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SOLUTE-GAS EQUILIBRIA IN
MULTI-ORGANIC AQUEOUS SYSTEMS

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I. INTRODUCTION

More than 40% of the U. S. population use groundwater for drinking, often without any treatment other than disinfection (1). Groundwaters are generally considered to be less susceptible than surface waters to contamination. However, improvements in analytical procedures and an increase in monitoring activity have uncovered a significant number of groundwaters contaminated with trichloroethylene (TCE) and other chlorinated organic solvents. Usually the water was being analyzed for trihalomethanes when the solvents were detected (2).

Dozens of wells serving several thousand people have been found to be contaminated in New England, New York (particularly Long Island), Pennsylvania, and Florida (1). In New Jersey, a recent study of 670 drinking and industrial wells uncovered contamination of 111 wells with toxic chemicals (3). The chemicals were mainly volatile, low-molecular-weight chlorinated solvents, including TCE, carbon tetrachloride, tetrachloroethylene, and trichloroethane. Some 450 wells in New Jersey have been shut down in the past three years, because of toxic contamination (3). Isolated incidences of solvent contamination of groundwaters have also been reported in California, Arizona, Michigan, and Virginia. Most of these incidences are suspected to have resulted from improper disposal of cleaning solvents, either through spreading on the land or at dump sites (4).

The Air Force routinely uses TCE and other chlorinated compounds as cleaning solvents in the maintenance of aircraft; TCE contamination of groundwater has been found in the vicinity of several Air Force bases. The Air Force has since been actively participating in research addressing the technology of TCE removal from contaminated groundwater, initially focusing on carbon adsorption to achieve removal to the 4.5 ppb action level given by the Environmental Protection Agency (EPA) for TCE. Additionally, research has been undertaken to evaluate the potential of air stripping for TCE removal.

Aeration -- either with a diffused air or packed bed system -- potentially offers a relatively inexpensive means for removal of highly volatile contaminants such as TCE. Conceivably it could be used as the sole treatment method in some instances, or as a pretreatment to carbon or resin adsorption, reducing overall costs by increasing the throughput volume per mass of adsorbent employed.

Diffused air stripping of TCE has been evaluated by EPA researchers (4) and their subcontractors (5), demonstrating perhaps 80-85% removal with 10 minutes contact time. Fundamentally, however, countercurrent packed bed stripping reactors offer significant advantages over diffused air systems, particularly in terms of the air/liquid ratio required to effect a particular removal. Consequently, the Air Force is constructing a pilot-scale packed tower facility to further investigate the potential of air stripping to remove TCE from contaminated groundwater at Wurtsmith AFB, Oscoda, Michigan.

Proper design of stripping tower facilities requires a model which relates process performance to design, operating, and environmental parameters. In particular, one would like to be able to model performance such that percent removal of a volatile such as TCE could be predicted as a function of packed volume, air and water flows, temperature (of critical concern in the Northeast and Midwest) and ionic strength. One would also like to be able to predict percent removal of volatile solvents in the presence of other volatile and nonvolatile solvents. Equations exist which allow performance prediction given values of the gas/liquid partition coefficients for the volatiles and the applicable mass transfer coefficients. However, data are lacking concerning the dependence of these equilibrium and kinetic coefficients on environmental conditions and operating parameters.

Previous USAF-sponsored studies conducted by this investigator (6) have been concerned with the modeling of stripping tower performance for TCE removal. The effects of temperature and ionic strength upon solution/gas equilibrium (i.e., Henry's Constant) have been evaluated only for a system containing TCE as the sole organic. Likewise, this simple chemical system was employed in investigations of the effects of temperature and fluid flow velocities on mass transfer kinetics. However, since the Air Force uses -- and disposes of -- a variety of chlorinated and aromatic solvents, it is likely that future applications of stripping technology may involve groundwater and/or wastewater systems containing organics other than TCE.

The previously-reported work of this investigator concluded with a recommendation that studies be broadened to include other volatile organics -- alone and in multiple-organic systems. The presence of additional organics (some perhaps not even strippable) likely to be found along with a particular volatile should be evaluated for mutual effects on stripping

potential. Henry's Constant and the applicable mass transfer coefficient ($K_L a$) may both be significantly affected by the presence of such compounds, either through effects on solvent-solute affinity, or by surface activity effects. It is likely, for example, that chlorobenzene (and other chlorinated compounds) and phenols will be present together in groundwaters or wastewaters contaminated with TCE, since these compounds are often used where TCE is, and are disposed of in the same manner.

Thus, the objective of this presently-reported research was to study the solution/gas equilibria of several relevant compounds. The effects of temperature, ionic strength, and presence of additional organics on Henry's Constant for a variety of significant organic compounds were evaluated. (The effect of these parameters on $K_L a$ is left for later investigation).

The compounds studied were: 1,1,1-trichloroethane; tetrachloroethylene; trichloroethylene; chloroform; methylene chloride; o-dichlorobenzene; and p-cresol. Selection of compounds was guided both by a concern to study organics of critical concern to the Air Force (o-dichlorobenzene, p-cresol, and methylene chloride are all used in paint-stripping solvents; tetrachloroethylene, 1,1,1-trichloroethane, and TCE are used as decarbonizers and degreasers) as well as by the desire to cover a broad range of volatilities (e.g., tetrachloroethylene versus p-cresol). Chloroform was included because it seems to be ubiquitous.

II. BACKGROUND

A Solution/Gas Equilibria Applied to Low-Solubility Contaminants

1. Henry's Law. Equilibrium between a solute and its vapor is generally modeled (7, 8) according to Henry's Law, which for dilute solutions is:

$$P = H C \quad (1)$$

where:

P = partial pressure of the solute
substance in the gas phase (atm);

C = solute concentration in the liquid phase (moles/m³);

H = Henry's Constant (m³-atm/mole).

For cases where ionic strength is appreciable, Equation 1 should properly be written in terms of activities, rather than concentrations; however, for total pressures less than 1 atm, partial pressure of a substance in the gas phase is a good approximation of its activity, and we may generally write,

$$P = H \gamma C \quad (2)$$

where:

γ = activity coefficient for the solute in liquid.

In order to model the performance of a packed stripping tower, we should like to know the variation of H with temperature, and the dependence of γ upon ionic strength. The literature is not extensive on these matters where chlorinated solvents of interest are concerned. Mackay and Leinonen (9), Mackay and Wolkoff (10), and Dilling (11) have used solubility and vapor pressure data to estimate Henry's Constants for volatile solvents -- but H-values obtained in this way, while they may give some idea of relative strippability among compounds, are only as good as the data used in the calculations. Solubility data in particular seem to vary greatly among literature sources. The EPA document, "Innovative and Alternative Technology Assessment Manual", (16) presents a Table of similarly-calculated Henry's Constants for the priority pollutants.

The dependence of Henry's Constant upon temperature must generally be further calculated using enthalpy of vaporization data in conjunction with the estimates of H at 20°C. Such enthalpy data are difficult to find and/or unacceptably inaccurate in many cases.

Even scarcer are data concerning the variation of γ with ionic strength. Butler (8) states that at concentrations less than 0.1 M, the activity of uncharged species is within 1% of molar concentration. For uncharged molecules of concentration less than 0.5 M, in solutions of ionic strength up to 5 M,

$$\log_{10} \gamma = kI \quad (3)$$

is a good approximation, with I = ionic strength (molar) and k = salting-out

coefficient (8). However, k values are not available for the organics of interest to this investigation.

2. Previous Studies by the Principal Investigator. Under sponsorship of the Air Force Summer Faculty Research Program, the Principal Investigator conducted equilibrium studies relating the gas/solution phase partitioning of TCE to temperature and ionic strength. Henry's Constant was determined for TCE in distilled, deionized and carbon-treated water over a temperature range from 10°C to 30°C -- the anticipated range of interest. The method of H determination was a variation of that used by Mackay et al. (13), the details of which are described elsewhere(6) and in the next section of this report. Essentially, the technique involved measurement of the rate of TCE removal from a batch, aqueous phase subjected to equilibrium diffused-air stripping at a known rate.

Over a limited range of temperature, the enthalpy of reaction may be considered a constant. In such cases, the variation of an equilibrium constant with temperature may be described by:

$$\ln \frac{H}{H_1} = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T} - \frac{1}{T_1} \right) \quad (4)$$

R = gas constant = $8.2056 \times 10^{-5} [(m^3 \cdot atm)/mole \cdot ^\circ K]$

H = Henry's Constant at T ($^\circ K$)

H₁ = Henry's Constant at T₁ ($^\circ K$)

ΔH° = Standard reaction enthalpy, assumed constant over the range from T to T₁.

Thus, a plot of $\ln H$ vs. $1/T$ should yield a straight line with a slope of $-\Delta H^\circ/R$. Henry's Constant data gathered in these earlier experiments over the range from 10°C to 30°C are shown plotted in Figure 1 in accordance with Equation 4. Linear regression gives the equation for H-dependence upon temperature shown in the Figure. From the slope of the regression, the standard enthalpy of volatilization is calculated to be 8560 cal/mole.

Ionic strength studies were conducted over the range from zero to 1 M at 20°C using KCl as electrolyte. The experimental procedure allowed, directly, only the determination of H_y. Using the H-value determined at I=0, however, allowed activity coefficients to be separately calculated from the H_y data obtained versus ionic strength. Figure 2 shows a plot of $\log_{10} \gamma$ versus

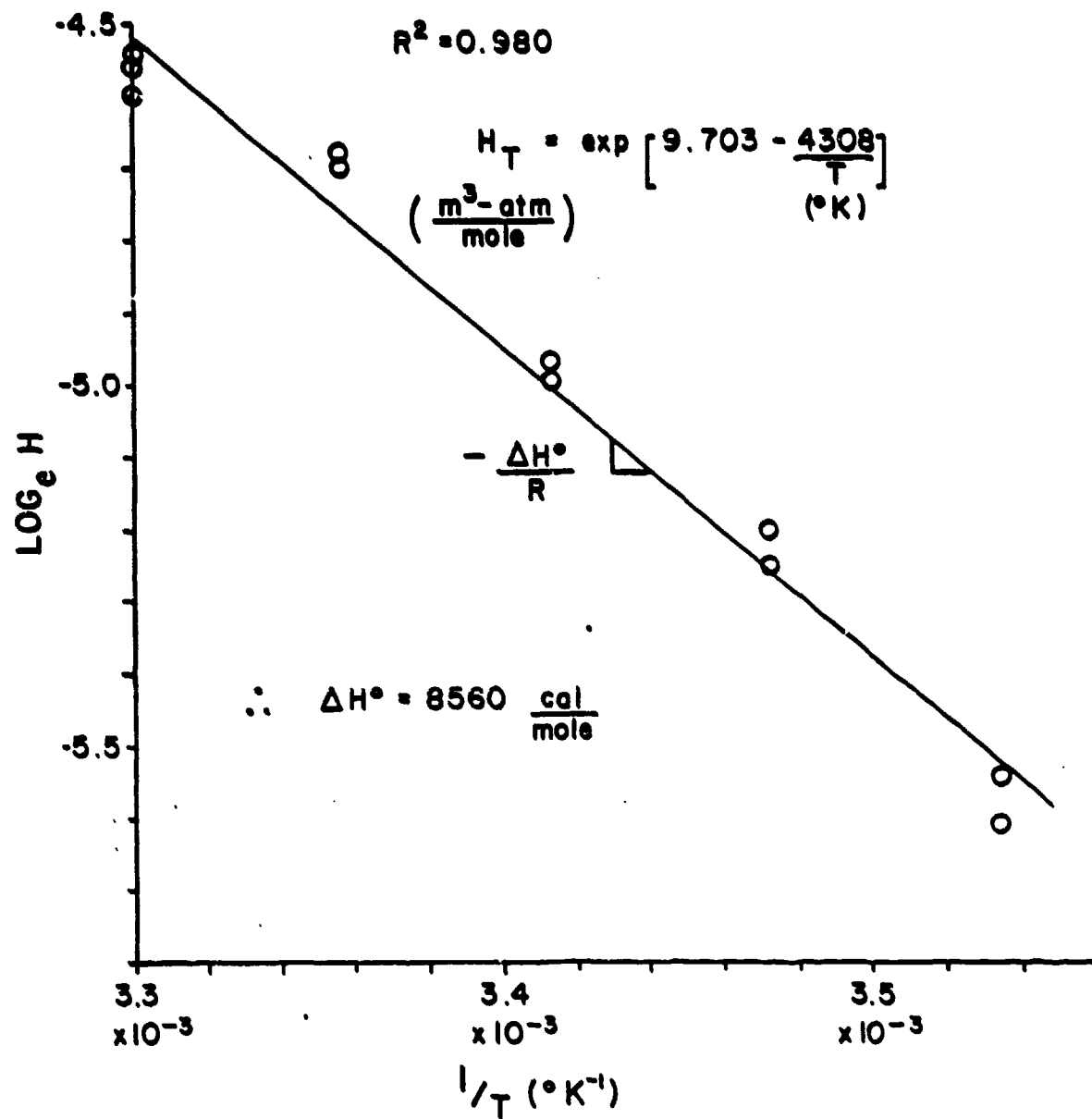


Figure 1. Temperature dependence of Henry's Constant for trichloroethylene.

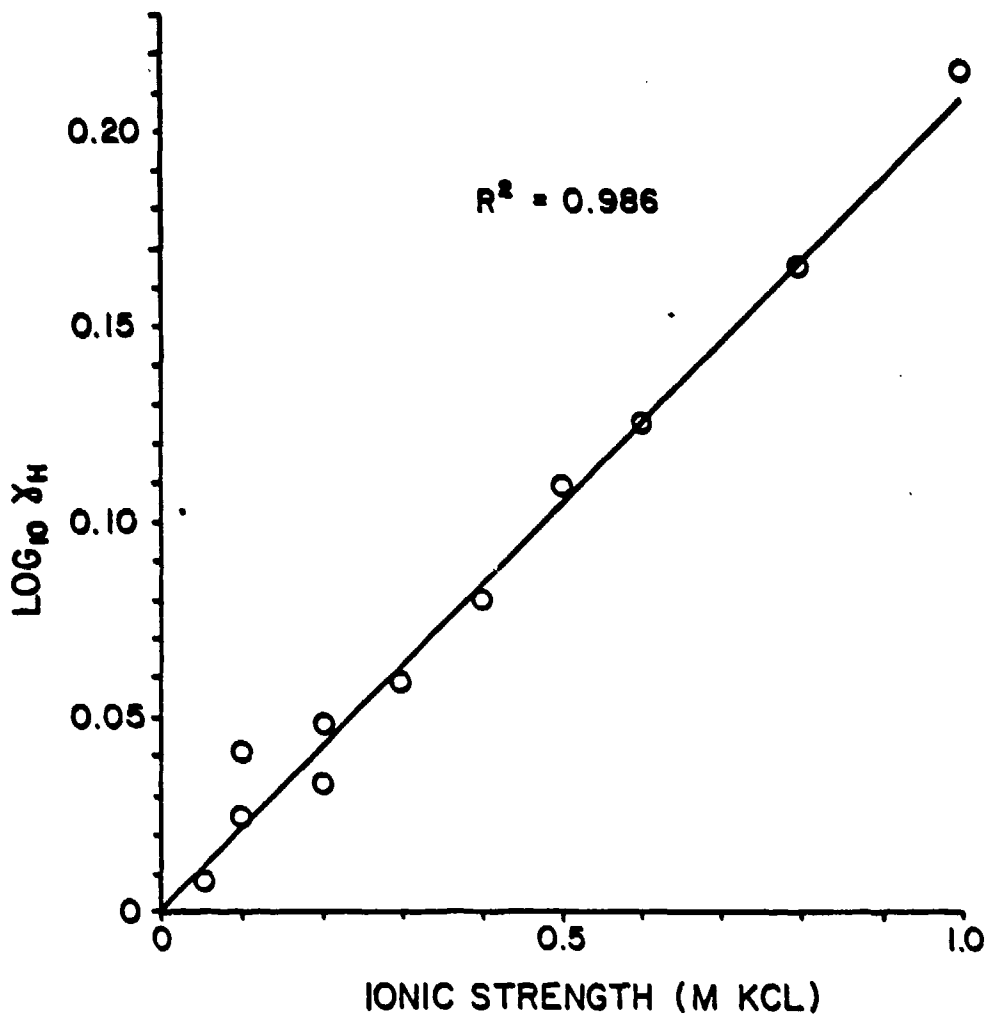


Figure 2. Effect of ionic strength on the activity coefficient for trichloroethylene (20°C).

ionic strength in accordance with the empirical model form commonly used for activity coefficients of uncharged solutes (Equation 3). The regression gives a salting-out coefficient of 0.21 l/mole for TCE in KCl solution at 20°C.

III. PROCEDURES

A. Program of Study.

Using the apparatus and techniques described below, values of Henry's Constant were determined for 1,1,1-trichloroethane, tetrachloroethylene, trichloroethylene, chloroform, methylene chloride, and o-dichlorobenzene in distilled water over a temperature range from 10°C to 30°C in the absence of additional organics. (Attempts to measure H-values for p-cresol proved fruitless; the extremely low volatility of this compound resulted in our not being able to detect any decrease in its concentration after one hour of stripping; we concluded that p-cresol is not practically strippable and conducted no further experiments with it).

In a second phase of study, the effects of ionic strength on the activity coefficients for aqueous tetrachloroethylene, chloroform, and methylene chloride were assayed using KCl over a range extending to 1.0 M concentration (25°C).

In a third phase of study, the six volatile compounds thus far studied alone (1,1,1-trichloroethane, tetrachloroethylene, TCE, chloroform, methylene chloride, and o-dichlorobenzene) were employed in experiments involving six-component mixtures. The six were added together to the batch stripping reactor in two separate series of experiments at two relative concentration levels (termed merely "high" and "low") which differed by an order of magnitude. The objective was to assess the effect of mutual presence of the six on the Henry's Constant of each.

In a fourth phase of study, Henry's Constants were measured for each of the six components listed above when each was added alone to distilled water containing 200 mg/l phenol at 25°C.

In a fifth phase of study, the six compounds were added together (at the "high" concentration level) to settled, municipal wastewater ("primary effluent") at 25°C. Effective Henry's Constants for each were determined in this matrix.

B. Compounds Chosen for Study

Data pertaining to the seven organic compounds used in this and the previous investigation (6) are contained in Table 1. It is apparent that significant discrepancies exist among some solubility data and reported estimates of Henry's Constants (particularly in the case of 1,1,1-trichloroethane). Discrepancies are also evident between estimated and measured H-values. Such discrepancies justify this presently-reported study.

All compounds studied were obtained in the highest purity commercially available; significant, spurious GC peaks were not evident using the headspace chromatographic technique (15) under the analytical conditions employed in this study.

C. Experimental Procedures

1. Measurement of Henry's Constant. The method for H-determination was a variation of that used by Mackay et al. (13). A tube reactor of one liter capacity was employed (Figure 3). An aqueous sample containing the organic solvent (or solvent mixture) of interest was placed in the reactor; air (breathing grade) was bubbled through the solution via a diffuser stone situated in the reactor bottom; the exit gas containing stripped solute then passed through a wet-test meter for flow-rate measurement. The entire reactor was surrounded by a water jacket for temperature control (the jacket water was continuously run through a circulator [Endocal model RTE-5, Neslab Inc.]), and the stripping gas was saturated with water vapor prior to its entry into the reactor. Samples of the reactor liquid were taken at time intervals, and the remaining organic concentration was assayed using the headspace gas chromatographic technique described by Dietz and Singley (15) (except in the case of p-cresol, where UV absorbance was used for concentration measurement).

The determination of Henry's Constant using the apparatus of Figure 3 depends upon two critical assumptions: (1) the liquid in the reactor is completely mixed; and (2) the gas exiting the reactor is at equilibrium with the uniform reactor liquid concentration. With these assumptions, equations may be derived which describe the stripping of a volatile solvent from the reactor with time.

With liquid samples removed at time intervals, the liquid volume decreases with each sequential sampling. Define:

Table 1. Pertinent Data for Compounds Studied
[from reference (14), except where otherwise noted].

MW	Density (a)	Boiling Point °C	Solubility in Water (b) mg/l	Vapor Pressure (pure) mm Hg	Henry's Constant m ³ -atm/mole (c)	
					Calculated	Measured
1,1,1-Trichloroethane	133.42	1.325 ²⁶	74.1	720 ²⁰ (11) 4400 ²⁰ (16)	100 ²⁹ .0	0.029 ²⁵ (11) 0.0041 ²⁰ (16) 0.0036 ²⁰ (12)
Tetrachloroethylene	165.85	1.624 ¹⁵	120.8	200 ²⁰ (14) 150 ²⁵ (16) 140 ²⁵ (11)	20 ²⁶ .3	0.027 ²⁵ (16) 0.023 ²⁰ (12) 0.029 ²⁵ (11)
Trichloroethylene	131.40	1.466 ²⁰	87.2	1000 ²⁵ (14) 1100 ²⁵ (11)	60 ²⁰ .0	0.012 ²⁵ (16) 0.010 ²⁰ (12) 0.0098 ²⁰ (11) 0.012 ²⁵ (11)
Chloroform	119.39	1.489 ²⁰	61.2	8200 ²⁰ (14) 7840 ²⁵ (16)	200 ²⁵ .9	0.0039 ²⁵ (16) 0.0034 ²⁰ (12)
Methylene Chloride	84.94	1.336 ²⁰	40.5	20,000 ²⁰ (14) 16,700 ²⁵ (16) 19,400 ²⁵ (11)	400 ²⁴ .1	0.0029 ²⁵ (16) 0.0025 ²⁰ (12) 0.0024 ²⁵ (11)
o-Dichlorobenzene	147.01	1.505 ²⁰	179	i (14) 100 ²⁵ (16)	120.0	0.0020 ²⁰ (16) 0.0017 ²⁰ (12)
p-Cresol	108.13	1.035 ²⁰	202	18,000 ²⁰ (14)	<1 ⁵³	

(a) Densities at superscript temperature (°C) relative to water at 4°C.

(b) Solubilities in water at superscript temperature (°C). References are given in parentheses.

(c) Henry's Constants calculated from solubilities and vapor pressures at superscript temperature (°C). References are given in parentheses. Measured values are reported for four of the compounds, with these references also given in parentheses.

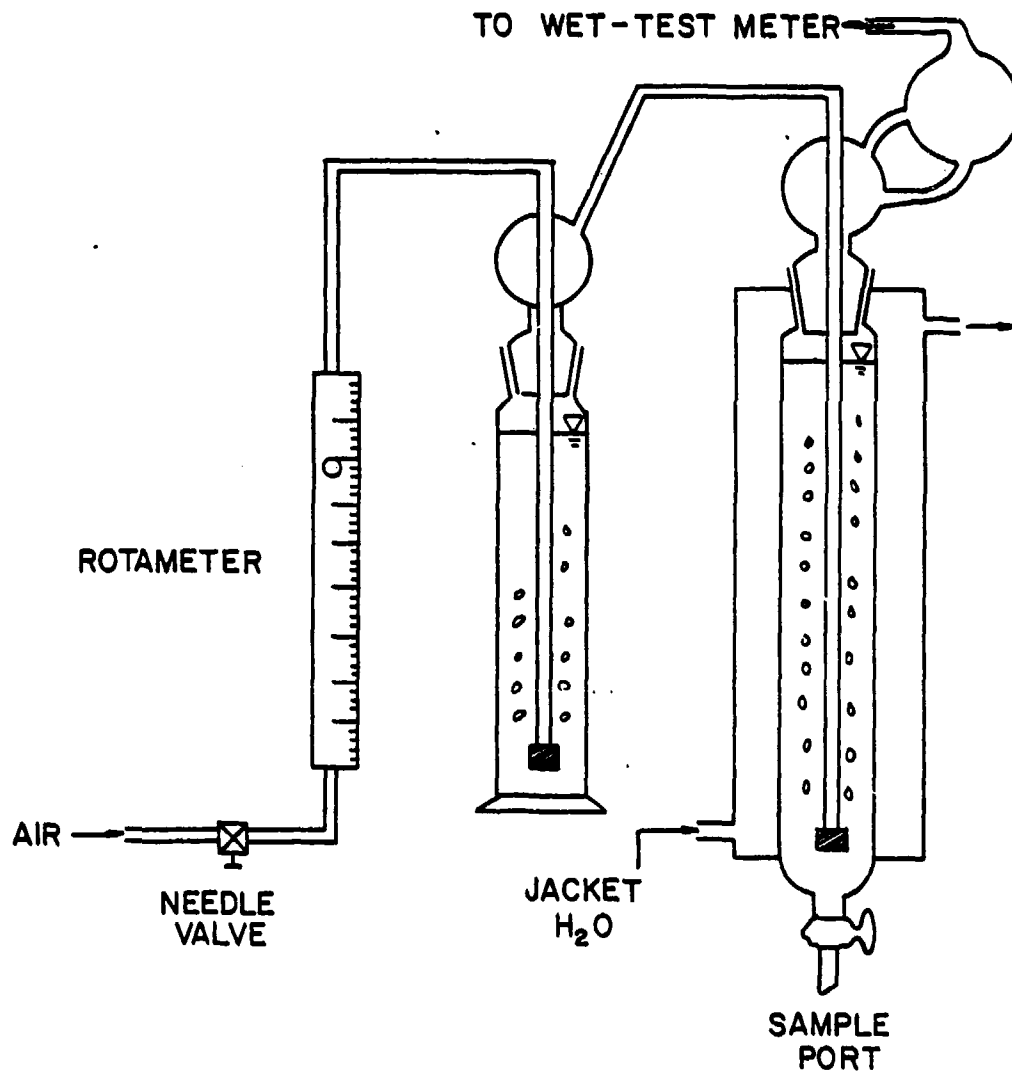


Figure 3. Apparatus for Henry's Constant determination.

$G = \text{m}^3/\text{min}$ air flow (measured at the temperature of the gas meter, T_g);

$R = \text{gas constant} = 8.2056 \times 10^{-5} (\text{m}^3\text{-atm})/(\text{mole}\text{-}^\circ\text{K})$;

$V_i = \text{reactor liquid volume during the } i\text{th interval } (\text{m}^3)$;

$C_i = \text{reactor concentration } (\text{moles}/\text{m}^3) \text{ at the end of the } i\text{th interval.}$

With our earlier assumptions regarding complete mixing and gas/liquid phase equilibration, then during the i th interval of purging,

$$V_i \left(\frac{dC}{dt} \right) = \frac{-PG}{RT_g} = \frac{-HYCG}{RT_g} \quad (5)$$

Integrate:

$$C_i = C_{i-1} \exp \left[\frac{-HYG\Delta t_i}{RT_g V_i} \right] \quad (6)$$

where:

$\Delta t_i = \text{time of } i\text{th interval (min)}$

Therefore:

$$\ln C_i = \ln C_0 - \frac{HYG}{RT_g} \sum_{j=1}^i \frac{\Delta t_j}{V_j} \quad (7)$$

where:

$C_0 = \text{initial, } t=0 \text{ concentration (moles}/\text{m}^3).$

Thus, a plot of $\ln(C_i/C_0)$ vs. $\sum \frac{\Delta t_j}{V_j}$ should yield a straight line with a slope equal to $-HYG/RT_g$. From this, HY may be evaluated.

Figure 4 is an example of a data plot from Henry's Constant determination in accordance with Equation 7. The precision is remarkable, as evidenced by the coefficient of determination (R^2) of 1.000. In no case was R^2 less than 0.98. Since these temperature studies employed distilled water, ionic strength (I) was zero and $\gamma = 1$; therefore, H itself could be evaluated as a function of temperature from the slopes of plots such as that of Figure 4.

(Studies were undertaken as outlined by Mackay *et al.* (13), using a range of initial system volumes and purging gas flow rates to demonstrate that the two critical assumptions of complete mixing and equilibration were satisfied.)

The procedure used in the temperature studies was as follows: One liter of distilled water was placed in the reactor; the air flow was turned on, adjusted within the range 350-390 ml/min (measured at the wet-test meter temperature, T_g) and allowed to flow through the reactor; the water jacket was adjusted to the desired study temperature; the system was thermally equilibrated for approximately one hour; the system temperatures (liquid, exit gas, and jacket water) were checked to verify thermal equilibration; a small volume (< 10 ml) of stock solution (prepared by saturating distilled water with the pure solvent of interest at 25°C) was added to the reactor; a mixing period of two minutes was allowed; 25 ml samples were taken from the reactor bottom at 1 - 5 minute intervals for 7 - 35 minutes (depending upon the organic studied); the samples were poured with a minimum of agitation into 120 ml serum bottles and crimp-capped with teflon-lined serum caps; the samples were thermally equilibrated to ambient temperature and phase equilibrated for 10 minutes using a wrist-action shaker; and 0.5 ml headspace samples were injected into a gas chromatograph. [Note: in the case of p-cresol, 25 ml samples which were removed from the reactor were directly analyzed by UV spectroscopy]. The initial value of organic concentration added to the reactor was selected to provide analytical convenience with the GC (or UV) technique employed; hence, these concentrations ranged from 1 mg/l (for o-dichlorobenzene) to 19 mg/l (for methylene chloride).

For the ionic strength and phenol studies, the above procedure was also followed, except that the initial liquid added to the reactor consisted of distilled water with either KCl or 200 mg/l phenol added to it.

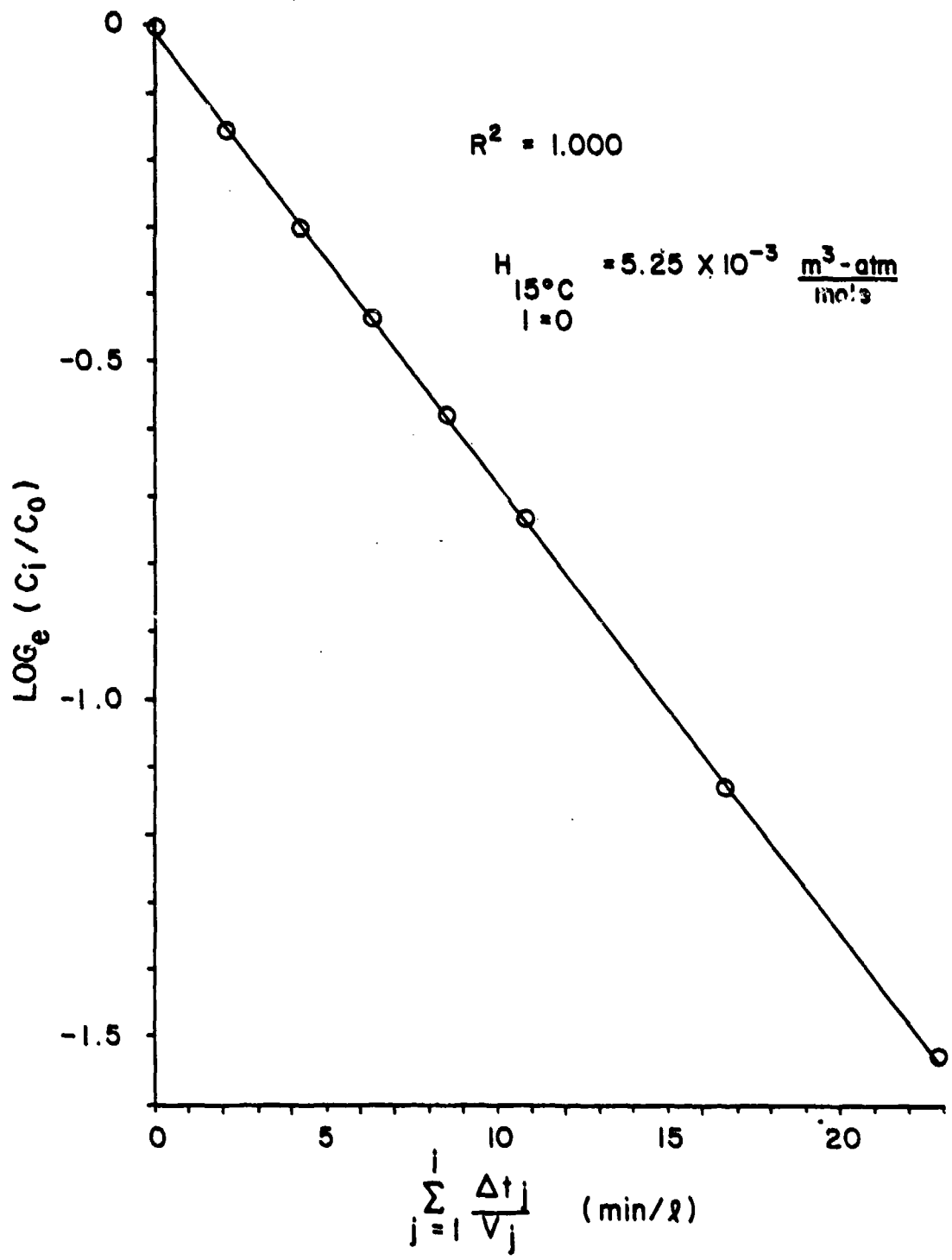


Figure 4. Example of data plot from Henry's Constant determination. (TCE, 15°C, zero ionic strength).

For the 25°C studies employing six-component mixtures, the procedure described in detail above was followed, except that instead of adding a small amount of single-solvent-saturated water to the thermally-equilibrated reactor contents, a mixture was prepared by combining aliquots of the saturated stock solutions from each of the six compounds. This mixture was added to the reactor to initiate the experiment. The proportion of each organic in the mixture was selected to give roughly equal initial GC peak heights for all six. The total volume of organic solvent mixture added to the reactor was appreciable -- 27.5 ml in the case of the "low" concentration level experiment, and 275 ml in the case of the "high" concentration level experiment. The initial volumes of distilled water equilibrated in the reactor were 972.5 ml and 725 ml, respectively. In order to prevent temperature change upon addition of the solvent mixtures, the saturated water/organic solvent stock solutions from which the mixtures were made were stored in a water bath at 25°C.

2. Headspace Chromatographic Technique. The technique used to assay remaining concentrations of all organics (except p-cresol) was that of headspace gas chromatography (15). The sampling and equilibration technique was described in the previous section. Here the GC operation is outlined.

A Varian Aerograph model 1410 gas chromatograph with flame-ionization detector was used in these studies. A 20-ft x 1/8-in stainless steel column packed with 10% SP-1000 on 80/100 Supelcoport (Supelco, Inc.) was employed for all GC analyses. In all cases, injector and detector temperatures were approximately 180°C. The carrier was N₂ (25 ml/min); air and H₂ flows were approximately 300 ml/min and 15 ml/min, respectively.

Two column temperatures were employed: 150°C (for o-dichlorobenzene); and 95°C (for all other organics studied). Because the GC was not capable of accurate, stable temperature programming, analyses were performed isothermally. That meant injecting headspace samples from each bottle twice, in experiments employing six-component mixtures. The GC column was set at 95°C, and single 0.5 ml gas samples from each serum bottle were injected to resolve and assay 1,1,1-trichloroethane (4 min 26 sec retention time), methylene chloride (4 min 50 sec retention time), TCE (6 min 30 sec retention time), chloroform (7 min retention time), and tetrachloroethylene (7 min 20 sec retention time). The column temperature was then increased

to 150°C, 0.5 ml gas samples from the previously-sampled serum bottles were again injected, and o-dichlorobenzene was assayed (15 minutes retention time).

For all six compounds, calibration curves were prepared prior to Henry's Constant determination to insure that GC peak height could legitimately be linearly related to aqueous concentration of the organic solvent. In subsequent experiments with the reactor apparatus, initial concentrations were selected which fell within the range of linear GC response. And then, because data analysis required knowledge only of concentration ratios (and never of concentration alone), peak heights were used exclusively in computation of data for Henry's Constant determination without ever resorting to a calibration curve for determination of actual concentration.

3. UV Analysis. Since it was expected that p-cresol would prove to be of low volatility, we decided to employ UV spectroscopy for direct assay of aqueous samples withdrawn from the reactor. A Beckman model 3600 double-beam UV-visible spectrometer was employed, with sample sipper.

p-Cresol showed absorption maxima at 195 nm and 220 nm, with the lower wavelength possessing five times the sensitivity of the higher wavelength. However, 220 nm was selected as the analytical wavelength, since the greater sensitivity was not needed, and absorbance at 220 nm was more linearly related to concentration over the range of interest (up to 5 mg/l) than at 195 nm. A suitable calibration curve was prepared at 220 nm. Absorbance was 0.260 units at 5 mg/l (1-cm cell; distilled water blank).

IV. RESULTS

A. Temperature Studies

The measured effects of temperature (10°C - 30°C) on Henry's Constants for 1,1,1-trichloroethane, tetrachloroethylene, chloroform, methylene chloride, and o-dichlorobenzene are depicted in Figures 5 through 9, plotted in accordance with Equation 4. These results -- along with those for TCE from earlier studies (Figure 1) -- are summarized in Table 2. For all compounds studied, the variation of measured H with temperature was found to be well-described by the model of Equation 4.

Though it was originally proposed also to determine H-values for

1,1,1-Trichloroethane

$$R^2 = 0.998$$

$$H_T = \exp \left(9.975 - \frac{4186}{T(\text{°K})} \right)$$

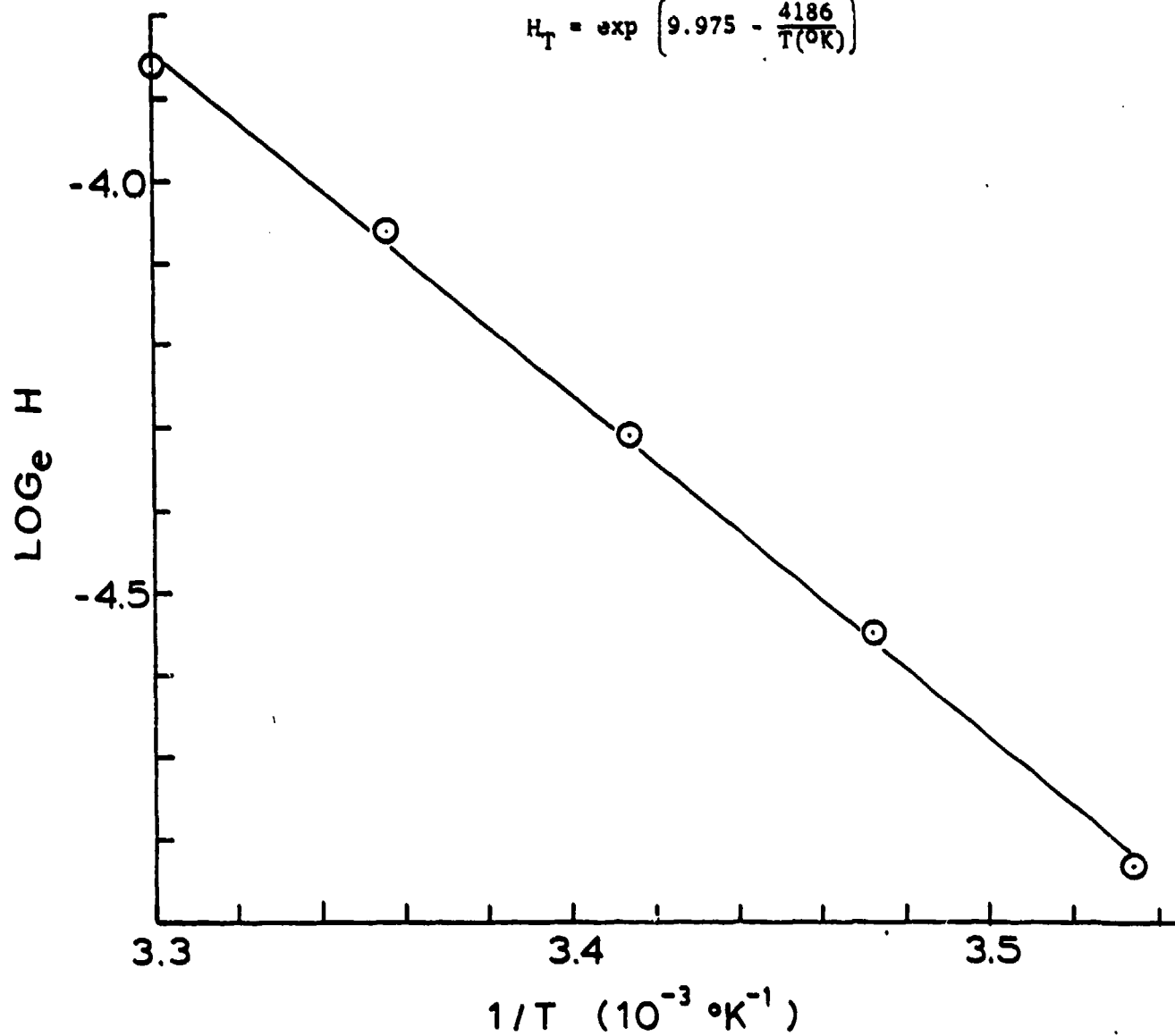


Figure 5. Variation of Henry's Constant with temperature for 1,1,1-trichloroethane (zero ionic strength).

Tetrachloroethylene

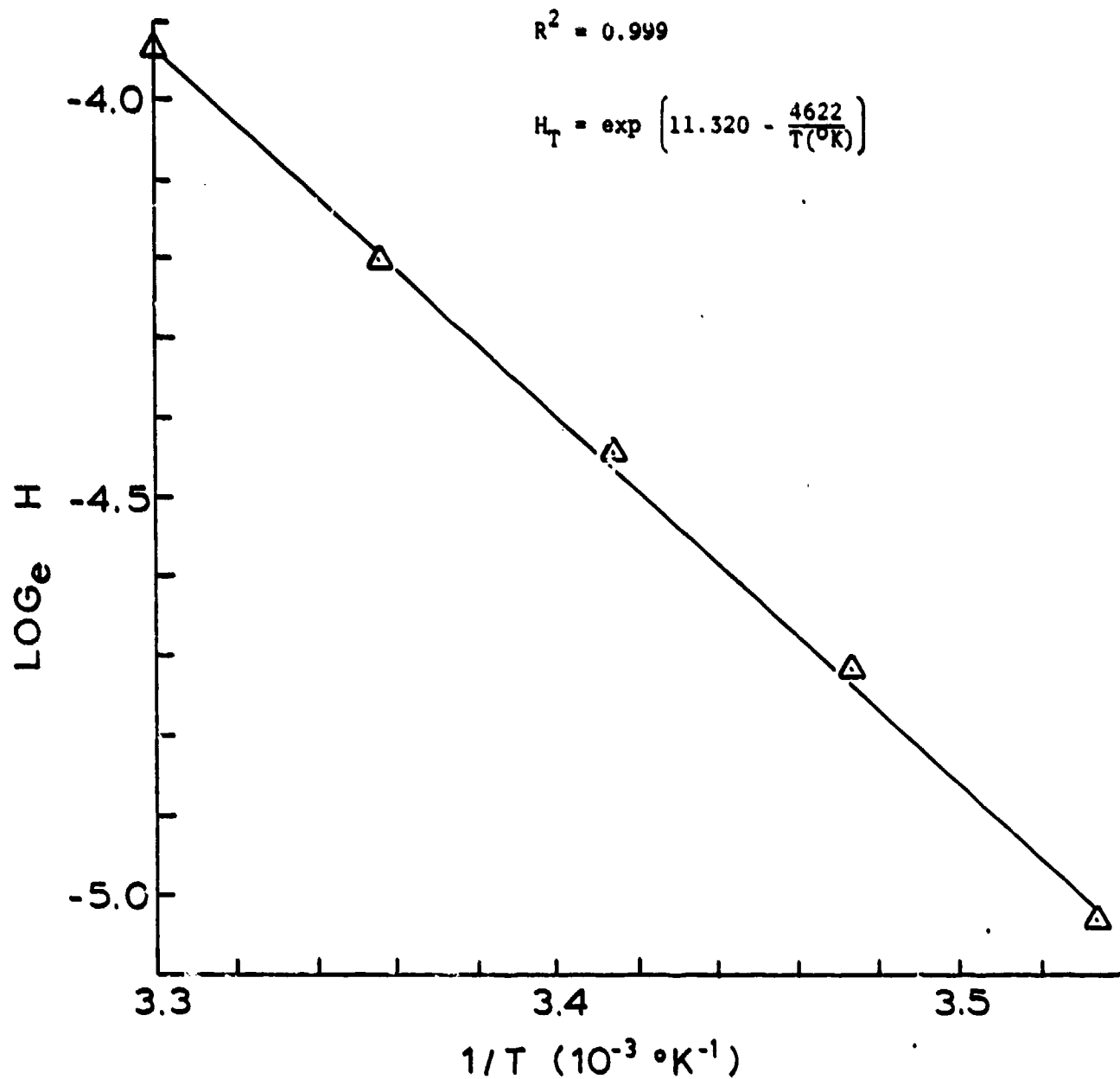


Figure 6. Variation of Henry's Constant with temperature for tetrachloroethylene (zero ionic strength).

Chloroform

$$R^2 = 0.995$$

$$H_T = \exp \left[8.956 - \frac{4322}{T(^{\circ}\text{K})} \right]$$

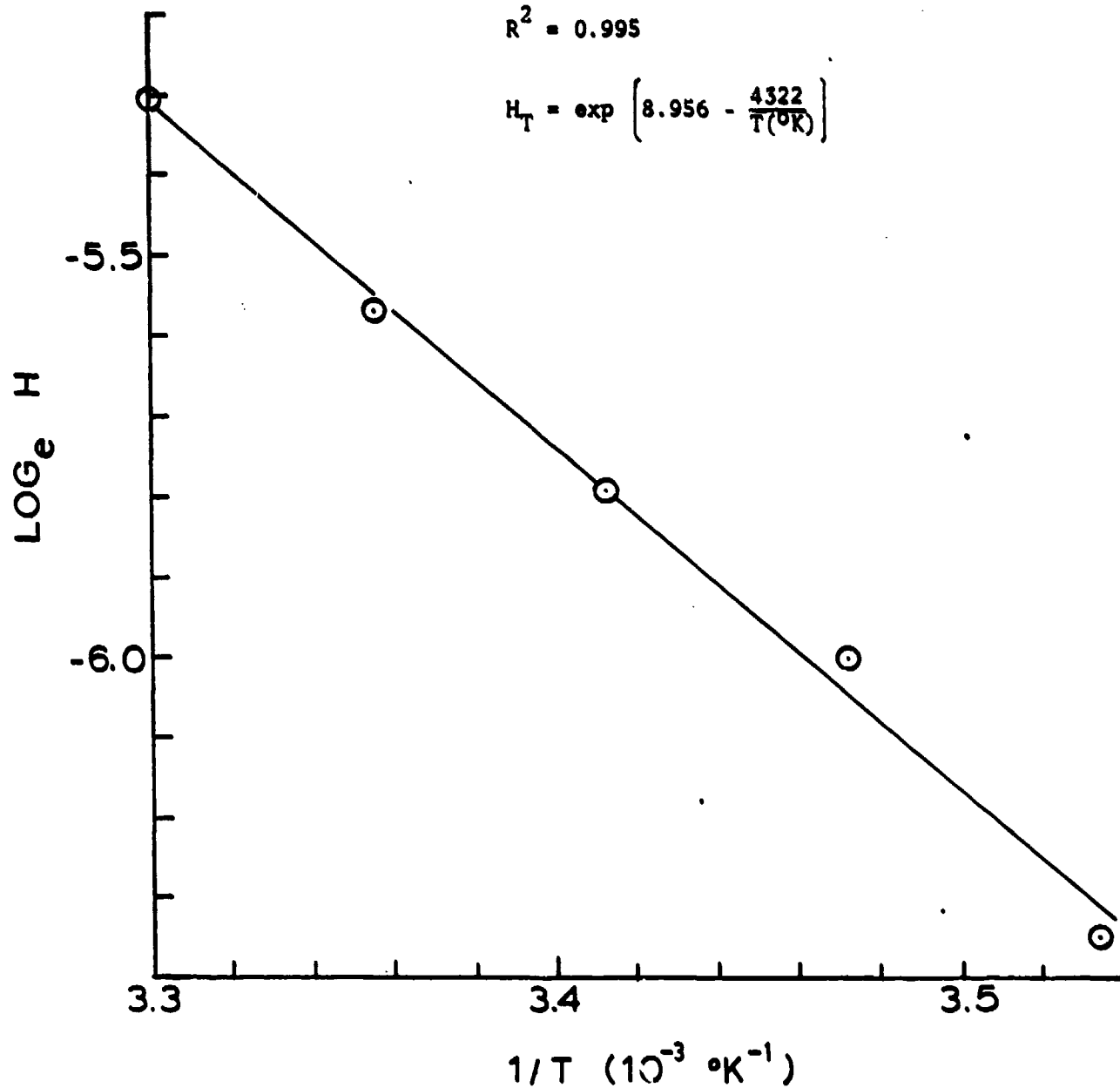


Figure 7. Variation of Henry's Constant with temperature for chloroform (zero ionic strength).

Methylene Chloride

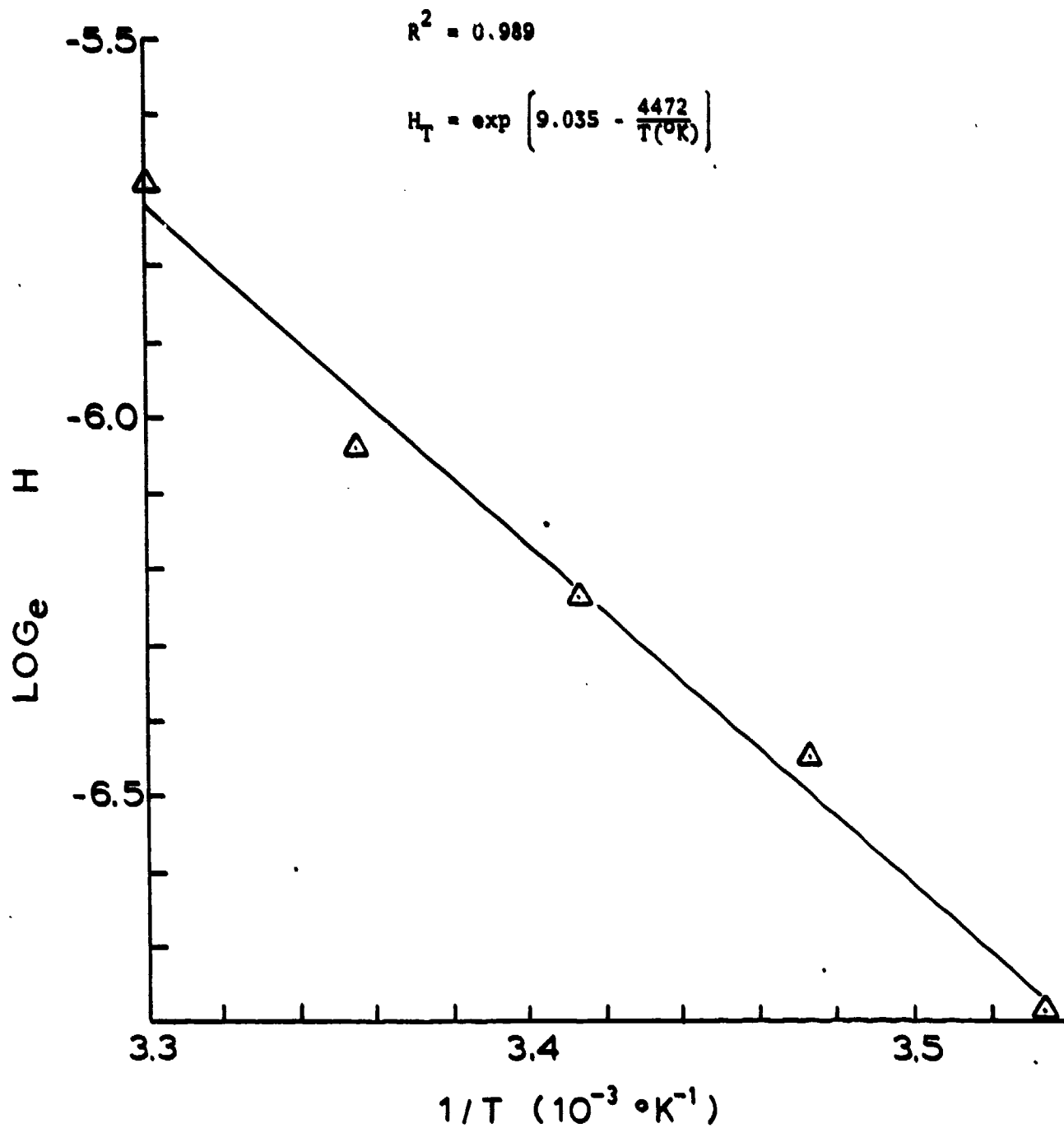


Figure 8. Variation of Henry's Constant with temperature for methylene chloride (zero ionic strength).

o-Dichlorobenzene

$$R^2 = 0.973$$

$$H_T = \exp \left[15.96 - \frac{6665}{T(^{\circ}\text{K})} \right]$$

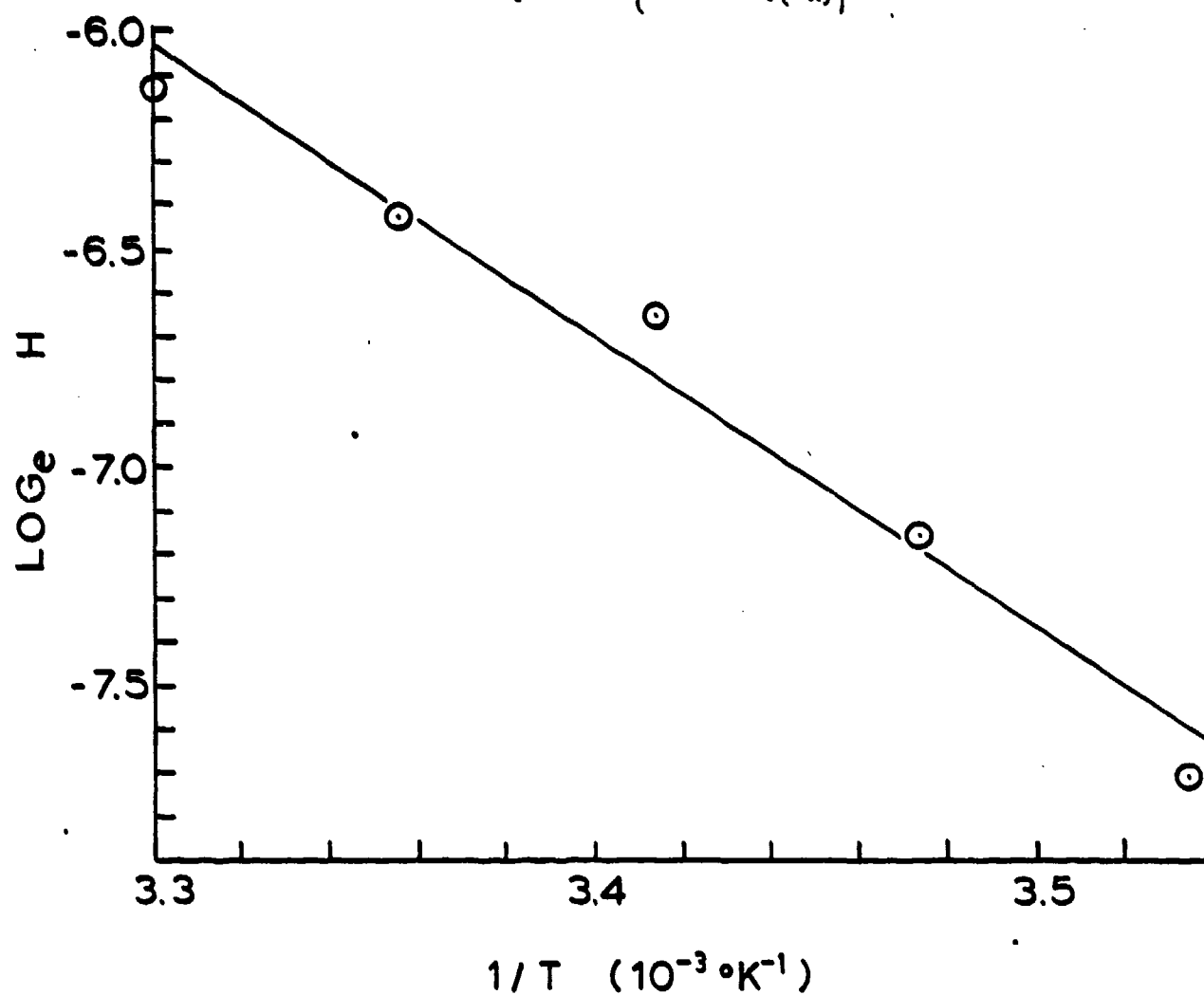


Figure 9. Variation of Henry's Constant with temperature for o-dichlorobenzene (zero ionic strength).

Table 2
Measured Henry's Constants for Selected
Chlorinated Solvents

Compound	Conc (mg/l)	$H_{20^{\circ}\text{C}}$ ($\text{m}^3\text{-atm/mole}$)	Temperature Dependence	
			Regression Equation	R^2
1,1,1-trichloroethane	3.6	0.0134	$H_T = \exp \left[9.975 - \frac{4186}{T(^{\circ}\text{K})} \right]$	0.998
tetrachloroethylene	3.0	0.0116	$H_T = \exp \left[11.32 - \frac{4622}{T(^{\circ}\text{K})} \right]$	0.999
trichloroethylene	2.0	0.00674	$H_T = \exp \left[9.703 - \frac{4308}{T(^{\circ}\text{K})} \right]$	0.980
chloroform	16	0.00304	$H_T = \exp \left[8.956 - \frac{4322}{T(^{\circ}\text{K})} \right]$	0.995
methylene chloride	19	0.00197	$H_T = \exp \left[9.035 - \frac{4472}{T(^{\circ}\text{K})} \right]$	0.989
o-dichlorobenzene	1.0	0.00113	$H_T = \exp \left[15.96 - \frac{6665}{T(^{\circ}\text{K})} \right]$	0.973

p-cresol, our attempts at this failed. When 5 mg/l p-cresol was placed in the equilibrium stripping reactor at 20°C, the UV absorbance (220nm) of the contents remained steady at 0.260 ± 0.001 units over the course of one hour's stripping with 360 ml/min air. We concluded that p-cresol was not sufficiently volatile to warrant H determination. It would have been impossible with our facilities to have held G and T_g constant for the lengthy stripping period required to investigate p-cresol. We performed no further studies with this compound.

B. Ionic Strength Studies

Figure 10 shows the effect of ionic strength (using KCl) upon the measured activity coefficients for tetrachloroethylene, methylene chloride, and chloroform at 25°C. The data were plotted according to the empirical model of Equation 3.

In the case of chloroform, good agreement with the model is evident over the full range of ionic strength investigated (up to 1 M KCl), yielding a salting-out coefficient, $k = 0.15$ l/mole.

For methylene chloride, the model appears valid only up to approximately

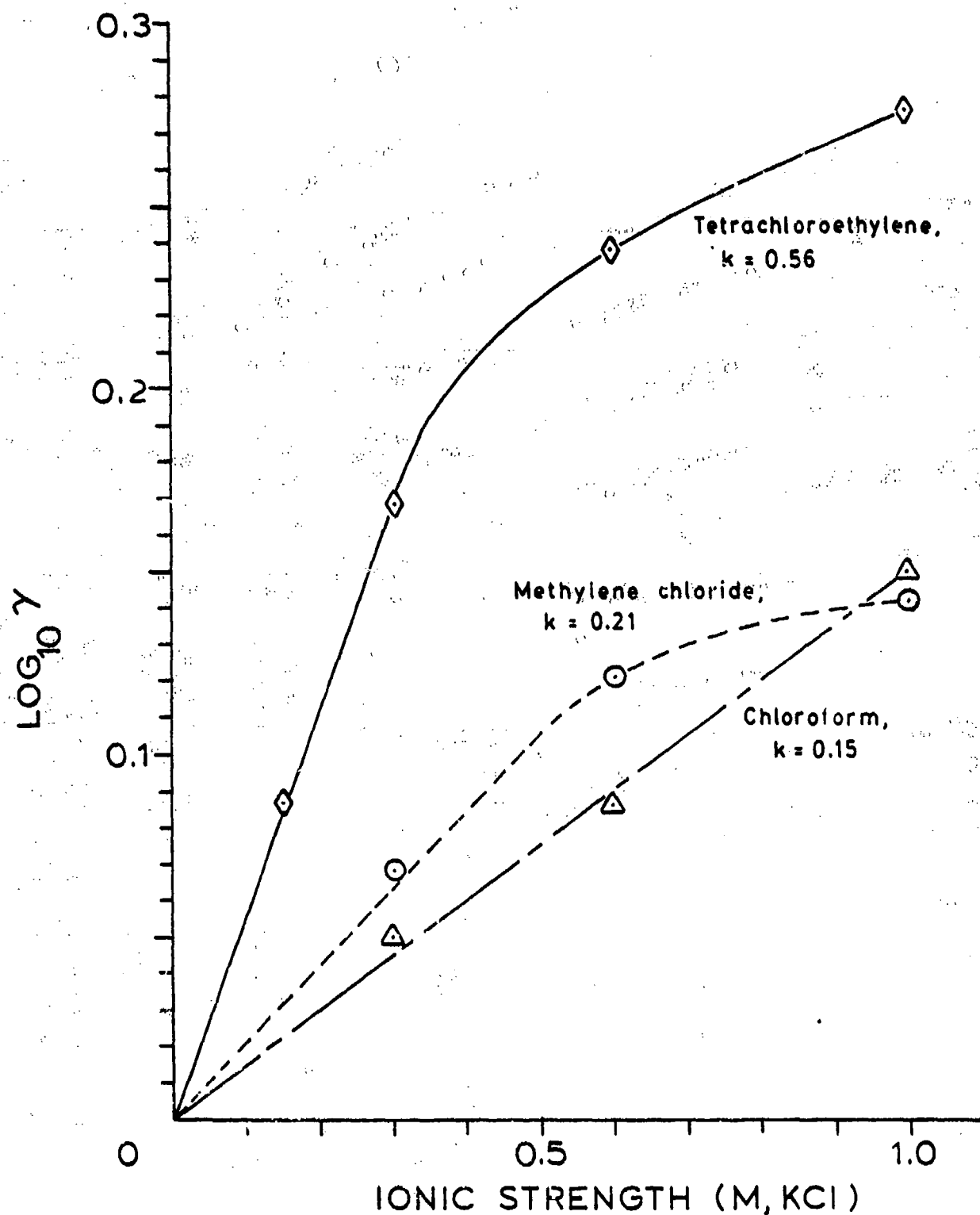


Figure 10. Effect of ionic strength (using KCl) on activity coefficients for tetrachloroethylene, methylene chloride, and chloroform in aqueous solution at 25°C.

0.6 M KCl. Below that concentration, $k = 0.21$ l/mole fits the rather limited data available. Coincidentally, this is the same k -value obtained earlier with TCE (Figure 2).

For tetrachloroethylene, the empirical model applies only up to $I = 0.3$ M KCl, with $k = 0.56$ l/mole.

What is evident from Figure 10 is that there are certainly great differences among the compounds of interest in the effect which ionic strength exerts on volatility. The KCl concentrations causing a 10% increase in the value of effective Henry's Constant are: 0.28 M, in the case of chloroform; 0.20 M, in the cases of methylene chloride and TCE; and 0.074 M, in the case of tetrachloroethylene.

Table 3 gives estimated ionic strengths for 31 natural waters characterized by Hem ("Study and Interpretation of the Chemical Characteristics of Natural Water", Geological Survey Water Supply Paper No. 1473 -- cited by Faust and Aly [17]). Ionic strengths were estimated using two methods: the empirical correlation of Langelier (18), relating ionic strength to total dissolved solids (TDS); and that of Russell (19), relating ionic strength to conductivity. While these water systems were not chosen on any statistically-valid, random basis, the data of Table 3 suggest that ionic strengths of natural, freshwater systems seldom exceed 0.074 M. Therefore, assuming that only errors greater than 10% are worth correcting, then in most freshwater systems, ionic strength corrections will be unnecessary -- even for tetrachloroethylene.

This is fortunate, for if one encounters a situation which requires ionic strength corrections (e.g., brackish, estuarine, or oceanic systems), a somewhat intractable problem is presented. KCl was selected arbitrarily as the electrolyte for use in this investigation. Garrels and Christ (7) report that for uncharged species, the value of the salting-out coefficient (k) depends somewhat upon the particular salt employed. Thus, there is little hope for development of a simple model relating γ to ionic strength in any real system comprised of many different dissolved salts. The data presented here -- based upon KCl electrolyte -- can only provide approximate corrections.

Table 3
 Estimated Ionic Strengths of Selected Natural
 Waters [after Hem, cited in reference (17)]

Water	Estimated Ionic Strength, M	
	1.6×10^{-5} (μmho)	2.5×10^{-5} (mg/l TDS)
Gila River, Gillespie Dam, Arizona	0.12	0.12
Well, Montecello, Arkansas	0.073	0.10
Pecos River, Artesia, New Mexico	0.057	0.065
Moreau River, Bixby, South Dakota	0.050	0.060
Well, Richland City, Montana	0.047	0.052
Jumping Springs, Eddy County, NM	0.040	0.060
Siegler Hot Springs, Lake County, CA	0.040	0.040
Wagon Wheel Gap hot spring, Mineral County, CO	0.039	0.039
Irrigation well, Maricopa County, NM	0.037	0.032
Shamokin Creek, Weightscale, PA	0.028	0.032
Spring on Havasu Creek, Grand Canyon, AZ	0.018	0.017
Oasis flowing well, Chaves County, NM	0.016	0.018
Well, Nelson Rd. Water Wks., Columbus, OH	0.014	0.014
Well No. 5, Sidney, Ohio	0.012	0.013
Industrial well, Williamset, MA	0.011	0.012
Well, Wake County, NC	0.011	0.011
Rattlesnake Spring, Eddy County, NM	0.010	0.010
Green Lake, Carlsbad Caverns, NM	0.0091	0.0080
City well, Bushton, Kansas	0.0087	0.0081
Drilled well, Milwaukee, Wisconsin	0.0082	0.0082
Kiskiminitas River, Leechburg, PA	0.0081	0.0065
Spring, Buell Park, Arizona	0.0073	0.0070
Spring, Jefferson County, Tennessee	0.0052	0.0045
Big Spring, Huntsville Alabama	0.0040	0.0035
Spring, Calhoun County, Alabama	0.0032	0.0027
Well, Baltimore County, MD	0.0031	0.0034
Partridge River, Aurora, Minnesota	0.0030	0.0039
Cumberland River, Smithland, KY	0.0028	0.0025
Well, public supply, Memphis, Tennessee	0.0026	0.0025
Wisconsin River, Muscoda, Wisconsin	0.0026	0.0027
City Well No. 4, Fulton, Mississippi	0.0011	0.0011

C. Multi-Component Studies

The six organics for which Henry's Constants were measured in previous, single-component experiments were studied in two experiments employing six-component mixtures at two relative concentration levels (Table 4).

Table 4
Concentrations Used in Six-Component Mixtures

Component	Component Concentrations in Mixtures (mg/l)	
	<u>Low Level</u>	<u>High Level</u>
1,1,1-trichloroethane	3.6	36
tetrachloroethylene	2	20
trichloroethylene	5	50
chloroform	16	160
methylene chloride	10	100
o-dichlorobenzene	0.5	5

It first had to be demonstrated that Henry's Constant for a single-component system is indeed constant over a range of concentration. Toward this end, H-values were determined at 25°C for TCE at 2 mg/l and 50 mg/l in distilled water. The values obtained were 0.00992 m³-atm/mole and 0.0103 m³-atm/mole -- the same within experimental error. Additionally, Henry's Constants were determined at 25°C for chloroform at 4 mg/l and 82 mg/l, yielding values of 0.00424 m³-atm/mole and 0.00428 m³-atm/mole, respectively. These results suggest that differences observed between the H-values for a compound in a multi-component mixture and for that same compound in a single-component experiment must be due to the presence of the other organics in the mixture. Furthermore, any differences observed between "low" and "high" level mixture experiments must be attributed to the difference in concentration of the other organics in the mixture, and not to the difference in concentration of the particular species whose H-values are being compared.

The results from the two sets of experiments employing six-component mixtures are summarized in Tables 5 and 6. Each of the two concentration levels was employed four times, yielding four H-values for each compound at each mixture concentration level. The mean and standard deviation

Table 5
Results From Multi-Component Studies ($H_{25^{\circ}C}$, m^3 -atm/mole)

Component	Low Level Mixture		High Level Mixture	
	Mean	Coeff. of Variation	Mean	Coeff. of Variation
1,1,1-trichloroethane	0.0177	2%	0.0210	1%
tetrachloroethylene	0.0172	1%	0.0211	2%
trichloroethylene	0.0115	2%	0.0122	2%
chloroform	0.00442	3%	0.00451	2%
methylene chloride	0.00243	5%	0.00252	5%
o-dichlorobenzene	0.00176	6%	0.00167	5%

Table 6
Results From Multi-Component Studies (cont.) [$H_{25^{\circ}C}$, m^3 -atm/mole]

Component	Measured Value, Pure H ₂ O	Low Level Mixture		High Level Mixture	
		Mean	$\Delta\%$ from Pure H ₂ O	Mean	$\Delta\%$ from Pure H ₂ O
1,1,1-trichloroethane	0.0173	0.0177	+ 2%	0.0210	+21%
tetrachloroethylene	0.0149	0.0172	+15%	0.0211	+42%
trichloroethylene	0.0101	0.0115	+14%	0.0122	+21%
chloroform	0.00411	0.00442	+ 8%	0.00451	+10%
methylene chloride	0.00239	0.00243	+ 2%	0.00252	+ 5%
o-dichlorobenzene	0.00164	0.00176	+ 7%	0.00167	+ 2%

(reported in the form of a coefficient of variation) of each determination is reported in Table 5. Table 6 compares the various mean H-values obtained from the multi-component experiments with the corresponding values obtained from experiments employing each component (alone) in pure water.

At the "low" concentration level, the only components for which H is significantly affected (with 95% confidence) by the presence of the other organics were tetrachloroethylene and trichloroethylene. At the "high" concentration level, Henry's Constants for 1,1,1-trichloroethane, tetrachloroethylene, trichloroethylene, and chloroform were significantly increased over their values in pure water. With the exception of 1,1,1-trichloroethane, the greater a compound's volatility, the more

its Henry's Constant appears to be increased (percentage-wise) by the presence of the other organics.

D. Phenol Studies

In order to examine further the effects noted in the previous phase of experimentation -- but in a simpler, more easily-defined system -- studies were undertaken in which the effective Henry's Constant for each compound was measured in a system containing that compound plus 200 mg/l phenol. Results are shown in Table 7.

Table 7
Results from Phenol Studies (H_{250C} , m^3 -atm/mole)

Component	Measured Value, Pure H ₂ O	With Phenol, 200 mg/l	
		Value	$\Delta\%$ from Pure H ₂ O
1,1,1-trichloroethane, 3.6 mg/l	0.0173	0.0208	+20%
tetrachloroethylene, 2 mg/l	0.0149	0.0195	+31%
trichloroethylene, 5 mg/l	0.0101	0.0131	+30%
chloroform, 16 mg/l	0.00411	0.00464	+13%
methylene chloride, 5 mg/l	0.00239	0.00266	+11%
o-dichlorobenzene, 0.5 mg/l	0.00164	0.00187	+14%

The Henry's Constants for all six compounds were significantly increased by the presence of 200 mg/l phenol. As in the previous phase of study, the more volatile the compound, the greater the percentage increase in its effective H (with the exception of 1,1,1-trichloroethane).

E. Primary Effluent Studies

Using the "high" level (Table 4) of the six-component mixture, Henry's Constant for each compound was measured in municipal primary effluent in a single experiment. Results are shown in Table 8. The proper comparison to make is with the set of H-values obtained from "high" level mixtures added to distilled water. This comparison is made in Table 8.

Primary effluent constituents apparently reduced effective H-values for all six compounds -- with the compounds of greater volatility exhibiting

Table 8
Results from Primary Effluent Studies ($H_{25^{\circ}C}$, m^3 -atm/mole)

Component	High Level Mix. in H_2O	High Level Mix. in Primary Effl.	% Δ
1,1,1-trichloroethane	0.0210	0.0148	-30%
tetrachloroethylene	0.0211	0.0141	-33%
trichloroethylene	0.0122	0.00928	-24%
chloroform	0.00451	0.00380	-16%
methylene chloride	0.00252	0.00233	- 8%
o-dichlorobenzene	0.00167	0.00159	- 5%

the greater percentage reductions. However, what we may be observing is not an effect on H, but an effect of surfactants upon mass-transfer rates.

The apparatus used to measure Henry's Constant has been extensively tested in "clean water" systems to assure that a reasonable approach to equilibrium is attained between the exit gas and the mixed reactor contents. However, as H increases and mass transfer rate decreases, this equilibrium assumption may be violated. The presence of surfactants in primary effluent (which would tend to decrease mass-transfer rates) may have caused the apparent values of H to decrease. Without testing the "approach-to-equilibrium" assumption by variation of reactor column depth, one cannot safely conclude that the observed decreases in H-values are real.

V. DISCUSSION

From a practical point of view, the effect of ionic strength on organic solvent volatility in aqueous solution is far less important a consideration than are the effects of other organics present in the system. It was determined that ionic strength must exceed 0.074 M (KCl) in order for the effective Henry's Constant to be increased by a mere 10% -- in the worst case (tetrachloroethylene). Granted, we have not investigated ionic-strength effects on 1,1,1-trichloroethane or o-dichlorobenzene. But all indications are that tetrachloroethylene is the one compound of the six studied whose volatility is most affected by solution conditions. Since most natural aqueous systems encountered will have ionic strengths far less than 0.074 M, our results suggest that ionic strength will not generally be

a factor of concern in applying our Henry's Constants to stripping application models.

What are far more troublesome are the sometimes significant effects which the presence of relatively small concentrations of organic solvents may have on the volatilities of other organic solvents. The concentrations used in the "low-level", six-component mixtures (Table 4) might reasonably be expected in contaminated natural waters; the "high-level" (Table 4) and phenolic (Table 7) mixtures could be representative of some industrial wastewaters. Unfortunately, no models exist to quantitatively describe the effects of uncharged species on the activity coefficients of other uncharged species. We had expected to find no such effects. Our experiments were, in fact, designed merely to verify this expectation, allowing us (we hoped) to dismiss such considerations from further study. Given our unexpected results, however, we must recommend additional research into the mutual interactions of chlorinated solvents in dilute aqueous solution.

VI. CONCLUSIONS

1. Henry's Constants were measured for six chlorinated solvents in pure water over the temperature range from 10°C to 30°C. The data obtained were adequately described by a regression equation.

2. The effect of ionic strength on organic solvent volatility in aqueous solution was determined to vary greatly among compounds. However, for ionic strengths less than 0.074 M KCl, activity corrections can be safely ignored.

3. Henry's Constants were measured for each of the six chlorinated solvents when present in six-component mixtures at two relative concentration levels. There was a significant increase in the volatility of each caused by the presence of the others. In general, the percentage increase was greater for the compounds possessing higher Henry's Constants.

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