

CHEMICAL THERMODYNAMICS  
AND THERMOCHEMISTRY

Relationship between Standard Enthalpies/Entropies  
of Formation and Topological Structural Characteristics  
for Saturated Hydrocarbons

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**Abstract**—QSPR models are proposed that satisfactorily describe the relationships between standard enthalpies/entropies of formation and topological indices in the form of Wiener and Randić indices and the sum of the squares of the eigenvalues from the adjacency matrix of a molecular graph. The models can be recommended for use in scientific and engineering calculations of thermodynamic functions.

**Keywords:** QSPR models, standard enthalpy and entropy, Wiener index, Randić index, topological parameters, eigenvalues, topological matrix

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INTRODUCTION

Calculating the thermodynamic characteristics of hydrocarbons is important to science and technology, particularly for predicting the direction of chemical transformations and the equilibrium dynamics of different technological processes. The existing ways of assessing standard enthalpies and heats of formation require quality and precision of an experiment. Relationships exist between these thermodynamic parameters and the topological characteristics of the structure of saturated hydrocarbons.

Methods based on a topological approach are now widely used to calculate thermodynamic characteristics, in which a relationship between structural chemical characteristics of a molecule being as parameters of molecular graphs and physicochemical properties is found. This approach has been widely used in recent years to predict the properties of organic compounds, and the corresponding empirical models are known as QSPR (Quantitative-Structure Properties Relationship) models. Assessing thermodynamic parameters, particularly standard enthalpies/entropies of formation for saturated hydrocarbons, is important in calculations for technological processes (e.g., alkylation, the pyrolysis of gases, and isomerization) and requires calculation of standard thermodynamic functions to estimate the direction of chemical reactions and equilibrium constants. Morovitz and Randić indices are used to estimate these characteristics [1].

Uryadov proposed using the so-called topological “moment of inertia” for a molecule to calculate heats of solvation [2]:

$$J_W = MW^{2/3},$$

where  $M$  is the molar weight and  $W$  is the Wiener index. Estimating thermodynamic parameters from this index gives the basis for finding nonlinear power QSPR models. The accuracy of calculations of standard enthalpies/entropies of formation and equilibrium constants has a considerable error despite the many works in this field, and there is a notable discrepancy between calculations and experimental results.

ANALYTICAL APPROACH

The aim of this work is to find a QSPR model that allows satisfactory calculations of standard enthalpies and entropies for saturated hydrocarbons. To solve this problem, we consider the standard enthalpies and entropies of formation of molecules as a nonlinear three-parameter function of their topological parameters. These parameters are the sum of the squares of the eigenvalues in a molecular graph (MG). This sum indirectly reflects the energy spectrum of the electronic states of molecules [3]:

$$L = \sum_{i=1}^n \lambda_i^2,$$

**Table 1.** Topological indices for saturated hydrocarbons

No.	Compound	$\rho$	$L$	$W$	$\gamma$	$\Theta$
1	Methane	0.000	0	0	0.00	0.00
2	Ethane	1.000	2	1	1.00	1.00
3	Propane	1.414	4	4	2.83	5.66
4	Butane	1.914	6	10	5.22	19.14
5	Pentane	2.414	8	20	8.29	48.28
6	Hexane	2.914	10	35	12.01	101.99
7	Heptane	3.414	12	56	16.40	191.18
8	Octane	3.914	14	84	21.46	328.78
9	Nonane	4.414	16	120	27.19	529.68
10	Decane	4.914	18	165	33.58	810.81
11	2-Methylpropane	1.732	6	9	5.20	15.59
12	2-Methylbutane	2.270	8	18	7.93	40.86
13	2-Methylpentane	2.770	10	32	11.55	88.64
14	3-Methylpentane	2.808	10	31	11.04	87.05
15	2,2-Dimethylbutane	2.561	10	28	10.93	71.70
16	2,3-Dimethylbutane	2.643	10	29	10.97	76.64
17	2-Methylhexane	3.270	12	52	15.90	170.04
18	3-Methylhexane	3.308	12	50	15.11	165.40
19	3-Ethylpentane	3.346	12	48	14.35	160.61
20	2,2-Dimethylpentane	3.061	12	46	15.03	140.79
21	2,3-Dimethylpentane	3.181	12	46	14.46	146.31
22	2,4-Dimethylpentane	3.126	12	48	15.36	150.04
23	3,3-Dimethylpentane	3.121	12	44	14.10	137.34
24	2,2,3-Trimethylbutane	2.943	12	42	14.27	123.62
25	2-Methylheptane	3.770	14	79	20.95	297.83
26	3-Methylheptane	3.808	14	76	19.96	289.41
27	4-Methylheptane	3.808	14	75	19.70	285.60
28	3-Ethylhexane	3.846	14	72	18.72	276.92
29	2,2-Dimethylhexane	3.561	14	71	19.94	252.81
30	2,3-Dimethylhexane	3.681	14	70	19.02	257.65
31	2,4-Dimethylhexane	3.664	14	71	19.38	260.14
32	2,5-Dimethylhexane	3.626	14	74	20.41	268.32
33	3,3-Dimethylhexane	3.621	14	67	18.50	242.63
34	3,4-Dimethylhexane	3.719	14	68	18.29	252.87
35	2-Methyl-3-ethylpentane	3.719	14	67	18.02	249.16
36	3-Methyl-3-ethylpentane	3.682	14	64	17.38	235.65
37	2,2,3-Trimethylpentane	3.481	14	63	18.10	219.33
38	2,3,3-Trimethylpentane	3.504	14	62	17.69	217.25
39	2,3,4-Trimethylpentane	3.553	14	65	18.29	230.97
40	2-Methyloctane	4.270	16	114	26.70	486.79
41	3-Methyloctane	4.308	16	110	25.53	473.89
42	4-Methyloctane	4.308	16	108	25.07	465.27
43	3-Ethylheptane	4.346	16	104	23.93	451.99
44	4-Ethylheptane	4.346	16	102	23.47	443.30
45	2,2-Dimethylheptane	4.061	16	104	25.61	422.31

**Table 1.** (Contd.)

No.	Compound	$\rho$	$L$	$W$	$\gamma$	$\Theta$
46	2,3-Dimethylheptane	4.181	16	102	24.40	426.44
47	4,4-Dimethylheptane	4.121	16	96	23.29	395.65
48	2-Methyl-3-ethylhexane	4.219	16	96	22.76	405.00
49	3-Methyl-3-ethylhexane	4.182	16	92	22.00	384.74
50	2-Methylnonane	4.770	18	158	33.12	753.67
51	3-Methylnonane	4.808	18	153	31.82	735.63
52	4-Methylnonane	4.808	18	150	31.20	721.21
53	5-Methylnonane	4.808	18	149	30.99	716.40
54	3-Ethyl-octane	4.846	18	145	29.92	702.68
55	2,2-Dimethyloctane	4.561	18	146	32.01	665.86
56	2,3-Dimethyloctane	4.681	18	143	30.55	669.35
57	3,4-Dimethyloctane	4.719	18	137	29.03	646.47
58	4-Propylheptane	4.846	18	138	28.48	668.76
59	2,2,3-Trimethylheptane	4.481	18	130	29.01	582.58

where  $L$  is the sum of the squares of the eigenvalues in the MG adjacency matrix, and  $\lambda_i$  are MG the eigenvalues.

The Wiener index is used to characterize the structures of hydrocarbons; it reflects the degree of bonding of carbon atoms in organic molecules, is determined through the half-sum of topological distances between all  $n$  atoms in MG, and is calculated using the formula

$$W = \frac{1}{2} \sum_{i=1}^n \sum_{\substack{j=1 \\ j \neq i}}^n d_{ij} + \sum_{i=1}^n d_{ii},$$

where  $d_{ij}$  are elements of the distances matrix for  $i$  and  $j$  atoms.

The Randić index, which characterizes the branching of a carbon skeleton and differs for hydrocarbon isomers (molecular connectivity index), is used to

**Table 2.** Coefficients from expressions (1) and (2) for calculating the standard enthalpies (kJ/mol) and entropies (J/(mol K)) of alkanes

$a_i$	(1)	(2)
$a_0$	-75	-80.6
$a_1$	-4.8	-78.091
$a_2$	-17.8	-4.0247
$a_3$	29.84	-0.035
$a_4$	0.035	111.575
$a_5$		-52.296
$a_6$		7.595

Coefficients were found via multifactorial regression analysis.

describe the branching of molecules [4]. It is calculated using the formula

$$\rho = \sum_{\substack{\text{over all} \\ \text{edges}}} \frac{1}{\sqrt{v_i v_j}},$$

where  $v_i$  is the number of edges in a graph that extend from the  $i$ th vertex and  $v_j$  is the number of edges of the graph that extend from the  $j$ th vertex.

To avoid the coincidence of indices for individual isomers, we propose a generalized index with the properties of Wiener and Randić indices. The index is the ratio of two indices:

$$\gamma(W, \rho) = \frac{W}{\rho} = \left[ \frac{1}{2} \sum_{i=1}^n \sum_{\substack{j=1 \\ j \neq i}}^n d_{ij} + \sum_{i=1}^n d_{ii} \right] \left[ \sum_{\substack{\text{over all} \\ \text{edges}}} \sqrt{v_i v_j} \right].$$

Unlike the Wiener index, the one proposed will differ for branched isomers (Table 1).

To consider the joint influence of the extent and branching of molecules, we propose an index equal to the product of Wiener and Randić indices:

$$\Theta = W\rho = \left( \frac{1}{2} \sum_{i=1}^n \sum_{\substack{j=1 \\ j \neq i}}^n d_{ij} + \sum_{i=1}^n d_{ii} \right) \left[ \sum_{\substack{\text{over all} \\ \text{edges}}} \sqrt{v_i v_j} \right].$$

In accordance with the QSPR approach, let us seek a nonlinear three-factor dependence that combines the thermodynamic properties and topological parameters of molecules (the so-called molecular descriptors) in the form of a multiparameter model:

$$\Delta H_{298}^0 = \Phi(\gamma, L, W, \Theta),$$

$$\Delta S_{298}^0 = \Phi(\gamma, L, W, \rho, \Theta),$$

**Table 3.** Comparison of experimental (I) and calculated (II) values of standard enthalpies ( $-\Delta H_{298}^0$ , in kJ/mol) of alkanes ( $\Delta$  is absolute error, in kJ/mol;  $s$  is relative error, %)

Compound	I	II	$\Delta$	$s$	Compound	I	II	$\Delta$	$s$
Methane	74.50	75.00	0.50	0.67	2,4-Dimethylhexane	219.20	217.62	-1.58	0.72
Ethane	83.80	85.53	1.73	2.06	2,5-Dimethylhexane	222.50	220.31	-2.19	0.99
Propane	104.70	106.41	1.71	1.64	3,3-Dimethylhexane	220.00	218.40	-1.60	0.73
Butane	126.80	126.39	-0.41	0.32	3,4-Dimethylhexane	212.70	214.42	1.72	0.81
Pentane	146.80	146.82	0.02	0.01	2-Methyl-3-ethylpentane	212.80	214.19	1.39	0.65
Hexane	166.90	167.67	0.77	0.46	3-Methyl-3-ethylpentane	214.90	215.07	0.17	0.08
Heptane	187.80	188.74	0.94	0.50	2,2,3-Trimethylpentane	220.00	223.43	3.43	1.56
Octane	208.80	209.76	0.96	0.46	2,3,3-Trimethylpentane	218.50	222.14	3.64	1.67
Nonane	229.03	230.32	1.29	0.56	2,3,4-Trimethylpentane	217.30	220.83	3.53	1.63
Decane	249.50	249.94	0.44	0.18	2-Methyloctane	235.90	236.18	0.28	0.12
2-Methylpropane	135.00	131.65	-3.35	2.48	3-Methyloctane	233.70	233.13	-0.57	0.24
2-Methylbutane	153.70	151.25	-2.45	1.59	4-Methyloctane	235.20	232.62	-2.58	1.10
2-Methylpentane	174.60	172.30	-2.30	1.32	3-Ethylheptane	231.50	229.84	-1.66	0.72
3-Methylpentane	172.00	170.70	-1.30	0.76	4-Ethylheptane	231.80	229.41	-2.39	1.03
2,2-Dimethylbutane	184.00	179.01	-4.99	2.71	2,2-Dimethylheptane	246.10	244.08	-2.02	0.82
2,3-Dimethylbutane	175.90	176.24	0.34	0.19	2,3-Dimethylheptane	235.90	237.38	1.48	0.63
2-Methylhexane	194.60	193.66	-0.94	0.48	4,4-Dimethylheptane	241.20	238.70	-2.50	1.04
3-Methylhexane	191.30	191.56	0.26	0.14	2-Methyl-3-ethylhexane	234.60	234.08	-0.52	0.22
3-Ethylpentane	189.66	189.63	-0.03	0.01	3-Methyl-3-ethylhexane	231.30	234.90	3.60	1.56
2,2-Dimethylpentane	205.80	200.58	-5.22	2.54	2-Methylnonane	256.50	256.46	-0.04	0.02
2,3-Dimethylpentane	194.10	195.66	1.56	0.80	3-Methylnonane	254.70	253.02	-1.68	0.66
2,4-Dimethylpentane	201.70	198.49	-3.21	1.59	4-Methylnonane	253.97	252.31	-1.66	0.66
3,3-Dimethylpentane	204.40	197.50	-6.90	3.38	5-Methylnonane	253.97	252.07	-1.90	0.75
2,2,3-Trimethylbutane	204.81	204.12	-0.69	0.34	3-Ethylloctane	251.08	249.14	-1.94	0.77
2-Methylheptane	215.40	215.08	-0.32	0.15	2,2-Dimethyloctane	267.00	265.19	-1.81	0.68
3-Methylheptane	212.50	212.49	-0.01	0.01	2,3-Dimethyloctane	256.60	257.59	0.99	0.39
4-Methylheptane	212.00	212.23	0.23	0.11	3,4-Dimethyloctane	253.38	254.12	0.74	0.29
3-Ethylhexane	210.70	209.87	-0.83	0.39	4-Propylheptane	251.08	247.73	-3.35	1.33
2,2-Dimethylhexane	224.60	222.38	-2.22	0.99	2,2,3-Trimethylheptane	261.83	265.03	3.20	1.22
2,3-Dimethylhexane	213.80	216.59	2.79	1.30					

where  $\Phi$  is a nonlinear function. We present the standard enthalpy/entropy of formation as a semiempirical function that depends on chemical nature and interaction energy of atoms, the order of mutual arrangement of atoms, and the branching of a molecular structure. This relationship can be presented using the expressions

$$\Delta H_{298}^0 = a_0 + a_1 \frac{W}{\rho} + a_2 L + a_3 W^{\frac{1}{3}} + a_4 W \rho, \quad (1)$$

$$\Delta S_{298}^0 = a_0 + a_1 L + a_2 \frac{W}{\rho} + a_3 W \rho + a_4 W^{\frac{1}{3}} + a_5 \rho^{\frac{1}{3}} + a_6 \rho^2, \quad (2)$$

where  $W$  is the Wiener index,  $L$  is the sum of the squares of the eigenvalues in the MG adjacency matrix,  $\rho$  is the Randić index, and  $a_n$  denotes the coefficients of the model. In analogy with the Uryadov index, the Wiener index is raised in power [2]. Calculations show that a 1/3 exponent ensures the best quality.

**Table 4.** Comparison of experimental (I) and calculated (II) values of standard entropies ( $-\Delta S_{298}^{\circ}$ , in J/(mol K)) of alkanes ( $\Delta$  is absolute error, in J/(mol K);  $s$  is relative error, %)

Compound	I	II	$\Delta$	$s$	Compound	I	II	$\Delta$	$s$
Methane	80.49	80.60	0.11	-0.13	2,4-Dimethylhexane	773.75	777.55	3.80	-0.49
Ethane	174.07	173.97	-0.10	-0.06	2,5-Dimethylhexane	779.45	777.39	-2.06	-0.26
Propane	269.65	270.94	1.29	-0.48	3,3-Dimethylhexane	783.81	784.30	0.49	-0.06
Butane	371.95	367.56	-4.38	-1.18	3,4-Dimethylhexane	770.39	776.83	6.44	-0.84
Pentane	463.51	463.38	-0.13	-0.03	2-Methyl-3-ethylpentane	778.11	777.86	-0.25	-0.03
Hexane	560.44	558.63	-1.81	-0.32	3-Methyl-3-ethylpentane	797.56	783.50	-14.06	-1.76
Heptane	657.37	653.70	-3.67	-0.56	2,2,3-Trimethylpentane	798.23	797.57	-0.66	-0.08
Octane	754.96	749.08	-5.88	-0.78	2,3,3-Trimethylpentane	795.21	797.21	1.99	-0.25
Nonane	851.35	845.33	-6.02	-0.71	2,3,4-Trimethylpentane	793.53	790.80	-2.73	-0.34
Decane	948.48	943.07	-5.42	-0.57	2-Methyloctane	859.27	859.76	0.49	-0.06
2-Methylpropane	381.00	378.53	-2.47	-0.65	3-Methyloctane	853.57	858.80	5.24	-0.61
2-Methylbutane	468.88	-475.84	6.97	-1.49	4-Methyloctane	855.25	859.90	4.65	-0.54
2-Methylpentane	568.49	572.02	3.53	-0.62	3-Ethylheptane	860.61	859.24	-1.37	-0.16
3-Methylpentane	566.14	572.36	6.22	-1.10	4-Ethylheptane	862.96	860.48	-2.48	-0.29
2,2-Dimethylbutane	590.96	590.95	-0.01	0.00	2,2-Dimethylheptane	886.10	881.29	-4.81	-0.54
2,3-Dimethylbutane	583.24	584.80	1.56	-0.27	2,3-Dimethylheptane	865.64	873.24	7.59	-0.88
2-Methylhexane	665.08	667.55	2.47	-0.37	4,4-Dimethylheptane	891.13	881.50	-9.63	-1.08
3-Methylhexane	659.38	668.03	8.65	-1.31	2-Methyl-3-ethylhexane	871.01	874.14	3.13	-0.36
3-Ethylpentane	672.99	668.70	-4.30	-0.64	3-Methyl-3-ethylhexane	873.36	879.69	6.33	-0.73
2,2-Dimethylpentane	692.92	688.07	-4.84	-0.70	2-Methylnonane	955.53	957.75	2.22	-0.23
2,3-Dimethylpentane	670.45	681.27	10.82	-1.61	3-Methylnonane	951.84	955.78	3.94	-0.41
2,4-Dimethylpentane	688.22	681.46	-6.76	-0.98	4-Methylnonane	953.11	956.69	3.58	-0.38
3,3-Dimethylpentane	702.31	687.73	-14.58	-2.08	5-Methylnonane	958.85	957.01	-1.84	-0.19
2,2,3-Trimethylbutane	701.23	700.72	-0.51	-0.07	3-Ethyloctane	958.85	955.02	-3.83	-0.40
2-Methylheptane	762.68	763.24	0.56	-0.07	2,2-Dimethyloctane	982.69	979.43	-3.26	-0.33
3-Methylheptane	756.31	763.16	6.86	-0.91	2,3-Dimethyloctane	962.24	970.05	7.81	-0.81
4-Methylheptane	764.69	764.05	-0.64	-0.08	3,4-Dimethyloctane	963.21	968.95	5.74	-0.60
3-Ethylhexane	764.02	764.25	0.23	-0.03	4-Propylheptane	967.97	957.62	-10.35	-1.07
2,2-Dimethylhexane	789.17	784.46	-4.72	-0.60	2,2,3-Trimethylheptane	988.87	991.69	2.82	-0.29
2,3-Dimethylhexane	769.39	777.38	7.99	-1.04					

Fifty-nine saturated hydrocarbons with known standard entropies/enthalpies of formation were chosen as our objects of study. The experimental thermodynamic functions were selected from the reference data in [5]. Table 1 shows the corresponding indices, calculated according to the specially developed program in [6]. Dependence coefficients (1) and (2) were calculated using a multifactorial regression analysis algorithm, the standard procedure of the least squares method. Table 2 shows the corresponding coefficients of dependences (1) and (2).

The quality of dependences (1) and (2) was assessed from their statistical characteristics—concor-

dance, multiple correlation, and standard error. Table 3 compares the reference and calculated values of a molar heat capacity under constant pressure.

Tables 3 and 4 indicate the average relative error does not exceed 1 and 0.57% for the standard enthalpy and entropy of formation, respectively. The quality of the models relative to experiments was estimated using the statistical characteristics given in Table 5.

To estimate the statistical reliability of the relationship, we use the correlative correction

$$S_r = \frac{1 - r^2}{\sqrt{n - 1}},$$

**Table 5.** Statistical parameters of model adequacy ( $s$  is standard error)

Value	$r$	$s$	$S_r$	$ r/S_r $
$\Delta H_{298}^\circ$	0.9986	2.29	0.0003	3330
$\Delta S_{298}^\circ$	0.9996	7.46	0.0001	9996

where  $S_r$  is the correlation correction,  $r$  is the coefficient of multiple correlation, and  $n$  is the number of investigated compounds.

The relationship cannot be considered random if

$$|r/S_r| \geq 3.$$

### CONCLUSIONS

The proposed QSPR models satisfactorily describe the relationships between standard enthalpies/entropies of formation and topological indices, which include the Wiener and Randić indices, along with the sum of the squares of the eigenvalues in an MG adjacency matrix. In comparison to the single-factor topological models proposed earlier, our models provide greater accuracy in assessing thermodynamic func-

tions. They may therefore be used in assessing chemical equilibria in the reactions of aliphatic hydrocarbons.

Our models can be recommended for scientific and engineering calculations of thermodynamic functions.

### REFERENCES

1. M. I. Stankevich, I. V. Stankevich, and N. S. Zefirov, *Russ. Chem. Rev.* **57**, 191 (1988).
2. V. G. Uryadov, Extended Abstract of Doctoral (Chem.) Dissertation (Tver. State Univ., Tver, 2011).
3. M. Yu. Dolomatov, N. A. Shamova, E. F. Trapeznikova, et al., *Khim. Tekhnol.*, No. 1, 45 (2016).
4. *Chemical Applications of Topology and Graph Theory*, Ed. by R. King, *Studies in Physical and Theoretical Chemistry* (Elsevier, Amsterdam 1983; Mir, Moscow, 1987, p. 560).
5. V. M. Tatevskii, *Physicochemical Properties of Individual Hydrocarbons* (Gostoptekhizdat, Moscow, 1960) [in Russian].
6. N. A. Shamova, M. Yu. Dolomatov, E. F. Trapeznikova, T. M. Aubekero, and A. V. Sten'kin, RF Patent No. 2015613203 (2015).

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