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DEVELOPMENT OF BENSON GROUP ADDITIVITY METHOD FOR ESTIMATION OF IDEAL GAS THERMODYNAMIC PROPERTIES OF POLYCYCLIC AROMATIC HYDROCARBONS

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ABSTRACT

The improved group additivity method has been applied to the prediction of ideal gas thermodynamic properties $C_p^\ominus$, $S^\ominus$ $-(G^\ominus - H_0^\ominus)/T$, $H^\ominus - H_0^\ominus$, $\Delta_f H^\ominus$ and log $K_f^\ominus$ between 100 and 1500 K for polycyclic aromatic hydrocarbons consisting of six-membered rings.

INTRODUCTION

The chemistry and thermodynamic properties of the polycyclic aromatic hydrocarbons (PCAHs) in the gas phase have been of interest for many years. Values for chemical thermodynamic properties of PCAHs are needed for the furthering of the study of coal pyrolysis chemistry. Following the recent observation that PCAHs are abundant in interstellar space, information is needed concerning the spectroscopic and thermodynamic properties of such compounds in the gas phase [1].

Values for chemical thermodynamic properties of PCAHs are scanty and often of low accuracy. Entropies and heat capacities are determined either calorimetrically or from structural data, vibrational assignments and statistical formulae. Only a few calorimetric and spectroscopic studies of PCAHs are available in the literature, and for this reason, the Benson group-contribution method [2,3] has been developed and extended by several authors [4–8]. Stein et al. [5] have applied group additivity techniques to the prediction of standard gas-phase heat capacity $C_p^\ominus(T)$ ($T = 300–1000$ K), entropy $S^\ominus$(298.15 K) and heat of formation $\Delta_f H^\ominus$(298.15 K) for PCAHs. The proposed scheme uses four group contributions to the thermodynamic properties. More recently, Stein and Fahr [6] have presented Benson group

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values with $C_p^\ominus$ values up to 3000 K. Alberty and Reif [7] have calculated values of $C_p^\ominus$, $S^\ominus$, $\Delta_f H^\ominus$ and $\Delta_f G^\ominus$ from 298.15 to 3000 K for PCAHs without D groups [C_{BF}–$(C_{BF})_3$] *.

In previous works [3–8], group contributions to the thermodynamic properties of PCAHs have been based on properties derived from experimental data for a small number of compounds. Recently, thermodynamic properties of 37 PCAHs have been calculated by the standard statistical mechanical method using the rigid rotor–harmonic oscillator approximation [9,10]. This, together with a new compilation of observed data for enthalpy of formation [11], provides a basis for further improvement and extension of the Benson group additivity method for PCAHs. The purpose of the present work is to improve Benson group values and to extend the group additivity scheme to cover all thermodynamic properties over a wide temperature range.

Comparisons of the entropy values calculated from vibrational assignments [9] with those estimated using the Benson method [5] show that they are very similar for PCAHs consisting of no more than two D groups (the average difference is 1.3 J K^{-1} mol^{-1}). The average difference between the calculated and estimated values for compounds consisting of more than two D groups is 11 J K^{-1} mol^{-1} [9]. Thus, the values for D groups evaluated from graphite [5] cannot any longer be regarded as reliable. In the present work, the values for group increments $C_p^\ominus(T)$, $S^\ominus$(298.15 K), $H^\ominus$(298.15 K) $- H^\ominus(0)$ and $\Delta_f H^\ominus$(298.15 K) are computed using the latest thermodynamic data [9,10]. The second aim of this study is to obtain information about all the thermodynamic properties of PCAHs ($C_p^\ominus(T)$, $S^\ominus(T)$, $-[G^\ominus(T) - H^\ominus(0)]/T$, $H^\ominus(T) - H^\ominus(0)$, $\Delta_f H^\ominus$(298.15 K) and log $K_f^\ominus(T)$) at various temperatures from 100 to 1500 K. Kudchadker et al. [8] have previously developed group additivity techniques for calculation of thermodynamic properties of PCAHs from 298.15 to 1500 K, but their values for D groups were obtained by extrapolating from graphite. For this reason, and because of the inaccuracy of vibrational frequency assignments for the key compounds, Kudchadker's scheme cannot be recommended for estimation of thermodynamic properties of PCAHs.

DETERMINATION OF GROUP CONTRIBUTION VALUES

The present group additivity scheme uses five groups. Figure 1 illustrates these groups in dibenzo[*bc*,*ef*]coronene. To simplify the figure, only sigma

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* The designation of four Benson groups is given in ref. 5. See also Fig. 1 in the present paper. According to Stein et al. [5], the D group is identical with a carbon atom present in a layer of graphite.

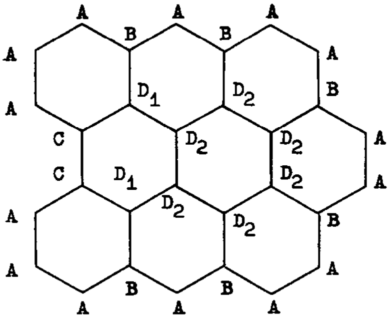

Fig. 1. Illustration of five kinds of carbon atoms in polycyclic aromatic hydrocarbons. Dibenzo[*bc*,*ef*]coronene consists of 14 A, 6 B, 2 C, 2 D_1 and 6 D_2 groups.

bonds have been shown. These groups are similar to those of Stein et al. [5] except that two kinds of D groups are employed in the present scheme.

Group A is the benzoid carbon atom carrying a hydrogen atom. Groups B and C are the aromatic carbon atoms common to two rings, and have no hydrogen atom. Groups D_1 and D_2 are the aromatic carbon atoms common to three rings, and these can be linked to B, C or D groups. The D_1 group is attached to two or three B or C groups. The D_2 group can be linked with no more than one B or C group. Stein et al. [5] do not distinguish between D_1 and D_2 groups, and their additive scheme gives less accurate values of thermodynamic properties for compounds with D groups. Thus, the $S^{\ominus}$(289.15 K) value for dibenzo[*bc*,*ef*]coronene estimated from the group additive increments of Stein et al. is 15 J K^{-1} mol^{-1} larger than that calculated from molecular constants by the statistical mechanical method. Using the present additive scheme, this discrepancy is decreased to 0.5 J K^{-1} mol^{-1}. Table 1 compares the group additivity values for the thermodynamic properties obtained in the present work with those of Stein et al. [5]. The values of the group contribution to $S^{\ominus}_{int}$(289.15 K) *, $H^{\ominus}$(298.15 K) − $H^{\ominus}$(0) and $C_p^{\ominus}(T)$ were derived from the thermodynamic properties calculated by statistical mechanical methods [9]. Of 37 PCAHs from $C_{10}H_8$ to $C_{32}H_{14}$, only the most simple compound, naphthalene, was excluded from consideration, as this improved slightly the agreement between the estimated and experimental entropy values for other compounds. The increments in $\Delta_f H^{\ominus}$(298.15 K) were based on thermochemical data reported by Pedley et al. [11]. Values of the group contributions to the thermodynamic properties were obtained by fitting thermodynamic properties calculated according to the additivity rules (P_{ADD}) to thermodynamic properties derived from the

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* The intrinsic entropy $S^{\ominus}_{int}$ is related to the observed entropy $S^{\ominus}$ by the relation $S^{\ominus}_{int} = S^{\ominus} + R\ln(\sigma/n)$, where σ is the symmetry number for the molecule, and n is the number of optical isomers.

TABLE 1

Group additivity values for PCAHs [a]

Group	$S^{\ominus}_{\text{int}}$(289.15 K) [b] (J K^{-1} mol^{-1})	$H^{\ominus}$(298.15 K) $- H^{\ominus}$ (0) (kJ mol^{-1})	$\Delta_f H^{\ominus}$ (298.15 K) (kJ mol^{-1})	$C_p^{\ominus}(T)$ (J K^{-1} mol^{-1})			
				100 K	200 K	298.15 K	300 K
A	49.387	2.371	11.569	5.150	9.563	14.777	14.875
	(48.242)		(13.807)				(13.556)
B	−23.189	1.072	28.858	2.356	5.763	9.375	9.442
	(−20.920)		(20.083)				(12.510)
C	−22.677	1.212	17.097	2.903	6.447	9.890	9.954
	(−20.920)		(15.481)				(12.510)
D_1	6.192	1.094	−2.710	1.116	5.704	9.464	9.527
	(7.615)		(6.067)				(8.703)
D_2	5.767	1.011	−2.710	1.101	5.135	8.724	8.787
	(7.615)		(6.067)				(8.703)

[a] Numbers in parentheses are the values obtained by Stein et al. [5].

[b] $S^{\ominus}_{\text{int}}(298.15\ \text{K}) = S^{\ominus}(298.15\ \text{K}) + R\ \ln(\sigma/n)$, where σ is the symmetry number, and n is the number of optical isomers.

data sources cited above (P_{EXP}) and using the least-squares method, minimizing the sum of the squares of the absolute deviations $\Sigma \mid P_{\text{EXP}} - P_{\text{ADD}} \mid^2$.

Entropies determined from calorimetric studies are known for only two of the PCAHs considered, namely, phenanthrene and pyrene. As can be seen from Table 2, the agreement between calculated and experimental entropies falls within the uncertainties of measurement. The average difference between entropy values estimated according to the group additivity scheme and values obtained by statistical calculation [9] is 0.45 J K^{-1} mol^{-1}. In the case of the scheme by Stein et al., this discrepancy is larger by a factor of ten.

Experimental data for naphthalene, anthracene, phenanthrene, pyrene, naphthacene, triphenylene, chrysene, benz[*a*]anthracene and benzo[*c*]phenanthrene [11] were considered for use in determining the group contribution values for $\Delta_f H^{\ominus}$. For naphthacene, triphenylene and benzo[*c*]phenanthrene, the discrepancy between the $\Delta_f H^{\ominus}$ values predicted by the additivity scheme and the experimental values proved to be essentially larger than the experimental uncertainties. It can therefore be expected that the accuracy of the measured values for these three compounds would be insufficient. Thus, with the exception of these three compounds, the group contribution values for $\Delta_f H^{\ominus}$ (Table 1) were derived from published data [11]. The average difference between the experimental and calculated values of $\Delta_f H^{\ominus}$ for the remaining compounds is 1.6 kJ mol^{-1}. It is difficult to estimate the uncertainties of calculated values of heat of formation because insufficient reliable experimental data are available. This is especially true for PCAHs containing D groups, as the $\Delta_f H^{\ominus}$ value for this group was based only on data reported for pyrene.

400 K	500 K	600 K	800 K	1000 K	1200 K	1400 K	1500 K
19.894	24.061	27.385	32.243	35.605	38.035	39.830	40.551
(18.577)	(22.845)	(26.359)	(31.547)	(35.187)			
12.839	15.698	17.990	21.178	23.122	24.348	25.155	25.456
(15.313)	(17.656)	(19.414)	(21.882)	(23.221)			
13.201	15.960	18.185	21.296	23.199	24.402	25.196	25.492
(15.313)	(17.656)	(19.414)	(21.882)	(23.221)			
12.611	15.092	17.035	19.685	21.271	22.263	22.910	23.152
(11.924)	(14.644)	(16.862)	(19.874)	(21.506)			
11.887	14.443	16.473	19.277	20.973	22.037	22.736	22.998
(11.924)	(14.644)	(16.862)	(19.874)	(21.506)			

The uncertainties in the entropies and heat capacities have been evaluated as 1–8 J K^{-1} mol^{-1}; uncertainties in the heats of formation may vary from 1 to 30 kJ mol^{-1}.

PREDICTION OF THERMODYNAMIC PROPERTIES AT VARIOUS TEMPERATURES

Using the group increment values obtained in the present work (Table 1), we can derive the thermodynamic properties $S^{\ominus}(298.15\ \mathrm{K})$, $H^{\ominus}(298.15\ \mathrm{K}) - H^{\ominus}(0)$, $-[G^{\ominus}(298.15\ \mathrm{K}) - H^{\ominus}(0)]/298.15$, $\Delta_f H^{\ominus}(298.15\ \mathrm{K})$ and $C_p^{\ominus}(T)$ for temperatures from 100 to 1500 K. To obtain the values of these thermodynamic properties at various temperatures, it is necessary to use an analytic expression for temperature dependence of heat capacity.

The values of heat capacities calculated from group increments were fitted to the following polynomial function

$$C_p^{\ominus}(T) = a + bT + cT^2 + dT^3 + eT^4 + fT^{-2} + jT^{-3} \qquad (1)$$

and the constants of eqn. (1) were determined by the least-squares method.

Using this analytic expression of heat capacity (eqn. (1)) and values of $S^{\ominus}(298.15\ \mathrm{K})$, $H^{\ominus}(298.15\ \mathrm{K}) - H^{\ominus}(0)$ and $\Delta_f H^{\ominus}(298.15\ \mathrm{K})$ evaluated by the group contribution method, the thermodynamic properties at other temperatures can be calculated by the well known equations

$$S^{\ominus}(T) = S^{\ominus}(298.15\ \mathrm{K}) + \int_{298.15}^{T} \frac{C_p^{\ominus}(T)}{T}\,\mathrm{d}T \qquad (2)$$

TABLE 2

Comparison of experimental and calculated entropies (in J K^{-1} mol^{-1})

Phenanthrene					Pyrene				
T (K)	Experimental [12]	Group additivity calculation			T (K)	Experimental [13]	Group additivity calculation		
		Stein et al. [5]	This work	Δ [a]			Stein et al. [5]	This work	Δ [a]
298.15		393.0	396.4		298.15		402.3	402.0	
372.4	443.0		443.1	−0.1	423.8	489.1 ± 1.1		488.6	0.5
380	447.6		447.8	−0.2	440	499.8 ± 0.9		499.6	0.2
390	453.3		454.1	−0.8	460	512.8 ± 1.5		513.2	−0.4
400	459.1		460.4	−1.3	480	525.7 ± 2.3		526.7	−1.0
410	465.0		466.7	−1.7					
420	471.2		472.9	−1.7					

[a] $\Delta = S^{\ominus}_{\mathrm{exp}}(T) - S^{\ominus}_{\mathrm{calc}}(T)$.

$$H^\ominus(T) - H^\ominus(0) = H^\ominus(298.15\ \mathrm{K}) - H^\ominus(0) + \int_{298.15}^{T} C_p^\ominus(T)\,\mathrm{d}T \tag{3}$$

$$\frac{-[G^\ominus(T) - H^\ominus(0)]}{T} = S^\ominus(T) - \frac{H^\ominus(T) - H^\ominus(0)}{T} \tag{4}$$

$$\ln K_\mathrm{f}^\ominus(T) = \frac{\Delta_\mathrm{f}S^\ominus(T)}{R} - \frac{\Delta_\mathrm{f}H^\ominus(T)}{RT} \tag{5}$$

The values of $\Delta_\mathrm{f}H^\ominus(T)$ and $\Delta_\mathrm{f}S^\ominus(T)$ at various temperatures were calculated using the values for $S^\ominus(T)$ and $H^\ominus(T) - H^\ominus(0)$ for C(graphite) and H_2(g).

The calculations of thermodynamic properties of PCAHs at different temperatures from 100 to 1500 K were carried out with the aid of a computer program, ADDITIV, written in Fortran IV. Input data for this program are: (1) the constants k_1, k_2, k_3, k_4 and k_5, which correspond to the numbers of A, B, C, D_1 and D_2 groups for a given PCAH; (2) the symmetry number σ and the number of optical isomers n, which are used in going from $S_\mathrm{int}^\ominus$ to $S^\ominus$; and (3) the number of carbon atoms n_C and the number of hydrogen atoms n_H. Given the above data, calculation of $C_p^\ominus(T)$ for temperatures from 100 to 1500 K, $S^\ominus$(298.15 K), $H^\ominus$(298.15 K) − $H^\ominus$(0) and $\Delta_\mathrm{f}H^\ominus$(298.15 K) is done using the equation

$$P = k_1\ \mathrm{A} + k_2\ \mathrm{B} + k_3\ \mathrm{C} + k_4\ \mathrm{D}_1 + k_5\ \mathrm{D}_2 \tag{6}$$

where P is any thermodynamic property. Calculation of other thermodynamic properties at various temperatures from 100 to 1500 K is then carried out using eqns. (1)–(5).

CONCLUSIONS

Using thermodynamic properties calculated by statistical mechanical methods, the group contribution method for PCAHs has been essentially improved. New group increment values and consideration of the analytic expression of heat capacity have enabled the calculation of all thermodynamic properties at various temperatures from 100 to 1500 K for PCAHs consisting of six-membered rings. The scheme presented here is an extension of Benson group additivity techniques. The method proposed is based on more reliable thermodynamic data, and hence is more accurate than previous estimation methods.

Reliable spectroscopic data needed for statistical calculations of thermodynamic functions are unexpectedly scarce, and in the Benson method, entropies and heat capacities calculated from spectroscopically determined vibrational frequencies are considered as measured valves [3]. In order to estimate the group contribution values for PCAHs we used thermodynamic properties calculated for a rather large number of compounds by statistical methods. The vibrational frequencies were calculated using the simple force field approximation. This approximation proved to be sufficiently reliable [9,10]. We believe that simple force approximations combined with group additivity techniques will allow the estimation of thermodynamic properties for many classes of organic compounds.

NOMENCLATURE

A, B, C, D_1, D_2	notation for five kinds of groups for PCAHs
a, b, c, d, e, f, j	constants of equation for $C_p^\ominus$ in the polynomial form
$C_p^\ominus$	standard heat capacity at constant pressure
$-(G^\ominus - H_0^\ominus)/T$	standard Gibbs energy
$H^\ominus - H_0^\ominus$	standard enthalpy
k_1, k_2, k_3, k_4, k_5	number of A, B, C, D_1 and D_2 groups in molecule
$\log K_f^\ominus$	logarithm of the equilibrium constant
n	number of optical isomers
P	any thermodynamic property
$S^\ominus$	standard entropy
$S_{int}^\ominus$	intrinsic entropy
T	temperature

Greek letters

$\Delta_f G^\ominus$	standard Gibbs energy of formation
$\Delta_f H^\ominus$	standard enthalpy of formation
$\Delta_f S^\ominus$	standard entropy of formation
σ	symmetry number

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