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°, S°, $\Delta_f H^\circ$, 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

the $[C_{FR}\text{-}(C_{FR})_3]$ group were derived from pyrene frequencies[36] 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° 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.[37]

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°_{int298}, C°_{P298}, C°_{P300}, C°_{P500}, C°_{P700}, C°_{P1000}, C°_{P1500}, C°_{P2000}, C°_{P2500}, and C°_{P3000}. In further steps in the calculation, the effect of symmetry number was included, and the heat capacity values were fit to the equation

$$C_P^\circ = a + \frac{b}{\sqrt{T}} + \frac{c}{T^2} + \frac{d}{T}, \tag{4}$$

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

$$S^\circ = S_0^\circ + a \ln T - 2bT^{-1/2} - (c/2)T^{-2} - d/T - R\ln(\mathrm{TSN}), \tag{5}$$

$$\Delta_f H^\circ = \Delta_f H_0^\circ + aT + 2bT^{1/2} - c/T + d\ln T - n_C(H^\circ - H^\circ_{298})_{\text{graphite}} - (n_H/2)(H^\circ - H^\circ_{298})_{H_2}. \tag{6}$$

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

The new value of the gas constant[38] and the new values for S° and $H^\circ - H^\circ(298.15\ \mathrm{K})$ for C(graphite) and H_2(g) were used.[39]

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.[40] This comparison has been made earlier with the Stull, Westrum, and Sinke[41] tables for benzene[26] and naphthalene[28] 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[42,43] 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 $H^\circ(\mathrm{I},T) - H^\circ(\mathrm{I},298.15\ \mathrm{K})$, the standard enthalpy for an isomer group relative to the isomer group at 298.15 K. Table 8 gives values for $H^\circ(\mathrm{I},T) - H^\circ(\mathrm{I},298.15\ \mathrm{K}) + \Delta_f H^\circ(\mathrm{I},298.15\ \mathrm{K})$, 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	-1.90
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	195.83	328.60	453.5	583.5	705.3	834.6
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 $\Delta_f G°(I)$ and $\Delta_f G_i^\circ$ 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.[44]

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 temperatures, 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°, $S°$, $\Delta_f H°$, and $\Delta_f G°$ 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
C14H10									
anthracene	.0121	.0123	.0518	.0932	.1418	.1929	.2233	.2431	.2569
phenanthrene	.9879	.9877	.9482	.9068	.8582	.8071	.7767	.7569	.7431
C18H12									
naphthacene	.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
C22H14									
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)naphthacene	.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
C26H16									
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	.1853	.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	188.4	189.3	300.9	378.7	447.0	504.0	532.9	549.9	560.8
phenanthrene	188.4	189.3	300.9	378.7	447.0	504.0	532.9	549.9	560.8
C18H12									
naphthacene	241.2	242.4	382.2	479.6	564.8	635.7	671.4	692.2	705.6
benz(a)anthracene	241.2	242.4	382.2	479.6	564.8	635.7	671.4	692.2	705.6
benzo(c)phenanthrene	236.8	238.0	380.9	478.5	563.4	633.8	669.1	689.7	702.9
chrysene	241.2	242.4	382.2	479.6	564.8	635.7	671.4	692.2	705.6
triphenylene	241.2	242.4	382.2	479.6	564.8	635.7	671.4	692.2	705.6
C22H14									
pentacene	294.1	295.4	463.4	580.4	682.6	767.4	809.9	834.6	850.4
dibenz(a,j)anthracene	294.1	295.4	463.4	580.4	682.6	767.4	809.9	834.6	850.4
benzo(b)chrysene	294.1	295.4	463.4	580.4	682.6	767.4	809.9	834.6	850.4
pentaphene	294.1	295.4	463.4	580.4	682.6	767.4	809.9	834.6	850.4
dibenzo(b,g)phenanthrene	289.7	291.1	462.2	579.4	681.2	765.5	807.6	832.1	847.7
benzo(c)chrysene	289.7	291.1	462.2	579.4	681.2	765.5	807.6	832.1	847.7
picene	294.1	295.4	463.4	580.4	682.6	767.4	809.9	834.6	850.4
benzo(a)naphthacene	294.1	295.4	463.4	580.4	682.6	767.4	809.9	834.6	850.4
dibenz(a,h)anthracene	294.1	295.4	463.4	580.4	682.6	767.4	809.9	834.6	850.4
benzo(b)triphenylene	294.1	295.4	463.4	580.4	682.6	767.4	809.9	834.6	850.4
benzo(a)triphenylene	289.7	291.1	462.2	579.4	681.2	765.5	807.6	832.1	847.7
C26H16									
1.	346.9	348.5	544.7	681.3	800.4	899.1	948.4	977.0	995.3
2.	346.9	348.5	544.7	681.3	800.4	899.1	948.4	977.0	995.3
3.	346.9	348.5	544.7	681.3	800.4	899.1	948.4	977.0	995.3
7.	342.5	344.2	543.4	680.2	799.0	897.2	946.1	974.5	992.5
8.	338.1	339.8	542.2	679.2	797.7	895.3	943.9	971.9	989.8
9.	346.9	348.5	544.7	681.3	800.4	899.1	948.4	977.0	995.3
10.	342.5	344.2	543.4	680.2	799.0	897.2	946.1	974.5	992.5
11.	346.9	348.5	544.7	681.3	800.4	899.1	948.4	977.0	995.3
12.	346.9	348.5	544.7	681.3	800.4	899.1	948.4	977.0	995.3
13.	346.9	348.5	544.7	681.3	800.4	899.1	948.4	977.0	995.3
14.	346.9	348.5	544.7	681.3	800.4	899.1	948.4	977.0	995.3
15.	342.5	344.2	543.4	680.2	799.0	897.2	946.1	974.5	992.5
16.	346.9	348.5	544.7	681.3	800.4	899.1	948.4	977.0	995.3
17.	346.9	348.5	544.7	681.3	800.4	899.1	948.4	977.0	995.3
18.	342.5	344.2	543.4	680.2	799.0	897.2	946.1	974.5	992.5
19.	342.5	344.2	543.4	680.2	799.0	897.2	946.1	974.5	992.5
20.	342.5	344.2	543.4	680.2	799.0	897.2	946.1	974.5	992.5
21.	342.5	344.2	543.4	680.2	799.0	897.2	946.1	974.5	992.5
22.	346.9	348.5	544.7	681.3	800.4	899.1	948.4	977.0	995.3
24.	342.5	344.2	543.4	680.2	799.0	897.2	946.1	974.5	992.5
25.	338.1	339.8	542.2	679.2	797.7	895.3	943.9	971.9	989.8
26.	346.9	348.5	544.7	681.3	800.4	899.1	948.4	977.0	995.3
27.	342.5	344.2	543.4	680.2	799.0	897.2	946.1	974.5	992.5
28.	346.9	348.5	544.7	681.3	800.4	899.1	948.4	977.0	995.3
29.	342.5	344.2	543.4	680.2	799.0	897.2	946.1	974.5	992.5
30.	338.1	339.8	542.2	679.2	797.7	895.3	943.9	971.9	989.8
31.	346.9	348.5	544.7	681.3	800.4	899.1	948.4	977.0	995.3
32.	342.5	344.2	543.4	680.2	799.0	897.2	946.1	974.5	992.5
33.	338.1	339.8	542.2	679.2	797.7	895.3	943.9	971.9	989.8
34.	346.9	348.5	544.7	681.3	800.4	899.1	948.4	977.0	995.3
35.	346.9	348.5	544.7	681.3	800.4	899.1	948.4	977.0	995.3
36.	342.5	344.2	543.4	680.2	799.0	897.2	946.1	974.5	992.5

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

T/K	298.15	300	500	700	1000	1500	2000	2500	3000
C6H6									
benzene	269.14	269.65	325.32	378.51	448.02	540.01	611.54	669.70	718.59
C10H8									
naphthalene	333.27	334.11	423.59	507.50	616.13	758.88	869.33	958.85	1033.94
C14H10									
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
C18H12									
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
C22H14									
pentacene	498.3	500.1	691.0	867.1	1093.1	1388.1	1615.3	1798.9	1952.6
dibenz(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
dibenzo(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
dibenz(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
C26H16									
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
C6H6									
benzene	82.80	82.70	73.39	67.52	63.02	61.37	62.25	63.44	64.02
C10H8									
naphthalene	150.57	150.45	139.40	132.62	127.93	127.67	130.52	133.41	135.05
C14H10									
anthracene	218.3	218.2	205.4	197.7	192.8	194.0	198.8	203.4	206.1
phenanthrene	209.1	209.0	196.2	188.5	183.6	184.8	189.6	194.2	196.9
C18H12									
naphthacene	286.1	285.9	271.4	262.8	257.8	260.3	267.1	273.4	277.1
benz(a)anthracene	276.9	276.7	262.2	253.6	248.6	251.1	257.9	264.2	267.9
benzo(c)phenanthrene	280.5	280.3	265.3	256.5	251.1	252.8	258.6	263.7	266.1
chrysene	267.7	267.5	253.0	244.4	239.3	241.9	248.7	255.0	258.7
triphenylene	258.5	258.3	243.8	235.2	230.1	232.7	239.5	245.8	249.5
C22H14									
pentacene	353.9	353.7	337.4	327.9	322.7	326.6	335.3	343.3	348.2
dibenz(a,j)anthracene	335.5	335.3	319.0	309.5	304.3	308.2	316.9	324.9	329.7
benzo(b)chrysene	335.5	335.3	319.0	309.5	304.3	308.2	316.9	324.9	329.7
pentaphene	344.7	344.5	328.2	318.7	313.5	317.4	326.1	334.1	339.0
dibenzo(b,g)phenanthrene	348.3	348.1	331.3	321.6	316.0	319.1	326.8	333.6	337.1
benzo(c)chrysene	339.0	338.9	322.1	312.4	306.8	309.9	317.6	324.4	327.9
picene	326.3	326.1	309.8	300.3	295.1	299.0	307.7	315.7	320.5
benzo(a)naphthacene	344.7	344.5	328.2	318.7	313.5	317.4	326.1	334.1	339.0
dibenz(a,h)anthracene	335.5	335.3	319.0	309.5	304.3	308.2	316.9	324.9	329.7
benzo(b)triphenylene	326.3	326.1	309.8	300.3	295.1	299.0	307.7	315.7	320.5
benzo(a)triphenylene	329.8	329.7	312.9	303.2	297.6	300.7	308.4	315.2	318.7
C26H16									
1.	412.4	412.2	394.2	383.8	378.4	383.7	394.4	404.1	410.0
2.	421.6	421.4	403.4	393.0	387.6	392.9	403.6	413.3	419.2
3.	403.2	403.0	385.0	374.6	369.2	374.5	385.2	394.9	400.8
7.	406.8	406.6	388.1	377.5	371.7	376.2	385.9	394.4	398.9
8.	410.4	410.2	391.3	380.4	374.3	378.0	386.6	393.9	397.1
9.	403.2	403.0	385.0	374.6	369.2	374.5	385.2	394.9	400.8
10.	397.6	397.4	378.9	368.3	362.5	367.0	376.7	385.2	389.7
11.	403.2	403.0	385.0	374.6	369.2	374.5	385.2	394.9	400.8
12.	394.0	393.8	375.8	365.4	360.0	365.3	376.0	385.7	391.6
13.	394.0	393.8	375.8	365.4	360.0	365.3	376.0	385.7	391.6
14.	412.4	412.2	394.2	383.8	378.4	383.7	394.4	404.1	410.0
15.	416.0	415.8	397.3	386.7	380.9	385.4	395.1	403.6	408.1
16.	403.2	403.0	385.0	374.6	369.2	374.5	385.2	394.9	400.8
17.	403.2	403.0	385.0	374.6	369.2	374.5	385.2	394.9	400.8
18.	416.0	415.8	397.3	386.7	380.9	385.4	395.1	403.6	408.1
19.	406.8	406.6	388.1	377.5	371.7	376.2	385.9	394.4	398.9
20.	406.8	406.6	388.1	377.5	371.7	376.2	385.9	394.4	398.9
21.	406.8	406.6	388.1	377.5	371.7	376.2	385.9	394.4	398.9
22.	394.0	393.8	375.8	365.4	360.0	365.3	376.0	385.7	391.6
24.	397.6	397.4	378.9	368.3	362.5	367.0	376.7	385.2	389.7
25.	392.0	391.8	372.9	362.0	355.9	359.5	368.2	375.5	378.7
26.	384.8	384.6	366.6	356.2	350.8	356.0	366.8	376.5	382.4
27.	388.4	388.2	369.7	359.1	353.3	357.8	367.5	376.0	380.5
28.	394.0	393.8	375.8	365.4	360.0	365.3	376.0	385.7	391.6
29.	397.6	397.4	378.9	368.3	362.5	367.0	376.7	385.2	389.7
30.	401.2	401.0	382.1	371.2	365.1	368.7	377.4	384.7	387.9
31.	403.2	403.0	385.0	374.6	369.2	374.5	385.2	394.9	400.8
32.	397.6	397.4	378.9	368.3	362.5	367.0	376.7	385.2	389.7
33.	401.2	401.0	382.1	371.2	365.1	368.7	377.4	384.7	387.9
34.	394.0	393.8	375.8	365.4	360.0	365.3	376.0	385.7	391.6
35.	384.8	384.6	366.6	356.2	350.8	356.0	366.8	376.5	382.4
36.	397.6	397.4	378.9	368.3	362.5	367.0	376.7	385.2	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
C6H6									
benzene	129.71	130.00	164.32	201.84	260.39	359.63	458.94	558.73	656.82
C10H8									
naphthalene	224.16	224.62	277.38	333.91	421.23	568.19	714.64	861.32	1005.52
C14H10									
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
C18H12									
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
C22H14									
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
C26H16									
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	1457.3	1810.5	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

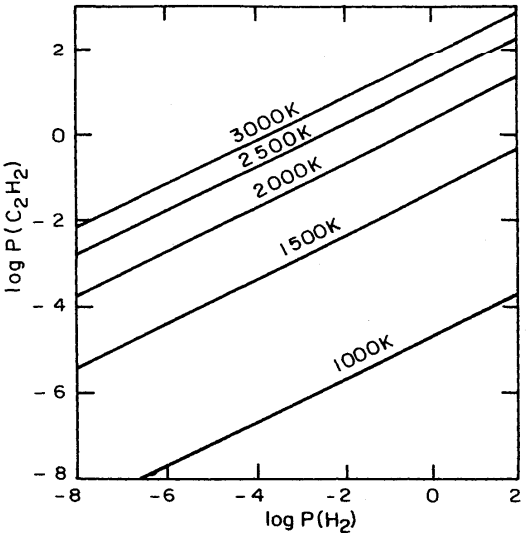

FIG. 2. Plot of Eq. (9) at several temperatures. To the right of these lines benzene is more stable than naphthalene and to the left naphthalene is more stable.

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

$$C_6H_6(g) + 2C_2H_2(g) = C_{10}H_8(g) + H_2(g). \quad (7)$$

If at equilibrium, $P(C_{10}H_8) = P(C_6H_6)$ then

$$K = P(H_2)/P(C_2H_2)^2, \quad (8)$$

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

$$\log P(C_2H_2) = -(1/2)\log K + (1/2)\log P(H_2). \quad (9)$$

Figure 2 shows $\log P(C_2H_2)$ as a function of $\log P(H_2)$ 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 $\Delta_f G°(I)$ 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 $C°_P(I)$, $S°(I)$, $\Delta_f H°(I)$, and $\Delta_f G°(I)$ per C_4H_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

$C°_{Pi}$ = standard heat capacity at constant pressure of isomer i, J K^{-1} mol^{-1}

$C°_P(I)$ = standard heat capacity at constant pressure of isomer group I, J K^{-1} mol^{-1}

$\Delta_f G°_i$ = standard Gibbs energy of formation of isomer i, kJ mol^{-1}

$\Delta_f G°(I)$ = standard Gibbs energy of formation of isomer group I, kJ mol^{-1}

$H°(I,T) - H°(I,298.15\ K)$ = standard enthalpy for isomer groups relative to isomer groups at 298.15 K, kJ mol^{-1}

$H°(I,T) - H°(I,298.15\ K) + \Delta_f H°(I,298.15\ K)$ = standard enthalpy for isomer groups relative to elements at 298.15 K, kJ mol^{-1}

$\Delta_f H°_i$ = standard enthalpy of formation of isomer i kJ mol^{-1}

$\Delta_f H°(I)$ = standard enthalpy of formation of isomer group I, 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

$S°_i$ = standard entropy of isomer i, J K^{-1} mol^{-1}

$S°(I)$ = standard entropy of isomer group I, J K^{-1} mol^{-1}

TSN = total symmetry number

y_i = mole fraction of isomer i within the isomer group

y_I = mole fraction of isomer group I in a mixture

9. Acknowledgments

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10. References

[1] J. D. Bittner and J. B. Howard, in "Eighteenth Symposium (International) on Combustion," The Combustion Institute, Pittsburg, PA, 198 p. 1105.

[2] J. D. Bittner and J. B. Howard, in *Particulate Carbon Formation during Combustion*, edited by D. C. Siegla and G. W. Smith (Plenum, New York 1981).

[3] J. B. Howard and J. D. Bittner, in *Soot in Combustion Systems*, edited by Lahaye and G. Prado (Plenum, New York, 1981), p. 56.

[4] J. D. Bittner, J. B. Howard, and H. B. Palmer, in Ref. 3, p. 95.

[5] J. A. Cole, J. D. Bittner, J. P. Longwell, and J. B. Howard, Combustic and Flame **56**, 51 (1984).

[6] A. Leger and J. L. Puget, Astron. Astrophys. **137**, L5 (1984).

[7] A. Leger, L. d'Hendecourt, and N. Boccara, *Polycyclic Aromatic Hydrocarbons in Astrophysics* (Reidel, Boston, MA, 1987).

[8]S. E. Stein, J. Phys. Chem. **82**, 566 (1978).
[9]S. E. Stein and B. D. Barton, Thermochim. Acta **44**, 265 (1981).
[10]M. J. Manka and S. E. Stein, J. Phys. Chem. **88**, 5914 (1984).
[11]S. E. Stein and A. Fahr, J. Phys. Chem. **89**, 3714 (1985).
[12]M. Frenklach and W. C. Gardiner, J. Phys. Chem. **88**, 6263 (1984).
[13]A. T. Balaban and F. Harary, Tetrahedron **24**, 2505 (1986).
[14]J. R. Dias, J. Chem. Inf. Comput. Sci. **22**, 15 (1982).
[15]J. R. Dias, J. Chem. Inf. Comput. Sci. **22**, 139 (1982).
[16]J. R. Dias, MATCH **14**, 83 (1983).
[17]J. R. Dias, J. Chem. Inf. Comput. Sci. **24**, 124 (1984).
[18]J. R. Dias, Can. J. Chem. **62**, 2914 (1984).
[19]J. R. Dias, Accounts Chem. Res. **18**, 241 (1985).
[20]J. R. Dias, J. Macromol. Sci. Chem. **A22**, 335 (1985).
[21]J. R. Dias, J. Mol. Struct. (Theochem) **137**, 9 (1986).
[22]J. R. Dias, J. Mol. Struct. (Theochem) **149**, 213 (1987).
[23]J. R. Dias, *Handbook of Polycyclic Hydrocarbons*, Part A: Benzenoid Hydrocarbons (Elsevier, Amsterdam, 1987).
[24]J. V. Knop, W. Müller, K. Szmanski, and N. Trinajstić, "Computer Generation of Certain Classes of Molecules"; SKTH/Kemija u industriji: Zagreb, 1985.
[25]R. A. Alberty and C. A. Gehrig, J. Phys. Chem. Ref. Data **13**, 1173 (1984).
[26]R. A. Alberty, J. Phys. Chem. Ref. Data **14**, 177 (1985).
[27]R. A. Alberty and C. A. Gehrig, J. Phys. Chem. Ref. Data **14**, 803 (1985).
[28]R. A. Alberty and T. M. Bloomstein, J. Phys. Chem. Ref. Data **14**, 821 (1985).
[29]R. A. Alberty and Y. S. Ha, J. Phys. Chem. Ref. Data **14**, 1107 (1985).
[30]B. D. Smith, AIChE J. **5**, 26 (1959).
[31]W. R. Smith and R. W. Missen, *Chemical Reaction Equilibrium Analysis: Theory and Algorithms* (Wiley, New York, 1982).
[32]R. A. Alberty, I&EC Fundamentals **22**, 318 (1983).
[33]S. W. Benson, *Thermochemical Kinetics* (Wiley, New York, 1976).
[34]S. E. Stein, D. M. Golden, and S. W. Benson, J. Phys. Chem. **81**, 314 (1977).
[35]S. E. Stein and A. Fahr, J. Phys. Chem. **89**, 3714 (1985).
[36]B. Nelander and S. J. Sunner, Chem. Phys. **44**, 2476 (1966).
[37]E. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, "The NBS tables of chemical thermodynamic properties," J. Phys. Chem. Ref. Data **11**, Suppl. 2 (1982).
[38]E. R. Cohen and B. N. Taylor, The 1986 Adjustment of the Fundamental Physical Constants, CODATA Bulletin, No. 63, 1986.
[39]M. W. Chase, C. A. Davies, J. R. Downey, D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF Thermochemical Tables*, 3rd ed., J. Phys. Chem. Ref. Data **14**, Suppl. No. 1 (1985).
[40]TRC Thermodynamic Tables, Hydrocarbons, Vols. 7 and 8, Thermodynamics Research Center, The Texas A&M University System, College Station, TX, 1986.
[41]D. R. Stull, E. F. Westrum, and G. E. Sinke, *The Chemical Thermodynamic Properties of Organic Compounds* (Wiley, New York, 1969).
[42]J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds* (Academic, New York, 1970).
[43]J. B. Pedley, R. D. Naylor, and S. P. Kirby, *Thermochemical Data of Organic Compounds*, 2nd ed. (Chapman and Hall, New York, 1986).
[44]J. Rigaudy and S. P. Klesney, *Nomenclature of Organic Chemistry Prepared for Publication* (Pergamon, New York, 1979).