

FOG-SMOG REACTOR AND PHOTOOXIDATION OF NAPHTHALENE WITHIN  
THE FOG CONDENSATE IN A UV LIGHT SETUP

A Thesis

Submitted to the Graduate Faculty of the  
Louisiana State University and  
Agricultural and Mechanical College  
in partial fulfillment of the  
requirements for the degree of  
Master of Science in Chemical Engineering

in

The Department of Chemical Engineering

by

Neha Shrikant Damle  
B.E. Pune University, Pune, India, 2006  
December 2008

## ACKNOWLEDGEMENTS

I would like to thank Dr. Valsaraj for his guidance, support and encouragement throughout my research work. I would like to thank Dr. Thompson and Dr. Henry for serving on my committee. The department of chemical engineering is thanked for two years of financial aid.

I want to thank my friends Amol, Akanksha, Anushree and Dhruva for their help with my thesis writing and my lab mates Jing Chen, Nicholas Ashley and Maoming Ren for helping me and sharing some of their experiences with me for the betterment of my research work. They have not just been lab mates, but teachers for me. I would like to thank Mr. Xiagang Xing for helping me with the Scanning Electron Microscope.

I would like to thank Paul, Joe and Fred for manufacturing reactor and other heat exchanger parts. I really appreciate their prompt support even though they had many other works to complete. My sincere thanks go to Darla, Melanie and Danny who helped me from time to time with my administrative requirements.

I would like to thank my mother and father and Pushkar, my fiancée for their continuous support and faith in me. This research work is dedicated to them and was impossible without their encouragement.

## TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	ii
LIST OF TABLES.....	v
LIST OF FIGURES.....	vi
ABSTRACT.....	viii
CHAPTER	
1. OVERVIEW.....	1
1.1 Polycyclic Aromatic Hydrocarbons.....	1
1.2 Fog and Smog: Formation, Types and Properties.....	3
1.3 Aerosols.....	4
1.4 The Scope of the Research.....	5
2. LITERATURE REVIEW.....	6
2.1 Experiment 1: Uptake of Naphthalene by Fog Droplets.....	6
2.1.1 Naphthalene.....	6
2.1.2 NaCl Aerosols.....	7
2.1.3 Partition Coefficients and Partitioning Phenomena.....	8
2.1.4 Atmospheric Fog Composition.....	12
2.1.5 Smog-Fog-Smog Cycle.....	14
2.1.6 Use of Reactors for Experiments.....	14
2.2 Experiment 2: Photooxidation of Naphthalene Within the Fog Condensate in UV Light.....	16
3. EXPERIMENT 1: UPTAKE OF NAPHTHALENE BY FOG DROPLETS.....	22
3.1 Materials and Methods.....	22
3.1.1 Materials and Methods for Sample Preparation.....	22
3.1.2 Equipment Specification and Techniques.....	23
3.2 Experimental Setup.....	25
3.3 Experimental Procedure.....	30
3.3.1 Calculation of Partition Coefficients.....	30
3.3.2 Photooxidation Reaction of Naphthalene and Fog Containing NaCl.....	32
3.4 Results and Discussion.....	32
3.4.1 Results and Discussion for the Naphthalene Uptake Experiment.....	32
3.4.2 Results and Discussion for the Photooxidation Reaction Experiment Inside the Reactor.....	37
4. EXPERIMENT 2: PHOTOOXIDATION OF NAPHTHALENE WITHIN THE FOG CONDENSATE IN A UV LIGHT SETUP.....	39
4.1 Materials and Methods.....	39
4.1.1 Chemicals.....	39
4.1.2 Methods and Techniques.....	40
4.2 Experimental Setup.....	40

4.3 Experimental Procedure.....	41
4.4 Results and Discussion.....	44
4.4.1 Analysis of a Product Formation Using the Reaction Mixture Containing NaCl.....	44
4.4.2 Analysis of a Product Formation Using the Reaction Mixture not Containing NaCl.....	50
5. CALCULATIONS.....	54
5.1 Calculations for Experiment 1 Explained in Chapter 3.....	54
5.1.1 Calculation for the Amount of NaCl Required for the Aerosol Solution..	54
5.1.2 Calculation for Naphthalene Concentration from HPLC Data.....	55
5.1.3 Calculation for $\Delta H$ and $\Delta S$ Values from Van't Hoff's Equation.....	57
5.2 Calculation for Experiment 2 Explained in Chapter 4.....	57
6. CONCLUSIONS.....	59
6.1 Partition Coefficient Experiments.....	59
6.2 Photooxidation Experiments.....	60
REFERENCES.....	61
VITA.....	66

## LIST OF TABLES

Table 1: Properties of PAH (Dabestani et al., 1999)..... 2

Table 2: Properties of Naphthalene..... 9

## LIST OF FIGURES

Figure 1: Growth Curves for Condensation and Dispersion Nuclei (Kramer et al., 2000).....	10
Figure 2: Partitioning Phenomenon.....	11
Figure 3: Relationship Between Enthalpy and Entropy for Different $N^*$ Values ( Davidovits et al., 1991).....	12
Figure 4: Average Contribution of Various Organic Compounds to the Dissolved Carbon in the Fog Water (Raja et al., 2007).....	15
Figure 5: Possible Mechanisms of a Photoreaction of PAH (Fasnacht et al., 2003).....	18
Figure 6: $C/C_0$ vs. Time for Benzopyrene and Chrysene (Miller et al., 2005).....	21
Figure 7: Experimental Setup for the Partition Coefficient Experiment.....	26
Figure 8: Aerosol Generator (Retrieved from <a href="http://www.TSI.com">www.TSI.com</a> ) .....	28
Figure 9: Fog Collector.....	30
Figure 10: Heat Exchanger Used for the Fog Condensation.....	31
Figure 11: Actual Structure of the Obtained NaCl Aerosol.....	33
Figure 12: Distribution and Abundance of Aerosols.....	34
Figure 13: $\ln K_{wa}$ vs $(1/T)$ for Naphthalene on Fog Droplets.....	36
Figure 14: Intelli-Ray 600 UV Light Setup (Taken From <a href="http://uvitroninternational.com">uvitroninternational.com</a> ).....	42
Figure 15: Arrangements of Vials Under UV Light (Front View).....	43
Figure 16: Spectrum of the Reaction Products of the Photooxidation Reaction of Naphthalene with Fog Consisting of NaCl.....	46
Figure 17: HPLC Trace Showing Phthalide Peak at the Retention Time 4.743 Seconds. Absorbance at 254 nm.....	47
Figure 18: Concentration vs. Time Curve for Decrease in Naphthalene.....	49
Figure 19: $\ln (C_{no}/C_n)$ vs. Time for Naphthalene.....	49
Figure 20: Increase in Benzaldehyde Concentration with Time.....	50
Figure 21: GC/MS Trace for Products of Photooxidation of Naphthalene in Water	

Without NaCl.....	51
Figure 22: HPLC Trace for Products of Photooxidation of Naphthalene Within Water without NaCl .....	52
Figure 23: Graph for Decrease in Naphthalene Concentration With Time for Photooxidation in Water without NaCl.....	53
Figure 24: Ln (C <sub>no</sub> /C <sub>n</sub> ) vs. time for naphthalene.....	53

## ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) form a major class of air pollutants. Naphthalene is a commonly found PAH in the atmosphere. Atmospheric fog water contains naphthalene absorbed from surrounding air. The partition coefficient of naphthalene is defined as the ratio of total naphthalene concentration in fog water to total naphthalene concentration in air. The purpose of this research was to determine the partition coefficients of naphthalene for varying reactor temperature.

Fog was artificially formed in a predesigned reactor. NaCl aerosols were used as condensation nuclei for fog formation. Fog droplets were exposed to naphthalene vapors in the reactor. The reactor provided 62 seconds residence time for fog droplets. Fog was then condensed using a heat exchanger at the reactor outlet. Compressed air was used as a carrier gas for the experiment. Naphthalene concentration in the collected condensate and exit gas was determined using High Performance Liquid Chromatography (HPLC). Partition coefficients were calculated at 334K, 346.5K, 361.5K and 371.5K. The experimental results indicated a decrease in partition coefficient with increasing temperature.

Earlier work has demonstrated presence of products of naphthalene photooxidation as 1-naphthol, naphthoquinones, benzoquinones, phthalide and 1,3-indandione. The aim of this research was also to determine products of naphthalene photooxidation reaction within the fog condensate containing water, naphthalene and NaCl under UV light. The fog condensate was exposed to UV light for time intervals between 0 to 5 hours. Experimental observations showed a decrease in naphthalene concentration with time. Overall reaction rate constant  $k$  for naphthalene was determined to be 0.00567/min and detected reaction products were phthalide and benzaldehyde. Same experiment was performed using a reaction mixture which consisted only of water and naphthalene with complete absence of NaCl which showed that the value of  $k$  was

decreased to 0.00147/min with complete absence of benzaldehyde in the reaction products. Along with phthalide, 1-3 indandione was also observed as a product of the reaction.

It was concluded from both the experiments that presence of NaCl changed product formation and reaction rate of naphthalene photooxidation and also lowered the value of partition coefficient at 298K as compared to pure water.

## **CHAPTER 1**

### **OVERVIEW**

Various industrial processes release different chemicals and gases in the atmosphere causing air pollution. Polycyclic aromatic hydrocarbons (PAH) form a major class of air pollutants. PAHs are also released by anthropogenic activities. Naphthalene, anthracene, pyrene and phenanthrene are some of the commonly found PAHs. PAHs are absorbed by water bodies that come in contact with them. Fog is one such entity, which concentrates gaseous PAHs. In the current research, the focus is on absorption of naphthalene by a laboratory created fog and photooxidation of this absorbed naphthalene within fog condensate in presence of UV light. The current chapter gives an overview of the concepts and terms used in this thesis.

#### **1.1 Polycyclic Aromatic Hydrocarbons (PAH)**

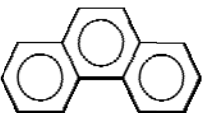
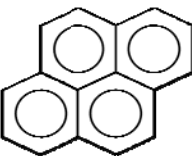


PAHs are two or more benzene rings fused together. They are stable and easily soluble in organic solvents and oils. They are hydrophobic and have high affinity toward organic compounds, therefore are readily adsorbed on soot particles, food and other organic matter. They are generally low vapor pressure compounds and can be classified on the basis of the number of aromatic rings that are fused together in a particular molecule. PAHs are found to be carcinogenic and mutagenic. This behavior of PAHs can be a function of their nonplanarity (Harvey et al., 1991). In general, non planar PAHs are less stable, more reactive and more toxic (Dabestani et al., 1991). As the number of rings in a PAH increase, its molecular weight increases which results in an increase in the number of isomers. Table 1 gives comparison of the main properties of these compounds.

Incomplete combustion of carbonaceous substances like wood, coal, cigarette, kerosene and smoke is the main source of PAHs (Jenkins et al, 1996). Household sources, industrial

sources and natural sources are three major sources of PAH production. Household sources include fireplaces, automobile and furnaces; industrial sources being oil power plants, waste incinerators, aluminum smelting and wood preservation. Natural sources are forest fires and volcanic eruptions (Nikolaou et al, 1984).

Along with air pollution, PAHs constitute even a major class of water polluting compounds since industrial waste water contains a major percentage of PAHs. Even though hundreds of PAHs are known, 17 have been listed as priority pollutants by Environmental Protection Agency (EPA)

Table 1: Properties of PAH (Dabestani et. al., 1999)

Property	Phenanthrene	Pyrene	Anthracene	Pentacene
Structure				
Molecular formula	$C_{14}H_{10}$	$C_{16}H_{10}$	$C_{14}H_{10}$	$C_{22}H_{14}$
Molecular weight (g/mol)	178.23	202.25	178.23	278.36
Solubility in water (mg/l at 20 °C)	1.28	0.135	1.3	Insoluble in water

Certain polycyclic aromatic hydrocarbons having very high molecular weights are

difficult to analyze because of an unavailability of reference standards. These high molecular weight PAHs are often obtained as products or intermediates in research experiments. Therefore, studies related to PAH identifications and reactions are going on for decades and new ways to identify the products and reaction mechanisms are being invented.

## **1.2 Fog and Smog: Formation, Types and Properties**

A large portion of water in the atmosphere is in the vapor phase (Acker et al., 2007). Fog is formed when vapor condenses on solid or liquid bodies. When water vapor in the atmosphere is cooled adiabatically, it deposits on aerosol particles present around. This leads to the formation of water droplets. Fog is formed in the form of such water droplets that are suspended in air near the earth's surface. A condensation nucleus acts as the surface on which a water film forms and grows during a fog droplet formation. Condensation growth occurs when the atmospheric temperature is lowered. Dust particles, oil aerosols and other solid aerosols can act as such condensation nuclei in fog formation. Fog and cloud droplets can be readily formed even by carbonaceous aerosols (Benner et al., 1993). Fog droplets have a wide size range. Their size can vary from a few micrometers to tens of micrometers (Raja et al., 2007). Fog reduces visibility and causes problems in real time remote sensing.

The difference between the temperature and a dew point should be less than or equal to 5°C and relative humidity should be near 100% for fog formation. Fog can form at much lower relative humidity than 100% when condensation nuclei are present abundantly and are hygroscopic (example, NaCl aerosols).

Sea fog, valley fog, steam fog and ice fog are some of the various types of fog. Fog can be produced in a laboratory and experiments can be performed using synthetically generated fog. Production of fog in a laboratory needs water vapor and aerosols that act as condensation nuclei. Such synthetically generated fog has previously been used to perform experiments. Condensation

nucleus is necessary for an artificial fog formation. In this experiment, NaCl aerosols were used as the condensation nuclei.

Smog is a combination of smoke and fog and results in air pollution. Smog can cause health hazards such as inflammation of breathing passages; adverse effects on lung working capacity, cough and different types of respiratory disorders. Polluted air containing acidic compounds such as nitric acid and hydrochloric acid can increase hygroscopy of aerosol particles effectively, affecting fog formation (Kokkola et. al., 2003). UV light present in the atmosphere causes smoke and fog to react, resulting in formation of many hazardous products. A special type of smog called photochemical smog forms as a result of secondary products formed from air pollutants. In this process of formation of photochemical smog, a photon collides with different air polluting molecules. The reaction leads to the formation of secondary compounds that combine with fog to produce smog.

One of the aims of this research was to study the reactions of fog condensate enriched with naphthalene under UV light and analyze the reaction products. Naphthalene being a typical air pollutant in the atmosphere was used to create smog in the laboratory for this project.

### **1.3 Aerosols**

Aerosols are minute particles suspended in air that are in solid or liquid form. Aerosols are a two phase system, solid or liquid suspended in gas. They are usually heavier than air and hence a continuous air current is needed to keep them suspended. Sources of aerosols are dust storms, volcanic eruptions, sea spray, grassland fires and most importantly, an incomplete combustion of hydrocarbons which releases aerosols in the form of heavy smoke. They vary greatly in their stability depending on the particle size and concentration (Hinds, Aerosol Technology).

Aerosols have a wide range of size and shape. The properties of aerosols depend on their size. Aerosols are measured in terms of either mass concentration ( $\text{g}/\text{m}^3$ ) or number concentration ( $\text{number}/\text{m}^3$ ). Aerosols when formed have electrostatic forces that need to be neutralized in order to use them for experimental purpose.

Some of the typical types of aerosols are bioaerosols, clouds, haze, fume, dust, smog and smoke. Aerosols have some commercial applications including spray dryers, production of pigments, carbon black and fiber optics. Aerosols affect visibility, climate and human health (Hinds, Aerosol technology).

#### **1.4 The Scope of the Research**

1. Use of NaCl aerosols as the condensation nuclei for fog droplet formation inside the reactor.
2. Determination of naphthalene concentrations in fog condensate and exit air.
3. Calculation of partition coefficients using concentration values at a particular reactor temperature and obtaining a plot of change in the reactor temperature and its effect on the partition coefficients.
4. Carrying out photo oxidation reaction of naphthalene within the collected condensate and studying a change in concentrations of reactants and products with time.

## CHAPTER 2

### LITERATURE REVIEW

Atmospheric fog absorbs surrounding organics, many of which come from air pollutants. This research concentrates on the uptake of polycyclic aromatic hydrocarbons by fog droplets and reaction of PAHs within a fog condensate in presence of UV light. Results of this research will help us understand what percentage of naphthalene (PAH) is absorbed by fog droplets and the resulting photoreactions that give various products that may or may not be harmful. This chapter of the thesis discusses some important concepts, properties and studies carried out by other researchers to understand similar phenomena. Knowing the results of their experiments and comparing them with the results of the current experiment, we can verify the data and draw important conclusions. The research has been divided into two separate experiments. The first set of experiments talks about the uptake of naphthalene by fog droplets at different reactor temperatures and the second set of experiments talks about photooxidation of naphthalene at given reaction conditions.

#### **2.1 Experiment 1: Uptake of Naphthalene by Fog Droplets**

Naphthalene is the most abundantly found polycyclic aromatic hydrocarbon in the industrial belt from Houston to Baton Rouge in USA. It is easily absorbed in bulk water and adsorbed on air-water interfaces at room temperature. The first set of experiments in this research focuses on the uptake of naphthalene gas by laboratory generated fog droplets. NaCl aerosols were used as condensation nuclei for fog droplet formation. Following sub-sections provide some information about properties of naphthalene and NaCl aerosols and findings of similar studies that had been carried out by researchers in the past.

##### 2.1.1 Naphthalene

Naphthalene is the most commonly found polycyclic aromatic hydrocarbon in pollutants

and has been used as a PAH in the current study. It is also one of those few PAHs found in nature that are in vapor form. A study carried out in Mumbai, India in recent years summarizes the concentrations of different pollutants at 9 different locations including canteens, movie theaters and restaurants. The results of this study indicate a significant presence of naphthalene as an air pollutant in seven out of nine places (Shrivastava et al., 2007).

Naphthalene is the smallest compound among the class of PAH that is also known by names such as naphthalin, naphthaline, naphthene and white tar. It is volatile and readily sublimates at room temperature. It has a characteristic odor that is detectable at 0.08 ppm. Sources of naphthalene are petroleum refineries, coal tar distillation, paper mills, motor vehicles exhaust, wood mills, antiseptics and lubricating fluids industries. Coal consists of 10-12% naphthalene. Naphthalene is also used as a raw material for different products and its industrial demands are increasing for the production of some major solutions like phthalic anhydride, azo dyes, surfactants and dispensers. Table 2 given below summarizes some of the important physical and chemical properties of naphthalene.

### 2.1.2 NaCl Aerosols

In this experiment, NaCl aerosols were used as condensation nuclei for production of fog in the laboratory. NaCl aerosols were specially used because of their large concentration in the atmosphere that can be illustrated by the fact that 1000-10000 ( $10^6$  metric tons/year) sea salts, which consist typically of NaCl aerosols, are emitted by sea sprays every year (Suhre et al., 1995). NaCl aerosols are hygroscopic and can form fog below 100% relative humidity. They have a characteristic cubical shape and have particle size range between 0.01 and 10  $\mu\text{m}$ . Due to their size range, they can be examined under a scanning electron microscope. NaCl aerosols are used typically as the test aerosols for direct and indirect atmospheric studies (Kramer et al, 2000). Figure 1 shows the growth curves for NaCl aerosols.

The typical growth curves were studied in the experiment (Kramer et al., 2000) and it was then concluded that growth of NaCl aerosols by condensation of water vapor depends on their diameter. As shown in figure 1, higher diameter of the condensation nuclei results in the smaller growth factor with increasing relative humidity; where a growth factor is the ratio of measured equivalent diameter  $D$  to the diameter of dry aerosol  $d$ .

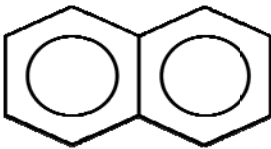
NaCl aerosols are generally produced in a laboratory by an aerosol generator or a nebulizer. Aerosol solutions used for the production of NaCl aerosols are salt solutions, typically consisting of alcohol, water and NaCl. Charge neutralizers are essential to remove a charge on NaCl aerosols.

In the current experiment, partition coefficients of naphthalene were calculated at various reactor temperatures. NaCl aerosols were used as the condensation nuclei for fog droplet formation in this experiment because of their hygroscopy and most importantly their abundance in the atmosphere. These aerosols also induced salinity to the fog condensate and reactions were performed later using this saline condensate.

### 2.1.3 Partition Coefficients and Partitioning Phenomena

Hundreds of different pollutants are present in the atmosphere. Different areas of the world have been studied for decades to understand the mechanism that controls the fate of these pollutants. From a complete class of pollutants, organics have been of a major interest to many researchers and it has been found that the main phenomena controlling their behavior is their equilibrium partitioning in two different phases (Hoff et al., 1993). Many studies explain that in case of the partitioning between air and water phases, air-water interface plays a significant role in chemical absorption influencing chemical effects (Chen et al., 2006)

Table 2: Properties of Naphthalene (Retrieved from [www.oehha.ca.gov](http://www.oehha.ca.gov))

Property	Value
Structure	
Molecular formula	C <sub>10</sub> H <sub>8</sub>
Molecular weight (g/mol)	128.17
Solubility in water (mg/l)	30
Density (g/cm <sup>3</sup> )	1.14
Appearance	Solid white flakes
Melting point (°C)	81.2
Boiling Point (°C)	218
Vapor pressure at 25 °C (N/m <sup>2</sup> )	11

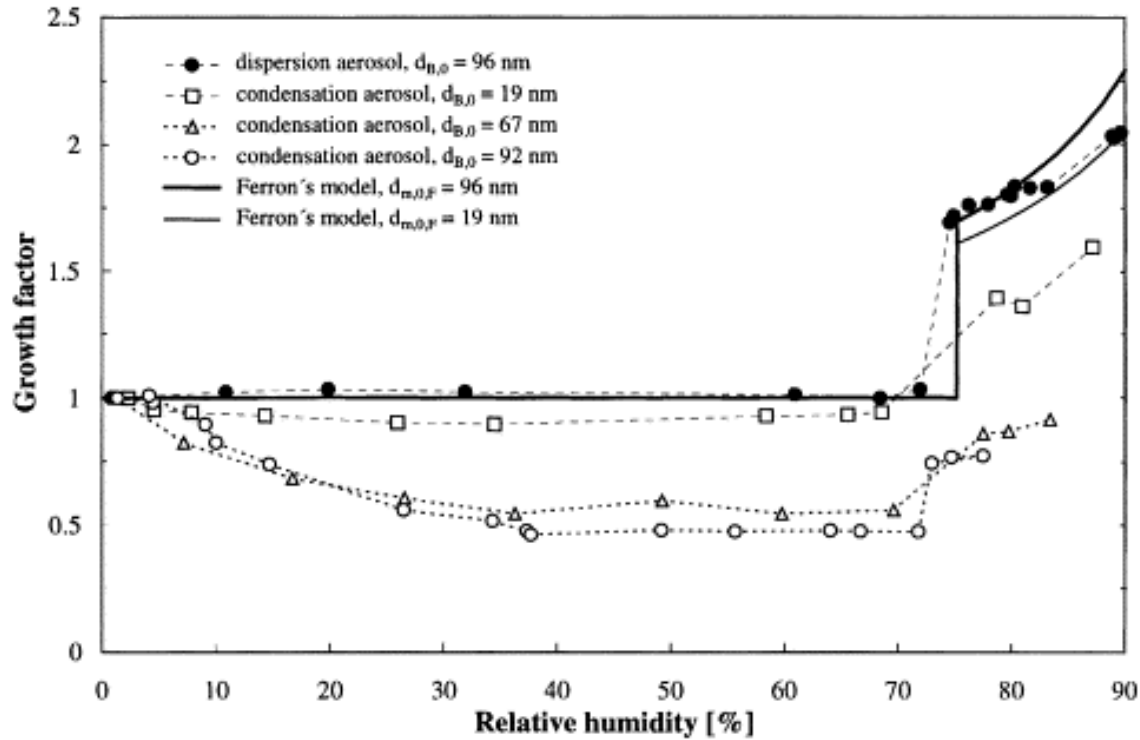


Figure 1: Growth curves for condensation and dispersion nuclei (Kramer et al., 2000)

Partition coefficient is defined as the ratio of a concentration of a trace gas in fog droplets to its concentration in surrounding air. Partition coefficient is a function of temperature. In this experiment a change in the value of partition coefficient with temperature was studied. Equation (1) given below gives a mathematical relation between the concentrations of naphthalene in water and air (Chen et al., 2006)

$$K_{WA} = \frac{C_W}{C_A} \quad (1)$$

Where, for the current research explained in the following chapters,  $C_A$  is the concentration of naphthalene in exit air and  $C_W$  is the total concentration of naphthalene in fog condensate and  $K_{WA}$  is the partition coefficient of naphthalene between exit air and fog condensate.

It has been found that partitioning of a chemical at an air-water interface is governed by mass accommodation coefficient  $\alpha$  which is a probability of a molecule of a chemical getting

adsorbed on an interface when it strikes the interface. Nathanson (Nathanson et al., 1996) explained this process of this adsorption as:



(Equation taken from Nathanson et al., 1996). Where, g represents a gas phase, s represents surface and l represents a liquid phase. A molecule in gas phase after striking the interface could either get adsorbed by the rate  $k_{ads}$  or get desorbed in the gas phase again by  $k_{desorb}$ . The molecule could further mix with the bulk liquid phase by transportation rate  $k_{sol}$ . So, a fate of the chemical truly depends on the ratio of  $k_{sol}$  and  $k_{desorb}$ . Figure 2 illustrates the above mentioned phenomenon.

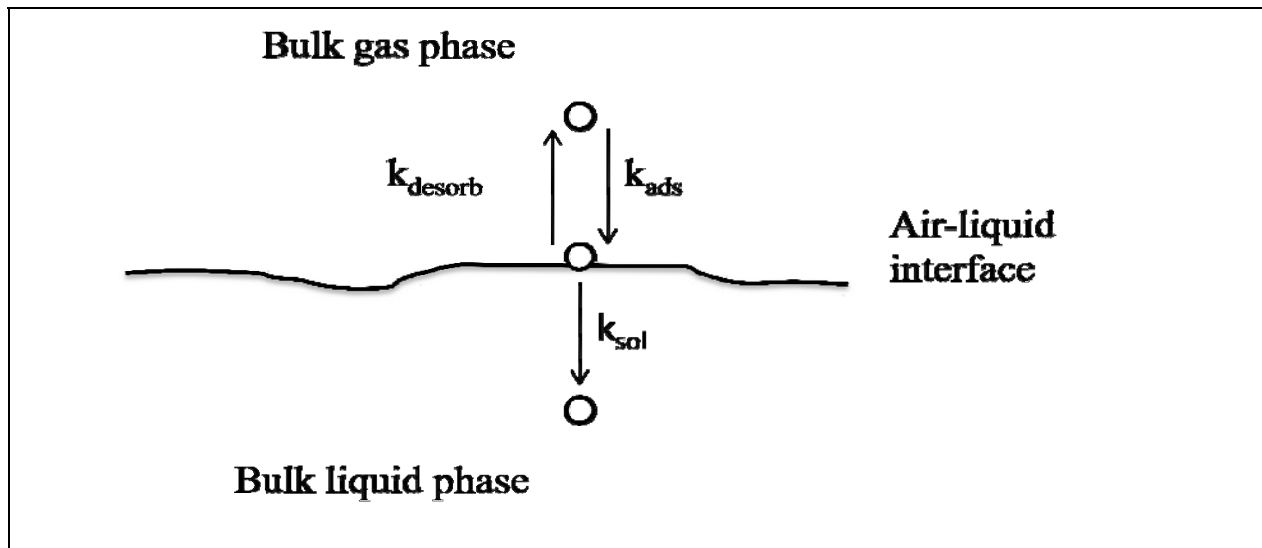


Figure 2: Partitioning phenomenon

Every adsorption process has a free energy associated with it at a particular temperature. The Gibbs' free energy can be divided to two parts as enthalpy and entropy associated with the process. Enthalpy value determines if the process is exothermic or endothermic. The sign of the enthalpy value determines the solubility and hence the process. Effect of temperature is dominant on partition constant at air-water interface. It has been observed that as temperature of a system

increases, solubility of a gas in water reduces because of an increase in negative enthalpy associated with the process. Work has been done to find the correlations between enthalpy and entropy associated with the process. According to Davidovits (Davidovits et al., 1991), this relationship can be presented with the help of the following figure. The graph shows the change of enthalpy with entropy for different values of  $N^*$ . The value of  $N^*$  represents the average number size of the critical cluster, meaning that for the case of  $N^*=2.4$ , it is the molecule of a chemical itself accompanied and coated by 1.4 water molecule.

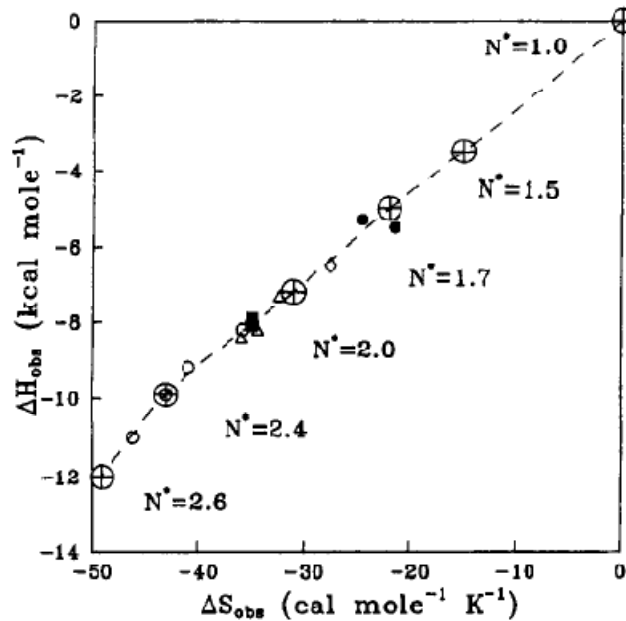


Figure 3: Relationship between enthalpy and entropy for different  $N^*$  values ( Davidovits et al., 1991)

There are several methods to find the partition coefficients. Some of them are actual concentration measurements (generally followed by many researchers) and determination of solubility by UV absorption.

#### 2.1.4 Atmospheric Fog Composition

Atmospheric fog readily absorbs surrounding pollutants. Solubility of pollutants in fog

varies with the atmospheric temperature and droplet diameter of fog. From the earlier study, it has been found that an increase in a fog droplet diameter lowers absorption of the surrounding PAHs. Extensive effort has been put into studying the chemical composition of naturally generated fog. It has typically been found that there is a wide range of organic and inorganic chemicals present in fog. These chemical compounds are present either as absorbed gases or condensation nuclei for fog formation.

Fog mostly consists of acidic compounds like nitric acid, formic acid, acetic acid, carbonyls and bi carbonyls, aromatic hydrocarbons like naphthalene, phenanthrene, benzene, long chain alkanes and other functional groups (Herckes et al., 2007). In a recent study, it has been found that fog in Houston and Baton Rouge consisted of ionic species of  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}_2^+$  and  $\text{Ca}_2^+$  (Raja et al., 2007). A work carried out in Agra, India showed that along with the components mentioned above, there were some acidic anions present such as  $\text{CH}_3\text{COO}^-$ ,  $\text{HCOO}^-$  (Lakhani et al., 2007). Due to the acidic and alkaline compounds mixed in fog, pH ranges from 2.6 to 7.2 depending on the location of fog collection (Raja et al., 2007).

Hydrophobic organic contaminants (HOC) are deposited on the ground due to fog water and rain water. It has been found that there is a greater influence of submicron particles in partitioning of HOCs. ( It was evident from the previous work that HOCs have affinity towards substrates such as dissolved organic matter present in fog and hence HOCs have major compositions in fog droplets (Poster et al., 1996)). It was found in the study carried out by Poster (Poster et al., 1996) that biphenyl compounds, phenanthrene, pyrene, chrysene, benzofluranthrene, indenopyrene and benzoperylene were present in major concentrations in rain and fog waters. In a study carried out by Poster (Poster et al., 1996) and Glotfelty ( Glotfelty et al., 1987) fog condensate was filtered or the submicron particles. It was observed that the

concentrations of PAHs measured in ambient air were lower by the factor of 100 than the ones present in fog water. This result indicated that fog was supersaturated with respect to ambient air concentrations. Many different compounds detected in fog are either present via absorption or photochemical reactions. Therefore, investigation of the reactions of different compounds in fog water becomes essential.

#### 2.1.5 Smog-Fog-Smog Cycle

Fog contents such as air pollutants and aerosols absorbed within the fog droplets settle on the earth's surface. These entities are deposited on the ground when fog dissipates. The smog-fog-smog cycle is the process where by enhanced secondary aerosols produced by fog processing further act as smog condensation nuclei for further fog (Raja et al., 2007).

In order to understand the fog processing and smog chemistry, collection and analysis of fog using different techniques is essential. Several studies have concluded the presence of carbonaceous compounds in collected fog samples from various locations. The sources of some of these compounds were identifiable, but many are still unidentifiable and predicted to be resulting from the photochemical reactions within fog. A study carried out in Baton Rouge, LA and Houston, TX showed a large number of compounds in the fog water (Raja et al., 2007). The result showed a contribution of different air pollutants toward the presence of dissolved carbon (DOC) in fog. The results are summarized in figure 4.

As shown in figure 4, more than 41.6 % unknown carbon has been detected in Baton Rouge and 37% has in Houston. To understand the sources of this non identifiable carbon, it is essential to carry out photochemical reactions on the artificially generated fog.

#### 2.1.6 Use of Reactor for Experiments

Environmental phenomena are recreated in the laboratory for the purpose of understanding them completely. Reactors are used for studying such environmental processes.

Experiments related to the uptake of gases by fog droplets or water films are typically carried out in suitable reactors. Chen (Chen et al., 2006) used a glass boat reactor for carrying out an experiment related to the uptake of PAHs by a thin water film. A falling droplet reactor was used by Raja (Raja et al., 2006) for studying partition coefficients of several PAHs in the water droplets and dependence of partition coefficients on droplet diameters.

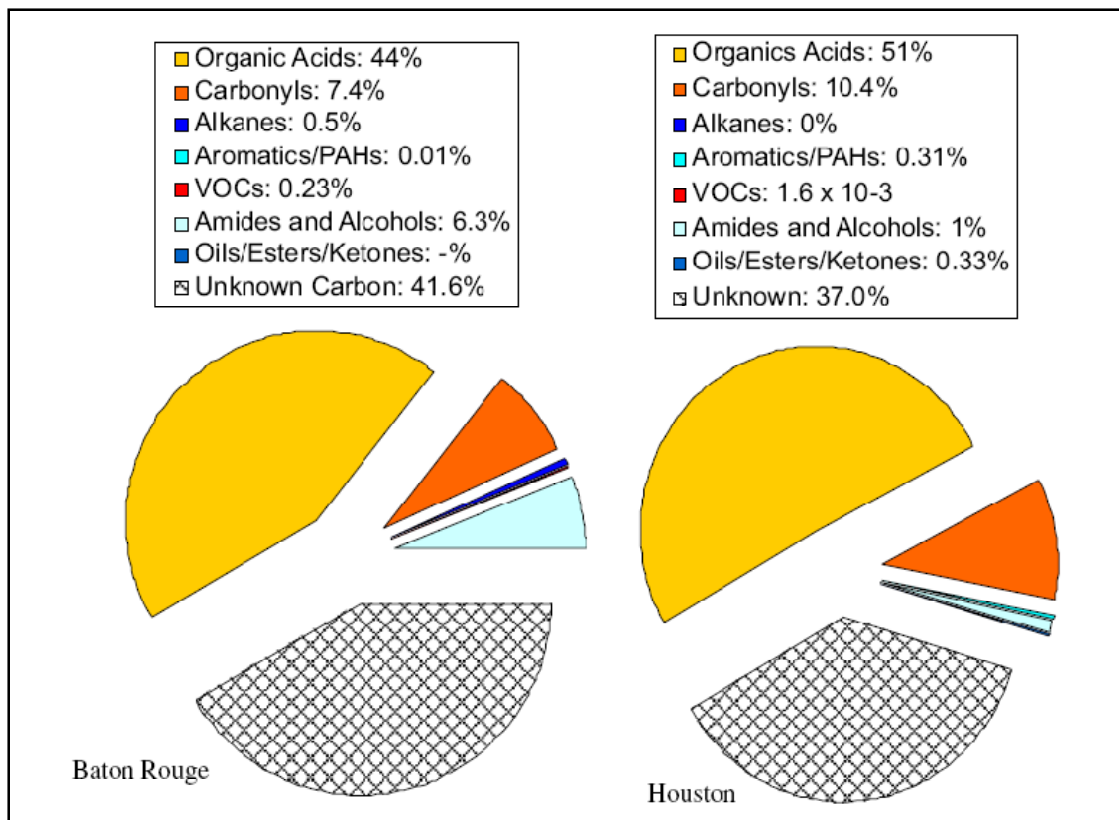


Figure 4: Average contributions of various organic compounds to the dissolved carbon in the fog water (Raja et al., 2007).

A setup consisting of a reactor was used by Benner (Benner et al., 1981) for studying oxidation of water droplets containing soot particles. A similar setup to the one mentioned for Benner’s experiment is used in this research for studying the uptake of naphthalene on the fog droplets that are synthesized artificially inside the reactor. Reactor length determined the

residence and reaction times for the complete process which may be less or more than the actual time taken for the similar process in the atmosphere.

## **2.2 Experiment 2: Photo Oxidation of Naphthalene Within the Fog Condensate in UV Light.**

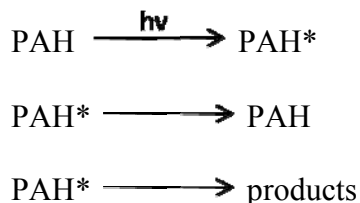
PAHs in air are not only adsorbed by fog droplets, but there also occurs a photo oxidation reaction of these PAHs in presence of naturally available UV light. Products of the reaction can be various depending upon the reaction conditions and catalysts available. The second set of experiments discusses a photo oxidation reaction of naphthalene in the collected fog condensate from experiment 1. This fog condensate also contained NaCl. Reaction products and reaction mechanism were observed to understand the effect of NaCl in a reaction mixture and compared to other work that has been done before. The Following section discusses a previous work carried out by others that provides necessary information about reaction products and mechanism under different reaction conditions. It also discusses different pathways in which the reaction can possibly proceed resulting in the observed products.

A photooxidation reaction is a type of reaction in which light induced oxidation of a reactant takes place due to oxygen or ozone. Products of these reactions may or may not be more toxic compared to the parent reactant. Other terms closely related to photo oxidation reactions are photoexcitation process in which a chemical species loses one or more electrons; photooxygenation process wherein an oxygen atom is retained in the product and photoinitiated oxygenation in which there is no electronic excitation of either the substrate or the oxygen (IUPAC compendium of chemical technology, vol2, 1997). Photocatalytic reactions use photons as catalyst and alter the reaction rates. Photocatalytic reactions have applications in water and sewage treatment.

Organic matter dissolved in water bodies, especially PAHs are known to absorb UV

greatly and undergo photooxidation reactions in the bulk phase. The two types of reactions of PAHs are homogeneous reactions that occur in bulk phases of air or water and heterogeneous reactions that occur at the interfaces. Photoreactions of PAHs occur at a faster rate via heterogeneous process on film surfaces compared to the rates at which they occur in homogeneous process (Streaowski et al., 2003). Photooxidation of PAHs in homogeneous process in a bulk phase of water has been studied. Photoinduced toxicity of some PAHs in aquatic plants and organisms has also been reported (Landrum et al., 1987; Huang et al., 1997).

Polycyclic aromatic hydrocarbons can be degraded in an aqueous medium by different processes of oxidation. PAHs can be oxidized by introducing ozone. In the experiment carried out by Beltran (Beltran et al., 1995), he studied the reaction mechanisms of PAHs anthracene and phenanthrene for 2 different cases namely UV pyrolysis and UV combined with ozone. According to his findings, UV radiation kinetics followed the simplified path given by reactions:



The expressions for the rate of change of PAH concentration were calculated depending on different reaction conditions used. It was also observed as a result of oxidations of PAHs, that if UV radiation is combined with ozone, then the rates of degradation are much faster than UV radiation alone. Therefore, the photodegradations of dissolved PAHs by natural UV light will be higher in the regions where higher ozone flux is available (Beltran et al., 1995).

Fasnacht and Blough (Fasnacht et al., 2003) carried out photodegradation of several PAHs in aqueous medium and gave a reaction pathway for the actual excitations and role of O<sub>2</sub> and OH<sup>-</sup> as explained in figure 5. Figure shows possible combinations of reaction pathways after

excitation of a single PAH molecule where P stands for a PAH molecule and P<sup>+</sup> is the resultant PAH cation radical.

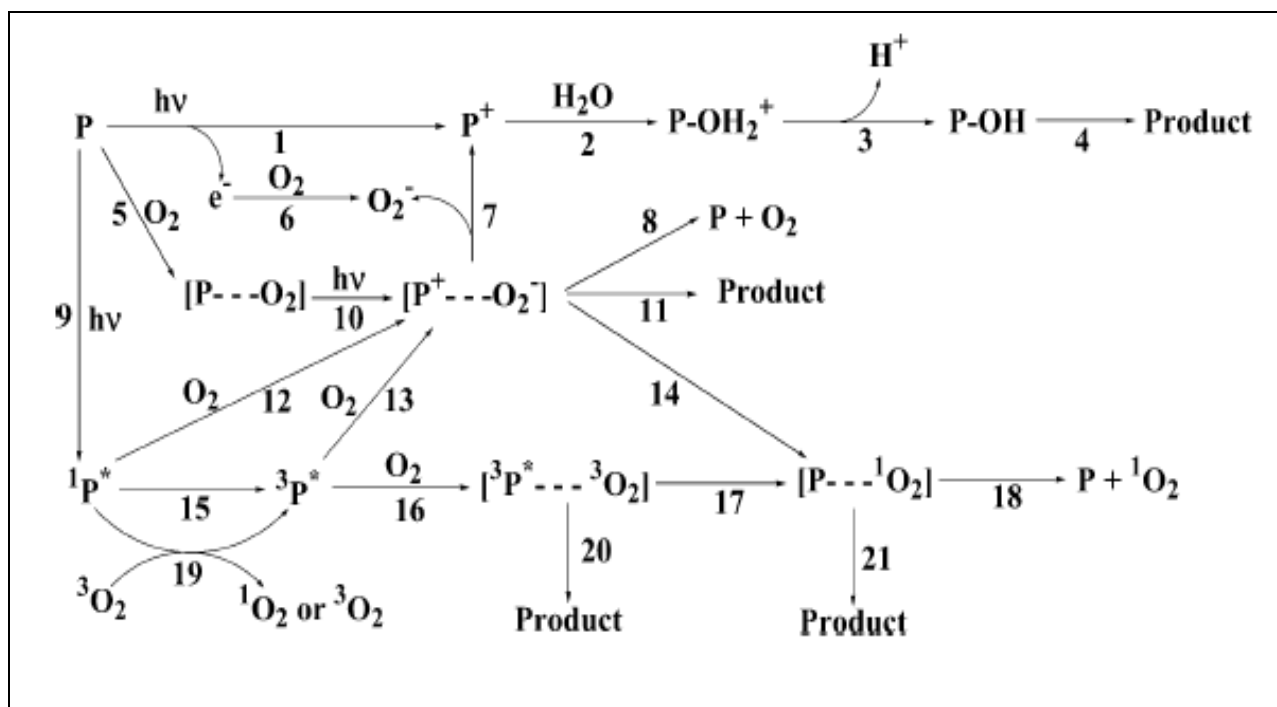


Figure 5: Possible mechanisms of a photoreaction of PAH (Fasnacht et al., 2003)

It has also been studied that, PAHs when dissolved in alkanes, form alkylated PAHs under UV light. The product formation is mainly because of the C-C and C=O/C-OH bonds formed. UV light was the major cause for the reaction to take place. Several products of anthracene and phenanthrene were detected and were produced from energy transfer by excited PAHs (Mahajan et al., 2002). Armstrong carried out a photooxidation of PAHs in sea water and concluded that the rate of photodegradation was very high in sea water as compared to pure water (Armstrong et al., 1966). Photoreactions of benzopyrene, chrysene and fluorine were studied by Miller (Miller et al., 2000). He concluded that UV spectrum and concentration of the PAHs are 2 major factors deciding the degradation rate. For a successful photoreaction, emission spectrum of UV should overlap the absorption spectrum of the main reactant. Reaction rates can also differ depending upon initial concentration of the target reactant. Figure 6 gives the

difference between the rate mechanism of benzopyrene (BAP) and chrysene (CHR) at their different initial concentrations.  $C/C_0\%$  vs. Time graph is plotted in the figure which indicates that at lower initial concentrations of the PAHs, rate of degradation was faster than the rate found at higher initial concentrations.

Photochemistry of organics has not only been studied in aqueous medium but also under different reaction conditions. Photoreactions of organics in water ice and ice-water interface have also been extensively studied. Photooxidation in ice takes place at higher rates than in the bulk air or water. This is because of a higher concentration of hydroxyl radicals available on ice surface (Domine et al., 2008). When photochemistry of monochlorophenols was studied in water ice, the reaction resulted in several different products because of the coupling reactions due to aggregation of monochlorophenol on the grain boundaries. The major products of the reaction were members of phenolic halogenated compounds. Photoreaction of PAHs in ice causes their reduction and leads to the formation of ketones, alcohols and bridging ethers. Ketones generally disturb aromaticity of the parent molecule but alcohols and ethers do not break the ring structure of PAH (Bernstein et al., 1999).

Naphthalene has been used as a PAH in the current study. Researchers have previously focused on the photodegradation of naphthalene and substituted naphthalene in different reaction conditions and with different catalysts. Wasserman (Wasserman et al., 2004) studied photooxidation reactions of methylnaphthalenes with a major reaction product as endoperoxide 1-5. It was observed that methyl substituted naphthalenes were more reactive than unsubstituted naphthalenes. A photolysis of naphthalene carried out on hexane film in absence of air resulted in 30% degradation of naphthalene. Major products of the reaction were 2-carboxybenzaldehyde and 3-phenyl-2-propanal. Experiments for naphthalene photodegradation in ultrapure water supported by  $TiO_2$  catalyst were carried out with the help of high and low pressure mercury

lamps. It was observed as a result of the experiment that a rate of photodegradation of naphthalene was higher for high pressure mercury lamp. The experiment also indicated that 25% to 40% conversion of naphthalene was observed depending on the type of lamp. The reaction did not leave any intermediates after 500 minutes of reaction (Garcia-Martinez et al., 2005).

Photodegradation of naphthalene on water films and bulk water were carried out by Chen (Chen et al., 2007) with a setup in which naphthalene flow was constant. UV lamps were used for photodegradation. The observed kinetics of the photoreaction were indicative of the importance of surface area to volume ratio for heterogeneous reactions as studied in the experiment. Humic acids present in surface water films was also an important factor affecting the rate of photoreactions. In the later experiment by Chen, the effect of surfactants on naphthalene photodegradation was studied with Suwannee River fulvic acid (SRFA). For low SRFA concentration, surface reactions of naphthalene on water were enhanced for thin water films than thicker films.

Different experiments carried out by researchers put some light on the factors that affect reaction rates and explain product formation mechanisms under different reaction conditions. The current research deals with different products of photooxidation reactions of naphthalene in fog condensate. The fog condensate also contained NaCl. From the earlier discussions regarding the factors affecting photodegradations, NaCl was expected to affect the product formation and rate mechanism.

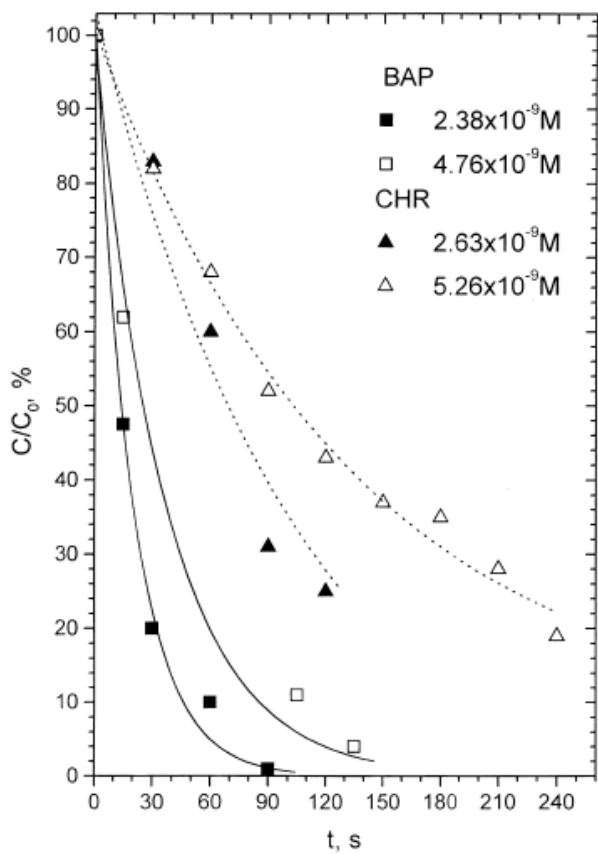


Figure 6:  $C/C_0$  vs. time for benzopyrene and chrysene (Miller et al., 2005)

## CHAPTER 3

### EXPERIMENT 1: UPTAKE OF NAPHTHALENE BY FOG DROPLETS

The scope of this experiment was to study the uptake of polycyclic aromatic hydrocarbon (naphthalene) and a relation between partition coefficients of naphthalene and various reactor temperatures.

#### 3.1 Materials and Methods

##### 3.1.1 Materials and Methods for Sample Preparation

Chemicals were required for the preparation of aerosol solution and titration solutions. Naphthalene was the most essential chemical that was used as a PAH for studying partition coefficients.

Aerosol Solution:

Aerosol solution was a 50% mixture of isopropanol reagent and water v/v. 1.36 grams of NaCl was thoroughly mixed into the solution for production of NaCl aerosols. Isopropanol reagent ( $\geq 98\%$ ) was obtained from Sigma Aldrich. NaCl was obtained from Fluka. All chemicals were used as such without dilution. The aerosol solution was covered properly after its preparation to avoid loss of isopropanol by evaporation. This precaution was essential to preserve the desired concentrations.

Titration chemicals:

Titration experiment required 0.1M  $\text{AgNO}_3$  solution and sodium chromate indicator.

$\text{AgNO}_3$  was ordered from Fluka. Sodium chromate was obtained from Sigma Aldrich. For preparing 0.1M solution of silver nitrate, following calculations were carried out.

$$\text{Molarity} = \frac{\text{moles of solute}}{1000\text{ml of solvent}} \quad (3)$$

For silver nitrate,

$$\frac{\left(\frac{x \text{ grams of silver nitrate}}{169}\right)}{1 \text{ liter of water}} = 0.1 \quad (4)$$

For preparation of 0.1M solution, 16.9 grams of silver nitrate was dissolved in 1 liter of water. 0.02 gram sodium chromate was dissolved in 1 liter of water.

Naphthalene:

Naphthalene ( $\geq 99.9\%$ ) was obtained from Sigma Aldrich. Gaseous naphthalene that was required for the experiment was obtained by passing a stream of compressed air through a packed bed of naphthalene. Packed bed of naphthalene consisted of 0.02g naphthalene per gram support.

Solvents:

Acetonitrile was used as a solvent for HPLC analysis. Acetonitrile ( $\geq 99\%$ ) ordered from Mallinckrodt Chemicals was used as purchased. In the latter part of this experiment as explained in 3.2, naphthalene from exit air was adsorbed on polymer. Acetonitrile was also used to dissolve this adsorbed naphthalene for determination of the naphthalene concentration in the exit air stream.

### 3.1.2 Equipment Specifications and Techniques

Aerosol Generator:

TSI made 3450 Vibrating Orifice Aerosol Generator was used (TSI incorporated, MN, USA) for production of NaCl aerosols. It was operated at a constant liquid feed rate through a vibrating orifice. Motor speed was set at  $0.1 \times 10^{-4}$  cm/s. Flow rate of the aerosol solution was kept at  $3.3 \text{ cm}^3/\text{min}$ .  $35 \text{ }\mu\text{m}$  orifice was used which produced NaCl aerosols ranging from 1 to  $40 \text{ }\mu\text{m}$  particle size. The orifice was made up of stainless steel. A syringe selected was 60 ml (as advised in the manual). A frequency of orifice vibration was set at 80 kHz. Neucleospots were

used as charge neutralizers for aerosols and were ordered from TSI. Weight of the aerosol generator was 20 pounds. The acrylic drying column height was 60 cm.

High Performance Liquid Chromatography (HPLC):

HPLC was used for detection of naphthalene in the samples. Advantages of using HPLC are as follows:

1. Number of steps required for the sample preparation are less than GC/MS
2. Liquid chromatographs can be connected to highly selective fluorescent detectors.
3. Liquid chromatographs can also be connected to UV detectors.

In the experiment, Agilent technologies 1100 series HPLC was used with

- a. Online degasser (model G1379A)
- b. Quaternary pump (model G1311A)
- c. Autosampler (model G1313A)
- d. Column thermostat (model G1316A)
- e. Diode array UV detector (DAD) (model G1315A)
- f. Mass spectrometer (model G1956B)

Ultra Aqueous C18 column having  $0.25\text{m} \times 0.0021\text{m}$  dimensions with  $5\ \mu\text{m}$  particle size was used. The method used for the detection of naphthalene was CHENUD1 for its accurate results.

Method Specifications are as Follows.

Stop time of fluorescence detector was 9 min. Detection wavelength was set at 254 nm. Solvents used were 30% water and 70% acetonitrile. Column flow rate was 0.5 ml/min. Autosampler had a normal injection mode. Injector volume was 25  $\mu\text{L}$ . Spectrum range for DAD was from 190 nm to 400 nm. Column thermostat was set at 30°C. Mobile phase started at 100% 5M Ammonia formate solution having pH 3.0. It was held for 10 minutes and then accelerated to

100% methanol in 60 minutes and was held there for 15 minutes. At this time the flow rate was  $2 \times 10^{-7} \text{ m}^3/\text{min}$ .

Scanning Electron Microscope (SEM):

Joel made 840A SEM was used to detect NaCl aerosols on the tape. The SEM had a variable accelerating voltage of 20,000V and accelerating current of 1 to 10 namp. Magnification range provided by the SEM was 10X to 300000X and maximum resolution was 10nm. Maximum 6 inch sample could be observed under the microscope and 360° complete rotation of the sample was possible.

### **3.2 Experimental Setup**

Figure 7 describes the experimental setup that was used to determine concentrations of naphthalene in fog condensate and exit air. Values of these concentrations at a particular reactor temperature were used to determine a value of partition coefficient of naphthalene. The experiment was repeated for different reactor temperatures.

Reactor:

Reactor was a 162 cm long glass column with an inner diameter of 4.5 cm. It had five inlets and one outlet. NaCl aerosols, water vapor, PAH (naphthalene), compressed air as a carrier gas and the probes for the temperature and relative humidity (RH) meter were introduced into the reactor through the five inlets. The outlet was connected to a heat exchanger. A heating tape was wound around the reactor body to vary its temperature. The reactor had a casing for UV light tubes that was used for photoreactions.

Reactor Inlets:

NaCl Aerosols:

The aerosol generator (figure 8) described in section 3.1.2 was used to produce NaCl aerosols. 1.36 grams of NaCl dissolved in the mixture of 50% isopropanol and water (by

volume) was used as an aerosol solution. Detailed calculation for these quantities is explained in chapter 5. 35 $\mu$ m orifice and 60 ml syringe was selected for the experiment. Aerosol solution was introduced into the aerosol generator using a syringe. NaCl aerosols were produced by means of a vibrating orifice in the aerosol generator.

Aerosols entered the drying column after coming out from the orifice. They were wet and charged after their production. In the drying column, a gentle lift was provided by the lift air supply and wet aerosols from the orifice were dried by an air drag. Charge on aerosols was removed by using charge neutralizers. These neutralizers were attached to the inner walls of the drying column with the scotch tape. These neutralizers are called as nucleospots.

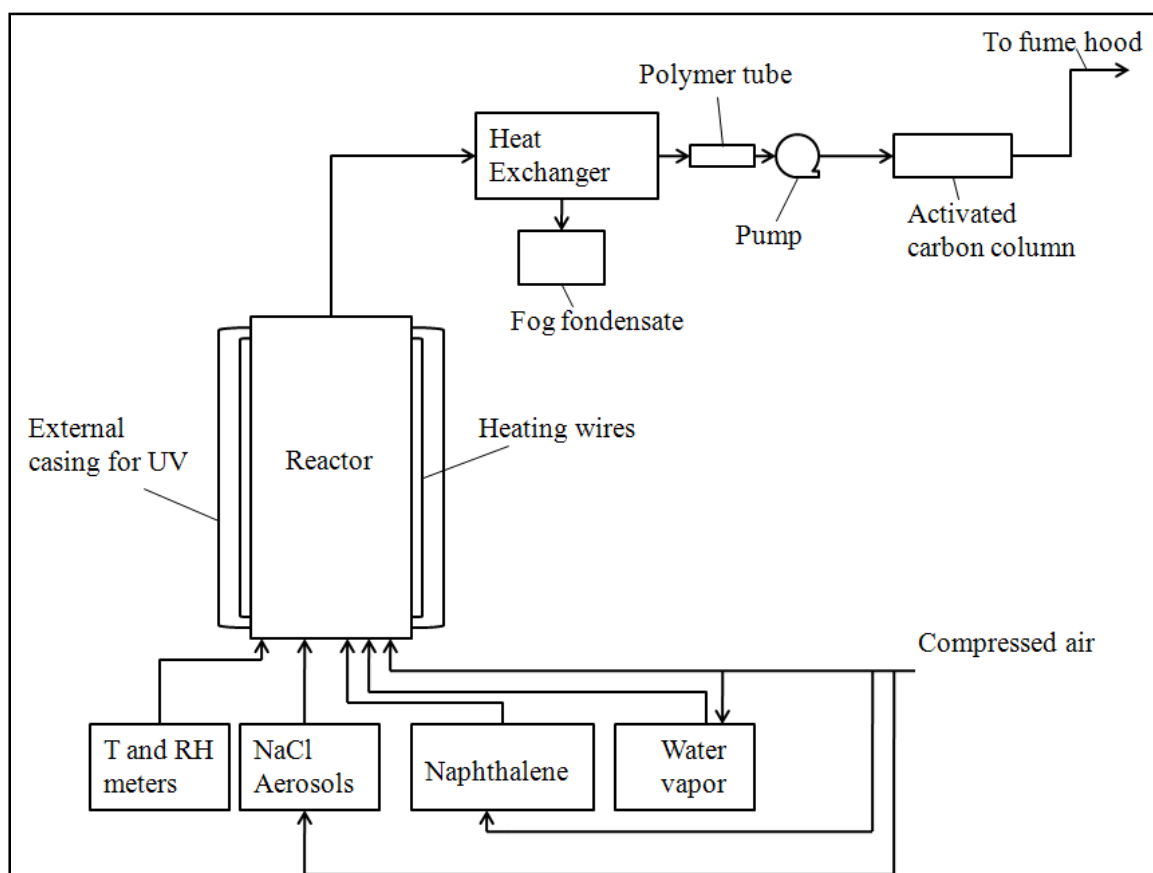


Figure 7: Experimental setup for the partition coefficient experiment

A flexible hose was used to carry NaCl aerosols from the drying column to the reactor.

One end of the flexible hose was connected to the end (top) of the drying column and other end of the flexible hose was connected to one of the inlets of the reactor. It was essential to ensure steady stream of NaCl aerosols from the flexible hose into the reactor. The experiment suggested in aerosol generator manual was performed for verification of an aerosol stream. For the verification experiment, Scotch tape was attached to the end of the flexible hose that was connected to the reactor inlet so that aerosols coming out from the flexible hose would stick to the tape instead of directly entering into the reactor. Then, the syringe was filled with an aerosol solution and fixed to an injection port of the aerosol generator. Syringe motor was started and aerosols were produced continuously. The syringe was refilled three to four times and the solution was introduced into the aerosol generator for production of a considerable number of aerosols.

Aerosol generator was then switched off. The tape attached to the flexible hose was removed and examined under a scanning electron microscope (SEM). Specifications of the SEM are explained in 3.1.2. NaCl aerosols were observed glued to the tape. Above experiment using a scotch tape proved that a stream of aerosols was entering into the reactor. Next step was to make sure that aerosols were reaching the reactor outlet that was at the top of the reactor. Experiment 1 required a humid environment inside the reactor. Therefore, to ensure an uplift of aerosols in the humid environment inside the reactor, a continuous supply of water vapor and a carrier gas was provided. The water vapor was supplied by boiling water. This procedure increased relative humidity of the reactor. A piece of Scotch tape was attached to the outlet of the reactor. Aerosol generator was started and similar procedure as explained earlier was followed. The tape was removed after producing sufficient number of aerosols and was examined under SEM.

#### Water Vapor:

Water was heated to 100°C in a beaker. A small stream of compressed air was passed

through the boiling water and introduced into the reactor through one of the inlets. This process resulted in 82% relative humidity inside the reactor.

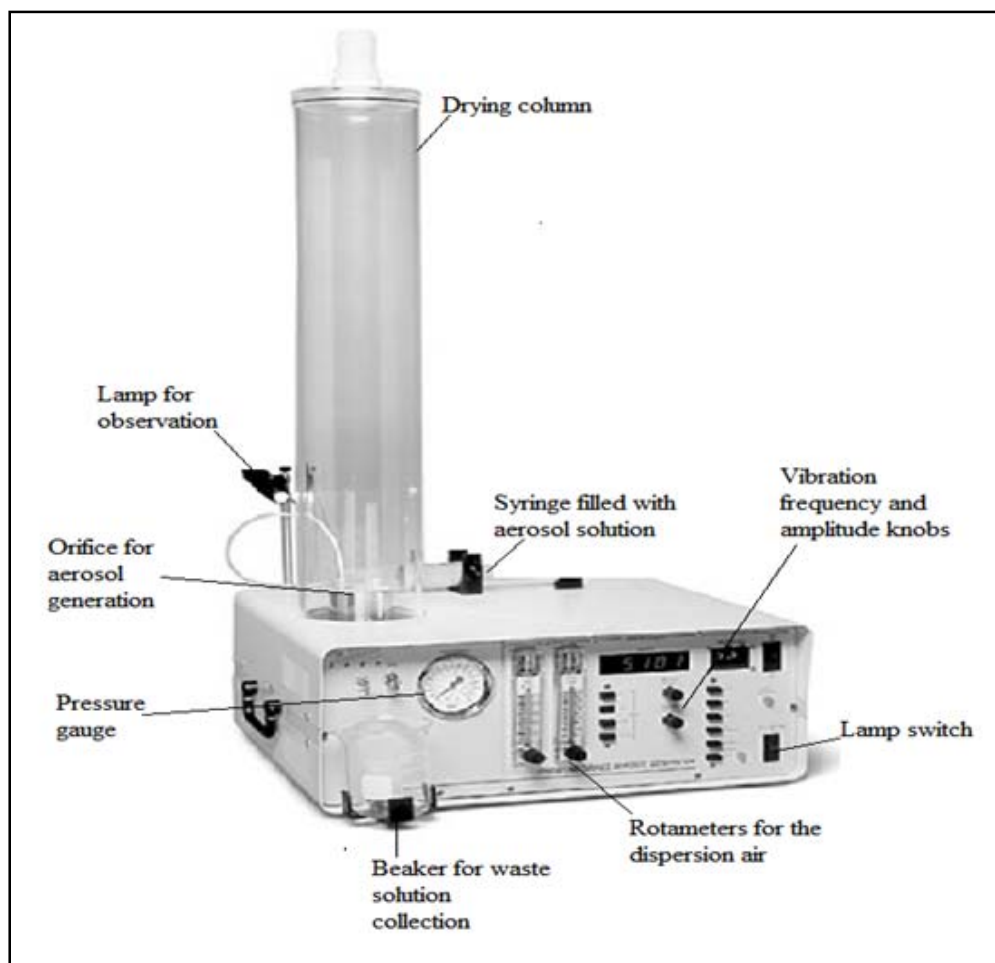


Figure 8: Aerosol generator (Retrieved from [www.TSI.com](http://www.TSI.com))

### Naphthalene:

To prepare a naphthalene source, chromosorb P was mixed with a solution of hexane containing pure naphthalene. Hexane was evaporated later which gave 0.02 grams naphthalene adsorbed per gram of support. 2 stainless steel columns were packed with 15 grams each of this chromosorb P as a naphthalene source. A stream of compressed air was passed through the packed naphthalene column. This stream was then introduced into the reactor through one of the inlets as a naphthalene source. The flow rate of compressed air containing naphthalene was set at

1977 ml/min.

#### Reactor Outlets:

The reactor had one outlet which was connected to a shell and tube heat exchanger. The initial experimental setup consisted of a passive fog collector. A typical fog collector used in a laboratory for fog collection is shown in figure 9. It had a rectangular hollow stainless steel casing within which was a set of parallel plates separated by 2.3 mm fixed at 35° to horizontal. Fog entered through the casing and separated from the carrier gas by impaction on the small gap between the parallel plates. Efficiency of the fog collector was determined to be only 22%. This efficiency was very low and unacceptable for the experiment. To increase the efficiency of fog condensation, a shell and tube heat exchanger was designed. Efficiency of the fog condensation by heat exchanger was determined experimentally and was found to be 86%.

#### The Heat Exchanger:

Figure 10 shows the shell and tube heat exchanger that was used for this experiment. Water was used as a shell side fluid. The shell had one inlet and one outlet for the cooling water. Port A was an inlet and port B was an outlet for the cooling water. The IWAKI made magnetic pump of 3 gpm capacity was used to circulate the cooling water. Inlet temperature of the cooling water was 280 K.

Reactor contents were used as a tube side fluid. The tube had three outlets and one inlet. Reactor contents entered the heat exchanger through port C. Reactor contents were separated as fog condensate and carrier gas after condensation. Fog condensate was collected from ports D and E and a carrier gas was pulled out by a Thomas made light pump of 4 gpm capacity connected after the heat exchanger through port F. A purpose of employing the light pump was to enhance flow of a carrier gas through the activated carbon columns connected to the outlet of the pump. This pump had 2 inlets and one outlet. A tube from the reactor outlet was connected to

one inlet of the pump and another tube whose one end was open to atmosphere was connected to the other inlet of the pump. This arrangement was made to avoid the excessive air pull by the pump from the reactor. The outlet of the pump was connected to activated carbon columns. The purpose of the activated carbon column was to adsorb any naphthalene in the exit air.

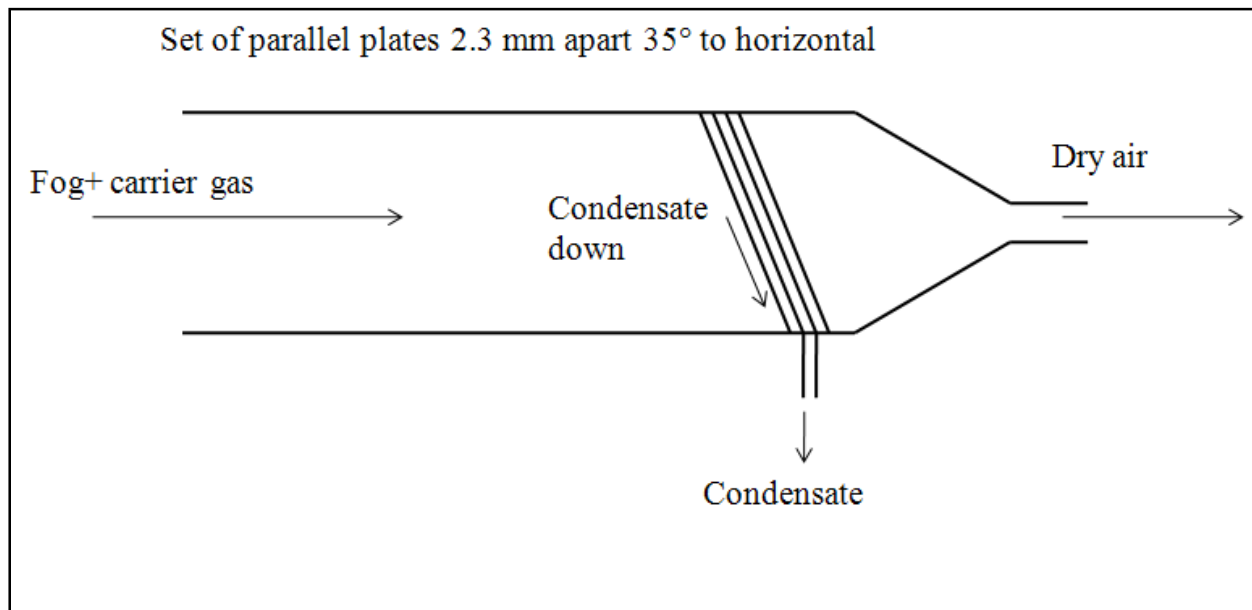


Figure 9: Fog collector

### 3.3 Experimental Procedure

#### 3.3.1 Calculation of the Partition Coefficients

A simultaneous inflow of naphthalene, aerosols, water vapor and the compressed air supply into the reactor was essential for the experiment. Temperature of the reactor was set at 334K. The mixture retained inside the reactor for 62 seconds. During the course of residence time of the mixture within the reactor, surrounding naphthalene was absorbed by the growing aerosols or fog droplets. The reactor contents were then passed through the heat exchanger connected to the outlet of the reactor where fog was condensed and collected.

Collected condensate contained aerosols and naphthalene. To ensure the presence of

sodium chloride in the collected condensate, the condensate was titrated against  $\text{AgNO}_3$  solution using sodium chromate as the titration indicator. A color change from no color to orange was indicative of the presence of chloride ions in the solution.

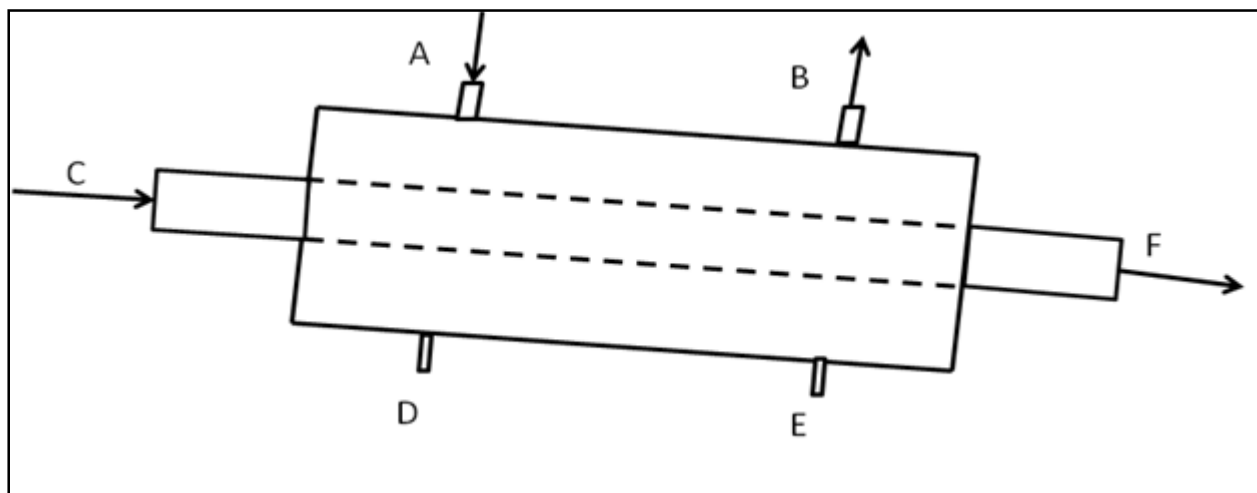


Figure 10: Heat exchanger used for the fog condensation

The concentration of naphthalene in the fog condensate was measured directly by HPLC analysis. For determination of naphthalene concentration in the exit air stream, a polymer tube was inserted in the tube connecting the reactor outlet to the pump inlet. Air stream was passed through the polymer tube and naphthalene in the exit air was adsorbed on the polymer. The tube was removed after 10 minutes and the contents were mixed with 5 ml acetonitrile. Naphthalene that was adsorbed on polymer was dissolved in acetonitrile. Polymer was insoluble in acetonitrile. After 7 to 8 hours of mixing time, 1 ml acetonitrile was removed and analyzed using HPLC.

Calculations for naphthalene concentrations (given in chapter 6) were performed. Values of the concentrations of naphthalene in fog condensate and exit air were obtained and a value of the partition coefficient was calculated using equation (1). The same experiment was repeated for reactor temperatures 346.5K, 361.5K, 371.5K and value of the partition coefficient at each

reactor temperature was calculated. A plot of different reactor temperatures and partition coefficients was obtained.

### 3.3.2 Photo Oxidation Reaction of Naphthalene and Fog Containing NaCl

The next step in experiment 1 after finding the values for partition coefficients was to study photo oxidation of naphthalene in fog containing NaCl as the condensation nuclei. Residence time provided by the reactor was 62 seconds. Reaction time was therefore also 62 seconds. To start the experiment, UV light tubes in the casing surrounding the reactor body were switched ON. The experiment was started exactly the same way as mentioned in section 3.3.1. The collected condensate was examined for the reaction products by using HPLC.

## 3.4 Results and Discussion

### 3.4.1 Results and Discussion for the Naphthalene Uptake Experiment

In the experiment, initially, a verification experiment was carried out in which a tape was attached to the flexible hose and to the reactor outlet as explained in 3.3.1 to ensure a steady stream of aerosols into the reactor. Figure 11 shows a close-up view of the NaCl aerosol obtained as a result when observed under the scanning electron microscope. The equivalent diameter of NaCl aerosols was in the range of 1-10 $\mu\text{m}$ . The specific aerosol shown in the following figure has a diameter close to 4  $\mu\text{m}$ . Figure 11 shows a typical shape of the NaCl aerosols. The NaCl aerosol was distorted cubical in shape. Shape depends on several factors such as diameter of the aerosol, vibration frequency of the orifice and stability of aerosols (Hinds, Aerosol Technology).

The next step was to ensure an uplift of aerosols inside the reactor. Figure 12 below shows an abundance of NaCl aerosols obtained. Careful observation shows presence of a water film around the aerosols. This proved that the aerosols were indeed formed with a water film and it was therefore possible to generate fog droplets within the reactor.

The next step was to ensure an uplift of aerosols inside the reactor. Figure 12 below

shows an abundance of NaCl aerosols obtained. Careful observation shows presence of a water film around the aerosols. This proved that the aerosols were indeed formed with a water film and it was therefore possible to generate fog droplets within the reactor.

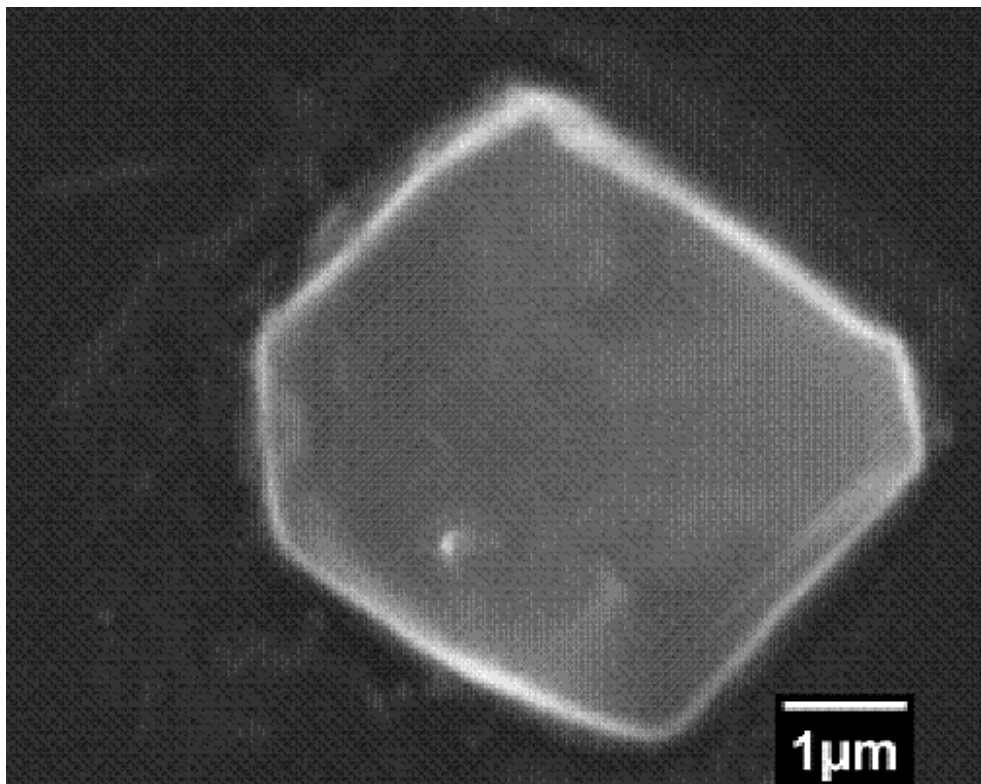


Figure 11: Actual structure of the obtained NaCl aerosol

The next step was to ensure an uplift of aerosols inside the reactor. Figure 12 below shows an abundance of NaCl aerosols obtained. Careful observation shows presence of a water film around the aerosols. This proved that the aerosols were indeed formed with a water film and it was therefore possible to generate fog droplets within the reactor.

The results of experiment 1 demonstrated that fog can be generated in a laboratory using the given setup. The experiment also showed that generated and grown NaCl aerosols which resulted in fog droplets were capable of absorbing gaseous naphthalene.

The partition coefficient of naphthalene was found to increase with the reactor

temperature as expected. Figure 13 shows a plot of  $\ln K_{wa}$  vs  $1/T$  ( $K^{-1}$ ). From the plotted graph, some important conclusions can be drawn.

Van't Hoff's equation can be explained as

$$\ln K_{wa} = \frac{-\Delta H_{obs}}{RT} + \frac{\Delta S_{obs}}{R} \quad (5)$$

Where,  $-\Delta H$  is the enthalpy and  $\Delta S$  is the entropy of the process.  $R$  is the universal gas constant and  $T$  is the temperature.

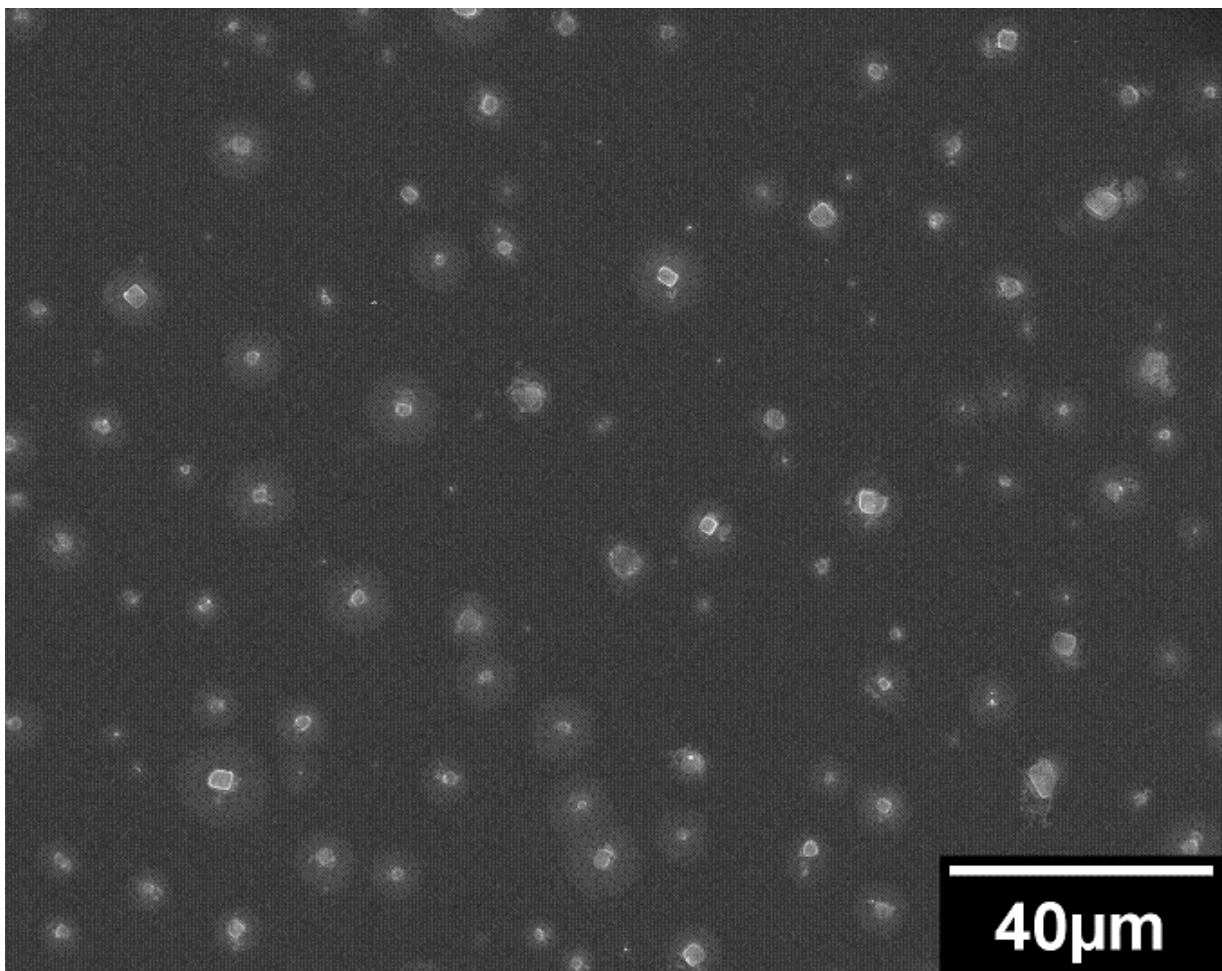


Figure 12: Distribution and abundance of aerosols

Following equation 5 and figure 13, two important values can be calculated. From the plotted graph,

$$\Delta H_{\text{obs}} = -18.44 \text{ kJ/mol}$$

$$\Delta S_{\text{obs}} = -35.45 \text{ J/mol K}$$

The correlation coefficient was 0.987 showing that over the mentioned temperature range, the fit was satisfactory. Both the enthalpy and entropy are negative indicating that the process was exothermic. With the obtained values of  $\Delta H$  and  $\Delta S$ ,  $\Delta G$  can be calculated by the equation

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

$$K_{\text{wa}} = \exp\left(\frac{-\Delta G}{RT}\right) \quad (7)$$

$\Delta G$  has a negative value for a used temperature range. This shows that higher energy was necessary to dissolve naphthalene in the fog droplets as the temperature increased. Therefore, in the actual experiment, observations indicated that a higher percentage of naphthalene was retained in exit air and this percentage increased as the temperature of the reactor was increased. If the above graph was extended to reach 298K, we get  $K_{\text{wa}}$  value for the current experiment as 24.11. This value can be compared to the  $K_{\text{wa}}$  value of pure water for previous experiments carried out by researchers. Alaei (Alaei et al., 1996) calculated  $K_{\text{wa}}$  to be 58 for bulk phase whereas NIST book gives the value of 64. This difference in the value of partition coefficient for pure water and current study was due to the induced salinity because of NaCl presence in the fog condensate. It has been observed that increasing concentration of NaCl decreases a partition coefficient value. A recent study carried out showed that the values of enthalpy and entropy associated with the partitioning process of naphthalene in a thin water film were -22 kJ/mol and -41 J/mol K (Chen et al., 2006). It was also observed that the value of  $K_{\text{wa}}$  increased with the decreasing thickness of the water film. On similar lines, it has been also shown that, there is a considerable increase in  $K_{\text{wa}}$  with decreasing fog droplet diameter (Moore et. al., 2003).

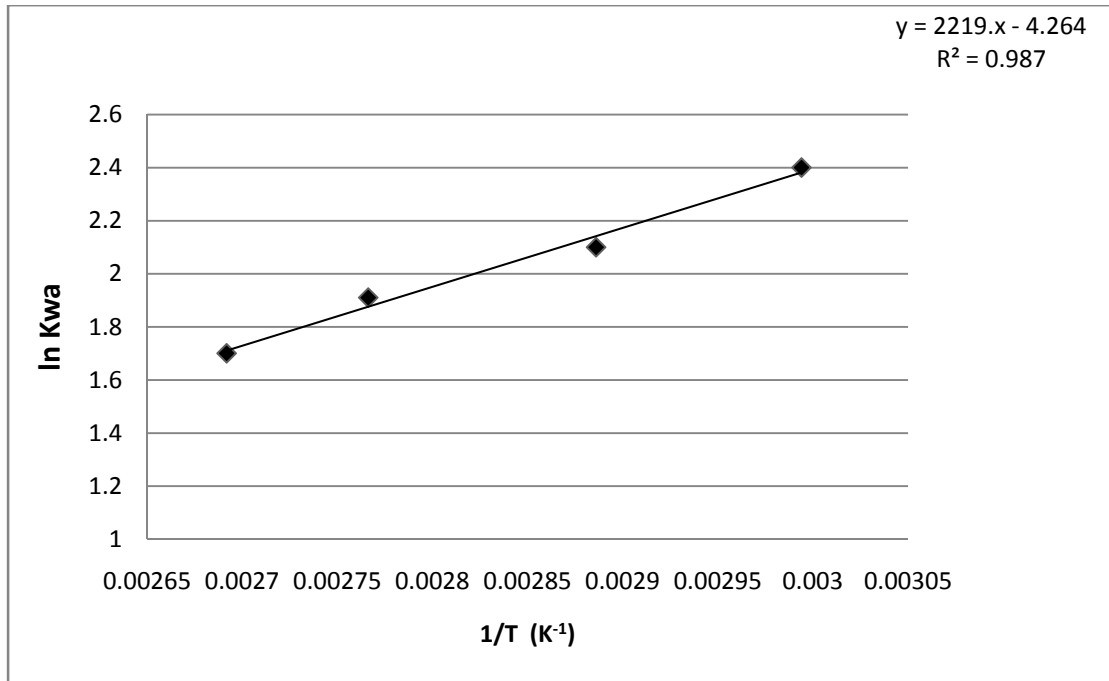
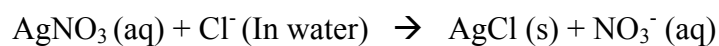


Figure 13:  $\ln K_{wa}$  vs  $1/T$  for naphthalene on fog droplets

$\Delta G$  has a negative value for a used temperature range. This shows that higher energy was necessary to dissolve naphthalene in the fog droplets as the temperature increased. Therefore, in the actual experiment, observations indicated that a higher percentage of naphthalene was retained in exit air and this percentage increased as the temperature of the reactor was increased. If the above graph was extended to reach 298K, we get  $K_{wa}$  value for the current experiment as 24.11. This value can be compared to the  $K_{wa}$  value of pure water for previous experiments carried out by researchers. Alaei (Alaei et al., 1996) calculated  $K_{wa}$  to be 58 for bulk phase whereas NIST book gives the value of 64. This difference in the value of partition coefficient for pure water and current study was due to the induced salinity because of NaCl presence in the fog condensate. It has been observed that increasing concentration of NaCl decreases a partition coefficient value. A recent study carried out showed that the values of enthalpy and entropy associated with the partitioning process of naphthalene in a thin water film were -22 kJ/mol and -41 J/mol K (Chen et al., 2006). It was also observed that the value of  $K_{wa}$  increased with the

decreasing thickness of the water film. On similar lines, it has been also shown that, there is a considerable increase in  $K_{wa}$  with decreasing fog droplet diameter (Moore et. al., 2003).

Titration was performed to verify presence of NaCl in the collected condensate. In the titration experiment, Ag in  $\text{AgNO}_3$  solution reacted with chloride ions to form AgCl solution and in presence of sodium chromate indicator. Color of the solution changed from colorless to light orange. The reaction occurred as per the following equation (The central science, experiment 7, retrieved from [www.earlham.edu](http://www.earlham.edu))



Calculations for determining NaCl concentration in water are detailed in calculations section of this chapter. NaCl concentration was determined from the known quantities such as molarity of  $\text{AgNO}_3$  solution, and volume of condensate and the volume of  $\text{AgNO}_3$  that was required for the reaction. The results showed that average concentration of 2.66 g/l of NaCl was present in the collected fog samples.

#### 3.4.2 Results and Discussion for the Photooxidation Reaction Experiment Inside the Reactor.

After successful completion of partition coefficient experiments, the same experiment was carried out with UV lights on the reactor switched on as explained in 3.3.2. Fog condensate was collected and analyzed on both GC/MS and HPLC. The reaction time was 62 seconds.

GC/MS and HPLC can only be used to detect organics if they are in measurable concentration ranges. Initial analysis did not show any observable reaction products which indicated that the products were present in minute quantities that were not detectable by GC/MS or they were not formed at all. Therefore, possibly, the products were present in minute concentration but were not detectable. One way to detect products was to concentrate them. For concentration of products, an experiment was performed where the products were extracted using hexane. Hexane serves as a better solvent for the organic products than water. A blow

down procedure was carried out for this solution. In this procedure, nitrogen was blown over the extracted hexane solution. Hexane, being more volatile than the products, evaporated progressively and products were concentrated in the residual hexane. These products were further analyzed on GC/MS. Similar procedure was carried out for HPLC using acetonitrile which is a good solvent for HPLC analysis. In both the cases, after concentration of the respective solutions, no product was detected. It was then concluded that there were no products of the reaction for the reaction time of 62 seconds. Therefore, a small reaction time was not enough for the product formation and a possibility of occurrence of the reaction inside the reactor was very rare. Experimental setup for a bulk phase reaction provided an adjustable reaction time. The reaction was carried out in a bulk phase with the UV light setup.

This chapter explained results and discussions related to the first part of the research. The following chapter will explain procedure and results for the second part of the research. Second part of the research was related to the photo oxidation reactions of naphthalene in the collected fog condensate under UV light in a bulk phase of water in the mentioned UV light setup.

## CHAPTER 4

### EXPERIMENT 2: PHOTOOXIDATION OF NAPHTHALENE WITHIN THE FOG CONDENSATE IN A UV LIGHT SETUP

Research experiments of uptake and UV induced photooxidation reactions of polycyclic aromatic hydrocarbons in water have been of major interest to many researchers for years. When water bodies and fog absorb surrounding pollutants that contain PAHs, UV light in the atmosphere oxidizes them in presence of water. This process results in numerous products of the reaction that get dissolved in surrounding water.

In this research, naphthalene was used as the most abundantly found PAH in class of pollutants. Photooxidation of naphthalene within fog condensate in presence of UV light was carried out and the process revealed some major products of the reaction. This chapter focuses on the reaction mechanism and different products that were obtained as a result.

#### 4.1 Materials and Methods

##### 4.1.1 Chemicals

Chemicals required for the experiment included calibration standards and solvents. Benzaldehyde ( $\geq 98.5\%$ ) was obtained from Alfa Aesar. It was used as a calibration standard for GC/MS analysis. For the calibration purpose, benzaldehyde was dissolved in hexane and calibrated for different concentrations. Hexane ( $\geq 98.5\%$ ) was ordered from Sigma Aldrich and used as an exchange solvent for GC/MS analysis. Acetonitrile ( $\geq 99\%$ ) was used as a solvent for the HPLC analysis. It was obtained from Mallinckrodt Chemicals. Phthalide and 1,3-indandione were required as calibration standards for the detected reaction products. Phthalide (98%) and 1,3-indandione ( $\geq 98\%$ ) were ordered from Sigma Aldrich. Helium and Argon were used as carrier gases. These were ordered from Capitol Welders as and when required.

#### 4.1.2 Methods and Techniques

##### Gas Chromatography with Mass Detection (GC/MS):

Agilent 6890N Gas chromatograph was used with a mass detector (5973) and an injector (7683). EPA 8270 method for semivolatiles was used for detection of reaction products. In the method, sample injection volume was 1 $\mu$ l and there were three pre injections and three post injections of the carrier solvent hexane. Agilent 19091S.433 column was used. Column flow was kept at 1 ml/min and pressure was 8.9 psi. Helium was used as a carrier gas with 250°C heater temperature. Injector was in a pulsed splitless mode. Oven temperature was initially held at 70°C for 5 minutes, then ramped to 270°C with 15°C/min and held for 7 minutes. It was then ramped up to 300°C with 15°C/min.

##### UV Light Setup:

UVITRON Intelli-ray 600; UV00000832 was used as the UV light setup for this experiment (UVITRON international, MA, USA). Intensity of the UV light and an exposure time were adjustable. The distance of a sample from the UV lamps was also adjustable. 140V 600 A metal halide lamps were used with 32 mm arc length and horizontal burning position. The lamp had a typical 1000 hours life. The radiation flux was 110W; 315-400nm. Operating temperature was 10 to 40° typical. Maximum 8"×6" curing area was available.

#### 4.2 Experimental Setup

The experiment described in chapter 1 indicated that the reaction time of 62 seconds was insufficient for the photooxidation reaction of naphthalene. So, a bulk phase reaction was carried out using collected fog condensate and a UV light setup in which UV exposure time and hence the reaction time was adjustable.

#### UV Light:

Figure 14 shows the UV light setup used for this experiment. The UV light source generated  $5 \text{ W/m}^2$  energy (photon flux) when set at 50% intensity with 6 inch distance between the samples and the UV light source. The setup was covered with a stainless steel sheet to protect surroundings.

#### Reaction Mixture:

The collected fog condensate from the experiment described in chapter 1 was used as the reaction mixture for this experiment. The reaction mixture did not have provision for a continuous inflow of naphthalene. The reaction ceased when the concentration of naphthalene in the condensate was very low. It was therefore necessary to ensure a considerable concentration of naphthalene in the condensate, essential for completion of the reaction. So, the condensate was enriched in naphthalene by bubbling naphthalene through the condensate for four to five hours.

### **4.3 Experimental Procedure**

The objectives of the experiment were as follows:

1. To find products of UV photo oxidation reaction of naphthalene in saline fog condensate.
2. To calculate a reaction rate constant for naphthalene degradation.
3. To observe concentration-time data for the major product formation.
4. To calculate a reaction rate constant for naphthalene degradation using a reaction mixture not containing NaCl and compare it with the results obtained in 2.

Five vials of 4 ml volume each were filled with the processed and condensate enriched with naphthalene and containing NaCl. All the vials were tightly closed and placed parallel to each other under the UV light. Placing the vials horizontally and parallel provided same surface area for the reaction to the contents in all five vials. The UV light was started and UV intensity

was adjusted to 10% of the actual intensity. A simplified arrangement is shown in figure 15. One vial was removed from the apparatus after every hour. The vial which was removed first had a lowest exposure time of one hour and last vial removed from the apparatus had an exposure time of five hours. Contents in each vial were analyzed on GC-MS and HPLC. HPLC was used because it can detect minute concentrations of the products and GC/MS was used for the direct identification of the products through a library search.



Figure 14: Intelli-ray 600 UV light setup (Taken from [uvitroninternational.com](http://uvitroninternational.com))

After the analysis of the reaction mixture in all five vials, additional verification experiments were performed to ensure that the products observed in analyses were the actual reaction products and not introduced from impure solvents. For these verification experiments, acetonitrile and hexane were analyzed separately in their pure forms on HPLC and GC respectively. Also, the products that were observed in the reaction were ordered from chemical

suppliers and analysis of the pure purchased chemicals was carried out to match their retention time with that of the observed products.

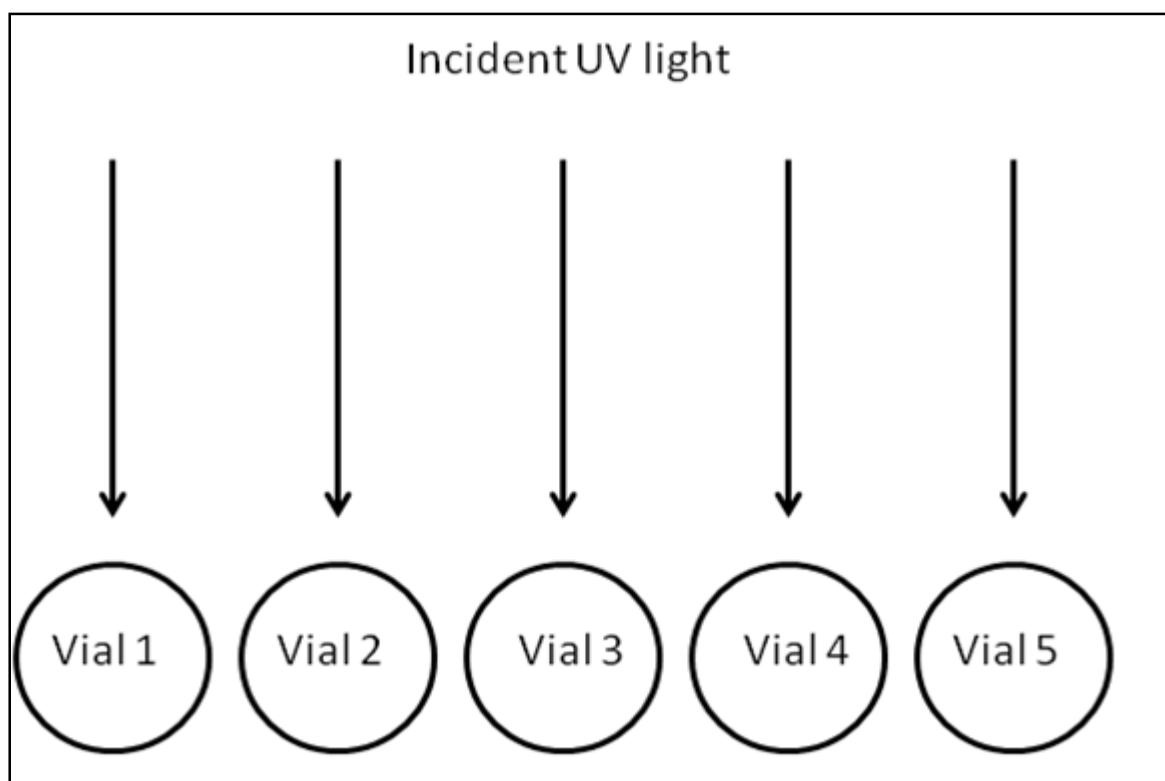


Figure 15: Arrangement of vials under UV light (Front view)

It was also important to observe difference in product formation by photo oxidation reaction of naphthalene in a fog condensate containing NaCl and in a fog condensate without NaCl. Another experiment was carried out with the reaction mixture containing water and naphthalene without any NaCl. For preparing this reaction mixture, naphthalene was bubbled through a condensed water vapor until its concentration reached 26 mg/l. This was used as a reaction mixture and placed in the UV light apparatus in vials as mentioned earlier. Each vial was removed after every one hour and decrease in naphthalene concentration was observed on GC. Also, products of the reaction were studied by HPLC and GC/MS analysis.

## 4.4 Results and Discussion

The reaction mixture consisted of naphthalene, water and sodium chloride. Photo oxidation reaction of naphthalene occurred in presence of an ultraviolet light. Presence of NaCl resulted in formation of different reaction products than those which were generally observed as a result of photo oxidation reaction of naphthalene with water not containing NaCl.

### 4.4.1 Analysis of a Product Formation Using the Reaction Mixture Containing NaCl.

The analysis of the reaction mixture in vials placed in the UV light setup was carried out using GC/MS and HPLC as mentioned in the procedural section 4.3. Benzaldehyde was detected as the major product of the reaction on GC/MS. HPLC was used to detect other products present in minute concentrations. The major product found using HPLC analysis was phthalide. Figure 16 shows the spectrum of GC/MS having both naphthalene and benzaldehyde. Naphthalene was seen at 10.4 minutes on and benzaldehyde peak was seen at 5.6 minutes. From the earlier work, benzaldehyde was never detected as the product of a photo oxidation reaction of naphthalene with pure water that did not contain NaCl.

From the work done by Chen (Chen et al., 2006), the main products of the reaction observed were coumarin, phthalide, 1,3-indandione and 1-naphthol. As explained by McConkey (McConkey et al., 2001), photooxidation of naphthalene in aqueous solution induced by natural sunlight revealed 11 major products and 40 minor products when analyzed on HPLC. Major products included 1-naphthol, coumarin, isobenzofuranone, 1,2-naphthoquinone. Apart from the photo oxidation of naphthalene in aqueous medium, other environmental conditions such as a photooxidation reaction of naphthalene in presence of titanium peroxide and hydrogen fluoride resulted in the similar products (Das et al., 1994). Studies related to products of naphthalene metabolism were carried out by Tingle, Wilson and other researchers (Tingle et al., 1993; Wilson et al., 1996). When the products of naphthalene in aqueous environments were compared to the

naphthalene metabolism products, they were found to be similar. As compared to all these products obtained in previous work, benzaldehyde was a new product. It was therefore suggested that presence of NaCl in the reaction mixture changed the reaction mechanism and the product formation.

A trace of HPLC analysis shown in figure 17 illustrates presence of phthalide as a major product of the reaction. Phthalide was the only product detected with HPLC analysis in a considerable concentration and matched with the earlier work done with water not containing NaCl. Figure shows the analysis of the reaction mixture on HPLC after 4 hours of reaction time. Phthalide presence was confirmed by matching the UV spectra and retention time of pure phthalide dissolved in acetonitrile. Retention time was matched with a tolerance of 0.1 minutes. Formation of 1,4-naphthalene endoperoxide could be the main cause for formation of phthalide with (2,4) photocycloaddition of oxygen as an intermediate for the reaction as explained by McConkey (McConkey et al., 2001).

The main focus of experiment 2 was to observe and study the decrease in concentration of the naphthalene and increase in concentration of benzaldehyde that was a reaction product with the reaction time of 5 hours. The aim of experiment 2 was to also calculate the reaction rate of naphthalene degradation from the available concentration-time data.

Figure 18 shows decrease in concentration of naphthalene (C<sub>n</sub>) with increasing time. The initial concentration was 26 mg/l. After 5 hours, 4.2 mg/l concentration of naphthalene was observed. For calculation of an overall reaction rate constant of naphthalene, order of the reaction was determined first. As explained in by Fogler (Fogler H. S., elements of Chemical Reaction Engineering, 3<sup>rd</sup> Ed.), verification of order of the reaction was done by plotting various graphs. The result showed that it was a first order reaction. The equation for finding reaction rate constant for first order reaction is

$$\ln\left(\frac{C_{no}}{C_n}\right) = k.t \quad (8)$$

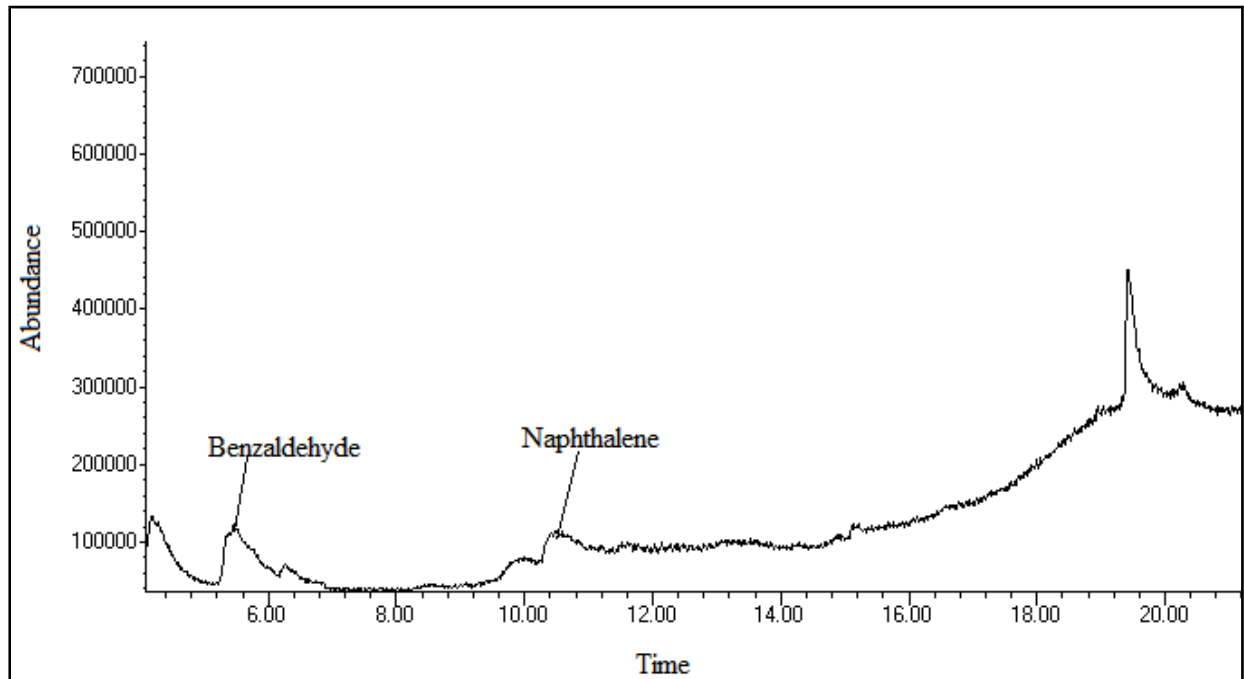


Figure 16: Spectrum of the reaction products of the photo oxidation reaction of naphthalene with fog water consisting of NaCl.

Figure 19 shows the graph that was obtained by plotting  $\ln(C_{no}/C_n)$  vs. time for the reaction, where  $C_{no}$  is the initial concentration of naphthalene. A linear fit was a very close match to the data points plotted with the correlation coefficient 0.977. The nature of the plot was indicative of the first order of the reaction (Foger, Elements of chemical reaction engineering; O. Levenspiel, Chemical reaction engineering).

With appropriate calculations (explained later in section 3.6 of this chapter), rate constant “k” for the overall reaction was found to be  $5.75 \times 10^{-3}$  /min. This value of the reaction rate constant was higher than the value obtained by Chen (Chen et al., 2006) that was of the order of  $10^{-4}$ . As discussed in the paper, reaction rate constant for different water film thicknesses was different. Naphthalene degradation rate constant was found to increase with decreasing film thickness. This was indicative of increase in the reaction rate value with increasing surface to

volume ratio.

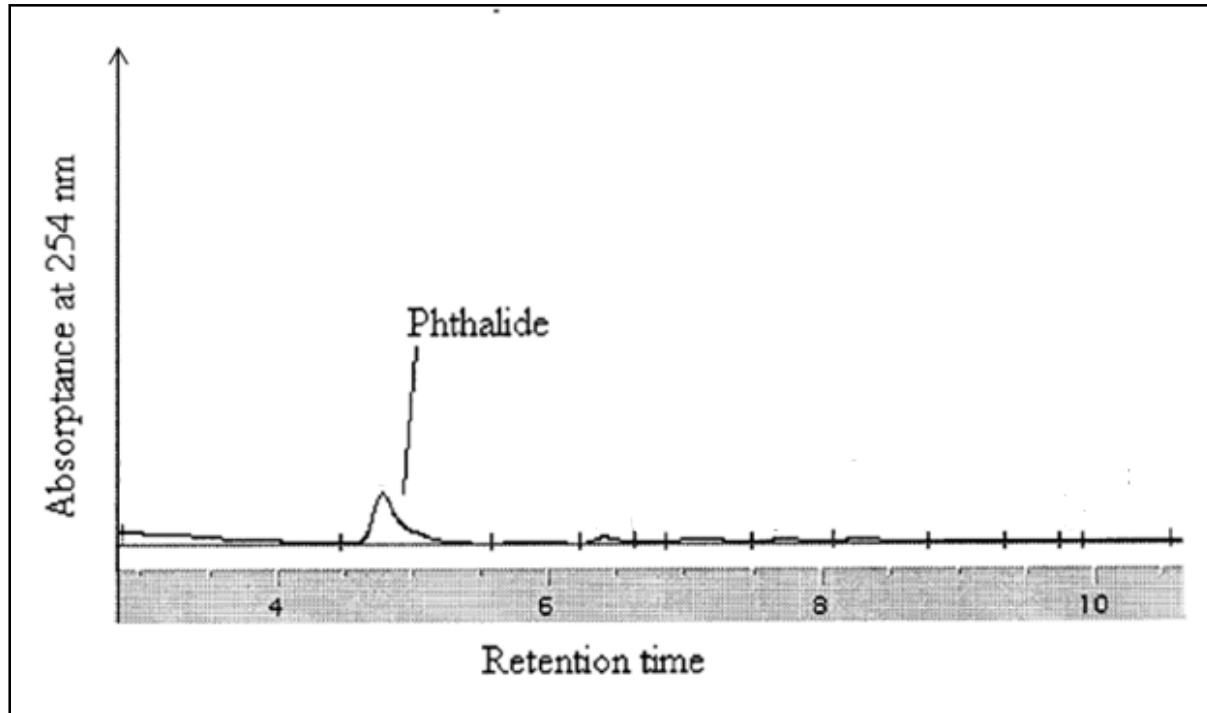


Figure 17: HPLC trace showing phthalide peak at the retention time of 4.743 seconds. Absorbance at 254 nm.

A similar approach can be put forth for a droplet reaction. The current photooxidation experiment was performed in a bulk phase of water. If photooxidation reaction of naphthalene was carried out within fog droplets, there could be the similar rate constant values. It could therefore be assumed that, if this reaction was carried out with the setup of experiment 1, and 5 hours of reaction time was provided, then the reaction rate constant would increase with decreasing droplet diameter depending on the concentration of naphthalene adsorbed on fog droplets.

Benzaldehyde was seen as a major reaction product with GC/MS analysis. Figure 20 gives an increase in benzaldehyde concentration with increasing time. From the available data, it was observed that benzaldehyde formation started between 2 to 3 hours. In the shape of the

curve, it can be seen that benzaldehyde formation was a first order reaction as explained by Fogler.

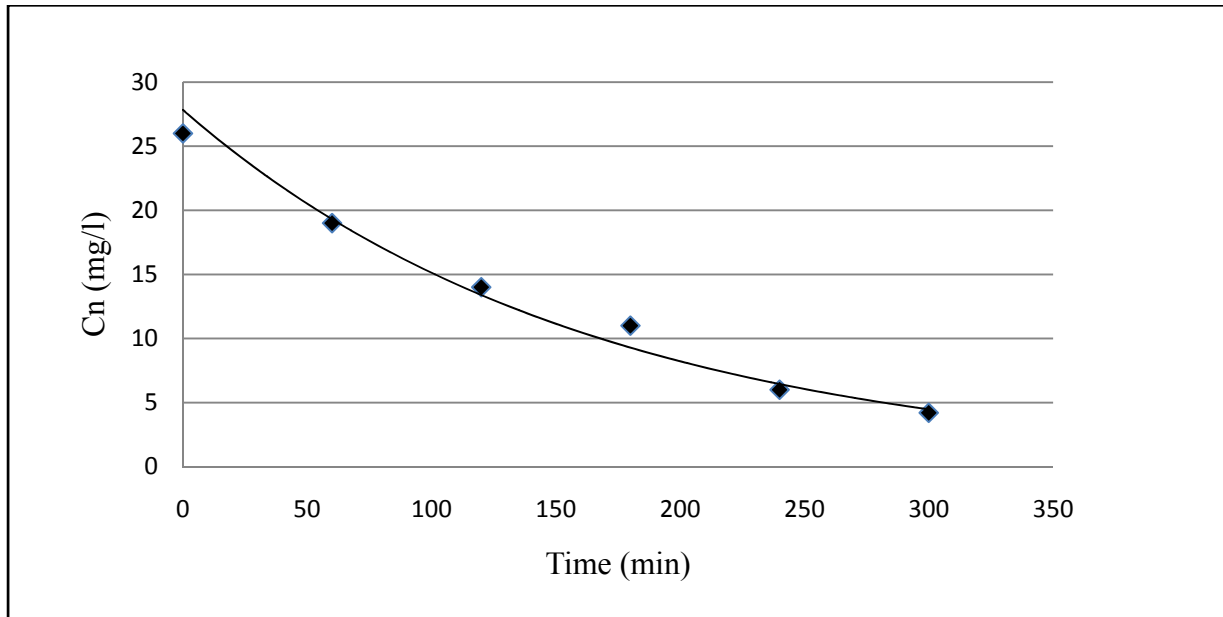


Figure 18: Concentration vs. time curve for decrease in naphthalene

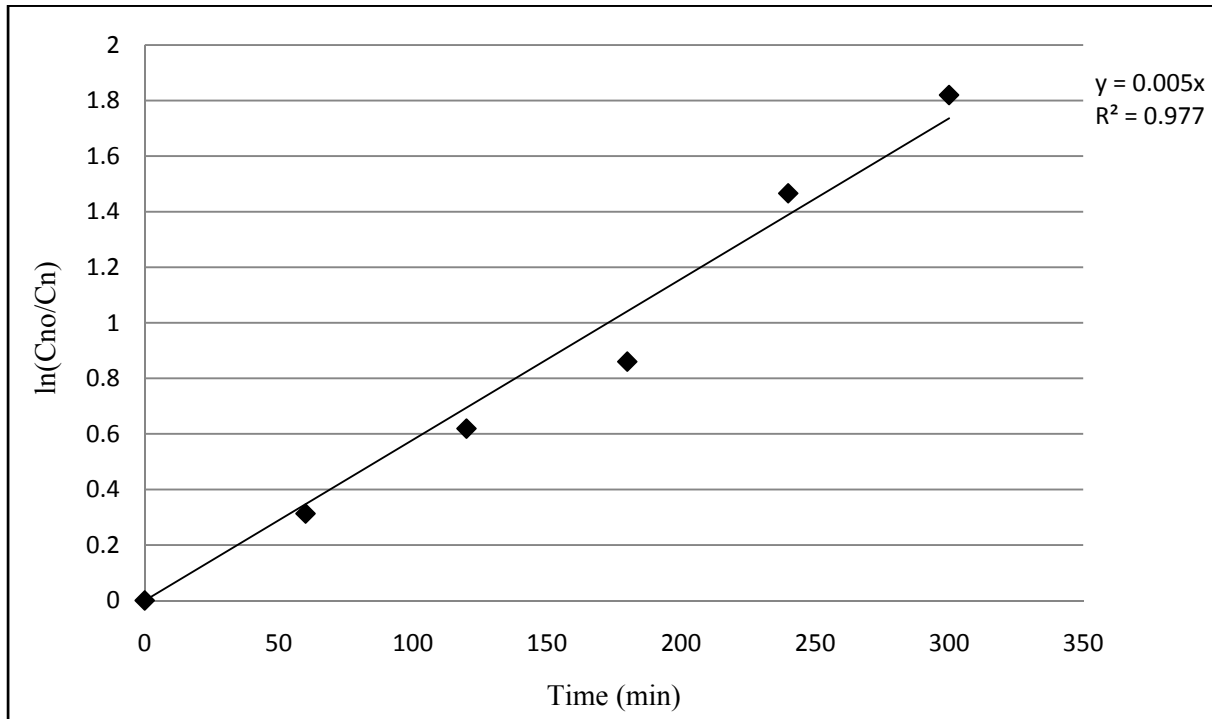


Figure 19:  $\ln(C_{no}/C_n)$  vs. time for naphthalene

Benzaldehyde has been observed as an intermediate during the photo degradation of naphthalene in previous work. In the research done by Guillard (Guillard et al., 1992) an experiment was carried out which focused on reaction products of a phototransformation of naphthalene adsorbed on  $\text{TiO}_2$ . This experiment resulted in 2 major products phthalic anhydride and benzoic acid. The intermediates for this reaction included 1,4-naphthoquinone and benzaldehyde. Benzaldehyde was an intermediate for benzoic acid formation. Similar products of the reaction were also observed from the adsorption of naphthalene on fly ash and ferric oxide in the same research, but with lesser concentrations. A similar work was also carried out by Fox (Fox et al., 1983). For substituted naphthalene and the results of the experiment of naphthalene oxidation showed presence of benzaldehyde. These studies have proved that benzaldehyde can be a product of naphthalene degradation. In the present research, benzaldehyde was observed under different reaction conditions than those used by Guillard and Fox. Reaction conditions can affect the overall reaction.

A study carried out by Armstrong (Armstrong et al., 1966) sheds some light on the rate constant for sea water oxidation of the dissolved organic matter. From his work, organic matter followed first order kinetics for carbon and rate constant for the degradation of the organic carbon was about 0.05/min. The present experiment had a major role of NaCl concentration in the reaction mixture. Similar to sea water reactions, NaCl may have altered the reaction rate and product formation in a photooxidation reaction of naphthalene in the current research.

A study carried out by Armstrong (Armstrong et al., 1966) sheds some light on the rate constant for sea water oxidation of the dissolved organic matter. From his work, organic matter followed first order kinetics for carbon and rate constant for the degradation of the organic carbon was about 0.05/min. The present experiment had a major role of NaCl concentration in

the reaction mixture. Similar to sea water reactions, NaCl may have altered the reaction rate and product formation in a photooxidation reaction of naphthalene in the current research.

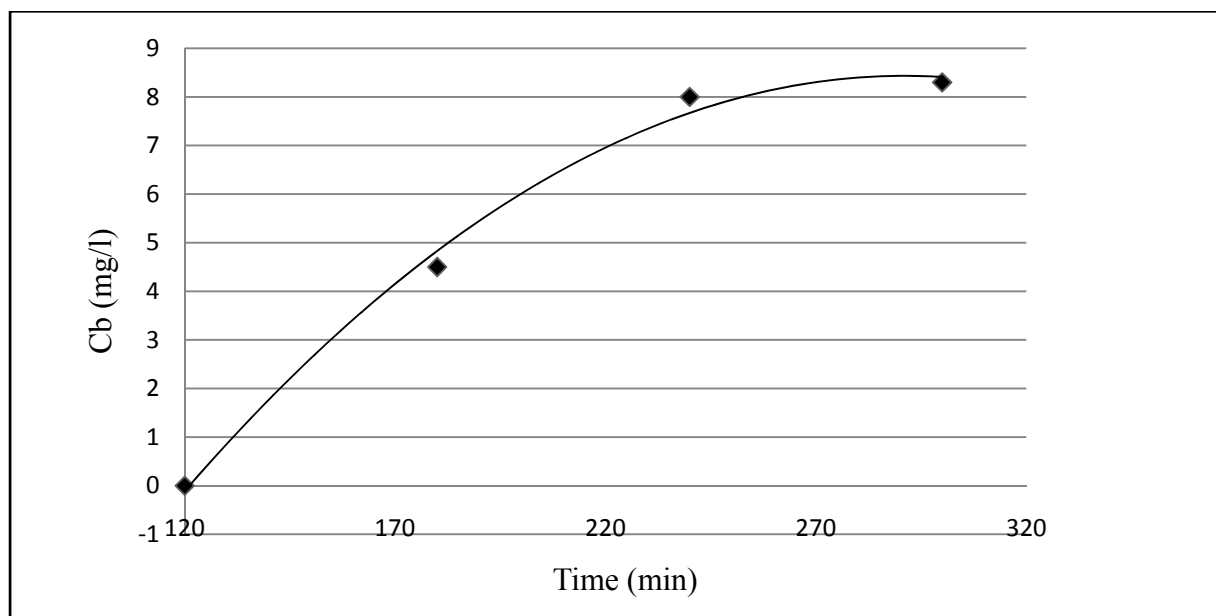


Figure 20: Increase in benzaldehyde concentration with time.

#### 4.4.2 Analysis of a Product Formation from the Reaction Mixture not Containing NaCl

A verification experiment as explained in 4.3 was carried out to ensure that there was no presence of benzaldehyde as one of the reaction products of naphthalene photooxidation within condensate not containing NaCl. This experiment was also performed to ensure that the reaction was giving all similar products that were observed in earlier studies. Figure 21 shows a GC/MS spectrum for analysis of the reaction mixture after 4 hours of reaction time. From the figure, it can be seen that there was no presence of benzaldehyde as a product of the reaction. Naphthalene peak is seen at 10.4 minutes. This result matches with other studies done with pure water as explained earlier in this section.

Identification of other products which were in small concentrations and undetectable on GC/MS was necessary. HPLC was used to detect those products. 1, 3- indandione and phthalide were observed as the major reaction products. They were confirmed by matching their respective

UV spectra and retention times to pure standards for HPLC. These were some of the products obtained in similar reactions in earlier research works. However, other products like naphthoquinones and naphthols were not observed on HPLC in the current experiment. They were either not present or were present in undetectably small concentrations. Figure 22 shows HPLC trace for the reaction products. 1,3-indandione can be seen at retention time of 3.754 minutes. Phthalide was observed at 4.451 minutes.

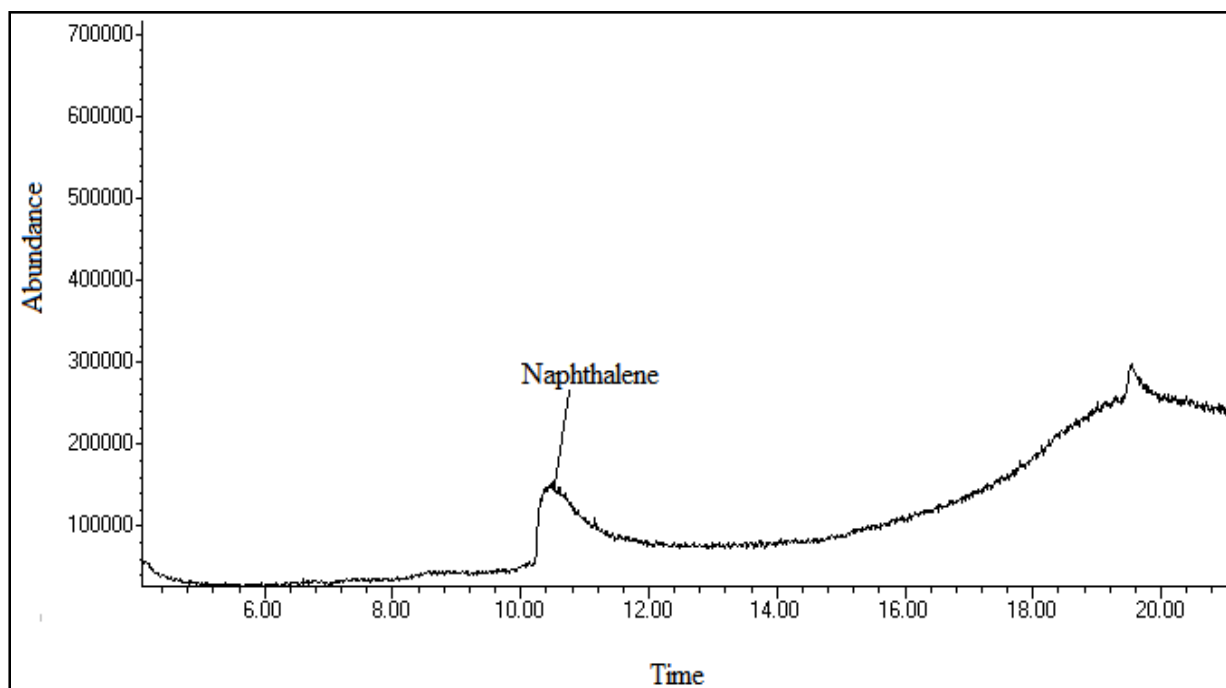


Figure 21: GC/MS trace for products of photooxidation of naphthalene in water without NaCl.

Decrease in concentration of naphthalene was also studied for this experiment with the obtained data. Figure 23 shows decrease in naphthalene concentration with time. The curve is similar to the one shown in figure 18. Fogler (Fogler, Elements of chemical reaction engineering) gives an explanation for nature of a curve and related reaction order. It was concluded by a data fit that it was a first order reaction. Chen (Chen et al., 2006) had concluded that similar reaction conditions resulted in a first order reaction of naphthalene. For the first order reaction, plot of  $\ln(C_{no}/C_n)$  vs. time was obtained as directed by Fogler to calculate the reaction rate constant.

Figure 24 shows the nature of this plot. A straight line passing through origin (0, 0) was obtained. With the similar calculations as explained above, the reaction rate constant for an overall reaction was observed to be  $1.47 \times 10^{-3}$  /min.

From the observed value of the reaction rate constant for photooxidation of naphthalene not containing NaCl it was evident that NaCl altered the overall rate of reaction. In the presence of NaCl, the reaction rate constant was higher than the one obtained in absence of NaCl.

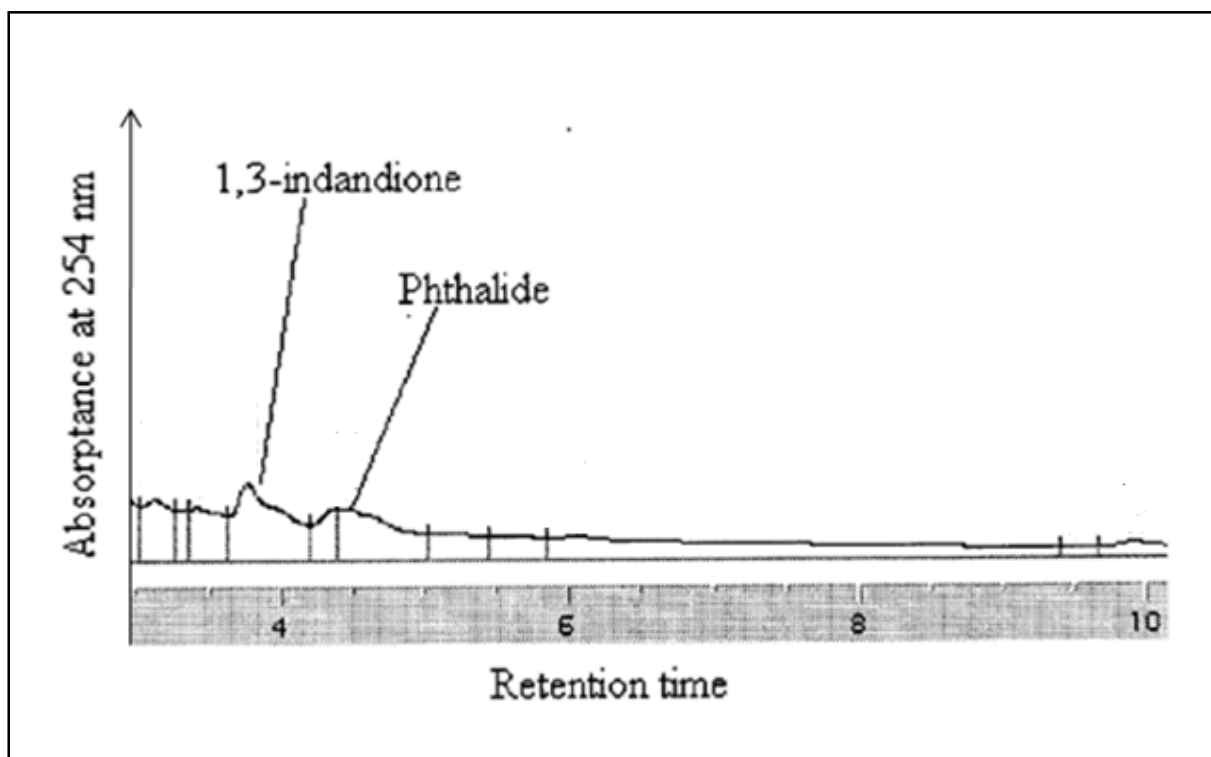


Figure 22: HPLC trace for products of photooxidation of naphthalene within water without NaCl.

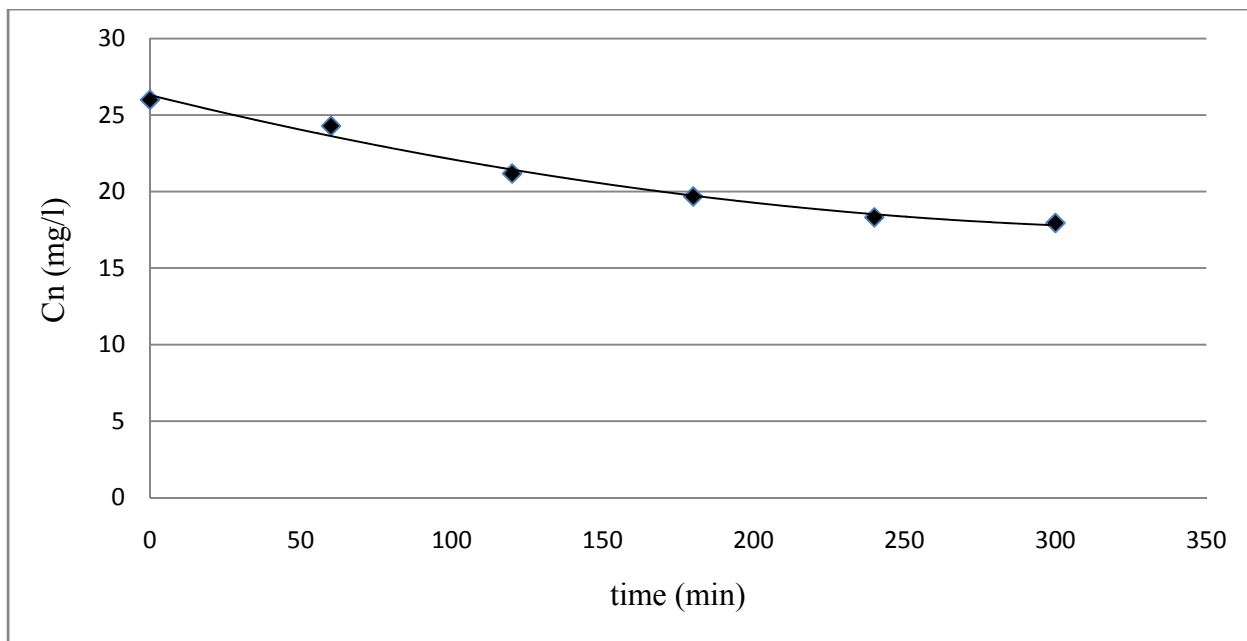


Figure 23: Graph for decrease in naphthalene concentration with time for photooxidation in water without NaCl.

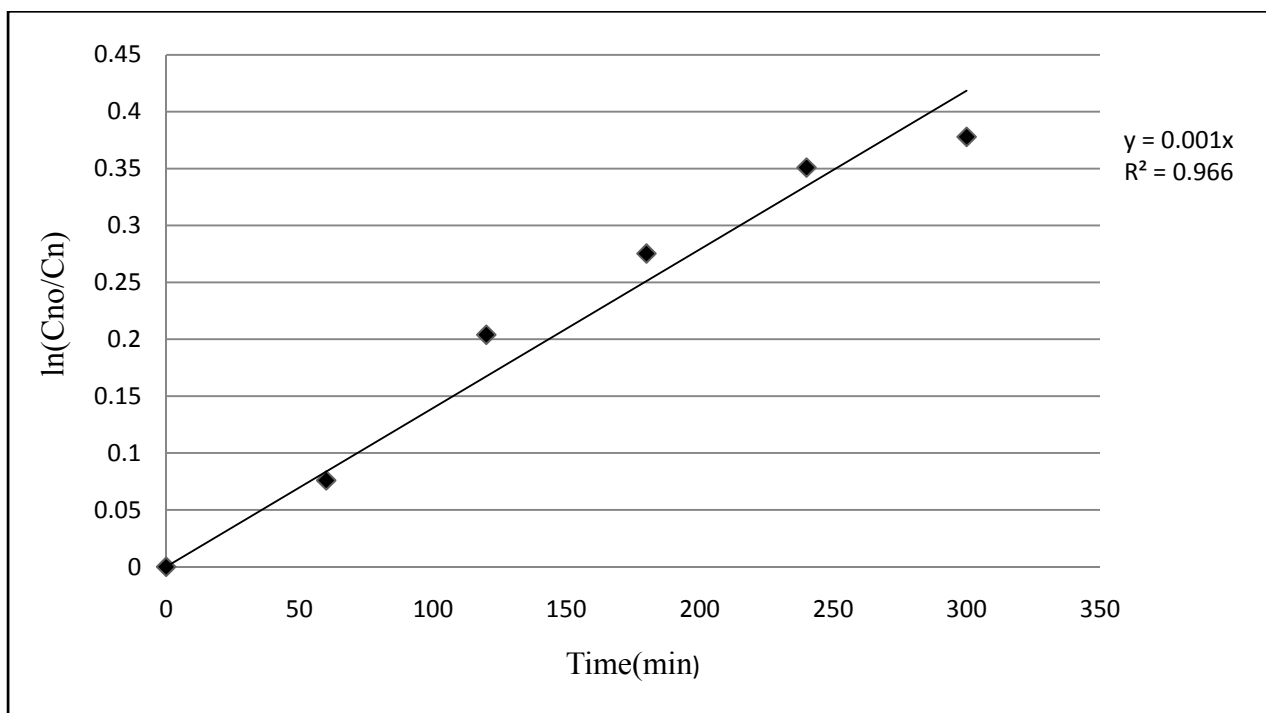


Figure 24:  $\ln(C_{no}/C_n)$  vs. time for naphthalene.

## CHAPTER 5

### CALCULATIONS

#### 5.1 Calculations for the First Experiment Explained in Chapter 3

##### 5.1.1 Calculation for the Amount of NaCl Required for the Aerosol Solution

NaCl aerosols were used in the experiment as condensation nuclei for fog droplet formation. The aerosol solution for production of NaCl aerosols consisted of 50% isopropanol and water by volume and 1.36 grams of pure NaCl crystals. The calculation of NaCl quantity is as follows, referred from the aerosol generator manual.

The desired size of the dry NaCl aerosol was 3.5 $\mu$ m. The diameter of the wet aerosols coming out from the orifice was 40  $\mu$ m (from the values mentioned in the table in the manual)

$$(C+I) = \left(\frac{D_p}{D_d}\right)^3 \quad (\text{retrieved from the aerosol generator manual}) \quad (8)$$

Where  $D_d$  is the droplet diameter of the wet aerosol coming out from the orifice,  $D_p$  is the aerosol particle diameter. C is the solute concentration of the NaCl and I is the impurity concentration.

$$(C + I) = \left(\frac{3.5}{40}\right)^3 = 0.00067$$

Considering the impurity was 0.00004.

$$C = 0.00064$$

For the calculation of the solute( NaCl ) needed, since measuring the volume of the solid is difficult, the volume was converted to weight using the dry density of NaCl which was 2.164 g/cm<sup>3</sup>

So, the final equation for the calculation of the solute quantity took the form:

$$\frac{0.00064 \text{ cm}^3 \text{ NaCl}}{1 \text{ cm}^3 \text{ solvent}} \times \frac{2.165 \text{ g NaCl}}{1 \text{ cm}^3 \text{ NaCl}} = \frac{0.00136 \text{ g NaCl}}{1 \text{ cm}^3 \text{ solvent}}$$

Therefore, 1.36 grams of NaCl was mixed in 1 liter of the solvent.

### 5.1.2 Calculation of Naphthalene Concentration from HPLC Data

HPLC was used in the experiment to determine concentrations of naphthalene in fog condensate and exit air. HPLC gives a peak for different analyzed compounds to represent their absorption. It was therefore essential to calculate actual concentration of naphthalene from the area under a peak provided by HPLC analysis.

The following section explains example calculations are the concentrations at a particular reactor temperature. Similar calculations were carried out for different reactor temperatures.

Using the definition of partition coefficient explained by equation (1) in section 2.1.3, calculations were first performed for obtaining actual concentration values and then calculating partition coefficient.

After obtaining values for area under the peak for naphthalene both in air and collected condensate from HPLC analysis, following calculation was performed.

Fixed values:

$F_n$  = Flow rate of carrier gas containing naphthalene = 1977 ml/min = 1.977 l/min

$T_a$  = Exposure time of polymer tube to air stream = 10 min

$C_s$  = Stability constant for naphthalene = 3.565

$T_w$  = Exposure time for fog and naphthalene = 62 seconds = 1.01 min

Velocity of carrier gas/reactor length =  $255.32/162 = 1.01$  min = 62 seconds

$V_g$  = volume of acetonitrile used for dissolving adsorbed naphthalene = 5 ml = 0.005 l

Variables:

$V_c$  = volume of condensate collected (l)

$A$  = Area under the peak

$C_a$  = Concentration of naphthalene in exiting air ( $\mu\text{g/l}$ )

C<sub>w</sub>= Concentration of naphthalene in collected condensate (µg/l)

Calculations for liquid condensate:

$$C_w = \frac{(A \times V_c \times C_s)}{(F_n \times T_w)} \quad (9)$$

Calculations for naphthalene in air:

$$C_A = \frac{(A \times V_g \times C_s)}{(F_n \times T_a)} \quad (10)$$

From these formulae, at 334 K

A= 1891 for liquid, 34500 for gas

V<sub>c</sub> = 102.5 ml

C<sub>s</sub> = 3.565

F<sub>n</sub> = 1.977 lpm

T<sub>w</sub> = 1.01 min

V<sub>g</sub> = 5 ml

T<sub>a</sub> = 10 min

Putting variables and constants in the above formulae

$$C_w = \frac{(1891 \times 0.1025 \times 3.565)}{(1.977 \times 1.01)} = 346.05$$

$$C_A = \frac{(34500 \times 0.005 \times 3.565)}{(1.977 \times 10)} = 31.1$$

So, from the definition, partition coefficient  $K_{wa} = \frac{346.05}{31.1} = 11.111$

This sample calculation was performed for 334K. Similar calculations were performed for temperatures 346.5K, 361.5K, 371.5K

These calculations carried out at different system temperature gave different values of partition coefficient.

### 5.1.3 Calculation for $\Delta H$ and $\Delta S$ from the Equation.

From the equation (5) mentioned in this chapter, a line with equation  $y = 2219x - 4.264$  was compared to the slope and intercept terms in the equation.

$$-\Delta H = 2219 \times 8.3142 = 18.449 \text{ KJ/mol}$$

$$\Delta S = -4.264 \times 8.3142 = -35.45 \text{ J/mol.K}$$

### 3.5.4 Calculation of NaCl concentration obtained in the collected condensate.

To achieve 0.1M silver nitrate solution, 16.9 g of silver nitrate was mixed in 1 liter of water.

$$M \text{ of } Cl^- = M \text{ of } AgNO_3 \times \frac{\text{ml of } AgNO_3}{\text{ml of Condensate}} \quad (11)$$

$$M \text{ of } Cl^- = 0.1 \times \frac{7.6}{10} = 0.076 \text{ M}$$

So, after multiplying by the molecular weight of chlorine,

$$\text{Concentration of NaCl obtained} = 2.66 \text{ g/l}$$

## 5.2 Calculations for Experiment 2 Explained in Chapter 4

The rate constant of overall reaction for decrease in naphthalene concentration was calculated as follows. Since the reaction is first order, the following equation holds good.

For first order reaction

$$\frac{dC_n}{dt} = k C_n \quad (12)$$

Integrating the above equation from  $C_{no}$  to  $C_n$  and from 0 to  $t$  gives

$$\ln \left( \frac{C_{no}}{C_n} \right) = k t \quad (13)$$

Taking the appropriate half life values of  $\ln(C_{no}/C_n) = 0.75$  and time = 130 minutes

$$k = 0.00576 \text{ /min.}$$

Similar to this procedure, a reaction rate constant for the reaction mixture not containing NaCl was calculated to be 0.00147/min.

## CHAPTER 6

### CONCLUSIONS

The research focused on partition coefficients of naphthalene for fog-air system and discussed the reaction products of absorbed naphthalene within the collected fog condensate containing NaCl in presence of UV light. The Following conclusions can be drawn from the experiments performed.

#### **6.1 Partition Coefficient Experiments**

Experiments demonstrated a successful method of creating fog in the reactor. Fog droplets formed with NaCl condensation nuclei could be examined under SEM and the droplet diameters were verified. From the experiments performed for partition coefficients of naphthalene it was observed that concentration of naphthalene in exit air started increasing and that in the fog condensate started decreasing with increasing reactor temperature. So, a conclusion can be drawn that the value of  $K_{wa}$  decreases with increasing reactor temperature. It can also be concluded that presence of NaCl as the condensation nuclei does not alter or reverse the relationship between partition coefficients and temperature when compared to other studies.

The observation suggested that the value of the partition coefficient at room temperature for naphthalene was lower than the value obtained for the similar systems in absence in NaCl in water. Therefore, it was concluded that salinity decreases the partition coefficient values at room temperature. This conclusion was consistent with the results presented by Alaei (Alaei et al., 2006).

It was also observable that though fog was formed inside the reactor, an attempt to carry out photooxidation reaction of naphthalene in 62 seconds reaction time inside the reactor was not successful. This meant that photooxidation reaction is not an instantaneous reaction and a bigger reactor or a recycle reactor which could provide much higher residence time was required to

carry out this type of a reaction inside the reactor. It can be recommended that, with the help of a bigger reactor, naphthalene as well as certain other polyaromatics can be studied for their photoreactions on fog droplets and products can be observed.

As explained above, instead of NaCl, other aerosols can be used as condensation nuclei and their effect on partitioning of organics can be studied as well.

## **6.2 Photooxidation Experiments**

The study of the naphthalene photooxidation reactions showed that with the used setup and given method, the reaction can take place and different products of the reaction can be analyzed with GC/MS and HPLC. Experiment showed that the overall rate of naphthalene photodegradation within water containing NaCl was  $5.76 \times 10^{-3}$ /min. The products of the reaction were mainly phthalide and benzaldehyde.

Another experiment was performed in absence of NaCl in water which showed that the overall rate of photodegradation of naphthalene was  $1.47 \times 10^{-3}$  /min. which was lower than the value mentioned above and the products of the reaction were 1,3-indandione and phthalide with complete absence of benzaldehyde. A conclusion was therefore drawn that under similar physical conditions for the reaction, presence of NaCl was responsible for the faster degradation of naphthalene and product formation. Benzaldehyde was detected as an intermediate in some of the reactions as discussed in section 3.6. With this experiment, it was shown that for the discussed physical conditions for the reaction and in the presence of NaCl, benzaldehyde can be obtained as a major reaction product.

## REFERENCES

- Alaee, M., Whittal, R.M. and William, M.J.S. 1996. The effect of water temperature and composition on Henry's law constant for various PAH's, *Chemosphere*, 32(6), 1153-1164.
- Alp, S., Erten, S., Karapire, C., Koz, B., Doroshenko, A.O. and Icli, S. 2000. Photoinduced energy-electron transfer studies with naphthalene diimides, *Journal of photochemistry and Photobiology A*, 135, 103-110.
- Armstrong, F.A.J., Williams, P.M. and Strickland, J.D.H. 1966. Photo-oxidation of organic matter in sea water by ultra-violet radiation, analytical and other applications, *Nature*, 5084, 481-483.
- Beltran, F.J., Ovejero, G., Gracia-Araya, J. F. and Rivas, J. 1995. Oxidation of polynuclear aromatic hydrocarbons in water. 2. UV radiation and ozonation in the presence of UV radiation, *Industrial and engineering chemistry research*, 34, 1607-1615.
- Benner, W.H., Brodzinsky, R. and Novakov, T. 1981. Oxidation of SO<sub>2</sub> in droplets which contain soot particles, *Atmospheric environment*, 16(6), 1333-1339.
- Bernstein, M.P., Standford, S. A., Allamandola, L.J., Gillette, J.S., Clemett, S.J. and Zare, R.N. 1999. UV irradiation of polycyclic aromatic hydrocarbons in ices: Production of alcohols, quinines and ethers, *Science*, 1135-1138.
- Chen, J., Ehrenhauser, F.S., Valsaraj, K.T. and Wornat, M.J. 2006. Uptake and UV-photooxidation of gas-phase PAHs on the surface of atmospheric water films 1. Naphthalene, *The journal of physical chemistry A*, 110(29), 9161-9168.
- Chen, J. and Valsaraj, K.T. 2007. Uptake and UV-photooxidation of gas phase polyaromatic hydrocarbons on the surface of atmospheric water films. 2. Effects of dissolved surfactants on naphthalene photooxidation, *The journal of physical chemistry A*, 111, 4289-4296.
- Dabestsani, R. and Ivanov, I.N. 1999. A compilation of physical, spectroscopic and photophysical properties of polycyclic aromatic hydrocarbons, *Photochemistry and photobiology*, 70(1), 10-34.
- Das, S., Muneer, M. and Gopidas, K.R. 1994. Photocatalytic degradation of wastewater pollutants. Titanium dioxide mediated oxidation of polynuclear aromatic hydrocarbons, *Journal of photochemistry and photobiology A: Chemistry* 77, 83-88.
- Davidovits, P., Jayne, J.T., Duan, S.X., Worsnop, D.R., Zahniser, M.S. and Kolb, C.E. 1991. Uptake of gas molecules by liquids, *Journal of physical chemistry*, 95, 6337-6340.
- Djikaev, Y.S. and Tabazadeh, A. 2003. Effect of adsorption on the uptake of organic trace gas by cloud droplets, *Journal of geophysical research*, 108(D22), 4689.

Domine, F. and Shepson, P.B. 2002. Air-snow interactions and atmospheric chemistry, *Atmospheric chemistry*, 297(5586), 1506

Donaldson, D.J. and Vaida, V. 2005. The influence of organic films at the air-aqueous boundary on atmospheric processes, *Chemical review*, 106, 1445-1461.

Dubowski, Y., Sumner, A.L., Menke, E.J., Gasper D.G., Newberg, J.T., Hoffman, R.C., Penner, R.M., Hemminger, J.C. and Finlayson-Pitts, B.J. 2004. Interactions of gaseous nitric acid with surfaces of environmental interest, *Physical chemistry chemical physics*, 6, 3879-3888.

Experiment 7, Measurement of chloride in natural waters: What impact does Richmond have on local rivers and streams?, Section 4.6 in chemistry, *The central science*, 9<sup>th</sup> Ed.

Fasnacht, M.P. and Blough, N.V. 2003. Mechanisms of the aqueous photodegradation of polycyclic aromatic hydrocarbons, *Environmental science and technology*, 37, 5767-5772.

Finlayson-Pitts, B.J. and Pitts, J.N.J. 2008. Tropospheric air pollution: ozone, airborne toxics, polycyclic aromatic hydrocarbons and particles, *American association for the advancement of science*, 276(5315), 1045-1052.

Fox, M.A., Chen, C. and Younathan, J.N.N. 1984. Oxidative cleavage of substituted naphthalenes induced by irradiated semiconductor powders, *Journal of organic chemistry*, 49, 1969-1974.

Fogler, H.S. 1999. Elements of chemical reaction engineering, 3<sup>rd</sup> Ed., Prentice hall of India, Delhi, India, pp.223-260.

Garcia-Martinez, M.J., Canoira, L., Blazquez G., Riva, I.D., Alcantara, R. and Llamas, J.F. 2005. Continuous photodegradation of naphthalene in water catalyzed by TiO<sub>2</sub> supported on glass raschig rings, *Chemical engineering journal*, 110, 123-128.

Goss, K. 2004. The air/surface adsorption equilibrium of organic compounds under ambient conditions, *Critical reviews in environmental science and technology*, 34, 339-389.

Goss, K. and Schwarzenbach, R.P. 1998. Gas/solid and gas/liquid partitioning of organic compounds: critical evaluation of the interpretation of equilibrium constants, *Environmental science and technology*, 32(14), 2025-2032.

Guillard, C., Delprat, H., Haong-Van, C. and Pichat, P. 1993. Laboratory study of the rates and products of the phototransformations of naphthalene adsorbed on samples of titanium dioxide, ferric oxide, muscovite and fly ash, *Journal of atmospheric chemistry*, 16, 47-59.

Harvey, R.G., Polycyclic Aromatic Hydrocarbons: Chemistry and Carcinogenicity, Cambridge University press, Cambridge.

Herckes, P., Chang, H., Leet, T. and Collette J.J.L. 2007. Air pollution processing by radiation fogs, *Journal of water, air and soil pollution*, 181, 65-75.

Hinds, W.C., *Aerosol technology*, 2<sup>nd</sup> Ed., Wiley interscience publications, NY, pp 1-14, 150-170, 304-315

Hoff, J.T., Mackay, D., Gillham, R. and Shiu, W.Y. 1993. Partitioning of organic chemicals at the air-water interface in environmental systems, *Environmental science and technology*, 27(10), 2174-2180.

IUPAC compendium of chemical technology 2, 1997.

Jenkins, B.M., Jones, A.D., Turns, S.Q. and Williams, R.B. 1996 a. Emissions factors for polycyclic aromatic hydrocarbons from biomass burning, *Environmental science and technology*, 30(8), 2462-2469.

Karthikeyan, K.G. and Chorover, J. 2000. Effects of solution chemistry on the oxidative transformation of 1-naphthol and its complexation with humic acid, *Environmental science and technology*, 34, 2939-2946.

Klanova, J., Klan, P., Nosek, J. and Holoubek, I. 2003. Environmental ice photochemistry, monochlorophenols, *Environmental science and technology*, 37, 1568-1574.

Kokkola, H., Romakkaniemi, S., Kulmala, M. and Laaksonene, A. 2003. A cloud microphysics model including trace gas condensation and sulfate chemistry, *Boreal environment research*, 8(4), 413-424.

Kramer, L., Poschl, U. and Niessner, R. 2000, Microstructural rearrangement of sodium chloride condensation aerosol particles on interaction with water vapor, *Journal of aerosols science*, 31(6), 673-685.

Lakhani, A., Parmar, R.S. and Sastangi, G.S. 2007. Chemistry of fogs in Agra, India: Influence of soil particulates and atmospheric gases, *Environmental monitoring and assessment*, 133(1-3), 435-445.

Landrum, P.F., Nihart, S.R., Eadie B.J. and Herche, L.R. 1987. Reduction in bioavailability of organic compounds to the Amphipod *ontoporeia-hoyi* by dissolved organic matter of sediment interstitial waters, 6(1), 11-20.

Levenspiel O. 1972. *Chemical reaction engineering*, 2<sup>nd</sup> Ed., Wiley Eastern university edition, Delhi, India.

Luttke, J. and Levsen, K. 1997. Phase partitioning of phenol and nitrophenols in clouds, *Atmospheric environment*, 31(16), 2649-2655.

Mahajan, T.B., Elsila, J.E., Deamer, D.W. and Zare, R.N. 2002. Formation of carbon-carbon bonds in the photochemical alkylation of polycyclic aromatic hydrocarbons, *Origins of life and evolution of biosphere*, 33, 17-35.

McConkey, B.J., Hewitt, L.M., Dixon D.J. and Greenberg, B.M. 2001. Natural sunlight induced photooxidation of naphthalene in aqueous solution, *Water, air and soil pollution*, 136, 347-359.

- Miller, J.S. and Olejnik, D. 2000. Photolysis of polycyclic aromatic hydrocarbons in water, *Water research*, 35(1), 233-243.
- Moore, K.F., Sherman, D.E., Reilly, J.E., Hannigan, M.P., Lee, T. and Collett J.L.J. 2003. Drop size-dependent chemical composition of clouds and fogs. Part II: Relevance to interpreting the aerosol/trace gas/fog system, *Atmospheric environment*, 38, 1403-1415.
- Moza, P.N., Hustert, K. and Kettrup, A. 1999. Photooxidation of naphthalene and phenanthrene in hexane as an oil film on water, *Chemosphere*, 39(4), 569-574.
- Nathanson, G.M., Davidovits, P., Worsnop, D.R. and Kolb, C.E. 1996. Dynamics and kinetics at gas liquid interface, *Journal of physical chemistry*, 100, 13007-13020.
- Poster, D.L. and Baker, J.E. 1996. Influence of submicron particles on hydrophobic organic contaminants in precipitation. 1. Concentrations and distributions of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in rainwater, *Environmental science and technology*, 30, 431-348.
- Raja, S. and Valsaraj, K.T. 2006. On the reactive uptake of gaseous PAH molecules by micron-sized atmospheric water droplets, *Atmospheric research*, 81, 277-292.
- Raja, S., Yaccone, F.S., Ravikrishna, R. and Valsaraj, K.T. 2002. Thermodynamic parameters for the adsorption of polycyclic aromatic hydrocarbon vapors at the gas-water interface, *Journal for chemical engineering data*, 47, 1213-1219.
- Raja, S. and Valsaraj, K.T. 2004. Adsorption and transport of gas-phase naphthalene on micron-size fog droplets in air, *Environmental science and technology*, 38, 763-768.
- Raja, S., Raghunathan R., Yu, X., Lee, T., Chen, J., Kommalapathi, R.R., Murugesan, K., Shen, X., Qingzhong, Y., Valsaraj, K.T. and Collett, J.L.J. 2008. Fog chemistry in the Texas-Louisiana gulf coast corridor, *Atmospheric environment*, 42, 2048-2061.
- Schwarz, F.P. and Wasik, S.P. 1977. A fluorescence method for the measurement of the partition coefficients of naphthalene, 1-methylnaphthalene, and 1-ethylnaphthalene in water, *Journal of chemical and engineering data*, 22(3), 270-273.
- Srivastava, A. and Devotta, S. 2007. Indoor air quality of public places in Mumbai, India in terms of volatile organic compounds, *Environmental monitoring and assessment*, 133, 127-138.
- Streaowski, R.S. and George, C.J. 2005. *Journal of chemical engineering data*, 50, 804-810
- Suhre, K., Andreae, M.O. and Rosset, R. 1995. Biogenic sulfur emissions and aerosols over the tropical south-atlantic. 2. One dimensional simulation of sulfur chemistry in the marine boundary layer, 100(D6), 11323-11334.

Tongle, M.D., Pirmohamed, M., Templeton, E., Wilson, A.S., Madden, S., Kitteringham, N.R. and Park, B.K. 1993. An investigation of formation of cytotoxic, genotoxic, protein reactive and stable metabolites from naphthalene by human liver microsomes, *Biochem. Pharmacol.*, 46, 1529-1538.

Voine, D., Maurino, V., Minero, C., Pelizzetti, E., Harrison, M.A.J., Olariu, R. and Arsene, C. 2006. Photochemical reactions in the tropospheric aqueous phase and on particulate matter, *Chemical society reviews*, 35, 441-453.

Wasserman, H.H., Wiberg, K.B., Larsen, D.L. and Parr, J. 2005. Photooxidation of methylnaphthalenes, *Journal of organic chemistry*, 70, 105-109.

## **VITA**

Neha Shrikant Damle was born in June, 1985, in Mumbai, India. She completed her high school studies and college from Pune, India. She graduated from Pune University, India, in August 2006 earning Bachelor of Engineering degree in the chemical engineering discipline. In August 2006, she was admitted to Louisiana State University, Chemical Engineering Department. There she worked under Dr. Kalliat T. Valsaraj and completed her research work successfully in May 2008. She is a present candidate for the degree of Master of Science in Chemical Engineering.