CHEMICAL THERMODYNAMICS OF POLYAROMATIC COMPOUNDS CONTAINING HETEROATOMS AND FIVE-MEMBERED RINGS

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ABSTRACT

An analysis of chemical thermodynamic properties of gaseous polynuclear aromatic compounds containing N-, S-, and O-heteroatoms and five-membered rings is presented. Standard enthalpies of formation, entropies and heat capacities taken from the literature, or derived from appropriate data, serve as the data base for this analysis. Enthalpies of formation are used to compute empirical resonance energies for polynuclear heteroaromatic structures which, in turn, allow critical examination of this property. An additive method is described for estimating entropies and heat capacities. New or revised values for thermodynamic properties for a number of polyaromatic substances are presented and recommended values for some common polyaromatics are given.

INTRODUCTION

At elevated temperatures organic substances tend to degrade to a mixture of low molecular weight gases and high molecular weight solids. At these temperatures, polynuclear heteroaromatic structures can be formed in substantial quantities, depending on particular reaction conditions and nature of reactants, even though the formation of nitrogen, oxygen, and sulfur as light gases is thermodynamically favored. Also, even though carbon tends to polymerize in benzenoid structures leading ultimately to graphite, five-membered ring structures are common pyrolysis products. The formation of substances containing polynuclear heteroaromatic and five-membered ring structures (PHFR) in high-temperature pyrolysis may be ascribed to their relative ease of formation and their resistance to free-radical attack.

Values for chemical thermodynamic properties of PHFR are scant and often of low accuracy. These values are needed for furthering the study of organic pyrolysis chemistry (e.g., coal pyrolysis) and an effort is made here to collect, calculate, evaluate, and extend this data. The basic goals of this work are to provide a data base for common PHFR usable for approximate equilibrium calculations and, where possible, to develop estimation methods for these properties.

The properties considered here are standard enthalpies of formation, entropies, and heat capacities. Enthalpies of formation are discussed independently since this property is strongly influenced by resonance stabiliza-

tion. An empirical resonance energy term is defined to allow comparison of resonance energies of different PHFR. A ring-additivity method is suggested for estimating entropies and heat capacities of PHFR. Recommended chemical thermodynamic properties of common PHFR are tabulated.

DATA BASE

Chemical thermodynamic properties of gas-phase PHFR and single-ring heteroaromatics obtained from the literature are listed in Table 1. It should be noted that published error limits given in Table 1 for enthalpies of formation of PHFR are generally based on experimental precision and in many cases are too small. For instance, the published gas-phase enthalpy of formation of indole was 44.6 ± 1.1 kcal mole^{-1} [1] until more accurate combustion measurements yielded 37.4 ± 0.4 kcal mole^{-1} [2]. Also, heats of sublimation at 298 K used for obtaining gas-phase enthalpies of PHFR from condensed phase values are, in many cases, of questionable reliability, as can be discerned by the sometimes large disagreement between different workers [3,4]. Therefore, available gas-phase enthalpies of formation of PHFR are generally somewhat less accurate than enthalpies of formation of substances of lower molecular weight and higher volatility. On the other hand, available enthalpies of formation, entropies and heat capacities for single-ring substances are quite reliable; these values form a good basis on which to build an approximation scheme for PHFR. There is a complete lack of published entropy and heat capacity data for gaseous PHFR.

Chemical thermodynamic properties of gas-phase PHFR that have been derived here for the first time or revised are compiled in Table 2. Enthalpies of formation given here (Table 2A) are the sum of condensed-phase enthalpies of formation taken from the literature and enthalpies of vaporization/ sublimation obtained from one of several sources: directly from the literature (fluorene); derived from vapor pressure data (quinoline, isoquinoline); estimated using values of similar substances (dibenzothiophene, benzothiophene); derived from vapor pressure and entropy values (quinoline, benzothiophene). Enthalpies of vaporization of quinoline and isoquinoline were derived from a least-squares fit of published vapor pressure data [5] to the Clausius—Clapeyron equation. The enthalpy of sublimation of dibenzothiophene was estimated as the average of measured enthalpies of sublimation of fluorene, carbazole and dibenzofuran (19.8 [6], 20.2 [1] and 21.2 [1] kcal mole^{-1}, respectively); for benzothiophene the average of the enthalpies of sublimation for supercooled indene and indole was used (15.0 [7a] and 16.7 [1] kcal mole^{-1}, respectively).

Gas-phase entropies obtained from thermal data for indan and indene are given in Table 2B. Uncertainties in their entropy of vaporization is the major source of error (2—3 cal mole^{-1} K^{-1}).

Entropies and heat capacities of carbazole, dibenzothiophene, anthracene, and acenaphthene (Table 2C,D) have been derived from published crystal structure data and complete vibrational assignments. Uncertainty of the lowest lying bending frequencies is expected to be the major factor limiting

TABLE 1

Chemical thermodynamic quantities from the literature

A. *Standard enthalpies of formation and intrinsic entropies for substances containing five-membered rings*
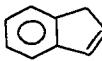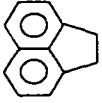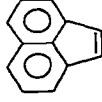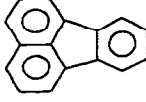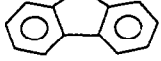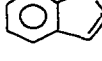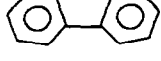
	$\Delta H^{o}_{f,298}$ (gas)	$S^{o}_{298,int}$ (gas)
1,3-Cyclopentadiene	31.94 ± 0.28 [a]	66.7 [b]
Indene	39.08 ± 0.37 [a]	
Acenaphthene	37.4 ± 0.7 [a]	
Acenaphthylene	61.6 ± 1.2 [a]	
Fluoranthene	69.78 ± 0.56 [a]	
Furan	−8.30 ± 0.15 [a]	65.2 [c]
Dibenzofuran	19.9 ± 1.2 [a]	
Pyrrole	25.88 ± 0.11 [a]	66.0 [d]
Indole	37.4 ± 0.4 [a,e]	
Carbazole	50.1 ± 0.9 [a]	
Thiophene	27.59 ± 1.5 [a]	68.0 [f]

Table 1 (continued)

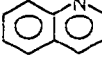*B. Standard enthalpies of formation (kcal mol^{-1}) for aromatic nitrogen heterocycles*
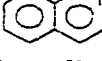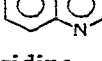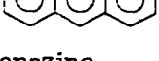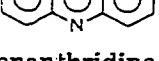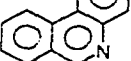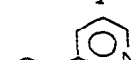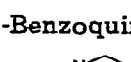
	$\Delta H^{\circ}_{f,298}$ (experimental)	$\Delta H^{\circ}_{f,298}$ (estimated) [n]	Δ
Pyridine	34.55 ± 0.12 [a]	33.8	+0.8
Pyrimidine	47.0 ± 0.3 [a]	47.8	−0.8
Pyrazine	46.9 ± 0.3 [a]	47.8	−0.9
Quinoline	51.8 ± [1] [g,m]	49.8	−2.0
Isoquinoline	48.2 ± [2] [g]	49.8	−1.6
Quinoxaline	62.7 ± 1 [h]	63.8	−1.9
Acridine	69.9 ± 1.7 [h]	68.4	+1.5
Phenazine	80.7 ± 1.5 [h]	82.4	−1.7
Phenanthridine	58.2 ± 1.3 [i]	64.0	−5.8
5,6-Benzoquinoline	55.9 ± 1.8 [i]	64.0	−8.1
7,8-Benzoquinoline	55.19 ± 1.2 [i]	64.0	−8.3

Table 1 (continued)

C. Heat capacities [p] (cal mole^{-1} K^{-1})

	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K	2000 K	2500 K
Cyclopentadiene [b]	18.56	23.94	29.46	33.96	40.67	45.38	52.34	55.80	57.66
Furan [e]	15.73	21.23	25.77	29.35	34.45	37.91	42.95	45.45	46.81
Pyrrole [d]	17.17	23.18	28.12	32.04	37.69	41.60	47.48	50.43	52.08
Pyridine [j]	18.76	25.31	30.91	35.44	42.06	46.59	53.13	56.31	58.03
Benzene [k]	19.71	26.95	33.10	38.06	45.35	50.39	57.78	61.42	63.41
Thiophene [f]	17.51	22.98	27.31	30.65	35.39	38.61	43.36	45.72	47.01
Naphthalene [l]	31.89	42.83	52.13	59.67	70.77	78.55	89.41	94.66	97.49

[a] J.D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, New York, 1970.

[b] R.M. Joshi, J. Polym. Sci., Part A-2, 8 (1970) 679.

[c] D.W. Scott, J. Mol. Spectrosc., 37 (1971) 77.

[d] D.W. Scott, W.T. Berg, I.A. Hosenlopp, W.N. Hubbard, J.F. Messerly, S.S. Todd, D.R. Douslin, J.P. McCollough and G. Waddington, J. Phys. Chem., 71 (1967) 2263.

[e] W.D. Good, J. Chem. Eng. Data, 17 (1972) 28.

[f] M. Rico, J.M. Orza and J. Morcillo, Spectrochim. Acta, 21 (1965) 689.

[g] See Table 2, this work.

[h] D.M. McEachern, O. Sandoval and J.C. Iniguez, J. Chem. Thermodyn., 7 (1975) 299.

[i] D.M. McEachern, J.C. Iniquez and H.C. Overlas, J. Chem. Eng. Data, 20 (1975) 226.

[j] J.P. McCollough, D.R. Douslin, J.F. Messerly, I.A. Hossenlopp, T.C. Kincheloe and Guy Waddington, J. Am. Chem. Soc., 79 (1957) 4290.

[k] T. Shimanouchi, Tables of Molecular Frequencies, Consolidated Volume I, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., 39 (1972).

[l] S.S. Mitra and H.J. Bernstein, Can. J. Chem., 37 (1959) 553.

[m] $S_{int}^{o} \equiv S^{o} + R \ln \sigma$, where σ is the rotational symmetry number.

[n] Obtained by adding 14.0 kcal/mole-N-atoms to enthalpies of formation of corresponding hydrocarbons, using heats of formation of hydrocarbons chosen in ref. 9.
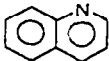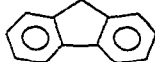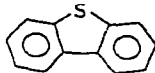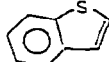
[o] Values in parentheses are estimates by the author.

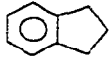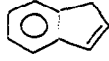[p] These values have been derived from the vibrational assignments given in each reference.

TABLE 2

Chemical thermodynamic quantities derived in this work

A. *Standard heats of formation (kcal mole⁻¹)*

	$\Delta H^o_{f,298}$ (condensed)	$\Delta H^o_{vap/sub,298}$	$\Delta H^o_{f,298}$ (gas)
Quinoline	37.44 ± [1] (l) [a]	14.4 ± [0.3] [b]	51.8 ± 1.3
		13.4 ± [1.5] [c]	50.8 ± 2.5
Isoquinoline	34.7 ± 0.2 (l) [c]	13.5 ± [1.5] [c]	48.2 ± 1.7
Fluorene	24.02 ± 0.31 (s) [q]	19.8 ± [1.5] [e]	43.8 ± 1.8
Dibenzothiophene	28.76 ± 0.35 (s) [f]	20.4 ± [1.5] [g]	49.3 ± 1.9
Benzothiophene	24.11 ± 0.22 (s) [f]	16.2 ± [0.3] [b]	40.3 ± 0.8
		15.9 ± [2] [g]	40.0 ± 2.2
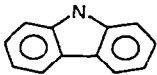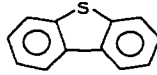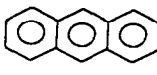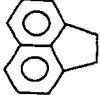
B. *Entropies (cal mole⁻¹ K⁻¹) from thermal data*

	S^o_{298} (liquid)	$\Delta S^o_{298,vap}$	S^o_{298} (gas)	$S^o_{298,intrinsic}$ (gas)
Indan	56.01 [h]	27.09 [i]	83.1	84.5
		27.80 [h]	83.8	85.2
Indene	51.19 [h]	29.35 [h]	80.5	80.5

the accuracy of these entropy values (2—3 cal mole⁻¹ K⁻¹). Heat capacity values are somewhat less sensitive to such uncertainties and are expected to be accurate to within 2 cal mole⁻¹ K⁻¹. Zwolinski and co-workers [7b] recently reported values for the ideal gas entropy and heat capacity of anthracene based on somewhat different vibrational models than those chosen in the present work. Their values agree with the present values within the above error limits.

Table 2 (continued)

C. Entropies (cal mole⁻¹ K⁻¹) from molecular properties

C. Entropies $(cal\,mole^{-1}\,K^{-1})$ from molecular properties

	$S^\circ_{298,vib}$	$S^\circ_{298,trans.rot.}$	S°_{298} (gas)	$S^\circ_{298,int}$ (gas)
Carbazole	22.50 [j]	71.84 [k]	92.9	94.3
Dibenzothiophene	21.26 [l]	72.67 [k]	92.5	93.9
Anthracene	22.21 [m]	72.51 [n]	92.0	94.7
Acenaphthene	18.00 [o]	70.86 [p]	87.5	88.9

(Table 2 continues overleaf)

ENTHALPIES OF FORMATION

To examine PHFR thermochemistry, it is useful to define an empirical resonance energy (ERE) term to account for resonance energy attributable to the heteroatomic ring. For substances containing a heteroatom in a five-membered ring, a suitable definition of ERE can be made with reference to the following series
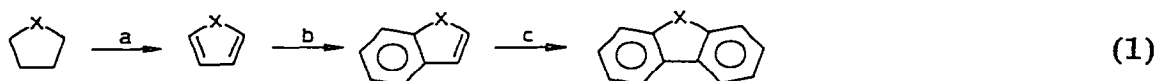
$$\bigotimes \xrightarrow{a} \bigotimes \xrightarrow{b} \bigotimes \xrightarrow{c} \bigotimes \qquad (1)$$

where X = CH$_2$, NH, O and S. The change in ERE for the ith step is defined as $\Delta ERE = \Delta H^0_{298}$ (i, CH$_2$) $- \Delta H^0_{298}$ (i, X). Here ΔH^0_{298} (i, CH$_2$) is the enthalpy difference in the ith step for the hydrocarbon case and ΔH^0_{298} (i, X) is the corresponding enthalpy difference for PHFR containing heteroatoms. Of course, any empirical definition of resonance energy inherently includes strain energy as well. Strain resulting from introduction of double bonds and the fusion of five and six-membered rings is probably relatively small; in any case, the above definition of ERE affords a useful means of comparing PHFR thermochemical stabilities. The hydrocarbon series is taken as reference since changes in resonance energies are expected to be small for steps a, b, and c in eqn. (1). Enthalpies of formation, ΔERE and $\Sigma \Delta ERE$ values for substances in sequence (1) are given in Table 3. $\Sigma \Delta ERE$ is the sum of ΔERE for steps a, b, and c and roughly corresponds to the net thermochemical

Table 2 (continued)

D. Heat capacities, $C^o_{P,T}$ (cal mole^{-1} K^{-1}), from molecular properties

	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K	2000 K	2500 K
Carbazole [j]	40.97	54.25	65.55	74.72	88.16	97.31	110.37	116.67	120.07
Dibenzothiophene [l]	39.52	52.18	62.99	71.80	84.68	93.41	105.73	111.59	114.72
Anthracene [m]	43.45	58.92	71.80	82.08	96.92	106.90	121.06	127.80	131.50
Acenaphthene [o]	39.10	52.66	64.13	73.43	87.15	96.56	110.03	116.51	119.97

[a] International Critcal Tables, V, McGraw-Hill, New York, 1928, p. 168.
[b] See Table 5.
[c] Derived from vapor pressure data given in ref. 5.
[d] D.R. Stull, E.F. Westrum and G.C. Sinke, The Chemical Thermodynamics of Organic Compounds, Wiley, New York, 1969.
[e] See ref. 6.
[f] W.D. Good, J. Chem. Eng. Data, 17 (1972) 158.
[g] Average of ΔH_{sub} for similar substances (see text).
[h] See ref. 7a.
[i] D. Ambrose and C.H.S. Sprake, J. Chem. Thermodyn., 9 (1976) 601.
[j] A. Bree and R. Zwarich, J. Chem. Phys., 49 (1968) 3344.
[k] R.M. Schaffrin and J. Trotter, J. Chem. Soc. A, (1970) 1561.
[l] A. Bree and R. Zwarich, Spectrochim. Acta., Part A, 27 (1971) 599.
[m] D.J. Evans and D.B. Scully, Spectrochim. Acta, 20 (1964) 891; N. Neta, M. Scrucco and S. Califano, Spectrochim. Acta, 22 (1966) 1981. C^o_P values obtained in ref. 7b are greater than these values by $\lesssim 1$ cal mole^{-1} K^{-1}. The lack of exact agreement is apparently due to different sources of vibrational frequencies.
[n] D.W.J. Cruickshank, Acta. Crystallogr., 9 (1956) 915.
[o] A. Bree, R.A. Kydd and T.N. Misra, Spectrochim. Acta., Part A, 25 (1969) 1815.
[p] H.W.H. Ehrlich, Acta Crystallogr, 10 (1957) 699.
[q] W.D. Good, private communication.

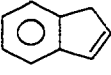stability attributable to the heteroatomic five-membered ring in each dibenzo-compound.
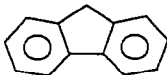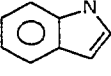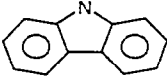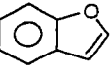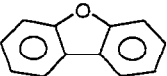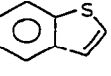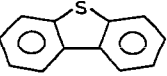
Of all of the series, the X = NH series shows the greatest amount of thermochemical stability due to the heteroatom; in fact, about half of ERE present in pyrrole is present in carbazole ($\Sigma\Delta$ERE = 11.3 kcal mole^{-1}). Thus, the pyrrolic ring system interacts strongly with adjacent aromatic structures and the enthalpies of formation for such substances show no signs of being estimable by additive methods.

For the X = O series, on the other hand, within experimental accuracy, far less resonance energy can be attributed to the heteroatomic ring. In fact, from a thermochemical viewpoint, the hetero-ring in dibenzofuran is not involved in the resonance system. The O atom in this compound effectively isolates the two resonance structures to which it is attached. Therefore, it seems reasonable to assign a single enthalpy of formation ring-group value of 14.1 kcal mole^{-1} for heteroatomic rings of the type present in dibenzofuran.

It is worth noting that for the X = NH and X = O series, MO calculations [8] based on the same experimental enthalpies of formation as employed here lead to similar conclusions about the thermochemistry of these heteroatoms in aromatic systems, namely, that the N atom contributes significantly

TABLE 3

Enthalpy of formation and empirical resonance energies [a]

			$\Sigma\Delta$ ERE
0.0 → 0.0 → 0.0 →			0.0
$\Delta H^{\circ}_{f,298}$ −18.4 31.9 39.1 43.8[b]			
23.6 → −4.3 → −8.0 →			11.3
$\Delta H^{\circ}_{f,298}$ −0.8 25.9 37.4[c] 50.1			
14.6 → −7.6 → −8.7 →			−1.7
$\Delta H^{\circ}_{f,298}$ −44.0 −8.3 [6.5][d] 19.9			
14.6 → −5.5 → −4.6 →			45
$\Delta H^{\circ}_{f,298}$ −8.1 27.6 40.3[e] 49.3[e]			

[a] All values are in kcal mole^{-1}; ΔERE are given above each arrow; except where noted all $\Delta H^{\circ}_{f,298}$ are taken from ref. 1.
[b] W.D. Good, private communication. Estimation methods [10] give a value of 45.
[c] Ref. 2.
[d] Estimated from relative resonance energy calcualtions given in ref. 8a using correct $\Delta H^{\circ}_{f,298}$ for furan and dibenzofuran.
[e] Given in Table 2.

to the "resonance energy" and the O atom does not. The magnitude of computed MO "resonance energy" differs from present values due to different definitions of resonance energy.

The thermochemical behavior for the X = S series is intermediate between the X = NH and X = O series and 4.5 kcal mole^{-1} of ERE is attributable to the ring containing sulfur in dibenzothiophene (11.3 kcal mole^{-1} remained in carbazole while −1.7 kcal mole^{-1} remained in dibenzofuran). Thiophene has the same ERE as furan, but loses less of this energy after fusion of benzenoid rings. Thus, in these substances, the S-heteroatomic ring interacts with the entire resonance system and no simple method for estimation of enthalpies of formation of related PHFR is apparent.

Substitution of a N atom for a benzenoid C—H group in polynuclear aromatic substances leads to an increase of ~14.0 kcal mole^{-1} (N atom)$^{-1}$ in the enthalpy of formation in benzene-, naphthalene- and anthracene-type structures (Table 1B). Use of this value with appropriate hydrocarbon enthalpies of formation leads to estimated values with an average deviation of ±1.3 kcal mole^{-1} for such structures; this is within the range of experimental uncertainty for naphthalene- and anthracene-type structures. In the phenanthrene ring system, such substitution apparently leads to structures with an additional stability of 8 ± 2 kcal mole^{-1}. These data lead to a difference in enthalpy of formation between anthracene-like structures and phenanthrene-like structures of ~12 kcal mole^{-1}, whereas the measured difference in enthalpies of formation of anthracene and phenanthrene is only ~5 kcal mole^{-1}. These results cannot be reproduced by existing theoretical calculations; in fact, MO calculations predict that substitution of a N atom for a benzenoid C—H group has no substantial effect on the magnitude of the resonance energy [8]. Until further experimental data are available, estimation of enthalpies of formation of benzenoid structures containing N-heteroatoms by any means must be regarded as uncertain.

ENTROPY AND HEAT CAPACITY

The principle of additivity of chemical thermodynamic properties, so successfully applied to acyclic substances, is expected to be directly applicable to entropy and heat capacity estimation of PHFR. This expectation is based on the relative insensitivity of vibrational frequencies and molecular geometry to the magnitude of resonance energy. In addition, within experimental accuracy, additivity of these properties has been shown to be applicable to benzenoid polynuclear aromatic substances [9]. Predictive methods developed for polycyclic hydrocarbons also support the idea of additivity for cyclic systems [10].

In principle, any of several existing additive methods can provide a framework for estimation of PHFR properties. In particular, the method presented by O'Neal and Benson [10a] could be extended to the classes of substances of interest in this paper. However, such methods make formal use of structural intermediates whose thermodynamic properties are not known, and several parameters would have to be introduced for each type of hetero-

ring. For the limited class of substances considered here, we feel that the number of variables introduced by previous methods is unneccessary, particularly in view of the amount of reliable data available. Hence, a more direct approach, employing "ring-group additivity", is used for PHFR. This direct extension of additive methods views each particular PHFR as being constructed from a single starting ring to which are added appropriate rings, one at a time, and is entirely consistent with the more general method of O'Neal and Benson. Each ring has a unique ring-group value for entropy and heat capacity; certain rings can be assigned enthalpy of formation values. Substituents and biphenyl-type linkages can be added as necessary utilizing existing group values [11]. Of course, additive methods for entropy yield intrinsic entropy, $S^0_{int} = S^0 - R \ln(n/\sigma)$, where n is the number of optical isomers and σ is the number of rotational isomers.

The ring-group entropy contribution of a benzenoid ring fused to a π-bond is taken as the average of the intrinsic entropy changes for the following condensations

69.3 [12]   83.2 [13]

$$\Delta S^0_{int,298} = 13.9 \text{ cal mole}^{-1} \text{ K} \quad (2)$$

74.3 [12]   88.4 [13]

$$\Delta S^0_{int,298} = 14.1 \text{ cal mole}^{-1} \text{ K}^{-1} \quad (3)$$

70.6 [12]   84.5
($\sigma = 2$)   85.2 (Table 2B)

$$\Delta S^0_{int,298} = 13.9 \text{ cal mole}^{-1} \text{ K}^{-1} \quad (4)$$
$$14.6$$

66.7   80.5
(Table 1A) (Table 2B)

$$\Delta S^0_{int,298} = 13.8 \text{ cal mole}^{-1} \text{ K}^{-1} \quad (5)$$
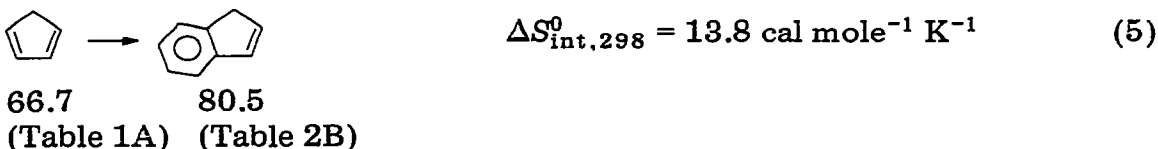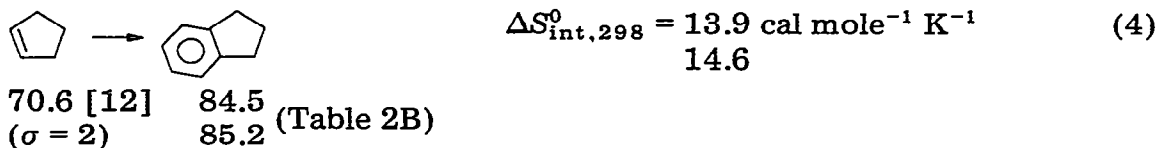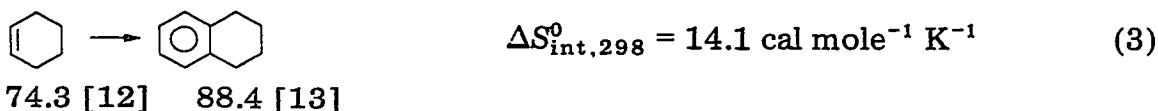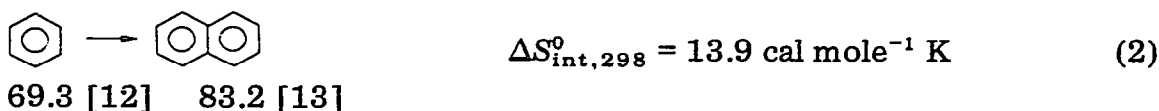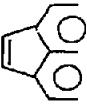
Intrinsic entropies and associated references are given beneath each compound. The constancy of these entropy changes implies that this ring-group value is quite reliable since it is not dependent on the detailed nature of the structure to which the ring is attached. Even the fusion of a benzenoid ring onto ethylene to form benzene results in an increase in standard intrinsic entropy of 14.1 cal mole^{-1} K^{-1} as shown in reaction (6). The heat capacity

55.2 [12]   69.3 [13]
($\sigma = 4$)

$$\Delta S^0_{int,298} = 14.1 \text{ cal mole}^{-1} \text{ K}^{-1} \quad (6)$$
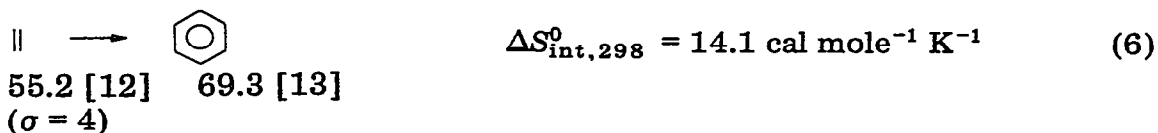
contribution of this ring-group is taken as $\Delta C^0_{P,T}$ for reaction (2) since $\Delta C^0_{P,T}$ values for the other reactions are not well established. Tables of heat capacities for benzene and naphthalene are given in Table 1C. Derived ring-group

TABLE 4

PHFC ring-group values

	$\Delta H^{\circ}_{f,298}$ (kcal mole^{-1})	$S^{\circ}_{298,\text{int}}$ (cal mole^{-1} K^{-1})	$C^{\circ}_{P,T}$ (cal mole^{-1} K^{-1})								
			300	400	500	600	800	1000	1500	2000	2500
A.	16.2 [14.0] [a]	14.0	12.18	15.88	19.03	21.61	25.42	28.16	31.63	33.24	34.08
B.		13.7	11.22	14.23	16.84	18.99	22.13	24.36	26.98	28.13	28.70
C.	19.3	11.4	11.03	12.87	15.39	17.51	20.74	23.15	26.19	27.62	28.33
D.		10.7	9.64	12.11	14.05	15.59	17.76	19.37	21.33	22.25	22.75
E.	[14.1] [b]	9.9	8.19	10.16	11.70	12.90	14.52	15.68	16.80	17.27	17.48
F.		12.7	9.98	11.91	13.24	14.20	15.46	16.38	17.21	17.54	17.68
G.		5.4	5.75	7.21	8.16	8.97	10.06	10.52	11.29	11.58	11.69

[a] For ring in phenanthrene-like system, see ref. 9.
[b] Only accurate for dibenzofuran-type systems.

values are tabulated in Table 4. Fusion of a benzene ring to a double-bonded substrate is labelled ring-group A in Table 4.

Note that the entropy of group A predicted by group additivity values given in ref. 9 is 1.5 cal mole^{-1} K^{-1} lower than the value chosen here. The present value is preferred since it is based on far more accurate entropy values and fits the experimental data given in ref. 9 within the stated error limits. The heat capacity estimates for group A from values given in ref. 9 are virtually the same as those used here.

It is also interesting to note that use of entropy estimates given in ref. 7a leads to the prediction that fusion of a benzenoid ring (group A) onto naphthalene to form anthracene and phenanthrene results in increases in intrinsic entropy of 13.6 and 12.7 cal mole^{-1} K^{-1}, respectively. Considering uncertainties in the entropies of anthracene and phenanthrene (± 1.2 cal mole^{-1} K^{-1} given in ref. 7b), these values are in reasonable agreement with the entropy value of 14 cal mole^{-1} K^{-1} chosen for group A.

Five-membered ring-groups C, D, E, and F were obtained in the following manner. Properties of indene, indole, benzofuran, and benzothiophene were estimated from corresponding properties of cyclopentadiene, pyrrole, furan and thiophene, respectively, using ring-group A values. Subtraction of the benzene value results in the desired ring-group value, as shown for the heat capacity of pyrrole ring-group D in eqn. (7).

$$\Delta C^0_{P,T}(\text{RG-D}) = C^0_{P,T}(\text{pyrrole}) + \Delta C^0_{P,T}(\text{RG-A}) - C^0_{P,T}(\text{benzene}) \qquad (7)$$

The five-membered ring structure in acenaphthylene is another common aromatic structure found in high-temperature hydrocarbon pyrolysis. Its ring-group values (RG-G) are obtained by subtracting properties of naphthalene from corresponding properties of acenaphthene, and correcting for unsaturation [10a].

Ring-group values (RG-B) for rings containing pyridene-type nitrogen atoms are obtained by comparing the properties of benzene to pyridine. For rings containing two such non-adjacent nitrogen atoms, ring-group values are obtained by simply assuming that such nitrogen atoms have independent

TABLE 5

Enthalpies of sublimation/vaporization from entropy and vapor pressure at 298 K [a]

	S^0_{298} (condensed)	S^0_{298} [b] (vapor)	ΔS	$P_{\text{vapor},298}$ (torr) [c]	$\Delta H_{298,\text{sub/vap}}$ [d]
Quinoline	51.9 (1) [e]	83.0	31.1	0.175	14.2
Benzothiophene	42.33 (s) [f]	82.0	39.7	0.22	16.6

[a] Entropy in cal mole^{-1} K^{-1} units, enthalpies in kcal mole^{-1}.
[b] From present additive methods.
[c] Determined in the authors' laboratory.
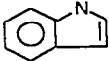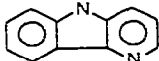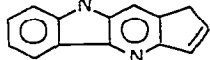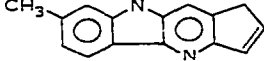[d] $R \ln P_{\text{vapor}} = (-\Delta H_{\text{sub/vap}}/T) + \Delta S_{\text{sub/vap}}$.
[e] G.S. Parks, S.S. Todd and W.A. Moore, J. Am. Chem. Soc., 58 (1936) 398.
[f] H.L. Finke, M.E. Gross, J.F. Messerly and G. Waddington, J. Am. Chem. Soc., 76 (1954) 854.

additive effects on entropy and heat capacity. This assumption is supported by the additivity of enthalpies of formation of such heterocycles (Table 1B).

An example of the use of ring-group values is given below.

Example: estimate S^0_{298} and $C^0_{P,1000}$ for the compound shown.

		Units are cal mol^{-1} K^{-1}	
		$\Delta S^0_{int,298}$	$\Delta C^0_{P,1000}$
		69.3	50.39
	RG-D	+10.7	+19.37
	RG-B	+13.7	+24.36
	RG-C	+11.4	+23.15
	Ref. 11	$-11.53 - [C_B - (H)]$	-8.41
		$-7.69 + [C_B - (C)]$	$+5.44$
		$+30.41 + [C - (H)_3(C)]$	$+14.77$
		$-2.18 - R \ln 3$	
		symmetry	
	Total $S^0_{298} = 114.1$		$C^0_{P,1000} = 129.1$

Estimated entropy values for gas-phase benzothiophene and quinoline in conjunction with thermal data for these substances, allows a reliable estimate of the heats of vaporization/sublimation of these substances (Table 5). The procedure is as follows. The entropy of vaporization/sublimation is found by subtracting measured condensed-phase entropies at 298 K from estimated gas-phase entropies at 298 K. A knowledge of the vapor pressures at 298 K then yields the heat of sublimation/vaporization through the Clausius—Calpeyron equation. We have measured these vapor pressures at 25°C in our laboratory using a differential pressure transducer as 0.22 torr for solid benzothiphene and 0.175 torr for liquid quinoline. These heats of vaporization/sublimation are probably as accurate as can be obtained by any means for these low vapor pressure materials, and are used to obtain gas-phase enthalpies of formation of quinoline and benzothiophene (Table 2A). Note that an error of 1 cal mole^{-1} K^{-1} in the entropy of vaporization/sublimation leads to an error of only 0.3 kcal mole^{-1} in the enthalpy of vaporization/sublimation at 298 K.

In Table 6, entropy and heat capacity values for anthracene, carbazole and dibenzothiophene obtained by the present additive method are compared to values given in Table 2B. Entropies and heat capacities are in reasonable

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TABLE 6

Comparison of ring-group entropy (cal mole^{-1} K^{-1}) and heat capacity (cal mole^{-1} K^{-1}) estimates to other values

| | S^o_{298} | S^o_{298} (addt'y) | $C^o_{P,T}$ [a] $-C^o_{P,T}$ (addt'y) | | | | | | | | |
			300	400	500	600	800	1000	1500	2000	2500
Anthracene	92.0 [a], 95.3 [b] 93.8 [c], 92.5 [d]	94.4	−0.5	+0.2	+0.6	+0.8	+0.8	+0.2	+0.2	+0.0	+0.1
Carbazole	92.9 [c]	92.7	−0.6	−0.7	−0.7	−0.5	−0.4	−0.5	−0.4	−0.2	−0.2
Dibenzothiophene	92.5 [a]	94.6	−2.3	−2.6	−2.4	−2.1	−1.6	−1.5	−0.9	−0.6	−0.5

[a] From vibrational model given in Table 2C and D.
[b] Experimental value reported in ref. 9.
[c] Ref. 7b.
[d] Value recommended in ref. 13.

TABLE 7

Recommended enthalpies of formation, entropies and heat capacities for common PHFR [a]

	$\Delta H_{f,298}^{o}$ (kcal mole⁻¹)	S_{298}^{o} (cal mole⁻¹ K⁻¹)	$C_{P,T}^{o}$ (cal mole⁻¹ K⁻¹)								
			300	400	500	600	800	1000	1500	2000	2500
Indene	39.08 [b]	80.5 [e]	30.7	39.8	48.5	55.6	66.1	73.5	84.0	89.0	91.7
Indole	37.4 [b]	80.1	29.4	39.1	47.2	53.7	63.1	69.8	79.1	83.7	86.2
Benzofuran	6.5 [f]	79.2	27.9	37.1	44.8	51.0	59.9	66.1	74.6	78.7	80.9
Benzothiophene	40.3 [d]	82.0	29.7	38.9	46.3	52.3	60.8	66.8	75.0	78.9	81.1
Fluorene	43.8 [d]	93.0	42.9	55.7	67.5	77.2	91.5	101.7	115.6	122.2	125.8
Carbazole	50.1 [b]	92.7	41.6	55.0	66.2	75.3	88.5	98.0	110.7	116.9	120.3
Dibenzofuran	19.9 [b]	91.8	40.1	53.0	63.8	72.6	85.3	94.3	106.2	111.9	115.0
Dibenzothiophene	49.3 [d]	94.6	41.9	54.8	65.3	73.9	86.2	95.0	106.6	121.1	115.2
Acenaphthylene	61.6 [b]	87.0	37.6	50.0	60.3	68.6	80.8	89.1	100.7	106.2	109.2
Fluoranthene	69.78 [b]	100.6	49.8	65.9	79.3	90.2	106.2	117.3	132.3	139.4	143.3
Quinoline	51.8 [c]	83.0	30.9	41.2	49.9	57.1	67.5	74.8	84.8	89.6	92.1
Isoquinoline	48.2 [c]	83.0	30.9	41.2	49.9	57.1	67.5	74.8	84.8	89.6	92.1

[a] Obtained by present additive methods, unless otherwise indicated.
[b] Table 1A, literature.
[c] Table 1B, literature.
[d] Table 2A, derived.
[e] Table 2B, derived.
[f] Table 3, estimated.

agreement for anthracene and carbazole. A rather large disagreement (2—3 cal mole^{-1} K^{-1}) is found for both the entropy and heat capacity of dibenzo-thiophene. This is most likely due to a faulty vibrational analysis for this molecule.

Finally, in Table 7 is given a listing of preferred chemical thermodynamic quantities for selected PHFR. For anthracene and phenanthrene, see ref. 7b.

SUMMARY

Chemical thermodynamic properties of PHFR have been collected and contrasted. Using these data, straightforward estimation methods have been constructed for entropy, heat capacity, and for a few particular structural types, heats of formation. Although these approximate methods are not as accurate as for numerous classes of acyclic substances, the accuracy is suitable for rough equilibrium calculations and serves as a foundation on which to build more accurate estimation methods as more data become available.

ACKNOWLEDGEMENTS

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