

Thermodynamic Analysis of the Effect of Temperature on VOCs Emission from Building Materials

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ABSTRACT: *This study attempts to interpret the physical mechanism of temperature affecting the emission of VOCs from building materials from the viewpoint of thermodynamics. VOCs adsorbed onto building materials are assumed to form a condensed thermodynamic system. The kinetic energy of VOCs molecules takes values from zero to infinite. It is assumed that only VOCs molecules with a kinetic energy greater than the critical value can escape from building materials. Based on the Maxwell velocity distribution function, the correlation between the initial concentration of VOCs within building materials and temperature is derived. By use of the Laplace transform technique and the theorem of the initial value, the correlation between the initial emission factor and temperature is further presented on the basis of the diffusion mechanism. The present thermodynamic model was validated through experimental data in the literature. A good agreement between the present thermodynamic model and experimental data is obtained. The present thermodynamic model can also explain the effect of temperature on the emission of other gases from materials.*

KEYWORDS: *Initial emittable concentration; Initial emission factor; Temperature; VOCs; Thermodynamic model; The kinetic theory of gases.*

INTRODUCTION

Volatile Organic Compounds (VOCs) emitted by numerous building materials, furniture, and household appliances have a severe adverse effect on Indoor Air Quality (IAQ) and human comfort, health, and productivity [1]. The emission of VOCs from building materials concerns the diffusion of VOCs within building materials and the adsorption/desorption of VOCs at the material-air interface. The key parameters influencing the emission of VOCs from building materials are the initial concentration ($C_{m,0}$), the diffusion coefficient (D_m), and the partition

coefficient (K_{ma}). Many experimental methods have been presented to measure these parameters [2–6]. Recently, a family of methods based on equilibrium state has been developed to measure the initial concentration and the partition coefficient at the material-air interface simultaneously [6–8].

The emission of VOCs from building materials is strongly affected by environmental conditions. When temperature increases, the diffusion coefficient increases [9] whereas the partition coefficient decreases [10].

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1021-9986/2023/2/558-564

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Moreover, the initial emission factor of VOCs usually increases [11,12]. Recently, the initial concentration emitted from building materials has been proved to depend on temperature [13,14]. Xiong *et al.* [15] developed an empirical correlation to describe the effect of temperature on the initial concentration. To the best knowledge of authors, a rigid physical interpretation of the effect of temperature on the emission of VOCs from building materials has not been proposed.

The objective of this paper is to derive a thermodynamic model describing the effect of temperature on the emission of VOCs from building materials. The presented theoretical model is constructed on the kinetic molecular theory of gases. The correlation is validated with the experimental data in literature.

THEORETICAL SECTION

Thermodynamic Model

When VOCs are adsorbed onto building materials, the occupied volume of VOCs becomes greatly small. VOCs adsorbed onto building materials form a condensed thermodynamic system. Only partial VOCs within the building materials can enter into the air at certain temperature. In the present study, the following assumptions are made

1- The adsorbed VOCs consists of enormous molecules of mass m in ceaseless random and rapid motion.

2- The speeds of individual VOCs molecule actually span a wide range.

3- Only molecules with the kinetic energy greater than critical energy level may escape from the building material and enter into the air.

The former two assumptions come from the kinetic molecular theory of gases, which has been thought to the most perfect theory that can derive quantitative correlation only from limited assumptions. Apparently, the numbers of VOCs molecules at each velocity level are different. It means that the kinetic energies of individual VOCs molecule are also different. The velocities of VOCs molecules comply with Maxwell velocity distribution function, which reads [16]

$$f(v) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT} \right)^{1.5} v^2 \exp\left(-\frac{mv^2}{2kT}\right) \quad (1)$$

Where, $f(v)$ is the velocity distribution function of the gas molecules with the velocity v , m is the molecular mass of VOCs, k is Boltzmann constant, v is the velocity, T is the absolute temperature.

Further, by defining

$$E = \frac{1}{2} mv^2 \quad (2)$$

the kinetic energy distribution function can be derived from Eq. (1), which reads

$$f(E) = \frac{2}{\sqrt{\pi}} \left(\frac{1}{kT} \right)^{1.5} E^{0.5} \exp\left(-\frac{E}{kT}\right) \quad (3)$$

Theoretically, the kinetic energy of a single molecule may be infinite. $f(E)$ obtains the minimum value when the kinetic energy takes the value of zero or infinite. The definition of distribution function of kinetic energy E is

$$f(E) = \frac{1}{n_0} \frac{dn}{dE} \quad (4)$$

Where, n_0 is the total number of molecules within the system, dn is the molecules located in the range E to $E+dE$. Thus, for a given thermodynamic system, the fraction of molecules with the kinetic energy greater than energy level E_0 can be obtained by the integration of Eq. (3) from E_0 to infinite

$$F_{E_0 \rightarrow \infty} = \int_{E_0}^{\infty} \frac{2}{\sqrt{\pi}} \left(\frac{1}{kT} \right)^{1.5} E^{0.5} \exp\left(-\frac{E}{kT}\right) dE \quad (5)$$

Where $F_{E_0 \rightarrow \infty}$ is the fraction of molecules with the kinetic energy greater than E_0 . Apparently, $F_{0 \rightarrow \infty} = 1$ exists according to Eq. (4). By performing integration by parts on Eq. (5), we can obtain

$$F_{E_0 \rightarrow \infty} = \frac{2}{\sqrt{\pi}} \exp\left(-\frac{E_0}{kT}\right) \left(\frac{E_0}{kT}\right)^{0.5} \times \left[1 + \left(\frac{kT}{2E_0}\right) - \left(\frac{kT}{2E_0}\right)^2 + 3\left(\frac{kT}{2E_0}\right)^3 - \dots \right] \quad (6)$$

E_0 is usually far greater than the product of temperature and Boltzmann constant, which means that the value of $kT/2E_0$ is quite small. By omitting the high-order terms in the bracket at the right-hand of Eq. (6), we can obtain

$$F_{E_0 \rightarrow \infty} = \frac{2}{\sqrt{\pi}} \exp\left(-\frac{E_0}{kT}\right) \left(\frac{E_0}{kT}\right)^{0.5} \quad (7)$$

Following assumption 3), there exists

$$F_{E_0 \rightarrow \infty} = \frac{C_{m,0}}{C_0} \quad (8)$$

Where C_0 is the total concentration in the building material, $C_{m,0}$ is the initial concentration. Thus, the initial concentration can be expressed as follows

$$\frac{C_{m,0}}{C_0} = \frac{2}{\sqrt{\pi}} \exp\left(-\frac{E_0}{kT}\right) \left(\frac{E_0}{kT}\right)^{0.5} \quad (9)$$

According to Eq.(9), the correlation between the temperature and the initial concentration can be expressed with two constants as follows:

$$C_{m,0} = \frac{A_1}{T^{0.5}} \exp\left(-\frac{B_1}{T}\right) \quad (10)$$

The transport of VOCs within building materials can be described by a transient diffusion equation.

$$\frac{\partial C_m}{\partial t} = D_m \frac{\partial^2 C_m}{\partial x^2} \quad (11)$$

Thus, the emission factor can be written as

$$R = -D_m \left. \frac{\partial C_m}{\partial x} \right|_{x=\delta} \quad (12)$$

Where R is the emission factor, C_m is the concentration of VOCs in the material, D_m is the diffusion coefficient of VOCs in the material, δ is the thickness of the material layer, x is the coordinate.

The boundary conditions and initial conditions of Eq. (11) have been described by several authors [17–19]. With the help of Laplace transform technique, Deng and Kim [17] obtained the analytical solutions of Eq. (11) in Laplace domain and time domain. The concentration in the material in Laplace domain can be expressed as follows [17]

$$\bar{C}_m = \frac{-(u^2 + \alpha)C_{m,0} \cosh\left(\frac{x}{\delta}u\right) + \frac{C_{m,0}}{\lambda}}{\lambda B_u} \quad (13)$$

with

$$u = \delta \sqrt{\lambda/D_m} \quad (14)$$

$$B_u = [K_{ma}\beta + (u^2 + \alpha)K_{ma}Bi_m^{-1}]u \sinh u + (u^2 + \alpha) \cosh u \quad (15)$$

where λ is Laplace variable, $\alpha = N\delta^2/D_m$ is the dimensionless air exchange rate, $\beta = L\delta$ is the dimensionless loading ratio.

Considering Eqs. (12) - (13), the emission factor in Laplace domain can be written as follows

$$\bar{R} = \frac{C_{m,0}D_m u \sinh u (u^2 + \alpha)}{\delta \lambda B_u} \quad (16)$$

By considering the initial value theorem of Laplace transform,

$$\lim_{t \rightarrow 0} f(t) = \lim_{\lambda \rightarrow \infty} \lambda F(\lambda) \quad (17)$$

we can obtain

$$R_0 = \frac{k_c C_{m,0}}{K_{ma}} \quad (18)$$

Where R_0 is the initial emission factor of VOCs from building materials, k_c is the mass transfer coefficient between the material surface and the bulk air. Eq. (18) shows that the initial emission factor of VOCs from building materials is independent from the diffusion coefficient of VOCs within building materials.

The mass transfer between the material surface and the bulk air is always equivalent to the diffusion flux of VOCs within the material.

$$-D_m \left. \frac{\partial C_m}{\partial x} \right|_{x=\delta} = k_c (C_{ai} - C_a) \quad (19)$$

Thus, h is proportional to the diffusion coefficient of VOCs in the material. The effect of temperature on the diffusion coefficient is usually described by Arrhenius equation

$$D_m = D_0 \exp\left(-\frac{E_d}{T}\right) \quad (20)$$

It means

$$k_c \propto D_0 \exp\left(-\frac{E_d}{T}\right) \quad (21)$$

The partition coefficient stands for the equilibrium of VOCs between the air phase and the adsorbed phase. The effect of temperature on the partition coefficient can be written as follows [10]

$$K_{ma} = P_1 T^{0.5} \exp\left(\frac{P_2}{T}\right) \quad (22)$$

Combination of Eqs. (10), (18), (21) and (22) yields the correlation between the initial emission factor and temperature with two constants, which reads

$$R_0 = \frac{A_2}{T} \exp\left(-\frac{B_2}{T}\right) \quad (23)$$

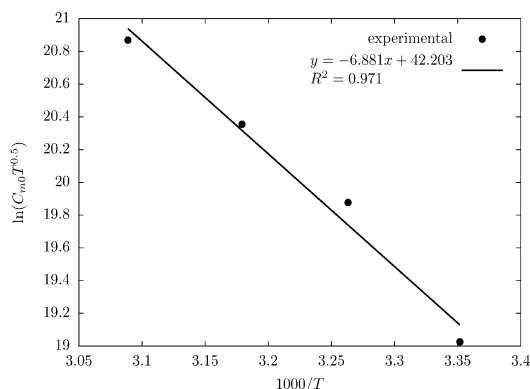
RESULTS AND DISCUSSION

Results

Xiong et al. [5] experimentally studied the impact of temperature on the initial emittable concentration of formaldehyde in medium density board using the multi-emission/flush regression method. The initial emittable concentrations of formaldehyde in medium density

Table 1: Initial emittable concentration of formaldehyde in medium density.

Temperature(K)	$C_{m,0}(10^7 \mu\text{g}/\text{m}^3)$
298.2	1.06
306.3	2.45
314.4	3.90
323.6	6.43

**Fig. 1: The initial concentration of formaldehyde in medium density board.**

at four temperatures were shown in Table 1. Fig. 1 shows the fitting of the present thermodynamic model to experimental data. Good agreement between the present thermodynamic model and the experimental data is obtained with the correlation coefficient (R^2) to be 0.971.

Lin *et al.* [20] carried out an 8-day experiment in an environmental test chamber to measure the emission of toluene and n-butyl acetate from wooden flooring. The effects of temperature, relative humidity (RH), air exchange rate on the emission were discussed in their study. The initial emittable concentrations of toluene and n-Butyl acetate under the condition of the same relative humidity are shown in table 2. As shown in Fig. 2, the correlation coefficients (R^2) for toluene and n-Butyl acetate are 0.924 and 0.847, respectively. In general, the results computed by the present thermodynamic model are in good agreement with the experimental data.

Crawford and Lungu [21] investigated the influence of temperature on styrene emission from a vinyl ester resin thermoset composite material. The relative humidity was kept in the range of 10-50%. Loading ratios were around 2 m^{-1} . The chamber volume was 175.5 L. The experiments

were carried out at 283.15 K, 293.15 K, 303.15 K, 313.15 K and 323.15 K. Fig. 3 shows the variation of initial emission factor along with temperature with the correlation coefficient (R^2) to be 0.973. They fitted the emission factor linearly with the correlation coefficient (R^2) to be 0.997. Although the latter is slightly higher than the value of the present thermodynamic model, the difference is not much and it is obtained empirically without physical background.

Lee and Kim [22] used a thermal extractor to measure the emission of VOCs from engineered flooring and laminate flooring at 298.15 K, 308.15 K and 318.15 K, respectively. The experiments were performed with a high loading ratio (79.85 m^{-1}) and a high air exchange rate (90 h^{-1}). The thermal extraction process lasted for 30 min after the emission began. The initial emission factors at different temperatures were obtained, as listed in table 3. Fig. 4 depict the simulated initial emission factors of TVOC and NVOC from engineered flooring and laminate flooring, respectively. The correlation coefficients (R^2) are 0.987 and 0.990 for TVOC and 0.827 and 0.981 for NVOC from engineered flooring and laminate flooring, respectively. Three correlation coefficients (R^2) are greater than 0.98 and the worst one (0.82227) for the assembly of NVOC and engineered flooring is also acceptable. Since the experiments of Lee and Kim [22] were carried out under a relatively extreme environmental conditions, it shows that the present thermodynamic model can be applied to a wide range of environmental conditions.

Discussion

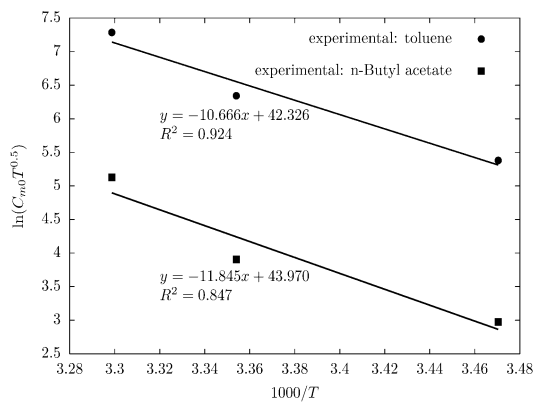
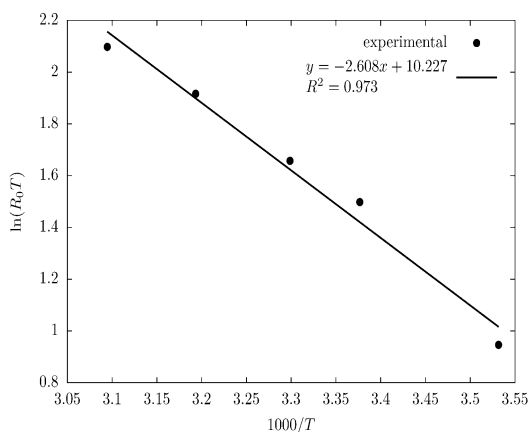
The kinetic molecular theory of gases is one of the most significant models in thermodynamics. Powerful quantitative conclusions such as the state equation of ideal gases can be derived only from limited assumptions. The derivation in the present study makes use of Maxwell velocity distribution function and the translational kinetic energy distribution function, which is totally based on the assumptions of the kinetic molecular theory of gases. The additional assumption made in the present study is that only molecules with the kinetic energy greater than energy level E_0 can escape from the building material and enter into the air. This is because that the interaction between VOCs molecules and building materials tends to keep VOCs molecules staying within building materials, which is just like the binding of earth to any object at the surface

Table 2: Initial emittable concentration from wooden flooring.

Temperature(K)	$C_{m,0}(\mu\text{g}/\text{m}^3)$	
	Toluene	n-Butyl acetate
288	404	36.4
298	1041	90.8
303	2650	306

Table 3: VOCs emission rate from the engineered flooring and laminate flooring results.

Compound Emission (mg/m ² h)	VOCs	298.15	Temperature(K)	318.15
engineered flooring	TVOC	0.787	2.081	4.103
	NVOC	0.073	0.362	0.550
	laminare flooring	TVOC	4.139	8.715
	NVOC	0.075	0.138	0.205

**Fig. 2: The initial concentrations of toluene and n-Butyl acetate in wooden flooring.****Fig. 3: The initial emission rate of Styrene from a vinyl ester resin thermoset composite material.**

of earth. Energy level E_0 actually plays a role similar to activation energy in chemical reaction since it appears at the same position as activation energy in the equation of reaction rate, which interprets the physical meaning of the constant B_1 in Eq. (10). Correspondingly, B_2 also plays a role of activation energy for the initial emission factor with a value greater than that of B_1 . On the other hand, although the present thermodynamic model is derived for considering the effect of temperature on VOCs emission, the derivation is also applicable to other gas molecules adsorbed on materials since Eqs. (1)- (10) doesn't concern any characteristics of VOCs and only assumptions of the kinetic molecular theory of gases are used. There exist some discrepancy between the experimental data and the present thermodynamic model, which can be ascribed into the difference between the real gas and the ideal gas and the simplification from Eq. (6) to Eq. (7). In general, the present thermodynamic model interprets the physical mechanism of temperature affecting VOCs emission from building material and obtained satisfactory result.

In the simplification from Eq. (6) to Eq. (7), high-order terms in the bracket at the right-hand in Eq. (6) have been omitted, which requires that kT should be far less than $2E_0$. This treatment has been widely adopted in physical chemistry since E_0 is thought to be large enough. It can prove the correctness of this treatment to evaluate the values of E_0 from the experimental data of VOCs emission. There exists $B_1 = E_0/k$ by comparing Eqs. (9) and (10). The absolute values of slope in Fig. 1-3 are 6.88048, 10.66582 and 11.8449, respectively. Considering the magnitude of

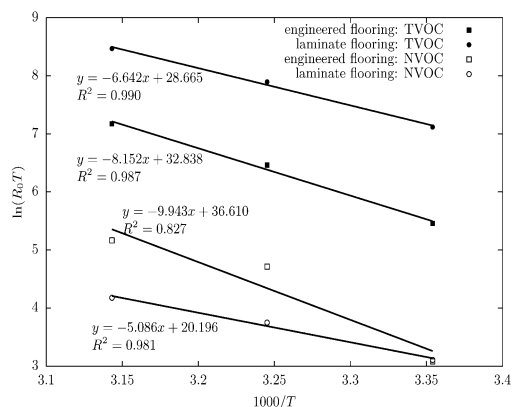


Fig. 4: The initial emission rate of TVOC and NVOC from engineered flooring and laminate flooring.

horizontal coordinate, the values of E_0/k are $6.880e+3$, $10.666e+3$ and $11.845e+3$, respectively. Temperatures are located in the range from 273.15 K to 323.15 K for all experiments. Thus, the values of $2E_0/kT$ for Figs. 1-3 are located in the range of 42 to 50, 66 to 78 and 72 to 86, respectively. Therefore, the sum of omitted high-order terms in the bracket of Eq. (6) is far less than unity. It means that the simplification from Eq. (6) to Eq. (7) is reasonable.

CONCLUSIONS

In the present study, a correlation describing the effect of temperature on the initial emittable concentration of VOCs has been developed based on the kinetic molecular theory of gases. With the help of Laplace transform, the initial emission factor is proved to be proportional to the mass transfer coefficient and the initial emittable concentration and inversely proportional to the partition coefficient. Based on the present thermodynamic model for the initial emittable concentration, the correlation between the temperature and the initial emission factor is constructed. The present thermodynamic model is validated through the experimental data in literatures. Good agreement is obtained between the experimental data and the present thermodynamic model.

Received : Feb. 2, 2022 ; Accepted : Apr. 25, 2022

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