Thermochimica Acta, 168 (1990) 179–186
Elsevier Science Publishers B.V., Amsterdam

GROUP ADDITIVITY SCHEME FOR CALCULATING THE CHEMICAL THERMODYNAMIC PROPERTIES OF GASEOUS POLYCYCLIC AROMATIC HYDROCARBONS CONTAINING FIVE-MEMBERED RINGS

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(Received 16 February 1990)

ABSTRACT

An additive method is described for estimation of ideal gas thermodynamic properties $C_p^\ominus$, $S^\ominus$, $-[G^\ominus - H^\ominus(0)]/T$, $H^\ominus - H^\ominus(0)$, $\Delta_f H^\ominus$ and log $K_f^\ominus$ from 100 to 1500 K for polycyclic aromatic hydrocarbons containing five-membered rings.

INTRODUCTION

Polycyclic aromatic hydrocarbons containing five-membered rings (PAHFR), together with other polynuclear aromatic compounds, are of special interest as products of coal pyrolysis processes. Few experimental data have been reported on chemical thermodynamic properties of gas-phase PAHFR. For two compounds, acenaphthene and fluorene, the entropy values, $S^\ominus(T)$, have been obtained from calorimetric measurements [1]. Less accurate values of $S^\ominus$(298.15 K) are known for indene and indan [2]. Gaseous heat of formation data, $\Delta_f H^\ominus$(298.15 K), are available for six PAHFR, i.e. indene, indan, acenaphthylene, acenaphthene, fluorene and fluoranthene [2,3].

Since data on thermodynamic properties (calorimetric or statistical) are lacking for most PAHFR, methods for estimating them have been proposed. Stein and Barton [2] have used the Benson group-additivity method [4,5] for estimation of thermodynamic properties ($S^\ominus$(298.15 K) $C_p^\ominus(T)$, $\Delta_f H^\ominus$(298.15 K)) of PAHFR containing indene and acenaphthylene fragments. These authors have estimated the thermodynamic properties for fluorene, acenaphthylene and fluoranthene using derived ring-group values.

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0040-6031/90/$03.50

The accuracy of these entropy values is 8–12 J K^{-1} mol^{-1}. Heat capacity values are expected to be accurate to within 8 J K^{-1} mol^{-1}.

Rehman and Lee [6] have derived self-consistent equations for calculating the ideal gas heat capacity, enthalpy and entropy based on formulae of statistical mechanics. These equations have been applied to compounds encountered in coal conversion operations. Eight parameters of these equations were determined by fitting all three equations simultaneously to the reported experimental data. Parameters determined for $C_p^{\ominus}(T)$, $S^{\ominus}(T)$ and $H^{\ominus}(T)-H^{\ominus}(0)$ allowed the thermodynamic properties between 298.15 and 1000 K for five PAHFR (indene, indan, acenaphthylene, acenaphthene, fluorene) to be calculated. However, such equations could not be obtained for other PAHFR due to the lacking of experimental data.

Recently, thermodynamic properties of 45 PAHFR have been calculated by the standard statistical mechanical method using the rigid rotor–harmonic oscillator approximation and estimated values of structural parameters and vibrational frequencies [7]. This, together with a compilation of observed data for enthalpy of formation [3], provides a basis for extension of the Benson group additivity method for PAHFR. The purpose of the present work is to obtain the group increment values for calculating the thermodynamic properties of PAHFR over a wide temperature range. In previous work [8], we have applied the group additivity method to the prediction of ideal gas thermodynamic properties for polycyclic aromatic hydrocarbons consisting of six-membered rings.

DETERMINATION OF GROUP CONTRIBUTION VALUES

Five kinds of groups for polycyclic aromatic hydrocarbons consisting of six-membered rings have been described in detail [8]. Figure 1 illustrates these groups. New groups arise with the fusion of five- and six-membered rings. Figure 2 presents different kinds of carbon atoms in five-membered

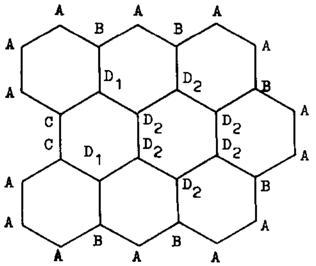


Fig. 1. Illustration of five kinds of carbon atoms in polycyclic aromatic hydrocarbons consisting of six-membered rings. Dibenzo[bc, ef]coronene consists of 14 A, 6 B, 2 C, 2 D_1 and 6 D_2 groups. To simplify this figure only the sigma bonds are shown.

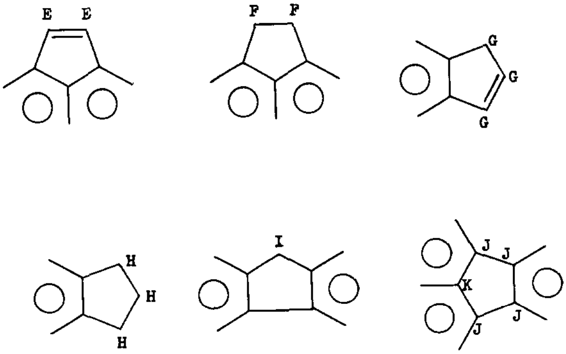
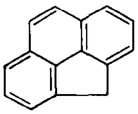
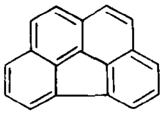


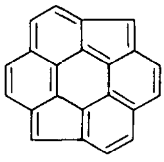
Fig. 2. Illustration of seven kinds of carbon atoms in five-membered rings of PAHFR. Acenaphthylene (E), acenaphthene (F), indene (G), indan (H), fluorene (I) and fluoranthene (J, K) ring groups are shown.

rings which occur most commonly in PAHFR. The E–I groups are the carbon atoms of five-membered rings and carry one or two hydrogen atoms. Carbon atoms common to five- and six-membered rings are considered as atoms of six-membered rings (B, C and D groups), except for the fluoranthene fragment. Fluoranthene has no carbon atoms present exclusively in a five-membered ring. The J and K groups represent the carbon atoms common to five- and six-membered rings and, as it will be seen below, their values are different from values of C and D_1 groups for benzenoid polycyclic aromatic hydrocarbons.

The groups in Figure 2 do not describe all possible PAHFR. Using these groups, we can not describe such structures as shown below.







However, there are no experimental data on the thermodynamic properties of such compounds and they are not considered in the present work.

Additivity values for A, B, C, D_1 and D_2 groups, presented in Table 1, were assumed to be the same as for polycyclic aromatic hydrocarbons consisting of six-membered rings only [8]. For the E, F, G, H, I, J and K groups, $S^{\ominus}_{\text{int}}(298.15\ \text{K})$, $H^{\ominus}(298.15\ \text{K}) - H^{\ominus}(0)$ and $C_p^{\ominus}(T)$ values were derived from the thermodynamic properties calculated by statistical mechanics methods for PAHFR from C_9H_8 to $C_{36}H_{12}$ [7]. Additivity values for the E group were based on data for 24 compounds containing the acenaphthylene fragments. Additivity values for the F and G groups were based on the data for 5 compounds with acenaphthene fragments and for 7 compounds

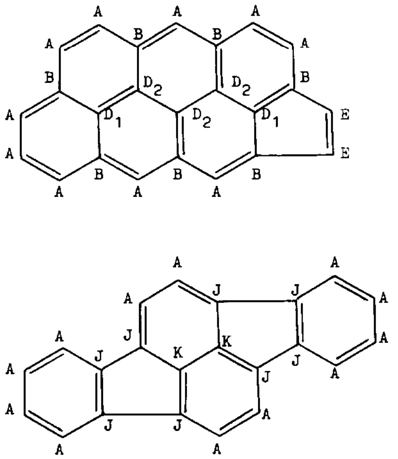


Fig. 3. Benz[mno]indeno[1,7,6,5-cdef]chrysene (top), which consists of 10 A, 7 B, 2 D_1, 3 D_2 and 2E groups: $P_{\text{add}} = 10\ A + 7\ B + 2\ D_1 + 3\ D_2 + 2\ E$. Indeno[1,2,3-cd]fluoranthene (bottom), which consists of 12 A, 8 J and 2 K groups: $P_{\text{add}} = 12\ A + 8\ J + 2\ K$.

with indene fragments. Values of the H and I group contributions were derived from the data for indan and fluorene, respectively. Data for 4 molecules with fluoranthene fragments were used for calculation of the J and K group values. Values of the group contributions to the thermodynamic properties were obtained by fitting thermodynamic properties calcu-

TABLE 1

Group additivity values for PAHFR

Group	$S^{\ominus}_{\text{int}}$(298.15 K) [a] ($J\ K^{-1}\ mol^{-1}$)	$H^{\ominus}$(298.15 K) − $H^{\ominus}$(0) ($kJ\ mol^{-1}$)	$\Delta_f H^{\ominus}$(298.15 K) ($kJ\ mol^{-1}$)
A	49.387	2.371	11.569
B	−23.189	1.072	28.858
C	−22.677	1.212	17.097
D_1	6.192	1.094	−2.710
D_2	5.767	1.011	−2.710
E	65.300	2.347	53.211
F	71.479	3.134	1.361
G	60.805	2.532	19.803
H	65.171	3.142	−14.431
I	83.412	2.704	−1.162
J	−20.007	1.801	17.097 [b]
K	26.059	−1.694	76.064

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

[b] Assumed J = C.

TABLE 1 (continued)

$C_p^{\ominus}(T)$ (J K^{-1} mol^{-1})											
100 K	200 K	298.15 K	300 K	400 K	500 K	600 K	800 K	1000 K	1200 K	1400 K	1500 K
5.150	9.563	14.777	14.875	19.894	24.061	27.385	32.243	35.605	38.035	39.830	40.551
2.356	5.763	9.375	9.442	12.839	15.698	17.990	21.178	23.122	24.348	25.155	25.456
2.903	6.447	9.890	9.954	13.201	15.960	18.185	21.296	23.199	24.402	25.196	25.492
1.116	5.704	9.464	9.527	12.611	15.092	17.035	19.685	21.271	22.263	22.910	23.152
1.101	5.135	8.724	8.787	11.887	14.443	16.473	19.277	20.973	22.037	22.736	22.998
4.874	9.042	14.132	14.227	19.036	23.027	26.235	30.971	34.282	36.686	38.469	39.185
7.836	11.811	18.096	18.229	25.354	31.684	36.938	44.931	50.663	54.871	57.999	59.226
5.626	9.762	15.429	15.542	21.320	26.204	30.155	36.037	40.184	43.204	45.441	46.339
8.372	11.523	17.628	17.761	24.968	31.427	36.801	44.976	50.826	55.112	58.292	59.569
6.184	8.976	16.355	16.516	24.789	31.673	37.085	44.938	50.413	54.394	57.342	58.526
4.552	9.334	12.796	12.853	15.681	17.975	19.808	22.369	23.944	24.943	25.605	25.855
−6.744	−9.104	−5.657	−5.559	−0.507	4.115	7.819	12.810	15.722	17.505	18.650	19.060

lated according to the additivity rules (P_{add}) to thermodynamic properties derived from statistical calculations (P_{calc}) using the least-squares method, then minimizing the sum of the squares of the absolute deviations $|P_{\mathrm{calc}} - P_{\mathrm{add}}|^2$. Examples of expressions for P_{add} are shown in Fig. 3. The average difference between values of thermodynamic functions estimated according to the group additivity scheme and values obtained by statistical calculation [7] is about 1 J K^{-1} mol^{-1} for $S^{\ominus}$(298.15 K) and $C_p^{\ominus}$(298.15 K).

TABLE 2

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

T (K)	Experimental [a]	Calculated			
		Self consistent equations (Ref. 6)	Group additivity method		
			Ref. 2	This work	Δ[b]
C_9H_8, *indene*					
298.15	336.8	336.7	–	333.6	3.2
C_9H_{10}, *indan*					
298.15	347.7	348.8	–	346.7	1.0
	350.6				3.9
$C_{12}H_8$, *acenaphthylene*					
298.15	–	361.6	364.0	357.8	–
$C_{12}H_{10}$, *acenaphthene*					
298.15	–	368.8		370.1	–
340	394.8	392.1		393.1	1.7
350	399.1	397.8		398.6	0.5
360	403.8	403.4		404.2	−0.4
366.56	407.2	407.0		407.8	−0.6
370	409.2	409.0		409.7	−0.5
380	414.7	414.6		415.2	−0.5
390	419.8	420.2		420.8	−1.0
400	425.8	425.8		426.3	−0.5
410	431.5	431.4		431.8	−0.3
$C_{13}H_{10}$, *fluorene*					
298.15	–	381.3	389.1	381.0	–
350	412.5	410.6	–	411.4	1.1
360	417.3	416.4	–	417.3	0.0
370	422.8	422.1	–	423.2	−0.4
380	428.6	427.8	–	429.1	−0.5
387.94	433.3	432.4	–	433.8	−0.5
$C_{16}H_{10}$, *fluoranthene*					
298.15	–	–	420.9	410.9	–

[a] See ref. 2 for indene and indan and ref. 1 for acenaphthene and fluorene.

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

The E–K increments of $\Delta_f H^\ominus(298.15\ \mathrm{K})$ were obtained from thermochemical data reported for indene, indan, acenaphthylene, acenaphthene, fluoranthene [3] and fluorene [2]. The values for each group were based only on data for one compound and thus the $\Delta_f H^\ominus(298.15\ \mathrm{K})$ group increments reproduce exactly the experimental values for heat of formation in the six compounds mentioned above.

CALCULATION OF THERMODYNAMIC PROPERTIES

Using the group increment values obtained in the present work (Table 1) and well known equations for thermodynamic functions (see eqns. (1)–(5) in ref. 8), we can derive the thermodynamic properties $C_p^\ominus(T)$, $S^\ominus(T)$, $-[G^\ominus(T) - H^\ominus(0)]/T$, $H^\ominus(T) - H^\ominus(0)$, $\Delta_f H^\ominus(T)$ and $\log K_f^\ominus(T)$ for temperatures from 100–1500 K for a large number of PAHFR.

Table 2 compares the entropies calculated in the present work with those determined from calorimetric studies and estimated by other authors. Reliable calorimetric entropy values are known for only two of the PAHFR considered, i.e. acenaphthene and fluorene. As can be seen from Table 2, the agreement between calculated and experimental entropies is close for these compounds. As for indene and indan, the difference between estimated and experimental values seems to fall within the uncertainties of measurement. Experimental entropies are not available for acenaphthylene and fluorene. Values estimated by various authors (see Table 2) agree within 10 J K^{-1} mol^{-1}.

The uncertainties in the $S^\ominus(298.15\ \mathrm{K})$ and $C_p^\ominus(298.15\ \mathrm{K})$ values have been evaluated as 3–15 J K^{-1} mol^{-1}, depending upon the number of fused rings, and uncertainties in the heat of formation can vary from 5–50 kJ mol^{-1}.

CONCLUSIONS

Using thermodynamic properties calculated by statistical mechanical methods, the Benson group additivity method has been developed for estimation of thermodynamic properties of PAHFR. Spectroscopic data needed for calculations of ideal gas thermodynamic properties are insufficiently reliable even for such relatively simple molecules as indene, fluorene and acenaphthene. In the present work the vibrational frequencies were calculated using the simple force field approximation. This approximation proved to be sufficiently reliable [7,9,10]. Obviously, the use of the estimated thermodynamic functions instead of experimental values reduces the accuracy of group contribution calculations, but the method proposed may be useful for calculation of thermodynamic properties of PAHFR because the experimental data are not available.

NOMENCLATURE

A, B, C, D_1, D_2, E, F, G, H, I, J, K	notation of group for PAHFR
$C_p^\ominus$	standard heat capacity at constant pressure
$-[G^\ominus - H^\ominus(0)]/T$	standard Gibbs energy
$H^\ominus - H^\ominus(0)$	standard enthalpy
$\log K_f^\ominus$	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

$\Delta_f H^\ominus$	standard enthalpy of formation
σ	symmetry number

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