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ON CALCULATION OF THERMODYNAMIC PROPERTIES OF POLYCYCLIC AROMATIC HYDROCARBONS

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ABSTRACT

Thermodynamic functions have been calculated for benzene, naphthalene, anthracene and phenanthrene in the ideal gas state using different sets of the experimental vibrational assignments and the sets of fundamentals obtained from normal coordinate analysis with various force fields. Results obtained were critically compared with available experimental and calculated data.

INTRODUCTION

As an extension of our studies of thermodynamic properties of individual substances [1,2] we proceed to calculation of thermodynamic functions for polycyclic aromatic hydrocarbons. Some preliminary results from our work on the technique of computation are presented. Spectroscopic data needed for calculations of ideal gas thermodynamic properties are insufficiently reliable even for such relatively simple molecules as naphthalene, anthracene and phenanthrene. Despite the abundant spectroscopic data for these compounds, the various interpretations have differed substantially from one another, and to achieve agreement of experimental values for entropy with those spectroscopically calculated, some experimental frequencies have often favored insufficiently valid interpretations (see, for example, refs. 3–5).

Cyvin et al. [6–20] have proposed for polycyclic aromatic hydrocarbons a simple force field approximation with only ten parameters (five parameters both for the in-plane and for the out-of plane vibrations). This simple force field has been successfully applied to a number of polycyclic aromatic hydrocarbons [6–20]. The purpose of this work is to show that the force field approximation of Cyvin et al. may be useful for calculation of thermodynamic properties of polycyclic aromatic hydrocarbons.

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TABLE 1

Comparison of experimental and calculated entropies for benzene

Temperature (K)	Entropy (J K^{-1} mol^{-1})		
	Experimental [21]	Calculated, present work [a]	
		Calculated from spectroscopic data [b]	Calculated from Cyvin's approximation [7,9]
298.15	269.7 ± 0.5	269.4	270.0
353.26	285.0 ± 0.5	284.7	285.7

[a] The product of the principal moments of inertia was calculated using the structural parameters determined by Tamagawa et al. [22] from combined electron diffraction and spectroscopic data.

[b] The vibrational assignment of Brodersen and Langseth [23] was adopted in this work except for six frequencies which were taken from more recent investigations [24–27].

We have calculated the thermodynamic functions of benzene, naphthalene, anthracene and phenanthrene using different sets of the experimental vibrational assignments and the sets of fundamentals obtained from computation with various force fields. To determine the degree of reliability and accuracy of the calculated thermodynamic properties, we have compared the spectroscopically calculated entropy values with the available experimental values (Tables 1–4).

RESULTS

Benzene

Different experimental and calculated frequencies have led to entropy values which are in agreement with experimental data. Table 1 shows the entropy values calculated with experimental frequencies [23–27] and with those obtained from the simple force field approximation of Cyvin et al. [7,9].

Naphthalene

Although in general there is a reasonable agreement between the calculated spectroscopic ideal gas state values for entropy and experimental entropy values (third law entropies), the available disagreement of experimental entropies has hampered the evaluation of the reliability of the different calculated entropy values (Table 2). (Only a large disagreement between the experimental entropies and calculated counterparts for recent

TABLE 2

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

Temperature (K)				Authors and year of cited references	
298.15	353.43	451.0	522.7	References for the experimental determination of entropy or its calculation	References for the vibrational assignments used in the entropy calculation
Experiment					
		405.2 ± 1.8	436.9 ± 1.8	Barrow, McClellan, 1951 [28]	
333.35 ± 0.53	357.87 ± 0.37			Chen et al., 1979 [3]	
334.0 ± 0.6		404.3 ± 0.5	436.2 ± 0.3	Lielmezs et al., 1981 [5] [a]	
Calculation with the experimental vibrational assignments					
336.5		405.5	437.1	McClellan, Pimentel, 1955 [29]	[b]
333.15	357.84	401.68	433.33	Chen et al., 1979 [3]	[b]
332.8	357.8	402.1	434.0	Lielmezs et al., 1981 [5]	[b]
333.4	358.2	402.2	433.9	This work [c]	Krainov, 1964 [30]
332.1	356.7	400.4	432.1	This work [c]	Ohno, 1978 [31] (in-plane); Pietilä, Stenman, 1978 [32] (out-of-plane)
337.7	363.1	407.9	440.0	This work [c]	Behlen et al., 1981 [33]
Calculations with the computed frequencies					
334.4	359.3	403.3	435.1	This work [c]	Krainov, 1964 [30]
333.4	358.0	401.8	433.4	This work [c]	Ohno, 1978 [31] (in-plane); Pietilä, Stenman, 1978 [32] (out-of-plane)
334.2	359.4	404.0	436.0	This work [c]	Cyvin et al., 1980 [6,9]

[a] Lielmezs et al. have compiled the third law entropies for naphthalene (see Table 5 in ref. 5). Their averaged values (except for the three extreme ones for 298.15 K) are presented in this Table.

[b] The frequencies were selected from different vibrational assignments in such a way as to give a better agreement between the calculated and experimental entropies.

[c] The product of the principal moments of inertia was calculated using the structural parameters determined by Ketkar and Fink [34] from electron diffraction data.

TABLE 3

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

Temperature (K)			Authors and year of cited references	
298.15	392.5	500	References for the experimental determination of entropy or its calculation	References for the vibrational assignments used in the entropy calculation
Experiment				
398.32			Stein et al., 1977 [35]	
393.1±5	457.6±5	514.9±5	Kudchadker et al., 1979 [4]	
Calculations with the experimental vibrational assignments				
392.6	451.6	518.0	Kudchadker et al., 1979 [4]	[a]
391.4	450.0	515.8	This work [b]	Bree, Kydd, 1969 [36]
385.0	442.9	508.4	This work [b]	Cyvin et al., 1980 [6,10]
Calculations with the compared frequencies				
385.6	443.6	509.2	This work [b]	Neto et al., 1966 [37] (in-plane) Evans, Scully, 1964 [38] (out-of-plane)
389.8	448.2	514.0	This work [b]	Krainov, 1964 [39]
389.8	449.2	515.9	This work [b]	Cyvin et al., 1980 [6,10]

[a] The frequencies were selected from different vibrational assignments in such a way as to give a better agreement between the calculated and experimental entropies.

[b] The product of the principal moments of inertia was calculated using the structural parameters determined by Ketkar et al. [40] from an electron diffraction study.

vibrational assignment of Behlen et al. [33] permits us to assume that the above assignment is erroneous.)

The thermodynamic properties of naphthalene in the ideal gas state have been calculated by many investigators (see [5]). McClellan and Pimentel [29] have adopted vibrational frequencies which gave good agreement between calculated entropies and the experimental values of Barrow and McClellan [28] (Table 2). Chen et al. [3] and Lielmezs et al. [5] have favored the vibrational assignments which gave a better fit between the calculated and experimental entropy values obtained by Chen et al. [3]. The entropy values calculated in the present work (Table 2) were obtained by using the different sets of experimental and computed frequencies. It should be noted that the simple force field approximation of Cyvin et al. [6,9] gives a good agreement between the calculated values for entropy and the experimental results obtained by averaging the values taken from the works of various investigators. (The latest were compiled by Lielmezs et al. [5] and their averaged values are presented in Table 2).

TABLE 4

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

Temperature (K)										Authors and year of cited references	
298.15	300	310	320	372.385	380	390	400	410	420	References for the experimental determination of entropy or its calculation	References for the vibrational assignments used in the entropy calculation
Experiment											
				443.04	447.58	453.29	459.09	464.96	471.24	Finke et al., 1977 [41]	
391.2	392.6	400.3	408.2							Kudchadker et al., 1979 [4]	
Calculation with the experimental vibrational assignments											
394.5	395.7	402.0	408.2	442.3	446.6	452.4	458.3	464.4	470.6	Kudchadker et al., 1979 [4]	[a]
396.7	397.9	404.2	410.6	444.0	448.9	455.2	461.6	467.9	474.3	This work [b]	Schettino et al., 1966 [42]
389.7	390.8	396.9	403.0	435.1	439.8	445.9	452.1	458.2	464.4	This work [b]	Bree et al., 1972 [43]
Calculations with the computed frequencies											
395.6	396.7	402.9	409.2	442.1	446.9	453.2	459.4	465.7	471.9	This work [b]	Schettino et al., 1966 [42] (in-plane); Bree et al., 1972 [43] (out-of-plane)
392.6	393.8	399.9	406.1	438.6	443.3	449.6	455.8	462.0	468.2	This work [b]	Altmann, Perkampus, 1979 [44] (in-plane); Bree et al., 1972 [43] (out-of-plane)
395.2	396.4	402.7	409.0	442.0	446.8	453.1	459.4	465.7	471.9	This work [b]	Cyvin et al., 1981 [14]

[a] The frequencies were selected from different vibrational assignments in such a way as to give a better agreement between the calculated and experimental entropies.

[b] The product of the principal moments of inertia was calculated using the structural parameters determined by Kay et al. [45] from a neutron diffraction study.

Anthracene

Large variations in the third law entropy values occur for anthracene due to the variation in the values for enthalpy of sublimation and vaporization. For that reason the comparison of experimental and spectroscopic entropies is of little interest. It should be noted, however, that entropy values calculated with the force field approximation of Cyvin et al. [6,10] are close to those calculated from the most reliable experimental vibrational assignment of Bree and Kydd [36] (Table 3).

Phenanthrene

Finke et al. [41] deduced the ideal gas thermodynamic properties for phenanthrene from 372 to 420 K using the experimental thermodynamic properties in the solid and liquid states obtained from the calorimetric measurements. Thus, reliable experimental entropy values are available for phenanthrene and the comparison of experimental and calculated values is especially interesting in this case.

The experimental vibrational assignment of Schettino et al. [42] leads to somewhat over-estimated entropy values, while the assignment of Bree et al. [43] leads to essentially under-estimated results (Table 4). Kudchadker et al. [4] selected a set of vibrational frequencies using these two assignments which gave a much better fit between the calculated and experimental entropy values than did the set of Schettino et al. or Bree et al. However, no normal coordinate analysis has confirmed the assignments of some frequencies adopted by Kudchadker et al. [4].

The simple force field of Cyvin et al. [14] as well as the more complex force field of Schettino et al. [42] (in-plane vibrations) and Bree et al. [43] (out-of-plane vibrations) gives entropy values which agree well with experimental data.

DISCUSSION

The group or bond additivity techniques have been extensively applied to the prediction of thermodynamic properties of organic compounds. Kudchadker et al. [46] have developed such a method for calculation of thermodynamic properties of polycyclic aromatic hydrocarbons. Using the available data on fundamental frequencies and molecular structure for key compounds such as benzene, naphthalene, anthracene, phenanthrene, pyrene, triphenylene and perylene and with the application of the concept of triatomic additivity [47] ideal gas thermodynamic properties for polycyclic aromatic hydrocarbons containing six membered rings have been predicted from 298.15 to 1500 K. The inaccuracies of this method resulted from the inaccuracy of vibrational frequency assignments for key compounds (errors in the structural parameters should not change the calculated thermodynamic functions greatly) and from the inaccuracies of the additivity scheme. The first type of inaccuracy, as is seen from the data presented in Tables 2–4, may be fairly large due to the complexity of vibrational spectra of polycyclic aromatic hydrocarbons. For that reason and taking into account results obtained in this work for naphthalene, anthracene and phenanthrene, we believe that the simple force field approximation of Cyvin et al. [6–20] is more suitable for the estimation of thermodynamic functions of polycyclic aromatic hydrocarbons than such methods as proposed by Kudchadker et al. [46]. Furthermore, a convenient procedure for computation of thermodynamic properties of polycyclic aromatic hydrocarbons can be developed on the basis of Cyvin's approximation because of its simplicity and small number of parameters. In principle such a procedure requires only the structural formula of a molecule to be known (the structural parameters, if unknown, can be easily estimated for this class of compounds).

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