Heats, Equilibrium Constants, and Free Energies of Formation of the Alkylbenzenes[1]

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For benzene, toluene, ethylbenzene, the three xylenes, normal and isopropylbenzene, the three methylethylbenzenes, the three trimethylbenzenes, and the higher normal alkylbenzenes, values are presented for the following thermodynamic properties for the gaseous state to 1,500° K: The heat-content function, $(H°-H_0°)/T$; the free-energy function, $(F°-H_0°)/T$; the entropy, $S°$; the heat content, $H°-H_0°$ the heat capacity, $C_p°$; the heat of formation from the elements, $\Delta Hf°$; the free energy of formation from the elements, $\Delta Ff°$; and the logarithm of the equilibrium constant of formation from the elements, $\log_{10} Kf$.

Equilibrium constants and concentrations are given in tabular and graphical form for the isomerization of the four C_8H_{10} alkylbenzenes and for the eight C_9H_{12} alkylbenzenes as a function of the temperature to 1,500° K. Equilibrium constants are also given in tabular and graphical form for some reactions involving alkylation (addition of olefin to benzene to form alkylbenzene), cyclization (conversion of paraffin to alkylbenzene plus hydrogen), and trimerization (of acetylene to form benzene and of methylacetylene to form 1,3,5-trimethylbenzene).

Contents

I. Introduction

As part of the work of the American Petroleum Institute Research Project 44 and the Thermochemical Laboratory at the National Bureau of Standards, values have been calculated for the heat-content function, free-energy function, entropy, heat content, and heat capacity for the 14 alkylbenzene hydrocarbons through C_9H_{12}, and for the higher normal monoalkylbenzenes, in the gaseous state to 1,500° K. These data have been combined with values of heats of formation at 25° C to calculate values of the heats, free eneries, and equilibrium constants of formation of these compounds in the gaseous state to 1,500° K. Equilibrium constants have been calculated for some reactions involving alkylation (addition of olefin to benzene to form alkylbenzene), cyclization (conversion of paraffin to alkylbenzene plus hydrogen), and trimerization (of acetylene to form benzene and of methylacetylene to form 1,3,5-trimethylbenzene).

II. Units and Constants

The unit of energy, atomic weights, and values of the fundamental constants used in this report are the same as those previously described [1].[4]

4 Figures in brackets indicate the literature references at the end of this paper.

III. Heat-Content Function, Free-Energy Function, Entropy, Heat Content, and Heat Capacity

The thermodynamic functions for benzene, toluene, o-, m-, and p-xylenes, and mesitylene were published by Pitzer and Scott [9]. The present calculations include minor revisions in these values to take account of more recent data, but they primarily concern the remaining alkylbenzenes through C_9H_{12} and the higher normal monoalkylbenzenes. The detailed methods, in which contributions from translation, over-all and internal rotation, and vibration are considered, were used for benzene and all its methyl derivatives and for ethylbenzene. The calculations for ethylbenzene and all methylbenzenes with ortho methyl groups contain certain additional approximations. The functions for n-propylbenzene and the higher normal alkylbenzenes, isopropylbenzene, and the three methylethylbenzenes, were estimated by a method of increments from the functions for the normal paraffin hydrocarbons and the lower alkylbenzenes.

1. Translational and Free Rotational Contributions

For this series of molecules the potential barriers to internal rotation are relatively low, and the moments of inertia are always fairly large; consequently, it is convenient to calculate the classical free internal rotational contribution and then to correct it in all cases for the potential barrier present. The alternate procedure of calculating directly the thermodynamic contributions for restricted internal rotations would be equally correct.

All the molecules considered in this section fall in the class studied by Pitzer and Gwinn [5], (symmetrical tops attached to a rigid frame) except ethylbenzene. However, it may be considered as a methylene group with a symmetrical methyl group and a balanced, but unsymmetrical phenyl group attached. By the term "balanced" it is meant that the center of gravity of the phenyl group is on the axis of rotation but that the two moments of inertia of the phenyl group perpendicular to the axis of rotation are not equal. An analysis of this type of problem, which shows that in such cases the various moments of inertia should be calculated for the equilibrium configuration of the molecule, is to be published elsewhere [4]. Although more general formulas are given there, they reduce to those already published [5] for this case.

The formulas of Pitzer and Gwinn [5], with the new physical constants mentioned above, combined with the equations for translation and over-

all rotation [1], yield the following equations for the total contribution of translation, over-all rotation, and free internal rotation:

$$(H° − H_0°)/T = C°_p = 7.9787 + 0.9936m \qquad (1)$$

$$−(F° − H_0°)/T = C_1 \log_{10} T + C_2 \qquad (2)$$

$$C_1 = 18.3026 + 2.2878m \qquad (3)$$

$$C_2 = 6.8635 \log_{10} M +$$
$$2.2878 \log_{10} A + 2.2878 \log_{10} B − 4.5757 \log_{10} \sigma$$
$$−2.5342m − 10.2960. \qquad (4)$$

In these equations, m is the number of internal rotations in the molecule; M is the molecular weight; A is the product of principal moments of inertia for over-all rotation, each in units of 10^{-39} g cm²; B is the product of reduced moments of inertia for internal rotation, each in units of 10^{-40} g cm²; and σ is the total symmetry number, the product of the over-all rotation symmetry number and all internal rotation symmetry numbers. The reduced moments of inertia for internal rotation were calculated from equations 1b and 1c of Pitzer and Gwinn, which give a second approximation to the reduced moments for molecules with several tops. However, for the molecules considered here, except perhaps ethylbenzene, there is no significant difference between the second approximation and the first approximation given by equation 1a of these authors.

The values for the bond lengths used in the calculations were chosen after a consideration of the published X-ray and electron-diffraction data. The benzene ring was assumed to be a plane hexagon, with carbon-carbon bond lengths of 1.39 angstroms. The other bond lengths, in angstroms, were 1.54 for the carbon-carbon bonds in the alkyl groups, including the bond joining the group to the ring [7], 1.09 for the carbon-hydrogen bonds in the alkyl groups, and 1.08 for the carbon-hydrogen bonds on the ring. Tetrahedral angles were assumed in the alkyl groups. These dimensions yield for the moment of inertia of the methyl group about its axis of rotation 5.30×10^{-40}. However, the moment of inertia of ethane about its threefold axis [8] should be double that of a methyl group giving for the latter 5.52×10^{-40}. Although no definite decision can be reached at this time, the larger value was used in all calculations for the methyl derivatives of benzene. The calculations for ethylbenzene had already been made with the smaller value and have not been changed.[5]

The values of the constants in eq 1 to 4 are summarized in table 1.

[5] The use of the higher value of the methyl moment of inertia for ethylbenzene would increase the entropy for free rotation by 0.04 cal/deg mole at all temperatures. As a result the potential barrier for the rotation of the phenyl (or ethyl) group evaluated later in this report from the experimental entropy would be increased from 1,080 to 1,130 cal/mole, which is well within the limit of other errors.

TABLE 1.—*Constants for the calculation of the translational and free rotational contributions to the thermodynamic functions*

Quantity	Symbol	Benzene	Toluene	Ethyl-benzene [b]	o-Xylene	m-Xylene	p-Xylene	1, 2, 2-Tri-methyl-benzene	1, 2, 4-Tri-methyl-benzene	1, 3, 5-Tri-methyl-benzene
Number of rotors	m	0	1	2	2	2	2	3	3	3
Symmetry number	σ	12	6	6	18	18	36	54	27	162
Molecular weight	M	78.108	92.134	106.160	106.160	106.160	106.160	120.186	120.186	120.186
Principal moments of inertia x10³⁹ [e]	$I_x°$	14.62	15.15	18.50	26.32	23.47	15.68	38.08	28.41	48.13
	$I_y°$	14.62	33.15	56.71	39.07	47.61	58.24	48.13	65.34	48.13
	I_z	29.24	47.77	68.51	64.32	70.02	72.86	84.62	92.16	94.67
Product of principal moments of inertia x10¹¹⁷	A	6,252	24,000	71,920	66,140	78,240	66,550	155,100	171,000	219,300
Product of reduced moments of inertia [a] [e]	B	---------	5.319	180.1 / [d]173.2	29.31	29.23	28.33	161.7	159.6	162.5
Constant of eq. 2 [e]	C_2	−0.422	−2.666	−4.763 / [d]−4.802	−8.834	−8.670	−10.239	−15.214	−13.752	−17.048

[a] All moments of inertia for internal rotation are expressed in units of 10^{-40} g cm².

[b] For the configuration in which the carbon atoms of the ethyl group lie in a plane perpendicular to the plane of the benzene ring.

[c] For the moment of inertia 5.52 for the methyl group; unless otherwise indicated.

[d] For the moment of inertia 5.30 for the methyl group; this value was used in the calculation of the thermodynamic functions for ethylbenzene.

[e] The principal z-axis is perpendicular to the plane of the benzene ring, except for ethylbenzene, for which it makes an angle of 11° with the perpendicular. The orientation of the principal x- and y-axes may be determined by inspection, except for 1,2,4-trimethylbenzene, for which the projection of the x-axis on the plane of the benzene ring makes an angle of 13° with a line passing through the 1 and 4 positions on the ring.

2. Vibrational Contributions

(a) Benzene, Toluene, the Xylenes, and Mesitylene

The vibrational assignments of Pitzer and Scott [9] for benzene,[6] toluene, the three xylenes, and mesitylene, were accepted without change. Such new data as have become available would not appear to make a complete reconsideration of the spectra of these compounds at this time worthwhile. However, the harmonic oscillator contributions to the thermodynamic functions were recomputed at 250° K and at 100-degree intervals from 300° to 1,500° K, using the tables of Sherman and Ewell [3] and the new values of the physical constants [1].

(b) Ethylbenzene

The vibrational frequencies of ethylbenzene were assigned on a semiempirical basis that involved a detailed consideration of only the lowest frequencies of vibration of the benzene ring and also of the frequencies associated with vibration of the ethyl group. The remaining frequencies were taken from the assignment for toluene [9]. A complete frequency assignment for ethylbenzene at this time is impracticable. The details of this assignment, together with the method of calculation, will be presented elsewhere [6]. The resulting frequencies as used in the thermodynamic calculations are listed in table 2.

(c) 1,2,3- and 1,2,4-trimethylbenzenes

The total vibrational contributions to the thermodynamic functions of 1,2,3- and 1,2,4-trimethylbenzene were estimated empirically from the values calculated for 1,3,5-trimethylbenzene (mesitylene) and the three xylenes. The differences in the vibrational contributions for the three xylenes are small, as may be seen from the values given in table 3 for the heat-content function, free-energy function, and heat capacity, at several temperatures. In view of the small differences in the functions obtained with the methyl groups ortho-, meta-, or para- to one another, it seems reasonable to conclude that these positional effects are approximately additive. This view does not take account of the effect of molecular

symmetry on the vibrations. However, symmetry affects the over-all distribution of frequen-

TABLE 2.—*Vibration frequencies of the ethylbenzene molecule*

Type of vibration [a]	Symmetry [b]	Frequency
		cm^{-1}
Vibrations principally characteristic of the benzene ring or phenyl radical:		
11 (C_2H_5 rocking)	A′	154
18b (C_2H_5 rocking)	A″	320
16a	A″	405
16b	A′	452
6a	A′	485
6b	A″	620
4	A′	695
10b	A′	730
12	A′	785
10a	A″	842
17b	A′	890
5	A′	943
17a	A″	985
1	A′	1,002
18a	A′	1,030
15	A″	1,070
9b	A″	1,155
9a	A′	1,175
7a ($C_6H_5-C_2H_5$ stretching)	A′	1,210
3	A″	1,282
19b	A″	1,310
19a	A′	1,483
8b	A″	1,586
8a	A′	1,603
14	A″	1,630
13 ⎫	A′	3,046
7b ⎪	A″	3,047
2 ⎬ C−H stretching	A′	3,062
20a ⎪	A′	3,080
20b ⎭	A″	3,080
Vibrations principally characteristic of the ethyl group:		
$C_6H_5-CH_2-CH_3$ angle bending	A′	380
CH_2 rocking	A″	775
CH_2-CH_3 stretching	A′	965
CH_3 rocking	A′	1,035
CH_3 rocking	A″	1,070
CH_2 twisting	A″	1,270
CH_2 rocking	A′	1,310
CH_3 symmetrical bending	A′	1,385
CH_2 symmetrical bending	A′	1,460
CH_3 unsymmetrical bending ⎰	A′	1,460
⎱	A″	1,460
CH_2 symmetrical stretching	A′	2,960
CH_2 unsymmetrical stretching	A″	2,960
CH_3 symmetrical stretching	A′	2,960
CH_3 unsymmetrical stretching ⎰	A′	2,960
⎱	A″	2,960
Internal rotations:		
$C_6H_5-C_2H_5$ rotation	A″	--------------
CH_3 rotation	A″	--------------

[a] The numbers refer to the normal modes of vibration for the benzene molecule, as given in figure 6 of reference [9].

[b] The ethylbenzene molecule, in the equilibrium configuration assumed, has the symmetry C_{1h}, with the symmetry plane perpendicular to the plane of the benzene ring. Vibrations of the type A′ and A″ are symmetric and antisymmetric, respectively, to reflection in the symmetry plane.

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[6] The recent vibrational assignment of Herzfeld, Ingold, and Poole [27] yields thermodynamic properties for benzene which do not differ significantly from those presented here. The largest differences are about 0.1 cal/deg mole in the entropy and heat capacity.

cies, and therefore the vibrational function, to a much smaller extent than it does the individual frequencies. It is easily verified that, on the basis of the assumption that positional effects are additive, the proper formulas are

(1,2,3-trimethylbenzene)＝(1,3,5-trimethylbenzene)＋2[(o-xylene)—(m-xylene)] (5)

(1,2,4-trimethylbenzene)＝(1,3,5-trimethylbenzene)＋[(o-xylene)＋(p-xylene)—2(m-xylene)] (6)
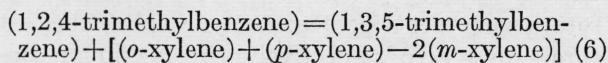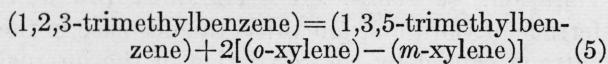
The vibrational functions for 1,2,3- and 1,2,4-trimethylbenzene were calculated by means of these formulas at each temperature. The resulting functions are compared with those for 1,3,5-trimethylbenzene at several temperatures in table 4.

3. Restricted Rotational Contributions

The calculation of the translational, total free (over-all and internal) rotational, and vibrational contributions to the thermodynamic functions have been described in the preceding sections for benzene, toluene, ethylbenzene, the three xylenes, and the three trimethylbenzenes. This completes the calculation for benzene and leaves only the restricted internal rotational contributions for the other molecules. The potential barriers

restricting internal rotation of the methyl groups in toluene and the three xylenes have been determined by comparison with the experimental entropies and heat capacities. The potential barrier for the methyl rotation in ethylbenzene was assigned a reasonable value empirically, and the barrier for the ethyl rotation was then obtained from the experimental entropy. The barriers for the methyl rotations in the trimethylbenzenes were assigned on the basis of the barriers in the xylenes. The details of these calculations will be presented in this section.

(a) Symmetry of Potential Barriers

The usual assumption has been made that the potential barrier for each internal rotation may be approximated by an n-fold cosine function and that interaction terms in the potential energy between different internal rotations may be neglected. The barrier for the methyl rotation in toluene is sixfold ($n=6$), and the barriers for the methyl groups in p- and m-xylenes must have essentially the same magnitude and symmetry as the barrier in toluene. The situation in o-xylene has been discussed by Pitzer and Scott [9], and their recommendation that the methyl groups be treated as independent rotors, with $n=3$, has been fol-

TABLE 3.—*Vibrational contributions for the xylenes*

T	Vibrational contribution in cal/deg mole								
	$(H°-H_0°)/T$			$(F°-H_0°)/T$			$C_p°$		
	o-Xylene	m-Xylene	p-Xylene	o-Xylene	m-Xylene	p-Xylene	o-Xylene	m-Xylene	p-Xylene
°K									
300	7.92	7.88	7.98	—4.62	—4.13	—4.33	19.88	20.30	20.13
500	16.40	16.58	16.52	—10.63	—10.17	—10.39	37.76	38.30	37.93
1,000	34.54	34.84	34.66	—27.96	—27.69	—27.80	63.93	64.24	64.03
1,500	46.55	46.83	46.66	—44.40	—44.25	—44.29	75.76	75.93	75.83

TABLE 4.—*Vibrational contributions for the trimethylbenzenes*

T	Vibrational contribution in cal/deg mole								
	$(H°-H_0°)/T$			$(F°-H_0°)/T$			$C_p°$		
	1,2,3-Trimethyl-benzene	1,2,4-Trimethyl-benzene	1,3,5-Trimethyl-benzene	1,2,3-Trimethyl-benzene	1,2,4-Trimethyl-benzene	1,3,5-Trimethyl-benzene	1,2,3-Trimethyl-benzene	1,2,4-Trimethyl-benzene	1,3,5-Trimethyl-benzene
°K									
300	10.27	10.34	10.19	—6.77	—6.48	—5.79	23.70	23.94	24.52
500	19.65	19.76	20.00	—13.96	—13.72	—13.06	43.62	43.79	44.69
1,000	40.36	40.49	40.97	—34.35	—34.20	—33.80	74.44	74.55	75.06
1,500	54.38	54.49	54.93	—53.55	—53.45	—53.25	88.61	88.67	88.94

lowed. The barrier for the ethyl (or phenyl) group rotation in ethylbenzene is twofold ($n=2$). Although the barrier in this case may deviate considerably from the simple cosine form, sufficient calorimetric data are not available to justify a more detailed treatment.

(b) Reduced Moments of Inertia

Although only the product of reduced moments of inertia was needed for the free-rotation calculation, individual values are required for restricted rotation calculations [5], since the partition function for each individual rotation is needed. In terms of our constants it is

$$Q_f = 2.7935 \ (10^{38} IT)^{\frac{1}{2}}/n, \tag{7}$$

where I is the reduced moment of inertia, T the absolute temperature, and n the symmetry number. The values of I were calculated from eq 1b and 1c of reference [5], and are listed in table 5.

TABLE 5.—*Reduced moments of inertia for internal rotation* [a] [b]

[Values in units of 10^{-40} g cm^2]

Toluene	5.32		
Ethylbenzene	[c] 5.18	33.5	
o-Xylene	5.41	5.41	
m-Xylene	5.41	5.41	
p-Xylene	5.32	5.32	
1,2,3-Trimethylbenzene	5.44	5.46	5.44
1,2,4-Trimethylbenzene	5.42	5.45	5.42
1,3,5-Trimethylbenzene	5.46	5.46	5.46

[a] The values refer to the groups in the order mentioned in the names for the trimethylbenzenes. The methyl group is given first for ethylbenzene. These values are rounded to three significant figures; hence their product will not agree exactly with that in table 1.

[b] For the moment of inertia 5.52 for the methyl group, unless otherwise indicated.

[c] For the moment of inertia 5.30 for the methyl group.

(c) Calculation of Potential Barriers from Experimental Entropies

The experimental entropies for these compounds, for the liquids under their saturation pressures, at 298.16° K, are given in the first row of table 6. These values have been taken as the standard entropy of the liquid, at 1-atmosphere pressure and 298.16° K, as the difference is only 0.002 or 0.003 cal/deg mole. The references to the sources of these values are given in the table. The second row gives the standard entropy of vaporization, $\Delta Sv°$, at 298.16° K, as taken from the work of Osborne and Ginnings [10], and reduced to the standard state [14]. The third row (sum of first and second) is the experimental

value for the standard entropy of the gas, at 1-atmosphere pressure and 298.16° K. The fourth row gives the sum of the calculated contributions to the standard entropy of the gas for translation, total free (over-all and internal) rotation, and vibration, at 298.16° K. The fifth row (difference of third and fourth) is the decrease in the entropy caused by the restriction of the internal rotations (except for benzene). Finally, the last three rows give respectively the maximum potential barrier consistent with the experimental entropy and its uncertainty, the probable barrier indicated by the experimental entropy value itself, and the minimum barrier consistent with the experimental entropy and its uncertainty.

All contributions of restricted rotation throughout this paper are taken from tables of Pitzer and Gwinn [5].

For ethylbenzene there are two separate potential barriers to be evaluated. The barrier for methyl rotation has been assumed to have the value of 3,400 cal/mole found in propane [12]. On this basis, 1.50 cal/deg mole of the entropy difference, $(S_f° - S°)$, is to be assigned to the methyl rotation, leaving 0.36 cal/deg mole as the contribution of the ethyl rotation, which leads to 1,080 cal/mole as the indicated value of the potential barrier for the ethyl (phenyl) rotation. In this case, the uncertainty in the calculated entropy of vibration and of restricted methyl rotation exceeds that of the experimental value. Hence, calculated maximum and minimum potential barriers would have no meaning.

The experimental value for the entropy of benzene gas at 298.16° K differs from the calculated value by 0.19 ±0.30 cal/deg mole. Even this insignificant difference is in the direction to be explained by the neglected anharmonicity of vibrations.

(d) Calculation of Potential Barriers from Experimental Heat Capacities

The comparison with the gaseous heat-capacity data of Gwinn, and of Pitzer and Scott [9], is shown in table 7. The experimental values are given in the third column, and the values calculated for the sum of translation, total free rotation (over-all and internal), and vibration are given in the fourth column. The difference of these values, given in the fifth column, is the increase in heat capacity owing to restriction of rotation (except for benzene). The values of the potential barriers indi-

TABLE 6.—*Potential barriers from entropy values at 298.16° K*

[Entropy, cal/degree mole; potential barrier, cal/mole]

	Benzene	Toluene	Ethylbenzene	o-Xylene	m-Xylene	p-Xylene
Experimental entropy:						
S° (liquid, 1 atm)ᵃ	41.49	52.39	60.99	58.80	60.42	59.20
Vaporization, ΔS_v°ᵇ	23.04	23.94	25.16	25.40	25.22	25.11
S° (gas, 1 atm)	64.53± 0.30	76.33 ±0.25	86.15 ±0.12	84.20 ±0.25	85.64 ±0.35	84.31 ±0.25
Calculated entropy of translation, vibration, and over-all and free internal rotation, S_f° (gas, 1 atm)	64.34	76.56	88.01	86.15	85.80	84.51
Difference ($S_f^{\circ} - S^{\circ}$)		0.23	1.86	1.95	0.16	0.20
Potential barrier:						
Maximum ᵈ		1,600	(ᵉ)	2,500	1,000	900
Most probable		1,000	ᵉ 1,080	2,200	550	600
Minimum ᵈ		0	(ᵉ)	2,000	0	0

ᵃ References: Benzene [17], toluene [18], ethylbenzene [19, 20], xylenes [9].
ᵇ Reference [14].
ᵉ For the ethyl (phenyl) rotation in ethylbenzene assuming a barrier of 3,400 cal/mole for the methyl rotation.

ᵈ Allowed by the experimental uncertainties.
ᵉ Uncertain—see text.

cated by the data are shown in the last column. These values are obviously subject to considerable uncertainty, in view of the estimated uncertainties in the experimental heat capacities, and the possible effects of error in vibrational assignment.

Scott and Mellors [11] have reported the value 38.06 ±0.20 cal/deg mole for the gaseous heat capacity (C_p°) of ethylbenzene at 373.16° K. This value was obtained by applying a calibration

TABLE 7.—*Potential barriers from gaseous heat-capacity data*

Compound	T	Heat capacity C_p°		Difference (experimental minus calculated)	Calculated potential barrier (V)
		Experimental ᵃ	Calculated (V=0)		
	° K	cal/deg mole	cal/deg mole		cal/mole
Benzene	388	26.0±0.3	25.96	0.04	
	417	28.1±0.3	27.85	.25	
	481	31.4±0.3	31.73	−.33	
Benzene	393	26.4±0.3	26.29	.11	
	428	28.4±0.3	28.55	−.15	
	463	30.3±0.3	30.70	−.40	
Toluene ᵇ	393	32.8±0.3	32.57	.23	1,000
	428	35.7±0.4	35.27	.43	1,500
	463	38.0±0.4	37.87	.13	750
o-Xylene ᵇ	393	40.2±0.4	38.62	1.58	1,900
	428	43.5±0.4	41.72	1.78	2,200
	463	46.0±0.5	44.72	1.28	1,800
m-Xylene ᵇ	393	39.1±0.4	39.12	−0.02	0
	428	42.4±0.4	42.25	.15	600
	463	45.4±0.4	45.24	.16	600
p-Xylene ᵇ	393	39.0±0.4	38.78	.22	650
	428	42.6±0.4	41.90	.70	1,300
	463	45.2±0.4	44.89	.31	850

ᵃ The first series for benzene is the data of Gwinn [9]; the remaining data are those of Pitzer and Scott [9].
ᵇ Toluene, m-xylene, and p-xylene calculated for a potential barrier of 6 maxima; o-xylene with a barrier of 3 maxima.

correction to the observed value of 37.71. The calculated value at this temperature for translation, total free rotation, and vibration is 36.56, leaving 1.50 cal/deg mole as the contribution of restricted rotation. Of this, 1.20 is to be assigned to the methyl rotation, assuming, as before, a 3,400 cal/mole barrier. The contribution of the ethyl rotation is therefore 0.30 cal/deg mole, which yields a value of 850 cal/mole for the barrier.

(e) Selected Values of Potential Barriers

The potential barriers selected on the basis of the entropy and heat-capacity data, and used in the calculation of the final values of the thermodynamic functions, may now be stated. The barriers for the methyl groups in toluene, p- and m-xylenes were assigned a value of 750 cal/mole, as the best average value indicated by the data on these compounds,[7] and a value of 2,100 cal/mole was assigned to the barriers in o-xylene. The differences between these values and the values reported previously [9] are attributable principally to changes in the calculated vibrational contributions resulting from the use of the new values of the fundamental physical constants [1]. The barrier for the ethyl group rotation in ethylbenzene was assigned the value 1,080 cal/mole indicated by the entropy. The entropies calculated with these barriers are compared with the experimental entropies at 298.16° K in table 8.

[7] This value of 750 cal/mole is to be regarded as an empirical parameter for best reproduction of thermodynamic functions. The low-temperature heat-capacity curves of toluene and m- and p-xylene make it improbable that the real value is this large—see Pitzer and Scott [9], page 826. The thermodynamic data are in reasonable accord with the 500 cal/mole value adopted previously [9].

Compound	Entropy, $S°$ (gas, 1 atm, 298.16° K)	
	Experimental	Calculated
	cal/deg mole	*cal/deg mole*
Benzene	64.53±0.30	64.34
Toluene	76.33±0.25	76.42
Ethylbenzene	86.15±0.12	86.15
o-Xylene	84.20±0.25	84.31
m-Xylene	85.64±0.35	85.49
p-Xylene	84.31±0.25	84.23

The barriers for the trimethylbenzenes were assigned empirically on the basis of the barriers in the xylenes, as follows: (1) 1,2,3-, and 1,2,4-trimethylbenzenes, one 750, and two 2,100 cal/mole barriers, each; (2) 1,3,5-trimethylbenzene, three 750 cal/mole barriers. The derivation of these values is obvious except in the case of the 750 cal/mole barrier assigned to the central methyl group in 1,2,3-trimethylbenzene. It is likely that the interactions of the central methyl group with the adjacent groups on either side increase about equally the maximum and minimum of the potential energy for the rotation, and do not, therefore, alter greatly the potential barrier (variation of potential energy) for the rotation.

4. Calculations by the Method of Increments

The thermodynamic functions for the C_9H_{12} alkyl benzenes, aside from the three trimethylbenzenes, were estimated from the functions for appropriate lower alkylbenzene and paraffin hydrocarbons. The formula used for the three methylethylbenzenes was

$$\text{1-methyl-}x\text{-ethylbenzene}=\text{1,}x\text{-dimethylbenzene} \\ +\text{ethylbenzene}-\text{toluene}+R\ln 2, \quad (8)$$
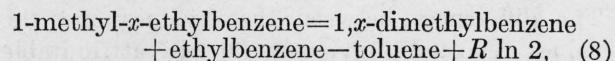
where $x=2,3,$ and 4   For propylbenzenes,

$$n\text{-propylbenzene}=\text{ethylbenzene}+n\text{-butane} \\ -\text{propane,} \quad (9)$$

$$\text{isopropylbenzene}=\text{ethylbenzene}+\text{isobutane} \\ -\text{propane}+R\ln (3/2). \quad (10)$$
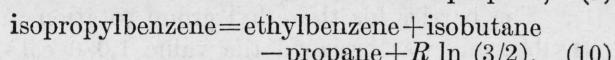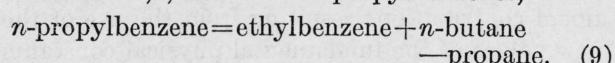
The higher normal alkylbenzenes, from n-butylbenzene ($C_{10}H_{14}$) to n-hexadecylbenzene ($C_{22}H_{38}$), were calculated from the formula

$$\text{normal alkylbenzene } (C_nH_{2n-8})=\text{ethylbenzene} \\ (C_8H_{10})+\text{normal paraffin } (C_{n-5}H_{2n-8}) \\ -\text{propane } (C_3H_8), \quad (n\geq9). \quad (11)$$
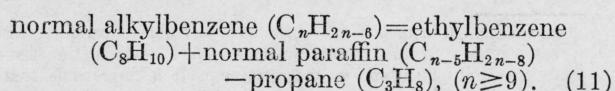
When $n=9$ this reduces to the formula for n-propylbenzene (C_9H_{12}) eq 9. The thermodynamic functions for isobutane were taken from reference [23], and for the normal paraffin hydrocarbons from reference [16]. The logarithmic terms correct for the discrepancies in total symmetry numbers for over-all and internal rotation in the formulas as written. They are to be included in the calculation of the entropy and the negative of the free-energy function, $-(F°-H_0°)/T$, but omitted in the calculation of the heat-content function and the heat capacity.

Some correction may be desirable for the changes in the barriers for rotation of the alkyl groups attached to the benzene ring, especially in 1-methyl-2-ethylbenzene and isopropylbenzene, but it was not considered worthwhile to estimate the corrections in view of the uncertainty of values calculated by the present method.

An indication of the accuracy of the values for n-propylbenzene may be obtained by comparing the directly calculated values for ethylbenzene with values calculated from the equation

$$\text{ethylbenzene}=\text{toluene}+\text{propane}-\text{ethane}. \quad (12)$$
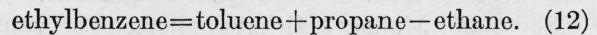
The differences, expressed as the value calculated from eq 12, less the directly calculated value, in cal/deg mole, at 300°, 900°, and 1,500° K, are 1.17, 0.10, and −0.17, for the free-energy function; −1.24, −0.67, and −0.42 for the heat-content function; and −0.92, −0.13, and −0.02 for the heat capacity. However, in this case the difference in the contribution of the methyl rotation in toluene and the ethyl rotation in ethylbenzene is considerable. Correction for the change in this contribution leads to differences of 0.04, −0.32, and −0.42, for the free-energy function; −0.29, −0.28, and −0.18, for the heat-content function; and −0.59, −0.09, and −0.01, for the heat capacity. A correction of this type should be unimportant in eq 9 for n-propylbenzene.

5. Tables of values of the thermodynamic properties

The resulting values of thermodynamic properties for the 14 alkylbenzenes through C_9H_{12} and for the higher normal monoalkylbenzenes are presented in tables 9 to 18, which give values of the heat-content function, $(H°-H_0°)/T$, the free-energy function, $(F°-H_0°)/T$, the entropy, $S°$, the heat content, $H°-H_0°$, and the heat capacity, $C_p°$, for the gas in the standard state at a pressure of 1 atmosphere.

Compound (gas)	For-mula	Temperature [a] in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat-content function,[b] $(H° — H_0^*)/T$, in cal/deg mole														
Benzene	C_6H_6	0	11.41	11.46	14.41	17.50	20.48	23.24	25.76	28.07	30.16	32.07	33.82	35.42	36.89	38.24
Methylbenzene (toluene)	C_7H_8	0	14.44	14.51	18.17	21.94	25.56	28.92	32.03	34.86	37.45	39.82	41.99	43.98	45.81	47.50
Ethylbenzene	C_8H_{10}	0	·17.89	17.97	22.44	26.99	31.33	35.35	39.03	42.38	45.45	48.25	50.82	53.18	55.34	57.35
1,2-Dimethylbenzene (o-xylene)	C_8H_{10}	0	18.70	18.78	23.23	27.61	31.78	35.66	39.23	42.52	45.53	48.30	50.84	53.17	55.32	57.31
1,3-Dimethylbenzene (m-xylene)	C_8H_{10}	0	17.86	17.94	22.31	26.72	30.94	34.88	38.52	41.86	44.93	47.74	50.32	52.69	54.87	56.88
1,4-Dimethylbenzene (p-xylene)	C_8H_{10}	0	17.97	18.04	22.32	26.66	30.83	34.74	38.36	41.69	44.76	47.56	50.14	52.52	54.70	56.72
n-Propylbenzene	C_9H_{12}	0	21.69	21.78	27.0	32.2	37.2	41.8	46.0	49.8	53.4	56.6	59.5	62.3	64.8	67.1
Isopropylbenzene (cumene)	C_9H_{12}	0	20.45	20.54	26.0	31.4	36.6	41.3	45.6	49.5	53.1	56.4	59.4	62.1	64.6	67.0
1-Methyl-2-ethylbenzene	C_9H_{12}	0	22.15	22.25	27.5	32.7	37.6	42.1	46.2	50.0	53.5	56.7	59.7	62.4	64.9	67.2
1-Methyl-3-ethylbenzene	C_9H_{12}	0	21.31	21.40	26.6	31.8	36.7	41.3	45.5	49.4	52.9	56.2	59.2	61.9	64.4	66.7
1-Methyl-4-ethylbenzene	C_9H_{12}	0	21.42	21.51	26.6	31.7	36.6	41.2	45.4	49.2	52.8	56.0	59.0	61.7	64.2	66.6
1,2,3-Trimethylbenzene (hemimellitene)	C_9H_{12}	0	22.10	22.19	27.0	32.0	36.6	41.1	45.2	48.9	52.4	55.6	58.6	61.3	63.9	66.2
1,2,4-Trimethylbenzene (pseudocumene)	C_9H_{12}	0	22.17	22.26	27.1	32.1	36.8	41.2	45.3	49.1	52.6	55.8	58.7	61.5	64.0	66.3
1,3,5-Trimethylbenzene (mesitylene)	C_9H_{12}	0	21.22	21.31	26.21	31.23	36.04	40.55	44.74	48.59	52.13	55.39	58.39	61.15	63.70	66.05

[a] Interpolation to other temperatures in the interval 298.16° to 1,500° K may be made by appropriate graphical or analytical methods. For temperatures between 200° and 298.16° K, values may be estimated by extrapolating the values for 300°, 400°, 500°, and 600° K. The values in this table are given to more significant figures than are warranted by the absolute accuracy of the individual values in order to retain the internal consistency of the several thermodynamic functions of a single substance, and also to retain the significance of the increment with temperature of a given thermodynamic function.

[b] The heat-content function $(H° — H_0^*)/T$, is the heat content at the given temperature less the heat content at 0°K, divided by the absolute temperature (°K) of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere).

Table 10.—Values [a] of the heat-content function, $(H° — H_0^*)/T$, for the normal alkylbenzenes, C_6 to C_{22}, for the ideal gaseous state, to 1,500° K

Compound (gas)	For-mula	Temperature [a] in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat-content function,[b] $(H° — H_0^*)/T$, in cal/deg mole														
Benzene	C_6H_6	0	11.41	11.46	14.41	·17.50	20.48	23.24	25.76	28.07	30.16	32.07	33.82	35.42	36.89	38.24
Methylbenzene (toluene)	C_7H_8	0	14.44	14.51	18.17	21.94	25.56	28.92	32.03	34.86	37.45	39.82	41.99	43.98	45.81	47.50
Ethylbenzene	C_8H_{10}	0	17.89	17.97	22.44	26.99	31.33	35.35	39.03	42.38	45.45	48.25	50.82	53.18	55.34	57.35
n-Propylbenzene	C_9H_{12}	0	21.69	21.78	27.0	32.2	37.2	41.8	46.0	49.8	53.4	56.6	59.5	62.3	64.8	67.1
n-Butylbenzene	$C_{10}H_{14}$	0	25.12	25.22	31.2	37.1	42.8	48.0	52.8	57.1	61.1	64.8	68.2	71.3	74.1	76.8
n-Amylbenzene	$C_{11}H_{16}$	0	28.55	28.67	35.4	42.0	48.3	54.2	59.5	64.4	68.9	73.0	76.8	80.3	83.5	86.4
n-Hexylbenzene	$C_{12}H_{18}$	0	31.98	32.11	39.6	46.9	53.9	60.4	66.3	71.7	76.7	81.2	85.4	89.3	92.8	96.1
n-Heptylbenzene	$C_{13}H_{20}$	0	35.41	35.56	43.8	51.8	59.5	66.6	73.1	79.0	84.4	89.4	94.0	98.3	102.2	105.7
n-Octylbenzene	$C_{14}H_{22}$	0	38.84	39.01	48.0	56.8	65.1	72.8	79.9	86.3	92.2	97.6	102.6	107.3	111.5	115.4
n-Nonylbenzene	$C_{15}H_{24}$	0	42.27	42.46	52.2	61.7	70.7	79.0	86.6	93.6	100.0	105.8	111.2	116.3	120.8	125.1
n-Decylbenzene	$C_{16}H_{26}$	0	45.70	45.90	56.4	66.6	76.3	85.3	93.4	100.9	107.8	114.1	119.9	125.3	130.2	134.7
n-Undecylbenzene	$C_{17}H_{28}$	0	49.13	49.35	60.6	71.5	81.9	91.5	100.2	108.2	115.5	122.3	128.5	134.3	139.5	144.4
n-Dodecylbenzene	$C_{18}H_{30}$	0	52.56	52.80	64.8	76.4	87.4	97.7	107.0	115.4	123.3	130.5	137.1	143.3	148.9	154.0
n-Tridecylbenzene	$C_{19}H_{32}$	0	55.99	56.24	69.1	81.3	93.0	103.9	113.8	122.8	131.1	138.7	145.7	152.3	158.2	163.7
n-Tetradecylbenzene	$C_{20}H_{34}$	0	59.42	59.59	73.3	86.2	98.6	110.1	120.5	130.0	138.8	146.9	154.4	161.3	167.6	173.4
n-Pentadecylbenzene	$C_{21}H_{36}$	0	62.85	63.14	77.5	91.2	104.2	116.3	127.3	137.3	146.6	155.1	163.0	170.3	176.9	183.0
n-Hexadecylbenzene	$C_{22}H_{38}$	0	66.28	66.58	81.7	96.1	109.8	122.5	134.1	144.6	154.4	163.3	171.6	179.3	186.3	192.7
Increment per CH_2 group		0	3.430	3.447	4.21	4.92	5.59	6.21	6.78	7.29	7.77	8.21	8.62	9.00	9.35	9.66

[a] See footnote "a" of table 9.

[b] The heat-content function, $(H° — H_0^*)/T$, is the heat content at the given temperature less the heat content at 0°K, divided by the absolute temperature (°K) of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere).

Heats and Free Energies of Alkylbenzenes

Compound (gas)	Formula	Temperature [a] in °K													
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
		Free-energy function,[b] $(F° − H_0^0)/T$, in cal/deg mole														
Benzene	C_6H_6	0	−52.93	−53.00	−56.69	−60.24	−63.70	−67.06	−70.34	−73.50	−76.57	−79.54	−82.40	−85.18	−87.85	−90.45
Methylbenzene (toluene)	C_7H_8	0	−61.98	−62.07	−66.74	−71.20	−75.52	−79.72	−83.79	−87.72	−91.53	−95.21	−98.77	−102.21	−105.53	−108.75
Ethylbenzene	C_8H_{10}	0	−68.26	−68.37	−74.14	−79.64	−84.94	−90.08	−95.05	−99.84	−104.47	−108.94	−113.25	−117.42	−121.44	−125.32
1,2-Dimethylbenzene (o-xylene)	C_8H_{10}	0	−65.61	−65.73	−71.74	−77.40	−82.81	−88.01	−93.01	−97.82	−102.46	−106.93	−111.24	−115.39	−119.42	−123.30
1,3-Dimethylbenzene (m-xylene)	C_8H_{10}	0	−67.63	−67.74	−73.50	−78.95	−84.20	−89.28	−94.18	−98.91	−103.48	−107.89	−112.15	−116.27	−120.25	−124.11
1,4-Dimethylbenzene (p-xylene)	C_8H_{10}	0	−66.26	−66.37	−72.15	−77.59	−82.83	−87.89	−92.76	−97.48	−102.02	−106.42	−110.66	−114.77	−118.74	−122.59
n-Propylbenzene	C_9H_{12}	0	−74.05	−74.19	−81.2	−87.8	−94.1	−100.1	−106.0	−111.6	−117.1	−122.3	−127.4	−132.2	−136.9	−141.5
Isopropylbenzene (cumene)	C_9H_{12}	0	−72.42	−72.54	−79.2	−85.6	−91.8	−97.8	−103.6	−109.2	−114.6	−119.8	−124.8	−129.6	−134.4	−138.9
1-Methyl-2-ethylbenzene	C_9H_{12}	0	−73.27	−73.41	−80.5	−87.2	−93.6	−99.8	−105.6	−111.3	−116.8	−122.0	−127.1	−132.0	−136.7	−141.2
1-Methyl-3-ethylbenzene	C_9H_{12}	0	−75.29	−75.42	−82.3	−88.8	−95.0	−101.0	−106.8	−112.4	−117.8	−123.0	−128.0	−132.9	−137.5	−142.1
1-Methyl-4-ethylbenzene	C_9H_{12}	0	−73.92	−74.05	−80.9	−87.4	−93.6	−99.6	−105.4	−111.0	−116.3	−121.5	−126.5	−131.4	−136.0	−140.5
1,2,3-Trimethylbenzene (hemimellitene)	C_9H_{12}	0	−71.40	−71.53	−78.4	−84.9	−91.2	−97.2	−102.9	−108.5	−113.8	−119.0	−123.9	−128.7	−133.4	−137.8
1,2,4-Trimethylbenzene (pseudocumene)	C_9H_{12}	0	−72.57	−72.70	−79.6	−86.2	−92.4	−98.4	−104.2	−109.8	−115.1	−120.3	−125.3	−130.1	−134.7	−139.2
1,3,5-Trimethylbenzene (mesitylene)	C_9H_{12}	0	−70.93	−71.06	−77.66	−84.04	−90.18	−96.08	−101.77	−107.26	−112.56	−117.68	−122.62	−127.40	−132.03	−136.50

[a] See footnote "a" of table 9.

[b] The free-energy function, $(F° − H_0^0)/T$, is the free energy (exclusive of nuclear spin) at the given temperature less the heat content at 0° K, divided by the absolute temperature (° K), of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere).

TABLE 12.—Values [a] of the free-energy function, $(F° − H_0^0)/T$, for the normal alkylbenzenes, C_6 to C_{22}, for the ideal gaseous state, to 1,500° K

Compound (gas)	Formula	Temperature [a] in °K													
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
		Free-energy function [b], $(F° − H_0^0)/T$, in cal/deg mole														
Benzene	C_6H_6	0	−52.93	−53.00	−56.69	−60.24	−63.70	−67.06	−70.34	−73.50	−76.57	−79.54	−82.40	−85.18	−87.85	−90.45
Methylbenzene (toluene)	C_7H_8	0	−61.98	−62.07	−66.74	−71.20	−75.52	−79.72	−83.79	−87.72	−91.53	−95.21	−98.77	−102.21	−105.53	−108.75
Ethylbenzene	C_8H_{10}	0	−68.26	−68.37	−74.14	−79.64	−84.94	−90.08	−95.05	−99.84	−104.47	−108.94	−113.25	−117.42	−121.44	−125.32
n-Propylbenzene	C_9H_{12}	0	−74.05	−74.19	−81.2	−87.8	−94.1	−100.1	−106.0	−111.6	−117.1	−122.3	−127.4	−132.2	−136.9	−141.5
n-Butylbenzene	$C_{10}H_{14}$	0	−79.79	−79.94	−88.0	−95.6	−102.8	−109.8	−116.6	−123.0	−129.3	−135.3	−141.1	−146.6	−152.0	−157.2
n-Amylbenzene	$C_{11}H_{16}$	0	−85.54	−85.72	−94.9	−103.5	−111.7	−119.6	−127.2	−134.5	−141.6	−148.3	−154.8	−161.1	−167.1	−173.0
n-Hexylbenzene	$C_{12}H_{18}$	0	−91.30	−91.49	−101.7	−111.4	−120.5	−129.4	−137.8	−146.0	−153.8	−161.3	−168.6	−175.6	−182.3	−188.8
n-Heptylbenzene	$C_{13}H_{20}$	0	−97.05	−97.27	−108.6	−119.2	−129.4	−139.1	−148.4	−157.4	−166.1	−174.4	−182.3	−190.0	−197.4	−204.5
n-Octylbenzene	$C_{14}H_{22}$	0	−102.80	−103.05	−115.5	−127.1	−138.2	−148.9	−159.1	−168.9	−178.3	−187.4	−196.1	−204.5	−212.5	−220.3
n-Nonylbenzene	$C_{15}H_{24}$	0	−108.56	−108.82	−122.3	−135.0	−147.1	−158.6	−169.7	−180.4	−190.6	−200.4	−209.9	−218.9	−227.7	−236.1
n-Decylbenzene	$C_{16}H_{26}$	0	−114.31	−114.60	−129.2	−142.9	−155.9	−168.4	−180.3	−191.8	−202.8	−213.4	−223.6	−233.4	−242.8	−251.8
n-Undecylbenzene	$C_{17}H_{28}$	0	−120.06	−120.38	−136.1	−150.8	−164.8	−178.1	−191.0	−203.3	−215.1	−226.4	−237.4	−247.9	−257.9	−267.6
n-Dodecylbenzene	$C_{18}H_{30}$	0	−125.81	−126.16	−142.9	−158.7	−173.6	−187.9	−201.6	−214.7	−227.4	−239.5	−251.1	−262.3	−273.1	−283.4
n-Tridecylbenzene	$C_{19}H_{32}$	0	−131.57	−131.93	−149.8	−166.6	−182.4	−197.6	−212.2	−226.2	−239.6	−252.5	−264.9	−276.8	−288.2	−299.1
n-Tetradecylbenzene	$C_{20}H_{34}$	0	−137.32	−137.71	−156.7	−174.5	−191.3	−207.4	−222.8	−237.6	−251.9	−265.5	−278.6	−291.3	−303.3	−314.9
n-Pentadecylbenzene	$C_{21}H_{36}$	0	−143.07	−143.49	−163.5	−182.4	−200.1	−217.1	−233.5	−249.1	−264.1	−278.5	−292.4	−305.7	−318.5	−330.7
nHexadecylbenzene	$C_{22}H_{38}$	0	−148.83	−149.26	−170.4	−190.2	−209.0	−226.9	−244.1	−260.6	−276.4	−291.6	−306.2	−320.2	−333.6	−346.4
Increment per CH_2 group		0	−5.753	−5.777	−6.87	−7.89	−8.84	−9.75	−10.63	−11.46	−12.26	−13.02	−13.76	−14.46	−15.13	−15.77

[a] See footnote "a" of table 9.

[b] The free-energy function $(F° − H_0^0)/T$, is the free energy (exclusive of nuclear spin) at the given temperature less the heat content at 0° K, divided by the absolute temperature (°K), of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere).

TABLE 13.—*Values* [a] *of the entropy, $S°$, for the 14 alkylbenzenes, C_6 to C_9, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature [a] in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
		Entropy,[b] $S°$, in cal/deg mole														
Benzene	C_6H_6	0	64.34	64.46	71.10	77.74	84.17	90.30	96.10	101.57	106.73	111.61	116.22	120.59	124.74	128.68
Methylbenzene (toluene)	C_7H_8	0	76.42	76.57	84.91	93.13	101.08	108.64	115.81	122.58	128.98	135.03	140.76	146.19	151.34	156.25
Ethylbenzene	C_8H_{10}	0	86.15	86.34	96.59	106.63	116.28	125.43	134.08	142.23	149.92	157.19	164.07	170.59	176.79	182.67
1,2-Dimethylbenzene (o-xylene)	C_8H_{10}	0	84.31	84.51	94.96	105.01	114.60	123.67	132.24	140.34	147.99	155.22	162.07	168.56	174.73	180.61
1,3-Dimethylbenzene (m-xylene)	C_8H_{10}	0	85.49	85.68	95.81	105.67	115.14	124.16	132.70	140.78	148.41	155.63	162.47	168.96	175.12	181.00
1,4-Dimethylbenzene (p-xylene)	C_8H_{10}	0	84.23	84.41	94.47	104.25	113.66	122.63	131.13	139.17	146.78	153.98	160.81	167.29	173.44	179.31
n-Propylbenzene	C_9H_{12}	0	95.74	95.97	108.1	119.9	131.2	141.9	152.0	161.5	170.5	178.9	186.9	194.5	201.7	208.6
Isopropylbenzene (cumene)	C_9H_{12}	0	92.87	93.08	105.2	117.0	128.3	139.0	149.2	158.7	167.6	176.1	184.2	191.8	199.0	205.9
1-Methyl-2-ethylbenzene	C_9H_{12}	0	95.42	95.66	108.0	119.9	131.2	141.8	151.9	161.4	170.3	178.8	186.8	194.3	201.6	208.4
1-Methyl-3-ethylbenzene	C_9H_{12}	0	96.60	96.83	108.9	120.5	131.7	142.3	152.3	161.8	170.7	179.2	187.2	194.7	201.9	208.8
1-Methyl-4-ethylbenzene	C_9H_{12}	0	95.34	95.56	107.5	119.1	130.2	140.8	150.8	160.2	169.1	177.5	185.5	193.1	200.3	207.1
1,2,3-Trimethylbenzene (hemimellitene)	C_9H_{12}	0	93.50	93.73	105.4	116.9	127.8	138.3	148.1	157.4	166.2	174.6	182.5	190.1	197.2	204.0
1,2,4-Trimethylbenzene (pseudocumene)	C_9H_{12}	0	94.73	94.96	106.7	118.2	129.2	139.6	149.5	158.8	167.7	176.0	184.0	191.5	198.7	205.5
1,3,5-Trimethylbenzene (mesitylene)	C_9H_{12}	0	92.15	92.37	103.87	115.28	126.22	136.64	146.51	155.85	164.69	173.07	181.01	188.56	195.73	202.55

[a] See footnote "a" of table 9.
[b] $S°$ is the entropy (exclusive of nuclear spin) of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere) at the temperature indicated.

TABLE 14.—*Values* [a] *of the entropy, $S°$, for the normal alkylbenzenes, C_6 to C_{22}, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature [a] in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
		Entropy,[b] $S°$, in cal/deg mole														
Benzene	C_6H_6	0	64.34	64.46	71.10	77.74	84.17	90.30	96.10	101.57	106.73	111.61	116.22	120.59	124.74	128.68
Methylbenzene (toluene)	C_7H_8	0	76.42	76.57	84.91	93.13	101.08	108.64	115.81	122.58	128.98	135.03	140.76	146.19	151.34	156.25
Ethylbenzene	C_8H_{10}	0	86.15	86.34	96.59	106.63	116.28	125.43	134.08	142.23	149.92	157.19	164.07	170.59	176.79	182.67
n-Propylbenzene	C_9H_{12}	0	95.74	95.97	108.1	119.9	131.2	141.9	152.0	161.5	170.5	178.9	186.9	194.5	201.7	208.6
n-Butylbenzene	$C_{10}H_{14}$	0	104.91	105.16	119.2	132.7	145.6	157.8	169.3	180.2	190.4	200.1	209.2	217.9	226.1	234.0
n-Amylbenzene	$C_{11}H_{16}$	0	114.09	114.38	130.2	145.5	160.0	173.8	186.7	198.9	210.4	221.3	231.6	241.4	250.6	259.4
n-Hexylbenzene	$C_{12}H_{18}$	0	123.28	123.61	141.3	158.3	174.5	189.8	204.1	217.7	230.5	242.5	254.0	264.8	275.1	284.8
n-Heptylbenzene	$C_{13}H_{20}$	0	132.46	132.83	152.4	171.1	188.9	205.7	221.5	236.4	250.5	263.8	276.4	288.3	299.6	310.3
n-Octylbenzene	$C_{14}H_{22}$	0	141.64	142.06	163.5	183.9	203.3	221.7	239.0	255.2	270.5	285.0	298.7	311.7	324.0	335.7
n-Nonylbenzene	$C_{15}H_{24}$	0	150.82	151.28	174.5	196.7	217.8	237.7	256.4	273.9	290.6	306.2	321.1	335.2	348.5	361.1
n-Decylbenzene	$C_{16}H_{26}$	0	160.01	160.50	185.6	209.5	232.2	253.6	273.8	292.7	310.6	327.5	343.5	358.6	373.0	386.5
n-Undecylbenzene	$C_{17}H_{28}$	0	169.19	169.73	196.7	222.3	246.6	269.6	291.2	311.4	330.6	348.7	365.9	382.1	397.5	412.0
n-Dodecylbenzene	$C_{18}H_{30}$	0	178.37	178.95	207.8	235.1	261.0	285.6	308.6	330.2	350.6	370.0	388.2	405.6	422.0	437.4
n-Tridecylbenzene	$C_{19}H_{32}$	0	187.56	188.18	218.8	247.9	275.5	301.5	326.0	348.9	370.7	391.2	410.6	429.0	446.4	462.8
n-Tetradecylbenzene	$C_{20}H_{34}$	0	196.74	197.40	229.9	260.7	289.9	317.5	343.4	367.7	390.7	412.4	433.0	452.5	470.9	488.2
n-Pentadecylbenzene	$C_{21}H_{36}$	0	205.92	206.62	241.0	273.5	304.3	333.5	360.8	386.4	410.7	433.7	455.4	476.0	495.4	513.7
n-Hexadecylbenzene	$C_{22}H_{38}$	0	215.11	215.85	252.1	286.3	318.8	349.4	378.2	405.2	430.8	454.9	477.8	499.4	519.9	539.1
Increment per CH2 group		0	9.183	9.224	11.08	12.80	14.43	15.97	17.40	18.75	20.03	21.24	22.38	23.46	24.48	25.43

[a] See footnote "a" of table 9.
[b] $S°$ is the entropy (exclusive of nuclear spin) of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere) at the temperature indicated.

Heats and Free Energies of Alkylbenzenes

Compound (gas)	Formula	Temperature [a] in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat content,[b] $(H° − H_0°)$, in cal/mole														
Benzene	C_6H_6	0	3401	3437	5762	8750	12285	16267	20612	25260	30163	35280	40590	46040	51640	57350
Methylbenzene (toluene)	C_7H_8	0	4306	4352	7269	10969	15334	20247	25621	31373	37449	43800	50390	57180	64130	71250
Ethylbenzene	C_8H_{10}	0	5335	5391	8976	13496	18799	24746	31222	38144	45448	53080	60980	69130	77480	86020
1,2-Dimethylbenzene (o-xylene)	C_8H_{10}	0	5576	5635	9291	13806	19070	24962	31386	38265	45531	53130	61000	69120	77450	85960
1,3-Dimethylbenzene (m-xylene)	C_8H_{10}	0	5325	5382	8925	13359	18563	24415	30817	37678	44933	52520	60390	68500	76820	85330
1,4-Dimethylbenzene (p-xylene)	C_8H_{10}	0	5358	5414	8929	13330	18499	24319	30690	37525	44755	52320	60170	68270	76580	85080
n-Propylbenzene	C_9H_{12}	0	6467	6534	10790	16090	22300	29250	36810	44860	53360	62200	71400	81000	90700	100600
Isopropylbenzene (cumene)	C_9H_{12}	0	6097	6162	10380	15700	21940	28900	36470	44560	53090	62000	71200	80800	90500	100400
1-Methyl-2-ethylbenzene	C_9H_{12}	0	6604	6674	11000	16330	22530	29460	36990	45040	53530	62400	71600	81100	90800	100700
1-Methyl-3-ethylbenzene	C_9H_{12}	0	6354	6421	10630	15890	22030	28910	36420	44450	52930	61800	71000	80500	90200	100100
1-Methyl-4-ethylbenzene	C_9H_{12}	0	6386	6453	10640	15860	21960	28820	36290	44300	52750	61600	70800	80200	89900	99900
1,2,3-Trimethylbenzene (hemimellitene)	C_9H_{12}	0	6590	6658	10810	15980	21990	28750	36130	44050	52430	61200	70300	79700	89400	99300
1,2,4-Trimethylbenzene (pseudocumene)	C_9H_{12}	0	6609	6677	10860	16030	22060	28830	36230	44160	52550	61300	70500	79900	89600	99500
1,3,5-Trimethylbenzene (mesitylene)	C_9H_{12}	0	6326	6392	10486	15616	21623	28386	35789	43728	52131	60930	70070	79500	89180	99080

[a] See footnote "a" of table 9.
[b] $(H° − H_0°)$ is the heat content at the given temperature less the heat content at 0° K of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere).

TABLE 16.—Values [a] of the heat content, $(H° − H_0°)$, for the normal alkylbenzenes, C_6 to C_{22}, for the ideal gaseous state, to 1,500° K

Compound (gas)	Formula	Temperature [a] in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat content,[b] $(H° − H_0°)$, in cal/mole														
Benzene	C_6H_6	0	3401	3437	5762	8750	12285	16267	20612	25260	30163	35280	40590	46040	51640	57350
Methylbenzene (toluene)	C_7H_8	0	4306	4352	7269	10969	15334	20247	25621	31373	37449	43800	50390	57180	64130	71250
Ethylbenzene	C_8H_{10}	0	5335	5391	8976	13496	18799	24746	31222	38144	45448	53080	60980	69130	77480	86020
n-Propylbenzene	C_9H_{12}	0	6467	6534	10790	16090	22300	29250	36810	44860	53360	62200	71400	81000	90700	100600
n-Butylbenzene	$C_{10}H_{14}$	0	7490	7566	12470	18540	25650	33590	42210	51400	61120	71300	81800	92600	103800	115100
n-Amylbenzene	$C_{11}H_{16}$	0	8512	8600	14150	21000	29000	37940	47630	57960	68900	80300	92100	104300	116800	129600
n-Hexylbenzene	$C_{12}H_{18}$	0	9535	9634	15840	23460	32350	42280	53050	64530	76670	89300	102500	116000	129900	144100
n-Heptylbenzene	$C_{13}H_{20}$	0	10558	10668	17520	25920	35710	46630	58470	71090	84440	98400	112800	127700	143000	158600
n-Octylbenzene	$C_{14}H_{22}$	0	11581	11702	19200	28380	39060	50980	63890	77650	92210	107400	123200	139400	156100	173100
n-Nonylbenzene	$C_{15}H_{24}$	0	12603	12736	20890	30840	42410	55330	69320	84220	99980	116400	133500	151100	169200	187600
n-Decylbenzene	$C_{16}H_{26}$	0	13626	13771	22570	33300	45760	59680	74740	90780	107760	125500	143800	162800	182300	202100
n-Undecylbenzene	$C_{17}H_{28}$	0	14649	14805	24260	35750	49120	64030	80160	97340	115530	134500	154200	174500	195400	216600
n-Dodecylbenzene	$C_{18}H_{30}$	0	15671	15839	25940	38210	52470	68380	85580	103910	123300	143500	164500	186200	208500	231100
n-Tridecylbenzene	$C_{19}H_{32}$	0	16694	16873	27620	40670	55820	72730	91000	110470	131080	152600	174900	197900	221600	245600
n-Tetradecylbenzene	$C_{20}H_{34}$	0	17717	17907	29310	43130	59170	77080	96420	117040	138850	161600	185200	209600	234700	260000
n-Pentadecylbenzene	$C_{21}H_{36}$	0	18740	18941	30990	45590	62520	81430	101850	123600	146620	170600	195600	221300	247700	274500
n-Hexadecylbenzene	$C_{22}H_{38}$	0	19762	19975	32680	48050	65880	85780	107270	130160	154400	179700	205900	233000	260800	289000
Increment per CH_2 group		0	1022.7	1034.1	1684	2458	3352	4349	5422	6564	7773	9030	10340	11700	13090	14490

[a] See footnote "a" of table 9.
[b] $(H° − H_0°)$ is the heat content at the given temperature less the heat content at 0° K of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere).

TABLE 17.—*Values* [a] *of the heat capacity,* C_p°, *for the 14 alkylbenzenes,* C_6 *to* C_9, *for the ideal gaseous state, to 1,500° K*

Compound (gas)	For-mula	Temperature [a] in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat capacity,[b] C_p°, in cal/deg mole														
Benzene	C_6H_6	0	19.52	19.65	26.74	32.80	37.74	41.75	45.06	47.83	50.16	52.16	53.86	55.32	56.58	57.67
Methylbenzene (toluene)	C_7H_8	0	24.80	24.95	33.25	40.54	46.58	51.57	55.72	59.22	62.19	64.73	66.90	68.77	70.38	71.78
Ethylbenzene	C_8H_{10}	0	30.69	30.88	40.76	49.35	56.44	62.28	67.15	71.27	74.77	77.77	80.35	82.57	84.49	86.16
1,2-Dimethylbenzene (o-xylene)	C_8H_{10}	0	31.85	32.02	41.03	49.11	55.98	61.76	66.64	70.80	74.35	77.40	80.02	82.28	84.24	85.93
1,3-Dimethylbenzene (m-xylene)	C_8H_{10}	0	30.49	30.66	40.03	48.43	55.51	61.43	66.41	70.63	74.23	77.31	79.95	82.22	84.19	85.89
1,4-Dimethylbenzene (p-xylene)	C_8H_{10}	0	30.32	30.49	39.70	48.06	55.16	61.12	66.14	70.39	74.02	77.13	79.80	82.09	84.07	85.79
n-Propylbenzene	C_9H_{12}	0	36.73	36.99	48.0	57.8	66.0	72.7	78.3	83.1	87.1	90.6	93.6	96.2	98.5	100.4
Isopropylbenzene (cumene)	C_9H_{12}	0	36.26	36.47	48.0	57.9	66.2	72.9	78.6	83.3	87.3	90.8	93.8	96.4	98.6	100.6
1-Methyl-2-ethylbenzene	C_9H_{12}	0	37.74	37.94	48.5	57.9	65.8	72.5	78.1	82.8	86.9	90.4	93.5	96.1	98.3	100.3
1-Methyl-3-ethylbenzene	C_9H_{12}	0	36.38	36.59	47.5	57.2	65.4	72.1	77.8	82.7	86.8	90.4	93.4	96.0	98.3	100.3
1-Methyl-4-ethylbenzene	C_9H_{12}	0	36.22	36.42	47.2	56.9	65.0	71.8	77.6	82.4	86.6	90.2	93.2	95.9	98.2	100.2
1,2,3-Trimethylbenzene (hemimellitene)	C_9H_{12}	0	36.85	37.04	46.9	56.1	64.0	70.9	76.7	81.6	85.9	89.5	92.7	95.4	97.8	99.8
1,2,4-Trimethylbenzene (pseudocumene)	C_9H_{12}	0	37.10	37.28	47.1	56.2	64.2	71.0	76.8	81.7	86.0	89.6	92.8	95.5	97.8	99.8
1,3,5-Trimethylbenzene (mesitylene)	C_9H_{12}	0	35.91	36.10	46.41	55.92	64.08	70.99	76.84	81.81	86.07	89.72	92.86	95.56	97.89	99.91

[a] See footnote "a" of table 9.
[b] C_p° is the heat capacity at constant pressure of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere) at the temperature indicated.

TABLE 18.—*Values* [a] *of the heat capacity,* C_p°, *for the normal alkylbenzenes,* C_6 *to* C_{22}, *for the ideal gaseous state, to 1,500° K*

Compound (gas)	For-mula	Temperature [a] in ° K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat capacity,[b] C_p°, in cal/deg mole														
Benzene	C_6H_6	0	19.52	19.65	26.74	32.80	37.74	41.75	45.06	47.83	50.16	52.16	53.86	55.32	56.58	57.67
Methylbenzene (toluene)	C_7H_8	0	24.80	24.95	33.25	40.54	46.58	51.57	55.72	59.22	62.19	64.73	66.90	68.77	70.38	71.78
Ethylbenzene	C_8H_{10}	0	30.69	30.88	40.76	49.35	56.44	62.28	67.15	71.27	74.77	77.77	80.35	82.57	84.49	86.16
n-Propylbenzene	C_9H_{12}	0	36.73	36.99	48.0	57.8	66.0	72.7	78.3	83.1	87.1	90.6	93.6	96.2	98.5	100.4
n-Butylbenzene	$C_{10}H_{14}$	0	42.42	42.73	55.1	66.3	75.4	83.1	89.4	94.9	99.5	103.5	106.9	109.9	112.5	114.7
n-Amylbenzene	$C_{11}H_{16}$	0	48.18	48.54	62.3	74.7	84.9	93.4	100.6	106.7	111.9	116.3	120.2	123.6	126.5	128.9
n-Hexylbenzene	$C_{12}H_{18}$	0	53.94	54.35	69.4	83.2	94.4	103.8	111.7	118.4	124.2	129.2	133.5	137.2	140.4	143.2
n-Heptylbenzene	$C_{13}H_{20}$	0	59.70	60.16	76.5	91.6	103.8	114.2	122.9	130.2	136.6	142.1	146.8	150.9	154.4	157.4
n-Octylbenzene	$C_{14}H_{22}$	0	65.46	65.97	83.6	100.0	113.3	124.5	134.0	142.0	149.0	154.9	160.1	164.6	168.4	171.7
n-Nonylbenzene	$C_{15}H_{24}$	0	71.22	71.78	90.8	108.5	122.8	134.9	145.1	153.8	161.4	167.8	173.4	178.2	182.4	185.9
n-Decylbenzene	$C_{16}H_{26}$	0	76.98	77.59	97.9	116.9	132.2	145.3	156.3	165.6	173.7	180.6	186.7	191.9	196.4	200.2
n-Undecylbenzene	$C_{17}H_{28}$	0	82.74	83.40	105.1	125.3	141.7	155.6	167.4	177.4	186.1	193.5	200.0	205.6	210.4	214.4
n-Dodecylbenzene	$C_{18}H_{30}$	0	88.50	89.21	112.2	133.8	151.2	166.0	178.6	189.2	198.5	206.4	213.3	219.3	224.4	228.7
n-Tridecylbenzene	$C_{19}H_{32}$	0	94.26	95.02	119.3	142.2	160.6	176.4	189.7	201.0	210.8	219.2	226.6	232.9	238.4	242.9
n-Tetradecylbenzene	$C_{20}H_{34}$	0	100.02	100.83	126.5	150.6	170.1	186.7	200.8	212.8	223.2	232.1	239.8	246.6	252.3	257.2
n-Pentadecylbenzene	$C_{21}H_{36}$	0	105.78	106.64	133.6	159.1	179.6	197.1	212.0	224.6	235.6	244.9	253.1	260.3	266.3	271.4
n-Hexadecylbenzene	$C_{22}H_{38}$	0	111.54	112.45	140.7	167.5	189.0	207.5	223.1	236.4	248.0	257.8	266.4	273.9	280.3	285.7
Increment per CH₂ group		0	5.760	5.810	7.13	8.44	9.47	10.37	11.14	11.79	12.37	12.86	13.29	13.67	13.99	14.25

[a] See footnote "a" of table 9.
[b] C_p° is the heat capacity at constant pressure of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere) at the temperature indicated.

Heats and Free Energies of Alkylbenzenes

IV. Heat of Formation, Free Energy of Formation, and Equilibrium Constant of Formation

1. Method and Data Used in the Calculations

The same method of calculation was used as described in Section IV–1 of reference [1].

For the heats of formation at 25° C of the alkylbenzenes in the gaseous state from the elements, solid carbon (graphite) and gaseous hydrogen, the values given in reference [2] were used.

2. Results

The resulting values of the thermodynamic properties for the formation of the 14 alkylbenzenes through C_9H_{12}, and of the higher normal monoalkylbenzenes, in the gaseous state, from the elements, solid carbon (graphite) and gaseous hydrogen, all at the given temperature, are presented in tables 19 to 24, which give values of the heat of formation, $\Delta Hf°$, the free energy of formation, $\Delta Ff°$, and the logarithm of the equilibrium constant of formation, $\log_{10} Kf$, to 1,500° K.

Figure 1 shows the thermodynamic stability of the normal monoalkylbenzenes in the gaseous state as a function of temperature, in the form of a plot of the standard free energy of formation, per carbon atom, divided by the absolute temperature. This plot may be compared with corresponding plots for the normal paraffins [13], the normal 1-alkynes [15], and the normal 1-alkenes [24].
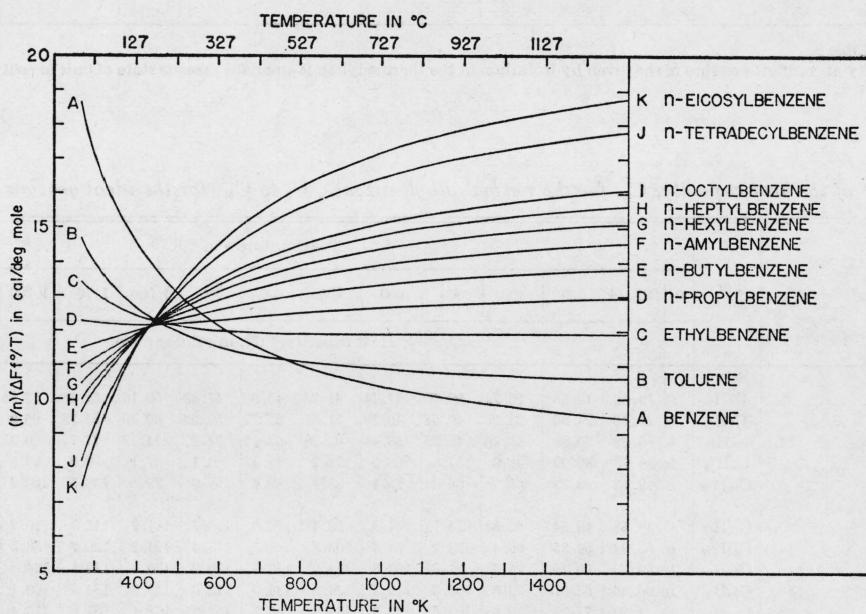
FIGURE 1.—*Thermodynamic stability of the normal monoalkylbenzenes in the gaseous state as a function of temperature.*

The scale of ordinates gives the value of $(1/n)$ $(\Delta Ff°/T)$ in calories per degree mole, where n is the number of carbon atoms per molecule, T is the absolute temperature in degrees Kelvin, and $\Delta Ff°$ is the standard free energy of formation of the hydrocarbon from the elements, solid carbon (graphite) and gaseous hydrogen, all at the given temperature, as given in tables 15 and 16. The scale of abscissas gives the temperature in degrees Kelvin.

TABLE 19.—*Values* [a] *of the heat of formation,* $\Delta Hf°$, *for the 14 alkylbenzenes,* C_6 *to* C_9, *for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature [a] in °K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat of formation [b], $\Delta Hf°$, in kcal/mole														
Benzene	C_6H_6	24.000	19.820	19.796	18.554	17.536	16.711	16.040	15.510	15.100	14.818	14.63	14.52	14.45	14.41	14.39
Methylbenzene (toluene)	C_7H_8	17.500	11.950	11.919	10.327	9.005	7.932	7.067	6.399	5.895	5.564	5.36	5.27	5.22	5.23	5.27
Ethylbenzene	C_8H_{10}	13.917	7.120	7.083	5.218	3.699	2.488	1.529	0.798	0.266	−0.061	−0.23	−0.28	−0.26	−0.18	−0.05
1,2-Dimethylbenzene (o-xylene)	C_8H_{10}	11.096	4.540	4.506	2.711	1.189	−0.062	−1.076	−1.858	−2.434	−2.799	−3.01	−3.08	−3.09	−3.04	−2.92
1,3-Dimethylbenzene (m-xylene)	C_8H_{10}	10.926	4.120	4.083	2.175	0.571	−.738	−1.792	−2.598	−3.191	−3.567	−3.78	−3.86	−3.88	−3.84	−3.73
1,4-Dimethylbenzene (p-xylene)	C_8H_{10}	11.064	4.290	4.253	2.317	.680	−.665	−1.751	−2.586	−3.207	−3.607	−3.84	−3.94	−3.97	−3.94	−3.84
n-Propylbenzene	C_9H_{12}	9.810	1.870	1.827	−0.31	−2.06	−3.44	−4.52	−5.34	−5.95	−6.30	−6.5	−6.5	−6.4	−6.2	−6.0
Isopropylbenzene (cumene)	C_9H_{12}	9.250	0.940	0.895	−1.28	−3.01	−4.37	−5.44	−6.24	−6.80	−7.13	−7.3	−7.2	−7.2	−7.0	−6.8
1-Methyl-2-ethylbenzene	C_9H_{12}	8.092	.290	.250	−1.82	−3.54	−4.93	−6.03	−6.88	−7.48	−7.84	−8.0	−8.0	−8.0	−7.9	−7.7
1-Methyl-3-ethylbenzene	C_9H_{12}	7.593	−.460	−.503	−2.68	−4.49	−5.93	−7.08	−7.95	−8.57	−8.94	−9.1	−9.2	−9.1	−9.0	−8.8
1-Methyl-4-ethylbenzene	C_9H_{12}	7.241	−.780	−.823	−3.03	−4.87	−6.35	−7.53	−8.43	−9.08	−9.47	−9.7	−9.7	−9.7	−9.6	−9.4
1, 2, 3-Trimethylbenzene (hemimellitene)	C_9H_{12}	5.527	−2.290	−2.332	−4.57	−6.46	−8.04	−9.31	−10.30	−11.04	−11.51	−11.8	−11.9	−11.9	−11.8	−11.7
1, 2, 4-Trimethylbenzene (pseudocumene)	C_9H_{12}	4.468	−3.330	−3.372	−5.59	−7.46	−9.02	−10.28	−11.26	−11.98	−12.45	−12.7	−12.8	−12.8	−12.7	−12.6
1, 3, 5-Trimethylbenzene (Mesitylene)	C_9H_{12}	4.241	−3.840	−3.883	−6.183	−8.107	−9.691	−10.960	−11.930	−12.643	−13.094	−13.34	−13.42	−13.42	−13.33	−13.18

[a] See footnote a of table 9.

[b] $\Delta Hf°$ represents the increment in heat content for the reaction of forming the given compound in the gaseous state from the elements carbon (solid graphite) and hydrogen (gaseous), with all the reactants and products in their appropriate standard reference states at the temperature indicated.

TABLE 20.—*Values* [a] *of the heat of formation,* $\triangle Hf°$, *for the normal alkylbenzenes,* C_6 *to* C_{22}, *for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature[a] in °K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat of formation,[b] $\triangle Hf°$, in kcal/mole														
Benzene	C_6H_6	24.000	19.820	19.796	18.554	17.536	16.711	16.040	15.510	15.100	14.818	14.63	14.52	14.45	14.41	14.39
Methylbenzene (toluene)	C_7H_8	17.500	11.950	11.919	10.327	9.005	7.932	7.067	6.399	5.895	5.564	5.36	5.27	5.22	5.23	5.27
Ethylbenzene	C_8H_{10}	13.917	7.120	7.083	5.218	3.699	2.488	1.529	0.798	0.266	−0.061	−0.23	−0.28	−0.26	−0.18	−0.05
n-Propylbenzene	C_9H_{12}	9.810	1.870	1.827	−0.31	−2.06	−3.44	−4.52	−5.34	−5.95	−6.30	−6.5	−6.5	−6.4	−6.2	−6.0
n-Butylbenzene	$C_{10}H_{14}$	5.89	−3.30	−3.35	−5.78	−7.78	−9.34	−10.56	−11.48	−12.14	−12.49	−12.6	−12.6	−12.5	−12.3	−12.0
n-Amylbenzene	$C_{11}H_{16}$	2.22	−8.23	−8.28	−11.00	−13.24	−14.99	−16.34	−17.35	−18.07	−18.43	−18.6	−18.5	−18.3	−18.0	−17.7
n-Hexylbenzene	$C_{12}H_{18}$	−1.46	−13.15	−13.21	−16.23	−18.71	−20.64	−22.12	−23.22	−23.99	−24.37	−24.5	−24.4	−24.1	−23.8	−23.4
n-Heptylbenzene	$C_{13}H_{20}$	−5.13	−18.08	−18.14	−21.45	−24.18	−26.28	−27.89	−29.09	−29.92	−30.31	−30.4	−30.3	−30.0	−29.5	−29.0
n-Octylbenzene	$C_{14}H_{22}$	−8.80	−23.00	−23.07	−26.67	−29.64	−31.93	−33.67	−34.96	−35.85	−36.25	−36.4	−36.2	−35.8	−35.3	−34.7
n-Nonylbenzene	$C_{15}H_{24}$	−12.48	−27.93	−28.00	−31.90	−35.10	−37.58	−39.45	−40.84	−41.78	−42.20	−42.3	−42.0	−41.6	−41.1	−40.4
n-Decylbenzene	$C_{16}H_{26}$	−16.15	−32.86	−32.94	−37.12	−40.57	−43.23	−45.23	−46.71	−47.70	−48.14	−48.2	−47.9	−47.5	−46.8	−46.1
n-Undecylbenzene	$C_{17}H_{28}$	−19.82	−37.78	−37.87	−42.34	−46.04	−48.88	−51.01	−52.58	−53.63	−54.08	−54.1	−53.8	−53.3	−52.6	−51.8
n-Dodecylbenzene	$C_{18}H_{30}$	−23.49	−42.71	−42.80	−47.56	−51.50	−54.52	−56.78	−58.45	−59.56	−60.02	−60.1	−59.7	−59.1	−58.3	−57.5
n-Tridecylbenzene	$C_{19}H_{32}$	−27.17	−47.63	−47.73	−52.79	−56.96	−60.17	−62.56	−64.32	−65.48	−65.96	−66.0	−65.6	−65.0	−64.1	−63.2
n-Tetradecylbenzene	$C_{20}H_{34}$	−30.84	−52.56	−52.66	−58.01	−62.43	−65.82	−68.34	−70.19	−71.41	−71.90	−71.9	−71.5	−70.8	−69.8	−68.9
n-Pentadecylbenzene	$C_{21}H_{36}$	−34.51	−57.49	−57.59	−63.23	−67.90	−71.47	−74.12	−76.06	−77.34	−77.84	−77.8	−77.4	−76.6	−75.6	−74.6
n-Hexadecylbenzene	$C_{22}H_{38}$	−38.19	−62.41	−62.52	−68.46	−73.36	−77.12	−79.90	−81.93	−83.26	−83.78	−83.8	−83.2	−82.4	−81.4	−80.3
Increment per CH_2 group		−3.673	−4.926	−4.931	−5.223	−5.465	−5.648	−5.778	−5.871	−5.927	−5.941	−5.93	−5.89	−5.83	−5.76	−5.69

[a] See footnote "a" of table 9.

[b] $\triangle Hf°$ represents the increment in heat content for the reaction of forming the given compound in the gaseous state from the elements carbon (solid, graphite) and hydrogen (gaseous), with all the reactants and products in their appropriate standard reference states at the temperature indicated.

TABLE 21.—*Values* [a] *of the free energy of formation,* $\Delta Ff°$, *for the 14 alkylbenzenes,* C_6 *to* C_9, *for the ideal gaseous state, to* 1,500° K

Compound (gas)	Formula	Temperature[a] in °K													
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
		Free energy of formation,[b] $\Delta Ff°$, in kcal/mole														
Benzene	C_6H_6	24.000	30.989	31.058	35.008	39.242	43.663	48.211	52.838	57.537	62.270	67.02	71.79	76.57	81.34	86.11
Methylbenzene (toluene)	C_7H_8	17.500	29.228	29.335	35.390	41.811	48.477	55.306	62.236	69.255	76.320	83.40	90.50	97.61	104.71	111.81
Ethylbenzene	C_8H_{10}	13.917	31.208	31.357	39.741	48.554	57.646	66.921	76.302	85.779	95.303	104.84	114.39	123.95	133.48	143.02
1,2-Dimethylbenzene (o-xylene)	C_8H_{10}	11.096	29.177	29.329	37.883	46.852	56.103	65.548	75.110	84.777	94.494	104.23	113.99	123.76	133.50	143.24
1,3-Dimethylbenzene (m-xylene)	C_8H_{10}	10.926	28.405	28.554	37.008	45.906	55.099	64.492	74.006	83.630	93.307	103.00	112.72	122.45	132.15	141.85
1,4-Dimethylbenzene (p-xylene)	C_8H_{10}	11.064	28.952	29.104	37.688	46.724	56.060	65.604	75.275	85.058	94.897	104.76	114.64	124.54	134.40	144.27
n-Propylbenzene	C_9H_{12}	9.810	32.810	33.000	43.73	54.94	66.48	78.22	90.09	102.07	114.08	126.1	138.2	150.3	162.3	174.3
Isopropylbenzene (cumene)	C_9H_{12}	9.250	32.738	32.934	43.96	55.46	67.29	79.33	91.48	103.74	116.06	128.4	140.7	153.1	165.4	177.6
1-Methyl-2-ethylbenzene	C_9H_{12}	8.092	31.323	31.514	42.26	53.48	65.02	76.78	88.65	100.64	112.67	124.7	136.8	148.9	160.9	173.0
1-Methyl-3-ethylbenzene	C_9H_{12}	7.593	30.217	30.406	41.05	52.20	63.68	75.38	87.20	99.14	111.14	123.2	135.2	147.2	159.2	171.2
1-Methyl-4-ethylbenzene	C_9H_{12}	7.241	30.281	30.472	41.25	52.54	64.16	76.02	88.00	100.10	112.26	124.4	136.6	148.8	161.0	173.2
1,2,3-Trimethylbenzene (hemimellitene)	C_9H_{12}	5.527	29.319	29.513	40.56	52.06	63.91	76.01	88.26	100.63	113.07	125.5	138.0	150.6	163.0	175.5
1,2,4-Trimethylbenzene (pseudocumene)	C_9H_{12}	4.468	27.912	28.104	39.02	50.39	62.11	74.07	86.17	98.41	110.71	123.0	135.4	147.8	160.1	172.4
1,3,5-Trimethylbenzene (mesitylene)	C_9H_{12}	4.241	28.172	28.369	39.558	51.223	63.237	75.495	87.903	100.443	113.045	125.67	138.32	150.98	163.60	176.23

[a] See footnote "a" of table 9.

[b] $\Delta Ff°$ represents the increment in free energy for the reaction of forming the given compound in the gaseous state from the elements carbon (solid, graphite) and hydrogen (gaseous), with all the reactants and products in their appropriate standard reference states at the temperature indicated.

Table 22.—Values [a] of the free energy of formation, $\Delta Ff°$, for the normal alkylbenzenes, C_6 to C_{22}, for the ideal gaseous state, to 1,500° K

Compound (gas)	Formula	Temperature[a] in °K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
		Free energy of formation,[b] $\Delta Ff°$, in kcal/mole														
Benzene	C_6H_6	24.000	30.989	31.058	35.008	39.242	43.663	48.211	52.838	57.537	62.270	67.02	71.79	76.57	81.34	86.11
Methylbenzene (toluene)	C_7H_8	17.500	29.228	29.335	35.390	41.811	48.477	55.306	62.236	69.255	76.320	83.40	90.50	97.61	104.71	111.81
Ethylbenzene	C_8H_{10}	13.917	31.208	31.357	39.741	48.554	57.646	66.921	76.302	85.779	95.303	104.84	114.39	123.95	133.48	143.02
n-Propylbenzene	C_9H_{12}	9.810	32.810	33.000	43.73	54.94	66.48	78.22	90.09	102.07	114.08	126.1	138.2	150.3	162.3	174.3
n-Butylbenzene	$C_{10}H_{14}$	5.89	34.62	34.86	47.98	61.65	75.70	89.97	104.38	118.90	133.48	148.1	162.7	177.3	191.9	206.5
n-Amylbenzene	$C_{11}H_{16}$	2.22	36.67	36.95	52.46	68.58	85.13	101.92	118.86	135.93	153.06	170.2	187.4	204.5	221.7	238.8
n-Hexylbenzene	$C_{12}H_{18}$	−1.46	38.72	39.04	56.94	75.51	94.56	113.87	133.35	152.96	172.64	192.3	212.0	231.8	251.4	271.1
n-Heptylbenzene	$C_{13}H_{20}$	−5.13	40.76	41.13	61.42	82.44	103.98	125.82	147.83	169.99	192.22	214.4	236.7	259.0	281.2	303.5
n-Octylbenzene	$C_{14}H_{22}$	−8.80	42.81	43.22	65.90	89.37	113.41	137.77	162.32	187.02	211.80	236.5	261.4	286.2	311.0	335.8
n-Nonylbenzene	$C_{15}H_{24}$	−12.48	44.86	45.31	70.38	96.30	122.84	149.72	176.80	204.04	231.38	258.7	286.0	313.4	340.7	368.1
n-Decylbenzene	$C_{16}H_{26}$	−16.15	46.91	47.40	74.85	103.24	132.27	161.68	191.28	221.07	250.95	280.8	310.7	340.6	370.5	400.5
n-Undecylbenzene	$C_{17}H_{28}$	−19.82	48.96	49.49	79.33	110.17	141.70	173.63	205.77	238.10	270.53	302.9	335.4	367.8	400.2	432.8
n-Dodecylbenzene	$C_{18}H_{30}$	23.49	51.00	51.58	83.81	117.10	151.12	185.58	220.25	255.13	290.11	325.0	360.0	395.0	430.0	465.1
n-Tridecylbenzene	$C_{19}H_{32}$	−27.17	53.05	53.67	88.29	124.03	160.55	197.53	234.74	272.16	309.69	347.1	384.7	422.3	459.8	497.4
n-Tetradecylbenzene	$C_{20}H_{34}$	−30.84	55.10	55.76	92.77	130.96	169.98	209.48	249.22	289.19	329.27	369.2	409.4	449.5	489.5	529.8
n-Pentadecylbenzene	$C_{21}H_{36}$	−34.51	57.15	57.85	97.25	137.89	179.41	221.43	263.70	306.22	348.85	391.4	434.0	476.7	519.3	562.1
n-Hexadecylbenzene	$C_{22}H_{38}$	−38.19	59.20	59.94	101.73	144.82	188.84	233.38	278.19	323.25	368.43	413.5	458.7	503.9	549.1	594.4
Increment per CH_2 group			−3.673	2.048	2.090	4.479	6.931	9.428	11.951	14.484	17.029	19.579	22.12	24.67	27.22	29.76	32.33

[a] See footnote "a" of table 9.

[b] $\Delta Ff°$ represents the increment in free energy for the reaction of forming the given compound in the gaseous state from the elements carbon (solid, graphite) and hydrogen (gaseous), with all the reactants and products in their appropriate standard reference states at the temperature indicated.

TABLE 23.—*Values* [a] *of the logarithm of the equilibrium constant of formation,* log $_{10}$ Kf, *for the 14 alkylbenzenes,* C_6 *to* C_9, *for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature [a] in °K													
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
		Logarithm of equilibrium constant of formation,[b] $\log_{10}$ Kf														
Benzene	C_6H_6	−∞	−22.7143	−22.6252	−19.1271	−17.1521	−15.9040	−15.0519	−14.4345	−13.9716	−13.6088	−13.3153	−13.0738	−12.8717	−12.6971	−12.5461
Methylbenzene (toluene)	C_7H_8	---do	−21.4236	−21.3698	−19.3356	−18.2752	−17.6574	−17.2671	−17.0018	−16.8171	−16.6794	−16.5699	−16.4825	−16.4102	−16.3455	−16.2900
Ethylbenzene	C_8H_{10}	---do	−22.8750	−22.8428	−21.7132	−21.2223	−20.9972	−20.8934	−20.8442	−20.8296	−20.8281	−20.8294	−20.8333	−20.8368	−20.8362	−20.8375
1, 2-Dimethylbenzene (*o*-xylene)	C_8H_{10}	---do	−21.3860	−21.3655	−20.6980	−20.4786	−20.4351	−20.4646	−20.5188	−20.5864	−20.6513	−20.7081	−20.7601	−20.8051	−20.8399	−20.8692
1, 3-Dimethylbenzene (*m*-xylene)	C_8H_{10}	---do	−20.8202	−20.8014	−20.2201	−20.0651	−20.0693	−20.1349	−20.2172	−20.3077	−20.3919	−20.4646	−20.5296	−20.5853	−20.6290	−20.6670
1, 4-Dimethylbenzene (*p*-xylene)	C_8H_{10}	---do	−21.2214	−21.2018	−20.5912	−20.4227	−20.4194	−20.4821	−20.5638	−20.6545	−20.7393	−20.8128	−20.8788	−20.9358	−20.9808	−21.0202
n-Propylbenzene	C_9H_{12}	---do	−24.049	−24.040	−23.894	−24.012	−24.215	−24.422	−24.610	−24.785	−24.932	−25.056	−25.168	−25.262	−25.336	−25.395
Isopropylbenzene (cumene)	C_9H_{12}	---do	−23.996	−23.992	−24.016	−24.241	−24.510	−24.768	−24.991	−25.192	−25.364	−25.509	−25.631	−25.732	−25.812	−25.880
1-Methyl-2-ethylbenzene	C_9H_{12}	---do	−22.960	−22.958	−23.090	−23.377	−23.684	−23.970	−24.218	−24.437	−24.624	−24.780	−24.914	−25.027	−25.119	−25.199
1-Methyl-3-ethylbenzene	C_9H_{12}	---do	−22.149	−22.150	−22.428	−22.816	−23.194	−23.533	−23.822	−24.075	−24.289	−24.468	−24.620	−24.749	−24.853	−24.945
1-Methyl-4-ethylbenzene	C_9H_{12}	---do	−22.195	−22.198	−22.537	−22.964	−23.371	−23.733	−24.040	−24.308	−24.535	−24.723	−24.885	−25.021	−25.133	−25.232
1, 2, 3-Trimethylbenzene (hemimellitene)	C_9H_{12}	---do	−21.490	−21.500	−22.159	−22.754	−23.279	−23.731	−24.110	−24.436	−24.712	−24.942	−25.140	−25.310	−25.450	−25.571
1, 2, 4-Trimethylbenzene (pseudocumene)	C_9H_{12}	---do	−20.459	−20.473	−21.319	−22.025	−22.622	−23.124	−23.541	−23.897	−24.196	−24.445	−24.657	−24.839	−24.990	−25.121
1, 3, 5-Trimethylbenzene (mesitylene)	C_9H_{12}	---do	−20.6497	−20.6666	−21.6131	−22.3891	−23.0336	−23.5702	−24.0136	−24.3904	−24.7055	−24.9678	−25.1916	−25.3815	−25.5390	−25.6761

[a] See footnote "a" in table 9.

[b] Log $_{10}$ Kf represents the logarithm (to the base 10) of the equilibrium constant for the reaction of forming the given compound in the gaseous state from the elements carbon (solid, graphite) and hydrogen (gaseous), with all the reactants and products in their appropriate standard reference states at the temperature indicated. Log $_{10}$ $Kf = -\Delta Ff°/0.00457566 T$; $\Delta Ff°$ in kcal/mole, T in °K.

TABLE 24.—*Values* [a] *of the logarithm of the equilibrium constant of formation,* $\log_{10} Kf$, *for the normal alkylbenzenes,* C_6 *to* C_{22}, *for the ideal gaseous state, to* 1,500° K

Compound (gas)	Formula	Temperature [a] in °K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
		Logarithm of equilibrium constant of formation,[b] $\log_{10} Kf$														
Benzene	C_6H_6	$-\infty$	−22.7143	−22.6252	−19.1271	−17.1521	−15.9040	−15.0519	−14.4345	−13.9716	−13.6088	−13.3153	−13.0738	−12.8717	−12.6971	−12.5461
Methylbenzene (toluene)	C_7H_8	do	−21.4236	−21.3698	−19.3356	−18.2752	−17.6574	−17.2671	−17.0018	−16.8171	−16.6794	−16.5699	−16.4825	−16.4102	−16.3455	−16.2900
Ethylbenzene	C_8H_{10}	do	−22.8750	−22.8428	−21.7132	−21.2223	−20.9972	−20.8934	−20.8442	−20.8296	−20.8281	−20.8294	−20.8333	−20.8368	−20.8362	−20.8375
n-Propylbenzene	C_9H_{12}	do	−24.049	−24.040	−23.894	−24.012	−24.215	−24.422	−24.610	−24.785	−24.932	−25.056	−25.168	−25.262	−25.336	−25.395
n-Butylbenzene	$C_{10}H_{14}$	do	−25.374	−25.392	−26.212	−26.948	−27.572	−28.090	−28.515	−28.873	−29.171	−29.419	−29.631	−29.811	−29.957	−30.082
n-Amylbenzene	$C_{11}H_{16}$	do	−26.876	−26.914	−28.660	−29.977	−31.006	−31.822	−32.472	−33.008	−33.450	−33.813	−34.124	−34.386	−34.604	−34.793
n-Hexylbenzene	$C_{12}H_{18}$	do	−28.377	−28.437	−31.107	−33.007	−34.440	−35.553	−36.429	−37.144	−37.729	−38.208	−38.616	−38.961	−39.250	−39.504
n-Heptylbenzene	$C_{13}H_{20}$	do	−29.878	−29.959	−33.554	−36.036	−37.874	−39.284	−40.386	−41.279	−42.008	−42.602	−43.109	−43.536	−43.896	−44.214
n-Octylbenzene	$C_{14}H_{22}$	do	−31.379	−31.482	−36.001	−39.066	−41.309	−43.015	−44.343	−45.414	−46.287	−46.996	−47.602	−48.112	−48.542	−48.925
n-Nonylbenzene	$C_{15}H_{24}$	do	−32.880	−33.004	−38.448	−42.095	−44.743	−46.746	−48.299	−49.549	−50.566	−51.391	−52.094	−52.687	−53.189	−53.635
n-Decylbenzene	$C_{16}H_{26}$	do	−34.382	−34.527	−40.896	−45.125	−48.177	−50.478	−52.256	−53.684	−54.845	−55.785	−56.587	−57.262	−57.835	−58.346
n-Undecylbenzene	$C_{17}H_{28}$	do	−35.883	−36.050	−43.343	−48.154	−51.611	−54.209	−56.213	−57.820	−59.124	−60.180	−61.080	−61.837	−62.481	−63.057
n-Dodecylbenzene	$C_{18}H_{30}$	do	−37.384	−37.572	−45.790	−51.184	−55.045	−57.940	−60.170	−61.955	−63.403	−64.574	−65.572	−66.412	−67.128	−67.767
n-Tridecylbenzene	$C_{19}H_{32}$	do	−38.885	−39.095	−48.237	−54.213	−58.479	−61.671	−64.127	−66.090	−67.682	−68.968	−70.065	−70.988	−71.774	−72.478
n-Tetradecylbenzene	$C_{20}H_{34}$	do	−40.386	−40.618	−50.684	−57.243	−61.913	−65.402	−68.083	−70.225	−71.961	−73.363	−74.557	−76.563	−76.420	−77.188
n-Pentadecylbenzene	$C_{21}H_{36}$	do	−41.888	−42.140	−53.132	−60.272	−65.347	−69.134	−72.040	−74.360	−76.240	−77.757	−79.050	−80.138	−81.066	−81.899
n-Hexadecylbenzene	$C_{22}H_{38}$	do	−43.389	−43.663	−55.579	−63.302	−68.781	−72.865	−75.997	−78.496	−80.519	−82.152	−83.542	−84.713	−85.713	−86.610
Increment per CH_2 group		do	−1.5012	−1.5226	−2.4472	−3.0295	−3.4341	−3.7312	−3.9568	−4.1352	−4.2790	−4.3944	−4.4926	−4.5752	−4.6463	−4.7106

[a] See footnote "a" of table 9.

[b] Log $_{10}$ Kf represents the logarithm (to the base 10) of the equilibrium constant for the reaction of forming the given compound in the gaseous state from the elements carbon (solid, graphite) and hydrogen (gaseous), with all the reactants and products in their appropriate standard reference states at the temperature indicated. Log $_{10}$ $Kf= -\Delta Ff°/0.00457566\,T$; $\Delta Ff°$ in kcal/mole, T in °K.

V. Free Energies and Equilibria of Isomerization

From the values in table 21 and 23, calculations were made of the values of the free energies and equilibrium constants for the isomerization of the C_8H_{10} and the C_9H_{12} alkylbenzenes, according to the reactions

$$C_8H_{10} \text{ (ethylbenzene, gas)} = C_8H_{10} \text{ (isomeric alkylbenzene, gas)} \tag{13}$$

$$C_9H_{12} \text{ (}n\text{-propylbenzene, gas)} = C_9H_{12} \text{ (isomeric alkylbenzene, gas).} \tag{14}$$
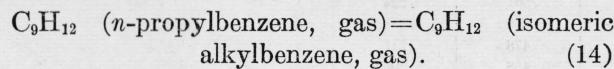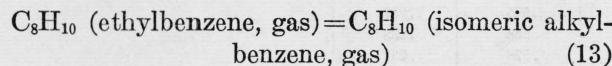
The resulting values are given in tables 25 and 26, under the following headings, for the isomerization reaction as written: $\Delta F^\circ/T$, the standard free-energy change divided by the absolute temperature; and K, the equilibrium constant. In tables 27 and 28 are given values of N, the mole fraction of the given isomer present at equilibrium with its other isomers. For any two isomers, the ratio of the corresponding values of K (or of N) in tables 25 and 27 gives the ratio of the amounts of those two isomers present at equilibrium with one another in the gas phase at the given temperature. For the purpose of retaining the significance of their change with temperature, the values in tables 25 to 28 are written with more figures than are warranted by the absolute uncertainty.

TABLE 25.—*Values of the free energies and equilibrium constants for the isomerization of ethylbenzene to the isomeric* C_8 *alkyl benzenes in the ideal gaseous state to 1,500° K*

Temperature	Ethylbenzene=o-xylene		Ethylbenzene=m-xylene		Ethylbenzene=p-xylene	
	$\Delta F^\circ/T$	K	$\Delta F^\circ/T$	K	$\Delta F^\circ/T$	K
°K						
298.16	−6.813	30.83	−9.402	113.45	−7.566	45.03
300	−6.760	30.02	−9.341	110.00	−7.509	43.76
400	−4.645	10.35	−6.832	31.12	−5.134	13.24
500	−3.403	5.54	−5.295	14.36	−3.659	6.30
600	−2.572	3.65	−4.246	8.47	−2.644	3.78
700	−1.962	2.68	−3.471	5.74	−1.882	2.58
800	−1.489	2.12	−2.869	4.24	−1.283	1.91
900	−1.113	1.75	−2.388	3.33	−0.801	1.50
1,000	−0.809	1.50	−1.996	2.73	−.406	1.23
1,100	−.555	1.32	−1.669	2.32	−.076	1.04
1,200	−.335	1.18	−1.390	2.01	+.208	0.90
1,300	−.145	1.08	−1.151	1.78	.453	.80
1,400	+.017	0.99	−0.948	1.61	.662	.72
1,500	.145	.93	−.780	1.48	.836	.66

TABLE 26.—*Values of the free energies and equilibrium constants for the isomerization of propylbenzene to the isomeric* C_9 *alkyl benzenes in the ideal gaseous state to 1,500° K*

Temperature	n-Propylbenzene=isopropylbenzene		n-Propylbenzene=1-methyl-2-ethylbenzene		n-Propylbenzene=1-methyl-3-ethylbenzene		n-Propylbenzene=1-methyl-4-ethylbenzene		n-Propylbenzene=1,2,3-trimethylbenzene		n-Propylbenzene=1,2,4-trimethylbenzene		n-Propylbenzene=1,3,5-trimethylbenzene	
	$\Delta F^\circ/T$	K	$\Delta F^\circ/T$	K	$\Delta F^\circ/T$	K	$\Delta F^\circ/T$	K	$\Delta F^\circ/T$	K	$\Delta F^\circ/T$	K	$\Delta F^\circ/T$	K
°K														
298.16	−0.24	1.13	−4.98	12.26	−8.69	79.28	−8.48	71.33	−11.71	362.4	−16.43	3897	−15.55	2503
300	−.22	1.12	−4.95	12.07	−8.65	77.70	−8.43	69.56	−11.62	346.3	−16.32	3687	−15.44	2368
400	+.56	0.75	−3.68	6.37	−6.70	29.1	−6.21	22.8	−7.94	54.4	−11.78	375	−10.43	190
500	1.05	.59	−2.91	4.32	−5.47	15.7	−4.79	11.1	−5.75	18.1	−9.09	97.0	−7.42	41.8
600	1.35	.51	−2.43	3.40	−4.67	10.5	−3.86	6.98	−4.28	8.62	−7.29	39.2	−5.40	15.1
700	1.58	.45	−2.07	2.83	−4.07	7.75	−3.16	4.90	−3.17	4.93	−5.94	19.9	−3.90	7.12
800	1.74	.42	−1.80	2.47	−3.61	6.15	−2.61	3.72	−2.29	3.17	−4.89	11.7	−2.73	3.95
900	1.86	.39	−1.59	2.24	−3.25	5.13	−2.19	3.01	−1.60	2.24	−4.06	7.71	−1.81	2.49
1,000	1.98	.37	−1.41	2.03	−2.94	4.39	−1.82	2.50	−1.01	1.66	−3.37	5.45	−1.04	1.69
1,100	2.07	.35	−1.26	1.88	−2.69	3.87	−1.52	2.15	−0.52	1.30	−2.80	4.09	−0.41	1.23
1,200	2.12	.34	−1.16	1.79	−2.51	3.54	−1.30	1.92	−.13	1.07	−2.34	3.25	+.11	0.95
1,300	2.15	.34	−1.07	1.71	−2.35	3.26	−1.10	1.74	+.22	0.90	−1.93	2.64	.55	.76
1,400	2.18	.33	−0.99	1.65	−2.21	3.04	−0.93	1.60	.52	.77	−1.58	2.22	.93	.63
1,500	2.22	.33	−.90	1.57	−2.06	2.82	−.75	1.46	.80	.67	−1.25	1.88	1.29	.52

Table 27.—*Values of the equilibrium concentrations for the isomerization of the C_8 alkylbenzenes in the ideal gaseous state to $1,500°$ K*

Temperature	Composition, in mole fraction, of equilibrium mixture of isomers			
	Ethylbenzene	o-Xylene	m-Xylene	p-Xylene
°K				
298. 16	0.0052	0.162	0.596	0.237
300	.0054	.163	.595	.237
400	.018	.186	.558	.238
500	.037	.204	.528	.232
600	.059	.216	.501	.224
700	.083	.224	.478	.215
800	.108	.228	.458	.206
900	.132	.231	.439	.198
1,000	.155	.232	.423	.190
1,100	.176	.233	.408	.183
1,200	.196	.232	.395	.177
1,300	.215	.231	.383	.171
1,400	.232	.230	.372	.166
1,500	.246	.229	.364	.161

Table 28.—*Values of the equilibrium concentration for the isomerization of the C_9 alkylbenzenes in the ideal gaseous state to $1,500°$ K*

Temperature	Composition, in mole fraction, of equilibrium mixture of isomers							
	n-Propyl-benzene	Isopropyl-benzene	1-Methyl-2-ethylbenzene	1-Methyl-3-ethylbenzene	1-Methyl-4-ethylbenzene	1,2,3-Trimethyl-benzene	1,2,4-Trimethyl-benzene	1,3,5-Trimethyl-benzene
°K								
298. 16	0.00014	0.00016	0.0018	0.011	0.010	0.052	0.564	0.361
300	.00015	.00017	.0018	.012	.011	.053	.561	.361
400	.0015	.0011	.009	.043	.033	.080	.553	.280
500	.005	.003	.023	.083	.059	.095	.511	.221
600	.012	.006	.040	.123	.082	.101	.459	.177
700	.020	.009	.058	.159	.100	.101	.407	.146
800	.031	.013	.076	.189	.114	.097	.359	.121
900	.041	.016	.092	.212	.124	.092	.320	.103
1,000	.052	.019	.106	.230	.131	.087	.287	.088
1,100	.063	.022	.119	.244	.135	.082	.258	.077
1,200	.072	.025	.129	.255	.139	.077	.235	.068
1,300	.081	.027	.139	.264	.141	.073	.214	.061
1,400	.089	.030	.147	.270	.142	.069	.197	.056
1,500	.098	.032	.154	.275	.142	.065	.183	.051

In figures 2 and 3 are plotted, as a function of the temperature, the values of $\Delta F°/T$ given in tables 25 and 26 for the isomerization of the C_8H_{10} and the C_9H_{12} alkybenzenes. These plots may be compared with corresponding plots for the paraffins [21, 22], the acetylenes [15], and the monoolefins [24]. From these charts, one may see at a glance, for any temperature in the given range, and within the limits of uncertainty of the calculations, which of the isomers is thermodynamically most stable (lowest value of $\Delta F°/T$) and which is the least stable (highest value of $\Delta F°/T$).

In figures 4 and 5 are plotted, as a function of temperature, for the C_8H_{10} and the C_9H_{12} alkyl-benzenes, respectively, the amounts, in mole fraction of each of the isomers present at equilibrium with its other isomers in the gas phase, as given in tables 27 and 28. The vertical width of each band gives the mole fraction for that isomer at the selected temperature. The mole fractions of the several isomers are plotted additively, so that their sum is unity at all temperatures.

In table 29 the directly measured equilibrium compositions for several reactions [9, 25] are compared with those calculated in this paper. The values agree within the combined limits of uncertainty of the experimental and calculated values.
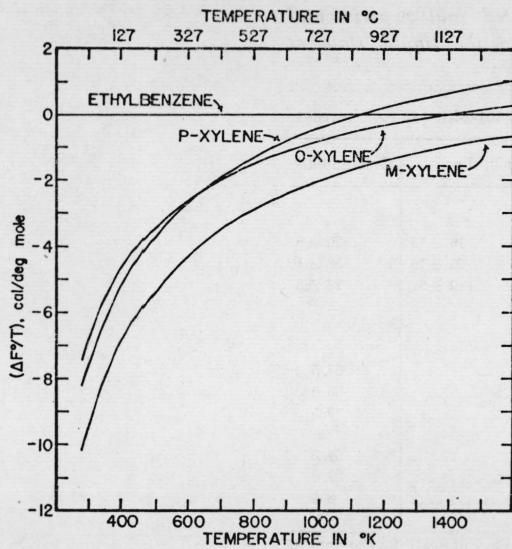
FIGURE 2.—*Free energy of isomerization of the* C_8H_{10} *alkylbenzenes.*

The scale of ordinates gives the value of $\Delta F^\circ/T$, in calories per degree mole, for the isomerization of ethylbenzene into the other isomers, in the gaseous state, as indicated. The scale of abscissas gives the temperature in degrees Kelvin.
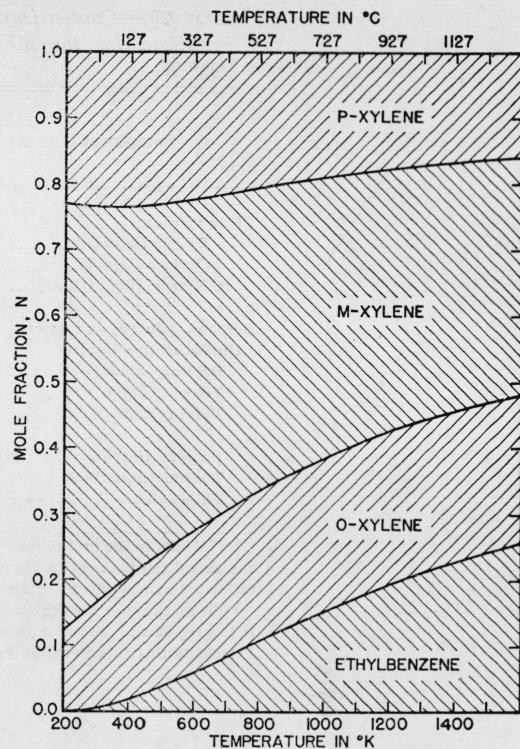

FIGURE 4.—*Equilibrium concentrations of the* C_8H_{10} *alkylbenzenes.*

The scale of ordinates measures the amount in mole fraction, and the scale of abscissas gives the temperature in degrees Kelvin and degrees centigrade. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present when at equilibrium with all of its other isomers, in the gas phase.
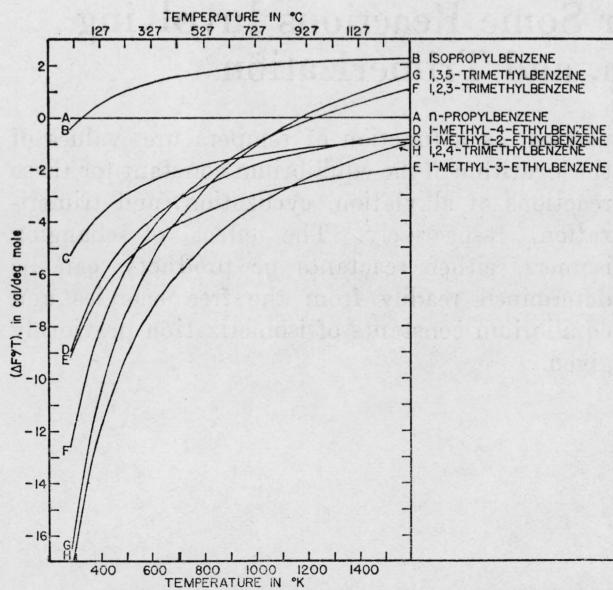
FIGURE 3.—*Free energy of isomerization of the* C_9H_{12} *alkylbenzenes.*

The scale of ordinates gives the value of $\Delta F^\circ/T$, in calories per degree mole, for the isomerization of *n*-propylbenzene into the other isomers, in the gaseous state, as indicated. The scale of abscissas gives the temperature in degrees Kelvin.
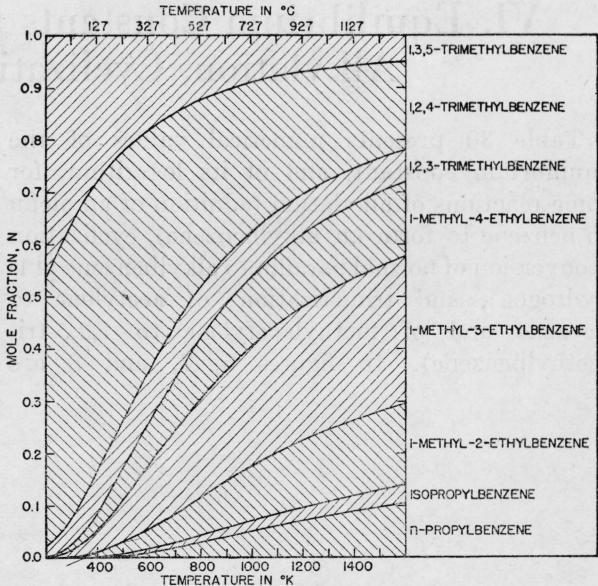

FIGURE 5.—*Equilibrium concentrations of the* C_9H_{12} *alkylbenzenes.*

The scale of ordinates measures the amount in mole fraction, and the scale of abscissas gives the temperature in degrees Kelvin and degrees centigrade. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present when at equilibrium with all of its other isomers, in the gas phase.

Heats and Free Energies of Alkylbenzenes

TABLE 29.—*Comparison of calculated and experimental equilibria for the alkylbenzenes in the liquid state at 323° K*

Component	Equilibrium composition in mole percent		
	Experimental [a]		Calculated [b]
Three xylenes:			
o-Xylene (liquid)_____	12 ±3	16 ±10	20 ±6
m-Xylene (liquid)_____	71 ±5	65 ±10	58 ±10
p-Xylene (liquid)_____	17 ±2	19 ±5	22 ±8
Benzene, toluene, and xylenes (initial composition):			
Benzene (liquid)=50_____	54	--------------	57.5
Toluene (liquid)=50_____	41	--------------	35.0
Total xylenes (liquid)=0___	4.7	--------------	7.5
Benzene (liquid)=55_____	58.5	--------------	54.5
Toluene (liquid)=36_____	36.5	--------------	27.0
Total xylenes (liquid)=9___	5.0	--------------	8.5

[a] The data in the first column are those of Pitzer and Scott [9]; the data in the second column are those of Norris and Vaala [25], with the uncertainties estimated by the present authors.

[b] These values are calculated from the thermodynamic functions given in this report and the vapor pressure data given in the tables of the American Petroleum Institute Research Project 44 [26].

VI. Equilibrium Constants for Some Reactions Involving Alkylation, Cyclization, and Trimerization

Table 30 presents numerical values of the equilibrium constant, and of its logarithm, for some reactions of alkylation (addition of an olefin to benzene to form an alkylbenzene), cyclization (conversion of normal paraffin to alkylbenzene plus hydrogen), and trimerization (of acetylene to benzene and of methylacetylene to 1,3,5-trimethylbenzene). In figures 6, 7, and 8 are plotted, as a function of temperature, values of the logarithm of the equilibrium constant for these reactions of alkylation, cyclization, and trimerization, respectively. The effect of changing isomers, either reactants or products, can be determined readily from the free energies and equilibrium constants of isomerization previously given.

TABLE 30.—*Values of equilibrium constants for reactions of alkylation, cyclization, and trimerization, to 1,500° K*

Reaction	Temperature in °K													
	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
	Logarithm of the equilibrium constant, $\log_{10} K$													
ALKYLATION														
C_6H_6 (benzene, gas)+C_2H_4 (ethylene, gas)=C_8H_{10} (ethylbenzene, gas)	11.7738	11.6605	7.0710	4.3417	2.5261	1.2382	0.2806	−0.4584	−1.0455	−1.5223	−1.9155	−2.2445	−2.5240	−2.7665
C_6H_6 (benzene, gas)+C_3H_6 (propylene, gas)=C_9H_{12} (n-propylbenzene, gas)	9.634	9.531	5.380	2.928	1.295	0.145	−.707	−1.365	−1.881	−2.302	−2.654	−2.947	−3.196	−3.403
C_6H_6 (benzene, gas)=C_3H_6 (propylene, gas)=C_9H_{12} (isopropylbenzene, gas)	9.686	9.579	5.257	2.698	1.000	−0.200	−1.088	−1.771	−2.314	−2.754	−3.117	−3.417	−3.672	−3.889
C_6H_6 (benzene, gas)+C_nH_{2n} (1-alkene, gas)=$C_nH_{2n+1}C_6H_5$ (n-alkylbenzene, gas); $n>3$	9.960	9.851	5.593	3.068	1.390	0.202	−0.680	−1.357	−1.895	−2.333	−2.698	−3.003	−3.262	−3.483
CYCLIZATION														
C_6H_{14} (n-hexane, gas)=C_6H_6 (benzene, gas)+$4H_2$ (gas)	−22.677	−22.406	−11.418	−4.712	−0.176	+3.097	5.566	7.494	9.041	10.308	11.365	12.258	13.021	13.686
C_7H_{16} (n-heptane, gas)=C_7H_8 (toluene, gas)+$4H_2$ (gas)	−19.892	−19.636	−9.184	−2.806	+1.502	4.613	6.956	8.785	10.251	11.448	12.448	13.294	14.018	14.654
C_8H_{18} (n-octane, gas)=C_8H_{10} (ethylbenzene, gas)+$4H_2$ (gas)	−19.840	−19.587	−9.144	−2.724	+1.597	4.718	7.067	8.905	10.378	11.584	12.588	13.441	14.172	14.817
C_9H_{20} (n-nonane, gas)=C_9H_{12} (n-propylbenzene, gas)+$4H_2$ (gas)	−19.516	−19.263	−8.849	−2.487	+1.813	4.918	7.259	9.085	10.553	11.751	12.746	13.591	14.318	14.968
C_nH_{2n+2} (n-paraffin, gas)=C_nH_{2n-6} (n-alkylbenzene, gas)+$4H_2$ (gas); $n>9$	−19.341	−19.092	−8.721	−2.393	+1.890	4.981	7.310	9.133	10.593	11.784	12.776	13.618	14.344	14.992
TRIMERIZATION														
$3C_2H_2$ (acetylene, gas)=C_6H_6 (benzene, gas)	87.2327	86.5922	60.4947	44.7349	34.1816	26.6256	20.9589	16.5390	13.0126	10.1321	7.7369	5.7151	3.9862	2.4941
$3C_3H_4$ (methylacetylene, gas)=C_9H_{12} (1,3,5-trimethylbenzene, gas)	81.191	80.916	55.895	40.845	30.789	23.598	18.205	14.012	10.664	7.930	5.657	3.740	2.102	0.688
ALKYLATION	Equilibrium constant, °K													
C_6H_6 (benzene, gas)+C_2H_4 (ethylene, gas)=C_8H_{10} (ethylbenzene, gas)	5.940×10^{11}	4.576×10^{11}	1.178×10^7	2.196×10^4	3.358×10^2	17.31	1.908	0.3480	9.005×10^{-2}	3.004×10^{-2}	1.215×10^{-2}	5.695×10^{-3}	2.992×10^{-3}	1.712×10^{-3}
C_6H_6 (benzene, gas)+C_3H_6 (propylene, gas)=C_9H_{12} (n-propylbenzene, gas)	4.30×10^9	3.40×10^9	2.40×10^5	8.47×10^2	19.72	1.397	1.96×10^{-1}	4.32×10^{-2}	1.31×10^{-2}	4.99×10^{-3}	2.22×10^{-3}	1.13×10^{-3}	6.37×10^{-4}	3.95×10^{-4}
C_6H_6 (benzene, gas)+C_3H_6 (propylene, gas)=C_9H_{12} (isopropylbenzene, gas)	4.85×10^9	3.79×10^9	1.81×10^5	4.99×10^2	10.00	0.631	8.16×10^{-2}	1.69×10^{-2}	4.85×10^{-3}	1.76×10^{-3}	7.64×10^{-4}	3.83×10^{-4}	2.13×10^{-4}	1.29×10^{-4}
C_6H_6 (benzene, gas)+C_nH_{2n} (1-alkene, gas)=$C_nH_{2n+1}C_6H_5$ (n-alkylbenzene, gas); $n>3$	9.12×10^9	7.10×10^9	3.92×10^5	1.17×10^3	24.55	1.592	0.209	4.40×10^{-2}	1.27×10^{-2}	4.64×10^{-3}	2.00×10^{-3}	9.93×10^{-4}	5.47×10^{-4}	3.29×10^{-4}
CYCLIZATION														
C_6H_{14} (n-hexane, gas)=C_6H_6 (benzene, gas)+$4H_2$ (gas)	2.10×10^{-23}	3.93×10^{-23}	3.82×10^{-12}	1.94×10^{-5}	0.667	1.25×10^3	3.68×10^5	3.12×10^7	1.10×10^9	2.03×10^{11}	2.32×10^{11}	1.81×10^{12}	1.05×10^{13}	4.85×10^{13}
C_7H_{16} (n-heptane, gas)=C_7H_8 (toluene, gas)+$4H_2$ (gas)	1.28×10^{-20}	2.31×10^{-20}	6.54×10^{-10}	1.56×10^{-3}	31.77	4.10×10^4	9.03×10^6	6.10×10^8	1.78×10^{10}	2.80×10^{11}	2.80×10^{12}	1.97×10^{13}	1.04×10^{14}	4.51×10^{14}

TABLE 30.—*Values of equilibrium constants for reactions of alkylytion, cyclization, and trimerization, to 1,500° K*—Continued

| Reaction	Temperature in °K													
	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
	Logarithm of the equilibrium constant, $\log_{10} K$													
CYCLIZATION—continued														
C_8H_{18} (n-octane, gas) = C_8H_{10} (ethylbenzene, gas) + $4H_2$ (gas)	1.45×10^{-20}	2.59×10^{-20}	7.18×10^{-10}	1.89×10^{-3}	39. 54	5.22×10^4	1.17×10^7	8.03×10^8	2.39×10^{10}	3.84×10^{11}	3.87×10^{12}	2.76×10^{13}	1.49×10^{14}	6.56×10^{14}
C_9H_{20} (n-nonane, gas) = C_9H_{12} (n-propylbenzene, gas) + $4H_2$ (gas)	3.05×10^{-20}	5.46×10^{-20}	1.42×10^{-9}	3.26×10^{-3}	65. 02	8.28×10^4	1.81×10^7	1.22×10^9	3.57×10^{10}	5.64×10^{11}	5.57×10^{12}	3.90×10^{13}	2.08×10^{14}	9.29×10^{14}
C_nH_{2n+2} (n-paraffin, gas) = C_nH_{2n-6} (n-alkylbenzene, gas) + $4H_2$ (gas); $n>9$	4.56×10^{-20}	8.09×10^{-20}	1.90×10^{-9}	4.04×10^{-3}	77. 70	9.57×10^4	2.04×10^7	1.36×10^9	3.92×10^{10}	6.08×10^{11}	5.97×10^{12}	4.15×10^{13}	2.21×10^{14}	9.82×10^{14}
TRIMERIZATION														
$3C_2H_2$ (acetylene, gas) = C_6H_6 (benzene, gas)	1.709×10^{87}	3.910×10^{86}	3.124×10^{60}	5.431×10^{44}	1.519×10^{34}	4.223×10^{26}	9.097×10^{20}	3.460×10^{16}	1.030×10^{13}	1.356×10^{10}	5.456×10^7	5.190×10^5	9.687×10^3	3.120×10^2
$3C_3H_4$ (methylacetylene, gas) = C_9H_{12} (1,3,5-trimethylbenzene, gas)	1.55×10^{81}	8.24×10^{80}	7.85×10^{55}	7.00×10^{40}	6.15×10^{30}	3.96×10^{23}	1.60×10^{18}	1.03×10^{14}	4.61×10^{10}	8.51×10^7	4.54×10^5	5.50×10^3	1.26×10^2	4.88
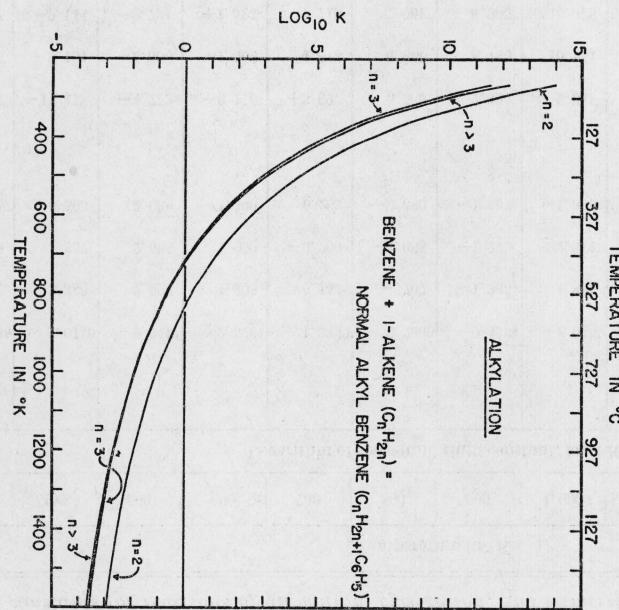
FIGURE 6.—*Logarithm of the equilibrium constant for some reactions of alkylation.*

The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for some reactions of alkylation (addition of an olefin to benzene to form an alkylbenzene), in the gaseous state. The scale of abscissas gives the temperature in degrees Kelvin and degrees centigrade. The corresponding numerical values are given in table 30.
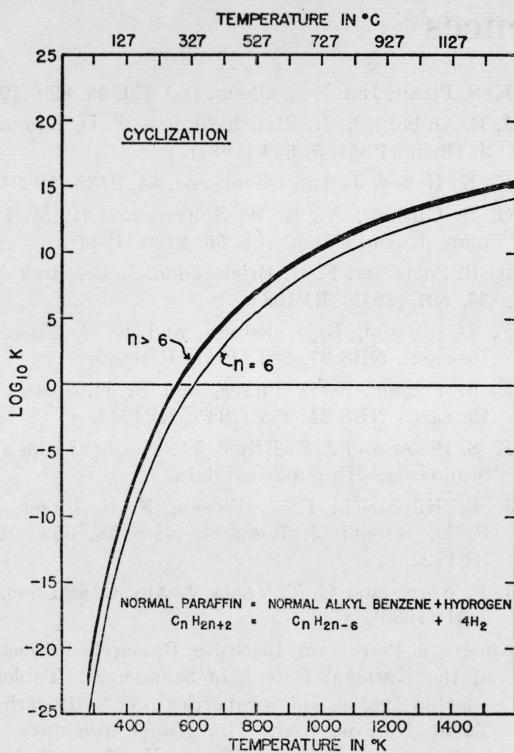
FIGURE 7.—*Logarithm of the equilibrium constant for some reactions of cyclization*

The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for the reaction of cyclization of a normal paraffin to form a normal alkylbenzene, in the gaseous state. The scale of abscissas gives the temperature in degrees Kelvin and degrees centigrade. The values calculated for *n*-heptane and higher paraffins fall within the width of the heavy line indicated. The corresponding numerical values are given in table 30.
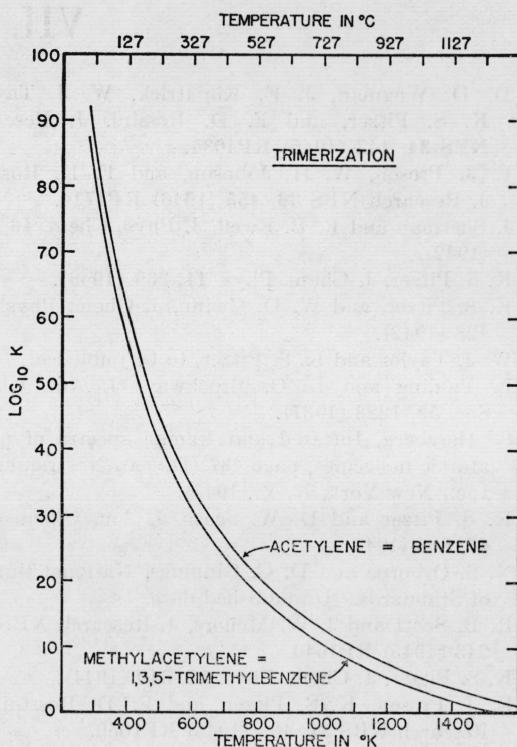
FIGURE 8.—*Logarithm of the equilibrium constant for some reactions of trimerization*

The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for some reactions of trimerization of alkynes to alkylbenzenes, in the gaseous state. The scale of abscissas gives the temperature in degrees Kelvin and degrees centigrade. The corresponding numerical values are given in table 30.

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