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R. Vijaya Kumar^a; K. Kishore^a

^a Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India

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CALCULATION OF HEATS OF VAPORIZATION OF LONG CHAIN MOLECULES BY GROUP CONTRIBUTION METHOD

R. VIJAYA KUMAR* and K. KISHORE

*Department of Inorganic and Physical Chemistry,
Indian Institute of Science, Bangalore-560012, India*

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Benson's additivity rule has been used to compute the heat of vaporization (ΔH_v°) of long chain molecules includes *n*-alkylcyclopentanes, *n*-alkylcyclohexanes and *n*-alkylbenzenes. From the error analysis empirical equations have been obtained which accurately predicts the ΔH_v° of these substituted *n*-alkanes. For simple *n*-alkanes it is observed that no modification is necessary in Benson's method. The present simple and elegant empirical approach can be utilized to calculate other thermodynamic properties of long chain molecules where such data are generally scarce.

Keywords: Thermochemistry; Polymers

1. INTRODUCTION

Thermodynamicists are always interested in developing accurate numerical methods which could be used to deduce thermodynamic properties of molecules from their structural features. Benson's additivity rule [1–3] are by far the best and most widely used for calculating various thermodynamic properties like heats of formation (ΔH_f°), heat capacity (C_p), entropy (S^0), *etc.*, due to the ready availability of group values. ΔH_v° is one of the most important thermodynamic

*Address for correspondence: Dept. of Chemistry, Bar Ilan University, Ramat Gan, Israel. e-mail: rangarv@mail.biu.ac.il

parameters in long chain molecules such as alkanes, esters and alcohols for assessing their plasticizing and lubricant properties. Generally, experimental ΔH_v^0 data on long chain molecules are scarce, and one has to resort to utilize theoretical thermochemical methods to compute the same. Benson's method gives very good ΔH_v^0 value for simple *n*-alkanes. However, this method is not so accurate for substituted *n*-alkanes. The main objective of the present investigation is to assess the error involved in the calculated ΔH_v^0 values and to propose empirical equations so that accurate ΔH_v^0 values could be obtained for substituted *n*-alkanes: *n*-alkylcyclopentanes, *n*-alkylcyclohexanes and *n*-alkylbenzenes. In the present investigation we have made an attempt to modify the Benson's additivity rule, from error analysis, and calculated the corrected ΔH_v^0 values of substituted *n*-alkanes.

2. METHODOLOGY

The structure of *n*-alkylcyclopentanes and *n*-alkylcyclohexanes species were split into the following groups: C-(H)₃(C), C-(H)₂(C)₂, C-(H)(C)₃ and C-(C)₄, and their respective group values for ΔH_v^0 are: 1.35, 1.19, 0.72 and 0 respectively. Similarly, for *n*-alkylbenzenes the groups are: C-(H)₃(C), C-(H)₂(C)₂, C-(C_b)(C)(H)₂, C-(C_b)(C)₂(H), C-(C_b)(C)₃, C-(C_b)₂(H), C-(C_b)(H)₃ and C-(C_b)₂(C), and their corresponding group values for ΔH_v^0 are: 1.35, 1.19, 1.02, 0.23, 0, 1.35, 1.35 and 0.98 respectively. The calculated ΔH_v^0 values (298°K) are given in Table I.

TABLE I Experimental, calculated, absolute error and corrected ΔH_v^0 in the substituted *n*-alkane series

Substituted <i>n</i> -alkanes	Mol. weight	ΔH_v^0 (kcal/mol)			
		Experimental	Calculated from Benson's method	Error	Calculated after adding the error
<i>n</i> -alkylcyclopentanes					
Cyclopentane	70	6.82	5.98	0.84	6.82
Methylcyclopentane	84	7.58	6.30	0.75	7.60
Ethylcyclopentane	98	8.72	8.02	0.70	8.72
<i>n</i> -propylcyclopentane	112	9.82	9.21	0.61	9.82
<i>n</i> -butylcyclopentane	126	11.00	10.40	0.60	11.00
<i>n</i> -pentylcyclopentane	140	12.18	11.59	0.59	12.18

TABLE I (Continued)

Substituted <i>n</i> -alkanes	Mol. weight	ΔH_v° (kcal/mol)			Calculated after adding the error
		Experimental	Calculated from Benson's method	Error	
<i>n</i> -hexylcyclopentane	154	13.16	12.78	0.58	13.36
<i>n</i> -heptylcyclopentane	168	14.54	13.97	0.57	14.54
<i>n</i> -octylcyclopentane	182	15.72	15.16	0.56	15.72
<i>n</i> -nonylcyclopentane	196	16.90	16.35	0.55	16.90
<i>n</i> -decylcyclopentane	210	18.08	17.54	0.54	18.08
<i>n</i> -undecylcyclopentane	224	19.26	18.73	0.53	19.26
<i>n</i> -dodecylcyclopentane	238	20.44	19.92	0.52	20.44
<i>n</i> -tridecylcyclopentane	252	21.62	21.11	0.51	21.62
<i>n</i> -tetradecylcyclopentane	266	22.80	22.30	0.50	22.81
<i>n</i> -alkylcyclohexane					
Cyclohexane	84	7.89	7.14	0.75	7.53
Methylcyclohexane	98	8.45	8.80	0.45	8.29
Ethylcyclohexane	112	9.67	9.21	0.46	9.35
<i>n</i> -propylcyclohexane	126	10.79	10.40	0.39	10.79
<i>n</i> -butylcyclohexane	140	11.95	11.50	0.36	11.97
<i>n</i> -pentylcyclohexane	154	13.14	12.70	0.36	13.15
<i>n</i> -hexylcyclohexane	168	14.32	13.90	0.35	14.32
<i>n</i> -heptylcyclohexane	182	15.50	15.10	0.34	15.50
<i>n</i> -octylcyclohexane	196	16.68	16.30	0.33	16.68
<i>n</i> -nonylcyclohexane	210	17.86	17.50	0.32	17.86
<i>n</i> -decylcyclohexane	224	19.04	18.70	0.31	19.04
<i>n</i> -undecylcyclohexane	238	20.22	19.90	0.30	20.22
<i>n</i> -dodecylcyclohexane	252	21.40	21.10	0.29	21.40
<i>n</i> -tridecylcyclohexane	266	22.58	22.30	0.28	22.58
<i>n</i> -tetradecylcyclohexane	280	23.76	23.40	0.27	23.76
<i>n</i> -alkylbenzenes					
Benzene	78	8.09	8.10	0.0	8.68
Methylbenzene	93	9.08	9.08	0.0	9.37
Ethylbenzene	107	10.09	10.10	0.0	10.13
<i>n</i> -propylbenzene	121	11.05	11.29	-0.2	11.07
<i>n</i> -butylbenzene	135	11.98	12.48	-0.5	11.99
<i>n</i> -pentylbenzene	149	13.16	13.67	-0.5	13.16
<i>n</i> -hexylbenzene	163	14.34	14.86	-0.5	14.34
<i>n</i> -heptylbenzene	177	15.52	16.05	-0.5	15.52
<i>n</i> -octylbenzene	191	16.72	17.24	-0.5	16.70
<i>n</i> -nonylbenzene	205	17.88	18.43	-0.6	17.88
<i>n</i> -decylbenzene	219	19.06	19.62	-0.6	19.06
<i>n</i> -undecylbenzene	233	20.24	20.81	-0.7	20.24
<i>n</i> -dodecylbenzene	247	21.42	22.00	-0.6	21.40
<i>n</i> -tridecylbenzene	261	22.60	23.19	-0.6	22.60
<i>n</i> -tetradecylbenzene	275	23.80	24.38	-0.6	23.78
<i>n</i> -pentadecylbenzene	289	25.00	25.57	-0.5	25.95
<i>n</i> -hexadecylbenzene	303	26.10	26.76	-0.7	26.13

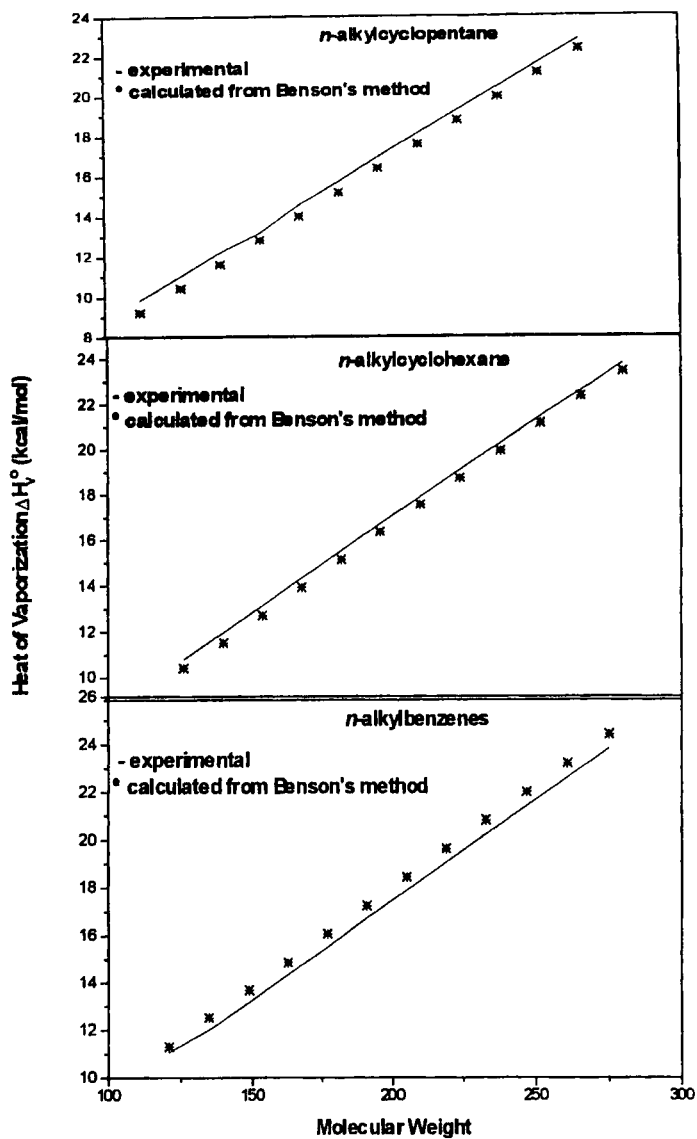


FIGURE 1 Variation of heats of vaporization as a function of molecular weight, in substituted *n*-alkanes.

3. RESULTS AND DISCUSSION

In the present investigation, the experimental ΔH_v^o of *n*-alkylcyclopentanes, *n*-alkylcyclohexanes and *n*-alkylbenzenes were taken from the literature [4]. The error in the calculated and experimental ΔH_v^o values are listed in Table I. They show +ve deviation in *n*-alkylcyclopentane and *n*-alkylcyclohexane series and -ve deviation in *n*-alkylbenzene series. Figure 1 displays the variation of ΔH_v^o as a function of molecular weight for *n*-alkylcyclopentanes, *n*-alkylcyclohexanes and *n*-alkylbenzenes respectively. Figure 1 shows a significant deviation between calculated and experimental ΔH_v^o values. This necessitates some improvement in Benson's group additivity methodology for substituted *n*-alkanes. To do this, the absolute error in the calculated ΔH_v^o values were plotted as a function of molecular weight, Figure 2 shows that error spectrum differs in the low molecular weight and high molecular weight regions, all of them show two distinct regions of deviation. The calculated error could be represented in terms of slope and intercept of a linear fit equation (see Tab. II). We have recalculated the ΔH_v^o by adding the corresponding error in the calculated ΔH_v^o obtained from Benson's method. The agreement between the calculated and experimental ΔH_v^o is shown in Figure 3. The dotted line represents the ideal line representing perfect mach

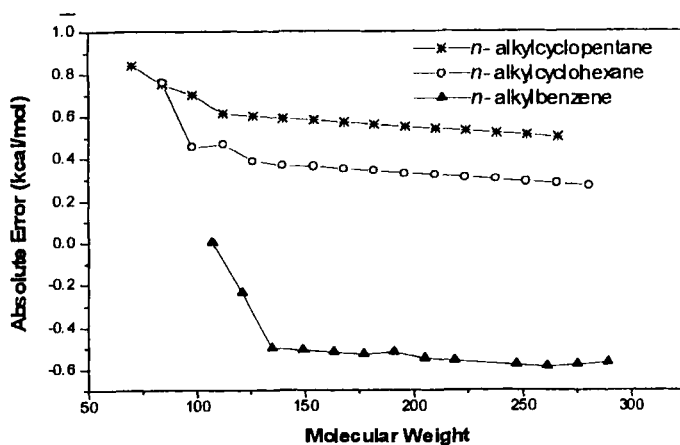


FIGURE 2 Absolute error as a function of molecular weight, in substituted *n*-alkanes.

TABLE II Empirical expressions for calculating errors in Benson's calculated values of ΔH_v°

Substituted <i>n</i> -alkanes	Mol. wt. range (Da)	Empirical equations
<i>n</i> -alkylcyclopentane	70–112	$Y = -5.0 \times 10^{-3}X + 1.19$
<i>n</i> -alkylcyclohexane	113 and above	$Y = -6.9 \times 10^{-4}X + 0.69$
<i>n</i> -alkylcyclohexane	84–126	$Y = -9.0 \times 10^{-3}X + 1.15$
<i>n</i> -alkylcyclohexane	127 and above	$Y = -8.0 \times 10^{-4}X + 0.49$
<i>n</i> -alkylbenzene	107–135	$Y = -9.0 \times 10^{-3}X + 2.06$
<i>n</i> -alkylbenzene	136 and above	$Y = 7.8 \times 10^{-4}X - 0.39$

Y = error in Benson's calculated values of ΔH_v° , X = molecular weight of the substituted *n*-alkanes.

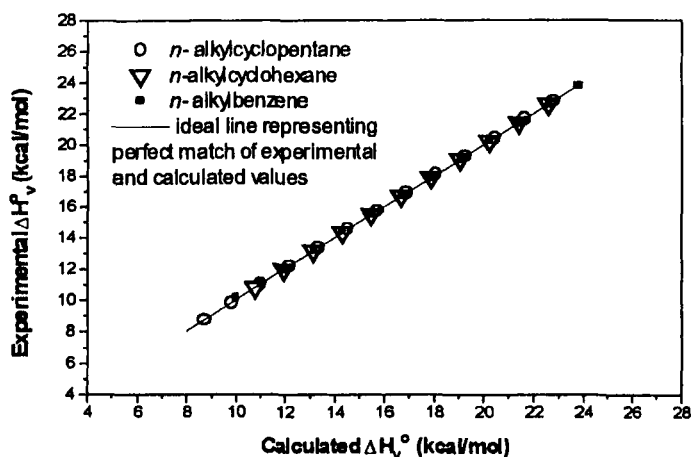


FIGURE 3 Calculated and experimental heats of vaporization from modified Benson's rule and its comparison with the corresponding experimental values.

between the experimental and the calculated ΔH_v° . The calculated values for all the three series of substituted *n*-alkanes fall on this line showing that modified Benson's method provides accurate data of ΔH_v° of substituted *n*-alkanes. It may be noted that some attempts have also been made earlier to represent the error as a fixed value [5, 6] but the present method is better as it considers the error as a function of molecular weight. We strongly believe that this approach could be extended not only for calculating the ΔH_v° of still high molecular weight substituted *n*-alkanes but also for obtaining other thermodynamic properties of long chain compounds.

4. CONCLUSIONS

Heat of vaporization of long chain molecules can be satisfactorily calculated by group contribution method. Although this is a totally empirical method and there is no simple method to calculate heat of vaporization of long chain molecules, the data obtained by this method is quite consistent with the values obtained by other methods.

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References

- [1] Benson, S. W. and Buss, J. H. (1958). *J. Chem. Phys.*, **29**, 546–572.
- [2] Benson, S. W., Cruickshank, F. R., Golden, D. M., Haugens, G. R., O'Neal, H. E., Rodgers, A. S., Shaw, R. and Walsh, R. (1969). *Chem. Rev.*, **69**, 279–313.
- [3] Benson, S. W. (1976). *Thermochemical Kinetics*. Wiley, New York, chapter 2.
- [4] Wilhoit, R. C. and Zwolinski, B. J. (1971). *Handbook of vapour pressure and heats of vaporization of hydrocarbons and related compounds*, American Petroleum Institute Research Project 44.
- [5] Ducros, M. and Sannier, H. (1982). *Thermochimica Acta*, **54**, 153–157.
- [6] Ducros, M., Gruson, J. F. and Sannier, H. (1980). *Thermochimica Acta*, **36**, 39–65.