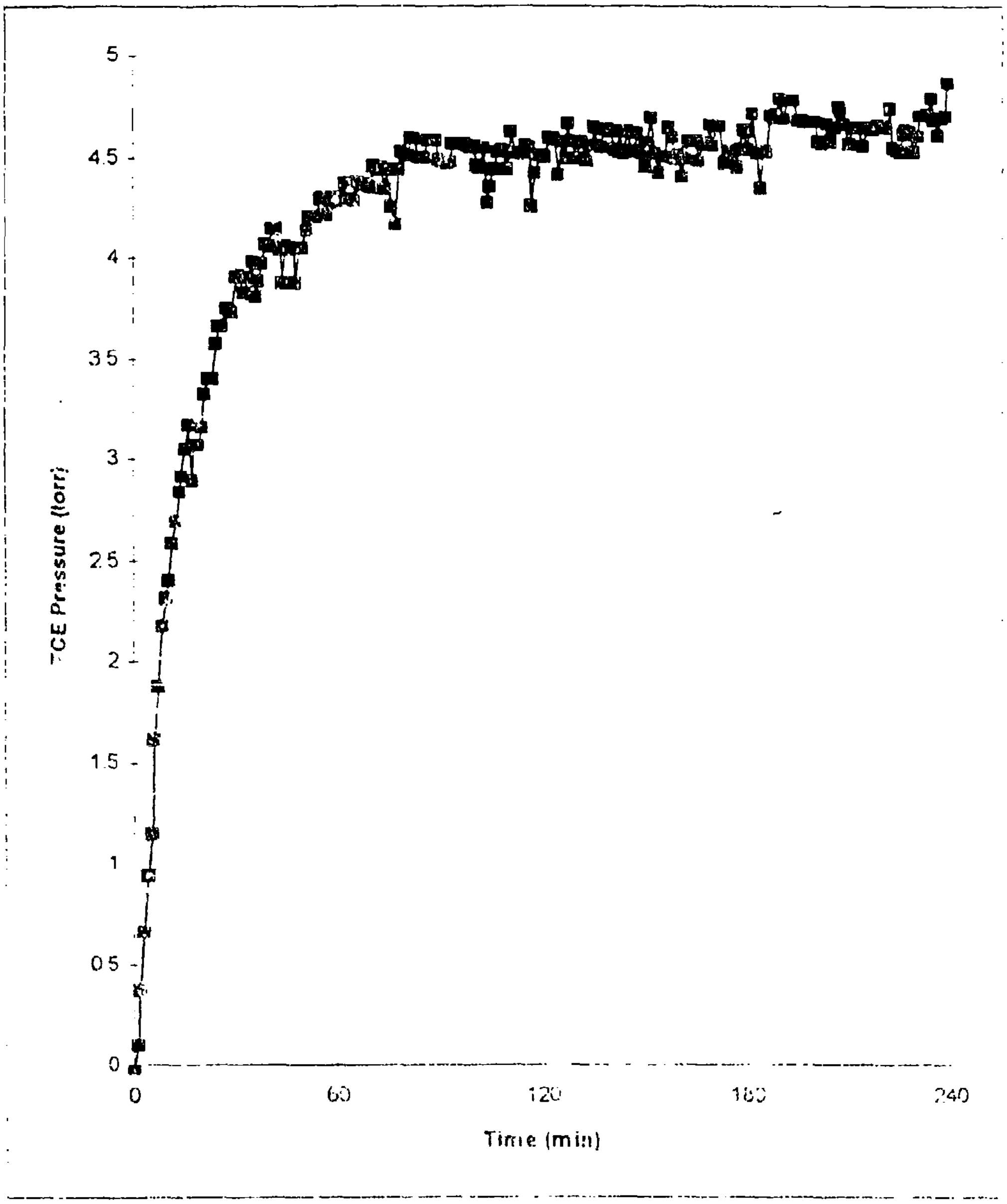


Figure 19: Actual Desorption of TCE under T = 64 C

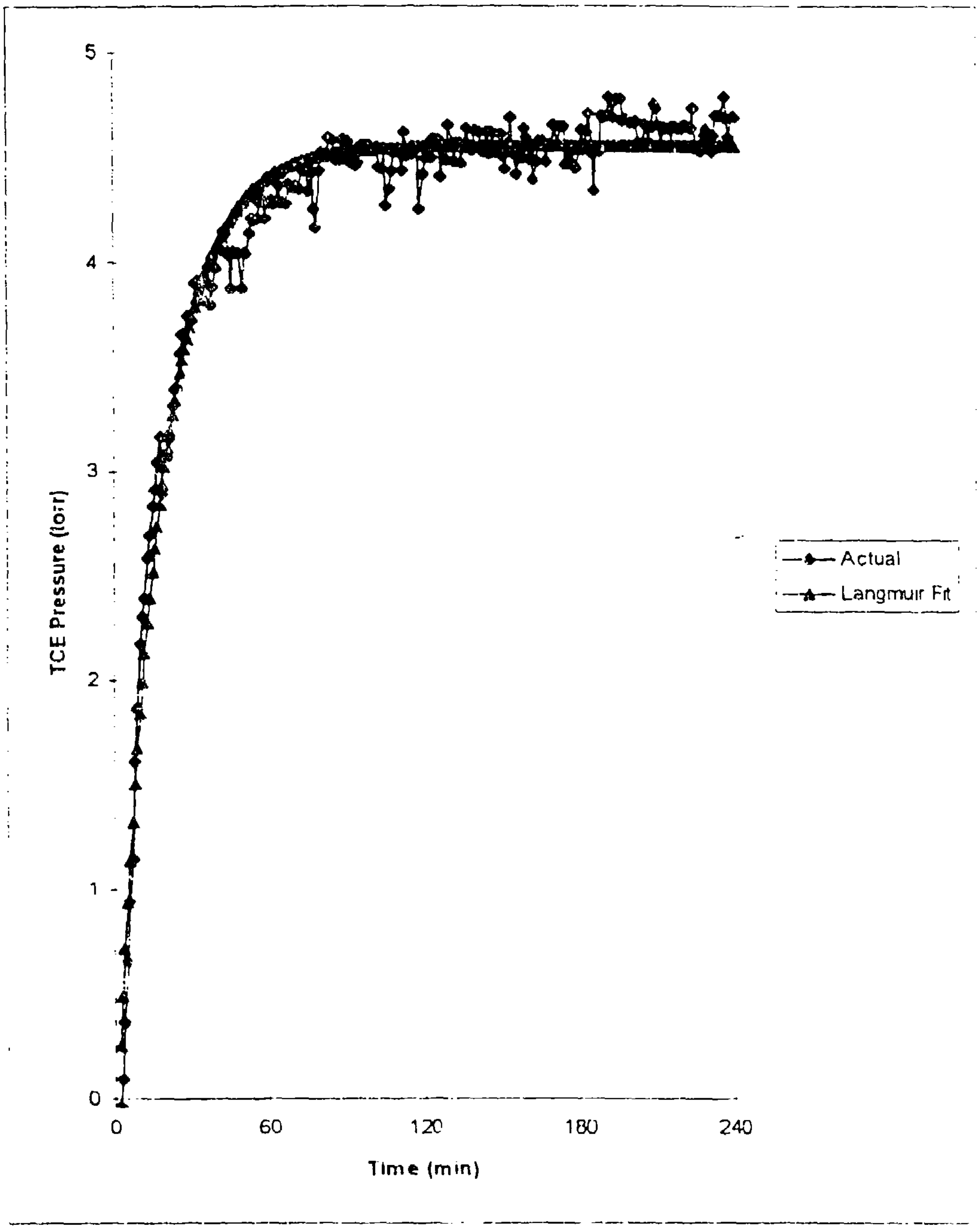


Figure 20: Langmuir Fit for TCE Desorption data at T = 64°C

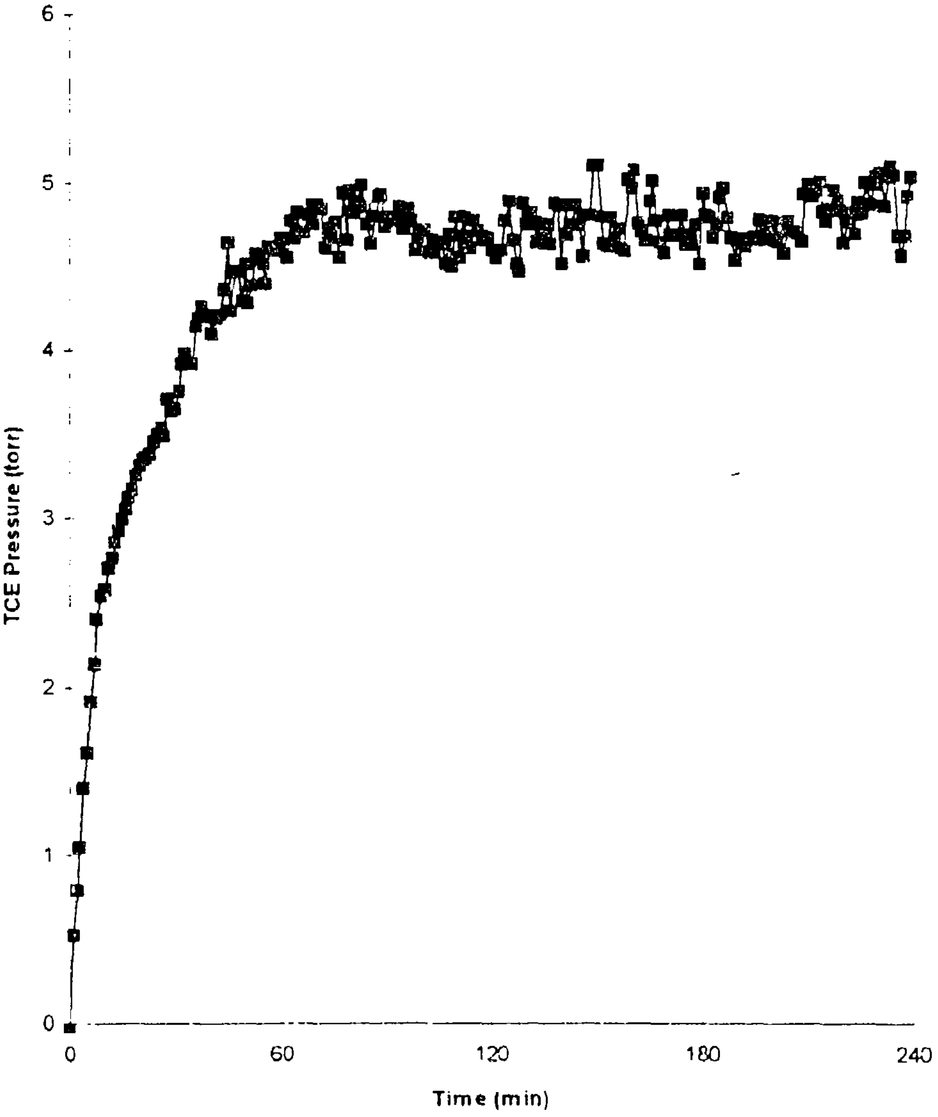


Figure 21: Actual Desorption of TCE under T = 70 C

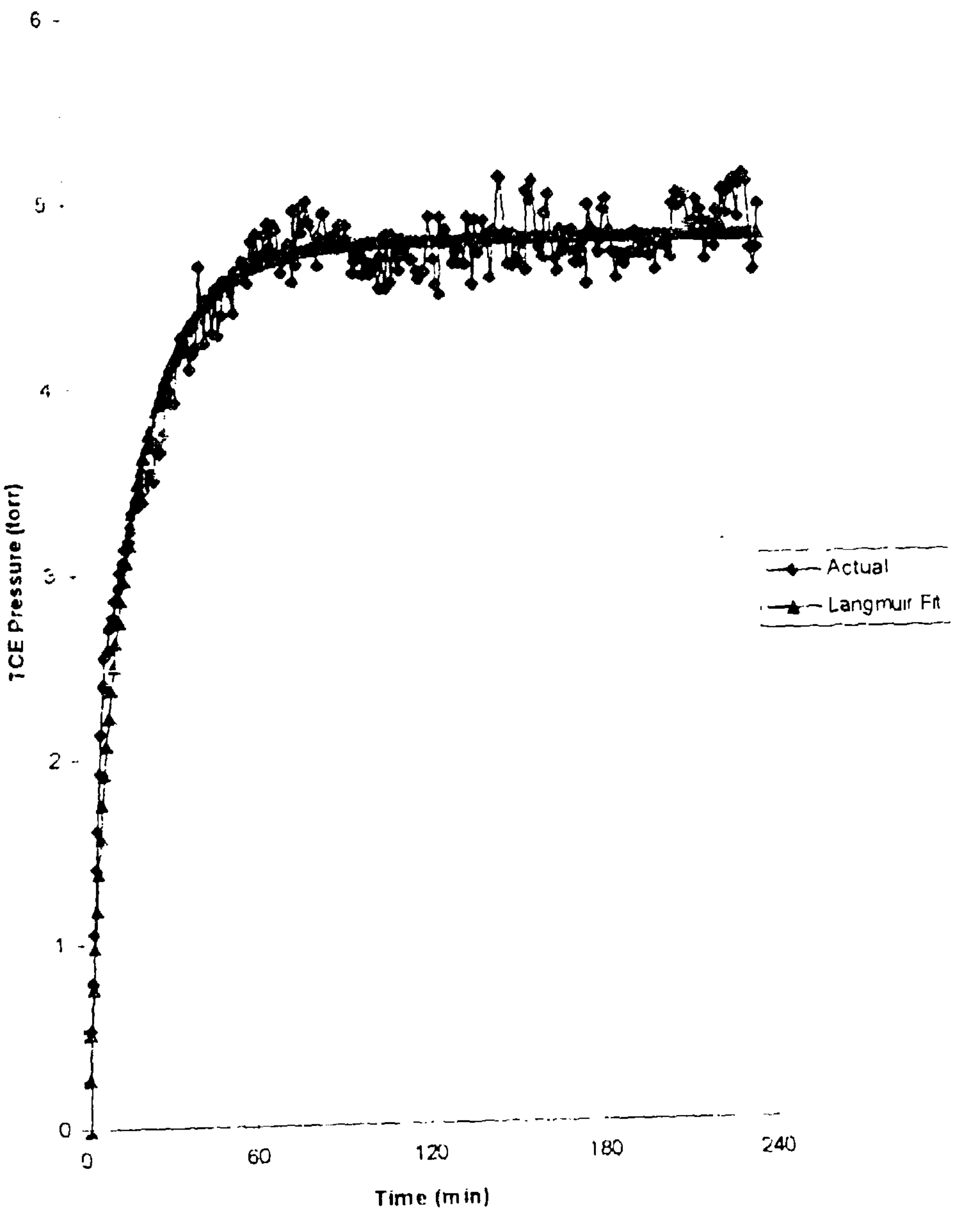


Figure 22: Langmuir Fit for TCE Desorption data at T = 70 C

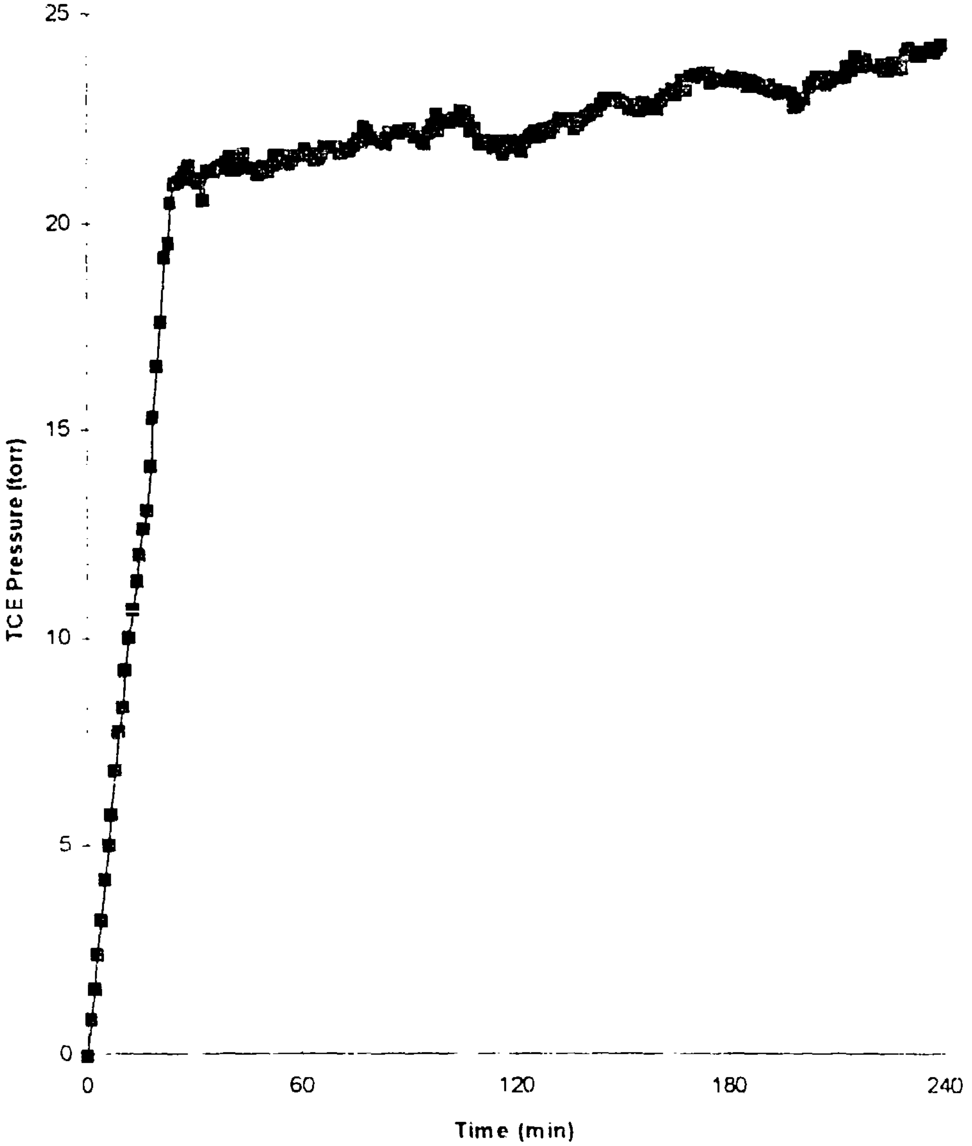


Figure 23: Actual Desorption of TCE under T = 100 C

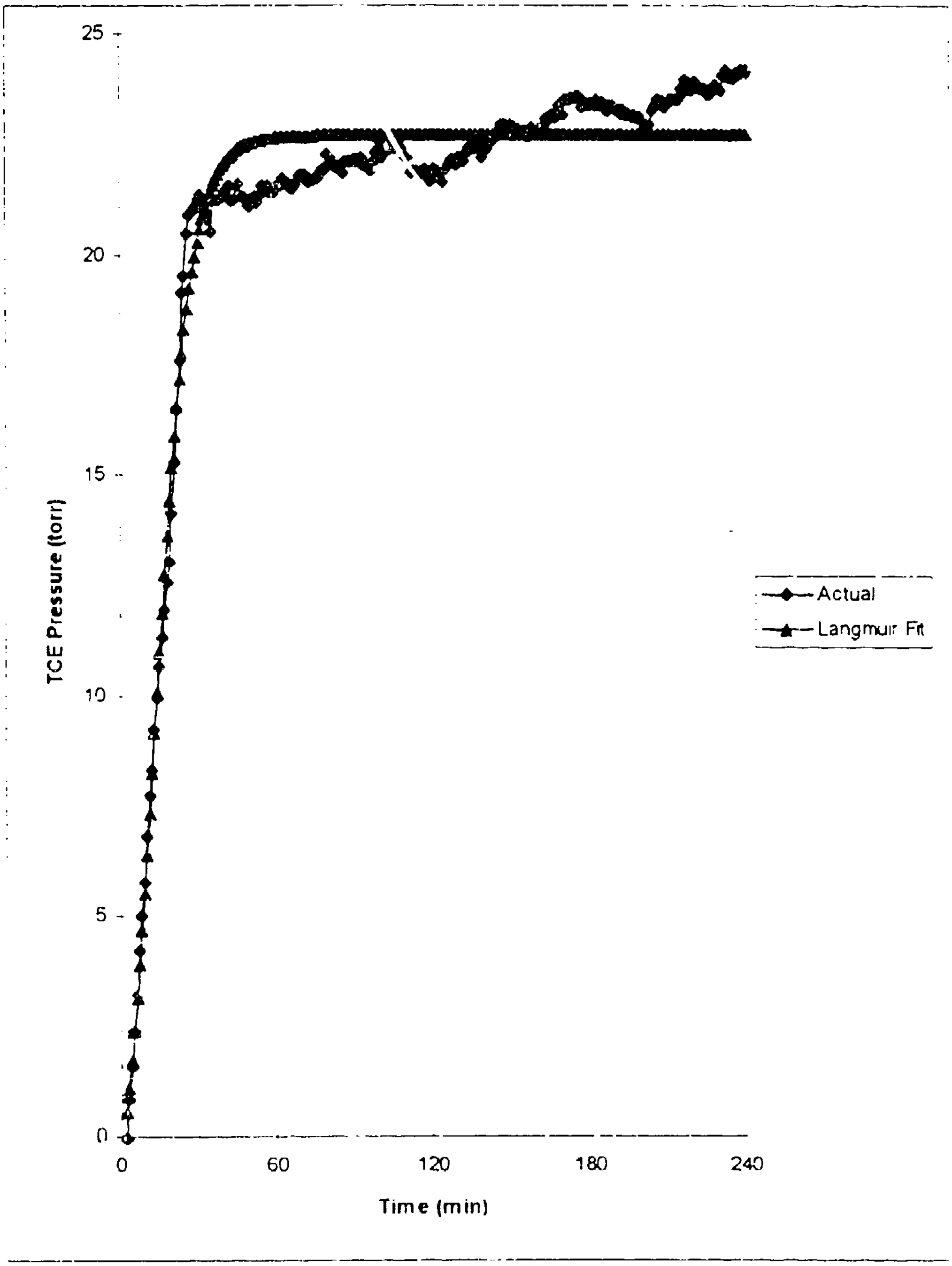


Figure 24: Langmuir Fit for TCE Desorption data at T = 100°C

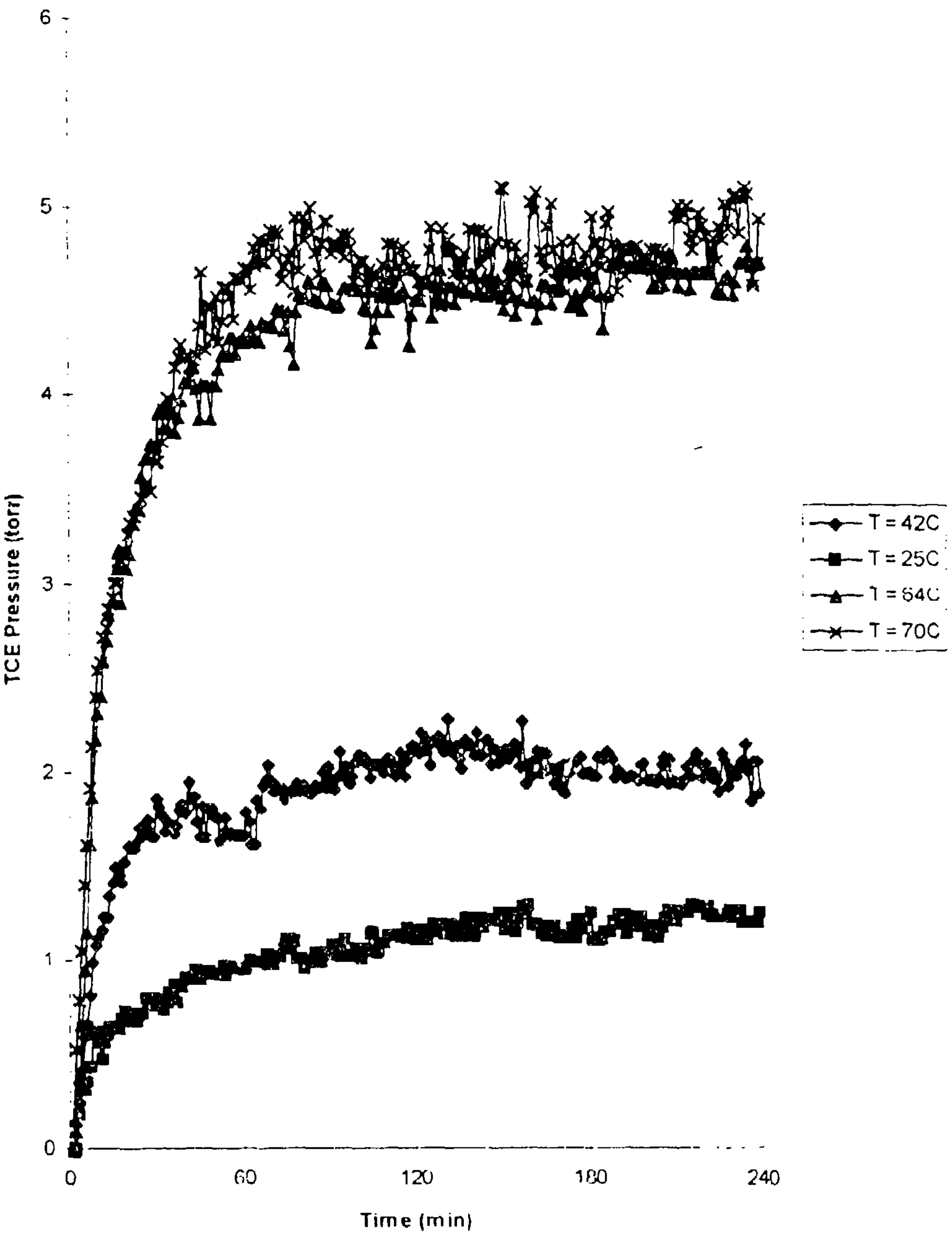


Figure 25: Actual data for TCE Desorption at 4 Temperatures

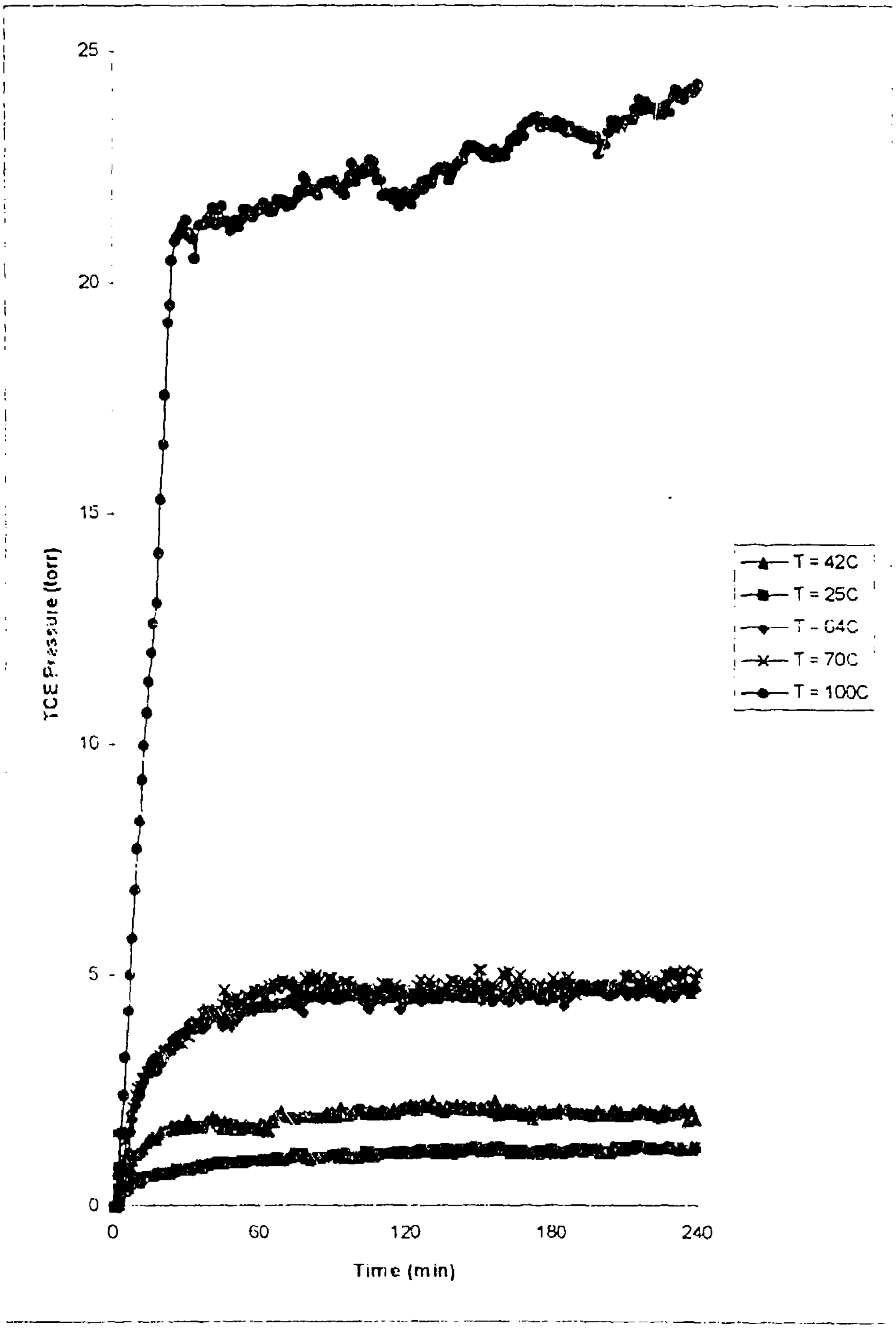


Figure 26: Actual data for TCE Desorption at 5 Temperatures

4.2 Interpretation and Analysis of The Results

4.2.1 Interpretation of the Results

TCE desorption from TCE contaminated plastic clay appears to be strongly correlated with temperature. This conclusion is supported both theoretically, by a scientific understanding of the mechanism of desorption of TCE and by the effects of temperature on the kinetics of this mechanism, and by experimental data on TCE desorption from Plastic Clay 98b. The five curves of Figure 25 indicate that the rate of desorption of TCE from plastic clay is very dependent on temperature. At room temperature (27°C), TCE desorbed at a slower rate and desorption reached a steady state with nearly 2 torr of TCE in the gas phase. At high temperatures, 100°C, TCE appeared to desorb faster and in a large quantity of nearly 24 torr.

The first stage of desorption (the fast stage) appears to also depend on temperature. During this stage of desorption (Figure 25), the graphs became steeper each time temperature was raised, indicating a correlation between the rate of desorption of TCE and temperature. At each temperature, the subsequent desorption stage is a steady state stage where TCE concentration appears to be unchanging. However, the time it took desorption to reach steady state conditions appears to be somewhat correlated to temperature. These time intervals decreased with increasing temperature. The graphs also show that regardless of temperature, desorption always reached a steady state characterized by a "constant" TCE concentration in the cell. These steady state conditions possibly indicate that the rates of adsorption and desorption of TCE became equal after the concentration of TCE in the cell reached a certain value under a specific temperature.

4.2.1.1 Surface Desorption

It is believed that the first TCE molecules that desorb from the soil were those that resided on the upper soil surface. The bonds between TCE and the soil surface are expected to be much weaker than those between TCE and the soil matrix. Thus these TCE molecules from the soil surface are the first ones that readily desorb and enter the gas phase. At room temperature, it is believed that most of the gas TCE in the cell has desorbed from the soil surface and only a very small fraction desorbed from the interior of the soil particles. As temperature increases, this soil surface TCE desorbs faster and subsequent desorption starts reaching the TCE in the sorbed phase inside the interior of the soil matrix. These conclusions are supported both theoretically by the fact that TCE diffusion in the soil matrix will limit the rate of desorption from the interior of the soil, and experimentally by the fact that after completely evacuating the cell down to vacuum, a much smaller quantity of TCE desorbed from the soil at a much slower rate (Appendix A, Figure 32).

4.2.1.2 Interior Desorption

Current remediation techniques succeed in removing most of the TCE on the soil surface. It was earlier stated in Chapter 2 of this thesis that a large fraction of TCE contamination is adsorbed or entrapped in the interior of the soil matrix. This fraction resists most common remediation techniques and forms a continuous source of TCE contamination. If not completely removed, this continuous contamination can last decades while contaminating larger quantities of soil and water. This is the case because TCE desorption from the interior of the soil particle at ambient temperatures takes longer periods of time.

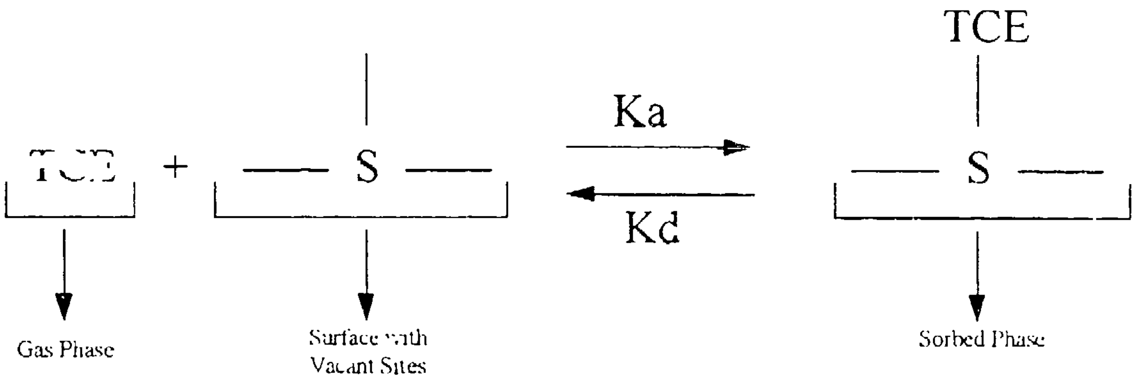
After the desorption from the soil surface is complete, desorption from the interior of the soil is initiated. The results of this study indicate that the rate of the interior desorption is slow at room temperature and increases with increasing temperature. To desert the solid phase and enter the gas phase, a TCE molecule must undergo some transitions. The bond that holds the TCE molecule to the soil particle must first be overcome. The TCE molecule will then leave the soil particle and enter the gas phase in the cell as the distance between the two becomes larger. At high temperatures, these transitions appear to occur faster and with high efficiency. This is theoretically supported by the fact that temperature is often used as a catalyst to increase the rate of a reaction.

Experimentally (Figure 25), the results of this study indicate that both the number of TCE molecules that undergo these transitions, or what can be called a "phase change" from the sorbed phase to the gas phase, and the rate of these transitions heavily depend on temperature. At room temperature, less than 1.5 torr of TCE desorbed from the soil. On the other hand, at 100°C, over 24 torr of TCE desorbed at a faster rate. The difference can be explained by the fact that higher temperatures are needed to increase the movement and the transition of molecules from the soil surface or from within the soil matrix to the gas phase.

4.2.2 Analysis of the Results:

4.2.2.1 The Langmuir Kinetic Model

If we assume that in order to desorb to the gas phase, a TCE molecule must leave the soil particle and enter the gas phase, then the desorption process would look like the following:



where:

S = soil particle;

Ka = TCE adsorption rate; and

Kd = TCE desorption rate.

By further assuming that a soil particle possesses more than one available site where a TCE molecule can bond to then if

$$\theta = \frac{\text{\#Sites where TCE is in soil}}{\text{Total \# of sites in soil}}$$

$$= \frac{\#\ \text{sites}}{\text{Unit surface area}};$$

V = Volume of cell; and

S = Surface area of soi

then the change in the number of TCE molecules in the gas phase will equal the change in the number of TCE sites which TCE bonds to. Mathematically written:

$$\frac{d}{dt}(fS\theta) = -d([TCE]V) \tag{4.1}$$

which gives

$$\frac{d\theta}{dt} = -\left(\frac{V}{fS}\right)d\frac{[TCE]}{dt} = -\beta d\frac{[TCE]}{dt} \tag{4.2}$$

where $\beta = -\frac{V}{fS}$

Thus

$$\frac{d[TCE]}{dt} = -K_a[TCE](1-\theta) + K_d\theta \tag{4.3}$$

Further, if we assume that

$$\theta(0) = \theta_0 \text{ and } [TCE](0) = 0$$

equation (4.2) becomes

$$\theta - \theta_0 = -\beta[\mathrm{TCE}] \tag{4.4}$$

or

$$\theta = \theta_0 - \beta[\mathrm{TCE}] \tag{4.5}$$

By letting [TCE] = y, equation (4.5) then becomes

$$\theta = \theta_0 - \beta y \tag{4.6}$$

Substituting equation (4.6) for θ in equation (4.3) gives:

$$\frac{d[\mathrm{TCE}]}{dt} = \frac{dy}{dt} = -\mathrm{K_a} y\left(1 - \theta_0 + \beta y\right) + \mathrm{K_d}\ \theta_0 - \beta y,$$

thus

$$\int_0^{[TCE]} \frac{dy}{\mathrm{K_d}\ \theta_0\ -\ \left[\mathrm{K_d}\beta - \mathrm{K_a}\left(1 - \theta_0\right)\right]y - \mathrm{K_a}\beta y^2} = \int_0^t dt \tag{4.7}$$

By letting:

$A = \mathrm{K_a}\beta$

$B = \mathrm{K_d}\beta - \mathrm{K_a}\left(1 - \theta_0\right)$

and

$C = \mathrm{K_d}\ \theta_0$

equation (4.7) becomes

$$\int_0^{[TCE]} \frac{dy}{\mathrm{A}y^2 + \mathrm{B}y + \mathrm{C}} = \int_0^t dt \tag{4.8}$$

To solve the integrals of equation (4.8), let

$$\Delta = B^2 - 4AC = K_d{}^2\beta^2 - 2K_d\beta K_a(1-3\theta_0) + K_a{}^2(1-\theta_0)^2 = \gamma^2$$

Therefore, the solution to equation (4.8) is

$$\frac{1}{\gamma}\ln\left(\frac{2Ay+B-\gamma}{2Ay+B+\gamma}\right)\Bigg|_0^{[TCE]} = t \qquad (4.9)$$

or

$$\left(\frac{2Ay+B-\gamma}{2Ay+B+\gamma}\right)\left(\frac{B-\gamma}{B+\gamma}\right) = e^{\gamma t} \qquad (4.10)$$

which leads to

$$y = [TCE]_t = \frac{(B^2-\gamma^2)(e^{\gamma t}-1)}{2A\left[(B+\gamma)-(B-\gamma)e^{\gamma t}\right]} \qquad (4.11)$$

However,

$$\frac{B^2-\gamma^2}{2A} = \frac{B^2-(B^2-4AC)}{2A} = \frac{4AC}{2A} = 2C = 2K_d\theta_0 \qquad (4.12)$$

and by further assuming that all the soil sites were initially filled with TCE or that the soil is initially saturated with TCE, $\theta = 1$ and equality (4.12) becomes

$$\frac{B^2-\gamma^2}{2A} = 2K_d$$

Therefore, equation (4.11) becomes

$$[TCE]_t = \frac{2K_d\left(e^{\gamma t} - 1\right)}{(B+\gamma) - (B-\gamma)e^{\gamma t}} \tag{4.13}$$

To determine the values for K_d and K_a, equation (4.13) was curve fitted to the experimental data. The results of this curve fit are displayed in the following table:

Temperature (°C)	K_d	K_d Sd Er	K_a	K_a Sd Er	R^2
27	0.0952	0.0124	0.0001	0.0013	0.70
40	0.1422	0.0132	1.1E-7	0.0041	0.8857
64	0.2616	0.0113	6.4E-7	0.0078	0.9716
70	0.2720	0.0132	1.2E-6	0.0013	0.9612
100	0.5037	0.0414	0.0102	0.0003	0.9661

4.2.2.2 Analysis of the Results

4.2.2.2.1 Molecular Interpretation of Temperature

The ideal gas law states the following:[30]

$$PV = NKT \tag{4.14}$$

where:

P = pressure in the cell in torr;

V = volume of the cell in cm^3 (held constant);

N = number of TCE molecules in the cell;

K = Boltzmann's constant; and

T = temperature in the cell in Kelvin.

Furthermore, it has been proven that the pressure of N molecules of an ideal gas contained in a volume V is proportional to the number of molecules per unit volume and to the average transitional kinetic energy per molecule.[30] That is:

$$P = \frac{2}{3}\frac{N}{V}\left(\frac{1}{2}mv^2\right) \tag{4.15}$$

where

P = total pressure on the cell wall;

N = number of molecules per unit volume;

V = volume of container (cell);

m = mass of a molecule; and

v = average molecular speed.

Rearranging equation (4.14) gives:

$$P = \frac{NKT}{V}$$

By using this expression for P, equation (4.15) becomes

$$T = \frac{2}{3K}\left(\frac{1}{2}mv^2\right) \tag{4.16}$$

That is, the absolute temperature of an ideal gas is a measure of the average of the square of the speed of its molecular constituents. By rearranging equation (4.16), the translational molecular kinetic energy can be related to the temperature as follows:

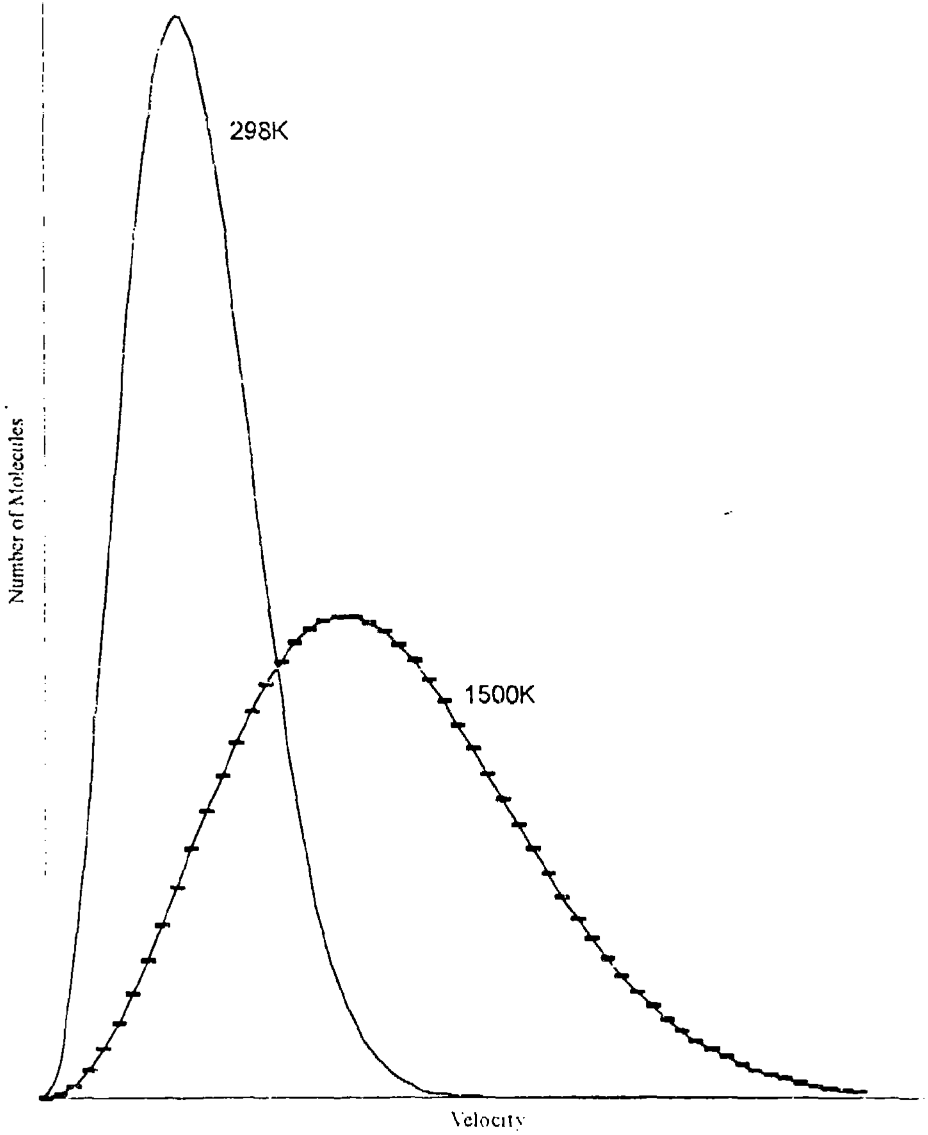


Figure 27: Effect of temperature on the average velocity of TCE molecules.

$$\frac{1}{2}mv^2 = \frac{3}{2}KT \qquad (4.17)$$

Solving for v in equation (4.17) gives:

$$v = \sqrt{\frac{3KT}{m}} \qquad (4.18)$$

The expression for molecular velocity in equation (4.18) shows that at a given temperature, a TCE molecule has a corresponding velocity. As temperature increase, this molecular speed increases and the molecule moves faster and possesses more energy (Figure 27). Thus, temperature has a considerable effect on the movement and translation of a molecule.

4.2.2.2.2 TCE-Soil Surface Bond

A soil particle is formed by several atoms including iron, aluminum, calcium, magnesium, and several others. These atoms coexist within the interior of the soil matrix and are held together by several energy bonds. These energy bonds transfer energy between each other and transfer some of this energy to the exterior of the soil particle. Since this study focused mostly on the soil surface desorption, it was assumed that a TCE molecule is in the sorbed phase when it is attached to the soil surface as drawn in Figure 28. In order for it to desorb to the vapor phase, a TCE molecule must first break the energy bond that is attaching it to the soil surface.

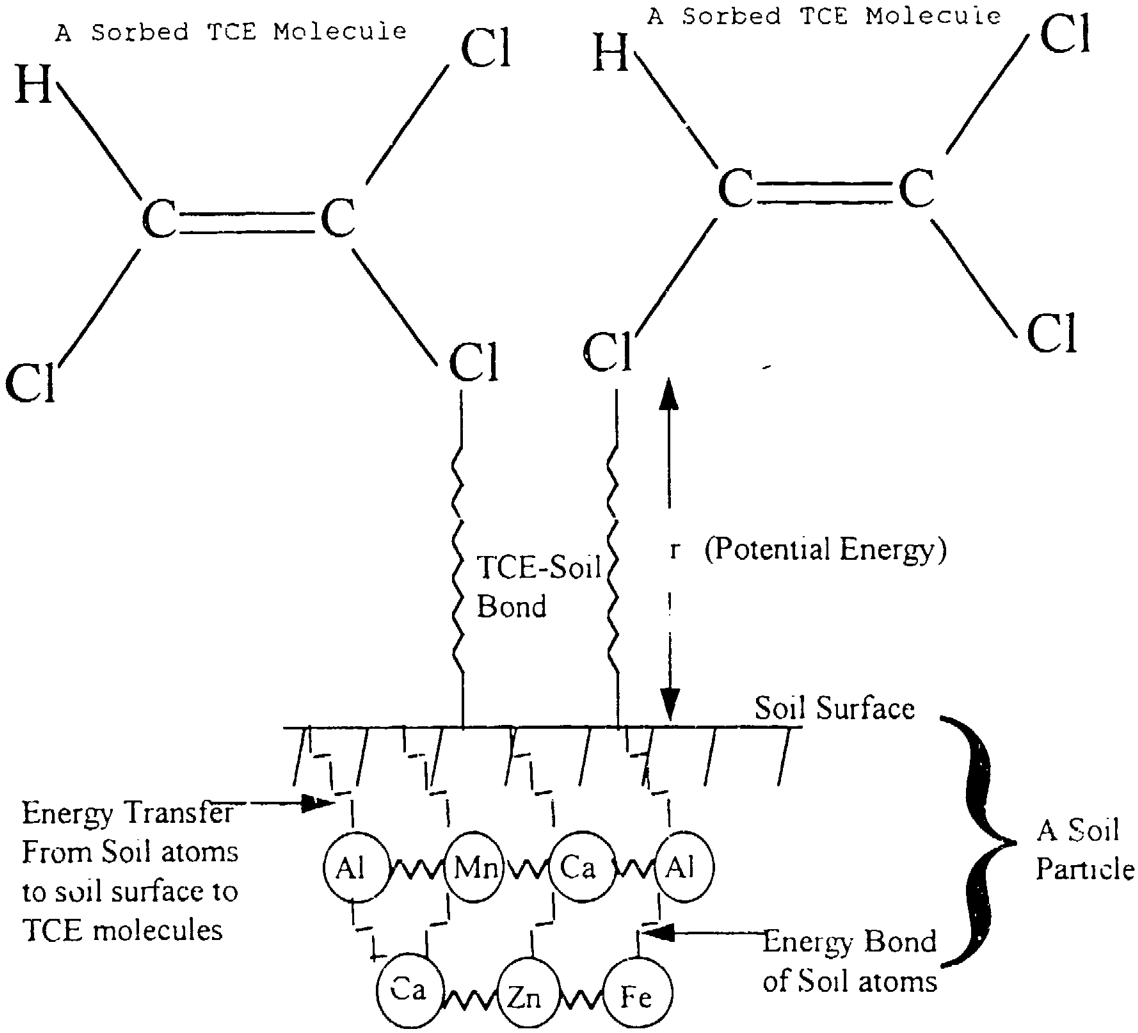


Figure 28: Diagram representing the bond attaching a TCE molecule to the surface of a soil particle.

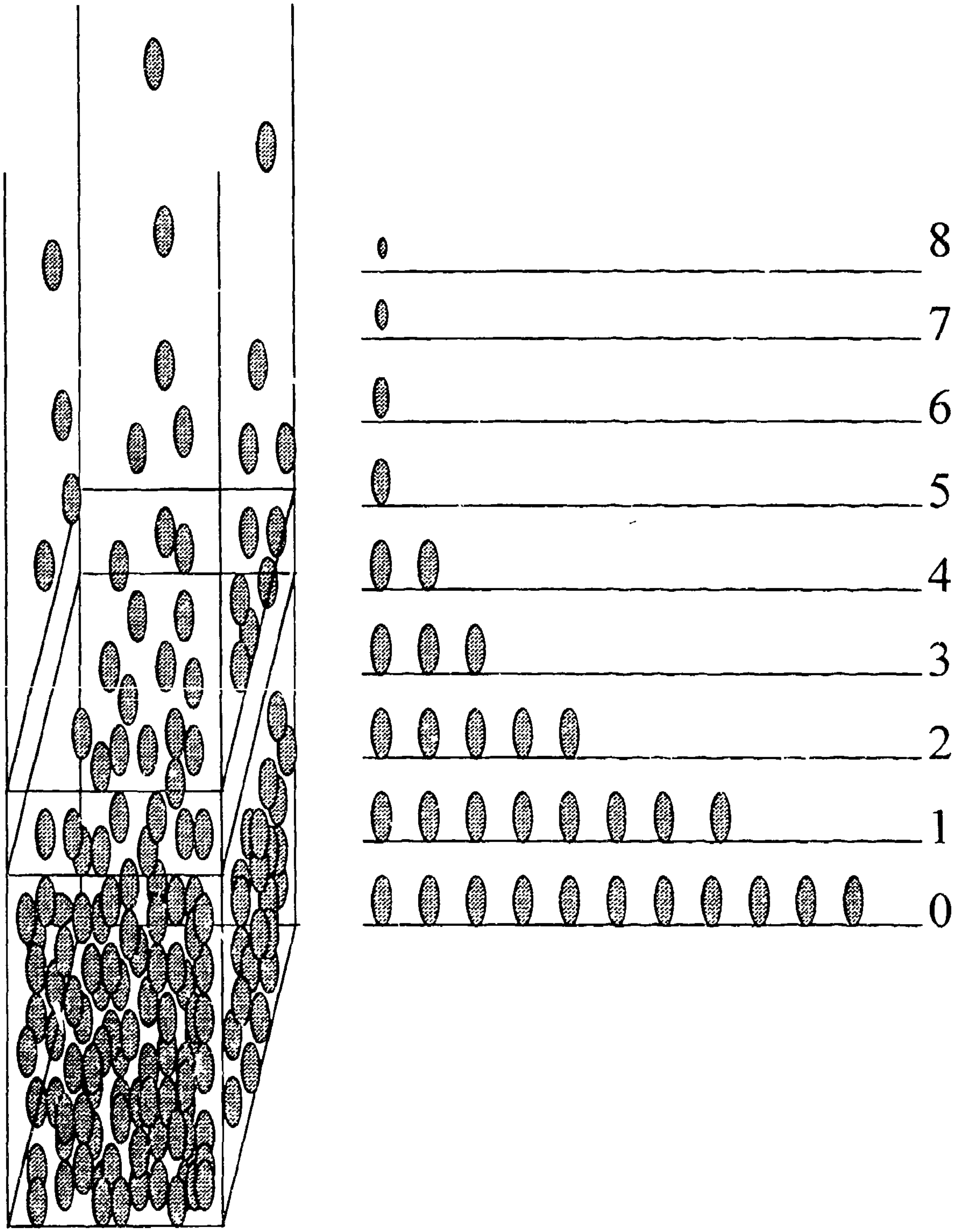


Figure 29: Distribution of TCE molecules among different energy levels

When temperature was raised, thermal energy within the experimental cell increased and was absorbed by the atoms of the soil particle. As a result, the vabrational and the translational energies within the matrix of the soil particle increased. A part of these energies was then transferred to the TCE-soil surface bond allowing the TCE molecule to vibrate much quicker, increasing its chances of detaching itself from the soil surface. As temperature was further raised, the amount of energy transferred to the TCE molecule increased, and the probability that this TCE molecule desorbs increased as well.

4.2.2.2.3 Temperature and Energy States of a Molecule

Molecules of a substance in the gas phase move with different speeds and possess different energies. In other words, there are several energy states where a molecule can reside depending on the amount of its total energy (Figure 29). At sufficiently low temperatures, almost no molecule can acquire enough energy by collision to reach an excited state and almost all molecules are in the ground state, moving very slowly. Simultaneously, very few molecules reside in the higher energy states and move with higher speeds. As temperature increases, the equilibrium number of molecules in each excited state increases and the amount of molecular vibrational energy increases. The translation from one energy level to another was found to be correlated with temperature because thermal energy is used by molecules to increase their kinetic energy, thus increasing their translational speed.

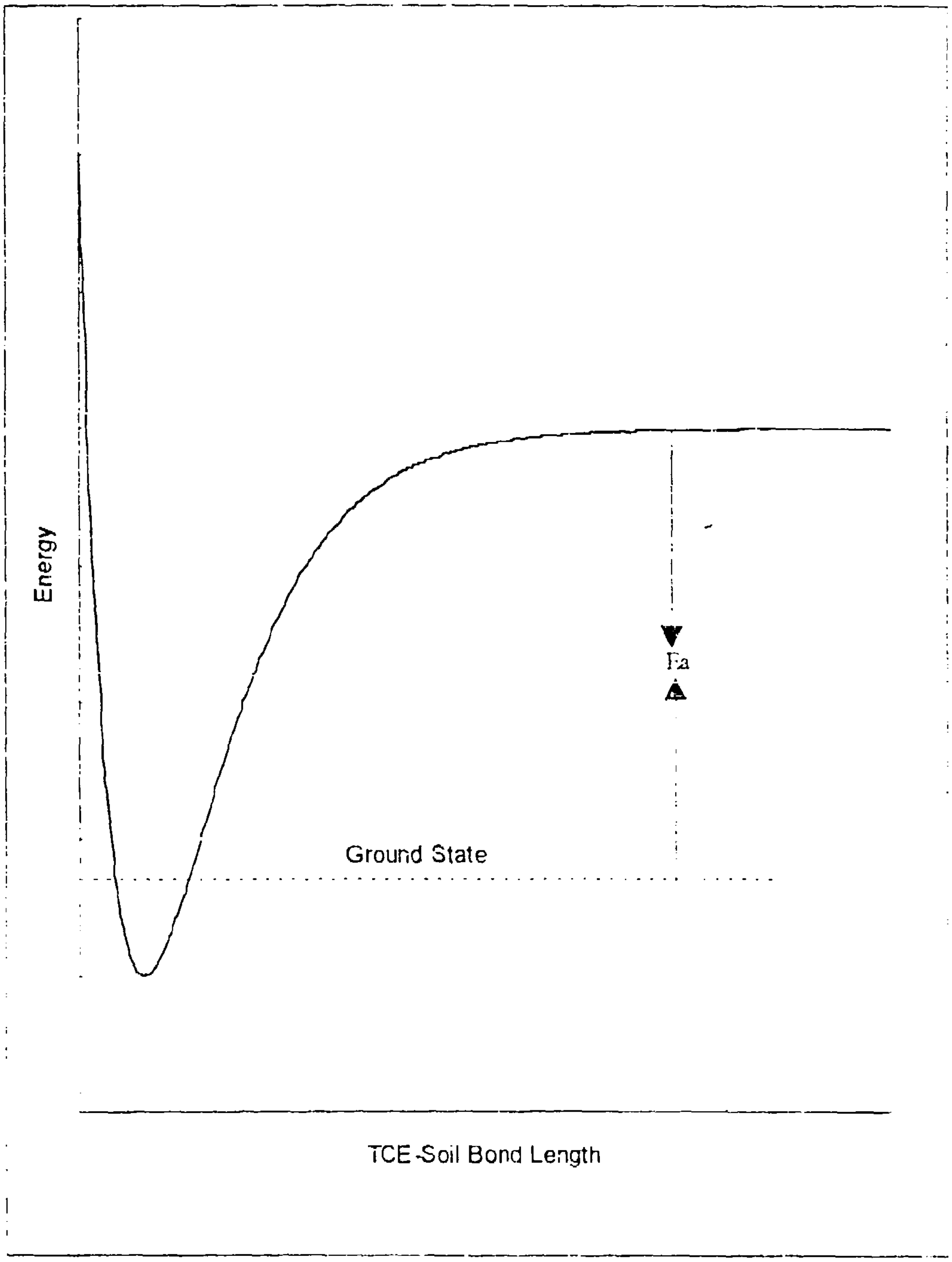


Figure 30 : Energy of TCE molecules as a function of soil bond length

At room temperature, most TCE molecules are in the ground state. These molecules are close to the soil surface and possess low kinetic energy and low translational speed. As temperature was raised, a large number of these molecules began acquiring thermal energy. This increase in temperature then allowed the molecules to move faster and to rise to higher energy levels. The result is large numbers of molecules with higher velocities in the excited states and fewer molecules in the ground state with lower velocities. In addition, the length of the TCE-soil bond of these excited molecules starts to increase with temperature, increasing the number of molecules that are entering the vapor phase (Figure 30). However, at any given temperature, there will always be a number of molecules in the ground state. This number decreases with increasing temperature.

4.2.2.2.4 Temperature and TCE Desorption Rates

It was theoretically expected that TCE desorption rate, K_d, is a function of temperature of the following form:

$$K_d(T) = K_0 e^{-\frac{L_a}{KT}} \tag{4.19}$$

where:

K_d = TCE desorption rate at temperature T;

K_0 = TCE desorption rate at infinite temperature;

K = Boltzmann constant = 10^{-23} J K^{-1}

T = absolute temperature (°K); and

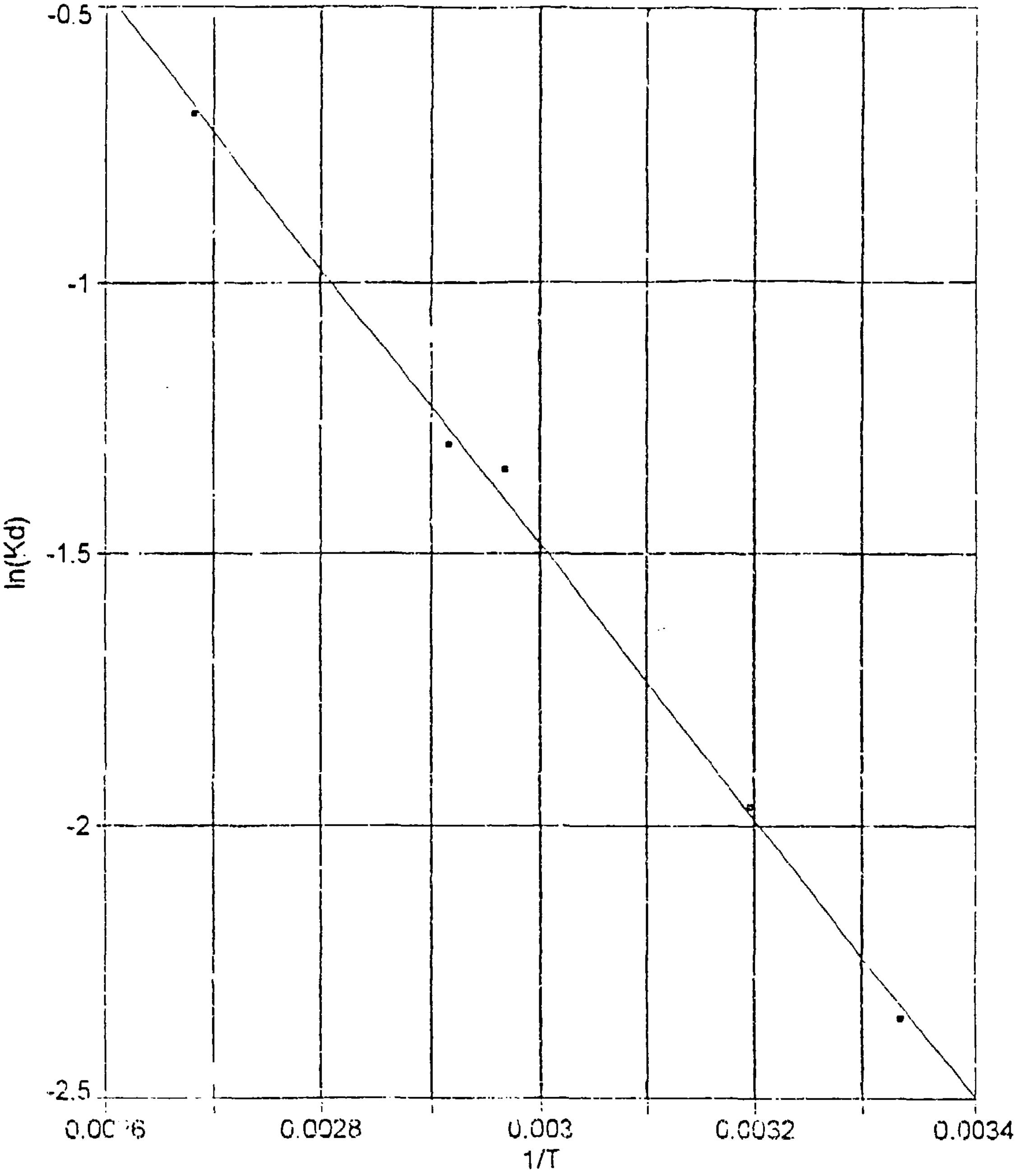


Figure 31: Langmuir Curve Fit of LN(Kd) vs. 1/T

E_a = energy that holds a TCE molecule to a soil particle. Equation (4.19) can also be written in the form:

$$\ln(K_d)_T = \ln(K_0) - \frac{E_a}{KT} \qquad (4.20)$$

Equation (4.20) indicates a linear relationship between $\ln(K_d)$ and $1/T$ with a negative slope of value E_a/K. After plotting ln(Kd) versus 1/T using the experimental data, the graph was nearly 100% linear with an R square of 0.996 and a fit standard error of 0.0288 (Figure 31). These values indicate that the desorption rates of TCE and temperature were consistent with equation (4.19). As temperature increases, the ratio $\frac{E_a}{KT}$ decreases and the term $e^{-\frac{E_a}{KT}}$ increases, increasing the value of K_d, the desorption rate of TCE at temperature T. Using regression analysis, the slope of this line is $-\frac{E_a}{K}$, and was found to be:

$$\frac{E_a}{K} = 2531.63 \ {}^{\circ}K$$

Initially, a TCE molecule is attached to a soil particle with a bond of energy E_a. This energy was computed using the experimental data and was found to be:

$$\begin{aligned} E_a &= K * \left(2531.63 \ {}^{\circ}K^{-1}\right) \\ &= \left(10^{-23} J^{\circ}K^{-1}\right) * \left(2531.63 \ {}^{\circ}K\right) * \left(6.24145 x 10^{18} eV / J\right) \\ &= 0.158 \, eV \end{aligned}$$

In order for it to desorb and enter the gas phase, a TCE molecule must acquire enough energy to overcome E_d and break the bond that ties it to the soil particle (Figure 28). Physically, when in the sorbed phase, a TCE molecule is at a distance d away from the surface of a soil particle. Therefore, in order for it to enter the vapor phase, a TCE molecule must gain enough energy that will help it break the soil bond, leave the soil surface, and be at a much further distance away from the soil particle. This energy and subsequent speed are gained as thermal energy from the cell temperature. Therefore, the higher the temperature in the cell, the more thermal energy is available for the TCE molecules, and the faster these TCE molecules are able to desorb. This thermal energy is used as transitional energy that allows the molecule to move faster to higher energy levels and enter the vapor phase.

4.2.2.2.5 Steady State Conditions of Desorption

The desorption graphs show that when steady state conditions are reached, the concentration of TCE in the gas phase appears to remain constant. This could mean that either the rates of desorption and adsorption of TCE in the cell are equal or that all TCE has desorbed from the soil and is in the gas phase. To solve the problem, an experiment was conducted to determine if a steady state condition had been reached. The outcome of this experiment is shown in Figure 32. After about four hours of desorption, the cell was evacuated to vacuum and the soil was allowed to desorb once more. After 4 hours of desorption, the concentration of TCE in the cell increased to about 0.5 torr. This indicates that there was more TCE in the soil and that the concentration gradient does in fact slow down desorption. From the same graph, it can be shown that the rate of desorption has decreased. This means that θ_0 is no longer equal to 1 at the beginning of the second desorption.

Finally, the results of the analysis indicate the presence of a simultaneous slow adsorption process ($K_a > 0$). Few TCE molecules are expected to go in a cycle of adsorption and desorption. Therefore, at any time, there is always some quantity of TCE left attached to the soil. This quantity is expected to decrease with increasing temperature. In this research, to make the adsorption rate approach zero, the cell must be evacuated periodically and the temperature must be increased.

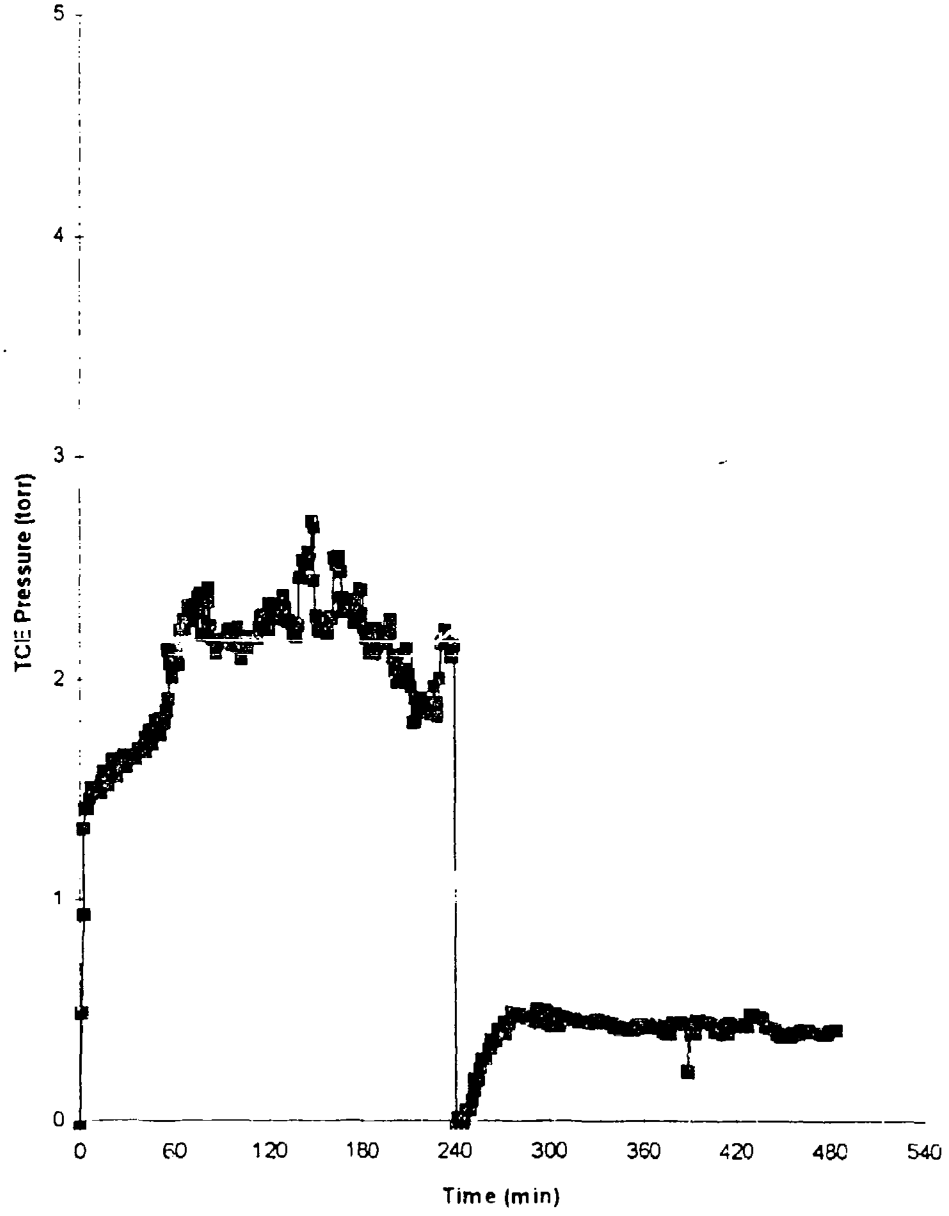


Figure 32. TCE desorption before and after evacuating the cell

V. Findings and Conclusions

5.1 Findings

The findings of this thesis include:

1. Ea = 0.158 eV is the energy of the bond that holds a TCE molecule to a plastic clay soil particle.
2. Desorption rates of TCE from plastic clay are correlated to temperature by the following function:

$$K_d(T) = K_0 e^{-\frac{E_a}{KT}}$$

Using the numerical values for E_a, K, and K_0, this equation can be written as:

$$K_d(T) = 6.11 e^{\frac{-2831.63\,(^\circ K)}{T\,(^\circ K)}} \quad \text{(molecule/m}^3\text{)/minute}$$

3. At infinite temperature, the desorption rate of TCE from plastic clay is:

$$K_{d(T \to \infty)} = 6.11 \ \text{(molecule/m}^3\text{)/minute}$$

5.2 Conclusions

The results of this study indicate that temperature influences the desorption rate of TCE from soil. At high temperatures, TCE desorbs at a faster rate and in larger quantities. This increase in temperature appears to allow a sorbed molecule to gain enough thermal energy to overcome the bond that ties it to the soil particle and enter the gas phase. If a TCE molecule is not supplied with any form of energy that it can use to overcome E_a, the molecule will stay attached to the soil particle and its chances of desorbing are very low. With no energy sources, TCE molecules will remain attached to the soil surface, may enter the soil matrix, will resist common remediation techniques, and will form a continuous source of contamination.

The analysis of the collected data during this study further indicates that the relation between TCE desorption rates and temperature did follow the Langmuir kinetic model. This model describes the mathematical relation between the vapor concentration and the sorbed concentration of a chemical. Therefore, by knowing the vapor concentration, it would be possible to determine the remaining sorbed concentration of TCE in the soil.

5.3 Recommendations

It appears from the results of this study that this optical absorption method must be somehow used in large scales in the outer environmental fields. To increase the efficiency of the remediation techniques and to lessen the resistance of those molecules in the sorbed phase, the contaminated site must be thermally heated. This could be done using Radiation heating or other type of heat sources. An example would be to use hot air during air injection techniques. This method may be economically impossible, but the efficiency will definitely be higher than when ambient air was used. It would also help a little if clean-up actions take place when the ambient temperature is at its peak.

A better way to conduct future desorption experiments would be to measure the chemical sorbed concentration prior and after desorption is complete. This way, it would be possible to quantify the desorbed quantity of the chemical and the amount that resisted desorption. These quantities may be represented as percentages of the initial sorbed concentration. Therefore, it will be possible to say that at this specific temperature, this much TCE desorbs and this much doesn't. The results would definitely be more useful in real world applications. After knowing the initial sorbed concentration, one would be able to determine the optimum temperature to use in order to decrease the sorbed concentration to below the maximum contamination level (MCL). This would both save extra spent money and assure the concentration is below the MCL.

Appendix A: Error Sources

The experiments of this study were designed to obtain consistent, correct, and accurate data. All identified error sources were minimized and corrected for. However, as with any experimental design, this research has a number of unavoidable error sources that must be corrected for. These errors were as follows:

1. Leak Errors and Concentration Gradient in the Cell

This was previously discussed in section 1.6. After performing several experiments to evaluate the leak rates in each cell, it was found that over a period of 4 hours, pressure in cell 1 increased to 0.4 torr while pressure in cell 2 increased to 0.28 torr. In addition, it was noticed that this leak approaches an asymptotic value. Compared to the desorption period (4 hours), this leak was considered negligible. Since air moves from high pressure to low pressure, the leak is assumed to be from the room into the cell ($P_{cell} \leq 70$ torr and $P_{room} \approx 760$ torr). At the same time, it was experimentally found that substances in the air do not absorb light within the frequency range 3060 to 3140 cm^{-1}. Therefore, a leak would negligibly affect the transmitted signal. However, it is believed that pressure and concentration gradients in the cell could affect the rate of TCE desorption from soil (Figure 32).

During the first 4 hours desorption experiment, the rate of TCE desorption was found to be increasing to a certain point then slows after TCE accumulates in the cell preventing more TCE from desorbing. This was experimentally determined by leaving the soil in the cell and drawing the cell down to vacuum for the second time. The results were more TCE desorbed out the soil but at a slower rate. As this operation was repeated several times, the rate starts getting slower and slower.

2. Room Temperature Changes

Throughout this research, room temperature ranged from 26 to 28°C. This change seemed to not affect TCE desorption from the soil.

3. Detector/Filter Errors

A study was performed to evaluate the decline of the sensitivity of both detectors over time using the same experimental cells but constantly maintained under vacuum. This study revealed that both detectors showed a slight decrease in intensity over the period of desorption. Theoretically, this decrease in intensity should be caused by an increase in the concentration of TCE in the cell. However, the cells were continuously under vacuum throughout the duration of the experiment. Therefore, when evaluating TCE desorption from soil, a partial decrease of the intensity over time is not caused by TCE, instead it was due to the decrease in the detector's sensitivity. This floats are further discussed in Appendix C.

4. Desorption due to Cell

One of the major obstacles in this study was the fact that the glassware and the O-rings both adsorbed and desorbed a partial quantity of TCE. To minimize these errors, the experimental cell was kept under vacuum for a period of 12 hours after each desorption experiment. This will allow the removal of TCE adsorbed to the cell. To further check this assumption, the cell was tested for adsorption and desorption. The results indicated that the amount of TCE desorbing from the cell was negligible compared to that desorbing from the soil. Furthermore, new O-rings (Teflon material) that do not adsorb organic compounds were used to minimize desorption due to the cell.

5. *Data Collection Errors*

Because of the electronic measurement devices used in this study, some errors could appear in the data collected due to all the connections between these components over time. These errors are expected to be minimum and were also accounted for in the correction for the detector float.

6. *Experimental Errors*

These errors are mainly due to the way experiments were conducted and the way soil was introduced in the cell, and others. These errors were also minimized by being consistent between experiments and by conducting all experiments in the same way and under same conditions. For example, the soils for all experiments were exposed for the same period of 2 days, the same quantity of soil was used in the five experiments, the soil was introduced and placed in the cell in the same way, and the cell alignments were nearly identical for all experiments.

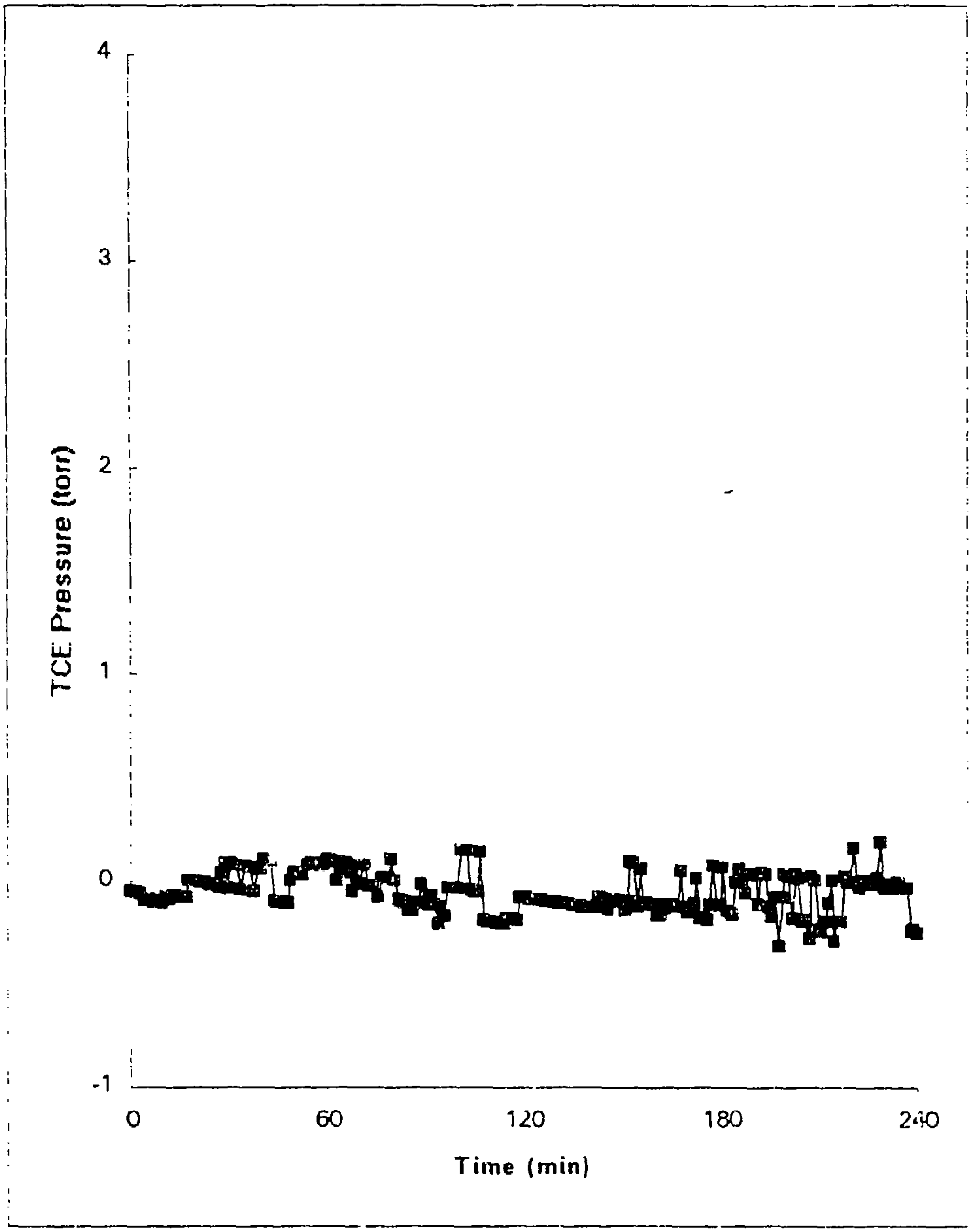


Figure 33: Effect of temperature on the structure of TCE

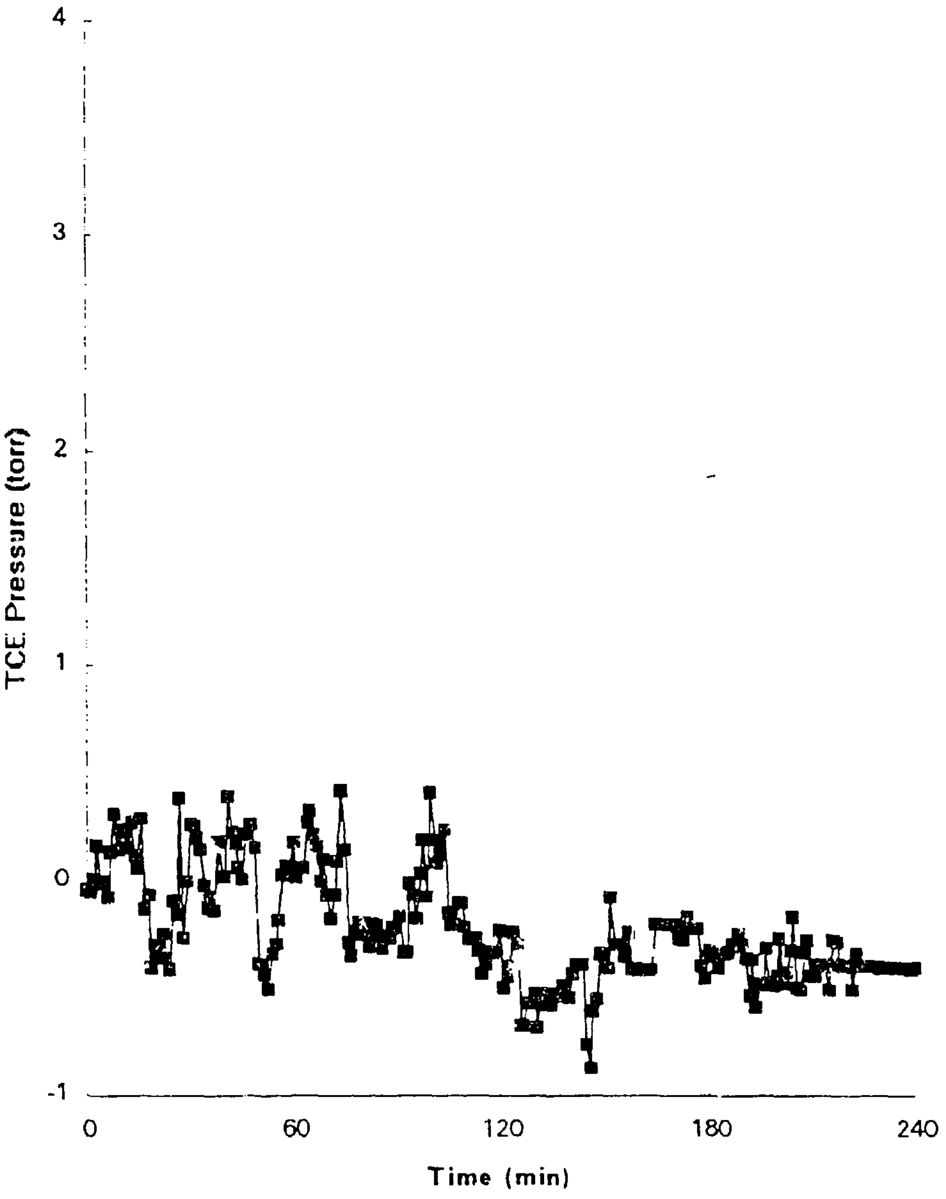


Figure 34: Effect of temperature on the signal's intensity

7. *Effect of Temperature on TCE*

An experiment was conducted to determine the effects of temperature on the structure and the integrity of TCE. To accomplish this, 10 torr of TCE were introduced into the cell and kept enclosed under a constant temperature of 100°C for a period of 5 hours. This experiment indicated that a temperature of 100°C does not have any effect on the integrity and the molecular structure of TCE (Figure 33). This again indicates that any drop in the signal was mainly due to an increase in the concentration of TCE in the cell.

8. *Effect of Temperature on The Intensity of the Signal*

An experiment was also performed to determine the effect of temperature on the intensity of the signal. This was done to determine whether the drop in the intensity of the signal was caused by the increase in temperature or by an increase in TCE concentration in the cell. This was accomplished by maintaining temperature at 100°C, closing the empty cell, and monitoring the change in the intensity of the transmitted signal for a period of 4 hours. The results indicated that temperature has a very negligible influence on the signal's intensity (Figure 34). For instance, a temperature of 100°C caused a drop in the signal that corresponds to a TCE pressure less than a half torr.

Appendix B: Correction of Cross Sectional Area of TCE

After a beam goes through the cell which contains TCE, its intensity, $I(\nu)$, which is frequency dependent, is subject to Beer's Law. After the beam leaves the cell and arrives at the filter placed on the detector, its intensity is reduced again because of TCE's unabsorbed wave numbers that pass through the filter. Therefore, the intensity, $I(\nu)$, recorded by the filter is equal to that intensity that would be recorded by the detector with no TCE and no filter in the path of the beam, I_{max}, multiplied by the fraction allowed by TCE, $[I/I_{max}]_{TCE}$, and further multiplied by the fraction allowed by the filter, $[I/I_0]_{filter}$ where:

$I(\nu)$ = recorded intensity with TCE and filter in the path of the beam;

I_0 = recorded intensity with no TCE in the cell;

I_{max} = recorded intensity with no TCE and no filter in the path of the beam;

$[I/I_0]_{filter}$ = fraction transmitted through filter only (no TCE); and

$[I/I_{max}]_{TCE}$ = fraction transmitted through TCE (no filter).

Because of Beer's Law,

$$\left[\frac{I}{I_{max}}\right]_{TCE} = e^{-\sigma(\nu)PL} \tag{B.1}$$

and because of the filter's transmitivity, T(λ), equation (B.1) becomes:

$$I(\nu) = I_{max} * T(\nu) * e^{-\sigma(\nu)lN} \qquad (B.2)$$

However, the detector "sees" the intensity:

$$I = \int_0^{\infty} T(\nu) I_0 e^{-\sigma(\nu)lN} d\nu \qquad (B.3)$$

Integration from 0 to $\propto$ was used in order to compute the intensity measured by the detector.

In the case where the cell contains no TCE (N = 0), equation (B.3) becomes:

$$I_0 = \int_0^{\infty} T(\nu) I_{in} d\nu \qquad (B.4)$$

However, our interest was to compute the signal change due TCE in the cell only. This change due to TCE alone was found by taking the ratio of equation (B.3) to equation (B.4). The result is:

$$\frac{I}{I_0} = \frac{Ln\left(\int^{\alpha} T(\nu) e^{-\sigma(\nu)lN} d\nu\right)}{Ln\left(\int^{\infty} T(\nu) d\nu\right)} \qquad (B.5)$$

Figure 35 graphically explains the correction. The filter allows transmission of only a fraction (t) of the entire light beam and this fraction must be within a certain frequency range

(T). Therefore, any frequency outside the range T will not be transmitted. TCE, on the other hand, allows transmission of all frequencies but those within the range A and only a fraction of the number of photons get through without being absorbed by the molecules of gas TCE in the cell according to Beer's Law: $e^{-\sigma lN}$. Therefore, to account for transmission due to both TCE in the cell and the filter on the detector, only the fraction $te^{-\sigma lN}$ was transmitted and was recorded by the detector. By referring to Figure 35, the shaded area is equal to $\left[t(T-A)+tAe^{-alN}\right]$, where a corresponds to the cross sectional area of TCE (σ), and equation (B.5) then becomes:

$$\left[\frac{I}{I_0}\right]_{EXP} = \frac{\left[t(T-A)+tAe^{-alN}\right]}{Tt}$$

(B.6)

or

$$\left[\frac{I}{I_0}\right]_{EXP} = \left(1-\frac{A}{T}\right)+\left(\frac{A}{T}\right)e^{-alN} \qquad \text{(B.7)}$$

Since the reduction of the signal due to TCE in the cell is

$$\left[\frac{I}{I_{max}}\right]_{TCE} = e^{-alN}$$

therefore, equation (B.7) becomes

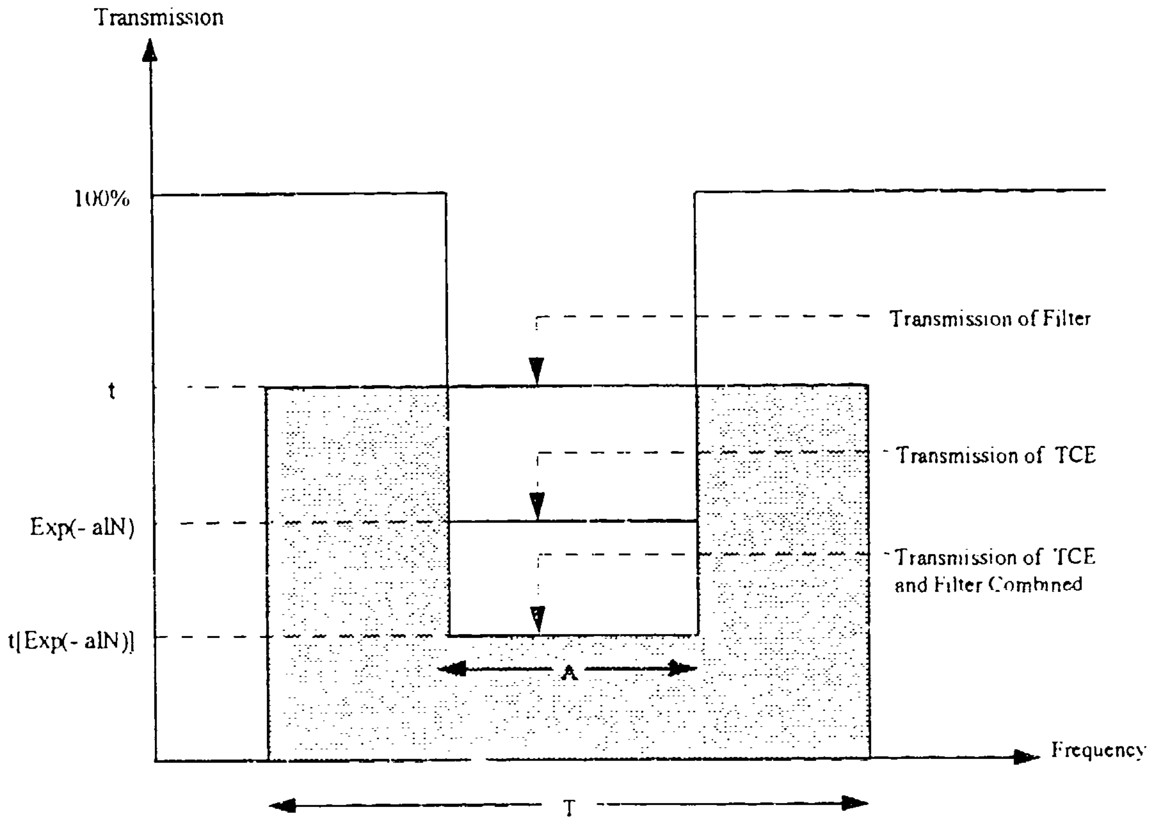


Figure 35: TCE and Filter Absorption Ranges

$$\left[\frac{I}{I_{max}}\right]_{TCE} = \frac{T}{A} * \left(\left[\frac{I}{I_0}\right]_{EXP} - \left(1 - \frac{A}{T}\right)\right) \qquad (B.8)$$

This is the correction that needs to be done in order to convert the reduction in the intensity $\left[\frac{I}{I_0}\right]_{EXP}$ to that due to TCE alone.

Therefore, to solve for signal changes caused by TCE only, the data recorded by the detector, I/I_0, must be used along with the values of T and A, found by a spectrometer, and substituted in equation (B.8). This correction will then lead to a linear relation between $\ln(I_t/I_0)$ and P, indicating a constant optical cross section of TCE (Figure 13).

After testing both filters and running a cross section experiment on both cells, the results for cell 1 with filter 1 were:

$$T = 43\ cm^{-1} \text{ and } A = 29\ cm^{-1}$$

These values were then used to compute the slope of the curve plot of $\ln(I_t/I_0)$ vs. Pressure. Using a regression analysis, and equation (B.7)

$$\begin{aligned}\sigma &= -1.0356x10^{-19} * T * \frac{\ln\left(\frac{I_t}{I_0}\right)}{PL} \\ &= -1.0356x10^{-19} * 300^{\circ}K * \frac{-0.04648}{43.5\ cm} \\ &= 3.32x10^{-20} cm^2 / molecule\end{aligned}$$

where 0.04648 is the slope of the plot of $\ln(I_t/I_0)$ against pressure. The same procedure was applied to cell 2.

To check the accuracy of these values, the data was further analyzed using the mathematical software table curve. $Ln(I_t/I_0)$ was plotted against pressure using the correction formula described by equation (B.8). In other words, the graph of $\ln(I_t/I_0)$ versus pressure (P) was plotted and fitted to the curve

$$Y = Ce^{-Bx} + (1 - C) \qquad \text{(B.9)}$$

where:

$$Y = \left[\frac{I}{I_0}\right]_{EXP}, \quad X = P, \quad B = -\frac{\sigma l}{RT}, \quad C = \frac{A}{T}$$

Using the actual data for I_t and pressure, Y and X were plotted and fitted to equation (B.9) by adjusting and fitting the values of B and C that would give the best fit. The result of this analysis were:

	B	C	R^2	σ	Correction
Cell1	0.0464	0.638	0.995	3.32×10^{-20}	$\left[\frac{I}{I_{max}}\right]_{TCE} = \left[\left(\frac{I}{I_0}\right)_{EXP} - 0.36\right] * 1.57$
Cell2	0.0469	0.623	0.996	3.35×10^{-20}	$\left[\frac{I}{I_{max}}\right]_{TCE} = \left[\left(\frac{I}{I_0}\right)_{EXP} - 0.38\right] * 1.61$
Averg	0.0466	0.630	N/A	3.335×10^{-20}	$\left[\frac{I}{I_{max}}\right]_{TCE} = \left[\left(\frac{I}{I_0}\right)_{EXP} - 0.37\right] * 1.59$

Therefore, by applying these correction to the experimental data, and by plotting the corrected data against experimental pressure, P, the results were linear graphs with constant slopes which indicate constant cross section areas for both cells (Figure 13).

This value of the cross section will then be used to find an expression for the pressure in the tube that is caused by TCE only (Appendix B).

Appendix C: Correction for Random Drift of Detectors

After performing two 36 hour tests on the detectors while maintaining both cells empty and continuously under vacuum, it was experimentally determined that both detectors experienced a decrease in the intensity over time for unknown reasons. Both test showed a fast decline in intensity in the first two hours followed by a leveling off. This decrease of intensity gave the false impression that there was an increase in the concentration of TCE in both cells which were continuously maintained under vacuum. This unknown drift was found to be random and indicated an increase in TCE pressure to a maximum of 4 torr. Unfortunately, there was no TCE in the cell. Therefore, a correction to account for this random drift had to be accomplished.

Using Table Curve, data from both experiments for each detector were plotted and fitted to a curve which was then used as the baseline correction for the drift. These curves are shown in Figures 36 and 37 and represent the following functions:

for cell 1

$$\frac{I_t}{I_0} = 0.9425 + 0.0593e^{-\left(\frac{min}{239.78}\right)} \qquad (C.1)$$

for cell 2

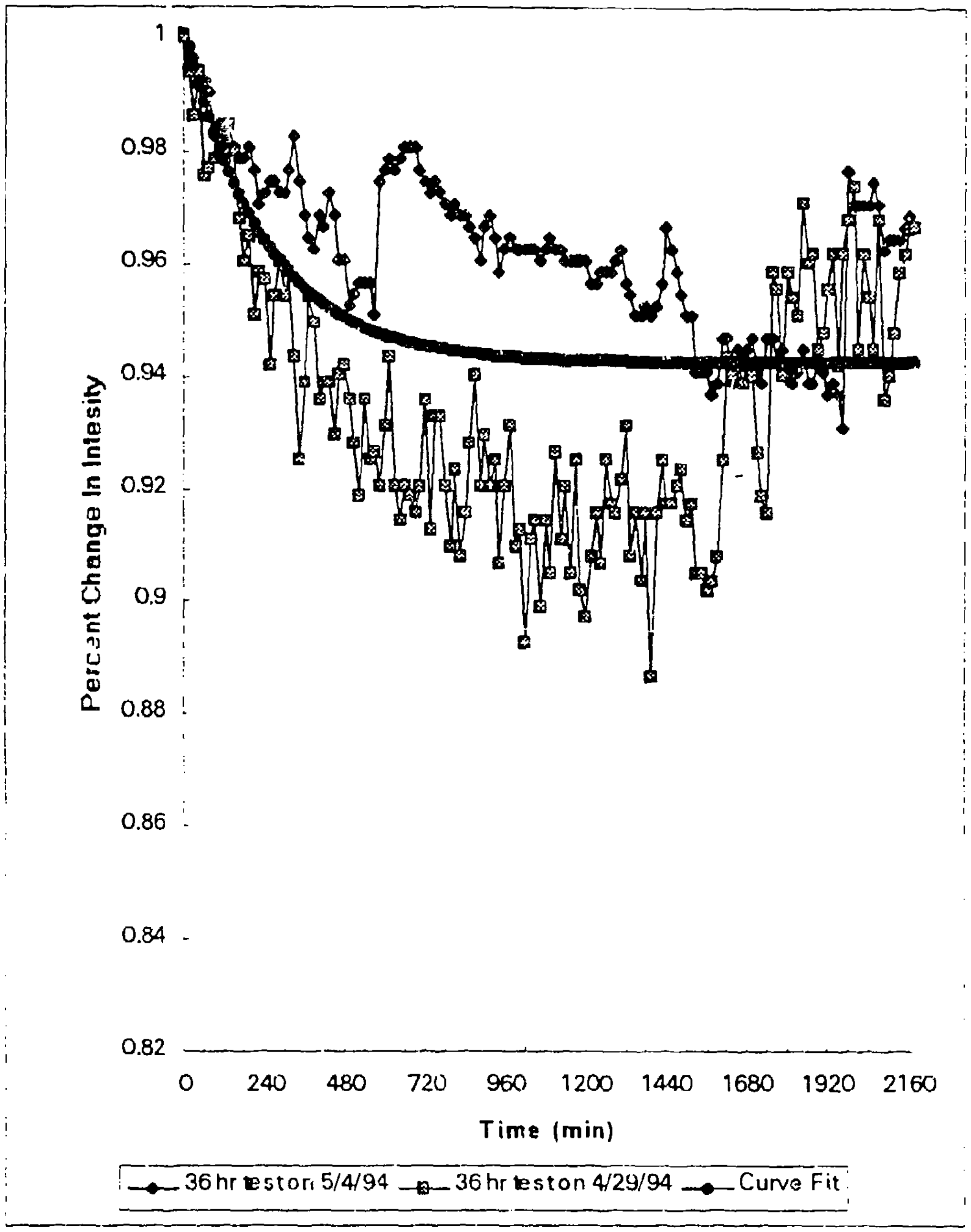


Figure 36 :Drift Correction of Detector 1

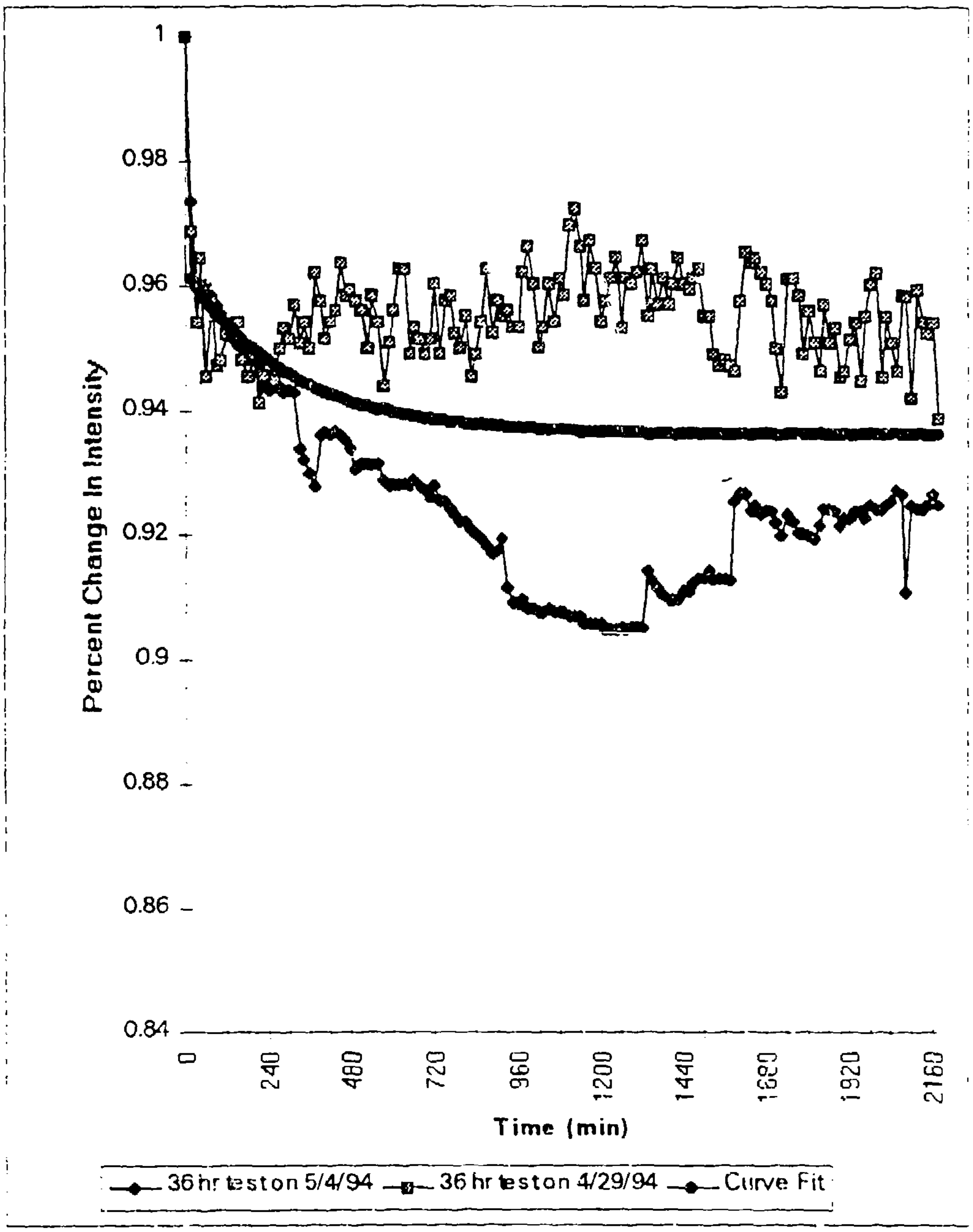


Figure 37: Drift Correction of Detector 2

$$\frac{I_t}{I_0} = 0.9362 + 0.0264e^{-\left(\frac{min}{300.33}\right)} \qquad (C.2)$$

where $\frac{I_t}{I_0}$ represent the percentage degradation in the signal over time and min indicates the time in minutes since the detectors are turned on.

To account for the drift, $\frac{I_0}{I_t}$ from the desorption experiment were multiplied by the ratio $\frac{I_0}{I_t}$ in equations (C.1) and (C.2). In other words, for each data point, the maximum (t = 0) transmitted signal, before any TCE desorbed from the soil, I_0 had to be multiplied by $\frac{I_0}{I_t}$ from equations (C.1) and (C.2) respectively. Mathematically:

$$P_t = -0.0714*(T+273)*\ln\left[\left(\frac{I_t}{I_0 * \frac{I_t}{I_{0,\,correction}}} - 0.37\right)*1.59\right] \qquad (C.3)$$

for each data point I_t.

Appendix D: Conversion of Signal Changes to Pressure of TCE

1. *TCE Pressure in the Cell*

Due to the possible presence of other species in the experimental cell, the Baratron pressure was believed not to be well consistent with TCE pressure. In addition, due to possible leaks into the cell, it was expected that the Baratron pressure would be larger than the pressure due to gas TCE alone in the cell. Therefore, by determining the pressure of TCE alone and comparing it to the Baratron pressure, the amount of any leaks into the cell was evaluated.

Using the Ideal Gas Law, the concentration of gas TCE in the cell could be written as:

$$N = \frac{n}{V} = \frac{P}{RT} \tag{D.1}$$

After rearranging Beer's law from

$$I_t = I_0 e^{-\sigma l N} \tag{D.2}$$

to

$$\ln\left(\frac{I_t}{I_0}\right) = -\sigma l N \tag{D.3}$$

and using equation (D.1), equation (D.3) becomes

$$\ln\left(\frac{I_t}{I_0}\right) = -\sigma l \left(\frac{P}{RT}\right) \tag{D.4}$$

or

$$P = -\frac{\left[RT * \ln\left(\frac{I_t}{I_0}\right)\right]}{\sigma l} \qquad (D.5)$$

Using the correction factors discussed in Appendix B, equation (D.5) becomes:

$$P = -\frac{\left[RT * \ln\left[\left(\frac{I_t}{I_0} - 0.37\right) * 1.59\right]\right]}{\sigma l} \qquad (D.6)$$

Since the temperature recorded by the computer was displayed in °C, a conversion from °C to °K was necessary. After making this temperature conversion and the substitution of numerical values for the constants l, σ, and R, equation (D.6) becomes:

$$P_t = -0.0714 * (T + 273) * \ln\left[\left(\frac{I_t}{I_0} - 0.37\right) * 1.59\right] \qquad (D.7)$$

where P has units of torr and the subscripts I indicates pressure computed using I_t (transmitted signal) and not that measured by the Baratron. This pressure is assumed to be due to the presence of TCE in the tube and that the decrease in the intensity of the transmitted signal is due only to absorption of photons by TCE and not by anything else. After evaluating the characteristics of cell 2, it was found that the equation for pressure in the cell due to TCE alone was the same as equation (D.7).

After it was found that both detectors experienced a drift (Appendix C). The drift corrections were further used in

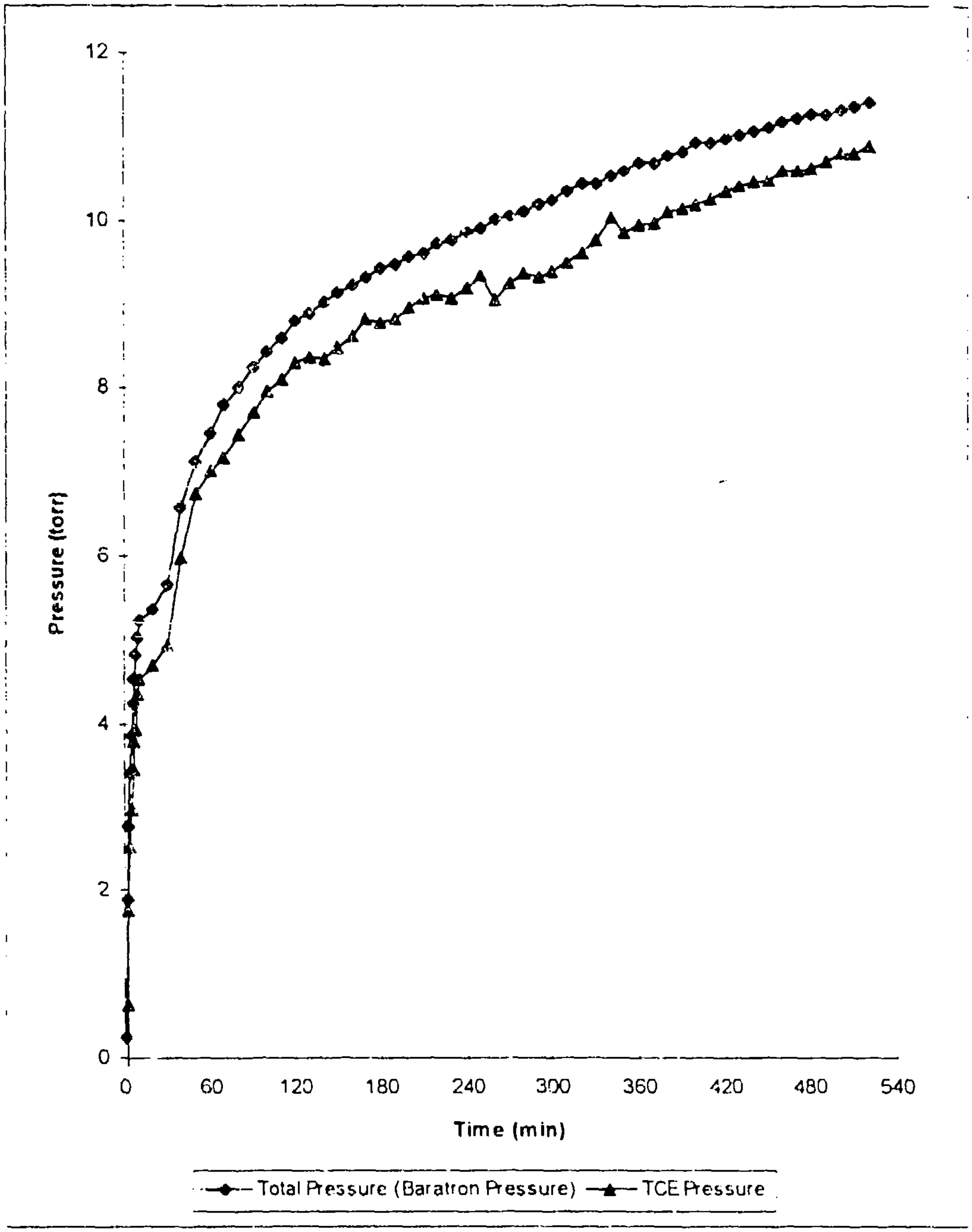


Figure 38: Comparison between Baratron pressure and TCE pressure

equation (D.7) to accurately obtain the pressure in the cells due only to TCE present in the cell. Therefore, equation (D.7) becomes:

$$P_t = -0.0714*(T+273)*\ln\left[\left(\frac{I_t}{I_0*(D_t)}-0.37\right)*1.59\right] \qquad (D.8)$$

where

I_0 = initial intensity (t = 0)including initial drift. This value is kept constant with changing in (D.8).

I_t = transmitted intensity at time t; and

D_t = detector drift at time t.

The same equation was used for both cells with D_t as the only changing parameter.

To measure the efficiency of the Baratron, P_t was plotted against the pressure recorded by the Baratron. This graph showed that the pressure of the Baratron was consistent and very close to the pressure due to the presence of TCE alone in the cell (Figure 39).

2. *TCE Concentration in molecules/cm^3*

Using Beer's Law and knowing the cross sectional area (σ), the initial and transmitted intensities (I_0 and I_t), and the path length (l), the concentration of TCE can be computed. Mathematically, after rearranging Beer's law:

$$N = \frac{\ln\left(\frac{I_t}{I_0}\right)}{\sigma l} \qquad (D.9)$$

After the corrections have been made (Appendix A), equation (D.9) becomes:

$$N = -\frac{\ln\left[\left[\left(\frac{I_t}{I_0}\right) - \frac{A}{T}\right] * \frac{T}{A}\right]}{\sigma l} \qquad (D.10)$$

or

$$N = -\frac{\ln\left[\left[\left(\frac{I_t}{I_0}\right) - \frac{A}{T}\right] * \frac{T}{A}\right]}{\left(3.334x10^{-20} cm^2 \,/\, molecule\right) * \left(43.5 cm\right)} \qquad (D.11)$$

where 43.5 cm is the length of the glass tube through which the light beam was traveling.

Simplifying equation (D.11) gives

$$N = -6.895x10^{17} * \ln\left[\left(\frac{I_t}{I_0} - 0.37\right) * 1.59\right] \qquad (D.12)$$

where

N = concentration of TCE in molecule/cm^3;

I_t = transmitted intensity in mVolts; and

I_0 = initial intensity (no TCE) in mVolts.

Therefore, it appears that by knowing I_t and I_0, the concentration of TCE in the cell can be computed. In other words, a change in the intensity of the transmitted signal automatically indicates the presence of a quantity of TCE in the cell.

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Vita

I was born and grew up in Fquih ben Salah, a small town in Morocco. At the age of 18, I attended college at the United State Air Force Academy, Colorado Springs, where I earned a B.S. in both Civil Engineering and Mathematical Sciences on June 2nd 1993. On June 3rd 1993, I flew to Dayto Ohio and started school at AFIT on June 7th to earn a Masters Degree in Environmental Engineering and Management.

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13. ABSTRACT (Maximum 200 words)

This thesis investigated the influence of temperature on the desorption rates of trichloroethylene (TCE) from plastic clay. It was expected that an increase in temperature will cause an increase in both the desorption rates of TCE and in the desorbed quantity. Previous studies on other chemicalsiindicated a faster decrease in the remaining sorbed concentration with an increase in temperature. This research made use of the infrared optical absorption technique. IR spectroscopy was used to measure the concentration of the vapor TCE that desorbed from the soil. The soil was exposed to liquid TCE fro 2 days tahn placed inside an enclosed glass tube and was allowed to desorb at a fixed temperature for a period of 4 hours. Similar experiments wer performed with temperature as the only variable. The results were an initial and rapid desorption followed by a leveling off. The rate of th initial desorption was found to increase with temperature and the quantity desorbed was also found to increase. The data was analyzed and was found to follow the Langmuir kinetic model.

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