

THERMODYNAMIC PROPERTIES OF SELECTED METHYLBENZENES FROM 0 TO 1000°K.

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Values of the heat capacity, the heat content function, the free energy function, the entropy, heat of formation and free energy of formation have been calculated at selected temperatures, from 0 to 1000°K. for eight methylbenzenes in the ideal gas state. All of the methylbenzenes for which vibrational assignments had not been made previously were included: namely, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, and three tetramethylbenzenes, pentamethylbenzene and hexamethylbenzene. Minor changes were made in the assignments for 1,2-dimethylbenzene published previously by Pitzer and Scott. The potential barrier associated with the hindered rotation of the *ortho*-methyl group in 1,2,4-trimethylbenzene was found to be 1400 cal./mole on the basis of frequency assignments and the experimental entropy. Employing this *ortho*-barrier for the methyl groups in the 1- and 3-positions in 1,2,3-trimethylbenzene, a barrier of 3200 cal./mole was found for the central methyl group. Comparison of the tetramethylbenzene isomerization equilibrium measured experimentally with that calculated from results of the statistical calculations shows good agreement.

Introduction

The thermodynamic properties of benzene and the C₇-, C₈- and C₉-methylbenzenes in the ideal gas state have been published by Taylor, *et al.*¹ The object of the present investigation was to establish reliable values of the heat capacity, the heat content function, the free energy function, and quantities derived from these for the tetra-, penta- and hexamethylbenzenes. Recently Kilpatrick and co-workers^{2,3} have determined entropies from low temperature heat capacity and other data for the 1,2,3- and 1,2,4-trimethylbenzenes. The availability of the entropy data permits a more precise assignment of the potential barriers associated with restricted rotation of the methyl groups for these molecules than has heretofore been possible.

Spectral Data.—Although infrared and Raman spectra for a number of the compounds studied were available from the literature,⁴⁻⁶ it was necessary to provide additional data. The near infrared spectra of pentamethylbenzene and hexamethylbenzene and the 15 to 35 μ infrared spectra of the eight hydrocarbons were determined in this Laboratory. Purities of the hydrocarbons were as follows: 1,2-dimethylbenzene, 99.93% (mole); 1,2,3-trimethylbenzene, 99.98%; 1,2,4-trimethylbenzene, 99.67%; 1,2,3,4-tetramethylbenzene, 99.92%; 1,2,3,5-tetramethylbenzene, 99.92%; 1,2,4,5-tetramethylbenzene, 99.86%; pentamethylbenzene, 95.8%; hexamethylbenzene, 95%. All of the hydrocarbons were API standards with the exception of penta- and hexamethylbenzenes, which were Eastman white label grade used without further purification. Spectral data in the 15–35 μ region were obtained with a Perkin-Elmer Model 112-C infrared spectrometer having cesium bromide optics.

Equilibrium Measurements.—Isomerization equilibria among the methylbenzenes were estab-

(1) W. J. Taylor, D. D. Wagman, M. G. Williams, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **37**, 95 (1946).

(2) R. D. Taylor, B. H. Johnson and J. E. Kilpatrick, *J. Chem. Phys.*, **23**, 1225 (1955).

(3) W. E. Putnam and J. E. Kilpatrick, unpublished data.

(4) American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, Catalogs of Infrared and Raman Spectral Data.

(5) K. W. F. Kohlrausch and A. Pongratz, *Monatsh.*, **64**, 361, 374 (1934).

(6) K. W. F. Kohlrausch and A. Pongratz, *Sitzb. Akad. Wiss. Wien.*, **143**, 275, 288, 358 (1934).

lished to compare with the equilibria calculated from free energies of formation. At 300°K. aluminum bromide and aluminum chloride, promoted with the corresponding hydrogen halides, were used as isomerization-disproportionation catalysts. The starting materials were 1,2,4-trimethylbenzene (95 mole %) (200 g.) and the anhydrous powdered aluminum halide (15–45 g.) in one series of experiments. Reaction times varied from 10–72 hours with the equilibrium vessels being provided with continuous stirring. In the second and third series of runs 5–20 mole % solutions of 1,2,4,5-tetramethylbenzene in benzene and 1,2,3,4-tetramethylbenzene (99.8% purity) were chosen as starting materials to establish the tetramethylbenzene equilibria. At 700°K. equilibria were established using a flow reactor having a volume of 150 ml. filled with an alumina-silica catalyst (SiO₂, 85.6%; Al₂O₃, 12.9%; H₂O, 1.5%) having a surface area of 303 m.²/g. The products from a given run were recirculated to the reaction zone at least three times to ensure that equilibrium had been attained. Hydrocarbon starting materials in the experiments at 700°K. were 1,2,4-trimethylbenzene, a solution of 1,2,4,5-tetramethylbenzene in benzene, and an equimolar mixture of 1,2,3,5- and 1,2,4,5-tetramethylbenzenes. It was assumed that equilibrium had been reached when no change in isomer concentration could be detected as contact time increased by a twofold factor.

Analysis of Products.—Reaction products from the isomerization-disproportionation experiments were analyzed, without the need for prior distillation, by a combination of infrared and mass spectrometric techniques. Penta- and hexamethylbenzene concentrations were determined from mass spectral patterns and the individual C₆–C₁₀ benzenes by infrared spectrometric analysis. Thus total aromatic concentrations for a given molecular weight value were obtained by two independent means. The infrared procedure provides corrections for deviations from Beer's law and utilizes a thick cell to minimize the effects of wave length shifts of the absorption bands.⁷

Discussion

Vibrational Assignments.—All of the methyl-

(7) R. B. Williams, S. H. Hastings and J. A. Anderson, Jr., *Anal. Chem.*, **24**, 1911 (1952).

TABLE I
FREQUENCY ASSIGNMENT FOR COMPOUNDS OF V_h AND C_{2v} SYMMETRY

Symmetry class V_h	Symmetry class C_{2v}	Freq. no.	Frequency in cm.^{-1}				
			Benzene	1,2,4,5-Tetra- methylbenzene	Penta- methylbenzene	1,2,3,5-Tetra- methylbenzene	1,2,3-Tri- methylbenzene
		1	993	508	568	573	654
		2	3062	1262	3050	3050	3046
A_{1g}	A_1	6a	606	430	484	330	514
		7a	3048	3033	786	1212	1240
		8a	1595	1620	1572	1614	1589
		9a	1178	346	353	1142	1163
		12	1010	582	682	736	654
		13	3060	1383	1371	1380	1377
B_{1u}		18a	1035	230	223	232	228
		19a	1485	1368	1450	1482	1386
		20a	3080	3050	1012	1293	3046
		3	1298	1202	892	1214	1220
B_{2g}	B_1	6b	606	346	340	551	509
		7b	3048	735	796	938	990
		8b	1595	1560	1572	1608	1553
		9b	1178	790	526	320	1191
		14	1693	1451	1450	1488	1653
		15	1170	844	307	232	306
B_{2u}		18b	1035	260	263	275	269
		19b	1485	1368	1346	1376	1377
		20b	3080	1280	1270	3050	3046
B_{1g}	A_2	10a	850	346	350	275	269
		16a	400	146	150	456	484
A_{1u}		17a	985	446	446	883	810
		4	685	690	326	330	709
B_{2g}	B_2	5	1016	867	526	512	938
		10b	850	260	712	705	269
B_{2u}		11	671	170	176	232	228
		16b	400	446	153	165	458
		17b	985	780	679	456	488

benzenes for which vibrational assignments have not been made previously were included in the present investigation: namely, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, the three tetramethylbenzenes, pentamethylbenzene and hexamethylbenzene. 1,2-Dimethylbenzene also was included since some changes in the published assignments were made. In making the frequency assignments extensive use was made of the Teller-Redlich product rule analog in the manner outlined by Pitzer and Scott.⁸ This procedure was essential for a number of reasons, including lack of polarization data for the available Raman spectra and an indication that certain thermodynamically-important low-frequency Raman bands were not observed. For the methylbenzenes there are thirty ring-frequencies; in addition, the hydrogens of each methyl group contribute nine degrees of freedom. Eight of these degrees of freedom will be vibrational modes and one will be the internal rotation of the methyl group against the remainder of the molecule. The methyl group vibrations are identified by Pitzer and Scott as follows: M_1 , one symmetrical stretching mode (2950 cm.^{-1}); M_2 , two unsymmetrical stretching modes (2950 cm.^{-1}); M_3 , one symmetrical bending mode (1380 cm.^{-1}); M_4 , two unsymmetrical bending modes (1450 cm.^{-1}); M_5 , two wagging modes (1050 cm.^{-1}). The frequencies of these vibrations do not vary greatly among the various methylbenzenes and

since they make comparatively small contributions to the thermodynamic properties, the average values cited above were employed, except for the wagging modes.

Tables I-III give the symmetry classes, vibrational modes, and frequency assignments for all of the methylbenzenes studied. The number system in the tables is that of Wilson.⁹ It is possible to calculate approximate values of τ for methyl substitution. For the methyl ring stretching modes the value of τ is the square root of the ratio of the mass of the hydrogen atom to the mass of the methyl group, *viz.*, $(1/15)^{1/2} = 0.258$. Similarly, the τ -value for each methyl bending mode is the ratio of the moment of inertia of a hydrogen atom referred to the benzene ring to the moment of inertia of the methyl group with respect to the point of attachment ($= 0.171$). There will be one methyl-ring stretching and two methyl-ring bending modes (in-plane and out-of-plane) for each methyl group. In order to determine the class into which a given methyl-ring vibration frequency will fall (with its attendant τ -value) one simply applies the covering operations of the appropriate point group to the symmetry of the vibration in question. It should be realized that within a symmetry class frequency assignments can be permuted to some extent among the various observed bands without affecting the values of τ calculated from the product rule. From the selec-

(8) K. S. Pitzer and D. W. Scott, *J. Am. Chem. Soc.*, **65**, 803 (1943).

(9) E. B. Wilson, *Phys. Rev.*, **45**, 706 (1934).

TABLE II
FREQUENCY ASSIGNMENTS FOR COMPOUNDS OF C_{2v} AND C_s
SYMMETRY

Symmetry class C _{2v} * C _s	Freq. no.	Frequency in cm. ⁻¹			
		Benzene	1,2-Dimethylbenzene	1,2,3,4-Tetramethylbenzene	1,2,4-Trimethylbenzene
A ₁	1	993	733	650	744
	2	3062	3062	1255	1239
	6a	606	582	325	474
	7a	3048	1223	1255	1239
	8a	1595	1584	1586	1615
	9a	1178	1185	1165	1150
	14	1693	1680	1455	1680
	15	1170	1156	240	928
	18b	1035	180	270	285
	19b	1485	1550	1380	1377
A'	20b	3080	3080	3050	3038
	3	1298	1287	1255	1212
B ₁	6b	606	583	550	541
	7b	3048	1275	1280	3038
	8b	1595	1606	1606	1571
	9b	1178	1145	320	321
	12	1010	740	550	557
	13	3060	3046	1380	3038
	18a	1035	256	240	285
	19a	1485	1585	1375	1377
	20a	3080	3080	3080	1239
	4	685	685	325	541
A ₂	5	1016	862	470	704
	10b	850	256	270	285
A''	16a	400	436	440	160
	17a	985	823	817	806
B ₂	10a	850	823	804	748
	11	671	256	240	240
	16b	400	405	155	439
	17b	985	862	485	874

tion rules¹⁰ it is found that there should be two fundamentals for 1,2,4,5-tetramethylbenzene (Point Group D_{2h}) which are inactive in both the infrared and Raman spectra. Hexamethylbenzene (D_{6h}) has nine inactive fundamental frequencies, as does benzene; the high degree of symmetry, however, greatly facilitates application of the product rule analog because the increased number of symmetry classes results in fewer vibration modes falling in a given class. The least certain of the assignments is probably that for 1,2,4-trimethylbenzene, the low symmetry of which does not permit as detailed an analysis of the vibrational spectrum as was possible for the other compounds. Agreement between the theoretical and calculated τ -values is within 1% for all compounds studied.

An additional check on the vibrational assignments is afforded by application of the vibrational sum rule as formulated by Bernstein.^{11,12} Strict application of this sum rule requires that parameters be evaluated which take into account differences in the sum of frequencies (over-all, in-plane and out-of-plane) for position isomers. This leads to absurd results and indicates that the data are not sufficiently accurate to evaluate these

(10) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

(11) H. J. Bernstein, *J. Chem. Phys.*, **20**, 263 (1952).

(12) Private communication.

TABLE III
FREQUENCY ASSIGNMENT FOR HEXAMETHYLBENZENE
Point Group D_{6h}
Frequency, cm.⁻¹

Symmetry class	Mode	Benzene	Hexamethylbenzene
A _{1g}	1	993	553
	2	3062	1385
A _{2g}	3	1298	508
	R _x	$\sqrt{I} = 17.06$	40.0
B _{2g}	4	685	313
	5	1016	378
E _{1g}	10	849	343
	R _x	$\sqrt{I} = 12.02$	28.2
	R _y	$\sqrt{I} = 12.02$	28.2
E _{2g}	6	606	343
	7	3047	783
A _{2u}	8	1596	1568
	9	1178	367
B _{1u}	11	671	171
	T ₂	$\sqrt{M} = 8.84$	12.73
B _{2u}	12	1011	553
	13	3046	1385
E _{1u}	14	1693	1462
	15	1170	229
E _{2u}	18	1035	229
	19	1485	1060
	20	3080	1272
	T _x	8.84	12.73
	T _y	8.84	12.73
E _{2u}	16	400	155
	17	985	450

differences (which are apparently small). If one assumes that there is no difference then it is possible to evaluate an average effect of methyl substitution on the various frequency sums. The out-of-plane sums show very good agreement and indicate that the assignments are reasonably certain. The over-all and in-plane sums show a higher variation on a wave number basis; however, on a percentage basis the agreement is even better.

Another useful check on the vibrational assignments is provided by the fact that certain frequencies are relatively unaffected by methyl substitution. Examination of Fig. 6 of reference 8 shows that in vibrational modes 7b, 9a, 10a, 17a and 20b the groups located on the vertical axis (in the plane of the drawing) are motionless during the vibration and hence should not affect the frequency appreciably. In modes 6b and 18a only a slight motion of these groups is indicated, so that here also the frequencies should be relatively unaffected by methyl substitution. Vibrations 7b and 20b apparently are misassigned by Pitzer and Scott for 1,3,5-trimethylbenzene, but since these fall in the same symmetry class the product rule is unaffected.

The vibrational contributions to the thermodynamic properties were programmed on an IBM Model 650 computer. Some of the regularities in the contributions to the heat capacity at 500°K. for the methylbenzenes are shown in Fig. 1. There appears to be a constant increment for each successive methyl group and the variation among position isomers is of the order of one cal./deg. mole.

Because of the uncertainties in the frequency assignments average values of the vibrational contributions were used for each set of isomers. This method of calculation amounts to an assumption that the vibrational contributions of isomers are identical. A further justification for employing average values for the vibrational contributions is that slightly better agreement in the experimental and calculated tetramethylbenzene isomerization equilibria at both 300 and 700°K. was obtained when using the average values.

Moments of Inertia and Barriers to Internal Rotation.—Carbon-carbon bond lengths in the planar benzene ring were taken as 1.39 Å. and carbon-carbon bond lengths between the methyl groups and the benzene ring were selected to be 1.54 Å. Bond lengths between the hydrogen and carbon atoms in the methyl groups and joining the benzene ring were 1.09 and 1.08 Å., respectively. Tetrahedral angles in the methyl groups were assumed in preparing coordinate tables. The symmetry numbers for over-all and internal rotation and the principal moments of inertia, for those compounds not previously reported,¹ are given in Table IV. The reduced moments of inertia for the restricted rotation calculations were computed from equations 1b and 1e in the paper by Pitzer and Gwinn.¹³ A value of 5.48×10^{-40} g. cm.² was used for the reduced moments of inertia of all the methyl groups in the tetra-, penta- and hexamethylbenzenes.

TABLE IV
MOLECULAR PARAMETERS

Compound	Symmetry no.	Principal moments of inertia, g. cm. ² × 10 ¹⁹		
		<i>I_x</i>	<i>I_y</i>	<i>I_z</i>
1,2,3,4-Tetramethylbenzene	162	69.92	41.91	109.75
1,2,3,5-Tetramethylbenzene	162	67.67	48.64	114.20
1,2,4,5-Tetramethylbenzene	324	35.12	80.54	116.43
Pentamethylbenzene	486	59.49	81.07	137.91
Hexamethylbenzene	8748	79.70	80.54	160.03

Cosine functions of the type $V(\phi) = \frac{1}{2} V_0(1 - \cos n\phi)$ were assumed to describe the internal rotation of the methyl groups. The barriers for *ortho* and central methyl groups ($n = 3$) were calculated from the entropy data of Kilpatrick, *et al.*,^{2,3} for 1,2,4- and 1,2,3-trimethylbenzenes. On the basis of the vibrational assignments and the entropy data, barriers for the *ortho* and central methyl groups are 1400 and 3200 cal./mole, respectively. The barrier for an isolated methyl group, as in methylbenzene or 1,4-dimethylbenzene was assigned a value of 750 cal./mole as had been selected previously.¹ Using the vibrational assignments in this study, the *ortho* barrier in 1,2-dimethylbenzene was computed as 1800 cal./mole from entropy data. It is quite possible that in certain cases, *e.g.*, for hexamethylbenzene, due to an interlocking effect the six barriers should be greater than 3200 cal./mole for each methyl group. Experimental entropy data for 1,2,3,4- and penta- and hexamethyl-

(13) K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

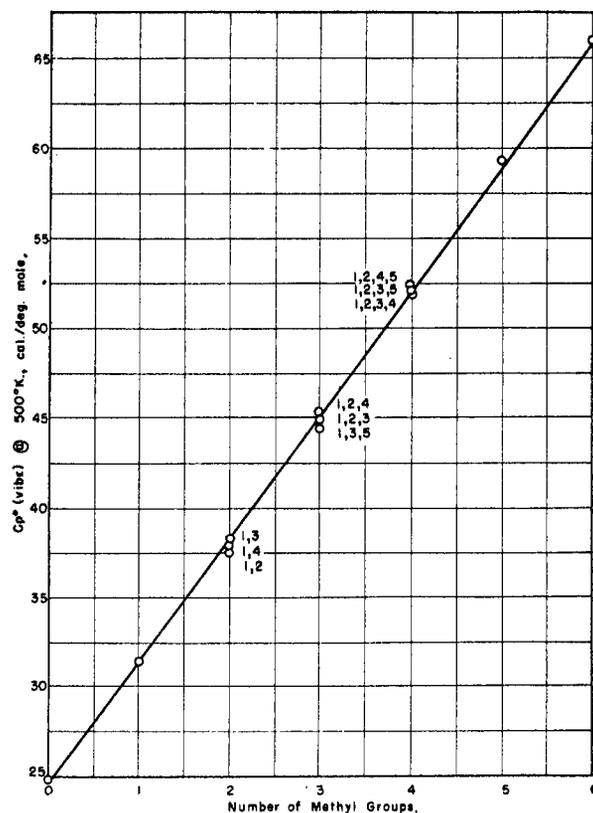


Fig. 1.—Effect of methyl substitution on heat capacity of benzene (vibrational).

benzene would, of course, be required before an answer to this question is possible. It is interesting to note, however, that in the isomerization-disproportionation experiments at 700°K. the reaction products contained about 2.0% (wt.) pentamethylbenzene and 0.1% hexamethylbenzene. The calculated concentrations were 6.5% and 0.3% penta- and hexamethylbenzene, respectively. Increasing the rotational barrier height would lower the calculated equilibrium concentrations of these components and give better agreement between theory and experiment, provided all the discrepancy can be attributed to an error in barrier assignment.

Thermodynamic Functions.—From the vibrational assignments, the moments and reduced moments of inertia, and the barriers to internal rotation described above, values of the thermodynamic functions $(H^\circ - H^\circ_0)/T$, $(F^\circ - H^\circ_0)/T$, S° , C_p° , at selected temperatures from 0 to 1000°K. were computed. The atomic weights of hydrogen and carbon were taken as 1.0080 and 12.010, respectively. Values of other natural constants were: Planck's constant, 6.624×10^{-27} erg. sec.; gas constant, 1.9863 cal./deg./mole; 1 calorie = 4.1833 international joules. The harmonic-oscillator rigid-rotor equations were used and it was assumed that the internal rotors could be treated independently. These thermodynamic quantities are presented in Table V.

Thermodynamic data for graphite and hydrogen given by Wagman, *et al.*,¹⁴ were used for the cal-

(14) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

TABLE V
 THERMODYNAMIC VALUES FOR EIGHT METHYLBENZENES

Temp., °K.	1,2- Dimethyl- benzene	1,2,3- Trimethyl- benzene	1,2,4- Trimethyl- benzene	1,2,3,4- Tetramethyl- benzene	1,2,3,5- Tetramethyl- benzene	1,2,4,5- Tetramethyl- benzene	Penta- methyl- benzene	Hexa- methyl- benzene
	$(H^\circ - H_0^\circ)/T$ (cal./deg. mole)							
298.16	18.83	22.26	22.05	26.22	26.01	26.72	29.40	32.91
300	18.91	22.35	22.14	26.33	26.12	26.83	29.52	33.04
400	23.32	27.44	27.08	32.42	32.07	32.61	36.64	41.28
500	27.67	32.54	31.94	38.43	37.90	38.23	43.60	49.37
600	31.82	37.33	36.73	43.93	43.34	43.53	49.89	56.48
700	35.66	41.81	41.19	49.03	48.41	48.54	55.68	62.92
800	39.21	45.93	45.30	53.71	53.08	53.13	60.95	68.81
900	42.50	49.72	49.10	57.98	57.36	57.38	65.75	74.10
1000	45.50	53.21	52.60	61.92	61.31	61.30	70.17	78.99
	$-(F^\circ - H_0^\circ)/T$ (cal./deg. mole)							
298.16	65.51	69.53	72.49	73.33	74.98	73.31	76.69	75.21
300	65.62	69.66	72.62	73.48	75.13	73.46	76.86	75.41
400	71.67	76.80	79.72	81.92	83.48	82.00	86.37	86.09
500	77.35	83.49	86.25	89.82	91.27	89.89	95.31	96.22
600	82.74	89.85	92.51	97.33	98.68	97.35	103.85	105.87
700	87.97	95.99	98.50	104.59	105.80	104.40	112.14	115.44
800	92.98	101.79	104.27	111.33	112.51	111.20	119.74	123.84
900	97.76	107.43	109.84	117.91	119.01	117.72	127.21	132.39
1000	102.40	112.83	115.17	124.20	125.24	123.93	134.34	140.33
	C_p° (cal./deg. mole)							
298.16	31.93	37.74	36.81	45.31	44.39	44.58	51.74	59.42
300	32.10	37.82	36.99	45.50	44.57	44.77	51.99	59.73
400	40.99	48.01	46.96	56.81	55.76	55.50	65.00	74.18
500	48.98	57.25	56.26	67.01	66.03	65.62	76.43	86.65
600	55.84	65.16	64.29	75.68	74.81	74.38	86.08	97.13
700	61.61	71.87	71.12	83.13	82.39	81.97	94.27	105.97
800	66.50	77.56	76.93	89.42	88.79	88.41	101.29	113.51
900	70.68	82.42	81.87	94.82	94.27	93.94	107.20	119.99
1000	74.24	86.58	86.10	99.47	99.01	98.71	112.33	125.55
	S° (cal./deg. mole)							
298.16	84.34	91.79	94.54	99.55	100.99	100.03	106.09	108.12
300	84.53	92.01	94.76	99.81	101.25	100.29	106.38	108.45
400	94.99	104.24	106.80	114.34	115.55	114.61	123.01	127.37
500	105.02	116.03	118.19	128.25	129.17	128.12	138.91	145.59
600	114.56	127.18	129.24	141.26	142.02	140.88	153.74	162.35
700	123.63	137.80	139.69	153.62	154.21	152.94	167.82	178.36
800	132.19	147.72	149.57	165.04	165.59	164.33	180.69	192.65
900	140.26	157.15	158.94	175.89	176.37	175.10	192.96	206.49
1000	147.90	166.04	167.77	186.12	186.55	185.23	204.51	219.32
	H_f° (kcal./mole)							
0	+11.057	+5.480	+4.503	-1.155	-1.782	-2.104	-7.608	-13.839
298.16	+4.540	-2.290	-3.330	-10.020	-10.710	-10.820	-17.800	-25.260
300	+4.505	-2.332	-3.372	-10.064	-10.754	-10.863	-17.852	-25.319
400	+2.709	-4.453	-5.574	-12.332	-13.097	-13.203	-20.329	-27.937
500	+1.178	-6.214	-7.491	-14.155	-15.047	-15.204	-22.273	-29.870
600	-0.079	-7.677	-9.014	-15.678	-16.659	-16.867	-23.883	-31.485
700	-1.115	-8.884	-10.251	-16.875	-17.936	-18.168	-25.126	-32.743
800	-1.916	-9.735	-11.216	-17.766	-18.897	-19.179	-25.946	-33.608
900	-2.488	-10.385	-11.920	-18.403	-19.588	-19.892	-26.680	-34.214
1000	-2.869	-10.776	-12.363	-18.742	-19.979	-20.311	-26.985	-34.436
	F_f° (kcal./mole)							
298.16	29.173	29.828	27.968	29.496	28.377	28.553	29.447	33.909
300	29.324	30.029	28.164	29.745	28.623	28.802	29.802	34.258
400	37.873	41.114	38.995	43.357	42.106	42.376	46.024	53.583
500	46.842	52.740	50.383	57.490	56.138	56.506	62.842	73.483
600	56.177	64.676	62.103	71.961	70.524	71.000	80.004	93.751
700	65.545	76.803	74.069	86.604	85.130	85.788	97.315	114.012
800	75.097	89.136	86.175	101.525	99.954	100.680	115.008	134.935
900	84.794	101.537	98.391	116.484	114.867	115.706	132.675	155.578
1000	94.517	114.020	110.703	131.525	129.858	130.846	150.442	176.503

culations. The heats of formation of gaseous penta- and hexamethylbenzene have not been reported.¹⁵ These heats of formation for gaseous $C_{11}H_{16}$ and $C_{12}H_{18}$ were estimated to have values -17.79 and -25.26 kcal./mole, respectively, at $298.16^\circ K$. The derived quantities ΔH_f° and ΔF_f° as a function of temperature are shown in Table V.

TABLE VI
COMPARISON OF CALCULATED AND EXPERIMENTAL
ISOMERIZATION EQUILIBRIA AMONG THE TRI-
AND TETRAMETHYLBENZENES

Component, mole %	Temp., $^\circ K. \rightarrow 300$		700	
	Exptl.	Calcd.	Exptl.	Calcd.
1,2,3-Trimethylbenzene	..	3	9	9
1,2,4-Trimethylbenzene	..	59	65	68
1,3,5-Trimethylbenzene	..	38	26	23
1,2,3,4-Tetramethylbenzene	8	8	22	18
1,2,3,5-Tetramethylbenzene	47	53	45	50
1,2,4,5-Tetramethylbenzene	45	39	33	32

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Isomerization Equilibria.—Data from the isomerization experiments are given in Table VI at 300 and $700^\circ K$. and are compared with the concentrations calculated using the free energies of formation from the present investigation. The agreement is believed to be within the limits imposed by probable errors in product analyses and assumptions in the statistical calculations.

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THE ELECTROPHORETIC MOBILITY OF DECYL-, DODECYL- AND TETRADECYLAMINE HYDROCHLORIDE MICELLES

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The electrophoretic mobilities of the decyl-, dodecyl- and tetradecylamine hydrochloride micelles were studied as functions of their concentrations in aqueous solutions. In addition the effect of ionic strength and temperature upon micelle mobility was studied for the dodecylamine hydrochloride micelle. Measurements on dodecylamine hydrochloride at temperatures of 18 , 25 and 35° give values of the mobilities of 3.74 , 4.43 and 5.56×10^{-4} cm.² per volt-sec. at the critical concentration. The determination of the mobilities of the decyl- and tetradecylamine hydrochloride micelles at 25° gave values of 3.62 and 5.75×10^{-4} cm.² per volt-sec. at the critical concentrations. The micelle mobilities are more dependent upon the ionic strength of the solution than upon the nature of the organic monomer ion.

Introduction

Within the past few years considerable progress has been made toward elucidating the nature of the particles existing in solution of colloidal electrolytes. McBain¹ was one of the first to recognize that these particles were formed by the association of simple molecules and/or ions into complex ions of colloidal dimensions. In recent years Debye and others²⁻⁴ have applied light scattering techniques to the determination of the molecular sizes of these colloidal electrolytes or micelles. For dodecylamine hydrochloride Debye found that the molecular weight at the critical concentration for the formation of micelles varies from $12,300$ in pure water to $31,400$ in a $0.045 M$ sodium chloride solution.

Little work has been directed toward elucidating the charge on these micelles. Van Rysselberghe⁵ has attempted to analyze the available conductivity and diffusion data for lauryl sulfonic acid and has obtained values for the charge on the micelle varying from -1 in dilute solutions to -89 in

0.6 molar solutions. Brady and Salley⁶ were able to estimate the percentage of the sodium ions which remained bound to the micelles of Aerosol OT and Aerosol MA by using a radioactive tracer technique but could not obtain an absolute value for the charge on the micelles. Hoyer and Mysels⁷ have suggested a micelle tagging technique based upon the preferential solubility of water insoluble dyes in the micelle. This technique was applied by Hoyer, Mysels and Stigter⁸ to the determination of the electrophoretic mobility of the potassium laurate and sodium lauryl sulfate micelle and by Stigter and Mysels⁹ to the determination of the mobility of the micelle of sodium lauryl sulfate in solutions of different ionic strengths. The last two authors interpreted their results in terms of Booth's theory¹⁰ of the electrophoresis of colloidal particles and arrived at a value of 23 for the charge on the sodium lauryl sulfate micelle at its critical concentration.

The present paper is concerned with the electrophoretic mobility of some aliphatic amine hydrochloride micelles, specifically those of decyl-,

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