Int. J. Chem. Sci.: 8(1), 2010, 9-21

ESTIMATION OF STANDARD GIBB'S FREE ENERGY FORMATION OF ALKANES IN GASEOUS STATE BY ELECTRONIC, SIZE AND STRUCTURAL PARAMETERS

P. S. VERMA[a], B. L. GORSI*, G. S. KALWANIA and LOVEL P. SINGH

Department of Chemistry, S. K.Govt. P. G. College, SIKAR (Raj.) INDIA
[a]Department of Chemistry, University of Rajasthan, JAIPUR (Raj.) INDIA

ABSTRACT

Standard Gibb's free energy formation (ΔG_f^0) of alkanes in gaseous state at 298.15 K is estimated by a quantitative correlationships with Kier's molecular connectivity index ($^1X^v$), Vander waal's volume (Vw), electrotopological state index (E) and refractotopological state index (R). The regression analysis reveals a significant linear correlationships of standard free energy of formation ($\Delta G_f^{\ 0}$) with these parameters.

Key words: Kier's molecular connectivity index ($^1X^v$); Vander waal's volume (Vw); Electrotopological state index (E); Refractotopological state index (R); Gibbs free energy of formation ($\Delta G_f^{\ 0}$).

INTRODUCTION

Thermodynamics is a phenomenological theory of matter. As such it draws its concepts directly from experiments[1]. Thermodynamics, which makes up a logical subject of great elegance, is a powerful method for studying chemical phenomena and can be developed quite independently of the atomic and molecular theory. Experimental measurements of some thermodynamic parameters involve experimental difficulties and they are not always feasible, and the corresponding methods posses real drawbacks[2,3].

Consequently, it is necessary to resort to a theoretical calculation of these parameters. This option is accessible because an important, fruitful and current field of research in contemporary chemistry is the model and prediction of physical properties of molecules[4,5].

This kind of study is based on the paradigm that physical properties of chemistry and biological activities are dependent on molecular structure. As a consequence, one of the

---

*Author for correspondence; E-mail: blgorsi.2007@yahoo.com

most important point in such research is the selection of adequate descriptors containing the information stored in the molecular structure[6].

Literature reveals that estimation of Gibb's free energy for a representative set of acyclic and aromatic compounds by mean of the semi empirical all -valence MNDO, AMI and PM3 molecular orbital methods[7], QSPR evaluation[8], inclusion of nearest neighbor interaction and additive concept group contribution of Benson[9] and Domalki[10] of amino acids[11], proteins[12,13] have been cited . This gives an impetus to correlate standard Gibb's free energy of formation with size, structure and electronic parameters of alkane molecules in gaseous state at 298.15 K. Previously, We have established a significant quantitative correlationship of diamagnetic susceptibilities with structural and size parameters, i.e., first order valence connectivity ($^1X^v$) and Vander waal's volume (Vw) of many organic compounds[14,15].

This paper deals with the estimation of standard Gibb's free energy of formation of alkanes by quantitative correlationship with first order valence connectivity ($^1X^v$), Vander waal's volume (Vw), electrotopological state index (E) and refractotopological state index (R).

Calculation of Kier's[16] molecular connectivity index ($^1X^v$)

It signifies the degree of branching or connectivity in a molecule, which is derived from the numerical extent of branching or connectivity in the molecular skeleton and was proposed by Randic[17]. It is calculated by hydrogen suppressed graph of the molecule and the first order valence connectivity ($^1X^v$) is given by eq. (1).

$$^1X^v = \sum (\delta i^v . \delta j^v)^{-1/2} \qquad \ldots(1)$$

Here, the sum is the overall connections or edges in hydrogen suppressed graph, δi^v and δj^v are numbers assigned to each atom reflecting the numbers of atoms adjacent or connected to atom (i) and (j), which are formally bonded.

The atomic connectivity term δi^v is defined as:

$$\delta i^v = \frac{Zi^v - hi}{z - Zi^v - 1} \qquad \ldots(2)$$

Where Zi^v = Number of valence electron of atom (i),

Z = Atomic number of atom (i) and

hi = Number of hydrogen atoms attached to atom (i)

Table 1 shows the atom connectivity (δi^v) values in different groups as calculated by eq.(2)

Table 1: Atom connectivity (δi^v) values in different groups

Groups	δi^v	Groups	δi^v
$-CH_3$	01	$=CH_2$	02
$\equiv CH$	03	- OH	05
$-NH_2$	03	O	06
-NH -	04	C = O	06
$- C \equiv N$	05	Furan O	06
- C = NH	04	O =N O	06
N or Pyridine N	05	H_2O	04
NH_3	02	F	(-) 20
NH_4	01	Cl	0.690
$> N^+ <$	06	Br	0.254
$= \overset{+}{N}H_2$	03	I	0.085

Calculation of Vander waal's volume (Vw)

It is calculated by assuming spherical shapes for all atoms in accordance with bonding[18]. Since Vander waal's radii are greater than covalent radii, the necessary corrections for overlapping of atomic orbitals and for branching in hydrocarbon chain are also taken from literature[19].

$$V_w = \sum n_i \; a_i. + [\sum \text{corrections for bonds} + \sum \text{corrections for no. of branching}] \quad \ldots(3)$$

Where, V_W = Vander waal's volume of the molecules,

ni = No. of atoms and

a_i = Vander's volume of atom i

Table 2 shows the Vander waal's volume of different atoms and Table 3 shows the correction values of Vander waal's volume for sphere overlapping due to covalent bonding and for branching.

Table 2: Vander waal's volume of different atoms

Atom	Sphere vol. 10^2 Å^3	Atom	Sphere vol. 10^2 Å^3	Atom	Sphere vol. 10^2 Å^3
C	0.206	H	0.056	N	0.141
O	0.115	S	0.244	F	0.115
Aliphatic Cl	0.206	Aromatic Cl	0.244	Aliphatic Br	0.244
Aromatic Br	0.287	Aliphatic I	0.335	Aromatic I	0.388

Table 3: Correction values of Vander waal's volume for sphere overlapping due to covalent bonding and for branching

Bond	Correction value 10^2 Å^3	Bond	Correction value 10^2 Å^3	Bond	Correction value 10^2 Å^3
C-C	-0.078	C-H	-0.043	C-N	-0.065
C-O	-0.056	C-S	-0.066	C-F	-0.056
Aliph. C-Cl	--0.058	Arom. C-Cl	-0.066	Aliph. C-Br	-0.060
Arom. C-Br	-0.068	Aliph. C-I	-0.063	Arom. C-I	-0.072
C-B	-0.113	H-H	-0.030	N-H	-0.038
N-N	-0.050	N-O	-0.042	N-S	-0.061
O-H	-0.034	O-B	-0.079	S-H	-0.040
S-S	-0.062	S-F	-0.052	C=C	-0.094
C=N	-0.072	C=O	-0.068	C=S	-0.081
N=N	-0.061	N=O	-0.053	S=O	-0.057
C≡C	-0.0101	C≡N	-0.079	Arom. C=C	-0.086
Branching for saturated bond except bonding with H	-0.050				

Calculation of electrotopological state index (E)

This index signifies the electronic effect of each atom on the other atom in the molecule as modified by molecular topology[20-22]. Each atom has an assigned intrinsic state valence I_i calculated as follows-

$$I_i = [(2/N)^2 \delta^v + 1]/\delta \qquad \ldots(4)$$

Where, N = Principal quantum number of the atom i,

δ^v = Number of valence electrons in the skeleton ($Z_v - h_i$), and

δ = Number of σ electrons in the skeleton ($\sigma - h$).

For a skeleton, Z_v = Total number of electrons on the atom,

σ = Number of electrons in the σ orbitals, and

h = Number of bonded hydrogen atom.

E-state for an atom i in molecule (S_i) is given by

$$S_i = I_i + \sum \Delta I_j \qquad \ldots(5)$$

ΔIj = quantifies the perturbation effect on the intrinsic atom value. This perturbation is assumed to be a function of the difference in the intrinsic values I_i and I_j -

$$\Delta I_j = \sum (I_i - I_j) / r_{ij}^2 \qquad \ldots(6)$$

Where, r_{ij} is the topological distance in the shortest path between ith and jth atoms.

The difference in intrinsic values ΔI_j for a pair of skeletal atoms encode both electronic and topological attributes that arise from electronegativity differences and skeletal connectivity. Therefore, the total of sum of the differences in intrinsic values, $\sum \Delta I_i$, due to perturbation for a whole molecule is zero, i.e. $\sum \Delta I_j = 0$ so,

$$S_i = I_i \qquad \ldots(7)$$

Therefore, E- state for a whole molecule = $\sum n_i S_i$ or $\sum n_i I_i$ …(8)

The intrinsic state valence I_i of atoms in some groups are listed in Table 4.

Table 4: Intrinsic state valence I_i of atoms in some groups

Group	I_i	Group	I_i	Group	I_i
> C <	1.250	>CH-	1.333	$-CH_2-$	1.5
> C =	1.667	-S-	1.833	$-CH_3$, = CH-, >N -	2.00
-I	2.12	≡ C-,-NH-	2.5	-Br	2.75
$= CH_2$, = N-	3.00	-SH	3.222	-O-	3.500
= CH, $-NH_2$	4.00	-Cl	4.111	≡ N,-OH	6.00
= O	7.00	-F	8.000		

Calculation of refractotopological state index (R)

It is developed from the chemical graph theory and the partition of the molar refractivity defined by Ghose and Crippen[23]. This index is based on the influence of dispersive forces of each atom on the other atom in the molecules modified by molecular topology.

The evaluation of the individual atomic refractivity value (Calculated by Ghose and Crippen[23] in Table 5) is based on the idea that the sum of the atomic values (α_i) being related to the molecular value of the molar refractivity.

$$R\ (\text{molecule})_{\text{calc}} = \sum n_i\ \alpha_i \qquad \ldots(9)$$

Where, n_i = No. of atoms; and

α_i = Atomic refractivity value

Table 5: Atomic refractivity values (as calculated by Ghose and Crippen) used in the analysis

Atom type	Atomic refractivity	Atom type	Atomic refractivity	Atom type	Atomic refractivity
C (sp^3)	2.816	C (sp^2)	3.828	C (sp)	3.897
C (Ar)	3.509	C=X	3.089	H	0.916
-O-	1.635	=O	1.796	O=N	2.141

Cont…

Atom type	Atomic refractivity	Atom type	Atomic refractivity	Atom type	Atomic refractivity
N (sp^3)	3.010	N (sp^2),N (sp)	3.201	N (Ar)	2.766
NO_2	3.505	Ar-N=X	3.810	F	1.063
Cl	5.611	Br	8.678	I	13.874
S (sp^3)	7.319	S (sp^2)	9.168	R-SO-R	6.076

RESULTS AND DISCUSSION

The molecular connectivity ($^1X^v$), Vander waal's volume (Vw), elctrotopological state index (E) and refractotopological state index (R) of some alkanes have been calculated as described above and are listed in Tables 6 and 7.

The experimental values of standard Gibb's free energy ((ΔG_f^0) of formation of alkanes in gaseous state are taken from literature[24-29]. The standard Gibb's free energy ((ΔG_f^0) are taken in kilocalories per mole at atmospheric pressure at 298.15 K. The correlation of ((ΔG_f^0) with first order valence connectivity ($^1X^v$), Vander waal's volume (Vw), electrotopological state index (E) and refractotopological state index (R) have been given by eq.(10),(11),(12) and (13), respectively.

$$\Delta G_f^0 = 4.022 (\pm 0.064)\ ^1X^v - 11.553 \qquad \ldots(10)$$

N = 44, r = 0.995, s = 0. 806, F (1, 42) = 3894.07

$$\Delta G_f^0 = 12.919 (\pm 0.249)\ Vw - 12.936 \qquad \ldots(11)$$

N = 43, r = 0.992, s = 0.918, F (1, 41) = 2694.913

$$\Delta G_f^0 = 1.370 (\pm 0.028)\ E - 14.736 \qquad \ldots(12)$$

N = 44, r = 0.991, s = 0.983, F (1, 42) = 2324.154

$$\Delta G_f^0 = 0.442 (\pm 0.008)\ R - 13.645 \qquad \ldots(13)$$

N = 46, r = 0.993, s = 0.887, F (1, 44) = 3230.126

In regression analysis, the statistical parameters are as:

N = Number of data points,

r = Correlation coefficient,

s = Standard deviation and

F = ratio between the variance of calculated and observed data

In the equation (10), (11), (12) and (13), the F values are significant at 99% level [F^1_{44} (0.01) = 7.31] and are accounting for 99%, 98.4%, 98.2% & 98.6% variance ($r^2 = 0.99$, 0.984, 0.982 & 0.986), respectively. High correlation coefficient ($r \approx 1.0$), low value of standard deviation ($s < 1.0$) and high values of F in all these equations show high level of significance.

Table 6: Experimental and theoretical calculated values of ΔG_f^0 by $^1X^v$ and V_w parameters in alkanes

Name of compound	$^1X^v$	V_w	ΔG_f^0		
			exp. value	Calc. Eq. 10	Calc. Eq. 11
Methane	0.000	0.258	-12.150	-11.150	*
Ethane	1.000	0.412	-7.840	-7.530	-7.613
Propane	1.414	0.566	-5.630	-5.860	-5.623
n-Butane	1.914	0.720	-4.100	-3.850	-3.634
2-Methyl propane	1.731	0.670	-4.990	-4.920	-4.280
n-Pantane	2.414	0.874	-2.000	-1.845	-1.644
2-Methyl butane	2.269	0.824	-3.540	-2.428	-2.290
n-Hexane	2.914	1.028	-0.060	0.166	0.345
2-Methyl pentane	2.769	0.978	-1.200	-0.417	-0.301
3-Methyl pentane	2.807	0.978	-0.510	-0.265	-0.301
2,2-Dimethyl butane	2.560	0.928	-2.300	-1.258	-0.947
2,3-Dimethyl butane	2.641	0.928	-0.980	-0.936	-0.947
Heptane	3.414	1.182	1.910	2.176	2.335
2-Meyhyl hexane	3.269	1.132	0.770	1.593	1.689
3-Mehtyl hexane	3.307	1.132	1.100	1.746	1.689
2,2-Dimethyl pentane	3.061	1.082	0.020	0.753	1.043
2,3-Dimethyl pentane	3.179	1.082	0.160	1.231	1.043
2,4-Dimethyl pentane	3.124	1.082	0.740	1.010	1.043

Cont…

Name of compound	$^1X^v$	V_w	ΔG_f^0		
			exp. value	Calc. Eq. 10	Calc. Eq. 11
2,2,3-Trimethyl butane	2.942	1.032	1.020	0.278	0.397
Octane	3.914	1.336	3.920	4.187	4.325
2-Methyl heptane	3.769	1.286	3.050	3.604	3.679
3-Methyl heptane	3.807	1.286	3.280	3.757	3.679
4-Methyl heptane	3.807	1.286	4.000	3.757	3.679
2,2-Dimethyl hexane	3.560	1.236	2.560	2.764	3.033
2,3-Dimethyl hexane	3.679	1.236	4.230	3.242	3.033
2,4-Dimethylhexane	3.662	1.236	2.800	3.174	3.033
2,5-Dimethylhexane	3.624	1.236	2.500	3.020	3.033
3,3-Dimethylhexane	3.620	1.236	3.170	3.005	3.033
3,4-Dimethylhexane	3.717	1.236	4.140	3.395	3.033
Nonane	4.414	1.490	5.930	6.198	6.314
2,2,3-Trimethylpentane	3.480	1.186	4.090	2.442	2.387
2,2,4-Trimethylpentane	3.415	1.186	3.270	2.181	2.387
2,3,3-Trimethylpentane	3.502	1.186	4.520	2.530	2.387
2,3,4-Trimethylpentane	3.551	1.186	4.520	2.727	2.387
3-Ethyl pentane	3.345	1.132	2.630	1.899	1.689
3-Methyl-3-ethyl pentane	3.680	1.236	4.760	3.246	3.033
2-Methyl-3-ethyl pentane	3.717	1.236	5.080	3.395	3.033
Undecane	5.414	1.798	9.940	10.220	10.293
Hexadecane	7.914	2.568	20.000	20.273	20.241
Nonadecane	9.414	3.030	26.030	28.306	26.210
Octadecane	8.914	2.876	24.020	24.295	24.221
Pentadecane	7.414	2.414	17.980	18.263	18.252
Tetradecane	6.914	2.260	15.970	16.252	16.262
Tridecane	6.414	2.106	13.970	14.241	14.273

Table 7: Experimental and theoretical calculated values of ΔG_f^0 by E and R parameters in alkanes

Name of compound	E	R	ΔG_f^0		
			Exp. value	**Calc. Eq. 12**	**Calc. Eq. 13**
Methane	*	6.478	-12.150	*	-10.781
Ethane	4.000	11.125	-7.840	-9.255	-8.725
Propane	5.500	15.771	-5.630	-7.200	-6.671
n-Butane	7.000	20.418	-4.100	-5.145	-4.616
2-Methyl propane	7.333	20.418	-4.990	-4.688	-4.616
n-Pentane	8.500	25.065	-2.000	-3.089	-2.561
2-Methyl butane	8.833	25.065	-3.540	-2.633	-2.561
2,2-Dimethyl propane	9.250	25.065	-0.364	-2.062	-2.561
n-Hexane	10.000	29.712	-0.060	-1.034	-0.506
2-Methyl pentane	10.333	29.712	-1.200	-0.578	-0.506
3-Methyl pentane	10.333	29.712	-0.510	-0.578	-0.506
2,2-Dimethyl butane	10.750	29.712	-2.300	*	-0.506
2,3-Dimethyl butane	10.666	29.712	-0.980	-0.121	-0.506
Heptane	11.500	34.359	1.910	1.021	1.549
2-Meyhyl hexane	11.833	34.359	0.770	1.478	1.549
3-Mehtyl hexane	11.833	34.359	1.100	1.478	1.549
2,2-Dimethyl pentane	12.250	34.359	0.020	2.049	1.549
2,3-Dimethyl pentane	12.166	34.359	0.160	1.934	1.549
2,4-Dimethyl pentane	12.166	34.359	0.740	1.934	1.549
2,2,3-Trimethyl butane	12.583	34.359	1.020	2.505	1.549
Octane	13.000	39.005	3.920	3.077	3.604
2-Methyl heptane	13.333	39.005	3.050	3.533	3.604
3-Methyl heptane	13.333	39.005	3.280	3.533	3.604

Cont…

Name of compound	E	R	ΔG_f^0		
			Exp. value	Calc. Eq. 12	Calc. Eq. 13
4-Methyl heptane	13.333	39.005	4.000	3.533	3.604
2,2-Dimethyl hexane	13.750	39.005	2.560	4.104	3.604
2,3-Dimethyl hexane	13.666	39.005	4.230	3.989	3.604
2,4-Dimethylhexane	13.666	39.005	2.800	3.989	3.604
2,5-Dimethylhexane	13.666	39.005	2.500	3.989	3.604
3,3-Dimethylhexane	13.750	39.005	3.170	4.104	3.604
3,4-Dimethylhexane	13.666	39.005	4.140	3.989	3.604
Nonane	14.500	43.652	5.930	5.132	5.659
2,2,3-Trimethylpentane	14.083	39.005	4.090	4.561	3.604
2,2,4-Trimethylpentane	14.083	39.005	3.270	4.561	3.604
2,3,3-Trimethylpentane	14.083	39.005	4.520	4.561	3.604
2,3,4-Trimethylpentane	13.999	39.005	4.520	4.446	3.604
3-Ethyl pentane	11.833	34.359	2.630	1.478	1.564
3-Methyl-3-ethyl pentane	13.750	39.005	4.760	4.104	3.604
2-Methyl-3-ethyl pentane	13.666	39.005	5.080	3.989	3.604
2,2,3,3-Tetramethylbutane	14.500	39.005	5.260	5.132	3.604
Undecane	17.500	52.946	9.940	9.243	9.769
Hexadecane	25.000	76.180	20.000	19.519	20.044
Nonadecane	29.500	90.120	26.030	25.685	26.209
Octadecane	28.000	85.473	24.020	23.630	24.153
Pentadecane	23.500	71.533	17.980	17.464	17.989
Tetradecane	22.000	66.886	15.970	15.409	15.934
Tridecane	20.500	62.239	13.970	13.353	13.879

CONCLUSION

The standard Gibb's free energy calculated from equations (10), (11), (12) and (13) are found to be very close to the experimental values (Tables 6 and 7). Therefore, these equations can be used to estimate standard free energy of alkane by simply calculating ($^1X^v$), (V_w), (E) and (R), respectively. This method of estimating standard Gibb's free energies of formation is easiest one and highly accurate.

REFERENCES

1. K. Huang, Statistical Mechanics, Wiley, New York, (1963) p. 3.
2. L. V. Vilkov and Yu. A. Pentin, Physical Methods of Research in Chemistry, Vysshaya Shkola, Moscow, (1987) p. 367.
3. D. R. Stull, E. F. Westrum and G. C. Sinke, The Chemical Thermodynamics of Organic Compounds, Wiley, New York (1969).
4. M. Randic and N. Trinajstic, New J. Chem., **18,** 179 (1994).
5. M. Randic, New J. Chem., **20,** 10019 (1996).
6. E. Estrada, O. Ivanciue, I. Gutman, A. Gutierrez and L. Rodriguez, New J. Chem., **22,** 819 (1998).
7. A. N. Pankratov, Afinidad, **56**, 257 (1999).
8. P. R. Duchowiczi, E. A. Castron, A. N. Pankratovz and De La Plata, PCS, Phy. Chem. /0207006.
9. S. W. Benson and J. H. Buss, J. Chem. Phy., **29,** 546 (1958).
10. E. S. Domalski and E. D.Hearing, J. Chem. Phys., **29,** 546 (1958).
11. J. O. Hutchens, A. G. Cole and J. W. Stout. , J. Biol. Chem., **239**, 591 (1964).
12. Z. Weng, C. Delisi and S. Vajda, Protein Science, **6,** 197 (1997).
13. Ajay and M. A. Murcko, J. Med. Chem., **38**, 4953 (1995).
14. B. L. Gorsi, G. S. Kalwania and M. Sharma, Indian J. Chem., **32 A,** 889 (1993).
15. B. L. Gorsi, G. S. Kalwania and M. Sharma, J. Indian Chem. Soc., **75,** 373 (1998).
16. L. B. Kier and L. H. Hall, Molecular Connectivity in Chemistry and Drug Research, Academic Press, New York (1976).
17. M. Randic, J. Am. Chem. Soc., **97,** 6609 (1975).
18. A. Bondi, J. Phy. Chem., **68,** 441 (1964).
19. A. Moriguchi, Chem. Pharm. Bull. (Jpn.) **23,** 247 (1975).

20. L. H. Hall, B. Mohney and L. B. Kier, The Electrotopological State, Structure Information at the Atomic Level for Molecular Graphs, J. Chem. Inf. Comput. Sci., **31,** 76 (1991**)**.

21. L. H. Hall, B. Mohney and L. B. Kier, The Electrotopological State: An Atom Index for QSAR, Quant. Struct-Act. Rel.**, 10,** 43 (1991**)**.

22. L. B. Kier and L. H. Hall, An Electrotopological State Index for Atoms in Molecules Pharm. Res., **7**, 801 **(**1990**)**.

23. A. K. Ghose and G. M. Crippen, J. Chem. Inf. Comput. Sci., **27**, 21 **(**1987**)**.

24. J. G. Aston and G. H. Messerly, J. Am. Chem. Soc., **62**, 1917 (1940**)**.

25. C. J. Dobratz, Ind. Eng. Chem., **33,** 759 **(**1941**)**.

26. D. R. Stull and F. D. Mayfield, Heat Capacities of Hydrocarbon Gases, Ind. Eng., **35,** 639 **(**1943**)**.

27. F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braum and G. C. Pimentel, Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, Carnegie Press, Pittsburgh, PA., (1953)**.**

28. J. B. Padley, R. D. Naylor and S. P. Kirby, Thermo-Chemical Data of Organic Compounds. Second Edition, Chapman and Hall, London and New York (1986).

29. John. A. Dean, Lange`s Hand Book of Chemistry 12th Edition, McGraw, Hill Book Co., New York (1970).

Revised : 01.10.2009 *Accepted : 03.10.2009*