

# Standard Chemical Thermodynamic Properties of Polycyclic Aromatic Hydrocarbons and Their Isomer Groups I. Benzene Series

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The polycyclic aromatic hydrocarbons can be organized into an infinite number of series in each of which successive isomer groups differ by  $C_4H_2$ . The first series starts with benzene, and chemical thermodynamic tables are presented here for  $C_6H_6$ ,  $C_{10}H_8$ ,  $C_{14}H_{10}$ ,  $C_{18}H_{12}$ ,  $C_{22}H_{14}$ , and  $C_{26}H_{16}$  in the ideal gas phase. Since chemical thermodynamic properties are known for only several polycyclic aromatic hydrocarbons, the properties of individual species have been estimated using Benson group values of Stein and Fahr for temperatures from 298.15 to 3000 K. Values of  $C_p^\circ$ ,  $S^\circ$ ,  $\Delta_f H^\circ$ , and  $\Delta_f G^\circ$  have been calculated in joules for a standard state pressure of 1 bar. The chemical thermodynamic properties of the isomer groups have also been calculated. This provides a basis for extrapolating to higher carbon numbers where it is not feasible to consider individual molecular species.

Key words: polycyclic aromatic hydrocarbons; Benson method; enthalpy of formation; heat capacity; entropy; Gibbs energy of formation; isomer group thermodynamic properties; isomer mole fractions; thermodynamic properties.

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## 1. Introduction

The chemical thermodynamic properties of the polycyclic aromatic hydrocarbons in the gas phase are of interest

because they are formed in flames<sup>1-5</sup> and are observed in the vicinity of carbon stars.<sup>6,7</sup> Stein and co-workers<sup>8-11</sup> have studied the thermodynamics and kinetics of the formation of polycyclic aromatic hydrocarbons in flames and have demonstrated the usefulness of thermodynamics in understanding the complicated reactions that are possible under flame conditions. A mechanism<sup>12</sup> has been suggested for the buildup of polycyclic aromatic hydrocarbons under these conditions.

Balaban and Harary<sup>13</sup> used graph theory to enumerate polycyclic aromatic hydrocarbons. More recently Dias<sup>14-23</sup> has developed a formula periodic table for benzenoid polycyclic aromatic hydrocarbons by using graph theoretical principles. Dias has discovered mathematical formulas relating numbers of atoms and rings that help clarify the systematics of the polycyclic aromatic hydrocarbons, and he has developed two concepts for the enumeration of their isomers.<sup>16-17</sup> In this paper we examine the benzene series that is represented by the first row in Dias' periodic table. One of the purposes is to see whether the increments in the thermodynamic properties per  $C_4H_2$  are constant enough so that properties of higher isomer groups may be estimated by linear extrapolation. Table 1 shows the first several isomer groups in the benzene series. The total numbers of isomers exclude structures that overlap, as in the helicene with six rings. The structures of the isomers in the benzene series through  $C_{26}H_{16}$  are given in Fig. 1.<sup>24</sup> To simplify this figure only sigma bonds are shown. Using current information on Benson groups it is not possible to estimate chemical thermodynamic properties of all of these isomers. Structure 12 of  $C_{22}H_{14}$  and structures 4-6, and 23 of  $C_{26}H_{16}$  can be regarded as helicenes in the sense that the hydrogen atom overlaps in the bay region prevent them from being planar molecules. Since the effect of this distortion on the Benson constants is not known, they have been omitted from the tables in this article. Since they would be expected to have significantly higher energies, they would not contribute very much to isomer group thermodynamic properties. The numbers of isomers for which thermodynamic properties are given in this article are given in the last column in Table 1.

This article is concerned only with polycyclic aromatic molecules with six-membered rings that are not radicals or diradicals or higher radicals. Since the number of isomers of polycyclic aromatic hydrocarbons increases rapidly with carbon number, it is convenient to use isomer group thermodynamic properties in calculations of equilibrium composi-

tions. The tables presented here are of the same type as those published for alkanes,<sup>25</sup> alkylbenzenes,<sup>26</sup> alkenes,<sup>27</sup> alkyl-naphthalenes,<sup>28</sup> and alkylcyclopentanes and cyclohexanes.<sup>29</sup>

## 2. Standard Thermodynamic Properties of Polycyclic Aromatic Isomer Groups

When isomers are in equilibrium, the standard Gibbs energy of formation  $\Delta_f G^\circ(I)$  of the isomer groups is defined by<sup>30,31</sup>

$$\Delta_f G^\circ(I) = -RT \ln \left( \sum_{i=1}^{N_I} \exp(-\Delta_f G_i^\circ/RT) \right), \quad (1)$$

where  $\Delta_f G_i^\circ$  is the standard Gibbs energy of formation of an individual isomer and  $N_I$  is the number of isomers in the group. The equilibrium mole fractions  $r_i$  of various isomers in a group can be calculated using

$$r_i = y_i/y_I = \exp[\Delta_f G^\circ(I) - \Delta_f G_i^\circ]/RT], \quad (2)$$

where  $y_I$  is the sum of the mole fractions of the individual isomers. The corresponding equations for the other standard thermodynamic properties  $C_p^\circ(I)$ ,  $S^\circ(I)$ , and  $\Delta_f H^\circ(I)$  can be derived by differentiating Eq. (1) with respect to temperature.<sup>32</sup> When standard Gibbs energies of formation of isomer groups are used in equilibrium calculations for ideal gases the equilibrium mole fractions of isomer groups are obtained.

For the polycyclic aromatic hydrocarbons the standard thermodynamic properties for an isomer group are interrelated by

$$\Delta_f G^\circ(I) = \Delta_f H^\circ(I) - T[S^\circ(I) - n_C S_{\text{graphite}}^\circ - (n_H/2)S_{H_2}^\circ(g)], \quad (3)$$

where  $n_C$  is the number of carbon atoms and  $n_H$  is the number of hydrogen atoms.

## 3. Calculations of Standard Thermodynamic Properties of Benzene Series Polycyclic Aromatic Hydrocarbons using the Benson Method

Experimental data on the polycyclic aromatic hydrocarbons are restricted to the smaller molecules. Fortunately, enough data were available for Stein, Golden, and Benson<sup>33,34</sup> to obtain group values for  $C_B-(H)$ ,  $C_{FR}-(C_{FR})(C_B)_2$ , and  $C_{FR}-(C_{FR})_2(C_B)$  groups; the group values of  $C_{FR}-(C_{FR})_3$  were evaluated from graphite. They also calculated the contribution for the 1,5H,H interaction in benzo[c]phenanthrene to  $\Delta_f H^\circ(298)$  to be 4.2 kcal mol<sup>-1</sup>. The average difference between predicted and measured  $\Delta_f H^\circ(298)$  for 11 polycyclic aromatic hydrocarbons was less than 2 kcal mol<sup>-1</sup> and generally was within experimental uncertainties. More recently, Stein and Fahr<sup>35</sup> have provided Benson group values with  $C_p^\circ$  values up to 3000 K. Although these values are similar to those of Stein, Golden, and Benson,<sup>34</sup> two major changes were made: (1) heat capacity values were calculated using the harmonic oscillator-rigid rotor approximation, and (2) values of  $C_p^\circ$  for

TABLE 1. Numbers of isomers in the benzene series of polycyclic aromatic hydrocarbons

Number of rings	Formulas	Total number	Number in tables
1	$C_6H_6$	1	1
2	$C_{10}H_8$	1	1
3	$C_{14}H_{10}$	2	2
4	$C_{18}H_{12}$	5	5
5	$C_{22}H_{14}$	12	11
6	$C_{26}H_{16}$	36	32
7	$C_{30}H_{18}$	118	0
8	$C_{34}H_{20}$	411	0

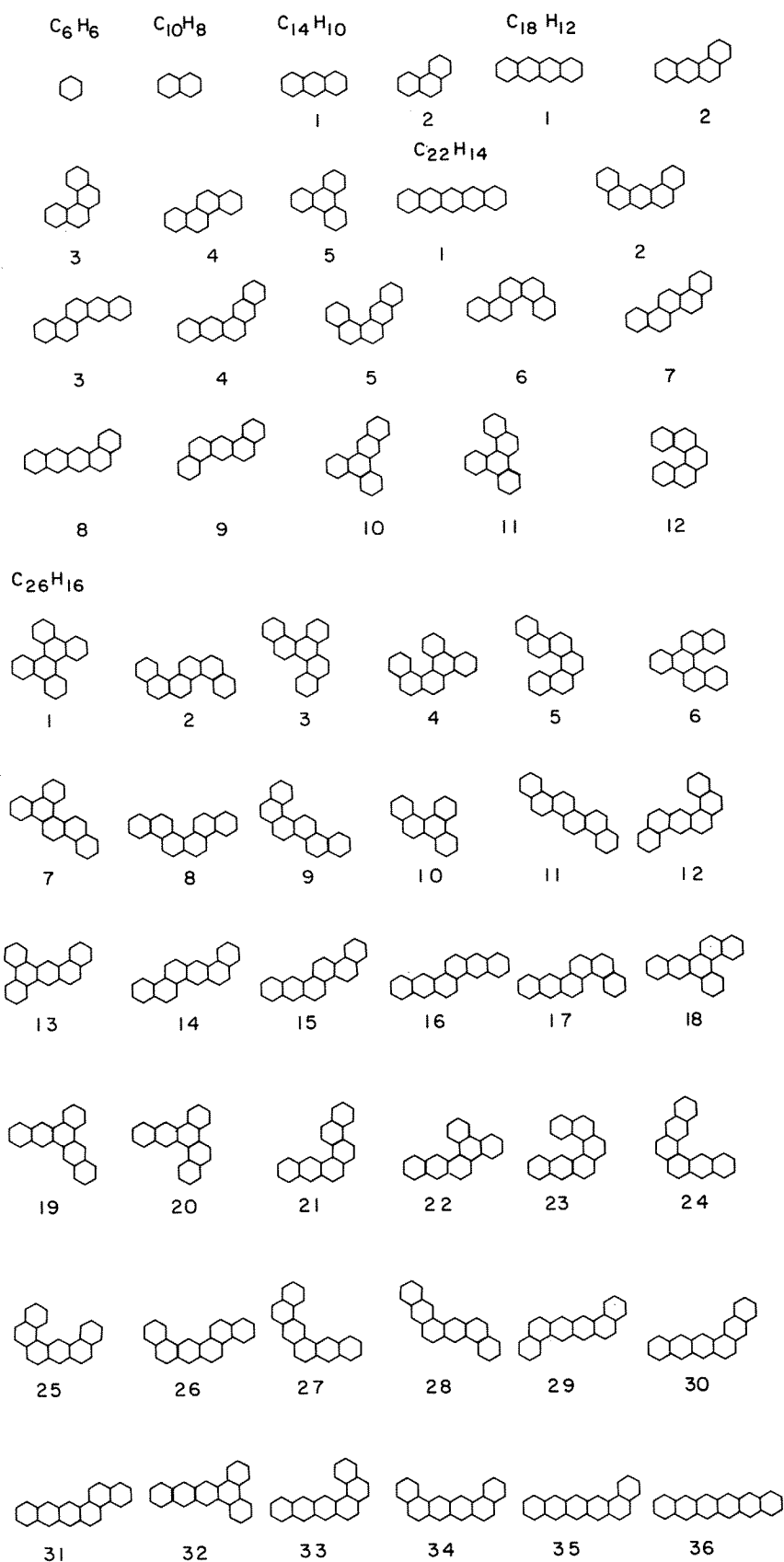


FIG. 1. Structures of isomers in the benzene series up to  $C_{26}H_{16}$ .

the  $[C_{FR} - (C_{FR})_3]$  group were derived from pyrene frequencies<sup>36</sup> rather than from graphite.

Two changes have been made in the methods used in previous articles in this series: (1) calculations were made directly in joules with Benson group values in joules and (2) a different function was used to represent  $C_p^\circ$  as a function of  $T$ . All values of thermodynamic quantities in this article are for a standard state pressure of 1 bar (0.1 MPa) in accordance with the recommendation of the International Union of Pure and Applied Chemistry.<sup>37</sup>

The matrix of numbers of contributions was multiplied by the matrix of the Benson values to obtain for each species the sum of the contribution to  $\Delta_f H^\circ_{298}$ ,  $S^\circ_{int298}$ ,  $C_p^\circ_{298}$ ,  $C_p^\circ_{300}$ ,  $C_p^\circ_{500}$ ,  $C_p^\circ_{700}$ ,  $C_p^\circ_{1000}$ ,  $C_p^\circ_{1500}$ ,  $C_p^\circ_{2000}$ ,  $C_p^\circ_{2500}$ , and  $C_p^\circ_{3000}$ . In further steps in the calculation, the effect of symmetry number was included, and the heat capacity values were fit to the equation

$$C_p^\circ = a + \frac{b}{\sqrt{T}} + \frac{c}{T^2} + \frac{d}{T}, \quad (4)$$

and the values of  $a$ ,  $b$ ,  $c$ , and  $d$  were used to calculate  $C_p^\circ$ ,  $S^\circ$ , and  $\Delta_f H^\circ$  from 298.15 to 3000 K.

$$S^\circ = S^\circ_0 + a \ln T - 2bT^{-1/2} - (c/2)T^{-2} - d/T - R \ln(TSN), \quad (5)$$

$$\begin{aligned} \Delta_f H^\circ &= \Delta_f H^\circ_0 + aT + 2bT^{1/2} - c/T + d \ln T \\ &\quad - n_C (H^\circ - H^\circ_{298})_{\text{graphite}} \\ &\quad - (n_H/2) (H^\circ - H^\circ_{298})_{H_2}. \end{aligned} \quad (6)$$

The values of  $\Delta_f G^\circ$  at various temperatures were then calculated using Eq. (3).

The new value of the gas constant<sup>38</sup> and the new values for  $S^\circ$  and  $H^\circ - H^\circ(298.15 \text{ K})$  for C(graphite) and  $H_2(g)$  were used.<sup>39</sup>

Table 2 gives the differences between properties of polycyclic aromatic hydrocarbons calculated using the Benson method and those given in the TRC Thermodynamic Tables for benzene, naphthalene, anthracene, and phenanthrene up to 1500 K.<sup>40</sup> This comparison has been made earlier with the Stull, Westrum, and Sinke<sup>41</sup> tables for benzene<sup>26</sup> and naphthalene<sup>28</sup> up to 1000 K. The largest difference in Table 2, that for naphthalene at 1500 K, is apparently due to a typographical error in the TRC tables. There are some differences between experimental values<sup>42,43</sup> and values calculated using the Benson method that might be reduced by the addition of more Benson groups, but the basic problem is the shortage of experimental data on the polycyclic aromatic hydrocarbons.

#### 4. Tables of Standard Thermodynamic Properties of Benzene Series Polycyclic Aromatic Isomer Groups

In Tables 3–8 all of the values have been estimated using the Benson method. Since the increments from one isomer group to the next are  $C_4H_2$  in each series, the increments in the properties are given for each series at each temperature. These increments provide a basis for a linear extrapolation of standard thermodynamic properties to polycyclic aromatic isomer groups to higher carbon number.

Table 7 gives  $H^\circ(I, T) - H^\circ(I, 298.15 \text{ K})$ , the standard enthalpy for an isomer group relative to the isomer group at 298.15 K. Table 8 gives values for  $H^\circ(I, T) - H^\circ(I, 298.15 \text{ K}) + \Delta_f H^\circ(I, 298.15 \text{ K})$ , the standard enthalpy for the isomer group relative to the elements of 298.15 K. This quantity allows the direct calculation of heat effects when the reactants and products are at different temperatures.

Table 2. Differences between properties of polycyclic aromatic hydrocarbons from the Benson method and from the Texas A and M tables

T/K	298	300	500	700	1000	1500
Standard heat capacity at constant pressure in J/K mol						
benzene	.31	.18	-.96	.28	-.03	-1.43
naphthalene	3.66	3.42	-.09	.89	-.01	-1.80
anthracene	5.57	5.21	-1.55	-.52	-1.31	-3.09
phenanthrene	1.61	1.32	-3.69	-1.56	-1.83	-3.35
Standard entropy in J/K mol						
benzene	-.05	-.05	-.73	-.82	-.72	-1.03
naphthalene	.12	.14	.19	.36	.58	.16
anthracene	2.35	2.38	2.14	1.82	1.56	.62
phenanthrene	-.46	-.49	-2.30	-3.19	-3.63	-4.82
Standard enthalpy of formation in kJ/mol						
benzene	.00	.00	-.16	-.20	-.15	-.62
naphthalene	-.01	.00	.18	.29	.42	-.25
anthracene	-9.36	-9.35	-9.23	-9.41	-9.69	-11.05
phenanthrene	2.03	2.09	1.60	1.11	.64	-.94
Standard Gibbs energy of formation in kJ/mol						
benzene	.11	.10	.22	.37	.44	.88
naphthalene	.06	.06	.04	-.04	-.47	28.45
anthracene	-9.91	-9.93	-10.38	-10.83	-11.75	-12.43
phenanthrene	2.32	2.34	2.63	3.13	3.74	5.81

Table 3. Standard heat capacity at constant pressure for benzene series polycyclic aromatic hydrocarbon isomer groups in J/K mol

T/K	C6H6	C10H8	C14H10	C18H12	C22H14	C26H16
298.15	82.75	135.58	189.8	257.0	295.1	359.8
300.00	83.20	136.26	190.7	258.5	296.5	361.5
500.00	138.39	219.65	302.9	422.1	467.8	555.4
700.00	177.06	277.90	380.5	499.6	584.7	686.9
1000.00	211.38	329.18	448.2	570.2	685.3	801.7
1500.00	240.68	372.37	504.8	635.9	768.0	897.4
2000.00	255.89	394.40	533.3	670.2	809.3	945.3
2500.00	265.05	407.45	550.2	690.5	833.3	973.1
3000.00	271.11	415.95	561.0	703.5	848.6	990.8

Table 3a. Increments per C4H2

T/K	C10-C6	C14-C10	C18-C14	C22-C18	C26-C22
298.15	52.83	54.2	67.2	38.1	64.7
300.00	53.06	54.4	67.8	38.1	64.9
500.00	81.26	83.3	119.2	45.7	87.5
700.00	100.84	102.6	119.1	85.1	102.1
1000.00	117.80	119.0	122.0	115.1	116.4
1500.00	131.68	132.4	131.1	132.1	129.4
2000.00	138.51	138.9	136.9	139.1	136.0
2500.00	142.40	142.7	140.3	142.8	139.8
3000.00	144.83	145.0	142.5	145.1	142.2

Table 4. Standard entropy for benzene series polycyclic aromatic hydrocarbon isomer groups in J/K mol

T/K	C6H6	C10H8	C14H10	C18H12	C22H14	C26H16
298.15	269.14	333.27	394.5	443.8	539.0	613.7
300.00	269.65	334.11	395.7	445.4	540.8	615.9
500.00	325.32	423.59	519.9	618.8	733.3	847.2
700.00	378.51	507.50	635.2	774.5	910.8	1056.6
1000.00	448.02	616.13	783.5	965.5	1138.1	1323.0
1500.00	540.01	758.88	977.3	1210.7	1433.8	1668.6
2000.00	611.54	869.33	1126.9	1398.8	1661.0	1934.0
2500.00	669.70	958.85	1247.8	1550.7	1844.4	2148.2
3000.00	718.59	1033.94	1349.2	1677.8	1997.8	2327.3

Table 4a. Increments per C4H2

T/K	C10-C6	C14-C10	C18-C14	C22-C18	C26-C22
298.15	64.13	61.2	49.3	95.2	74.7
300.00	64.46	61.6	49.7	95.4	75.1
500.00	98.28	96.3	98.9	114.5	113.9
700.00	128.99	127.7	139.4	136.3	145.8
1000.00	168.11	167.3	182.1	172.6	184.8
1500.00	218.87	218.5	233.3	223.1	234.8
2000.00	257.79	257.5	271.9	262.2	273.0
2500.00	289.15	289.0	302.9	293.7	303.8
3000.00	315.35	315.2	328.7	319.9	329.5

Table 5. Standard enthalpy of formation for benzene series polycyclic aromatic hydrocarbon isomer groups in kJ/mol

T/K	C6H6	C10H8	C14H10	C18H12	C22H14	C26H16
298.15	82.80	150.57	209.2	259.4	329.7	391.4
300.00	82.70	150.45	209.1	259.3	329.5	391.3
500.00	73.39	139.40	196.7	251.4	313.8	375.8
700.00	67.52	132.62	189.4	248.8	305.2	367.0
1000.00	63.02	127.93	184.9	247.1	301.1	362.5
1500.00	61.37	127.67	186.5	250.7	305.7	367.6
2000.00	62.25	130.52	191.6	257.1	314.5	377.0
2500.00	63.44	133.41	196.4	262.7	322.0	385.0
3000.00	64.02	135.05	199.2	265.5	325.9	388.7

Table 5a. Increments per C4H2

T/K	C10-C6	C14-C10	C18-C14	C22-C18	C26-C22
298.15	67.77	58.7	50.2	70.2	61.8
300.00	67.75	58.7	50.2	70.2	61.8
500.00	66.01	57.3	54.7	62.5	61.9
700.00	65.10	56.8	59.5	56.4	61.7
1000.00	64.91	57.0	62.2	53.9	61.4
1500.00	66.30	58.9	64.1	55.1	61.8
2000.00	68.27	61.1	65.5	57.3	62.6
2500.00	69.98	63.0	66.3	59.3	63.0
3000.00	71.03	64.2	66.2	60.5	62.8

Table 6. Standard Gibbs energy of formation for benzene series polycyclic aromatic hydrocarbon isomer groups in kJ/mol

T/K	C6H6	C10H8	C14H10	C18H12	C22H14	C26H16
298.15	129.71	224.16	310.4	391.7	479.3	564.7
300.00	130.00	224.62	311.0	392.5	480.3	565.7
500.00	164.32	277.38	382.7	484.2	585.6	686.8
700.00	201.84	333.91	458.6	577.8	696.0	812.9
1000.00	260.39	421.23	575.0	719.1	864.5	1005.1
1500.00	359.63	568.19	769.9	954.6	1145.6	1325.8
2000.00	458.94	714.64	963.7	1188.3	1424.2	1643.8
2500.00	558.73	861.32	1157.3	1422.0	1702.5	1961.5
3000.00	656.82	1005.52	1347.7	1651.7	1976.1	2274.0

Table 6a. Increments per C4H2

T/K	C10-C6	C14-C10	C18-C14	C22-C18	C26-C22
298.15	94.45	86.2	81.3	87.7	85.3
300.00	94.62	86.4	81.5	87.8	85.5
500.00	113.06	105.3	101.5	101.4	101.2
700.00	132.07	124.7	119.2	118.2	116.9
1000.00	160.84	153.7	144.2	145.4	140.6
1500.00	208.57	201.7	184.7	191.0	180.2
2000.00	255.69	249.0	224.7	235.9	219.5
2500.00	302.59	296.0	264.6	280.6	259.0
3000.00	348.71	342.2	304.0	324.4	297.9

Table 7. Standard enthalpy for benzene series polycyclic aromatic hydrocarbon isomer groups relative to isomer groups at 298.15 K in kJ/mol

T/K	C6H6	C10H8	C14H10	C18H12	C22H14	C26H16
298.15	.00	.00	.0	.0	.0	.0
300.00	.15	.25	.4	.5	.5	.7
500.00	22.43	36.01	50.0	69.8	77.4	92.9
700.00	54.26	86.21	118.9	162.8	183.6	218.2
1000.00	113.03	178.04	244.2	324.1	375.7	443.2
1500.00	226.96	354.79	484.3	627.5	741.7	871.0
2000.00	351.52	547.11	744.7	955.1	1137.2	1333.1
2500.00	481.86	747.73	1015.7	1295.4	1548.1	1813.0
3000.00	616.00	953.72	1293.7	1644.2	1968.9	2304.3

Table 7a. Increments per C4H2

T/K	C10-C6	C14-C10	C18-C14	C22-C18	C26-C22
298.15	.00	.0	.0	.0	.0
300.00	.10	.1	.1	.1	.1
500.00	13.58	13.9	19.9	7.6	15.5
700.00	31.95	32.7	43.9	20.8	34.6
1000.00	65.00	66.2	79.9	51.6	67.5
1500.00	127.84	129.5	143.2	114.2	129.3
2000.00	195.60	197.5	210.4	182.2	195.9
2500.00	265.86	268.0	279.7	252.7	264.9
3000.00	337.72	340.0	350.5	324.7	335.4

Table 8. Standard enthalpy for benzene series polycyclic aromatic hydrocarbon isomer groups relative to the elements at 298.15 K in kJ/mol

T/K	C6H6	C10H8	C14H10	C18H12	C22H14	C26H16
298.15	82.80	150.57	209.2	259.4	329.7	391.4
300.00	82.95	150.82	209.6	259.9	330.2	392.1
500.00	105.23	186.57	259.2	329.2	407.0	484.3
700.00	137.06	236.77	328.1	422.2	513.2	609.6
1000.00	195.82	328.60	453.5	583.5	705.3	824.6
1500.00	309.76	505.36	693.5	887.0	1071.3	1262.5
2000.00	434.32	697.68	953.9	1214.5	1466.9	1724.6
2500.00	564.66	898.29	1225.0	1554.9	1877.8	2204.5
3000.00	698.80	1104.28	1502.9	1903.6	2298.5	2695.7

Table 8a. Increments per C4H2

T/K	C10-C6	C14-C10	C18-C14	C22-C18	C26-C22
298.15	67.77	58.7	50.2	70.2	61.8
300.00	67.86	58.8	50.3	70.3	61.9
500.00	81.35	72.6	70.0	77.8	77.3
700.00	99.71	91.4	94.1	91.0	96.3
1000.00	132.77	124.9	130.0	121.8	129.3
1500.00	195.60	188.2	193.4	184.4	191.1
2000.00	263.36	256.2	260.6	252.4	257.7
2500.00	333.63	326.7	329.9	322.9	326.7
3000.00	405.48	398.6	400.7	394.9	397.2

## 5. Equilibrium Mole Fractions Within Benzene Series Polycyclic Aromatic Isomer Groups

The equilibrium mole fractions within isomer groups calculated from standard Gibbs energies of formation are given in Table 9 for the ideal gas state. Since the uncertainties in  $\Delta_f G^\circ(I)$  and  $\Delta_f G^\circ_i$  are about the same, the uncertainty in the difference is nearly independent of the relative values of the two parameters, but the absolute uncertainty does increase with temperature.

Compounds are named in tables according to the IUPAC Revised and Collected Recommendations for the Nomenclature of Organic Chemistry, 1978.<sup>44</sup>

Table 9 shows that there are significant changes in the distribution of isomers within an isomer group when the temperature is changed from 298 to 3000 K. At higher tem-

peratures, the relative stabilities are determined primarily by the entropy. The distribution becomes more uniform as the temperature is raised.

## 6. Standard Thermodynamic Properties of Individual Polycyclic Aromatic Hydrocarbons

The values of  $C_p^\circ$ ,  $S^\circ$ ,  $\Delta_f H^\circ$ , and  $\Delta_f G^\circ$  calculated using the Benson method for the polycyclic aromatic hydrocarbons are given in Tables 10–13 with energy in joules for a standard state pressure of 1 bar.

## 7. Discussion

The standard Gibbs energies of formation of the polycyclic aromatic hydrocarbons give their stabilities with re-

Table 9. Equilibrium mole fractions within benzene series polycyclic aromatic hydrocarbon isomer groups

T/K	298.15	300	500	700	1000	1500	2000	2500	3000
<b>C14H10</b>									
anthracene	.0121	.0123	.0518	.0932	.1418	.1929	.2233	.2431	.2569
phenanthrene	.9879	.9877	.9482	.9068	.8582	.8071	.7767	.7569	.7431
<b>C18H12</b>									
naphthalene	.0000	.0000	.0011	.0034	.0064	.0095	.0115	.0130	.0142
benz(a)anthracene	.0033	.0034	.0387	.0661	.0769	.0794	.0801	.0811	.0824
benzo(c)phenanthrene	.0119	.0125	.2420	.5090	.6829	.7703	.7983	.8099	.8150
chrysene	.0672	.0686	.1773	.1608	.1164	.0830	.0697	.0632	.0596
triphenylene	.9177	.9155	.5409	.2606	.1174	.0579	.0404	.0328	.0287
<b>C22H14</b>									
pentacene	.0000	.0000	.0000	.0001	.0003	.0008	.0012	.0015	.0018
dibenz(a,j)anthracene	.0014	.0015	.0036	.0050	.0060	.0067	.0071	.0073	.0075
benzo(b)chrysene	.0029	.0029	.0072	.0099	.0121	.0135	.0141	.0146	.0150
pentaphene	.0000	.0000	.0004	.0010	.0020	.0032	.0041	.0047	.0052
dibenzo(b,g)phenanthrene	.0005	.0005	.0098	.0315	.0708	.1251	.1620	.1872	.2051
benzo(c)chrysene	.0209	.0213	.0895	.1530	.2142	.2617	.2817	.2915	.2967
picene	.0590	.0585	.0328	.0242	.0183	.0141	.0123	.0114	.0108
benzo(a)naphthalene	.0001	.0001	.0008	.0020	.0040	.0064	.0081	.0094	.0104
dibenz(a,h)anthracene	.0014	.0015	.0036	.0050	.0060	.0067	.0071	.0073	.0075
benzo(b)triphenylene	.0590	.0585	.0328	.0242	.0183	.0141	.0123	.0114	.0108
benzo(a)triphenylene	.8547	.8551	.8196	.7441	.6481	.5475	.4901	.4538	.4291
<b>C26H16</b>									
1.	.0000	.0000	.0000	.0001	.0001	.0002	.0003	.0004	.0005
2.	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0001	.0001
3.	.0000	.0000	.0001	.0001	.0002	.0002	.0003	.0003	.0003
7.	.0002	.0002	.0017	.0038	.0063	.0090	.0107	.0119	.0129
8.	.0006	.0007	.0107	.0291	.0558	.0871	.1064	.1190	.1276
9.	.0000	.0000	.0001	.0001	.0002	.0002	.0003	.0003	.0003
10.	.0036	.0036	.0079	.0092	.0095	.0094	.0093	.0093	.0093
11.	.0000	.0000	.0001	.0002	.0004	.0005	.0005	.0006	.0007
12.	.0010	.0010	.0013	.0012	.0011	.0010	.0009	.0009	.0009
13.	.0010	.0010	.0013	.0012	.0011	.0010	.0009	.0009	.0009
14.	.0000	.0000	.0000	.0001	.0001	.0002	.0003	.0004	.0005
15.	.0000	.0000	.0001	.0004	.0010	.0021	.0031	.0038	.0045
16.	.0000	.0000	.0001	.0002	.0004	.0005	.0005	.0006	.0007
17.	.0000	.0000	.0001	.0002	.0004	.0005	.0005	.0006	.0007
18.	.0000	.0000	.0002	.0008	.0021	.0043	.0061	.0077	.0089
19.	.0002	.0002	.0017	.0038	.0063	.0090	.0107	.0119	.0129
20.	.0002	.0002	.0017	.0038	.0063	.0090	.0107	.0119	.0129
21.	.0002	.0002	.0017	.0038	.0063	.0090	.0107	.0119	.0129
22.	.0005	.0005	.0006	.0006	.0005	.0005	.0005	.0005	.0005
24.	.0072	.0073	.0157	.0184	.0190	.0188	.0186	.0186	.0187
25.	.5308	.5315	.4497	.3438	.2554	.1906	.1610	.1442	.1334
26.	.0405	.0398	.0115	.0058	.0032	.0020	.0016	.0014	.0014
27.	.2932	.2910	.1439	.0893	.0575	.0393	.0323	.0289	.0270
28.	.0005	.0005	.0006	.0006	.0005	.0005	.0005	.0005	.0005
29.	.0072	.0073	.0157	.0184	.0190	.0188	.0186	.0186	.0187
30.	.0259	.0265	.0983	.1414	.1688	.1822	.1851	.1859	.1845
31.	.0000	.0000	.0001	.0001	.0002	.0002	.0003	.0003	.0003
32.	.0072	.0073	.0157	.0184	.0190	.0188	.0186	.0186	.0187
33.	.0518	.0531	.1965	.2828	.3376	.3645	.3703	.3705	.3690
34.	.0010	.0010	.0013	.0012	.0011	.0010	.0009	.0009	.0009
35.	.0202	.0199	.0058	.0029	.0016	.0010	.0008	.0007	.0007
36.	.0072	.0073	.0157	.0184	.0190	.0188	.0186	.0186	.0187

Table 10. Standard heat capacity at constant pressure for polycyclic aromatic hydrocarbons in J/K mol

T/K	298.15	300	500	700	1000	1500	2000	2500	3000
C6H6 benzene	82.75	83.20	138.39	177.06	211.38	240.68	255.89	265.05	271.11
C10H8 naphthalene	135.58	136.26	219.65	277.90	329.18	372.37	394.40	407.45	415.95
C14H10 anthracene phenanthrene	188.4 188.4	189.3 189.3	300.9 300.9	378.7 378.7	447.0 447.0	504.0 504.0	532.9 532.9	549.9 549.9	560.8 560.8
C18H12 naphthacene benz(a)anthracene benzo(c)phenanthrene chrysene triphenylene	241.2 241.2 236.8 241.2 241.2	242.4 242.4 238.0 242.4 242.4	382.2 382.2 380.9 382.2 382.2	479.6 479.6 478.5 479.6 479.6	564.8 564.8 563.4 564.8 564.8	635.7 635.7 633.8 635.7 635.7	671.4 671.4 669.1 671.4 671.4	692.2 692.2 689.7 692.2 692.2	705.6 705.6 702.9 705.6 705.6
C22H14 pentacene dibenz(a,j)anthracene benzo(b)chrysene pentaphene dibenzo(b,g)phenanthrene benzo(c)chrysene picene benzo(a)naphthacene dibenz(a,h)anthracene benzo(b)triphenylene benzo(a)triphenylene	294.1 294.1 294.1 294.1 289.7 289.7 294.1 294.1 294.1 294.1 289.7	295.4 295.4 295.4 295.4 291.1 291.1 295.4 295.4 295.4 295.4 295.4	463.4 463.4 463.4 463.4 462.2 462.2 463.4 463.4 463.4 463.4 463.4	580.4 580.4 580.4 580.4 579.4 579.4 580.4 580.4 580.4 580.4 580.4	682.6 682.6 682.6 682.6 681.2 681.2 682.6 682.6 682.6 682.6 682.6	767.4 767.4 767.4 767.4 765.5 765.5 767.4 767.4 767.4 767.4 767.4	809.9 809.9 809.9 809.9 807.6 807.6 809.9 809.9 809.9 809.9 809.9	834.6 834.6 834.6 834.6 832.1 832.1 834.6 834.6 834.6 834.6 834.6	850.4 850.4 850.4 850.4 847.7 847.7 850.4 850.4 850.4 850.4 850.4
C26H16 1. 2. 3. 7. 8. 9. 10. 11. 12. 13. 14. 15. 16. 17. 18. 19. 20. 21. 22. 24. 25. 26. 27. 28. 29. 30. 31. 32. 33. 34. 35. 36.	346.9 346.9 346.9 342.5 338.1 346.9 342.5 346.9 346.9 346.9 346.9 342.5 346.9 346.9 342.5 342.5 342.5 342.5 346.9 342.5 342.5 338.1 346.9 342.5 346.9 342.5 338.1 346.9 346.9 342.5 346.9 342.5	348.5 348.5 348.5 344.2 339.8 348.5 344.2 348.5 348.5 348.5 348.5 344.2 348.5 348.5 344.2 344.2 344.2 344.2 348.5 344.2 344.2 339.8 348.5 344.2 348.5 344.2 339.8 348.5 348.5 344.2 348.5 344.2	544.7 544.7 544.7 543.4 542.2 544.7 543.4 544.7 544.7 544.7 544.7 543.4 544.7 544.7 543.4 543.4 543.4 543.4 544.7 544.2 543.4 542.2 544.7 544.7 543.4 544.7 542.2 544.7 544.7 544.7 544.7 544.7	681.3 681.3 681.3 680.2 679.2 681.3 680.2 681.3 681.3 681.3 681.3 680.2 680.2 681.3 680.2 680.2 680.2 680.2 681.3 680.2 680.2 679.2 681.3 680.2 681.3 680.2 679.2 681.3 680.2 681.3 680.2 680.2	800.4 800.4 800.4 799.0 797.7 800.4 799.0 800.4 800.4 800.4 800.4 799.0 800.4 800.4 799.0 799.0 799.0 799.0 800.4 797.7 799.0 797.7 800.4 799.0 800.4 799.0 797.7 800.4 800.4 800.4 800.4 800.4	899.1 899.1 899.1 897.2 895.3 899.1 897.2 899.1 899.1 899.1 899.1 897.2 899.1 899.1 897.2 897.2 897.2 897.2 899.1 897.2 897.2 895.3 899.1 897.2 899.1 895.3 899.1 899.1 899.1 899.1 899.1	948.4 948.4 948.4 946.1 943.9 948.4 946.1 948.4 948.4 948.4 948.4 946.1 948.4 948.4 946.1 946.1 946.1 946.1 948.4 946.1 946.1 943.9 948.4 946.1 948.4 943.9 948.4 948.4 948.4 948.4 948.4	977.0 977.0 977.0 974.5 971.9 977.0 974.5 977.0 977.0 977.0 977.0 974.5 977.0 977.0 974.5 974.5 974.5 974.5 977.0 974.5 974.5 971.9 977.0 974.5 977.0 971.9 977.0 977.0 977.0 977.0 977.0	995.3 995.3 995.3 992.5 989.8 995.3 992.5 995.3 995.3 995.3 995.3 992.5 995.3 995.3 992.5 992.5 992.5 992.5 995.3 992.5 992.5 989.8 995.3 992.5 995.3 989.8 995.3 995.3 995.3 995.3 995.3



Table 11. Standard entropy of polycyclic aromatic hydrocarbons in J/K mol

T/K	298.15	300	500	700	1000	1500	2000	2500	3000
<b>C6H6</b>									
benzene	269.14	269.65	325.32	378.51	448.02	540.01	611.54	669.70	718.59
<b>C10H8</b>									
naphthalene	333.27	334.11	423.59	507.50	616.13	758.88	869.33	958.85	1033.94
<b>C14H10</b>									
anthracene	388.3	389.4	512.7	627.3	775.1	968.6	1118.0	1238.9	1340.1
phenanthrene	394.0	395.2	518.5	633.1	780.9	974.4	1123.7	1244.6	1345.9
<b>C18H12</b>									
naphthacene	443.3	444.8	601.9	747.2	934.1	1178.4	1366.6	1518.9	1646.4
benz(a)anthracene	454.8	456.3	613.4	758.7	945.6	1189.9	1378.2	1530.4	1657.9
benzo(c)phenanthrene	477.5	479.0	634.9	779.9	966.3	1209.9	1397.6	1549.3	1676.3
chrysene	449.0	450.5	607.6	753.0	939.9	1184.1	1372.4	1524.6	1652.1
triphenylene	439.9	441.4	598.5	743.8	930.7	1175.0	1363.3	1515.5	1643.0
<b>C22H14</b>									
pentacene	498.3	500.1	691.0	867.1	1093.1	1388.1	1615.3	1798.9	1952.6
di-benz(a,j)anthracene	504.0	505.9	696.8	872.8	1098.8	1393.9	1621.1	1804.7	1958.3
benzo(b)chrysene	509.8	511.6	702.5	878.6	1104.6	1399.6	1626.8	1810.4	1964.1
pentaphene	504.0	505.9	696.8	872.8	1098.8	1393.9	1621.1	1804.7	1958.3
di-benzo(b,g)phenanthrene	538.3	540.1	729.8	905.5	1131.1	1425.5	1652.0	1835.1	1988.3
benzo(c)chrysene	538.3	540.1	729.8	905.5	1131.1	1425.5	1652.0	1835.1	1988.3
picene	504.0	505.9	696.8	872.8	1098.8	1393.9	1621.1	1804.7	1958.3
benzo(a)naphthacene	509.8	511.6	702.5	878.6	1104.6	1399.6	1626.8	1810.4	1964.1
di-benz(a,h)anthracene	504.0	505.9	696.8	872.8	1098.8	1393.9	1621.1	1804.7	1958.3
benzo(b)triphenylene	504.0	505.9	696.8	872.8	1098.8	1393.9	1621.1	1804.7	1958.3
benzo(a)triphenylene	538.3	540.1	729.8	905.5	1131.1	1425.5	1652.0	1835.1	1988.3
<b>C26H16</b>									
1.	564.8	567.0	791.7	998.4	1263.6	1609.4	1875.5	2090.4	2270.3
2.	553.3	555.4	780.2	986.9	1252.0	1597.8	1864.0	2078.9	2258.8
3.	559.0	561.2	785.9	992.7	1257.8	1603.6	1869.7	2084.7	2264.5
7.	593.3	595.4	818.9	1025.3	1290.0	1635.2	1900.7	2115.1	2294.5
8.	616.0	618.1	840.4	1046.5	1310.8	1655.3	1920.2	2134.1	2313.0
9.	559.0	561.2	785.9	992.7	1257.8	1603.6	1869.7	2084.7	2264.5
10.	587.5	589.7	813.2	1019.6	1284.3	1629.4	1894.9	2109.4	2288.8
11.	564.8	567.0	791.7	998.4	1263.6	1609.4	1875.5	2090.4	2270.3
12.	564.8	567.0	791.7	998.4	1263.6	1609.4	1875.5	2090.4	2270.3
13.	564.8	567.0	791.7	998.4	1263.6	1609.4	1875.5	2090.4	2270.3
14.	564.8	567.0	791.7	998.4	1263.6	1609.4	1875.5	2090.4	2270.3
15.	587.5	589.7	813.2	1019.6	1284.3	1629.4	1894.9	2109.4	2288.8
16.	564.8	567.0	791.7	998.4	1263.6	1609.4	1875.5	2090.4	2270.3
17.	564.8	567.0	791.7	998.4	1263.6	1609.4	1875.5	2090.4	2270.3
18.	593.3	595.4	818.9	1025.3	1290.0	1635.2	1900.7	2115.1	2294.5
19.	593.3	595.4	818.9	1025.3	1290.0	1635.2	1900.7	2115.1	2294.5
20.	593.3	595.4	818.9	1025.3	1290.0	1635.2	1900.7	2115.1	2294.5
21.	593.3	595.4	818.9	1025.3	1290.0	1635.2	1900.7	2115.1	2294.5
22.	559.0	561.2	785.9	992.7	1257.8	1603.6	1869.7	2084.7	2264.5
24.	593.3	595.4	818.9	1025.3	1290.0	1635.2	1900.7	2115.1	2294.5
25.	610.3	612.4	834.7	1040.7	1305.0	1649.5	1914.4	2128.3	2307.2
26.	564.8	567.0	791.7	998.4	1263.6	1609.4	1875.5	2090.4	2270.3
27.	593.3	595.4	818.9	1025.3	1290.0	1635.2	1900.7	2115.1	2294.5
28.	559.0	561.2	785.9	992.7	1257.8	1603.6	1869.7	2084.7	2264.5
29.	593.3	595.4	818.9	1025.3	1290.0	1635.2	1900.7	2115.1	2294.5
30.	616.0	618.1	840.4	1046.5	1310.8	1655.3	1920.2	2134.1	2313.0
31.	559.0	561.2	785.9	992.7	1257.8	1603.6	1869.7	2084.7	2264.5
32.	593.3	595.4	818.9	1025.3	1290.0	1635.2	1900.7	2115.1	2294.5
33.	621.8	623.9	846.2	1052.2	1316.5	1661.0	1925.9	2139.8	2318.7
34.	564.8	567.0	791.7	998.4	1263.6	1609.4	1875.5	2090.4	2270.3
35.	559.0	561.2	785.9	992.7	1257.8	1603.6	1869.7	2084.7	2264.5
36.	593.3	595.4	818.9	1025.3	1290.0	1635.2	1900.7	2115.1	2294.5

Table 12. Standard enthalpy of formation for polycyclic aromatic hydrocarbons in kJ/mol

T/K	298.15	300	500	700	1000	1500	2000	2500	3000
C <sub>6</sub> H <sub>6</sub> benzene	82.80	82.70	73.39	67.52	63.02	61.37	62.25	63.44	64.02
C <sub>10</sub> H <sub>8</sub> naphthalene	150.57	150.45	139.40	132.62	127.93	127.67	130.52	133.41	135.05
C <sub>14</sub> H <sub>10</sub> anthracène phenanthrene	218.3 209.1	218.2 209.0	205.4 196.2	197.7 188.5	192.8 183.6	194.0 184.8	198.8 189.6	203.4 194.2	206.1 196.9
C <sub>18</sub> H <sub>12</sub> naphthacene benz(a)anthracene benzo(c)phenanthrene chrysene triphenylene	286.1 276.9 280.5 267.7 258.5	285.9 276.7 280.3 267.5 258.3	271.4 262.2 265.3 253.0 243.8	262.8 253.6 256.5 244.4 235.2	257.8 248.6 251.1 239.3 230.1	260.3 251.1 252.8 241.9 232.7	267.1 257.9 258.6 248.7 239.5	273.4 264.2 263.7 255.0 245.8	277.1 267.9 266.1 258.7 249.5
C <sub>22</sub> H <sub>14</sub> pentacene dibenz(a,j)anthracene benzo(b)chrysene pentaphene dibenzo(b,g)phenanthrene benzo(c)chrysene picene benzo(a)naphthacene dibenz(a,h)anthracene benzo(b)triphenylene benzo(a)triphenylene	353.9 335.5 335.5 344.7 348.3 339.0 326.3 344.7 335.5 326.3 329.8	353.7 335.3 335.3 344.5 348.1 338.9 326.1 344.5 335.3 326.1 329.7	337.4 319.0 319.0 328.2 331.3 322.1 309.8 328.2 319.0 309.8 312.9	327.9 309.5 309.5 318.7 321.6 312.4 300.3 318.7 309.5 300.3 303.2	322.7 304.3 304.3 313.5 316.0 306.8 295.1 313.5 304.3 295.1 297.6	326.6 308.2 308.2 317.4 319.1 309.9 299.0 317.4 308.2 299.0 300.7	335.3 316.9 316.9 326.1 326.8 317.6 307.7 321.6 316.9 307.7 308.4	343.3 324.9 324.9 334.1 333.6 324.4 315.7 334.1 324.9 315.7 315.2	348.2 329.7 329.7 339.0 337.1 327.9 320.5 339.0 329.7 320.5 318.7
C <sub>26</sub> H <sub>16</sub> 1. 2. 3. 7. 8. 9. 10. 11. 12. 13. 14. 15. 16. 17. 18. 19. 20. 21. 22. 24. 25. 26. 27. 28. 29. 30. 31. 32. 33. 34. 35. 36.	412.4 421.6 403.2 406.8 410.4 403.2 397.6 403.2 394.0 394.0 412.4 416.0 403.2 403.2 416.0 406.8 406.8 406.8 394.0 397.6 392.0 384.8 388.4 394.0 397.6 401.2 403.2 397.6 401.2 394.0 384.8 397.6	412.2 421.4 403.0 406.6 410.2 403.0 397.4 403.0 393.8 393.8 412.2 415.8 403.0 403.0 415.8 406.6 406.6 406.6 393.8 397.4 391.8 384.6 388.2 393.8 397.4 401.0 403.0 397.4 401.0 393.8 384.6 397.4	394.2 403.4 385.0 388.1 391.3 385.0 378.9 385.0 375.8 375.8 394.2 397.3 385.0 385.0 397.3 388.1 388.1 388.1 375.8 378.9 372.9 366.6 369.7 375.8 368.3 382.1 385.0 378.9 382.1 375.8 366.6 378.9	383.8 393.0 374.6 377.5 380.4 374.6 368.3 374.6 365.4 365.4 383.8 386.7 374.6 374.6 386.7 377.5 377.5 377.5 365.4 368.3 362.0 356.2 359.1 365.4 360.0 368.3 371.2 374.6 368.3 371.2 365.4 356.2 368.3	378.4 387.6 369.2 371.7 374.3 369.2 362.5 369.2 360.0 360.0 378.4 380.9 369.2 369.2 380.9 371.7 371.7 371.7 360.0 362.5 355.9 350.8 353.3 357.8 360.0 362.5 365.1 369.2 368.7 365.1 368.7 356.0 366.0 362.5	383.7 392.9 374.5 376.2 378.0 374.5 376.0 374.5 385.2 376.0 383.7 385.4 374.5 374.5 385.4 376.2 385.9 385.9 376.0 367.0 359.5 356.0 357.8 365.3 367.0 368.7 374.5 368.7 368.7 367.0 377.4 366.8 367.0	394.4 403.6 385.2 385.9 386.6 385.2 385.2 385.2 394.9 376.0 394.4 395.1 385.2 385.2 395.1 385.9 385.9 385.9 376.0 376.7 368.2 366.8 367.5 376.0 376.0 385.2 377.4 385.2 376.7 377.4 376.0 366.8 376.7	404.1 413.3 394.9 394.4 393.9 394.9 394.9 394.9 394.9 394.9 404.1 403.6 394.9 394.9 403.6 394.4 394.4 394.4 385.7 385.2 375.5 376.5 376.0 385.7 384.7 384.7 384.7 384.7 384.7 384.7 384.7 385.2	410.0 419.2 400.8 398.9 397.1 400.8 389.7 400.8 391.6 391.6 410.0 408.1 400.8 400.8 408.1 398.9 398.9 398.9 391.6 389.7 378.7 382.4 380.5 391.6 389.7 387.9 400.8 389.7 387.9 387.9 382.4 382.4 389.7

Table 13. Standard Gibbs energy of formation for polycyclic aromatic hydrocarbons in kJ/mol

T/K	298.15	300	500	700	1000	1500	2000	2500	3000
<b>C6H6</b>									
benzene	129.71	130.00	164.32	201.84	260.39	359.63	458.94	558.73	656.82
<b>C10H8</b>									
naphthalene	224.16	224.62	277.38	333.91	421.23	568.19	714.64	861.32	1005.52
<b>C14H10</b>									
anthracene	321.3	322.0	395.0	472.4	591.2	790.5	988.6	1186.7	1381.6
phenanthrene	310.4	311.0	382.9	459.1	576.2	772.6	967.9	1163.1	1355.1
<b>C18H12</b>									
naphthacene	418.5	419.3	512.6	610.8	761.2	1012.7	1262.6	1512.2	1757.7
benz(a)anthracene	405.9	406.7	497.7	593.6	740.5	986.2	1230.3	1474.2	1714.0
benzo(c)phenanthrene	402.7	403.4	490.1	581.7	722.3	957.9	1192.1	1426.3	1656.8
chrysene	398.4	399.2	491.3	588.4	737.0	985.7	1232.6	1479.4	1722.0
triphenylene	391.9	392.7	486.7	585.6	736.9	990.2	1241.7	1493.0	1740.2
<b>C22H14</b>									
pentacene	515.7	516.7	630.3	749.3	931.2	1235.0	1536.5	1837.6	2133.8
dibenz(a,j)anthracene	495.6	496.6	609.0	726.9	907.0	1207.9	1506.6	1804.8	2098.1
benzo(b)chrysene	493.8	494.8	606.1	722.8	901.2	1199.3	1495.1	1790.4	2080.9
pentaphene	504.8	505.8	618.2	736.1	916.2	1217.1	1515.8	1814.0	2107.4
dibenzo(b,g)phenanthrene	498.1	499.1	604.8	716.1	886.5	1171.5	1454.5	1737.4	2015.6
benzo(c)chrysene	488.9	489.9	595.6	706.9	877.3	1162.3	1445.3	1728.2	2006.4
picene	486.4	487.4	599.8	717.7	897.8	1198.7	1497.4	1795.6	2088.9
benzo(a)naphthacene	503.1	504.0	615.3	732.0	910.4	1208.5	1504.3	1799.6	2090.1
dibenz(a,h)anthracene	495.6	496.6	609.0	726.9	907.0	1207.9	1506.6	1804.8	2098.1
benzo(b)triphenylene	486.4	487.4	599.8	717.7	897.8	1198.7	1497.4	1795.6	2088.9
benzo(a)triphenylene	479.7	480.7	586.4	697.7	868.1	1153.1	1436.1	1718.9	1997.2
<b>C26H16</b>									
1.	600.2	601.4	732.9	870.5	1080.4	1430.8	1778.2	2125.0	2466.2
2.	612.9	614.1	747.9	887.8	1101.1	1457.9	1810.6	2163.0	2510.0
3.	592.7	593.9	726.6	865.3	1077.0	1430.2	1780.6	2130.2	2474.3
7.	586.1	587.2	713.2	845.4	1047.3	1384.6	1719.3	2053.6	2382.5
8.	582.9	584.0	705.6	833.5	1029.1	1356.2	1681.0	2005.8	2325.4
9.	592.7	593.9	726.6	865.3	1077.0	1430.2	1780.6	2130.2	2474.3
10.	578.6	579.7	706.9	840.2	1043.9	1384.0	1721.6	2058.8	2390.6
11.	591.0	592.2	723.7	861.3	1071.2	1421.6	1769.0	2115.8	2457.0
12.	581.8	583.0	714.5	852.1	1062.0	1412.4	1759.8	2106.6	2447.8
13.	581.8	583.0	714.5	852.1	1062.0	1412.4	1759.8	2106.6	2447.8
14.	600.2	601.4	732.9	870.5	1080.4	1430.8	1778.2	2125.0	2466.2
15.	597.0	598.2	725.3	858.6	1062.3	1402.4	1740.0	2077.2	2409.0
16.	591.0	592.2	723.7	861.3	1071.2	1421.6	1769.0	2115.8	2457.0
17.	591.0	592.2	723.7	861.3	1071.2	1421.6	1769.0	2115.8	2457.0
18.	595.3	596.4	722.4	854.6	1056.5	1393.8	1728.5	2062.8	2391.7
19.	586.1	587.2	713.2	845.4	1047.3	1384.6	1719.3	2053.6	2382.5
20.	586.1	587.2	713.2	845.4	1047.3	1384.6	1719.3	2053.6	2382.5
21.	586.1	587.2	713.2	845.4	1047.3	1384.6	1719.3	2053.6	2382.5
22.	583.5	584.7	717.4	856.1	1067.8	1421.0	1771.3	2121.0	2465.1
24.	576.9	578.0	704.0	836.2	1038.1	1375.4	1710.1	2044.4	2373.3
25.	566.2	567.3	690.1	819.1	1016.5	1346.5	1674.2	2001.8	2324.2
26.	572.6	573.8	705.3	842.9	1052.8	1403.2	1750.6	2097.4	2438.6
27.	567.7	568.8	694.8	827.0	1028.9	1366.2	1700.9	2035.2	2364.1
28.	583.5	584.7	717.4	856.1	1067.8	1421.0	1771.3	2121.0	2465.1
29.	576.9	578.0	704.0	836.2	1038.1	1375.4	1710.1	2044.4	2373.3
30.	573.7	574.8	696.4	824.3	1019.9	1347.0	1671.8	1996.6	2316.2
31.	592.7	593.9	726.6	865.3	1077.0	1430.2	1780.6	2130.2	2474.3
32.	576.9	578.0	704.0	836.2	1038.1	1375.4	1710.1	2044.4	2373.3
33.	572.0	573.1	693.5	820.3	1014.2	1338.4	1660.3	1982.1	2298.9
34.	581.8	583.0	714.5	852.1	1062.0	1412.4	1759.8	2106.6	2447.8
35.	574.3	575.5	708.2	846.9	1058.6	1411.8	1762.1	2111.8	2455.8
36.	576.9	578.0	704.0	836.2	1038.1	1375.4	1710.1	2044.4	2373.3

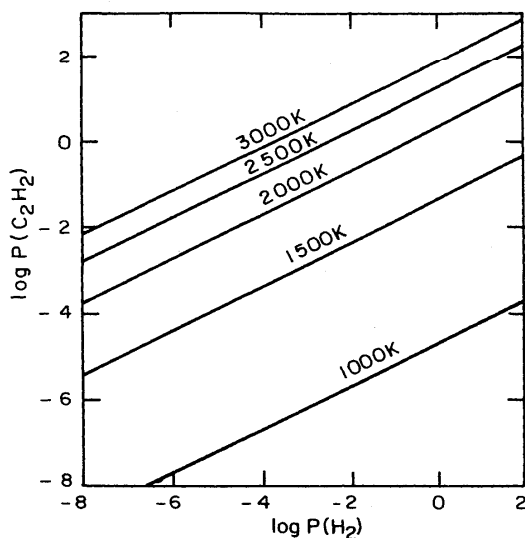
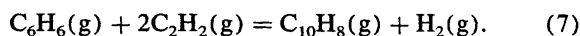


FIG. 2. Plot of Eq. (9) at several temperatures. To the right of these lines benzene is more stable than naphthalene and to the left naphthalene is more stable.

spect to graphite and molecular hydrogen at 1 bar, but the sequence of decreasing stability depends upon the partial pressure of hydrogen. The choice of graphite and molecular hydrogen is, of course, arbitrary and in thinking about the relative stabilities of the various polycyclic aromatic hydrocarbons in flames, it is of more interest to consider their formation from acetylene. For example, naphthalene can be formed from benzene by the reaction



If at equilibrium,  $P(\text{C}_{10}\text{H}_8) = P(\text{C}_6\text{H}_6)$  then

$$K = P(\text{H}_2)/P(\text{C}_2\text{H}_2)^2, \quad (8)$$

where  $K$  is the equilibrium constant for reaction 7 expressed in terms of pressures. Thus

$$\log P(\text{C}_2\text{H}_2) = - (1/2)\log K + (1/2)\log P(\text{H}_2). \quad (9)$$

Figure 2 shows  $\log P(\text{C}_2\text{H}_2)$  as a function of  $\log P(\text{H}_2)$  for several temperatures. If at a given temperature the point representing an equilibrium system lies to the right of the line, benzene will be present at a higher partial pressure than naphthalene. To the left of the line naphthalene is more stable. Since the increment in  $\Delta_f G^\circ(\text{I})$  in going from an isomer group to the next higher isomer group is nearly the same, this plot applies approximately to any successive pair of isomer groups. Therefore Fig. 1 provides a quick method for determining whether growth to higher isomer groups of polycyclic aromatic hydrocarbons will occur spontaneously.

The increments in  $C_p^\circ(\text{I})$ ,  $S^\circ(\text{I})$ ,  $\Delta_f H^\circ(\text{I})$ , and  $\Delta_f G^\circ(\text{I})$  per  $\text{C}_4\text{H}_2$  are very nearly constant at a given temperature. This means that the isomer group thermodynamic properties at higher carbon numbers, where it is not feasible to deal with individual molecular species, can be estimated in the temperature range 298 to 3000 K.

The polycyclic aromatic hydrocarbons provide a good example of the usefulness of isomer group thermodynamic

properties because the number of components that have to be considered in the calculation of an equilibrium composition is very much reduced by considering isomer groups.

## 8. Nomenclature

- $C_{pi}^\circ$  = standard heat capacity at constant pressure of isomer  $i$ ,  $\text{J K}^{-1} \text{mol}^{-1}$
- $C_p^\circ(\text{I})$  = standard heat capacity at constant pressure of isomer group  $\text{I}$ ,  $\text{J K}^{-1} \text{mol}^{-1}$
- $\Delta_f G_i^\circ$  = standard Gibbs energy of formation of isomer  $i$ ,  $\text{kJ mol}^{-1}$
- $\Delta_f G^\circ(\text{I})$  = standard Gibbs energy of formation of isomer group  $\text{I}$ ,  $\text{kJ mol}^{-1}$
- $H^\circ(\text{I}, T) - H^\circ(\text{I}, 298.15 \text{ K})$  = standard enthalpy for isomer groups relative to isomer groups at 298.15 K,  $\text{kJ mol}^{-1}$
- $H^\circ(\text{I}, T) - H^\circ(\text{I}, 298.15 \text{ K}) + \Delta_f H^\circ(\text{I}, 298.15 \text{ K})$  = standard enthalpy for isomer groups relative to elements at 298.15 K,  $\text{kJ mol}^{-1}$
- $\Delta_f H_i^\circ$  = standard enthalpy of formation of isomer  $i$ ,  $\text{kJ mol}^{-1}$
- $\Delta_f H^\circ(\text{I})$  = standard enthalpy of formation of isomer group  $\text{I}$ ,  $\text{kJ mol}^{-1}$
- $n_C$  = number of carbon atoms in a molecule
- $n_H$  = number of hydrogen atoms in a molecule
- $N_I$  = number of isomers in an isomer group
- $r_i$  = equilibrium mole fraction of species  $i$  in an isomer group
- $S_i^\circ$  = standard entropy of isomer  $i$ ,  $\text{J K}^{-1} \text{mol}^{-1}$
- $S^\circ(\text{I})$  = standard entropy of isomer group  $\text{I}$ ,  $\text{J K}^{-1} \text{mol}^{-1}$
- TSN = total symmetry number
- $y_i$  = mole fraction of isomer  $i$  within the isomer group
- $y_I$  = mole fraction of isomer group  $\text{I}$  in a mixture

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