Gas-Film Coefficients for the Volatilization of Ketones from Water

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SYMBOLS

Symbol	*Definition*
A	Cross-sectional area for volatilization, in square meters.
a_A	Pre-exponential constant in the equation relating the gas-film coefficient and temperature, in meters per day.
a_G	Constant in the equation relating the gas-film coefficient and the molecular diffusion coefficient, in meters per day.
a_w	Constant corresponding to the gas-film coefficient at zero windspeed, in meters per day.
B_1	Constant in the relation between boiling temperature and the logarithm of the ratio of the volatilization times for the compound of interest and the reference compound (Marwedel equation), in kelvins.
B_2	Pre-exponential constant in the relation between vapor pressure and boiling temperature (Marwedel equation), in kilopascals.
b_A	Exponential constant in the equation relating the gas-film coefficient and temperature, in reciprocal kelvins.
b_G	Constant in the equation relating the gas-film coefficient and molecular weight, in meters per day.
b_0	Constant in the regression of the volatilization flux as a function of vapor pressure, molecular weight, and temperature, in grams per minute per square meter.
b_w	Constant in the function relating the gas-film coefficient and windspeed, in meters per day per unit of windspeed in meters per second raised to the power c_w.
b_1	Exponent of vapor pressure in the regression of the volatilization flux as a function of vapor pressure, molecular weight, and temperature, dimensionless.
b_2	Exponent of molecular weight in the regression of the volatilization flux as a function of vapor pressure, molecular weight, and temperature, dimensionless.
b_3	Exponent of temperature in the regression of the volatilization flux as a function of vapor pressure, molecular weight, and temperature, dimensionless.
C_1	Dimension characteristic of the surface from which evaporation occurs (Dorsey factor), in millimeters.
C	Concentration in the bulk liquid phase, in gram moles per cubic meter.
C_E	Concentration in the bulk liquid phase in equilibrium with the bulk air phase, in gram moles per cubic meter.
C_i	Concentration in the liquid phase at the interface, in gram moles per cubic meter.
c_w	Exponent of windspeed in the function relating the gas-film coefficient and windspeed, dimensionless.
D_G	Molecular diffusion coefficient of the compound of interest in air, in square meters per day.
D_{GREF}	Molecular diffusion coefficient of the reference compound in air, in square meters per day.
d	Slope of the regression of the logarithm of the vapor pressure versus reciprocal absolute temperature, in kelvins.
f	Intercept of the regression of the logarithm of the vapor pressure versus reciprocal absolute temperature, in kilopascals.
H	Henry's law constant, in kilopascals cubic meter per gram mole.
Int	Intercept of the regression of the logarithm of the volatilization flux as a function of the logarithm of the vapor pressure, in grams per minute per square meter.

K_{OG}	Overall mass-transfer coefficient based on the gas phase, in meters per day.
K_{OL}	Overall mass-transfer coefficient based on the liquid phase, in meters per day.
k_G	Gas-film coefficient, in meters per day.
k_{GFIELD}	Gas-film coefficient for the compound of interest for a stream or river, in meters per day.
k_{GREF}	Gas-film coefficient for the reference compound, in meters per day.
$k_{GREF\ (FIELD)}$	Gas-film coefficient for the reference compound for a stream or river, in meters per day.
k_{GWATER}	Gas-film coefficient for the evaporation of water, in meters per day.
k_L	Liquid-film coefficient, in meters per day.
L_G	Thickness of the gas film, in millimeters.
log_e	Natural logarithm.
M	Molecular weight, in grams per gram mole.
N	Mass flux, in gram moles per day per square meter.
n	Index of the degree of mixing in the exponent of the molecular diffusion coefficient in the Pasquill equation, dimensionless.
P	Partial pressure in the bulk gas phase, in kilopascals.
P_E	Partial pressure in the bulk gas phase in equilibrium with the bulk liquid phase, in kilopascals.
P_i	Partial pressure in the gas phase at the interface, in kilopascals.
P_S	Vapor pressure, in kilopascals.
P_{S_T}	Vapor pressure at absolute temperature T, in kilopascals.
R	Ideal gas constant, in kilopascals cubic meter per gram mole per kelvin.
S_c	Schmidt number, equal to the viscosity divided by the product of the density and the molecular diffusion coefficient, dimensionless.
T	Absolute temperature, in kelvins.
T_{bp}	Normal boiling temperature, in kelvins.
T_{bpi}	Normal boiling temperature of compound i, in kelvins.
T_1	Temperature of the vapor pressure data correlated with normal boiling temperature, in kelvins.
t	Time, in minutes.
U	Windspeed, in meters per second.
U_*	Shear velocity, in meters per second.
W	Weight, in grams.
α	Ratio of the concentration at the liquid surface to the concentration in the bulk liquid phase (Chiou equation), dimensionless.
β	Evaporation coefficient dependent on atmospheric pressure and the rate of mixing in the air phase (Chiou equation), dimensionless.
ΔH_V	Heat of vaporization, in kilojoules per gram mole.
$\dfrac{\Delta W}{\Delta t}$	Volatilization rate, in grams per minute.
$\dfrac{\Delta W}{A\Delta t}$	Volatilization flux, in grams per minute per square meter.
$\left(\dfrac{\Delta t}{\Delta W}\right)_i$	Volatilization time for compound i, in minutes per gram.
$\left(\dfrac{\Delta t}{\Delta W}\right)_{REF}$	Volatilization time for the reference compound, in minutes per gram.

η	Exponent of the molecular diffusion coefficient in the relation between the gas-film coefficient and the molecular diffusion coefficient, dimensionless.
μ_G	Viscosity of the air, in grams per day per meter.
π	The constant 3.1416, dimensionless.
ρ_G	Density of the air, in grams per cubic meter.
ψ	Ratio of the gas-film coefficient for the compound of interest to the gas-film coefficient for a reference compound, dimensionless.

Conversion Factors

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

Multiply SI unit	By	To obtain inch-pound unit
millimeter (mm)	0.03937	inch (in.)
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)
square meter (m^2)	10.765	square foot (ft^2)
square meter per day (m^2/d)	10.765	square foot per day (ft^2/d)
gram (g)	0.002205	pound (lb)
gram per gram mole (g/g mol)	1.000	pound per pound mole (lb/lb mole)
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 cubic meter (g mol/m^3)	6.243×10^{-5}	pound mole per cubic foot (lb mol/ft^3)
gram per milliliter (g/mL)	62.43	pound per cubic foot (lb/ft^3)
minute per gram (min/g)	453.6	minute per pound (min/lb)
milliliter (mL)	2.642×10^{-4}	gallon (gal)
kilopascal (kPa)	101.325	standard atmosphere (atm)
kilopascal cubic meter per gram mole [kPa • m^3/(g mol)]	158.1	standard atmosphere cubic foot per pound mole (atm • ft^3/lb mol)
kilopascal cubic meter per gram mole kelvin [kPa • m^3/(g mol • K)]	87.83	standard atmosphere cubic foot per pound mole degree rankine [atm • ft^3/(lb mol • °R]
joule per gram mole kelvin [J/(g mol • K)]	60.19	calory per pound mole degree rankine [cal/(lb mol • °R)]
kilojoules per gram mole kelvin [kJ/(g mol • K)]	60.19	kilocalory per pound mole degree rankine [kcal/(lb mol • °R)]

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:
$$°F = (K - 273.15)(1.8) + 32.0$$

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

Abstract

Volatilization is a significant process in determining the fate of many organic compounds in streams and rivers. Quantifying this process requires knowledge of the mass-transfer coefficient from water, which is a function of the gas-film and liquid-film coefficients. The gas-film coefficient can be determined by measuring the flux for the volatilization of pure organic liquids.

Volatilization fluxes for acetone, 2-butanone, 2-pentanone, 3-pentanone, 4-methyl-2-pentanone, 2-heptanone, and 2-octanone were measured in the laboratory over a range of temperatures. Gas-film coefficients were then calculated from these fluxes and from vapor pressure data from the literature.

An equation was developed for predicting the volatilization flux of pure liquid ketones as a function of vapor pressure and molecular weight. Large deviations were found for acetone, and these were attributed to the possibility that acetone may be hydrogen bonded. A second equation for predicting the flux as a function of molecular weight and temperature resulted in large deviations for 4-methyl-2-pentanone. These deviations were attributed to the branched structure of this ketone.

Four factors based on the theory of volatilization and relating the volatilization flux or rate to the vapor pressure, molecular weight, temperature, and molecular diffusion coefficient were not constant as suggested by the literature. The factors generally increased with molecular weight and with temperature. Values for acetone corresponded to ketones with a larger molecular weight, and the acetone factors showed the greatest dependence on temperature. Both of these results are characteristic of compounds that are hydrogen bonded.

Relations from the literature commonly used for describing the dependence of the gas-film coefficient on molecular weight and molecular diffusion coefficient were not applicable to the ketone gas-film coefficients. The dependence on molecular weight and molecular diffusion coefficient was in general U-shaped with the largest coefficients observed for acetone, the next largest for 2-octanone, and the smallest for 2-pentanone and 3-pentanone.

The gas-film coefficient for acetone was much more dependent on temperature than were the coefficients for the other ketones. Such behavior is characteristic of hydrogen-bonded substances. Temperature dependencies of the other ketones were about twice the theoretical value, but were comparable to a literature value for water.

Ratios of the ketone gas-film coefficients to the gas-film coefficients for the evaporation of water were approximately constant for all the ketones except for acetone, whose values were considerably larger. The ratios increased with temperature; however, the increases were small except for acetone. These ratios can be combined with an equation from the literaure for predicting the gas-film coefficient for evaporation of water from a canal to predict the gas-film coefficients for the volatilization of ketones from streams and rivers.

INTRODUCTION

The fate of organic compounds in the waters of our environment is determined by the complex interactions of chemical, biological, and physical processes. Possible chemical processes include hydrolysis, photolysis, chemical reactions, and complexation with metal ions. Possible biological processes include microbial degradation and absorption by biota. Possible physical processes include convective mass transport, dispersion, sorption by sediments, and volatilization. Not all of these processes are important for all compounds in all situations. The relative importance of the various processes depends on the characteristics of both the organic compound and the water body of interest.

Many organic compounds have appreciable volatility, and therefore it is expected that volatilization is likely to be a significant process in determining their fate. Volatilization is the transfer of an organic compound from water across the water-air interface into the air. This process is commonly described by the two-film model of Lewis and Whitman (1924), which assumes uniformly mixed water and air phases separated by thin films of water and air in which mass transfer is by molecular diffusion. Equilibrium conditions are assumed at the interface between the phases, with the equilibrium usually expressed in terms of Henry's law.

The three parameters of the two-film model are the gas-film coefficient, the liquid-film coefficient, and the Henry's law constant. The film coefficients have different significances, depending on the characteristics of the organic compound. For volatile compounds with low solubility in water, it has been shown (Mackay, 1977; Mackay and others, 1979;

Smith and others, 1980; and Rathbun and Tai, 1982b) that virtually all resistance to volatilization is in the liquid film. Therefore, only the liquid-film coefficient is necessary for predicting the volatilization rates of these compounds. Conversely, for volatile compounds with appreciable solubility in water, it has been shown (Rathbun and Tai, 1982a) that the gas film also offers significant resistance to volatilization. Therefore, both film coefficients are necessary for predicting the volatilization rate of these compounds.

Much of the previous experimental research on the volatilization of organic compounds from water has been directed toward compounds for which the liquid-film resistance is dominant, as reported, for example, in the studies of Dilling and others (1975), Dilling (1977), Mackay and others, (1979), Smith and others (1980), Rathbun and Tai (1981, 1984a), and Roberts and Dandliker (1983).

Some studies have considered compounds for which the gas-film resistance is significant. These include Southworth (1979), Smith and Bomberger (1980), Smith and others (1981), and Rathbun and Tai (1982a). The present study is also concerned with the gas-film coefficient, with emphasis on measurements for acetone, 2-butanone, 2-pentanone, 3-pentanone, 4-methyl-2-pentanone, 2-heptanone, and 2-octanone. These compounds are a homologous series of straight-chain ketones, with the exception of 4-methyl-2-pentanone, which has a branched structure.

These ketones are solvents widely used for a variety of purposes. Acetone, 2-butanone, and 4-methyl-2-pentanone were among the 34 large-volume industrial solvents whose use was analyzed by Lee and others (1979). These authors concluded that 4-methyl-2-pentanone was one of the 12 solvents having a potentially high risk to man.

The widespread use of these ketones has resulted in their appearance in various waters of the environment. A survey of organic compounds in various types of waters showed that acetone was the compound most frequently found, and other ketones were also detected (Shackelford and Keith, 1976). A survey of trace organic compounds in the finished drinking waters of 10 cities in the United States showed that only acetone and chloroform were present in all the waters (Office of Toxic Substances, 1975). A number of ketones were found in the drinking water of Cincinnati, Ohio (Coleman and others, 1980). Ketones were found in environmental water, drinking water, and industrial effluent water samples (Nowicki and others, 1979), and in water effluents from oil shale processing procedures (Pellizzari and others, 1979). Acetone and 2-butanone were found in leachates from landfills (Khare and Dondero, 1977), and acetone may also be present in wastewaters from sewage treatment plants operated above optimum capacity, where it is formed as an intermediate decomposition product (Abrams and others, 1975). Under some conditions, acetone may be a precursor in the formation of chlorinated hydrocarbons during chlorination of drinking water supplies (Stevens and others, 1976). Acetone is also

apparently produced by some algae during their growth processes and during bacterial decay of algae mats (Adams and others, 1975). The biological significance of several ketones was summarized by Verschueren (1977).

The widespread occurrence of these ketones in the environment necessitates an understanding of their behavior in water. Because these compounds are volatile, volatilization is likely to be a significant process in determining their fate. This report presents the results of a study of the gas-film coefficients of seven ketones. These coefficients are necessary in predicting the volatilization rates of ketones from water.

THEORY

The Two-Film Model

A schematic representation of the two-film model (Lewis and Whitman, 1924) is shown in figure 1. A dynamic steady-state condition is assumed at the interface; therefore, the fluxes of the compound being transferred through the two films are the same. Writing a flux equation for each film and equating gives

$$N = \frac{k_G}{RT} (P_i - P) = k_L (C - C_i) \qquad (1)$$

where

N is the mass flux, in gram moles per day per square meter;

k_G is the gas-film coefficient, in meters per day;

k_L is the liquid-film coefficient, in meters per day;

P_i is the partial pressure of the compound in the gas phase at the interface, in kilopascals;

P is the partial pressure of the compound in the bulk gas phase, in kilopascals;
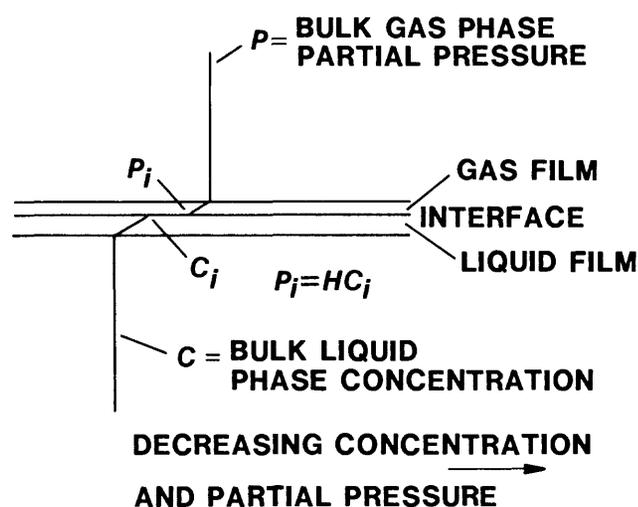
Figure 1. Schematic representation of the two-film model.

C is the concentration of the compound in the bulk liquid phase, in gram moles per cubic meter;

C_i is the concentration of the compound in the liquid phase at the interface, in gram moles per cubic meter;

T is the absolute temperature, in kelvins; and

R is the ideal gas constant, in kilopascals cubic meter per gram mole per kelvin.

Because the solutions of interest in environmental situations are almost always dilute, it follows that Henry's law is a valid representation of the assumed equilibrium conditions at the interface and also between the bulk properties. Therefore,

$$P_i = H C_i, \qquad (2)$$

and

$$P_E = H C, \qquad (3)$$

where H is the Henry's law constant (in kilopascals cubic meter per gram mole) and P_E is the partial pressure of the compound (in kilopascals) in equilibrium with the bulk liquid concentration C.

The interfacial concentration, C_i, and partial pressure, P_i, are difficult to measure and therefore the procedure followed in the two-film model is to rewrite the flux equations in terms of overall driving forces and overall mass-transfer coefficients. The result is

$$N = \frac{K_{OG}}{RT} (P_E - P) = K_{OL} (C - C_E), \qquad (4)$$

where C_E is the water concentration (in gram moles per cubic meter) in equilibrium with the partial pressure P, and K_{OG} and K_{OL} are the overall mass-transfer coefficients based on the gas and liquid phases, respectively (in meters per day).

By combining equation 1 with equations 2 and 3 and comparing the result with equation 4, it follows that

$$\frac{1}{K_{OG}} = \frac{1}{k_G} + \frac{H}{RTk_L} . \qquad (5)$$

Because the reciprocal of a transfer coefficient is the resistance to mass transfer, it can been seen that the left-hand side of equation 5 is the overall resistance to mass transfer and the two terms on the right-hand side are the resistances of the gas and liquid films, respectively. Therefore, it follows that

percentage resistance
in the gas film
$$= \frac{\dfrac{1}{k_G}}{\dfrac{1}{k_G} + \dfrac{H}{RTk_L}} \times 100 \qquad (6)$$

$$= \frac{100\,RT}{\dfrac{Hk_G}{k_L} + RT} . \qquad (7)$$

Equation 7 shows that the maximum percentage resistance in the gas film occurs when the k_G/k_L ratio is small, and conversely that the minimum resistance occurs when the k_G/k_L ratio is large.

Rathbun and Tai (1982b) selected on the basis of data from the literature three pairs of gas-film and liquid-film coefficients considered appropriate for streams and rivers of the United States. These coefficients were used with equation 7 and a temperature of 298.2 K to calculate the percentage resistance in the gas film as a function of the Henry's law constant, and the results are plotted in figure 2. The minimum gas-film coefficient was paired with the maximum liquid-film coefficient, and conversely the maximum gas-film coefficient with the minimum liquid-film coefficient, to obtain the maximum possible range of percentage resistances.

The results presented in figure 2 show that for the three pairs of coefficients, more than 90 percent of the resistance to volatilization is predicted to be in the liquid film for organic compounds with Henry's law constants between about 7×10^{-3} and 0.27 kPa • m³/g mol. A review of Henry's law constants in the literature (Mackay and Yuen, 1980; Mackay and Shiu, 1981) shows that there are numerous organic compounds having constants in this range or larger. Therefore, the liquid-film coefficient for the volatilization of these compounds from water can be determined directly by measuring the rate of change of concentration with time in the water.

The figure 2 results also show that for the three pairs of coefficients, more than 90 percent of the resistance to volatilization is predicted to be in the gas film for organic compounds with Henry's law constants between about 8×10^{-5} and 3.3×10^{-3} kPa • m³/g mol. There are, however, fewer organic compounds with Henry's law constants in this range (Mackay and Yuen, 1980). One reason is that because volatilization is less likely to be important for compounds in this range, the Henry's law constants have not been measured or calculated.

HENRY'S LAW CONSTANT, IN KILOPASCALS CUBIC METER PER GRAM MOLE
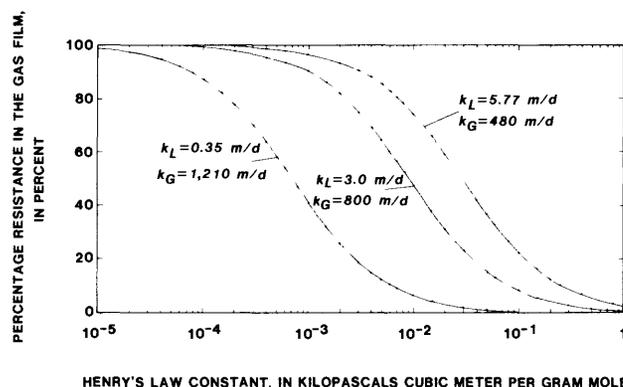
Figure 2. Percentage resistance in the gas film as a function of the Henry's law constant.

In the intermediate range of Henry's law constants, both films are predicted to have significant resistance to volatilization. Examples of compounds having Henry's law constants in this range are the seven ketones (acetone, 2-butanone, 2-pentanone, 3-pentanone, 4-methyl-2-pentanone, 2-heptanone, and 2-octanone) that are the subject of this study. Rathbun and Tai (1982a) estimated the Henry's law constants for these ketones to range from 4.10×10^{-3} kPa • m^3/g mol for acetone to 18.3×10^{-3} kPa • m^3/g mol for 2-octanone. The figure 2 results show that both films are predicted to have significant resistance to volatilization for these values of Henry's law constants.

The fact that both film resistances are significant complicates the measurement of the film mass-transfer coefficients because in general only an overall mass-transfer coefficient can be measured experimentally. One procedure is to determine the film coefficients indirectly from measurements of the overall coefficients for the ketone and oxygen, as described by Rathbun and Tai (1982a). The gas-film coefficient, however, in this procedure is calculated from the intercept of a correlation, and therefore extrapolation to the intercept could result in errors.

An alternative is to use the rationalization (Whitney and Vivian, 1949; Chiou and others, 1980) that there is no concentration gradient, and therefore no liquid-film resistance, in the volatilization of pure compounds. Thus, the gas-film coefficient can be calculated from measurements of the volatilization rates of pure compounds.

If $\Delta W/\Delta t$ is the volatilization rate (in grams per minute) and A is the cross-sectional area (in square meters) through which the volatilization is occurring, then

$$N = \frac{\Delta W}{A\Delta t} \frac{1440}{M},$$ (8)

where M is the molecular weight (in grams per gram mole) and 1440 is the number of minutes in a day. Combining equations 8 and 4 gives

$$K_{OG} = \frac{1440RT}{M} \frac{\Delta W}{A\Delta t} \left(\frac{1}{P_E - P}\right).$$ (9)

In the volatilization of a pure liquid, there is no liquid-film resistance and therefore it follows that the overall mass-transfer coefficient K_{OG} is identical to the gas-film coefficient k_G. Also, the equilibrium partial pressure P_E is the vapor pressure of the liquid P_S at the temperature of the liquid, and the partial pressure in the air phase is usually negligible relative to the vapor pressure. With these considerations, equation 9 becomes

$$k_G = \frac{1440RT}{MP_S} \frac{\Delta W}{A\Delta t},$$ (10)

which permits the gas-film coefficient to be calculated from measurements of the volatilization rate of a pure liquid and its vapor pressure, molecular weight, and temperature.

Fundamentals of the Volatilization Process

The molecules of a liquid are in continual motion, and those molecules near the surface with sufficient energy to overcome the attractive forces of the surrounding molecules can escape into the air phase, a process resulting in volatilization. If this process occurs into a closed volume, then an equilibrium will be established between the air and liquid phases, with the pressure in the air phase equal to the vapor pressure of the liquid at the temperature of the liquid. If this process occurs into an open volume large enough such that saturation with the vapor does not occur, then volatilization occurs until all the liquid has volatilized. The pressure exerted by the liquid during this process is the vapor pressure corresponding to the liquid temperature.

Application of the kinetic theory of gases and the ideal gas law (Glasstone, 1946) to the volatilization process gives

$$\Delta W/\Delta t = P_S A(M/2\pi RT)^{1/2} .$$ (11)

Equation 11 gives the rate at which gas molecules condense on the surface of the liquid and assumes that every molecule hitting the surface is retained. In some cases, an accommodation coefficient is added to the right-hand side of equation 11 to account for molecules that hit the surface and are not retained. Equation 11 also gives the rate at which molecules volatilize from the liquid surface, and this rate is the maximum rate possible when P_S is the vapor pressure.

Volatilization of a liquid requires input of heat because the average gas molecule has more thermal energy than the average liquid molecule. This energy is called the heat of vaporization, ΔH_V. In general, the higher the heat of vaporization, the stronger are the intermolecular forces of attraction (Mortimer, 1967). The most common method of estimating heats of vaporization is from vapor pressure data and the Clausius-Clapeyron equation (Reid and others, 1977).

Thermodynamic arguments (Glasstone, 1946) have suggested that the ratio of the heat of vaporization of a liquid and its normal boiling temperature should be approximately 96 J/(g mol • K). This generalization, known as Trouton's rule, has been found to be only approximately correct. For non-hydrogen-bonded liquids with a molecular weight of about 100 and a boiling temperature that is not too high, the Trouton constant is about 88 J/(g mol • K). For hydrogen-bonded liquids such as water and ethanol, the Trouton constant is 109 and 113 J/(g mol • K), respectively. Glasstone (1946) concluded that whenever there is regularity of structure or restriction to movement of the liquid molecules as a result of either hydrogen bonding or the shape of the molecules, then the increase in randomness or entropy during volatilization will be higher than normal. This is true for hydrogen-bonded liquids and long-chain molecules, and deviations from Trouton's rule should be expected for these substances.

Hydrogen Bonding

A hydrogen bond is formed when a hydrogen atom of a molecule acts as a proton donor and coordinates with an atom of another molecule that acts as an electron donor. This other atom is usually oxygen, and the oxygen atom may be in the same type of molecule or in a molecule of another compound in the mixture. The bond energy is usually only of the order of 10 to 15 kJ, but hydrogen bonding in many cases significantly affects the physical and chemical properties of compounds and mixtures of compounds. These differences in properties are often the result of the increase in molecular weight as a result of the hydrogen-bond formation. The hydrogen bond has been discussed in detail by Pimental and McClellan (1960).

Molecules have been divided into four classes depending on their ability to form hydrogen bonds (Pimental and McClellan, 1960). Class A includes compounds with sufficient halogens to activate the hydrogen to cause it to act as a proton donor. An example is chloroform. Class B compounds contain only an electron donor (usually oxygen, nitrogen, or fluorine). Examples are ketones, aldehydes, ethers, tertiary amines, esters, and olefins. Therefore, in theory, the molecules of these compounds can form hydrogen bonds only with other molecules containing a proton donor, not with each other. Class AB includes compounds with both proton donors and electron donors. Examples are water, alcohols, organic acids, and amines. The molecules of these compounds can form hydrogen bonds with each other and with molecules of class A and class B compounds. Class N includes compounds that cannot form hydrogen bonds. Examples are carbon tetrachloride, carbon disulfide, and saturated hydrocarbons. These are only general guidelines as to which types of compounds form hydrogen bonds. In some cases, steric hindrance as a result of molecular geometry may prevent the formation of hydrogen bonds when the guidelines suggest bonds should be formed.

Pimental and McClellan (1960) list a number of physical and chemical properties that may be modified as a result of hydrogen bonding. Among these are frequency shifts of the IR and Raman bands, freezing and boiling points, deviations from ideal gas and solution laws, dielectric properties, and electrical conductivities. In the case of very strong hydrogen bonds, the liquid and vapor densities, vapor pressure, solubility, molar volume, parachor, viscosity, and heat of vaporization may be modified also. Usually these properties are changed sufficiently to require special consideration for associated compounds in any correlation of behavior on the basis of molecular weight. Another physical property not discussed by Pimental and McClellan (1960) is the molecular diffusion coefficient, which as been shown by Anderson and others (1958) to depend strongly on the degree of hydrogen bonding.

Because ketones are placed in class B by Pimental and McClellan (1960), one would expect that ketone molecules

do not form hydrogen bonds with each other, and therefore that pure ketones are not hydrogen bonded. There is also other evidence (Pimental and McClellan, 1960) that ketones (in particular, acetone) are not hydrogen bonded.

However, there is also some evidence that acetone is hydrogen bonded. One observation is based on vapor-liquid equilibrium data for a binary system where the second component is a class N compound, which cannot form hydrogen bonds (for example, carbon tetrachloride or carbon disulfide). Ideal solution laws say that the total pressure above a binary solution of acetone and carbon tetrachloride should vary linearly with mole fraction between the vapor pressures of the pure components (Prutton and Maron, 1951), as shown by the dashed line in figure 3. Actual vapor pressure data (Brown and Smith, 1957) at 318.2 K vary as shown by the solid line in figure 3. Such positive deviations from the ideal solution behavior are characteristic of mixtures of classes AB and N compounds (Prutton and Maron, 1951); thus these results suggest that acetone molecules form hydrogen bonds with themselves. This suggestion is supported by the conclusion of Huyskens and Nauwelaerts (1980) that acetone has a significant dipole moment and can undergo self-association through a dipole-dipole interaction. One explanation for the behavior shown in figure 3 is that the dilution of the acetone by the carbon tetrachloride makes it more difficult for the acetone molecules to form hydrogen bonds with each other, which results in the increased vapor pressure.

A second observation is based on the molecular diffusion coefficient for a binary system where the second component is a class N compound (for example, the system of
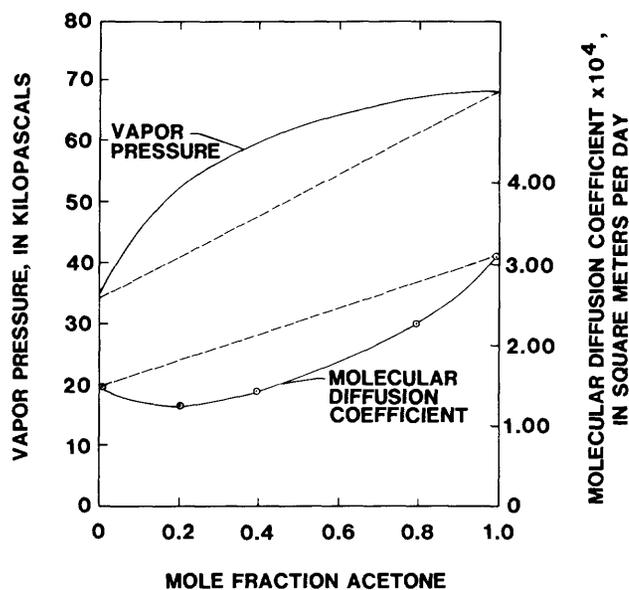
Figure 3. Vapor pressure and molecular diffusion coefficient as a function of the mole fraction of acetone for the system acetone–carbon tetrachloride.

acetone and carbon tetrachloride). Deviations from ideal behavior in this case should be the result of the characteristics of the acetone alone. Molecular diffusion coefficients from the literature (Anderson and others, 1958) for the system acetone-carbon tetrachloride are plotted in figure 3 as a function of the mole fraction of acetone. It was previously suggested (Caldwell and Babb, 1956) that the molecular diffusion coefficient in an ideal system should vary linearly with mole fraction between the molecular diffusion coefficients of each of the two components in infinitely dilute solutions. If this is true, then the acetone-carbon tetrachloride molecular diffusion coefficient should vary with mole fraction as shown by the dashed line in figure 3. Deviations from this ideal behavior are apparent.

Comparison of the relation shown in figure 3 with molecular diffusion coefficient data for the ethanol–carbon tetrachloride and methanol–carbon tetrachloride systems (Anderson and Babb, 1963) shows that the general shapes of the curves are similar, although the acetone system does not show nearly as much increase in the molecular diffusion coefficient in the dilute solution range as do the alcohol systems. This rapid increase was attributed (Anderson and Babb, 1963) to the diluting effect of the carbon tetrachloride on the hydrogen-bonded alcohols which resulted in smaller sizes and smaller numbers of the hydrogen-bonded species of the alcohols and correspondingly large diffusion coefficients. A similar explanation for the behavior of the acetone–carbon tetrachloride system seems logical, except that the acetone is less hydrogen bonded than the two alcohols. The results presented in figure 3 show definite deviations from ideal behavior, and hydrogen bonding seems to be a logical explanation.

Vapor pressure data (Fowler and Norris, 1955) at 323.2 K and molecular diffusion coefficient data at 298.2 K (Anderson and Babb, 1962) were also available for the system 2-butanone–carbon tetrachloride, and these data are presented in figure 4. Deviations from the ideal solution laws are similar to those for the acetone–carbon tetrachloride system, which suggests that the 2-butanone is also hydrogen bonded. Neither vapor pressure nor molecular diffusion coefficient data in binary systems with an inert component were available for the other ketones.

The discussion of hydrogen bonding of ketones was limited to a consideration of self-association, that is, hydrogen bonding of molecules to other molecules of the same kind. This limitation was imposed because pure ketones were the objective of study in this report for reasons discussed previously. In an environmental situation, however, the concentrations of interest will be very dilute solutions in water. Water is in the AB class, and thus water molecules can form hydrogen bonds with each other as well as with ketones. Anderson and others (1958) presented molecular diffusion coefficient data for the acetone-water system, and large deviations from the ideal linear dependence on mole fraction
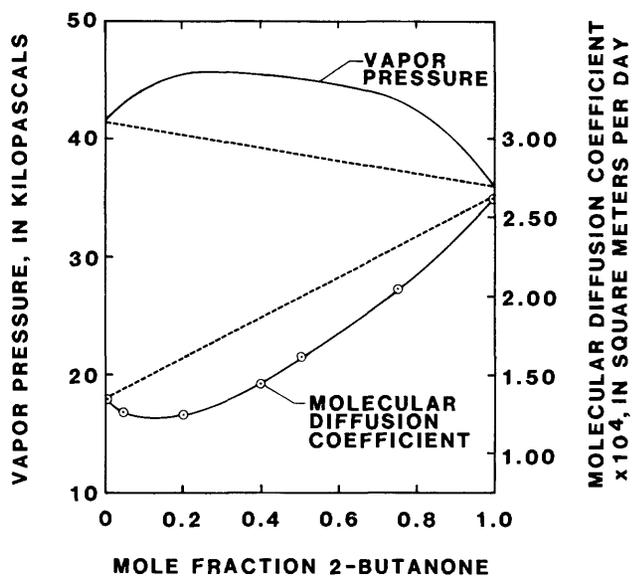
Figure 4. Vapor pressure and molecular diffusion coefficient as a function of the mole fraction of 2-butanone for the system 2-butanone–carbon tetrachloride.

were found. They concluded that the many possible molecular interactions in this system precluded a theoretical discussion of its behavior. Huyskens and Nauwelaerts (1980) studied solutions of acetone, 2-butanone, 2-pentanone, and 3-pentanone in water and concluded that most of the ketone molecules had formed hydrogen bonds with the water molecules. Thus, interpretation of the behavior of these ketones in the environment could be complicated by this bonding process.

VOLATILIZATION OF ORGANIC COMPOUNDS

The volatilization of organic compounds has been studied for a variety of reasons. These include the determination of the persistence of chemical warfare agents in the field (Hine, 1924) and of the drying times for lacquers and varnishes (Wade, 1942). Other studies have been concerned with the hydrodynamics underlying the volatilization process (Pasquill, 1943), the basic physical chemistry of the process (Marwedel and Hauser, 1948; Marwedel, 1950; 1953), and chemical engineering applications of volatilization (Powell and Griffiths, 1935). More recent studies have been concerned with environmental aspects, including volatilization of pesticides (Hartley, 1969) and of organic liquid pollutants from water (Chiou, 1980; Chiou and others, 1980; 1983). Details and results of these studies are briefly reviewed in the following sections.

Hine (1924)

Hine (1924) studied the evaporation of four organic solvents in a wind tunnel. His work was directed toward

testing the fundamental relation that the number of moles of a liquid volatilized per unit time from a specific area is proportional to the vapor pressure of the liquid and the windspeed.

Volatilization rates for chlorobenzene, m-xylene, nitrobenzene, and toluene were determined for a range of windspeeds. These rates were interpolated at specific windspeeds by assuming that the ratio of the volatilization rate to vapor pressure increased linearly with windspeed. Experimental errors resulted from variations in the windspeed and from uncertainties as to the exact liquid surface temperature in some experiments. It was concluded, with consideration of these errors, that there were no systematic deviations from the relation that the volatilization rate in moles per unit time was proportional to the vapor pressure.

Converting the mass rate to a mole rate results in the relation

$$\frac{\Delta W/\Delta t}{MP_S} = \text{constant}, \tag{12}$$

which is valid for a specific windspeed.

Wade (1942)

Wade (1942) studied the volatilization of six organic solvents and water in a small wind tunnel. Measurements with water, acetone, ethyl acetate, benzene, toluene, trichloroethylene, and carbon tetrachloride suggested that the evaporation rate was proportional to the molecular weight to the 0.71 power. It follows from the equation of Wade (1942) that the quantity $\Delta W/\Delta t/(P_S M^{0.71})$ should be a constant for a specific windspeed.

Dorsey (1940)

Dorsey (1940) reviewed various equations for predicting the evaporation rate of water. Using a diffusion approach and the perfect gas law, he developed the expression

$$\Delta W/\Delta t = C_1 D_G M P_S/RT, \tag{13}$$

where C_1 is a dimension characteristic of the surface from which evaporation is occurring and D_G is the molecular diffusion coefficient in air. For a series of compounds volatilizing from the same surface area under the same mixing conditions in the air, it follows from equation 13 that

$$\frac{(\Delta W/\Delta t)(RT)}{MP_S D_G} = C_1 = \text{constant}, \tag{14}$$

where the constant has dimensions of length.

Pasquill (1943)

Pasquill (1943) used a turbulent diffusion approach to the problem of volatilization from a flat liquid surface into a turbulent airstream. He concluded from this theoretical analysis that the relative volatilization rates should be proportional to the product of the molecular weight and the vapor pressure and inversely proportional to the temperature. He then checked this relation, using both his data on three organic liquids and water and the data of Wade (1942), and found large variations. In addition, he noted that the range of physical properties was much wider when water was included. This may explain why some of the earlier researchers [for example, Hine (1924)], who did not consider water, concluded that the volatilization rate was proportional to the product of the molecular weight and the vapor pressure. Pasquill (1943) also pointed out that there was no physical basis for the 0.71 power dependence on the molecular weight determined empirically by Wade (1942).

Pasquill (1943) then rationalized that the ultimate limiting process in the transport of mass is molecular diffusion. Modifying his approach, he developed the expression

$$\frac{(\Delta W/\Delta t)(RT)}{MP_S D_G^{2n/(2+n)}} = \text{constant}, \tag{15}$$

where n is an index of the degree of mixing in the air. An n value of 0.25 corresponds to the one-seventh power law–velocity profile. Equation 15 is valid for a specific windspeed. Pasquill (1943) concluded that adding the molecular diffusion coefficient factor as shown in equation 15 resulted in a more constant ratio than without this factor. The Pasquill factor is identical to the Dorsey factor except for the power dependence on the molecular diffusion coefficient.

Marwedel (1950, 1953) and Marwedel and Hauser (1948)

Marwedel (1950, 1953) and Marwedel and Hauser (1948) measured the volatilization rates of a number of organic liquids by determining the weight loss with time from a series of shallow glass dishes. They suggested the relations

$$T_{bp_i} = B_1 \log_e [(\Delta t/\Delta W)_i/(\Delta t/\Delta W)_{REF}]_T \tag{16}$$

and

$$\log_e P_{S_T} = \log_e B_2 - T_{bp}/B_1 \tag{17}$$

where T_{bp_i} is the normal boiling temperature of compound i (in kelvins); $\Delta t/\Delta W$ is the reciprocal of the volatilization rate, or the volatilization time (the time in minutes for 1.0 g to volatilize); P_{S_T} is the vapor pressure at absolute temperature T; B_1 and B_2 are constants for each homologous series of compounds; and the i and REF subscripts denote the compound of interest and a reference compound, respectively. Equations 16 and 17 are applicable to the specific temperature T (in kelvins). Marwedel used n-propanol as the reference compound.

Equations 16 and 17 show that the volatilization time $\Delta t/\Delta W$ can be predicted for any member of a homologous

series if vapor pressure data, the boiling temperatures, and a volatilization time for one member of the series are available. The equations must be applied at a specific temperature T. The volatilization time can then be used with equation 10 to calculate the gas-film coefficient.

Equation 17 is identical in form to the equation obtained by combining the Clausius-Clapeyron equation with Trouton's rule (Marwedel, 1950). Values of B_1 and B_2 calculated from this theoretical equation were in fair agreement with values determined from experimental data.

A similar equation was presented later by Mackay, Bobra, and others (1982). They concluded for a Trouton constant of 86.4 J/(g mol $\cdot$ K) that the slope of a logarithmic vapor pressure versus normal boiling temperature plot should be $-10.6/T_1$, where T_1 is the temperature (in kelvins) of the vapor pressure data. This relation has the form

$$\log_e P_S = -10.6 (T_{bp}/T_1 - 1). \tag{18}$$

Mackay, Bobra, and others (1982) proposed equation 18 as one means of estimating vapor pressure data as a function of boiling temperature. They suggested that if the slope deviates by more than about 10 percent from the value in equation 18, then the molecules of the compound should have exceptional properties.

Mackay, Shiu, and others (1982) also applied equation 18 to a series of compounds at a constant temperature of 298.2 K. In this case, equation 18 becomes identical in form to equation 17 proposed by Marwedel (1950, 1953) and Marwedel and Hauser (1948). The result is a linear relation between the logarithm of the vapor pressure at a specific temperature and the boiling temperature of a series of compounds.

Hartley (1969)

Hartley (1969) was interested in developing a method for measuring the volatilization losses of pesticides from soil surfaces. Because direct measurements of pesticide loss were inaccurate, he tried to develop a relation between the volatilization rates of pesticides and a reference compound, using water and several organic liquids as the reference compound. His development was based on the rationalization that the volatilization rate should be proportional to the product of the molecular diffusion coefficient of the compound in air and the saturation vapor concentration, which is proportional to the product of the vapor pressure P_S and the molecular weight M. Because Graham's law of diffusion suggests that the molecular diffusion coefficient is inversely proportional to the square root of the molecular weight, it follows that Hartley's relation has the form

$$\Delta W/\Delta t \propto P_S \sqrt{M}, \tag{19}$$

where $\Delta W/\Delta t$ is the volatilization rate. This is comparable to equation 11 if the temperature is constant.

Equation 19 suggests that the expression

$$\frac{\Delta W/\Delta t}{P_S \sqrt{M}} = \text{constant} \tag{20}$$

holds for all compounds under constant conditions of windspeed and temperature. Hartley (1969) found that the ratio was reasonably constant for the less volatile compounds, but that the ratios were smaller for the more volatile compounds. This difference was attributed to reduced volatilization rates as a result of the energy demands for volatilization, which were not provided for in the experimental apparatus. Hartley (1969) concluded that the volatilization rate could be predicted on the basis of equation 20 and vapor pressure data if data for a reference substance that is not too volatile are known for identical conditions.

The Knudsen Equation and the Modifications of Chiou and Others (1980, 1983)

The rate of volatilization of a liquid is dependent upon the escaping tendency of the liquid molecules, the diffusion of those molecules escaping the liquid through the air film at the surface, and the mixing of the molecules in the bulk air phase (Tinsley, 1979). Thermal effects may also be important because the system must supply the heat of vaporization for those molecules leaving the liquid. The most important factors, however, are the escaping tendency and diffusion. These have been combined to give the Knudsen equation for volatilization of a pure liquid into a vacuum. This equation has the form (Tinsley, 1979; Chiou and others, 1980)

$$\Delta W/\Delta t = AP_S (M/2\pi RT)^{1/2}, \tag{21}$$

where the escaping tendency is described by the vapor pressure P_S and diffusion is described by Graham's law which has the molecular diffusion coefficient inversely proportional to the square root of the molecular weight M. Equation 21 is identical to equation 11 obtained from the kinetic theory of gases and the ideal gas law.

Equation 21 was modified by Chiou and others (1980, 1983) to give the volatilization rate of a component from solution as

$$\Delta W/\Delta t = \alpha \beta AP_E (M/2\pi RT)^{1/2}, \tag{22}$$

where β is the evaporation coefficient dependent on the atmospheric pressure and the rate of mixing in the air phase, α is the ratio of the concentration at the liquid surface to the concentration in the bulk liquid phase, and P_E is the partial pressure of the component in equilibrium with the bulk liquid concentration.

The parameter β has a maximum of unity for volatilization into a vacuum, and therefore it will be less than unity for

environmental situations. In effect, $1/\beta$ is the resistance factor for the air phase with respect to a vacuum, and $1/\alpha\beta$ is the total resistance for the system. Chiou and others (1980) measured β for a number of pure compounds and concluded that the average value for still air was 1.98×10^{-5} with a standard deviation of 9 percent. Most of these measurements were at temperatures between 296.2 and 298.2 K; however, five measurements were at 276.7 K. It was concluded on the basis of these limited data that β was practically independent of temperature for this temperature range.

The parameter α is unity for pure substances because no concentration gradient can exist. Also, the equilibrium pressure P_E for pure substances becomes the vapor pressure P_S. For dilute aqueous solutions, α depends on the Henry's law constant and the degree of mixing in the water phase (Chiou and others, 1980).

THE GAS-FILM COEFFICIENT

The gas-film coefficient k_G is the mass transfer coefficient for the transport of compounds through the air film of the two-film model (Lewis and Whitman, 1924). Because all the resistance to the volatilization of pure liquids is in the air film and because considerable data exist on the volatilization, or evaporation, of water, the mass transfer coefficient for the volatilization of water $k_{G_{WATER}}$ is often used as a basis for estimating the gas-film coefficients for volatilization of organic compounds from water (Liss and Slater, 1974; Rathbun and Tai, 1983). This requires some means of adjusting the coefficients for water to the coefficients for the organic compounds. These adjustment procedures are usually based on the molecular diffusion coefficient or the molecular weight (Rathbun and Tai, 1983). The dependence of the gas-film coefficient on the molecular diffusion coefficient and the molecular weight are discussed in the following sections. Also discussed are the dependencies of the gas-film coefficient on temperature and windspeed.

Dependence on Molecular Weight

The gas-film coefficient k_G is generally assumed to depend on molecular weight (Liss and Slater, 1974; Rathbun and Tai, 1983) according to

$$k_G = b_G M^{-0.5}, \tag{23}$$

where b_G is a constant. This equation is based on Graham's law of diffusion, which assumes that the molecular diffusion coefficient D_G is proportional to $M^{-0.5}$. Therefore, this adjustment procedure inherently assumes $k_G \propto D_G^{1.0}$, which is contrary to much of the experimental data in the literature (Tamir and Merchuk, 1978). Also, doubts exist (Rathbun and Tai, 1983) about the application of Graham's law to the gas film of the two-film model, and the molecular diffusion coefficient depends on the molecular arrangement or cross-sectional area, not just on the weight of the molecule (Mackay, Shiu, and others, 1982). Despite these questions, equation 23 has been widely used (Liss and Slater, 1974; Mackay and Leinonen, 1975; Dilling, 1977; Southworth, 1979; Thibodeaux, 1979), probably because of the ready availability of molecular weights.

Dependence on Molecular Diffusion Coefficient

The gas-film coefficient k_G is generally assumed to depend on the molecular diffusion coefficient according to

$$k_G = a_G D_G^n, \tag{24}$$

where a_G is a constant, D_G is the molecular diffusion coefficient of the compound in air, and n is a coefficient. The value of n depends on the model. The two-film model (Lewis and Whitman, 1924) suggests that n is 1.0, the penetration model (Danckwerts, 1951) estimates that n is 0.5, and the film-penetration model (Dobbins, 1964) gives a range for n varying from 0.5 for high mixing conditions to 1.0 for low mixing conditions. A heat transfer–mass transfer analogy (Sherwood and Pigford, 1952) suggests that n is 0.667. Tamir and Merchuk (1978) reviewed experimental determinations of n and found values between 0.15 and 1.0. They conducted their own experiments covering an 18-fold variation in the molecular diffusion coefficient and obtained a best-fit value of 0.684 for a number of different substances, including six organic liquids and water. They later (Tamir and others, 1979) revised this value to 0.632, stating that this value was appropriate for low concentrations where bulk motion was negligible, such as in environmental systems. For volatilization of pure liquids, bulk motion is likely to be significant (that is, mass-transfer rates are relatively large). Therefore, 0.684 should be used for n.

Mackay and Yeun (1983) suggested on the basis of the chemical engineering literature that the difference between molecular properties of various compounds should be adjusted by using the Schmidt number to the -0.67 power. The Schmidt number is equal to the viscosity μ_G divided by the product of the molecular diffusion coefficient D_G and the density ρ_G or

$$S_c = \mu_G / D_G \rho_G. \tag{25}$$

It follows, therefore, that the gas-film coefficient is proportional to the molecular diffusion coefficient to the 0.67 power, in general agreement with the experimental results of Tamir and Merchuk (1978). Mackay and Yeun (1983) used this relation in correlating their laboratory data with other laboratory data and limited field data, and the results were satisfactory.

Dependence on Temperature

A basic equation (Liss and Slater, 1974) of the two-film model is

$$k_G = D_G/L_G, \qquad (26)$$

where L_G is the thickness of the gas film. Equation 26 results from the assumption that mass transport in the air film is entirely by molecular diffusion.

Temperature affects the gas-film coefficient through its effect on both the molecular diffusion coefficient and the physical properties of air that contribute to the determination of the film thickness. It has been suggested (Haslam and others, 1924) that

$$L_G \propto \left(\frac{\mu_G}{\rho_G}\right)^{2/3}, \qquad (27)$$

where μ_G and ρ_G are the viscosity and density of the air, respectively. For gases, μ_G/ρ_G increases (Haslam and others, 1924) as the temperature increases, and thus L_G also increases as the temperature increases. Various correlations (Reid and others, 1977) for predicting the molecular diffusion coefficient of gases have the coefficient depending on temperature to the 1.5 to 2.0 power. Thus, combining equations 26 and 27 suggests that the temperature dependence of the gas-film coefficient will depend on the relative magnitudes of the dependencies of the molecular diffusion coefficient and the film thickness on temperature. It seems likely, however, that since both factors increase with temperature, the effects will tend to cancel and thus will result in little temperature dependence of the gas-film coefficient.

A similar conclusion was reached by Mackay, Shiu, and others (1982) on the basis of an analysis of the Schmidt number. They suggested that the viscosity of equation 25 varied with the 0.5 power of temperature, the density with the -1.0 power, and the diffusion coefficient with the 1.5 power, which results in no predicted dependence of the Schmidt number on temperature. Because the gas-film coefficient was assumed proportional to the Schmidt number to the -0.67 power in their correlations, this in turn suggests no dependence of the gas-film coefficient on temperature.

Models other than the two-film model predict a fractional dependence of the gas-film coefficient on the molecular diffusion coefficient, as shown by equation 24. If the experimental value of 0.632 (Tamir and others, 1979) is used for η and if 1.75 is used as the average power dependence on temperature of the molecular diffusion coefficient (Reid and others, 1977), then the result is a temperature dependence of about 0.4 percent/K.

Rathbun and Tai (1983) determined the temperature dependence of the gas-film coefficient for the evaporation of water in a laboratory study covering the temperature range from 291.2 to 321.2 K. The gas-film coefficient increased

0.94 percent/K, which suggests that the effect of temperature on the molecular diffusion coefficient was greater than the effect on the other physical properties of the film. Upper and lower confidence limits at the 95-percent level for this value were 1.06 percent and 0.82 percent, respectively, which indicates a fairly large amount of scatter in the data. This larger-than-expected temperature dependence could be the result of a temperature effect on the degree of hydrogen bonding and its resultant effect on the molecular diffusion coefficient. This point is discussed in more detail later.

Dependence on Windspeed

The uniformly mixed air and water phases of the two-film model (Lewis and Whitman, 1924) result from mixing caused by turbulence in the air and water. This mixing also determines the thickness of the air and water films and thereby the magnitudes of the gas-film and liquid-film mass-transfer coefficients.

Turbulence basically results from two processes. In streams and rivers, turbulence in the water is caused by shear at the bottom and on the banks of the channel, and turbulence in the air results from wind effects. In lakes and ponds, turbulence in both the water and the air largely occurs as a result of wind effects. There is no sharp division between the types of water bodies, however. In deep, sluggish rivers, the effect of wind on mixing in the water may be much more significant than the effect of the bottom and the bank shear forces.

There is also no sharp division between the air and water phases, in that turbulence in one phase may affect the film coefficient for the other phase. For example, it is generally accepted (Rathbun and Tai, 1982a) that virtually all the resistance to the absorption of oxygen by water is in the liquid film. However, it is also well known (Rathbun, 1977) that wind significantly increases the oxygen absorption coefficient, which suggests that turbulence in the air has some effect on the liquid-film thickness. Conversely, a laboratory study (Rathbun and Tai, 1983) of the evaporation of water showed, with one exception, that the gas-film coefficient did not depend on mixing conditions in the water. In the exception, the effect of mixing in the water was statistically significant at the 5-percent level; however, the actual differences were less than 5 percent. It was concluded that there might be a slight dependence of the gas-film coefficient on mixing conditions in the water. This conclusion is consistent with the observation of Jobson (1980) that the evaporation rate in a canal is larger than in a lake for low windspeeds.

In general, the gas-film coefficient depends largely on mixing conditions in the air, and these conditions are usually characterized by the windspeed. There have been several studies of the effect of wind on the gas-film coefficient, and all of these have been based on the evaporation of water. Laboratory studies included those by Liss (1973) and

Mackay, Shiu, and others (1982). Liss (1973) obtained seven gas-film coefficients in a wind-water tunnel for windspeeds ranging from 1.6 to 8.2 m/s. Mackay, Shiu, and others (1982) obtained six gas-film coefficients in a wind-wave tank for windspeeds ranging from 5.96 to 13.2 m/s. These laboratory gas-film coefficients are plotted as a function of windspeed in figure 5.

Also shown in figure 5 are limited data for the ocean. These include seven values from Sverdrup (1937) and one value from the study of Pond and others (1971), as reported by Mackay, Shiu, and others (1982). In addition, lines are displayed in figure 5 for three predictive equations, the laboratory and field equations of Mackay, Shiu, and others (1982) and the equation of Rathbun and Tai (1983). Mackay, Shiu, and others (1982) developed their equations on the basis of their laboratory water evaporation data, which showed that the ratio of the gas-film coefficient k_G to the wind shear velocity U_* was reasonably constant. This ratio (k_G/U_*) was then assumed to be proportional to the Schmidt number to the -0.67 power, largely on the basis of the form of mass-transfer correlations from the chemical engineering literature. For the laboratory equation, the wind shear velocity was related to the windspeed through a drag coefficient correlation. For the field equation, the drag coefficient equation of Smith (1980) was used to relate the shear velocity and the windspeed. The equation of Rathbun and Tai (1983) was based on water evaporation data for a canal in southern California (Jobson and Sturrock, 1979; Jobson, 1980).

The results presented in figure 5 show, except at low windspeeds, that both the experimental and predicted laboratory coefficients are larger than the field coefficients. The two field equations agree reasonably well, although the Rathbun and Tai (1983) equation gives larger coefficients for windspeeds less than about 10 m/s and smaller coefficients above this windspeed. The field equation of Mackay, Shiu, and others (1982) was based on a drag coefficient relation for lakes and oceans, whereas the equation of Rathbun and Tai (1983) was based on evaporation data for a canal. Thus, the larger coefficients at low windspeeds for the latter equation are consistent with the conclusion of Jobson (1980) that evaporation rates at low windspeeds are larger in canals than in lakes.
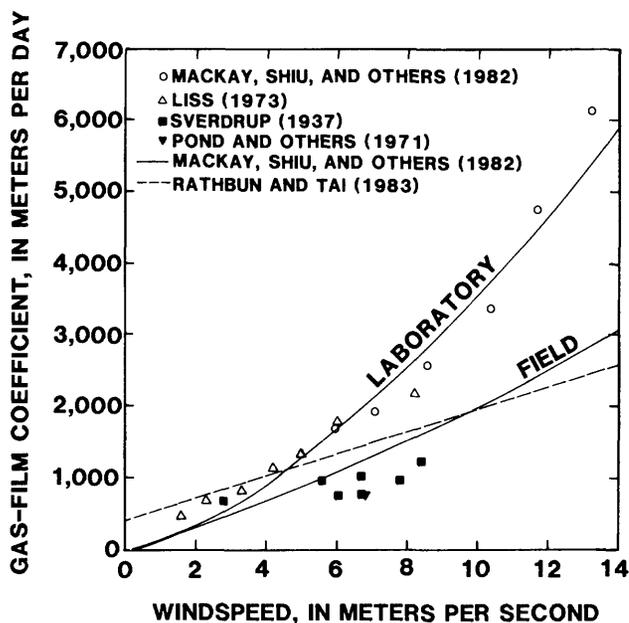
A significant difference between the equations is the behavior at zero windspeed. The Rathbun and Tai (1983) equation predicts a coefficient of 416 m/d, whereas both of the equations of Mackay, Shiu, and others (1982) predict a coefficient of zero at zero windspeed. Both the laboratory and field experimental data shown in figure 5 suggest a coefficient at zero windspeed significantly larger than zero, however. To test this suggestion, both the laboratory and field data were fit to a function of the form $a_w + b_w U^{c_w}$, where a_w is a constant corresponding to the gas-film coefficient at zero windspeed, b_w and c_w are constants, and U is the windspeed in meters per second. Both a nonlinear least squares procedure and a linear least squares procedure with U^{c_w} as the independent variable were used. In the linear procedure, the constant c_w was varied for each calculation until the root-mean-square error of prediction was minimized. Identical results were obtained for the two regression procedures.

For the laboratory data, the best-fit value of a_w was 655 m/d with 95-percent confidence limits of $\pm$ 154 m/d. Because the two highest laboratory data points seemed to deviate considerably from the general trend of the other points, these two points were excluded and the regressions recomputed. The best fit value of a_w was then 331 m/d with 95-percent confidence limits of $\pm$ 141 m/d. For the limited field data, the best fit value of a_w was 802 m/d with 95-percent confidence limits of $\pm$ 126 m/d. Thus, in each case, the constant a_w was significantly different from zero at the 95-percent level of significance. The values were also comparable to the 416 m/d value of the Rathbun and Tai (1983) equation.

Mackay and Yeun (1983) concluded on the basis of a review of the literature that the best estimate of the gas-film coefficient for zero windspeed is 86 $\pm$ 43 m/d. Using the Fuller and others (1966) procedure, as described by Reid and others (1977), the estimated molecular diffusion coefficient for water in air is 2.18 m^2/d at 298.2 K. If this value is used in equation 26, it leads to gas-film thicknesses of 25 and 5.2 mm, respectively, for the Mackay and Yeun (1983) and Rathbun and Tai (1983) estimates of the gas-film coefficient at zero windspeed. Film thicknesses for the best-fit values of the gas-film coefficients at zero windspeed from the regression analysis of the data in figure 5 were 3.3 and 6.6 mm for the two treatments of the laboratory data and 2.7 mm for the field data.

Figure 5. Gas-film coefficient as a function of windspeed.

There are other limited data in the literature. Wolff and van der Heijde (1982) obtained a gas-film thickness of 120 mm, a value that would seem to be too large. Correlating Sverdrup's data (1937) for film thickness with windspeed and extrapolating to zero gives thicknesses of 4.4 and 4.0 mm for a rough and a smooth ocean surface, respectively. The available evidence suggests, therefore, that gas-film thicknesses at zero windspeed range between 3 and 25 mm. Scatter in the results undoubtedly occurs because of the difficulty of producing perfect no-wind conditions (that is, transport solely by molecular diffusion). The slightest deviation from this condition results in greatly increased transport rates.

Predicting Gas-Film Coefficients for Streams

A procedure for predicting the gas-film coefficient for the volatilization of organic compounds from streams and rivers can be developed from equation 24. Writing this equation for the compound of interest and a reference compound and taking ratios gives

$$k_G/k_{G_{REF}} = (D_G/D_{G\ REF})^n = \psi \qquad (28)$$

where ψ is a constant independent of turbulence conditions. If k_G and $k_{G_{REF}}$ are measured under identical conditions (for example, in the laboratory to determine ψ), then the assumption is that the same value of ψ applies under all conditions (for example, in a stream or river). Therefore, it follows that

$$k_{G_{FIELD}} = \psi k_{G_{REF}\ (FIELD)}, \qquad (29)$$

where $k_{G_{FIELD}}$ is the gas-film coefficient for the volatilization of the compound of interest from a stream or river, ψ is the constant determined under controlled laboratory conditions, and $k_{G_{REF}\ (FIELD)}$ is the gas-film coefficient for the volatilization of the reference compound under field conditions.

It is convenient to use water as the reference compound for several reasons discussed previously. To reiterate, water is one of the few compounds for which all the resistance to volatilization is in the gas film. Also, field data exist on the gas-film coefficient for the volatilization of water, and in particular an equation (Rathbun and Tai, 1983) exists for predicting the gas-film coefficient as a function of windspeed for a canal. Flow conditions in the canal were considered a reasonable approximation of flow conditions in streams and rivers, so that this equation can then be used in conjunction with equation 29 and laboratory-determined values of ψ to predict gas-film coefficients for the volatilization of organic compounds from streams and rivers.

DESCRIPTION OF APPARATUS

Volatilization rates were measured in the apparatus shown in figure 6. The apparatus was a two-chamber system,
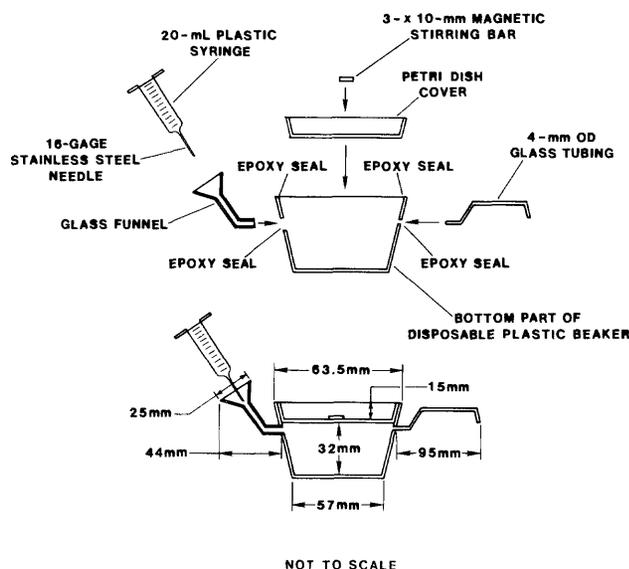
Figure 6. Apparatus for volatilization measurements: Top, components of the apparatus; Bottom, assembled apparatus.

with the top serving as the volatilization chamber and the bottom serving as the temperature-control part of the system. This bottom chamber supplied the heat of vaporization of the volatile organic liquids so that the volatilization rate could be measured at a constant temperature.

A cover glass for a 60- X 15-mm petri dish was used as the top chamber. The bottom part of a disposable plastic beaker, cut so that the petri dish cover fit into it, was used as the bottom chamber. The two chambers were sealed together with epoxy. An inlet to the bottom chamber was constructed from a 25-mm-diameter glass funnel. An outlet from the bottom chamber was constructed from a piece of 4-mm OD glass tubing, as shown in figure 6. The inlet and outlet were positioned just below the level of the bottom of the top chamber. They were attached to the bottom chamber with epoxy.

Temperature control was obtained by pumping water from the reservoir of a constant-temperature bath through the bottom chamber at a constant rate using an FMI[1] positive displacement metering pump powered by a 12-V battery. The water was pumped from the bath into a head device consisting of the body of a 20-mL disposable plastic syringe and a 16-gage stainless-steel needle, as shown in figure 6. The end of the needle was positioned in the top of the funnel just above the water surface. Flow through the bottom chamber was controlled by varying the output of the pump and by varying the elevation of the discharge point of the chamber outlet by attaching short pieces of plastic tubing of different lengths.

These two factors were adjusted so that the bottom chamber and the drain line were full and the funnel was about half-full. This insured a constant weight of water in the system during an experiment. The water was collected in an aspirator bottle and then discharged to a drain. Tygon lines between the water bath and the pump and between the pump and the head device were covered with fiberglass insulation to minimize heat transfer.

The volatilization apparatus was placed on a small magnetic stirrer that was located on an Ohaus model 1500 D electronic balance. This system was placed in a fume hood with a rated face velocity of 38 m/min. Figure 7 shows schematically the arrangement of the equipment. Placing the system in a fume hood allowed the volatilized compounds to be removed and ensured that the partial pressure in the air above the volatilization chamber was negligibly small with respect to the vapor pressure. This was one of the assumptions in the development of equation 10 presented previously. The type of airflow produced by the fume hood, however, did not permit measurement of the windspeed over the volatilization chamber, as is done in some studies.

The temperature of the liquid in the volatilization chamber was measured with a digital thermometer with a liquid thermistor probe. This thermometer was calibrated at the beginning of each day with a mercury thermometer with 0.1-K divisions. Air temperature in the room immediately in front of the hood was measured with the mercury thermometer.

PROCEDURE FOR THE EXPERIMENTS

The procedure used for the experiments consisted of measuring the weight of organic liquid in the volatilization chamber as a function of time. The first step was to start the waterflow through the bottom chamber and to allow the system to equilibrate, as determined by the weight indicated by the balance. The balance had four options with respect to the averaging time period used for determining the weight. An intermediate time period was used in this study. Once equilibrium was established, the balance was tared to zero.

The next step was to add the organic liquid to the volatilization chamber with a pipet and to allow the system to equilibrate with respect to temperature as indicated by the digital thermometer. In some experiments with the more volatile compounds and (or) high temperatures, it was necessary to make small extra additions of the compound because it was desired to have the volatilization chamber nearly full at the beginning of data collection. After the temperature had stabilized, data collection was initiated. This consisted of recording the balance reading and the compound temperature at fixed intervals of time together with auxiliary data such as the air temperature, the water temperature in the circulator bath, and the water level in the syringe of the head device.

The time interval between balance readings was such that a minimum of about 1.0 g of the compound volatilized between readings, and an experiment usually consisted of 10
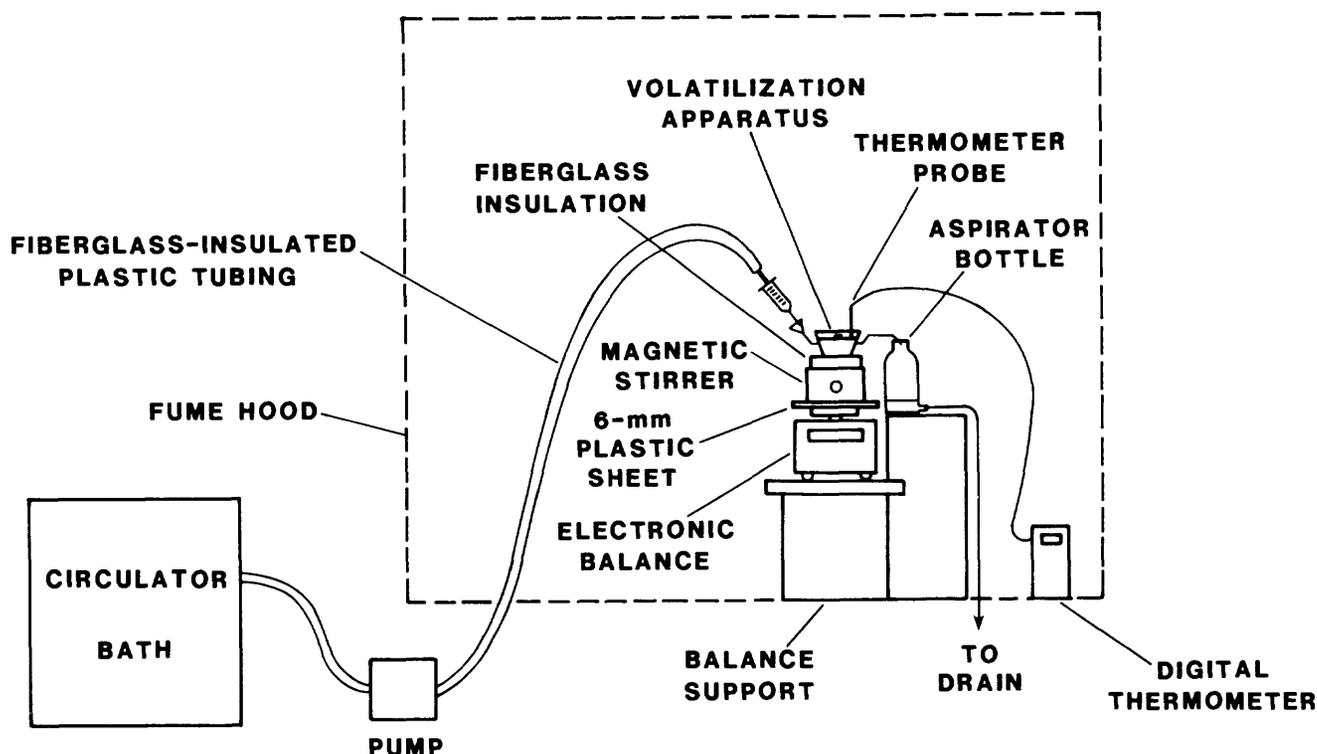

Figure 7. The volatilization apparatus and auxiliary equipment.

readings. About half the compound in the chamber vol-
atilized during an experiment. Exceptions to this procedure
were several experiments for 2-heptanone and 2-octanone at
low temperatures, where volatilization rates were low. Time
intervals ranged from 1.0 min for acetone experiments at high
temperatures to about 4 h for 2-octanone experiments at low
temperatures. Two experiments were usually done at each
condition, with the exception of several of the low volatiliza-
tion rate conditions.

The compound in the volatilization chamber was stirred
with a 3-mm-diameter by 10-mm-long Teflon stirring bar.
The stirring rate was about 350 r/min (revolutions per minute)
for all experiments. This stirring rate caused a visible disturb-
ance of the liquid surface, but a vortex was not formed.
Therefore, the stirring was assumed to have negligible effect
on the area for volatilization, and the cross-sectional area of
the volatilization chamber was used for A in equation 10. This
area was 2.71×10^{-3} m^2, as computed from the diameter of
the chamber measured using calipers and a scale.

The temperature of the compound in the volatilization
chamber was generally constant within ± 0.5 K of the aver-
age temperature during an experiment. This temperature,
however, could be predetermined only approximately. It
depended on a combination of the temperature of the water
being pumped through the bottom chamber and the vol-
atilization characteristics of the compound being studied.
The pumping rate of the water and the room temperature may
also have had some effect. The water temperature in the
constant-temperature bath could be varied between 274.2 and
344.2 K. It was this temperature range and the volatilization
characteristics of each compound that determined the tem-
perature range that could be studied for each ketone using the
apparatus shown in figures 6 and 7.

The volatilization rate $\Delta W/\Delta t$ was determined as the
slope of a least-squares fit of the weight versus time data.
Examples of the data from a high volatilization rate experi-
ment and a low volatilization rate experiment are shown in
figure 8. Volatilization rates determined in this way were
converted to volatilization fluxes $\Delta W/A\Delta t$ by dividing by the
area A for volatilization. The temperature was the arithmetic
average of the temperatures observed during an experiment.

Several problems with respect to the experimental pro-
cedure were of concern in this study. First was the drop in
temperature that occurs when an organic liquid volatilizes. To
measure volatilization rates at a reasonably constant tem-
perature, some means of supplying heat to the liquid was
necessary. This was accomplished using the two-chamber
device described previously and shown in figure 6.

A second problem was the wall effect or rim effect that
causes the volatilization rate to change as the liquid level in
the volatilization chamber drops. Experiments in which the
volatilization rates increased (Powell and Griffiths, 1935;
Wade, 1942; Pasquill, 1943) and decreased (Powell and
Griffiths, 1935; Hartley, 1969) have been reported. The
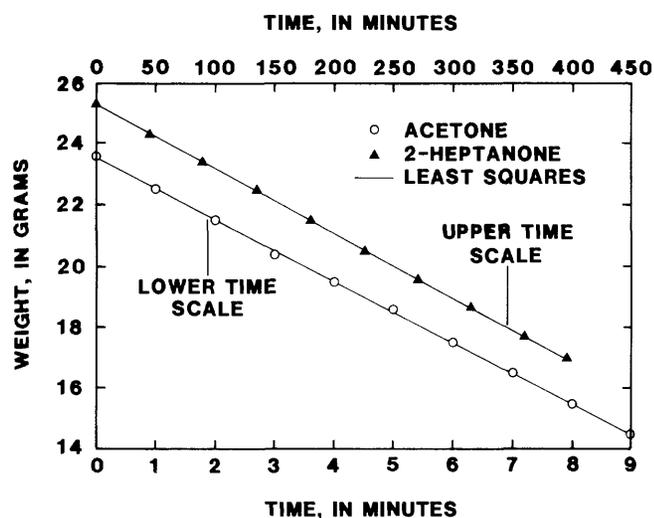
Figure 8. Weight of organic liquid in the volatilization
chamber as a function of time.

increased rates were hypothesized to be the result of increased
turbulence from flow over the rim of the volatilization cham-
ber, whereas the decreased rates were conjectured to be due to
the shielding effect of the rim and the buildup of a stagnant
layer above the liquid surface.

A third problem was the possibility of absorption of
water vapor from the air by the hygroscopic organic liquids
and of condensation of water vapor on the sides of the
apparatus during low-temperature experiments. It has pre-
viously been reported (Wade, 1942; Galstaun, 1950) that such
effects cause erratic volatilization rates.

In the present study, the first step in the analysis of the
data from each experiment was to plot the weight as a func-
tion of time, such as is shown in figure 8. Therefore, any
effects of the second and third problems should be seen as
changes in the slopes of these plots or scatter in the data.
Because slope changes were not seen and the scatter in the
data was small (fig. 8), it was concluded that the second and
third problems had no significant effects on the results of this
study. The first problem (that of supplying the heat of vapor-
ization) was solved using the two-chamber device, as dis-
cussed previously.

Water Evaporation Experiments

The apparatus shown in figures 6 and 7 was used to
measure the evaporation rate of water under airflow condi-
tions identical to those used for the ketones. The experimental
procedure was the same as described previously for the ke-
tones, except that the wet-bulb and dry-bulb temperatures of
the air immediately above the apparatus were measured
periodically with a psychrometer. These measurements were
necessary because the partial pressure of water in the air was
not negligible relative to the water-vapor pressure, as was true

for the organic compounds. The evaporation rate for water was also slower; therefore, each experiment generally was continued for about 8 hours. The water experiments were limited to a water temperature in the constant temperature bath of 298.2 K, which resulted in average temperatures for the experiments ranging from 296.0 to 297.0 K.

Measurement of the wet-bulb and dry-bulb temperatures permits calculation of the gas-film coefficient for the evaporation of water for the humidity conditions existing in the laboratory at the time of the experiments. Some researchers correct the evaporation rate to dry air conditions. It is the evaporation rate that is changed by this correction, however, not the gas-film coefficient. The gas-film coefficient is a function only of mixing conditions in the air phase.

PRESENTATION AND DISCUSSION OF RESULTS

The results are presented and discussed in terms of two parameters, the volatilization flux (which was measured experimentally) and the gas-film coefficient (which was calculated from the volatilization flux). These two parameters are discussed in terms of their dependence on vapor pressure, temperature, molecular weight, and other properties of the molecules. The basic experimental volatilization flux data were used in some analyses. In other analyses requiring data at specific temperatures, the basic data were smoothed and interpolated to obtain data at the desired temperatures. The experimental volatilization fluxes and temperatures and computed vapor pressures and gas-film coefficients are presented in tables 14 through 20 in the appendix. Four significant figures are shown for computation purposes. Values should be rounded to three significant figures for application purposes.

Volatilization Flux and Vapor Pressure

The nature of the volatilization process suggests that the volatilization flux should be strongly dependent on the vapor pressure. To check the internal consistency of the experimental data, the logarithm of the volatilization flux was correlated with the logarithm of the vapor pressure; the fluxes are plotted as a function of the vapor pressure on logarithmic-logarithmic scales in figures 9 and 10. Percentage differences in the volatilization fluxes for duplicate experiments ranged from 0 to 6.06 percent and averaged 2.24 percent for 46 pairs.

Vapor pressure data from the literature (Stull, 1947; Fuge and others, 1952; Ambrose and others, 1975) were used for this purpose. During the early stages of this study, inconsistencies were noted in some of the results, and these were determined to be because of errors in the standard handbook (Weast, 1966) vapor pressures for 2-pentanone, 3-pentanone, 4-methyl-2-pentanone, and 2-heptanone. Handbook vapor pressures for these compounds were from 54 to 66 percent
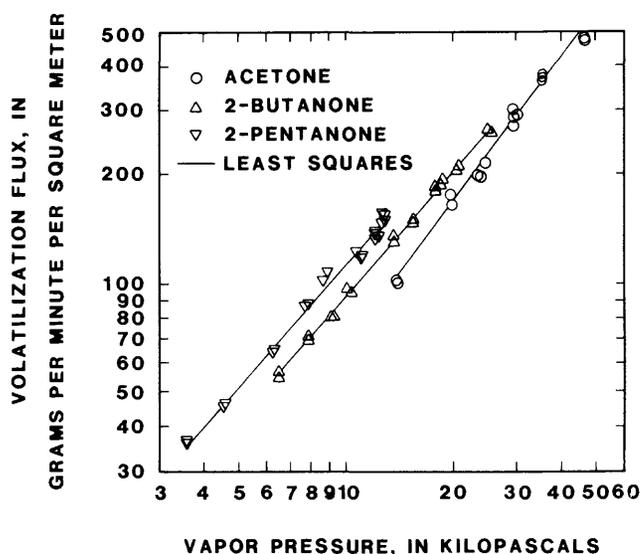
Figure 9. Volatilization flux as a function of vapor pressure for acetone, 2-butanone, and 2-pentanone.
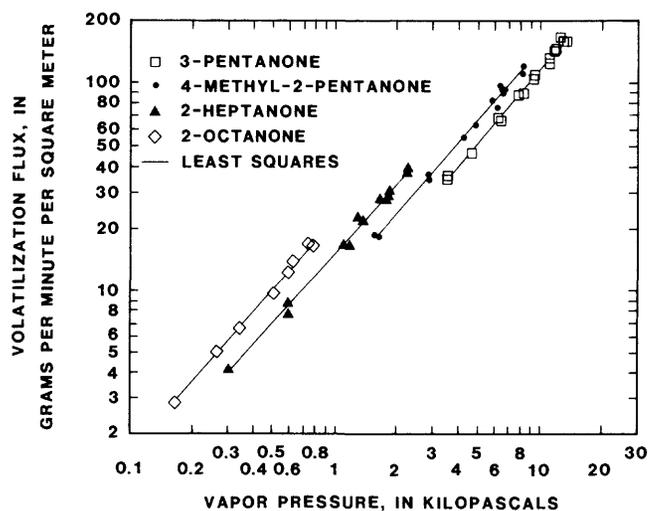
Figure 10. Volatilization flux as a function of vapor pressure for 3-pentanone, 4-methyl-2-pentanone, 2-heptanone, and 2-octanone.

smaller than the more recent data from the literature referenced above. Other data for 2-octanone, however, were not found, and therefore the handbook data originally from Stull (1947) were used for this compound.

The slopes and intercepts of the regression lines shown in figures 9 and 10 are given in table 1, as is the root-mean-square error defined as

$$\text{Error} = \left\{ \sum_{i=1}^{n} \frac{[(\Delta W/A\Delta t)_{EXP} - (\Delta W/A\Delta t)_{CALC}]^2}{n} \right\}^{1/2} \times \frac{100n}{\sum_{i=1}^{n} (\Delta W/A\Delta t)_{EXP}}, \quad (30)$$

Table 1. Slopes, intercepts, and root-mean-square errors of linear regressions of the logarithm of the volatilization flux as a function of the logarithm of the vapor pressure

Compound	Slope	Intercept $[(g/min)/m^2]$	Error (percent)
Acetone	1.32	3.25	4.36
2-butanone	1.14	6.67	2.48
2-pentanone	1.13	8.32	4.80
3-pentanone	1.16	8.06	3.34
4-methyl-2-pentanone	1.13	10.9	4.97
2-heptanone	1.12	15.1	4.08
2-octanone	1.14	22.3	3.25

where the *EXP* and *CALC* subscripts indicate experimental and calculated values, respectively, and n is the number of points. The small errors, which are indicative of the small scatter of the data around the regression lines in figures 9 and 10, suggest that the experimental data are internally consistent.

The slopes given in table 1 are virtually the same, with the exception of the value for acetone. The larger value for acetone is consistent with the expectation that acetone is likely to be hydrogen bonded. The slope represents the rate of change of the volatilization flux with respect to vapor pressure, and because vapor pressure increases with temperature, the slope may also be considered as representative of the rate of change of the volatilization flux with respect to temperature. Because the extent of hydrogen bonding decreases as the temperature increases, the larger slope for acetone is consistent with the behavior of a hydrogen-bonded substance.

The intercepts *Int* given in table 1 increase with molecular weight M according to

$$Int = 1.29 \exp(0.0218\,M), \tag{31}$$

where acetone has been excluded from consideration. The average power dependence of the volatilization flux on vapor pressure from table 1 (excluding acetone) is 1.14. Combining this power dependence with equation 31 gives

$$\Delta W/A\Delta t = 1.29\, P_S^{1.14} \exp[(0.0218\,M)], \tag{32}$$

which can be used to predict the volatilization flux as a function of vapor pressure and molecular weight for any of the ketones except acetone.

Volatilization fluxes calculated from equation 32 are presented as a function of the experimental volatilization fluxes on logarithmic-logarithmic scales in figure 11. The root-mean-square error defined by equation 30 was 7.17 percent for equation 32.

Acetone volatilization fluxes calculated from equation 32 are shown in figure 11 for comparison. The acetone fluxes
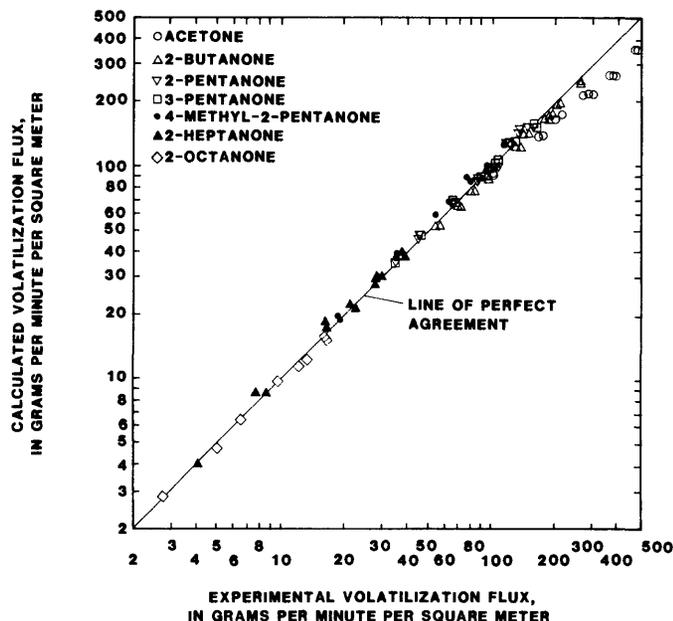
Figure 11. Volatilization flux calculated from equation 32 as a function of the experimental volatilization flux.

are underpredicted. This result is consistent with the suggestion that acetone is hydrogen bonded, because the molecular weight of a hydrogen-bonded substance is larger than the stoichiometric molecular weight. The molecular weight necessary to make the volatilization flux calculated from equation 32 agree with the experimental flux for the highest flux acetone experiment is 71.23, which is larger than the stoichiometric weight of 58.08.

The deviation of the acetone points from the line of perfect agreement increases as the volatilization flux increases (fig. 11). This probably occurs because the 1.14 power dependence on the vapor pressure of equation 32 is not sufficiently large enough to compensate for the 1.32 power dependence observed experimentally for acetone.

Interpolation of the Volatilization Flux Data

The exact temperature at which each volatilization experiment occurred could not be predetermined exactly for reasons discussed in the section on the experimental procedures. Therefore, an interpolation procedure was necessary to obtain volatilization fluxes at specific temperatures. Two methods were used. The first consisted of correlating the logarithm of the volatilization flux as a function of the reciprocal absolute temperature. This procedure was based on the rationalization that the volatilization flux should be strongly dependent on vapor pressure, and vapor pressure is commonly correlated as a function of reciprocal absolute temperature. This method worked well, and details have been presented previously (Rathbun and Tai, 1984b).

The second procedure consisted of calculating the gas-film coefficient k_G from equation 10 using both the experimental values of the volatilization fluxes and temperatures and the vapor pressure data from the literature (Stull, 1947; Fuge and others, 1952; Ambrose and others, 1975). The logarithms of these gas-film coefficients were then correlated with temperature T (in kelvins) according to an Arrhenius-type equation commonly used for expressing the temperature dependence of rate constants for environmental chemical and physical processes. This equation has the form

$$k_G = a_A \exp (b_A T), \tag{33}$$

where a_A and b_A are constants.

Plots of the gas-film coefficient on a logarithmic scale as a function of absolute temperature are presented in figures 12, 13, and 14. The slopes and intercepts of the least-squares regression lines shown in these figures and the root-mean-square errors calculated from equation 30 are given in table 2. The slopes and intercepts correspond to the constants b_A and a_A, respectively, in equation 33.

Figure 13. Gas film coefficient as a function of temperature for 4-methyl-2-pentanone and 2-heptanone.

Figure 12. Gas-film coefficient as a function of temperature for acetone, 2-butanone, and 2-pentanone.
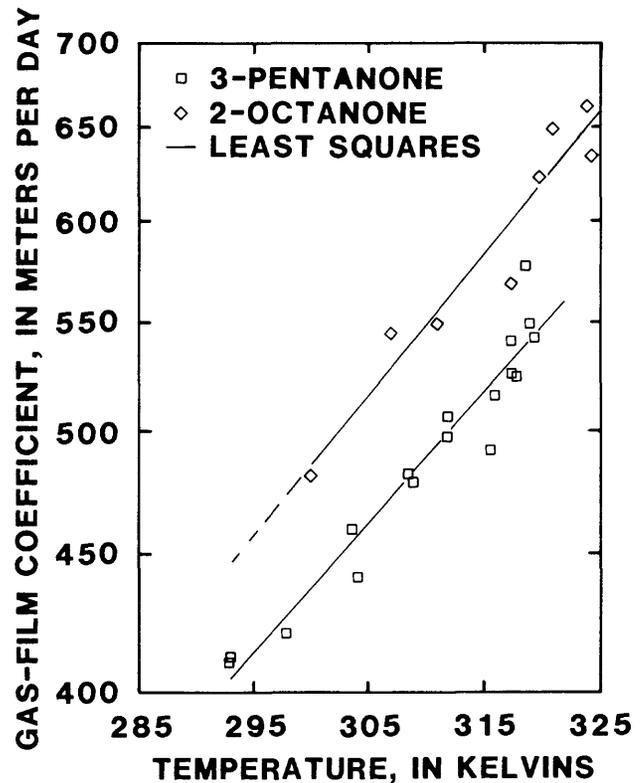
Figure 14. Gas-film coefficient as a function of temperature for 3-pentanone and 2-octanone.

Table 2. Slopes, intercepts, and root-mean-square errors of linear regressions of the logarithm of the gas film coefficient as a function of absolute temperature

Compound	Slope (K^{-1})	Intercept (m/d)	Error (percent)
Acetone	0.0174	3.33	4.09
2-butanone	.00991	24.3	2.34
2-pentanone	.00978	22.9	4.36
3-pentanone	.0112	15.0	2.74
4-methyl-2-pentanone	.0101	21.4	4.30
2-heptanone	.0107	17.8	4.57
2-octanone	.0121	12.8	2.93

There is considerable apparent scatter in the data presented in figures 12, 13, and 14, unlike the volatilization flux on a logarithmic scale versus reciprocal absolute temperature plots presented elsewhere (Rathbun and Tai, 1984b). The errors presented in table 2, however, are approximately the same as those presented elsewhere (Rathbun and Tai, 1984b) for the logarithm of volatilization flux versus reciprocal absolute temperature correlations. The apparent scatter in figures 12, 13, and 14 is because the gas-film coefficient varies only over a part of one log cycle, whereas the volatilization flux varies over two to three log cycles.

Volatilization fluxes were calculated at specific temperatures from equation 10 and gas-film coefficients interpolated at the same temperature using the regression coefficients from table 2. These fluxes were virtually identical to volatilization fluxes interpolated using the regression coefficients presented by Rathbun and Tai (1984b) for the logarithm of volatilization flux versus reciprocal absolute temperature correlations. It was concluded that the two interpolation procedures were comparable.

Figures 12, 13, and 14 show that the experimental temperatures ranged from about 281 K for two acetone experiments to about 324 K for two 2-octanone experiments. This complete temperature range could not be covered, however, for each of the compounds studied. As discussed in the experimental procedures section, the temperature range studied for each compound was determined by the volatilization characteristics of the compound and the temperature range of the water circulator bath. Therefore, discussion of temperature effects on the volatilization flux and the gas-film coefficient are limited to the range from 293.2 to 313.2 K. Since the highest experimental temperature for acetone was 308.1 K and the lowest experimental temperature for 2-octanone was 300.0 K, some extrapolation of the experimental data was necessary for these two compounds. These extrapolations are shown by the dashed lines in figures 12 and 14. Experimental data for the other compounds covered the 293.2 to 313.2 K range.

The 293.2 to 313.2 K temperature range is the upper part of the temperature range of importance in environmental studies. Extrapolation of the results to lower temperatures

should be done only with caution because of the previously discussed temperature dependence of hydrogen bonding.

Volatilization Flux and Empirical Correlations

A consideration of the fundamentals of the volatilization process as presented previously suggests that the volatilization flux should be a function of the vapor pressure, molecular weight, and temperature of the liquid. An empirical approach to describing the volatilization flux is to assume a function of the form

$$\Delta W/A\Delta t = b_0 P_S^{b_1} M^{b_2} T^{b_3}, \qquad (34)$$

where b_0 is a regression constant and b_1, b_2, and b_3 are exponents on the variables in the regression equation. The usual procedure is to linearize equation 34 by taking logarithms to give

$$\log_e (\Delta W/A\Delta t) = \log_e b_0 + b_1 \log_e P_S + b_2 \log_e M + b_3 \log_e T \qquad (35)$$

Multiple linear regression analysis can then be applied to equation 35 to determine the best-fit values of the regression coefficients and the constant.

Application of this procedure to the basic experimental data resulted in the equation

$$\Delta W/A\Delta t = 1.27 \times 10^{-11} P_S^{0.798} M^{-0.486} T^{5.25}. \qquad (36)$$

The error defined by equation 30 was 10.0 percent for equation 36. The error actually should be computed in terms of the logarithms of the experimental and calculated volatilization fluxes because minimization is with respect to the logarithm of the volatilization flux, as shown by equation 35. If this error is computed, then the result is 1.54 percent. The error based on the arithmetic fluxes may have more practical significance, however, because the researcher is generally interested in how well an equation predicts the volatilization flux, not the logarithm of the volatilization flux.

The volatilization fluxes calculated from equation 36 are plotted as a function of the experimental volatilization fluxes on logarithmic-logarithmic scales in figure 15. Average errors for the individual ketones ranged from 10.9 percent for 4-methyl-2-pentanone to 4.20 percent for 3-pentanone with the overall error being 10.0 percent, as stated previously.

Because the vapor pressure is strongly dependent on the temperature, it might be argued that including both temperature and vapor pressure in the regression analysis was redundant. Therefore, an analysis using temperature and molecular weight as the variables was completed, resulting in exponents of 18.4 and −5.40 for temperature and molecular weight, respectively. The error defined by equation 30,
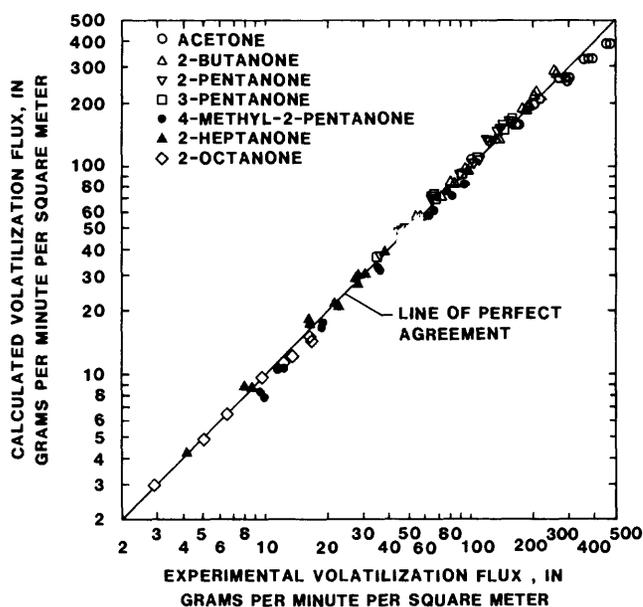
Figure 15. Volatilization flux calculated from equation 36 as a function of the experimental volatilization flux.

however, was 29.7 percent, much higher than the 10.0-percent value for the three-parameter equation. The fit for the two-parameter equation, therefore, was not nearly as good, and it was not considered further.

Volatilization Flux and Other Molecular Properties

Other molecular properties such as the molar volume are sometimes used for relating physical properties of a homologous series of compounds. It follows from the definition of molar volume that if the liquid density of a series of compounds is approximately constant, then the dependencies of the volatilization flux on molecular weight and on molar volume will be virtually identical.

Densities of the seven ketones range from 0.792 g/mL for acetone at 293.2 K to 0.822 g/mL for 2-heptanone at 288.2 K (Hodgman, 1951). Thus, there is little dependence of the density on molecular weight, and a virtually constant relation exists between molar volume and molecular weight for these ketones. Therefore, only the dependence of volatilization flux on molecular weight was considered in this report.

The logarithms of the smoothed volatilization flux data at temperatures of 293.2, 298.2, 303.2, 308.2, and 313.2 K were correlated with molecular weight. It was found that the points for 4-methyl-2-pentanone were considerably above the regression lines for each temperature. Computation of the 95 percent confidence limits for the regression lines showed that points for all the ketones except 4-methyl-2-pentanone were within these limits. Expanding the confidence limits to the

99.5-percent level resulted in a confidence band about twice as wide; however, the 4-methyl-2-pentanone points were still outside the limits. Also, the root-mean-square errors of prediction for 4-methyl-2-pentanone were about 6.0 times larger than the average errors for the other ketones. Therefore, the 4-methyl-2-pentanone points were rejected as outliers and the correlations recomputed.

For the recomputed correlations, the slopes, intercepts, and root-mean-square errors defined by equation 30 are presented in table 3. The volatilization flux is plotted on a logarithmic scale as a function of molecular weight for temperatures of 293.2, 303.2, and 313.2 K in figure 16. The points for 4-methyl-2-pentanone are shown for comparison. The points for 293.2 and 303.2 K fall approximately on the regression lines for 303.2 and 313.2 K, respectively, and the point for 313.2 K falls above the regression line. The experimental fluxes for 4-methyl-2-pentanone were 83, 76, and 72 percent larger at temperatures of 293.2, 303.2, and 313.2 K, respectively, than fluxes calculated from the regression coefficients given in table 3 for a straight-chain ketone of the
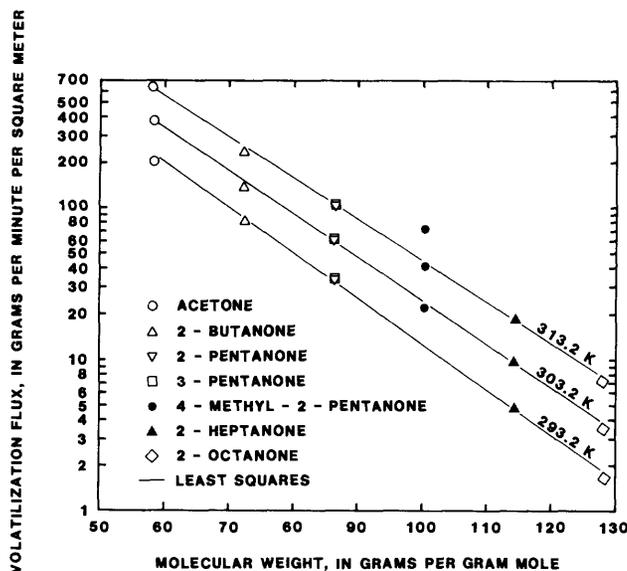
Figure 16. Volatilization flux as a function of molecular weight for temperatures of 293.2, 303.2, and 313.2 K.

Table 3. Slopes, intercepts, and root-mean-square errors of linear regressions of the logarithm of the volatilization flux as a function of molecular weight

Temperature (K)	Slope (g mol/g)	Intercept $\times 10^{-4}$ [(g/min)/m^2]	Error (percent)
293.2	-0.0695	1.33	9.18
298.2	-.0677	1.57	5.92
303.2	-.0660	1.83	3.80
308.2	-.0644	2.13	4.07
313.2	-.0628	2.47	6.18

same molecular weight. A possible explanation for these higher-than-expected fluxes is that the branched structure of this ketone inhibits hydrogen bonding and other molecular interactions.

The fact that the points for 4-methyl-2-pentanone for 293.2 and 303.2 K fall approximately on the regression lines for 303.2 and 313.2 K, respectively, suggests that the effect of branching is equivalent to about a 10-K change in temperature, in agreement with the expectation that the extent of hydrogen bonding increases as the temperature decreases. This result again suggests that the straight-chain ketones are hydrogen bonded to some extent.

The absolute values of the slopes and the intercepts in table 3 decrease and increase with temperature, respectively. The logarithms of the slopes and intercepts were correlated with temperature T and the results combined to give the equation

$$\log_e \Delta W/A\Delta t = 3.77 \exp(0.00315\ T)$$
$$- (0.309\ M) \exp(-0.00509\ T). \quad (37)$$

Equation 37 was then applied to the basic experimental data, with the exception of 4-methyl-2-pentanone. The overall error defined by equation 30 was 7.62 percent. Volatilization fluxes predicted from equation 37 are plotted as a function of the experimental volatilization flux on logarithmic-logarithmic scales in figure 17. The points agree closely with the line of perfect agreement.

The calculated volatilization fluxes for 4-methyl-2-pentanone are also plotted in figure 17 as a function of the experimental flux. The deviations of the points for this
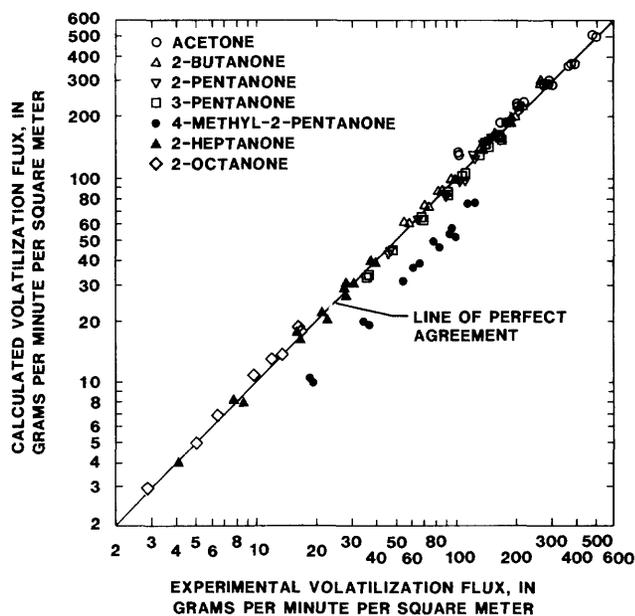
Figure 17. Volatilization flux calculated from equation 37 as a function of the experimental volatilization flux.

branched ketone are obvious, with the experimental fluxes ranging from 34 to 47 percent larger than the calculated fluxes. Therefore, it is expected that equation 37 will work well for predicting volatilization fluxes as a function of temperature and molecular weight for straight-chain ketones, but that it should not be used for branched or cyclic ketones.

Application of Experimental Data to Equations from the Literature

The objective of many of the previous studies of volatilization was to find a constant relation among the variables affecting the volatilization process. These included vapor pressure, molecular weight, molecular diffusion coefficient, and temperature. A brief summary of the development of these relations was presented previously. Application of these relations to the volatilization flux data of this study is discussed in the following sections.

Volatilization Fluxes and the Equations of Chiou and Others (1980, 1983)

For volatilization of pure liquids, α in equation 22 is 1.0 and P_E is identical to P_S. For volatilization under constant mixing conditions in the air, β should be constant. For these conditions, it follows from equation 22 that

$$(\Delta W/A\Delta t/P_S)(2\pi RT/M)^{1/2} = \beta = \text{constant}. \quad (38)$$

Values of the Chiou factor β, defined by equation 38, were calculated from the basic experimental data, and the mean values and the coefficients of variation for each compound are presented in table 4. Mean values are four to six times larger than the value observed by Chiou and others (1980) for still-air conditions. These larger values are consistent with the expectation that the factor should increase as the degree of mixing in the air phase increases, with the factor ultimately reaching its theoretical limit of 1.0 for the optimum condition of volatilization into a vacuum. The coefficients of variation are comparable to the 9-percent value observed by Chiou and others (1980); therefore, the conclusion might be that the

Table 4. Mean values and coefficients of variation of the Chiou factor β for the basic experimental data

Compound	Mean value x10^5	Coefficient of variation (percent)
Acetone	7.98	12.8
2-butanone	7.49	7.95
2-pentanone	8.04	8.32
3-pentanone	8.25	8.91
4-methyl-2-pentanone	8.89	9.40
2-heptanone	9.82	10.0
2-octanone	11.9	9.49

Chiou factor is approximately constant, as expected for a specific experimental configuration.

However, the mean values presented in table 4 suggest, with the exception of acetone, that the factor increases with molecular weight. Because acetone is expected to be hydrogen bonded, the molecular weight is expected to be larger than the stoichiometric weight. Interpolating a plot of the mean values as a function of molecular weight gives a molecular weight of about 83 for the acetone value of 7.98×10^{-5}. This molecular weight is consistent with a small degree of hydrogen bonding.

Plots of the Chiou factor calculated from equation 38 as a function of temperature are presented in figures 18, 19, and 20, and it is apparent from these figures that the factor also depends on temperature. The lines shown in these figures are least-squares lines, and the slopes and intercepts are given in table 5. Also given in table 5 are the root-mean-square errors defined by equation 30 and the percentage increase in the factor per kelvin at 298.2 K. The percentage increase is maximum for acetone, which is consistent with the expected temperature dependence of hydrogen bonding. An unexpected result is the relatively large value for 2-octanone.

Figure 19. Chiou factor β as a function of temperature for 2-pentanone and 3-pentanone.

Volatilization Times and the Equations of Marwedel (1950, 1953) and Marwedel and Hauser (1948)

The logarithms of vapor pressure data from the literature (Stull, 1947; Fuge and others, 1952; Ambrose and others, 1975) were correlated with normal boiling temperatures from Hodgman (1951) for the six normal ketones, as suggested by equation 17. The branched ketone, 4-methyl-2-pentanone, was not considered because the constants in the Marwedel equations differ, depending on the homologous series. Slopes, intercepts, and root-mean-square errors defined by equation 30 are presented in table 6 for five temperatures, and the vapor pressures are plotted on a logarithmic scale as a function of the normal boiling temperature in figure 21 for temperatures of 293.2, 303.2, and 313.2 K. The points for 4-methyl-2-pentanone are shown in figure 21 for comparison. The vapor pressures for this ketone are about 30 percent larger than the values predicted by the regression lines, which shows that the vapor pressure for the branched ketone is higher than it would be for a straight-chain ketone with the same boiling temperature. This may occur because branching inhibits the formation of hydrogen bonds.

Figure 18. Chiou factor β as a function of temperature for acetone and 2-butanone.
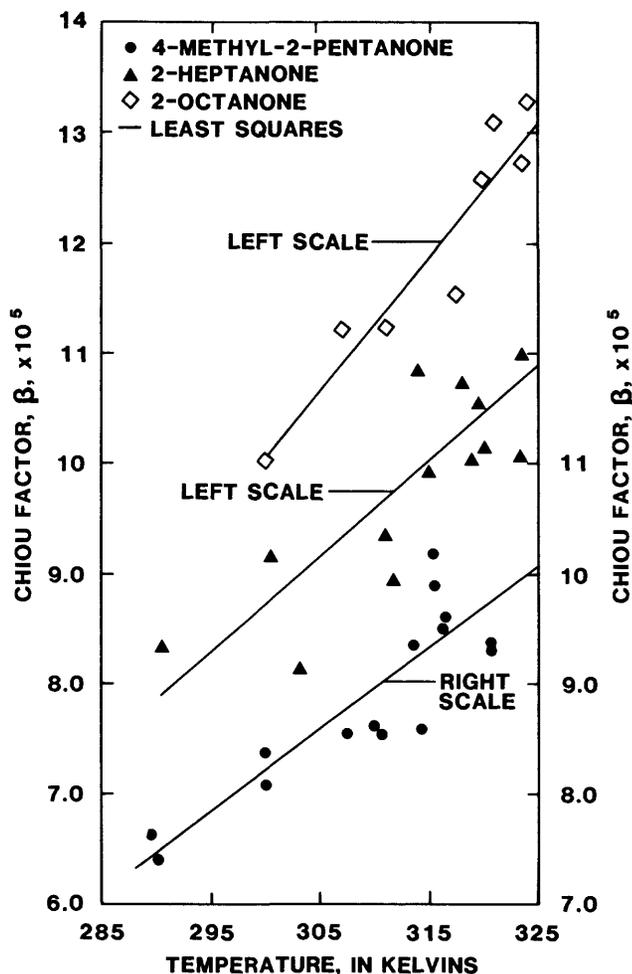
Figure 20. Chiou factor β as a function of temperature for 4-methyl-2-pentanone, 2-heptanone, and 2-octanone.

If the slopes in table 6 are multiplied by the corresponding temperature, the results are −13.8, −13.6, −13.5, −13.4, and −13.3. These values in an absolute sense are 25 to 30 percent larger than the theoretical value of −10.6 from equation 18, which is based on the Trouton constant. Because the Trouton constant is proportional to the heat of vaporization, this difference suggests that the heat of vaporization of these ketones are larger than normal, and this is one characteristic of hydrogen-bonded compounds (Pimental and McClellan, 1960).

The slopes decrease with temperature, which indicates that the vapor pressure depends less on boiling temperature as the temperature increases. This decrease may be the result of decreased hydrogen bonding as the temperature increases. Decreased hydrogen bonding with temperature increase may also explain the small but consistent improvement in the regression fit, as indicated by the decreasing error in table 6.

The errors for the individual ketones were relatively large, and there was a consistent pattern. The predicted values for acetone and 2-octanone were always larger than the

Table 5. Slopes, intercepts, and root-mean-square errors of linear regressions of the Chiou factor as a function of temperature, and percentage increases in the factor per kelvin at 298.2 K

Compound	Slope x10⁶ (K⁻¹)	Intercept x10⁴	Error (percent)	Percentage increase per Kelvin at 298.2 K (percent)
Acetone	1.20	−2.74	3.64	1.46
2-butanone	.609	−1.08	2.25	.83
2-pentanone	.636	−1.17	4.30	.87
3-pentanone	.773	−1.57	2.84	1.06
4-methyl-2-pentanone	.731	−1.37	4.31	.91
2-heptanone	.861	−1.71	4.70	1.01
2-octanone	1.22	−2.66	2.95	1.25
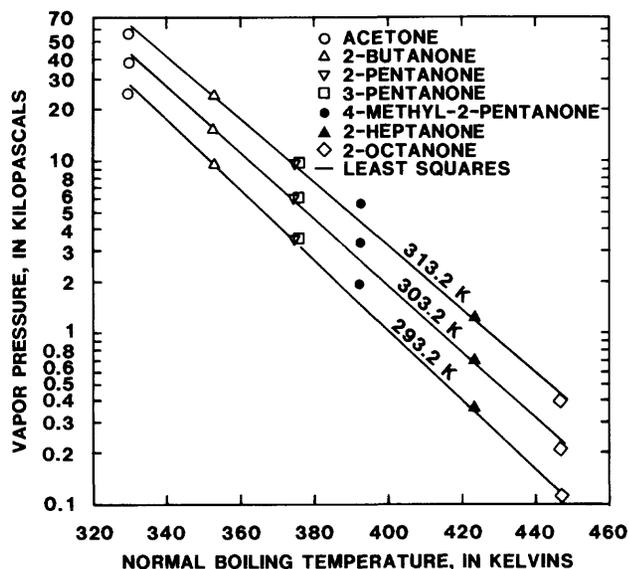
Figure 21. Vapor pressures at three temperatures as a function of normal boiling temperature.

Table 6. Slopes, intercepts, and root-mean-square errors of linear regressions of the logarithm of the vapor pressure at five temperatures as a function of normal boiling temperature

Temperature (K)	Slope (K⁻¹)	Intercept x10⁻⁸ (kPa)	Error (percent)
293.2	−0.0469	1.45	18.8
298.2	−.0457	1.22	18.3
303.2	−.0446	1.03	17.6
308.2	−.0435	.886	17.0
313.2	−.0425	.758	16.3

experimental values (fig. 21), and the percentage errors were largest for these ketones, ranging from +10 to +12 percent. The predicted and experimental values for 2-butanone were always nearly identical, with the percentage error less than 0.5 percent. The predicted values for the other three ketones were always smaller than the experimental values, with percentage errors ranging from −4 to −11 percent. The plots in figure 21 show this behavior.

The experimental vapor pressures shown for acetone in figure 21 are less than predicted on the basis of the regression lines. This behavior is consistent with the suggestion that acetone is hydrogen bonded, because hydrogen bonding reduces the vapor pressure (Pimental and McClellan, 1960). The behavior of 2-octanone is more difficult to explain because it is not expected to be hydrogen bonded. Even if the acetone points are neglected, however, there is a tendency for a slight curvature in the points shown in figure 21.

The logarithm of the volatilization time (the reciprocal of the volatilization rate) was correlated with the normal boiling temperature, as suggested by equation 16. The smoothed volatilization rate data at temperatures of 293.2, 298.2, 303.2, 308.2, and 313.2 K were used. Rate data were obtained by multiplying the flux data by the area for volatilization. Slopes, intercepts, and root-mean-square errors defined by equation 30 are given in table 7. Volatilization times in minutes per gram for temperatures of 293.2, 303.2, and 313.2 K are plotted on a logarithmic scale in figure 22 as a function of the normal boiling temperature. Points for 4-methyl-2-pentanone, although not included in the regression analysis, are shown for comparison. Experimental volatilization times for this branched ketone are less than would be predicted from the regression equations for the straight-chain ketones. This may occur because branching inhibits the formation of hydrogen bonds, and therefore volatilization is comparatively easier. The solid lines shown in figure 22 are the regression lines, the constants for which are given in table 7.

The dashed lines in figure 22 are the result of combining equations 16 and 17. The slopes given in table 6 for the regressions of the logarithm of the vapor pressure as a function of the boiling temperature are equal to $1/B_1$ in equation 17. Using these values in equation 16 with the experimental data of 2-pentanone (the reference substance) gives the

Figure 22. Volatilization time at three temperatures as a function of normal boiling temperature.

dashed lines. Any of the ketones could have been used as the reference substance, but choosing one near the middle of the boiling temperature range results in more nearly equal errors at the ends of the boiling temperature range. If acetone or 2-octanone had been chosen as the reference substance, then the error would have increased from zero at one end of the temperature range to a maximum at the other end. It is apparent that the closer the unknown is to the reference substance, the more accurate is the prediction of the volatilization time because of the slightly different slopes of the solid and dashed lines in figure 22.

The percentage errors of prediction of the dashed lines for acetone are −25.5, −18.9, and −12.5 percent for 293.2, 303.2, and 313.2 K, respectively. The corresponding values for 2-octanone are +37.1, +41.2, and +46.2 percent. Prediction errors for the other ketones are within these extremes. These errors are very sensitive to the slopes of the lines in figure 22 because the plot is logarithmic. It was determined that the slopes of the dashed lines need to be reduced by only about 10 percent to have almost perfect agreement over the entire temperature range.

It is concluded that the method of estimating volatilization times from equations 16 and 17 is satisfactory if the required information is available. Volatilization times estimated from these equations can be converted to the gas-film coefficient of the two-film model using equation 10.

Volatilization Rates and the Dorsey (1940) Factor

The Dorsey (1940) factor (defined by equation 14) was calculated from the basic experimental data. Molecular diffu-

Table 7. Slopes, intercepts, and root-mean-square errors of linear regressions of the logarithm of the volatilization time as a function of normal boiling temperature

Temperature (K)	Slope (K^{-1})	Intercept x10^6 (min/g)	Error (percent)
293.2	0.0416	1.80	8.49
298.2	.0405	1.96	7.00
303.2	.0395	2.12	5.74
308.2	.0385	2.30	4.49
313.2	.0375	2.48	3.59

sion coefficients for the seven ketones in air were predicted using the procedure of Fuller and others (1966), as described by Reid and others (1977). This procedure assumes that the molecular diffusion coefficient increases with the 1.75 power of the absolute temperature. Mean values of the Dorsey factor and the coefficients of variation for each compound are presented in table 8. The coefficients of variation are smaller than those in table 4, which suggests that the Dorsey (1940) factor for a specific compound is more constant than the Chiou factor. However, the mean values in table 8 show the same increase with molecular weight as the values shown in table 4. Also, the value for acetone is comparable to that for 2-pentanone, which suggests that the molecular weight for acetone is 86 (the same as for 2-pentanone). This corresponds to the value of 83 predicted for acetone on the basis of the Chiou factor.

Consideration of the temperature dependence of the Dorsey factor resulted in plots similar in form to those for the temperature dependence of the Chiou factor (figs. 18, 19, and 20). Percentage increases per kelvin at 298.2 K ranged from 1.08 percent for acetone to 0.41 percent for 2-butanone. The percentage increases were smaller than for the Chiou factor (table 5); however, the trend with molecular weight was the same. In each case, the largest percentage increase occurred for acetone, the smallest for 2-butanone, and then an increase with molecular weight to 2-octanone. This similarity is not unexpected, because the same temperature dependence for the molecular diffusion coefficient was assumed for all the compounds.

Volatilization Rates and the Pasquill (1943) Factor

The Pasquill (1943) factor (defined by equation 15) was calculated with $n = 0.25$ from the basic experimental data and molecular diffusion coefficients estimated as described previously. Because of the fractional power of the molecular diffusion coefficient and the resultant mixture of units on the Pasquill factor, the mean values presented in table 9 are relative to that for acetone. The coefficients of variation are also presented in table 9.

The coefficients of variation are larger than those for the Dorsey (1940) factor in table 8 and comparable to but slightly

Table 8. Mean values and coefficients of variation of the Dorsey factor for the basic experimental data

Compound	Mean value (mm)	Coefficient of variation (percent)
Acetone	1,690	9.79
2-butanone	1,610	4.44
2-pentanone	1,700	5.67
3-pentanone	1,740	5.68
4-methyl-2-pentanone	1,920	6.17
2-heptanone	2,120	6.94
2-octanone	2,570	6.43

Table 9. Mean values of the Pasquill factor relative to the acetone value, and coefficients of variation for the basic experimental data

Compound	Mean value relative to acetone value	Coefficient of variation (percent)
Acetone	1.00	13.1
2-butanone	.871	8.27
2-pentanone	.880	8.58
3-pentanone	.903	9.21
4-methyl-2-pentanone	.920	9.70
2-heptanone	.971	10.3
2-octanone	1.13	9.77

larger than those for the Chiou factor in table 4. The mean values again show, with the exception of acetone, the increase with molecular weight seen in tables 4 and 8. In table 9, however, the value for acetone is relatively larger, with the value falling between those for 2-heptanone and 2-octanone. This would suggest an apparent molecular weight for acetone of about 120, which indicates that the acetone was completely dimerized (that is, two molecules joined by a hydrogen bond).

Consideration of the temperature dependence of the Pasquill factor resulted in plots similar in form to those for the temperature dependence of the Chiou factor (figs. 18, 19, and 20) but with more scatter. Percentage increases per kelvin at 298.2 K ranged from 1.49 percent for acetone to 0.87 percent for 2-butanone. The percentage increases were about the same as for the Chiou factor (table 5), and the trend with molecular weight was the same as for both the Chiou and Dorsey factors. These similarities are not unexpected because of the similar forms of the factors and the use of the same temperature dependence for the molecular diffusion coefficient for the two factors requiring this variable.

Volatilization Rates and the Hartley (1969) Factor

The Hartley (1969) factor (defined by equation 20) was calculated from smoothed values of the volatilization rates at 293.2, 298.2, 303.2, 308.2, and 313.2 K and the corresponding vapor pressures from the literature (Stull, 1947; Fuge and others, 1952; Ambrose and others, 1975). Values of the factor at 293.2, 303.2, and 313.2 K are plotted in figure 23 as a function of molecular weight, which is used to indicate the compound.

The factor should be independent of molecular weight for each temperature according to equation 20. The results in figure 23 show that the factor is not constant but that the variability is relatively small. Coefficients of variation about the mean values are ± 11, ± 13, and ± 14 percent for 293.2, 303.2, and 313.2 K, respectively. It is significant, however, that the variability is not random, but rather the factor appears to depend systematically on the molecular weight.
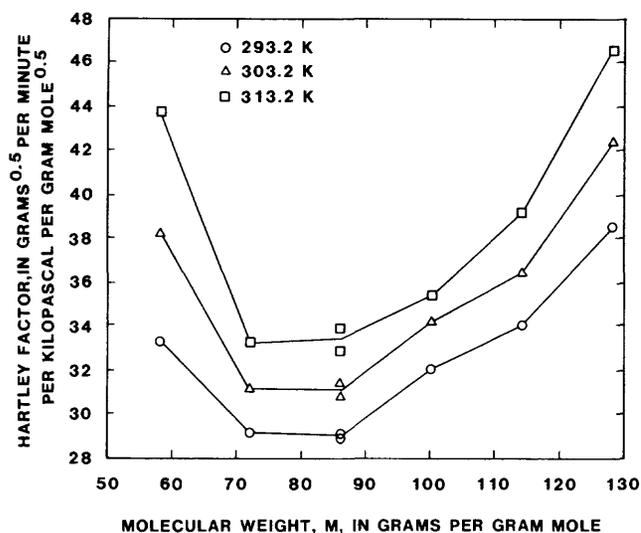
Figure 23. Hartley factor at three temperatures as a function of molecular weight.

Consideration of figure 23 might suggest that the acetone factors are larger than might be expected on the basis of the other ketones. This suggestion is consistent with the belief that acetone is hydrogen bonded, because the stoichiometric molecular weight was used in computing the factors. The molecular weight of a hydrogen-bonded compound is larger than the stoichiometric weight, however, and the use of a larger weight in equation 20 would result in smaller factors.

The acetone molecular weights necessary to flatten the curves in figure 23 (that is, make the factors for acetone identical to those for 2-butanone) were computed. Values of 69.1, 79.9, and 91.4 were found for 293.2, 303.2, and 313.2 K, respectively. These values are consistent with a small degree of hydrogen bonding, as is expected for acetone. The increase with temperature, however, is inconsistent with the suggestion that the degree of hydrogen bonding should decrease as temperature increase.

This analysis neglects the effect of hydrogen bonding on the vapor pressure, and there is undoubtedly some effect on this property also. It is apparent, however, that the Hartley factor is not constant for the ketones considered in this study.

Heat of Vaporization

Heats of vaporization at 298.2 K for the seven ketones were calculated from vapor pressure data from the literature (Stull, 1947; Fuge and others, 1952; Ambrose and others, 1975) using the Douglass-Avakian method of differentiation (Reid and others, 1977). These calculated values are plotted as a function of molecular weight on logarithmic-logarithmic scales in figure 24. Also shown in figure 24 are measured values at 298.2 K for four of the ketones (Uchytilova and others, 1983). Calculated values are 1.19, 1.16, 1.23, and
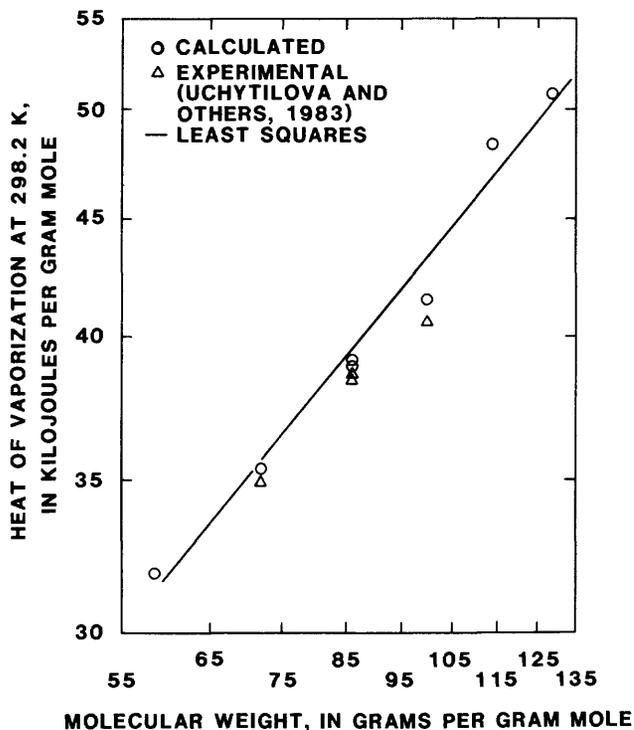
Figure 24. Heat of vaporization at 298.2 K as a function of molecular weight.

2.26 percent larger than the measured values for 2-butanone, 2-pentanone, 3-pentanone, and 4-methyl-2-pentanone, respectively. The line shown in figure 24 was determined by correlating the logarithm of the heat of vaporization as a function of the logarithm of the molecular weight. The result was a dependence on the molecular weight to the 0.605 power, in reasonable agreement with Wall and others (1970), who found the heat of vaporization of a series of linear alkanes to be dependent on the 0.667 power of the number of carbon atoms in the molecule.

Heats of vaporization at the normal boiling temperature were calculated for the seven ketones by using the Riedel method (Reid and others, 1977). Critical constants were from the compilation of Reid and others (1977), except for 2-heptanone and 2-octanone, whose constants were estimated using methods given by Reid and others (1977).

Calculated heats of vaporization are given in table 10. Also given in table 10 are values measured by Uchytilova and others (1983) for four of the ketones. The calculated values are 2.46, 2.30, 1.70, and 2.64 percent larger than the measured values for 2-butanone, 2-pentanone, 3-pentanone, and 4-methyl-2-pentanone, respectively. The good agreement suggests that the Riedel method works well for this series of compounds, and therefore the calculated values for the other three ketones are probably reasonable.

Trouton constants (the ratio of the heat of vaporization at normal boiling temperature to the normal boiling tem-

Table 10. Calculated and experimentally determined heats of vaporization at the normal boiling temperature, normal boiling temperatures, and Trouton constants

| Compound | Heat of vaporization at normal boiling temperature | | Normal boiling temperature (K) | Trouton constants [J/(g mol·K)] |
	Calculated (kJ/g mol)	Experimental[1] (kJ/g mol)		
Acetone	30.15	---	329.4	91.5
2-butanone	32.07	31.30	352.8	90.9
2-pentanone	34.21	33.44	375.5	91.1
3-pentanone	34.02	33.45	375.1	90.7
4-methyl-2-pentanone	35.38	34.47	392.2	90.2
2-heptanone	39.69	---	423.2	93.8
2-octanone	42.58	---	446.6	95.3

[1]Uchytilova and others (1983).

perature) are also given in table 10. The values for acetone through 4-methyl-2-pentanone are slightly larger than the generally accepted value of 88, and the values for 2-heptanone and 2-octanone are somewhat larger. These Trouton constants suggest that the ketones are not hydrogen bonded to any appreciable extent.

The Gas-Film Coefficient

Gas-film coefficients were calculated from the experimental measurements of the volatilization flux, the temperature, vapor pressure data from the literature (Stull, 1947; Fuge and others, 1952; and Ambrose and others, 1975) and equation 10. The dependencies of these gas-film coefficients on the molecular diffusion coefficient, molecular weight, and temperature are discussed in the following sections. Also presented are several equations for predicting the gas-film coefficient of ketones as a function of molecular weight and temperature. Finally, the results of the water evaporation experiments are discussed. These results, when combined with the ketone volatilization results, permit the estimation of the gas-film coefficients for the volatilization of ketones from streams and rivers.

Dependence on Molecular Weight

The gas-film coefficient at 298.2 K is plotted as a function of the molecular weight on logarithmic-logarithmic scales in figure 25. Also shown in figure 25 is a line representing equation 23, which states that the gas-film coefficient should decrease as the reciprocal of the square root of the molecular weight. The constant in equation 23 was adjusted so that the line passed through the data point for 2-pentanone.

The dependence of the gas-film coefficient on molecular weight is U-shaped, with the coefficient decreasing from acetone through 2-pentanone and then increasing for 4-methyl-2-pentanone, 2-heptanone, and 2-octanone. It is apparent that the simple dependence on molecular weight as given by equation 23 does not describe the dependence of the gas-film coefficient on molecular weight for this series of ketones.
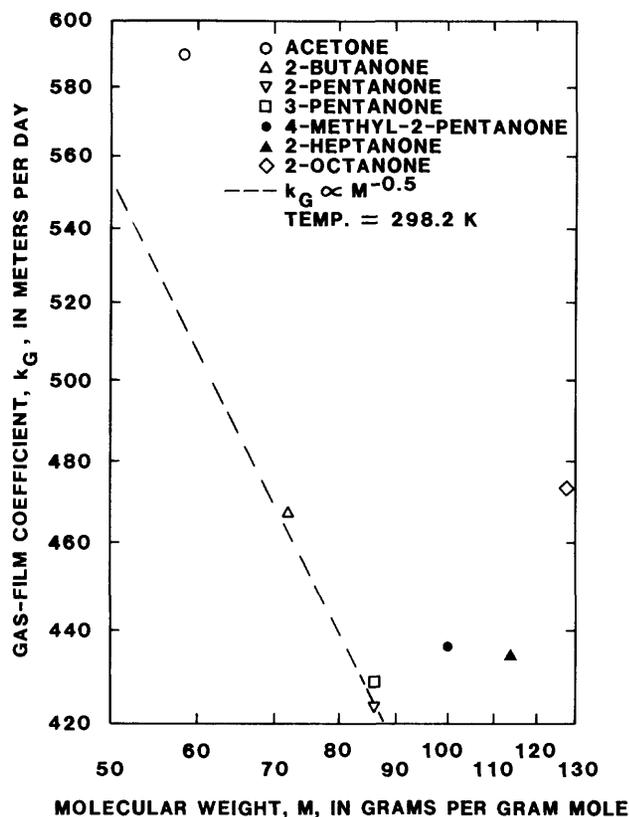
Figure 25. Gas-film coefficient at 298.2 K as a function of molecular weight.

Dependence on Molecular Diffusion Coefficient

Molecular diffusion coefficients for the seven ketones in air were predicted using the procedure of Fuller and others (1966), as described by Reid and others (1977). The gas-film coefficient interpolated at 298.2 K as described previously is plotted as a function of the molecular diffusion coefficient on logarithmic-logarithmic scales in figure 26. Also shown in figure 26 is a line representing equation 24, with a value of 0.684 for η. This value is appropriate for volatilization of pure liquids where bulk motion is likely to be significant (Tamir and others, 1979). The constant in equation 24 was adjusted so that the line passed through the point for 2-pentanone.

The dependence of the gas-film coefficient on the molecular diffusion coefficient is virtually a mirror image of the dependence on the molecular weight (fig. 25), with the gas-film coefficient decreasing for 2-octanone through 2-pentanone and then increasing rapidly for 2-butanone and acetone. It is apparent that the simple dependence on molecular diffusion coefficient as given by equation 24 does not describe the dependence of the gas-film coefficient on molecular diffusion coefficient for this series of ketones.

Dependence on Temperature

The dependence of the gas-film coefficient on temperature was discussed previously in the section on
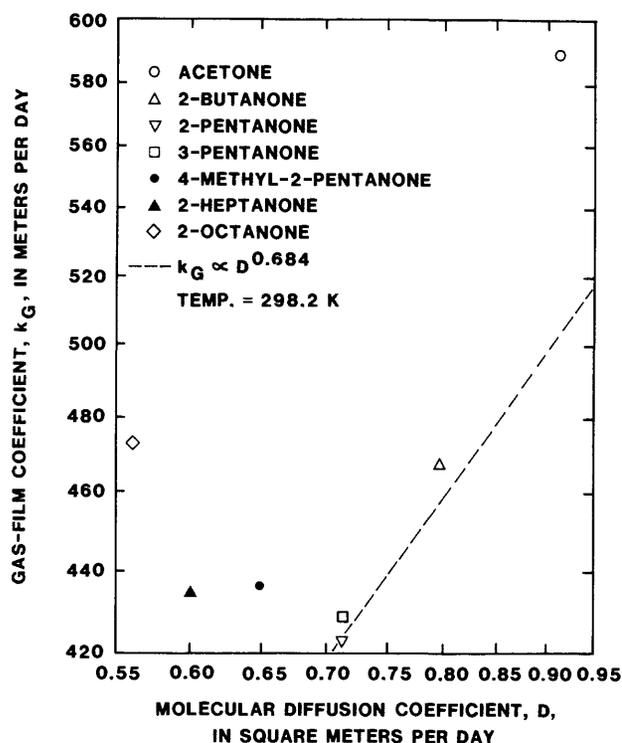
Figure 26. Gas-film coefficient at 298.2 K as a function of molecular diffusion coefficient.

Interpolation of the Volatilization Flux Data. The temperature dependence (as expressed by equation 33) was used to interpolate the experimental data to obtain values at specific temperatures. Slopes, intercepts, and root-mean-square errors of linear regressions of the logarithm of the gas-film coefficient as a function of temperature as suggested by equation 33 were presented in table 2.

The slopes from table 2, when multiplied by 100, correspond to the percentage increase in the gas-film coefficient per kelvin. These values range from about 1.7 percent for acetone to about 0.98 percent for 2-pentanone. However, the value for acetone is considerably larger than the values for the other ketones. This result is consistent with the expectation that acetone is hydrogen bonded, and the temperature dependence of the hydrogen bonds is manifested in the greater temperature dependence of the gas-film coefficient.

All these values are at least two times larger than the 0.4 percent/K value presented previously. This value was predicted on the basis of the combination of the dependence of the molecular diffusion coefficient on temperature and the dependence of the gas-film coefficient on the molecular diffusion coefficient. Also, the values, with the exception of that of acetone, are comparable to the experimental value of 0.94 percent/K found for water (Rathbun and Tai, 1983). Water is known to be hydrogen bonded, and thus the large value found for it is not without explanation. The large values of the temperature dependencies of the gas-film coefficients for the ketones was unexpected, however, with the possible exception of acetone.

Predictive Equations

The gas-film coefficient is a function of volatilization flux, vapor pressure, temperature, and molecular weight (as shown by equation 10). Several equations have been presented previously (eqs. 32, 36, and 37) for predicting volatilization flux as a function of vapor pressure, temperature, and molecular weight. Therefore, if an equation can be developed for predicting vapor pressure as a function of molecular weight and temperature, then the equations can be combined to give an equation for predicting the gas-film coefficient as a function of molecular weight and temperature.

Vapor pressure data were calculated from equations in the literature (Fuge and others, 1952; Ambrose and others, 1975) at temperatures of 293.2, 298.2, 303.2, 308.2, 313.2, 318.2, and 323.2 K or interpolated at these temperatures from tabular data (Stull, 1947). This procedure was necessary to get the data into a common form of dependence on temperature, because Ambrose and others (1975) used the Antoine equation (Reid and others, 1977) for presenting their data, whereas Fuge and others (1952) used the Kirchhoff equation (Reid and others, 1977) and Stull (1947) presented tabular data.

These vapor pressure data (in kilopascals) were then correlated with reciprocal absolute temperatures (in kelvins) according to

$$\log_e P_S = f - d/T, \tag{39}$$

where f and d are constants. Slopes and intercepts corresponding to d and f, respectively, are presented in table 11. The slopes and intercepts in table 11 were correlated with molecular weight M, which resulted in the equation

$$\log_e P_S = 16.1 \; \exp \; (0.00194M)$$

$$- \frac{2,540}{T} \exp \; (0.00689M). \tag{40}$$

Vapor pressures were calculated from equation 40 for all the ketones for the temperatures observed in the volatilization experiments and then compared with vapor pressures

Table 11. Slopes and intercepts of linear regressions of the logarithm of the vapor pressure as a function of reciprocal absolute temperature

Compound	Slope (K)	Logarithm intercept (kPa)
Acetone	-3,780	16.1
2-butanone	-4,180	16.5
2-pentanone	-4,600	17.0
3-pentanone	-4,620	17.0
4-methyl-2-pentanone	-4,920	17.5
2-heptanone	-5,710	18.5
2-octanone	-6,100	18.5

calculated from specific equations for each ketone from the original vapor pressure data references (Stull, 1947; Fuge and others, 1952; Ambrose and others, 1975). Root-mean-square differences of the form of equation 30 ranged from 1.13 percent for 2-butanone to 50.6 percent for 4-methyl-2-pentanone with an overall error for all the ketones of 15.5 percent. The error of 15.0 percent for acetone was also relatively large.

Equation 40 was combined with equation 10 and the equation presented by Rathbun and Tai (1984b) for predicting the volatilization flux, and the resultant equation was used to predict the gas-film coefficient as a function of molecular weight and temperature. The overall root-mean-square error calculated from an equation of the form of equation 30 was 7.25 percent, with errors for the individual ketones ranging from 4.54 percent for 4-methyl-2-pentanone to 9.88 percent for acetone. The small error for 4-methyl-2-pentanone was surprising in view of the large error of equation 40 in predicting vapor pressures for this ketone. There were apparently compensating errors in the calculation of the gas-film coefficient.

Equation 40 was also combined with equations 10 and 36 to predict the gas-film coefficient as a function of molecular weight and temperature. Calculated gas-film coefficients are plotted as a function of the experimental gas-film coefficient on logarithmic-logarithmic scales in figure 27. The overall root-mean-square error was 5.86 percent, with errors for the individual ketones ranging from 2.78 percent for 2-butanone to 8.59 percent for acetone. The gas-film coefficients are underpredicted at the upper part of the range. These coefficients are some of the data for acetone and
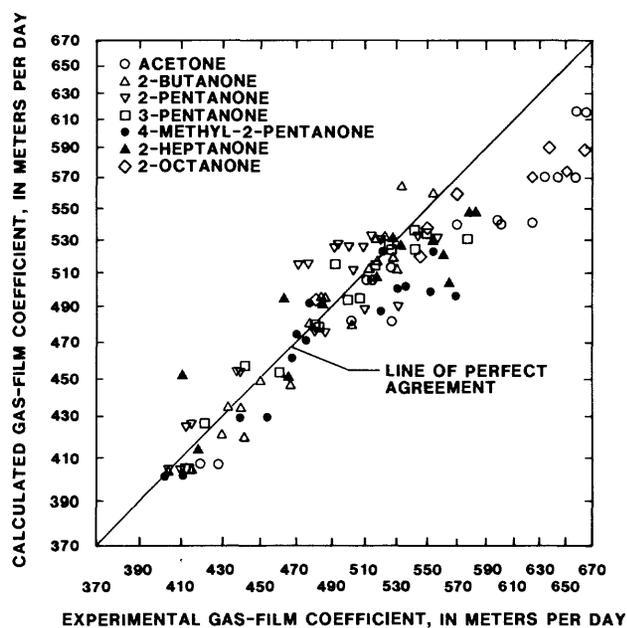
2-octanone. Figure 15 shows that the volatilization fluxes for most of the acetone points and for the higher of the 2-octanone points are underpredicted also, and this would contribute to the underprediction shown in figure 27. In general, however, the overall error of 5.86 percent is satisfactory.

Two other equations were presented previously for predicting the volatilization flux as a function of vapor pressure and molecular weight (eq. 32) and temperature and molecular weight (eq. 37). In the case of equation 32, it was necessary to exclude acetone because the slope and intercept of the logarithm of the volatilization flux as a function of the logarithm of the vapor pressure did not follow the pattern of the other ketones.

If the vapor pressure data are recorrelated excluding acetone and if the resultant equation is combined with equations 10 and 32 as before, then the result is an equation that predicts the gas-film coefficient with an overall root-mean-square error of 5.70 percent. This equation has less value, however, because of the exclusion of acetone.

In the case of equation 37, it was necessary to exclude 4-methyl-2-pentanone for the reason shown in figure 16. If the vapor pressure data are recorrelated excluding 4-methyl-2-pentanone, and if the resultant equation is combined with equations 10 and 37 as before, then the result is an equation that predicts the gas-film coefficient with an overall root-mean-square error of 11.9 percent. Thus, this equation is of less value than those presented previously, both because the error is larger and because it was necessary to exclude 4-methyl-2-pentanone.

In recorrelating the vapor pressure data excluding acetone and 4-methyl-2-pentanone, it was found that the equation constants differed little from those in equation 40, which was developed for all seven ketones. The distribution of the errors changed significantly, however. This indicates the sensitivity of the vapor pressure to molecular weight, which is a result of the logarithmic form of equation 40.

Water Evaporation Experiments

Results of the water evaporation experiments are given in table 12. Each experiment consisted of six or seven determinations of the gas-film coefficient, and the coefficients of variation of these determinations for each experiment are also given in table 12. The overall average gas-film coefficient for the evaporation of water in the six experiments was 824 m/d with a coefficient of variation of ± 3.24 percent. The overall average water temperature was 296.4 K.

ψ Factors

Volatilization fluxes at 293.2, 298.2, 303.2, and 313.2 K were interpolated from the basic experimental data by assuming that the logarithm of the flux varied linearly with reciprocal absolute temperature (Rathbun and Tai, 1984b).

Figure 27. Calculated gas-film coefficients as a function of the experimental gas-film coefficient.

Table 12. Gas-film coefficients for the evaporation of water

Experiment	Number of points	Gas-film coefficient (m/d)	Coefficient of variation (percent)	Water temperature (K)
1	6	851	8.38	296.0
2	7	836	14.1	296.0
3	7	818	12.7	296.2
4	7	794	13.6	296.2
5	6	792	11.7	296.9
6	6	851	7.56	297.0

These fluxes were then used with vapor pressures from the literature (Stull, 1947; Fuge and others, 1952; Ambrose and others, 1975) to calculate the gas-film coefficients for these temperatures from equation 10. Gas-film coefficients for the evaporation of water at these temperatures were obtained by adjusting the average value from table 12 to the appropriate temperature using the temperature dependence function determined by Rathbun and Tai (1983). Values of ψ were then calculated from equation 28 using water as the reference compound, and the results are presented in table 13.

The values of ψ are reasonably constant, with the exception of the acetone values, which are larger. The overall average ψ value excluding acetone is 0.534 with a coefficient of variation of ± 4.78 percent. If acetone is included, the average is increased to 0.562 and the coefficient of variation becomes ± 13.5 percent.

The ψ factors increase with temperature, although the increases are small except for acetone. Percentage increases for the 20-K temperature range given in table 13 range from 16.4 percent for acetone to 0.59 percent for 2-pentanone. Equation 28 suggests that ψ is independent of temperature only if the temperature dependencies of the molecular diffusion coefficients are exactly the same; therefore, the small increases for five of the ketones are not unreasonable. The behavior for acetone could be explained on the basis of a decrease in the extent of hydrogen bonding as the temperature increases. Water itself is also extensively hydrogen bonded, but the temperatures considered here are much closer to the boiling temperature of acetone than to that of water. Therefore, it might be expected that the extent of hydrogen bonding

would decrease faster for acetone than for water in this temperature range, which would result in an increasing ψ factor, as was observed.

This explanation is not applicable to 2-octanone, however. Because the extent of hydrogen bonding decreases as the size and complexity of the molecule increase (Pimental and McClellan, 1960), 2-octanone is the least likely of the seven ketones to be hydrogen bonded. Also, the relative constancy of the ψ factors for all the other ketones except acetone suggests that probably only acetone is appreciably hydrogen bonded.

Another possible explanation is that the vapor pressure data for 2-octanone are erroneous. As discussed previously, significant errors were found in the standard handbook (Weast, 1966) vapor pressure data for 2-pentanone, 3-pentanone, 4-methyl-2-pentanone, and 2-heptanone. A review of the literature revealed no sources of new data for 2-octanone, and since the handbook data (Weast, 1966) were reported in the year 1895, the accuracy of the data might be questioned. However, when vapor pressure data at 298.2 K for the seven ketones were plotted as a function of the normal boiling temperature, no large discrepancies were found for 2-octanone.

Consideration of the gas-film coefficients for the seven ketones at a specific temperature (figs. 12, 13, and 14) shows that acetone has the largest coefficient and 2-octanone has the next largest. The differences among the ketones are not random, however. There is a definite pattern for the gas-film coefficient to decrease from acetone to 2-butanone to 2-and 3-pentanone, and then for the coefficient to increase for 4-methyl-2-pentanone, 2-heptanone, and 2-octanone. This behavior is contrary to the commonly accepted dependence of the gas-film coefficient on molecular weight (fig. 25) and on the molecular diffusion coefficient (fig. 26), as discussed previously, and indicates that molecular weight and the molecular diffusion coefficient are not adequate descriptors of the volatilization characteristics of these ketones. These results suggest that all these ketones may possibly be hydrogen bonded to varying degrees, and further research is needed to explain the volatilization characteristics of these compounds.

The ψ factors presented in table 13 can, however, be used to predict gas-film coefficients for the volatilization of these ketones from streams and rivers. The procedure is to use the equation of Rathbun and Tai (1983), which predicts the gas-film coefficient for the evaporation of water from a canal as a function of windspeed and water temperature. Flow conditions in the canal were considered a reasonable approximation of flow conditions in streams and rivers, so that the predicted gas-film coefficient is applicable to streams and rivers. Once this gas-film coefficient has been predicted, it is used with equation 29 and the appropriate value of ψ from table 13 to predict the ketone gas-film coefficient. It is probably reasonable to extrapolate the ψ values in table 13 to lower temperatures for all the ketones except acetone because of the

Table 13. ψ factors at temperatures of 293.2, 298.2, 303.2, 308.2, and 313.2 K, and percentage increases with temperature

Compound	$\psi = k_G/k_{G\,WATER}$					Percentage increase
	293.2 K	298.2 K	303.2 K	308.2 K	313.2 K	
Acetone	0.676	0.704	0.732	0.760	0.787	16.4
2-butanone	.556	.558	.560	.561	.563	1.26
2-pentanone	.506	.506	.507	.508	.509	.59
3-pentanone	.508	.512	.516	.521	.527	3.74
4-methyl-2-pentanone	.520	.521	.523	.525	.527	1.35
2-heptanone	.518	.519	.521	.525	.529	2.12
2-octanone	.554	.565	.574	.584	.593	7.04

small dependencies of ψ on temperature. For acetone, such an extrapolation might result in large errors because of the large temperature dependence of ψ and the previously discussed temperature dependence of the extent of hydrogen bonding.

Hydrogen Bonding

Most of the evidence assembled from the literature by Pimental and McClellan (1960) suggests that ketones, particularly acetone, are not hydrogen bonded. Other evidence presented previously, such as vapor pressure data and molecular diffusion coefficient data for the binary systems acetone-carbon tetrachloride and 2-butanone-carbon tetrachloride, suggests that acetone and 2-butanone are hydrogen bonded to some extent. More recent work (Huyskens and Nauwelaerts, 1980) also suggests that acetone could be hydrogen bonded.

Results of the present study in general suggest a small degree of hydrogen bonding for acetone. The slope of the correlation of the logarithm of the volatilization flux as a function of reciprocal absolute temperature was much larger for acetone than for the other ketones. Also, the temperature dependence of the gas-film coefficient was much larger for acetone than for the other ketones, and the acetone-water gas-film coefficient ratio increased with temperature, whereas the ratios for the other ketones were much less dependent on temperature. These observations are consistent with the accepted large temperature dependence of the degree of hydrogen bonding.

The acetone results for many of the other analyses also differed considerably from the results for the other ketones. These differences suggested acetone molecular weights of 71, 83, 86, and 120 g/g mol compared with the stoichiometric weight of 58.08 g/g mol; these values indicate a small degree of hydrogen bonding. Analysis of the Hartley (1969) factor, however, suggested molecular weights of 69, 80, and 91 g/g mol at temperatures of 293.2, 303.2, and 313.2 K, respectively. These molecular weights are consistent with a small degree of hydrogen bonding, but the increase with temperature is inconsistent with the accepted temperature dependence of the degree of hydrogen bonding.

The vapor pressure of acetone was less than expected on the basis of the vapor pressures of the other ketones, and a reduced vapor pressure is characteristic of hydrogen-bonded substances. Heats of vaporization approximated from slopes of the logarithm of the vapor pressure at a specific temperature as a function of boiling temperature were 25 to 30 percent larger than expected, and this discrepancy is characteristic of hydrogen-bonded substances. However, the Trouton constants were only several percent larger than the expected value, and this difference suggests very little hydrogen bonding.

The branched structure of 4-methyl-2-pentanone was expected to inhibit the formation of hydrogen bonds. It was found that the vapor pressure for this ketone was about 30

percent larger than that predicted on the basis of a logarithm of vapor pressure versus boiling temperature plot for the linear ketones, in agreement with the expected behavior. Also, the points for this ketone deviated considerably from the points for the linear ketones in plots of the logarithm of the volatilization flux as a function of molecular weight.

The behavior of 2-octanone in general was not as expected. Because the degree of hydrogen bonding decreases as molecular size increases, it was expected that 2-octanone would have the least tendency of any of the ketones to form hydrogen bonds. However, the temperature dependencies of both the β factor of Chiou and others (1980, 1983) and the ketone-water gas-film coefficient ratio were larger than expected on the basis of the other ketones, excluding acetone. Also, the vapor pressure of 2-octanone was less than expected on the basis of the vapor pressures of the other ketones. An exact explanation for these differences is not possible on the basis of the information presently available.

To summarize, most of the results of this study suggest that acetone is hydrogen bonded to some extent. There are, however, several results that do not support this conclusion. It is believed that this is because the degree of hydrogen bonding is small, and therefore the experimental errors in some cases are sufficiently large to obscure the results. The results for 4-methyl-2-pentanone are consistent with the suggestion that this ketone is not hydrogen bonded because of its branched structure. The results for 2-octanone were not as expected, and these differences cannot be explained with the information now available.

Deviations from expected behavior were discussed in this report in terms of hydrogen bonding. This is a logical choice because of the presence of the oxygen electron donor in the ketone molecules. Other molecular interactions are possible, however. A complete discussion of all types of possible molecular interactions that could account for the observed behavior of the ketones studied is beyond the scope of this report.

SUMMARY AND CONCLUSIONS

Volatilization fluxes for acetone, 2-butanone, 2-pentanone, 3-pentanone, 4-methyl-2-pentanone, 2-heptanone, and 2-octanone were measured in the laboratory over a range of temperatures. Gas-film coefficients for quantifying the volatilization of these ketones from water were calculated using the volatilization fluxes and vapor pressure data from the literature. The data were analyzed in terms of the dependence of the volatilization flux on vapor pressure, temperature, and molecular weight and the dependence of the gas-film coefficient on molecular weight, molecular diffusion coefficient, and temperature. Several predictive equations for both the volatilization flux and the gas-film coefficient were developed. Gas-film coefficients for the evaporation of water were measured under the same conditions used for the volatilization measurements for the ket-

ones. These water and ketone gas-film coefficients can be combined with an equation for predicting the gas-film coefficient for the evaporation of water from a canal to estimate the gas-film coefficients for the volatilization of these ketones from streams and rivers. This procedure assumes that flow conditions in the canal were a reasonable approximation of flow conditions in streams and rivers.

Specific conclusions resulting from this study are as follows:

1. Development of an equation for predicting the volatilization flux as a function of vapor pressure and molecular weight resulted in large deviations for acetone. Excluding acetone from consideration resulted in an equation with a root-mean-square error of prediction of 7.17 percent. The difference in behavior for acetone was attributed to the possibility that it may be hydrogen bonded.

2. Volatilization fluxes interpolated from the experimental data by assuming a logarithmic dependence on reciprocal absolute temperature were found to be virtually identical to fluxes calculated from gas-film coefficients interpolated by assuming a logarithmic dependence on temperature.

3. An empirical correlation approach resulted in an equation with the volatilization flux dependent on vapor pressure to the 0.798 power, molecular weight to the -0.486 power, and absolute temperature to the 5.25 power. Comparison of the experimental volatilization fluxes with predicted values gave a root-mean-square error of 10.0 percent. Comparison of the logarithm of the experimental volatilization fluxes with the logarithm of the predicted values gave an error of 1.54 percent.

4. Development of an equation for predicting the volatilization flux as a function of molecular weight and temperature resulted in large deviations for 4-methyl-2-pentanone. Excluding this ketone from consideration resulted in an equation with a root-mean-square error of 7.62 percent. Experimental volatilization fluxes for 4-methyl-2-pentanone ranged from 34 to 47 percent larger than fluxes calculated from the equation. The larger fluxes for 4-methyl-2-pentanone were attributed to the fact that the ketone has a branched structure that may inhibit the formation of hydrogen bonds relative to straight-chain ketones.

5. Four factors based on equations from the literature combining volatilization flux or rate with vapor pressure, molecular weight, temperature, and molecular diffusion coefficient were calculated, and none were found to be constant as predicted. In general, the factors increased with molecular weight, with acetone differing in behavior from the other ketones. Values for acetone corresponded to compounds with larger molecular weight, which is consistent with the suggestion that acetone is hydrogen bonded. The factors also increased with temperature, contrary to expectations, and the rate of increase was largest for acetone. This behavior is also characteristic of a compound subject to hydrogen bonding.

6. An equation for predicting the volatilization time, which is the reciprocal of the volatilization rate, was developed by correlating the logarithm of vapor pressure with normal boiling temperature and using 2-pentanone as a reference compound. Comparison of the experimental and predicted volatilization times showed satisfactory agreement. The branched ketone 4-methyl-2-pentanone was excluded from this development because the vapor pressure versus boiling temperature dependence was different from that of the straight-chain ketones. Vapor pressures for this ketone were about 30 percent larger than values predicted from the vapor pressure versus boiling temperature relations for the straight-chain ketones.

7. Heats of vaporization at 298.2 K estimated from vapor pressure data were in good agreement with experimental values from the literature for four of the ketones. The heat of vaporization depended on the molecular weight to the 0.605 power. Heats of vaporization at the normal boiling temperature were calculated from an equation in the literature and found to be in good agreement with values from the literature for four of the ketones. Values of the Trouton constant calculated from the heats of vaporization at the normal boiling temperature suggested that the ketones are not hydrogen bonded to any appreciable extent.

8. Relations from the literature commonly used for describing the dependence of the gas-film coefficient on molecular weight and the molecular diffusion coefficient were not applicable to the gas-film coefficients for the ketones. In general, the largest gas-film coefficients were observed for acetone. The coefficients then decreased through 2-butanone and 2- and 3-pentanone and then increased for 2-heptanone and 2-octanone. Values for 4-methyl-2-pentanone were generally comparable to the values for 2-heptanone.

9. The temperature dependence of the gas-film coefficient was much larger for acetone than for the other ketones, in agreement with the suggestion that acetone is hydrogen bonded. Percentage increases per kelvin ranged from about 1.7 percent for acetone to about 0.98 percent for 2-pentanone. These values are larger than the 0.4 percent/K value predicted on the basis of the temperature dependence of the molecular diffusion coefficient. However, excluding acetone, the values generally agree with the literature value of 0.94 percent/K for the temperature dependence of the gas-film coefficient for water evaporation.

10. An equation was developed for predicting vapor pressures of the ketones as a function of molecular weight and temperature. Combining this equation with two of the equations developed for predicting the volatilization flux resulted in two equations for predicting the gas-film coefficient as a function of molecular weight and temperature. Root-mean-square errors of prediction for the experimental data were 7.25 percent and 5.86 percent for these equations.

11. Ratios of the gas-film coefficient for the volatilization of the ketones to the gas-film coefficient for the evapora-

tion of water were approximately constant for all the ketones, with the exception of acetone. Values for acetone were considerably larger. The ratios increased with temperature, although the increases were small except for acetone. These ratios, when combined with an equation from the literature for predicting the gas-film coefficient for evaporation of water from a canal, can be used to predict the gas-film coefficient for volatilization of ketones from streams and rivers. This procedure assumes that flow conditions in the canal were a reasonable approximation of flow conditions in streams and rivers.

12. Dependencies on temperature of the volatilization fluxes and gas-film coefficients of acetone in general did not follow the trends with molecular weight observed for the other ketones. This difference in behavior was attributed to a small degree of hydrogen bonding for acetone. Deviations for 4-methyl-2-pentanone were attributed to the branched structure of this ketone, which hinders the formation of hydrogen bonds. Dependencies on temperature of some of the factors and coefficients for 2-octanone were larger than expected, because 2-octanone was believed to have the least tendency of any of the ketones studied to form hydrogen bonds. An explanation for these observations was not possible with the information presently available.

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Table 14. Experimental volatilization fluxes and temperatures and computed vapor pressures and gas-film coefficients for acetone

Volatilization flux [(g/min)/m^2]	Temperature (K)	Vapor pressure[1] (kPa)	Gas-film coefficient[2] (m/d)
302.8	297.4	29.84	622.7
292.9	297.6	30.14	596.9
274.4	297.2	29.56	569.2
290.7	297.3	29.73	600.0
215.1	293.2	24.73	526.0
370.1	301.8	35.92	641.6
377.5	301.7	35.86	655.4
365.0	301.8	35.92	632.7
175.1	288.2	19.73	527.5
166.7	288.2	19.73	502.3
102.8	280.9	13.93	427.8
101.5	281.1	14.06	418.6
483.4	307.9	46.19	664.9
479.1	308.0	46.36	656.8
199.9	292.0	23.46	513.5
199.7	292.0	23.53	511.4

[1]Computed from an equation based on the data of Ambrose and others (1975).

[2]Computed from equation 10.

Table 15. Experimental volatilization fluxes and temperatures and computed vapor pressures and gas-film coefficients for 2-butanone

Volatilization flux [(g/min)/m^2]	Temperature (K)	Vapor pressure[1] (kPa)	Gas-film coefficient[2] (m/d)
187.3	307.5	18.54	516.3
193.4	307.8	18.74	528.0
97.01	294.7	10.19	466.1
95.28	295.1	10.40	449.3
206.1	309.9	20.54	516.9
210.7	310.2	20.79	522.2
81.11	292.4	9.106	432.9
81.99	292.3	9.079	438.8
71.73	289.4	7.817	441.4
70.00	289.5	7.853	428.9
56.97	285.9	6.541	414.0
54.61	285.8	6.510	398.6
137.2	300.8	13.66	502.1
131.4	301.0	13.76	477.4
150.1	303.7	15.62	485.2
149.4	303.7	15.60	483.3
265.1	314.5	25.05	553.2
262.0	315.2	25.76	532.8
180.1	306.8	17.94	512.0
185.1	306.6	17.83	529.0

[1]Computed from an equation based on the data of Ambrose and others (1975).

[2]Computed from equation 10.

Table 16. Experimental volatilization fluxes and temperatures and computed vapor pressures and gas-film coefficients for 2-pentanone

Volatilization flux [(g/min)/m^2]	Temperature (K)	Vapor pressure[1] (kPa)	Gas-film coefficient[2] (m/d)
123.3	315.0	10.75	502.8
120.4	315.6	11.08	476.9
118.4	315.6	11.07	469.4
103.2	310.6	8.766	508.6
108.9	310.9	8.896	529.7
45.24	297.5	4.549	411.7
46.05	297.8	4.614	413.5
87.78	308.0	7.746	485.7
87.78	308.4	7.871	478.5
35.12	293.0	3.560	402.2
36.03	293.2	3.600	408.3
64.72	303.6	6.231	438.8
64.94	303.8	6.272	437.6
158.8	318.6	12.66	556.4
157.2	318.9	12.83	543.4
139.7	317.7	12.15	508.2
137.9	318.1	12.37	493.2
147.1	318.4	12.57	518.4
148.1	318.8	12.79	513.6
134.6	317.6	12.10	491.7
137.0	317.7	12.14	499.0

[1]Computed from an equation based on the data of Ambrose and others (1975).

[2]Computed from equation 10.

Table 17 Experimental volatilization fluxes and temperatures and computed vapor pressures and gas-film coefficients for 3-pentanone

Volatilization flux [(g/min)/m^2]	Temperature (K)	Vapor pressure[1] (kPa)	Gas-film coefficient[2] (m/d)
124.5	315.6	11.10	492.3
130.8	315.7	11.12	516.4
106.2	311.7	9.244	498.4
108.9	311.8	9.314	507.3
46.86	297.8	4.619	420.4
142.4	317.3	11.96	525.6
147.1	317.3	12.00	541.4
145.2	317.8	12.23	524.9
89.56	308.6	7.966	482.7
89.56	308.7	8.028	479.2
35.58	292.8	3.532	410.4
35.98	293.0	3.563	411.7
67.68	303.6	6.216	459.8
66.42	304.0	6.368	441.2
160.5	319.1	12.96	549.7
165.1	318.6	12.68	577.1
160.2	319.3	13.13	542.2

[1]Computed from an equation based on the data of Ambrose and others (1975).

[2]Computed from equation 10.

Table 18. Experimental volatilization fluxes and temperatures and computed vapor pressures and gas-film coefficients for 4-methyl-2-pentanone

Volatilization flux [(g/min)/m^2]	Temperature (K)	Vapor pressure[1] (kPa)	Gas-film coefficient[2] (m/d)
36.08	299.7	2.846	454.4
35.16	299.9	2.873	438.8
54.43	307.3	4.270	468.3
94.58	316.2	6.694	534.2
93.69	316.2	6.681	530.2
80.74	313.4	5.821	519.8
76.68	314.1	6.032	477.5
62.07	309.7	4.848	474.2
63.10	310.2	4.968	471.1
18.52	289.9	1.614	397.7
18.73	289.6	1.581	410.1
96.20	315.2	6.385	567.9
94.58	315.5	6.476	551.0
112.2	320.6	8.249	521.7
119.3	320.6	8.261	553.5

[1]Computed from an equation based on the data of Fuge and others (1952).

[2]Computed from equation 10.

Table 19. Experimental volatilization fluxes and temperatures and computed vapor pressures and gas-film coefficients for 2-heptanone

Volatilization flux [(g/min)/m^2]	Temperature (K)	Vapor pressure[1] (kPa)	Gas-film coefficient[2] (m/d)
8.627	300.4	0.5858	464.5
21.62	314.7	1.385	515.9
22.45	313.8	1.312	563.4
27.78	317.8	1.653	560.7
30.01	319.6	1.821	553.0
16.43	310.8	1.106	484.8
16.36	311.6	1.156	462.8
4.103	290.5	.3005	416.4
7.767	300.6	.5926	413.7
38.23	323.5	2.246	578.1
38.19	323.4	2.238	579.6
28.72	319.6	1.825	528.0
27.77	318.9	1.751	531.0

[1]Computed from an equation based on the data of Ambrose and others (1975).

[2]Computed from equation 10.

Table 20. Experimental volatilization fluxes and temperatures and computed vapor pressures and gas-film coefficients for 2-octanone

Volatilization flux [(g/min)/m^2]	Temperature (K)	Vapor pressure[1] (kPa)	Gas-film coefficient[2] (m/d)
2.869	299.9	0.1670	481.6
12.27	319.7	.5882	623.2
13.49	320.7	.6220	650.3
9.727	317.2	.5068	569.2
6.505	311.0	.3447	548.7
5.063	307.0	.2666	544.8
16.24	324.4	.7749	635.4
16.61	324.1	.7589	663.1

[1]Computed from an equation based on data from Stull (1947).

[2]Computed from equation 10.