General and Inorganic Chemistry

Fourier series approximation of the density of substances

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The expediency of approximation of physicochemical parameters using Fourier series is illustrated using density as an example.

Key words: additive methods; analytical functions; approximation; Fourier series; power series; trigonometrical basis.

The power series method for the approximation of density (ρ) presented in the previous work,[1] despite its advantages over additive schemes, has several essential disadvantages conditioned by properties of power series:

1. An approximated function must be analytical over the whole expansion range. However, for many physicochemical values, including ρ, even continuity is doubtful, to say nothing of analyticity.

2. Over the whole expansion range, the approximated function values depend on its properties at a single point, the center of expansion. Therefore, empirical expansion constants depend on the selection of this center.

3. At the fixed expansion power, the calculation error depends on the argument and regularly increases with increasing distance from the expansion center.

Fourier series are free of these disadvantages for the following reasons:

1. The function being approximated f need not be analytical or even continuous. Integrability of f^2 over the expansion range is enough. This condition can be considered as fulfilled for ρ^2 because substances with ρ^2 greater than that for Os (506.3 g^2 cm^{-6}) are unknown so far.

2. Approximated values of the function depend on its properties over the whole expansion range and not at some fixed point. Therefore, empirical constants are determined by the reference selection and expansion power only.

3. Owing to the uniform convergence of Fourier series to the approximated function, the calculation error depends only randomly on the argument.

These facts evoke interest in the Fourier series approximation of physicochemical parameters of C,H,N,O-containing substances. In this work, we attempt to use Fourier series for the approximation of density. The trigonometric basis traditional for Fourier series was used. Expansion constants were determined on the same reference selections and by the same procedure[1,2] as previously: regression analysis, sequential inclusion of

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 22—24, January, 1994.

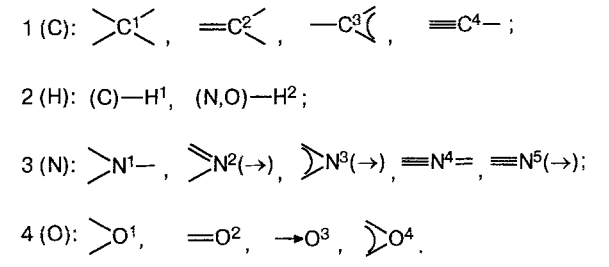
1066-5285/94/4301-0013 $12.50

variables, least-squares method. The same types of arguments were accepted as initial:[1]

1. For normalized compositions with enthalpy of formation* (NCE): $h = \mathrm{th}(\Delta H^0_f)$ and $f'_i = f_i/\Sigma f_i$, where f_i are stoichiometric coefficients of substances with the empirical formula $C_{f_1}H_{f_2}N_{f_3}O_{f_4}$.

2. For molecular formulas with enthalpy of formation (MFE): h and $x_i = \mathrm{th}[\lg(1 + f_i)]$.

3. For expanded molecular formulas (EMF): $y_k = \mathrm{th}[\lg(1 + q^j_i)]$, where q^j_i are coefficients at the jth-type of atoms of the i-th element. As previously,[1] for C, H, N, O (1st, 2nd, 3d, and 4th elements, respectively) 15 atomic types are specified:[1]



The index k at the argument y_k is determined as follows: for C $k = j$; for H $k = j + 4$; for N $k = j + 6$; for O $k = j + 11$.

* Here, as previously,[1] ΔH^0_f refers to 1 g of a substance.

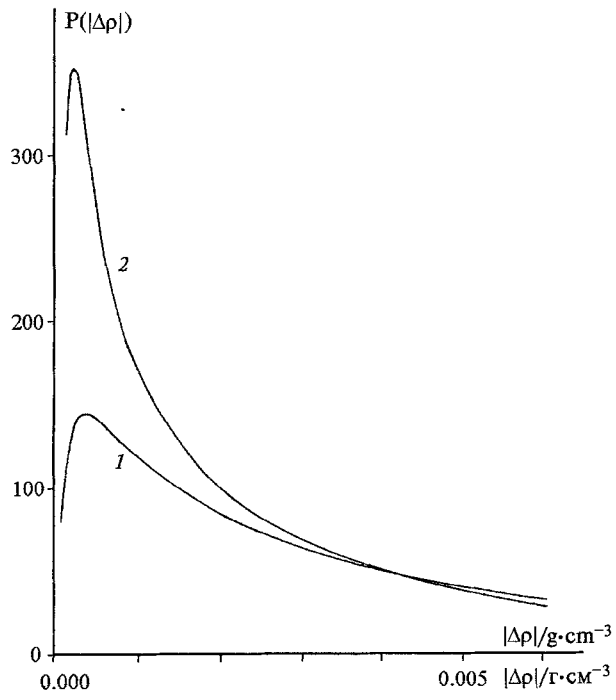


Fig. 1. Logarithmic normal distribution P(|Δρ|) in the reference selection in the approximation of ρ based on TEF by a Taylor series restricted by the 3d power (*1*) and by a trigonometric Fourier series restricted by the 3d harmonics (*2*).

Table 1. Numbers of non-zero expansion constants (n^T_k for Taylor series and n^F_k for Fourier series), correlation coefficients (r(%)), and mean absolute errors (Δρ/g cm^{-3}) and error dispersions (σ/g cm^{-3}) at the expansion of ρ to different (k) powers (harmonics)

Basis	k	n_k^T (n_k^F)	Distribution parameter	Taylor series		Fourier series	
				Reference	Control	Reference	Control
			r	80.6	70.9	90.5	82.8
	1	5(7)	|Δρ|	0.141	0.144	0.105	0.115
			σ	0.114	0.137	0.094	0.095
			r	90.8	85.7	92.5	88.1
NCE	2	13(26)	|Δρ|	0.101	0.105	0.087	0.103
			σ	0.084	0.091	0.072	0.083
			r	92.0	87.3	93.5	87.8
	3	24(62)	|Δρ|	0.091	0.106	0.070	0.104
			σ	0.070	0.084	0.073	0.075
			r	79.1	74.2	84.2	78.5
	1	6 (8)	|Δρ|	0.135	0.141	0.123	0.131
			σ	0.085	0.171	0.073	0.157
			r	92.9	91.4	95.0	92.6
MFE	2	17(39)	|Δρ|	0.084	0.090	0.072	0.085
			σ	0.063	0.078	0.055	0.063
			r	95.1	90.3	96.2	91.9
	3	33(79)	|Δρ|	0.067	0.093	0.055	0.082
			σ	0.056	0.062	0.050	0.065
			r	88.7	—	92.4	90.4
	1	15(27)	|Δρ|	0.107	—	0.101	0.124
			σ	0.112	—	0.078	0.111
			r	96.8	95.9	97.3	97.2
EMF	2	76(144)	|Δρ|	0.069	0.074	0.054	0.069
			σ	0.061	0.063	0.049	0.058
			r	98.3	98.0	99.2	98.2
	3	226(340)	|Δρ|	0.038	0.050	0.023	0.048
			σ	0.035	0.043	0.021	0.042

Arguments of Fourier trigonometric series are obtained from the initial arguments of the power series by multiplying the latter by π. The search for significant members of the series was performed up to the third harmonics, inclusive. The obtained formulas are not presented here, because each of them occupies several pages. Table 1 presents parameters of the normal distribution[3] and mean absolute errors determined for control and reference selections using new calculation formulas together with similar characteristics of the reference selection, which were recorded in the approximation of density by Taylor series restricted by the third power.[1]

The plots of the logarithmic normal distribution[3] of the absolute errors for two different approximation methods of ρ are presented in Fig. 1. The comparison of these plots clearly demonstrates the advantages of Fourier series for the approximation of density. Experimental and calculated values of density for some reference and control substances are given in Table 2.

Table 2. Experimental and calculated values of density for some reference (*) and control substances

Substance	ρ/g cm^{-3}			
	Exp.	SCE	EFE	TEF
Diamond*	3.515	2.900	3.511	3.514
Graphite*	2.265	2.878	3.267	2.262
Water*	1.000	1.055	0.994	1.006
Hydrazoic acid*	1.127	1.123	1.127	1.131
Nitroglycerin*	1.610	1.605	1.592	1.611
Carbamide*	1.335	0.982	1.050	1.528
Triethylamine*	0.730	0.736	0.764	0.739
Ethylcarbamide	1.042	1.064	1.026	1.066
Hexogen*	1.810	1.830	1.872	1.834
Octogen	1.840	1.833	1.835	1.848
Trotyl*	1.640	1.650	1.648	1.645
Hexanitrobenzene	2.000	1.884	2.029	1.991
Sorguyl	2.010	2.019	1.943	1.886
Benzene	0.879	1.448	1.149	1.061
Adamantane	1.070	0.835	1.426	0.881
Hydrocyanic acid*	0.688	1.402	0.861	0.695
Naphthalene	1.168	1.164	1.110	1.149
Aniline	1.022	1.022	1.010	1.026
Phenol	1.071	0.950	1.094	1.045
Toluene	0.867	1.210	1.284	1.054
Dimethylamine	0.680	0.711	0.599	0.690

Thus, the expediency of approximation of physicochemical parameters using Fourier series is illustrated using the density of C,H,N,O-containing substances as an example. It should be noted that besides traditional trigonometric basis, any other *infinite dimensional orthonormalized functional basis* can be used for this purpose. We believe that Haar and Rademacher—Walsh functions[4] are especially promising in this respect.

The authors are grateful to Mr. S. A. Telyakovskii for valuable consultations and very timely critical comments about the methods used.

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Received September 15, 1993