Application of the Two-Film Model to the Volatilization of Acetone and t-Butyl Alcohol from Water as a Function of Temperature

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Application of the Two-Film Model to the Volatilization of Acetone and t-Butyl Alcohol from Water as a Function of Temperature

By R. E. RATHBUN and D. Y. TAI

U.S. GEOLOGICAL SURVEY WATER-SUPPLY PAPER 2318

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SYMBOLS AND DEFINITIONS

		Units
A	Cross-sectional area for volatilization	Square meters
a_E	Pre-exponential constant in the general equation for the temperature dependence of a rate constant	Reciprocal days
a_G	Pre-exponential constant in the equation for the temperature dependence of the gas-film coefficient	Meters per day
a_H	Pre-exponential constant in the equation for the temperature dependence of the Henry's law constant	Kilopascals cubic meter per gram mole
a_k	Constant in the equation relating the film coefficient and the molecular-diffusion coefficient	Meters to the $(1-2\nu)$ power times days to the $(\nu-1)$ power
a_L	Pre-exponential constant in the equation for the temperature dependence of the liquid-film coefficient	Meters per day
a_ν	Pre-exponential constant in the equation for the temperature dependence of the vapor pressure	Kilopascals
a_γ	Pre-exponential constant in the equation for the temperature dependence of the activity coefficient	---
a_1	Constant in the empirical equation relating the liquid-film coefficient to the stirrer Reynolds number and the Schmidt number	Meters per day
b_G	Exponential constant in the equation for the temperature dependence of the gas-film coefficient	Kelvins
b_H	Exponential constant in the equation for the temperature dependence of the Henry's law constant	Kelvins
b_L	Exponential constant in the equation for the temperature dependence of the liquid-film coefficient	Kelvins
b_ν	Exponential constant in the equation for the temperature dependence of the vapor pressure	Kelvins
b_γ	Exponential constant in the equation for the temperature dependence of the activity coefficient	Kelvins
b_1	Exponent on the stirrer Reynolds number in the empirical equation relating the liquid-film coefficient to the stirrer Reynolds number and the Schmidt number	---

		Units
b_2	Exponent on the Schmidt number in the empirical equation relating the liquid-film coefficient to the stirrer Reynolds number and the Schmidt number	---
C	Concentration of the solute in the bulk-liquid phase	Gram moles per cubic meter
C_d	Concentration of the solute in the stream water at the downstream point	Milligrams per liter
C_E	Concentration of the solute in the bulk-liquid phase which would be in equilibrium with the bulk-gas phase partial pressure, p	Gram moles per cubic meter
C_i	Concentration of the solute in the water at the interface between the air and water phases	Gram moles per cubic meter
C_o	Concentration of the solute in the water at time zero	Gram moles per cubic meter
C_s	Concentration of dissolved oxygen in water in equilibrium with the oxygen in the atmosphere	Gram moles per cubic meter
C_u	Concentration of the solute in the stream after mixing of the wastewater with the stream water	Milligrams per liter
D	Molecular-diffusion coefficient	Square meters per day
D_{AC}	Molecular-diffusion coefficient of acetone in water	Square meters per day
D_{ORG}	Molecular-diffusion coefficient of an organic substance in water	Square meters per day
D_{OXY}	Molecular-diffusion coefficient of oxygen in water	Square meters per day
D_{TBA}	Molecular-diffusion coefficient of t-butyl alcohol in water	Square meters per day
D_1	Molecular-diffusion coefficient for solute 1	Square meters per day
D_2	Molecular-diffusion coefficient for solute 2	Square meters per day
E	Activation energy for a chemical, biological, or physical process	Joules per gram mole
ERR	Normalized root-mean-square error of prediction for an equation	Percent
f	Fugacity of a solute in a water solution	Kilopascals

		Units
f_R	Reference fugacity for the solute	Kilopascals
H	Henry's law constant	Kilopascals cubic meter per gram mole
H_{AC}	Henry's law constant for acetone in water	Kilopascals cubic meter per gram mole
H_{OXY}	Henry's law constant for oxygen in water	Kilopascals cubic meter per gram mole
H_{TBA}	Henry's law constant for TBA in water	Kilopascals cubic meter per gram mole
K	Rate constant for a chemical,biological, or physical process	Reciprocal days
K_o	Rate constant for a chemical, biological, or physical process at temperature, T_o	Reciprocal days
K_{OL}	Overall mass-transfer coefficient for volatilization based on the liquid phase	Meters per day
$K_{OL_{AC}}$	Overall mass-transfer coefficient for volatilization of acetone from water based on the liquid phase	Meters per day
$K_{OL_{TBA}}$	Overall mass-transfer coefficient for volatilization of t-butyl alcohol from water based on the liquid phase	Meters per day
K_2	Reaeration coefficient for the absorption of oxygen by a stream or river	Reciprocal days
k	Film coefficient for mass transfer	Meters per day
k_G	Mass-transfer coefficient for the gas film, usually called the gas-film coefficient	Meters per day
$k_{G_{AC}}$	Gas-film coefficient for acetone	Meters per day
$k_{G_{ORG}}$	Gas-film coefficient for an organic solute	Meters per day
$k_{G_{REF}}$	Gas-film coefficient for the reference substance	Meters per day
$k_{G_{TBA}}$	Gas-film coefficient for t-butyl alcohol	Meters per day
$k_{G_{WAT}}$	Gas-film coefficient for the volatilization of water	Meters per day
k_{G_1}	Gas-film coefficient for solute 1	Meters per day

		Units
k_{G_2}	Gas-film coefficient for solute 2	Meters per day
$\left(k_{G_{ORG}}/k_{G_{WAT}}\right)_{DISH}$	Ratio of the gas-film coefficients for the volatilization of an organic solute and water from the dish volatilization apparatus	---
$\left(k_{G_{ORG}}/k_{G_{WAT}}\right)_{BATH}$	Ratio of the gas-film coefficients for the volatilization of an organic solute and water from the stirred water bath	---
k_L	Mass-transfer coefficient for the liquid film, usually called the liquid-film coefficient	Meters per day
$k_{L_{AC}}$	Liquid-film coefficient for acetone	Meters per day
$k_{L_{ORG}}$	Liquid-film coefficient for an organic solute	Meters per day
$k_{L_{OXY}}$	Liquid-film coefficient for the absorption of oxygen by water	Meters per day
$k_{L_{REF}}$	Liquid-film coefficient for the reference substance	Meters per day
$k_{L_{TBA}}$	Liquid-film coefficient for t-butyl alcohol	Meters per day
k_{L_1}	Liquid-film coefficient for solute 1	Meters per day
k_{L_2}	Liquid-film coefficient for solute 2	Meters per day
L	Thickness of the film	Meters
log_e	Natural logarithm	---
M	Molecular weight	Grams per gram mole
M_1	Molecular weight of solute 1	Grams per gram mole
M_2	Molecular weight of solute 2	Grams per gram mole
N	Mass flux of the solute	Gram moles per day per square meter
n	Number of data points	---
p	Partial pressure of the solute in the bulk-gas phase	Kilopascals
p_i	Partial pressure of the solute in the air at the interface between the air and water phases	Kilopascals
p_s	Vapor pressure of the pure solute	Kilopascals

		Units
R	Ideal gas constant	Kilopascals cubic meter per gram mole per kelvin
Re	Stirrer Reynolds number, equal to the stirrer speed times the square of the stirrer-blade width times the water density divided by the water viscosity	---
r_G	Resistance of the gas film to volatilization	Days per meter
r_L	Resistance of the liquid film to volatilization	Days per meter
r_{OL}	Overall resistance to volatilization, based on the liquid phase	Days per meter
Sc	Schmidt number, equal to the viscosity of water divided by the product of the molecular-diffusion coefficient and the water density	---
Sc_{OXY}	Schmidt number for oxygen in water	---
s	Stirrer speed	Revolutions per second
T	Temperature	Kelvins
T_o	Lower temperature limit of integration	Kelvins
t	Time	Days
U	Mean water velocity in a stream or river	Meters per day
V	Volume of the liquid phase	Cubic meters
Var_{CALC}	Calculated value of the variable in the computation of the normalized root-mean-square error of prediction; dimensions depend on variable under consideration	---
Var_{EXP}	Experimental value of the variable in the computation of the normalized root-mean-square error of prediction; dimensions depend on variable under consideration	---
w	Width of the stirrer blade	Meters
x	Mole fraction of the solute	Gram moles of solute per total gram moles in the system
Y	Mean water depth	Meters
Z	Distance downstream from the point of the waste discharge to the water supply intake	Meters

		Units
α	Pre-exponential constant in the general empirical equation for the temperature dependence of a rate constant for a chemical, biological, or physical process	Reciprocal days
β	Exponential constant in the general empirical equation for the temperature dependence of a rate constant for a chemical, biological, or physical process	Reciprocal kelvins
γ	Activity coefficient for the solute in water	---
$\Delta W/A\Delta t$	Volatilization flux	Grams per minute per square meter
ν	Exponent on the molecular-diffusion coefficient in the relation between the film coefficient and the molecular-diffusion coefficient	---
θ	Temperature coefficient for expressing empirically the temperature dependence of a rate coefficient for a chemical, biological, or physical process, equal to the exponential of β	---
μ	Viscosity of water	Grams per meter per second
ρ	Density of water	Grams per cubic meter
ϕ	Constant in the reference-substance concept for the liquid film; equal to the ratio of the liquid-film coefficient for the volatilization of an organic solute to the liquid-film coefficient for the volatilization of a reference substance	---
ψ	Constant in the reference-substance concept for the gas film, equal to the ratio of the gas-film coefficient for the volatilization of an organic solute to the gas-film coefficient for the volatilization of a reference substance	---

CONVERSION FACTORS

The following factors may be used for converting the International System of Units (SI) used in this report to inch-pound units.

Multiply SI units	By	To obtain inch-pound units
	Length	
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
	Flow	
day per meter (d/m)	0.3048	day per foot (d/ft)
meter per second (m/s)	3.281	foot per second (ft/s)
meter per minute (m/min)	3.281	foot per minute (ft/min)
meter per day (m/d)	3.281	foot per day (ft/d)
	Area	
square meter (m^2)	10.76	square foot (ft^2)
square meter per day (m^2/d)	10.76	square foot per day (ft^2/d)
	Volume	
cubic meter (m^3)	35.31	cubic foot (ft^3)
liter (L)	0.03531	cubic foot (ft^3)
milliliter per minute (mL/min)	3.531×10^{-5}	cubic foot per minute (ft^3/min)
	Mass	
milligram per liter (mg/L)	6.243×10^{-5}	pound per cubic foot (lb/ft^3)
gram per gram mole (g/g mol)	1.000	pound per pound mole (lb/lb mol)
gram per minute per square meter [$(g/min)/m^2$]	2.048×10^{-4}	pound per minute per square foot [$(lb/min)/ft^2$]
gram mole per day per square meter [$(g\ mol/d)/m^2$]	2.048×10^{-4}	pound mole per day per square foot [$(lb\ mol/d)/ft^2$]
gram per cubic meter (g/m^3)	6.243×10^{-5}	pound per cubic foot (lb/ft^3)
gram mole per cubic meter ($g\ mol/m^3$)	6.243×10^{-5}	pound mole per cubic foot ($lb\ mol/ft^3$)
gram per meter per second [(g/m)/s]	6.720×10^{-4}	pound per foot per second [(lb/ft)/s]
	Pressure	
kilopascal (kPa)	101.325	standard atmosphere (atm)
kilopascal cubic meter per gram mole ($kPa \cdot m^3/g\ mol$)	158.1	standard atmosphere cubic foot per pound mole ($atm \cdot ft^3/lb\ mol$)
kilopascal cubic meter per gram mole per kelvin [$(kPa \cdot m^3/g\ mol)/K$]	87.83	standard atmosphere cubic foot per pound mole per degree Rankine [$(atm \cdot ft^3/lb\ mol)/°R$]
	Energy	
joule per gram mole (j/g mol)	108.34	calorie per pound mole (cal/lb mol)

Temperature

Temperature in kelvins (K) may be converted to degrees Celsius (°C) as follows:

$$°C = K - 273.15$$

Temperature in kelvins (K) may be converted to degrees Rankine (°R) as follows:

$$°R = (K - 273.15)\ (1.8) + 491.7$$

Temperature in kelvins (K) may be converted to degrees Fahrenheit (°F) as follows:

$$°F = (K - 273.15)\ (1.8) + 32.0$$

Application of the Two-Film Model to the Volatilization of Acetone and t-Butyl Alcohol from Water as a Function of Temperature

By R. E. Rathbun *and* D. Y. Tai

Abstract

The two-film model is often used to describe the volatilization of organic substances from water. This model assumes uniformly mixed water and air phases separated by thin films of water and air in which mass transfer is by molecular diffusion. Mass-transfer coefficients for the films, commonly called film coefficients, are related through the Henry's law constant and the model equation to the overall mass-transfer coefficient for volatilization. The films are modeled as two resistances in series, resulting in additive resistances.

The two-film model and the concept of additivity of resistances were applied to experimental data for acetone and t-butyl alcohol. Overall mass-transfer coefficients for the volatilization of acetone and t-butyl alcohol from water were measured in the laboratory in a stirred constant-temperature bath. Measurements were completed for six water temperatures, each at three water mixing conditions. Wind-speed was constant at about 0.1 meter per second for all experiments. Oxygen absorption coefficients were measured simultaneously with the measurement of the acetone and t-butyl alcohol mass-transfer coefficients. Gas-film coefficients for acetone, t-butyl alcohol, and water were determined by measuring the volatilization fluxes of the pure substances over a range of temperatures. Henry's law constants were estimated from data from the literature. The combination of high resistance in the gas film for solutes with low values of the Henry's law constants has not been studied previously.

Calculation of the liquid-film coefficients for acetone and t-butyl alcohol from measured overall mass-transfer and gas-film coefficients, estimated Henry's law constants, and the two-film model equation resulted in physically unrealistic, negative liquid-film coefficients for most of the experiments at the medium and high water mixing conditions. An analysis of the two-film model equation showed that when the percentage resistance in the gas film is large and the gas-film resistance approaches the overall resistance in value, the calculated liquid-film coefficient becomes extremely sensitive to errors in the Henry's law constant. The negative coefficients were attributed to this sensitivity and to errors in the estimated Henry's law constants.

Liquid-film coefficients for the absorption of oxygen were correlated with the stirrer Reynolds number and the Schmidt number. Application of this correlation with the experimental conditions and a molecular-diffusion coefficient adjustment resulted in values of the liquid-film coefficients for both acetone and t-butyl alcohol within the range expected for all three mixing conditions. Comparison of Henry's law constants calculated from these film coefficients and the experimental data with the constants calculated from literature data showed that the differences were small relative to the errors reported in the literature as typical for the measurement or estimation of Henry's law constants for hydrophilic compounds such as ketones and alcohols.

Temperature dependence of the mass-transfer coefficients was expressed in two forms. The first, based on thermodynamics, assumed the coefficients varied as the exponential of the reciprocal absolute temperature. The second empirical approach assumed the coefficients varied as the exponential of the absolute temperature. Both of these forms predicted the temperature dependence of the experimental mass-transfer coefficients with little error for most of the water temperature range likely to be found in streams and rivers.

Liquid-film and gas-film coefficients for acetone and t-butyl alcohol were similar in value. However, depending on water mixing conditions, overall mass-transfer coefficients for acetone were from two to four times larger than the coefficients for t-butyl alcohol. This difference in behavior of the coefficients resulted because the Henry's law constant for acetone was about three times larger than that of t-butyl alcohol. Combination of the experimental coefficient ratios with the two-film model equation was used to develop an equation for estimating the acetone volatilization coefficient from coefficients for t-butyl alcohol and the Henry's law constants.

Ratios of the liquid-film coefficients for the volatilization of acetone and t-butyl alcohol to the liquid-film coefficients for the absorption of oxygen were independent of temperature and mixing conditions in the water. Ratios of the gas-film coefficients for the volatilization of acetone and t-butyl alcohol to the gas-film coefficient for the volatilization of water were, for practical purposes, independent of temperature. Constancy of these ratios was used with the two-film model to develop an equation for predicting the volatilization coefficients of acetone and t-butyl alcohol for streams and rivers. Application of the equation requires these laboratory-determined ratios, an estimate of the Henry's law constant, and estimates of the oxygen absorption and water volatilization coefficients for the stream or river.

INTRODUCTION

Organic substances discharged into the surface waters of the environment and organic substances occurring naturally in these waters are subject to a variety of chemical, biological, and physical processes (Kuwabara and Helliker, in press). Possible chemical processes include complexation-dissociation, precipitation-dissolution, oxidation-reduction, and photolysis. Possible biological processes include bacterial degradation and absorption and release by biota. Possible physical processes include convective mass transport, dispersion, volatilization, and adsorption and desorption by sediments. The fate of organic substances in streams and rivers is determined by complex interactions of these processes.

Not all of these processes are important for all compounds. The relative importance of the various processes depends on the characteristics of both the water body and the organic substance. However, the large number of organic substances in use by society precludes research on all processes for all substances that might be found in streams and rivers. The alternative is research on a specific substance selected as a model for a class of compounds.

Selection of a model compound may be on the basis of chemical structure or a similarity in a physical property. A physical property of importance in several processes is water solubility. For example, Chiou and others (1979) showed that sorption of a wide variety of organic compounds by sediments was dependent on water solubility. Mackay and Yuen (1980) showed that the coefficient for the volatilization of organic compounds from water was dependent on water solubility through its effect on the Henry's law constant. Solubility is undoubtedly important in the other processes also, because water is the matrix in which the processes are occurring.

A number of organic compounds with various solubilities could be used as model substances. In the initial study (Rathbun and others, 1982), acetone, which is infinitely soluble in water, was chosen as a model substance for the class of very soluble organic compounds. There were several reasons for selecting acetone. It is a widely used solvent, and a survey of organic compounds in various types of waters showed that it occurred most frequently (Shackelford and Keith, 1976). Acetone under some conditions may be a precursor in the formation of trihalomethanes during the chlorination of drinking water (Stevens and others, 1976). Other reports discussing the environmental significance of acetone, as well as other ketones, have been published (Rathbun and Tai, 1982a, 1986a).

The initial laboratory study (Rathbun and others, 1982) concluded that volatilization and bacterial degradation were likely to be the dominant processes in determining the fate of acetone in streams and rivers. Volatilization of organic substances from water is usually described by the two-film model (Lewis and Whitman, 1924), which assumes that all the resistance to volatilization is in thin films of water and air at the interface between the phases. The resistances of these films are assumed to be in series and, therefore, additive. This model, however, and the concept of additivity of resistances have not been tested extensively for substances with large solubilities such as acetone, for which the gas-film resistance is expected to be large.

In the laboratory study of the processes affecting the fate of acetone in water (Rathbun and others, 1982), the variables could be controlled such that the primary-process effects could be isolated. In the planned field studies, however, such variable control was impossible. Therefore, some procedure for separating the effect of volatilization from that of bacterial degradation on the fate of acetone in streams and rivers was sought.

The procedure selected was to use a second compound which would have volatilization characteristics similar to those of acetone but which would be much more resistant to bacterial degradation. Such a compound would, in theory, permit separating the effects of volatilization and bacterial degradation. The compound selected for this purpose was t-butyl alcohol (TBA), which also is infinitely soluble in water. TBA was expected to have volatilization characteristics similar to those of acetone but, because of its branched structure, to be much more resistant to bacterial degradation than acetone.

Two other variables that affect the volatilization of organic substances from water, but that cannot be controlled in field situations, are water temperature and windspeed. The need for additional research on the effect of temperature on the volatilization process, especially at low windspeeds, has been noted (Mackay and others, 1982). Other investigators (Wolff and van der Heijde, 1981; Klopffer and others, 1982) also have pointed out the lack of information on the temperature dependence of the volatilization coefficient.

This report describes the results of the study to

(1) determine the volatilization characteristics of acetone and TBA from water for a range of water mixing conditions and temperatures;

(2) determine the oxygen absorption coefficients for the same mixing conditions and temperatures in order to characterize the liquid-film coefficient;

(3) determine the gas-film coefficients for the volatilization of acetone, TBA, and water;

(4) check the applicability of the two-film model and the concept of additivity of resistances for very soluble compounds;

(5) determine the temperature dependences for the mass-transfer coefficients;

(6) determine the relative volatilization characteristics of acetone and TBA; and

(7) develop an equation for predicting volatilization coefficients for acetone and TBA for streams and rivers.

Experiments in the present study were limited to a single low windspeed of about 0.1 m/s. However, this is the condition expected to prevail much of the time in streams and rivers, and under this condition of relatively low volatilization rates, acetone and TBA concentrations in the water are most likely to cause water-quality problems.

THEORY OF THE TWO-FILM MODEL OF THE VOLATILIZATION OF ORGANIC COMPOUNDS FROM WATER

The Two-Film Model

The two-film model (Lewis and Whitman, 1924) is frequently used to describe the volatilization of organic compounds from water in environmental situations. The model assumes uniformly mixed water and air phases separated by thin films of water and air in which mass transfer is by molecular diffusion. Details of the two-film model and development of the model equations have been presented previously (Liss and Slater, 1974; Mackay and Cohen, 1976). Therefore, only equations necessary for the discussions of this report are presented herein. Two concepts of the two-film model are discussed.

The first concept is that mass transfer through the films is by molecular diffusion. This results in the equation (Liss and Slater, 1974)

$$k=D/L \ , \tag{1}$$

where k is the mass-transfer coefficient for the film (m/d), D is the molecular-diffusion coefficient (m^2/d) for the solute transferring through the film, and L is the film thickness (m). Equation 1 may be written for either the liquid or the gas film.

It is generally agreed (Mackay and others, 1982) that the film coefficient does not vary linearly with the molecular-diffusion coefficient as shown by equation 1. Instead, a dependence is generally assumed having the form

$$k=a_k D^{\nu} , \tag{2}$$

where a_k is a constant ($m^{1-2\nu}d^{\nu-1}$) and the value of the exponent ν depends on the model assumed. The two-film model predicts a value of 1.0 as shown by equation 1. The penetration model (Danckwerts, 1951) predicts a value of 0.5 for ν, and the film-penetration model (Dobbins, 1964) predicts a value varying from 0.5 for high mixing conditions to 1.0 for low mixing conditions. Experimental values generally range between 0.5 and 0.8. Values most often recommended (Mackay and others, 1982) and most often used are 0.5 when k is the liquid-film coefficient and 0.67 when k is the gas-film coefficient.

The second concept is that the resistances of the gas and liquid films are additive. Writing flux equations for the transport of a solute through the two films gives

$$N=k_L(C-C_i) \tag{3}$$

and

$$N=(k_G/RT)(p_i-p) \ , \tag{4}$$

where N is the mass flux of the solute [(g mol/d)/m^2]; k_L is the mass-transfer coefficient for the liquid film, usually called the liquid-film coefficient (m/d); C_i is the concentration of the solute in the water at the interface between the phases (g mol/m^3); C is the concentration of the solute in the bulk-liquid phase (g mol/m^3); k_G is the mass-transfer coefficient for the gas film, usually called the gas-film coefficient (m/d); R is the ideal gas constant [(kPa·m^3/g mol)/K]; T is the absolute temperature (K); p_i is the partial pressure of the solute in the gas film at the interface (kPa); and p is the partial pressure of the solute in the bulk gas phase (kPa). The fluxes through the two films given by equations 3 and 4 are equal because the two-film model assumes a dynamic steady-state condition. Thus, there can be no mass accumulation at any point in the system.

The concentration, C_i, and the partial pressure, p_i, at the interface cannot be easily measured, however. To eliminate these variables, the flux equation is rewritten in terms of an overall concentration-difference driving force and an overall mass-transfer coefficient. The result is

$$N=K_{OL}(C-C_E) \ , \tag{5}$$

where K_{OL} is the overall mass-transfer coefficient (m/d) for volatilization based on the liquid phase and C_E is the concentration (g mol/m^3) in the bulk-liquid phase which would be in equilibrium with the bulk-gas phase partial pressure, p.

The equilibrium conditions are expressed by Henry's law in the form

$$p_i=HC_i \tag{6}$$

and

$$p = HC_E\ , \tag{7}$$

where H is the Henry's law constant (kPa·m^3/g mol).

Combining equations 3, 4, 6, and 7 and comparing with equation 5 shows that

$$1/K_{OL} = 1/k_L + RT/Hk_G. \tag{8}$$

Reciprocals of mass-transfer coefficients are equivalent to resistances to mass transfer. Therefore, equation 8 may also be written

$$r_{OL} = r_L + r_G, \tag{9}$$

where r_{OL} is the overall resistance to volatilization (d/m), r_L is the resistance of the liquid film (d/m), and r_G is the resistance of the gas film (d/m). Comparing equations 8 and 9, it follows that

$$r_{OL} = 1/K_{OL}, \tag{10}$$

$$r_L = 1/k_L, \text{ and} \tag{11}$$

$$r_G = RT/Hk_G. \tag{12}$$

Equations for the percentage resistances in the gas and liquid films may be derived from equations 10, 11, and 12. For the gas film, the result is

$$\text{percentage resistance in the gas film} = (1\text{-}K_{OL}/k_L)(100). \tag{13}$$

Similarly, for the liquid film, the result is

$$\text{percentage resistance in the liquid film} = (1\text{-}RTK_{OL}/Hk_G)(100). \tag{14}$$

Other forms of these equations are possible. These particular forms were presented here because they were the most appropriate for the intended purposes that will be discussed later.

Equation 8 is the basic equation of the two-film model, and it is apparent from equation 9 that the two-film model assumes that the film resistances are additive. Equation 8, however, is directly applicable only under certain limiting conditions. These conditions place restrictions on the experimental verification of the two-film model and the concept of the additivity of resistances.

Limiting Forms of the Model

Equation 8 relates the liquid-film and the gas-film coefficients to the overall mass-transfer coefficient through the Henry's law constant. The overall mass-transfer coefficient is directly measurable; however, the liquid-film and the gas-film coefficients are in general not directly measurable because values for the concentration and partial pressure of the solute at the interface (eqs. 3 and 4) are needed. Under certain limiting conditions, however, the film coefficients can be measured.

For a solute with a large value of the Henry's law constant, such as oxygen, the term $RT/H\,k_G$ in equation 8 is negligible with respect to the term $1/k_L$. It follows that the liquid-film coefficient, k_L, is for practical purposes identical to the overall mass-transfer coefficient, K_{OL}.

For a solute with an extremely small value of the Henry's law constant, the term $1/k_L$ is negligible with respect to the term RT/Hk_G. It follows that the gas-film coefficient, k_G, is for practical purposes identical to the overall mass-transfer coefficient K_{OL}. In this situation, however, volatilization is not likely to be a significant fate-determining process because of the small Henry's law constant. This constant is basically an air-water partition coefficient, and a very small value indicates a preference for remaining in the water.

The effect of the Henry's law constant on the relative magnitudes of the liquid-film and gas-film resistances is not symmetrical, however. A large Henry's law constant results in a very small gas-film resistance relative to the liquid-film resistance, but a small Henry's law constant does not result conversely in a very small liquid-film resistance relative to the gas-film resistance. This apparent contradiction occurs because of differences in the magnitudes of the film coefficients. An approximate range of liquid-film coefficients for streams and rivers is from 0.35 m/d to 5.77 m/d, and an approximate range of gas-film coefficients is from 480 m/d to 1,210 m/d (Rathbun and Tai, 1982b). A major factor contributing to the difference in the magnitudes of the coefficients is the 10^4 times larger molecular-diffusion coefficients in air than in water.

For solutes with small to intermediate values of the Henry's law constant, such as acetone and TBA, both terms in equation 8 are significant; and the film coefficients cannot be determined from the limiting forms of the two-film model.

The gas-film coefficient can be determined, however, by measuring the volatilization flux of the pure solute. The basis of this procedure is the rationalization (Whitney and Vivian, 1949) that there can be no concentration gradient and, therefore, no liquid-film resistance in a pure liquid.

Thus, measurements of the gas-film coefficient and the overall mass-transfer coefficient, together with calculation of the Henry's law constant, permit application of the two-film model and the concept of additivity of resistances through equation 8. However, this procedure has, under certain conditions, a disadvantage previously discussed (Whitney and Vivian, 1949). When mixing conditions in the air are low, resulting in a small gas-film coefficient, and when the solute has a small Henry's law constant, a large percentage of the resistance is in the gas film. As a result, the RT/Hk_G term in equation 8 will approach the value of the $1/K_{OL}$ term. Thus, the difference in two numbers of comparable magnitude is being used to calculate the liquid-film coefficient, and any experimental errors in determining these terms will be magnified in the computation of the liquid-film coefficient.

Previous Applications of the Model

The two-film model was developed for chemical engineering applications. The concept of film resistances has been tested extensively in these applications, for which the objective generally is to maximize the contact between gas and liquid flows. As a result of these tests, the film-resistance concept has been used as the basis for numerous correlations of both mass- and heat-transfer coefficients.

Tests of the two-film model for environmental air-water systems, however, have been limited. Many of the studies of the volatilization of organic substances from water have been restricted to solutes with large values of the Henry's law constant. For these solutes, one of the limiting forms of the two-film model discussed previously prevails, and the liquid-film coefficient is virtually identical to the overall mass-transfer coefficient for volatilization. For solutes with smaller values of the Henry's law constant, such as acetone and TBA, for which both film resistances are significant, there has been little research and the model has not been tested extensively.

Four studies of particular relevance to the present work are summarized in the following paragraphs. One of these (King, 1964) is a theoretical analysis of the concept of the additivity of resistances, and the other three (Goodgame and Sherwood, 1954; Atlas and others, 1982; Mackay and others, 1982) are experimental studies.

King (1964)

A theoretical analysis of the two-film model was conducted, and the results suggested that the resistances are additive if five conditions are fulfilled: (1) constancy of the Henry's law constant, (2) no significant resistance other than the liquid and gas films, (3) application of the concept of addition of the film resistances under hydrodynamic conditions identical to those under which the resistances were measured, (4) no interactions between the film coefficients, and (5) constancy of the term Hk_G/k_L at all points of the interface. The relevance of these conditions in several types of chemical engineering applications was discussed. In environmental situations, questions may be raised about several of these conditions, as discussed in the following paragraphs.

Condition (1) requires that the Henry's law constant be independent of concentration. Because environmental concentrations are likely to be very dilute, Henry's law should be applicable and the constant should be independent of concentration.

Condition (2) requires that there be no significant resistance to volatilization other than the liquid and gas films. Researchers generally agree (for example, Mackay and others, 1982) that the interface offers no resistance to mass transfer if the interface is clean; and, therefore, there should be no resistance other than the liquid and gas films for this situation. However, in environmental waters, the presence of surface films of both natural and manmade organic substances is likely. These films affect volatilization by presenting an additional diffusional resistance and also by affecting the hydrodynamics and thermodynamics of the process as a result of changes in the physical properties of the water in the interfacial region (Mackay, 1982). These effects do not necessarily invalidate the concept of additivity of resistances, but require the addition of other resistance terms to the model equation. However, the effect of surface films is generally neglected because we cannot quantitatively determine the effect. Further research in this area is needed.

Condition (3) requires that the hydrodynamic conditions for the situation in which the resistances are to be added be the same as for the measurements of the individual resistances. For use in streams and rivers, gas-film coefficients of organic substances are usually determined by measuring the volatilization fluxes of the pure substances, as discussed previously. Because such measurements are generally not practical in a stream or river, condition (3) may not be fulfilled. However, the reference-substance concept (Rathbun and Tai, 1986b) can be used. This concept, discussed in more detail later, assumes that the ratio of the gas-film coefficient of an organic compound to that of a reference substance is independent of the hydrodynamic conditions in the air, primarily the windspeed in the case of the gas-film coefficient. The ratio is determined in the laboratory and used with an environmentally determined gas-film coefficient for the reference substance to estimate the gas-film coefficient for the organic compound in the stream or river. Assuming the ratio is independent of the hydrodynamics is, therefore, much less restrictive than assuming the gas-film coefficients are independent of the hydrodynamics.

Liquid-film coefficients of organic substances are usually determined in laboratory stirred baths, and the hydrodynamics are likely to be different from the hydrodynamics in streams and rivers. But, again, the reference-substance concept can be used for the liquid-film coefficient (Rathbun and Tai, 1984a). This concept assumes that the ratio of the liquid-film coefficient of an organic compound to that of a reference substance is independent of the hydrodynamic conditions, primarily the turbulent mixing conditions in the water in the case of the liquid-film coefficient. This laboratory ratio is used with an environmentally determined liquid-film coefficient for the reference substance to estimate the liquid-film coefficient for the organic compound in the stream or river. Assuming this ratio is independent of the hydrodynamics is, therefore, much less restrictive than assuming the liquid-film coefficients are independent of the hydrodynamics.

Condition (4) requires that the two film coefficients be independent of each other. The liquid-film coefficient must be determined only by mixing conditions in the water and the gas-film coefficient only by mixing conditions in the air. Such a situation is likely for most streams and rivers. However, for lakes and ponds, much of the mixing in both the air and water probably results from wind effects. In this situation, the liquid-film and gas-film coefficients are likely to show dependence on each other.

Some experimental evidence supports condition (4); other evidence does not. Rathbun and Tai (1983) found that, for practical purposes, the gas-film coefficient for the volatilization of water from a stirred bath was independent of mixing conditions in the water. Also, the liquid-film coefficient for the volatilization of ethylene dibromide from water in a stirred bath was independent of windspeed (Rathbun and Tai, 1987). Conversely, the absorption of oxygen by water is assumed to be controlled almost exclusively by the liquid-film resistance. Yet several studies summarized by Rathbun (1977) suggest that wind significantly affected the absorption of oxygen by streams and rivers. It is expected that condition (4) will be reasonably true for most streams and rivers, but that, in some situations, there may be effects of mixing in the one phase on the film coefficient for the other phase.

Condition (5) requires that the term Hk_G/k_L be constant at all points of the interface. This condition might be questioned for streams and rivers because velocity and depth distributions affect mixing conditions in the water and, thus, the liquid-film coefficient. Also, topography and stream direction relative to prevailing winds determine the effect of the wind on the mixing conditions in the air above the stream and, thus, the gas-film coefficient.

Experimental verification of condition (5) would be difficult, if not impossible. Theoretical calculations (King, 1964) for a number of surface lifetime distribution models suggested that errors would generally be less than 10 percent. However, for the extreme case of a liquid surface with half the surface inactive, the error could be as large as 50 percent for small values of the term Hk_G/k_L. Also, a hypothetical example (Mackay and others, 1982) using a roll cell model of volatilization predicted the error would be 5 percent. Generalizations to streams and rivers are not possible at the present time, however.

Goodgame and Sherwood (1954)

The concept of additivity of resistances was checked in a laboratory absorption vessel. The gas-film coefficient was determined by measuring the volatilization of water into air. This process is assumed to be controlled completely by the gas film because pure water can have no concentration gradient. Thus, the gas-film coefficient can be measured directly. The liquid-film coefficient was determined by measuring the absorption of carbon dioxide by water. This slightly soluble gas has a large Henry's law constant, such that more than 99.99 percent of the resistance to absorption is in the liquid film. Thus, the liquid-film coefficient can be measured directly for carbon dioxide.

Acetone and ammonia were chosen for evaluation of the two-film model because both film resistances were expected to be important in the volatilization of these solutes. Measured overall mass-transfer coefficients for acetone and ammonia were compared with coefficients calculated from the two-film model equation (eq. 8). Liquid-film and gas-film coefficients for acetone and ammonia were calculated from equation 2 with a value of 0.50 for the exponent ν for both the liquid-film and gas-film coefficients. The a_k constants were determined using the measured film coefficients for carbon dioxide and water.

Measured overall mass-transfer coefficients differed from the calculated coefficients by -4.1 percent for acetone and +2.1 percent for ammonia. Percentage resistances in the liquid film were 62 percent for acetone and 45 percent for ammonia. It was concluded that the two-film model and the concept of additivity of resistances were valid for these two solutes and that the possibility of substantial resistance at the interface was incompatible with the experimental results.

The gas-film coefficient for the volatilization of water in these experiments was 1,190 m/d at 298.2 K. This coefficient is near the upper limit of the normal range of coefficients that might be observed in the environment for streams and rivers (Rathbun and Tai, 1982b). Therefore, these experiments were for relatively high mixing conditions in the air phase. The liquid-film coefficient for carbon dioxide was 0.87 m/d, which is in the lower part of the normal range of coefficients that might be observed in the environment for streams and rivers (Rathbun and Tai, 1982b). Therefore, these experiments were for relatively low mixing conditions in the water phase.

Atlas and others (1982)

The two-film model was evaluated for predicting the volatilization of a series of high-molecular-weight organic compounds from water and seawater in a laboratory stirred tank. The gas-film coefficient was determined by measuring the volatilization of water and the liquid-film coefficient was determined by measuring the absorption of oxygen by water.

The coefficients were used in equation 2 to compute values of the constants, a_k, for the gas-film and liquid-film coefficients. These equations were then used with estimated values of the molecular-diffusion coefficients to compute gas-film and liquid-film coefficients for the organic compounds.

Measured overall mass-transfer coefficients for eight compounds were compared with coefficients calculated from the two-film model equation (eq. 8). Results were in excellent agreement except for dieldrin and di-n-butyl phthalate. Differences for these two compounds were attributed to difficulties in determining accurate values of the Henry's law constant. Using Henry's law constants based on literature data resulted in better agreement for these two compounds. It was concluded that the two-film model adequately predicted the volatilization coefficients of a series of eight high-molecular-weight compounds.

These measurements were for water gas-film coefficients ranging from 410 m/d to 2,200 m/d and for oxygen liquid-film coefficients ranging from 2.6 m/d to 8.9 m/d. Therefore, these measurements covered the approximate range of coefficients expected in environmental situations for streams and rivers (Rathbun and Tai, 1982b), with the possible exception of low mixing conditions in the water phase. Henry's law constants were in the intermediate range where both film resistances offered significant resistance to volatilization.

Mackay and others (1982)

In a laboratory volatilization apparatus, the two-film model was evaluated for predicting the volatilization of a series of organic compounds from water. Mixing in both the air and water was caused by air flowing tangentially around the wall of a circular tank. Four air flow rates were used, and surface waves resulted for all flow rates. Thus, these experiments were for high mixing conditions in both the air and water phases.

The original intent of this study was to verify the two-film model by measuring overall mass-transfer coefficients for volatilization of a series of solutes having a wide range of Henry's law constants. The basis of this intent was the two-film model equation (eq. 8) arranged in the form

$$1/K_{OL} = 1/k_L + (RT/H)(1/k_G). \tag{15}$$

Equation 15 suggests that a plot of the reciprocal of the overall mass-transfer coefficient as a function of the term RT/H for a series of solutes having various Henry's law constants should have a slope equal to the reciprocal of the gas-film coefficient and an intercept equal to the reciprocal of the liquid-film coefficient. This analysis, however, neglects the fact that the liquid-film and gas-film coefficients depend on the molecular properties of the solutes and, therefore, will not be constant as required by the intended application of equation 15.

Volatilization coefficients were measured for a series of 20 organic compounds having Henry's law constants ranging from 1.6 kPa·m^3/g mol for carbon tetrachloride to 8.8×10^{-4} kPa·m^3/g mol for cyclohexanol. Measurements were done at an ambient temperature of 295 ± 2 K.

Analysis of the data according to equation 15 did not result in a good fit of the data. Difficulties were attributed to differences in the film coefficients for the solutes, differences that were neglected in the proposed use of equation 15; errors in the Henry's law constants, particularly for the alcohols and the ketones; wave-damping effects of the more polar compounds; and other experimental errors.

The data were reanalyzed using a procedure in which the liquid-film and gas-film coefficients were assumed to be proportional to the molecular-diffusion coefficient raised to some power ν as shown by equation 2. These equations were then substituted into the two-film model equation (eq. 8). Sum-of-squares minimization of the experimental data resulted in best-fit values for ν of 0.70 for the liquid-film coefficient and 0.59 for the gas-film coefficient. It was found, however, that the error minimization was very insensitive to values of ν in the range between 0.5 and 0.8. This was attributed to the fact that variations in the molecular-diffusion coefficients for the different solutes were very small relative to variations in the mixing conditions and the Henry's law constants. Thus, the experimental data did not permit exact determinations of the ν values for the liquid- and gas-film coefficients.

Other experimental studies and theoretical considerations, however, strongly suggest that ν should be 0.50 for the liquid-film coefficient and 0.67 for the gas-film coefficient. Therefore, the experimental data were reanalyzed using these ν values. Comparison of calculated and experimental overall mass-transfer coefficients for the 20 solutes showed good agreement, and it was concluded that the two-film model and the concept of additivity of resistances are valid. It was also concluded that the interface offered no resistance to volatilization.

The Henry's Law Constant

Previous discussion of the two-film model indicates the importance of the Henry's law constant. It is used to express the equilibrium between the partial pressure and the concentration of the solute at the interface and also between the bulk-solution properties (eqs. 6 and 7). As a result, it appears in the two-film model equation (eq. 8) relating the liquid-film and gas-film coefficients to the overall mass-transfer coefficient for volatilization.

In its simplest form, the Henry's law constant is an air-water partition coefficient. It relates the partial pressure of a solute above a solution (kPa) to the concentration of the solute in the solution (g mol/m^3) at equilibrium. This can be written as

$$p=HC. \tag{16}$$

Thus, the larger the Henry's law constant, the larger is the partial pressure of the solute above a solution of a specific concentration and the greater is the tendency for the solute to volatilize or partition into the air.

The fugacity of the solute above the solution is given by (Mackay and Shiu, 1975)

$$f=x\gamma f_R\ , \tag{17}$$

where f is the fugacity (kPa), x is the mole fraction of the solute in the liquid, γ is the liquid-phase activity coefficient, and f_R is the reference fugacity (kPa). The activity coefficient is defined on the Raoult's Law convention in which the coefficient is unity when the mole fraction is unity. For dilute solutions at low pressures, the fugacity is approximately equal to the partial pressure and the reference fugacity may be taken as the vapor pressure of the pure solute at the temperature of interest. Combining equations 16 and 17 with these changes and rearranging give

$$H=(x/C)\gamma p_s, \tag{18}$$

where p_s is the vapor pressure of the pure solute (kPa).

For very dilute aqueous solutions, it can be shown that

$$x=(18)\ (10^{-6})\ (C), \tag{19}$$

and combining with equation 18 gives

$$H=(18)\ (10^{-6})\ (\gamma)(p_s). \tag{20}$$

Equation 20 is used to calculate Henry's law constants from activity coefficients and vapor pressure data from the literature.

For the purpose of this report, the activity coefficient in equation 20 will be considered as that at infinite dilution. This is done because several procedures for estimating or measuring the activity coefficient give the coefficient at infinite dilution. In actuality, the coefficient should be for some finite but very small concentration. Thus, any effect of concentration on the activity coefficient between this very small concentration and zero is being neglected. This effect should be small. For example, an acetone concentration of 100 mg/L would be considered high for environmental waters. However, the acetone mole fraction for this concentration is only 3.10×10^{-5}, and any effect of a mole fraction change in concentration of this magnitude or less should be small.

Several procedures are available for obtaining activity coefficients at infinite dilution. One is to compute the activity coefficients in the dilute-solution range from isothermal vapor-liquid equilibrium data and extrapolate to zero concentration. Plots of the activity coefficient or the logarithm of the activity coefficient as a function of the mole fraction or of the logarithm of the activity coefficient as a function of the square of the mole fraction may be used. This procedure is usually limited by the fact that there will generally be only two or three points in the dilute 0.01- to 0.05-mole fraction range of the organic compound. This is particularly significant for the acetone-water and TBA-water systems because these systems are highly nonideal, with large positive deviations from Raoult's law. As a result, a very small change in the liquid concentration results in a very large change in the vapor composition in the dilute organic concentration range. Consequently, the organic activity coefficient also changes rapidly with concentration in this range.

Isobaric vapor-liquid equilibrium data can also be used. They are less satisfactory than isothermal data, however, because extrapolation to infinite dilution requires assuming that the activity coefficient is independent of temperature. The activity coefficient is independent of temperature for athermal solutions, but varies with reciprocal absolute temperature for regular solutions. Neither of these extreme approximations is valid, but the assumption of dependence on reciprocal absolute temperature is generally the better of the two (Reid and others, 1977). For highly nonideal systems such as acetone-water and TBA-water, the activity coefficient is expected to depend on temperature. Therefore, use of isobaric vapor-liquid equilibrium data is subject to this restriction.

A second procedure (Mash and Pemberton, 1980) is to use the various equations such as Redlick-Kister, van Laar, Wilson, NRTL, and UNIQUAC to fit the activity coefficient data over the mole fraction range from 0.1 to 0.9 and then calculate the limiting activity coefficients from the equations. However, the different equations gave different values when fit to the same data. Also, it has been pointed out (Schreiber and Eckert, 1971) that the Wilson equation gives good fits of the activity coefficients in the concentrated solution range and that the fits were relatively insensitive to errors in the limiting activity coefficients. Conversely, however, to get even a moderately good estimate of the limiting activity coefficient from data in the concentrated solution range requires extremely accurate data.

A third procedure is to use the empirical predictive equations of Pierotti and others (1959). However, empirical equations are only as good as the activity coefficient data upon which they were based, and these data were probably subject to the same limitations in their determination as those just discussed.

A fourth procedure which has been developed in recent years is the direct determination of infinite-dilution activity coefficients by gas chromatography. This procedure involves measuring the retention time of a solute in an inert carrier gas passing through a column containing a solvent-coated solid support. The advantages and disadvantages of this procedure have been summarized (Thomas and others, 1982). Measured coefficients are considered accurate to within 15 percent except when the activity coefficients are larger than 100. Such large coefficients usually occur when water is the solvent; therefore, the procedure is likely to be less accurate for water systems. However, in the case of acetone and TBA, which have properties in some ways similar to those of water, the activity coefficients are less than 100 for the temperatures considered in this study.

Several methods can be used to directly measure the Henry's law constant. These can be broadly classified as static and dynamic methods. The static method consists of equilibrating a water solution of the solute of interest in a closed container with head space. Measurement of the solute concentrations in the water and air phases permits calculation of the Henry's law constant. However, because environmental concentrations are very small, this procedure requires measurement of very small concentrations. The alternative is to use higher concentrations, but this would require extrapolation to concentrations appropriate for environmental situations. Also, in the case of very soluble compounds such as acetone and TBA that have small values of the Henry's law constants, the concentrations in the air phase will be very small. Thus, the static method is expected to be subject to large errors for compounds with low values of the Henry's law constant.

The dynamic method consists of purging the solute from a known volume of water with a known flow rate of air under conditions such that the solute concentration in the exit air is in equilibrium with the concentration in the water (Mackay and others, 1979). The Henry's law constant is calculated from a plot of the water concentration as a function of time; and thus, any dependence of the Henry's law constant on concentration can be determined. Analysis of this method (Mackay and others, 1982) suggests, however, that the time required for establishment of equilibrium for solutes, such as acetone and TBA, with small values of the Henry's law constant is too long for practical purposes.

An alternative procedure was developed (Mackay and others, 1982) for solutes with small values of the Henry's law constant. The procedure is based on the ratio of the Henry's law constant for the solute to the Henry's law constant for water. This ratio was measured using a low temperature distillation process. Comparison of measured ratios with calculated ratios for a series of alcohols and ketones showed generally good agreement for the alcohols but large discrepancies for three of the ketones. They concluded that the experimental values from this procedure can be expected to be only within a factor of two of the true value for these types of compounds.

Consideration of the various procedures for estimating or measuring the activity coefficients and the Henry's law constants of acetone and TBA in infinite dilution in water suggests that these coefficients and constants could be subject to large errors. These errors result from the highly nonideal properties of the acetone-water and TBA-water solutions and also the fact that both the solutes are infinitely soluble in water, resulting in small Henry's law constants.

Laboratory Studies

Laboratory studies of the various chemical, biological, and physical processes that determine the fate of organic substances in streams and rivers have the advantage that conditions can generally be controlled so that only one process is occurring. This condition permits a study of the fundamental principles involved in that process. Results of these single-process studies can be combined later in a multi-process model of the fate of organic substances, if desired.

Laboratory volatilization studies are commonly done in a stirred water bath in which water mixing conditions and the temperature are closely controlled. Mixing conditions in a stirred bath are usually described (Davies, 1972) by the stirrer *Re* (Reynolds) number which has the form

$$Re = sw^2\rho/\mu \ , \tag{21}$$

where s is the stirrer speed (rev/s), w is the width of the stirrer blade (m), ρ is the water density (g/m^3), and μ is the water viscosity [(g/m)/s].

The characteristics of the solute volatilizing from the water are usually described (Mackay and others, 1982) by the *Sc* (Schmidt) number which has the form

$$Sc = \mu/\rho D \ , \tag{22}$$

where the molecular-diffusion coefficient, D, accounts for the difference in diffusion characteristics of the various solutes.

These numbers can be combined into an empirical predictive equation for the liquid-film coefficient for volatilization. The result is

$$k_L = a_1 Re^{b_1} Sc^{b_2} , \qquad (23)$$

where the constants a_1, b_1, and b_2 are determined by regression analysis of experimental data. This is usually done by taking logarithms of equation 23 to linearize the equation. The *Sc* number also accounts for temperature changes, in addition to accounting for changes in the diffusion characteristics of the various solutes.

Different statistics are used to measure how well an empirical equation such as equation 23 fits experimental data. In this report, the normalized rms (root-mean-square) error expressed as a percentage will be used. This error, *ERR*, is calculated from

$$ERR = \left[\frac{\sum_{i=1}^{n} (Var_{EXP} - Var_{CALC})^2}{n} \right]^{0.5} \frac{(100)\,(n)}{\sum_{i=1}^{n} Var_{EXP}} , \qquad (24)$$

where *Var* is the variable of interest that is being predicted, n is the number of data points, and the *EXP* and *CALC* subscripts indicate the experimental and calculated values of the variable, respectively.

Reference Substance Concept

Although laboratory studies allow examination of single-process effects on volatilization, it is usually agreed (Mackay and Yeun, 1983) that laboratory volatilization coefficients are generally higher than volatilization coefficients observed in the field. The reference-substance concept, however, permits the application of laboratory data to the development of predictive equations for streams and rivers. The basis of the reference-substance concept is the assumption that the ratio of the film coefficient for an organic substance to the film coefficient for a reference substance is independent of mixing conditions in the particular phase of importance.

For the liquid film, the reference substance concept is expressed as

$$k_{L_{ORG}} / k_{L_{REF}} = \phi , \qquad (25)$$

where ϕ is a constant independent of mixing conditions in the water and the *ORG* and *REF* subscripts indicate the organic solute and the reference substance, respectively. Oxygen is commonly used as the reference substance for the liquid film for two reasons. First, virtually all the resistance to the absorption of oxygen by streams and rivers is in the liquid film (Mackay and Yuen, 1980). Second, numerous equations exist (Rathbun, 1977) for predicting oxygen absorption coefficients as a function of the hydraulic and geometric properties of streams and rivers. Equation 25 has been verified for a number of organic compound-oxygen pairs (Smith and others, 1980; Rathbun and Tai, 1981, 1984a).

For the gas film, the reference-substance concept is expressed as

$$k_{G_{ORG}} / k_{G_{REF}} = \psi , \qquad (26)$$

where ψ is a constant independent of mixing conditions in the air. Water is commonly used as the reference substance for the gas film for two reasons. First, volatilization of a pure substance is controlled completely by the gas-film resistance, as discussed previously. Second, an equation exists (Rathbun and Tai, 1983) for predicting the gas-film coefficient for the volatilization of water from a canal as a function of windspeed and water temperature. This equation, based on data from a canal study (Jobson and Sturrock, 1979; Jobson, 1980), was assumed applicable to other open-channel flows such as streams and rivers. The original wind function for the canal has been applied to two water-quality modeling studies (Faye and others, 1979; Jobson, 1985) on the Chattahoochee River near Atlanta, Georgia. A wind function 70 percent of the value for the canal was used for the Chattahoochee River. As a result of the generally good agreement in these studies, Jobson (1985) concluded that the canal wind function was a valid predictor of the wind function for streams and rivers. Equation 26 has been verified for the ethylene dibromide-water pair of compounds (Rathbun and Tai, 1986b). The reference substance concept for both the liquid film and the gas film has been discussed also by Chiou and others (1983).

Combining equations 25 and 26 with equation 8 gives an equation for predicting volatilization coefficients for organic substances in streams and rivers. This equation has the form

$$1/K_{OL} = 1/\phi k_{L_{REF}} + RT/H\psi k_{G_{REF}} . \qquad (27)$$

Application of equation 27 requires the following steps:

1. determination in the laboratory of the value of ϕ from measurements of the liquid-film coefficients for the organic solute and for oxygen,
2. determination in the laboratory of the value of ψ from measurements of the gas-film coefficients for the organic solute and for water,
3. estimation or measurement of the Henry's law constant for the solute,
4. estimation of the oxygen absorption coefficient from the hydraulic and geometric properties of the stream or river,
5. estimation of the gas-film coefficient for the volatilization of water from the average windspeed and water temperature for the stream or river,

6. computation of the overall mass-transfer coefficient for volatilization from equation 27, and
7. use of this overall mass-transfer coefficient to estimate the volatilization of the solute from the stream or river.

Use of equation 27 in this way permits determining the volatilization coefficient of an organic solute for a stream or river without having to physically introduce the solute into the stream or river.

Temperature Dependence

Temperature dependences of rate constants for chemical, biological, and physical processes are commonly expressed by the van't Hoff-Arrhenius equation (Rich, 1973). This equation is

$$\frac{d\log_e(K)}{dT}=E/RT^2, \qquad (28)$$

where K is the rate constant (d^{-1}) for the specific process and E is the activation energy for the process (j/g mol).

Integrating equation 28 between limits of T_o and T gives

$$\log_e(K/K_o)=E(T-T_o)/(RTT_o), \qquad (29)$$

where K_o is the rate coefficient at temperature T_o. We assumed in this integration that the activation energy, E, was independent of temperature.

Two approaches have been used in applying equation 29. The first approach is to rearrange the equation into an exponential form giving

$$K=a_E exp(-E/RT), \qquad (30)$$

where the constant a_E is given by

$$a_E=K_o exp(E/RT_o). \qquad (31)$$

Equation 30 has a sound thermodynamic basis, the only assumption being that the activation energy is independent of temperature. This should be a good assumption for the limited range of temperatures observed in streams and rivers.

The second approach is to assume that the product TT_o does not vary appreciably over the range of temperatures observed in streams and rivers. With this assumption, the quantity E/RTT_o in equation 29 is approximately constant. It follows that equation 29 can be written as

$$K=(K_o)\theta^{(T-T_o)}, \qquad (32)$$

where θ is the temperature coefficient given by

$$\theta=exp(E/RTT_o) \qquad (33)$$

Equation 32 is equivalent to assuming empirically a simple exponential temperature dependence for the rate constant of the form

$$K=(\alpha)exp(\beta T), \qquad (34)$$

where α and β are constants. Writing equation 34 for a temperature of T_o and taking the ratio to equation 34 gives

$$K/K_o=exp[\beta(T-T_o)], \qquad (35)$$

which can also be written

$$K=(K_o)\theta^{(T-T_o)}, \qquad (36)$$

with

$$\theta=exp\beta \qquad (37)$$

Equation 36 is identical to equation 32.

Equation 36 has been used to express the temperature dependence of the oxygen absorption coefficient for streams and rivers, and Metzger (1968) summarized the results of a number of studies at several mixing rates. He concluded that the temperature coefficient, θ, is not constant, but depends on the degree of mixing in the water and also on the temperature level.

Analysis of equations 30 and 36 shows that equation 36 predicts a constant percentage increase in the rate coefficient per kelvin temperature increase but that equation 30 predicts a percentage increase per kelvin that depends on the temperature level. This may explain why the temperature coefficient, θ, has to vary to fit experimental data over a temperature range. Also inherent in the definition of θ is the assumption that the temperature range is small so that the TT_o product is approximately constant, as discussed previously.

There have been few studies of the temperature dependence of the volatilization of organic solutes from water, as discussed previously. For the purpose of this study, therefore, temperature dependencies of the form of equation 30 were assumed. These have the form

$$k_L=a_L exp(-b_L/T) \qquad (38)$$

and

$$k_G=a_G exp(-b_G/T), \qquad (39)$$

where a(m/d) and b(K) are constants and the L and G subscripts indicate the liquid and gas films, respectively.

The Henry's law constant also depends on temperature. This constant is equal to the product of the activity coefficient and the vapor pressure of the pure solute, as shown by equation 20. The temperature dependence of the vapor pressure is commonly described by the Clapeyron equation (Reid and others, 1977), which generally results in a good fit over small temperature ranges. This equation has the form

$$p_s = a_v exp(-b_v/T) \ , \qquad (40)$$

where a_v(kPa) and b_v(K) are constants.

The temperature dependence of the activity coefficients varies, depending on the type of solution (Reid and others, 1977). A good approximation for a moderate temperature range is the empirical equation

$$\gamma = a_\gamma exp(-b_\gamma/T) \ , \qquad (41)$$

where a_γ and b_γ(K) are constants. It is expected that the temperature dependence of the activity coefficient will be small compared with the temperature dependence of the vapor pressure.

Combining equations 40 and 41 with equation 20 gives

$$H = a_H exp(-b_H/T) \ , \qquad (42)$$

where

$$a_H = (18)(10^{-6})(a_v)(a_\gamma) \qquad (43)$$

and

$$b_H = b_v + b_\gamma \ . \qquad (44)$$

An equation of the form of equation 42 has been used previously (Leighton and Calo, 1981; Lincoff and Gossett, 1984) to express the temperature dependence of the Henry's law constant.

Finally, equations 38, 39, and 42 can be combined with equation 8 to obtain an equation for the temperature dependence of the overall mass-transfer coefficient for volatilization. The result is

$$K_{OL} = \left[\frac{exp(b_L/T)}{a_L} + \frac{RT \ exp \ [(b_H + b_G)/T]}{a_H a_G} \right]^{-1} \ . \qquad (45)$$

Bacterial Degradation

Bacterial degradation of organic substances in streams and rivers is a complex subject, beyond the scope of this report. A brief discussion of the general principles of bacterial degradation as they relate to acetone and TBA is presented, however.

The degradation of organic substances in streams and rivers results from use of the substances by bacteria as food or energy for the purpose of cell growth (Dugan, 1972). These reactions are catalyzed by enzymes specific for particular reactions. Therefore, the ability of bacteria to degrade specific organic substances depends on the chemical structure of the substance and the ability of the bacteria to adapt to this structure. Adaptation may have already occurred as a result of prior exposure of the bacteria to the specific organic substances. If not, then adaptation may occur (Dugan, 1972) by a temporary change in the organism's characteristics that allows production of the necessary enzyme or by mutation that results in a permanent change in the organism. Other environmental factors important in bacterial degradation are temperature, light, pH, and the concentrations of nutrients, dissolved oxygen, trace elements, and other organic compounds that might inhibit the reactions.

The bacterial degradation of hydrocarbons has been reviewed by Zobell (1950) and Humphrey (1967). Zobell (1950) concluded that virtually all kinds of hydrocarbons are susceptible to bacterial degradation, but that the ability of bacteria to attack hydrocarbons is highly specific. He also concluded that aliphatic hydrocarbons are degraded more readily than aromatic or naphthenic compounds, and that the ease of degradation appeared to increase with chain length up to a length of from 15 to 20 carbon atoms. Humphrey (1967) concluded that straight chain alkanes are more easily degraded than branched chains, that compounds containing one methyl branch are degraded only when the molecule contains a sufficiently long unbranched chain, and that compounds with multiple methyl branches are not degraded.

The literature on the bacterial degradation of acetone was reviewed (Rathbun and others, 1982), with the conclusion that it should be readily degraded. Laboratory results (Rathbun and others, 1982) showing rapid acetone degradation after an adaptation period supported this conclusion.

The generalizations with respect to the effect of structure on bacterial degradation suggest that TBA should be relatively resistant to bacterial degradation because of its branched structure. Tallon (1969) noted that branching markedly increased resistance to bacterial degradation in the treatment of sewage, with TBA having considerable resistance to degradation but with n-butyl and sec-butyl alcohols readily degrading. Using both acclimated and nonacclimated bacteria, Stover and McCartney (1984) compared two BOD (biochemical oxygen demand) tests for 20 organic compounds. They found no degradation of TBA with the nonacclimated bacteria and only very limited degradation with the acclimated bacteria. Acetone was rapidly degraded in all the tests.

Finally, one test was conducted using the same respirometer procedure and strain of bacteria used previously (Rathbun and others, 1982) in the study of the bacterial degradation of acetone. It was found (D. J. Shultz, written commun., 1978) that the acetone concentration was reduced to about 10 percent of its initial value in 1.0 day and to virtually zero after 1.25 days. The TBA concentration, however, was virtually unchanged after 25 days. It was concluded that TBA was not degraded by this particular strain of bacteria.

These results should not be interpreted to suggest that TBA is recalcitrant; that is, completely resistant to bacterial degradation. The results do suggest, however, that TBA is much more resistant to bacterial degradation than is acetone. Therefore, over the timeframe of a volatilization study, the assumption that TBA is inert to bacterial degradation seems reasonable.

APPARATUS AND PROCEDURES FOR THE EXPERIMENTS

Overall mass-transfer coefficients and gas-film coefficients for describing the volatilization of acetone and TBA from water were measured over a range of temperatures. Specific details of these measurements are described in the following paragraphs.

Overall Mass-Transfer Coefficients

Overall mass-transfer coefficients for the volatilization of acetone and TBA from water were measured simultaneously with the oxygen absorption coefficients in a stirred constant-temperature water bath. The stainless-steel bath was 460 mm wide by 910 mm long, with a maximum depth of 305 mm. A water depth of 267 mm was used for all experiments, giving a water volume of 112 L. Distilled water was used. The bath was equipped with a heater and a temperature controller. Water temperatures above ambient were obtained with the heater, and water temperatures below ambient were obtained by pumping a water-antifreeze mixture from an auxiliary low-temperature circulator through a stainless-steel coil on the bottom of the bath.

Mixing in the water was obtained with an oscillating plate on the bottom of one end of the bath and a variable-speed stirrer with a 50.8-mm-diameter blade located near the center of the bath. This blade was a left-hand propeller in the sense that the water was forced downward when the stirrer was rotating clockwise when viewed from above (Bates and others, 1966). Three water mixing conditions, designated low, medium, and high, were used for temperatures of 279, 285, 291, 298, 305, and 313 K. Stirrer *Re* numbers for these three mixing conditions were 26,000, 71,000, and 108,000, respectively, at 298 K. Qualitatively, the low mixing condition had a virtually placid water surface, the medium mixing condition had gentle surface motion with ripples over much of the water surface, and the high mixing condition had considerable surface motion with ripples over the entire water surface. Revolution rates of the stirrer were measured with a digital tachometer. Oscillation rate of the plate was determined by counting and timing with a stopwatch. This rate was 21 oscillations/min for all experiments. Most of the mixing resulted from the stirrer rather than the plate, however.

The water bath was placed in a fume hood with a face velocity of 30 m/min to obtain a constant flow of air over the bath. This air flow removed the acetone and TBA as they volatilized, maintaining the concentrations in the air above the bath at zero. Windspeed that resulted from this air flow across the bath surface was estimated to be about 0.1 m/s. This air flow was constant for all experiments. The procedure for the experiments consisted of reducing the dissolved oxygen concentration in the bath water by stripping with nitrogen gas, adding a quantity of acetone and TBA sufficient to give the desired initial concentration in the bath water, mixing at a constant rate, and sampling as a function of time. Samples were obtained from middepth of the bath by siphoning with a glass siphon. Run durations ranged from about 6 hours for the high-mixing, high-temperature condition to about 2.5 days for the low-mixing, low-temperature condition. Seven samples for determination of the acetone and TBA concentrations and five samples for determination of the dissolved oxygen concentration were collected in each experiment. Samples for acetone and TBA were collected in 60-mL glass bottles with ground-glass stoppers, and samples for dissolved oxygen were collected in 300-mL BOD bottles. Samples for acetone and TBA were usually analyzed on the day of the experiment. Samples for dissolved oxygen were fixed immediately with the Winkler reagents and the analyses completed within several hours.

Acetone and TBA concentrations in the water samples were determined by a purge-and-trap procedure followed by analysis in a gas chromatograph with a flame ionization detector. The purge-and-trap procedure was done with a Tekmar[1] model LSC-2 sample concentrator. Samples were purged for 10 min with a helium flow rate of 20 mL/min and then desorbed into the chromatograph by heating at 453 K for 2.0 min. The concentrator trap was Tenax, and the trap was baked at 473 K for 3.0 min between samples.

The chromatograph was a Varian model 2700. The column was a 1.83-m length of 3.18-mm O.D. nickel alloy tubing packed with SP-1000. The column was operated isothermally at 348 K, and the detector was at 473 K. Helium was used as the carrier gas at a flow rate of 60 mL/min. This analytical system gave very sharp peaks for acetone and TBA.

Samples of standards were analyzed each day that samples from experiments were analyzed, and standard

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[1] Use of firm and trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

curves were drawn. Analyses of replicates of standards resulted in coefficients of variation ranging from ±1.9 to ±3.1 percent for acetone and ±1.4 to ±3.7 percent for TBA.

Dissolved oxygen concentrations were determined using a modified Winkler technique in which titrations were done directly in the sample bottles (Rathbun and others, 1978).

A modified form of equation 5 was used in the data analysis. A mass balance for the solute shows that the flux, N, can also be expressed as

$$N=-\left(\frac{V}{A}\right)\left(\frac{dC}{dt}\right), \tag{46}$$

where V is the volume of the liquid phase (m^3), A is the surface area (m^2), and t is time (d). The negative sign occurs because the concentration is decreasing with time. For a reasonably flat water surface,

$$Y=V/A\ , \tag{47}$$

where Y is the mean water depth (m). Combining equations 5, 46, and 47 gives

$$\frac{dC}{dt}=(K_{OL}/Y)(C_E-C)\ , \tag{48}$$

and integrating gives

$$(C_E-C)=(C_E-C_O)exp(-K_{OL}t/Y)\ , \tag{49}$$

where C_O is the concentration (g mol/m^3) of the solute in the water at time zero.

For acetone and TBA, it is assumed, as discussed previously, that the fume hood removes these compounds as soon as they volatilize so that their concentrations in the air above the water may be assumed zero. As a result, the concentration, C_E, in the water in equilibrium with this concentration is zero also. Therefore, for acetone and TBA, equation 49 reduces to

$$C=C_Oexp(-K_{OL}t/Y)\ . \tag{50}$$

For oxygen, the equilibrium concentration is the saturation concentration of the water in equilibrium with the atmospheric oxygen. Designating this concentration C_S, equation 49 for oxygen becomes

$$C_S-C=(C_S-C_O)exp(-K_{OL}t/Y)\ . \tag{51}$$

Volatilization coefficients for acetone and TBA were computed from equation 50, and oxygen absorption coefficients were computed from equation 51 using a two-parameter nonlinear least-squares procedure (Rathbun and Tai, 1984b) and the experimental concentration-time data. Saturation concentrations for oxygen for use in equation 51 were from Mortimer (1981).

Gas-Film Coefficients

Gas-film coefficients for acetone, TBA, and water were determined by measuring the volatilization fluxes of the pure substances. The basis of the technique, which assumes no liquid-film resistance for a pure liquid, has been discussed previously (Chiou and others, 1980; Rathbun and Tai, 1984c, 1986a).

Briefly, the procedure consisted of measuring the rate of change as a function of time of the weight of the pure substance in a small glass dish on an electronic balance. Temperature control was maintained by pumping water at a constant rate and constant temperature through a plastic cup under the glass dish. Fluxes were calculated from the rate of change of the weight with time and from the cross-sectional area for volatilization. Gas-film coefficients were calculated from an equation previously derived (Rathbun and Tai, 1984c). This equation is

$$k_G=(1440)\ \frac{RT}{Mp_s}\ \frac{\Delta W}{A\Delta t}\ , \tag{52}$$

where M is the molecular weight (g/g mol), $\Delta W/A\Delta t$ is the volatilization flux [(g/min)/m^2], and 1440 is the number of minutes per day.

Gas-film coefficients for the volatilization of water from the stirred water bath used in the acetone and TBA studies were determined previously (Rathbun and Tai, 1983). The apparatus and experimental conditions, including water depth, water mixing conditions, water temperatures, and air-flow conditions were identical to those used in the present study. At a windspeed of about 0.1 m/s, the gas-film coefficient for water was independent of water mixing conditions but dependent on temperature according to

$$k_{G_{WAT}}=32.6exp(0.00934\ T)\ , \tag{53}$$

where the WAT subscript indicates water. Equation 53 is of the empirical exponential temperature-dependence form (eq. 34). The reciprocal temperature-dependence form (eq. 30) has a sounder thermodynamic basis, however, and this form was generally used in this report. The data of Rathbun and Tai (1983) were, therefore, reanalyzed according to this form, giving

$$k_{G_{WAT}}=1.01\times10^4exp(-879/T)\ . \tag{54}$$

Equation 54 has an rms error of the form of equation

24 of ±3.53 percent, whereas equation 53 has an rms error of ±3.60 percent. Thus, the errors for equations 53 and 54 show little difference. These equations are based on 40 measurements of the gas-film coefficient for temperatures ranging from 291.3 K to 321.2 K.

Equation 54 was used with the reference-substance concept for the gas-film coefficient (eq. 26) and with experimental values of the ψ factor to calculate gas-film coefficients for acetone and TBA for the stirred water bath. This procedure assumes that

$$\psi = \left(k_{G_{ORG}} / k_{G_{WAT}} \right)_{DISH} = \left(k_{G_{ORG}} / k_{G_{WAT}} \right)_{\mathrm{BATH}}, \quad (55)$$

which permits calculation of $k_{G_{ORG}}$ for the bath. Equation 55 is based on the fundamental assumption of the reference-substance concept that ψ is independent of mixing conditions in the air phase.

PRESENTATION AND DISCUSSION OF RESULTS OF THE APPLICATION OF THE TWO-FILM MODEL TO THE VOLATILIZATION OF ORGANIC COMPOUNDS FROM WATER

Overall Mass-Transfer Coefficients

The experimental overall mass-transfer coefficients are presented in table 1 as a function of water temperature and stirrer *Re* number. The difference in dependence of the overall coefficients on mixing conditions in the water is apparent. At 279 K, there is virtually no dependence of the TBA coefficient on stirrer *Re* number, whereas the acetone coefficient increased 51.0 percent and the oxygen coefficient 818 percent from the low to the high stirrer *Re* number. At 313 K, the TBA coefficient increased 68.4 percent, the acetone coefficient 97.8 percent, and the oxygen coefficient 575 percent from the low to the high stirrer *Re* number. This difference in behavior is a result of the difference in Henry's law constants, in addition to differences in the diffusion characteristics, for the three solutes.

Table 1 also shows the results of six replicate experiments. Runs replicated were those in which one or more of the experimental coefficients differed considerably from the expected values. Comparison of the 18 pairs of coefficients for the six replicates shows that 12 of the percentage differences were less than 5 percent and six were larger, ranging from 9.13 percent to 25.3 percent. No single pair of experiments contained three large differences, however, suggesting the errors were the result of random effects rather than a systematic change in experimental conditions. Average percentage differences for the six pairs of replicated experiments were 8.04 percent for acetone, 6.39 percent for TBA, and 5.96 percent for oxygen.

In addition to the usual experimental errors, two factors undoubtedly contributed to these percentage differences. First, the variable-speed stirrer had to be replaced during the data collection because the stirrer would no longer provide the mixing rate needed for the high mixing condition. About half the experiments were done with the initial stirrer, the other half with a new stirrer of the same type. This new stirrer was located as nearly as possible at the same position and same orientation as the initial stirrer. Also, the same stirrer blade was used with both stirrers. A comparison of experiments with the initial and new stirrers at the same mixing and temperature conditions showed no consistent differences. Small differences undoubtedly occurred, however, because of slight changes in the position and orientation of the stirrer blade.

Second, the experiments for this study were conducted over a relatively long timespan. One preliminary experiment was done about 3 yr before the conclusion of the study, and the rest of the experiments were done over a 1-yr time period, with a break in the middle of about 6 mo during which time other studies were being done. This preliminary run at a temperature of 298.4 K and a stirrer Reynolds number of 2.68×10^4 (table 1) was one of the replicated experiments discussed previously. Percentage differences were 10.2 percent, 4.44 percent, and 0.39 percent for acetone, TBA, and oxygen, respectively, indicating a reproducibility comparable to that of the other replicates.

The effect of temperature on the mass-transfer coefficients shown in table 1 will be discussed later in the section on temperature dependence.

Gas-Film Coefficients

Experimental volatilization fluxes for acetone, TBA, and water are plotted on a logarithmic scale in figure 1 as a function of reciprocal absolute temperature. The water fluxes were adjusted to dry air conditions using relative humidities of the laboratory air measured during the experiments. Duplicate experiments were done at each temperature. Percentage differences ranged from 0.73 percent to 4.33 percent and averaged 2.42 percent for acetone, ranged from 0.10 percent to 3.37 percent and averaged 1.49 percent for TBA, and ranged from 0.45 percent to 9.15 percent and averaged 3.88 percent for water.

The lines in figure 1 are least-squares fits of the experimental data. Regression equations for these lines were used to interpolate fluxes at specific temperatures and also to extrapolate fluxes to a temperature of 279 K. Flux measurements were restricted generally to temperatures

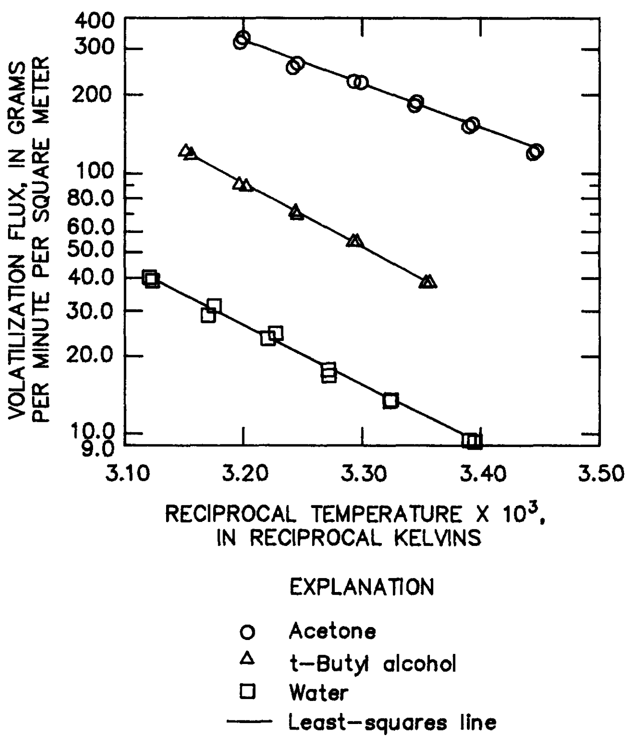

Figure 1. Experimental volatilization fluxes on a logarithmic scale as a function of reciprocal absolute temperature for acetone, t-butyl alcohol, and water.

above 293 K by experimental limitations discussed previously (Rathbun and Tai, 1984c) and in the case of TBA, by its freezing point of 298.6 K.

Interpolated fluxes were combined with vapor pressure data from the literature (Parks and Barton, 1928; Ambrose and others, 1975; Jobson and Sturrock, 1979) and equation 52 to compute gas-film coefficients. These gas-film coefficients were used to form the ψ factor defined by equation 26, with water as the reference substance. Factors were computed for temperatures of 279, 285, 291, 298, 305, and 313 K. Values for acetone ranged from 0.489 to 0.491 and averaged 0.490 with a coefficient of variation of ±0.22 percent. Values for TBA ranged from 0.441 to 0.458 and averaged 0.452 with a coefficient of variation of ±1.46 percent. These values suggested a slight dependence on temperature. However, for practical purposes, ψ was considered independent of temperature.

These ψ values for the dish apparatus were converted to gas-film coefficients for acetone and TBA for the stirred water bath using equations 54 and 55. The results for a windspeed of about 0.1 m/s were

$$k_{G_{AC}} = 4.95 \times 10^3 exp(-879/T) \qquad (56)$$

and

$$k_{G_{TBA}} = 4.56 \times 10^3 exp(-879/T) \ , \qquad (57)$$

where the *AC* subscript indicates acetone and the *TBA* subscript indicates t-butyl alcohol.

Equations 56 and 57 are applicable to the particular air-flow conditions over the stirred water bath generated by the fume hood. The actual windspeed was not measured, but it was estimated to be about 0.1 m/s, as discussed previously.

Henry's Law Constants

Henry's law constants for acetone were calculated from equation 20, vapor pressure data from the literature (Ambrose and others, 1975), and activity coefficients estimated from vapor-liquid equilibrium data (Beare and others, 1930; Othmer and others, 1944; Pierotti and others, 1959; Lichtenbelt and Schram, 1985), or activity coefficients measured directly (Mash and Pemberton, 1980). Henry's law constants were also measured directly in four studies (Burnett, 1963: Nelson and Hoff; 1968; Buttery and others, 1969; Ioffe and Vitenberg, 1984). Results are plotted on a logarithmic scale in figure 2 as

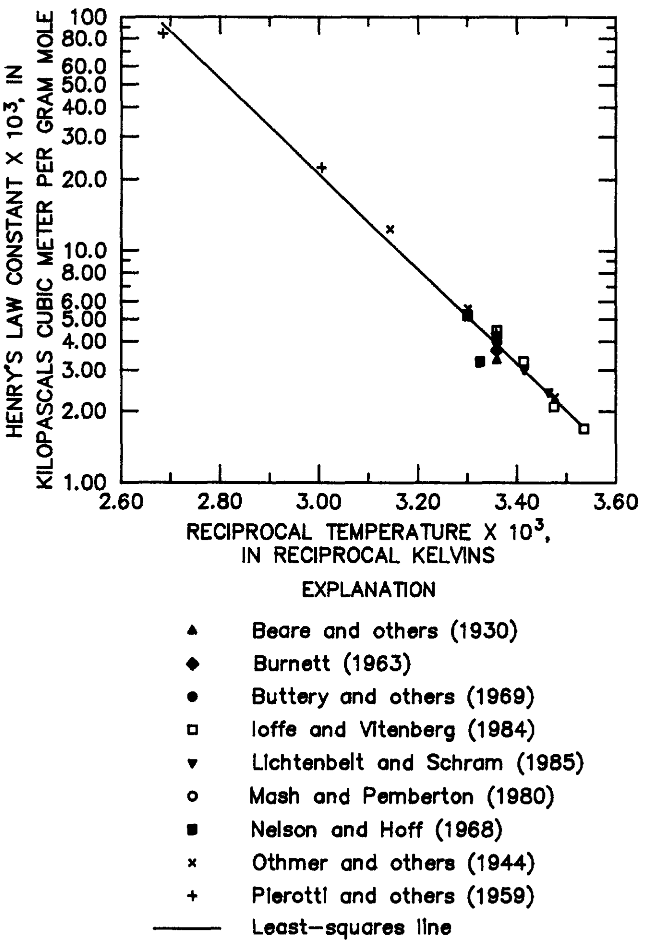

Figure 2. Henry's law constants on a logarithmic scale as a function of reciprocal absolute temperature for acetone.

a function of reciprocal absolute temperature as suggested by equation 42. The line is a least-squares fit having the form

$$H_{AC}=2.64\times 10^{4} exp(-4{,}690/T) \qquad (58)$$

Henry's law constants for TBA were calculated from equation 20, vapor pressure data from the literature (Parks and Barton, 1928), and activity coefficients estimated from vapor-liquid equilibrium data (Kenttamaa and others, 1959; Pierotti and others, 1959; Ziak and others, 1974), or activity coefficients measured directly (Mash and Pemberton, 1980). Results are plotted on a logarithmic scale in figure 3 as a function of reciprocal absolute temperature as suggested by equation 42. The line is a least-squares fit having the form

$$H_{TBA}=3.31\times 10^{6} exp(-6{,}470/T)\ . \qquad (59)$$

Three of the points at the lower end of the temperature range deviated considerably from the expected linear dependence of the logarithm of the constant on reciprocal absolute temperature. These points were based on limited data (Pierotti and others, 1959) of only two values at each temperature and, thus, their accuracy might be questioned. Also extrapolation to zero concentration was limited to a linear extrapolation. Therefore, these points were not considered in the regression analysis.

Henry's law constants for oxygen were calculated from precise measurements (Benson and Krause, 1976) of the Bunsen coefficient and the gas compressibilities. Results are plotted on a logarithmic scale in figure 3 as a function of reciprocal absolute temperature. The line is a least-squares fit having the form

$$H_{OXY}=2.24\times 10^{4} exp(-1{,}680/T)\ , \qquad (60)$$

where the *OXY* subscript indicates oxygen. The Henry's law constant for oxygen is considerably less dependent on temperature than is the TBA constant and is considerably larger.

Liquid-Film Coefficients

Liquid-film coefficients for acetone and TBA were calculated from equation 8, the experimental overall mass-transfer coefficients and temperatures from table 1, gas-film coefficients from equations 56 and 57, and Henry's law constants from equations 58 and 59. Results were not as expected. For the high and medium stirrer *Re* numbers, almost all the liquid-film coefficients for both acetone and TBA were negative. For the low stirrer *Re* number, the coefficients were small and in general increased with temperature as expected.

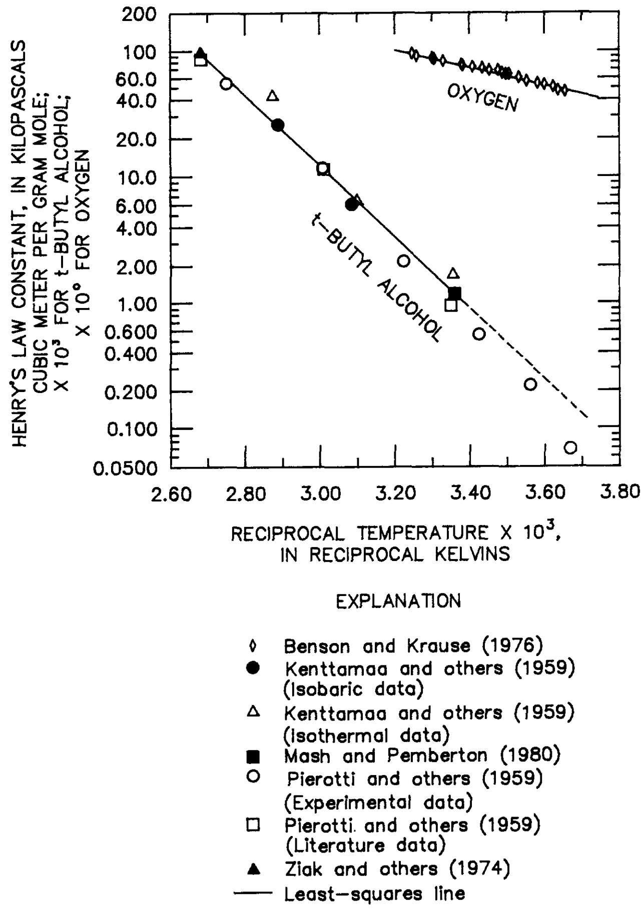

Figure 3. Henry's law constants on a logarithmic scale as a function of reciprocal absolute temperature for t-butyl alcohol and oxygen.

Negative liquid-film coefficients have no physical meaning, however, so an explanation for the negative coefficients was sought. The initial conclusion might be that the concept of additivity of resistances used in the two-film model and the derivation of equation 8 is not valid. However, equation 8 and the errors involved in determining the factors of this equation should be analyzed first.

Whitney and Vivian (1949) stated that determining liquid-film coefficients by measuring overall coefficients and gas-film coefficients was difficult because errors in these determinations are magnified when the liquid-film coefficient is determined by difference. This is most likely to be a problem when the liquid-film resistance is small (high stirrer *Re* number and large liquid-film coefficient) and when the gas-film resistance is high (low mixing conditions in the air phase and small gas-film coefficient). This condition requires taking the difference of two numbers approximately the same in value. Considering the probable distribution of errors, then, a negative liquid-film coefficient can easily result.

The overall mass-transfer coefficients and the gas-film coefficients were measured using established procedures. Errors in the determination of these coefficients are generally less than 5 percent, with an occasionally larger error. The Henry's law constants are considerably less accurately known, however.

Errors could occur in both the limiting activity coefficient and the vapor pressure data used in calculating the Henry's law constant. Errors in vapor pressure data in the literature are well known (Hoffman, 1984). In the present study, several sources of vapor pressure data for acetone and TBA were compared with the data used in the computation of the activity coefficients, and no large discrepancies were found.

Errors in the activity coefficients are more likely, however. Both the acetone-water and TBA-water systems have large positive deviations from Raoult's law. As a result, the vapor concentration in equilibrium with the liquid concentration increases extremely rapidly in the dilute concentration range of the organic compound. Accurate vapor-liquid equilibrium data in this concentration range are, therefore, difficult to obtain. Also, because the investigator is generally interested in the entire concentration range, only two or three points are usually measured in the dilute organic concentration range. Finally, because the activity coefficient is varying most rapidly with concentration in this dilute concentration range, extrapolation to zero concentration is subject to considerable error. Underestimation of the activity coefficient is most likely because it is increasing rapidly as the organic compound concentration decreases.

Henry's law constants for acetone were also calculated from measurements of the distribution coefficient for the acetone-water system. These measurements are subject to some unknown error because they must be for a finite concentration rather than an infinitely dilute solution. These concentrations, however, are usually small and, therefore, this error is probably small. But the error cannot be determined because generally only one concentration is considered and extrapolation is not possible.

The Henry's law constants in figures 2 and 3 also show considerable variation. For acetone, the values at 298 K have ±15 percent variation around the least-squares value. For TBA, the experimental values range from −17 percent to +37 percent of the least-squares value at 298 K. Other evidence from the literature suggests that the Henry's law constants for hydrophilic compounds may be subject to large errors. Distribution coefficients for polar liquids determined by different methods and from different data sets were found (Ioffe and Vitenberg, p. 13, 1984) to diverge by "several tens of percent." Measurements of the overall mass-transfer coefficients for the volatilization of a series of compounds and fitting the data to the two-film model suggested (Mackay and others, 1982) that the Henry's law constant estimated from literature data for 3-heptanone was about a factor of 10 too small. Also, the value for cyclohexanol determined by fitting of the volatilization data appeared (Mackay and others, 1982) to be about a fourth of the value estimated from literature data. Finally, the difficulty of measuring Henry's law constants for hydrophilic compounds is noted by the conclusion (Mackay and others, 1982) that data for ketones and alcohols are less satisfactory, but that the results are generally within a factor of two and, therefore, reasonable. These results suggest that Henry's law constants for acetone and TBA can be subject to large errors.

The sensitivity of the calculation of the liquid-film coefficient to errors in the Henry's law constant is best demonstrated by an example. Consider the high-*Re*-number experiment for TBA at 298.2 K for which the overall mass-transfer coefficient was 0.164 m/d (table 1). The gas-film coefficient for TBA computed from equation 57 was 238 m/d. Substituting these values into equation 8 and rearranging gives

$$1/k_{L_{TBA}} = 6.10 - 0.0104/H_{TBA} \ . \tag{61}$$

Values of k_L were computed from equation 61 as a function of H_{TBA} and the results are plotted in figure 4. When the value of H_{TBA} is such that the right side of equation 61 is zero, the liquid-film resistance is zero and the liquid-film coefficient is infinite. As the Henry's law constant approaches this value, the computed liquid-film coefficient is very dependent on errors in the Henry's law constant (fig. 4). If the Henry's law constant is less than this value, negative liquid-film coefficients result, and these are physically unrealistic, as discussed previously.

Percentage errors in computed liquid-film coefficients are shown in figure 5 for three values of the Henry's law constant. These errors were calculated from liquid-film coefficients obtained from equation 61 for a range of Henry's law constants. The value of 1.86×10^{-3} kPa·m^3/g mol falls on the flat part of the curve in the right part of figure 4. Even though the film coefficient appears to have little dependence on the Henry's law constant at this point, figure 5 shows that very large errors result in the computed liquid-film coefficient for small errors in the Henry's law constant. The lines for the other two Henry's law constants show that as the constant becomes further removed from the value of the constant at the discontinuity, the dependence of the errors in the liquid-film coefficient on errors in the Henry's law constant decreases.

These considerations lead us to conclude that the negative liquid-film coefficients obtained for the high and medium stirrer *Re* numbers were very likely the result of errors in the Henry's law constants. An alternative method of data analysis was developed, therefore.

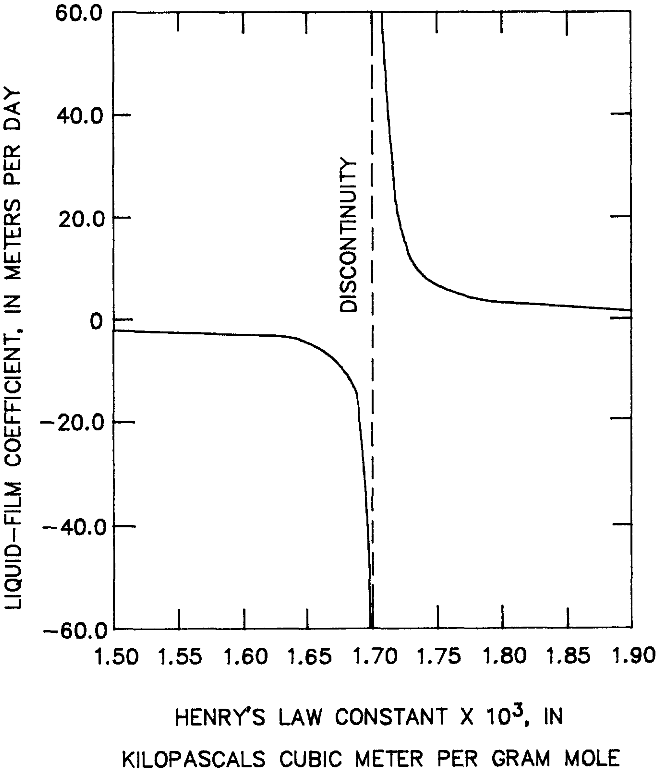

Figure 4. Computed liquid-film coefficients for t-butyl alcohol as a function of Henry's law constant for a high-mixing-condition experiment at 298.2 K.

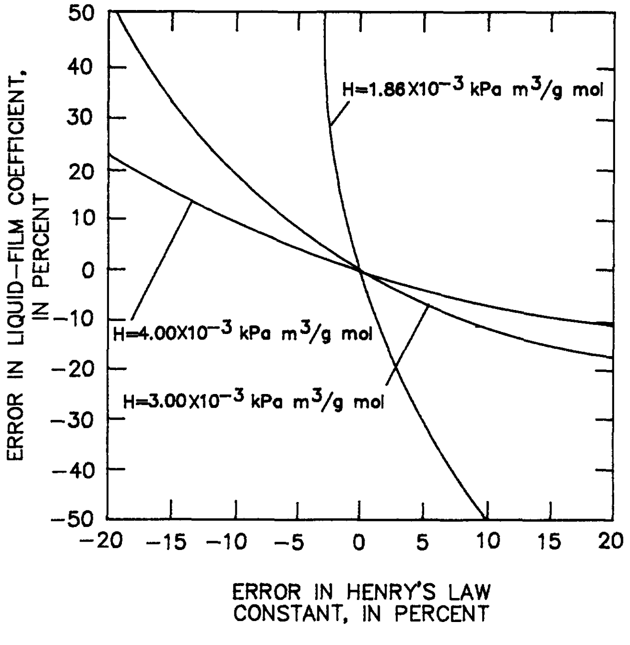

Figure 5. Percentage errors in the computed liquid-film coefficient for t-butyl alcohol as a function of the percentage error in the Henry's law constant for a high-mixing-condition experiment at 298.2 K.

Alternative Data Analysis Procedure

The alternative data analysis procedure was based on the concept that the liquid-film coefficient is proportional to the molecular diffusion coefficient raised to some power ν as shown by equation 2. Writing this equation for an organic compound and for oxygen as the reference substance and taking ratios gives

$$k_{L_{ORG}} / k_{L_{OXY}} = \left(D_{ORG} / D_{OXY} \right)^{\nu} = \phi \ . \qquad (62)$$

Equation 62 is a combination of equations 2 and 25. Constancy of ϕ has been verified (Smith and others, 1980; Rathbun and Tai, 1981; Rathbun and Tai, 1984a) for a number of organic compound/oxygen pairs.

The alternative procedure consists of the following steps:

1. development of a correlation for the liquid-film coefficient from equation 23 and the oxygen mass-transfer coefficient data in table 1;
2. calculation of liquid-film coefficients for acetone and TBA from this correlation, estimated molecular-diffusion coefficients, and equation 62;
3. calculation of Henry's law constants from equation 8, the liquid-film coefficients from step 2, the overall mass-transfer coefficients from table 1, and the gas-film coefficients calculated from equations 56 and 57; and
4. evaluation of the Henry's law constants to determine if reasonable values have been obtained. Also, the liquid-film coefficients are evaluated to determine if reasonable dependencies on stirrer *Re* numbers and temperature are obtained.

A similar approach based on equation 8 has been used in previous evaluations (Goodgame and Sherwood, 1954; Atlas and others, 1982; Mackay and others, 1982) of the two-film model and the concept of additivity of resistances.

Molecular-Diffusion Coefficients

Molecular-diffusion coefficients of the three solutes in water are needed to apply equation 62. There were relatively few data in the literature (Tyn and Calus, 1975) for the acetone-water system, and these covered only the limited temperature range from 288 to 298 K. Also, there were irregularities in the logarithm diffusion coefficient versus reciprocal absolute temperature plot frequently used (Reid and others, 1977) to describe the temperature dependence of diffusion coefficients. Therefore, the Stokes-Einstein approach (Reid and others, 1977) was used. This approach assumes

$$D\mu/T = \text{constant} \ , \qquad (63)$$

where μ is the viscosity of the water. This equation is the basis for most empirical equations for molecular-diffusion coefficients at infinite dilution.

The logarithm of viscosity data for water from a standard reference (Hodgman, 1951) was correlated with reciprocal absolute temperature and the resultant equation combined with equation 63. The combined equation was then calibrated to determine the constant using the acetone diffusion coefficient measured (Anderson and others, 1958) at 298.3 K using a precise interferometric technique. The resulting equation was

$$D_{AC} = (4.00 \times 10^{-4})(T)exp(-2{,}080/T) \tag{64}$$

where D_{AC} is the molecular-diffusion coefficient for acetone at infinite dilution in water (m^2/d).

There were relatively few data in the literature (Dunning and Washburn, 1952; Tyn and Calus, 1975; Ito and others, 1981) for the TBA-water system, and the three values at 298 K ranged from $6.31 \times 10^{-5} m^2/d$ to $8.47 \times 10^{-5} m^2/d$. These three values, however, scattered reasonably well about the best-fit value at this temperature. The data also covered a fairly wide temperature range from 277.2 K to 310.2 K. Linear regression of the logarithm of the diffusion coefficient as a function of reciprocal absolute temperature gave

$$D_{TBA} = 2.09exp(-3{,}050/T), \tag{65}$$

where D_{TBA} is the molecular-diffusion coefficient of TBA at infinite dilution in water (m^2/d).

The molecular-diffusion coefficient of oxygen in water has been extensively studied. A review (St-Denis and Fell, 1971) of the data showed 38 measurements between temperatures of 283 and 333 K. This review also showed that the 12 measurements at 298 K ranged from 16.2×10^{-5} to 22.5×10^{-5} m^2/d.

Another analysis (Duda and Vrentas, 1968) of the oxygen molecular-diffusion coefficient data suggested that the data at 298 K were divided approximately into two groups, with one group having a mean value of about 22×10^{-5} m^2/d and the other a value of about 17×10^{-5} m^2/d. Arguments were presented (Duda and Vrentas, 1968) suggesting that the high values may be in error because they were measured using a technique known to give high diffusion coefficients. Also, several of the measurements of the low values were in the presence of extraneous substances such as hemoglobin, potassium chloride, sodium chlorate, and gelatin, which may have affected the diffusion coefficient measurements in some way. Because of these considerations, only two data sets (Baird and Davidson, 1962; Duda and Vrentas, 1968) were considered in the present study for the determination of the molecular-diffusion coefficient-versus-temperature relation for oxygen. The result was

$$D_{OXY} = 1.20exp(-2{,}630/T), \tag{66}$$

where D_{OXY} is the molecular-diffusion coefficient of oxygen in water (m^2/d).

Liquid-Film Coefficient Correlation

A correlation for predicting the liquid-film coefficient was developed from equation 23 using the overall mass-transfer coefficient data from table 1 for the absorption of oxygen. Inherent in this procedure is the assumption that the resistance to the absorption of oxygen by water is virtually all in the liquid film. This assumption can be verified using equation 8 along with the oxygen overall mass-transfer coefficients from table 1, Henry's law constants from equation 60, and gas-film coefficients for the volatilization of water computed from equation 54 and adjusted to oxygen using equation 2.

Molecular-diffusion coefficients for water and oxygen in air were estimated at temperatures of 279, 298, and 313 K using the Brokaw method as described by Reid and others (1977). A value of 0.50 was used for ν in equation 2. However, the diffusion coefficient ratios were 0.970, 0.957, and 0.948 for temperatures of 279, 298, and 313 K; and, therefore, the value of the exponent had little effect and there was little adjustment. Percentage resistances in the liquid film predicted from equation 14 for three stirrer *Re* numbers at each of the three temperatures are presented in table 2. The results show that virtually all resistance to the absorption of oxygen by water is in the liquid film for the conditions of this study. It follows for practical purposes that the overall mass-transfer coefficient for the absorption of oxygen may be considered identical to the liquid-film coefficient.

Diffusion coefficients for oxygen in water were computed from equation 66 for the various experimental temperatures. Viscosity and density data for water were obtained from a standard reference (Hodgman, 1951). These data were combined with measurements of the stirrer revolution rate for each experiment and the width of the stirrer blade (50.8 mm) to give the stirrer *Re* number and the *Sc* number (eqs. 21 and 22). Correlation of the overall mass-transfer coefficients for oxygen with these numbers gave

$$k_{L_{OXY}} = 2.10 \times 10^{-7} Re^{1.45} Sc^{0.062} . \tag{67}$$

Logarithms of the liquid-film coefficients calculated from equation 67 are plotted as a function of the logarithm of the experimental liquid-film coefficient in figure 6. Equation 67 has an rms error of ±11.6 percent.

The exponent of 1.45 on the stirrer *Re* number is in reasonable agreement with values from the literature (Davies, 1972) which are generally in the range of 1.2 to 1.4. The exponent of 0.062 on the *Sc* number is considerably less than the generally accepted value, which

Table 1. Experimental overall mass-transfer coefficients

Temperature (K)	Reynolds number $\times 10^{-4}$	Overall mass-transfer coefficient (m/d)		
		Acetone	t-Butyl alcohol	Oxygen
279.2	1.64	0.100	0.0247	0.405
279.0	4.10	.122	.0267	1.64
279.2	6.52	.151	.0239	3.72
285.0	1.93	.156	.0406	.515
285.2	1.95	.121	.0356	.506
285.2	4.83	.166	.0380	1.83
285.2	7.64	.210	.0442	4.12
291.4	2.29	.197	.0642	.560
291.6	5.78	.269	.0722	2.61
291.2	9.13	.318	.0794	4.62
291.2	9.14	.331	.0870	5.47
298.2	2.57	.269	.115	.761
298.4	2.68	.298	.110	.764
298.4	7.06	.393	.142	2.93
298.2	10.72	.476	.164	5.48
298.4	10.89	.462	.159	5.26
305.0	3.05	.392	.181	.887
305.0	7.88	.602	.240	4.25
305.0	12.56	.711	.277	6.99
313.2	3.56	.541	.297	1.23
313.2	3.51	.557	.308	1.38
313.2	9.37	.846	.408	5.17
313.2	14.72	1.04	.476	8.40
313.2	14.62	1.07	.500	8.30

Table 2. Predicted percentage resistances in the liquid film for the absorption of oxygen by water

Temperature (K)	Reynolds number $\times 10^{-4}$	Overall mass-transfer coefficient (m/d)	Gas-film coefficient (m/d)	Henry's law constant (kPa·m^3/g mol)	Percentage resistance in liquid film
279.2	1.64	0.405	435	54.5	100.00
	4.10	1.64			99.98
	6.52	3.72			99.96
298.2	2.57	.761	516	80.0	100.00
	7.06	2.93			99.98
	10.7	5.48			99.97
313.2	3.56	1.23	591	105	100.00
	9.37	5.17			99.98
	14.7	8.40			99.96

is in the range of 0.50 to 0.67. This was not unexpected, however, because only oxygen was considered in the development of equation 67; and, therefore, the true effect of the molecular-diffusion coefficient was not determined. The small coefficient on the *Sc* number apparently indicates only the temperature effect on the diffusion coefficient of the oxygen and the physical properties of the water.

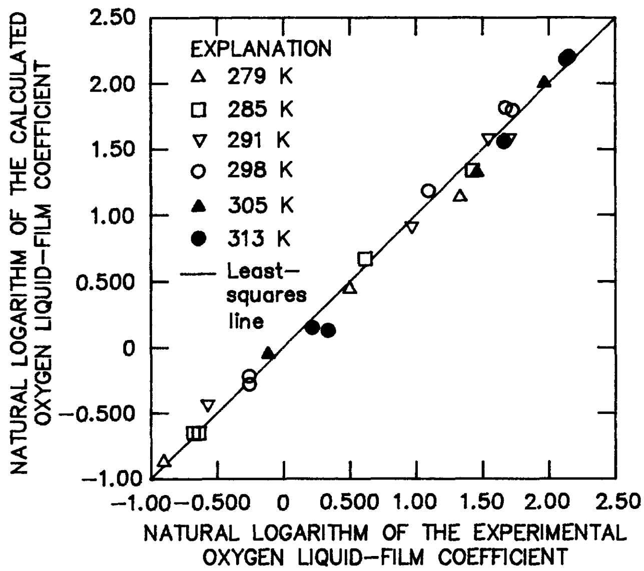

Figure 6. Natural logarithms of the calculated liquid-film coefficients for oxygen as a function of the natural logarithm of the experimental liquid-film coefficient for oxygen.

Liquid-Film Coefficients for Acetone and t-Butyl Alcohol

Liquid-film coefficients for oxygen were computed from equation 67 and the appropriate stirrer *Re* and *Sc* numbers for each experiment. These coefficients were adjusted to liquid-film coefficients for acetone and TBA using equation 62 and diffusion coefficients calculated from equations 64, 65, and 66. A value of 0.50 was used for the exponent ν, as was done in previous applications of the two-film model and the concept of additivity of resistances (Goodgame and Sherwood, 1954; Atlas and others, 1982; Mackay and others, 1982).

Liquid-film coefficients for acetone for the low, medium, and high mixing conditions are presented in tables 3, 4, and 5, respectively. Similarly, coefficients for TBA for the three mixing conditions are presented in tables 6, 7, and 8, respectively. Each table is for a low, medium, or high mixing condition for which the mixing conditions in the constant temperature bath, as indicated by the revolution rate of the stirrer, were constant. The stirrer *Re* number, however, in each case increased because

Table 3. Computed liquid-film coefficients, Henry's law constants, and percentage differences in the Henry's law constants for acetone at the low mixing condition

Temperature (K)	Stirrer Reynolds number $\times 10^{-4}$	Liquid-film coefficient (m/d)	Computed Henry's law constant$\times 10^3$ (kPa·m^3/g mol)		Percentage difference
			equation 8	equation 58	
279.2	1.64	0.340	1.55	1.33	16.5
285.0	1.93	.417	2.60	1.89	37.6
285.2	1.95	.425	1.76	1.90	-7.37
291.4	2.29	.519	3.17	2.71	17.0
298.4	2.68	.594	5.71	3.95	44.6
298.2	2.57	.630	4.49	3.91	14.8
305.0	3.05	.739	7.64	5.55	37.7
313.2	3.56	.894	11.9	8.30	43.4
313.2	3.51	.875	13.4	8.26	62.2

Table 4. Computed liquid-film coefficients, Henry's law constants, and percentage differences in the Henry's law constants for acetone at the medium mixing condition

Temperature (K)	Stirrer Reynolds number $\times 10^{-4}$	Liquid-film coefficient (m/d)	Computed Henry's law constant$\times 10^3$ (kPa·m^3/g mol)		Percentage difference
			equation 8	equation 58	
279.0	4.10	1.29	1.48	1.33	11.3
285.2	4.83	1.58	1.93	1.90	1.58
291.6	5.78	1.98	3.10	2.72	14.0
298.4	7.06	2.56	4.42	3.93	12.5
305.2	7.88	2.92	6.91	5.61	23.2
313.2	9.37	3.63	9.61	8.26	16.3

Table 5. Computed liquid-film coefficients, Henry's law constants, and percentage differences in the Henry's law constants for acetone at the high mixing condition

Temperature (K)	Stirrer Reynolds number $\times 10^{-4}$	Liquid-film coefficient (m/d)	Computed Henry's law constant$\times 10^3$ (kPa·m^3/g mol)		Percentage difference
			equation 8	equation 58	
279.2	6.52	2.52	1.75	1.33	31.6
285.2	7.64	3.07	2.35	1.91	23.0
291.2	9.13	3.85	3.47	2.68	29.5
291.2	9.14	3.85	3.63	2.66	36.5
298.2	10.7	4.70	5.06	3.91	29.4
298.4	10.9	4.80	4.87	3.95	23.3
305.0	12.6	5.74	7.42	5.55	33.7
313.2	14.7	6.98	10.7	8.26	29.5
313.2	14.6	6.91	11.1	8.26	34.4

Table 6. Computed liquid-film coefficients, Henry's law constants, and percentage differences in the Henry's law constants for t-butyl alcohol at the low mixing condition

Temperature (K)	Stirrer Reynolds number $\times 10^{-4}$	Liquid-film coefficient (m/d)	Computed Henry's law constant$\times 10^3$ (kPa·m^3/g mol)		Percentage difference
			equation 8	equation 59	
279.2	1.64	0.261	0.324	0.284	14.1
285.0	1.93	.329	.526	.460	14.3
285.2	1.95	.335	.452	.463	-2.38
291.4	2.29	.419	.822	.756	8.73
298.4	2.68	.524	1.44	1.27	13.4
298.2	2.57	.494	1.56	1.25	24.8
305.0	3.05	.629	2.56	2.04	25.5
313.2	3.56	.782	4.52	3.55	27.3
313.2	3.51	.765	4.87	3.52	38.4

Table 7. Computed liquid-film coefficients, Henry's law constants, and percentage differences in the Henry's law constants for t-butyl alcohol at the medium mixing condition

Temperature (K)	Stirrer Reynolds number $\times 10^{-4}$	Liquid-film coefficient (m/d)	Computed Henry's law constant$\times 10^3$ (kPa·m^3/g mol)		Percentage difference
			equation 8	equation 59	
279.0	4.10	0.987	0.326	0.282	15.6
285.2	4.83	1.24	.444	.463	-4.10
291.6	5.78	1.60	.819	.762	7.48
298.4	7.06	2.13	1.58	1.26	25.4
305.2	7.88	2.48	2.63	2.06	27.7
313.2	9.37	3.17	4.42	3.52	25.6

Table 8. Computed liquid-film coefficients, Henry's law constants, and percentage differences in the Henry's law constants for t-butyl alcohol at the high mixing condition

Temperature (K)	Stirrer Reynolds number $\times 10^{-4}$	Liquid-film coefficient (m/d)	Computed Henry's law constant$\times 10^3$ (kPa·m^3/g mol)		Percentage difference
			equation 8	equation 59	
279.2	6.52	1.94	0.287	0.284	1.06
285.2	7.64	2.42	.510	.467	9.21
291.2	9.13	3.11	.885	.745	18.8
291.2	9.14	3.11	.973	.739	31.7
298.2	10.7	3.90	1.77	1.25	41.6
298.4	10.9	3.99	1.71	1.27	34.6
305.0	12.6	4.88	2.91	2.04	42.6
313.2	14.7	6.11	4.88	3.52	38.6
313.2	14.6	6.05	5.15	3.52	46.3

of the effect of temperature on the viscosity and density of the water.

Unlike the negative values obtained previously, the liquid-film coefficients for both acetone and TBA for the three mixing conditions are within the range expected. All the coefficients show the expected increase with mixing intensity, as indicated by the stirrer *Re* number, and the expected increase with temperature. The temperature dependence of the liquid-film coefficients will be discussed in more detail in the next section.

The liquid-film coefficients from tables 3 through 8 were used along with the experimental overall mass-transfer coefficients from table 1 and the gas-film coefficients from equations 56 and 57 to calculate from equation 8 the values of the Henry's law constants necessary for the concept of additivity of resistances to be valid. These Henry's law constants were then compared with the constants calculated from equations 58 and 59, which, as previously discussed, were developed on the basis of activity-coefficient and vapor pressure data from the literature. The results are presented in tables 3, 4, and 5 for acetone and tables 6, 7, and 8 for TBA.

The average percentage differences in the Henry's law constants in tables 3, 4, and 5 for acetone were 29.6, 13.1 and 30.1 for the low, medium, and high mixing conditions, respectively. The corresponding values for TBA in tables 6, 7, and 8 were 18.2, 16.3, and 29.4 percent. These differences are small relative to the errors that might be expected in the direct measurement of Henry's law constants for hydrophilic compounds or the estimation of these constants from vapor pressure and activity-coefficient data.

The fact that the calculated Henry's law constants are in reasonable agreement with the constants estimated from vapor pressure and activity-coefficient data suggests that the two-film model and the concept of additivity of resistances are useful for interpreting the volatilization from water of very soluble compounds such as acetone and TBA. This evaluation admittedly was somewhat indirect. However, the present state of our experimental ability precludes direct measurement of the film coefficients, which would permit a direct evaluation of the two-film model. Previous evaluations of the model (Goodgame and Sherwood, 1954; Atlas and others, 1982; Mackay and others, 1982) were also of this indirect form.

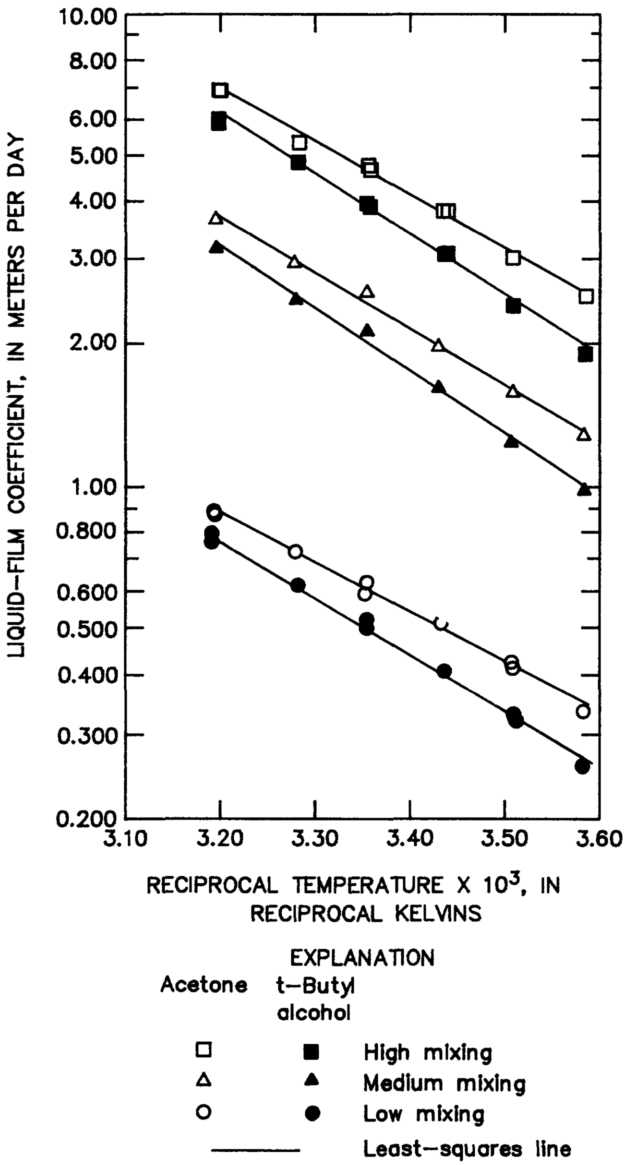

Figure 7. Liquid-film coefficients on a logarithmic scale as a function of reciprocal absolute temperature for acetone and t-butyl alcohol.

Temperature Dependence

Liquid-Film Coefficients

Liquid-film coefficients for acetone and TBA from tables 3 through 8 are plotted on a logarithmic scale in figure 7 as a function of reciprocal absolute temperature as suggested by equation 38. The overall mass-transfer coefficients for oxygen from table 1, which are considered to be virtually identical to the liquid-film coefficients, as discussed previously, are plotted on a logarithmic scale in figure 8 as a function of reciprocal absolute temperature. The lines in these figures are least-squares fits of the data.

Slopes, intercepts, and rms errors of the linear regressions are presented in table 9. On the basis of these errors, we concluded that an exponential function of the reciprocal absolute temperature of the form of equation 38 accurately predicted the temperature dependences of the liquid-film coefficients of acetone, TBA, and oxygen.

The liquid-film coefficient data were also analyzed

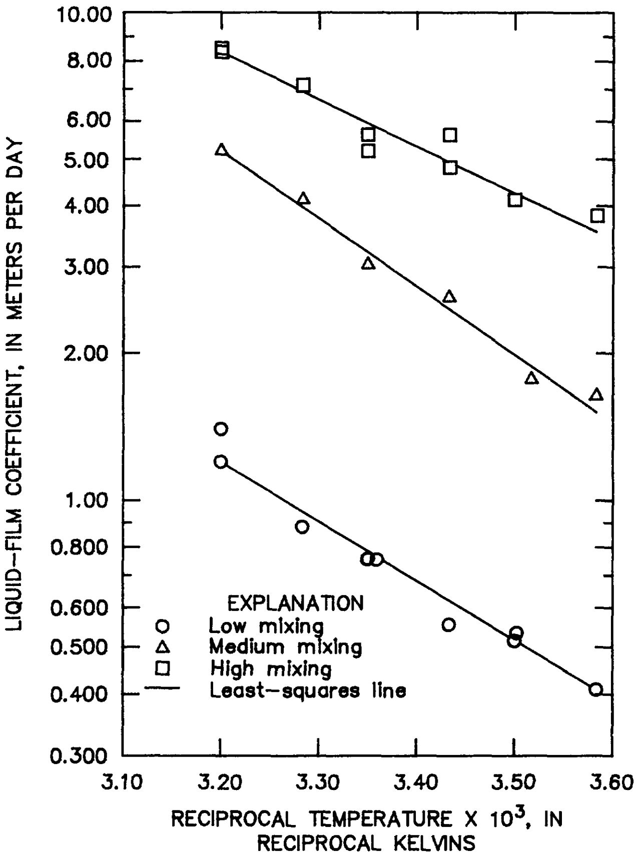

Figure 8. Liquid-film coefficients on a logarithmic scale as a function of reciprocal absolute temperature for oxygen.

according to equation 34. Slopes, intercepts, rms errors, and the temperature coefficient, θ, defined by equation 37 are presented in table 10. On the basis of these errors, we concluded that an exponential function of the absolute temperature of the form of equation 34 accurately predicted the temperature dependences of the liquid-film coefficients of acetone, TBA, and oxygen.

Comparison of the slopes in tables 9 and 10 showed no obvious dependence on mixing condition for acetone and TBA. Coefficients of variation of the slopes in table 9 were ±5.10 percent for acetone and ±4.66 percent for TBA. Coefficients of variation of the slopes in table 10 were ±5.46 percent for acetone and ±4.95 percent for TBA. Also the largest slope for both acetone and TBA was for the medium mixing condition. We concluded, therefore, that the temperature dependences of the liquid-film coefficients for acetone and TBA did not depend on the water mixing conditions.

For oxygen, however, the variation was considerably larger. Coefficients of variation of the slopes were ±19.4 percent for the table 9 values and ±19.6 percent for the table 10 values. The slope for the high mixing condition was significantly different from the slopes for the low and medium mixing conditions. A similar conclusion is also evident for the temperature coefficient, θ.

This result is in general agreement with previous results on the temperature dependence of the absorption of oxygen. Metzger (1968) analyzed the data of six studies and concluded that the temperature coefficient, θ, decreased as the mixing intensity increased. Values ranged from 1.047 to 1.008, with most being less than the 1.0241 value of Elmore and West (1961). This latter value is the one most commonly used for expressing the temperature dependence of the oxygen absorption coefficient. The value of the temperature coefficient for the high mixing condition from table 10 agrees well with this value. The values for the low and medium mixing conditions are higher, however.

The errors in tables 9 and 10 for acetone and TBA are smaller than the errors for oxygen. This decrease in the errors apparently resulted from the smoothing of the data that occurred during the procedure used to calculate the liquid-film coefficients for acetone and TBA.

The temperature dependence of the liquid-film coefficient for the volatilization of organic compounds from water has not been studied in any detail. Therefore, data for comparison with the acetone and TBA results were not available. Additional research in this area is needed, as noted previously (Mackay and others, 1982).

Table 9. Slopes, intercepts, and root-mean-square errors of linear regressions of the logarithm of the liquid-film coefficient as a function of reciprocal absolute temperature

Solute	Mixing condition	Slope (K)	Intercept $\times 10^{-3}$ (m/d)	Error (percent)
Acetone	Low	-2,410	2.00	2.22
	Medium	-2,670	18.9	2.99
	High	-2,560	24.6	2.34
t-Butyl alcohol	Low	-2,750	5.08	2.08
	Medium	-3,010	48.6	3.07
	High	-2,930	72.6	1.88
Oxygen	Low	-2,940	14.7	7.55
	Medium	-3,080	98.0	5.25
	High	-2,110	6.88	5.79

Table 10. Slopes, intercepts, and root-mean-square errors of linear regressions of the logarithm of the liquid-film coefficient as a function of temperature, and temperature coefficients

Solute	Mixing condition	Slope (K^{-1})	Intercept (m/d)	Error (percent)	Temperature coefficient
Acetone	Low	0.0274	0.302	2.95	1.0278
	Medium	.0305	1.11	3.99	1.0310
	High	.0290	2.21	2.89	1.0294
t-Butyl alcohol	Low	.0312	.228	3.01	1.0317
	Medium	.0344	.833	4.24	1.0350
	High	.0332	1.66	3.12	1.0338
Oxygen	Low	.0335	.329	6.69	1.0341
	Medium	.0353	1.28	5.33	1.0359
	High	.0240	3.14	5.39	1.0243

Overall Mass-Transfer Coefficients

The experimental overall mass-transfer coefficients for acetone and TBA from table 1 are plotted on a logarithmic scale in figures 9 and 10 as a function of reciprocal absolute temperature. The lines are least-squares fits of the data. Slopes, intercepts, and rms errors of the regressions are presented in table 11. The errors are somewhat larger than the errors for similar regressions of the liquid-film coefficients given in table 10. Figures 9 and 10 show, however, no systematic deviations from the assumed linear relation between the logarithm of the coefficient and reciprocal absolute temperature.

The slopes in table 11 show a slight tendency to increase as the degree of mixing increases. This increase is similar to that shown in table 10 for the slopes of the regressions for the liquid-film coefficients. The overall mass-transfer coefficient, however, is not a single coefficient, but is a combination of the liquid-film and gas-film coefficients and the Henry's law constant as indicated by equation 8. Of these three coefficients, only the liquid-film coefficient is expected to depend on mixing conditions in the water. Therefore, the similarity in the dependence of the slopes on mixing conditions is as should be expected.

Because the overall mass-transfer coefficient depends on the gas-film and liquid-film coefficients and the Henry's law constant, the approach used in figures 9 and 10 is empirical. This approach does, however, provide an adequate fit to the data for temperatures from 279 to 313 K, which covers most of the range of temperatures likely to be encountered in streams and rivers.

A fundamentally better approach is to combine the temperature dependences of the gas-film and liquid-film coefficients and the Henry's law constant with the two-film-model equation (eq. 8) to predict the temperature dependence of the overall mass-transfer coefficient. The result is equation 45, presented previously.

Equations for the temperature dependence of the Henry's law constant for use in equation 45 were obtained from the constants computed in the alternative data analysis procedure. Linear regression of the logarithms of these constants from tables 3 through 8 as a function of reciprocal absolute temperature gave the equations

$$H_{AC} = 1.44 \times 10^5 exp(-5{,}130/T) \tag{68}$$

and

$$H_{TBA} = 3.99 \times 10^7 exp(-7{,}150/T) \ . \tag{69}$$

In the determination of these equations, the Henry's law constants for the three mixing conditions were combined into one group for each of the two compounds because the constants in tables 3 through 8 showed no obvious dependence on mixing conditions. Combining these constants is consistent with the fact that the Henry's law constant is an equilibrium parameter rather than a kinetic parameter. The rms errors were ±12.1 percent for equation 68 and ±8.18 percent for equation 69. The errors are less than the errors of ±18.2 percent for equation 58 and ±22.0 percent for equation 59, which shows the smoothing effect of the analysis procedure used to determine the Henry's law constants upon which equations 68 and 69 are based.

The exponents in equations 68 and 69 are 9.38 percent larger and 10.5 percent larger in an absolute sense than the exponents in equations 58 and 59, respectively. The generally good agreement between the exponents says that the temperature dependences of the two sets of Henry's law constants are approximately the same, thus giving additional support to the alternative data analysis procedure.

Substituting, into equation 45, slopes and intercepts from equations 56 and 57 for the temperature dependence of the gas-film coefficient and substituting equations 68 and 69 for the temperature dependence of the Henry's law constant gives equations for the temperature dependence of the experimental overall mass-transfer coefficients. For acetone, this equation has the form

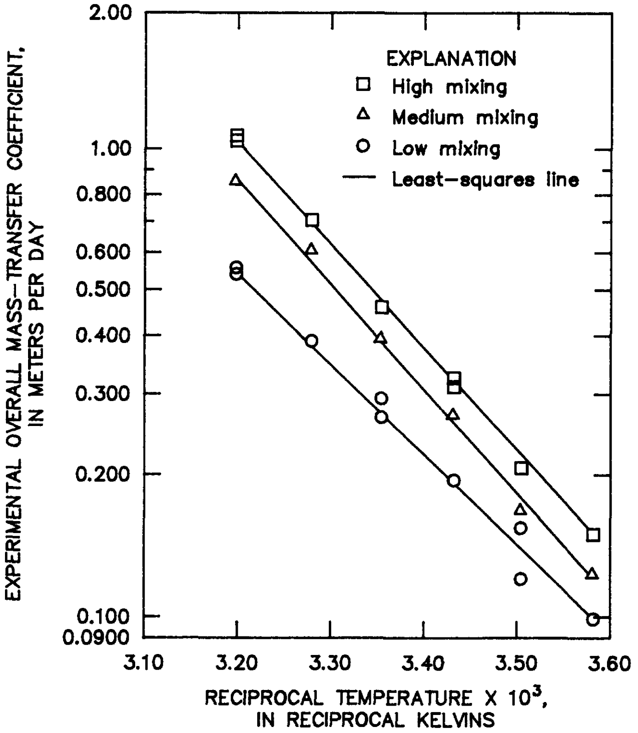

Figure 9. Experimental overall mass-transfer coefficients on a logarithmic scale as a function of reciprocal absolute temperature for acetone.

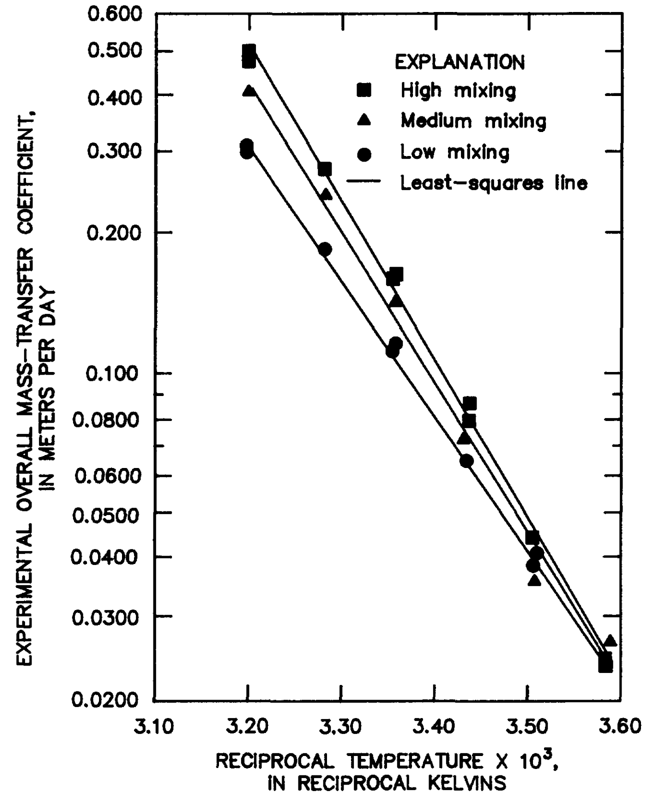

Figure 10. Experimental overall mass-transfer coefficients on a logarithmic scale as a function of reciprocal absolute temperature for t-butyl alcohol.

Table 11. Slopes, intercepts, and root-mean-square errors of linear regressions of the logarithm of the overall mass-transfer coefficient as a function of reciprocal absolute temperature

Solute	Mixing condition	Slope (K)	Intercept×10^{-7} (m/d)	Error (percent)
Acetone	Low	-4,420	0.0745	4.49
	Medium	-5,110	1.08	4.44
	High	-5,050	1.08	2.47
t-Butyl alcohol	Low	-6,550	37.4	4.05
	Medium	-7,290	539	5.27
	High	-7,740	2760	7.98

$$K_{OL_{AC}} = [a_{L_{AC}}^{-1} exp(b_{L_{AC}}/T) + 1.17\times 10^{-11}(T)exp(6{,}010/T)]^{-1} \qquad (70)$$

and for *TBA*

$$K_{OL_{TBA}} = [a_{L_{TBA}}^{-1} exp(b_{L_{TBA}}/T) + 4.57\times 10^{-14}(T)exp(8{,}030/T)]^{-1} \qquad (71)$$

The a_L factors are the intercepts given previously in table 9 for the regression equations for the temperature dependence of the liquid-film coefficient. The b_L factors are the negatives of the slopes in table 9. Single values cannot be used for these factors in equations 70 and 71 because the liquid-film coefficient depends on mixing conditions in the water.

Overall mass-transfer coefficients for acetone and TBA were calculated from equations 70 and 71 at temperatures of 279.2 K, 285.2 K, 291.2 K, 298.2 K, 305.2 K, and 313.2 K. Logarithms of the calculated coefficients are plotted as a function of reciprocal absolute temperature in figure 11 for acetone and in figure 12 for TBA. The lines in these figures are for least-squares

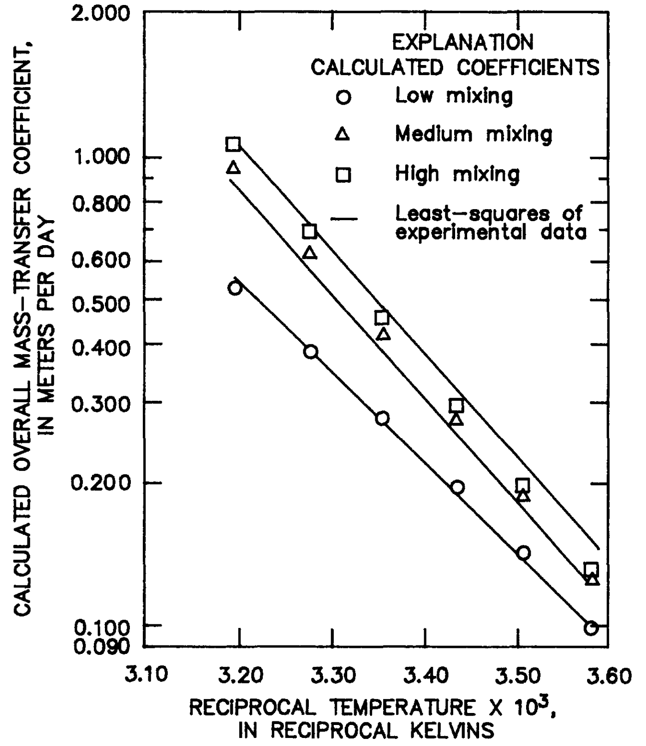

Figure 11. Calculated overall mass-transfer coefficients on a logarithmic scale as a function of reciprocal absolute temperature for acetone.

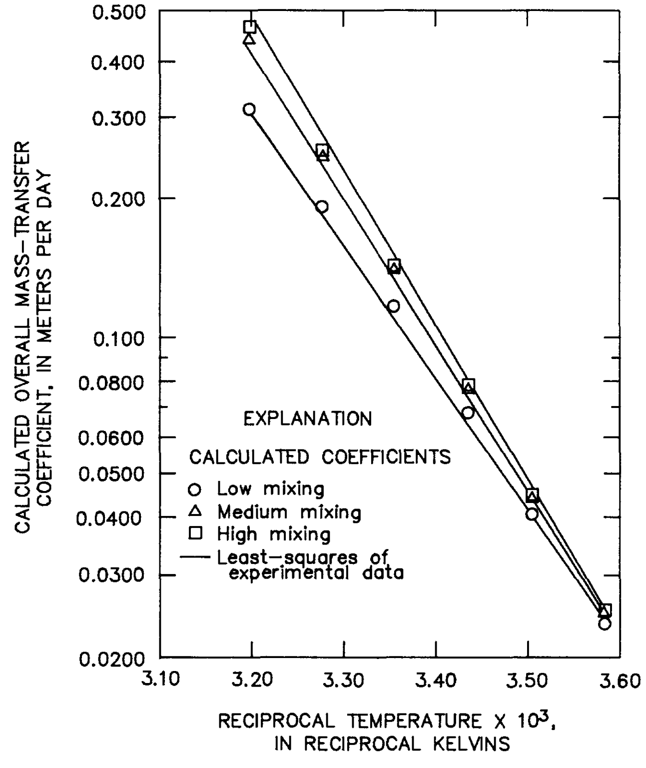

Figure 12. Calculated overall mass-transfer coefficients on a logarithmic scale as a function of reciprocal absolute temperature for t-butyl alcohol.

regressions of the logarithms of the experimental data from table 1 as a function of reciprocal absolute temperature.

Figures 11 and 12 show that the calculated overall mass-transfer coefficients generally scatter about the least-squares lines based on the experimental data. We conclude that the fundamental approach of combining the temperature dependences of the liquid-film coefficient, the gas-film coefficient, and the Henry's law constant through the two-film-model equation gives a temperature dependence comparable to that obtained by assuming empirically that the overall coefficient depends on the reciprocal of the absolute temperature.

Distribution of Resistances

The percentage resistances in the gas film were calculated from equation 13; the liquid-film coefficients came from tables 3 through 8 and the overall mass-transfer coefficients came from table 1. The results are plotted for acetone in figure 13 and for TBA in figure 14.

Figures 13 and 14 show that the percentage resistance in the gas film for a specific mixing condition decreases as the temperature increases. This decrease occurs apparently because the product of the Henry's law constant and the gas-film coefficient increases with temperature more rapidly than the product of the liquid-film coefficient and the temperature. This can be shown as follows:

Combine equations 8 and 13 to eliminate the overall mass-transfer coefficient. The result is

$$\begin{array}{l}\text{percentage resistance}\\ \quad\text{in the gas film}\end{array} = \left(1-\frac{1}{1+RTk_L/Hk_G}\right)100\ . \quad (72)$$

Dependence of the percentage resistance on temperature thus depends on the relative temperature dependencies of the variables in the Tk_L/Hk_G ratio. As an example, consider the low mixing condition for acetone and a temperature increase from 279 to 313 K. Equation 38 with constants from table 9 predicts that the liquid-film coefficient will increase by a factor of 2.56. Similarly, equation 56 predicts that the gas-film coefficient will increase by a factor of 1.41, equation 68 predicts that the Henry's law constant will increase by a factor of 7.37, and the absolute temperature increases by a factor of 1.12. Substituting these factors into the Tk_L/Hk_G ratio shows that this ratio at 313 K is 0.276 of the value at 279 K. Consideration of equation 72 shows that the percentage resistance in the gas film decreases when this ratio decreases.

From a physical point of view, the decrease may be explained as follows: The Henry's law constant is

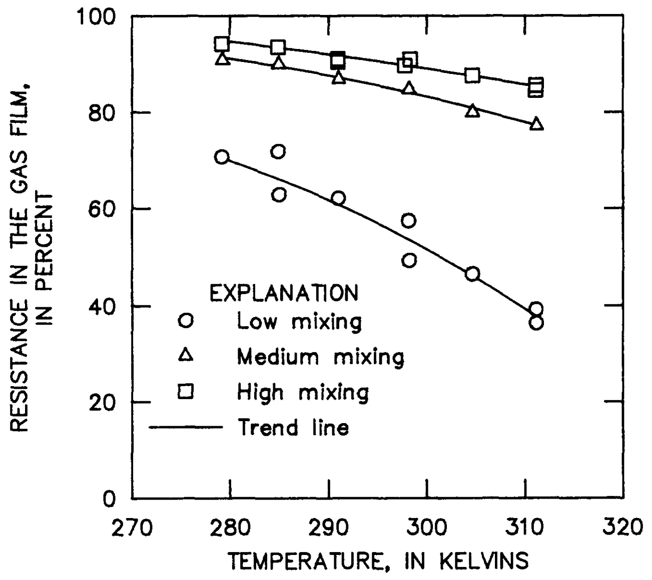

Figure 13. Percentage resistances in the gas film as a function of temperature for acetone.

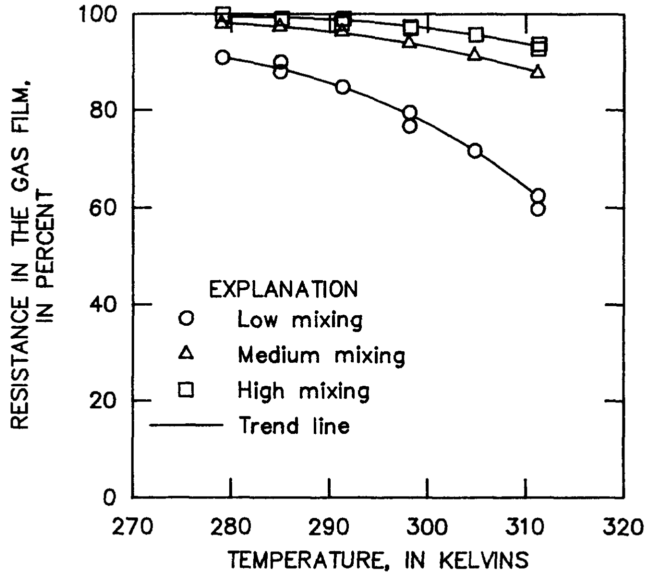

Figure 14. Percentage resistances in the gas film as a function of temperature for t-butyl alcohol.

basically an air-water partition coefficient for the solute. This constant increases with temperature and the larger the Henry's law constant, the greater is the tendency for the solute to transfer to the air phase and the lesser is the gas-film resistance to the transfer. It was previously shown that gas-film resistance to the absorption of oxygen, which has a large Henry's law constant, is negligible with respect to the liquid-film resistance. Similarly, it is well known (Mackay and others, 1979; Smith and others, 1981; Rathbun and Tai, 1982b), when a series of solutes is considered, that the significance of the gas-film resistance decreases as the Henry's law constant increases. Analogously then, the significance of the gas-film resistance should decrease for a specific solute when the Henry's law constant increases as a result of a temperature increase.

Figures 13 and 14 also show for any specific temperature that the percentage resistance in the gas film increases from the low to the high mixing conditions. We previously determined (Rathbun and Tai, 1983) that mixing conditions in the water had a generally insignificant effect on the gas-film resistance. Therefore, the increase in the percentage resistance in the gas-film resistance is a result of a decrease in the liquid-film resistance as the mixing conditions were increased.

Finally, figures 13 and 14 show for the conditions of this study that a large percentage of the resistance was in the gas film, particularly for the high and medium mixing conditions. Percentage resistances ranged from 84.5 to 94.0 and from 76.7 to 90.5 for the high and medium mixing conditions for acetone, respectively. Corresponding values for TBA were 91.7 percent to 98.8 percent and 87.1 percent to 97.3 percent. As this percentage resistance approaches 100, the gas-film resistance approaches the overall resistance in value. It is at this point, as discussed previously, that the calculated liquid-film coefficients become extremely sensitive to errors in the Henry's law constant, and that negative liquid-film coefficients may result. This combination of high resistance in the gas film for solutes with low values of the Henry's law constants has not been checked previously for applicability of the two-film model. However, work of a somewhat different nature on solutes of this type has been presented previously (Chiou and others, 1980, 1983).

Predictive Equations

Laboratory Data

Combining equations 56, 62, 64, 66, 67, and 68 with equation 8 gives an equation for predicting the overall mass-transfer coefficient for the volatilization of acetone from water in the stirred bath used in this study. The result is

$$K_{OL_{AC}} = [2.60 \times 10^{8} Re^{-1.45} Sc_{OXY}^{-0.0616} T^{-0.500} exp(-275/T) + 1.17 \times 10^{-11} T exp(6{,}010/T)]^{-1} \,. \tag{73}$$

Combining equations 57, 62, 65, 66, 67, and 69 with equation 8 gives a similar equation for TBA. The result is

$$K_{OL_{TBA}} = [3.61 \times 10^{6} Re^{-1.45} Sc_{OXY}^{-0.0616} exp(210/T) + 4.57 \times 10^{-14} T exp(8{,}030/T)]^{-1} \tag{74}$$

Overall mass-transfer coefficients for acetone computed from equation 73 are plotted in figure 15 as a function of the experimental overall mass-transfer coefficients from table 1. The rms error was ±6.63 percent. Percentage errors for the individual experiments ranged from -17.3 to +14.0 and averaged 0.28. We conclude that equation 73 provides a good fit of the acetone experimental data.

Overall mass-transfer coefficients for TBA computed from equation 74 are plotted in figure 16 as a function of the experimental overall mass-transfer coefficients from table 1. The rms error was ±7.57 percent. Percentage errors for the individual experiments ranged from -14.8 to +12.6 and averaged 0.06. We also conclude that equation 74 provides a good fit of the TBA experimental data.

The good fits shown in figures 15 and 16 were expected because the experimental overall mass-transfer coefficients were used as the independent variables, and these same coefficients also were used in obtaining the liquid-film coefficient relations for deriving equations 73 and 74. Therefore, some self-correlation is involved in figures 15 and 16. The results show, however, that the experimental results can be described by the basic equation of the two-film model (eq. 8).

Equations 73 and 74 apply to the stirred bath used in this study. Laboratory studies such as this contribute to understanding the fundamentals of the volatilization process. However, volatilization coefficients determined in the laboratory are generally not directly transferable to field situations. Laboratory data can be used in conjunction with the reference-substance concept to develop an equation for predicting volatilization coefficients for streams and rivers, as discussed previously.

Streams and Rivers

Use of equation 27 to predict volatilization coefficients of acetone and TBA for streams and rivers requires laboratory determinations of the ϕ and ψ factors, estimation of the Henry's law constants, estimation of the liquid-film coefficient for oxygen absorption, and estimation of the gas-film coefficient for water volatilization for the stream or river of interest.

Liquid-film coefficients for acetone, $k_{L_{AC}}$, from tables 3, 4, and 5 are plotted in figure 17 as a function of the liquid-film coefficient for oxygen from table 1. According to equation 25, the slope of the least-squares line forced through the origin in this figure is ϕ, and this value is 0.802. Figure 17 shows that a reasonably constant relation exists between the liquid-film coefficients for acetone and oxygen over a wide range of water mixing conditions and temperatures. The rms error for this regression was ±10.6 percent. It was concluded that the reference-substance concept is applicable to the liquid-film coefficients for the acetone-oxygen pair, in agreement with previous results (Smith and others, 1980; Rathbun and Tai, 1981, 1984a) for other organic substances.

Liquid-film coefficients for TBA, $k_{L_{TBA}}$, from tables 6, 7, and 8 are plotted in figure 18 as a function of the liquid-film coefficient for oxygen from table 1. The slope of the least squares line corresponding to ϕ is 0.671. Figure 18 shows that a reasonably constant relation

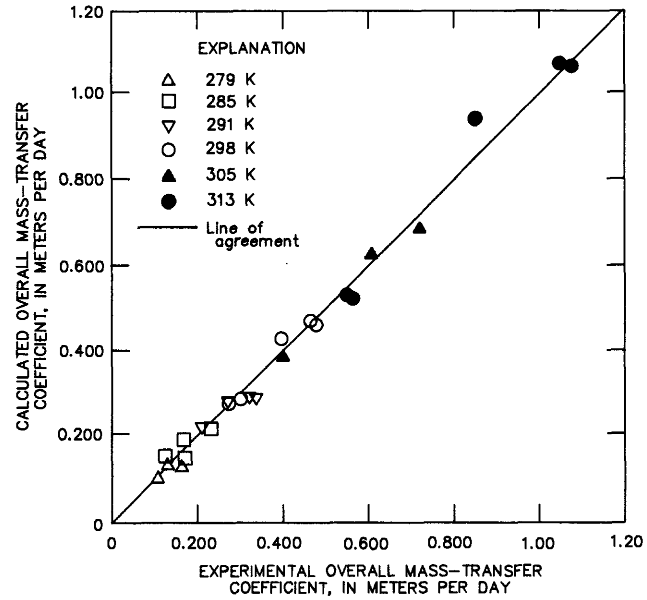

Figure 15. Calculated overall mass-transfer coefficients as a function of the experimental overall mass-transfer coefficient for acetone.

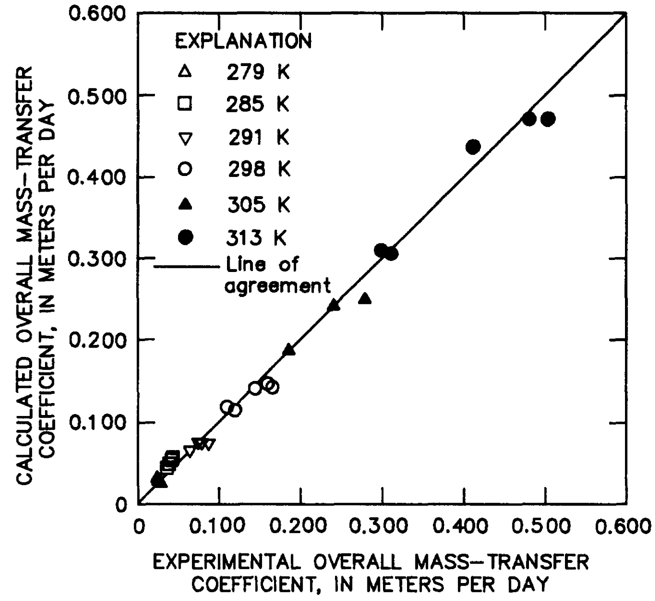

Figure 16. Calculated overall mass-transfer coefficients as a function of the experimental overall mass-transfer coefficient for t-butyl alcohol.

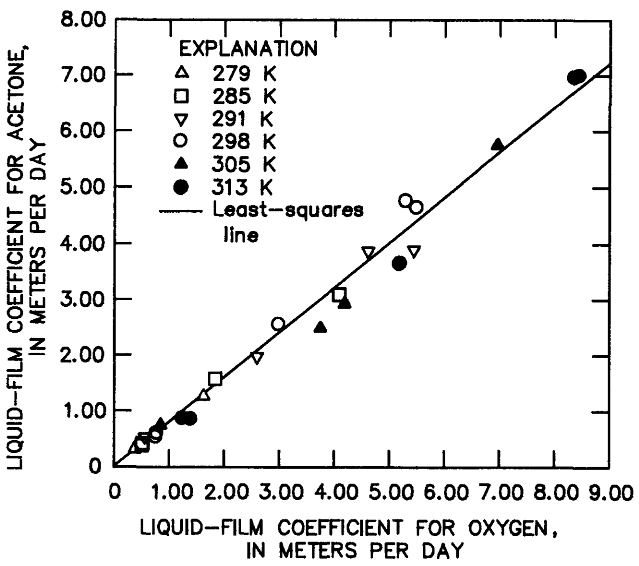

Figure 17. Liquid-film coefficients for acetone as a function of the liquid-film coefficient for oxygen.

exists between the liquid-film coefficients for TBA and oxygen over a wide range of water mixing conditions and temperatures. The rms error for this regression was ±14.2 percent. It was concluded that the reference-substance concept is applicable to the liquid-film coefficients for the TBA-oxygen pair.

The ψ factors for the gas-film coefficient ratios for acetone-water and TBA-water were presented previously. Values of ψ were 0.490 for acetone and 0.452 for TBA, and it was concluded for practical purposes that these values were independent of temperature. The usual assumption of the reference-substance concept is that ψ is also independent of windspeed. This constancy was not tested in the present study, but it is a reasonable and customary assumption (Smith and others, 1981; Mackay and others, 1982; Rathbun and Tai, 1983). Also, constancy of ψ with respect to windspeed has been verified recently for the ethylene dibromide-water pair of compounds (Rathbun and Tai, 1986b).

The estimation of the Henry's law constant was discussed previously. Equations 68 and 69 can be used to estimate this constant for acetone and TBA, respectively.

The liquid-film coefficient for oxygen absorption in streams and rivers is related to the reaeration coefficient by the equation

$$k_{L_{OXY}} = K_2 Y \, , \tag{75}$$

where K_2 is the reaeration coefficient (d^{-1}). The reaeration coefficient has been extensively studied, and numerous equations exist (Rathbun, 1977) for predicting this coefficient for streams and rivers as a function of the hydraulic and geometric properties. Questions still exist regarding the reaeration coefficient, however, because the various predictive equations give a wide range of predicted coefficients for a specific set of hydraulic and geometric conditions. Therefore, we suggest that the several equations judged best (Rathbun, 1977) be used to estimate reaeration coefficients, that any obvious outlier values be discarded, and that an average of the remaining values be used to compute the oxygen absorption coefficient from equation 75 for use in equation 27.

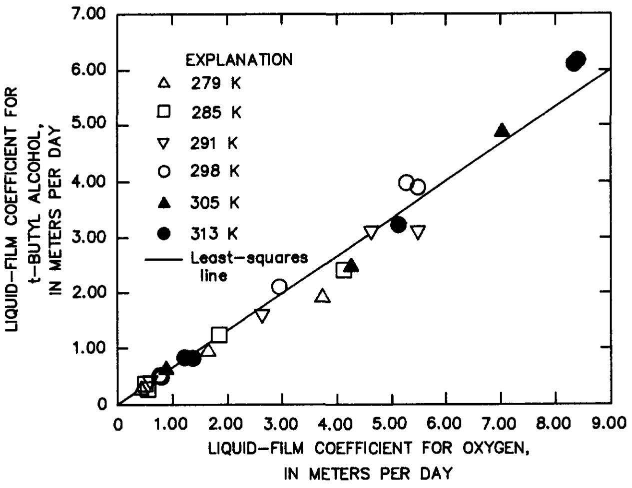

Figure 18. Liquid-film coefficients for t-butyl alcohol as a function of the liquid-film coefficient for oxygen.

The gas-film coefficient for the volatilization of water from streams and rivers can be estimated from an equation (Rathbun and Tai, 1983) expressing the coefficient as a function of the average windspeed and water temperature. This equation has not been used extensively, but Jobson (1985) recently concluded that the wind function upon which this equation is based is a valid predictor of the wind function for streams and rivers. Therefore, gas-film coefficients predicted from this equation should not be subject to large errors.

The difficulty of estimating Henry's law constants for compounds with appreciable water solubility was discussed previously. Therefore, overall mass-transfer coefficients estimated from equation 27 should be used with this consideration in mind. However, the percentage errors are not expected to be nearly as large as in the calculation of the liquid-film coefficients. This is true because of the difference in the mathematical operations. In the case of the overall mass-transfer coefficient and equation 27, the operation is addition and the error is not magnified. In the case of the liquid-film coefficient and equation 61, the operation is subtraction of two numbers of about the same magnitude. As a result, any error is magnified, as discussed previously.

Application of the Predictive Equation

Example

Application of the predictive equation (eq. 27) for streams and rivers is demonstrated through an example. Consider a reach of stream into which a wastewater is discharged which results in concentrations of 100 mg/L each of acetone and TBA in the stream water. The manager of a drinking water facility must estimate what the concentrations of acetone and TBA will be at his intake point 40 km downstream. For the purpose of this illustration, it is assumed that only volatilization affects the concentrations of acetone and TBA.

Assume a mean water velocity of 0.33 m/s, a mean depth of flow of 0.27 m, a channel slope of 0.0015 m/m, and a mean water temperature of 296.0 K. The problem is to estimate the concentrations at the intake point for three average windspeeds of 0.10 m/s, 2.0 m/s, and 5.0 m/s.

Steps in the application of equation 27 were presented previously. The first step is to determine in the laboratory the liquid-film coefficient ratio, ϕ. These values were 0.802 for acetone and oxygen (fig. 17) and 0.671 for TBA and oxygen (fig. 18).

The second step is to determine in the laboratory the gas-film coefficient ratio, ψ. These values presented previously were 0.490 for acetone and water and 0.452 for TBA and water.

The third step is to estimate the Henry's law constants for a temperature of 296.0 K from equations 68 and 69. The results were 4.42×10^{-3} kPa·m^3/g mol for acetone and 1.29×10^{-3} kPa·m^3/g mol for TBA.

The fourth step is to estimate the reaeration coefficient for the stream reach using equations from the literature (Rathbun, 1977). The equations of Langbein and Durum (1967), Isaccs and Gaudy (1968), Thackston and Krenkel (1969), Padden and Gloyna (1971), Parkhurst and Pomeroy (1972), Tsivoglou and Wallace (1972), and Bansal (1973) were used for this purpose. Results were adjusted to the mean water temperature of 296.0 K using the temperature correction factor of Elmore and West (1961). Estimated coefficients ranged from 5.29 d^{-1} to 10.4 d^{-1}, and there were no obvious outliers. The mean was 8.41 d^{-1} with a coefficient of variation of ±28.0 percent. This coefficient, which is for the better of the predictive equations, gives an indication of the errors involved in predicting reaeration coefficients. The mean reaeration coefficient was converted to the oxygen absorption coefficient using equation 75. The result was a coefficient of 2.27 m/d.

It is generally agreed (Rathbun, 1977) that wind significantly affects the reaeration coefficient under some conditions. The present state of our knowledge (Frexes and others, 1984), however, is such that wind effects cannot be quantitatively incorporated into predictive equations. Therefore, for the purpose of this example, wind effects on the reaeration coefficient have been neglected.

The fifth step is to estimate the gas-film coefficient for the volatilization of water from the stream reach using an equation from the literature (Rathbun and Tai, 1983). Results for a water temperature of 296.0 K and average windspeeds of 0.10 m/s, 2.0 m/s, and 5.0 m/s were 419 m/d, 706 m/d, and 1,160 m/d, respectively. These water coefficients were adjusted to gas-film coefficients for acetone and TBA using equation 26 and the ψ values from the second step. The results are presented in table 12.

The sixth step is to calculate the overall mass-transfer coefficients for acetone and TBA from equation 27 and the parameter values from the preceding steps. The results are presented in table 12.

The final step is to calculate the concentrations predicted at the downstream point from the equation (Rathbun and Tai, 1982b)

$$C_d = C_u exp(-K_{OL}Z/YU) \,, \tag{76}$$

where C_u is the concentration (mg/L) in the stream at the point of discharge after mixing of the wastewater with the stream water, Z is the distance (m) from the point of the discharge to the water intake point, C_d is the concentration (mg/L) in the stream water at this downstream point, and U is the mean water velocity (m/d). Predicted concentrations of acetone and TBA at the downstream point are presented in table 12. Equation 76 is a simplified description of the actual situation used to demonstrate the effect of volatilization. In the actual stream situation, concentrations would also be reduced by the effects of dispersion, bacterial degradation, and possibly other processes.

The results in table 12 show that windspeed significantly affects the volatilization of both compounds from water. The results also show that acetone volatilizes considerably faster than TBA, despite the fact that the liquid-film coefficients were similar. This difference occurs because of the larger Henry's law constant for acetone, indicating a greater preference to partition into the air phase.

Finally, the behavior of acetone and TBA in this example was compared with the behavior of an organic compound with a large value of the Henry's law constant such as 1,1,1-trichloroethane. The constant for this compound was estimated to be 2.84 kPa·m^3/g mol, and the ϕ factor was determined to be 0.596 (Rathbun and Tai, 1984a). The ψ factor has not been measured; however, it is expected to be unimportant because the gas-film resistance should be negligible for a compound with this Henry's law constant. Two values, 0.35 and 0.70, were used to cover the possible range of values. Calculation

Table 12. Gas-film coefficients, overall mass-transfer coefficients, and predicted concentrations of acetone and t-butyl alcohol at a point 40 kilometers downstream from an upstream concentration of 100 mg/L

Windspeed (m/s)	Gas-film coefficient (m/d)		Overall mass-transfer coefficient (m/d)		Concentration (mg/L)	
	Acetone	t-Butyl alcohol	Acetone	t-Butyl alcohol	Acetone	t-Butyl alcohol
0.1	205	189	0.306	0.0930	20.4	61.7
2.0	346	319	.463	.151	9.02	45.6
5.0	568	524	.654	.233	3.34	29.8

of the concentrations at the downstream intake point showed that the concentrations were virtually independent of the assumed ψ value, virtually independent of the windspeed, and less than 0.1 mg/L. This example demonstrates the importance of the Henry's law constant in determining the partitioning of an organic substance between the water and air phases.

Estimation of the ϕ and ψ Factors

Steps one and two of the procedure for estimating overall mass-transfer coefficients for the volatilization of organic substances from streams and rivers suggest laboratory determinations of the ϕ and ψ factors. However, laboratory determinations of these factors may not always be possible or necessary. Limitations of time and funds may preclude measuring these factors for all organic substances for which volatilization may be a significant fate-determining process. Also, in many qualitative modeling efforts, estimates of these factors may be adequate.

Two procedures are commonly used to estimate ϕ and ψ values when experimental values are not available. The first is based on the assumption that the film coefficient is proportional to the molecular-diffusion coefficient raised to some power ν as expressed previously by equation 2. Writing equation 2 for two solutes designated 1 and 2, taking ratios to eliminate the constant a_k, and combining with equation 25 gives

$$\phi = k_{L_2}/k_{L_1} = (D_2/D_1)^{\nu} \ . \tag{77}$$

Following the same procedure for the gas-film coefficients and combining with equation 26 gives

$$\psi = k_{G_2}/k_{G_1} = (D_2/D_1)^{\nu} \ , \tag{78}$$

where the molecular-diffusion coefficients can be estimated using procedures from the literature (Reid and others, 1977).

As discussed previously, theoretical values of ν range from 0.50 to 1.00, depending on the model of the mass-transfer process selected. Experimental values for the liquid-film coefficient generally range from 0.50 to 0.80, with 0.50 being the value generally recommended (Mackay and others, 1982). Experimental values of ν for the gas-film coefficient include 0.684 (Tamir and Merchuk, 1978) and 0.50 (Yadav and Sharma, 1979), with 0.67 being the value generally recommended (Mackay and others, 1982).

The second procedure is based on the assumption that the film coefficient is inversely proportional to the square root of the molecular weight. Using the same procedure as for equations 77 and 78, it follows that

$$\phi = k_{L_2}/k_{L_1} = (M_1/M_2)^{0.50} \tag{79}$$

and

$$\psi = k_{G_2}/k_{G_1} = (M_1/M_2)^{0.50} \ . \tag{80}$$

The basis of this procedure is Graham's law of diffusion (Glasstone, 1946) which states that the rate of molecular diffusion is inversely proportional to the square root of the molecular weight. It follows, therefore, that equations 79 and 80 assume that the film coefficients are proportional to the molecular-diffusion coefficient to the 1.0 power, as is true for the two-film model.

Values of ϕ were calculated from equation 77 for a temperature of 298.2 K for comparison with the experimental values. Molecular-diffusion coefficients for acetone, TBA, and oxygen in water were calculated from equations 64, 65, and 66, respectively. A value of 0.50 was used for ν. Calculated values of ϕ were 0.792 for acetone and 0.653 for TBA, in good agreement with the experimental values of 0.802 for acetone and 0.671 for TBA, respectively. This good agreement was to be expected, however, because it was assumed in the data analysis procedure that the liquid-film coefficients for acetone and TBA varied with the molecular-diffusion coefficient raised to the 0.50 power.

Values of ϕ calculated from equation 79 were 0.742 for acetone and 0.657 for TBA. These values are 7.48

percent smaller than the experimental value of 0.802 for acetone and 2.09 percent smaller than the experimental value of 0.671 for TBA.

Values of ψ were calculated from equation 78 for a temperature of 298.2 K for comparison with the experimental values. Molecular-diffusion coefficients for acetone, TBA, and water in air were calculated using the Brokaw method as described by Reid and others (1977). A value of 0.67 was used for ν. Calculated values of ψ were 0.607 for acetone and 0.531 for TBA. These values are 23.9 percent larger than the experimental value of 0.490 for acetone and 17.5 percent larger than the experimental value of 0.452 for TBA.

Water has unusual physical properties, and predicting its molecular-diffusion coefficient in air might be subject to more error than predictions for the other two solutes. If a ratio of the experimental ψ factors for acetone-water and TBA-water is formed, then the water coefficient is eliminated and a ψ ratio of 1.08 is obtained. Estimating ψ according to equation 78 using the molecular-diffusion coefficients for acetone and TBA gives a value of 1.14, which is 5.56 percent larger than the experimental value of 1.08.

Values of ψ calculated from equation 80 were 0.557 for acetone and 0.493 for TBA. These values are 13.7 percent larger than the experimental value of 0.490 for acetone and 9.07 percent larger than the experimental value of 0.452 for TBA. If water is eliminated by taking ratios as before, the result is a predicted value of 1.13, which is 4.63 percent larger than the experimental ratio of 1.08.

We conclude that both of the procedures for estimating the ϕ and ψ factors provide adequate estimates for the experimental data of this study. The second procedure, however, based on molecular weights, does not have a good theoretical basis and it has not been extensively verified. Despite these limitations, it has been used frequently, apparently because of the ready availability of molecular weights.

Relative Volatilization Characteristics of Acetone and t-Butyl Alcohol

The relative volatilization characteristics of acetone and TBA are of interest because of the intention to use TBA in an attempt to separate the effects of volatilization and bacterial degradation on the fate of acetone in streams and rivers. Physical properties of these organic substances that might be of importance in determining volatilization characteristics are presented in table 13. The molecular weights and solubilities are from a standard reference (Hodgman, 1951), and the vapor pressures were calculated from equations based on data from the literature (Parks and Barton, 1928; Ambrose and others, 1975). Molecular-diffusion coefficients and Henry's law constants were computed from equations 64 and 65 and equations 68 and 69, respectively. Analysis of the data in table 13 suggests that the volatilization characteristics of acetone and TBA should be similar, but that acetone probably will volatilize from water more rapidly than TBA because of the smaller molecular weight and the larger vapor pressure and molecular-diffusion coefficient.

Values of the organic solute/oxygen liquid-film coefficient ratio, ϕ, presented previously were 0.802 for acetone and 0.671 for TBA. Taking a ratio of these ratios to eliminate the oxygen coefficient gives a value of 1.20, which suggests that the liquid-film coefficient for acetone is on the average 20 percent larger than the liquid-film coefficient for TBA.

Similarly, values of the organic solute/water gas-film coefficient ratio, ψ, presented previously, were 0.490 for acetone and 0.452 for TBA. Taking a ratio of these ratios, as before, to eliminate the water coefficient gives a value of 1.08, which suggests that the gas-film coefficient for acetone is on the average 8 percent larger than the gas-film coefficient for TBA. These results suggest that mass transfer through the water and air films, which is assumed to be controlled entirely by molecular diffusion, is similar for acetone and TBA, with the acetone transferring slightly faster.

In the case of the overall volatilization coefficient, however, equilibrium considerations as expressed by the Henry's law constant, in addition to the molecular-diffusion considerations, are important. Table 13 shows that the Henry's law constant for acetone is 3.16 times larger than the constant for TBA at 298.2 K. Therefore, larger differences might be expected for the overall mass-transfer coefficients. Experimental overall mass-transfer coefficients for acetone from table 1 are plotted in figure 19 as a function of the overall mass-transfer coefficient

Table 13. Physical properties of acetone and t-butyl alcohol at 298.2 K

Compound	Molecular weight (g/g mol)	Water solubility (g/m^3)	Vapor pressure (kPa)	Molecular-diffusion coefficient × 10^4 (m^2/d)	Henry's law constant × 10^3 (kPa·m^3/g mol)
Acetone	58.08	∞	30.87	1.12	4.86
t-Butyl alcohol	74.12	∞	5.61	.755	1.54

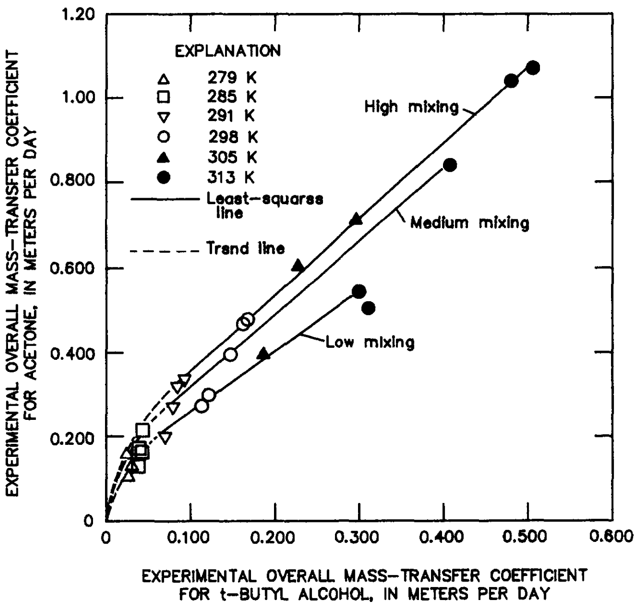

Figure 19. Experimental overall mass-transfer coefficients for acetone as a function of the experimental overall mass-transfer coefficient for t-butyl alcohol.

for TBA. The solid lines are least-squares fits of the data over the range for which a visual inspection suggested a linear relation between the coefficients. The dashed lines are trend lines in the region of very small coefficients. These lines were drawn on the basis of the several data points in this region as well as the requirement that the acetone coefficient must be zero when the TBA coefficient is zero.

Figure 19 shows that the overall mass-transfer coefficients for acetone are about two to four times larger than the coefficients for TBA, in contrast to the film coefficients for which the two substances have more similar values. Also, the difference in the mass-transfer coefficient increases as the mixing intensity in the water increases. These differences occur because of the relatively large difference in the Henry's law constants and the resultant difference in the distribution of the resistance between the two films.

Despite these differences, the TBA coefficients can still be used to estimate the overall mass transfer of acetone for comparison with experimental values. The procedure is to write the two-film model equation (eq. 8) for acetone and TBA, take a ratio, and substitute numerical values for the film-coefficient ratios from the ϕ and ψ values presented previously. The result is

$$K_{OL_{AC}} = (1.30)\left(K_{OL_{TBA}}\right)\left(H_{AC}/H_{TBA}\right)\left[\frac{\left(H_{TBA}\right)\left(k_{G_{TBA}}\right)/\left(k_{L_{TBA}}\right)+RT}{(1.08)\left(H_{AC}\right)\left(k_{G_{TBA}}\right)/\left(k_{L_{TBA}}\right)+1.20\,RT}\right], \qquad (81)$$

which expresses the overall mass-transfer coefficient for the volatilization of acetone in terms of the TBA coefficients and the Henry's law constants. Comparison of coefficients calculated from equation 81 with measured values for streams and rivers should theoretically indicate how much of the loss of acetone was the result of volatilization and how much was the result of bacterial degradation, assuming these are the only two processes affecting the fate of acetone.

Equation 81 was checked by applying it to the experimental data of this study. Overall mass-transfer coefficients for TBA were from table 1; liquid-film coefficients for TBA were from tables 6, 7, and 8; gas-film coefficients for TBA were from equation 57; and Henry's law constants were from equations 68 and 69. Overall mass-transfer coefficients for acetone, calculated from equation 81, are plotted in figure 20 as a function of the experimental coefficients from table 1. The rms error was ±7.24 percent. Figure 20 shows that equation 81 adequately predicts the overall mass-transfer coefficients for acetone over a wide range of water temperatures and mixing conditions.

However, in one respect, this is not a completely valid test of equation 81 because the numerical constants were determined from the same data used in evaluating the equation. In another respect, a fundamental assumption of the reference-substance concept is that the values of ϕ and ψ factors are independent of mixing conditions in the respective water and air phases. Therefore, from this assumption, equation 81 should be valid, whatever the conditions. This fundamental assumption of the reference-substance concept cannot at present be verified

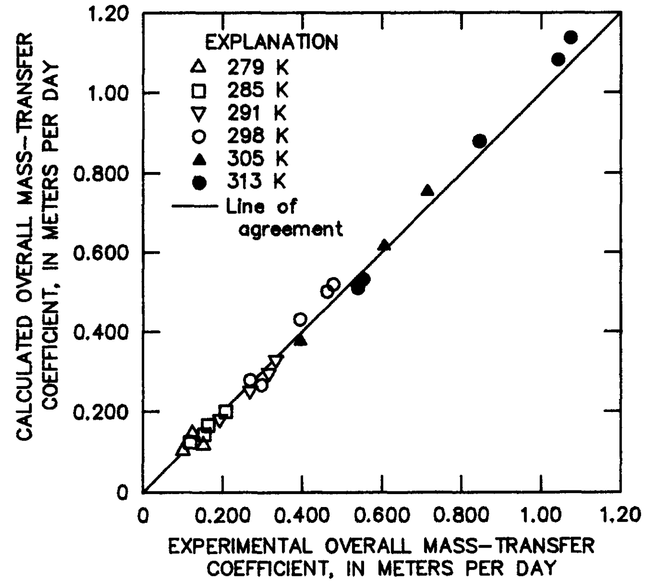

Figure 20. Calculated overall mass-transfer coefficients for acetone as a function of the experimental overall mass-transfer coefficient for acetone.

because liquid-film and gas-film coefficients for organic substances cannot be measured directly in streams and rivers.

Applicability of the Two-Film Model

Application of the two-film model and the concept of additivity of resistances is difficult because the film coefficients can be measured directly only under special limiting conditions. Previous applications of the model (Goodgame and Sherwood, 1954; Atlas and others, 1982; Mackay and others, 1982) assumed *a priori* that both the liquid-film and gas-film coefficients depended on the molecular-diffusion coefficient raised to some power. This assumption permitted direct empirical fits of experimental data (Mackay and others, 1982) or allowed adjustments of coefficients for solutes such as oxygen, carbon dioxide, and water to coefficients for other solutes (Goodgame and Sherwood, 1954; Atlas and others, 1982). These three solutes have Henry's law constants such that virtually all resistance to volatilization is in one film or the other. Thus, the liquid-film coefficients can be measured directly for oxygen and carbon dioxide, and the gas-film coefficient can be measured directly for water.

The present study eliminated the diffusion-coefficient assumption for the gas-film coefficient by measuring the gas-film coefficients directly. This procedure, in theory, should have permitted direct calculation of the liquid-film coefficient from the two-film model, measured values of the overall mass-transfer and gas-film coefficients, and estimated values of the Henry's law constant. However, the resultant liquid-film coefficients were negative for most of the medium- and high-mixing-condition experiments, and negative mass-transfer coefficients have no physical meaning. An alternative data analysis procedure assuming dependence of the liquid-film coefficient on the molecular-diffusion coefficient raised to the 0.50 power resulted in liquid-film coefficients within the range of values expected for the three mixing conditions considered.

Thus, this study and the three studies cited previously are not really tests of the two-film model but are, more correctly, tests of the concept of additivity of resistances. This concept is valuable, however, because it allows estimation of the significance of mixing conditions in the air and water phases for specific organic solutes. The significant factor is the Henry's law constant of the solute. Knowledge of this constant together with typical values of the liquid-film and gas-film coefficients permits qualitative estimation of which mixing conditions will have significant effects on the volatilization process.

The two-film model, however, provides no information on the magnitudes of the film coefficients. Therefore, the reference-substance concept is used to relate the liquid-film and gas-film coefficients for the organic substance to solutes for which these coefficients can be measured or estimated. The basis of the reference-substance concept is the assumption that solutes with similar values of the Henry's law constants will have similar values of the film coefficients and that the ratios of these coefficients will be independent of mixing conditions in the respective phases. The reference substances are also chosen so that information exists on the film coefficients for these substances for streams and rivers. Such information, together with the two-film model and the reference-substance concept, permits estimation of volatilization coefficients of organic substances for streams and rivers without having to physically introduce the organic substance into the stream or river. Such information is valuable to water-quality modelers who must estimate the effect of volatilization on the fate of organic substances discharged or accidentally spilled into streams and rivers.

The present study considered the volatilization of two hydrophilic solutes, acetone and TBA, from water for a low windspeed condition. Although some inconsistencies were found, apparently because of errors in the estimated Henry's law constants, we concluded that the concept of additivity of resistances as expressed by the two-film model was useful for these two solutes.

The present study, however, was limited almost exclusively to distilled water experiments. One experiment not discussed previously was conducted using water from a small outdoor model stream. This stream contained natural vegetation and organic detritus and was, in most respects, virtually identical to a natural stream. Procedures for this experiment were the same as those for the distilled water experiments discussed previously, with one difference. The oxygen absorption coefficient was not measured because of possible biological effects on the dissolved oxygen concentration. This experiment at a water temperature of 297.8 K and a stirrer *Re* number of 2.70×10^4 gave overall mass-transfer coefficients for the volatilization of acetone and TBA of 0.267 m/d and 0.108 m/d, respectively, in good agreement with results for distilled water experiments at a similar temperature and stirrer *Re* number (table 1).

The most likely cause for differences between laboratory and field mass-transfer coefficients is not a difference in water quality, but the presence of surface films on the natural water bodies. As mentioned previously, however, there has been little research on the effects of surface films. The study of these films is complicated by difficulties in sampling the films to determine chemical composition and difficulties in determining thicknesses of the films. Also, the composition is likely to be highly site specific.

The state of our knowledge of surface films was summarized by Mackay (1982). The general conclusion was that organic substances in natural waters accumulate at the interface in films which reduce volatilization. The extent of the reduction is dependent on the coherence of the film, its chemical composition and thickness, and the characteristics of the volatilizing substance. The reduction is the result of two effects. The first is the hydrodynamic effect, which is a damping of surface waves and turbulence as a result of changes in the physical properties of the water in the interfacial region. The second is the added resistance of the film to the molecular diffusion of the volatilizing substance through the interfacial region.

Mackay (1982) rationalized that the hydrodynamic effect is most likely to affect the gas-film resistance and that the surface-film-resistance effect will depend on the characteristics of the volatilizing substance. For substances with large values of the Henry's law constant such as oxygen and slightly soluble hydrocarbons and halogenated hydrocarbons, the surface-film resistance will likely be small because these substances are probably as soluble or more soluble in the surface-film material than they are in water. Therefore, the volatilization of these substances will most likely be retarded as a result of the hydrodynamic effect.

Conversely, for compounds with small values of the Henry's law constant such as acetone and TBA (considered in this study) and also water itself, the surface-film resistance may be large because the substances are as soluble or more soluble in the water than in the surface-film material. Therefore, the volatilization of these substances will be retarded as a result of both the hydrodynamic effect and the surface-film resistance. Mackay (1982) concluded his analysis with the suggestion that general predictions on the effects of surface films on volatilization cannot be made, except possibly to speculate that volatilization will usually be reduced. Additional research on surface films is needed.

The predictive equations developed in this study, such as equations 45, 70, 71, and 81, are for distilled water conditions. Because surface films on natural waters probably reduce volatilization, any coefficient predicted with these equations should be considered as an upper limit. The extent of the reduction as a result of a surface film cannot be estimated, as discussed previously. However, the importance of the coverage and coherence of the film on the surface has been emphasized (Mackay and others, 1982). Because the maintenance of a coherent film on the surface of a flowing stream or river would appear difficult, surface films will likely have less effect in streams and rivers than in other types of environmental waters.

SUMMARY AND CONCLUSIONS

Overall mass-transfer coefficients for the volatilization of acetone and t-butyl alcohol from water in a stirred constant-temperature bath were measured simultaneously with the oxygen absorption coefficient. Coefficients were measured for low, medium, and high water mixing conditions and for six water temperatures. A constant windspeed of about 0.1 m/s over the bath was used for all experiments. Gas-film coefficients for acetone, t-butyl alcohol, and water were determined by measuring the volatilization fluxes of the pure substances for a range of temperatures and a windspeed of about 0.1 m/s. These measured coefficients were combined with Henry's law constants estimated from literature data to apply the concept of additivity of resistances as expressed by the two-film model. Temperature dependencies of the various coefficients were determined. The relative volatilization characteristics of acetone and t-butyl alcohol were also determined. Finally, the results were combined with the reference-substance concept and the two-film model equation to develop an equation for estimating the volatilization coefficients of acetone and t-butyl alcohol for streams and rivers.

Specific conclusions resulting from this study are as follows:

1. Liquid-film coefficients for acetone and t-butyl alcohol calculated from the two-film model equation, measured values of the overall mass-transfer coefficients and gas-film coefficients, and Henry's law constants estimated from literature data were negative for most of the medium and high water mixing conditions. Negative film coefficients have no physical meaning, however.
2. An analysis of the errors involved in calculating liquid-film coefficients from measured values of the overall mass-transfer coefficients and gas-film coefficients and from estimated Henry's law constants showed that the calculated liquid-film coefficients were extremely sensitive to errors in the Henry's law constants for low windspeeds, where the gas-film resistance is large, such as was true in this study. We concluded that the negative liquid-film coefficients were the result of errors in the estimated Henry's law constants for acetone and t-butyl alcohol.
3. A correlation of the liquid-film coefficients for the absorption of oxygen by water with the stirrer Reynolds number and the Schmidt number predicted the experimental data with a normalized root-mean-square error of ±11.6 percent.
4. Liquid-film coefficients for acetone and t-butyl alcohol, predicted from the correlation for oxygen liquid-film coefficients by assuming a 0.50 power dependence on the molecular-diffusion coefficient, were within the range expected for the three water mixing conditions and showed the expected dependence on temperature.
5. Henry's law constants for acetone and t-butyl alcohol, calculated from the two-film model equation, the predicted liquid-film coefficients, and the measured overall mass-transfer and gas-film coefficients, were almost always larger than constants estimated from literature vapor-liquid equilibrium data, activity coefficient

data, vapor pressure data, and air-water partition coefficient data. Average differences for acetone were 29.6, 13.1, and 30.1 percent for the low, medium, and high mixing conditions, respectively. Average differences for t-butyl alcohol were 18.2, 16.3, and 29.4 percent for the low, medium, and high mixing conditions, respectively. These percentage differences were small relative to the errors reported in the literature as typical in the measurement or estimation of Henry's law constants for hydrophilic compounds such as ketones and alcohols. We concluded that the two-film model and the concept of additivity of resistances are useful for interpreting the volatilization of acetone and t-butyl alcohol from water.

6. The temperature dependences of the liquid-film coefficients for acetone and t-butyl alcohol were accurately predicted using functions of both the exponential of reciprocal absolute temperature and the exponential of the absolute temperature. Errors for the two types of temperature dependence were similar. Maximum normalized root-mean-square error of prediction was ±4.24 percent for the medium mixing condition for t-butyl alcohol for the absolute-temperature-dependence equation. The slopes of the two equations for both acetone and t-butyl alcohol were independent of water mixing conditions.

7. The temperature dependence of the liquid-film coefficients for oxygen were accurately predicted using the two equations of the same form as for acetone and t-butyl alcohol. Maximum normalized root-mean-square error of prediction was ±7.55 percent for the low mixing condition for the reciprocal-absolute-temperature-dependence equation. The values of the slopes of the predictive equations for the high mixing condition were significantly smaller than the values for the low and medium mixing conditions. This finding is in general agreement with the literature, which suggests that the temperature dependence of the process of oxygen absorption decreases as the mixing intensity increases. The value of the temperature coefficient for the high mixing condition was comparable to literature values; however, the values for the low and medium mixing conditions were higher.

8. The temperature dependence of the overall mass-transfer coefficients for the volatilization of acetone and t-butyl alcohol was adequately predicted empirically assuming a dependence on the exponential of the reciprocal absolute temperature. Maximum normalized root-mean-square error was ±7.98 percent for the high mixing condition for t-butyl alcohol. Combining the temperature dependences of the liquid-film and gas-film coefficients and the Henry's law constants with the two-film model equation resulted in predicted overall mass-transfer coefficients for acetone and t-butyl alcohol that generally scattered around the experimental data.

9. Percentage resistance in the gas film decreased as the temperature increased for all three mixing conditions for both acetone and t-butyl alcohol. This decrease was attributed to the fact that the Henry's law constant and gas-film coefficient product increased with temperature more rapidly than did the liquid-film coefficient and temperature product. Percentage resistance for a specific temperature increased as the mixing intensity increased because of the reduced liquid-film resistance.

10. Equations were derived for predicting the laboratory data by combining the two-film model equation with the Reynolds number-Schmidt number correlation for the liquid-film coefficient, and temperature-dependence equations for the molecular-diffusion coefficients, the Henry's law constant, and the gas-film coefficient. These derived equations predicted the acetone overall mass-transfer coefficient data with a normalized root-mean-square error of ±6.63 percent and t-butyl alcohol data with an error of ±7.57 percent.

11. Comparison of the liquid-film coefficient ratios showed that the liquid-film coefficient for acetone was, on the average, 20 percent larger than the liquid-film coefficient for t-butyl alcohol. Comparison of the gas-film coefficient ratios showed that the gas-film coefficient for acetone was, on the average, 8 percent larger than the gas-film coefficient for t-butyl alcohol. Overall mass-transfer coefficients for acetone, however, were, depending on water mixing conditions, about two to four times larger than the coefficients for t-butyl alcohol. The difference was the result of the fact that the Henry's law constant for acetone is about three times larger than the constant for t-butyl alcohol. Combining these ratios with the two-film model equation permitted development of an equation for predicting the overall mass-transfer coefficient for acetone as a function of the coefficients for t-butyl alcohol and the Henry's law constants.

12. Ratios of the liquid-film coefficients for acetone and t-butyl alcohol to the oxygen absorption coefficient were independent of water mixing conditions and temperature. Values of this ratio, ϕ, were 0.802 for acetone and 0.671 for t-butyl alcohol. Constancy of this ratio is the basis for the reference-substance concept for the liquid-film coefficient.

13. Ratios of the gas-film coefficients for acetone and t-butyl alcohol to the water volatilization coefficient were, for practical purposes, independent of temperature. Values of this ratio, ψ, were 0.490 for acetone and 0.452 for t-butyl alcohol. Constancy of this ratio is the basis for the reference-substance concept for the gas-film coefficient.

14. Values of the ratio, ϕ, estimated using the diffusion-coefficient procedure were 0.792 for acetone and 0.653 for t-butyl alcohol, in good agreement with the experimental values of 0.802 and 0.671. Values estimated using the molecular-weight procedure were 0.742 for acetone and 0.657 for t-butyl alcohol, also in good agreement

with the experimental values. We concluded that both estimation procedures gave adequate predictions of the experimental ϕ values for acetone and t-butyl alcohol.

15. Values of the ratio, ψ, estimated using the diffusion-coefficient procedure, were 0.607 for acetone and 0.531 for t-butyl alcohol. These values are 23.9 percent larger than the experimental value of 0.490 for acetone and 17.5 percent larger than the experimental value of 0.452 for t-butyl alcohol. Values estimated using the molecular-weight procedure were 0.557 for acetone and 0.493 for t-butyl alcohol. These values are 13.7 percent larger than the experimental value of 0.490 for acetone and 9.07 percent larger than the experimental value of 0.452 for t-butyl alcohol. We concluded that both estimation procedures gave adequate predictions of the experimental ψ values for acetone and t-butyl alcohol.

16. The constancy of the ϕ and ψ ratios for acetone and t-butyl alcohol was used to develop an equation for predicting volatilization coefficients for these solutes for streams and rivers. This equation was developed by combining in the two-film model equation the laboratory values of ϕ and ψ with the Henry's law constant and field values of the liquid-film coefficient for oxygen absorption and of the gas-film coefficient for water volatilization. Application of this equation permits determination of volatilization coefficients for acetone and t-butyl alcohol without having to physically introduce these substances into the stream or river.

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