Comments

Comments on "Thermodynamic Properties of Dibenzo-*p*-dioxin, Dibenzofuran, and Their Polychlorinated Derivatives in the Gaseous and Condensed Phases. 2. Thermodynamic Properties of Condensed Compounds" (Iorish, V. S.; Dorofeeva, O. V.; Moiseeva, N. F. *J. Chem. Eng. Data* 2001, *46,* 286-298)

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Recently, Iorish et al. derived several thermodynamic data for a range of chlorine-substituted dioxins (PCDDs) and dibenzofuranes (PCDFs) from various correlations for experimental data. In their study, they derived melting temperatures (T_m) from a correlation between experimental melting temperatures and calculated moments of inertia for congeners with the same molecular symmetry groups.[1] They reported uncertainties in estimated melting temperatures of 20 to 30 K for both the PCDDs and the PCDFs. The aim of this Comment is to demonstrate that the melting temperatures can also be estimated from the experimental data gathered in ref 1 by a simple procedure, avoiding the complicated use of structural parameters for the calculation of moments of inertia and leading to a lower uncertainty.

For PCDDs, the authors observed the enthalpy of fusion (ΔH_m) to be linearly correlated with the chlorine substitution number, *n* (data for 11 PCDDs). An initial comparison of the entropy of fusion (ΔS_m), calculated from the experimental T_m and ΔH_m data in ref 1 and corrected for molecular symmetry, suggested this entropy also to be linearly related to the chlorine substitution number. Therefore, it can be expected that melting temperatures would be described by

$$T_m = \Delta H_m/\Delta S_m = (5370n + 15700)/(An + B - R \ln \delta) \quad (1)$$

where the expression in the numerator is the correlation of ΔH_m with *n* from ref 1 and where the expression in the denominator is the dependence of ΔS_m, with correction for the symmetry number (δ), on *n*; *R* is the gas constant. The experimental T_m values cited in ref 1 for 25 PCDDs fitted to eq 1 with $A = 7.37 \pm 0.39$ J/mol·K and $B = 50.8 \pm 1.6$ J/mol·K. Figure 1 plots the experimental T_m versus the estimated T_m. On average, the difference between experimental and estimated values is 16 K, which is at the lower end of the uncertainty range given in ref 1.

For four PCDFs, ΔH_m was found to be equal to $3870n + 21400$ J/mol·K [1]. The fitting of 59 experimental PCDF T_m values to eq 2 afforded $C = 5.00 \pm 0.28$ J/mol·K and $D = 61.2 \pm 1.3$ J/mol·K.

$$T_m = \Delta H_m/\Delta S_m = (3870n + 21400)/(Cn + D - R \ln \delta) \quad (2)$$

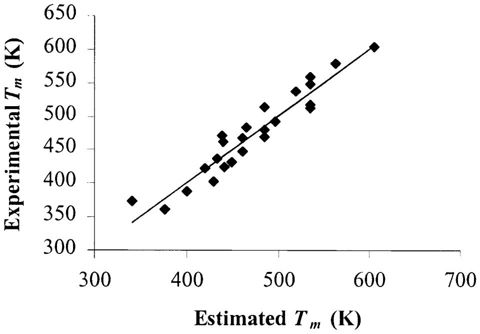

Figure 1. Experimental versus estimated melting temperatures for PCDDs. The line is the $y = x$ line.

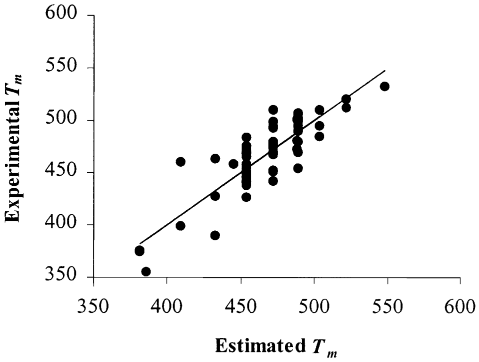

Figure 2. Experimental versus estimated melting temperatures for PCDFs. The line is the $y = x$ line.

For the PCDFs, Figure 2 plots the experimental T_m versus the estimated T_m. On average, the difference between experimental and estimated values is 14 K, which is a factor of 2 better than the uncertainty given by Iorish et al.

Literature Cited

(1) Iorish, V. S.; Dorofeeva, O. V.; Moiseeva, N. F. Thermodynamic Properties of Dibenzo-*p*-dioxin, Dibenzofuran, and Their Polychlorinated Derivatives in the Gaseous and Condensed Phases. 2. Thermodynamic Properties of Condensed Compounds. *J. Chem. Eng. Data* **2001**, *46*, 286−298.

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