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THERMODYNAMIC CONDITIONS FOR THE FORMATION OF DIOXINS AND FURANS

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Introduction

Knowledge of the thermodynamics of polychlorinated dibenzo-*p*-dioxins and dibenzo-furans (PCDD/Fs) is very important in understanding the formation mechanism of PCDD/Fs in thermal processes. It would assist in the effective control or elimination of the PCDD/Fs emissions from thermal combustion and reduction processes. Unfortunately, due to the large number of these compounds (as many as 212) and the extreme toxicity of certain isomers, experimental information on their thermodynamic properties is difficult to obtain. In the absence of experimental data, some estimations and theoretical predictions on thermodynamic properties of PCDD/Fs have been reported¹⁻⁶.

Spencer and Neuschütz have predicted concentrations of 2,3,7,8-TCDD under various conditions of concentration and temperature¹. Shaub has developed a group contribution method to estimate the heats of formation of polychlorinated dioxins using values derived from chlorinated phenols to represent the dioxin chlorination². In addition to the effect of replacing a hydrogen atom with a chlorine atom, Iorish considered the *ortho*-, *meta*- and *para*-interactions between chlorine atoms and chlorine and oxygen atoms³. Thompson has estimated the gas phase enthalpies of formation of PCDDs and PCDFs, and simulated fuel rich combustion products in the C, H, O, Cl system including to PCDD/Fs⁴. Unsworth used a molecular orbital program, MOPAC, which implements four different semi-empirical Hamiltonians (MNDO, AM1, MINDO/3 and PM3), and tested the accuracy of the predictions⁵. Saito and Fuwa have evaluated the thermodynamic properties of PCDD/Fs using a semi-empirical molecular orbital method with the PM3 Hamiltonian⁶.

In the present work, three thermodynamic databases have been used to simulate PCDD/Fs formation and PCDD/Fs isomer distributions in thermal processes.

Thermodynamic Calculations

With the exception of the data for PCDD/Fs, all thermodynamic values for the substances taking part in, or being formed during the thermal processes taken into consideration, were extracted from the SGTE (the Scientific Group Thermodata Europe) pure substances database⁷. The thermodynamic databases of PCDD/Fs were derived using the MNDO method⁵, the PM3 method⁶ and the group additivity approach³, respectively. The equilibrium calculations were carried out using the thermodynamic package, ChemApp⁸.

Thermodynamic Conditions of PCDD/Fs Formation

Industrial measurements indicate that partial pressures of PCDD/Fs in the off-gas of iron ore sinter plants before gas cleaning are about 10^{-13} to 10^{-11} bar⁹. The conditions for the PCDD/Fs formation, in which the partial pressures of PCDDs and PCDFs reach 10^{-13} and 10^{-11} bar,

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respectively, can be calculated for different chlorine contents and C/H molar ratios. The concentrations of the major components in the sinter plant off-gas (13% O₂, 7% CO₂, 1% CO, 76% N₂, 3% H₂O and 0.01% Cl) are used as input conditions in the present calculations¹⁰. The formation of various PCDD and PCDF isomers have similar behavior according to our calculations. Therefore only 2,3,7,8-TCDD and 2,3,7,8-TCDF are presented in this section. It should be noted that all PCDFs have been excluded from the calculations where the condition for 2,3,7,8-TCDD formation are determined. The calculated values for PCDDs are extremely low if PCDFs are included in the calculations. The chlorine content in the calculations was chosen as a parameter, and set to values of 0.01%, 0.1%, and 1% for the calculations. The shaded regions, which indicate PCDD and PCDF partial pressures of at least 10⁻¹³ bar and 10⁻¹¹ bar respectively, increase with increasing the chlorine content. The PCDD/Fs only form in extremely low oxygen partial pressure, or P_{O₂} < 10⁻³⁵ bar, as shown in Figure 1.

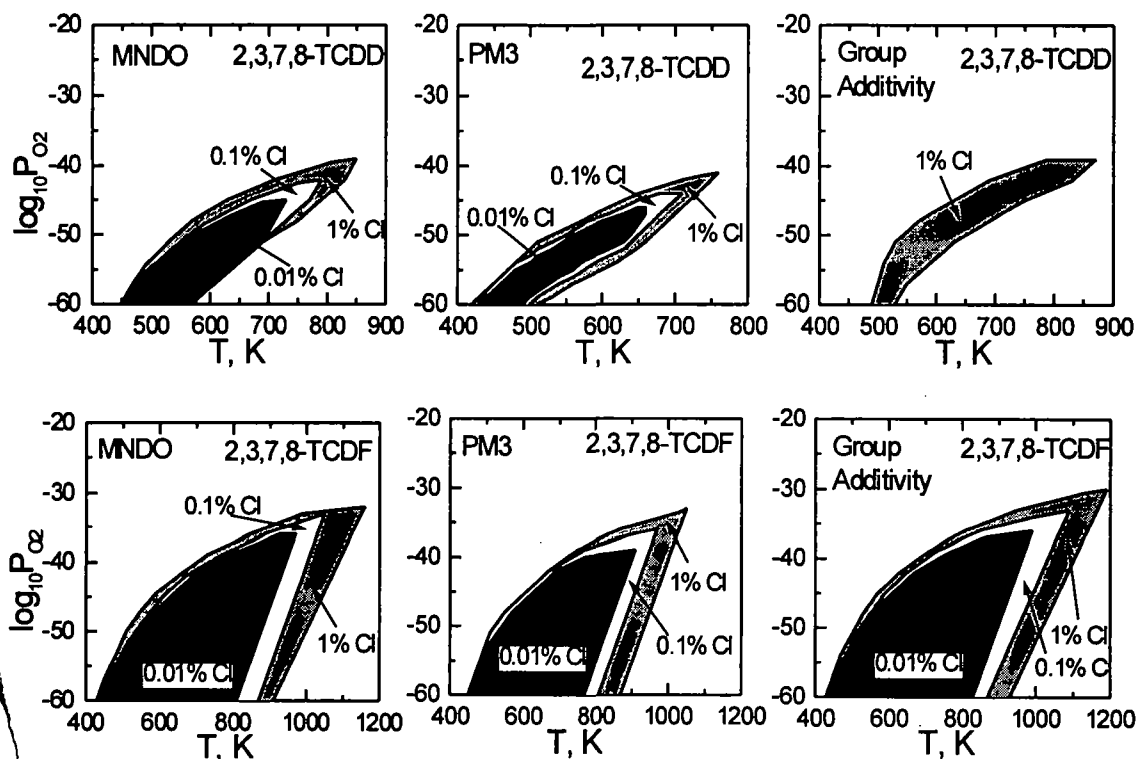


Fig. 1. Calculated regions in which the partial pressures of 2,3,7,8-TCDD and 2,3,7,8-TCDF reach 10⁻¹³ and 10⁻¹¹ bar, respectively (using the three different databases)

Thermodynamic Modelling of PCDD/Fs Isomer Distributions

The PCDD/Fs isomer distribution is one of the important criteria to decide whether the PCDD/Fs formation is thermodynamically controlled⁵. To predict the equilibrium isomer

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distribution in the gas phase of a thermal process, the equilibrium between n isomers of a PCDD or PCDF group D may be considered, equation 1:



The equilibrium isomer fraction, X_i , of D_i in group D may be calculated from the Gibbs energy of formation of each isomer using the following equation⁵:

$$[X_i] = \frac{\exp(-\Delta G_i^0 / RT)}{\sum_{i=1}^n \exp(-\Delta G_i^0 / RT)} \quad (2)$$

According to the above equation, only the temperature and the Gibbs energies of formation of PCDD/Fs affect the isomer distributions of PCDD/Fs if the PCDD/Fs formation is controlled thermodynamically. The other operating conditions, such as oxygen partial pressure, and the concentrations of reactants (O_2 , CO , CO_2 , H_2O , Cl or some chlorinated precursors), have no influence on the PCDD/Fs isomer distribution.

To compare the reliability of the three databases, the predicted values of the toxic PCDD/Fs isomer fractions are compared with the experimental values during iron ore sinter⁹, electrical arc furnace⁹, pilot incinerator¹¹ and wood combustion systems^{12,13}. The temperature at the sample points in the pilot incinerator was 530K¹¹. So the equilibrium isomer fractions at 530K have been calculated. They are compared with the measured values, shown in Figure 2. The comparison shows that the calculated isomer fractions of the toxic PCDD/Fs using the database derived from the MNDO method are in a good agreement with the experimental values, while only part of the predicted isomer fractions of the toxic PCDD/Fs using the database derived from the PM3 method are in an agreement with these values, and most predicted values using the database derived from the Group Additivity method do not agree with the measured values.

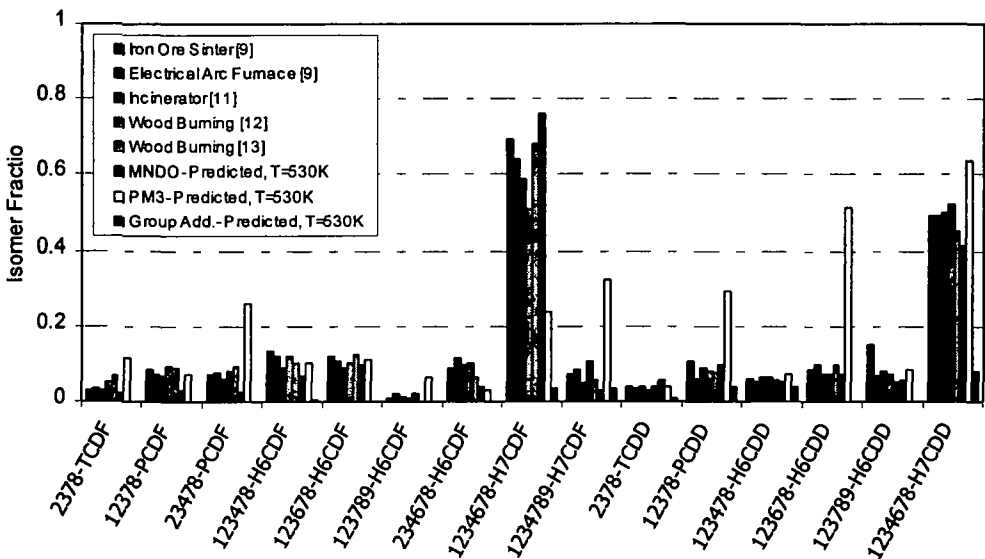


Fig. 2. Comparison of the prediction of toxic PCDD/Fs isomer distribution with the measured data

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Conclusions

Three thermodynamic databases of PCDD/Fs, derived using the group additivity approach and two computational molecular modelling methods, MNDO and PM3, respectively, combined with the SGTE database have been used to model PCDD/Fs formation and PCDD/Fs isomer distribution. The results show that similar conditions of PCDD/Fs formation are found using the different databases. The effect of temperature on PCDD/Fs formation in the thermal processes is presented. Isomer distributions of toxic PCDD/Fs are also predicted and compared with the measured data. An excellent agreement between the predictions and the measured values is obtained using the MNDO method. It is suggested that the PCDD/Fs isomer distribution may be thermodynamically controlled.

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