Approximation of enthalpy of formation by Fourier series

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A possible approximation of the enthalpy of formation of C,H,N,O-containing compounds by trigonometric Fourier series has been shown.

Key words: approximation, enthalpy of formation, trigonometric Fourier series.

In the preceeding paper,[1] a method was suggested for approximating the density (ρ) of substances by Fourier series, and the efficiency of similar approximations for other physicochemical parameters was proposed. In this work, this supposition has been checked for the enthalpy of formation (ΔH^0_f) of C,H,N,O-containing compounds.

Presently available methods for the determination of ΔH^0_f are either restricted to one or another class of compounds,[2] are based on a very large set of descriptors,[3] or are rather complicated and tedious (for example, methods of molecular mechanics and quantum chemistry[4]). However, the properties of the Fourier series[5] allow one to manage with a comparatively small set of descriptors and, at the same time, to cover a rather wide range of compounds (in our case, the range of C,H,N,O-containing substances).

The Fourier-series expansion coefficients for ΔH^0_f were determined by the same methods by which the expansion coefficients for ρ were obtained in the previous work,[1] however, only descriptors of expanded molecular formulas (EMF) were used in this case as the basis for the argument, because the other two bases (normed composition and molecular formula) are quite inappropriate for representing ΔH^0_f. Like previously, the argument of the series has the form:

$$y_k = \pi \mathrm{th}[\lg(1 + q^j_i)],$$

where q^j_i is the number of atoms of the i-th element related to the j-th type. As previously[1] the atomic types are determined for C, H, N, O, (1st, 2nd, 3d, and 4th elements, respectively) (Scheme 1). The index k in argument y_k is established as follows: for C: $k = j$; for H: $k = j + 4$; for N: $k = j + 6$, and for O: $k = j + 11$.

The reference series consisted of 478 compounds related to various structural classes;[6,7] 52 substances entered the control series. Table 1 presents the parameters of the error distribution for the reference and control series for the expansion of ΔH^0_f in different harmonics. It can be seen that the representation of ΔH^0_f by more than two harmonics for a given list of descriptors worsens these parameters in the control sample and, hence, reduces the accuracy of calculations of ΔH^0_f by the suggested method. Table 2 contains calculated and experimental ΔH^0_f values for some "reference" and "control" compounds.

Scheme 1

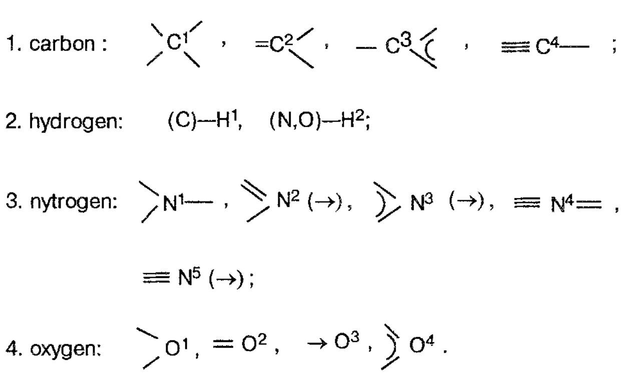

Table 1. Correlation coefficients (r), average absolute errors ($|\overline{\Delta(\Delta H^0_f)}|$), and error dispersions (σ) in reference and control samples for expansion of ΔH^0_f up to h-th harmonics

h	r(%)	$\lvert\overline{\Delta(\Delta H^0_f)}\rvert$ kcal mol^{-1}	σ kcal mol^{-1}	Note
1	93.1	27.1	26.9	Reference
	85.3	23.2	21.6	Control
2	98.2	13.5	12.2	Reference
	95.4	13.6	11.9	Control
3	99.3	7.2	6.5	Reference
	88.2	22.0	18.3	Control

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Table 2. Experimental and calculated $\Delta H^0{}_f$ values for support (*) and control substances

Substance	$\Delta H^0{}_f$/kcal mol^{-1}	
	Experiment	Calculation
1-Methyl-2-methoxydiazene oxide	2.5	−5.9
Oxalic acid	−198.4	−183.6
Pyrazole	28.3	28.4
Imidazole	14.5	28.4
1,3,5-Triazine	40.2	41.1
1-Methylamino-5-methyltetrazole	47.8	59.2
2-Nitrofuran	−24.9	−37.1
Dimethylfurazan	13.4	24.1
Butane 1,4-dinitrate	−78.0	−91.5
Butane 1,2,3,4-tetranitrate	−114.0	−121.2
Pyridazine	53.7	40.2
Pyrrole	21.2	12.3
1-(2-Propenyl)-aziridine	38.2	68.1
1,3,5-Triamino-2,4,6-trinitrobenzene	−37.0	−15.9
Aminocarbonylpentane	−101.6	−92.7
Hexanitrobenzene	48.0	44.3
1-Amino-5-phenyltetrazole	74.3	71.3
Phenylfurazan	58.5	59.9
1,2,3,4-Tetrazole	56.7	60.3
Water*	−27.5	−59.8
Ammonium nitrate*	−87.9	−93.4
Hydrazoic acid*	64.4	60.4
Nitroglycerin*	−87.6	−94.4
Cyclopentane azide*	42.8	45.4
Adamantane*	−31.6	−22.6
Trinitronaphthalene*	5.7	−1.7
Octogen*	18.0	9.7
Hexogen*	14.7	19.2

Thus, we have shown that $\Delta H^0{}_f$ can be successfully approximated using the Fourier-series expansion. The obtained approximation formula is quite appropriate for fast estimation of $\Delta H^0{}_f$ for C,H,N,O-containing substances, despite its awkwardness due to which it is not presented here. (The authors are ready to provide the approximation formula.)

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