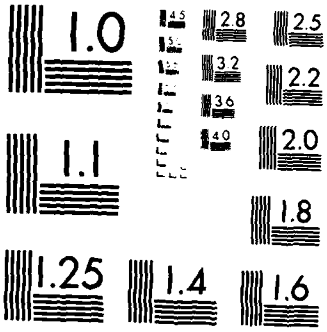
AD-A129 727 PACKED TOWER AIR STRIPPING OF TRICHLOROETHYLENE FROM 1/1
DILUTE AQUEOUS SOLUT..(U) CORNELL UNIV ITHACA NY DEPT
OF ENVIRONMENTAL ENGINEERING J M GOSSETT APR 83
UNCLASSIFIED AFESC/ESL-TR-81-38 F49620-79-C-0038 F/G 15/5 NL



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963 A

(12

ESL-TR-81-38

PACKED TOWER AIR STRIPPING OF TRICHLOROETHYLENE FROM DILUTE AQUEOUS SOLUTION

JAMES M. GOSSETT
ENVIRONICS DIVISION
ENVIRONMENTAL ENGINEERING BRANCH

APRIL 1983

FINAL REPORT
JUNE - AUGUST 1980

AFESC

ENGINEERING & SERVICES LABORATORY
AIR FORCE ENGINEERING & SERVICES CENTER
TYNDALL AIR FORCE BASE, FLORIDA 32403

NOTICE

PLEASE DO NOT REQUEST COPIES OF THIS REPORT FROM HQ AFESC/RD (ENGINEERING AND SERVICES LABORATORY). ADDITONAL COPIES MAY BE PURCHASED FROM:

NATIONAL TECHNICAL INFORMATION SERVICE
5285 PORT ROYAL ROAD
SPRINGFIELD, VIRGINIA 22161

FEDERAL GOVERNMENT AGENCIES AND THEIR CONTRACTORS REGISTERED WITH DEFENSE TECHNICAL INFORMATION CENTER SHOULD DIRECT REQUESTS FOR COPIES OF THIS REPORT TO:

DEFENSE TECHNICAL INFORMATION CENTER
CAMERON STATION
ALEXANDRIA, VIRGINIA 22314

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER
ESL TR 81-38

2. GOVT ACCESSION NO.
AD-A129 727

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
PACKED TOWER AIR STRIPPING OF TRICHLOROETHYLENE FROM DILUTE AQUEOUS SOLUTION

5. TYPE OF REPORT & PERIOD COVERED
FINAL REPORT JUN-AUG 1980

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
JAMES M. GOSSETT

8. CONTRACT OR GRANT NUMBER(s)
F49620-79-C-0038

9. PERFORMING ORGANIZATION NAME AND ADDRESS
AIR FORCE ENGINEERING AND SERVICES CENTER
HQ AFESC/RDVW
TYNDALL AFB FL 32403

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
PE 62601F
JON 19002025

11. CONTROLLING OFFICE NAME AND ADDRESS
AIR FORCE ENGINEERING AND SERVICES CENTER
HQ AFESC/RDVW
TYNDALL AFB FL 32403

12. REPORT DATE
APRIL 1983

13. NUMBER OF PAGES
38

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report)
UNCLASSIFIED

15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES
Availability of this report is specified on reverse of Front Cover.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Trichloroethylene
Packed Tower
Air Stripping
Pollution Control
Water Treatment
Groundwater
Mass Transfer
Henry's Law
Water Pollution Control

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Air stripping is among the technologies being considered by the Air Force for TCE removal from contaminated groundwaters. The most promising stripper configuration is that of the countercurrent flow, packed column. This study was undertaken to model the performance of such a stripping reactor applied to

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

TCE removal. Equations are presented which related efficiency to packed volume, air and liquid flows, gas/liquid partition coefficient (Henry's constant, H) and overall mass transfer coefficient ($K_L a$). A major objective of this study was to quantify the effect of temperature and ionic strength on H, and of temperature, air flow and liquid flow on $K_L a$.

Henry's constant was measured by an equilibrium, mixed batch reactor technique, over a temperature range from 10° to 30°C, and a range of ionic strengths from 0 to 1 Molar Potassium Chloride. The effect of temperature was of practical significance; the effect of ionic strenth was not.

$K_L a$ was determined for 5/8 - inch (1.59 cm) plastic Pall rings over a range of temperature from 10° to 30°C. The effect was significant, and equations are presented for calculating the dependency. Air and liquid flow velocity did not affect $K_L a$ over the range examined.

PREFACE

This research was sponsored by the Air Force Office of Scientific Research through a contract with the Southeastern Center for Electrical Engineering Education as part of the USAF Summer Faculty Research Program. The author and principal investigator was Dr. James M. Gossett, Environmental Engineering Department, Cornell University under Contract F49620-79-C-0038. The research was performed at the Air Force Engineering and Services Center (AFESC), Environics Division, Tyndall AFB, Florida 32403. The AFESC project officer was Major Stephen G. TerMaath, RDVW.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

Stephen G. TerMaath
STEPHEN G. TERMAATH, Major, USAF, BSC
Chief, Environmental Engineering Branch
Project Officer

Francis B Crowley III
FRANCIS B. CROWLEY III, Colonel, USAF
Director, Engineering and Services
Laboratory

Michael J. Ryan
MICHAEL J. RYAN, Lt Col, USAF, BSC
Chief, Environics Division

Accession For
NTIS GRA&I ☒
DTIC TAB ☐
Unannounced ☐
Justification

By
Distribution/

Availability Codes

Dist	Avail and/or Special
A	

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

GLOSSARY OF TERMS

A	cross-sectional area of tower (m^2)
a	interfacial area per unit bulk volume (m^2/m^3)
C	solute concentration in the liquid gas phase ($moles/m^3$)
C_o	initial ($t=0$) concentration ($moles/m^3$)
C_i	reactor TCE concentration ($moles/m^3$) at the end of the ith interval
C_1, C_2	influent, effluent TCE concentrations in liquid phase ($moles/m^3$)
C_1^*, C_2^*	influent, effluent theoretical TCE concentrations in liquid phase if at equilibrium with the effluent, influent gas phase partial pressures ($moles/m^3$)
G	m^3/min air flow (measured at the temperature of the gas meter, T_g)
H	Henry's constant (m^3-atm/mole)
H_T	Henry's constant at temperature T (°K)
$\Delta H°$	standard reaction enthalpy (cal/mole), constant over the range from T to T_1
I	ionic strength (molar)
K	salting-out coefficient
K_L	overall mass transfer coefficient based upon the liquid phase $\dfrac{\text{moles solute stripped}}{\text{min - interfacial area - moles/m}^3\text{ gradient}}$
L	water flow (m^3/min)
M	molar concentration (moles/liter)
P	partial pressure of the solute substance in the gas phase (atm)
P_1, P_2	effluent, influent TCE partial pressures in the gas phase (atm)
R	gas constant $= 8.2056 \times 10^{-5}$ (m^3-atm)/(mole-°K) $=$ 1.987 calorie/mole-°K
R^2	coefficient of determination
T	temperature (°K)

T_g	temperature at the gas meter (°K)
Δt_i	time of ith interval (min)
V_i	reactor liquid volume during the ith interval (m^3)
z	height of packing (m)
Z_T	packed height (m)
γ	activity coefficient for the solute in the liquid phase

SECTION I

INTRODUCTION

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 related solvents. Usually, the water was being analyzed for trihalomethanes when the solvents were detected.(1)

Dozens of wells serving several thousand people have been found to be contaminated in New England, New Jersey, New York (particularly Long Island), Pennsylvania, and Florida.(1) 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.(2)

The Air Force routinely used 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, primarily 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(2) and their contractors(3), demonstrating perhaps 80 to 85 percent 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(4). Consequently, the Air Force plans construction of pilot-scale packed tower facilities to further investigate the potential of air stripping to remove TCE from contaminated groundwater at Wurtsmith AFB, Oscoda, Michigan.

In order to design stripping tower facilities, Air Force engineers need to be able to relate process performance to design, operating, and environmental parameters. In particular, it would be desirable to model performance such that percent removal 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. Equations exist which allow performance prediction, given values of the gas/liquid partition coefficient for TCE and the applicable mass transfer coefficient. However, data are lacking concerning the dependence of these equilibrium and kinetic parameters on flow rates, temperature, and salinity.

SECTION II

OBJECTIVES

The main objective of this project was to model performance of stripping towers for TCE removal as a function of process and environmental parameters. In particular, the functional relationship between percent removal and bed volume, air and water flow rates, temperature, and ionic strength was sought. Work was carried out in two phases: (1) equilibrium studies relating the gas/liquid phase partitioning of TCE to temperature and ionic strength were performed; and (2) the kinetics of packed tower stripping were investigated in order to evaluate the effects of temperature and flow rates upon the mass transfer coefficient.

SECTION III

EQUILIBRIUM STUDIES

1. BACKGROUND

Equilibrium between a solute and its vapor is generally modeled(5,6) according to Henry's Law, which for dilute solutions, is:

$$P = HC \qquad (1)$$

where:

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

C = solute concentration in the liquid phase (moles/m^3)

H = Henry's constant (m^3-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 proximation of its activity, and the equation may be written,

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

where:

γ = activity coefficient for the solute in liquid phase.

In order to model the performance of a packed stripping tower, the variation of H with temperature, and the dependence of γ upon ionic strength must be known. The literature is not extensive on these matters where TCE is concerned. An H-value of 1.0 x 10^{-2} m^3-atm/mole has been reported for TCE in water at 20°C(7), but the origins of this particular value are rather obscure, and the temperature dependence is unknown.

No literature concerning the variation of γ with ionic strength was found. Butler(6) states that at concentrations less than 0.1 M, the activity of uncharged species is within 1 percent of molar concentration. For uncharged molecules of concentration less than 0.5 M, in solutions of ionic strength up to 5 M,

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

is a good approximation, with I = ionic strength (molar) and k = salting-out coefficient(6).

2. OBJECTIVES

The objectives of this phase were to evaluate the effect of temperature on Henry's constant (H) and the effect of ionic strength on the activity coefficient (γ) for TCE.

3. PROCEDURES

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 for H determination was a variation of that used by Mackay et al.(8)

A tube reactor of 1-liter capacity was employed (Figure 1). A water sample containing TCE (generally at 2200 ug/l initial concentration) was placed in the reactor; air ("zero grade") was bubbled through the solution via a diffuser stone situated in the reactor bottom; the exit gas containing stripped TCE 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 Lauda K-2/R circulator), 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 TCE concentration was assayed, using the headspace gas chromatographic technique described by Dietz and Singley(9).

The determination of Henry's constant using the apparatus of Figure 1 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 TCE concentration. With these assumptions, equations may be derived which describe the stripping of TCE from the reactor with time.

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

G = m^3/min air flow (measured at the temperature of the gas meter, T_g)

R = gas constant - 8.2056×10^{-5} (m^3-atm)/(mole- °K)

V_i = reactor liquid volume during the ith interval (m^3)

C_i = reactor TCE concentration (moles/m^3) at the end of the ith interval

With the earlier assumptions regarding complete mixing and gas/liquid phase equilibrium, during the ith interval of purging,

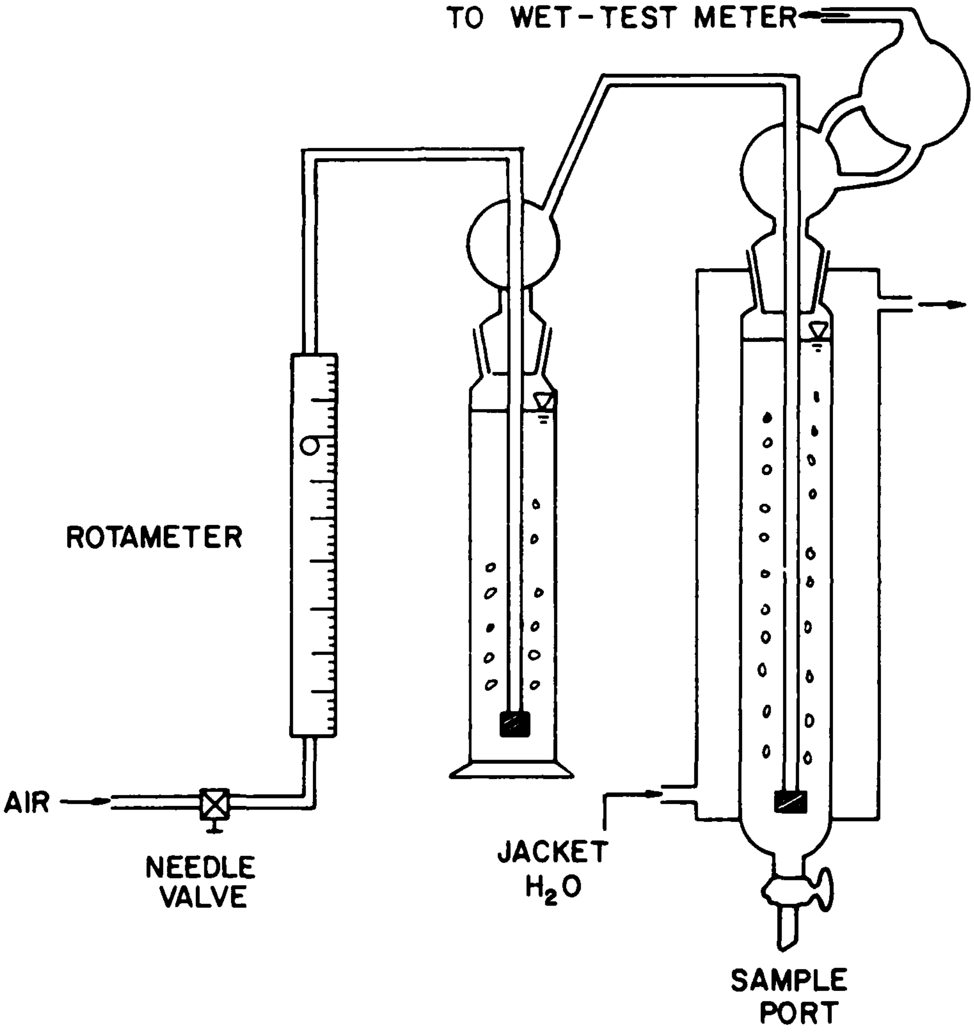


Figure 1. Apparatus for Henry's Constant Determination.

$$V_i \left(\frac{dC}{dt}\right) = \frac{-PG}{RT_g} = \frac{-H\gamma CG}{RT_g} \qquad (4)$$

Integrate:

$$C_i = C_{i-1} \exp\left[\frac{-HG\gamma\Delta t_i}{RT_g\ V_i}\right] \qquad (5)$$

where:

t_i = time of ith interval (min)

Therefore:

$$\ln C_i = \ln C_o - \frac{H\gamma G}{RT_g} \sum_{j=1}^{i} \frac{\Delta t_j}{V_j} \qquad (6)$$

where:

C_o = initial, t=0, concentration (moles/m^3)

Thus, a plot of ln (C_i/C_o) vs $\sum_{j=1}^{i} \frac{\Delta t_j}{V_j}$ should yield a straight line with a slope equal to $-H\gamma G/RT_g$. From this, $H\gamma$ may be evaluated. (Studies were undertaken as outlined by Mackay et al(8), using a range of initial 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:

a. One liter of distilled water was placed in the reactor.

b. The air flow was turned on, adjusted to 315 ml/min (measured at the wet-test meter temperature of 22°C) and allowed to flow through the reactor.

c. The water jacket was adjusted to the desired study temperature.

d. The system was thermally equilibrated for approximately 1 hour.

e. The system temperatures (liquid, exit gas, and jacket water) were checked to verify thermal equilibrium.

f. 2 ml of TCE-saturated water were added to the reactor (yielding approximately a 2200 ug/l concentration).

g. A mixing period of 1 minute was allowed.

h. 25 ml samples were taken from the reactor bottom at 2-5 minute intervals for 15-20 minutes.

Samples from the equilibrium experiments were handled as follows:

a. The 25 ml samples were poured with a minimum of agitation into 120 ml serum bottles and crimp-capped with Teflon®-lined serum caps.

b. The samples were thermally equilibrated to ambient temperature and phase equilibrated for 10 minutes using a wrist-action shaker.

c. 0.5 ml headspace samples were injected into a gas chromatograph.

d. A Varian Aerograph Model 2800 was used with 10 feet of 10 percent SP-1000 on 100/120 Supelcoport (Supelco, Inc.), operated isothermally at 100°C, retention time = 4.5 minutes. See Figure 2 for a sample calibration curve.

For the ionic-strength studies, the above procedure was also followed, except the initial liquid added to the reactor was distilled water with a known content of potassium chloride (KCl).

4. RESULTS

Figure 3 is an example of a data plot from Henry's constant determination in accordance with Equation (6). The precision is remarkable, as evidenced by

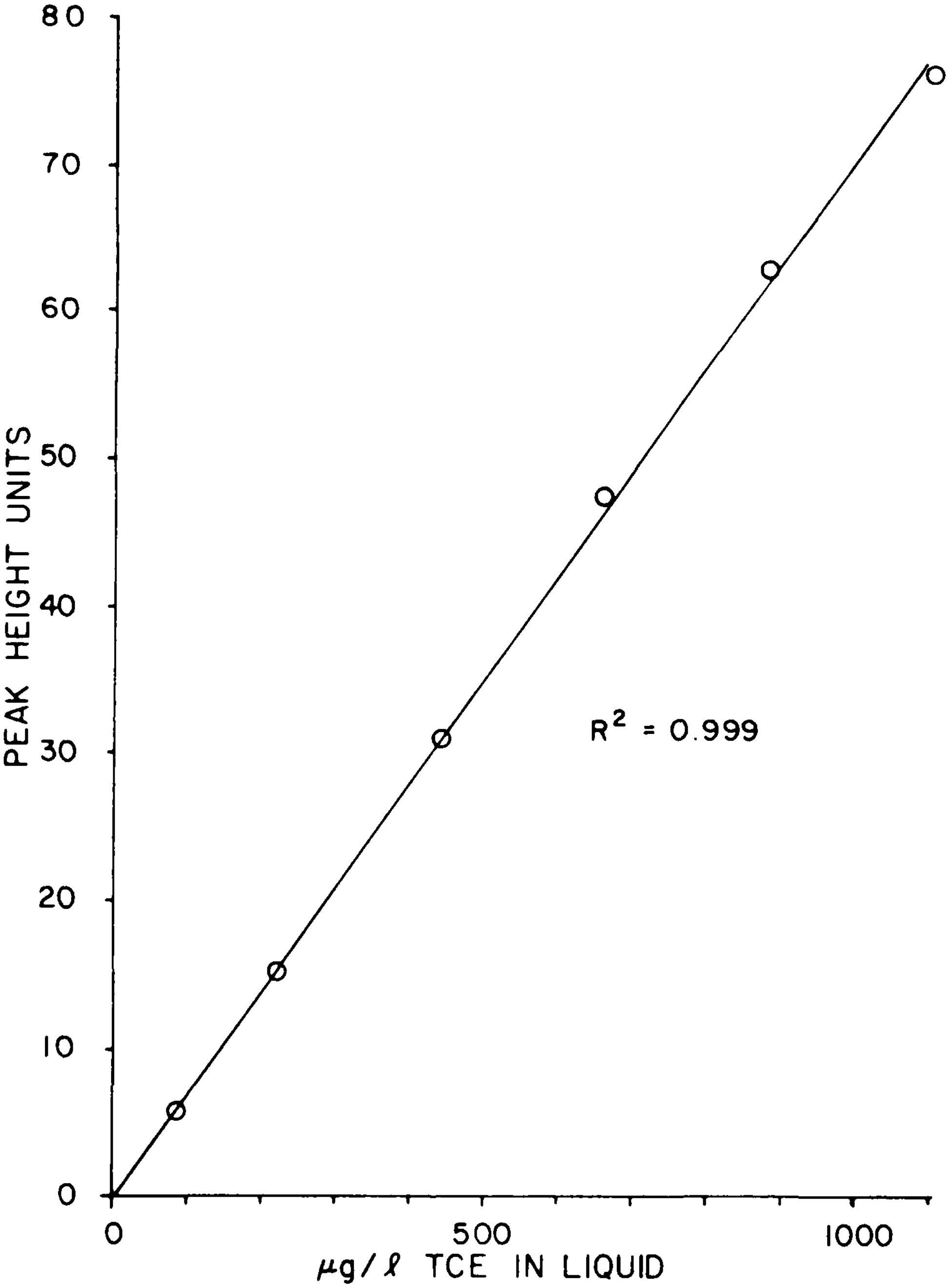


Figure 2. Sample Calibration Curve for Headspace Chromatographic Technique of TCE Measurement

the coefficient of determination (R^2) of 1.000. In no case was R^2 less than 0.99. 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 3.

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:

$$\ln \frac{H}{H_1} = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T} - \frac{1}{T_1} \right) \tag{7}$$

where:

H = Henry's constant at T (°K)

H_1 = Henry's constant at T_1 (°K)

ΔH° = standard reaction enthalpy, assumed constant over the range from T to T_1

Thus, a plot of lnH versus 1/T should yield a straight line with a slope of $-\Delta H^\circ/R$.

The Henry's constant data gathered in these experiments over the range from 10° to 30°C are shown plotted in Figure 4 in accordance with Equation (7). Linear regression gives the following equation for H dependence on temperature:

$$H_T \left\{ \frac{m^3\text{-atm}}{\text{mole}} \right\} = \exp \left[9.703 - \frac{4308}{T} \right] \tag{8}$$

From the slope of the regression, the standard enthalpy of volatilization at 10° - 30°C is calculated to be 8560 cal/mole. (Lange's handbook gives standard enthalpy of formation data for gaseous and liquid TCE at 25°C

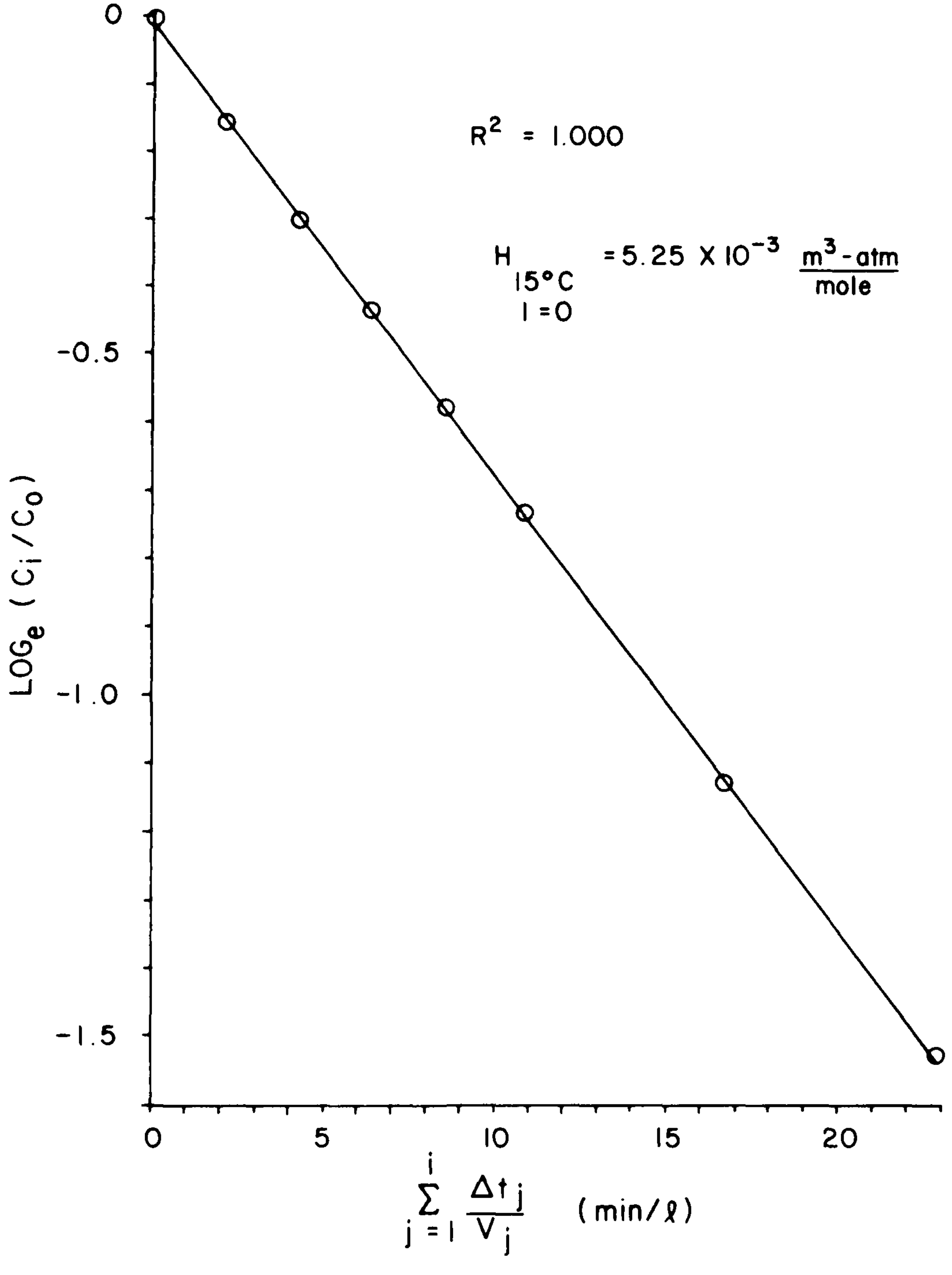


Figure 3. Example of Data Plot from Henry's Constant Determination

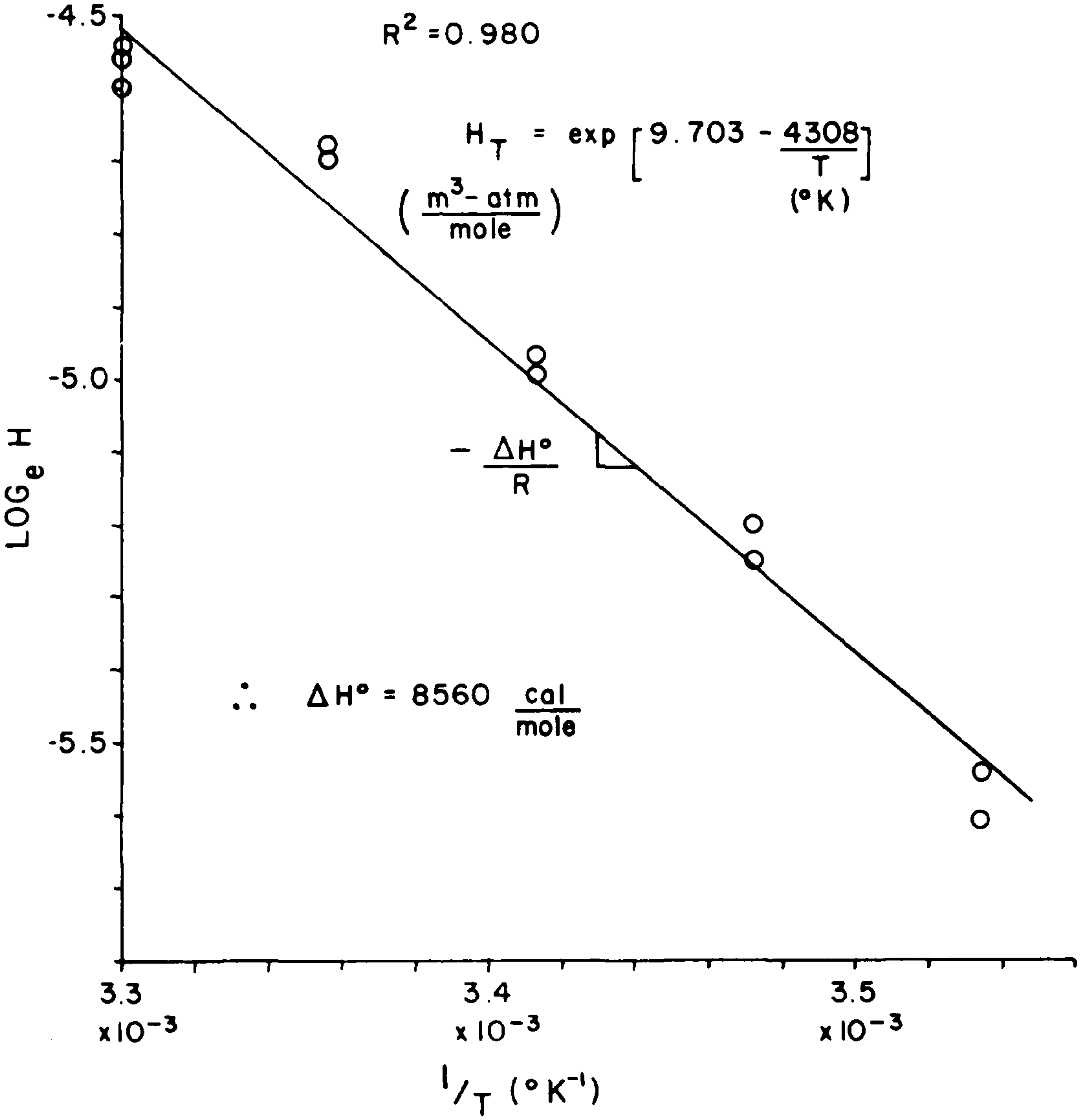


Figure 4. Temperature Dependence of Henry's Constant

which yields a $\Delta H°$ value of 8240 cal/mole upon calculation -- this is within 4 percent of the value arrived at from these experiments.)

Ionic strength studies were conducted over the range from zero to 1 M at 20°F using KCl as electrolyte. The experimental procedure allowed, directly, only the determination of $H\gamma$. Using the H-value determined at I = 0 via Equation (6), however, activity coefficients could be separately calculated from the $H\gamma$ data obtained versus ionic strength. Figure 5 shows a plot of $\log_{10} \gamma$ versus ionic strength in accordance with the empirical model of Equation (3). The model appears adequate. The regression gives a salting-out coefficient of 0.207.

5. DISCUSSION

The effect of temperature on Henry's constant is quite pronounced, as shown in Table 1.

Table 1. EFFECT OF TEMPERATURE ON HENRY'S CONSTANT*

T(°C)	H (m^3 - atm/mole)
10	0.401×10^{-2}
15	0.522×10^{-2}
20	0.674×10^{-2}
25	0.862×10^{-2}
30	1.09×10^{-2}

*Calculated via Equation (8).

The single reported literature value of 1.0×10^{-2} m^3-atm/mole (7) at 20°C differs significantly from the 20°C value found in these experiments. No explanation is apparent, but this author has no knowledge of the basis for the literature value. The precision of the experiments reported herein, and the agreement with the literature value of $\Delta H°$ is circumstantial evidence supporting experimental results.

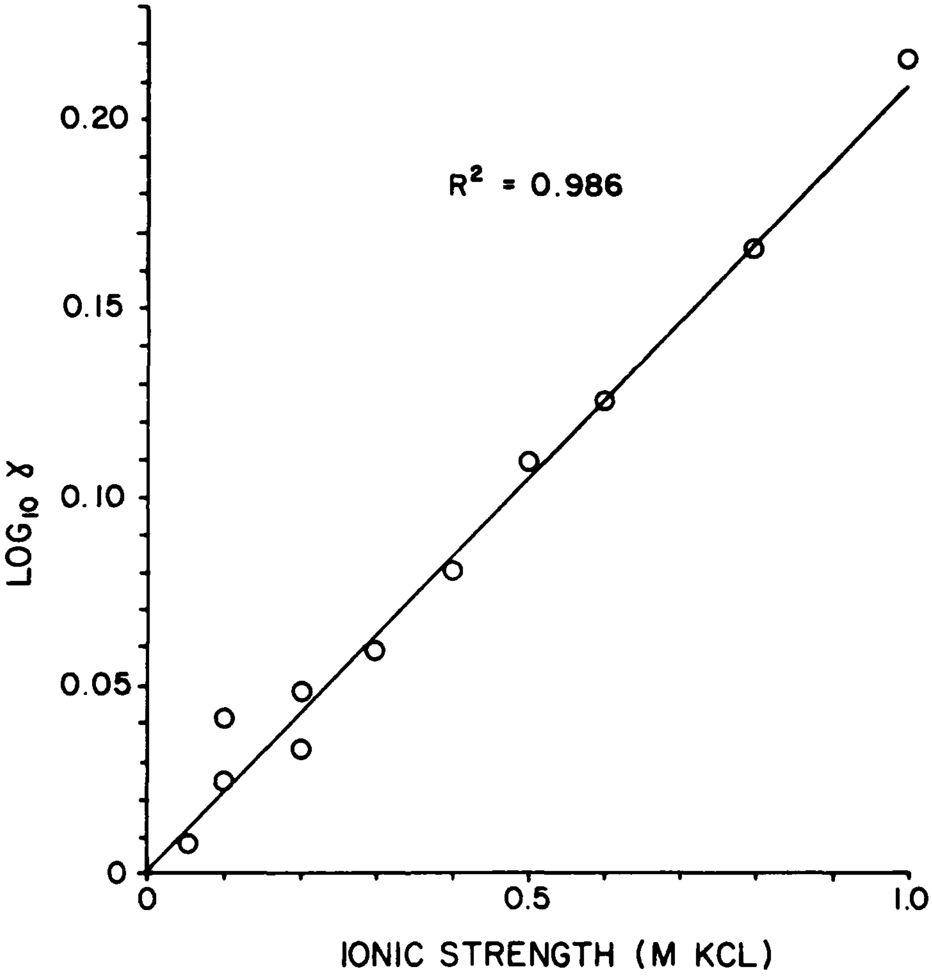


Figure 5. Effect of Ionic Strength on Activity Coefficient for TCE (20°C)

The effect of ionic strength appears to be very minimal. At I = 0.1 M (KCl), the activity coefficient is 1.05 -- meaning only a 5-percent change in the effective H-value if the concentration of TCE is used as an approximation of its activity. For most applications, then, ionic strength corrections will prove to be unnecessary. If needed, however, the results from these experiments provide the means.

SECTION IV

PACKED TOWER KINETIC STUDIES

1. BACKGROUND

Figure 6 schematically represents a countercurrent flow, packed bed stripping tower. Equations describing performance of such systems are well developed in standard texts and references.(4, 11)

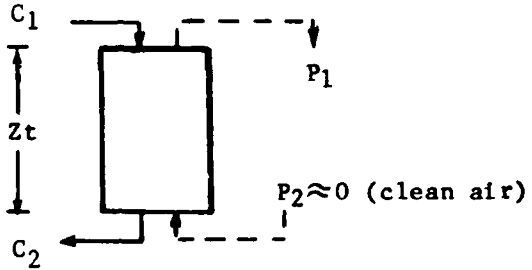


Figure 6. Packed Bed Schematic for Countercurrent Operation.

Define:

L = water flow (m^3/min)

G = gas flow (m^3/min at temperature = T_g)

C_1, C_2 = influent, effluent TCE concentration in liquid phase (moles/m^3)

P_1, P_2 = effluent, influent TCE partial pressures in the gas phase (atm)

C_1^*, C_2^* = influent theoretical TCE concentrations in liquid phase if at equilibrium with the effluent, influent gas phase partial pressures (moles/m^3). This is (ignoring activity corrections),

$$C_1^* = P_1/H$$

$$C_2^* = P_2/H$$

H = Henry's constant (m^3-atm/mole)

Z_T = packed height (m)

A = cross-sectional area of tower (m^2)

a = interfacial area per unit bulk volume (m^2/m^3)

K_L = overall mass transfer coefficient based upon the liquid phase

$$\left(\frac{\text{moles solute stripped}}{\text{min - interfacial area - moles/m}^3\text{ gradient}}\right)$$

Normally, these last two quantities are not separately specified, but are employed instead as the single quantity product, K_La.

Making two assumptions leads to a simple analytical solution. The assumptions are:

1. Both the gas and liquid phases are dilute with respect to the mole fraction of TCE in them. Thus, a linear operating line results.
2. A linear equilibrium line exists (i.e., Henry's Law holds).

The solution (4,11) is

$$L(C_1 - C_2) = K_La\,\overline{(C - C^*)}_L\,AZ_T \qquad (9)$$

moles/min

where:

$$\overline{(C - C^*)_L} = \text{log-mean driving force}$$

$$= \frac{(C_1 - C_1^*) - (C_2 - C_2^*)}{\ln[(C_1 - C_1^*)/(C_2 - C_2^*)]} \qquad (10)$$

But $C_1^* = P_1/H$ and $C_2^* = P_2/H = 0$ (if clean influent air is used). Also, from a mass balance consideration,

$$L(C_1 - C_2) = \frac{G\,(P_1 - \cancelto{0}{P_2})}{RT_g} \qquad (11)$$

Upon substitution and rearrangement, the following alternative forms of the same equation result:

$$Z_T = \frac{L}{A} \; \frac{\ln\left[\dfrac{C_1}{C_2} - \dfrac{LRT_g}{GH}\left(\dfrac{C_1}{C_2} - 1\right)\right]}{K_La\left(1 - \dfrac{LRT_g}{GH}\right)} \qquad (12)$$

or

$$\frac{C_1}{C_2} = \frac{\exp\left[\dfrac{Z_TA}{L}\left(1 - \dfrac{LRT_g}{GH}\right)K_La\right] - \dfrac{LRT_g}{GH}}{1 - \dfrac{LRT_g}{GH}} \qquad (13)$$

Equation (12) allows calculation of the required packed height -- given some required efficiency -- for specified values of flow rates, H, and K_La. Equation (13) allows calculation of the expected performance, given values of Z_T, flows, H and K_La. Thus, factors which influence H and K_La will affect performance.

From studies described in the previous section, the effects of temperature and ionic strength on H are now known. Factors influencing K_La for TCE include temperature, liquid and gas flow rates, and type of packing.(4,11)

2. OBJECTIVES

The objectives of this second experimental phase were to quantify the effects of temperature and flow rates on the overall mass transport coefficient, K_La. (A single packing material was used -- 5/8-inch plastic Pall rings.) Such study was necessary in order to enable proper design and analysis of packed bed countercurrent strippers.

3. EXPERIMENTAL

The experimental strategy involved the measurement of K_La in a packed tower operated isothermally at temperatures from 10° - 30°C, holding L and G constant. Then L was varied at constant G, with temperature held constant at 30°C. Finally, G was varied at constant L, with T = 30°C.

a. Measurement of K_La.

If a packed tower were provided with liquid sampling ports at various heights, z, from the bottom, then the concentration of TCE at height z (C_z) would be given by the following analogue of Equation (13):

$$\frac{C_z}{C_2} = \frac{\exp\left[\frac{zA}{L}\left(1 - \frac{LRT_g}{GH}\right)K_La\right] - \frac{LRT_g}{GH}}{1 - \frac{LRT_g}{GH}} \qquad (14)$$

Rearranging gives:

$$\ln\left[\frac{C_z}{C_2}\left(1 - \frac{LRT_g}{GH}\right) + \frac{LRT_g}{GH}\right] = \frac{zA}{L}\left(1 - \frac{LRT_g}{GH}\right)K_La \qquad (15)$$

Thus, if C_z data are taken at steady state for various heights, z, a plot of the left hand side of Equation (15) versus

$$\frac{zA}{L}\left(1 - \frac{LRT_g}{GH}\right)$$ should yield a straight line of slope, K_La.

b. Packed Bed Stripping Reactor.

The experimental apparatus is shown in Figure 7. The reactor consisted of a 2.9 m x 19 cm (ID) Plexiglass® column outfitted as shown and packed with 1.59 cm plastic Pall rings. The packing retention plate was a Plexiglass® disk drilled with holes. A liquid redistribution disk was situated approximately at the packing midpoint. Seven liquid sampling ports were constructed of PVC piping (1.27 cm OD) which was longitudinally cut to form troughs near the inner ends. These sample ports were located at z = 0.0857, 0.391, 0.695, 1.000, 1.610, 1.915, and 2.219 meters. (This last port was resting on top of the packing.) The effluent sample port represented the z = 0 sample, even though there was a 20 cm free fall between it and the bottom of the packing. Any difference in TCE concentration between true z = 0 and the point of effluent sampling was ignored.

Liquid was applied to the bed by pumping from a 2000-liter reservoir through a conventional shower nozzle. The flow passed through a calibrated rotameter prior to the shower nozzle. The liquid temperature was adjustable by varying the initial mix of tap water and chilled tap water used to prepare the TCE feed. (The chilled water came from pumped storage in a large refrigerated room.)

A reservoir of air was provided to the bottom of the column from an air-conditioner. The minimum temperature which could be consistently supplied was 9°C. The temperature of the air reservoir below the packed bed reactor was

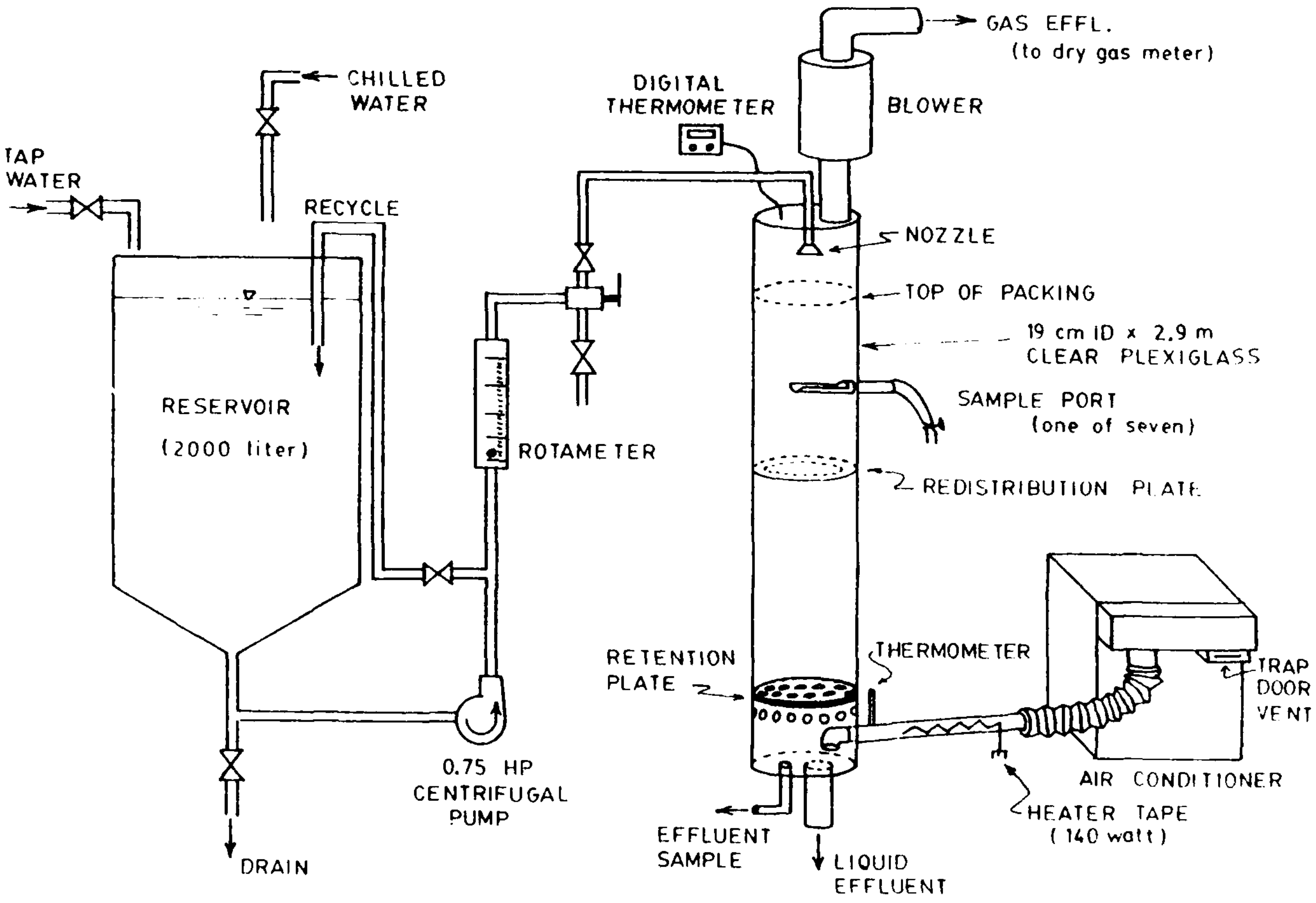


Figure 7. Packed Bed Stripping Apparatus.

controlled by a combination of adjusting the air-conditioner output (via its own fan speed and purposeful venting from a trap door in a manifold) and by varying the voltage applied to a 140-watt heating tape placed inside the duct. The goal was to provide constant temperature air (from 10 - 30°C) to the column bottom in excess of the flow demanded by the blower situated above the bed. It was this blower which determined the actual flow throughput. The excess air supplied to the column bottom from the air-conditioning system merely exited through holes below the packing retention plate. The air flow passing through the column exited through a dry gas meter for flow rate measurement.

c. Procedures.

A 2 ml quantity of TCE was added to 2 liters of tap water, capped, and allowed to mix for a period of 2 or more hours in order to dissolve as much of the TCE as possible. A mixture of tap and chilled waters totaling 1500 liters was placed in the reservoir. The TCE solution was added, then the reservoir was mixed by pumping in a recycle mode (Figure 7) for 20 minutes. Meanwhile, the air conditioning/heating system was started and adjusted to provide the desired air temperature to the column bottom. The blower was then turned on to start the air flow through the reactor. The liquid flow was diverted from its recycle mode to flow to the column through the rotameter.

The reactor was allowed to equilibrate for 20 minutes prior to taking samples for concentration measurements. (Studies where samples were taken at time intervals from 1 to 60 minutes after flow commencement demonstrated that equilibration was indeed rapid -- probably less than a minute was really necessary.) Flow data were recorded, and temperatures of reservoir liquid,

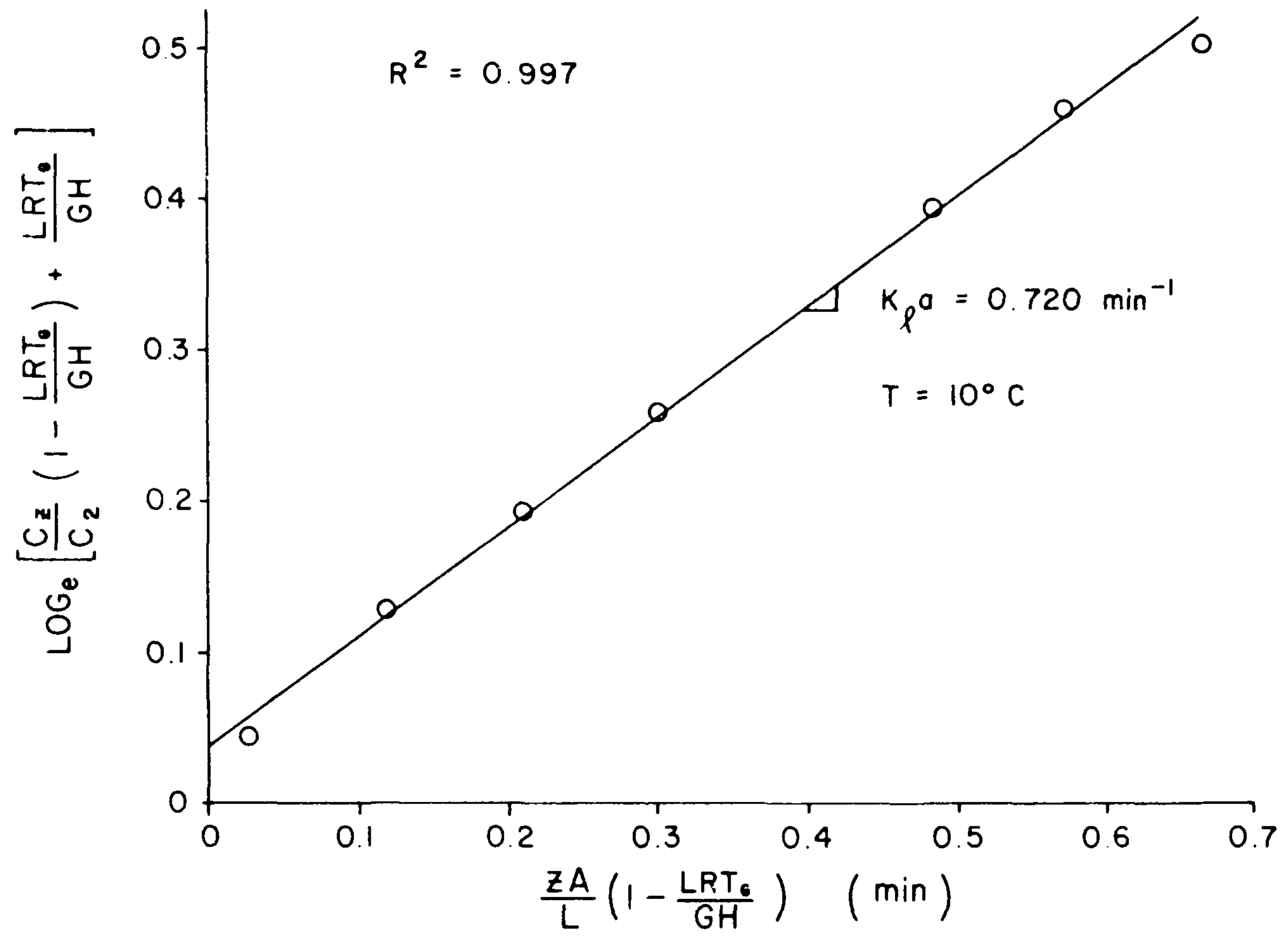


Figure 8. Example of Data Plot from Packed Bed Reactor Studies.

effluent liquid, influent air and effluent air were taken. All temperatures were within ± 1°C of the desired set point.

Liquid samples of 25 ml volume were collected from the reservoir (surface and bottom, to demonstrate uniformity), the reactor effluent, and each of the seven packed bed sampling ports. The samples were carefully poured into 120 ml serum bottles, sealed with Teflon®-lined serum bottle crimp caps, and equilibrated (as described in a previous section) prior to concentration measurement using the headspace chromatographic technique.

4. RESULTS

An example of results from these kinetic studies is shown in Figure 8. The data appear to fit the model of Equation (15) very well. Notice, however, that the regression lines do not pass through the origin, as predicted by Equation (15). This is probably due to the fact that the effluent concentration is not a good measure of the C_2 value, which is properly defined to be the concentration at $z = 0$ (a point where no sample port existed). An error in C_2, however, does not appreciably affect the slope of the regression (or K_La determination), but merely shifts the line vertically.

The effect of temperature on K_La is shown in Figure 9. Liquid surface loading rate was 0.857 $m^3/min/m^2$ in all cases; air surface loading rate was 6.4 m^3 (STP)/min/m^2 (surface area was defined on the basis of column cross-sectional area, 0.02835 m^2). The plot of $\ln K_La$ versus $1/T$ was chosen because it was suspected that the Arrhenius model of temperature effect on reaction rate might be appropriate. The coefficient of determination was 0.95. The regression equation yields:

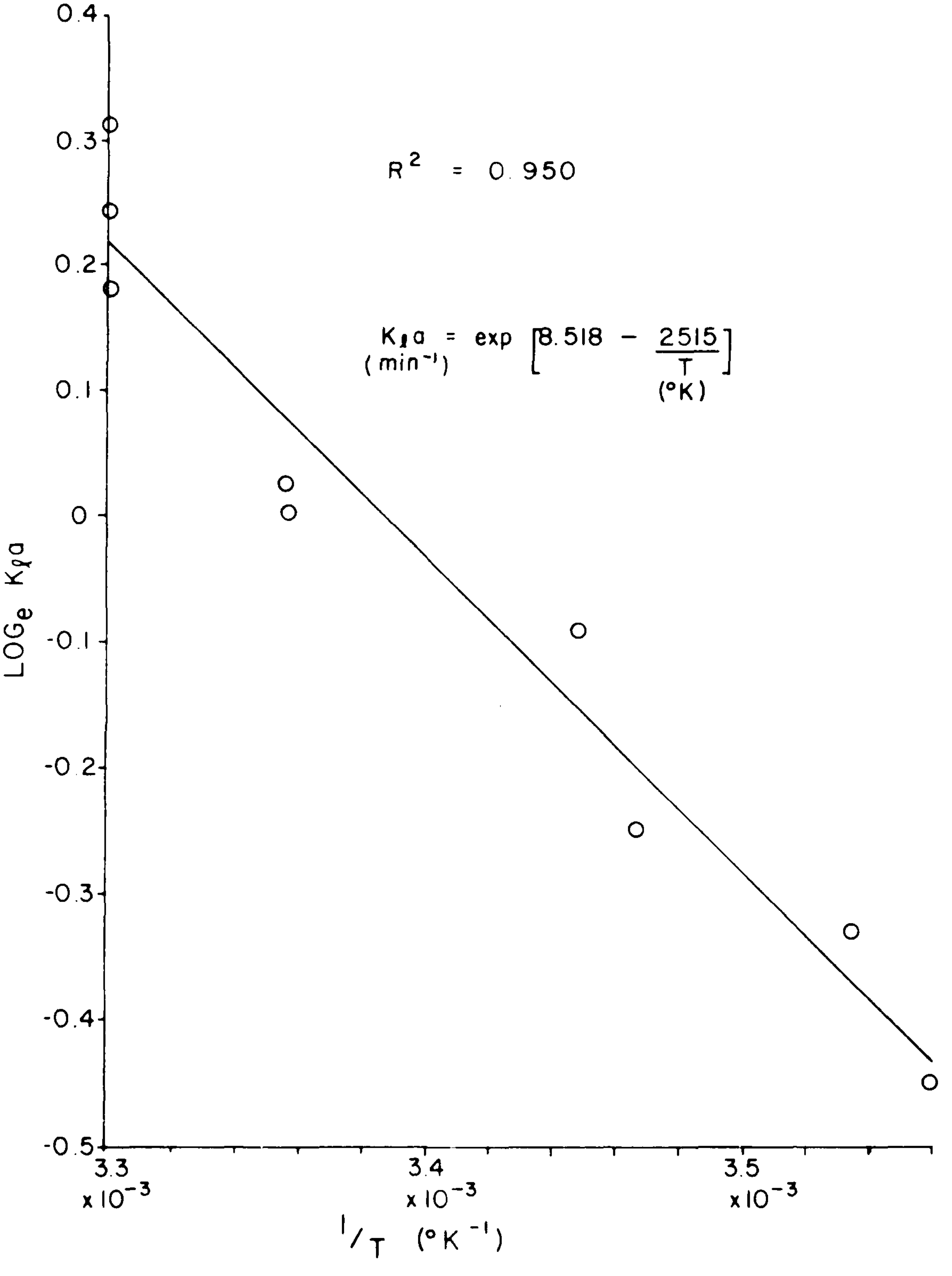


Figure 9. Effect of Temperature $K_L a$.

$$K_La\ (\mathrm{min}^{-1}) = \exp\left[8.518 - \frac{2515}{T\ (\text{as }^\circ K)}\right] \qquad (16)$$

Predicted K_La values are shown in Table 2 for selected temperatures.

TABLE 2. K_La VERSUS TEMPERATURE*

T (°C)	K_La (min^{-1})
10	0.691
15	0.807
20	0.936
25	1.082
30	1.243

*Calculated from Equation (16)

The effect of liquid flow velocity on K_La was evaluated at 30°C using a liquid loading which varied from 0.635 to 1.160 $m^3/min/m^2$, with air velocity held constant at 6.4 m^3(STP)/min/m^2. The range of liquid flows studied, while rather small, was the maximum possible with the pump and rotameter provided. Results are shown in Figure 10. There is no apparent significant effect of liquid loading on K_La.

The effect of air velocity on K_La was evaluated at 30°C over a range from 3.17 to 12.49 m^3(STP)/min/m^2, with a constant liquid loading of 0.857 $m^3/min/m^2$. Results are shown in Figure 11. No significant effect is apparent. It should be pointed out that even at the highest air velocity studied, the air pressure drop across the bed was only about 2.1 cm (H_2O)/m)of packing (0.25 in/ft), a value which indicates operation well below the load point.

5. DISCUSSION

The effect of temperature on K_La was quite significant and should be taken into account according to Equation (16). Mackay and Leninonen(13) have stated that for most compounds of importance, the stripping rate is insensitive to temperature; however, these results do not bear out that statement.

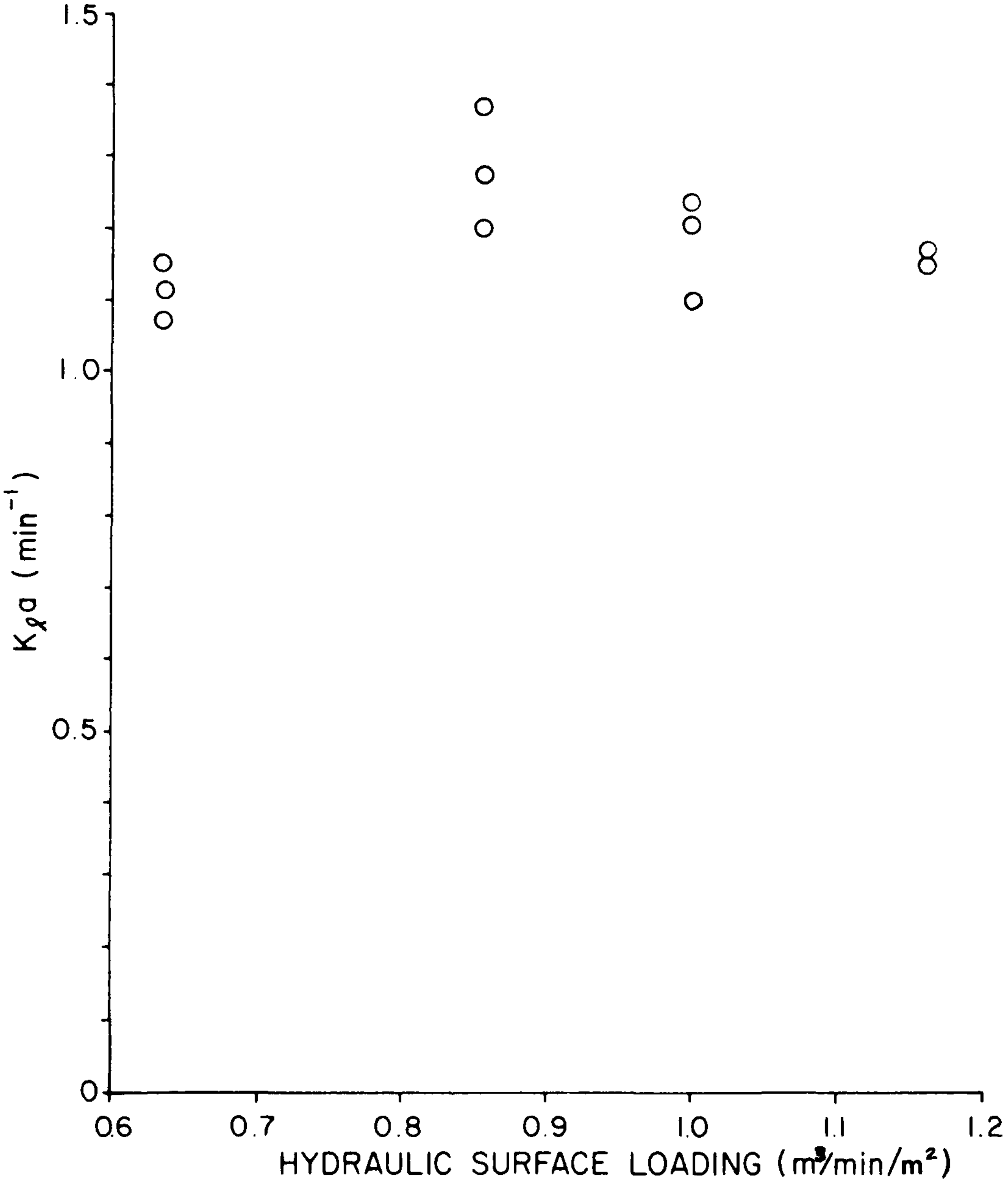


Figure 10. Effect of Hydraulic Loading on $K_L a$.

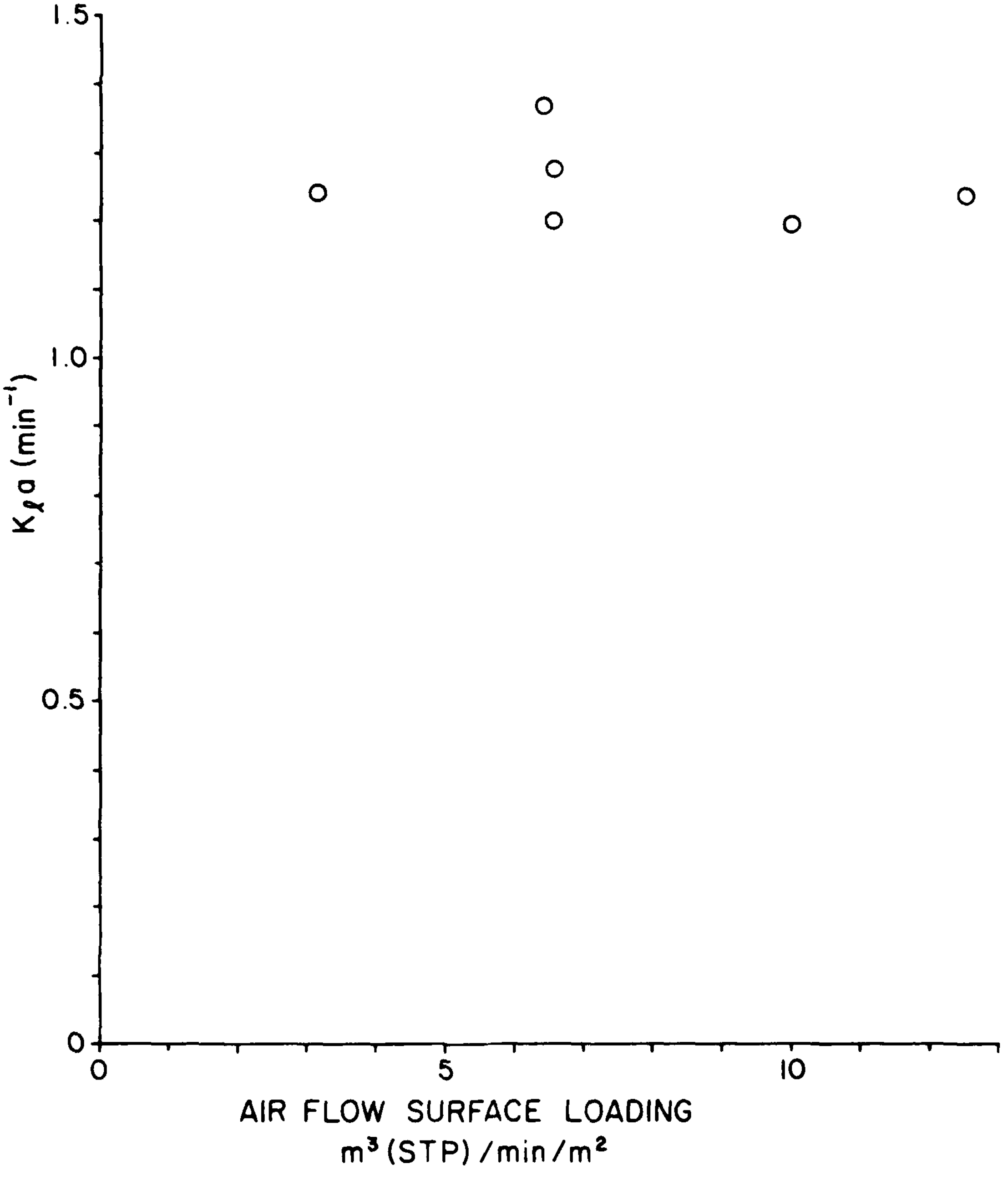


Figure 11. Effect of Air Flow on $K_L a$.

MacKay and Leinonen(13) have also suggested that for compounds with Henry's constant exceeding 1.6 x 10^{-4} m^3atm/mole, the liquid phase resistance will dominate transfer kinetics. Such is the case with TCE. Thus, it is not surprising to find that air flow velocity has negligible effect on K_La. However, the finding that liquid flow rate also has no effect (over the limited range investigated) is more puzzling. Perhaps the answer is that in these experiments, the expected increase in K_L caused by increased liquid turbulence was offset by a decrease in interfacial surface area per volume (a), leading to a relatively constant K_La. Certainly "a" will decrease at some point as L increases. However, the fact that these experiments appeared to operate under conditions of rather low air head loss, apparently well below the load point, makes this explanation uncertain.

With the packing material used in these experiments, and over the range of temperatures and flow velocity studies, Equations (13), (8), and (16) can be used together to predict performance of a countercurrent stripper as a function of packed volume per liquid flow, air/water ratio, and temperature. Examples are provided by Figures 12, 13, and 14. It appears from Figures 12 and 13 that little is to be gained in exceeding air/water ratios of about 10-15m^3 (STP)/m^3.

Predictions made using Equation (13) will be underestimates of observed performance, in that additional removals will result from the free-fall drops occurring between the distribution nozzle and the top of the packing, and between the bottom of the packing and the effluent drain. The former may be quite significant in some cases -- depending upon the temperature and nozzle configuration. In these studies, the "nozzle removal" was as much as 30 percent at 30°C, and as little as 10 percent at 10°C (for G/L = 7.5 m^3(STP)/m^3).

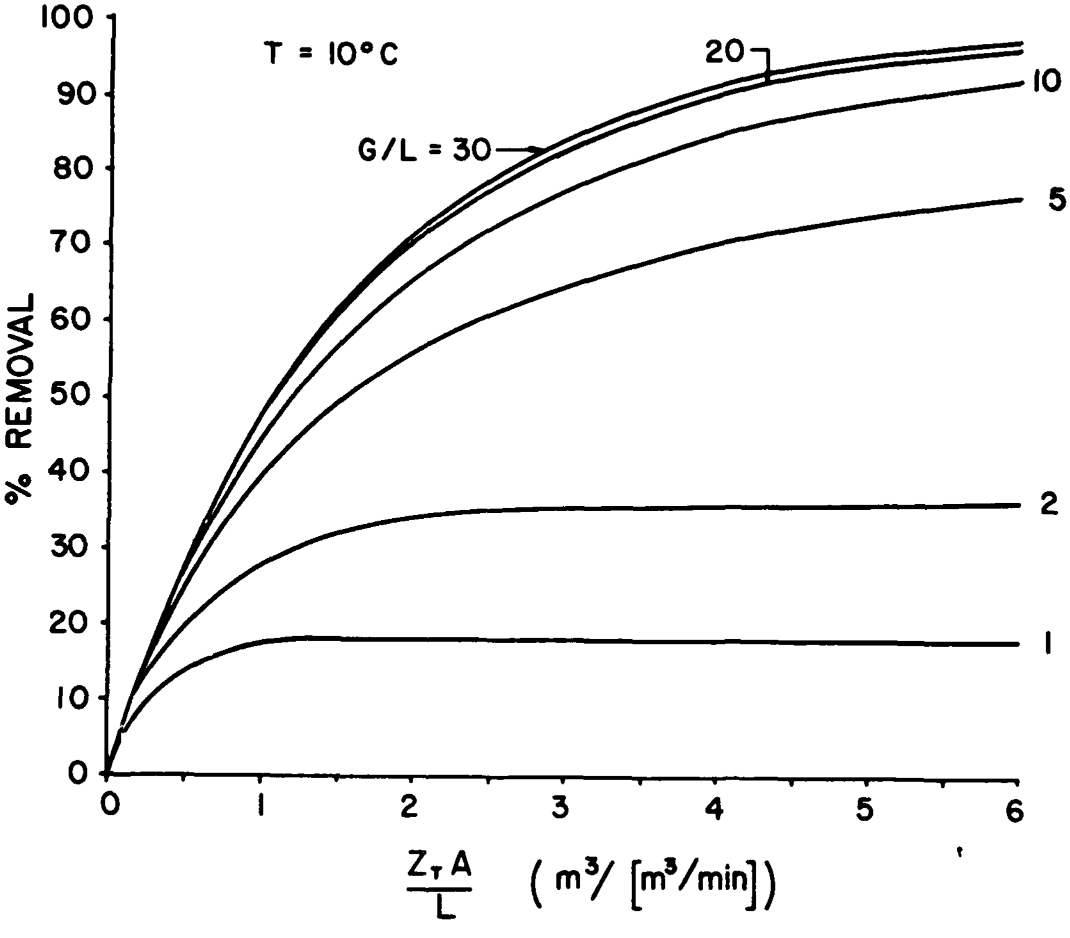


Figure 12. Predicted Percent Removal of TCE Versus Packed Volume Per Liquid Flow Rate, at Various Volume Ratios of Air (STP)/Water.

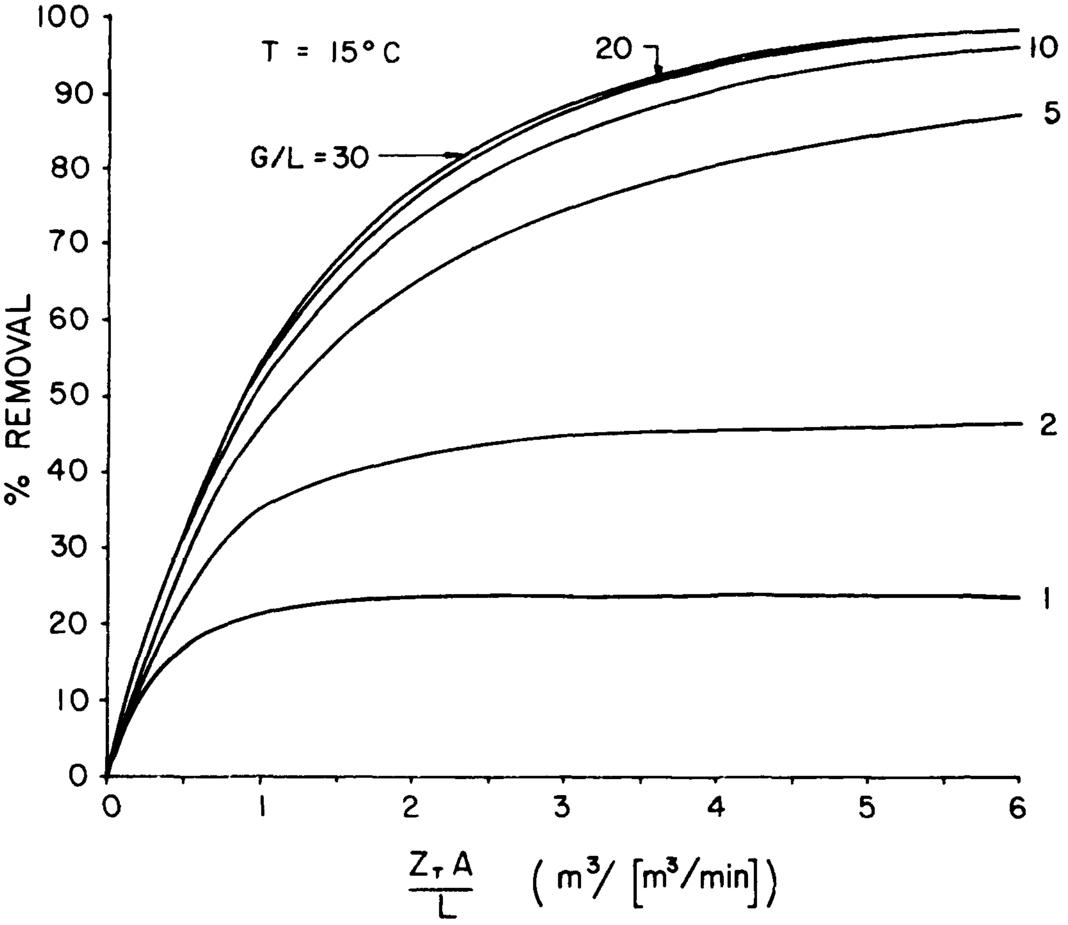


Figure 13. Predicted Percent Removal of TCE Versus Packed Volume Per Liquid Flow Rate, at Various Volume Ratios of Air (STP)/Water.

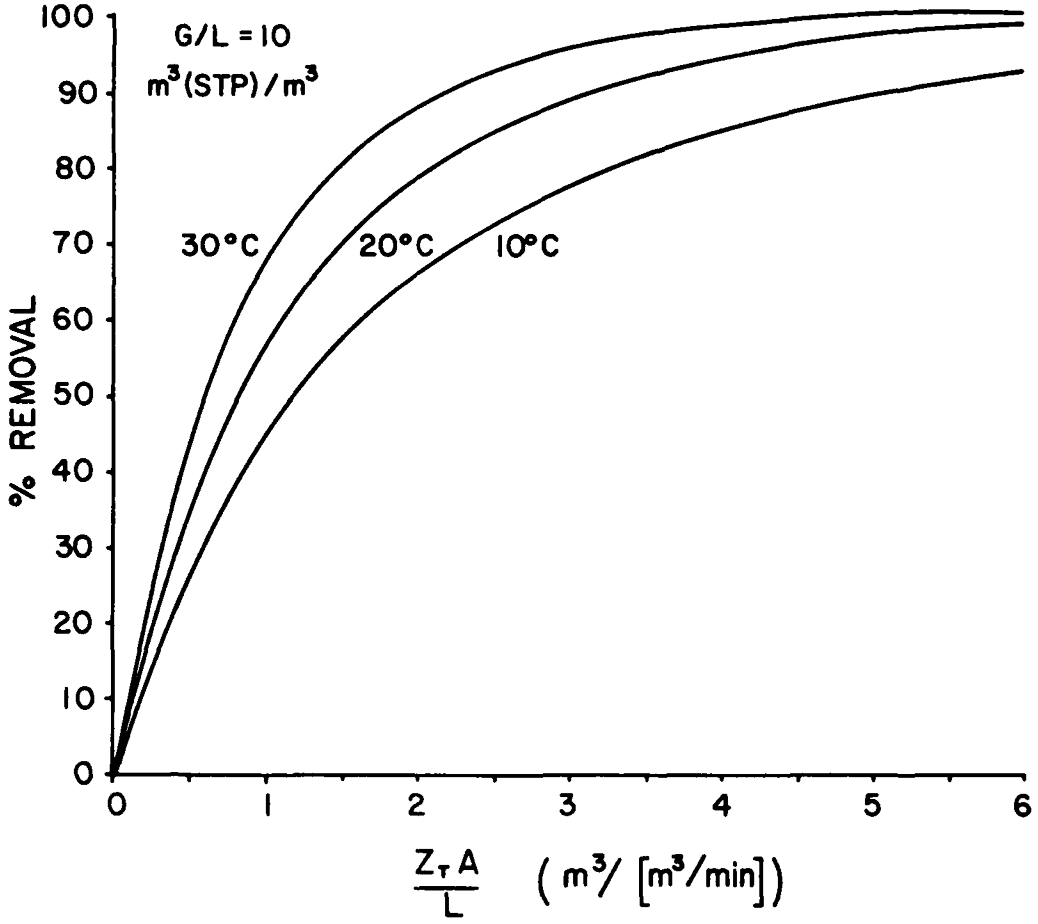


Figure 14. Predicted Percent Removal of TCE Versus Packed Volume Per Liquid Flow Rate, at Three Different Temperatures For G/L = 10m^3 (STP)/m^3.

SECTION V

CONCLUSIONS

1. The effect of temperature on Henry's constant for TCE was evaluated; the variation was well described by the equation:

$$H_T \left\{\frac{m^3\text{-atm}}{\text{mole}}\right\} = \exp\left[9.703 - \frac{4308}{T(\text{as}^\circ K)}\right]$$

2. The effect of ionic strength on the effective H is of little practical concern over the range of salinity values expected to be encountered. At I = 0.1 M(KCl), the effective H (based on molar TCE concentration instead of activity) is only 5 percent higher than the true H.

3. The overall mass transfer coefficient, K_La, applicable to a countercurrent flow packed bed (5/8 in Pall rings) reactor for TCE stripping was affected by temperature significantly, but not by liquid or gas flow rates used in these studies. The temperature effect is described by:

$$K_La\ (\text{min}^{-1}) = \exp\left[8.518 - \frac{2515}{T\ (\text{as}^\circ K)}\right]$$

4. Studies have shown that little gain in performance accrues by increasing the air/water ratio beyond about 10 to 15 m^3(STP)/m^3.

SECTION VI

RECOMMENDATIONS

1. An economic evaluation should be undertaken to determine the optimum system design for a combination air stripping/carbon adsorption facility for TCE removal. There is an infinite set of values for packed bed length, diameter, and air/liquid ratio which will yield a desired removal efficiency in the stripping reactor. Additionally, there is an infinite set of coupled individual stripper/carbon adsorption efficiencies which will result in some desired overall removal efficiency. A cost model should be developed to optimize the overall system design. Only in this way can the true potential of air stripping be evaluated.

2. The presence of additional organics (some perhaps not even strippable) likely to be found along with TCE should be evaluated for an effect on TCE stripping. Henry's constant and mass transfer coefficient (K_La) 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 chlorobenzenes and other chlorinated compounds will coexist in groundwaters contaminated with TCE, since these compounds are often used in addition to TCE and are disposed of in the same manner.

3. Mass transfer data should be gathered for other packings in order to provide a range of design choices.

4. Thermal studies should be undertaken to evaluate and model the freezing potential and effects on performance of subzero air when used for TCE stripping. At northern facilities, the groundwater may be fairly uniform in

temperature throughout the year, but the air is not. Nonisothermal models should be investigated and potential for freezing assessed.

5. A much fuller range of liquid and air flow rates should be examined. The liquid distribution system used in these studies was incapable of approaching the flood point, and therefore may not typify conditions likely to be encountered in optimal design.

REFERENCES

1. Roebeck, G. G., Memorandum to F. T. Mayo, Director, Municipal Environmental Research Laboratory, U.S. EPA, Cincinnati, Ohio, Subject: Progress on Major Priority Issue -- Contaminated Groundwater, October 23,1979.

2. Symons, J. M., et al., Removal of Organic Contaminants From Drinking Water Using Techniques Other Than Granular Activated Carbon Alone: A Progress Report , Drinking Water Research Division, Municpal Environmental Research Laboratory, U.S. EPA, Cincinnati, Ohio, May 1979.

3. Ruggiero, D., "Glen Cove, Long Island: Project Experiences," Region III Technology Transfer Seminar on Trichloroethylene Contamination of Ground Water, Philadelphia, PA, November 8, 1979.

4. Perry, R. H., et al., Chemical Engineer's Handbook, 5th Edition, McGraw-Hill, 1973.

5. Garrels, R. M., and C. L. Christ, Solutions, Minerals, and Equilibria, New York, Harper & Row, 1965.

6. Butler, J. N., Ionic Equilibrium, Reading, MA, Addison-Wesley, 1964.

7. U.S. EPA, Innovative and Alternative Technology Assessment Manual (Draft), EPA-43019-78-009, 1978.

8. Mackay, D., et al., "Determination of Air-Water Henry's Law Constants for Hydrophobic Pollutants ," Envir. Sci. and Technol., 13 (3), 333-337, 1979.

9. Dietz, E. A., Jr., and K. F. Singley, "Determination of Chlorinated Hydrocarbons in Water by Headspace Gas Chromatography, " Analytical Chemistry, 51 (11), 1809, 1979.

10. Lange's Handbook, 11th ed. 1973.

11. McCabe, W. L. and J. C. Smith, Unit Operations of Chemical Engineering, 3rd ed., New York, McGraw-Hill, 1976.

12. Sherwood and Hollaway, "Performance of Packed Towers -- Liquid Film Data for Several Packings," Trans. Am. Inst. Chem. Engrs., 36, 39, 1940.

13. MacKay, D., and P. J. Leinonen, "Rate of Evaporation of Low-Solubility Contaminants from Water Bodies to Atmosphere," Envir. Sci. and Technol., 9, 1178, 1975.