Thermodynamic Properties of Dibenzo-*p*-dioxin, Dibenzofuran, and Their Polychlorinated Derivatives in the Gaseous and Condensed Phases. 2. Thermodynamic Properties of Condensed Compounds

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Thermodynamic data including enthalpies of formation and fusion, entropies, and heat capacities have been derived for dibenzo-*p*-dioxin, dibenzofuran, and their polychlorinated derivatives in the solid and liquid states. The evaluated data are based on recent experimental determinations of enthalpies of formation of dibenzo-*p*-dioxin, 1-chlorodibenzo-*p*-dioxin, 2-chlorodibenzo-*p*-dioxin, and 2,3-dichlorodibenzo-*p*-dioxin, improved statistical thermodynamics calculations, several published vapor pressure measurements, melting temperatures, enthalpies of fusion, and various correlations. The consistent database is intended for simulation of the processes leading to the formation of these pollutants. This second part of our work describes evaluations for solid and liquid dibenzo-*p*-dioxin, dibenzofuran, and their polychlorinated derivatives together with vapor pressure data treatment to derive a consistent set of thermodynamic data.

Introduction

The past decade has seen considerable progress in studies of the thermodynamic properties of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) due to various experimental and theoretical investigations.[1−22] However, the creation of a thermodynamic database requires the development of a data set which is consistent with all available information, the general laws of thermodynamics, and some correlations.

The present paper combines data for gaseous and condensed phases to derive such a consistent data set for all the compounds considered.

Entropies and Heat Capacities of Condensed Compounds

Experimental values of the entropy and heat capacity for the condensed phase are known for dibenzofuran (DF) only.[23] Estimations of the condensed phase entropy and heat capacity for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin have been made[24] using Shaub's gaseous phase data[25] and vapor pressure data.[2,26] Some very rough assumptions concerning the heat capacities of solid and liquid polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans have been made by Rordorf.[5]

In the absence of experimental data for dibenzo-*p*-dioxin (DD), polychlorinated dibenzo-*p*-dioxins, and polychlorinated dibenzofurans, some estimations are needed. Domalski and Hearing[26] have demonstrated that the estimation of thermodynamic properties of condensed phases of organic compounds can be carried out in a satisfactory manner using an additivity method developed and used primarily for the gas phase. Due to a lack of experimental data, Domalski and Hearing[26] could not generate all group values needed for calculating the thermodynamic properties of DD and PCDDs. Consequently, the entropy and heat capacity values of solid DD were estimated in this work using an alternative procedure, referred to as "the difference method", which is completely consistent with group additivity. Using the experimental data for model compounds,[23,27−29] the thermodynamic properties, namely the enthalpy of formation, the heat capacity, and the entropy of solid DD, can be determined from the following relationships ($\Delta_f H^o$ values are in kJ·mol^{-1}, C_p^o and S^o are in J·K^{-1}·mol^{-1}):

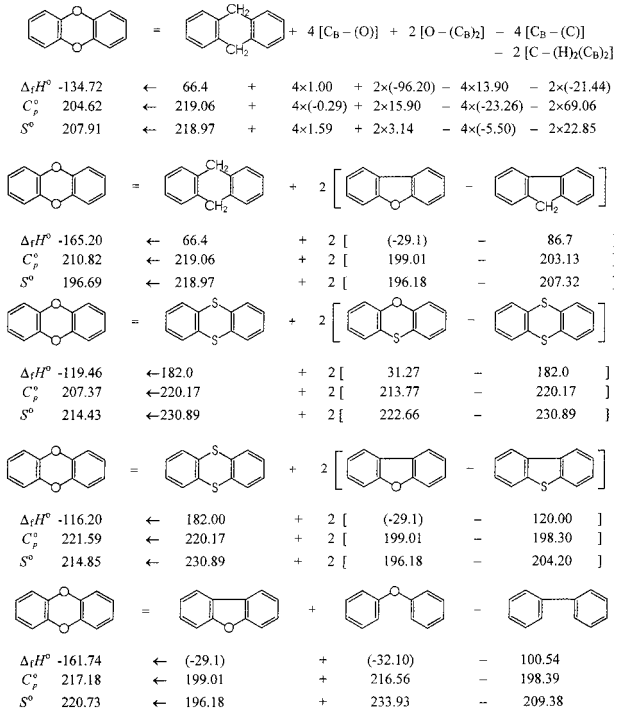

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Table 1. Experimental Investigations of Dibenzo-*p*-dioxin, Dibenzofuran, and Their Polychlorinated Derivatives

substance		
full name	short name	properties[a] and references
dibenzo-*p*-dioxin	DD	VP,GS(30−60);[3,5] $\Delta_f H$, $\Delta_{sub} H$, $\Delta_{fus} H$[22]
1-chlorodibenzo-*p*-dioxin	1-MCDD	VP,GS(30−65);[3,5] $\Delta_f H$, $\Delta_{sub} H$, $\Delta_{fus} H$[20]
2-chlorodibenzo-*p*-dioxin	2-MCDD	VP,GS(32−75);[3,5] $\Delta_f H$, $\Delta_{sub} H$, $\Delta_{fus} H$[18]
2,3-dichlorodibenzo-*p*-dioxin	2,3-DCDD	VP,GS(33−101);[3,5] $\Delta_f H$, $\Delta_{sub} H$, $\Delta_{fus} H$[19]
2,7-dichlorodibenzo-*p*-dioxin	2,7-DCDD	VP,GS(41−101)[3,5]
2,8-dichlorodibenzo-*p*-dioxin	2,8-DCDD	VP,GS(32−90)[3,5]
1,3,7-trichlorodibenzo-*p*-dioxin	1,3,7-T3CDD	VP,GS(37−100)[3,5]
1,2,4-trichlorodibenzo-*p*-dioxin	1,2,4-T3CDD	VP,GS(37−101)[3,5]
1,3,6,8-tetrachlorodibenzo-*p*-dioxin	1,3,6,8-T4CDD	VP,GS(unknown)[10]
1,2,3,4-tetrachlorodibenzo-*p*-dioxin	1,2,3,4-T4CDD	VP,GS(60−120);[3,5] VP,GC(90−150)[9]
1,2,3,7-tetrachlorodibenzo-*p*-dioxin	1,2,3,7-T4CDD	VP,GS(unknown)[10]
2,3,7,8-tetrachlorodibenzo-*p*-dioxin	2,3,7,8-T4CDD	$\Delta_{fus} H$;[42] VP,GS(30−71);[6] VP,GS(25)[8]
1,3,6,8-tetrachlorodibenzo-*p*-dioxin	1,3,6,8-T4CDD	VP,GS(20−100))[7]
1,2,3,7,8-pentachlorodibenzo-*p*-dioxin	1,2,3,7,8-PCDD	VP,GC(90−150)[9]
1,2,3,4,7-pentachlorodibenzo-*p*-dioxin	1,2,3,4,7-PCDD	VP,GS(unknown)[10]
1,2,3,4,7,8-hexachlorodibenzo-*p*-dioxin	1,2,3,4,7,8-H6CDD	VP,GS(unknown); VP,GC(90−150)[9]
1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin	1,2,3,4,6,7,8-H7CDD	VP,GS(unknown),[10] VP,GC(90−150)[9]
octachlorodibenzo-*p*-dioxin	OCDD	VP,GS(20−100)[7]
		VP,GS(111−201);[3,5] VP,GC(90−150)[9]
dibenzofuran	DF	VP,GS(30−60)[3,5]
		VP,EM(85−330); $\Delta_f H$, $\Delta_{sub} H$, $\Delta_{fus} H$, $C_p°(T)$, $H°(T) - H°(0)$[23]
3,6-dichlorodibenzofuran	3,6-DCDF	VP,GS(32−101)[3,5]
2,4,8-trichlorodibenzofuran	2,4,8-T3CDF	VP,GS(45−150)[3,5]
2,3,7,8-tetrachlorodibenzofuran	2,3,7,8-T4CDF	VP,GC(90−150)[9]
1,2,3,7,8-pentachlorodibenzofuran	1,2,3,7,8-PCDF	VP,GC(90−150)[9]
2,3,4,7,8-pentachlorodibenzofuran	2,3,4,7,8-PCDF	VP,GC(90−150)[9]
1,2,3,4,8-pentachlorodibenzofuran	1,2,3,4,8-PCDF	VP,GC(unknown)[10]
1,2,4,7,8-pentachlorodibenzofuran	1,2,4,7,8-PCDF	VP,GS(unknown)[10]
1,2,3,4,7,8-hexachlorodibenzofuran	1,2,3,4,7,8-H6CDF	VP,GS(unknown);[10] VP,GC(90−150)[9]
1,2,3,6,7,8-hexachlorodibenzofuran	1,2,3,6,7,8-H6CDF	VP,GC(90−150)[9]
1,2,3,7,8,9-hexachlorodibenzofuran	1,2,3,7,8,9-H6CDF	VP,GC(90−150)[9]
2,3,4,6,7,8-hexachlorodibenzofuran	2,3,4,6,7,8-H6CDF	VP,GC(90−150)[9]
1,2,4,6,7,8-hexachlorodibenzofuran	1,2,4,6,7,8-H6CDF	VP,GS(unknown)[10]
1,2,4,6,8,9-hexachlorodibenzofuran	1,2,4,6,8,9-H6CDF	VP,GS(unknown)[10]
1,2,3,4,6,7,8-heptachlorodibenzofuran	1,2,3,4,6,7,8-H7CDF	VP,GS(unknown);[10] VP,GC(90−150)[9]
1,2,3,4,7,8,9-heptachlorodibenzofuran	1,2,3,4,7,8,9-H7CDF	VP,GC(90−150)[9]
1,2,3,4,6,7,9-heptachlorodibenzofuran	1,2,3,4,6,7,9-H7CDF	VP,GS(unknown)[10]
1,2,3,4,6,8,9-heptachlorodibenzofuran	1,2,3,4,6,8,9-H7CDF	VP,GS(unknown)[10]
Octaclorodibenzofuran	OCDF	VP,GS(111−201)[3,5]

[a] VP,GS = vapor pressure by gas saturation method; VP,GC = vapor pressure by gas chromatographic method; VP,EM = vapor pressure by ebulliometric measurements; temperature range is in parentheses (in °C). $\Delta_f H$, $\Delta_{sub} H$, $\Delta_{fus} H$ = enthalpies of formation, sublimation, and melting respectively. $C_p°(T)$ = heat capacity. $H°(T) - H°(0)$ = enthalpy change.

Combining all estimations and taking into account results of similar estimations for thianthrene,[30,31] one can obtain (−139 ± 25) kJ·mol^{-1}, (215 ± 10) J·K^{-1}·mol^{-1}, and (215 ± 15) J·K^{-1}·mol^{-1} for the enthalpy of formation, heat capacity, and entropy of DD, respectively. The estimated enthalpy of formation value is in very good agreement with the experimental value[22] (−148.7 ± 4) kJ·mol^{-1}. This leads us to believe that the other estimations for $S°$ and $C_p°$ are also reliable and that real uncertainties are much less.

Using the estimated data for dibenzo-*p*-dioxin, experimental data for dibenzofuran, and increments for chlorine substitutions developed by Domalski and Hearing,[26] standard entropies and heat capacities for all solid PCDDs and PCDFs were estimated from the equations

$$S°(\text{PCDD}) = S°(\text{DD}) + nS°[\text{C}_\text{B} - (\text{Cl})] - nS°[\text{C}_\text{B} - (\text{H})] \quad (1)$$

$$C_p°(\text{PCDD}) = C_p°(\text{DD}) + nC_p°[\text{C}_\text{B} - (\text{Cl})] - nC_p°[\text{C}_\text{B} - (\text{H})] \quad (2)$$

$$S°(\text{PCDF}) = S°(\text{DF}) + nS°[\text{C}_\text{B} - (\text{Cl})] - nS°[\text{C}_\text{B} - (\text{H})] \quad (3)$$

$$C_p°(\text{PCDF}) = C_p°(\text{DF}) + nC_p°[\text{C}_\text{B} - (\text{Cl})] - nC_p°[\text{C}_\text{B} - (\text{H})] \quad (4)$$

where n is the number of chlorine atoms in the PCDD or PCDF molecule;

$$S°[\text{C}_\text{B} - (\text{Cl})] = 43.37 \text{ J·K}^{-1}\text{·mol}^{-1};$$

$$C_p°[\text{C}_\text{B} - (\text{Cl})] = 33.55 \text{ J·K}^{-1}\text{·mol}^{-1}$$

$$S°[\text{C}_\text{B} - (\text{H})] = 22.75 \text{ J·K}^{-1}\text{·mol}^{-1};$$

$$C_p°[\text{C}_\text{B} - (\text{H})] = 20.13 \text{ J·K}^{-1}\text{·mol}^{-1}$$

The estimations for entropies were used only as initial values for the vapor pressure data treatment described below. Final entropies were selected as a result of the treatment.

Vapor pressure values over solid and liquid PCDDs and PCDFs have been investigated in many studies, as presented in Table 1. Direct determinations of enthalpies of formation, sublimation, and melting are also cited in the table. The goal of this work was to develop a data set which is sufficiently consistent with all of these data as well as with the thermodynamic functions for gaseous compounds calculated in Part 1 of this work.[32]

To carry out "Second and Third Law" calculations using the vapor pressure data, some assumptions concerning the temperature dependence of the heat capacities for the solid

Table 2. Experimental[23] and Calculated Heat Capacity Values for the Liquid Dibenzofuran in Stable and Subcooled (below 355 K) Regions

T	$C_{p,l}$(exp)	$C_{p,l}$(calc)	$100\{C_{p,l}(\text{exp}) - C_{p,l}(\text{calc})\}$
K	J·K^{-1}·mol^{-1}	J·K^{-1}·mol^{-1}	$C_{p,l}$(exp)
298.15	237.57	235.30	0.96
300	238.51	236.18	0.98
320	248.35	245.78	1.04
340	257.81	255.44	0.92
360	266.98	265.08	0.71
380	275.90	274.61	0.47
400	284.63	283.98	0.23
420	293.21	293.11	0.03
440	301.66	302.01	−0.12
460	310.00	310.65	−0.21
480	318.25	319.05	−0.25
500	326.42	327.21	−0.24
520	334.53	335.14	−0.18
540	342.59	342.87	−0.08
560	350.60	350.43	0.05
580	358.57	357.86	0.20
600	366.50	365.21	0.35
620	374.41	372.57	0.49
640	382.28	380.03	0.59
660	390.14	387.72	0.62
680	397.97	395.86	0.52
700	405.78	404.81	0.24

and liquid compounds must be made. For the solid state we suggest a linear function of the form[33]

$$C_p^\circ(T)/R = C_p^\circ(298.15\ \text{K})/R + 1.51n(T/\text{K} - 298.15)/(T_{fus}/\text{K}) \quad (5)$$

where the numerical coefficient was obtained from experimental data for related compounds, n is the number of atoms in the molecule, and T_{fus} is the melting temperature.

The heat capacities of liquid PCDDs and PCDFs were estimated on the basis of the calculated data for gases (see Part 1 of this work)[32] and the Bondi−Rowlinson equation[34,35] for the difference between gaseous and liquid heat capacities:

$$(C_{pL}^\circ - C_{pG}^\circ)/R = 2.56 + 0.436(1 - T_r)^{-1} + \omega[2.91 + 4.28(1 - T_r)^{1/3}T_r^{-1} + 0.296(1 - T_r)^{-1}] \quad (6)$$

where $T_r = T/T_c$, T_c is the critical temperature, and ω is the acentric factor.

Critical temperatures were estimated using the group contribution technique developed by Somayajulu.[36] Additional increments for dibenzofuran ($n_t = 6.227$, $n_p = 8.011$) based on experimental [23] T_c and P_c values were added to the Somayajulu set. The boiling points and acentric factors as well as enthalpies of fusion were calculated within the framework of the vapor pressure correlation described in the next section. We used dibenzofuran as a test of the quality of eq 6. Calculated heat capacities for liquid dibenzofuran ($T_c = 924$ K, $\omega = 0.397$) are compared with experimental values in Table 2. Agreement between the experimental and calculated values is excellent.

The estimated heat capacities for liquid PCDDs are in satisfactory agreement with the values predicted by the additivity method,[26] especially at the melting points, despite the fact that the method relates to room temperature. The conclusion is demonstrated in Table 3 for selected compounds.

Vapor Pressure Treatment and Thermal Functions Estimation

Rordorf[3] suggested a very convenient way to process vapor pressure data which gives not only the enthalpy of sublimation but the enthalpy of melting and boiling point. The approach is based on the Fishtine[37] formula for the entropy and enthalpy of vaporization at the boiling point T_b:

Table 3. Heat Capacity Estimations for the Liquid PCDDs at the Melting Points

compound	C_p(est by eq 4) J·K^{-1}·mol^{-1}	C_p(est by additive method[26]) J·K^{-1}·mol^{-1}
DD	305	310
1-CDD	316	324
2-CDD	313	317
23-DCDD	358	353
137-T3CDD	375	348
2378-T4CDD	438	407
OCDD	503	477

$$\Delta_v S(T_b) = 1.01(36.61 + R \ln T_b/K) + R \ln(1.01325) \quad (7)$$

where the last term is introduced to take into account the standard pressure $P^o = 1$ bar, adopted in this study

$$\Delta_v H(T_b) = 1.01T_b(36.61 + R \ln T_b/\text{K}) \quad (8)$$

Using the estimated heat capacities, one obtains the temperature dependencies of the liquid-phase vapor pressures and the enthalpies and entropies of vaporization and can therefore evaluate these parameters for the melting point. The enthalpies and entropies of sublimation at T_{fus} are then calculated using the enthalpies of fusion from the correlation. Experimental vapor pressure data over the solid compound are extrapolated to the melting point, where they equal the vapor pressure of the liquid. The temperature (T_b), for which the extrapolated entropy (enthalpy) of vaporization equals the values predicted by the Fishtine's formula, is thus determined together with the enthalpy of fusion at T_{fus}.

We used Rordorf's experimental data[3,5] and his approach only for the enthalpy of fusion estimation, taking into account a more reliable assumption about heat capacities and a "Third Law" vapor pressure data treatment. The latter allowed us to obtain consistency between vapor pressure data and the results of direct enthalpy of sublimation measurements via the variation of solid-state entropy. We could not use vapor pressure data for some other PCDDs and PCDFs (see Table 1) due to lack of numerical data in ref 10.

Rordorf[5] presented his data in the form of equations for vapor pressure dependence on temperature:

$$\ln P = \Delta_s S/R + \Delta_{sub}H/RT \quad (9)$$

where $T_1 < T < T_2$ is the range of experimental measurements.

The "Second Law" standard enthalpy of sublimation and entropy for the solid state are calculated from the data using the formulas

$$S_{solid}^{\ o}(298.15\ \text{K}) = S_{gas}^{\ o}(298.15\ \text{K}) - \Delta_{sub}S(T_{mid}) - [\Delta_{sub}S(298.15\ \text{K}) - \Delta_{sub}S(T_{mid})] \quad (10)$$

$$\Delta_{sub}H^\circ(298.15\ \text{K}) = \Delta_{sub}H(T_{mid}) - [\Delta_{sub}H(T_{mid}) - \Delta_{sub}H^\circ(298.15\ \text{K})] \quad (11)$$

where $T_{mid} = 2(T_1T_2)/(T_1 + T_2)$.

Quantities in brackets are calculated using the difference between the heat capacities of the gaseous and solid phases.

Table 4. Results of Vapor Pressure Data Treatment

substance	method	S_{solid}(298.15 K) J·K^{-1}·mol^{-1}	Δ_{sub}(298.15 K) kJ·mol^{-1}	$\delta_{inf}H(T_{fus})$/kJ·mol^{-1} exp data	t_b/°C Fishtine's correlation this work	t_b/°C Fishtine's correlation ref 3	t_b/°C calc in this work
DD	II Law	204.8	92.9	25.7	298.5	283.5	
	III Law	215.0	89.7	21.4	305.2		
	III Law	211.5	90.8	23.0 **21.9**,[22] 23.2[5]	302.3		296.1
1-CDD	II Law	237.0	99.3	25.6	335.4	315.5	
	III Law	235.6	99.7	26.1	335.0		
	III Law	243.6	97.0	22.9 **20**,[20] 23.2[5]	337.9		316.6
2-CDD	II Law	237.2	98.1	23.8	335.9	316	
	III Law	235.6	98.7	24.4	335.6		
	III Law	238.3	97.8	23.4 **22.1**,[18] 23.1[5]	336.5		327.3
23-DCDD	II Law	259.3	107.5	28.8	373.9	358	
	III Law	256.2	108.5	30.2	371.2		
	III Law	255.4	108.9	30.7 **27.1**[19]	370.9		352.1
27-DCDD	II Law	272.2	106.9	28.0	386.7	374.5	384.1
	III Law	256.2	112.3	36.8	366.8		
28-DCDD	II Law	259.4	110.1	26.6	398.9	382.5	396.3
	III Law	256.2	111.1	28.1	396.4		
137-T3CDD	II Law	282.0	117.4	31.2 **30.8**[5]	413.3	398	409.6
	III Law	276.9	119.2	33.5	409.7		
124-T3CDD	II Law	263.8	120.1	37.2	389.8	375	393.2
	III Law	276.9	115.6	31.5	396.0		
1234-TCDD	II Law	307.6	120.4	33.0	429.7	419	426.6
	III Law	297.5	124.0	38.1	421.9		
2378-TCDD	II Law	316.7	124.6	38.9	457.8	446.5	
	III Law	297.5	130.8	52.9	411.8		
	III Law	312.0	127.7	41.4 **38.9**[38]	461.5		442.9
OCDD	II Law	397.8	153.3	59.6	513.0	510	502.4
	III Law	380.0	160.8	72.1	485.6		
36-DCDF	II Law	231.2	112.1	37.2 **32.4**[a]	358.2	357	368.4
248-T3CDF	II Law	259.1	114.4	32.0	397.0	392.5	395.5
OCDF	II Law	369.5	151.9	52.4	531.0	537	528.1

[a] Cited in ref 3 as B. F. Rordorf, B. Nickler, and A. Geoffroy, unpublished result.

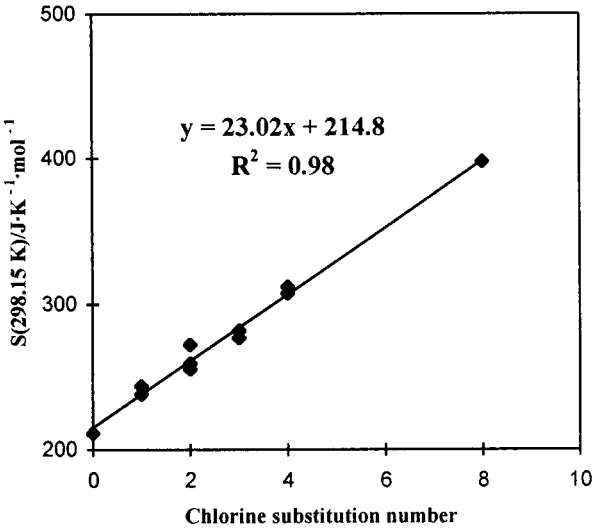

Figure 1. Standard entropy correlation for PCDDs.

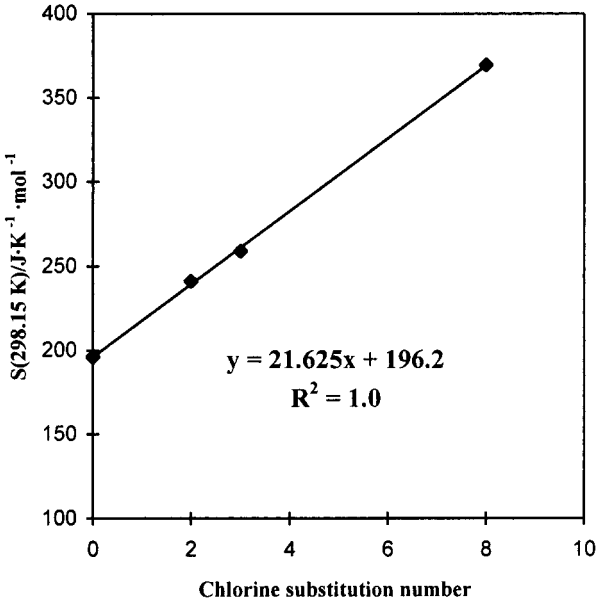

Figure 2. Standard entropy correlation for PCDFs.

In the absence of experimental vapor pressure data we calculated the values from eq 9 at two temperatures T_{min} and T_{max} and used them for a "Third Law" treatment:

$$\Delta_{sub}H°(298.15\ K) = (\Delta_{sub}H°(298.15\ K)_1 + \Delta_{sub}H°(298.15\ K)_2)/2 \quad (12)$$

where

$$\Delta_{sub}H°(298.15\ K)_1 = -RT_1 \ln P_1 + T_1\Delta_{sub}\Phi(T_1)$$

$$\Delta_{sub}H°(298.15\ K)_2 = -RT_2 \ln P_2 + T_2\Delta_{sub}\Phi(T_2)$$

and

$$\Phi(T) = S(T) - (H°(T) - H°(298.15\ K))/T$$

Assuming the uncertainties of the "Second Law" enthalpies of sublimation are twice those associated with direct determination of the quantity, we fitted entropy values for the solid phase to obtain respective average "Third Law" enthalpies of sublimation.

The results of the data processing are presented in Table 4.

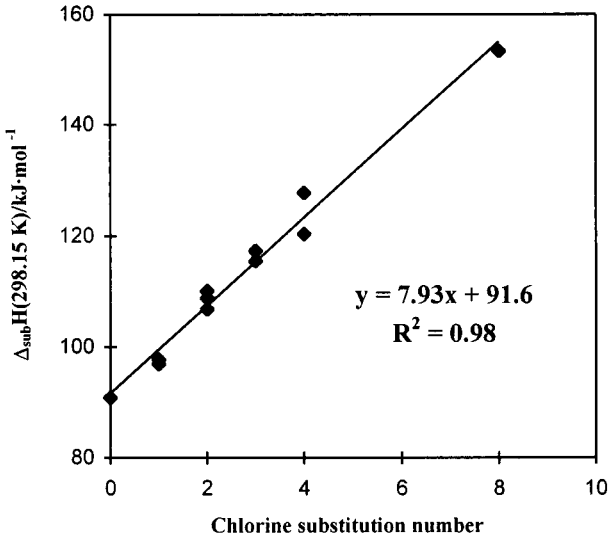

Figure 3. Enthalpy of sublimation correlation for PCDDs.

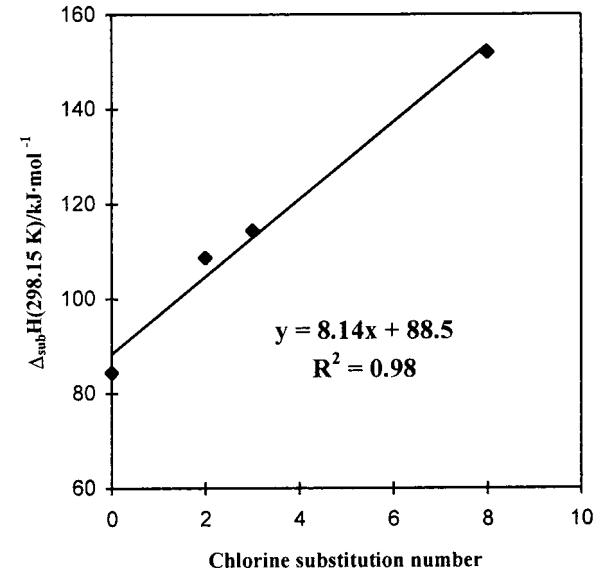

Figure 4. Enthalpy of sublimation correlation for PCDFs.

Table 5. Estimated Critical Temperatures and Acentric Factors

substance	T_c/K	ω
DD	827	0.463
1-CDD	846	0.485
2-CDD	861	0.485
23-DCDD	887	0.507
27-DCDD	932	0.507
28-DCDD	950	0.507
137-T3CDD	958	0.527
124-T3CDD	935	0.527
1234-TCDD	972	0.547
2378-TCDD	995	0.547
OCDD	1041	0.625
DF[23]	824	0.397
36-DCDF	923	0.452
248-T3CDF	951	0.472
OCDF	1088	0.574

"Third Law" calculations were carried out twice: using a priori estimated entropies and "adjusted" entropies as mentioned above.

In the cases where the enthalpy of sublimation was not determined directly, we adopted "Second Law" results with two exceptions, namely 1,2,4-trichlorodibenzo-*p*-dioxin (1,2,4-T3DD) and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-T4DD). Visual examination of the graph for vapor pressure dependence on temperature[2] shows explicit irregularities for 1,2,4-T3CDD. For the case of 2,3,7,8-T4CDD we take into account the accurate vapor pressure data given in ref 8. To achieve consistency within the four measured vapor pressure points in ref 6, we have to change both the enthalpy of sublimation and the entropy for the solid phase.

All the final data adopted in the present work are presented in bold type in Table 4. These are the values used for the calculation of boiling temperatures (see Table 4) and the subsequent correlations. The data for dibenzofuran were adopted from ref 23. The obtained standard entropies and enthalpies of sublimation and melting were correlated

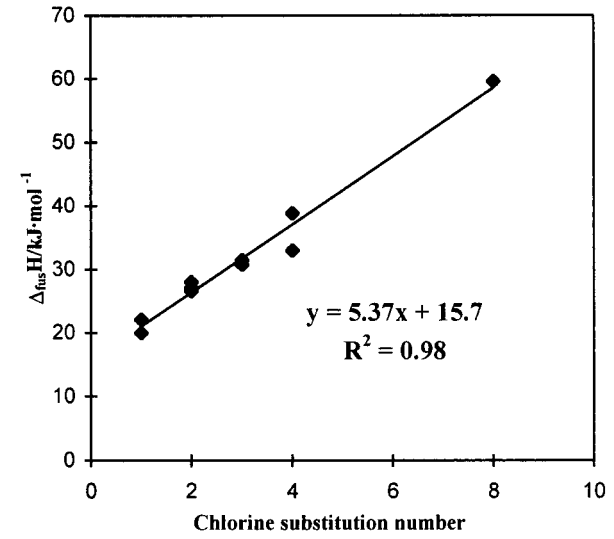

Figure 5. Enthalpy of fusion correlation for PCDDs.

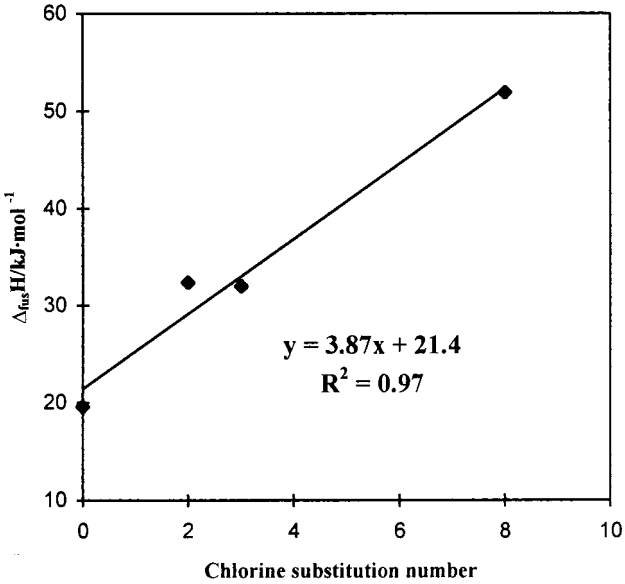

Figure 6. Enthalpy of fusion correlation for PCDFs.

Table 6. Vapor Pressure log(*P*/bar) at 298.15 K: Comparison of Values Evaluated in This Work and Measured by the Gas Chromatographic Method[9] and by the Gas Saturation Method[5]

substance	this work	ref 9	ref 5
1,2,3,4-T4CDD	−10.2	−10.6	−10.2
1,2,3,7,8-PCDD	−11.5	−11.9	−12.2
1,2,3,4,7,8-H6CDD	−12.9	−12.9	−13.3
1,2,3,4,6,7,8-H7CDD	−13.7	−13.4	−14.1
OCDD	−15.0	−14.6	−15.0

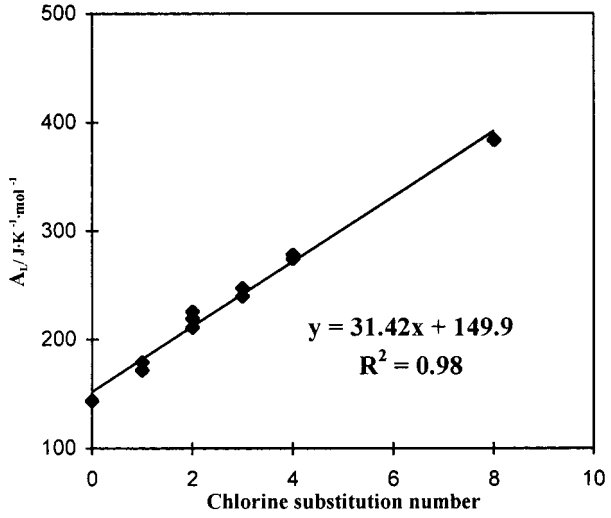

Figure 7. A_L coefficient in heat capacity equation correlation for PCDDs.

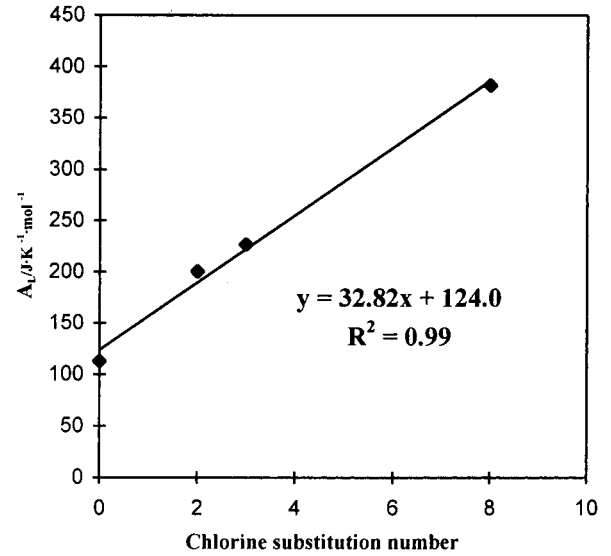

Figure 8. A_L coefficient in heat capacity equation correlation for PCDFs.

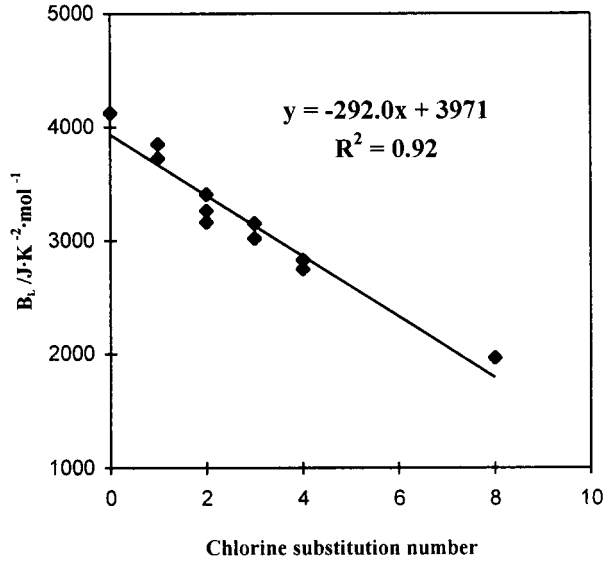

Figure 9. B_L coefficient in heat capacity equation correlation for PCDDs.

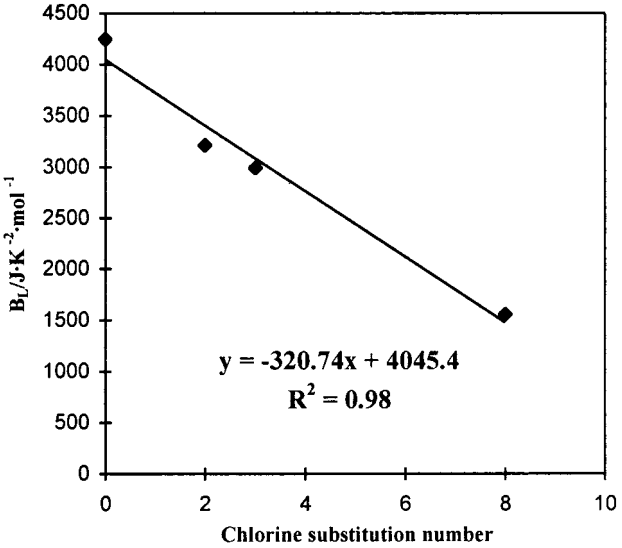

Figure 10. B_L coefficient in heat capacity equation correlation for PCDFs.

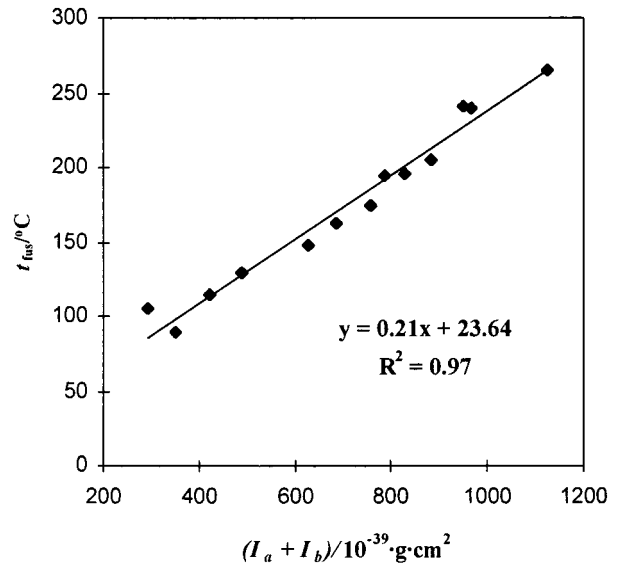

Figure 11. Melting temperature correlation for the case C_s molecular symmetry of PCDDs.

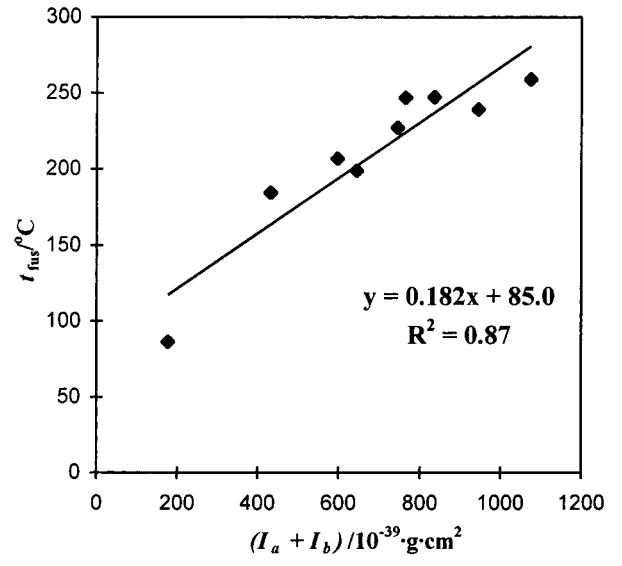

Figure 12. Melting temperature correlation for the case C_{2v} molecular symmetry of PCDFs.

Table 7. Evaluated Thermodynamic Properties of DD and PCDDs

substance	$\Delta_{sub}H^{o\,a}$ kJ·mol^{-1}	$\Delta_fH^{o\,a}$ kJ·mol^{-1}	$S^{\circ\,a}$ J·K^{-1}·mol^{-1}	T_{fus} K	$\Delta_{fus}H$ kJ·mol^{-1}	A_S J·K^{-1}·mol^{-1}	B_S J·K^{-2}·mol^{-1}	A_L J·K^{-1}·mol^{-1}	B_L J·K^{-2}·mol^{-1}	C_p/J·K^{-1}·mol^{-1} (at the following T/K) 298.15	300	400	500	600	700	800	900	1000	T_{fus} (solid) K	T_{fus} (liquid) K
DD	90.8	−148.7	211.5	392.5	21.9	5.16	7038.04	143.45	4127.06	215.0	216.3	308.5	349.8	391.1					281.4	305.4
1-MCDD	97.0	−183.4	243.6	374.0	20.0	8.28	7386.23	171.79	3852.67	228.5	229.9	325.9	364.4	403.0	441.5				284.5	315.9
2-MCDD	97.8	−187.6	238.3	360.8	22.1	0.22	7656.49	178.91	3722.98	228.5	229.9	327.8	365.1	402.3	439.5				276.4	313.2
2,3-DCDD	108.9	−220.5	255.4	431.6	27.1	51.20	6399.63	211.07	3410.96	242.0	243.2	307.2	381.6	415.7	449.8				327.4	358.3
2,7-DCDD	106.9	−227.3	272.2	482.7	28.0	71.38	5722.74	225.79	3165.14	242.0	243.1	300.3	384.0	415.7	447.3				347.6	378.6
2,8-DCDD	110.1	−230.5	259.4	424.2	26.6	47.84	6512.04	219.38	3265.02	242.0	243.2	308.3	382.6	415.3	447.9				324.1	357.9
1,3,7-T3CDD	117.4	−264.1	282.0	421.7	30.8	60.19	6550.65	247.30	3020.73	255.5	256.7	322.2	398.3	428.5	458.7	489.0			336.4	374.7
1,2,4-T3CDD	115.6	−265.5	276.9	401.7	31.5	50.47	6876.83	239.75	3152.04	255.5	256.8	325.5	397.4	428.9	460.4	491.9			326.7	366.4
1,2,3,4-T4CDD	120.4	−287.6	307.6	462.2	33.0	90.81	5976.59	278.41	2750.54	269.0	270.1	329.9	415.9	443.4	470.9	498.4	526.0		367.0	405.5
2,3,7,8-T4CDD	127.7	−291.7	312.0	578.2	38.9	126.56	4777.45	274.42	2830.49	269.0	269.9	317.7	365.4	444.3	472.6	500.9	529.2		402.8	438.1
OCDD	153.3	−428.5	397.8	604.2	59.6	186.69	4571.85	384.04	1964.83	323.0	323.8	369.6	415.3	461.0	521.6	541.2	560.9	580.5	462.9	502.7
Estimation for Known Melting Temperatures																				
1,3-DCDD	107.5	−223.6	260.8	387.2	26.4	29.29	7134.39	212.74	3387.00	242.0	243.3	348.2	382.1	416.0	449.8				305.5	343.9
2,3,7-T3CDD	115.4	−257.6	283.9	435.7	31.8	66.47	6340.14	244.16	3095.00	255.5	256.7	320.1	398.9	429.9	460.8	491.8			342.7	379.0
1,2,3,7-T4CDD	123.3	−291.9	306.9	446.7	37.2	84.62	6183.99	275.58	2803.00	269.0	270.1	332.0	415.7	443.8	471.8	499.8	527.9		360.8	400.8
1,3,7,8-T4CDD	123.3	−291.8	306.9	467.5	37.2	92.83	5908.82	275.58	2803.00	269.0	270.1	329.2	415.7	443.8	471.8	499.8	527.9		369.0	406.6
1,2,3,4,7-PCDD	131.3	−329.1	329.9	468.7	42.6	106.78	5893.70	307.00	2511.00	282.5	283.6	342.5	432.6	457.7	482.8	507.9	533.0		383.0	424.7
1,6-DCDD	107.5	−227.9	260.8	471.2	26.4	67.21	5862.42	212.74	3387.00	242.0	243.1	301.7	382.1	416.0	449.8				343.4	372.3
1,2,4,7,8-PCDD	131.3	−333.6	329.9	479.2	42.6	110.63	5764.54	307.00	2511.00	282.5	283.6	341.2	432.6	457.7	482.8	507.9	533.0		386.8	427.3
1,3,6,8-T4CDD	123.3	−296.3	306.9	492.5	37.2	101.77	5608.85	275.58	2803.00	269.0	270.0	326.1	415.7	443.8	471.8	499.8	527.9		378.0	413.6
1,2,4,6,7,9-H6CDD	139.2	−367.9	352.9	512.2	47.9	135.20	5393.11	338.42	2219.00	296.0	297.0	350.9	404.9	471.6	493.8	515.9	538.1		411.4	452.1
1,2,3,7,8-PCDD	131.3	−321.7	329.9	513.7	42.6	122.17	5377.36	307.00	2511.00	282.5	283.5	337.3	391.0	457.7	482.8	507.9	533.0		398.4	436.0
1,2,3,7,8,9-H6CDD	139.2	−356.0	352.9	516.7	47.9	136.61	5346.13	338.42	2219.00	296.0	297.0	350.5	403.9	471.6	493.8	515.9	538.1		412.8	453.1
1,2,3,4,6,7,8−H7CDD	147.1	−393.1	375.9	537.7	53.3	156.33	5137.32	369.84	1927.00	309.5	310.5	361.8	413.2	485.5	504.7	524.0	543.3	562.5	432.5	473.4
1,2,3,4,7,8-H6CDD	139.2	−358.8	352.9	547.2	47.9	145.49	5048.12	338.42	2219.00	296.0	296.9	347.4	397.9	471.6	493.8	515.9	538.1		421.7	459.8
1,2,3,6,7,8-H6CDD	139.2	−356.0	352.9	558.7	47.9	148.59	4944.21	338.42	2219.00	296.0	296.9	346.4	395.8	471.6	493.8	515.9	538.1		424.8	462.4
Estimation of Melting Points and Other Properties																				
1,2-DCDD	107.5	−219.1	260.8	384	26.4	27.37	7198.65	212.74	3387.00	242.0	243.3	348.2	382.1	416.0	449.8				303.6	342.7
1,4-DCDD	107.5	−226.8	260.8	411	26.4	41.82	6714.13	212.74	3387.00	242.0	243.2	310.4	382.1	416.0	449.8				318.0	352.1
1,7-DCDD	107.5	−227.9	260.8	395	26.4	33.55	6991.33	212.74	3387.00	242.0	243.3	348.2	382.1	416.0	449.8				309.8	346.6
1,8-DCDD	107.5	−227.9	260.8	392	26.4	31.80	7050.10	212.74	3387.00	242.0	243.3	348.2	382.1	416.0	449.8				308.0	345.4
1,9-DCDD	107.5	−227.9	260.8	409	26.4	40.62	6754.33	212.74	3387.00	242.0	243.2	310.8	382.1	416.0	449.8				316.8	351.2
1,2,3-T3CDD	115.4	−253.4	283.9	407	31.8	53.12	6787.74	244.16	3095.00	255.5	256.8	324.6	398.9	429.9	460.8	491.8			329.3	370.1
1,2,6-T3CDD	115.4	−257.6	283.9	412	31.8	55.40	6711.42	244.16	3095.00	255.5	256.7	323.9	398.9	429.9	460.8	491.8			331.6	371.5
1,2,7-T3CDD	115.4	−257.6	283.9	429	31.8	63.67	6433.88	244.16	3095.00	255.5	256.7	321.0	398.9	429.9	460.8	491.8			339.9	377.0
1,2,8-T3CDD	115.4	−257.6	283.9	425	31.8	61.71	6499.72	244.16	3095.00	255.5	256.7	321.7	398.9	429.9	460.8	491.8			337.9	375.7
1,2,9-T3CDD	115.4	−257.6	283.9	403	31.8	51.08	6856.31	244.16	3095.00	255.5	256.8	325.3	398.9	429.9	460.8	491.8			327.3	368.8
1,3,6-T3CDD	115.4	−262.1	283.9	412	31.8	55.40	6711.42	244.16	3095.00	255.5	256.7	323.9	398.9	429.9	460.8	491.8			331.6	371.5
1,3,8-T3CDD	115.4	−262.1	283.9	429	31.8	63.67	6433.88	244.16	3095.00	255.5	256.7	321.0	398.9	429.9	460.8	491.8			339.9	377.0
1,3,9-T3CDD	115.4	−262.1	283.9	409	31.8	53.98	6759.04	244.16	3095.00	255.5	256.8	324.3	398.9	429.9	460.8	491.8			330.2	370.6
1,4,6-T3CDD	115.4	−265.3	283.9	398	31.8	48.38	6946.97	244.16	3095.00	255.5	256.8	368.0	398.9	429.9	460.8	491.8			324.6	367.2
1,4,7-T3CDD	115.4	−265.3	283.9	415	31.8	57.23	6650.05	244.16	3095.00	255.5	256.7	323.2	398.9	429.9	460.8	491.8			333.4	372.7
1,7,8-T3CDD	115.4	−257.6	283.9	421	31.8	59.96	6558.34	244.16	3095.00	255.5	256.7	322.3	398.9	429.9	460.8	491.8			336.2	374.5
1,2,3,6-T4CDD	123.3	−291.9	306.9	437	37.2	80.54	6321.15	275.58	2803.00	269.0	270.2	333.4	415.7	443.8	471.8	499.8	527.9		356.7	398.1
1,2,3,8-T4CDD	123.3	−291.9	306.9	456	37.2	88.49	6054.48	275.58	2803.00	269.0	270.1	330.7	415.7	443.8	471.8	499.8	527.9		364.7	403.5
1,2,3,9-T4CDD	123.3	−291.9	306.9	432	37.2	78.27	6396.95	275.58	2803.00	269.0	270.2	334.2	415.7	443.8	471.8	499.8	527.9		354.5	396.6
1,2,4,6-T4CDD	123.3	−303.8	306.9	427	37.2	76.18	6467.27	275.58	2803.00	269.0	270.2	334.9	415.7	443.8	471.8	499.8	527.9		352.4	395.3
1,2,4,7-T4CDD	123.3	−303.8	306.9	448	37.2	85.03	6170.50	275.58	2803.00	269.0	270.1	331.8	415.7	443.8	471.8	499.8	527.9		361.2	401.0
1,2,4,8-T4CDD	123.3	−303.8	306.9	446	37.2	84.49	6188.40	275.58	2803.00	269.0	270.1	332.0	415.7	443.8	471.8	499.8	527.9		360.7	400.7

1,2,4,9-T4CDD	123.3	−303.8	306.9	424	37.2	75.00	6506.71	275.58	2803.00	269.0	270.2	335.3	415.7	443.8	471.8	499.8	527.9		351.2	394.6
1,2,6,7-T4CDD	123.3	−287.3	306.9	508	37.2	106.79	5440.60	275.58	2803.00	269.0	270.0	324.4	378.8	443.8	471.8	499.8	527.9		383.0	417.9
1,2,6,8-T4CDD	123.3	−291.8	306.9	449	37.2	85.71	6147.59	275.58	2803.00	269.0	270.1	331.6	415.7	443.8	471.8	499.8	527.9		361.9	401.5
1,2,6,9-T4CDD	123.3	−295.0	306.9	431	37.2	77.86	6410.74	275.58	2803.00	269.0	270.2	334.3	415.7	443.8	471.8	499.8	527.9		354.1	396.3
1,2,7,8-T4CDD	123.3	−287.3	306.9	463	37.2	90.97	5971.29	275.58	2803.00	269.0	270.1	329.8	415.7	443.8	471.8	499.8	527.9		367.2	405.2
1,2,7,9-T4CDD	123.3	−291.8	306.9	445	37.2	84.11	6201.18	275.58	2803.00	269.0	270.1	332.2	415.7	443.8	471.8	499.8	527.9		360.3	400.4
1,2,8,9-T4CDD	123.3	−287.3	306.9	465	37.2	91.95	5938.23	275.58	2803.00	269.0	270.1	329.5	415.7	443.8	471.8	499.8	527.9		368.2	406.0
1,3,6,9-T4CDD	123.3	−299.5	306.9	433	37.2	79.01	6372.45	275.58	2803.00	269.0	270.2	333.9	415.7	443.8	471.8	499.8	527.9		355.2	397.1
1,3,7,9-T4CDD	123.3	−296.3	306.9	474	37.2	95.31	5825.51	275.58	2803.00	269.0	270.1	328.3	415.7	443.8	471.8	499.8	527.9		371.5	408.5
1,4,6,9-T4CDD	123.3	−302.7	306.9	482	37.2	98.08	5732.76	275.58	2803.00	269.0	270.1	327.4	415.7	443.8	471.8	499.8	527.9		374.3	410.6
1,4,7,8-T4CDD	123.3	−295.0	306.9	472	37.2	94.48	5853.28	275.58	2803.00	269.0	270.1	328.6	415.7	443.8	471.8	499.8	527.9		370.7	407.8
1,2,3,4,6-PCDD	131.3	−329.1	329.9	450	42.6	99.38	6141.98	307.00	2511.00	282.5	283.6	345.1	432.6	457.7	482.8	507.9	533.0		375.6	419.9
1,2,3,6,7-PCDD	131.3	−321.7	329.9	482	42.6	111.67	5729.50	307.00	2511.00	282.5	283.6	340.9	432.6	457.7	482.8	507.9	533.0		387.9	428.1
1,2,3,6,8-PCDD	131.3	−326.2	329.9	482	42.6	111.67	5729.50	307.00	2511.00	282.5	283.6	340.9	432.6	457.7	482.8	507.9	533.0		387.9	428.1
1,2,3,6,9-PCDD	131.3	−329.4	329.9	461	42.6	103.94	5989.07	307.00	2511.00	282.5	283.6	343.5	432.6	457.7	482.8	507.9	533.0		380.1	422.8
1,2,3,7,9-PCDD	131.3	−326.2	329.9	480	42.6	110.84	5757.43	307.00	2511.00	282.5	283.6	341.1	432.6	457.7	482.8	507.9	533.0		387.1	427.5
1,2,3,8,9-PCDD	131.3	−321.7	329.9	475	42.6	109.15	5814.12	307.00	2511.00	282.5	283.6	341.7	432.6	457.7	482.8	507.9	533.0		385.4	426.3
1,2,4,6,7-PCDD	131.3	−333.6	329.9	468	42.6	106.44	5904.92	307.00	2511.00	282.5	283.6	342.6	432.6	457.7	482.8	507.9	533.0		382.7	424.5
1,2,4,6,8-PCDD	131.3	−338.1	329.9	469	42.6	106.88	5890.20	307.00	2511.00	282.5	283.6	342.5	432.6	457.7	482.8	507.9	533.0		383.1	424.7
1,2,4,6,9-PCDD	131.3	−341.3	329.9	450	42.6	99.65	6132.87	307.00	2511.00	282.5	283.6	345.0	432.6	457.7	482.8	507.9	533.0		375.9	420.1
1,2,4,7,9-PCDD	131.3	−338.1	329.9	468	42.6	106.44	5904.93	307.00	2511.00	282.5	283.6	342.6	432.6	457.7	482.8	507.9	533.0		382.7	424.5
1,2,4,8,9-PCDD	131.3	−333.6	329.9	464	42.6	105.11	5949.54	307.00	2511.00	282.5	283.6	343.1	432.6	457.7	482.8	507.9	533.0		381.3	423.6
1,2,3,4,6,7-H6CDD	139.2	−358.8	352.9	496	47.9	129.98	5568.42	338.42	2219.00	296.0	297.0	352.7	449.4	471.6	493.8	515.9	538.1		406.2	448.5
1,2,3,4,6,8-H6CDD	139.2	−363.3	352.9	498	47.9	130.69	5544.59	338.42	2219.00	296.0	297.0	352.5	449.4	471.6	493.8	515.9	538.1		406.9	449.0
1,2,3,4,6,9-H6CDD	139.2	−366.5	352.9	499	47.9	130.82	5540.29	338.42	2219.00	296.0	297.0	352.4	449.4	471.6	493.8	515.9	538.1		407.0	449.0
1,2,3,6,8,9-H6CDD	139.2	−367.9	352.9	501	47.9	131.71	5510.27	338.42	2219.00	296.0	297.0	352.1	407.2	471.6	493.8	515.9	538.1		407.9	449.6
1,2,3,6,7,9-H6CDD	139.2	−379.8	352.9	531	47.9	141.05	5196.92	338.42	2219.00	296.0	297.0	348.9	400.9	471.6	493.8	515.9	538.1		417.3	456.4
1,2,4,6,8,9-H6CDD	139.2	−379.8	352.9	507	47.9	133.69	5443.85	338.42	2219.00	296.0	297.0	351.4	405.9	471.6	493.8	515.9	538.1		409.9	451.0
1,2,3,4,6,7,9 −H7CDD	147.1	−405.0	375.9	521	53.3	151.33	5305.14	369.84	1927.00	309.5	310.5	363.5	416.6	485.5	504.7	524.0	543.3	562.5	427.5	470.2

[a] At 298.15 K.

Table 8. Evaluated Thermodynamic Properties of DF and PCDFs

substance	$\Delta_{sub}H^{o\,a}$ kJ·mol^{-1}	$\Delta_fH^{o\,a}$ kJ·mol^{-1}	$S^{o\,a}$ J·K^{-1}·mol^{-1}	T_{fus} K	$\Delta_{fus}H$ kJ·mol^{-1}	A_S J·K^{-1}·mol^{-1}	B_S J·K^{-2}·mol^{-1}	A_L J·K^{-1}·mol^{-1}	B_L J·K^{-2}·mol^{-1}	C_p/J·K^{-1}·mol^{-1} (at the following T/K) 298.15	300	400	500	600	700	800	900	1000	T_{fus} (solid) K	T_{fus} (liquid) K
DF	84.4	−29.1	196.2	355.3	19.6	−15.0	7177.6	85.0	5490.2	199.0	200.3	284.3	327.7	368.7					240.0	264.0
3,6-DCDF	108.7	−114.6	241.2	460.2	32.4	55.2	5729.7	200.7	3213.9	226.0	227.1	284.4	361.4	393.6	425.7				318.8	348.6
2,4,8-T3CDF	114.4	−146.6	259.1	427.2	32.0	55.5	6172.4	226.8	2991.6	239.5	240.7	302.4	376.3	406.3	436.2	466.1			319.1	354.5
OCDF	151.9	−312.6	369.5	532.2	51.9	159.3	4954.5	382.1	1561.4	307.0	307.9	357.5	407.0	475.8	491.4	507.0	522.6	538.2	422.9	465.2
Estimation for Known Meting Temperatures																				
3-MCDF	96.6	−71.9	217.8	374.7	25.3	2.7	7037.3	156.8	3724.7	212.5	213.8	305.8	343.1	380.3	417.5				266.3	296.4
2-MCDF	96.6	−71.9	217.8	375.2	25.3	3.0	7027.9	156.8	3724.7	212.5	213.8	305.8	343.1	380.3	417.5				266.6	296.6
2,4,6-T3CDF	112.9	−145.1	261.1	389.7	33.0	37.8	6766.4	222.5	3083.2	239.5	240.8	345.8	376.6	407.5	438.3				301.4	342.6
2,3-DCDF	104.8	−101.9	239.5	399.4	29.1	29.2	6601.2	189.6	3403.9	226.0	227.2	325.8	359.8	393.9	427.9				292.8	325.6
2,3,4,6-T4CDF	121.1	−175.2	282.7	426.7	36.9	68.8	6179.6	255.3	2762.4	253.0	254.2	315.9	393.4	421.0	448.7	476.3			332.4	373.1
2,4,6,7-T4CDF	121.1	−175.1	282.7	437.4	36.9	73.3	6027.7	255.3	2762.4	253.0	254.1	314.4	393.4	421.0	448.7	476.3			336.9	376.1
1,2,3,7-T4CDF	121.1	−175.2	282.7	440.9	36.9	74.7	5979.9	255.3	2762.4	253.0	254.1	313.9	393.4	421.0	448.7	476.3			338.4	377.1
1,2,3,4-T4CDF	121.1	−173.8	282.7	441.9	36.9	75.1	5966.4	255.3	2762.4	253.0	254.1	313.8	393.4	421.0	448.7	476.3			338.8	377.4
1,3,4,7,8-PCDF	129.2	−217.0	304.3	442.2	40.8	88.7	5963.0	288.1	2441.7	266.5	267.6	327.2	410.2	434.6	459.0	483.4			352.4	396.1
2,3,4,7-T4CDF	121.1	−175.2	282.7	445.9	36.9	76.7	5912.8	255.3	2762.4	253.0	254.1	313.2	393.4	421.0	448.7	476.3			340.4	378.5
2,3,4,8-T4CDF	121.1	−175.2	282.7	449.7	36.9	78.2	5863.5	255.3	2762.4	253.0	254.1	312.7	393.4	421.0	448.7	476.3			341.8	379.5
1,3,6,7-T4CDF	121.1	−175.1	282.7	449.9	36.9	78.3	5860.3	255.3	2762.4	253.0	254.1	312.7	393.4	421.0	448.7	476.3			341.9	379.6
1,3,6,8-T4CDF	121.1	−179.6	282.7	450.7	36.9	78.6	5850.5	255.3	2762.4	253.0	254.1	312.6	393.4	421.0	448.7	476.3			342.2	379.8
1,2,3,4,8-PCDF	129.2	−212.5	304.3	450.7	40.8	92.1	5850.5	288.1	2441.7	266.5	267.6	326.1	410.2	434.6	459.0	483.4			355.7	398.1
1,2,4,6,7-PCDF	129.2	−217.0	304.3	452.2	40.8	92.7	5831.1	288.1	2441.7	266.5	267.6	325.9	410.2	434.6	459.0	483.4			356.3	398.5
1,4,6,7-T4CDF	121.1	−178.3	282.7	453.7	36.9	79.7	5811.8	255.3	2762.4	253.0	254.1	312.2	393.4	421.0	448.7	476.3			343.4	380.6
1,2,4,6,7,9-H6CDF	137.3	−263.4	326.0	453.7	44.6	106.7	5811.8	320.9	2121.0	280.0	281.1	339.2	427.0	448.2	469.4	490.6			370.4	417.1
2,8-DCDF	104.8	−110.7	239.5	457.7	29.1	54.2	5761.0	189.6	3403.9	226.0	227.1	284.7	359.8	393.9	427.9	462.0			317.9	345.4
1,2,7,9-T4CDF	121.1	−175.1	282.7	457.7	36.9	81.2	5761.0	255.3	2762.4	253.0	254.1	311.7	393.4	421.0	448.7	476.3			344.9	381.7
2,3,8-T3CDF	112.9	−140.6	261.1	463.2	33.0	69.8	5692.6	222.5	3083.2	239.5	240.6	297.5	376.6	407.5	438.3	469.1			333.4	365.3
1,2,4,8-T4CDF	121.1	−187.1	282.7	465.2	36.9	84.0	5668.1	255.3	2762.4	253.0	254.1	310.7	393.4	421.0	448.7	476.3			347.7	383.8
1,2,3,4,6-PCDF	129.2	−212.5	304.3	467.7	40.8	98.4	5637.8	288.1	2441.7	266.5	267.6	323.9	410.2	434.6	459.0	483.4			362.1	402.3
1,3,4,6,7-PCDF	129.2	−217.0	304.3	468.4	40.8	98.7	5628.8	288.1	2441.7	266.5	267.6	323.8	410.2	434.6	459.0	483.4			362.3	402.5
2,3,6,7-T4CDF	121.1	−170.6	282.7	468.7	36.9	85.3	5625.8	255.3	2762.4	253.0	254.1	310.3	393.4	421.0	448.7	476.3			348.9	384.7
2,3,4,7,8-PCDF	129.2	−205.1	304.3	469.4	40.8	99.0	5616.8	288.1	2441.7	266.5	267.5	323.7	410.2	434.6	459.0	483.4			362.7	402.7
1,2,4,7,9-PCDF	129.2	−221.5	304.3	469.7	40.8	99.1	5613.8	288.1	2441.7	266.5	267.5	323.7	410.2	434.6	459.0	483.4			362.8	402.8
1,2,3,4,6,9-H6CDF	137.3	−250.1	326.0	469.7	44.6	112.6	5613.8	320.9	2121.0	280.0	281.0	337.2	427.0	448.2	469.4	490.6			376.3	420.5
1,2,3,8-T4CDF	121.1	−175.2	282.7	470.7	36.9	86.0	5601.9	255.3	2762.4	253.0	254.0	310.1	393.4	421.0	448.7	476.3			349.6	385.3
2,4,6,8-T4CDF	121.1	−179.6	282.7	472.2	36.9	86.5	5584.1	255.3	2762.4	253.0	254.0	309.9	393.4	421.0	448.7	476.3			350.2	385.7
1,2,6,7-T4CDF	121.1	−170.6	282.7	472.7	36.9	86.7	5578.2	255.3	2762.4	253.0	254.0	309.8	393.4	421.0	448.7	476.3			350.3	385.8
2,3,4,6,7-PCDF	129.2	−205.1	304.3	474.9	40.8	101.0	5551.8	288.1	2441.7	266.5	267.5	323.1	410.2	434.6	459.0	483.4	507.9		364.6	404.1
2,3,6,8-T4CDF	121.1	−175.1	282.7	475.7	36.9	87.7	5543.0	255.3	2762.4	253.0	254.0	309.5	393.4	421.0	448.7	476.3	503.9	531.5	351.4	386.7
1,2,4,6,8-PCDF	129.2	−221.5	304.3	477.7	40.8	101.9	5519.8	288.1	2441.7	266.5	267.5	322.7	410.2	434.6	459.0	483.4	507.9		365.6	404.7
1,2,3,6,7-PCDF	129.2	−205.1	304.3	479.2	40.8	102.5	5502.5	288.1	2441.7	266.5	267.5	322.6	410.2	434.6	459.0	483.4	507.9		366.1	405.1
1,2,3,6,8,9-H6CDF	137.3	−251.5	326.0	479.7	44.6	116.1	5496.8	320.9	2121.0	280.0	281.0	336.0	427.0	448.2	469.4	490.6	511.8		379.8	422.7
1,3,7,9-T4CDF	121.1	−179.6	282.7	480.2	36.9	89.3	5491.1	255.3	2762.4	253.0	254.0	308.9	393.4	421.0	448.7	476.3	503.9		352.9	387.9
1,2,7,8-T4CDF	121.1	−170.6	282.7	483.7	36.9	90.5	5451.3	255.3	2762.4	253.0	254.0	308.5	393.4	421.0	448.7	476.3	503.9		354.1	388.9
1,2,3,4,6,8,9-H7CDF	145.5	−288.9	347.6	484.7	48.5	131.3	5440.1	353.7	1800.2	293.5	294.5	348.9	443.8	461.8	479.8	497.8	515.8		395.0	441.0
1,2,3,4,7,9-H6CDF	137.3	−246.9	326.0	489.7	44.6	119.5	5384.5	320.9	2121.0	280.0	281.0	334.9	427.0	448.2	469.4	490.6	511.8		383.1	424.8
2,3,4,6,8-PCDF	129.2	−209.6	304.3	492.7	40.8	106.9	5351.7	288.1	2441.7	266.5	267.5	321.0	410.2	434.6	459.0	483.4	507.9		370.6	408.4
1,2,6,7,8-PCDF	129.2	−205.1	304.3	493.7	40.8	107.3	5340.9	288.1	2441.7	266.5	267.5	320.9	410.2	434.6	459.0	483.4	507.9		370.9	408.6
1,2,4,6,7,8-H6CDF	137.3	−251.5	326.0	494.7	44.6	121.1	5330.1	320.9	2121.0	280.0	281.0	334.3	427.0	448.2	469.4	490.6	511.8		384.7	425.8
1,2,3,4,7,8,9-H7CDF	145.5	−277.0	347.6	495.2	48.5	134.8	5324.7	353.7	1800.2	293.5	294.5	347.7	443.8	461.8	479.8	497.8	515.8		398.4	442.9
1,2,3,7,8-PCDF	129.2	−205.1	304.3	499.2	40.8	109.0	5282.0	288.1	2441.7	266.5	267.5	320.3	410.2	434.6	459.0	483.4	507.9		372.7	410.0

1,2,3,4,7,8-H6CDF	137.3	−242.4	326.0	499.2	44.6	122.5	5282.0	320.9	2121.0	280.0	281.0	333.8	427.0	448.2	469.4	490.6	511.8		386.2	426.8
2,3,7,8-T4CDF	121.1	−170.6	282.7	500.7	36.9	96.0	5266.2	255.3	2762.4	253.0	254.0	306.6	359.3	421.0	448.7	476.3	503.9		359.7	393.6
1,2,3,4,6,7-H6CDF	137.3	−242.4	326.0	500.7	44.6	123.0	5266.2	320.9	2121.0	280.0	281.0	333.6	386.3	448.2	469.4	490.6	511.8		386.7	427.1
1,3,4,6,7,8-H6CDF	137.3	−251.5	326.0	502.7	44.6	123.6	5245.3	320.9	2121.0	280.0	281.0	333.4	385.9	448.2	469.4	490.6	511.8		387.3	427.5
1,2,3,6,7,8-H6CDF	137.3	−239.6	326.0	506.2	44.6	124.7	5209.0	320.9	2121.0	280.0	281.0	333.1	385.2	448.2	469.4	490.6	511.8	533.0	388.4	428.3
1,2,3,4,6,8-H6CDF	137.3	−246.9	326.0	506.9	44.6	124.9	5201.3	320.9	2121.0	280.0	281.0	333.0	385.0	448.2	469.4	490.6	511.8	533.0	388.6	428.4
1,2,3,4,6,7,8-H7CDF	145.5	−277.0	347.6	509.7	48.5	139.3	5173.2	353.7	1800.2	293.5	294.5	346.2	397.9	461.8	479.8	497.8	515.8	533.8	402.9	445.5
1,2,4,7,8-PCDF	129.2	−217.0	304.3	510.2	40.8	112.4	5168.1	288.1	2441.7	266.5	267.5	319.1	370.8	434.6	459.0	483.4	507.9	532.3	376.1	412.7
2,3,4,6,7,8-H6CDF	137.3	−239.6	326.0	512.7	44.6	126.7	5142.9	320.9	2121.0	280.0	281.0	332.4	383.8	448.2	469.4	490.6	511.8	533.0	390.3	429.7
1,2,4,6,8,9-H6CDF	137.3	−263.4	326.0	520.2	44.6	128.9	5068.8	320.9	2121.0	280.0	280.9	331.6	382.3	448.2	469.4	490.6	511.8	533.0	392.5	431.2
1,2,3,7,8,9-H6CDF	137.3	−239.6	326.0	520.7	44.6	129.0	5063.9	320.9	2121.0	280.0	280.9	331.6	382.2	448.2	469.4	490.6	511.8	533.0	392.7	431.3
Estimation of Melting Temperatures and Other Properties																				
1-MCDF	96.6	−71.9	217.8	385.6	25.3	8.6	6837.7	156.8	3724.7	212.5	213.8	305.8	343.1	380.3	417.5				272.3	300.4
4-MCDF	96.6	−71.9	217.8	389.7	25.3	10.8	6764.9	156.8	3724.7	212.5	213.8	305.8	343.1	380.3	417.5				274.5	302.0
1,2-DCDF	104.8	−101.9	239.5	402.2	29.1	30.6	6555.0	189.6	3403.9	226.0	227.2	292.8	359.8	393.9	427.9				294.2	326.6
1,3-DCDF	104.8	−106.4	239.5	406.8	29.1	32.8	6481.7	189.6	3403.9	226.0	227.2	292.0	359.8	393.9	427.9				296.4	328.1
1,4-DCDF	104.8	−109.6	239.5	401.7	29.1	30.3	6564.0	189.6	3403.9	226.0	227.2	292.9	359.8	393.9	427.9				294.0	326.4
1,6-DCDF	104.8	−110.7	239.5	403.7	29.1	31.3	6531.3	189.6	3403.9	226.0	227.2	292.5	359.8	393.9	427.9				294.9	327.0
1,7-DCDF	104.8	−110.7	239.5	410.3	29.1	34.4	6426.2	189.6	3403.9	226.0	227.2	291.5	359.8	393.9	427.9				298.1	329.3
1,8-DCDF	104.8	−110.7	239.5	405.2	29.1	32.0	6507.5	189.6	3403.9	226.0	227.2	292.3	359.8	393.9	427.9				295.6	327.6
1,9-DCDF	104.8	−110.7	239.5	408.7	29.1	33.7	6451.5	189.6	3403.9	226.0	227.2	291.7	359.8	393.9	427.9				297.3	328.7
2,4-DCDF	104.8	−106.4	239.5	408.6	29.1	33.6	6453.0	189.6	3403.9	226.0	227.2	291.7	359.8	393.9	427.9				297.3	328.7
2,6-DCDF	104.8	−110.7	239.5	415.7	29.1	36.9	6343.0	189.6	3403.9	226.0	227.2	290.6	359.8	393.9	427.9				300.5	331.1
2,7-DCDF	104.8	−110.7	239.5	424.7	29.1	40.9	6208.0	189.6	3403.9	226.0	227.2	289.2	359.8	393.9	427.9				304.6	334.2
3,4-DCDF	104.8	−101.9	239.5	407.5	29.1	33.1	6470.0	189.6	3403.9	226.0	227.2	291.9	359.8	393.9	427.9				296.8	328.4
3,7-DCDF	104.8	−110.7	239.5	445.2	29.1	49.4	5922.7	189.6	3403.9	226.0	227.1	286.3	359.8	393.9	427.9				313.1	341.2
4,6-DCDF	104.8	−110.7	239.5	420.5	29.1	39.1	6270.0	189.6	3403.9	226.0	227.2	289.9	359.8	393.9	427.9				302.7	332.8
1,2,3-T3CDF	112.9	−136.4	261.1	419.8	33.0	52.3	6280.5	222.5	3083.2	239.5	240.7	303.5	376.6	407.5	438.3	469.1			315.9	351.9
1,2,4-T3CDF	112.9	−148.3	261.1	417.8	33.0	51.4	6310.0	222.5	3083.2	239.5	240.7	303.8	376.6	407.5	438.3	469.1			315.0	351.3
1,2,6-T3CDF	112.9	−140.6	261.1	425.8	33.0	54.9	6192.3	222.5	3083.2	239.5	240.7	302.6	376.6	407.5	438.3	469.1			318.5	353.7
1,2,7-T3CDF	112.9	−140.6	261.1	433.7	33.0	58.3	6079.4	222.5	3083.2	239.5	240.6	301.4	376.6	407.5	438.3	469.1			321.9	356.2
1,2,8-T3CDF	112.9	−140.6	261.1	426.2	33.0	55.1	6185.9	222.5	3083.2	239.5	240.7	302.5	376.6	407.5	438.3	469.1			318.7	353.9
1,2,9-T3CDF	112.9	−140.6	261.1	410.6	33.0	48.0	6421.6	222.5	3083.2	239.5	240.7	304.9	376.6	407.5	438.3	469.1			311.7	349.0
1,3,4-T3CDF	112.9	−148.3	261.1	419.4	33.0	52.1	6287.1	222.5	3083.2	239.5	240.7	303.5	376.6	407.5	438.3	469.1			315.7	351.8
1,3,6-T3CDF	112.9	−145.1	261.1	428.5	33.0	56.1	6152.7	222.5	3083.2	239.5	240.6	302.2	376.6	407.5	438.3	469.1			319.7	354.6
1,3,7-T3CDF	112.9	−145.1	261.1	438.6	33.0	60.3	6011.5	222.5	3083.2	239.5	240.6	300.7	376.6	407.5	438.3	469.1			323.9	357.7
1,3,8-T3CDF	112.9	−145.1	261.1	433.2	33.0	58.0	6086.5	222.5	3083.2	239.5	240.6	301.5	376.6	407.5	438.3	469.1			321.7	356.0
1,3,9-T3CDF	112.9	−145.1	261.1	417.5	33.0	51.2	6315.0	222.5	3083.2	239.5	240.7	303.8	376.6	407.5	438.3	469.1			314.9	351.2
1,4,6-T3CDF	112.9	−148.3	261.1	419.6	33.0	52.2	6282.7	222.5	3083.2	239.5	240.7	303.5	376.6	407.5	438.3	469.1			315.8	351.8
1,4,7-T3CDF	112.9	−148.3	261.1	429.8	33.0	56.6	6133.9	222.5	3083.2	239.5	240.6	302.0	376.6	407.5	438.3	469.1			320.3	355.0
1,4,8-T3CDF	112.9	−148.3	261.1	426.6	33.0	55.2	6180.5	222.5	3083.2	239.5	240.7	302.5	376.6	407.5	438.3	469.1			318.9	354.0
1,4,9-T3CDF	112.9	−148.3	261.1	413.0	33.0	49.2	6383.2	222.5	3083.2	239.5	240.7	304.5	376.6	407.5	438.3	469.1			312.8	349.8
1,6,7-T3CDF	112.9	−140.6	261.1	424.2	33.0	54.2	6215.6	222.5	3083.2	239.5	240.7	302.8	376.6	407.5	438.3	469.1			317.8	353.2
1,6,8-T3CDF	112.9	−145.1	261.1	422.2	33.0	53.3	6245.4	222.5	3083.2	239.5	240.7	303.1	376.6	407.5	438.3	469.1			317.0	352.6
1,7,8-T3CDF	112.9	−140.6	261.1	425.4	33.0	54.7	6197.3	222.5	3083.2	239.5	240.7	302.6	376.6	407.5	438.3	469.1			318.4	353.6
2,3,4-T3CDF	112.9	−136.4	261.1	422.9	33.0	53.6	6234.5	222.5	3083.2	239.5	240.7	303.0	376.6	407.5	438.3	469.1			317.3	352.8
2,3,6-T3CDF	112.9	−140.6	261.1	436.5	33.0	59.4	6040.4	222.5	3083.2	239.5	240.6	301.0	376.6	407.5	438.3	469.1			323.1	357.0
2,3,7-T3CDF	112.9	−140.6	261.1	448.7	33.0	64.3	5876.3	222.5	3083.2	239.5	240.6	299.4	376.6	407.5	438.3	469.1			328.0	360.8
2,4,7-T3CDF	112.9	−145.1	261.1	441.1	33.0	61.3	5977.0	222.5	3083.2	239.5	240.6	300.4	376.6	407.5	438.3	469.1			325.0	358.5
2,6,7-T3CDF	112.9	−140.6	261.1	439.9	33.0	60.8	5993.5	222.5	3083.2	239.5	240.6	300.6	376.6	407.5	438.3	469.1			324.5	358.1
3,4,6-T3CDF	112.9	−140.6	261.1	426.6	33.0	55.3	6179.8	222.5	3083.2	239.5	240.7	302.5	376.6	407.5	438.3	469.1			318.9	354.0
3,4,7-T3CDF	112.9	−140.6	261.1	441.1	33.0	61.3	5977.2	222.5	3083.2	239.5	240.6	300.4	376.6	407.5	438.3	469.1			325.0	358.5
1,2,3,6-T4CDF	121.1	−175.2	282.7	446.4	36.9	76.9	5906.2	255.3	2762.4	253.0	254.1	313.2	393.4	421.0	448.7	476.3	503.9		340.6	378.6
1,2,3,9-T4CDF	121.1	−175.2	282.7	431.2	36.9	70.7	6113.9	255.3	2762.4	253.0	254.1	315.3	393.4	421.0	448.7	476.3	503.9		334.4	374.4
1,2,4,6-T4CDF	121.1	−187.1	282.7	440.7	36.9	74.7	5982.0	255.3	2762.4	253.0	254.1	313.9	393.4	421.0	448.7	476.3	503.9		338.3	377.0

Table 8 (Continued)

substance	$\Delta_{sub}H^{o\,a}$ / kJ·mol^{-1}	$\Delta_fH^{o\,a}$ / kJ·mol^{-1}	$S^{o\,a}$ / J·K^{-1}·mol^{-1}	T_{fus} / K	$\Delta_{fus}H$ / kJ·mol^{-1}	A_S / J·K^{-1}·mol^{-1}	B_S / J·K^{-2}·mol^{-1}	A_L / J·K^{-1}·mol^{-1}	B_L / J·K^{-2}·mol^{-1}	C_p/J·K^{-1}·mol^{-1} (at the following T/K)									T_{fus} (solid) / K	T_{fus} (liquid) / K
										298.15	300	400	500	600	700	800	900	1000		
Estimation of Melting Temperatures and Other Properties (Continued)																				
1,2,4,7-T4CDF	121.1	−187.1	282.7	451.7	36.9	79.0	5837.3	255.3	2762.4	253.0	254.1	312.5	393.4	421.0	448.7	476.3	503.9		342.6	380.1
1,2,4,9-T4CDF	121.1	−187.1	282.7	429.5	36.9	70.0	6138.8	255.3	2762.4	253.0	254.1	315.5	393.4	421.0	448.7	476.3	503.9		333.6	373.9
1,2,6,8-T4CDF	121.1	−175.1	282.7	447.7	36.9	77.4	5889.0	255.3	2762.4	253.0	254.1	313.0	393.4	421.0	448.7	476.3	503.9		341.1	379.0
1,2,6,9-T4CDF	121.1	−178.3	282.7	435.0	36.9	72.3	6061.3	255.3	2762.4	253.0	254.1	314.7	393.4	421.0	448.7	476.3	503.9		335.9	375.4
1,2,8,9-T4CDF	121.1	−170.6	282.7	450.0	36.9	78.3	5859.2	255.3	2762.4	253.0	254.1	312.7	393.4	421.0	448.7	476.3	503.9		342.0	379.6
1,3,4,6-T4CDF	121.1	−187.1	282.7	441.0	36.9	74.8	5978.6	255.3	2762.4	253.0	254.1	313.9	393.4	421.0	448.7	476.3	503.9		338.4	377.1
1,3,4,7-T4CDF	121.1	−187.1	282.7	453.8	36.9	79.8	5809.4	255.3	2762.4	253.0	254.1	312.2	393.4	421.0	448.7	476.3	503.9		343.5	380.7
1,3,4,8-T4CDF	121.1	−187.1	282.7	450.1	36.9	78.4	5857.1	255.3	2762.4	253.0	254.1	312.7	393.4	421.0	448.7	476.3	503.9		342.0	379.6
1,3,4,9-T4CDF	121.1	−187.1	282.7	433.5	36.9	71.7	6082.5	255.3	2762.4	253.0	254.1	315.0	393.4	421.0	448.7	476.3	503.9		335.3	375.0
1,3,6,9-T4CDF	121.1	−182.8	282.7	440.0	36.9	74.4	5991.6	255.3	2762.4	253.0	254.1	314.0	393.4	421.0	448.7	476.3	503.9		338.0	376.8
1,3,7,8-T4CDF	121.1	−175.1	282.7	459.5	36.9	81.9	5737.8	255.3	2762.4	253.0	254.1	311.4	393.4	421.0	448.7	476.3	503.9		345.6	382.2
1,4,6,8-T4CDF	121.1	−182.8	282.7	443.0	36.9	75.6	5951.3	255.3	2762.4	253.0	254.1	313.6	393.4	421.0	448.7	476.3	503.9		339.2	377.7
1,4,6,9-T4CDF	121.1	−186.0	282.7	450.1	36.9	78.4	5857.4	255.3	2762.4	253.0	254.1	312.7	393.4	421.0	448.7	476.3	503.9		342.0	379.6
1,4,7,8-T4CDF	121.1	−178.3	282.7	449.8	36.9	78.3	5861.0	255.3	2762.4	253.0	254.1	312.7	393.4	421.0	448.7	476.3	503.9		341.9	379.5
1,6,7,8-T4CDF	121.1	−175.2	282.7	439.3	36.9	74.1	6001.1	255.3	2762.4	253.0	254.1	314.1	393.4	421.0	448.7	476.3	503.9		337.7	376.6
3,4,6,7-T4CDF	121.1	−170.6	282.7	474.8	36.9	87.5	5552.4	255.3	2762.4	253.0	254.0	309.6	393.4	421.0	448.7	476.3	503.9		351.1	386.5
1,2,3,4,7-PCDF	129.2	−212.5	304.3	472.0	40.8	100.0	5585.9	288.1	2441.7	266.5	267.5	323.4	410.2	434.6	459.0	483.4	507.9		363.6	403.3
1,2,3,4,9-PCDF	129.2	−212.5	304.3	447.1	40.8	90.7	5896.5	288.1	2441.7	266.5	267.6	326.6	410.2	434.6	459.0	483.4	507.9		354.4	397.3
1,2,3,6,8-PCDF	129.2	−209.6	304.3	473.6	40.8	100.5	5566.9	288.1	2441.7	266.5	267.5	323.2	410.2	434.6	459.0	483.4	507.9		364.2	403.7
1,2,3,6,9-PCDF	129.2	−212.8	304.3	458.0	40.8	94.9	5756.9	288.1	2441.7	266.5	267.6	325.1	410.2	434.6	459.0	483.4	507.9		358.5	399.9
1,2,3,7,9-PCDF	129.2	−209.6	304.3	466.7	40.8	98.1	5649.7	288.1	2441.7	266.5	267.6	324.1	410.2	434.6	459.0	483.4	507.9		361.7	402.0
1,2,3,8,9-PCDF	129.2	−205.1	304.3	458.0	40.8	94.9	5756.4	288.1	2441.7	266.5	267.6	325.1	410.2	434.6	459.0	483.4	507.9		358.5	399.9
1,2,4,6,9-PCDF	129.2	−224.7	304.3	452.9	40.8	92.9	5821.6	288.1	2441.7	266.5	267.6	325.8	410.2	434.6	459.0	483.4	507.9		356.6	398.7
1,2,4,8,9-PCDF	129.2	−217.0	304.3	454.7	40.8	93.6	5797.8	288.1	2441.7	266.5	267.6	325.6	410.2	434.6	459.0	483.4	507.9		357.3	399.1
1,2,6,7,9-PCDF	129.2	−217.0	304.3	460.7	40.8	95.9	5722.9	288.1	2441.7	266.5	267.6	324.8	410.2	434.6	459.0	483.4	507.9		359.5	400.6
1,3,4,6,8-PCDF	129.2	−221.5	304.3	469.4	40.8	99.1	5616.5	288.1	2441.7	266.5	267.5	323.7	410.2	434.6	459.0	483.4	507.9		362.7	402.7
1,3,4,6,9-PCDF	129.2	−224.7	304.3	455.5	40.8	93.9	5788.5	288.1	2441.7	266.5	267.6	325.5	410.2	434.6	459.0	483.4	507.9		357.6	399.3
1,3,4,7,9-PCDF	129.2	−221.5	304.3	466.0	40.8	97.8	5658.1	288.1	2441.7	266.5	267.6	324.1	410.2	434.6	459.0	483.4	507.9		361.5	401.9
1,3,6,7,8-PCDF	129.2	−209.6	304.3	475.4	40.8	101.2	5545.4	288.1	2441.7	266.5	267.5	323.0	410.2	434.6	459.0	483.4	507.9		364.8	404.2
1,4,6,7,8-PCDF	129.2	−212.8	304.3	463.2	40.8	96.8	5691.4	288.1	2441.7	266.5	267.6	324.5	410.2	434.6	459.0	483.4	507.9		360.5	401.2
1,2,3,4,8,9-H6CDF	137.3	−242.4	326.0	477.2	44.6	115.3	5525.5	320.9	2121.0	280.0	281.0	336.3	427.0	448.2	469.4	490.6	511.8	533.0	378.9	422.1
1,2,3,6,7,9-H6CDF	137.3	−251.5	326.0	488.6	44.6	119.1	5396.2	320.9	2121.0	280.0	281.0	335.0	427.0	448.2	469.4	490.6	511.8	533.0	382.8	424.5
1,3,4,6,7,9-H6CDF	137.3	−263.4	326.0	505.2	44.6	124.4	5219.2	320.9	2121.0	280.0	281.0	333.2	385.4	448.2	469.4	490.6	511.8	533.0	388.1	428.1
1,2,3,4,6,7,9-H7CDF	145.5	−288.9	347.6	505.5	48.5	138.0	5215.3	353.7	1800.2	293.5	294.5	346.6	398.8	461.8	479.8	497.8	515.8	533.8	401.7	444.7

[a] At 298.15 K.

Table 9. Uncertainties of Evaluated and Predicted Thermodynamic Data Adopted in This Study

substance	$\delta(\Delta_f H)$	$\delta S^o(298.15\ K)$	$\delta C_p^o(298.15\ K)$	$\delta C_p(T_{fus})_{solid}$	$\delta C_p(T_{fus})_{liquid}$	$\delta(\Delta_{fus}H)$	δT_{fus}
	kJ·mol^{-1}	J·K^{-1}·mol^{-1}	J·K^{-1}·mol^{-1}	J·K^{-1}·mol^{-1}	J·K^{-1}·mol^{-1}	kJ·mol^{-1}	K
DD	4	3	5	8	9	1	1
1-MCDD	5	3	7	9	9	1	1
2-MCDD and MCDFs	10	3	7	8	9	1	1
2,3-DCDD	7	4	7	10	11	1	1
2,7-DCDD	11	4	7	10	11	3	1
2,8-DCDD	10	4	7	10	11	3	1
other DCDDs and all DCDFs	11	6	7	10	11	4	20[a]
1,3,7-T3CDD	12	5	8	10	11	2	1
1,2,4-T3CDD	13	5	8	10	11	4	1
other T3CDDs and all T3CDFs	14	8	8	10	11	4	25[a]
1,2,3,4-T4CDD	16	6	8	11	12	5	1
2,3,7,8-T4CDD	16	8	8	12	13	2	1
other T4CDDs and all T4CDFs	20	10	8	12	13	6	30[a]
PCDDs and PCDFs	30	13	8	12	13	6	30[a]
H6CDDs and H6CDFs	35	16	9	12	14	7	30[a]
H7CDDs and H7CDFs	40	20	9	13	14	7	30[a]
OCDD and OCDF	50	8	10	14	15	8	1

[a] The uncertainties of predicted melting temperatures. Uncertainties of experimental melting temperatures are 1−2 K (see 3).

with chlorine substitution for PCDDs and PCDFs as shown in Figures 1−6, and corresponding equations have been calculated. The equations $y = f(x)$ are shown in these and subsequent figures together with the correlation coefficients R.

To calculate heat capacity values using eq 6, critical temperatures and acentric factors were obtained from the following formulas:[34,36]

$$T_c = T_b + T_b/(a_t + b_t N_t) \quad (13)$$

where

$$a_t = 1.242, \quad b_t = 0.138, \quad N_t = 7.027 + x0.642,$$
$$\text{and } x = \text{chlorine substitution}$$

$$\omega = 31g(1.01325P_c)(T_b/T_c)/7\{1 - (T_b/T_c)\} - 1 \quad (14)$$

where

$$P_c/\text{bar} = M/(a_p + b_p N_p), \quad M = \text{molecular weight},$$
$$a_p = 0.339, \quad b_p = 0.226, \quad \text{and } N_p = 8.721 + x1.409$$

One or two iterations are required to achieve consistency of the critical parameters (see Table 5) and the corresponding heat capacities with vapor pressure data and to calculate the boiling temperatures using Fishtine's correlation, as compared with the direct procedure using adopted thermodynamic values. The boiling temperatures' comparison in Table 4 shows that the validity of Fishtine's correlation differs for the different compounds.

The heat capacities obtained as a result of our estimations, and the vapor pressure correlation, were represented by simple equations: for the solid ($C_p(T) = A_S + B_S T/10000$) and for the liquid ($C_p(T) = A_L + B_L T/10000$). The coefficients are presented in Table 7. The A_L and B_L coefficients are correlated with chlorine substitution, as shown in Figures 7−10.

Thermodynamic properties for PCDDs and PCDFs with known melting temperatures (as cited in ref 8), calculated using the derived correlations, are presented in Tables 7 and 8.

Melting Temperatures' Estimation

There are 25 PCDDs and 59 PCDFs for which melting temperatures are unknown. An estimation of the melting temperatures for organics is somewhat complicated because of the explicit nonadditive behavior of the property.[3] We found it possible to correlate melting temperatures with moments of inertia for PCDDs and PCDFs with the same molecular symmetry groups. The moments of inertia ($I_a + I_b$) were calculated using structural parameters adopted in Part 1 of this work.[32] Examples of the correlations are shown in Figures 11 and 12 for the case of C_s molecular symmetry of PCDDs and C_{2v} molecular symmetry of PCDFs.

Using the correlations considered, we estimated the melting points for all of these PCDDs and PCDFs together with other properties (see Tables 7 and 8), as outlined above.

Enthalpies of Formation of Condensed Compounds

The experimental values of the enthalpies of formation are known for dibenzo-*p*-dioxin, dibenzofuran, 1-chlorodibenzo-*p*-dioxin, 2-chlorodibenzo-*p*-dioxin, and 2,3-dichlorodibenzo-*p*-dioxin. There are some doubts[39] about the reliability of the experimental value for 2-chlorodibenzo-*p*-dioxin,[18] and we do not adopt this value. Enthalpies of formation of 2-chlorodibenzo-*p*-dioxin and other PCDDs and all PCDFs need to be estimated. For this purpose we used enthalpies of formation of gaseous compounds obtained in Part 1 of this work[32] and experimental and estimated enthalpies of sublimation. The adopted values of the enthalpies of formation are presented in Tables 7 and 8.

Comparison of Vapor Pressure Data

The estimated vapor pressure data are in good agreement with experimental values obtained for selected liquid PCDDs by a gas chromatographic method[9] (see Table 6). Experimental and predicted data[5] are presented in the same table for comparison.

Uncertainties in the Evaluated and Predicted Data

Most of the uncertainty is critically dependent on uncertainties adopted for the gas-phase properties. Taking into account these uncertainties, the following estimations can be made.

For the enthalpies of formation (excluding DD, 1-CDD, and 2,3-DCDD, where experimental uncertainties should be adopted) uncertainties are determined by gas-phase

estimation uncertainties and uncertainties in enthalpies of sublimation. We adopted the difference between $\Delta_s H$ values obtained by "III Law" and "II Law" treatments as a measure of the uncertainty of the enthalpy of sublimation. For the estimated enthalpies of sublimation for other PCDDs and all PCDFs we adopted uncertainties of (10−40) kJ·mol^{-1} depending on the chlorine substitution.

Uncertainties in entropies of solid PCDDs and PCDFs are determined by gas-phase calculation uncertainty and by the quality of our correlation. We adopted uncertainties equal to that for the gas phase for those cases where vapor pressure measurements were used and added a contribution from uncertainty of correlation (5−20) J·K^{-1}·mol^{-1} depending on the chlorine substitution for other cases.

Uncertainties in heat capacities depend on the quality of the primary estimation for DD, the group contribution technique for solid PCDDs and PCDFs, and eq 4 for liquid compounds. Taking into account the conclusion of ref 26 and a test for eq 6 presented above, we adopted uncertainties in heat capacities of 3−5% for all PCDDs and PCDFs in the solid and liquid states.

Adopted uncertainties in enthalpies of fusion are 1 kJ·mol^{-1} for measured quantities and (2−5) kJ·mol^{-1} for predicted values.

The correlation quality of the melting temperatures is different for different symmetry groups. A detailed examination of the various possible uncertainties in predicted values allowed adoption of uncertainties (20−30) K for all estimated melting temperatures.

All adopted uncertainties are presented in Table 9.

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