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# The Gas-Phase Heats of Formation of *n*-Alkanes as a Function of the Electrostatic Potential Extrema on their Molecular Surfaces

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**Abstract.** The hybrid density functional B3LYP is employed to map the molecular electrostatic potentials on the surfaces of twenty normal alkanes, ( $C_nH_{2n+2}$ ),  $n = 1-20$ . It is shown that gas-phase heats of formation of the alkanes can be represented quantitatively in terms of the potential, where a general equation of the heat of formation is introduced as a function of potentials' extrema,  $V_{S,\min}$  and  $V_{S,\max}$  with average absolute error of 0.028 kcal/mol and a standard deviation of 0.048 kcal/mol. This should be viewed as a success of the B3LYP functional and the molecular surface electrostatic potential as tools of chemistry. The predicted gas-phase heats of formation of thirty normal alkanes ( $n = 21-50$ ) are reproduced and compared to their experimental counterparts when available.

**Key words:** Alkane, MSEP, B3LYP, Heat of formation

## Introduction

Several computational applications have been crucial to predict thermochemical properties of real and hypothetical systems, mainly where experimental data are lacked.<sup>1-5</sup> The system's standard heat of formation  $\Delta_f H^\circ$  is an example of such properties, where it has been under the focus of both chemists and physicists for different classes of organic compounds due to the property's role toward developing new energetic materials such as fuels and propellants.<sup>6</sup> The researchers have sought accurate computational approaches that may produce an average error of about 1 kcal. In this regard the semi empirical methods presented a well received compromise between the accuracy of the calculated  $\Delta_f H^\circ$  and the computations' costs. Then number of computational approaches at a fairly high level of accuracy is developed to produce gas-phase standard heats of formation,  $\Delta_f H^\circ_{\text{gas}}$ .<sup>7-11</sup> Politzer *et al* suggests a direct approach of density functional theory, DFT that is based upon calculating  $\Delta_f H$  for the formation of the molecules from its elements.<sup>7</sup> Kemeny *et al* used high level

*ab-initio* at the coupled cluster FFSD(T) level with augmented correlation-consistent basis sets extrapolated to the complete basis set limit to study  $\Delta_f H$  of phosphorus nitride.<sup>8</sup> Cioslowski *et al* used atomic equivalents, bond density functions, and corrections for molecular charge and spin multiplicity to convert B3LYP based energies to  $\Delta_f H$ .<sup>9,12</sup> This approach calculated reasonable  $\Delta_f H$  for a wide range of molecules and ions with a standard deviation of a 5.84 kcal/mol. Guthrie applied B3LYP functional to calculate the total molecular energy and then converted it to analogous  $\Delta_f H$  using various new parameterization schemes. The scheme of Ibrahim and Schleyer relied on the impact of the atoms attached to the central atom in the molecule produced an average error of 2 kcal/mol for the molecules employed.<sup>13</sup> Redfern *et al* concluded that the G3 enthalpies of formation of the n-alkanes deviate with experiment by less than 2 kcal/mol and pointed out to a small accumulation of error that increases the deviation with chain length.<sup>10</sup> For a set of 62 compounds an atom equivalents scheme with 11 parameters was described by Yala to convert *ab-initio* based energies to  $\Delta_f H$  with a deviation of 1.80 kcal/mol.<sup>14</sup> Similarly, Allinger and others showed that for various families of compounds including alkanes a bond contributions scheme can be used to convert *ab-initio* energies into heats of formation with good accuracy.<sup>15</sup> An assessment of B3LYP functional in its application to alkane concluded that simple conversion of the functional energies to heats of formation gives good results for alkanes of only 1-3 carbons but gives increasingly poor results for larger ones such as in case of hexadecane where the deviation is -30.3 kcal/mol.<sup>10</sup> Most recently, Hu and others combined an algorithm of quantum mechanical calculations and neural-network correction to evaluate  $\Delta_f H$  for 180 small to medium sized organic molecules at 298 K. Their achievement at B3LYP/6-311+G(d,p) level was noticeable.<sup>1</sup>

For the last thirty years the molecular surface electrostatic potential, MSEP has been successfully employed as a tool of studying physics and chemistry, variety of molecular properties can be expressed analytically in terms of some statistically defined quantities that feature the MSEP map.<sup>16</sup> Such properties include boiling points, critical constants, heats of vaporization, sublimation and fusion, free energies of solvation, solubilities of different components, partition coefficients, and surface tensions.<sup>17-19</sup> The electrostatic potential  $V(\mathbf{r})$  as defined by eq.(1) is produced in the space around a molecule by its nuclei and electrons.<sup>28</sup>  $Z_A$  is the charge on nucleus A that is located at distance  $R_A$  and  $\rho(\mathbf{r})$  is the electronic density function that can be defined in terms of a specific contour. The overall sign of the produced potential anywhere in the molecular vicinity depends upon the role's extent of either the nuclei or the electrons.

$$V(r) = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r') dr'}{|r' - r|} \quad (1)$$

The most negative and most positive values of  $V(\mathbf{r})$  are sites-specific in the total three-dimensional space of the molecule quantities designated respectively  $V_{S,\min}$  and  $V_{S,\max}$ . Introducing quantitative relationships and developing analytical expressions that involve one or both the quantities is becoming a broad field of research in condensed-phase systems.<sup>29</sup>

The objective of this work is to correlate the experimentally determined  $\Delta_f H^\circ_{\text{gas}}$  of the normal alkanes of interest with the numerical values of  $V_{S,\min}$  and / or  $V_{S,\max}$  on the MSEP calculated by the DFT functional B3LYP. The ultimate achievement would include introducing a new empirical equation for  $\Delta_f H^\circ_{\text{gas}}$  of normal alkanes as a function of the molecules potentials' extrema.

A great deal of interest has been shown in applications similar to the current one where the calculations of MSEP have been employed as an indicator or predictor of the molecular behavior. Such studies, for example, included correlations between theoretical and experimental determination of heat of formation of certain aliphatic nitro compounds, and correlation of boiling points of compounds with the 3/4 power of the polarizabilities of the outer atoms, where polarizability relates to both molecular surface area and volume.<sup>22-24</sup>

## Experimental

### *Methods and Procedure*

The optimized geometries of twenty different *n*-alkanes listed in **Table 1** were computed at the density functional B3LYP and 6-31G\*\* basis set using Gaussian 98 package.<sup>25</sup> The produced wave functions were used to calculate the B3LYP/6-31++G\*\* electron densities and electrostatic potentials,  $V(\mathbf{r})$  as given in eq. (1). We choose a contour of  $\rho(\mathbf{r}) = 0.001$  au to be the molecular surface, where Bader *et al* showed that this contour for a group of hydrocarbons encompasses more than 97% of the total electronic charge of the system.<sup>26</sup> The experimentally predetermined  $\Delta_f H^\circ_{\text{gas}}$  of the listed alkanes are linearly correlated with the computed potentials'  $V_{S,\text{min}}$  and / or  $V_{S,\text{max}}$  on the MSEP using SPSS statistical software.<sup>34</sup> As a comment on the level of theory employed in this work, the trends in the characterization of the surface potentials in terms of their minima and maxima should be qualitatively reasonably independent of the computational level of theory; although not the numerical coefficients.<sup>17</sup>

## Results and Discussion

In **Table 1** the experimentally determined  $\Delta_f H^\circ_{\text{gas}}$  for twenty normal alkanes along with both  $V_{S,\text{min}}$  and  $V_{S,\text{max}}$  computed on their MSEP as described above. It can be seen that  $\Delta_f H^\circ_{\text{gas}}$  generally increases in same order as does any of the alkane's molecular weight, number of carbon atoms ( $N_C$ ), molecular volume (Vol). However, a primary statistical analysis preferred a correlation that includes  $N_C$ . A linear correlation with a regression coefficient of  $R^2 = 1.00$  is represented by a straight line equation where  $\Delta_f H^\circ_{\text{gas}} = -4.9333 * N_C - 10.305$ . The average absolute error for this correlation is 0.17 kcal / mol while the standard deviation is 0.056 kcal / mol.

However, employing the computed  $V_{S,\text{min}}$  and/or  $V_{S,\text{max}}$  altogether with  $N_C$  as independent variables in seeking a linear correlation with the experimental  $\Delta_f H^\circ_{\text{gas}}$  would enhance the average standard deviation for the twenty normal alkanes down to 0.028 kcal/mol. The experimental  $\Delta_f H^\circ_{\text{gas}}$  works as a function of the three variables such that  $\Delta_f H^\circ_{\text{gas}} = (-10.335 - 0.00412 * V_{S,\text{max}} - 0.0881 * V_{S,\text{min}} - 4.958 * N_C)$ . The standard error in the calculated values is 0.048 Kcal / mol, indicating excellent agreement between the variables. **Figure 1** shows a linear plot of the experimental and the predicted values of  $\Delta_f H^\circ_{\text{gas}}$  with  $R^2 = 1.00$ . It is noticeable that in any of the correlations the inclusion of the data related to methane ( $N_C = 1$ ) would slightly affect the regression negatively.

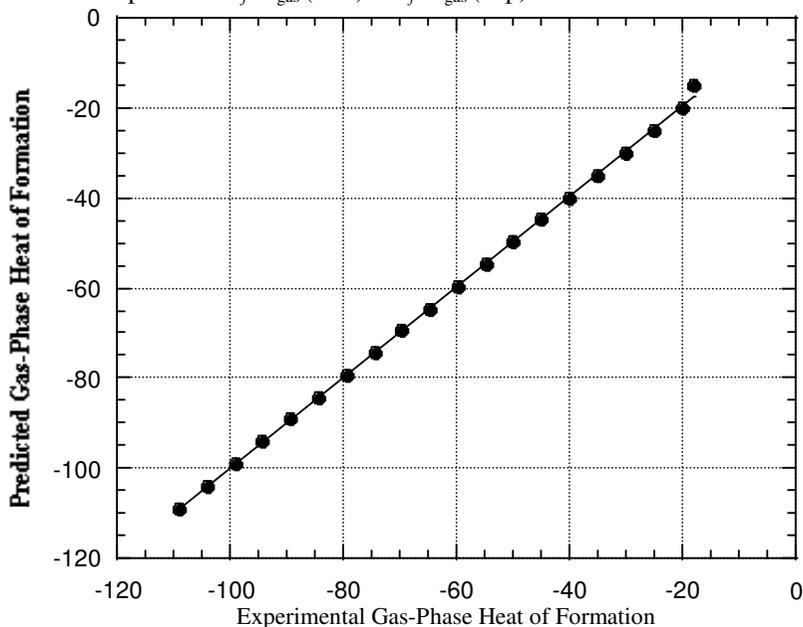
The correlated equation can be used to reproduce  $\Delta_f H^\circ_{\text{gas}}$  for such compounds that are not reported in the literature. For example,  $\Delta_f H^\circ_{\text{gas}}$  for  $C_{30}H_{62}$ ,  $C_{40}H_{82}$  and  $C_{100}H_{202}$  equal to -158.30, -207.64, and -503.64 Kcal / mol respectively. **Table 2** lists the predicted values of  $\Delta_f H^\circ_{\text{gas}}$  for *n*-alkanes, where  $n = 21-50$ , and compared with the experimental counterparts when available.

**Table 1** Gas-phase heats of formation  $\Delta_f H^\circ_{\text{gas}}$ , calculated  $V_{S,\text{min}}$ , and  $V_{S,\text{max}}$  computed at B3LYP/6-31++G\*\*, (kcal mol<sup>-1</sup>)

N <sub>C</sub>	n-alkane	V <sub>min</sub>	V <sub>max</sub>	$\Delta_f H^\circ_{\text{gas}}$ (298 K)	
				Exp. <sup>a</sup>	Calc.
1	CH <sub>4</sub>	-0.872	0.606	-17.89	-15.25
2	C <sub>2</sub> H <sub>6</sub>	-1.418	0.569	-20.04 ± 0.07	-20.15
3	C <sub>3</sub> H <sub>8</sub>	-2.275	0.763	-25.02 ± 0.12	-25.02
4	C <sub>4</sub> H <sub>10</sub>	-1.430	0.715	-30.03 ± 0.16	-30.07
5	C <sub>5</sub> H <sub>12</sub>	-1.805	1.100	-35.08 ± 0.14	-34.98
6	C <sub>6</sub> H <sub>14</sub>	-1.830	0.973	-39.96 ± 0.19	-39.94
7	C <sub>7</sub> H <sub>16</sub>	-1.991	1.302	-44.89 ± 0.19	-44.90
8	C <sub>8</sub> H <sub>18</sub>	-2.519	1.494	-49.82 ± 0.16	-49.81
9	C <sub>9</sub> H <sub>20</sub>	-2.509	1.568	-54.66 ± 0.24	-54.78
10	C <sub>10</sub> H <sub>22</sub>	-2.845	1.919	-59.67 ± 0.26	-59.71
11	C <sub>11</sub> H <sub>24</sub>	-3.226	2.498	-64.60 ± 0.30	-64.65
12	C <sub>12</sub> H <sub>26</sub>	-3.629	3.066	-69.52 ± 0.34	-69.59
13	C <sub>13</sub> H <sub>28</sub>	-4.108	4.006	-74.45 ± 0.39	-74.49
14	C <sub>14</sub> H <sub>30</sub>	-4.561	4.789	-79.38 ± 0.43	-79.44
15	C <sub>15</sub> H <sub>32</sub>	-5.064	5.978	-84.30 ± 0.48	-84.33
16	C <sub>16</sub> H <sub>34</sub>	-5.393	6.619	-89.22 <sup>b</sup>	-89.30
17	C <sub>17</sub> H <sub>36</sub>	-5.822	7.687	-94.20 ± 2.4	-94.21
18	C <sub>18</sub> H <sub>38</sub>	-6.105	8.114	-99.08 ± 2.7	-99.16
19	C <sub>19</sub> H <sub>40</sub>	-6.484	9.007	-104.00 ± 2.9	-104.08
20	C <sub>20</sub> H <sub>42</sub>	-3.764	2.510	-108.93 ± 0.74	-109.04

<sup>a</sup> unless otherwise indicated, experimental data are from NIST, <http://webbook.nist.gov/chemistry/><sup>b</sup> <http://www.chemic.org/kdb/kdb/hcprop/showprop.php?cmpid=16>

**Figure 1.** calculated  $\Delta_f H^\circ_{\text{gas}}$  plotted against the experimental  $\Delta_f H^\circ_{\text{gas}}$  for 20 *n*-alkanes using the concluded relationship;  $\Delta_f H^\circ_{\text{gas}} = (-10.335 - 0.00412 * V_{S,\text{max}} - 0.0881 * V_{S,\text{min}} - 4.958 * N_C)$ . the line drawn corresponds to  $\Delta_f H^\circ_{\text{gas}}(\text{calc}) = \Delta_f H^\circ_{\text{gas}}(\text{exp})$ .



**Table 2.** Predicted Gas-phase heats of formation  $\Delta_f H^\circ_{\text{gas}}$ , as a function of calculated  $V_{S,\text{min}}$ , and  $V_{S,\text{max}}$  computed at B3LYP/6-31++G\*\*, (kcal mol<sup>-1</sup>)

$N_C$	n-alkane	Calc. $\Delta_f H^\circ_{\text{gas}}$	$N_C$	n-alkane	Calc. $\Delta_f H^\circ_{\text{gas}}$
21	C <sub>21</sub> H <sub>44</sub>	-113.98	36	C <sub>36</sub> H <sub>74</sub>	-188.04
22	C <sub>22</sub> H <sub>46</sub>	-118.92	37	C <sub>37</sub> H <sub>76</sub>	-192.97
23	C <sub>23</sub> H <sub>48</sub>	-123.86	38	C <sub>38</sub> H <sub>78</sub>	-197.91
24	C <sub>24</sub> H <sub>50</sub>	-128.79	39	C <sub>39</sub> H <sub>80</sub>	-202.85
25	C <sub>25</sub> H <sub>52</sub>	-133.73	40	C <sub>40</sub> H <sub>82</sub>	-207.78
26	C <sub>26</sub> H <sub>54</sub>	-138.67	41	C <sub>41</sub> H <sub>84</sub>	-212.72
27	C <sub>27</sub> H <sub>56</sub>	-143.60	42	C <sub>42</sub> H <sub>86</sub>	-217.66
28	C <sub>28</sub> H <sub>58</sub>	-148.54	43	C <sub>43</sub> H <sub>88</sub>	-222.60
29	C <sub>29</sub> H <sub>60</sub>	-153.48	44	C <sub>44</sub> H <sub>90</sub>	-227.53
30	C <sub>30</sub> H <sub>72</sub>	-158.41	45	C <sub>45</sub> H <sub>92</sub>	-232.47
31	C <sub>31</sub> H <sub>64</sub>	-163.35	46	C <sub>46</sub> H <sub>94</sub>	-237.41
32	C <sub>32</sub> H <sub>66</sub>	-168.29	47	C <sub>47</sub> H <sub>96</sub>	-242.34
		Exp: -166.5 ± 2.2			
33	C <sub>33</sub> H <sub>68</sub>	-173.23	48	C <sub>48</sub> H <sub>98</sub>	-247.28
34	C <sub>34</sub> H <sub>70</sub>	-178.16	49	C <sub>49</sub> H <sub>100</sub>	-252.22
35	C <sub>35</sub> H <sub>72</sub>	-183.10	50	C <sub>50</sub> H <sub>102</sub>	-257.15

## Conclusion

The extrema of electrostatic potential mapped on the molecular surfaces of normal alkanes can work as a function of the gas-phase heat of formation. The property correlated linearly to the potential's minima and maxima, along with the number of carbons in the alkane. The introduced function can be employed to predict  $\Delta_f H^\circ_{\text{gas}}$  for any alkane with very small deviation.

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