# Effects of thermodynamics parameters on mass transfer of volatile pollutants at air-water interface

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## Abstract

A transient three-dimensional coupling model based on the compressible volume of fluid (VOF) method was developed to simulate the transport of volatile pollutants at the air-water interface. VOF is a numerical technique for locating and tracking the free surface of water flow. The relationships between Henry's constant, thermodynamics parameters, and the enlarged topological index were proposed for nonstandard conditions. A series of experiments and numerical simulations were performed to study the transport of benzene and carbinol. The simulation results agreed with the experimental results. Temperature had no effect on mass transfer of pollutants with low transfer free energy and high Henry's constant. The temporal and spatial distribution of pollutants with high transfer free energy and low Henry's constant was affected by temperature. The total enthalpy and total transfer free energy increased significantly with temperature, with significant fluctuations at low temperatures. The total enthalpy and total transfer free energy increased steadily without fluctuation at high temperatures.
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*Keywords:* Henry's constant; Mass transfer at interface; Thermodynamics parameters; Topological index; Volatile pollutants

## 1. Introduction

Accurately predicting the temporal and spatial distribution of volatile pollutants in water and air after leakage can provide an important insight for health evaluation of hydrosphere ecosystems. However, mass transfer of volatile pollutants at the air-water interface is a complex process and we do not yet have a deep and accurate understanding of its mechanisms and factors (Jähne and Haubecker, 1998; Bade, 2009; Wang et al., 2011). This affects the prediction results of the temporal and spatial distribution of volatile pollutants. Thus, it is necessary

to reach a better understanding of mass transfer of volatile pollutants at the air-water interface.

In computational fluid dynamics, the volume of fluid (VOF) method is a numerical technique for locating and tracking the air-water interface (Larmaei and Mahdi, 2010). A transient three-dimensional coupling transport model based on the compressive VOF method was used to simulate mass transfer at the air-water interface (Chen and Jiang, 2010). Henry's constant is an important parameter in a coupling transport model for volatile pollutants. It relates not only to the thermodynamics parameters, such as the transfer free energy and the standard enthalpy, but also to the molecular structure of pollutants (Cheng et al., 2004; Amelia et al., 2011; Duran et al., 2010). Quantitative structure-activity/property relationships (QSAR/QSPR) represent an attempt to correlate activities or properties with structural descriptors of compounds. There are many methods for quantifying molecular structures, of which the topological index is the most popular since it can be obtained directly from molecular structures and rapidly

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computed for large numbers of molecules. The first reported use of a topological index in chemistry was by Wiener in his study of paraffin boiling points (Wiener, 1947). Degeneracy and low discriminating power have been the two shortcomings of Wiener's index, resulting in ambiguity and uniqueness in its properties. This is one major reason that Wiener's index has not seen widespread use in the QSAR/QSPR community (Bajaj et al., 2004). The enlarged topological index of distance matrix $W^*$ has been defined to forecast Henry's constants of some alkylbenzene and alcohol compounds in standard conditions (Yang et al., 2004). At present, the relationship between Henry's constant and the molecular structure of pollutants in nonstandard conditions has not been established. Mathematical models have been developed to describe the relationships between Henry's constant, thermodynamics parameters, and $W^*$ in nonstandard conditions in this study.

Thermodynamics parameters such as the transfer free energy and the standard enthalpy have been used for volatilization study in recent years. The transfer free energy and the standard enthalpy are defined for per mole of pollutants and they are independent of time. However, mass transfer at the air-water interface in sudden water pollution relates to time. Thus, the transfer free energy and the standard enthalpy cannot be used as effective thermodynamic parameters in sudden water pollution. Total transfer free energy and total enthalpy were defined to analyze the changes of thermodynamics parameters with time at different temperatures. The total transfer free energy and total enthalpy for mass transfer at the air-water interface are discussed below.

## 2. Model development

### 2.1. Mathematical equations for transportation

The equations for compressive VOF are as follows (Chen and Jiang, 2010):

$$\frac{\partial \rho}{\partial t} + \frac{\partial (\rho u_i)}{\partial x_i} = 0 \tag{1}$$

$$\frac{\partial (\rho u_j)}{\partial t} + \frac{\partial (\rho u_j u_i)}{\partial x_i} = \frac{\partial}{\partial x_j}\left(\eta_t \frac{\partial u_j}{\partial x_i}\right) - \frac{\partial p}{\partial x_j} + \rho f_j \tag{2}$$

$$\frac{\partial \alpha}{\partial t} + \frac{\partial (u_i \alpha)}{\partial x_i} - \frac{\partial}{\partial x_i}\left[\frac{(u_{Gi} - u_{Li})(1-\alpha)\alpha \rho_G}{\rho}\right] = 0 \tag{3}$$

where $\rho$ and $\rho_G$ are the densities of the fluid in the computational cell and air, respectively, in kg/m$^3$; $t$ is time, in s; the subscripts $i$ and $j$ are equal to 1, 2, or 3, representing the three directions in the Cartesian coordinate system; $u$, $u_L$, and $u_G$ are the velocities of the fluid in the computational cell, water, and air, respectively, in m/s; $\eta_t$ is the turbulent dynamic viscosity, in m$^2$/s, which can be calculated with the realizable $k$-$\varepsilon$ model; $f$ is the body force, in m/s$^2$; $p$ is the pressure, in Pa; and $\alpha$ is the water volumetric fraction of the computational cell.

The air-water coupling transport model for volatile pollutants is written as follows (Chen and Jiang, 2010):

$$\frac{\partial C}{\partial t} + \frac{\partial (u_i C)}{\partial x_i} + \frac{\partial}{\partial x_i}\left[(u_{Gi} - u_{Li})\alpha(1-\alpha)\frac{H_{aw} - 1}{\alpha + (1-\alpha)H_{aw}}C\right] =$$
$$\frac{\partial^2}{\partial x_i \partial x_i}\left[\frac{E_i\alpha + (1-\alpha)H_{aw}D}{\alpha + (1-\alpha)H_{aw}}C\right] \tag{4}$$

where $C$ is the total concentration of pollutants in the computational cell, in kg/L; $H_{aw}$ is Henry's constant; and $D$ and $E_i$ are the turbulent mass diffusivities in air and water, respectively, in m$^2$/s.

### 2.2. Henry's constant and thermodynamics parameters

The driving force of volatile pollutants' transportation is the difference in chemical potential related to activity coefficients. Mass transfer at the air-water interface is at instantaneous equilibrium. The equilibrium constant is called Henry's constant (Schwarzenbach et al., 2003):

$$H_{aw} = \exp\left(-\frac{RT\ln\gamma_a - RT\ln\gamma_w}{RT}\right) = \exp\left(-\frac{\Delta_{12}G}{RT}\right) \tag{5}$$

where $\gamma_a$ and $\gamma_w$ are the activity coefficients of volatile pollutants in air and water, respectively; $\Delta_{12}G$ is the transfer free energy, in J/mol; $R$ is the gas constant, which is 8.314 J/(mol·K); and $T$ is the Kelvin temperature.

Taking the derivative of Eq. (5) with respect to temperature and using the Gibbs-Helmholtz equation (Lucia and Henley, 2013) yield:

$$\frac{d(\ln H_{aw})}{dT} = -\frac{1}{R}\frac{d(\Delta_{12}G/T)}{dT} = \frac{1}{R}\frac{\Delta_{12}H}{T^2} \tag{6}$$

where $\Delta_{12}H$ is the standard enthalpy, in J/mol. It is considered constant over a small temperature range. Henry's constant in nonstandard conditions is obtained from Eq. (6):

$$\ln H_{aw} = -\frac{\Delta_{12}H}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) + \ln H_0 \tag{7}$$

where $H_0$ is Henry's constant in standard conditions with $T_0 = 298$ K.

Henry's constant relates not only to the thermodynamics parameters but also to the molecular structure of pollutants. There are many methods of quantifying the molecular structure, of which the topological index is the most popular since it can be obtained directly from molecular structures and rapidly computed for large numbers of molecules. The enlarged topological index of distance matrix $W^*$ was defined as $W^* = MSI$, where $M = (m_1, m_2, \cdots, m_n)$, $S = (S_{kj})_{n \times n}$, $I = (I_1, I_2, \cdots, I_n)^T$, $m_k$ is the number of bonded electrons, $I_k$ is electronegativity, $S_{kj} = 1/R_{kj}$, and $R_{kj}$ is the sum of the bond length from $k$ to $j$. The linear relationships between $\ln H_0$ and $W^{*0.5}$ of alkylbenzene, alcohol, aldehyde, and hydrocarbon are listed in Table 1 (Yang et al., 2004).