

# Prediction of the Net Heats of Combustion of Organic Halogenated Compounds based on the Atomic Contribution Method

## 원자기여법에 근거한 유기 할로젠 화합물의 순연소열 예측

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### 요 약

연소열은 인화성 물질의 화재·폭발 위험성을 결정하는 주요한 물성치이다. 할로젠화 유기화합물의 순연소열을 예측하기 위해서, 원자기여법에 기반을 둔 경험식들이 개발되어 왔다. 본 연구에 개발된 경험식을 Cardozo와 Hanley의 경험식들과 비교해 보았다. A.A.D.를 보면 알 수 있듯이 본 연구에서 제안된 경험식으로 계산된 값이 실험값에 가장 근접해 있음을 확인하였다. 따라서, 본 연구에서 제안된 경험식은 여타 할로젠화 유기화합물의 연소열을 예측하는데 도움을 줄 것으로 사료된다.

### ABSTRACT

The heat of combustion is one of the major physical properties used to determine the fire and explosion hazards of the flammable substances. Empirical equations have been developed to predict the net heats of combustion of organic halogenated compounds based on the atomic contribution method. The method developed in this study was compared with Cardozo's method and Hanley's method. As can be seen from the average absolute deviation(A.A.D.), the proposed equation was found to be best. The proposed equation may serve as an estimation scheme for the heats of combustion of the other organic halogenated compounds.

**Keywords :** Heat of Combustion, Organic Halogenated, Atomic Contribution Method, Flammable Substances, Fire and Explosion Hazards

## 1. Introduction

Flammable substances are frequently used in chemical process industries. The thermochemical parameters necessary for safe handling, transport, process design and operation of flammable substances are lower flammability limits(LFL), upper flammability limits(UFL), flash point, AIT(minimum autoignition temperature or spontaneous ignition temperature), minimum ignition energy, and minimum oxygen concentration for flame propagation.<sup>1)</sup>

In addition, the heats of combustion of flammable substances are also important. They can be used to estimate the potential fire hazards of flammable substances once they ignite and burn.

The heat of combustion is of practical interest not only in relation to fire hazard but also in combustion system such as engine, reactor etc.. Also, the heat of combustion is a physical property of particular interest to the chemical engineer responsible for the safe operation in the industrial plants.

Recently, in order to obtain data of flammability limits and flame temperature in the lower flammability limits, the research for the heat of combustion

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has been carried out.

Benson<sup>2)</sup> reported that there is another way to obtain the gross heat of combustion of a substance, which is calculated by using the heat of formation of a combustion substance and the heat of formation of its combustion products. Balcan *et al.*<sup>3)</sup> reported that the heat of combustion of several substituted naphthalenes have been determined using an adiabatic bomb calorimeter. Suzuki<sup>4)</sup> reported that the LFL of organic compounds can be estimated with the gross heat of combustion. Hshieh<sup>5)</sup> has reported the methods for predicting heat of combustion and LFL of organosilicon compounds.

The literature data on the net combustion of organic halogenated compounds are rather scarce. Therefore, the objective of this study is to derive empirical equation to estimate the net heat of combustion of organic halogenated compounds based on the atomic contribution method and to provide basic data to prevent fire and explosion.

## 2. Prediction Equation of the Heat of Combustion

The heat of combustion of a substance is the heat evolved when the substance is converted to the standard oxidation products by reaction with oxygen.

The gross heat of combustion is normally measured in an oxygen bomb calorimeter. The gross heat of combustion is determined considering the water formed is in liquid state.

The net heat of combustion is calculated from the gross heat of combustion considering the water formed is in gaseous state.

Thus, the difference between the gross and the net heat of combustion is the heat of condensation of water. In view of their utility in the fire safety, the net heat of combustion is more important than the gross heat of combustion because the water formed in the fire is in gaseous state.

Generally, the data of the heat of combustion can be obtained in the literatures.<sup>6,7)</sup>

Cardozo<sup>8)</sup> has proposed a rather simple method to estimate the heat of combustion. The heat of combustion is defined as the difference in enthalpy of a compound and that of its products of combustion in

gaseous state, all at 298.15 K and 1 atm. The products of combustion are assumed to be H<sub>2</sub>O(g), CO<sub>2</sub>(g), SO<sub>2</sub>(g), N<sub>2</sub>(g), and HX(g), where X is a halogen atom. Since product water is in gaseous state, this enthalpy of combustion would be termed the net heat of combustion.

In the calculation an equivalent chain length N is defined as:

$$N = N_c + \sum_i \Delta N_i \quad (1)$$

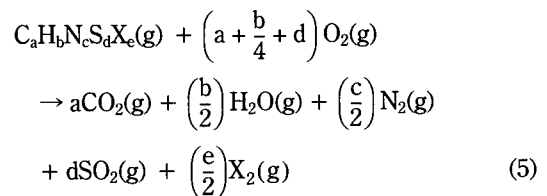
Here N<sub>c</sub> is the total number of carbon atoms in a molecule, while ΔN<sub>i</sub> values are correction factors for functional groups and chain branching. Once N has been determined, the heat of combustion (in kJ/mol) is determined from eq. (2) through eq. (4).

$$\Delta H_c^0(g) = -198.42 - 615.14N \quad (2)$$

$$\Delta H_c^0(l) = -196.98 - 610.13N \quad (3)$$

$$\Delta H_c^0(s) = -206.21 - 606.56N \quad (4)$$

Recently, Hanley<sup>9)</sup> proposed the method to estimate the heat of combustion of the organic compounds. The following reaction represents the complete combustion of an organic halogenated compounds:



where "C" represents carbon, "H" hydrogen, "N" nitrogen, "S" sulfur, and "X" halogens. He has presumed that all carbon is oxidized to CO<sub>2</sub>; all sulfur is oxidized to SO<sub>2</sub>; all halogens in the substance react to form molecular halogens; all hydrogen is oxidized to water; all nitrogen in the flammable species is converted to molecular nitrogen; and all oxygen is available for oxidation of other constituents.

The heat of combustion of an organic halogenated compound at 298.15 K (ΔH<sub>c</sub><sup>0</sup>) can be calculated as follows.

$$\Delta H_c^0 = aH_{f,CO_2}^0 + \left(\frac{b}{2}\right)H_{f,H_2O}^0 + dH_{f,SO_2}^0 - H_{f,C_aH_bN_cS_dX_e}^0 \quad (6)$$

where  $H_{f,C_aH_bN_cS_dX_e}^0$  is the heat of formation of organic halogenated compound, and other  $H_f^0$  are the heats of formation of  $CO_2$ ,  $H_2O$ , and  $SO_2$ , respectively.

### 3. Prediction of the Heat of Combustion by Means of Atomic Contribution Method

#### 3.1 Multiple Regression Analysis

Regression analysis is a statistical tool for evaluating the relationship of one or more independent variables  $X_1, X_2, \dots, X_k$  to a single, continuous dependent variable(response),  $Y$ . It is most often used when the independent variables cannot be controlled, as when collected in a sample survey or other observational study. Nevertheless, it is equally applicable to more controlled experimental situations.

Multiple regression analysis can be regarded as an extension of straight-line regression analysis (which involves only one independent variable) to the situation where there is more than independent variable to be considered.<sup>10,11)</sup>

One example of multiple regression model is given by any second- or higher-order polynomial. The addition of higher-order terms (e.g., an  $X^2$  or  $X^3$  term) to the model can be considered as equivalent to the addition of new independent variables. Thus, if we rename  $X$  as  $X_1$  and  $X^2$  as  $X_2$ , the second-order model is

$$Y = \beta_0 + \beta_1X + \beta_2X^2 + e \quad (7)$$

can be rewritten as

$$Y = \beta_0 + \beta_1X_1 + \beta_2X_2 + e \quad (8)$$

Of course, in polynomial regression we really have only one basic independent variable, the others being simple mathematical functions of this basic variable. In more general multiple regression problems, however, the number of basic independent

variables may be greater than one. The general form of a regression model for  $k$  independent variables is given by

$$Y = \beta_0 + \beta_1X_1 + \beta_2X_2 + \dots + \beta_kX_k + e \quad (9)$$

where  $\beta_0, \beta_1, \beta_2, \dots, \beta_k$  are the regression coefficient that need to be estimated. The independent variables  $X_1, X_2, \dots, X_k$  may all be separate basic variables, or some may be functions of a few basic variables.

In general, the least squares method is chosen as the best-fitting model which minimizes the sum of squares of the distances between the observed responses and those predicted by the fitted model.<sup>12,13)</sup>

#### 3.2 Evaluation Criteria Used

##### 3.2.1 Average absolute percent errors(A.A.P.E.)

It is a non-dimensional quantity that permits an accurate quantitative comparison between the reported value and predicted value. The average absolute percent errors(A.A.P.E.) is:

$$A.A.P.E. = \frac{\sum \left| \frac{\Delta H_p - \Delta H_r}{\Delta H_r} \right|}{n} \times 100 \quad (10)$$

where  $\Delta H_p$  is the predicted value of the heat of combustion,  $\Delta H_r$  is the reported value of the heat of combustion and  $n$  is the number of data.

##### 3.2.2 Average absolute deviations(A.A.D.)

It is another index, replacing A.A.P.E. in situation when an accurate quantitative comparison between the reported value and estimated value are attempted. The average absolute deviations(A.A.D.)<sup>14)</sup> is:

$$A.A.D. = \frac{\sum |\Delta H_p - \Delta H_r|}{n} \quad (11)$$

where  $\Delta H_p$  is the predicted value of the heat of combustion,  $\Delta H_r$  is the reported value of the heat of combustion and  $n$  is the number of data.

##### 3.2.3 The coefficient of determination( $r^2$ ) and standard deviation

The determination of determination  $r^2$  measures the proportion of the variation in the response around the mean that can be attributed to terms in the model rather than to random error and it is determined by

$$r^2 = \frac{SS_R}{SS_{yy}} = 1 - \frac{SS_E}{SS_{yy}} \quad (12)$$

where  $SS_E$  is the sum of squares of the residual errors  $\left( = \sum_{i=1}^n (y_i - Y_i)^2 \right)$  where  $Y_i$  is the predicted value by the fitted model.  $SS_R$  is the sum of squares due to regression  $\left( = \sum_{i=1}^n (Y_i - \bar{y})^2 \right)$  where  $\bar{y}$  is the overall average of  $y_i$ .  $SS_{yy}$  is the total sum of squares about the mean given by

$$SS_{yy} = SS_E + SS_R = \sum_{i=1}^n (y_i - \bar{y})^2$$

The standard deviation(S) is:

$$S = \sqrt{\frac{\sum (y_i - \bar{y})^2}{n - 1}} \quad (13)$$

where  $n$  is the number of data.

### 3.3 The Proposed Equation Based on Atomic Contribution Method

The multiple regression analyses of these 28 compounds resulted in the best-fit empirical equation for estimating the net heats of combustion of organic halogenated compounds by means of the atomic group contribution method. The empirical equation is:

tion for estimating the net heats of combustion of organic halogenated compounds by means of the atomic group contribution method. The empirical equation is:

For the net heat of combustion,

$$\begin{aligned} \Delta H_{cn}^0 \text{ (kJ/mole)} = & 427.2364 \times (C) + 89.4466 \times (H) \\ & - 195.8868 \times (O) - 181.5104 \times (F) \\ & - 40.8723 \times (Cl) + 6.2078 \times (Br) \end{aligned} \quad (14)$$

where C, H, O, F, Cl and Br represent the number of individual atom in the empirical equation of organic halogenated compounds. Fig. 1 shows the comparison between the reported net heats of combustion and the predicted net heats of combustion.

## 4. Results and Discussion

The method developed in this work is based on the atomic group contribution method.

The atomic group contribution method only requires the empirical equation of compounds and the contribution of each atom in the empirical equation.

Fig. 1 shows the comparison between the reported net heats of combustion and the predicted net heats of combustion based on atomic group contribution

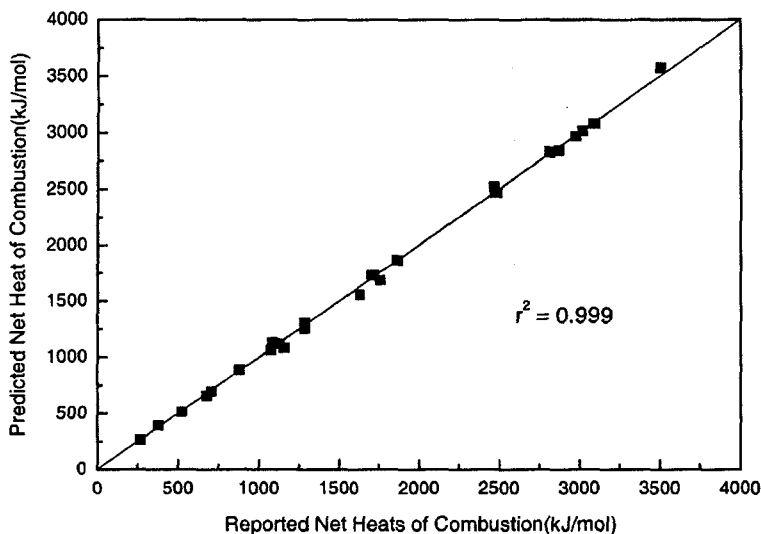


Fig. 1. Comparison between reported net heats of combustion and predicted net heats of combustion for organic halogenated compounds.

**Table 1.** Reported net heats of combustion and predicted net heats of combustion by atomic contribution method for organic halogenated compounds

No.	Nomenclatures	Molecular Fomular	$\Delta H_r$	$\Delta H_f$	Hanley	Cardozo	$\Delta H_p$
1	Fluoromethane	CH <sub>3</sub> F	521.9	-237.8	518.4	653.62	514.07
2	Chloromethene	CH <sub>3</sub> Cl	675.4	-81.9	674.34	641.32	654.70
3	Tirchloromethane	CHCl <sub>3</sub>	380	-103.6	410.8	296.84	394.07
4	Tetrachloromethane	CCl <sub>4</sub>	265.3	-95.8	297.7	124.6	263.75
5	Bromomethane	CH <sub>3</sub> Br	705.4	-35.5	718.56	629.01	695.58
6	Fluoroethane	C <sub>2</sub> H <sub>5</sub> F	1127	-263.2	1128.3	1268.76	1120.19
7	Cloroethane	C <sub>2</sub> H <sub>5</sub> Cl	1284.9	-112.1	1279.43	1256.46	1260.83
8	Bromoethane	C <sub>2</sub> H <sub>5</sub> Br	1285	-90.1	1327.08	1244.16	1307.91
9	1-Chloropropane	C <sub>3</sub> H <sub>7</sub> Cl	1867	-131.9	1893.8	1871.6	1866.96
10	2-Chloropropane	C <sub>3</sub> H <sub>7</sub> Cl	1863	-144.9	1881.9	1871.6	1866.96
11	1.1-Dichloropropane	C <sub>3</sub> H <sub>6</sub> Cl <sub>2</sub>	1720	-95.6	1810.3	1699.36	1736.64
12	1.2-Dichloropropane	C <sub>3</sub> H <sub>6</sub> Cl <sub>2</sub>	1707	-162.8	1740.42	1699.36	1736.64
13	Vinyl chloride	C <sub>2</sub> H <sub>3</sub> Cl	1155	37.3	1185.33	1140.20	1081.94
14	Chlorobenzene	C <sub>6</sub> H <sub>5</sub> Cl	2976	11.0	2976.5	2999.15	2969.78
15	Fluorobenzene	C <sub>6</sub> H <sub>5</sub> F	2814.5	-116.0	2799.5	3011.46	2829.14
16	Bromobenzene	C <sub>6</sub> H <sub>5</sub> Br	3019.2	60.9	3070.60	2986.85	3016.86
17	1.1-Dichloroethane	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	1084	-127.7	1141.27	1084.22	1130.52
18	Allyl chloride	C <sub>3</sub> H <sub>5</sub> Cl	1758	-0.63	1784.48	1871.6	1688.07
19	n-Chlorobutane	C <sub>4</sub> H <sub>9</sub> Cl	2486	-154.6	2508.27	2486.74	2473.10
20	iso-Butylchloride	C <sub>4</sub> H <sub>9</sub> Cl	2474	-161.2	2500.9	2486.74	2473.10
21	Chloropentane	C <sub>5</sub> H <sub>11</sub> Cl	3097	-175.0	3122.64	3101.88	3079.22
22	tert-Chloropentane	C <sub>5</sub> H <sub>11</sub> Cl	3089	-	N · F	3101.88	3079.22
23	n-Butyl bromide	C <sub>4</sub> H <sub>9</sub> Br	2469	-107.1	2555	2474.44	2520.17
24	Propargyl bromide	C <sub>3</sub> H <sub>3</sub> Br	1628	-	N · F	1666.14	1556.26
25	Benzyl chloride	C <sub>7</sub> H <sub>7</sub> Cl	3503	-32.6	3568.2	3595.22	3575.91
26	o-Dichlorobenzene	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	2871	30.2	2874.8	2823.22	2839.46
27	Acetyl chloride	C <sub>2</sub> H <sub>3</sub> OCl	879	-	N · F	902.14	886.05
28	Ethylene chlorohydrin	C <sub>2</sub> H <sub>5</sub> ClO	1072	-	N · F	1105.14	1064.94
Average Absolute Deviation (A.A.D.)					31.83	47.47	23.34

\*N · F : Not Found

(kJ/mol)

method. Fig. 1 demonstrate the excellent predictions of the heats of combustion of organic halogenated compounds.

The reported net heats of combustion and the predicted net heats of combustion based on Hanley's method, Cardozo's method, and the method developed in this paper for 28 organic halogenated compounds are listed in Table 1.

As can be seen from A.A.D in Table 1, the method proposed in this study is superior to the Hanley's method and Cardozo's method.

The average absolute deviations is 23.34 kJ/mol. The average absolute percent errors(A.A.P.E.) is 1.62% and the coefficient of determination( $r^2$ ) is 0.999. The estimated values by the proposed equation were in good agreement with the reported values.

Overall, the average absolute percent errors for predicting the net heats of combustion for organic halogenated compounds is 0.02%~4.41%.

## 5. Conclusions

The net heats of combustion of organic halogenated compounds can be predicted using the following equation based on the atomic group contribution method:

$$\begin{aligned} \Delta H_{\text{cn}}^0 \text{ (kJ/mole)} = & 427.2364 \times (\text{C}) + 89.4466 \times (\text{H}) \\ & - 195.8868 \times (\text{O}) - 181.5104 \times (\text{F}) \\ & - 40.8723 \times (\text{Cl}) + 6.2078 \times (\text{Br}) \end{aligned}$$

The proposed method in this paper was compared with Cardozo's method and Hanley's method. As seen from the average absolute deviation(A.A.D.), the proposed equation was found to be best.

## Nomenclature

- N : equivalent chain length  
 $N_c$  : total number of carbon atoms in the molecule  
 n : number of data  
 $N_i$  : correction factors for functional groups and chain branching  
 $\Delta H_{\text{cn}}$ : net heat of combustion (kJ/mol)  
 $\Delta H_p$ : predicted value of the heat of combustion (kJ/mol)  
 $\Delta H_r$ : reported value of the heat of combustion (kJ/mol)  
 $\Delta H_c^0$ : heat of combustion (kJ/mol)  
 $\Delta H_f^0$ : heat of formation (kJ/mol)  
 X : independent variable  
 Y : single, continuous dependent variable  
 $Y_i$  : predicted value by the fitted model  
 $\beta$  : regression coefficient  
 $r^2$  : coefficient of determination  
 S : standard deviation  
 SS : sum of squares

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