ABSTRACT

Volatilization of VOCs from Complex Wastewaters

by

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A variety of volatile organic solvents used in the pharmaceutical and specialty chemical industries end up in wastewater collection and treatment systems. EPA has classified these VOCs into groups depending on their potential to volatilize from the wastewaters. In making this classification, Henry's Law, which is valid at very low concentrations, has been used to describe the vapor-liquid equilibrium. But, in reality the concentrations observed in the wastewaters are often too high for Henry's Law to be valid and it is inappropriate to assume that equilibrium has been achieved for every compound.

This project evaluates the volatilization rates, both experimental and theoretical, of VOCs (namely methanol, acetone and dimethyl sulfoxide (DMSO)) under a number of different operating scenarios. These different scenarios (e.g., quiescent, agitated, aerated, different free surface area exposed to the ambient air, different shapes of the vessel etc.) are supposed to closely simulate the range of different conditions that the VOCs are subjected to in the wastewater collection and treatment facilities in the industry. The aim is to determine how closely these compounds reach the equilibrium described by the Henry's Law, when subjected to the different scenarios.

VOLATILIZATION OF VOLATILE ORGANIC COMPOUNDS FROM COMPLEX WASTEWATERS

by
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This thesis is dedicated to
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CHAPTER 1

INTRODUCTION

Volatile Organic Compounds, abbreviated as VOCs, are hydrocarbons having high enough vapor pressures to be able to leave the liquid solution and exist in vapor state. They are the precursors of oxidants (or ozone) because of reactions in the atmosphere involving nitrogen oxides and sunlight. This can be shown by the classic Haagen-Smit (15) reaction, which some four decades ago described the formation of photochemical smog, and is now well understood.

$$\text{VOCs} + NO_x + h\nu\ (\lambda < 430\text{nm}) \rightarrow O_3 + \text{'other products'}$$

This ozone adds to the air pollution because its the major constituent in the formation of smog. The Clean Air Act, as amended in 1990, requires EPA to promulgate standards for various industrial groups that emit hazardous air pollutants (HAP). As a result, EPA has proposed the national emission standards for hazardous air pollutants (NESHAP) for the emission of certain organic hazardous air pollutants from various industries.

1.1 Types of Industries Emitting VOCs

Wastewaters containing various amounts and types of organic contaminants are mostly common in the following types of industries.

- The Organic Chemicals, Plastics and Synthetic Fibers Manufacturing Industry
- The Pesticides Manufacturing Industry;
- The Pharmaceutical Manufacturing Industry; and
- The Hazardous Waste Treatment, Storage and Disposal Facilities Industry;

Many of the chemical processes employed within these industries use organic compounds as raw materials, solvents, catalysts and extractants. In addition, many of these processes also generate similar organic by-products during reaction steps.

1.2 Sources of VOC's Emission

If a material balance is done about a plant, considering only inlet and outlet streams from a plant, it is seen that some materials are being lost. In the manufacture of chemical products, wastewater streams are generated which contain organic compounds. These organic containing wastewater streams result from both the direct and indirect contact of water with organic compounds. The wastewater is collected and treated in a variety of ways. Generally, wastewater passes through a series of collection and treatment units before being discharged from a facility. Many of these collection and treatment system units are open to the atmosphere and allow organic-containing wastewaters to contact ambient air. Whenever this happens, there is a potential for VOC emissions. The organic pollutants volatilize in an attempt to exert their partial pressure above the wastewater. In doing so, the organics are emitted to the ambient air surrounding the collection and treatment units.

The EPA document EPA-450/3/90-004 entitled "Industrial Wastewater Volatile Organic Compound Emissions -- Background Information For BACT/LAER Determinations" describes the different kinds of collection and treatment units like drains, manholes, junction boxes, lift stations, sewers, trenches, equalization basins, clarifiers and aeration basins. It expresses concern that contaminants (VOCs), escape these units as fugitive emissions and thus avert treatment.

1.3 Factors Affecting the VOC Emission

The magnitude of VOC emissions depends greatly on many factors such as :

-*Wastewater characteristics:* Both the concentration and physical properties of the specific organic compounds present in the wastewater affect the emissions. The volatility of the organics in water is the most significant physical property affecting the rate of emission. The Henry's Law constant (H) for an organic compound provides an indication of this physical property. Values for Henry's constant are determined by measuring the equilibrium concentrations of an organic compound in the vapor and aqueous phases, in the limit as both the concentrations tend to zero. However, the organic compound's vapor pressure and water solubility are sometimes used, when laboratory data are not

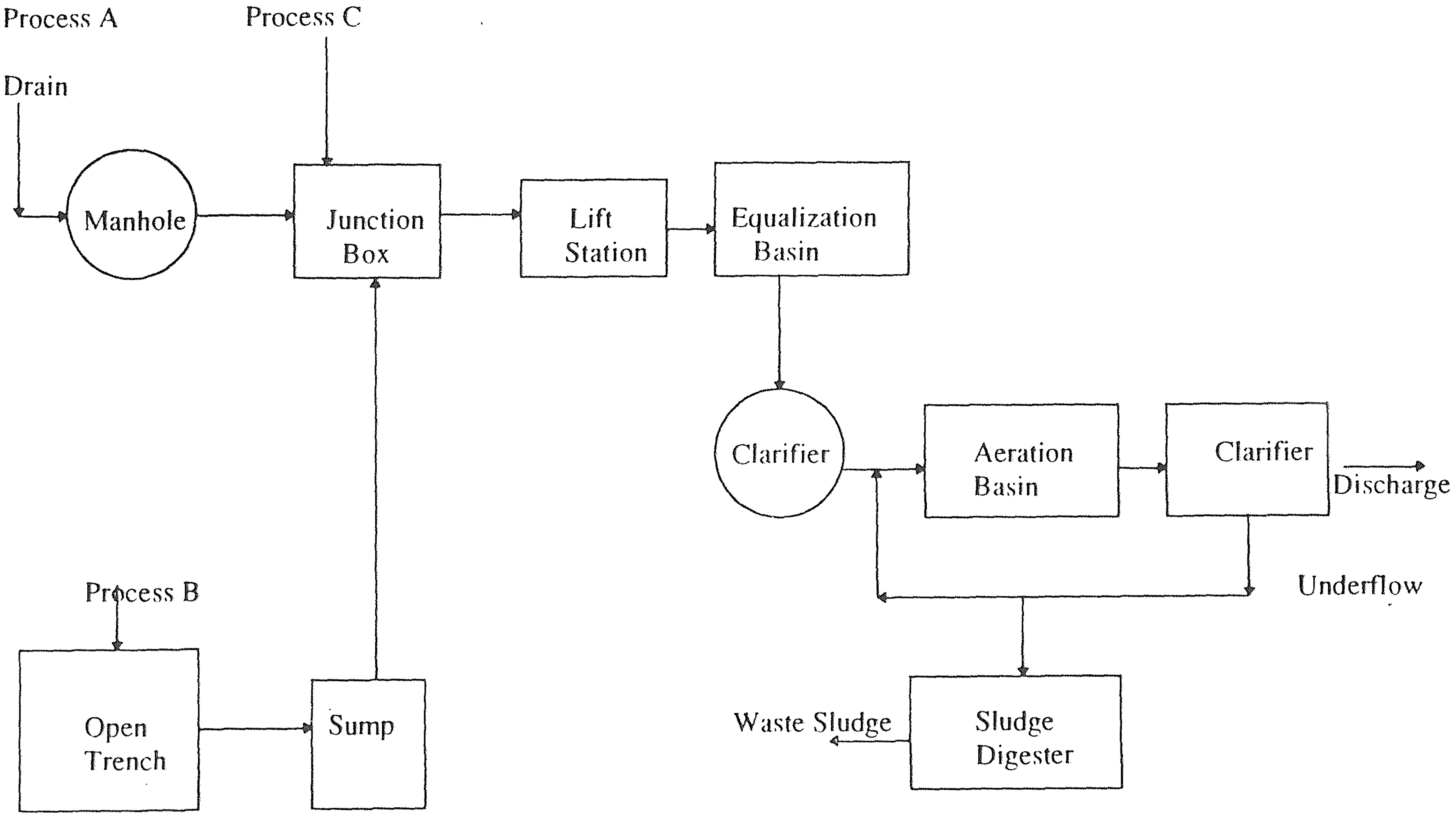


Figure 1.1: Typical Wastewater Collection and Treatment Scheme

available, to estimate values of Henry's constant. Using these data the value of H is calculated by computing the ratio of the compound's vapor pressure to its water solubility at the same temperature. Organic compounds with low water solubilities and high vapor pressures exhibit the highest values for Henry's constant and therefore, these compounds tend to volatilize into the vapor phase most readily.

-*The temperature of the wastewater:* Because the temperature of the wastewater affects the Henry's Law constant, its value will affect emissions.

- *The design of the individual collection and treatment units:* Collection and treatment schemes are facility specific. The flow rate and organic composition of wastewater streams at a particular facility are functions of the processes used. The wastewater flow rate and composition, in turn, influence the sizes (e.g. surface area exposed to ambient air) and types of collection and treatment units that must be employed at a given facility. Figure (1.1) illustrates a typical scheme for collecting and treating process wastewater generated at a facility and the opportunity for volatilization of organics.

- *Climactic factors:* Emission rates from a drain are also affected by climactic factors. These include ambient air temperature, wind speed and wind direction. Differences in temperature between the ambient air and the vapors in the headspace in the collection and treatment units establish pressure and density gradients. These gradients generate bulk vapor flow from the headspace towards the atmosphere. This bulk flow increases convective mass transfer of organic compounds to the air surrounding the unit. Wind speed has a similar effect. For example, it creates a lower pressure at the mouth of the drains, manholes etc. which "pulls" vapors from the sewer line headspace. This pressure gradient, therefore, increases the convective mass transfer of organic compounds to air surrounding the collection system. Wind blowing into annular upstream opening will also increase the volatilization rate of the organics.

All of these factors as well as the general scheme used to collect and treat facility wastewater have a major effect on VOC emissions.

1.4 Control Strategies

Since the VOC emissions during collection and treatment of industrial wastewater can be significant, measures to control these emissions need to be considered. Three control strategies are known. The first control strategy is waste minimization through process modification of operating practices, preventive maintenance, recycling, or segregation of waste streams. The second control strategy is to reduce the organic content of the wastewater through treatment before the stream contacts ambient air. The third strategy is to control emissions from collection and treatment system components until the organic compounds are either recovered or destroyed. Although the third strategy is feasible in some cases, the more universally applicable treatment technology is to reduce the quantity of waste generated or reduce the organic content of the wastewater at the point of generation.

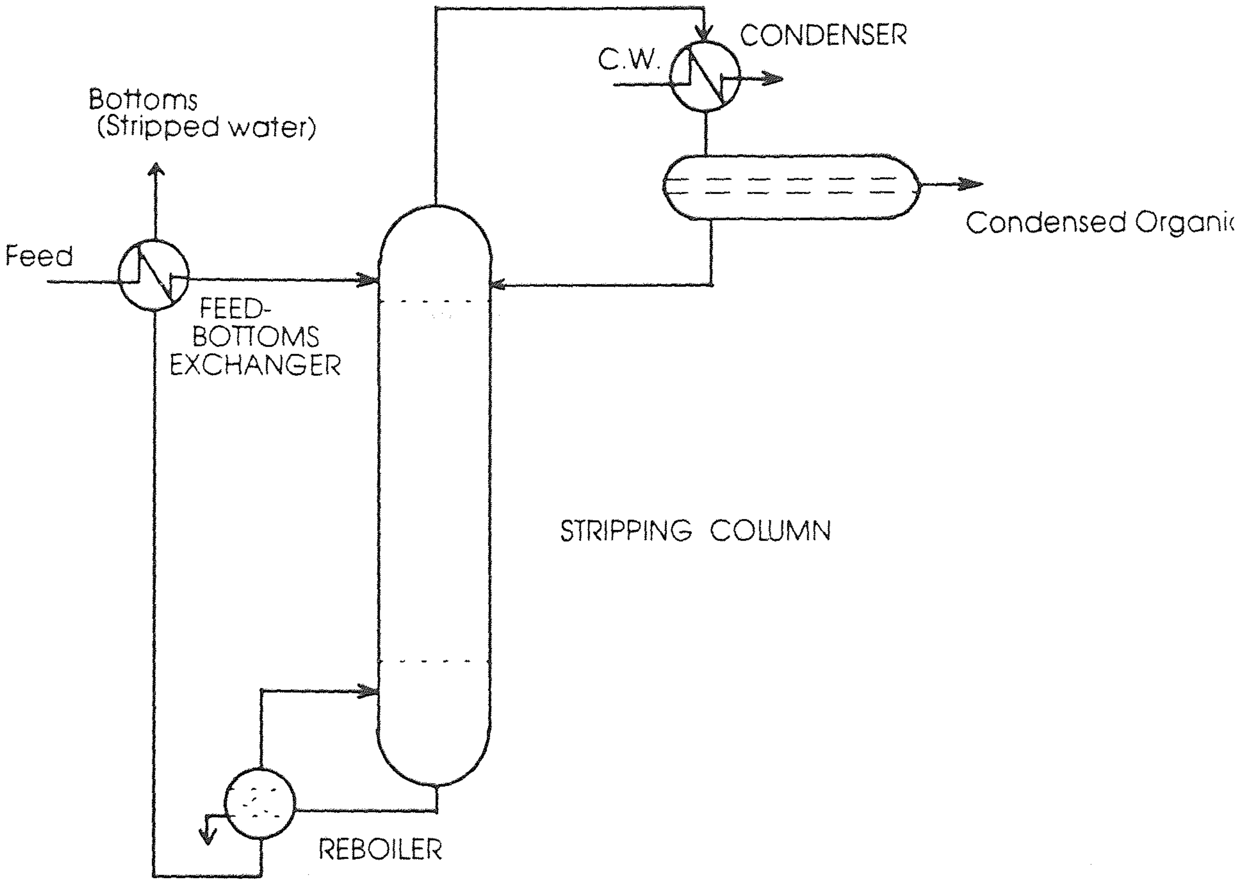


Figure 1.2: Typical flow diagram for a steam stripping system

One type of treatment technology available and currently in use at many facilities is steam stripping. Because steam stripping removes the organic compounds most likely to be emitted downstream (most volatile compounds), it is an effective technique for reducing VOC emissions from wastewater. It involves the fractional distillation of wastewater to remove organic compounds. The basic principle of steam stripping is the direct contact of steam with wastewater. This contact provides heat for vaporization of the more volatile organic compounds. The overhead vapor containing water and organics is condensed and separated (usually in a decanter) to recover the organics. A typical steam stripping strategy is shown in the Figure(1.2). These recovered organics are usually either recycled or incinerated in an on-site combustion device.

While biological treatment units and other technologies may be used to comply with the hazardous organic national emission standards for hazardous air pollutants (HON), they must achieve a comparable control efficiency as the reference control technology, which has been proposed to be a design steam stripper. The degree of control achieved with biological treatment systems depends on the biodegradability of the compounds and the system design. In some cases, high removal efficiencies have been reported, and industry sources have claimed that control performance for all degradable organics is generally quite good with overall removals exceeding 80 to 85 percent of the volatiles. Information on performance and characteristics of biological treatment units (e.g., retention time, aeration rates, aeration gas, mixed liquor suspended solids) will be needed from as many Synthetic Organic Chemical Manufacturing Industry sources as possible.

1.5 Format proposed by EPA and its Contradictions

The format proposed by EPA for reduction of wastewater stream volatile organic hazardous air pollutants (VOHAP) concentration is based on the organic hazardous air pollutant (HAP) removal efficiency of a steam stripper. The compounds were grouped with others having similar removal efficiencies and then each group was assigned a target removal efficiency. The removal efficiencies for the compounds were predicted based on physical and chemical properties of the chemicals, the design steam stripper conditions etc. As a result, three strippability groups were formed. The target removal efficiency for each strippablility group is shown in the following table (1.1).

TABLE 1.1.- Organic Strippability Groups and Target Removal Efficiencies

Strippability Group	Target Removal Efficiency (Percent)
A..........................	99
B..........................	95
C..........................	70

One concern, raised by industry representatives, is the range of required removal efficiencies of Hazardous Air Pollutants (HAPs) within each strippability group, as shown in the table (1.1) (16). The concern is that the ranges represented in each strippablility group could hinder a compliance demonstration for specific HAPs that cannot individually attain removal efficiencies at the level assigned to the strippability group. This could result because each strippability group is comprised of several HAPs and each HAP in each strippability group does not necessarily have the same removal efficiency that is assigned to the strippability group. For example, the removal efficiency that is achievable for a particular HAP in Strippability Group B might be 92 percent, while the target removal efficiency for Strippability Group B is 95 percent. EPA is considering whether it is more appropriate to develop more strippability groups with smaller ranges of removal efficiencies in each group, or to assign an individual target removal efficiency for each HAP.

To make the determination of whether to revise the strippability groups, additional information is needed for the current physical/chemical properties data base (16). Specifically, the information needed includes: (1) Experimental data and documentation for Henry Law constants at 25 ^{o}C and 100 ^{o}C (2) documentation (e.g. reaction kinetics) for HAPs that cannot readily exist in wastewater (e.g. due to rapid hydrolysis); and (3) documentation of HAPs that are difficult to remove by steam stripping. This information would be compared against the documentation EPA used to derive the fraction emitted values and strippability factors used in the development of the proposed regulation.

The pharmaceutical steam stripping pilot study also demonstrated poor steam stripping of oxygenated organic compounds. Methanol , which is in Group C and so has target removal efficiency 70 percent, averaged 46.8 percent for 11 separate steam stripping tests on two different feed streams (17). These tests, with actual wastewaters treated in a large pilot-scale steam stripper, demonstrate that EPA's strippability estimates are inaccurate for some compounds and cannot be achieved. Furthermore, this pilot study pointed out that for non-ideal VOHAP/aqueous systems, very good data are required to reliably predict stripper performance using a simulation model, including ASPEN. This is not a failure of the simulation model, but rather represents the use of inappropriate assumptions and characteristics for the wastewater being stripped.

There are a number of organic HAPs that EPA originally considered as candidates for identification as VOHAPs. Examples of such HAPs include chemicals such as phenol, ethylene glycol, and p-cresol, which are poorly steam stripped, if at all, and which by EPA's own calculations have a very low potential to emit from Synthetic Organic Chemical Manufacturing Industry (SOCMI) wastewater collection and treatment systems.

EPA's estimates of the strippability of the compounds that it has excluded from the rule, when compared to the Agency's predicted emissions from wastewater collection and treatment units, justifies the decision not to regulate such compounds. The Agency's calculations for the three example compounds listed above are as follows (17):

Chemical	Percent steam stripped	Percent emitted
p-cresol	8	10
ethylene glycol	0	1
phenol	9	11

As noted in these comments, EPA's estimates of its RCT steam stripper performance are grossly overoptimistic, while its estimates of emissions during wastewater collection and treatment are overstated - especially for biological treatment. It is apparent even from these figures, however, that if a compound cannot be stripped by steam at a temperature of 100 °C in a treatment unit that is designed to maximize removal, it is not going to be emitted from a collection system and wastewater treatment units that typically operate at temperatures of 30 to 40 °C.

In addition, the compounds that EPA has excluded from regulation are biodegradable and are very effectively treated in SOCMI wastewater treatment systems. Chemicals such as phenol, ethylene glycol and the cresols are all very biodegradable and are essentially 100 percent removed in biological treatment plants. Chemical Manufacturers Association (CMA) strongly supports EPA's decision to exclude chemicals with minimal potential to be emitted from wastewater management systems from regulation as VOHAPs. The scientific data that supports this decision are complete and conclusive.

Although the Agency has excluded a number of organic HAPs from regulation by the wastewater Hazardous Organic National Emission Standards for hazardous air pollutants (HON), there remain a number of chemicals on the VOHAP list that have little potential to be emitted during wastewater collection and treatment and that are poorly removed by the RCT steam stripper. These compounds should also be excluded from regulation.

Methanol is one good example of such a compound. It also is good example of how EPA's methodology overestimates wastewater system emissions for some chemicals. The Enviromega tests showed that methanol was not measurably emitted from drop structures or process drains under any of the conditions examined, which represented the range of conditions found in full scale collection systems (17). In addition, it is well documented that methanol is biodegradable in acclimated biological treatment units. What is surprising is that EPA's methodology predicts that 27.8 percent of the methanol in wastewater will be emitted during collection and treatment. This overprediction is not unique to methanol, it is also likely to be present in the predicted emissions for other VOHAPs with chemical properties similar to methanol.

As a part of technical basis for estimating emissions, EPA developed scenarios representing Synthetic Organic Chemical Manufacturing Industry

(SOCMI) wastewater collection and treatment systems. Equilibrium and mass transfer equations were used to model the emissions from the waste management units(e.g., individual drain systems, wastewater tanks, biological treatment units, etc.) in each of the scenarios.

Industry representatives questioned whether the scenarios are representative of SOCMI wastewater collection and treatment systems. Specifically, industry representatives pointed out that many facilities have installed traps on drains and seals on the waste management units, therefore controlling some air emissions from the systems. In response to these concerns, CMA developed an alternative scenario based on input from CMA member companies and provided it to EPA.

EPA may revise the scenarios and because industry representatives have expressed concerns about some of the models used for estimating emissions from waste management units, EPA will be re-evaluating some models between proposal and promulgation. Revisions to the models will reflect technical issues. The EPA requests results of studies measuring air emissions from waste management units, especially individual drain systems (e.g. drains, manholes, sumps, and junction boxes) as well as wastewater tanks and biological treatment units.

Industry has stated that biological treatment units should be given more serious consideration as reference control technology, which has been proposed to be a design steam stripper. According to CMA, many of the chemicals in the

Group B and Group C can be degraded in biological treatment systems more efficiently than they can be steam stripped. CMA also suggested that some of the compounds of the very volatile Group A can be effectively biodegraded in typical SOCMI wastewater treatment systems using enhanced biological treatment. Consequently, EPA plans to evaluate the performance achieved by individual drain systems and biological treatment systems at existing facilities and then to reassess the source-wide floor. To do this analysis, a number of technical issues need to be resolved. Specific issues that must be resolved include; appropriate biokinetic data and appropriate models to predict rates of volatilization.

CHAPTER 2

BACKGROUND

The maximum extent to which a compound may volatilize occurs when the liquid phase containing the compound is in thermodynamic equilibrium with the vapor or gas phase into which the compound is volatilizing. Therefore the rate at which a compound volatilizes from the liquid phase is proportional to the difference between 1) the partial pressure of the compound in the gas phase and 2) the partial pressure that the compound would have in the gas phase if a state of equilibrium existed between the two phases. In most cases, we do not expect this equilibrium to occur due to mass transfer limitations. The proportionality constant is determined by the mass transfer characteristics of a given installation, that is if the phases are in contact long enough for the equilibrium to be established by diffusion of the compound from the liquid phase to the gas or vapor phase. But in most cases it is sufficiently large enough to allow the assumption that equilibrium is achieved.

For thermodynamic equilibrium between a liquid and a vapor phase, the appropriate starting equation is (13):

$$\hat{f}_i\,(liquid) = \hat{f}_i\,(vapor)$$

where $\hat{f}_i$ is the fugacity of compound i in the indicated phase. For species i in vapor mixtures

$$\hat{f}_i\,(vapor) = y_i \hat{\phi}_i P$$

But for most practical applications, the pressure is low enough to assume that the vapor behaves as an ideal gas (i.e. $\hat{\phi}_i = 1$). Therefore the vapor-phase fugacity is given by

$$\hat{f}_i\,(vapor) = y_i P = p_i \qquad (1)$$

where p_i is the partial pressure of component i, which is defined as the system pressure, P, multiplied by the component mole fraction in the vapor phase, y_i.

The liquid phase, on the other hand, is almost always a non-ideal mixture. This is generally true for mixtures between water and organic compounds. Liquid phase fugacity is given by:

$$\hat{f}_i\,(liquid) = x_i \gamma_i f_i^{\circ}$$

where x_i is the component mole fraction in the liquid phase and γ_i is the component activity coefficient in the liquid phase. By definition,

$$\gamma_i \equiv \frac{\hat{f}_i}{x_i f_i}$$

where f_i is the fugacity of the pure species i

f_i^o is the standard state fugacity for the component in the liquid phase.

In terms of excess Gibbs free energy, activity coefficient is given by,

$$\ln\gamma_i = [\frac{\partial(nG^E/RT)}{\partial n_i}]_{P,T,n_j} \tag{2}$$

where G^E = excess Gibbs energy of the solution,

n = total number of moles of the solution,

n_i = number of moles of species i,

P = total pressure,

T = solution temperature,

R = Gas constant.

The activity coefficient is a measure of the non-ideality of the liquid mixture relative to the standard state that has been chosen for each component. f_i^o can be either the Lewis-Randall (LR) standard state or the Henry's Law standard state. f_i° (LR) represents the fugacity f_i of pure i as it actually exists and is given by,

$$\lim_{x_i \to 1} \frac{\hat{f}_i}{x_i} = f_i$$

Therefore, f_i° (LR) $= f_i$, which is given by

$$f_i = \phi_i^{sat} P_i^{sat} \exp \frac{V_i^{l}(P - P_i^{sat})}{RT}$$

At low pressure, $\phi_i^{sat} = 1$ and the exponential factor (Poynting factor) differs from unity by only a few parts per thousand, and thus may be neglected. The LR standard state fugacity (at low pressures) is simply the pure component vapor pressure. Thus f_i° for the Lewis-Randall standard state is replaced by $P_i^{sat}(P_i^{\circ})$. For miscible mixtures, such as those involving similar organic compounds, the usual standard state is the Lewis-Randall (LR) state. However, for solvent/solute mixtures and mixtures in which certain compounds are always dilute, the usual standard state is the Henry's Law standard state. In this case, f_i° is replaced by the Henry's Law constant $H_{i,j}$ which is defined by:

$$H_{i,j} = \lim_{x_i \to 0} \frac{\hat{f}_i}{x_i} \qquad (3)$$

P_i^o is characteristic of only component i, $H_{i.j}$ is characteristic of both component i and the solvent j in which it is dissolved. Thus if there is a change in the composition of the solvent, the Henry's Law constant for compound i will also change.

From equation (1) and (3) it is can be seen that at low pressures the value of Henry's constant can be determined experimentally by:

$$H_{i,j} = \lim_{x_i \to 0} \frac{y_i P}{x_i}$$

According to the definition, all mixtures will behave ideally by Henry's Law as the composition tends to zero. That is, the activity coefficient for Henry's Law becomes equal to unity. The range of composition in which the activity coefficient in close enough to unity and can be neglected is regarded as the range of composition in which Henry's Law is valid for describing the thermodynamic equilibrium. If its not in this range then an "effective" Henry's constant can be used (18):

This "effective" Henry's constant is not a constant. It varies with composition as the activity coefficient varies. In most cases, the activity coefficient decreases as the composition increases. Therefore, the "effective" Henry's constant also decreases as composition increases. Also, since the activity coefficient and the true Henry's constant are both temperature dependent, so of course the "effective" Henry's constant is also a function of temperature.

As already mentioned, Henry's constant $H_{i,j}$ can be measured at low pressures by the limiting value of the ratio of the vapor-phase partial pressure to the liquid-phase composition. However, not all systems have had reliable Henry's constants reported. But there are methods of estimating the values, if the experimental values are not available or are unreliable. Methods based on the prediction of the liquid phase activity coefficients are the ones normally used. The standard state usually used in these methods is the Lewis-Randall standard state.

$$\hat{f}_i\,(liquid) = x_i \gamma_i (LR)\, P_i^{\circ}$$

where the activity coefficient is based on the Lewis-Randall standard state. But if we substitute this equation in the following equation,

$$H_{i,j} = \lim_{x_i \to 0} \frac{\hat{f}_i\,(liquid)}{x_i}$$

which is a limiting case of the concentration tending to be negligible (infinite dilution), then the activity coefficient becomes the activity coefficient at infinite dilution.

$$H_{i,j} = \gamma^{\infty}_{i,j}(LR)\,P_i^{sat}$$

The superscript on the activity coefficient indicates that we require the value at infinite dilution, and the additional subscript indicates the solvent. In terms of "effective" Henry's constant:

$$H^{eff}_{i,j} = \gamma_{i,j}(LR)\,P_i^{sat}$$

Activity coefficients γ_i have traditionally been calculated from correlating equations for G^E/RT by application of equation 2. The excess Gibbs energy is a function of T, P and composition, but for liquids at low to moderate pressures it is a very weak function of P. Under these conditions, its pressure dependence and therefore the pressure dependence of the activity coefficients are usually

$$\frac{G^E}{RT} = g(x_1, x_2, \dots\dots\dots\dots, x_N) \qquad \text{(constant T)}$$

For binary systems the function often most conveniently represented by an equation is $G^E / x_1 x_2 RT$, and one procedure is to express this function as a power series in x_1:

$$\frac{G^E}{x_1 x_2 RT} = a + b\,x_1 + c\,x_1^{\,2} + \dots\dots\dots \quad \text{(constant T)}$$

Since $x_1 = 1 - x_2$ for binary system of species 1 and 2, x_1 can be taken as the single independent variable. An equivalent power series with certain advantages is known as the Redlich/Kister expansion (13):

$$\frac{G^E}{x_1 x_2 RT} = B + C(x_1 - x_2) + D(x_1 - x_2)^2 + \dots$$

In application, different truncations of this series are appropriate. For each particular expression representing $G^E / x_1 x_2 RT$, specific expressions for ln γ_1 and lnγ_2 result from application of Eq. (2).

For example, if D = 0, then

$$\frac{G^E}{x_1 x_2 RT} = B + C(x_1 - x_2)$$

and in this case $G^E / x_1 x_2 RT$ is linear in x_1. Multiplication of B by $x_1 + x_2$ (=1) gives

$$\frac{G^E}{x_1 x_2 RT} = B(x_1 + x_2) + C(x_1 - x_2)$$

or

$$\frac{G^E}{x_1 x_2 RT} = (B + C)\, x_1 + (B - C)\, x_2$$

Letting B + C = A_{21} and B - C = A_{12}, we have

$$\frac{G^E}{x_1 x_2 RT} = A_{21} x_1 + A_{12} x_2$$

The corresponding equation for the activity coefficients are

$$\ln\gamma_1 = x_2^2 [A_{12} + 2(A_{21} - A_{12})\, x_1]$$

$$\ln\gamma_2 = x_1^2 [A_{21} + 2(A_{12} - A_{21})\, x_2]$$

These are the Margules equations, which have been used in this project to evaluate the liquid phase activity coefficients. Another well-known equation is obtained when we write the reciprocal expression x_1x_2RT/G^E as a linear function of x_1. This equation is known as the van Laar equation. The Redlich/Kister expansion, the Margules equations, and the van Laar equations are all special cases of a very general treatment based on rational functions, i.e., on equations for G^E given by ratios of polynomials. They provide great flexibility in the fitting of vapor-liquid equilibrium (VLE) data for binary systems. However, they have scant theoretical foundation, and as a result there is no rational basis for their extension to multicomponent systems. Moreover, they do not incorporate an explicit temperature dependence for the parameters, though this can be supplied on an ad hoc basis.

Modern theoretical developments in the molecular thermodynamics of liquid-solution behavior are based on the concept of local composition. Within a liquid solution, local compositions, different from the overall mixture composition, are presumed to account for the short-range order and non random molecular orientations that result from differences in molecular size and intermolecular forces. One model of solution of behavior which uses this concept is the Wilson equation. The success of this equation in the correlation of VLE data prompted the development of alternative local-composition models, most notably NRTL (Non-Random-Two-Liquid) equation of Renon and Prausnitz. and the UNIQUAC (UNIversal QUAsi-Chemical) equation of Abrams and Prausnitz. A further significant development, based on the UNIQUAC equation is the UNIFAC method. The UNIFAC method for evaluation of activity coefficients depends on the concept that a liquid mixture may be considered a solution of the structural units (called the subgroups) from which the molecules are formed rather than a solution of the molecules themselves. While using these methods, however it must be kept in mind that they are approximate methods.

The following table gives the Henry's Constant for some organic compounds.

Table 2.1 Henry's Constants for Organic Compounds in water at 25 °C

Values from Ref 6 are at 20 °C
All values reported in atm-m3/mol except the ones
*means values evaluated using Margules equation by taking vapor to liquid mole fraction ratio

Compound	Ref[1]	Ref[2]	Ref[3]	Ref[4]	Ref[5]	Ref[6]	Ref[7]	UNIFAC
Chloromethane		8.26×10^{-3}	9.38×10^{-3}			8.0×10^{-3}		
Dichloromethane		2.48×10^{-3}	2.57×10^{-3}					2.58×10^{-3}
Chloroform		4.05×10^{-3}	3.75×10^{-3}			3.4×10^{-3}		4.04×10^{-3}
Carbon Tetrachloride		2.94×10^{-2}	1.97×10^{-2}			2.5×10^{-2}		2.96×10^{-2}
Bromomethane		6.78×10^{-3}	5.26×10^{-3}			9.3×10^{-2}		
Chloroethane		6.92×10^{-3}	1.13×10^{-2}					5.78×10^{-3}
1,1-Dichloroethane		5.87×10^{-3}	5.72×10^{-3}			5.1×10^{-3}		9.73×10^{-3}
1,2-Dichloroethane		1.18×10^{-3}	1.09×10^{-3}		1.1×10^{-3}	1.1×10^{-3}		1.21×10^{-3}
1,1,1-Trichloroethane			2.76×10^{-2}		4.9×10^{-3}	3.6×10^{-3}		8.41×10^{-3}
1,1,2-Trichloroethane		9.61×10^{-4}	1.18×10^{-3}			7.8×10^{-4}		1.20×10^{-3}
1,1,2,2-Tetrachloroethane		3.30×10^{-4}	4.74×10^{-4}		4.2×10^{-4}	4.2×10^{-4}		1.45×10^{-3}
Hexachloroethane		2.24×10^{-2}				1.1×10^{-3}		
1,1-Dichloroethylene		2.29×10^{-2}	0.131			0.17		
1,2-Transdichloroethylene		6.67×10^{-3}				5.7×10^{-3}		
Trichloroethylene		1.17×10^{-2}	1.16×10^{-2}			1.0×10^{-2}		
Tetrachloroethylene		2.69×10^{-2}	2.27×10^{-2}			2.3×10^{-2}		
1,2-Dichloropropane		2.67×10^{-3}			2.8×10^{-3}	2.0×10^{-3}		2.4×10^{-3}
n-Butyl alcohol	8.90×10^{-6}							8.47×10^{-6}
1,3-Butadiene	0.142	7.13×10^{-2}	7.36×10^{-2}					1.02×10^{-2}
Vinyl chloride		2.24×10^{-2}	2.32×10^{-2}			6.4		
Acrylonitrile					6.3×10^{-5}	6.3×10^{-5}		
Bis(2-chloroisopropyl)ether						1.1×10^{-4}		4.53×10^{-4}
Benzene		5.57×10^{-3}	5.55×10^{-3}		6.0×10^{-3}	4.6×10^{-3}		5.79×10^{-3}

Table 2.1 (continued) Henry's Constants for Organic Compounds in water at 25 °C

Values from Ref 6 are at 20 °C

All values reported in atm-m3/mol except the ones with *

*means values evaluated using Margules equation by taking vapor to liquid mole fraction ratio

Compound	Ref[1]	Ref[2]	Ref[3]	Ref[4]	Ref[5]	Ref[6]	Ref[7]	UNIFAC
Chlorobenzene		4.54×10^{-3}	3.45×10^{-3}			4.0×10^{-3}		2.9×10^{-3}
1,2-Dichlorobenzene		2.95×10^{-3}	1.88×10^{-3}		1.9×10^{-3}	1.7×10^{-3}		1.2×10^{-3}
1,3-Dichlorobenzene		3.24×10^{-3}	3.55×10^{-3}		2.6×10^{-3}	2.7×10^{-3}		1.35×10^{-3}
1,4-Dichlorobenzene		4.33×10^{-3}	1.60×10^{-3}			2.1×10^{-3}		1.20×10^{-3}
1,2,4-Trichlorobenzene								5.48×10^{-4}
Hexachlorobenzene		0.412	4.93×10^{-5}					7.36×10^{-8}
Nitrobenzene					2.4×10^{-5}	1.1×10^{-5}		2.62×10^{-5}
Phenol	4.54×10^{-7}				1.3×10^{-6}	2.7×10^{-7}		4.02×10^{-7}
2-Chlorophenol						2.1×10^{-5}		
2,4-Dichlorophenol						4.2×10^{-5}		
Pentachlorophenol						2.1×10^{-6}		
2-Nitrophenol						7.6×10^{-5}		5.76×10^{-7}
Toulene	6.68×10^{-3}	6.36×10^{-3}	6.61×10^{-3}			5.7×10^{-3}		4.87×10^{-3}
2,4-Dimethylphenol				5.9×10^{-7}				2.59×10^{-6}
4,6-Dinitro-o-cresol						1.7×10^{-7}		
Ethylbenzene		8.04×10^{-3}	7.90×10^{-3}			5.7×10^{-3}		6.69×10^{-3}
Dimethyl phthalate						4.2×10^{-7}		3.46×10^{-7}
Diethyl phthalate				1.7×10^{-5}				9.72×10^{-7}
Di-n-butyl phthalate						6.3×10^{-5}		1.42×10^{-9}
Bis (2-ethylhexyl) phthalate				1.2×10^{-7}				
Naphthalene	1.18×10^{-3}	1.23×10^{-3}	4.24×10^{-4}			3.6×10^{-4}		2.60×10^{-4}
Anthracene			5.92×10^{-5}			1.4×10^{-3}		2.13×10^{-4}
Phenanthrene			3.95×10^{-5}					6.68×10^{-4}

Table 2.1 (continued) Henry's Constants for Organic Compounds in water at 25 $^{\circ}$C

Values from Ref 6 are at 20 $^{\circ}$C

All values reported in atm-m3/mol except the ones with *

*means values evaluated using Margules equation by taking vapor to liquid mole fraction ratio

Compound	*	Ref[8]	Ref[3]	Ref[4]	Ref[5]	Ref[6]	Ref[7]	UNIFAC
Pyrene			1.18×10^{-5}	1.3×10^{-6}				7.0×10^{-23}
1,2-Benzanthracene			1.38×10^{-4}	1.2×10^{-7}				
3,4-Benzopyrene			4.4×10^{-10}					
Fluoranthene			2.17×10^{-3}	1.0×10^{-5}				3.8×10^{-18}
Isophorone						4.2×10^{-6}		4.6×10^{-5}
Acenaphthene			2.37×10^{-4}			1.9×10^{-4}		5.02×10^{-4}
Acrolein						9.7×10^{-5}		9.55×10^{-5}
Chrysene				1.5×10^{-6}				
Fluorene			8.39×10^{-5}					1.05×10^{-3}
Aldrin			2.76×10^{-5}			2.1×10^{-3}		
Dieldrin			1.09×10^{-6}			1.7×10^{-7}		
Chlordane							3.64×10^{-3}	
4,4 DDT			5.23×10^{-5}			3.4×10^{-5}	9.52×10^{-4}	
Heptachlor						2.3×10^{-3}		
Alpha BHC						2.0×10^{-3}		
Beta BHC						1.1×10^{-2}		
PCB 1242 / Arochlor		3.43×10^{-4}				4.9×10^{-4}		
PCB 1221 / Arochlor		2.28×10^{-4}						
PCB 1248 / Arochlor		4.40×10^{-4}				3.0×10^{-3}		
PCB 1260 / Arochlor		3.36×10^{-4}				6.1×10^{-3}		
Toxaphene						6.3×10^{-2}		
Methanol	0.314							
Acetone	2.02							
DMSO	1.53×10^{-3}							

CHAPTER 3

EXPERIMENTAL METHOD

The experimental portion of the project consisted of verification of Henry's constant and determination of volatilization rates of the targeted compounds from water solutions under a number of different scenarios. These experiments used different amounts of stirring and aeration in order to simulate the range of conditions possible in practice.

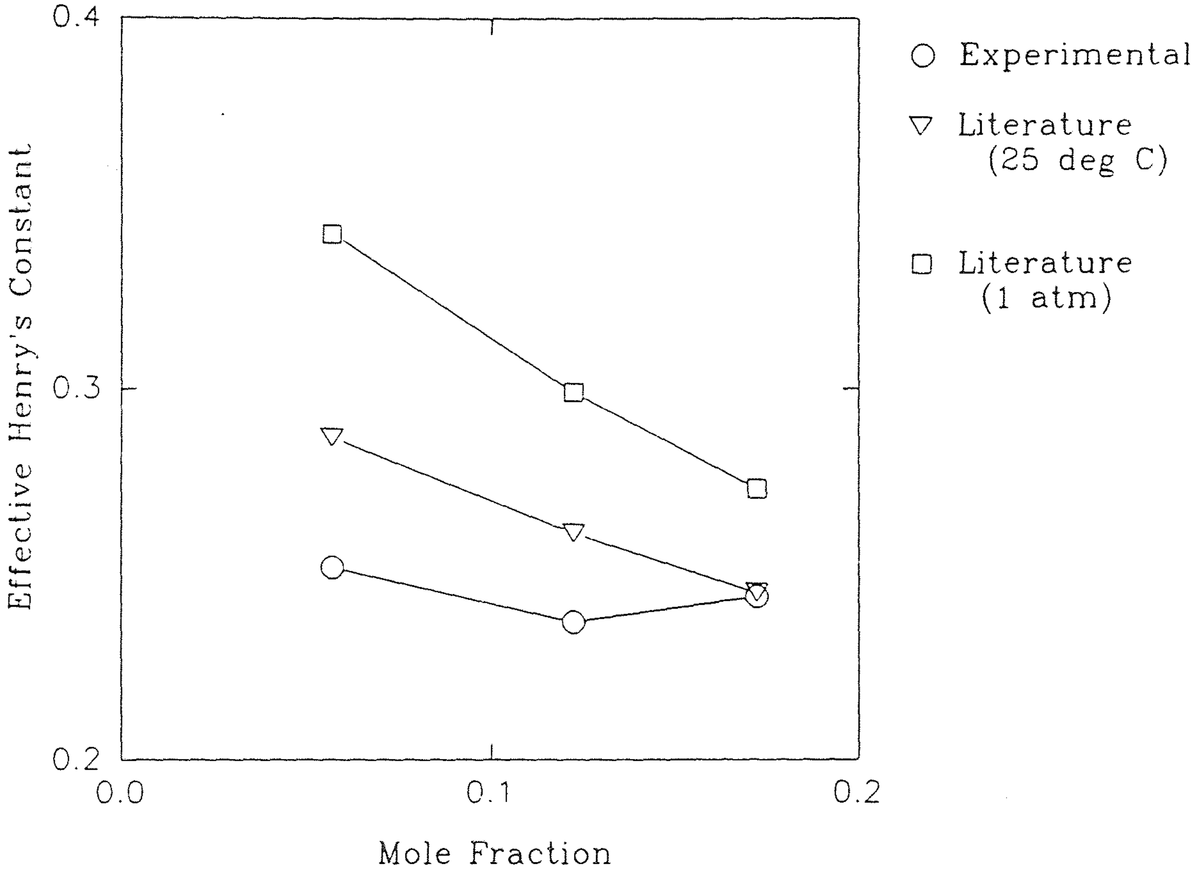
Verification of Henry's Constant was studied for methanol. For determining the Henry's Constant three different concentrations of aqueous methanol solution were prepared and were kept in sealed serum bottles, each having about 50 percent of head space for the vapors. A time period of 7 days was given to make sure that vapor-liquid equilibrium is achieved. After about a week the vapor and liquid concentrations were measured separately using gas chromatography.

A typical experiment for all the compounds consisted of placing an amount of water with a known composition of the organic compound into an open 1000 ml beaker. The beaker was then subjected to the chosen treatment. such as aeration through a diffusion stone with a measured air rate or stirring at known rate. For the sake of comparison, a control beaker (no aeration or stirring) was also kept for the same duration of time. Samples of the solution were taken at various times over the course of a couple of hours or days depending on its volatilization rate. Also noted were the change in volume of the solution. Chemical analysis of the samples then yielded the compositions, and a material balance gave the amount that had volatilized.

Chemical analysis was done using Varian 3400 gas chromatography equipment. Carrier gas (nitrogen) was maintained at a flow rate of 25-30 ml/min for methanol and acetone; and 35 ml/min for Dimethyl sulfoxide. Injector temperature for methanol and acetone was 150°C, and for DMSO was 250°C. The column temperature for methanol and acetone was about 55°C, and for DMSO was 215°C.The detector temperature for all the three compounds was maintained at 250°C. For the detector, the hydrogen flowrate was 30 ml/min and the air flowrate was 300 ml/min.

To study the effect of free surface area, solutions were treated in cylinders (minimum free surface area), beakers and open pans (maximum free surface area). Further, the effect of the shape of equipment on the rate of volatilization was studied. For this, comparison was made on the volatilization rates from beakers and conical flasks.

Graph 4.1.1 Effective Henry's Constant for Methanol



CHAPTER 4

RESULTS AND DISCUSSION

4.1 Methanol

Following are the results for Henry's constant for three different concentrations:

4.1.1 Results for the Effective Henry's Constant

Table 4.1.1 Effective Henry's Constants

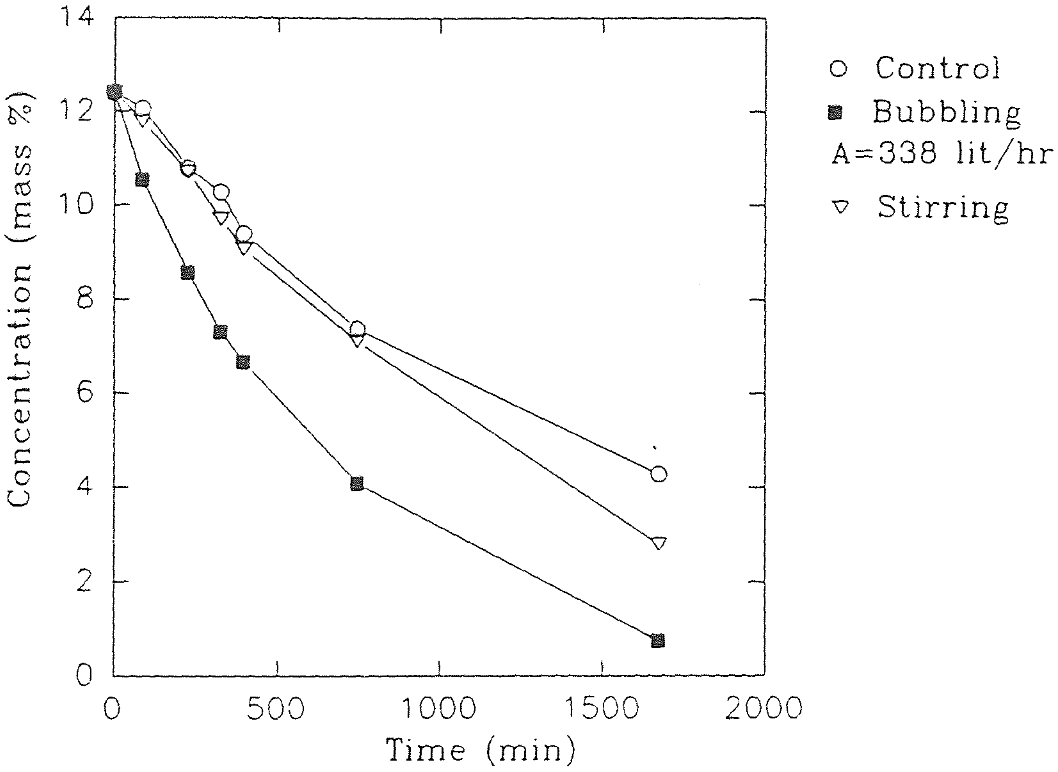
Liquid Mole Fraction	Experiment	Literature (25 °C)	Literature (1 atm)
0.0568	0.252	0.287	0.342
0.1225	0.237	0.261	0.299
0.1725	0.244	0.245	0.273

The experimental values have been found by determining the liquid and vapor phase mole fraction, and dividing the vapor phase mole fraction by the liquid phase mole fraction. The theoritical Henry's constant values have been found using the Margules equation at constant temperature (25^{o}C) and at constant pressure (1 atm). The experimental Henry's Constant values verify, within experimental error range, the ones obtained from the literature.

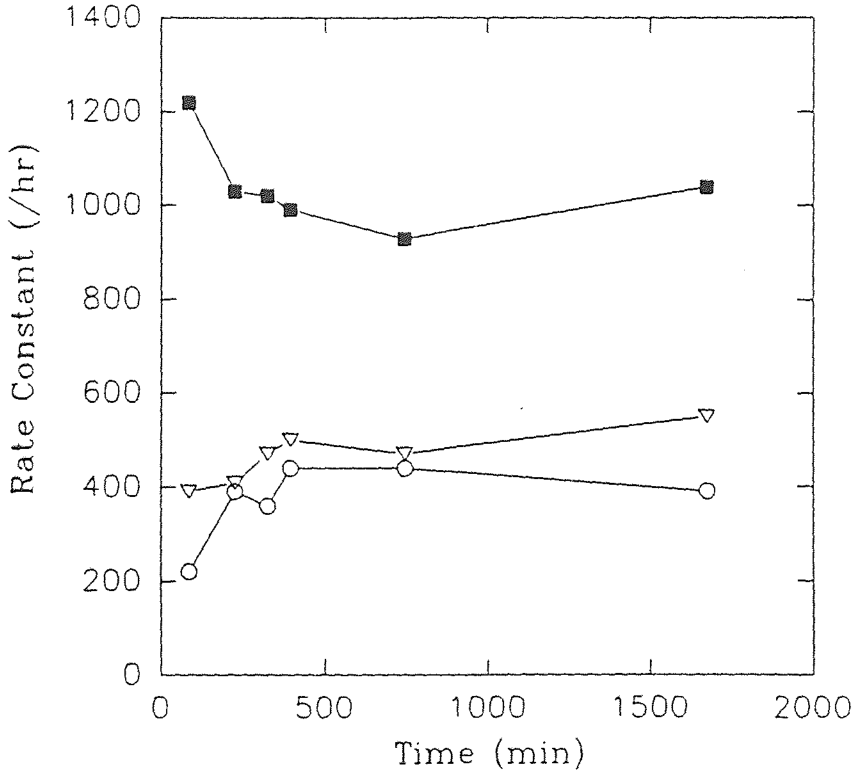
The following data shows the volatilization results of methanol for the typical experimental set up described in chapter 3. For every table with suffix 'a',

4.1.2 Aeration and Stirring Results (Methanol in beakers)

Graph 4.1.2a Concentration(mass %) With Time (min)



Graph 4.1.2b Rate Constant (/hr) with Time (min)



which shows mass percent change with time, there is a corresponding table with suffix 'b'. The 'b' table presents the experimental rate constants evaluated using the data in the corresponding 'a' table. The 'b' table also shows theoretical values of the rate constants in parantheses, evaluated assuming equilibrium (discussed below). Corresponding to each table is a graph with the same number as the table.

4.1.2 Stirring and Aeration Results (All Beakers)

Table 4.1.2a Concentration (mass percent) trend with Time (min)

Time (min)	Control	Stirring - Beaker	Bubbling - Beaker A = 340 lit/hr
0	12.4	12.4	12.4
85	12.1	11.8	10.5
225	10.8	10.7	8.6
325	10.3	9.7	7.3
395	9.4	9.1	6.7
745	7.4	7.1	4.1
1675	4.3	2.8	0.7

Table 4.1.2b Rate Constant (/hr) trend with Time (min)

Time (min)	Control	Stirring - Beaker	bubbling - Beaker A = 340 lit/hr
85	220	390	1220 (1530)
225	390	410	1030 (1650)
325	360	470	1020 (1800)
395	440	500	990 (1860)
745	440	470	930 (2050)
1675	390	550	1040 (2760)

The values reported for the rate constants have been multiplied by 10000 hr.

The data presented above are a representative data for methanol in the cases of control, stirring, and bubbling. More tables for stirring and different rates of aeration have been included in the appendix A-1.

The absolute maximum volatilization rate for a contaminant can be determined by assuming that the gas phase is saturated with the contaminant. If so, then thermodynamic equilibrium exists between the gas and liquid phases. For a sufficiently dilute component, this equilibrium is described by Henry's Law; if not, then it can be described by an "effective" Henry's Law, as described earlier. In the latter (more general) case, we would thus have:

$$\frac{y_i P}{x_i} = H_{i,j}^{eff} = \gamma_i (LR) P_i^{sat} \qquad (4)$$

Again, as the composition becomes ever more dilute, each of these quantities becomes the true Henry's Law constant. Written in this form, however, the equation has general validity at low pressures, and the activity coefficient can be estimated by standard methods such as using the Margules equation, the van Laar equation or UNIFAC. If one prefers to use experimental values for Henry's constant while not neglecting the composition dependence of the activity coefficient, then the following form can be used:

$$\frac{y_i P}{x_i} = H^{eff}_{i,j} = \frac{\gamma_i(LR)}{\gamma_i^{\infty}(LR)} H_{i,j} \qquad (5)$$

In the above equation, both the actual activity coefficient and its value at infinite dilution can be estimated by one of the standard methods discussed above, while still using a measured value of the Henry's Law constant.

The system used can be considered as a semi-batch reactor. The dry air enters the reactor, which contains the aqueous solution of the contaminant, and carries with it water and the contaminant. The flowrate of the air has been calculated using a calibrated rotameter. The following material balance can be written for the contaminant leaving the system, which is also the rate of volatilization of the contaminant.

$$-\frac{d(x_i \rho_L V)}{dt} = y_i \rho_v A$$

where V is the volume of the liquid solution, A is the flowrate of the gas phase, and ρ_L, and ρ_V are the molar densities of the two phases. Substituting y_i from (4) or (5), assuming ρ_L and V to be constant.

$$-\frac{d x_i}{dt} = \frac{\rho_v A x_i \gamma_i(LR) P_i^{sat}}{\rho_v VP} = \frac{\rho_v A x_i \gamma_i(LR) H_{i,j}}{\rho_L V \gamma_i^{\infty}(LR) P}$$

Further assuming that the densities, aeration rate, liquid volume and activity coefficient remain constant, the equation may readily be solved by integration to give,

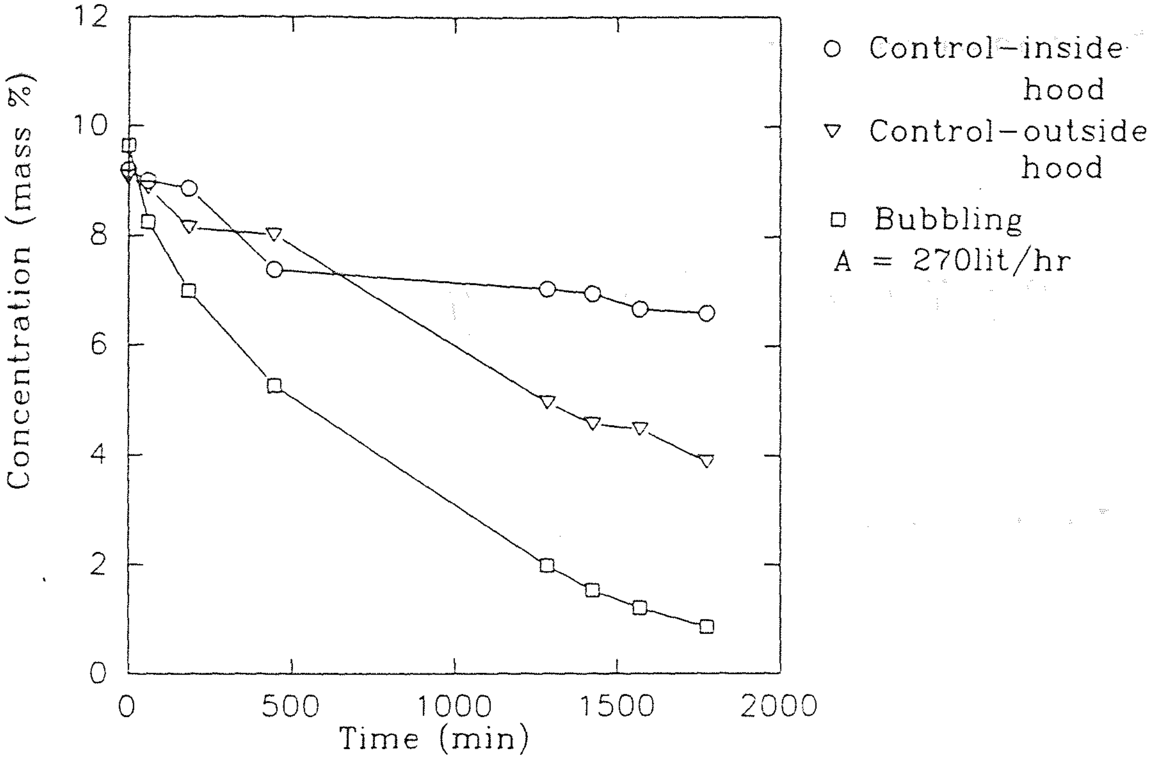
$$\ln\left[\frac{x_{io}}{x_i}\right]=\left[\frac{\rho_V A}{\rho_L V}\right]\left[\frac{\gamma_i (LR) P_i^{sat}}{P}\right]\Delta t=\left[\frac{\rho_V A}{\rho_L V}\right]\left[\frac{\gamma_i (LR) H_{i,j}}{\gamma_i^{\infty} (LR) P}\right]\Delta t$$

The above equation assumes that over small time increments all of the variables, except x_i,are constant. This gives first-order disappearance of the contaminant. In reality, the activity coefficient changes with composition, usually increasing with decreases in composition. The other variable is the volume of the solution, which will also decrease with time because the solvent (water) evaporates with time. Thus the change of both of these variables with time will cause the VOC to disappear from the solution a little faster than what will be predicted by the first order kinetics. In the above equation, the factors multiplied by the Δt represent the pseudo-first order rate constant for the volatilization of a contaminant, assuming that thermodynamic equilibrium exists between the liquid and the vapor phases.

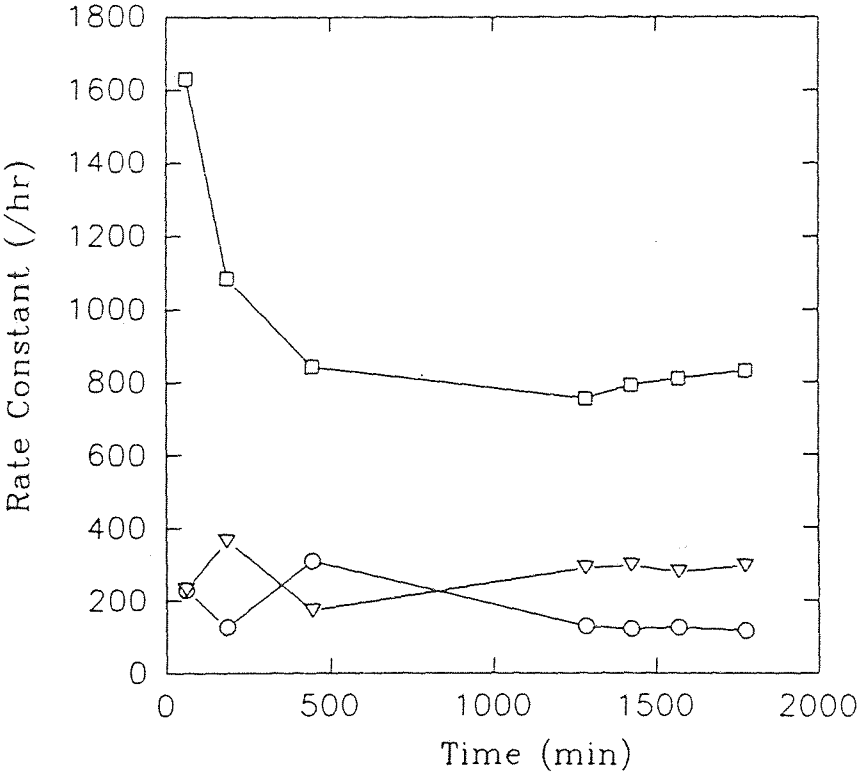
It is seen from the results obtained that the experimental volatilization rate is always less than the corresponding calculated (theoretical) rate constants for the bubbling (aerated) systems. This shows that at no point during bubbling is

4.1.3Hood Contribution to the Volatilization Rate (Beakers)

Graph 4.1.3a Concentration (mass %) with Time (min)



Graph 4.1.3b Rate Constant (/hr) with Time (min)



equilibrium achieved for the aerated systems. Stirring increases volatilization rate 1.5-2 times compared to the control. But, since stirring gives lesser turbulence than bubbling, therefore the experimental rate constants for stirring are less than aeration. As expected, the control has the lowest experimental rate constant. All of these experiments were carried inside the hood in the laboratory.

4.1.3 Hood Contribution to the Volatilization Rate (All Beakers)

Table 4.1.3a Concentration (mass percent) trend with Time (min)

Time	Control - outside hood	Control - inside hood	Bubbling A = 270lit / hr
0	9.2	9.07	9.65
60	9.02	8.87	8.25
185	8.86	8.14	6.99
445	7.38	8.02	5.27
1285	7.06	4.98	1.99
1425	6.97	4.58	1.53
1570	6.69	4.49	1.21
1775	6.61	3.89	0.86

Table 4.1.3b Rate Constant (/hr) trend with Time (min)

Time (min)	Control - outside	Control - inside	Bubbling A = 270 lit / hr
60	229	232	1631 (1161)
185	127	365	1085 (1233)
445	308	172	842 (1333)
1285	128	289	753 (1674)
1425	121	296	790 (1704)
1570	126	277	808 (1792)
1775	115	294	831 (1913)

The values reported for the rate constants have been multiplied by 10000 hr.

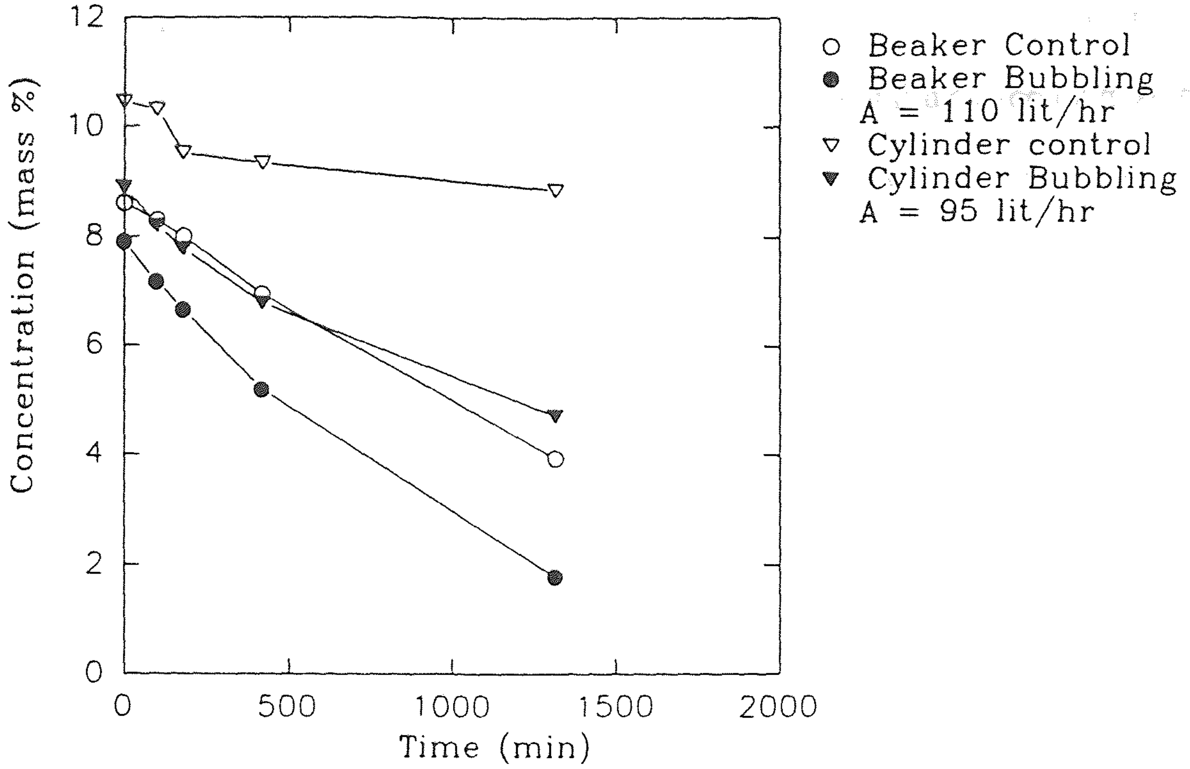
Volatilization inside the hood is the extreme scenario because there is a continuous overflow of air inside the hood. Therefore we can expect the maximum possible rate constants of methanol. To study the contribution of hood to the volatilization rate, the above experiment was conducted. It is evident from the above data that the experimental value of the rate constant for volatilization from control outside the hood is less than 50% of the one outside the hood.

4.1.4. Aeration Results (Different Free Surface Area)

The following data represent the effect of the free surface area (surface area of the methanol aqueous solution in the container exposed to air) on the rate of volatilization of methanol for bubbling. Each of the containers has the same volume of the aqueous solution of methanol. But obviously, the cylinder provides the least surface area, about 16 sq. cm, beaker provides about 100 sq. inches and the pan provides the maximum, about 740 sq. cm). All these containers have almost the same initial concentration, very close air bubbling rate and same initial volume. Also, all these containers were kept inside the hood. Therefore, by keeping all these parameters the same or very close to each other, attempt was made to find the effect of exposed surface area on the rate of volatilization. Following are representative data for the effect of free surface area on volatilization of VOCs. More data have been included in Appendix A-2

4.1.4 Aeration Results (Methanol-Different Free Surface Area)

Graph 4.1.4a Concentration(mass%) with Time (min)



Graph 4.1.4b Rate Constant (/hr) with Time (min)

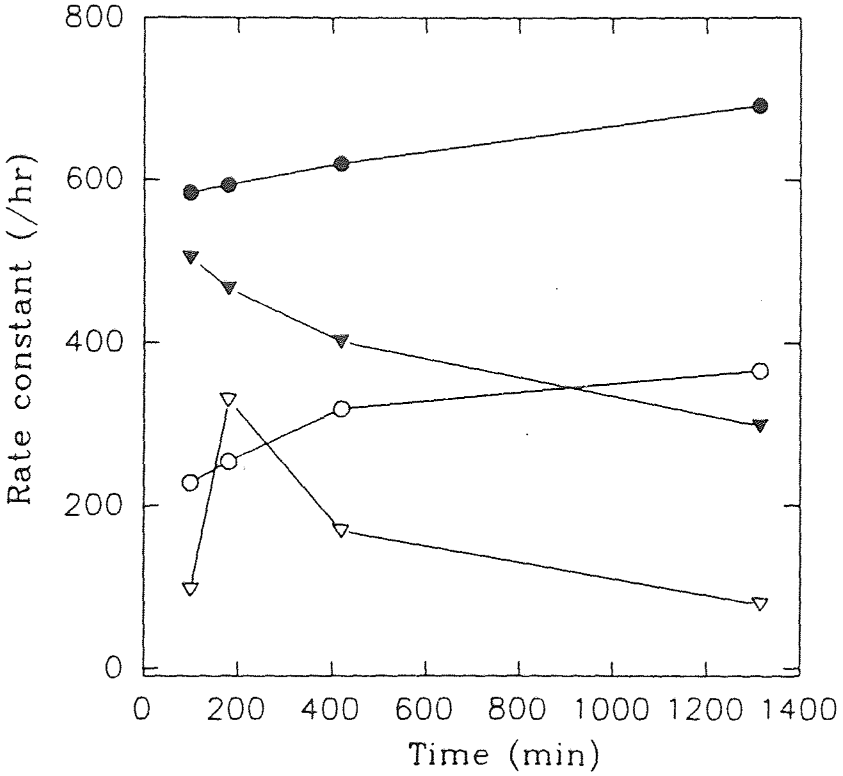


Table 4.1.4a Concentration (mass percent) trend with Time (min)

Time (min)	Beaker-Control	Beaker-Bubbling	Cylinder Control	Cylinder Bubbling
0	8.61	7.9	10.45	8.89
100	8.3	7.17	10.29	8.2
180	8.0	6.65	9.51	7.77
420	6.94	5.18	9.33	6.78
1315	3.94	1.78	8.87	4.71

Table 4.1.4b Rate Constant (/hr) trend with Time (min)

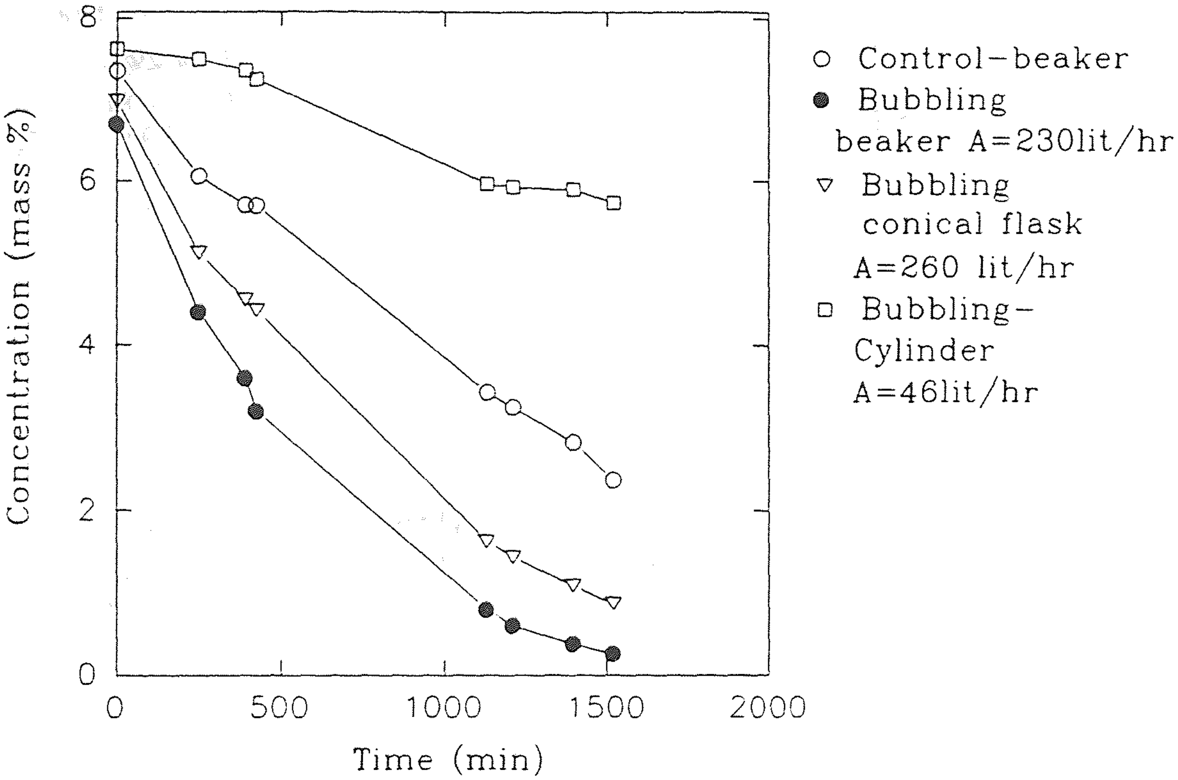
Time (min)	Beaker - Control	Beaker-Bubbling (A=110 lit/hr)	Cylinder - Control	Cylinder - Bubbling (A = 95 lit /hr)
100	229	584	97	504
		(852)		(719.2)
180	254	593	329	466
		(868)		(729.8)
420	319	620	169	401
		(919)		(760.13)
1315	366	692	78	298
		(1125)		(869.5)

The values reported for the rate constants have been multiplied by 10000 hr.

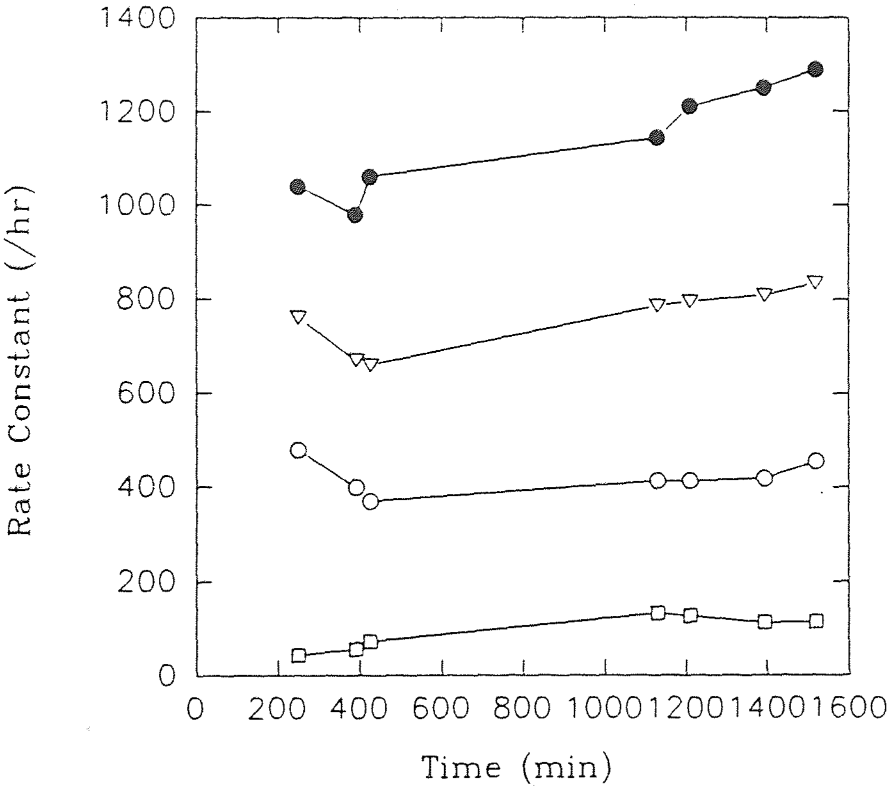
Normally, one would expect the cylinder to have the maximum rate of volatilization. Since all the containers have the same initial volume, the residence time for the bubbles in the solution is greatest in the case of the cylinder and lowest in the case of the pan. This would give the bubbles a chance to carry more methanol to the surface. But it is observed that the pan has the maximum rate of volatilization, the beaker has a lower rate and the cylinder has the lowest rate. This shows that the free surface area has a more dominant role to play. More VOC is available at the surface to escape the solution, if the surface area exposed to air is more, which increases the rate of volatilization.

4.1.5 Aeration (Methanol-Different Surface & Shape)

Graph 4.1.5a Concentration (mass%) with Time (min)



Graph 4.1.5b Rate Constant (/hr) with Time (min)



4.1.5 Aeration Results (Different Free Surface Area and Different Shape)

Table 4.1.5a Concentration (mass percent) trend with Time (min)

Time	Control beaker	Bubbling beaker A = 230 lit/hr	Bubbling conical flask A = 260 lit/hr	Bubbling cylinder A = 46lit/hr
0	7.35	6.7	6.98	7.62
250	6.06	4.4	5.12	7.49
390	5.71	3.6	4.55	7.36
425	5.7	3.2	4.42	7.25
1130	3.44	0.8	1.63	5.98
1210	3.26	0.6	1.44	5.94
1395	2.83	0.38	1.09	5.91
1520	2.37	0.26	0.87	5.75

Table 4.1.5b Rate Constant (/hr) trend with Time (min)

Time (min)	Control beaker	Bubbling Beaker A = 230 lit/hr	Bubbling conical flask A = 260 lit /hr	Bubbling cylinder A = 46 lit/hr
250	478	1040 (1510)	760 (1690)	43 (279)
390	399	980 (1570)	670 (1858)	56 (283)
425	370	1060 (1570)	660 (1862)	73 (283)
1130	413	1143 (2003)	786 (2268)	133 (299)
1210	413	1210 (2140)	795 (2310)	127 (303)
1395	419	1250 (2180)	808 (2320)	113 (303)
1520	455	1290 (2220)	834 (2370)	114 (303)

The values reported for the rate constants have been multiplied by 10000 hr.

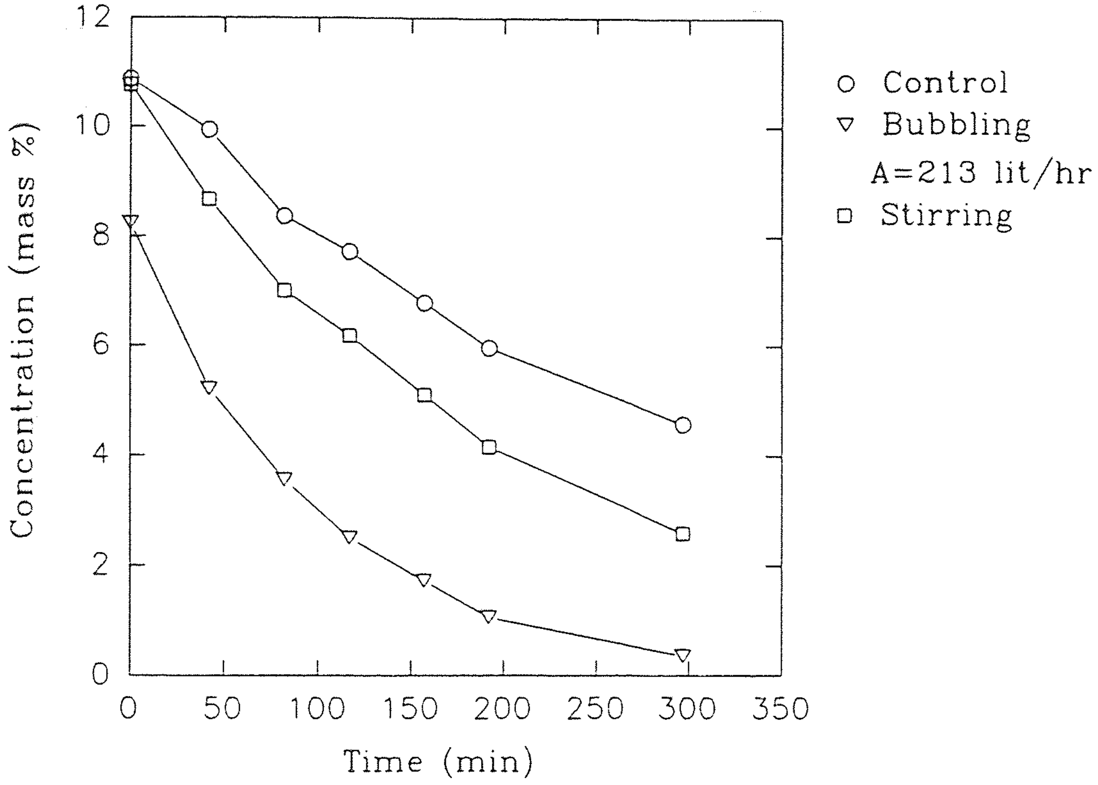
To study the effect of the shape of the equipment on the rate of volatilization, the above results were obtained. Here a conical flask was taken along with the beaker and the cylinder. The conical flask has almost the same rate of bubbling, rather more, as the beaker and same volume of solution (450 ml). But the free surface area in the case of the conical flask, for the volume taken (450 ml), is more than the beaker. The results show that the rate of volatilization is greater for the beaker than for the conical flask even though the rate of bubbling and the free surface area are larger for the conical flask. This can happen because the shape of the conical flask is such that it tapers with the height. This makes the area available for the saturated air to get carried away by the fresh air flowing at the mouth of the flask very much less. Thus the amount of VOC laden air replaced by the fresh ,VOC free air, is more in case of the beaker, which allows more VOC to volatilize into the fresh air so as to make up for the depleted VOC. That is, convective mass transfer in the vapor phase is greater in the case of the beaker (wide mouth container) than the conical flask.

4.2 Acetone

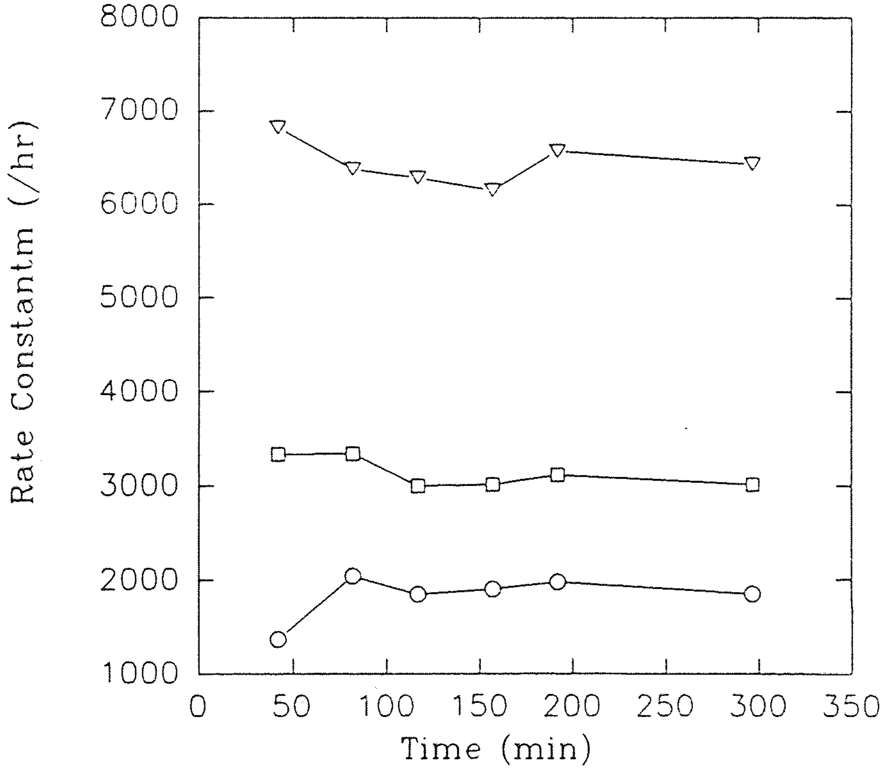
The two methyl groups in the structure of acetone affect its solubility in water. As an indication of this, its infinite dilution activity coefficient in water is 9.3 (as compared to 2.3 for methanol). It has a higher vapor pressure than methanol (0.304 atm as compared to 0.17 atm for methanol). Therefore, the higher activity coefficient results in a higher Henry's constant than methanol, which should

4.2.1 Aertion and Stirring (Acetone in Beakers)

Graph 4.2.1a Concentration (mass %) with Time (min)



Graph 4.2.1b Rate Constant (/hr) with Time (min)



correspondingly increase the volatilization rate. But the difference in the properties of methanol and acetone (as discussed above) is not that much. Therefore a close resemblance is expected between the results of these two compounds.

Results from one of the experiments for the volatilization of acetone are presented in the following tables and graphs.

4.2.1 Aeration and Stirring Results (All Beakers)

Table 4.2.1a Concentration (mass percent) trend with Time (min)

Time (min)	Control	Stirring	Bubbling A = 213 lit / hr
0	10.87	10.77	8.24
42	9.94	8.67	5.22
82	8.37	7.02	3.56
117	7.74	6.21	2.52
157	6.81	5.12	1.72
192	5.98	4.17	1.06
297	4.57	2.58	0.36

Table 4.2.1b Rate Constant (/hr) trend with Time (min)

Time (min)	Control	Stirring	Bubbling A = 213 lit / hr
42	1370	3330	6820 (7131)
82	2040	3340	6380 (7510)
117	1850	3000	6290 (7667)
157	1900	3010	6160 (7797)
192	1980	3120	6580 (7902)
297	1850	3010	6440 (8385)

All the reported values for the rate constants have been multiplied by 10000 hr.

More experimental results for aeration and stirring for acetone are included in the Appendix B-1. With these experiments, its observed again that stirring increases the rate by 1.5-2 times. Aeration promotes volatilization, but equilibrium is certainly not reached. This can be seen by comparing the aeration rate constant to the theoretical value which assumes that equilibrium is reached.

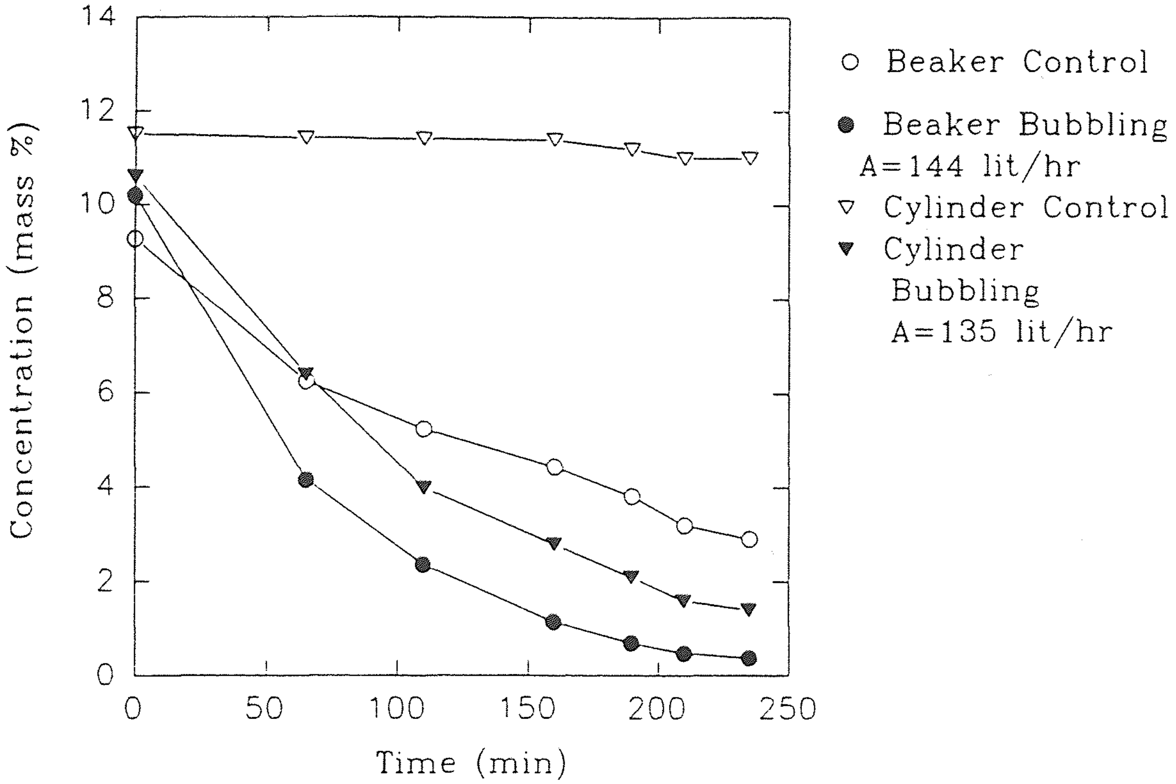
4.2.2 Aeration Results (Different Free Surface Area)

Again, to study the effect of the free surface area on the rate of volatilization, other parameters (initial volume, rate of aeration, initial concentration and hood contribution) were kept as close to each other as possible. It is very difficult to maintain the same aeration rate for beaker and cylinder because of the difference in calibration of the two rotameters The same trend was observed as in the case of methanol. That is, an increase in the free surface area (from cylinder to beaker) increases the rate of volatilization.

Also, at increased surface area (beaker) the increase in the rate constant from control to bubbling is not that much (3-4 times) as it is for lower surface area (75-90 cylinder). This indicates that at increased free surface area, diffusion mass transfer does not play a very determining role in the volatilization of acetone. This can be observed again in the following representative data. More experimental results to study the effect of free surface area have been included in the Appendix B-2.

4.2.2Aeration Results for Acetone (Different Surface Areas)

Graph 4.2.2a Concentration (mass %) with Time (min)



Graph 4.2.2b Rate Constant (/hr) with Time (min)

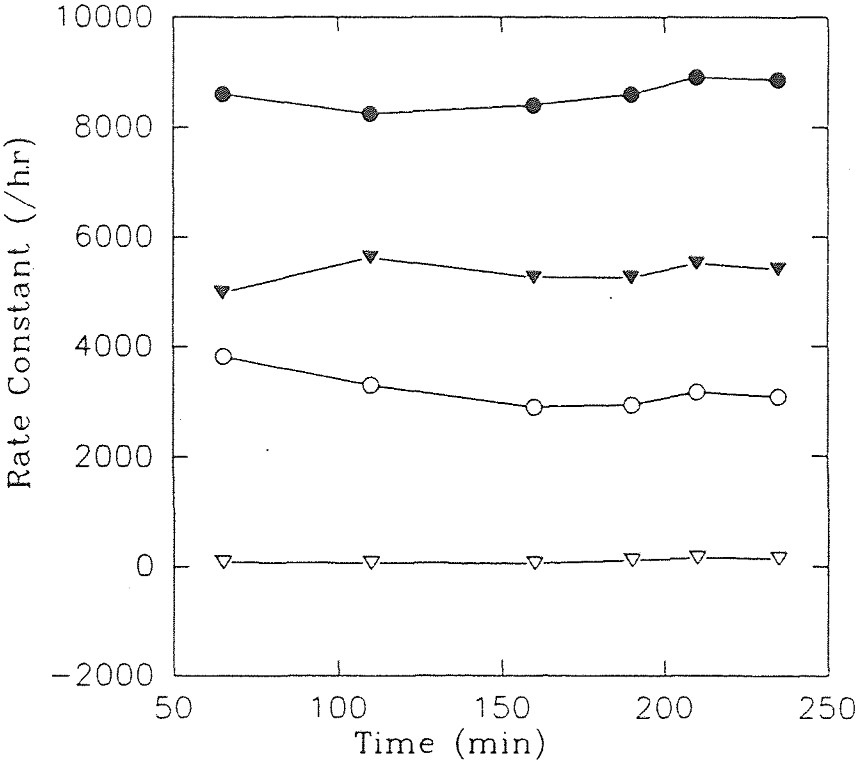


Table 4.2.2a Concentration (mass percent) trend with Time (min)

Time (min)	Beaker-Control	Beaker-Bubbling (A = 144 lit / hr)	Cylinder Control	Cylinder Bubbling (A = 135 lit / hr)
0	9.27	10.2	11.5	10.6
65	6.26	4.17	11.42	6.4
110	5.25	2.37	11.41	4.0
160	4.45	1.15	11.41	2.8
190	3.82	0.71	11.2	2.1
210	3.21	0.48	11.0	1.6
235	2.91	0.34	11.0	1.4

Table 4.2.2b Rate Constant (/hr) trend with Time (min)

Time (min)	Beaker - Control	Beaker-Bubbling (A = 144 lit / hr)	Cylinder - Control	Cylinder - Bubbling (A = 135 lit / hr)
65	3825	8611 (8813)	78.2	4984 (7165)
110	3288	8251 (9597)	49.9	5627 (7989)
160	2884	8403 (10171)	34.3	5258 (8313)
190	2926	8604 (10440)	100.8	5254 (8417)
210	3158	8913 (10488)	153	5523 (9068)
235	3077	8870 (10706)	137	5409 (9117)

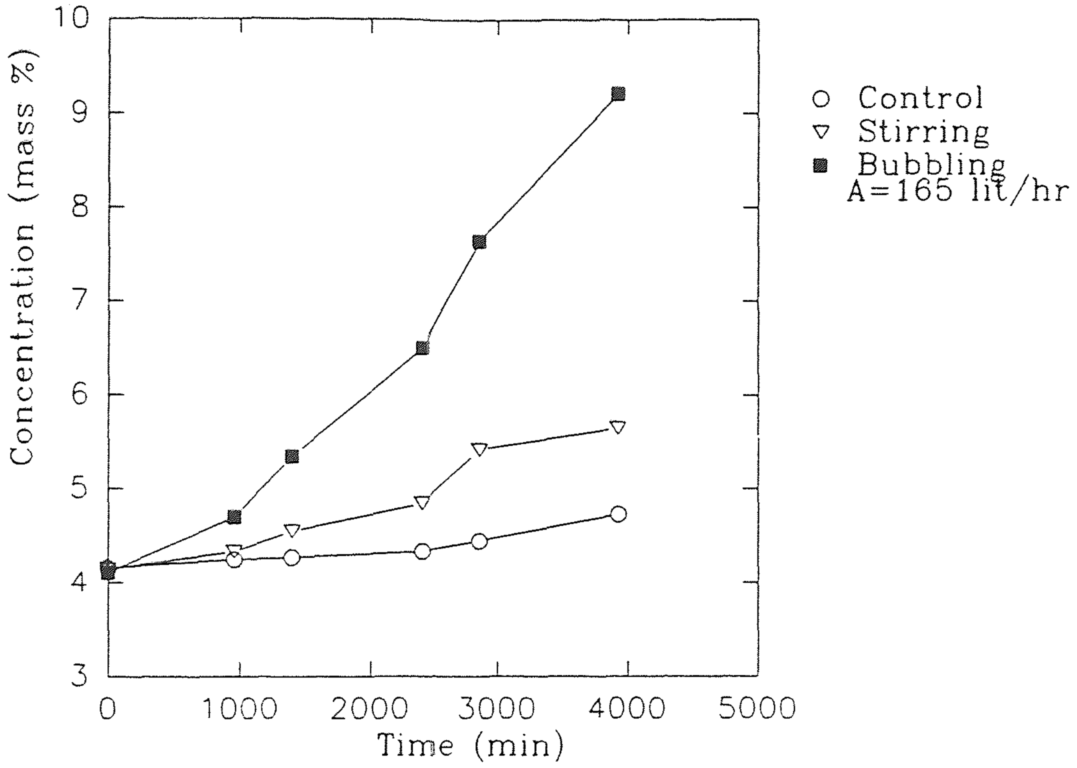
The values reported for the rate constants have been multiplied by 10000 hr.

4.3 Dimethyl sulfoxide (DMSO)

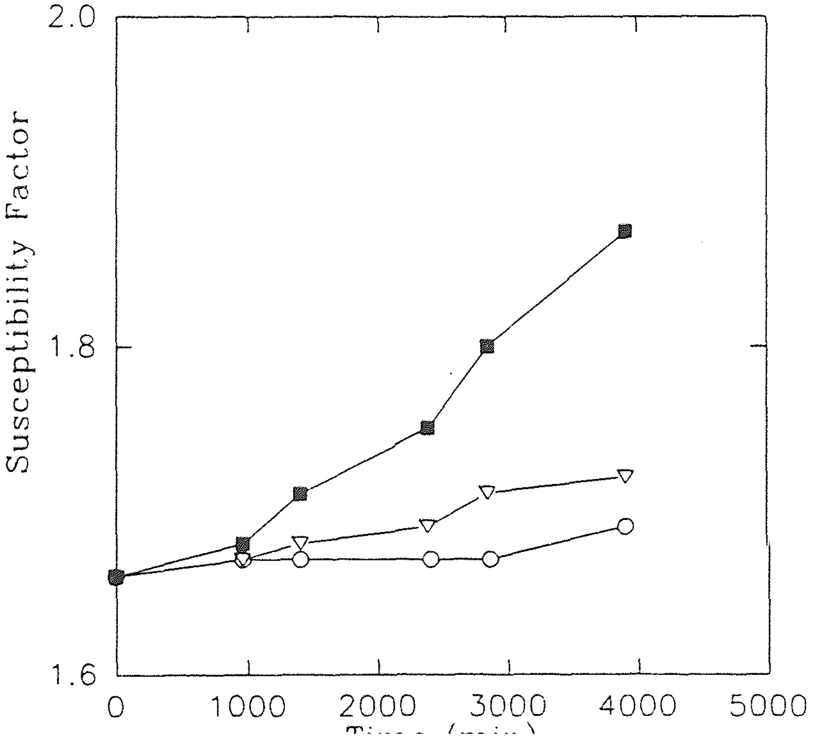
DMSO has a very low activity coefficient (less than 1) indicating that its an associative system. As a result, its Henry's constant in water is small. Also, its pure component vapor pressure is very small (0.6 mm Hg). These factors suggest that the volatilization of DMSO must be negligible. Following are the results for the volatilization of DMSO. Here, instead of rate constants, the tables

4.3.1 Aeration and Stirring (DMSO in Beakers)

Graph 4.3.1a Concentration (mass %) with Time



Graph 4.3.1b Susceptibility Factor with Time (mir



and graphs with suffix 'b' depict the behavior of the volatilization susceptibility factor (for definition, see below) with time. Following is the data from one of the experiments for stirring and aeration scenarios. More data have been included in the Appendix C.

4.3.1 Stirring and Aeration Results (All Beakers)

Table 4.3.1a Concentration (mass percent) trend with Time (min)

Time (min)	Control	Stirring	Bubbling A = 221 lit/hr
0	4.162	4.14	4.11
960	4.253	4.33	4.70
1400	4.268	4.55	5.34
2400	4.327	4.84	6.50
2860	4.441	5.41	7.65
3925	4.727	5.64	9.21

Table 4.3.1a Susceptibility Factor trend with Time (min)

Time (min)	Control	Stirring	Bubbling A = 221 lit/hr
0	1.66	1.66	1.66
960	1.67	1.67	1.68
1400	1.67	1.68	1.71
2400	1.67	1.69	1.75
2860	1.67	1.71	1.80
3925	1.69	1.72	1.87

The values for the susceptibility factor have been multiplied by a factor of 1000.

From the results, it is evident that an aqueous solution of DMSO gets concentrated over time, whether it is a control, stirring or aeration scenario. This shows that water evaporates faster than DMSO. Hence DMSO can not be stripped from its aqueous solution, no matter how long it is left. For the volatilization of DMSO, the same material balance can be written:

$$\frac{d(x_i \rho_L V)}{dt} = -y_i \rho_v A \qquad (6)$$

Here the volume V is not a constant. The water evaporates with an attempt to establish an equilibrium between the liquid and the vapor phase. That is for water:

$$y_2 \hat{\phi}_2 P = x_2 \gamma_2 P_2^{sat}$$

and for DMSO:

$$y_1 \hat{\phi}_1 P = x_1 \gamma_1 P_1^{sat}$$

Since at low pressures, $\hat{\phi}_i = 1$, and considering the water to be nearly pure, it can thus be shown that the above equation for water becomes:

$$y_2 P = P_2^{sat}$$

Thus the rate at which the water evaporates, assuming the entering air is dry and that the exiting air is saturated with water would be given by:

$$\frac{d(\rho_L V)}{dt} = -\frac{P_2^{sat}}{P}\rho_V A \qquad (7)$$

By dividing the equations 6 and 7 we can find out which substance volatilizes more quickly. On comparing this ratio of the contaminant to the mole fraction of the contaminant, it can be determined whether the solution will become more dilute or more concentrated with the passage of time. This ratio is:

$$\frac{\text{Volatilization rate of the contaminant}}{\text{Volatilization rate of water}} = x_i \gamma_i(LR)\frac{P_1^{sat}}{P_2^{sat}} = x_i \frac{\gamma_i(LR)}{\gamma_i^{\infty}(LR)}\frac{H_{i,j}}{P_2^{sat}}$$

To compare this ratio to the mole fraction of the contaminant we can divide it by x_i. This quantity is called the "volatilization susceptibility factor".

$$\gamma_i(LR)\frac{P_1^{sat}}{P_2^{sat}} = \frac{\gamma_i(LR)}{\gamma_i^{\infty}(LR)}\frac{H_{i,j}}{P_2^{sat}}$$

If this "volatilization susceptibility factor" is less than one, then the solution will become more concentrated. If it is approximately equal to one, then the solution will not change in concentration. If the factor is greater than unity, than the solution will become more dilute. This happens for methanol which has volatilization susceptibility factor value of around 11. The analogous value for will not change in concentration. If the factor is greater than unity, than the solution will become more dilute. This happens for methanol which has volatilization susceptibility factor value of around 11. The analogous value for dimethylsuphoxide is around 0.0016. This makes it obvious that dimethyl sulfoxide will definitely concentrate over time.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

The volatilization rates of three compounds have been studied under different scenarios. The three compounds were methanol, acetone and dimethyl sulfoxide. The different scenarios were quiescent liquid, agitation (stirring), bubbling, different free surface area and different shapes of the container.

Dimethyl sulfoxide does not volatilize at all. In fact, DMSO concentrates over a period of time as water evaporates faster than DMSO.

Methanol and acetone volatilized slowly from quiescent solutions, slightly faster from agitated solutions and even faster from aerated.

Stirring the solution at medium to high speed increases the rate of volatilization (experimental rate constant) by 1.5-2.0 times in both methanol and acetone.

Generally, it has been observed that bubbling increases the rate of volatilization by almost the same factor (2.5-4.0 times) in both methanol and acetone in beakers (for the same kinds of aeration rates).

The rate of volatilization was seen to be affected by the free surface exposed to the ambient air. Increase in the exposed surface area, in case of methanol, increased the rate of volatilization by 1.3-2.5 times (for nearly the same aeration rates). For acetone this factor ranged from 1.3-1.7. This shows that methanol volatilization is more sensitive to the free surface exposed to the ambient air.

For smaller free surface areas (like the cylinder) it has been observed that acetone is much more mass transfer limited. That is, by providing bubbling the rate constant for acetone increases by about 75-90 times (as compared to methanol 3-4 times for the same bubbling rate). Also, for higher free surface area (like pan) the volatilization rate for methanol is affected very less by the bubbling (about 1.3 times).

Further, it has been observed for methanol that rate of volatilization decreases if the shape of the container (like the conical flask) is such that it will hold back the saturated air from being carried away with the air, thus reducing the driving force for volatilization.

This observation, affect of the free surface exposed to the atmosphere and shape of the container, can definitely affect the design of the collection and treatment units like drains, manholes, trenches, equalization basins etc. It would be preferable to shape the collection and treatment units in such a way so as to reduce the free surface exposed to the atmosphere and to have narrower mouths (to reduce the convective mass transfer) , thus reducing the rate of volatilization of the VOCs from wastewater.

Some more study needs to be done on the investigation of more complex volatilization scenarios involving multiple solvents or solutes and multiple phases (liquid or solid). Additional contaminants (either solid or another liquid phase) may affect the solubility of the VOC under consideration. Presence of solid, either organic or inorganic, can provide an alternate destination for the dissolved VOC. The VOC may adsorb onto the solid, thereby lowering the volatilization rate of the compound. If a second liquid phase is present, and if the compound is more soluble in it, then it can lower the volatilization rate of the compound from water. Or if the second phase is lighter than water, thus forming a layer on top of water, it may significantly lower the volatilization rate of the VOC from water.

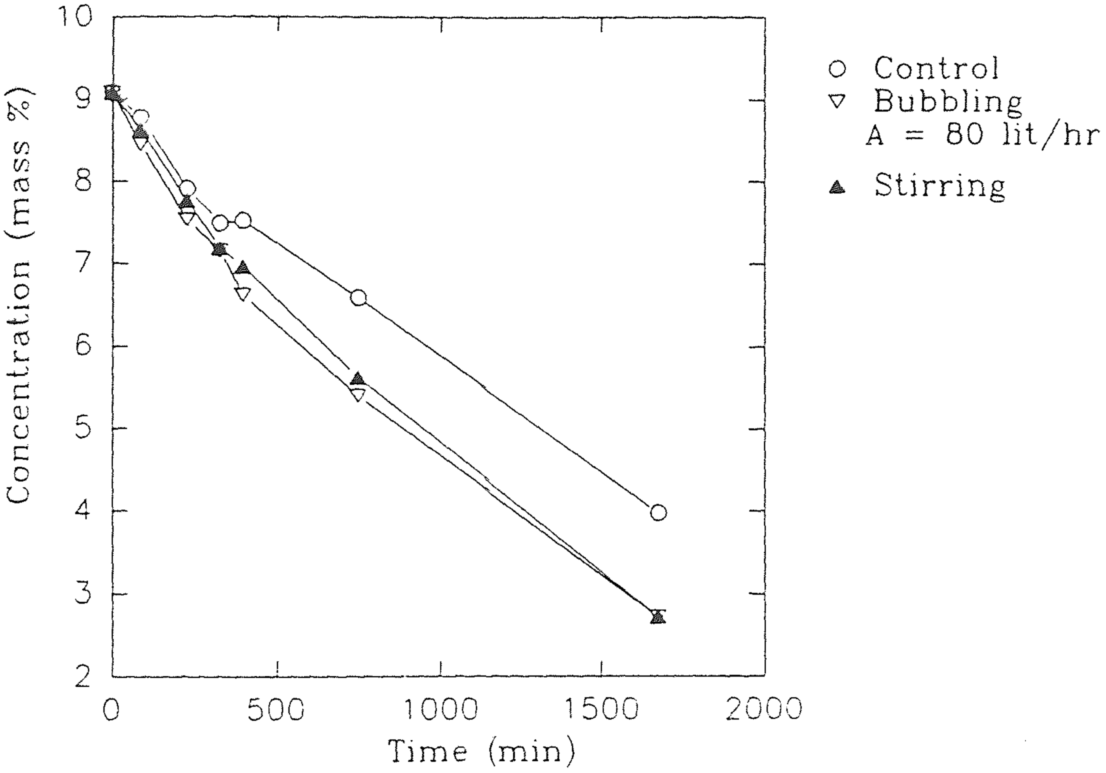
Also, evaluation of the feasibility of steam stripping for the compounds chosen is required.

APPENDIX A-1

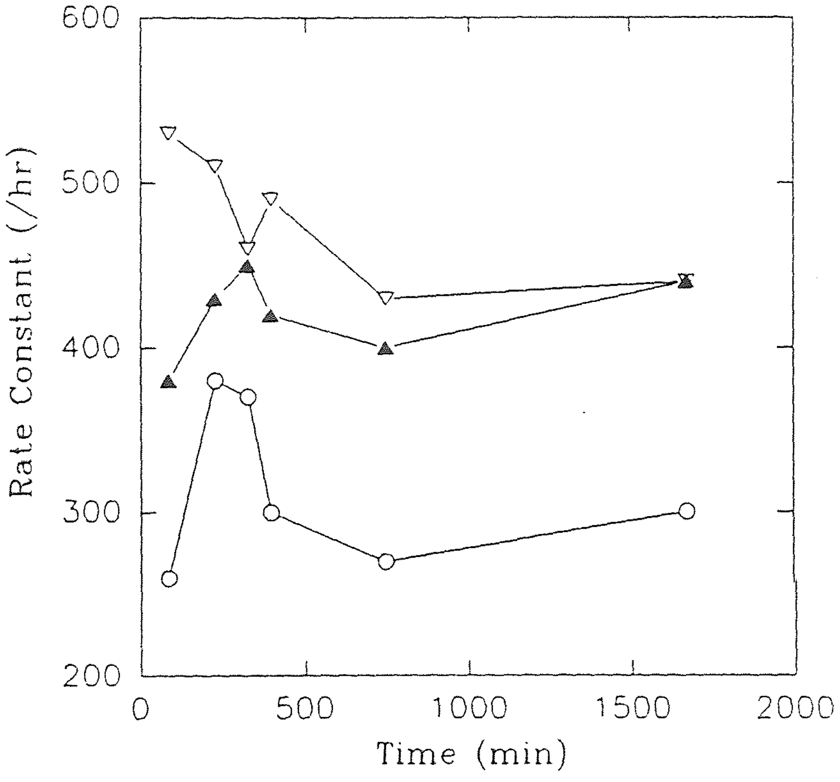
Results for Methanol in Beakers

A-1.1 Aeration and Stirring (Methanol in Beakers)

Graph A-1.1a Concentration (mass %) with Time (min)



Graph A-1.1b Rate Constant (/hr) with Time (min)



A-1.1 Stirring and Aeration Results for Methanol (All Beakers)

TableA-1.1a Concentraton (mass percent) trend with time (min)

Time (min)	Control	Stirring - Beaker	Bubbling - Beaker A = 80 lit/hr
0	9.10	9.10	9.10
85	8.77	8.62	8.45
225	7.91	7.77	7.54
325	7.50	7.19	7.16
395	7.53	6.97	6.63
745	6.60	5.63	5.41
1675	3.98	2.72	2.72

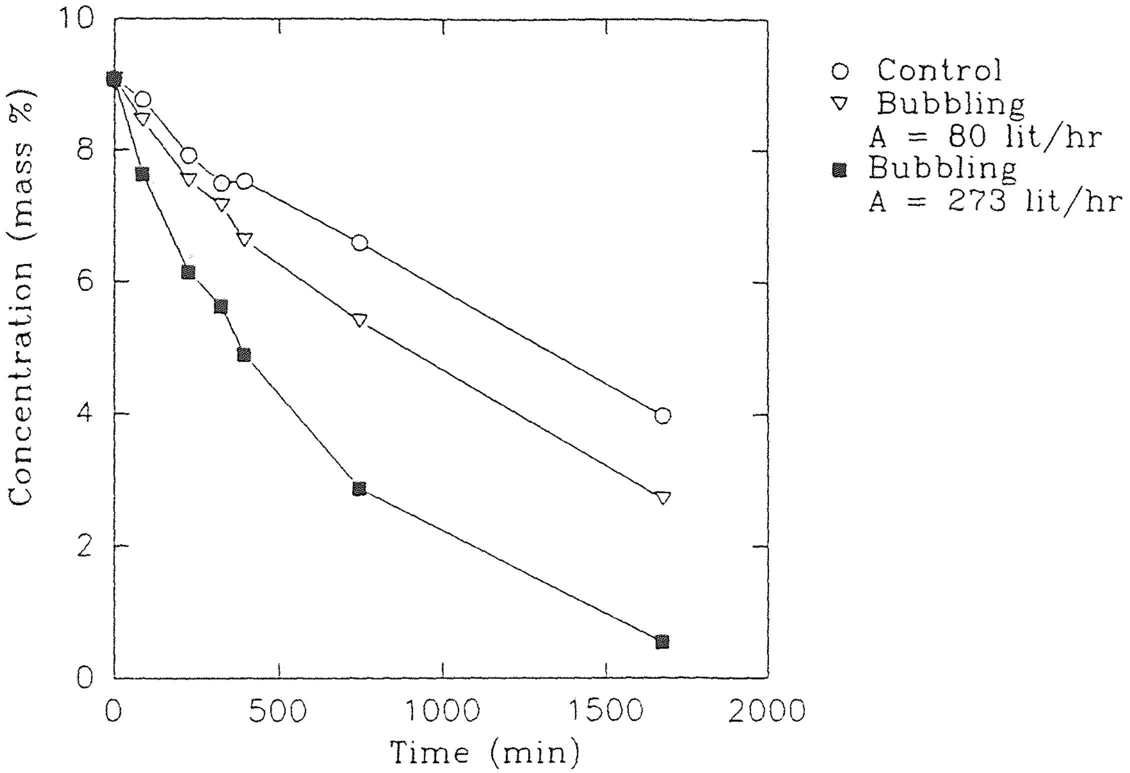
Table A-1.1b Rate constant (/hr) trend with time (min)

Time	Control	Stirring - Beaker	Bubbling - Beaker A = 80 lit/hr
85	260	380	530 (420)
225	380	430	510
325	370	450	460
395	300	420	490
745	270	400	430
1675	300	440	440 (580)

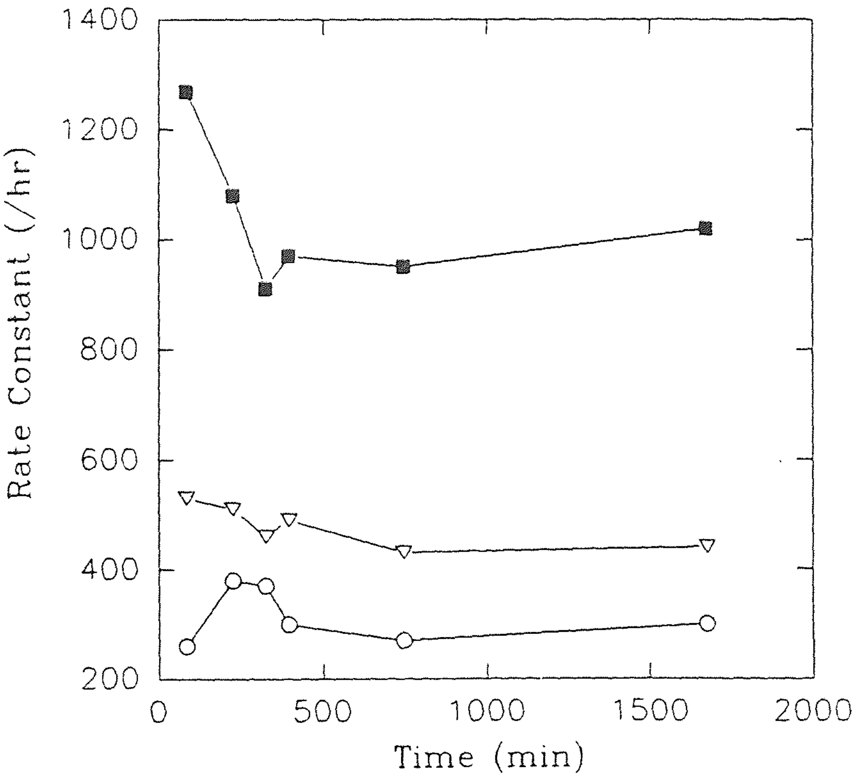
The values reported for the rate constants have been multiplied by 10000 hr.

A-1.2 Aeration Results for Methanol In Beakers

Graph A-1.2a Concentration (mass %)with Time (min)



Graph A-1.2b Rate Constant (/hr) with Time(min)



A-1.2 Aeration Results for Methanol
(All Beakers)

Table A-1.2a Concentration (Mass Percent) Trend With Time (Min)

Time (min)	Control - Beaker	Bubbling - Beaker A = 80 lit/hr	Bubbling - Beaker A = 275 lit/hr
0	9.08	9.08	9.08
85	8.77	8.45	7.64
225	7.91	7.54	6.14
325	7.50	7.16	5.62
395	7.53	6.63	4.89
745	6.60	5.41	2.88
1675	3.98	2.72	0.55

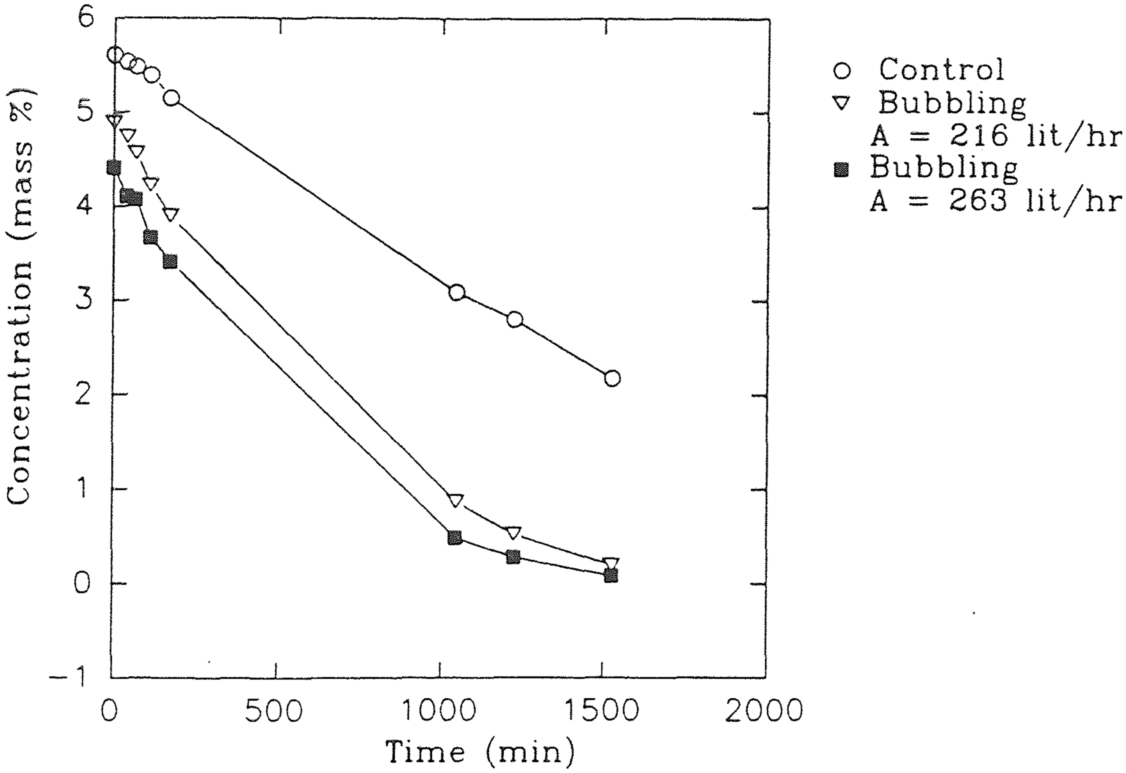
Table A-1.2b Rate Constant Trend (/Hr) With Time (Min)

Time (min)	Control - Beaker	Bubbling - Beaker A = 80 lit/hr	Bubbling - Beaker A = 275 lit/hr
85	260	530 (420)	1270 (1470)
225	380	510	1080
325	370	460	910
395	300	490	970
745	270	430	950
1675	300	440 (580)	1020 (2590)

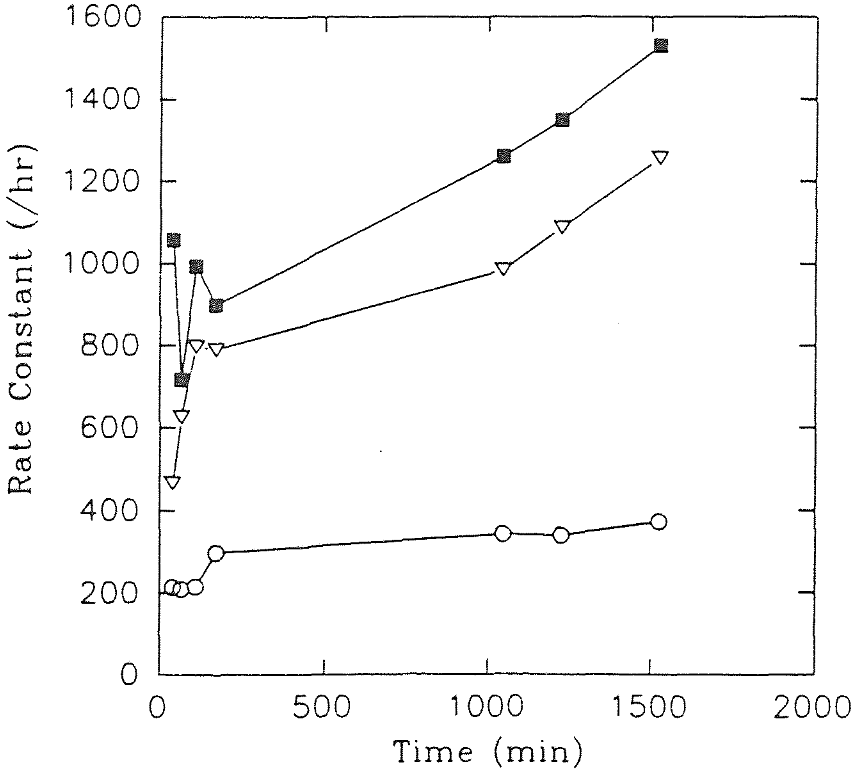
· The values reported for the rate constants have been multiplied by 10000 hr.

A-1.3 Aeration Results for Methanol in Beakers

Graph A-1.3a Concentrarion (mass %) with Time (min)



Graph A-1.3b Rate Constant (/hr) with Time (min)



A-1.3 Aeration Results for Methanol
(All Beakers)

Table A-1.3a Concentration (Mass Percent) Trend With Time (Min)

Time (min)	Control	Bubbling A = 216 lit/hr	Bubbling A = 263 lit/hr
0	5.61	4.89	4.41
40	5.53	4.74	4.11
67	5.48	4.56	4.07
111	5.39	4.22	3.67
172	5.15	3.9	3.41
1047	3.10	0.88	0.49
1227	2.81	0.53	0.28
1527	2.18	0.20	0.09

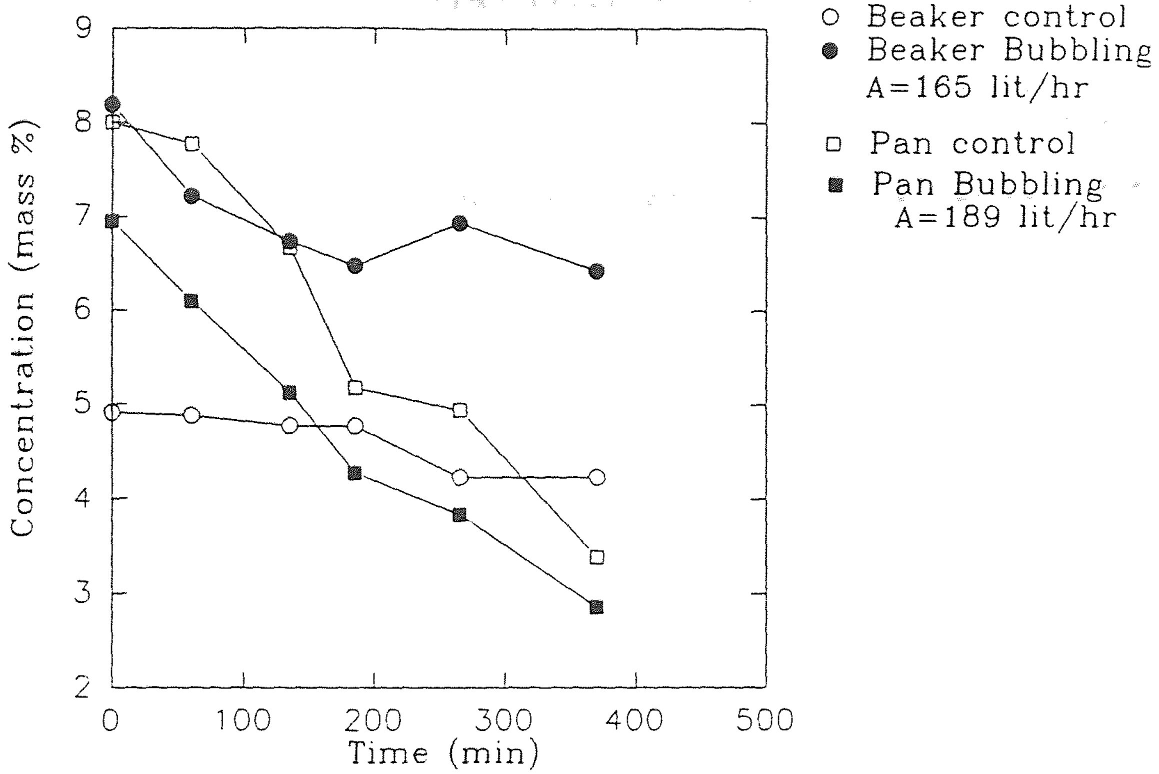
Table A-1.3b Rate Constants (/hr) trend with Time (min)

Time (min)	Control	Bubbling A = 216 lit / hr	Bubbling A = 263 lit /hr
40	215	467 (798)	1057 (960)
67	210	626	718
111	216	797	993
172	298	789	897
1047	340	983	1259
1227	338	1087	1348
1527	371	1256 (2076)	1529 (2490)

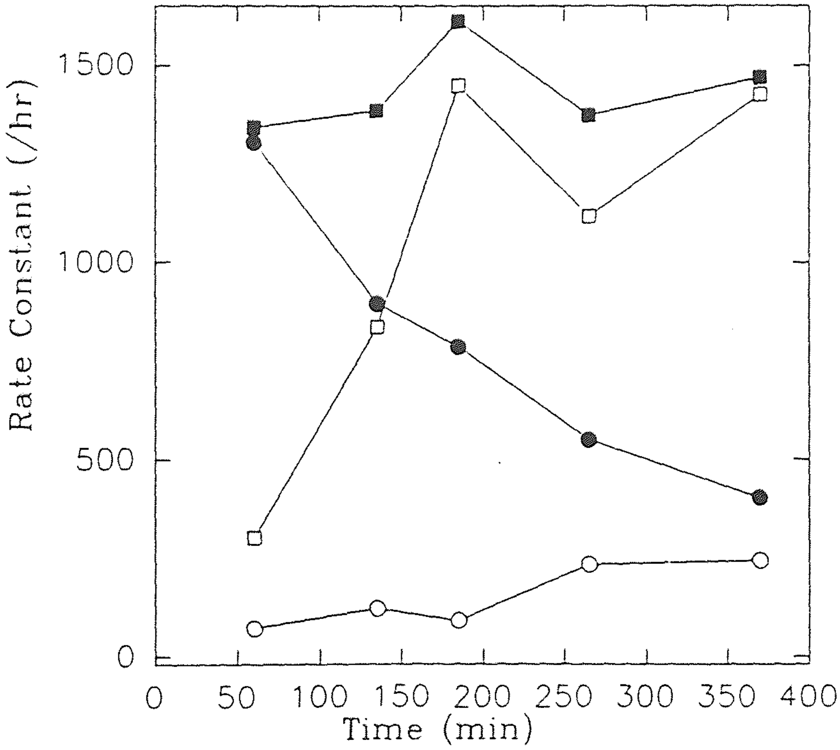
The values reported for rate constants have been multiplied by 1000 hr.

A-2.1 Aeration (Methanol-Different Surface Areas)

Graph A-2.1a Concentration (mass%) with Time (min)



Graph A-2.1 Rate Constant (/hr) with Time (min)



APPENDIX A-2

Aeration Results for Methanol (Different Free Surface Areas)

Table A-2.1a Concentration (Mass Percent) trend with Time (min)

Time (min)	Beaker-Control	Beaker-Bubbling (A=165 lit/hr)	Pan Control	Pan Bubbling (A=189 lit/hr)
0	4.91	8.19	8.00	6.95
60	4.88	7.22	7.77	6.10
135	4.78	6.74	6.67	5.13
185	4.78	6.48	5.18	4.28
265	4.24	6.95	4.95	3.84
370	4.24	6.44	3.39	2.86

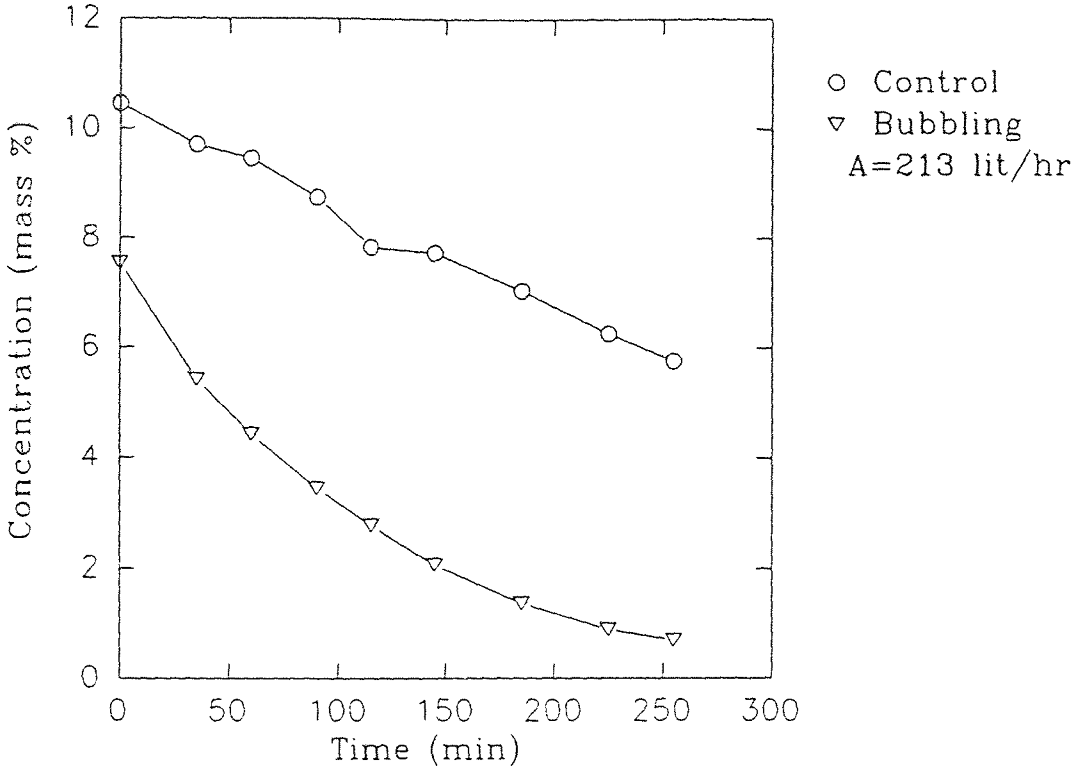
Table A-2.1b Rate Constant (/hr) trend with Time (min)

Time (min)	Beaker - Control	Beaker-Bubbling (A = 165 lit / hr)	Pan - Control	Pan - Bubbling (A = 189 lit / hr)
60	71	1305 (1018)	302	1343 (1337)
135	122	895 (1074)	835	1386 (1584)
185	89	785 (1113)	1451	1611 (1809)
265	233	548 (1167)	1118	1375 (2280)
370	243	403 (1267)	1426	1470 (3474)

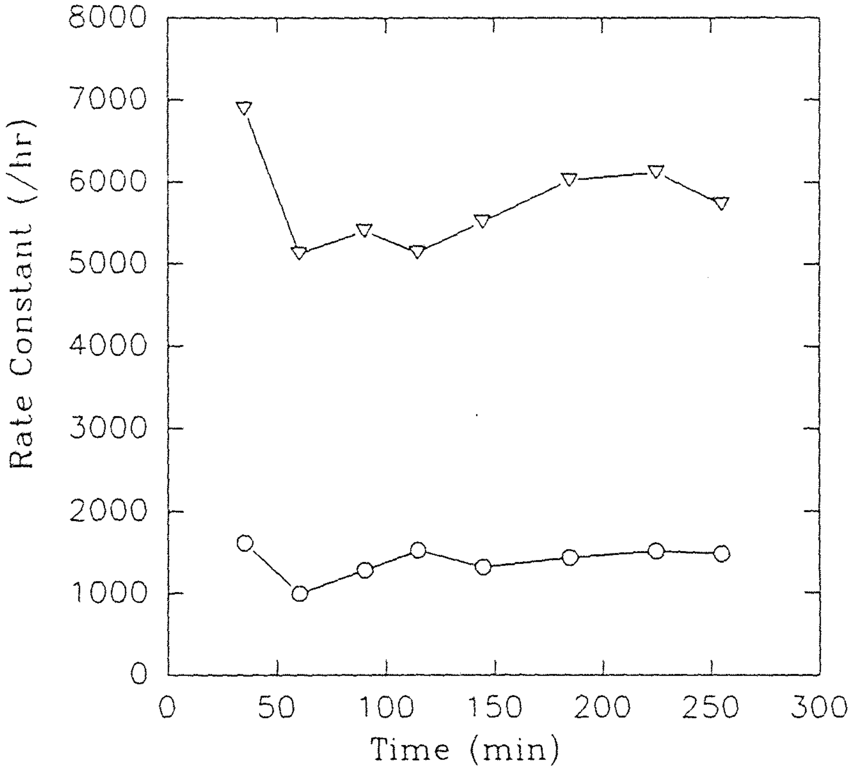
The values reported have been multiplied by 10000 hr.

B-1.1 Aeration Results for Acetone in Beakers

Graph B-1.1a Concentration (mass %) with Time (min)



Graph B-1.1b Rate Constant (/hr) with Time (min)



APPENDIX B-1

Results for Acetone in Beakers

B-1.1 Aeration Results for Acetone (All Beakers)

Table B-1.1a Concentration (Mass Percent) Trend With Time (Min)

Time (min)	Control	Bubbling A = 213 lit / hr
0	10.45	7.53
35	9.70	5.42
60	9.45	4.43
90	8.74	3.45
115	7.85	2.79
145	7.75	2.07
185	7.06	1.36
225	6.27	0.88
255	5.76	0.69

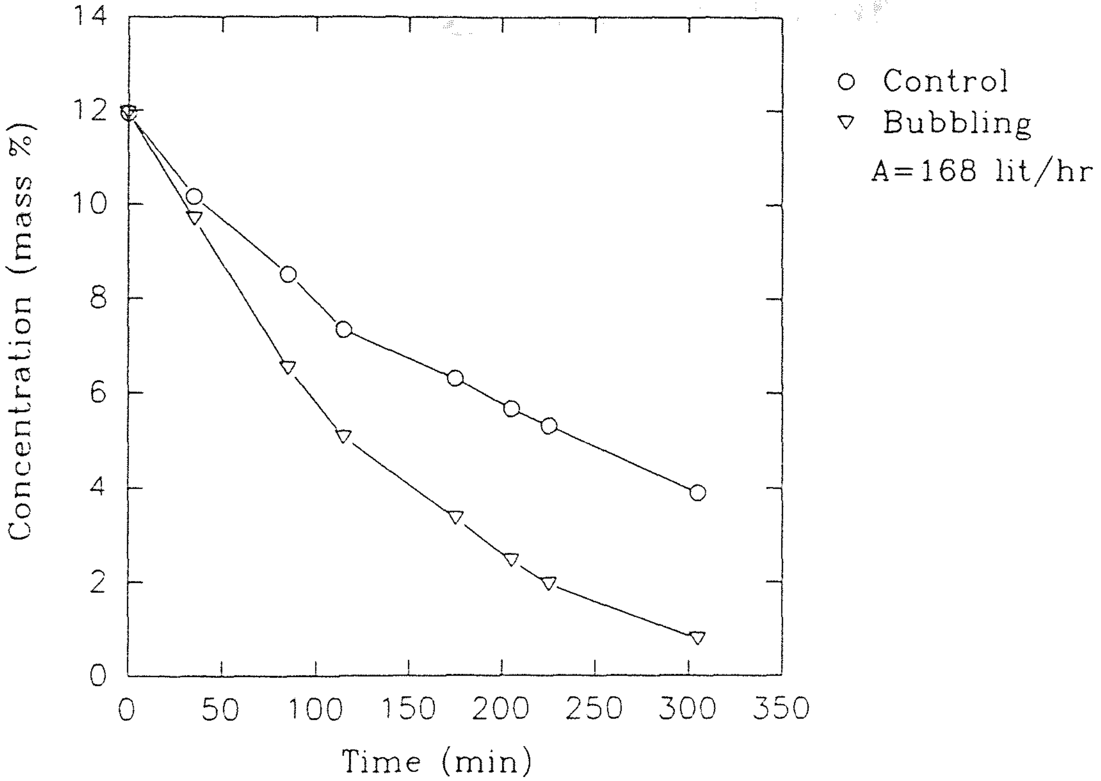
Table B-1.1b Rate Constant (/Hr) Trend With Time (Min)

Time (min)	Control	Bubbling A = 213 lit / hr
35	1611	6890 (7210)
60	996	5120 (7500)
90	1280	5400 (7860)
115	1520	5140 (8370)
145	1310	5510 (8490)
185	1430	6023 (8610)
225	1510	6120 (8690)
255	1480	5730 (8730)

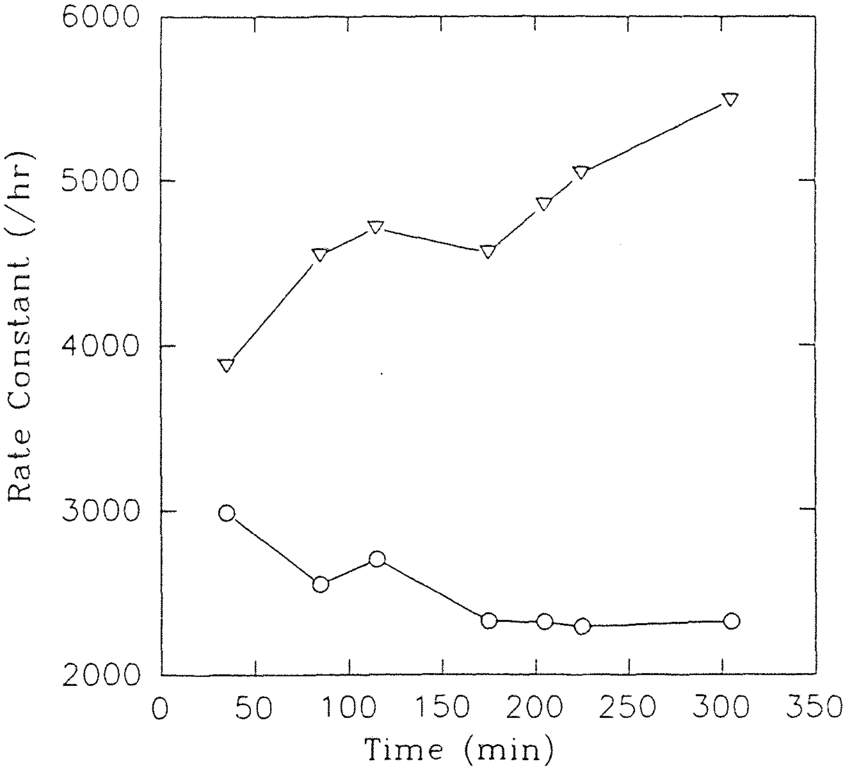
The values reported have been multiplied by 10000 hr

B−1.2 Aeration Results for Acetone in Beakers

Graph B−1.2a Concentration (mass%) with Time (min)



Graph B−1.2b Rate Constant (/hr) with Time (min)



B-1.2 Aeration Results for Acetone
(All Beakers)

Table B-1.2a Concentration (Mass Percent) Trend With Time (Min)

Time (min)	Control	Bubbling A = 168 lit /hr
0	11.95	11.95
35	10.17	9.69
85	8.53	6.53
115	7.36	5.09
175	6.32	3.36
205	5.67	2.44
225	5.31	1.94
305	3.89	0.79

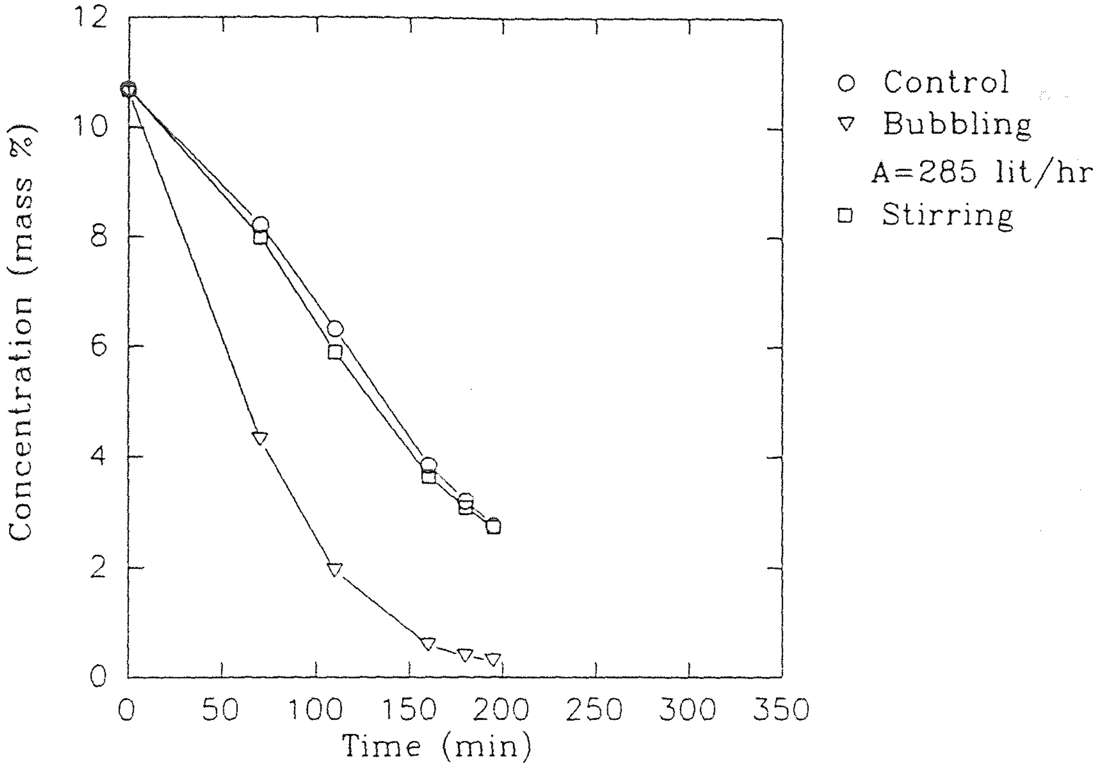
Table B-1.2b Rate Constant (/Hr) Trend With Time (Min)

Time (min)	Control	Bubbling A = 168 lit / hr
35	2990	3880 (5180)
85	2550	4545 (6100)
115	2700	4710 (6280)
175	2324	4560 (6500)
205	2317	4850 (6760)
225	2290	5040 (7050)
305	2321	5490 (7290)

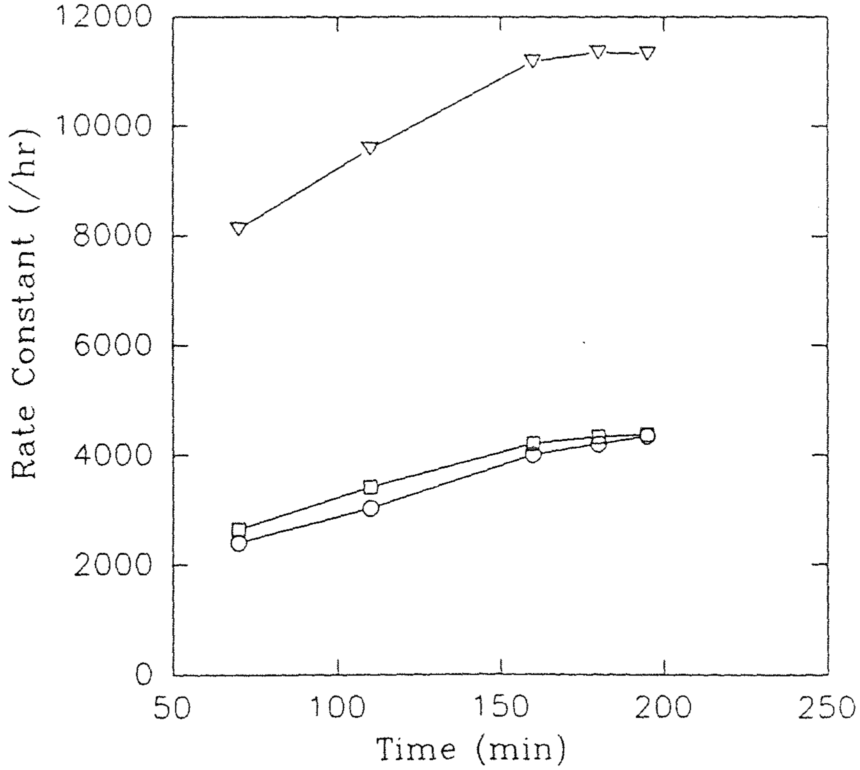
The values reported for the rate constant have been multiplied by 10000 hr.

B-1.3 Aeration Results for Acetone in Beakers

Graph B-1.3a Concentration (mass%) with Time (min)



Graph B-1.3b Rate Constant (/hr) with Time (min)



B-1.3 Aeration and Stirring Results for Acetone (All Beakers)

Table B-1.3a Concentration (Mass Percent) Trend With Time (Min)

Time (min)	Control	Stirring	Bubbling A = 285 lit /hr
0	10.69	10.69	10.63
70	8.23	8.00	4.32
110	6.33	5.92	1.95
160	3.86	3.66	0.58
180	3.21	3.09	0.38
195	2.77	2.73	0.29

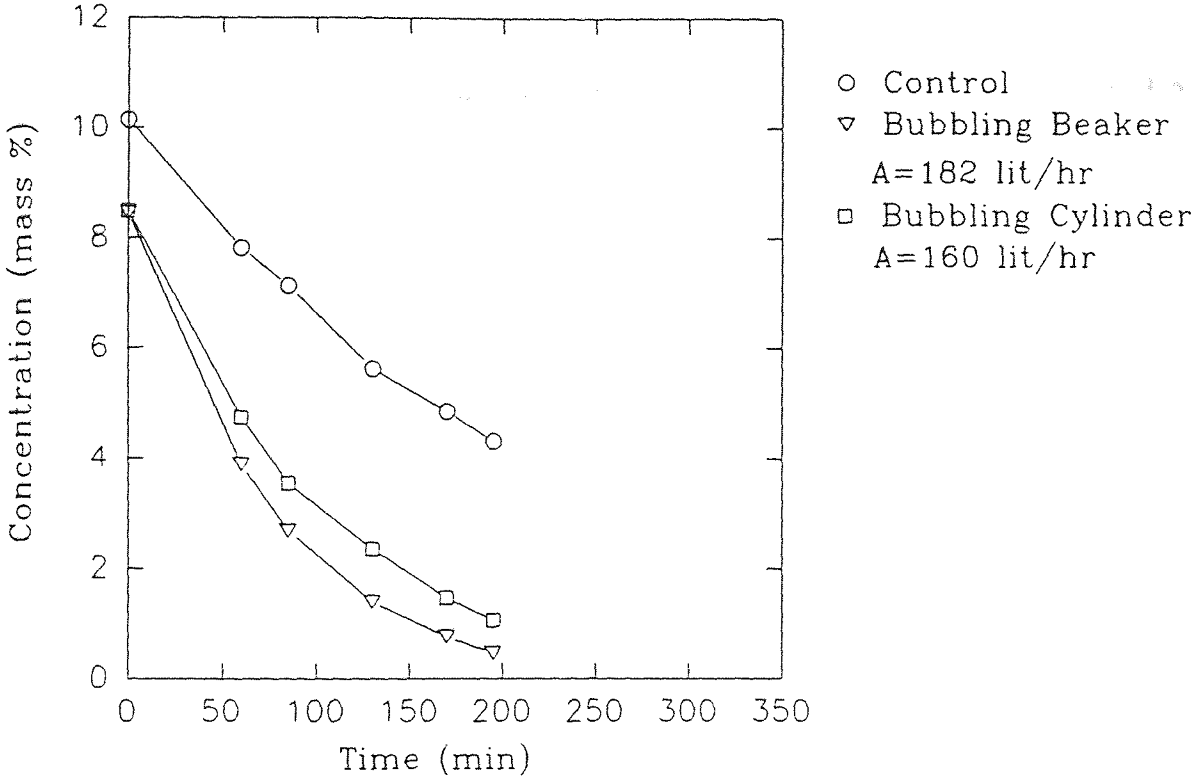
Table B-1.3b Rate Constant (/Hr) Trend With Time (Min)

Time (min)	Control	Stirring	Bubbling A = 285 lit / hr
70	2400	2650	8111 (9986)
110	3030	3410	9585 (10571)
160	4000	4210	11181 (11281)
180	4190	4320	11346 (11547)
195	4330	4370	11321 (11568)

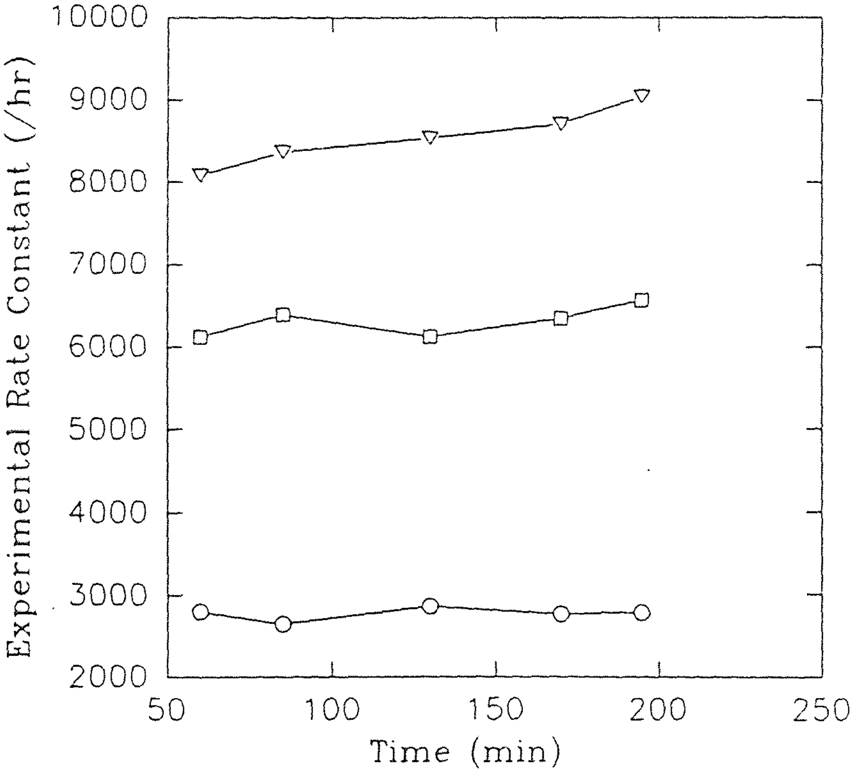
The values reported for the rate constants have been multiplied by 10000 hr.

B-2.1 Aeration Results for Acetone in Beakers

Graph B-2.1a Concentration (mass %) with Time (min)



Graph B-2.1b Rate Constant with Time (min)



APPENDIX B-2

Aeration Results for Acetone
(Different Free Surface Area)

Table B-2.1a Concentration (Mass Percent) Trend With Time (Min)

Time (min)	Control	Bubbling - Beaker A = 182 lit / hr	Bubbling - Cylinder A = 160 lit / hr
0	10.15	8.46	8.49
60	7.81	3.89	4.73
85	7.13	2.69	3.55
130	5.64	1.40	2.35
170	4.85	0.76	1.47
195	4.30	0.47	1.06

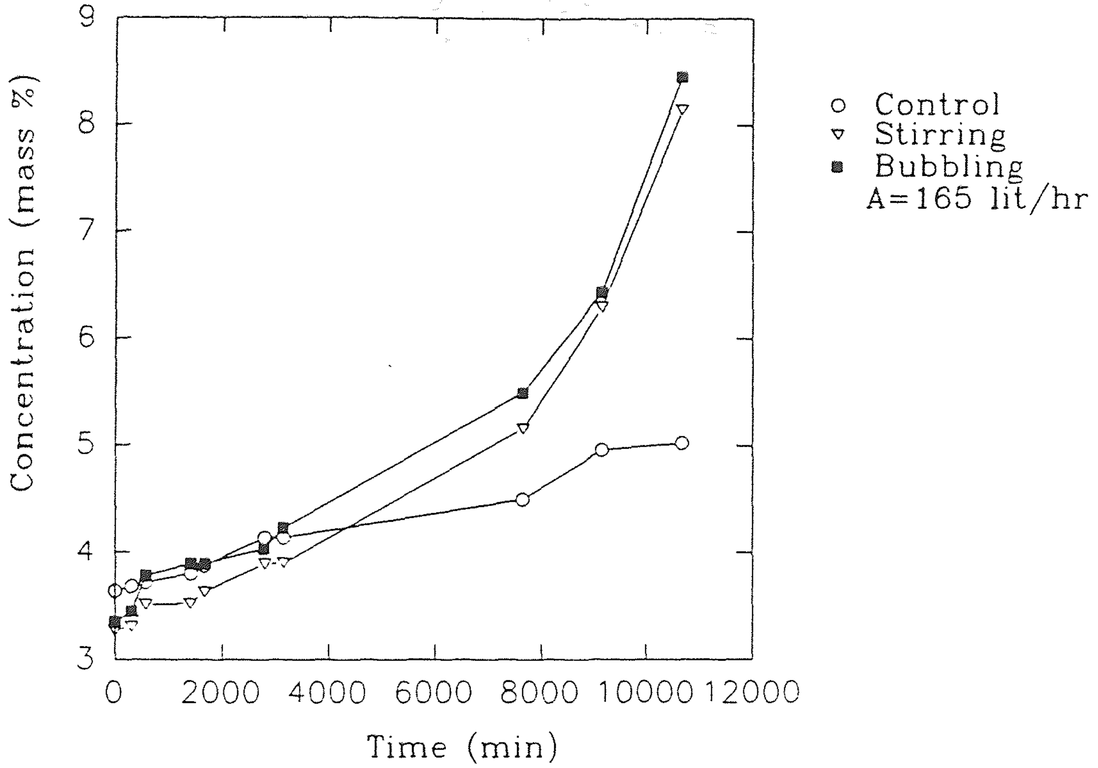
Table B-1.2b Rate Constant (/Hr) Trend With Time (Min)

Time (min)	Control	Bubbling - Beaker A = 182 lit / hr	Bubbling - Cylinder A = 160 lit / hr
60	2800	8080 (10760)	6120 (9460)
85	2650	8370 (11020)	6390 (10170)
130	2870	8540 (11670)	6125 (10590)
170	2770	8710 (11820)	6350 (10780)
195	2780	9040 (12270)	6570 (11050)

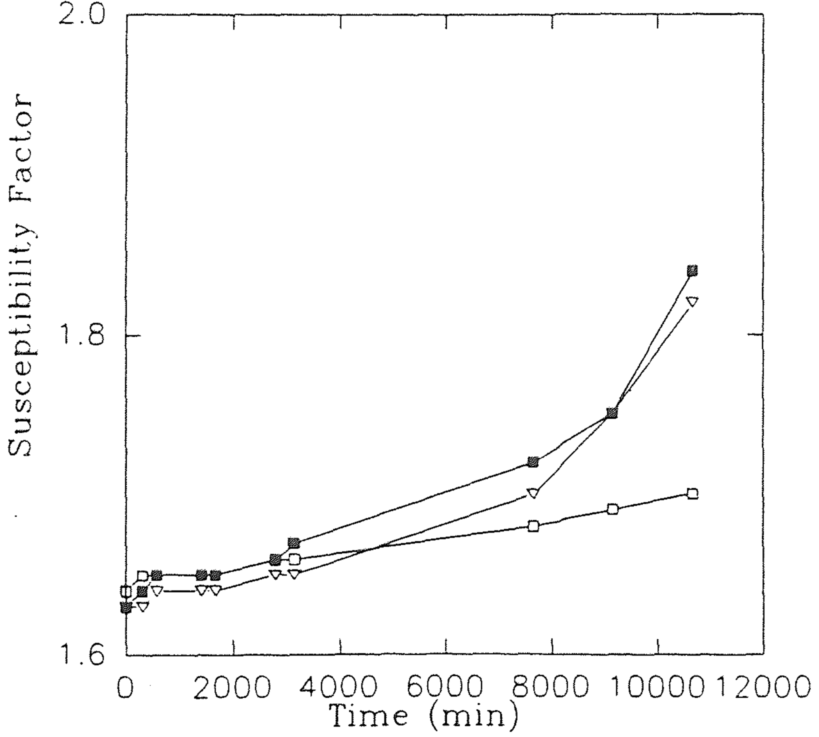
Each of values reported for the rate constants have been multiplied by 10000 hr.

C-1 Aeration and Stirring (DMSO in Beakers)

Graph C-1a Concentration(mass %) with Time (min)



Graph C-1bSusceptibility Factor with Time (min)



APPENDIX C-1

Stirring and Aeration Results for DMSO
(All Beakers)

Table C-1a Concentration (Mass Percent) Trend With Time (Min)

Time (min)	Control	Stirring	Bubbling A = 165 lit/hr
0	3.64	3.27	3.35
90	3.67	3.31	3.35
240	3.68	3.31	3.45
310	3.68	3.31	3.45
580	3.72	3.51	3.78
1415	3.80	3.52	3.89
1680	3.87	3.63	3.89
2795	4.14	3.89	4.03
3145	4.14	3.90	4.23
7655	4.50	5.16	5.50
9160	4.96	6.30	6.44
10675	5.02	8.14	8.45

Table C-1b Volitilization Susceptibility Factor Trend With Time

Time (min)	Control	Stirring	Bubbling A = 165 lit/hr
0	1.64	1.63	1.63
90	1.65	1.63	1.63
240	1.65	1.63	1.64
310	1.65	1.63	1.64
580	1.65	1.64	1.65
1415	1.65	1.64	1.65
1680	1.65	1.64	1.65
2795	1.66	1.65	1.66
3145	1.66	1.65	1.67
7655	1.68	1.70	1.72
9160	1.69	1.75	1.75
10675	1.70	1.82	1.84

The values for the susceptibility factor have been multiplied by a factor of 1000 .

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