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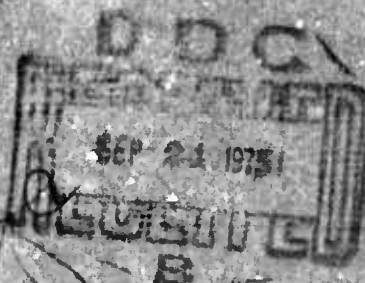
**Precipitation Scavenging
of Organic Contaminants**

Final Report

July 1975

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20. Abstract (continued)

Mathematical expressions were formulated to describe the observed solubility behavior, and these were incorporated into the EPAEC scavenging model to predict concentrations of these materials in rain for comparison with experimental measurements. Agreement between experiment and theory was found to improve over previous estimates, which were based upon less accurate solubility data. Diethylamine results showed generally good agreement, while those for ethyl acetoacetate exhibited considerable deviation. Disagreement in this latter case was attributed primarily to the neglect of aqueous-phase mixing effects in the model calculations.

PRECIPITATION SCAVENGING OF ORGANIC CONTAMINANTS

FINAL REPORT

Richard N. Lee and Jeremy M. Hales

July 1975

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**Atmospheric Sciences Department ✓
Battelle, Pacific Northwest Laboratories ✓
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SUMMARY

A gas-chromatographic technique has been employed to measure the solubilities of diethylamine and ethyl acetoacetate in water at low concentrations. Diethylamine solubility was found to increase with decreasing concentration and increasing acidity. Ethyl acetoacetate solubility was found to decrease with decreasing concentration.

Mathematical expressions were formulated to describe the observed solubility behavior, and these were incorporated into the EPAEC scavenging model to predict concentrations of these materials in rain for comparison with experimental measurements. Agreement between experiment and theory was found to improve over previous estimates, which were based upon less accurate solubility data. Diethylamine results showed generally good agreement, while those for ethyl acetoacetate exhibited considerable deviation. Disagreement in this latter case was attributed primarily to the neglect of aqueous-phase mixing effects in the model calculations.

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CHAPTER I.

INTRODUCTION

The objective of the research described in this report is the measurement of the water solubility of diethylamine and ethyl acetoacetate at low concentrations. Interest in this information has arisen from previous Army research (LEE and HALES (1974)) dealing with precipitation scavenging of organic compounds, which demonstrated a marked deviation between observed and predicted scavenging rates.

The basis for predicting scavenging rates in this former work was the EPAEC scavenging code, which had been demonstrated previously to predict sulfur dioxide scavenging with reasonable accuracy (DANA, HALES, and WOLF (1973)). An analysis of the results indicates that the most probable reason for the large disagreement exhibited in the case of the organic materials was poor estimates of the water solubility of these compounds, which were required as model input.

If solubility is expressed in terms of the equation

$$p = H'c_g \quad , \quad (1)$$

where p (atm.) is the partial pressure of vapor in the gas phase associated with an equilibrium aqueous-phase concentration c_g (moles/ml), then the solubility parameters H' (atm. ml/mole) can be predicted as shown in Table 1 (LEE and HALES (1974)). Observed washout concentrations are compared with those predicted using these solubility estimates in Tables 2-6.

Additional calculations have been performed showing that much better agreement between experiment and theory can be achieved using higher solubilities in the case of diethylamine, and lower ones in the case of ethyl acetoacetate. This rather weak evidence that the solubility data in Table 1 is inappropriate, is supported by the highly approximate nature of the calculations leading to these values. Estimates for both compounds were based upon

TABLE 1. ESTIMATED SOLUBILITIES OF ETHYL ACETOACETATE
AND DIETHYLAMINE IN WATER AT 5°C

Compound	H ⁱ (atm. ml/mole)
Ethyl acetoacetate	0.25
Diethylamine	11.

TABLE 2. OBSERVED VERSUS PREDUCTED WASHOUT CONCENTRATIONS - EEA

Rain Collector Station	Measured Concentration C _{obs.}	Predicted Concentration C _{Hⁱ=0.25}	Rain Collector Station	Measured Concentration C _{obs.}	Predicted Concentration C _{Hⁱ=0.25}
A 3	<0.10 ppm	0.04 ppm	B 8	--	0.05 ppm
4	0.16	0.18	9	--	0.21
5	0.50	0.71	10	--	0.67
6	1.1	2.41	11	1.0 ppm	1.68
7	1.5	7.96	12	0.70	3.18
8	1.6	27.7	13	1.2	4.43
9	1.5	13.9	14	0.78	4.21
10	1.2	4.48	15	0.73	2.54
11	1.0	1.12	16	0.33	0.97
12	0.32	0.25	17	0.35	0.27
13	0.10	0.05	18	0.12	0.06

TABLE 3. OBSERVED VERSUS PREDICTED WASHOUT CONCENTRATIONS - EEA

Rain Collector Station	Measured Concentration C _{obs.}	Predicted Concentration C _{Hⁱ=0.25}	Rain Collector Station	Measured Concentration C _{obs.}	Predicted Concentration C _{Hⁱ=0.25}
A 1	<0.10 ppm	0.27 ppm	B 5	<0.10 ppm	--
2	<0.10	0.89	6	0.26	--
3	0.80	2.38	7	0.16	0.16 ppm
4	1.0	5.23	8	0.31	0.49
5	1.5	9.99	9	0.36	1.23
6	2.0	28.7	10	0.31	2.44
7	1.6	9.99	11	0.27	3.73
8	0.77	5.23	12	0.37	4.31
9	0.20	2.38	13	0.28	3.73
10	0.11	0.89	14	0.12	2.44
11	<0.10	0.27	15	<0.10	1.23
12	<0.10	--	16	<0.10	0.49
13	<0.10	--	17	<0.10	0.16
			18	<0.10	

TABLE 4. OBSERVED VERSUS PREDICTED WASHOUT CONCENTRATIONS - DEA

Rain Collector Station	Measured Concentration $C_{obs.}$	Predicted Concentration $C_{H'=11}$	Rain Collector Station	Measured Concentration $C_{obs.}$	Predicted Concentration $C_{H'=11}$
A 4	0.6 ppm	--	B 11	0.9 ppm	0.002 ppm
5	0.7	--	12	1.7	0.021
6	2.1	0.005 ppm	13	2.2	0.112
7	1.4	0.042	14	2.7	0.304
8	1.3	0.225	15	3.0	0.425
9	2.1	0.628	16	2.1	0.304
10	2.5	0.898	17	2.8	0.112
11	1.0	0.628	18	1.1	0.021
12	0.6	0.225	19	1.2	0.002
13	0.1	0.042			
14	0.1	0.005			

TABLE 5. OBSERVED VERSUS PREDICTED WASHOUT CONCENTRATIONS - DEA

Rain Collector Station	Measured Concentration $C_{obs.}$	Predicted Concentration $C_{H'=11}$	Rain Collector Station	Measured Concentration $C_{obs.}$	Predicted Concentration $C_{H'=11}$
A 6	0.19 ppm	--	A 12	0.21 ppm	--
7	0.55	--	13	0.42	--
8	0.62	0.014 ppm	14	1.3	--
9	0.96	0.357	15	1.3	0.013 ppm
10	1.3	1.4	16	1.7	0.19
11	1.0	0.357	17	2.2	0.48
12	0.85	0.014	18	1.7	0.19
13	0.56	--	19	1.4	0.013
14	0.39	--	20	1.8	
			21	1.3	
			22	0.80	
			23	0.45	

TABLE 6. OBSERVED VERSUS PREDICTED WASHOUT CONCENTRATIONS - DEA

Rain Collector Station	Measured Concentration $C_{obs.}$	Predicted Concentration $C_{H'=11}$	Rain Collector Station	Measured Concentration $C_{obs.}$	Predicted Concentration $C_{H'=11}$
A 8	0.17 ppm	--	A 12	0.28 ppm	--
9	0.47	--	13	0.41	--
10	0.37	0.01 ppm	14	0.47	--
11	0.43	0.24	15	0.47	0.001 ppm
12	0.57	0.70	16	0.47	0.019
13	0.32	0.24	17	--	0.112
14	0.48	0.02	18	0.63	0.207
15	0.17		19	0.56	0.112
			20	0.43	0.019
			21	0.43	0.001
			22	0.42	--

high-concentration data which was extrapolated over long ranges to the lower concentrations and temperatures experienced in this study. A number of factors could possibly render such estimates invalid, including the effects of dissociation, association, and sequestering by trace impurities. The following sections of this report describe the measurements performed during the course of this investigation, and the application of these results in conjunction with the EPAEC scavenging model to obtain refined washout estimates.

CHAPTER II.

APPARATUS AND TECHNIQUE

Although a number of conventional techniques are available for measurement of the solubility of gases in liquids (cf. HILDEBRAND and SCOTT (1950)), the low-concentration conditions of the present study preclude the use of most such methods. The basic requirements of this research are ones of accurately setting and maintaining a known low concentration of solute in either the gaseous (or aqueous) phase, while accurately measuring the corresponding equilibrium concentration in its aqueous (or gaseous) counterpart.

The basic approach of setting a known gaseous-phase concentration and measuring its aqueous-phase counterpart was attempted during the initial periods of this study. The initial method of maintaining gaseous-phase concentrations was the diffusion-capillary technique, as shown in Figure 1. With this technique diluent air was passed at a known flow rate past a vertical glass capillary containing a small amount of the pure organic, which was allowed to diffuse into the diluent stream. The dilute mixture then flowed into a solubility cell where it was bubbled through a water sample. Upon approaching saturation with respect to the concentration of the solute in the gas stream, the sample was removed, and analyzed chemically to determine the equilibrium concentration, and thus the solubility.

In theory this technique should be totally adequate for the purpose of the present study. A straightforward integration of the diffusion equation shows that the rate of diffusion of solute from the glass capillary should be given by

$$\text{Flow rate (moles/t)} = \frac{D C_{eq} A}{l} \quad (2)$$

where D is the diffusion coefficient of solute in diluent, C_{eq} is its equilibrium gas-phase concentration (a function of temperature), A is the bore area of the capillary, and l is the distance from the top of the capillary

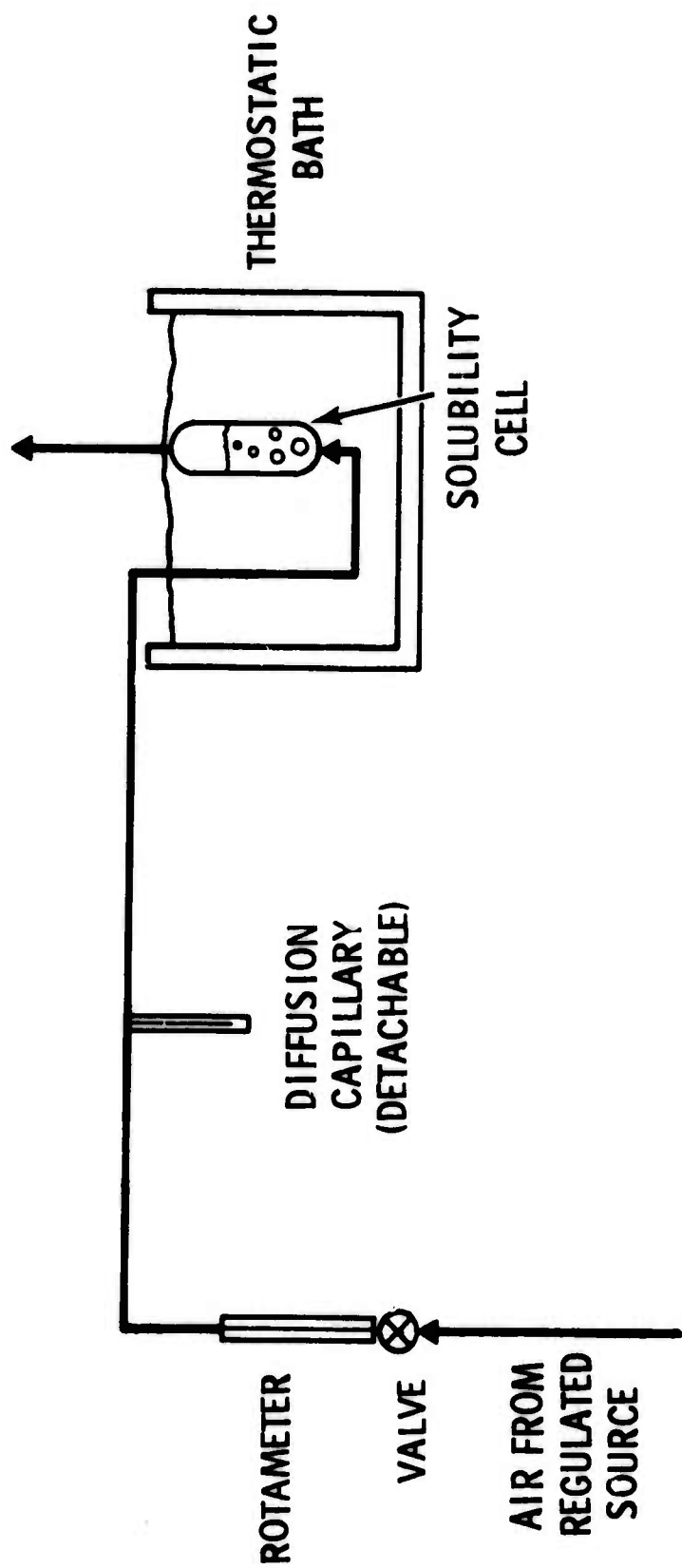


Figure 1. Simplified Schematic of Initial Solubility - Measurement Apparatus

to the surface of the liquid. From equation (2) it is evident that concentration of solute in the gaseous phase should be controllable through manipulation of a number of variables; and, provided that temperature and l can be maintained constant, this type of unit should provide the long-term stabilized gas concentrations required for this study.

Initial tests with this apparatus, however, proved unsatisfactory. It was extremely difficult to obtain a reliable calibration of the diffusion capillary, and highly erratic gaseous concentrations were observed during solubility tests. After substantial amounts of testing it became evident that pressure fluctuations caused by formation of bubbles in the solubility cell were propagating upstream, causing spurious mixing in the diffusion capillary. Since there was no straightforward or reliable way of countering this effect, the diffusion-capillary approach was abandoned from further consideration during this study.

In view of this finding, a second dilution technique, involving the use of permeation tubes, was tested. Small quantities of the solute compounds were encased in polyethylene vials, and located in the diluent gas stream in place of the diffusion capillary. While these units provided marginal success in dampening short-term concentration fluctuations, they proved unsuccessful in providing the long-term stability required for these experiments.

An additional difficulty involved with the initial experiments was the long time period necessary for the approach to equilibrium conditions. This feature can be illustrated by rewriting equation (1) in terms of a partition coefficient, K , which relates gas- and liquid-phase concentrations:

$$\begin{aligned} C_g &= K C_l \\ &= p/RT \quad \text{assuming ideal-gas behavior} \end{aligned} \tag{1A}$$

Here C_g (moles/ml) is the gas-phase concentration of solute, rather than its partial pressure, which appeared in (1). Since

$$K = \frac{H'}{RT} \approx \frac{H'}{25000} \quad , \quad (3)$$

it is obvious that extremely large volumes of gas must be passed through initially pure water in the solubility cell before equilibrium conditions are approached, thus requiring intolerably long experiment times.

Because of these difficulties a reverse experiment, based upon fixing known concentrations of solute in the aqueous phase and measuring equilibrium gas-phase concentrations was tested. Shown in Figure 2, this experiment involved bubbling ultrapure helium (supplied by the U. S. Bureau of Mines) from a regulated cylinder through a flow meter, a heat-transfer coil, and finally a solubility cell, containing a known solution of solute in triple-distilled, organic-free water. Helium, thus saturated with solute, was conducted into a gas-chromatograph sampling valve where it was subsequently injected into a chromatograph for analysis. The chromatograph was a flame ionization unit, manufactured by Analytical Instruments Development, Inc.

Owing to the high purity of both the solvent gas and the water, the solute vapor was the only organic in the chromatograph sample, and thus the separation requirements were minimal. All that was required was separation of the solute peak from the minimal air peak, and this was accomplished using an unpacked 1/8" stainless steel column, approximately 100 cm long. A typical peak from an ethyl acetoacetate sample is shown in Figure 3.

In contrast to the previous experiments, the behavior discussed in conjunction with equations (1A) and (3) is one sense advantageous for the present technique. Since the partition coefficient is small for both ethyl acetoacetate and diethylamine, comparatively large quantities of divent gas can be passed through the solubility cell with negligible change in liquid phase concentration. This results in a relatively stable system, providing ample time for decay of transients prior to final measurement.

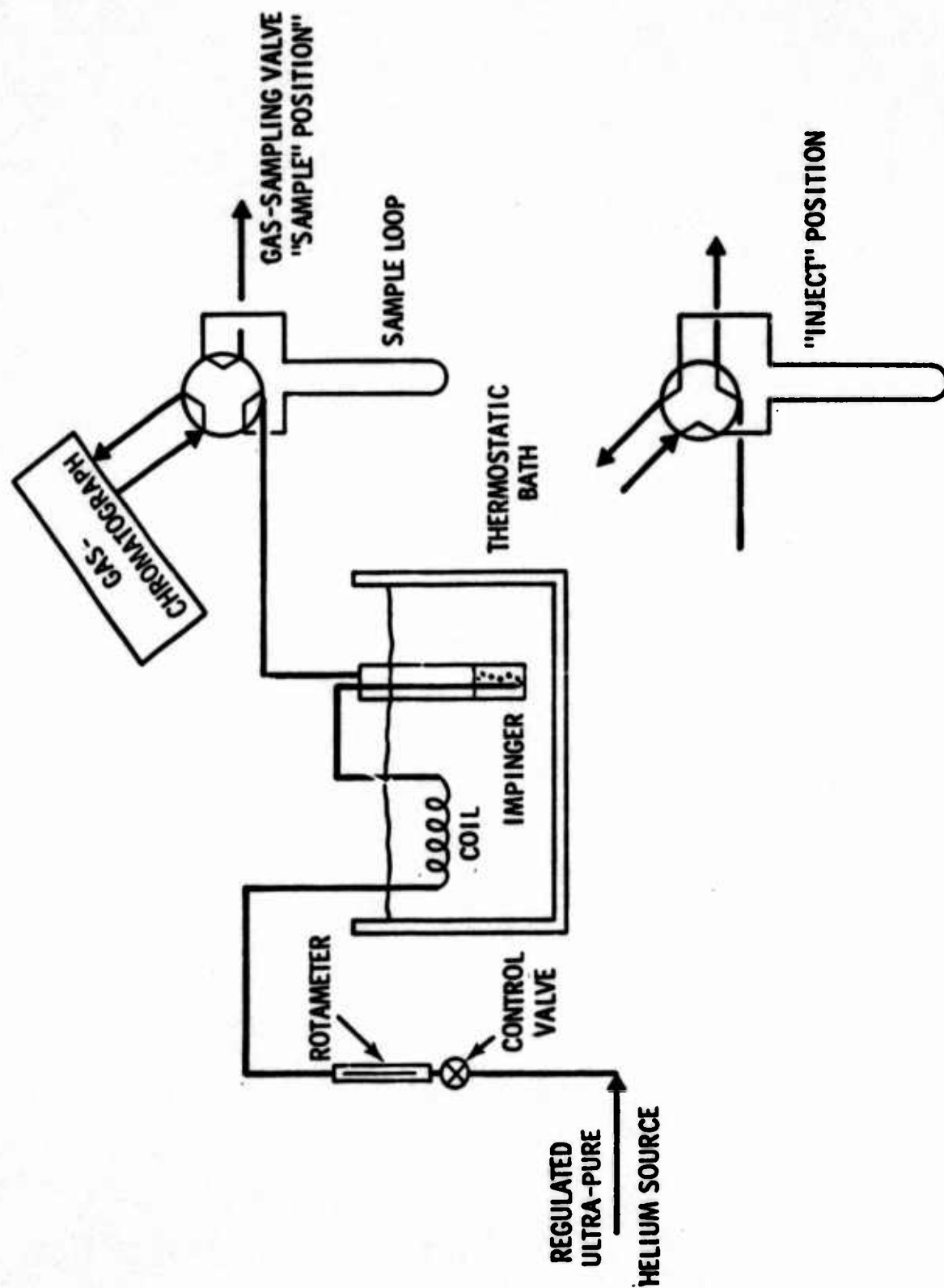


Figure 2. Schematic of Final Solubility - Measurement Apparatus

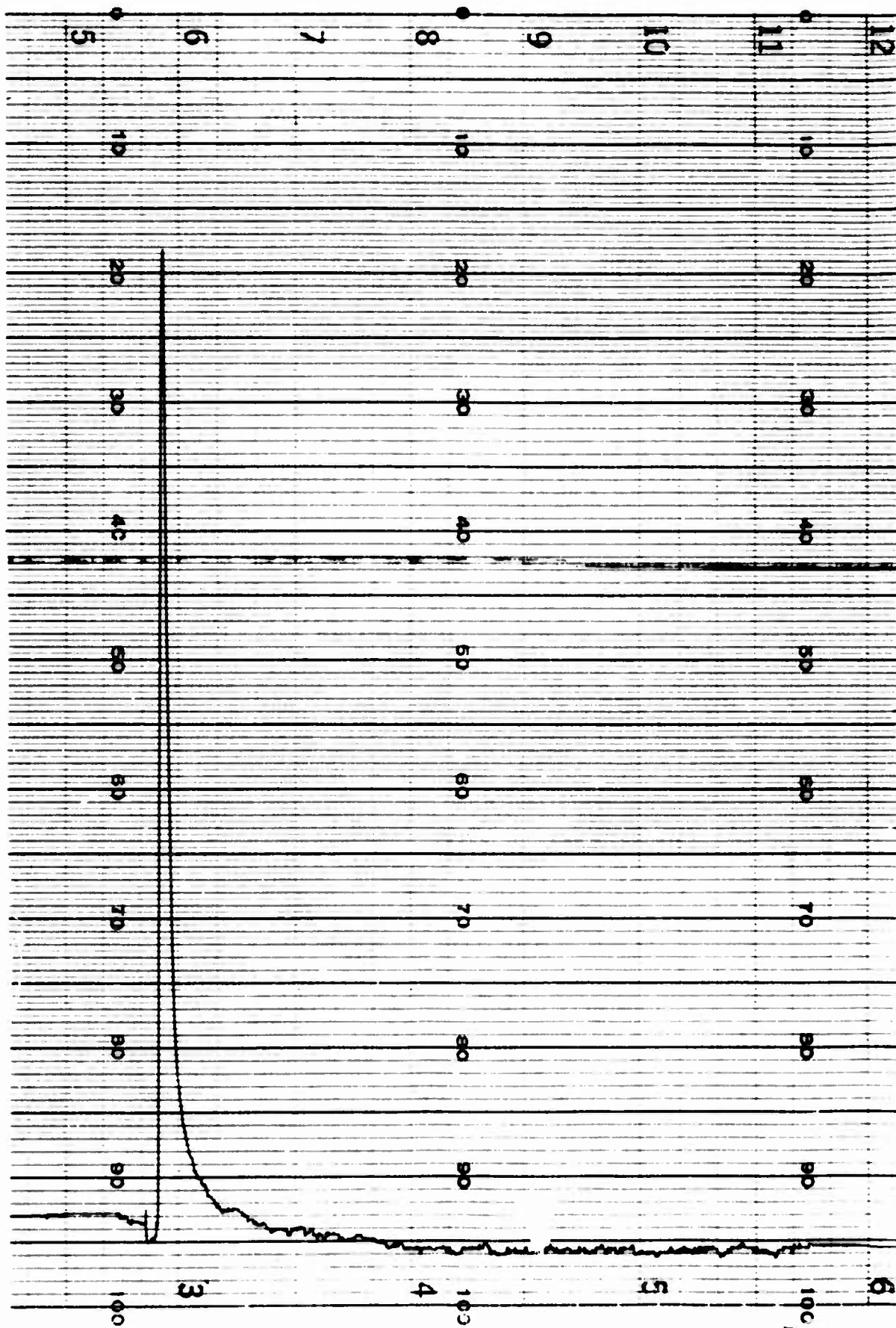


Figure 3. Typical Chromatogram for Ethyl Acetoacetate Analysis.

In another sense, however, this behavior is disadvantageous. Gas-phase concentrations, rather than those in the aqueous phase, are measured in this approach; and because of the low value of K this required the observation of comparatively low concentrations, which are more difficult to measure. Owing to this feature solubilities at gas-phase concentrations below a few tenths of a part per million could not be determined using this technique.

Additional aspects of this experimental method give rise to other potential measurement errors. The method depends upon the assumption that the gas stream leaving the liquid is saturated with solvent, and this in turn requires that the carrier gas be passed through the system at a rate sufficiently slow to ensure that mass transfer from the liquid to the gas had proceeded essentially to completion. In addition, too high a gas flow rate could possibly entrain liquid droplets, and deposit them in the line between the solubility cell and the chromatograph sampling valve, where they might desorb additional solute and thus produce high results.

Both of the above effects were examined by varying the gas flow rate through a test mixture and observing the resulting concentrations of solute in the gas stream. From these tests it was determined that gas concentration was virtually independent of flow rate for the solubility cell employed (250 ml Smith-Greenburg impinger containing 40 ml liquid), at flow rates below about 40 ml/minute. Above 40 ml/minute higher concentrations were observed, ostensibly from entrainment of liquid droplets. For this reason, all solubility experiments were conducted at nominal flow rates of 10 ml/minute.

A typical solubility experiment was conducted as follows: A solution of known solvent concentration was prepared by volumetric dilution in triple-distilled water, and 40 ml of this solution was placed in the solubility cell. The cell was in turn placed in the thermostatic bath (normally at 5°C) and allowed to approach thermal equilibrium. Upon approaching the bath temperature the gas flow was turned on, and the resulting concentration of solute in the gas was monitored until all transients had passed, and the true equilibrium concentration was attained.

The gas chromatograph was calibrated each day that solubility measurements were performed. This was accomplished using a syringe pump, which injected an air-solute mixture into a constant flow of helium at selected flow rates. Known concentrations of solute in air were loaded into the syringe by withdrawing volumes of vapor at equilibrium with the liquid phase at a known temperature from an expanding-volume vessel. Vapor pressures of the solutes were calculated for this purpose from the expressions

$$\ln p = \frac{-6098}{T} + 20.21 \quad \text{for ethyl acetoacetate ,} \quad (4)$$

and

$$\ln p = \frac{-3765}{T} + 18.089 \quad \text{for diethylamine ,} \quad (5)$$

where p is vapor pressure in mm Hg, and T is in degrees Kelvin. Plots of the calibration curves produced in this manner, along with the numerical data, are given in the Appendix.

The flow rate of diluent gas was monitored with a rotameter, which had been calibrated using a wet test meter. Flow rates from the syringe pump were calibrated using a soap-film flowmeter. All tubing downstream from the mixing points of both the calibration apparatus and solubility cell was 1/4 inch Teflon, to minimize sorption of the organic vapors.

CHAPTER III.

EXPERIMENTAL RESULTS

The experimental results of this study are given in Tables 7 and 8. These include the data obtained for both solutes at 5.0°C, in addition to data for higher temperatures. Data at 5.0°C for acidified water solutions (HCl added) for diethylamine are given as well. These results will be discussed in the following chapter.

TABLE 7. SUMMARY OF SOLUBILITY MEASUREMENTS FOR DIETHYLAMINE

Solution Temperature	Molarity Added Acid	Solute Concentration in liquid	Solute Mixing Ratio in Gas
°K	molar	moles/ml	ppm
278.2	0	1.22×10^{-6}	2.7
278.2	0	2.43×10^{-6}	6.0
278.2	0	4.87×10^{-6}	23.7
278.2	0	4.87×10^{-6}	24.2
278.2	0	9.73×10^{-5}	41.4
278.2	0	9.63×10^{-5}	355
278.2	2.50×10^{-3}	2.37×10^{-6}	1.5
278.2	2.50×10^{-3}	4.75×10^{-6}	6.4
278.2	2.50×10^{-3}	9.49×10^{-6}	32.7
278.2	2.50×10^{-3}	9.40×10^{-5}	347
279.9	0	9.73×10^{-6}	43.2
282.1	0	9.73×10^{-6}	44.8
291.6	0	9.73×10^{-6}	137

TABLE 8. SUMMARY OF SOLUBILITY MEASUREMENTS FOR ETHYL ACETOACETATE

Solution Temperature °K	Solute Concentration in Liquid moles/ml	Solute Mixing Ratio in Gas ppm
278.2	7.85×10^{-6}	4.7
278.2	3.94×10^{-6}	3.1
278.2	7.88×10^{-5}	12.7
278.2	7.88×10^{-5}	12.3
278.2	7.16×10^{-6}	3.2
278.2	3.75×10^{-6}	2.7
278.2	1.92×10^{-6}	2.0
269.2	7.16×10^{-6}	11.0

CHAPTER IV.

DISCUSSION OF RESULTS

EXPERIMENTAL ERRORS

Accuracy of the experimental results was principally dependent upon the accuracy of the gas-phase concentration measurements. These measurements depended, in turn, upon the calibration of the gas-chromatograph, and the degree of error involved in reading chromatograph output. The minimum detectable gas-phase concentrations were of the order of a few tenths of a part per million for both diethylamine and ethyl acetoacetate, with ethyl acetoacetate exhibiting somewhat higher sensitivity. At higher concentrations, serial measurements indicated a reproducibility of about $\pm 5\%$. These features give rise to an overall repeatability* of the measurements corresponding to the equations

$$E = 0.5 + .05 \chi \text{ ppm for diethylamine} \quad (6)$$

and

$$E = 0.3 + .05 \chi \text{ ppm for ethyl acetoacetate} \quad (7)$$

where E is the expected error, and χ is the measured mixing ratio in parts per million.

Calibration of the gas chromatograph involved the same peak-reading errors as the sampling procedure. Serial analyses of calibration mixtures indicated a similar repeatability; thus a conservatively large error estimate is obtained for the combination of the effects simply by doubling the above expressions

$$E_{\text{TOT}} = 1 + 0.1 \chi \text{ ppm for diethylamine} \quad (8)$$

and

$$E_{\text{TOT}} = 0.6 + 0.1 \chi \text{ ppm for ethyl acetoacetate} \quad (9)$$

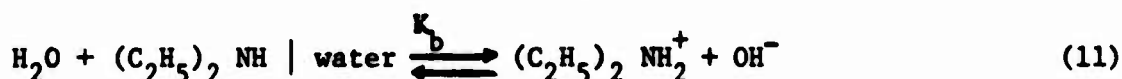
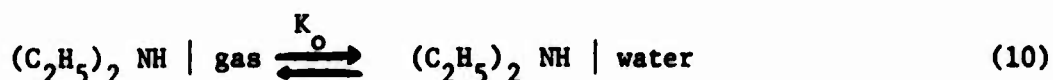
As stated previously, additional errors arising from temperature control, flow control, standards preparation, and entrainment and disequilibrium

*using a consistent calibration standard.

effects were comparatively minor; hence (8) and (9) should represent the total expected error reasonably well except for the case of low-concentration ethyl acetoacetate, which was found to vary radically with concentration and possibly lead to higher errors. This aspect will be discussed later in this chapter, where this compound is addressed more specifically.

DIETHYLAMINE

In analyzing the diethylamine solubility data it is helpful to set forth a mechanism for interaction of this material with water. Ostensibly, this interaction consists of an absorption from the gas phase with a subsequent ionization in water solution. Representing these steps in the conventional manner, we have



where the equilibrium constants K_o and K_b are given by

$$K_o = \frac{[(C_2H_5)_2 NH \mid \text{water}]}{[(C_2H_5)_2 NH \mid \text{gas}]} \quad (12)$$

$$K_b = \frac{[(C_2H_5)_2 NH_2^+][OH^-]}{[(C_2H_5)_2 NH \mid \text{water}]} \quad (13)$$

Since total dissolved diethylamine exists as two species, i.e.,

$$DEA_T = [(C_2H_5)_2 N_2H^+] + [(C_2H_5)_2 NH \mid \text{water}] \quad (14)$$

one can formulate an expression relating gaseous to dissolved solute

$$[(C_2H_5)_2 NH \mid \text{gas}] = \frac{DEA_T [OH^-]}{K_o (K_b + [OH^-])} \quad (15)$$

An accompanying expression for $[OH^-]$ can be obtained by employing the equilibrium relationship for dissociation of water

$$K_w = [H_3O^+] [OH^-] \quad (16)$$

with the ion balance for the solution

$$[OH^-]_{TOTAL} = [OH^-]_w + [OH^-]_{DEA} \quad (17)$$

The result is

$$[OH^-]_{TOTAL}^3 + (H_3O^+_{don} + K_b) [OH^-]_{TOTAL}^2 + (-K_w - K_b \text{ DEA}_T + H_3O^+_{don} K_b) [OH^-]_{TOTAL} - K_b K_w = 0 \quad (18)$$

which expresses the OH^- concentration from all sources, $[OH^-]_{TOTAL}$, as a cubic equation. In the above equations, OH^-_w and OH^-_{DEA} denote OH^- arising from ionization of water and diethylamine, respectively. $H_3O^+_{don}$ is the hydrogen ion contributed to the system from sources other than dissociation of water; this term accounts for the influence of acid on the solubility of diethylamine.

If values of the equilibrium constants were known, one could proceed immediately to solve (15) and (18) to obtain a family of curves relating the partial pressure of diethylamine above water solutions. Indeed, values for K_w are well established (RIEMAN, NEUSS, and NAIMAN (1951)) and a few measurements of K_b are available in the literature, which can be extrapolated to temperature conditions of interest with good reliability. Utilizing the data of Evans and Hayamann (1951) for this purpose in conjunction with the van't Hoff expression, one obtains the form

$$\ln K_b = - 8.4726 + \frac{211.715}{T} \quad (19)$$

Solving equation (18) for values of K_w and K_b appropriate to 5°C (1.86×10^{-14} and 4.48×10^{-4} , respectively) the results given in Table 9 are obtained.

TABLE 9. ROOTS OF EQUATION 18 FOR VARIOUS CONDITIONS

Dissolved Diethylamine Concentration	OH ⁻ Concentration H ₃ O ⁺ _{don} = 0	OH ⁻ Concentration H ₃ O ⁺ _{don} = 2.5 x 10 ⁻³
molar	molar	molar
1 x 10 ⁻³	4.82 x 10 ⁻⁴	1.24 x 10 ⁻¹²
5 x 10 ⁻³	1.29 x 10 ⁻³	3.41 x 10 ⁻⁴
1 x 10 ⁻²	1.90 x 10 ⁻³	8.78 x 10 ⁻⁴
5 x 10 ⁻²	4.51 x 10 ⁻³	3.37 x 10 ⁻³
1 x 10 ⁻¹	6.47 x 10 ⁻³	5.30 x 10 ⁻³

Since K_0 is the only remaining parameter in equations (15) and (18) it can be adjusted to fit the experimental results. If the mechanism set forth in this section is correct, then the experimental data should conform to the solutions to (15) and (18) over the complete range of variables.

A visual fit of the data to these equations suggested that K_0 at 5°C should be approximately equal to 5060, and a corresponding comparison of the experimental and theoretical results is given in Figure 4. Here it should be emphasized again that the curves were adjusted to the data by choosing an appropriate value of K_0 . The good fit to all of the data points over the ranges of concentration and acidity investigated, however, suggests that the postulated mechanism is a valid one, and provides a basis for the calculation of solubility under all low-concentration conditions.

ETHYL ACETOACETATE

In contrast to the basic behavior of diethylamine, ethyl acetoacetate exhibits mildly acedic behavior in water solution. Its small dissociation constant, however, of the order of 2×10^{-11} (EIDINOFF (1945)), limits the significance of dissociation phenomena insofar as solubility is concerned, except possibly at extremely low concentrations or under highly basic conditions. This compound also enters into a tautomerization reaction and

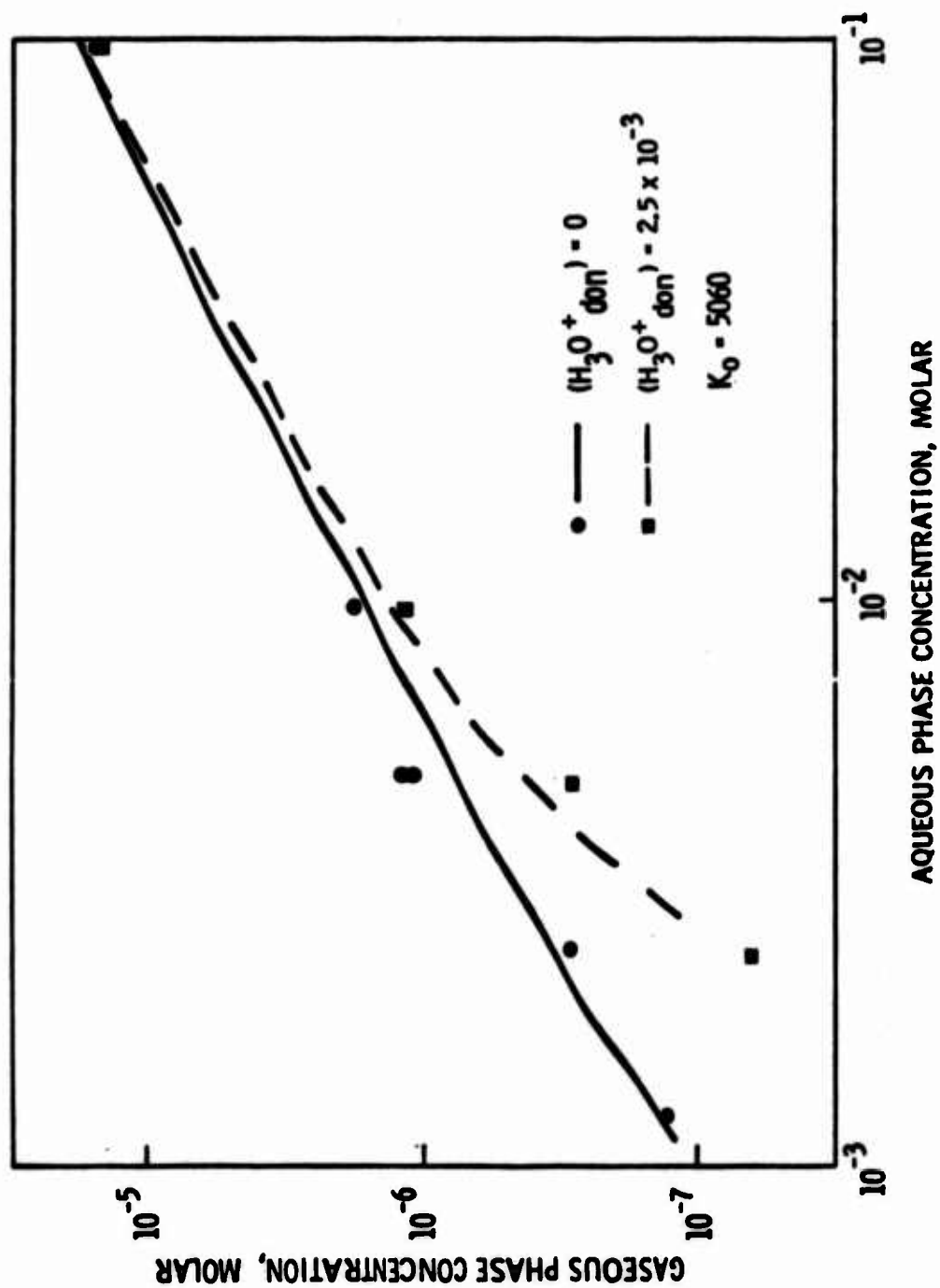


Figure 4. Experimental and Theoretical Solubilities for Diethylamine at 5°C.

exists in both keto and enol forms, which have distinctly different chemical characteristics (cf. MORRISON and BOYD (1959), RIDDICK and BUNGER (1970)). At room temperature ethyl acetoacetate contains about eight percent of the enol form.

Because of the noted complexity of the ethyl acetoacetate system, it is most expedient here to express the solubility data presented in the previous chapter directly in terms of the solubility parameter H' . This is done in the graph in Figure 5 where H' is plotted as a function of solute concentration in the liquid phase. Of particular interest here is the rapid decrease of solubility (increase of H') at concentrations lower than about 10^{-3} molar. This feature made accurate measurements of solubility more difficult under such conditions, since slight changes of solute concentration had pronounced effects on the corresponding values of H' .

It is difficult to explain the phenomena exhibited in Figure 5. Although the complex chemistry of ethyl acetoacetate may be the cause of this behavior, it seems more likely that it is based in the strongly self-associated nature of this compound. This type of behavior is conventionally associated with positive deviations from Raoult's Law (DENBIGH (1957)), and rests simply in the fact that clusters of solute molecules can exist at considerably lower energy than solvent-solute associated molecules. At very low concentrations, where solute-solute interactions become less likely, the resulting high energy state will be reflected in an increase in solute vapor pressure.

Such behavior implies that a limiting value of H' will be approached at concentrations approaching zero. This value was determined from the 5°C data by plotting the logarithm of H' versus concentration and linearly extrapolating to zero:

$$H'_0 = 1.4 \text{ atm. ml/mole} .$$

Combining this with a visual fit to the low-concentration data provides the empirical form for the water solubility of ethyl acetoacetate at 5°C :

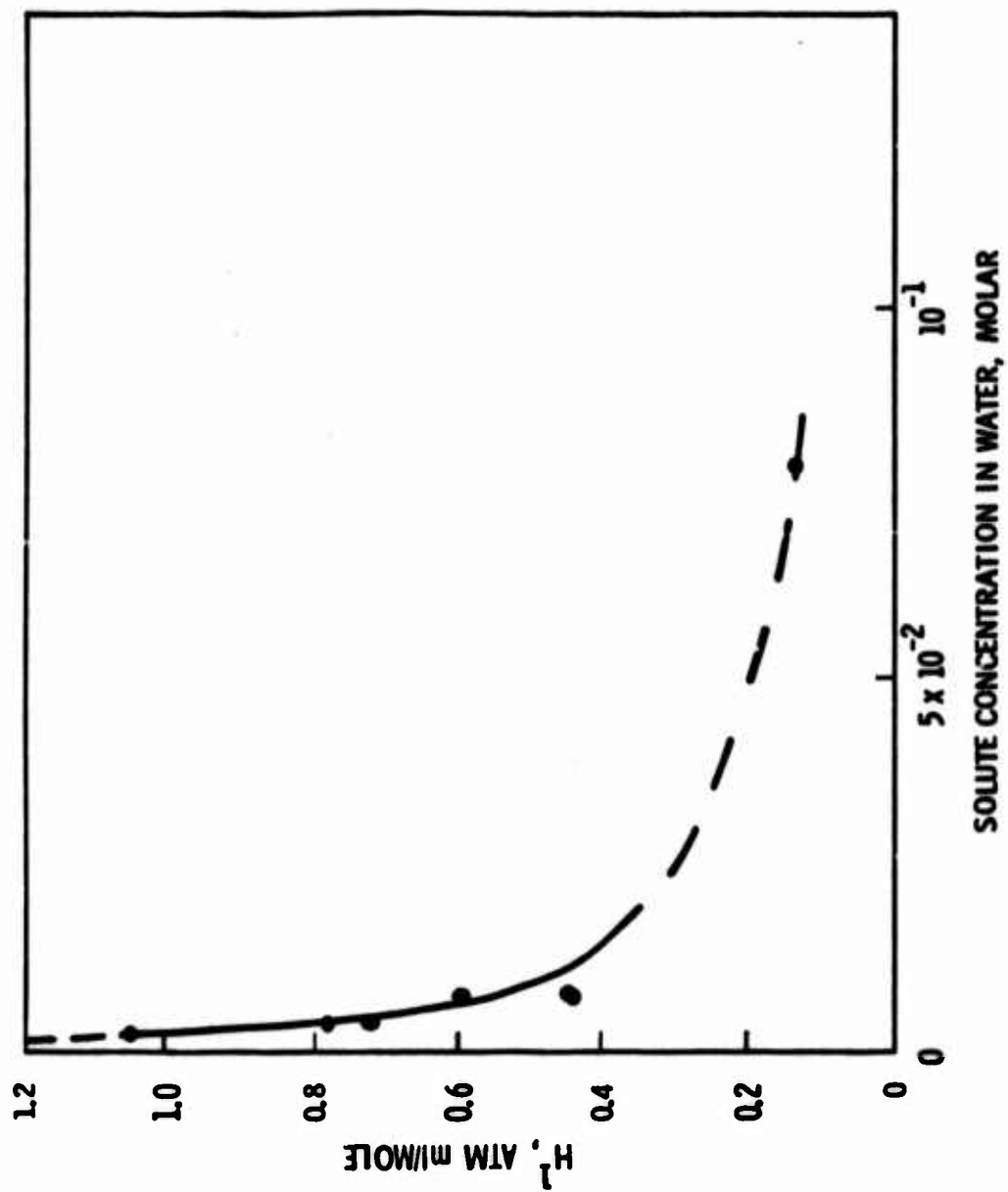


Figure 5. Experimental Solubilities for Ethyl Acetoacetate.

$$H' = 1.4 - 1.68 \times 10^5 C \text{ atm. ml/mole} \quad (20)$$

$$(0 < C < 5 \times 10^{-6})$$

where C is solute concentration in the liquid phase in moles/ml.

TEMPERATURE DEPENDENCE

Although the bulk of data obtained in this project were acquired at 5°C. additional results, obtained at higher temperatures, allow estimates of temperature dependence of the solubilities of both diethylamine and ethyl acetoacetate. For diethylamine, the temperature dependence of both K_b and K_w are known; thus if that of K_o can be determined total temperature dependence can be assessed.

Applying (15) and (18) to the experimental data point for 291.6 °K in Table 7 results in a corresponding value for K_o of approximately 1380. Utilizing an equation of the form (19) and fitting the 278.2 °K and 291.6 °K results gives

$$\ln K_o = -19.75 + \frac{7866}{T} \quad (21)$$

A similar treatment can be used to derive an analagous equation for ethyl acetoacetate, although this must be considered highly approximate in view of the complicated behavior of this substance discussed previously. Using the data points at 7.16×10^{-6} moles/cc at 278.2 and 296.2 degrees K (H' of .45 and 1.54 atm. ml/mole, respectively) in conjunction with an equation of the form (19) gives

$$\ln H' = 19.446 - \frac{5632}{T} \quad (22)$$

at 7.16×10^{-6} moles/cc. Changes in H' at other concentrations can be estimated to a first approximation, at least, by assuming proportionate changes with changes in temperature.

CHAPTER V.

REVISED SCAVENGING CALCULATIONS

The measurements obtained in this study showed the solubilities of diethylamine and ethyl acetoacetate, respectively, to be higher and lower than estimated from previous measurements. As mentioned in the first chapter, this is consistent with the comparison of predicted and measured washout rates of these compounds, and it is of interest here to perform revised estimates based upon the newly-acquired solubility data.

Such estimates, based upon EPAEC calculations in conjunction with the solubility equations (15), (18), and (20) are shown in Tables 10-14, which may be compared directly with Tables 2-6 in Chapter I. From these results the following observations can be made:

- o estimates based on the revised solubility data are in significantly better agreement with observation than previous estimates,
- o better agreement between observation and theory occurs for the more distant sampling line (line B) than for the inner sampling line (line A),
- o Diethylamine measurements exhibit closer agreement with theory than do those for ethyl acetoacetate.

In the case of ethyl acetoacetate it is readily apparent that, although the modification of the solubility estimates did enhance the agreement between observation and theory, calculated concentrations typically exceed experimental values by a factor of five or more. This behavior indicates that scavenging is influenced by additional rate phenomena, and suggests that liquid-phase mixing within the raindrops may be emerging as an important factor in this respect.

Liquid-phase mixing is dependent upon molecular and convective transport processes within falling raindrops, and its influence should increase as the diffusion coefficient and solubility of the material become small. Since no diffusivity data are available for the ethyl acetoacetate-water system this effect is difficult to assess. Assuming a moderately low diffusion coefficient for this material, however, it is not unreasonable to expect a factor

TABLE 10. REVISED PREDICTIONS OF WASHOUT CONCENTRATIONS

Experiment 1 (EAA)

Rain Collector Station	Measured Concentration C _{obs.}	Predicted Concentration C	Rain Collector Station	Measured Concentration C _{obs.}	Predicted Concentration C
A 3	<0.10 ppm	--	B 8	--	--
4	0.16	0.03 ppm	9	--	0.81 ppm
5	0.50	0.27	10	--	1.48
6	1.1	1.55	11	1.0 ppm	2.15
7	1.5	6.34	12	0.70	2.46
8	1.6	14.43	13	1.2	2.98
9	1.5	6.34	14	0.78	2.46
10	1.2	1.55	15	0.73	2.15
11	1.0	0.27	16	0.33	1.48
12	0.32	0.03	17	0.35	0.81
13	0.1	--	18	0.12	--

TABLE 11. REVISED PREDICTIONS OF WASHOUT CONCENTRATIONS

Experiment 2 (EAA)

Rain Collector Station	Measured Concentration C _{obs.}	Predicted Concentration C	Rain Collector Station	Measured Concentration C _{obs.}	Predicted Concentration C
A 1	<.10 ppm	0.22 ppm	B 5	<0.10 ppm	0.69 ppm
2	<.10	0.69	6	0.26	1.0
3	0.80	1.8	7	0.16	1.3
4	1.0	3.6	8	0.31	1.6
5	1.5	5.9	9	0.36	1.8
6	2.0	9.4	10	0.31	1.9
7	1.6	5.9	11	0.27	2.0
8	0.77	3.6	12	0.37	1.9
9	0.20	1.8	13	0.28	1.8
10	<0.10	0.69	14	0.12	1.6
11	<0.10	0.22	15	<0.10	1.3
12	<0.10	0.06	16	<0.10	1.0
13	<0.10		17	<0.10	0.69
			18	<0.10	

TABLE 12. REVISED PREDICTIONS OF WASHOUT CONCENTRATIONS

Experiment 3 (DEA)

Rain Collector Station	Measured Concentration C _{obs.}	Predicted Concentration C	Rain Collector Station	Measured Concentration C _{obs.}	Predicted Concentration C
A 4	0.6 ppm	--	B 11	0.9 ppm	0.7 ppm
5	0.7	--	12	1.7	1.4
6	2.1	--	13	2.2	2.0
7	1.4	0.2 ppm	14	2.7	2.5
8	1.3	1.4	15	3.0	2.8
9	2.1	4.9	16	2.1	2.5
10	2.5	7.3	17	2.8	2.0
11	1.0	4.9	18	1.1	1.4
12	0.6	1.4	19	1.2	0.7
13	<0.1	0.2			
14	<0.1	--			

TABLE 13. REVISED PREDICTIONS OF WASHOUT CONCENTRATIONS

Experiment 4 (DEA)

Rain Collector Station	Measured Concentration C _{obs.}	Predicted Concentration C	Rain Collector Station	Measured Concentration C _{obs.}	Predicted Concentration C
A 6	.19 ppm	.1 ppm	B 12	.21 ppm	--
7	.55	.01	13	.42	.15 ppm
8	.62	.46	14	1.3	1.0
9	.96	5.2	15	1.3	2.1
10	1.2	11.2	16	1.7	3.3
11	1.0	5.2	17	2.2	4.6
12	.85	.46	18	1.7	3.3
13	.56	.01	19	1.4	2.1
14	.39	--	20	1.8	1.0
			21	1.3	.15
			22	.80	--
			23	.45	--

TABLE 14. REVISED PREDICTIONS OF WASHOUT CONCENTRATIONS

Experiment 5 (DEA)

Rain Collector Station	Measured Concentration C _{obs.}	Predicted Concentration C	Rain Collector Station	Measured Concentration C _{obs.}	Predicted Concentration C
A 8	0.17 ppm	--	B 12	0.28 ppm	.1 ppm
9	0.47	.02 ppm	13	0.41	.2
10	0.37	.41	14	0.47	.8
11	0.43	3.1	15	0.47	1.3
12	0.57	6.0	16	0.47	1.7
13	0.32	3.1	17	--	2.2
14	0.48	.41	18	0.63	1.7
15	0.17	.20	19	0.56	1.3
			20	0.43	.8
			21	0.43	.2
			22	0.42	.1

of ten reduction in washout concentrations from this effect. Quantitative assessments of the effects of liquid mixing, if diffusion coefficients are known, can be performed by the EPAEC model (DANA, HALES, and WOLF (1973)).

Scavenging calculations for diethylamine are complicated by the presence of atmospheric CO_2 , which forms acid upon dissolution in water and thus modifies diethylamine solubility. Conversely, dissolved diethylamine modifies the solubility of CO_2 in water, and the simultaneous presence of these materials should enhance the scavenging rates of both. The EPAEC model cannot account for scavenging of multiple, reactive components*, and for this reason we have chosen to account approximately for the influence of CO_2 by choosing a nominal constant, associated value of $[\text{H}_3\text{O}^+_{\text{don}}] = 3.2 \times 10^{-6}$ molar. This approximation should be reasonably valid for this purpose owing to the relatively slow dissociation rate of CO_2 in water, and to the rather secondary effects of hydrogen ion on solubility in this concentration range.

As seen from the data in Tables 18-20, the computed washout concentrations for the innermost arc appear to be somewhat higher and more constricted in the crosswind direction than those actually observed. Such behavior is typical of similar measurements for SO_2 under such conditions, and is thought to be caused primarily by undercutting by the rain and meandering by the true plume, which is approximated as a point source in the EPAEC model. The agreement between experiment and theory on the outer sampling line is excellent; this is undoubtedly caused in part by fortuity, but is considered also to be strong supporting evidence for this modeling approach. From these investigations it is concluded that although a number of microphysical phenomena may emerge as rate-influencing steps in the gas-scavenging process, the modeling approach presented in this and the previous report provides a reasonable and convenient means for generalized gas-scavenging analysis.

*A new code, Scavenging Model Incorporating Chemical Kinetics (SMICK) has recently been developed at this laboratory for this purpose under contract to the EPA.

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APPENDIX A

CHROMATOGRAPH CALIBRATIONS AND RAW DATA

DIETHYLAMINE

Chromatograph Calibrations

9 July 75

<u>PPM DEA</u>	<u>PEAK HT</u>
4.43	29
8.87	85
17.7	240
44.3	1190
88.7	3170
177	9290

11 July 75

225	9980
450	21800

Solubility Measurements

<u>Liquid Conc.</u>	<u>[H_{don}]</u>	<u>PEAK HT</u>
<u>moles/ml</u>	<u>molar</u>	
1.22 x 10 ⁻⁶	0	12
2.43 x 10 ⁻⁶	0	43
2.37 x 10 ⁻⁶	2.5 x 10 ⁻³	5
4.87 x 10 ⁻⁶	0	378
4.75 x 10 ⁻⁶	2.5 x 10 ⁻³	48
4.87 x 10 ⁻⁶	0	392
9.73 x 10 ⁻⁶	0	917
9.49 x 10 ⁻⁶	2.5 x 10 ⁻³	632
9.73 x 10 ⁻⁶ (6,7°C)	0	982
9.73 x 10 ⁻⁶ (8,9°C)	0	1040
9.73 x 10 ⁻⁶ (18,4°C)	0	6080

Solubility Measurements (continued)

<u>Liquid Conc.</u> <u>moles/ml</u>	<u>[H_{don}]</u> <u>molar</u>	<u>PEAK HT</u>
9.63×10^{-5}	0	17200
9.40×10^{-5}	2.5×10^{-3}	16900

ETHYL ACETOACETATE

Chromatograph Calibrations

6 July 75

<u>PPM EAA</u>	<u>PEAK HT</u>
1.95	55
3.90	136
7.80	288
15.6	708

11 July 75

0.74	13
1.48	38
2.96	102
5.92	248
11.8	610

Solubility Measurements

<u>Liquid Conc.</u> <u>moles/ml</u>	<u>PEAK HT</u>
6 July 75	
7.88×10^{-6}	162
3.94×10^{-6}	98
11 July 75	
7.88×10^{-5}	720
7.88×10^{-5}	690
7.16×10^{-6}	112
3.75×10^{-6}	88
1.92×10^{-6}	60
7.16×10^{-6} (23.0°C)	592