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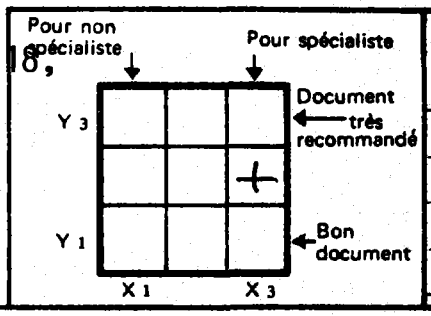
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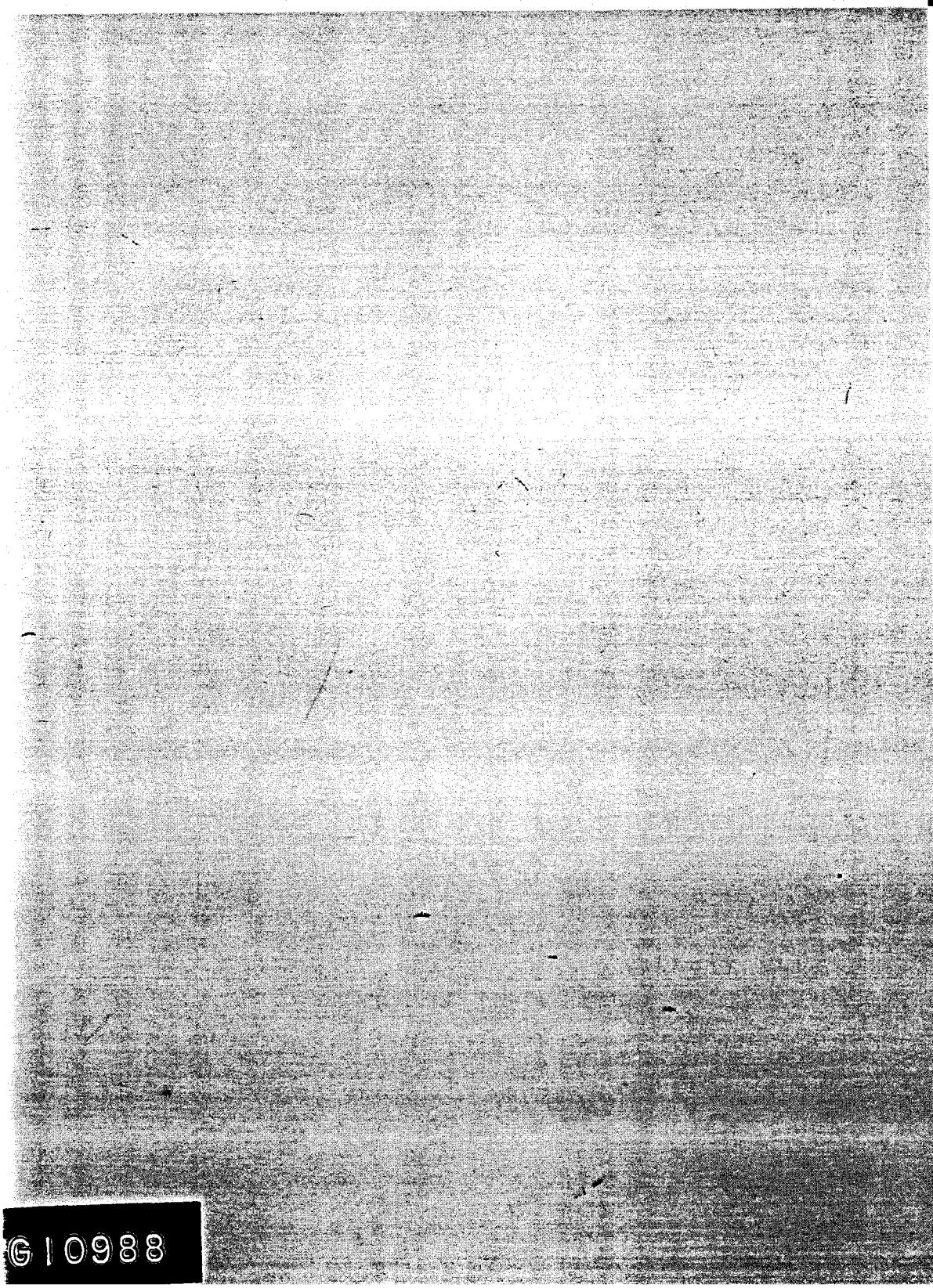
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Description d'un modèle mathématique permettant de prévoir et optimiser la volatilisation de composés volatils : Acétone et Alcool butylique

20 figures
13 tableaux

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

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

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

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

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

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

| | | *Units* |
|---|---|---|
| $\alpha$ | Pre-exponential constant in the general empirical equation for the temperature dependence of a rate constant for a chemical, biological, or physical process | Reciprocal days |
| $\beta$ | Exponential constant in the general empirical equation for the temperature dependence of a rate constant for a chemical, biological, or physical process | Reciprocal kelvins |
| $\gamma$ | Activity coefficient for the solute in water | --- |
| $\Delta W/A\Delta t$ | Volatilization flux | Grams per minute per square meter |
| $\nu$ | Exponent on the molecular-diffusion coefficient in the relation between the film coefficient and the molecular-diffusion coefficient | --- |
| $\theta$ | Temperature coefficient for expressing empirically the temperature dependence of a rate coefficient for a chemical, biological, or physical process, equal to the exponential of $\beta$ | --- |
| $\mu$ | Viscosity of water | Grams per meter per second |
| $\rho$ | Density of water | Grams per cubic meter |
| $\phi$ | Constant in the reference-substance concept for the liquid film; equal to the ratio of the liquid-film coefficient for the volatilization of an organic solute to the liquid-film coefficient for the volatilization of a reference substance | --- |
| $\psi$ | Constant in the reference-substance concept for the gas film, equal to the ratio of the gas-film coefficient for the volatilization of an organic solute to the gas-film coefficient for the volatilization of a reference substance | --- |

## CONVERSION FACTORS

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

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

*Temperature*

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

$$°C = K-273.15$$

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

$$°R = (K-273.15)\ (1.8) + 491.7$$

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

$$°F = (K-273.15)\ (1.8) + 32.0$$

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

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

**Abstract**

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

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

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

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

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

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

Ratios of the liquid-film coefficients for the volatilization of acetone and t-butyl alcohol to the liquid-film coefficients for the absorption of oxygen were independent of temperature and mixing conditions in the water. Ratios of the gas-film coefficients for the volatilization of acetone and t-butyl alcohol to