[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Thermodynamics and Molecular Structure of Benzene and Its Methyl Derivatives[1]

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Besides the obvious importance of thermodynamic data on benzene and its simpler methyl derivatives, this series of compounds is interesting because of the various possibilities for rotation of the methyl groups with respect to the ring. Since the benzene ring is planar while the methyl group has a three-fold axis of symmetry, the potential energy for internal rotation in toluene must have a six-fold symmetry (six maxima and minima per rotation). In the only other case of this type yet investigated, nitromethane, the potential barrier was found to be very small, leading to essentially free rotation above room temperature.[3,4] In *o*-xylene, however, interactions between the two methyl groups may be expected.

Other interesting points investigated include the freezing behavior of the ternary system, *o*, *m*, and *p*-xylene, the equilibrium composition of the xylenes, and the equilibrium of the reaction: 2 toluene = benzene + xylene. The latter data lead to quite accurate energy relationships between these hydrocarbons.

Part I. Thermodynamic Measurements on the Pure Substances. The Heat Capacities, Heats of Fusion and Vaporization, Vapor Pressures and Entropies of Benzene, Toluene and the Xylenes

In this part thermodynamic measurements are described which include typical low temperature calorimetric studies of the three xylenes. In addition, the vapor pressures up to 60°, and the heat capacities of the vapors have been measured. Insofar as such measurements could not be found in the literature, they were also made for benzene and toluene.

Purification of Materials.—The xylenes used for the measurements on the solid and liquid were purified by fractional crystallization and distillation. The device used for the fractional crystallization is shown schematically in Fig. 1. It was made of glass and was sufficiently compact to fit into a large dewar containing the cooling bath. A mixture of the material to be crystallized and a suitable solvent was introduced into bulb A. A slow stream of dry air entering tube C and bubbling up through the sintered glass plate, E, prevented any liquid from flowing down through the sintered glass plate while crystallization was taking place. After crystallization had reached the desired state, the air stream was stopped and air pressure was applied through tube D, forcing the mother liquor out through the sintered glass plate and over into bulb, B, leaving the crystals in bulb, A. The apparatus was then removed from the cooling bath and disconnected at the ground glass joint, F. As the crystals melted, the liquid drained from the bulb and was collected. After several such crystallizations, the product obtained was refluxed with molten sodium metal and then distilled in order to remove water and solvent which had adhered to the crystals.

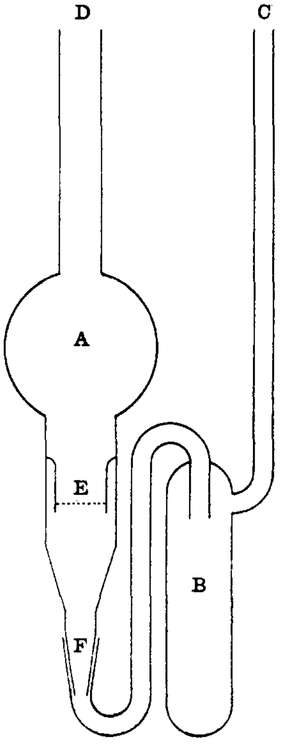

Fig. 1.—The apparatus for purification by fractional crystallization.

The *o*-xylene was Eastman Kodak Company best grade product. Heat capacity measurements on a sample of this original material in the region below the melting point indicated considerable impurity. In addition, there was an isothermal absorption of heat at about 210°K., presumably caused by the melting of a eutectic mixture with *m*-xylene impurity. This material was crystallized three times, using acetone as a sol-

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(1) Portions of this paper were presented in the Symposium on Low Temperature Research at the Buffalo meeting of the American Chemical Society, September, 1942.

(2) Du Pont Fellow in Chemistry, 1941–1942. Part I of this paper is essentially an abstract of the Ph.D. Dissertation of Donald W. Scott, University of California, 1942.

(3) K. S. Pitzer and W. D. Gwinn, THIS JOURNAL, 63, 3313 (1941).

(4) T. De Vries and B. T. Collins, *ibid.*, 64, 1224 (1942).

vent and an acetone–dry-ice mixture for the cooling bath. Heat capacity measurements below the melting point on a sample of the material so obtained showed less premelting than previously and the absorption of heat at 210°K. was considerably diminished. This material was further purified by crystallizing it three times from methyl alcohol solvent, again using an acetone–dry-ice cooling bath. This final product, after drying and distilling in a 2-ft. glass bead packed column, was used in all measurements on the solid and liquid. The premelting effect and the change of melting point with per cent. melted indicated 0.12 mole per cent. liquid soluble, solid insoluble impurity. The absorption of heat at 210°K. had virtually disappeared, amounting to only about four calories per mole. This can be accounted for by assuming that 0.10 mole per cent. or 5/6 of the total impurity was *m*-xylene. A portion of the material removed from the calorimeter after the completion of the heat capacity measurements was employed in the vapor pressure experiments. For the gas heat capacity measurements, which are not sensitive to small amounts of impurity, and which require a larger amount of material, Eastman Kodak Co. *o*-xylene was used without further purification.

The *m*-xylene was likewise Eastman Kodak Company best grade product. It was crystallized three times from acetone and three times from methyl alcohol, using an acetone–dry-ice cooling bath. After drying and distilling in a column of about 25 theoretical plates, the product so obtained was used for the gas heat capacity measurements. Subsequent measurements of the melting point and heat capacity below the melting point showed that the material was not pure *m*-xylene, but approximately the eutectic mixture of *m*- and *p*-xylenes (about 13% *p*-xylene). This material was further purified by fractional sulfonation, fractional hydrolysis, followed by fractional crystallization from acetone solvent, drying, and distilling in the 25-plate column. The melting point behavior of the product obtained in this manner indicated that it contained 2.34 ± 0.05 mole per cent. liquid soluble, solid insoluble impurity, of which all except 0.22 mole per cent. was *p*-xylene. Since time did not permit further purification, this material was used for all measurements on the solid and liquid. After completion of the heat capacity measurements, a portion of the material removed from the calorimeter was employed in the vapor pressure experiments. Since the impurity present in the sample was predominantly *p*-xylene, it was possible to make corrections for it, exactly in the case of the heat capacities of the solid, and to a satisfactory approximation in the case of the other thermal quantities. More will be said about these corrections in later paragraphs.

The *p*-xylene was also Eastman Kodak Company best grade product. It was crystallized three times from acetone and three times from methyl alcohol, using ice water as a cooling bath. It was then dried and distilled in a column of about 25 theoretical plates, one portion of the middle fraction being used for the gas heat capacity measurements and another portion for the measurements on the solid and liquid. This latter contained 0.02 mole per cent. of liquid soluble, solid insoluble impurity, as shown by the premelting effect and the change of melting point with per cent. melted. A portion of the material removed from the calorimeter after completion of the heat capacity measurements was used in the vapor pressure experiments.

Toluene was obtained from a commercial source. It was purified by freezing it on a coil of copper tubing through which liquid air was circulated. When about a half or two-thirds of the original material was frozen, the solid was allowed to melt and was again subjected to the same process. After several repetitions of this process, about a fifth of the starting material remained as a final product. This was dried by refluxing with molten sodium and distilled in the 25-plate column. Separate portions of the middle fraction, which distilled within a tenth degree range, were used for the gas heat capacity and the vapor pressure measurements.

Commercial benzene was refluxed with metallic sodium and distilled, the middle fraction being used for the gas heat capacity measurements. The carbon tetrachloride sample was likewise the middle fraction obtained by distilling a commercial product.

Melting Points.—The melting points were observed as a function of the per cent. melted. The data are shown in Table I. The "fraction melted" in Table I is strictly the fraction of the heat of fusion of the sample which has been introduced. The difference is significant only for *m*-xylene with its large impurity. The true melting points were calculated assuming Raoult's law. For purposes of comparison, values taken from the recent literature are also included in the table.

The data for *m*-xylene are shown graphically in Fig. 2 where the temperature is plotted *vs.* the reciprocal of the fraction melted. The latter quantity is proportional to the concentration of the solute since the quantity of solute is constant and its concentration varies inversely with the fraction of the solvent melted. The upper branch of the curve represents the melting of pure *m*-xylene and extrapolates to the true melting point, 225.27°K. Its slope gives the total impurity 2.34%. The lower branch of the curve represents the melting of the *m-p* eutectic which extrapolates to 220.2°K., and its slope gives the impurity other than *p*-xylene, 0.22%. From the point of intersection and the heat of fusion data given below one may calculate the composition of the eutectic to be 12.9% *p*-xylene.

TABLE I

THE MELTING POINTS OF THE XYLENES (ICE POINT = 273.16°K.)

o-Xylene	
Per cent. melted	Observed temperature, °K.
31	247.66
55	247.71
78	247.75
True melting point	247.82 ± 0.1°K.
Parks, Huffman and Daniels[5]	247.8°K.
White and Rose[6]	247.86°K.
m-Xylene	
Per cent. melted	Observed temperature, °K.
5.3	218.85
13.8	219.67
21.4	221.12
30.0	222.26
46.5	223.40
62.8	223.86
85.4	224.23
Melting point of sample	224.38°K.
Melting point of pure *m*-xylene	225.27 ± 0.15°K.
Parks, Huffman and Daniels[5]	219.6°K.
White and Rose[6]	225.27°K.
Timmermans and Hennaut-Roland[7]	225.8°K.
Nakatsuchi[8]	224.2°K.
p-Xylene	
Per cent. melted	Observed temperature, °K.
20	286.36
38	286.37
56	286.38
True melting point	286.39 ± 0.05°K.
Parks, Huffman and Daniels[5]	286.3°K.
White and Rose[6]	286.37°K.

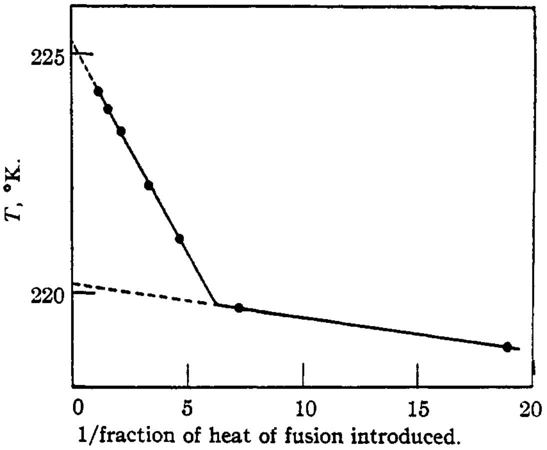

Fig. 2.—The melting behavior of the *m*-xylene sample.

Solid and Liquid Heat Capacities.—The apparatus was a low temperature, vacuum insulated calorimeter which has been used in previous work in this Laboratory and has been described in the literature.[9] It was used without change for the measurements on *o*-xylene. For the measurements on *m*- and *p*-xylene, the thermometer was replaced with a new pure platinum strain-free resistance thermometer This consists of a spiral of 0.1 mm. c. p. platinum wire wound on a mica cross and has an ice-point resistance of 83.318 ohms. It was calibrated at the oxygen, ice, steam and sulfur points according to the international temperature scale. The equation obtained was

$$R = 83.318\ [1 + 0.00397202t - 0.59115 \times 10^{-6}t^2 - 4.384 \times 10^{-12}t^3(t - 100)]$$

Below 90°K. it was calibrated by comparison with the hydrogen triple point, hydrogen vapor pressures, oxygen transitions and triple point, and oxygen vapor pressures. The vapor pressure equations and melting points for hydrogen and oxygen given by Henning and Otto[10] were used. The value, 43.76°K., for the oxygen transition has been reported by both Giauque and Johnson,[11] and Henning and Otto.[10] Using the resistance–temperature tables of Hoge and Brickwedde[12] for pure platinum in this range as a

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(5) Parks, Huffman and Daniels, THIS JOURNAL, **52**, 1547 (1930).

(6) White and Rose, *Bur. Standards J. Research*, **9**, 711 (1932).

(7) Timmermans and Hennaut-Roland, *J. chim. phys.*, **27**, 401 (1930).

(8) Nakatsuchi, *J. Soc. Chem. Ind., Japan*, **32**, suppl. bind., 333 (1929).

(9) (a) Latimer and Greensfelder, THIS JOURNAL, **50**, 2202 (1928). (b) Brown, Smith, and Latimer, *ibid.*, **58**, 1758 (1936). (c) Pitzer and Coulter, *ibid.*, **60**, 1310 (1938).

(10) Henning and Otto, *Physik. Z.*, **37**, 633 (1936).

(11) Giauque and Johnston, THIS JOURNAL, **51**, 2300 (1929).

(12) Hoge and Brickwedde, *J. Research, Nat. Bur. Standards*, **22**, 351 (1939).

base, a deviation plot was made on which these calibration points satisfactorily determined the curve.

The heat capacity data are listed in Tables II, III and IV and shown graphically in Fig. 3. The *m*-xylene heat capacities have been corrected for the *p*-xylene impurity. This correction never exceeded 0.05 cal./deg. mole. Table V lists values at even temperatures taken from a smooth curve through the experimental points. All data are reported in terms of the defined calorie equal to 4.1833 Int. joules and on the basis of 273.16°K. for the ice-point. All weights were reduced to *in vacuo*. The error in these results should not exceed 0.2% except at the highest and lowest temperatures and just below the melting points. In the case of *m*- and *p*-xylene the measurements were extended to temperatures above room temperature. In this region the accuracy falls off rapidly because of large radiation losses and the uncertainty in the results may well exceed 1%. It must be remembered that the data in this region are not used in the entropy calculation.

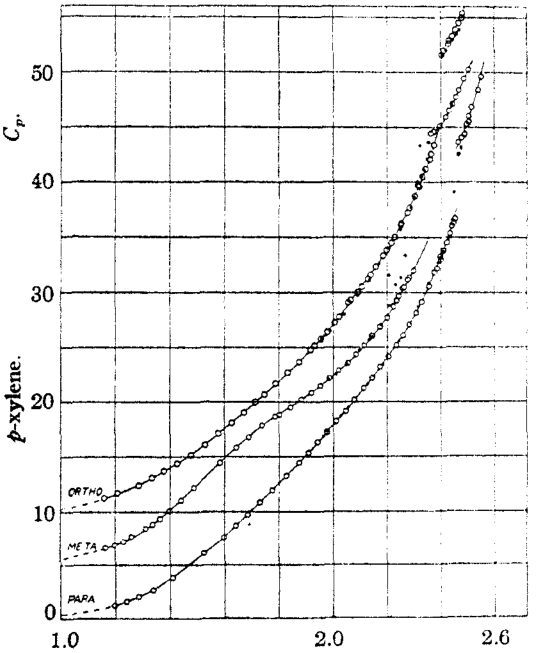

Fig. 3.—The experimental heat capacity data for solid and liquid xylenes. Open circles, this research; solid circles, Parks, Huffman, and Daniels.[5] Vertical scales are offset for clarity.

The heat capacities of these substances above 90°K. have been measured previously by Parks, Huffman and Daniels.[5] Their data are plotted in Fig. 3 for comparison. The melting point which they report for *m*-xylene, 219.6°K., seems to indicate that their sample of this substance was not pure *m*-xylene but approximately the eutectic mixture with *p*-xylene. This probably accounts for the large deviations in their points near the melting point.

Figure 4 shows the smooth curves for all three xylenes for the purpose of comparison. The heat capacities at 20°K. are in the inverse order of the melting points. This would be expected if both effects result from varying degrees of firmness of crystal binding. The relatively marked hump in *m*-xylene near 50°K. and the more gradual one in *p*-xylene near 100°K. may be caused by the beginning of rotation of methyl groups. It will be shown later that the methyl groups rotate freely in these molecules in the gas phase. The data of Kelley[13] show a similar hump for toluene as would be expected if this idea is correct. Internal rotation is well restricted in *o*-xylene so that no hump should appear.

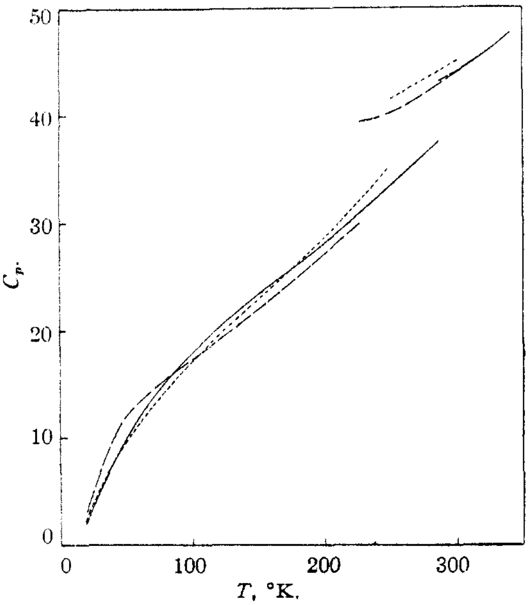

Fig. 4.—Smoothed curves showing the heat capacity of the three xylenes: ortho, dotted curve; meta, dashed; para, solid.

The heat capacities of *m*- and *p*-xylenes are essentially equal in both liquid and gaseous states. The data for the gases are given below. The heat capacity of liquid *o*-xylene is about one calorie per degree higher and a similar difference is shown by the gas. Thus if one removes internal heat capacity effects, all liquid xylenes are

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[13] Kelley, THIS JOURNAL, 51, 2733 (1929).

TABLE II

THE HEAT CAPACITY OF *o*-XYLENE

Sample: 52.00 g. (0.4898 mole)

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole
14.42	1.290	152.77	23.28
16.15	1.704	157.35	23.78
19.32	2.417	164.13	24.51
21.76	3.113	168.52	25.00
23.88	3.698	177.71	26.08
26.69	4.393	178.76	26.18
30.10	5.219	188.33	27.25
33.78	6.127	191.54	27.67
37.86	7.149	199.91	28.73
42.43	8.126	205.98	29.71^b
47.00	9.060	207.71	29.64
51.87	9.970	210.38	30.36^b
56.05	10.72	215.18	30.47^a
61.48	11.68	220.59	31.22^a
67.93	12.68	221.07	31.23^a
75.06	13.72	229.14	32.15^a
82.41	14.78	230.92	32.65^a
85.26	15.22	237.06	33.51^a
90.20	15.85		
94.85	16.44	247.82 melting point	
101.25	17.26		
105.07	17.80	251.65	41.66
114.09	19.07	256.79	42.04
115.54	19.19	268.19	42.65
123.93	20.05	268.81	42.92
127.36	20.43	276.52	43.31
134.52	21.24	284.82	43.96
137.80	21.60	293.52	44.56
144.04	22.32	301.31	45.05
		301.86	45.39

[a] Corrected for premelting. [b] Includes heat to melt the eutectic mixture.

TABLE III

THE HEAT CAPACITY OF *m*-XYLENE

Sample: 66.14 g. (0.6230 mole)

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole
14.62	1.686	148.49	21.89
15.76	1.938	157.61	22.72
16.96	2.283	167.15	23.73
18.19	2.712	171.79	24.25
20.54	3.501	175.85	24.66
21.71	3.881	181.56	25.39
23.10	4.389	183.93	25.46
25.03	5.072	186.72	25.66
27.63	6.053	189.84	26.15
30.69	7.019	191.66	26.35
38.40	9.433	198.42	26.97
43.80	10.80		
48.78	11.77		
54.79	12.83	225.27 melting point	
61.01	13.63		
63.45	13.80	231.40	39.45
69.57	14.49	237.18	39.62
76.38	15.21	249.43	40.12
83.11	15.82	262.62	40.92
89.83	16.47	268.83	41.49
97.07	17.11	276.80	42.10
104.89	17.85	276.97	42.02
113.15	18.57	284.83	42.78
121.54	19.32	292.93	43.40
130.26	20.14	305.27	44.36
139.78	21.03	318.16	45.26

TABLE IV

THE HEAT CAPACITY OF *p*-XYLENE

Sample: 68.40 g. (0.6443 mole)

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole
15.76	1.210	211.11	29.18
17.42	1.588	224.90	30.64
19.32	2.039	236.25	31.89
21.80	2.674	240.69	32.28
25.68	3.809	247.48	33.13
33.58	6.154	254.85	33.94
39.73	7.692	261.10	34.66
43.86	8.732	262.89	34.73
48.62	9.776	267.69	35.44^a
53.68	10.88	272.16	36.16^a
59.56	11.98	275.28	36.40^a
66.77	13.22	276.58	36.44^a
74.40	14.46	276.74	36.44^a
80.30	15.33	279.66	36.84^a
86.95	16.33		
94.32	17.26	286.39 melting point	
102.27	18.24		
110.72	19.17	292.02	43.62
119.64	20.24	301.10	43.98
129.01	21.25	310.04	44.42
138.65	22.24	314.69	45.23
148.69	23.23	318.47	45.99
159.04	24.22	319.24	45.50
169.68	25.23	327.36	46.85
179.55	26.19	338.96	48.38
189.86	27.16	345.49	48.42
200.15	28.21	354.65	49.62

[a] Corrected for premelting.

the same, which supports the idea that Raoult's law should apply accurately to these systems.

Heat of Fusion.—The heats of fusion were measured with different rates of heating and no trend was observed. Table VI lists the results and, for comparison, the values reported by other investigators. In correcting the heat of fusion of the *m*-xylene sample for the *p*-xylene impurity, the heat of fusion of *p*-xylene at 225.27°K. was calculated from the value obtained at 286.39°K. using values of ΔC_p calculated on the assumption that the apparent molal heat capacity of *p*-xylene in the *m*-xylene is 1.004 times that of liquid *m*-xylene. This correction is not very sensitive to the assumption made in regard to ΔC_p. For example, if we had instead assumed a constant ΔC_p of fusion of 5.4, this would have changed the value for the heat of fusion of pure *m*-xylene by only 2 calories.

TABLE V

THE HEAT CAPACITIES OF THE XYLENES AT EVEN TEMPERATURES

T, °K.	Heat capacity, cal./deg. mole		
	o-Xylene	*m*-Xylene	*p*-Xylene
15	1.30	1.74	1.03
20	2.63	3.28	2.25
25	3.97	5.08	3.72
30	5.19	6.80	5.17
35	6.42	8.43	6.50
40	7.60	9.86	7.76
45	8.65	11.06	8.94
50	9.63	12.04	10.07
60	11.41	13.25	12.05
70	12.98	14.54	13.76
80	14.43	15.54	15.27
90	15.82	16.49	16.68
100	17.13	17.41	17.96
110	18.41	18.28	19.14
120	19.59	19.15	20.26
130	20.72	20.11	21.32
140	21.86	21.03	22.34
150	22.96	21.97	23.33
160	24.03	22.96	24.28
170	25.18	24.04	25.26
180	26.32	25.06	26.22
190	27.47	26.11	27.17
200	28.65	27.15	28.13
210	29.85	28.19	29.13
220	31.13	29.22	30.13
230	32.48	39.40	31.18
240	33.82	39.71	32.28
250	41.52	40.17	33.40
260	42.29	40.78	34.54
270	42.87	41.50	35.68
280	43.58	42.53	36.83
290	44.30	43.13	43.27
300	45.02	43.93	44.07
320		45.6	45.6
340			48.0
360			50.4

It is difficult to reconcile the value reported by Parks, Huffman and Daniels for *o*-xylene with the results of the present research. Such a large discrepancy could scarcely have arisen from a different manner of treating the premelting heat.

TABLE VI

THE HEATS OF FUSION

Time of energy input, minutes	Heat of fusion, cal./mole
o-Xylene	
19	3250
24	3245
27	3255
Average	3250 ± 10
Parks, Huffman, and Daniels[5]	3116
Rossini[14]	3330 ± 70
Nakatsuchi[8]	3100
m-Xylene (impure sample)	
27	2780
32	2796
39	2776
Average	2784 ± 15
Heat of fusion of pure *m*-xylene	2765 ± 20
Parks, Huffman, and Daniels[5]	2734
Rossini[14]	2760 ± 50
Nakatsuchi[8]	2800
p-Xylene	
33	4089
51	4085
54	4097
Average	4090 ± 20
Parks, Huffman, and Daniels[5]	4047
Nakatsuchi[8]	4100

Vapor Pressures and Heats of Vaporization.—The vapor pressure apparatus consisted of a sample bulb connected to a mercury manometer, both of which were completely immersed in a water thermostat with a plate glass window. The difference in height of the mercury column was read with a cathetometer of 0.05 mm. sensitivity. Temperatures were determined with a mercury-in-glass thermometer calibrated by the U. S. Bureau of Standards which could be read to 0.01°. To thoroughly dry and degas the samples, the following procedure was employed. The sample was introduced into a bulb connected to the sample bulb through a phosphorus pentoxide tube. It was frozen with liquid air and the system was evacuated to a pressure of 10^{-5} mm. The sample was distilled into the sample bulb, then distilled back into the original bulb, and finally distilled back into the sample bulb, thus having passed through the phosphorus pentoxide tube three times. At the end of each distillation the sample was again frozen with liquid air and the system evacuated to a pressure of 10^{-5} mm. The phosphorus pentoxide tube and the second bulb were then sealed off from the remainder of the system. Finally, about a third of the sample was allowed to evaporate by pumping on it while it was at room temperature. The fact that the measured vapor pressures did not change as further quantities of the sample were pumped off was taken as evidence of ample drying and degassing and the absence of significant amounts of impurity of different volatility.

The manometer readings were reduced to 0° and standard acceleration of gravity. The large diameter of the manometer arms, 15 mm., made capillary depression corrections negligible. The

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[14] Rossini, *Bur. Stand. J. Res.*, **11**, 533 (1933).

data were fitted to three-constant equations. The coefficient of the logarithmic term was obtained by a process of trial and error and the remaining two constants were calculated by the method of least squares. The equations obtained are

(1) Toluene 0–50°

$$\log_{10}p = -2866.53/T - 6.7 \log_{10}T + 27.6470$$

(2) *o*-Xylene 0–60°

$$\log_{10}p = -3327.16/T - 8.0 \log_{10}T + 31.7771$$

(3) *m*-Xylene 0–60°

$$\log_{10}p = -2871.66/T - 5.0 \log_{10}T + 22.9270$$

(4) *p*-Xylene 13.23–60° (liquid)

$$\log_{10}p = -3080.31/T - 6.7 \log_{10}T + 27.8581$$

(5) *p*-Xylene 0–13.23° (solid)

$$\log_{10}p = -3141.33/T + 11.6092$$

Equation 5 was calculated from equation 4 and the measured heat of fusion. Table VII shows a comparison of the observed and calculated values. It can be seen that the equations reproduce the data to within the sensitivity of the cathetometer (0.05 mm.).

TABLE VII

VAPOR PRESSURES

Substance	T, °C.	p (obs.) mm. Hg	p (calcd.) mm. Hg
Toluene	0.0	6.75	6.75
	12.5	14.40	14.38
	25.0	28.40	28.45
	37.5	52.70	52.65
	50.0	92.00	91.98
o-Xylene	0.0	1.30	1.27
	12.5	3.00	3.04
	25.0	6.60	6.64
	37.5	13.50	13.45
	50.0	25.50	25.48
	60.0	40.60	40.63
m-Xylene	0.0	1.75	1.71
	12.5	3.90	3.94
	25.0	8.35	8.39
	37.5	16.65	16.66
	50.0	31.20	31.17
	60.0	49.50	49.49
p-Xylene	0.0	1.35[a]	1.29[a]
	12.5	4.05[a]	4.10[a]
	25.0	8.90	8.87
	37.5	17.50	17.55
	50.0	32.60	32.61
	60.0	51.35	51.32

[a] Solid.

The vapor pressures of toluene given by the "I. C. T." are in good agreement with the results of this research, the former being higher by a few tenths of a per cent. The vapor pressures of the xylenes have been reported by Linder,[15] Rintelen, Saylor and Gross,[16] Kassel,[17] and Stuckey and Saylor.[18] The results reported by the last-named authors are in excellent agreement with those reported here. This is not true for the others.

The heats of vaporization at 298.16°K. were calculated by means of the Clapeyron equation. Corrections for gas imperfections were made by means of the Berthelot equation of state, using critical constants from the "I. C. T." for toluene and from the measurements of Altschul[19] for the xylenes. Because of the low vapor pressures of these substances, this correction is rather small, being 26, 10, 12 and 11 calories for toluene, *o*-, *m*- and *p*-xylenes, respectively. The calculated heats of vaporization at 298.16°K. are

Toluene	9,115 ± 50 cal./mole
o-Xylene	10,470 ± 50 cal./mole
m-Xylene	10,160 ± 50 cal./mole
p-Xylene	10,110 ± 50 cal./mole

The correction of the *m*-xylene heat of vaporization for the *p*-xylene impurity in the sample was not significant.

Entropies.—The entropy calculations are summarized in Table VIII. The calculation for benzene uses the value for the liquid at 298.16°K. given by Ahlberg, Blanchard and Lundberg[20] together with vaporization data from the work of Fiock, Ginnings and Holton.[21] The value of the entropy of liquid toluene at 298.16°K. is that reported by Kelley.[13] The double Debye functions (*i. e.*, for six degrees of freedom) used to extrapolate the xylene heat capacities to 0°K. fit the measured heat capacities up to 25 or 30°K. Calculations showed that corrections for gas imperfections were negligible. The entropy of *m*-xylene was calculated in two separate ways. In the first, the entropy was calculated in the conventional manner, using values of the thermal quantities corrected for the *p*-xylene impurity. In the second, the entropy of a mole of substance of the composition of the sample was first calculated and then corrected for the entropy of mixing and the *p*-xylene impurity. The two methods give concordant results. The second method avoids any assumptions which could possibly be subject to question and therefore is to be preferred insofar as there is any difference at all.

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[15] Linder, *J. Phys. Chem.*, **35**, 351 (1931).

[16] Rintelen, Saylor and Gross, THIS JOURNAL, **59**, 1129 (1937).

[17] Kassel, *ibid.*, **58**, 670 (1936).

[18] Stuckey and Saylor, *ibid.*, **62**, 2922 (1940).

[19] Altschul, *Z. physik. Chem.*, **11**, 577 (1893).

[20] Ahlberg, Blanchard and Lundberg, *J. Chem. Phys.*, **5**, 539 (1937).

[21] Fiock, Ginnings and Holton, *J. Research Natl. Bur. Standards*, **6**, 881 (1931).

TABLE VIII
ENTROPY CALCULATIONS
Units: cal. per degree mole

	Benzene		
298.16°K.	Liquid (Ahlberg, *et al.*[20])	41.49	
	Vaporization (Fiock, *et al.*[21])	27.05	
	Compression R ln (0.1235)	-4.15	
	Gas, 1 atm., 298.16°K.		64.39 ± 0.3
	Toluene		
298.16°K.	Liquid (Kelley[13])	52.40	
	Vaporization 9115/298.16	30.57	
	Compression $-R$ ln 760/28.45	-6.53	
	Gas, 1 atm., 298.16°K.		76.44 ± 0.3
	o-Xylene		
0.00–14.13°K.	Extrapolation $2D(131.5/T)$	0.40	
14.13–247.82	Solid, graphical integration	37.32	
247.82	Fusion, 3250/247.82	13.12	
247.82–298.16	Liquid, graphical integration	7.96	
	Entropy of liquid at 298.16°K.		58.80
298.16	Vaporization 10,470/298.16	35.12	
	Compression $-R$ ln 760/6.64	-9.42	
	Gas, 1 atm., 298.16°K.		84.50 ± 0.3
	m-Xylene (1st method)		
0.00–14.13°K.	Extrapolation $2D(117/T)$	0.54	
14.13–225.27	Solid, graphical integration	36.13	
225.27	Fusion 2765/225.27	12.26	
225.27–298.16	Liquid, graphical integration	11.49	
	Entropy of liquid at 298.16		60.42
298.16	Vaporization 10,160/298.16	34.08	
	Compression $-R$ ln 760/8.39	-8.95	
	Gas, 1 atm. 298.16°K.		85.55 ± 0.4
	m-Xylene (2nd method)		
0.00–14.13°K.	Extrapolation $2D(118/T)$	0.53	
14.13–224.38	Solid, graphical integration	36.02	
220.20–224.38	Fusion	12.46	
224.38–298.16	Liquid, graphical integration	11.65	
298.16	Vaporization 10,160/298.16	34.08	
	Compression $-R$ ln in 760/8.39	-8.95	
	Entropy of one mole of substance of the composition of the sample	85.79	
	Entropy of mixing	-0.22	
		85.57	
	Entropy of 0.0234 mole *p*-xylene	-1.97	
	Entropy of 0.9766 mole *m*-xylene	83.60	
	Entropy of one mole *m*-xylene, gas, 1 atm. 298.16°K., 83.60/0.9766		85.60 ± 0.3
	p-Xylene		
0.00–15.85°K.	Extrapolation $2D(142/T)$	0.44	
15.85–286.39	Solid, graphical integration	42.73	
286.39	Fusion 4090/286.39	14.28	
286.39–298.16	Liquid, graphical integration	1.75	
	Entropy of liquid at 298.16°K.		59.20
298.16	Vaporization 10,110/298.16	33.91	
	Compression $-R$ ln 760/8.87	-8.84	
	Gas, 1 atm., 298.16°K.		84.27 ± 0.3

Gas Heat Capacities.—The gas heat capacities were measured in a flow type calorimeter which has been described previously.[3,22] The high boiling points of toluene and the xylenes made it necessary to carry out the measurements under reduced pressure except at the higher temperatures. Corrections for gas imperfections were made by means of the Berthelot equation of state, using critical constants from the "I. C. T." for benzene, toluene and carbon tetrachloride and those reported by Altschul[19] for the xylenes. The data are given in Table IX and are shown graphically in Fig. 7 of Part V. Within experimental error, meta and para xylenes have the same gaseous heat capacity. This fact makes unnecessary any correction for the *p*-xylene impurity in the *m*-xylene sample used for these measurements. It is difficult to estimate the uncertainty in these gas heat capacity values; they have been somewhat arbitrarily assigned an uncertainty of 1%. The measurement on carbon tetrachloride was made after the completion of the measurements on the other substances. The fact that the value obtained agrees with that calculated from the vibrational assignment of Vold[23] (21.84 cal./deg. mole at 393°K.) serves as a check on the reliability of these measurements. The heat capacity of gaseous benzene has also been measured by Dr. W. D. Gwinn of this Laboratory, using a different calorimeter. His data agree well with the present results and have been included in Table IX. Bennewitz and Rossner's[24] value for the heat capacity of toluene gas (33.6 cal./deg. mole at 410°K.) is significantly lower than the results reported here (about 2%). These results are compared with calculated values in Fig. 7, Part V.

TABLE IX

GAS HEAT CAPACITIES

Substance	T, °K.	P, atm.	C_p, cal./deg. mole	$C_p - C_p^0$	C_p^0, cal./deg. mole
Benzene	393	1	26.7	0.3	26.4 ± 0.3
	393	0.19	26.5	.1	26.4 ± .3
	428	1	28.6	.2	28.4 ± .3
	463	1	30.5	.2	30.3 ± .3
Benzene by Dr. W. D. Gwinn	388	1	26.3	.3	26.0 ± .3
	417	1	28.4	.3	28.1 ± .3
	481	1	31.6	.2	31.4 ± .3
Toluene	393	0.53	33.0	.2	32.8 ± .3
	428	1	36.0	.3	35.7 ± .4
	463	1	38.3	.3	38.0 ± .4
o-Xylene	393	0.22	40.3	.1	40.2 ± .4
	428	0.73	43.7	.2	43.5 ± .4
	463	1	46.3	.3	46.0 ± .5
m-Xylene	393	0.22	39.2	.1	39.1 ± .4
	428	0.69	42.7	.3	42.4 ± .4
	463	1	45.7	.3	45.4 ± .4
p-Xylene	393	0.22	39.1	.1	39.0 ± .4
	428	0.73	42.9	.3	42.6 ± .4
	463	1	45.5	.3	45.2 ± .4
CCl_4	393	1	22.2	.3	21.9 ± .2

Part II. Thermodynamic Measurements on Mixed Systems

Equilibrium and Heat Content Relationships between Benzene, Toluene, and Each of the Xylenes. The Freezing Point Diagram of the Ternary System *o*-, *m*-, and *p*-Xylenes

Inspection of the available heat of combustion data for the xylenes led to the conclusion that the differences between isomers could not be determined with any reliability by this method. By comparison, the data of Norris and Vaala[25] indicated that satisfactory values could probably be obtained by direct equilibrium studies using aluminum halide–hydrogen halide catalysts.

The freezing point studies were undertaken primarily as an aid in the analysis of xylene mixtures. However, they offer an interesting measure of the accuracy to which these mixtures follow Raoult's law.

The Freezing Point of Xylene Mixtures.—By use of the accurate melting points and heats of fusion of Part I, together with thermodynamics and Raoult's law, the complete freezing point diagram of the xylenes was calculated. A value of 3R (5.96 cal./degree) was assumed for ΔC_p of fusion for each xylene, by comparison of the various heat capacity curves. Its exact value is unimportant. Kravchenko[26] has already published such a calculation but did not have as accurate physical constants available. The results of the calculations of this research are shown in Table X and in Fig. 5.

The data on the impure *m*-xylene sample provide an excellent check on these calculations at

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(22) Pitzer, THIS JOURNAL, 63, 2413 (1941).

(23) Vold, *ibid.*, 57, 1192 (1935).

(24) Bennewitz and Rossner, *Z. physik. Chem.*, B39, 126 (1938).

(25) Norris and Vaala, THIS JOURNAL, 61, 2131 (1939).

(26) Kravchenko, *Acta physicochim. U. S. S. R.*, 14, 279 (1941).

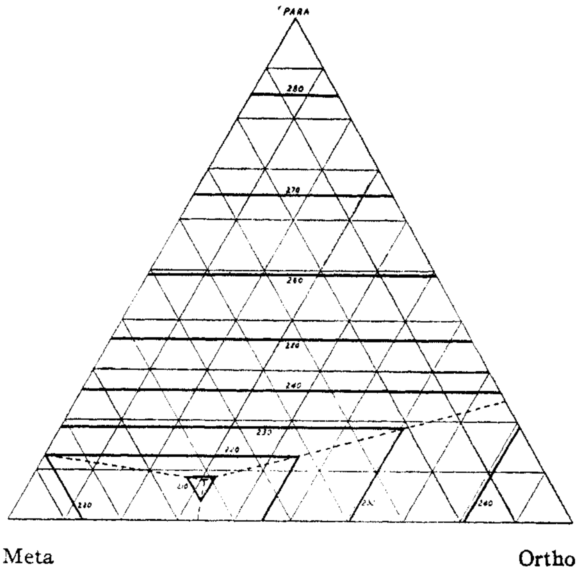

Fig. 5.—The freezing point diagram for the ternary system *o*- *m*- and *p*-xylene.

the meta–para eutectic as shown in Table X.

TABLE X

EUTECTIC POINTS IN THE TERNARY SYSTEM *o*-, *m*-, *p*-XYLENE

Composition calcd.	Calcd.	Temperature, °K. exp. (this research)	exp. (Nakatsuchi[9])
13.0% para, 87.0% meta[a]	220.3	220.2 ± 0.2	216.2 ± 3
24.3% para, 75.7% ortho	237.6	...	237.7 ± 0.4
66.6% ortho, 33.4% meta	211.2	211.4 ± 1	210.2 ± 1
30.5% *o*-, 61.4% *m*-, 8.1% *p*-	208.5	209 ± 1	...

[a] Experimental composition (this research) 12.9% para, 87.1% meta.

Analysis of Xylene Mixtures.—Norris and Vaala analyzed their xylene mixtures for *p*-xylene by the depression of the freezing point of pure *p*-xylene on addition of the unknown sample, and for *o*-xylene by oxidation to phthalic acids and separation of phthalic anhydride. The percentage of meta was then obtained by difference.

It was found possible to simplify this procedure considerably by the substitution of a refractive index measurement for the oxidation to phthalic acids. The refractive indices of the pure xylenes are (at 25°) ortho, 1.5030; meta, 1.4946; para, 1.4931. Thus the refractive index is primarily dependent on the ortho concentration although the para content must be known independently for exact work. Actual analyses were carried out by first determining the para content, then making up knowns with the same para content and with ortho contents near that of the unknown. Since all samples of interest were near the equilibrium composition, only that region was actually investigated experimentally.

A simple Abbe refractometer sufficed for analyses to one or two per cent. The final results were checked with an interferometer. The latter instrument had such sensitivity as to have permitted analyses to a few hundredths of one per cent. if there had been any need of such accuracy (and if the freezing point measurements, for para content, were correspondingly accurate).

If analyses were desired covering the entire composition range, it would be a simple matter to set up a graph showing constant refractive index curves on the ternary composition axes.

With the Abbe instrument it is barely possible to detect the difference between the true refractive index of a mixture and that calculated as the sum of the mole fractions times the refractive indices of the pure substances.

Equilibrium among the Xylenes.—An examination of the data of Norris and Vaala,[25] reproduced in Table XI, shows that these workers definitely obtained equilibrium between meta and para-xylene. In fact their data indicate the reaction to be going past equilibrium which is of course impossible and must be due to experimental error, probably in analysis. With respect to *o*-xylene, however, their results are less certain. Starting with either meta or para, 14% ortho was obtained after five hours while seventy-five hours gave only 16% ortho. This strongly suggests that equilibrium was attained, but this composition was never reached starting from pure ortho. Only one experiment was done with ortho, of only five-hour duration.

TABLE XI

EQUILIBRIUM COMPOSITION OF THE XYLENES FROM EXPERIMENTS BY NORRIS AND VAALA

(Temperature, 50°C.)

Initial composition	Expts.	Time, hr.	% still xylene	Final composition, % ortho	meta	para
meta	1	5	88	14	74	12
meta	7	18–75	72–85	16	65–69	15–19
para	1	5	83	14	76	10
ortho	1	5	94	40	55	5

It seemed desirable to show definitely that starting with pure *o*-xylene the concentration of that isomer would approach the value near 14%. In our experiments starting with pure *o*-xylene excessive side reaction occurred before this end was attained. However, by starting with a mixture of *o*-xylene with toluene and benzene, the net side reactions were reduced to a small percentage and the desired result demonstrated. The numerical data are shown in Table XII together with other results which confirm the work of Norris and Vaala. As "best" values of the equilibrium composition of the liquid at 50°, one may take 12 ± 3% ortho, 71 ± 5% meta, 17 ± 2% para. These figures will not change very rapidly with temperature. Considering the vapor pressures of each isomer (given in Part I) the values for the gas phase become 10% ortho, 72% meta and 18% para with the same limits of error as in the liquid. The equilibrium composition at other temperatures will be presented below.

TABLE XII

EQUILIBRIUM COMPOSITION OF THE XYLENES FROM EXPERIMENTS OF THIS RESEARCH

(Catalyst: $AlBr_3$ + HBr anhydrous)

Initial composition	Temp., °C.	Time, days	Side reaction, %	Final composition, % ortho	meta	para
p-Xylene	30	2	20[a]	12	72	16
Benzene + toluene	50	5	15[a]	13	71	16
o-Xylene (excess) + benzene + toluene	50	6	20[a]	12	71	17

[a] In the first experiment "side reactions" include the formation of toluene, in the second and third this is, of course, excluded.

Equilibrium between Benzene, Toluene and Xylene.—So far as we are aware, a measure of the equilibrium of this reaction has not been attained previously. Table XIII shows the results of two final experiments (following many exploratory runs) which limit the equilibrium constant

$$K = N_{\text{Benzene}}N_{\text{Xylene}}/N^2_{\text{Toluene}} \quad (N = \text{mole fraction})$$

to the range 0.15 to 0.22. In this expression the total xylene is considered. The xylenes present were of equilibrium composition at the end of both experiments, as would be expected.

Considering the various vapor pressures involved and assuming Raoult's law; one obtains values for the equilibrium constant in the gas phase which do not differ appreciably from those for the liquid.

TABLE XIII

EQUILIBRIUM MEASUREMENTS ON THE REACTION

2 Toluene = Benzene + Xylene

(Temperature, 50°C.; Catalyst, $AlBr_3$ + HBr anhydrous)

Initial composition, % Benzene	Toluene	Xylene	Time, days	Side reactions, %	Final composition, % Benzene	Toluene	Xylene	*K*
50	50	0	5	15	54	41	4.7	0.15
55	36	9	6	20	58.5	36.5	5.0	0.22

The analyses for benzene, toluene and total xylene were made by fractional distillation in a column of approximately 25 theoretical plates.

Catalysts and Side Reactions.—Norris and Vaala used anhydrous aluminum chloride with and without hydrogen chloride for catalysts. A few experiments employed ferric chloride. All gave essentially the same results. It was found in this research that anhydrous aluminum chloride gave little or no reaction in the absence of hydrogen chloride. Exploratory experiments also indicated that anhydrous aluminum bromide and hydrogen bromide was a more effective catalyst than the chlorides. Therefore all final experiments were made with the latter substances.

The aluminum bromide was prepared by direct union of the elements; the hydrogen bromide by the action of bromine on phenol. The concentration used was about 5 mole per cent. aluminum bromide (as Al_2Br_6). For each mole of aluminum bromide present, approximately two moles of hydrogen bromide were passed into the mixture. At the end of the desired time the catalyst was destroyed by pouring the mixture on cracked ice and subsequent shaking of the hydrocarbon phase with portions of pure water.

It was found in general that tar-forming side reactions proceeded fastest with the more highly methylated compounds. Thus in the last experiment in Table XIII the ratio of total methyl groups present to benzene rings present decreased during the course of the reaction. Another side reaction which it was desirable to suppress was that forming tri- and tetramethylbenzenes. This would tend to consume xylene and to prevent equilibrium measurements on other reactions until equilibrium amounts of these substances were formed.

By starting with mixtures rich in benzene and

TABLE XIV

THERMODYNAMIC CONSTANTS FOR CERTAIN REACTIONS

All values for gases at 50°C., 323°K.; units, cal. and cal./degree

Reaction	Δ*F*	Δ*H*	Δ*S*
m-Xylene = *p*-xylene	890 ± 100	460 ± 150	−1.33 ± 0.3
m-Xylene = *o*-xylene	1270 ± 150	950 ± 200	−1.00 ± .3
p-Xylene = *o*-xylene	380 ± 250	490 ± 250	+0.33 ± .3
m-Xylene = xylene (equil. mixt.)	−210 ± 40	180 ± 40	1.20 ± .2
2 Toluene = benzene + xylene (equil.)	1100 ± 200	600 ± 300	−1.54 ± .6
2 Toluene = benzene + *m*-xylene	1310 ± 200	420 ± 300	−2.74 ± .6

toluene it was possible to obtain, at equilibrium, measurable amounts of xylene but practically negligible amounts of trimethylbenzenes. This condition also tended to suppress the tar forming side reactions.

Free Energies and Heat Contents.—Using the data presented in the preceding sections together with the entropy values obtained in Part I, one obtains the results shown in Table XIV. Although the values are strictly for the gas phase at 50°, they are only slightly different in the liquid phase. A change to 25° has similarly only a small effect. Further thermodynamic calculations and discussion will be presented after the vibration frequencies and statistical mechanical analysis is completed.

Part III. The Vibration Frequencies of Benzene

Before considering the vibration frequencies of the methyl derivatives, it is desirable to make a complete, although not absolutely certain, vibrational assignment for benzene itself. The most recent researches in this field are those by Ingold and his collaborators[27] and by Langseth and Lord[28] on the spectra of the deuterated benzenes, making use of the Teller–Redlich product rule. These authors give extensive discussions of the theoretical aspects of this problem, hence they will not be repeated here. The present status may be described briefly as follows. Of the twenty fundamental frequencies of benzene, eleven are active in either the Raman or infrared spectra and are definitely established. According to Wilson's[29] numbering scheme, see Fig. 6, these are 1, 2, 6, 7, 8, 9, 10, 11, 18, 19, 20. Vibrations 12 and 13 have been definitely placed by Langseth and Lord through consideration of the deuterated benzene spectra. These authors also established rather definitely the product of frequencies 4 and 5 by the same method and assigned no. 16 to the weak Raman line at 400 cm.$^{-1}$ which appears in violation of the selection rules. This leaves four frequencies for which tentative values were suggested in the cases of no. 3 and 17 and none given for no. 14 and 15.

Although no new spectral data are available, reliable heat capacity values for gaseous benzene are presented in Part I of this paper which can be used to check a tentative complete assignment. Also, it is believed that several of the missing fundamental frequencies can be found among the weak lines in the Raman and infrared spectra of liquid benzene. The line at 400 cm.$^{-1}$ has already been assigned as no. 16. These frequencies are forbidden by the selection rules but do appear, presumably because of the perturbing effect of liquid forces. Particularly to be considered are lines which occur in the infrared absorption of the liquid but are absent for the gas.

Several normal coördinate analyses were made using approximate but reasonable potential functions.[30] These served to indicate approximately where a given line should appear, but did not give exact enough agreement to justify presentation in detail. The normal coördinates shown in Fig. 6 resulted from these calculations. Although these data are only of semi-quantitative significance, they were valuable in connection with the assignments for the methyl derivatives.

Planar Hydrogen Bending Vibrations 3 and 15.—To start the assignments, let us consider first nos. 3 and 15. Normal coördinate calculations place these frequencies in the range 1150–1350 cm.$^{-1}$ with no. 3 probably the higher. In Table XV the lines in the Raman and infrared spectra of benzene are listed. All lines are included except those so weak as to be of doubtful existence. On this basis 1298 is an obvious choice for no. 3. Before adopting it, however, the spectra of the para benzenes d_2 and d_4 must be considered, because no. 3 becomes Raman active and Langseth and Lord suggested the value 1195 on this basis. Table XVI gives these data in the region of interest. No. 3 falls in the symmetry group B_{2g} along with another hydrogen planar bending mode, 9*b*. These two modes become hopelessly mixed in the deuterated compounds. We follow Langseth and Lord in arbitrarily calling 3 the higher frequency in d_2, and 9*b* the higher in the d_4 compound. Following Langseth and Lord for all other frequencies in this symmetry group but using 1298 for no. 3 in benzene, one calculates 1266 for no 3 in para benzene d_2. Considering anharmonicity, this is in satisfactory

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(27) Angus, Bailey, Hale, Ingold, Leckie, Raisin, Thompson and Wilson, *J. Chem. Soc.*, 912–987 (1936); *Nature*, **139**, 880 (1937).

(28) Langseth and Lord, *Kgl. Danske Videnskab. Selskab, Math-fys. Medd.*, **16**, No. 6, 1–85 (1938).

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

(30) Use was made of the formulas of Manneback, *Am. Soc. Sci. Bruxelles*, Ser. B, **55**, 129 (1935); Barnard Manneback and Verleysen, *ibid.*, Ser. I, **59**, 376 (1939); **60**, 45 (1940).

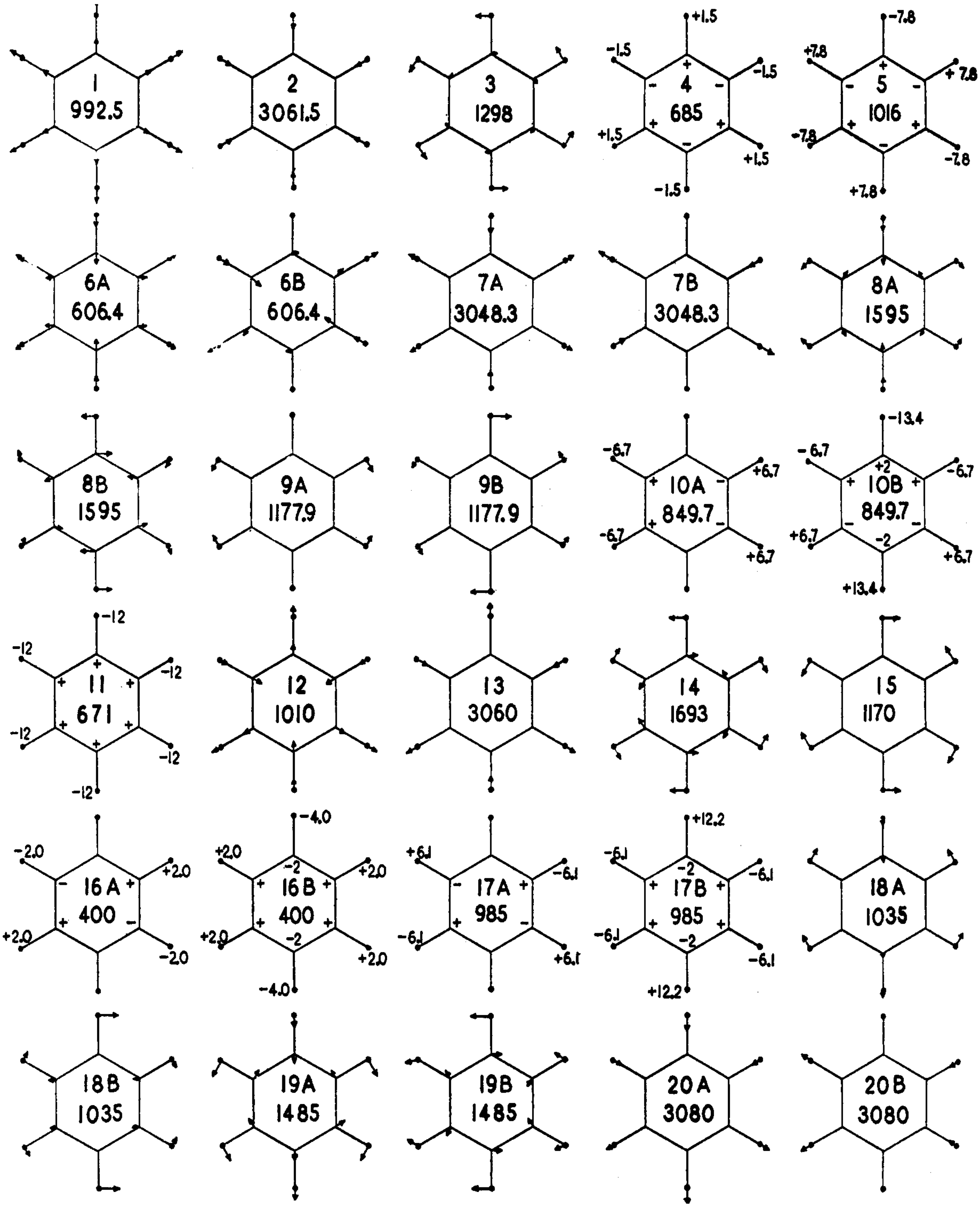

Fig. 6.—The frequencies and normal modes of vibration of benzene; + and − refer to motions perpendicular to the plane of the ring.

agreement with the observed line at 1273 cm.$^{-1}$. For no. 9*b* in para benzene d_4 one calculates 1242 cm.$^{-1}$ as compared to the observed line at 1253 cm.$^{-1}$. Finally, the discarded lines at 1175 and 1137 cm.$^{-1}$ can be satisfactorily accounted for. Thus the value 1298 is quite satisfactory for no. 3.

The only other available line in this range for no. 15 is at 1170 cm.$^{-1}$. This lies almost within experimental error of the Raman line at 1178 cm.$^{-1}$. However, in cases where definitely the same frequency is observed in both spectra the average difference is 2 cm.$^{-1}$ and the largest is 4 cm.$^{-1}$. Thus it seems best to adopt 1170 for no. 15, realizing that it is not absolutely certain but cannot be far wrong.

TABLE XV

SPECTRA OF BENZENE

Infrared		Raman	
Gas	Liquid	liquid	Assignment
		$\underline{\underline{400}}$ w	(16)
	$\underline{610}$ w	606 s (d)	(6)
671 s	671 s		(11)
		$\underline{\underline{685}}$ w	(4)
	$\underline{\underline{773}}$ w		2(16) = 800
	$\underline{849}$ m	849 s (d)	(10)
	$\underline{\underline{985}}$ w		(17)
		992 s (p)	(1)
1037 s	1033 s	$\underline{1030}$ w	(18)
	$\underline{\underline{1170}}$ m		(15)
		1178 s (d)	(9)
	$\underline{\underline{1298}}$ w		(3)
1377 w	1381 m		(16) + (17) = 1385 ?
1485 s	1480 s	$\underline{1478}$ w	(19)
	$\underline{\underline{1529}}$ w		(10) + (11) = 1520
	$\underline{1584}$ m	1585 s (d)	(8) = 1596
	$\underline{1604}$ m	1606 s (d)	(1) + (16) = 1598
1617 w			(6) + (18) = 1643, or (6) + (17) = 1591 ?
	$\underline{\underline{1669}}$ w		(1) + (11) = 1663
		$\underline{\underline{1693}}$ w	(14) also 2 (10) = 1698
1808 m	1810 m		(10) + (17) = 1834 see text
1965 m	1963 m		(5) + (17) = 2001

s, strong; m, medium; w, weak; (p) polarized; (d) depolarized. Singly underscored values are lines appearing in that spectrum in violation of "selection rules" but which are permitted in some other spectrum; doubly underscored values are lines which appear only in violation of "selection rules."

TABLE XVI

SPECTRA OF PARA BENZENES d_2 AND d_4 IN THE RANGE 1100–1400 CM.$^{-1}$

Obs. L + L	Assignment L + L	This research
	para-$C_6H_4D_2$	
1167 (2)	(3)	resonance (9*a*) with 2(6*a*) = 1186
1175 (4)	(9*a*)	
1273 (0*d*)	2(4) = 1268	(3)
	para-$C_6H_2D_4$	
1137 (1)	(9*b*)	2(6*b*) $\leq$ 1170; (10b) + (16*a* or *b*) $\cong$ 1125
1253 (1*d*)	(6) + (10*a*) = 1247	(9*b*)

Carbon Bond Stretching Vibration 14.—This frequency may be expected in the range 1500–1900 cm.$^{-1}$, probably above 1600 cm.$^{-1}$. Langseth and Lord found that no. 8 (1596 in benzene) showed no sign of interaction with a nearby fundamental in those unsymmetrically deuterated benzenes where 8 and 14 fall in the same symmetry class. On that basis they stated that no. 14 lies outside the range 1560–1640 cm.$^{-1}$ in benzene. Table XV shows the infrared lines at 1529, 1669, and the Raman line at 1693 as possibilities. Each line, however, can be accounted for as an allowed combination tone. The Raman line at 1693 is selected primarily because combination tones are much more likely to appear in the infrared than in the Raman spectrum.

Out of Plane Vibrations 4, 5 and 17.—Langseth and Lord considered seriously two different assignments for vibration 5 in para benzene d_2, sym. d_3 and para d_4. The values were either 966, 914 and 927 cm.$^{-1}$, respectively, or 1273, 1226 and 1253. These authors selected the former alternative for the good reason that there is no other satisfactory explanation of the strong parallel infrared band at 914 cm.$^{-1}$ for sym. benzene d_3, whereas 1226 is a weaker band of unknown structure. We may now add the additional reasons that the 1273 and 1253 lines have now been assigned as planar hydrogen bending frequencies. Possibly the 1226 band should be similarly assigned; however, it would be appearing in violation of selection rules. The product of frequencies 4 and 5 which are inactive in benzene itself is now fixed. However the 685 line in the Raman spectrum lies just where no. 4 would be expected. Adopting this value one calculates 1016 cm.$^{-1}$ for no. 5. No line has been observed in either spectrum at this location, but it would be hard to find because of strong neighboring lines. Furthermore, even though some "inactive" fundamentals do appear in violation of the ordinary selection rules, one certainly cannot as yet be sure that all should.

In order to locate no. 17 one considers the spectrum of sym. benzene d_3, where it becomes Raman active, in addition to that of benzene itself. Langseth and Lord suggested 815 cm.$^{-1}$ for no. 17 in the sym. d_3. This value for no. 17 is unsatisfactory because the calculated heat capacity for benzene is then too high and because it leads to an unreasonable potential function. Further evidence is found in the very recent data on the heat capacity of solid benzene d_6 obtained by Ziegler and Andrews[30a] which led them to suggest that the Langseth and Lord assignment (815 cm.$^{-1}$) for no. 17 was too low.

[30a] Ziegler and Andrews, THIS JOURNAL, **64**, 2482 (1942).

TABLE XVII

FUNDAMENTAL FREQUENCIES OF BENZENE, SYM. BENZENE d_3 AND BENZENE d_6

Symmetry classes		No.	C_6H_6			sym. $C_6H_3D_3$			C_6D_6		
A_1'	A_{1g}	1	992	R(p)	—	955	R(p)	—	945	R(p)	(IR)
		2	3062	R(p)	—	3055	R(p)	—	2292	R(p)	—
	B_{1u}	12	(1011)	—	—	1002	R(p)	—	977	(R)	(IR)
		13	(3046)	—	—	2284	R(p)	—	(2268)		
A_2'	A_{2g}	3	1298	—	(IR)	1226	—	(IR)?	1010	(R)?	(IR)?
	B_{2u}	14	1693	(R)	—	—			(1665)	—	—
		15	1170	—	(IR)	—			(841)	—	—
E'	E^+_g	6	606	R(d)	(IR)	592	R	IR	578	R(d)	(IR)
		7	3047	R(d)	—	2272	R	IR	2265	R(d)	—
		8	1596	R(d)	(IR)	1574	R	IR	1556	R(d)	(IR)
		9	1178	R(d)	—	1100	R	IR	868	R(d)	(IR)
	E^-_u	18	1037	(R)	IR	833	R	IR	813	—	IR
		19	1485	(R)	IR	1405	R	IR	1333	(R)	IR
		20	3080	—	IR	3055	R	IR	2294	—	IR
A_2''	B_{2g}	4	685	(R)	—	691	—	IR	—		
		5	(1016)	—	—	914	—	IR	—		
	A_{2u}	11	671	—	IR	533	—	IR	503	—	IR
E''	E^-_g	10	849	R(d)	(IR)	710	R(d)	—	661	R(d)	(IR)
	E^+_u	16	400	(R)		374	R		~350	(R)	
		17	985	—	(IR)	(950)	R?	—	790	(R)	—

Parentheses indicate appearance in spectra of liquids in violation of the simple selection rules for gases. Letters indicate appearance in the indicated spectrum, dashes indicate absence, no mark indicates that spectrum was not taken in that region. (p), polarized, (d), depolarized.

A satisfactory assignment for vibration 17 is the weak infrared band at 985 cm.$^{-1}$ in benzene and the weak Raman line at 790 cm.$^{-1}$ in benzene d_6. This places the line at 950 in sym. benzene d_3 where it should be Raman active but would be masked by the very strong line at 955 cm.$^{-1}$. The 985 infrared band in benzene is a mere shoulder on the strong band at 1037, and might easily be explained as no. 1 (992 cm.$^{-1}$). However, it is very difficult to explain the rather strong infrared bands at 1810 and 1965 cm.$^{-1}$ which appear for both gas and liquid except as the allowed combination tones (10) + (17) and (5) + (17), respectively. Both calculated values are a bit high, but this could be easily corrected by lowering 17 to about 970 cm.$^{-1}$ which would still be consistent with the shoulder on the 1037 infrared band. It might also be desirable to lower 5 a few units, a perfectly permissible change. These last considerations offer considerable support to an otherwise doubtful assignment.

Conclusion.—The complete Raman and infrared spectra (barring lines so extremely weak as to be doubtful) as listed in Table XV are now satisfactorily explained. All of the fundamental frequencies are reasonable in terms of approximate potential functions. Table XVII lists these frequencies. A majority of these values have been given previously.[27,28] The heat capacity calculated using this assignment is in excellent agreement with the experimental values as shown in Fig. 7 of Part V. Even with all this evidence one cannot definitely conclude that this assignment is correct, but rather one must say that it is by far the most probable in view of the available information.

Several authors[27,28,29] have given sets of symmetry coördinates for benzene. So far as the writer is aware, however, Fig. 6 gives the true normal coöordinates of benzene for the first time. The values are of course only semi-quantitative, having arisen from approximate potential functions. They will be very useful, nevertheless, in discussing substituted benzenes.

Part IV. The Vibration Frequencies of Toluene, *o*-, *m*- and *p*-Xylenes and Mesitylene

The Raman spectra, including polarization data, and the infrared absorption spectra, have been measured for one or more of these substances by several workers.[31–40] Some of these authors

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(31) Ananthakrishnan, *Proc. Indian Acad. Sci.*, **3A**, 52 (1936) (Raman for toluene).

(32) Kohlrausch, *Wien Ber.*, **142**, 637 (1933) (Raman for toluene).

identified certain lines, but no attempt at complete assignments has been made heretofore. We have available, in addition to the spectra, accurate values of the heat capacity and entropy for all substances except mesitylene and a complete vibrational assignment for benzene including the normal coördinates.

A very important aid has been the use of an approximate product rule *analogous* to the Teller–Redlich product rule for isotopic substitution. With the substitution of methyl groups for hydrogen atoms, not only the mass but also the force constants and bond distances change. In addition the methyl group has internal vibrations which may interact with ring motions. However, these complicating effects should be nearly the same for each substituted methyl group. Therefore, although the product ratio cannot be calculated accurately from theory, its value should remain closely constant for similar groups of vibrations in the various molecules. Actually the values obtained are very close to those calculated by considering only changes in mass and bond distance.

The product ratio may be defined as follows

$$\tau = \frac{\prod\limits_i \nu_{s_i} \prod\limits_j I_{u_j}^{1/2} \prod\limits_k M_{u_k}^{1/2}}{\prod\limits_i \nu_{u_i} \prod\limits_j I_{s_j}^{1/2} \prod\limits_k M_{s_k}^{1/2}}$$

where s indicates the value for the substituted compound and u that for the unsubstituted, ν is a vibration frequency, I a moment of inertia and M a mass. The products are to be taken over all the degrees of freedom of a given symmetry class. This definition differs from that commonly used for the isotopic product rule by including the masses and moments of inertia in the observed product. This is desirable because no exact theoretical formula for τ can be given in this case, hence we wish to put all observed τ's on a directly comparable basis.

One can calculate approximate theoretical τ's for methyl substitution as follows. For each methyl-ring stretching motion the value is the square root of the mass ratio, $(1/15)^{1/2} = 0.258$. For each bending motion one considers the moments of inertia of the attached group with respect to the point of attachment on the ring obtaining $(1.2/41)^{1/2} = 0.171$.

Throughout this work we have ignored the spectrum in the region around 3000 cm.$^{-1}$ because, although there are always several lines, there are never enough resolved to account for all expected. We have arbitrarily assigned benzene-H stretching modes the value from benzene and C-H stretching within a methyl group the value 2950 cm.$^{-1}$.

Mesitylene.—Let us consider first the substance of highest symmetry and therefore greatest simplicity, *sym*-trimethylbenzene. Table XVIII gives first the symmetry classes and their selection rules, second the benzene and methyl group (M) vibrations falling in these various classes, third the frequencies for benzene, fourth the assigned frequencies for mesitylene, fifth the appearance of these lines in the spectra, and finally the product ratios. The various benzene vibrations are depicted in Fig. 6. The methyl group motions are as follows: M1, sym. stretching; M2, unsym. stretching; M3, sym. bending; M4, unsym. bending within the methyl group; M6, wagging of the whole methyl group. The even numbered motions are degenerate in a methyl halide. In these compounds the degeneracy is removed, the vibration appearing in two different symmetry groups. The letters R and IR indicate appearance in the corresponding spectrum, —indicates absence, no mark indicates that the spectrum was not taken or not examined in this region and parentheses indicate appearance in violation of selection rules. The state of polarization is given for the Raman lines where it is known.

Although the actual modes become so mixed up as to make numbering arbitrary, there can be no doubt about the members of the totally symmetric, A_1, class. For the calculation of the product ratio one must decide between 1300 and 1380 as no. 13 and M3. Since a strong, polarized line always appears at 1380 cm.$^{-1}$ in methyl substituted benzenes, whereas the line below it varies from 1200 to 1300 cm.$^{-1}$, the assignment of 1380 to M3 is definite. One then obtains the

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(33) (a) Kohlrausch and Pongratz, *Monatsh*, **63**, 427 (1933) (Raman for the xylenes); (b) *Wien Ber.*, **143**, 358 (1934) (Raman for mesitylene).

(34) Cabannes and Rousset, *Ann. Phys.*, **19**, 229 (1933), (Raman for toluene).

(35) Narkiewicz, *Z. Physik*, **96**, 177 (1935) (Raman for xylenes).

(36) Desreux, *Bull. soc. chim.*, [5] **3**, 1659 (1936) (Raman for all subst.).

(37) Venkateswaran, *Phil. Mag.*, **15**, 263 (1933); *Proc. Roy. Soc.* (London), **128A**, 252 (1930) (Raman for mesitylene).

(38) Lambert and Lecompte, *Ann. phys.*, [10], **18**, 329 (1932); [11] **10**, 503 (1938) (infrared for all subst.); Lecompte, *J. Phys. Radium*, **8**, 489 (1937); **9**, 13 (1938).

(39) Coblenz, *Astrophys. J.*, **20**, 207 (1904) (infrared for all but *m*-xylene)

(40) Barchewitz and Perodi, *J. Phys. Radium*, **10**, 142 (1939).

TABLE XVIII

VIBRATIONAL ASSIGNMENT FOR MESITYLENE

(Methyl groups in positions 1, 3, 5)

Symmetry class	No.	Benzene	Mesitylene			Ratio of products
A_1 $R_{(p)}$ —	1	992	998	R(p)	—	0.244
	2	3062	(3062)			
	12	1011	575	R(p)	?	
	13	3046	1300	R(p)	—	
	M3	—	1380	R(p)	—	
	M1	—	(2950)			
E' $R_{(d)}$, IR	6	606	515	R(d)	IR	.0425 ‖ (.171) (.248)
	7	3047	(3047)			
	8	1596	1610	R(d)	IR	
	9	1178	1160	R	IR	
	18	1037	230	R(d)		
	19	1485	1385	?	IR	
	20	3080	930	R	IR	
	xy trans.	M = 78	M = 120			
	M6	—	1025	—	IR	
	M4	—	1470	—	IR	
	M3	—	1380	R	—	
	M2	—	(2950)			
	M1	—	(2950)			
E'' $R_{(d)}$ —	10	849	275	R(d)		.171
	16	400	(439)	(obs. in meta xylene)		
	17	985	847	R(d)	—	
	xy rot.	I = 145	I = 481			
	M6	—	(1200)	—	—	
	M4	—	1440	R	—	
	M2	—	(2950)			
A'' — IR	4	685	690	—	IR	179
	5	1016	840	—	IR	
	11	671	182	(R)		
	z trans.	M = 78	M = 120			
	M6	—	1025	—	IR	
	M4	—	1480	—	IR	
	M2	—	(2950)			
A_2' — —	3	1298	(1220)	—	—	(.171)
	14	1693	(1650)	—	—	
	15	1170	(390)	—	—	
	z rot.	I = 291	I = 947			
	M6	—	(1200)			
	M4	—	(1450)			
	M2	—	(2950)			

product ratio, 0.244, which is somewhat lower than the theoretical, 0.258, due almost certainly to a slightly lower force constant for C–C than for C–H bond stretching.

In assigning the degenerate modes it is desirable to note that certain of the frequencies should be either exactly or approximately the same as in the *m*-xylene. There the degeneracy is removed, one component changing and the other not. From Fig. 6, Part III, it is apparent nos. 6b, 9a, 10a, 16a, 17a and 18a should fall in this general category, some changing very slightly, 10, 16 and 17 not at all. With this in mind, and the selection rules, the assignment of Table XVIII is quite definite. No line appears in the mesitylene spectra where no. 16 would be expected. A very weak line is observed at 439 cm^{-1} in the Raman for *m*-xylene, which is assigned to 16a there, and can be taken for 16 in mesitylene. The product rule is well satisfied.

In the A_2'' class which is only active in the infrared, one would expect no. 4 to be raised slightly. 5 and 11 will recombine to give an out of plane motion of the hydrogens (arbitrarily called 5) and one of the methyl groups. The former should be near the average of 5 and 11 in benzene, the latter very low. Thus 690 and 840 are very satisfactory for 4 and 5. The infrared spectrum does not continue to long enough wave lengths to find 11. Two doubtful Raman lines have been reported, each by only one investigator, at 145 and 182 cm.$^{-1}$. The higher fits the product rule better and is therefore adopted.

The frequencies in the A_2' group are quite arbitrary since they are inactive in both the Raman and infrared. However, they are of such a nature as to make reasonably accurate estimates possible.

Probably the most important results arising from the mesitylene assignment are the reliable values of the product ratios in the A_1, E', and E'' classes.

p-**Xylene.**—The assignments for this substance, and those to follow, were made by the same general methods. With the aid of the polarization data and considerations of general reasonableness the A_{1g} class is quite definite. The product ratio seems a trace small but is satisfactory. The only point requiring comment in remaining Raman active classes is the use of 313 for both no. 9b and 10b. One might wish to assign the faint line at 389 cm.$^{-1}$ to one or the other of these vibrations. The product rule prevents this unless utterly unreasonable values are assigned to other frequencies.

In the infrared active classes the assignments are quite satisfactory. There are no data below 500 cm.$^{-1}$ but the frequencies (18b) = 232 and (11) = 170 appear in combination tones: 540 obs. = (9b) + (18b) = 545 calcd. and 635 obs. = (6a) + (11) = 630 calcd. Vibration 16b must lie fairly near 400 cm.$^{-1}$; thus the faint Raman line at 389 is quite acceptable. Nos. (11) and (16b) appear in the Raman in violation of selection rules. The completely inactive class A_{1u} fortunately comprises vibrations essentially unchanged from benzene so that no real doubt arises here.

On the whole the assignment for *p*-xylene may be classed as very satisfactory.

m-**Xylene.**—As has been already mentioned, a number of the frequencies in the *m*-xylene should be the same as in mesitylene and have been so assigned. The symmetry C_{2v} of *m*-xylene (and of toluene and *o*-xylene) permits all lines in the Raman and all but one class in the infrared. Thus, although all frequencies may be expected in the spectra, the selection rules are of little help in sorting them out. This must be compensated by reasoning which may be described as interpolation between benzene and mesitylene. Everything considered the assignment is quite satisfactory, although it is certainly not unique.

TABLE XIX

VIBRATIONAL ASSIGNMENT FOR *p*-XYLENE

(Methyl groups in positions 1 and 4)

Symmetry class	No.	Benzene	*p*-Xylene			Ratio of products
A_{1g} $R_{(p)}$ –	1	992	826	R(p)	—	0.238
	2	3062	(3062)			
	6a	606	460	R(p)		
	7a	3047	1204	R(p)	—	
	8a	1596	1616	R	—	
	9a	1178	1182	R	—	
	M3	—	1377	R(p)	—	
	M1	—	(2950)			
B_{1g} $R_{(d)}$ –	10a	849	811	R	—	.95
	x rot.	I = 145	I = 156			
	i rot.	—	I = 5.09			
B_{2g} $R_{(d)}$ –	4	685	697	R	—	.179
	5	1016	959	R	—	
	10b	849	~313	R ?	—	
	y rot.	I = 145	I = 578			
	M6	—	1152	R	—	
	M4	—	1451	R(d)	—	
	M2	—	(2950)			
B_{3g} $R_{(d)}$ –	3	1298	~1200	R ?	—	.170
	6b	606	644	R(d)	—	
	7b	3047	(3047)			
	8b	1596	1575	R(d)	(IR?)	
	9b	1178	313	R(d)		
	z rot.	I = 291	I = 724			
	M6	—	1152	R	—	
	M4	—	1451	R ?	—	
	M2	—	(2950)			
A_{1u} — —	16a	400	(400)	—		.99
	17a	985	971	(R)	(IR?)	
	i rot.	—	I = 5.09			
B_{1u} — IR	12	1010	720	—	IR	.245
	13	3046	(3046)			
	18a	1037	1030	—	IR	
	19a	1485	1525	—	IR	
	20a	3080	1200	—	IR	
	x trans.	M = 78	M = 106			
	M3	—	1380	—	IR	
	M1	—	(2950)			
B_{2u} — IR	14	1693	1640	—	IR	.171
	15	1170	1100	—	IR	
	18b	1037	(232)	—	IR ?	
	19b	1485	1450	—	IR	
	20b	3080	(3080)			
	y trans.	M = 78	M = 106			
	M6	—	~1100	—	IR ?	
	M4	—	~1450	—	IR ?	
	M2	—	(2950)			
B_{3u} — IR	11	671	170	(R)		.172
	16b	400	389	(R)		
	17b	985	800	—	IR	
	z trans.	M = 78	M = 106			
	M6	—	~1100	—	IR	
	M4	—	~1450	—	IR ?	
	M2	—	(2950)			

o-**Xylene.**—By far this is the worst assignment of the group. Two Raman active frequencies (16a and 18a) must lie in the 300–500 range where none are observed. Nor can the remaining fre-

TABLE XX

VIBRATIONAL ASSIGNMENT FOR *m*-XYLENE

(Methyl groups in positions 3 and 5)

Symmetry class	No.	Benzene	*m*-Xylene			Ratio of products
A_1 $R_{(p)}$ IR	1	992	998	R(p)	—	(0.0422) ‖ (.171)(.247)
	2	3062	(3062)			
	6a	606	538	R	—	
	7a	3047	(3047)			
	8a	1596	1592	R		
	9a	1178	1167	R	—	
	12	1011	724	R	—	
	13	3046	(3046)			
	18a	1037	224	R		
	19a	1485	(1320)	—		
	20a	3080	1247	R(p)	—	
	x trans.	M = 78	M = 106			
	M6	—	1090	R	IR	
	M4	—	1448	R	IR	
	M3	—	1375	R(p)		
	M2	—	(2950)			
	M1	—	(2950)			
B_1 $R_{(d)}$ IR	3	1298	1262	R	—	(.0419) ‖ (.171)(.245)
	6b	606	514	R	IR	
	7b	3047	945	R	IR	
	8b	1596	1613	R(d)		
	9b	1178	1152	R	IR	
	14	1693	(1660)	—		
	15	1170	1197			
	18b	1037	310	R	IR	
	19b	1485	(1470)	—		
	20b	3080	(3080)			
	y trans.	M = 78	M = 106			
	z rot.	I = 291	I = 699			
	M6	—	1031	R	IR	
	M4	—	1448	R	IR	
	M3	—	(1350)	—	—	
	M2		(2950)			
	M1		(2950)			
A_2 $R_{(d)}$ —	10a	849	276	R		.169
	16a	400	439	R		
	17a	985	830	R ?	—	
	x rot.	I = 145.3	I = 475			
	i rot.	—	I = 5.23			
	M6	—	1090	R	—	
	M4	—	(1470)	?	?	
	M2	—	(2950)			
B_2 $R_{(d)}$ IR	4	685	690	—	IR	.177
	5	1016	890	—	IR	
	10b	849	770	R	IR	
	11	671	200	R		
	16b	400	485	R	IR	
	17b	985	880	—	IR	
	y rot.	I = 145.3	I = 233			
	z trans.	M = 78	M = 106			
	i rot.	—	I = 5.23			
	M6	—	1031	R	IR	
	M4	—	(1470)	?	?	
	M2	—	(2950)			

quencies be reliably enough assigned to permit definite product rule calculations for these two. Many of the individual frequencies are definite, but many others are merely reasonable. In a

TABLE XXI

VIBRATIONAL ASSIGNMENT FOR *o*-XYLENE

(Methyl groups in positions 2 and 3)

Symmetry class	No.	Benzene	*o*-Xylene			Ratio of products
A_1 $R_{(p)}$, IR	1	992	733	R(p)	?	(0.409) ‖ (.170)(.240)
	2	3062	(3062)			
	6a	606	582	R(p)	IR	
	7a	3047	1223	R(p)	?	
	8a	1596	1584	R	IR	
	9a	1178	1117	R	IR	
	14	1693	(1680)	—		
	15	1170	1156	R	—	
	18b	1037	180	R		
	19b	1485	(1550)		—	
	20b	3080	(3080)			
	y trans.	M = 78	M = 106			
	M6	—	1051	R(p)	?	
	M4	—	1450	R	IR	
	M3	—	1386	R(p)	—	
	M2	—	(2950)			
	M1	—	(2950)			
B_1 R, IR	3	1298	1240	—	IR	(.0420) ‖ (.172)(.244)
	6b	606	506	R(d)	IR	
	7b	3047	1275	—	IR	
	8b	1596	1606	R(d)	IR	
	9b	1178	1015	—	IR	
	12	1011	740	?	IR	
	13	3046	(3046)			
	18a	1037	(360)	—		
	19a	1485	1450	R	IR	
	20a	3080	(3080)			
	z rot.	I = 291	I = 639			
	x trans.	M = 78	M = 106			
	M6	—	1156	R	—	
	M4	—	1450	R	IR	
	M3	—	1376	R	—	
	M2	—	(2950)			
	M1	—	(2950)			
A_2 $R_{(d)}$ −	4	685	(685)	—	—	(.173)
	5	1016	862	R	—	
	10b	849	256	R		
	16a	400	(430)	—	—	
	17a	985	823	R	—	
	y rot.	I = 145.3	I = 261			
	i rot.	—	I = 5.17			
	M6	—	1156	R	—	
	M4	—	1450	R	IR	
	M2	—	(2950)			
B_2 $R_{(d)}$, IR	10a	849	770	—	IR	.170
	11	671	640	—	IR	
	16b	400	148	R		
	17b	985	982	R	IR	
	x rot.	I = 145.3	I = 388			
	z trans.	M = 78	M = 106			
	i rot.	—	I = 5.17			
	M6	—	1156	R	—	
	M4	—	1450	R	IR	
	M2	—	(2950)			

statistical sense it is supported by the heat capacity and entropy calculations.

Toluene.—This assignment is quite definite. The Raman polarization data are more extensive, which is very helpful. On the basis of polarization data and general reasonableness one may consider the A$_1$ class as definitely correct. Vibration 9a should be unchanged from benzene, where it is depolarized. Thus it is not surprising that it should be reported as depolarized in toluene even though it falls in the totally symmetric-polarized class. The A$_2$ class, although Raman active by group theory, actually consists of vibrations unchanged from benzene. Hence, one expects to find 10a of moderate intensity, 16a very weak, and 17a not observed at all. This is exactly the actual state of affairs. The remaining classes B$_1$ and B$_2$ are not quite as definite but are entirely satisfactory. The very weak 467 cm.$^{-1}$ line assigned to 16b is reported as polarized, whereas it should be depolarized. However, it cannot be a totally symmetric fundamental, nor can it be accounted for as an overtone of that symmetry. Therefore we feel justified in disregarding the polarization data.

Methyl Group Vibrations.—Discussion of the internal vibrations of the methyl groups has been largely omitted above because they are essentially the same from one molecule to another. M1 and M2 are near 2950 cm.$^{-1}$ and in virtually every case the lines overlap one another so that too few are resolved. M3 lies very close to 1380 cm.$^{-1}$ in all cases and is easily identified. Similarly M4 is found very near 1450 cm.$^{-1}$ in every case. The various components are virtually never resolved. In *o*-xylene Desreux reports continuous absorption from 1442 to 1464 cm.$^{-1}$. Only M6 appears to vary appreciably in frequency and its identification is in many cases difficult. The expected range is 1000–1200 cm.$^{-1}$. These values are all entirely reasonable by comparison to the methyl halides and other simple molecules containing methyl groups.

TABLE XXII

VIBRATIONAL ASSIGNMENT FOR TOLUENE

(Methyl group in position 1)

Symmetry class	No.	Benzene	Toluene			Ratio of products
A$_1$ R$_{(p)}$, IR	1	992	1002	R(p)	IR?	0.246
	2	3062	(3062)			
	6a	606	521	R(p)	IR ?	
	7a	3047	1210	R(p)	—	
	8a	1596	1603	R	IR	
	9a	1178	1175	R(?)	IR	
	12	1011	785	R(p)	IR	
	13	3046	(3046)			
	18a	1037	1030	R(p)	IR	
	19a	1485	1483	R(p)	IR	
	20a	3080	(3080)			
	x trans.	M = 78	M = 92			
	M3	—	1380	R(p)	IR	
	M1	—	(2950)			
B$_1$ R$_{(d)}$, IR	3	1298	1282	R(d)	—	.177
	6b	606	622	R(d)	IR	
	7b	3047	(3047)			
	8b	1596	1586	R	IR	
	9b	1178	1155	R	IR	
	14	1693	1630	R	—	
	15	1170	1070	—	IR	
	18b	1037	340	R(d)		
	19b	1485	1310	R	IR	
	20b	3080	(3080)			
	y trans.	M = 78	M = 92			
	z rot.	I = 291	I = 494			
	M6	—	1060		IR ?	
	M4	—	1495	R	IR	
	M2	—	(2950)			
A$_2$ R$_{(d)}$$^{-}$	10a	849	842	R	?	1.0
	16a	400	405	R(d)	—	
	17a	985	(985)	—	—	
	x rot.	I = 145.3	I = 150.6			
	i rot.	—	I$_r$ = 5.08			
B$_2$ R$_{(d)}$, IR	4	685	695	—	IR	.179
	5	1016	943	—	IR	
	10b	849	730	R	IR	
	11	671	216	R		
	16b	400	467	R(?)		
	17b	985	890	R(d)	IR	
	y rot.	I = 145.3	I = 350			
	z trans.	M = 78	M = 92			
	M6	—	1190	R(d)	IR	
	M4	—	1455	R	IR	
	M2	—	(2950)			

Discussion

For the sake of brevity, tables of all observed lines and their assignments have been omitted This is quite justifiable since the difficulty is not to account in some way for all observed lines, but rather to show which of the many possible assignments is the correct one.

One very striking feature of the Raman spectra of these and other benzene derivatives is the behavior of the strong line near 1000 cm.$^{-1}$. Kohlrausch[41] first discussed certain features of this line, but Langseth and Lord have explained it more completely. We wish to add certain other features. Vibrations 1 and 12 are separated by symmetry in benzene itself (or any completely substituted derivative), but their frequencies are so nearly equal that any small perturbation will cause them to recombine with one another. Specifically, if the perturbation affects one or more of the 1, 3 and 5 positions but does not affect the 2, 4 or 6 positions, then two "trigonal vibrations" arise from the sum and difference of 1 and 12. Here in one case only the 1, 3, 5 carbons move; in the other the 2, 4, 6 atoms move. The 2, 4, 6 trigonal mode then takes almost exactly the average of frequencies 1 and 12 which is 1001.5 cm.$^{-1}$. Thus toluene, *m*-xylene, and

(41) Kohlrausch, *Naturwissenschaften*, **25**, 635 (1937).

mesitylene have lines at 1002, 998, and 998 cm.$^{-1}$, respectively. Similarly, iodo, bromo, chloro, *m*-dichloro and *sym*-trichlorobenzenes[42,43] show, respectively, 1001, 1002, 1004, 999 and 995 cm.$^{-1}$ lines. Intensity and polarization data make this situation even more striking. This line is always one of the most intense lines of the spectrum and is highly polarized.

Similar results arise when three of the positions remain substituted with a given group. Thus the 1, 3, 5 trigonal mode in mesitylene gives a line 575 cm.$^{-1}$ which is very intense and strongly polarized. In 1,2,3,5-tetramethylbenzene[36] (isodurene) we find a line at 573 cm.$^{-1}$. In hexamethylbenzene[36] the motion changes to no. 1 and takes the slightly lower value 550 cm.$^{-1}$. Likewise in the chloro compounds, 1,3,5-trichloro, 1,2,3,5-tetrachloro, pentachloro, and hexachlorobenzenes show lines at 375, 380, 383, and 375 cm.$^{-1}$, all very intense.

Compounds in which both the 1, 3, 5 and 2, 4, 6 sets of positions are partially substituted show no comparable lines in this region. Thus for *o*-xylene they are at 827 and 1204 cm.$^{-1}$. In view of these facts it appears as if this feature could be used safely for determining the positions of substituents under suitable conditions.

Comparisons of calculated and observed heat capacities and entropies are made in Part V. It is sufficient to state here that the agreement is everywhere satisfactory.

Part V. Statistically Calculated Thermodynamic Quantities. Internal Rotation of Methyl Groups Attached to a Benzene Ring. General Discussion

As was stated in the general introduction, one of the primary purposes of this research was the determination of the barriers to internal rotation in this series of substances. We are now ready to calculate these quantities. Certain other phases also deserve discussion.

Statistically Calculated Entropies.—The molecules in this series fall in the class of rigid frames with attached symmetrical tops. Therefore, their moments of inertia for over-all rotation are independent of internal rotation. Furthermore, the tops are very light compared to the frame. Hence they may be treated by the methods of Pitzer and Gwinn.[44] It is convenient to calculate the various quantities assuming free rotation (zero potential barrier), and then to take the corrections for restriction of rotation from the tables given there. Other necessary parameters, masses, moments of inertia, and vibration frequencies are given in the tables of Part IV. The entropy results are summarized in Table XXIII. The complete symmetry number for the whole molecules is readily computed by taking the symmetry number for the corresponding benzene substituted with single atoms (such as chlorine) and multiplying it by three for each methyl group. Thus for benzene $\sigma = 12$, for toluene $\sigma = 6$, for *o*- and *m*-xylene, $\sigma = 18$, for *p*-xylene $\sigma = 36$, and for mesitylene $\sigma = 162$. The factoring of these numbers for the various degrees of freedom is much more complex and will not be discussed since it is of no importance for the desired calculations. It affects the itemization in Table XXIII but not the totals.

Values of the quantity $S + R \ln \sigma$ are also given in Table XXIII since they permit comparisons on a more equitable basis.

One may note from Table XXIII first, that the entropy of benzene checks well within the estimated error. Second, the entropies of toluene, *m*-xylene and *p*-xylene all agree with the values calculated for free internal rotation within the respective experimental errors. However, the calculated entropies are all higher than the experimental values, which suggests a slight restricting barrier. Third, the calculated entropy of *o*-xylene is definitely too large, indicating considerable restriction of rotation. Finally, the values of $S + R \ln \sigma$ increase by increments of about 11 cal. per degree per methyl group, excepting of course *o*-xylene. If one assumes this value, and that the entropy decrease for *o*-xylene (1.7 cal./deg.) is generally applicable whenever two methyl groups are adjacent, one may estimate the entropies of two more highly substituted benzenes as shown in Table XXIV.

When three or more methyl groups are adjacent even higher restrictions to rotation with correspondingly larger entropy decreases may be expected. Quantitative predictions, however, are not yet possible.

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(42) Murray and Andrews, *J. Chem. Phys.*, **1**, 406 (1933); Swaine and Murray, *ibid.*, **1**, 513 (1933).

(43) Dadieu, Pongratz and Kohlrausch, *Monatsh*, **61**, 426 (1932).

(44) Pitzer and Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

TABLE XXIII

STATISTICALLY CALCULATED ENTROPIES

All values for hypothetical ideal gases at 298.16°K. and 1 atm. Units: cal. per degree mole

Entropy terms	Benzene	Toluene	*o*-Xylene	*m*-Xylene	*p*-Xylene	Mesitylene
Translation and over-all rot.	59.73	66.60	66.53	66.72	66.56	65.92
Vibr.	4.70	7.94	12.47	11.97	12.26	15.62
Free internal rotation	...	2.19	7.17	7.19	5.76	10.80
Calcd.-free rot.	64.43	76.73	86.17	85.88	84.58	92.34
Exper.	64.39 ± .3	76.44 ± .3	84.50 ± .3	85.60 ± .3	84.27 ± .3	....
$S_f - S$	...	0.29	1.67	0.28	0.31	...
S calcd. ($V_0 = 2000$)			84.53			
S calcd. + $R \ln \sigma$	69.37	80.26	91.91	91.61	91.68	102.43
S exp. + $R \ln \sigma$	69.33 ± .3	79.97 ± .3	90.24 ± .3	91.34 ± .3	91.39 ± .3	....

TABLE XXIV

ESTIMATED ENTROPIES FOR SOME METHYL BENZENES

(All values for hypothetical ideal gases at 298.16°K. and 1 atm.)

Subst.	$S + R \ln \sigma$	σ	S (cal./deg.)
1,2,4-Trimethylbenzene (pseudocumene)	100.7	27	94.2
1,2,4,5-Tetramethylbenzene (durene)	110.0	324	98.5

Statistically Calculated Heat Capacities.—The calculated heat capacity curves for the various gases are compared with the experimental points in Fig. 7. Potential barriers of 500 cal./mole were assumed except for *o*-xylene where the value is 2000 cal./mole. Considering all the data it appears likely that the experimental points for each substance show too much curvature because of some systematic error, possibly arising from the thermometer. The values for benzene below 400°K. from some of the other experimenters are likely to be too high because of gas imperfections.

The agreement is evidently satisfactory for benzene and for toluene, *m*-, and *p*-xylene assuming relatively free rotation of the methyl groups. In the case of *o*-xylene it is apparent as it was for the entropy that considerable restriction of rotation must be present.

Potential Barriers Restricting Internal Rotation.—The discussion above shows that for *m*- and *p*-xylene and toluene a very low potential barrier agrees with the experimental data. The gas heat capacity data set the more stringent upper limit, namely, about 1000 cal./mole.

It is of course true that the vibrational assignments are subject to question; however, no simple adjustment there will allow a higher potential barrier and still give agreement with both heat capacity and entropy. Thus increasing the potential barrier to internal rotation lowers the calculated entropy and raises the heat capacity. Lowering one or more vibration frequencies would increase the entropy but would also increase the heat capacity.

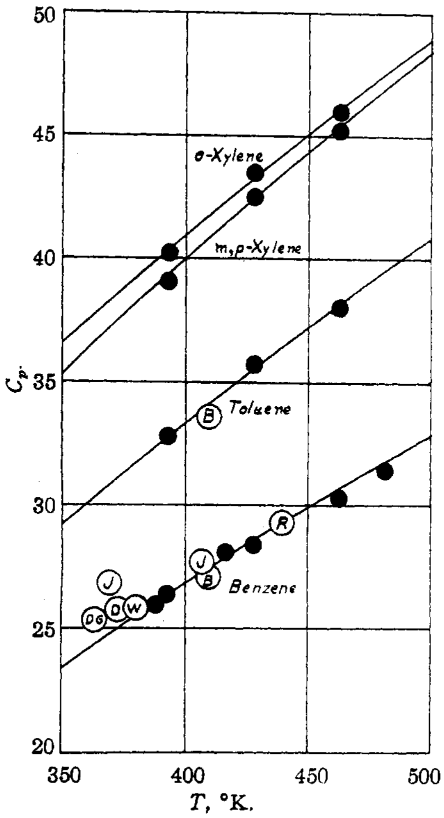

Fig. 7.—The heat capacity in the gas state of benzene, toluene, and the three xylenes: circles are experimental values; solid, this research; open, see footnotes. Curves are calculated: B, Bennewitz and Rossner[24]; D, Déjardin, *Ann. Phys.*, [9] **11**, 253 (1919); DG., Dixon and Greenwood, *Proc. Roy. Soc.* London, **105A**, 199 (1924); J, Jatkar, *J. Ind. Inst. sci.*, **22A**, Pt. II, p. 19 (1939); R, Regnault, *Mém. de l'acad. sci. France*, **26**, 1 (1862); W, Wiedemann, *Ann. chim. phys.*, **2**, 195 (1877). The very recent results of Montgomery and De Vries (THIS JOURNAL, **64**, 2375 (1942)) are not shown on the graph. They are about 1% higher than the curve for benzene and 2-3% for toluene.

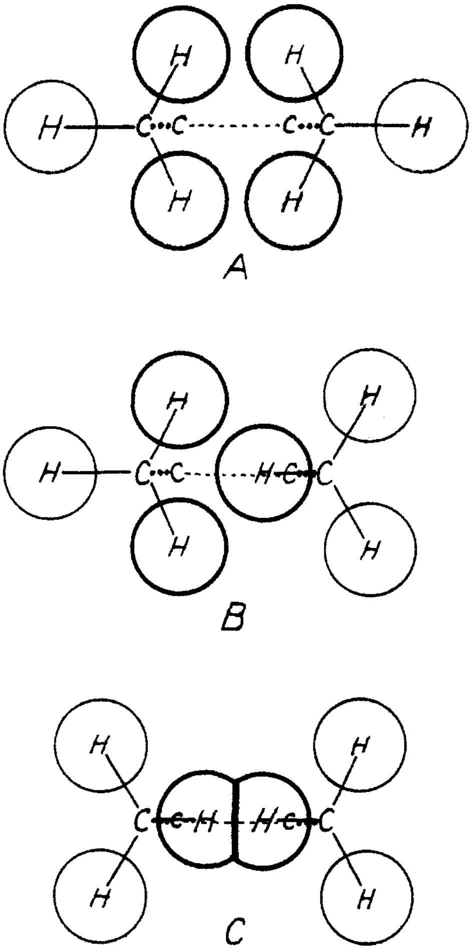

Fig. 8.—Schematic drawing illustrating various orientations of methyl groups in *o*-xylene.

At this point it is also of interest to recall the humps in the heat capacity curves of solid toluene, *m*- and *p*-xylene which were attributed in Part I to the beginning of internal rotational motion of some sort in the range 50–100°K. Forces arising from neighboring molecules must play some part in this effect so that it is impossible to make a simple quantitative interpretation. However, it seems unlikely that these results could be consistent with potential barriers in the free molecules much larger than about 500 cal. per mole.

In toluene or *m*- or *p*-xylene a very small potential barrier is quite reasonable, because the symmetry indicates six maxima and minima per revolution and no particularly large forces would be expected. A low barrier was also found for nitromethane where the symmetry calls for six maxima.

It is difficult to set up a really satisfactory potential function for *o*-xylene. Two extreme approximations may be described as (I)—no interaction term coupling the rotation of one methyl group to the other, just cosine type potential barriers acting on each methyl separately and (II)—only an interaction term such that the two methyls are like gears which can rotate freely in mesh but resist stripping. Examination of a scale model shows that neither approximation is reasonable. As can be seen from Fig. 8, methyl groups are not good gears. The meshed position, B in Fig. 8, involves no serious steric repulsions and the out of mesh position A is also reasonable on the same basis. Only positions near C should be of high energy on this basis. However, if only positions near C are set at high energy then agreement cannot be obtained with the experimental entropy. If one takes approximation (I) with A as the minimum position then B is higher in energy by V_0 while C is higher by $2V_0$. Actually position C should probably be still higher in energy but the effect of this would not be too large. Thus it seems best to use approximation (I) even though it cannot be entirely correct.

Another difficulty in the way of any exact analysis for *o*-xylene is the uncertainty of the vibrational assignment.

Using approximation (I) one finds from the entropy value a potential barrier height, V_0 = 2000 cal./mole. This gives the curve on Fig. 7 for the heat capacity which is in good agreement with experimental points. Therefore, this approximation should be reasonably satisfactory for further thermodynamic calculations.

Calculated Thermodynamic Functions.—The free energy function, $(H^0_0 - F^0_T)/T$, the heat content function, $H^0_T - H^0_0$, and the heat capacity have been calculated for gaseous benzene, toluene, all three xylenes, and mesitylene at various temperatures up to 1500°K. and are listed in Tables XXV to XXVII. The vibrational analyses of Parts III and IV are used together with a mean value of 500 cal. per mole

TABLE XXV

THE FREE ENERGY FUNCTION

$(H^0_0 - F^0_T)/T$ IN CAL. PER DEGREE MOLE

			Xylene			
T	Benzene	Toluene	ortho	meta	para	Mesitylene
298.16	52.98	62.20	65.74	67.89	66.48	71.07
400	56.75	66.97	71.88	73.75	72.36	77.98
500	60.32	71.44	77.57	79.21	77.82	84.38
600	63.81	75.75	82.93	84.43	83.03	90.46
800	70.42	84.02	93.18	94.42	92.96	102.02
1000	76.66	91.75	102.63	103.72	102.23	112.87
1500	90.60	109.03	123.52	124.44	122.89	136.82

TABLE XXVI

THE HEAT CONTENT FUNCTION $H^0_T - H^0_0$ IN KCAL.

T	Benzene	Toluene	Xylene ortho	Xylene meta	Xylene para	Mesitylene
298.16	3.415	4.314	5.604	5.330	5.364	6.290
400	5.78	7.27	9.31	8.91	8.91	10.46
500	8.79	10.98	13.84	13.36	13.33	15.59
600	12.32	15.35	19.10	18.57	18.51	21.61
800	20.66	25.64	31.42	30.86	30.72	35.80
1000	30.22	37.50	45.57	44.97	44.80	52.16
1500	57.5	71.3	86.1	85.4	85.2	99.2

TABLE XXVII

THE HEAT CAPACITY

C_p IN CAL. PER DEGREE MOLE

T	Benzene	Toluene	Xylene ortho	Xylene meta	Xylene para	Mesitylene
298.16	19.64	24.80	31.93	30.38	30.24	35.65
400	26.84	33.25	41.08	40.01	39.68	46.32
500	32.96	40.58	49.16	48.46	48.10	55.87
600	37.87	46.64	56.01	55.56	55.22	64.08
800	45.14	55.78	66.70	66.51	66.22	76.94
1000	50.25	62.27	74.36	74.29	74.08	86.14
1500	57.77	71.81	85.98	85.95	85.85	100.03

for the potential barriers to internal rotation for toluene, *m* and *p*-xylene, and mesitylene. For the rotation of the two methyl groups in *o*-xylene two independent three-fold potential barriers of 2000 cal. per mole height were assumed as discussed above.

The entropy is readily obtainable from the tabulated functions by the equation

$$S = \frac{H^0_T - H^0_0}{T} + \frac{H^0_0 - F^0_T}{T}$$

We may now compute the change in heat capacity with vaporization and compare the result with the coefficients of the log terms in the vapor pressure equations. The values of ΔC_p from heat capacity data are, for *o*-, *m*-, and *p*-xylene, respectively, −13.0, −13.4 and −13.7, while from the vapor pressure equations the values are −15.9, −13.3 and −9.9 cal. per degree. A consideration of the possible errors shows that the vapor pressure measurements must have been of high accuracy in order to have obtained ΔC_p values as satisfactory as these. The values from heat capacity data are, of course, the more reliable.

It is now possible to use the more reliable ΔC_p values to fix the coefficients of the log terms in the vapor pressure equations and evaluate the remaining constants to best fit the data. Such equations should be more reliable for extrapolation beyond the measured range but would not differ significantly within that range. However, increasing gas imperfection makes extrapolation to higher temperatures impractical while extrapolation to lower temperatures seems unimportant. Consequently it was not deemed worthwhile to revise the vapor pressure equations.

Heat Contents at the Absolute Zero.—Using the equilibrium results of Part II together with the values of $(H^0_0 - F^0_T)/T$ from Table XXV one obtains the results in Table XXVIII. Also included there are values of the heats of formation from the elements derived from heat of combustion data. The values 782.0 ± 1.0 and 935.5 ± 1.5 kcal. per mole were adopted for the heats of combustion of benzene and toluene, respectively, after considering the data of Richards and co-workers[45] and those of Roth and von Auwers.[46] Using the present results for the toluene–benzene–xylene reaction, one calculates for *o*-, *m*- and *p*-xylene, respectively, 1090.4, 1089.4 and 1089.9 kcal., which may be compared with revised values[45d] from Richards of 1090.8, 1090.8 and 1087.0 and with Roth's value for *m*-xylene 1089.5 kcal. It is apparent that the differences between the isomers as found by Richards bear no connection to the true differences. This is not surprising when one considers the very large total heat of combustion being measured.

Calculated Values for Certain Equilibria.—By using the data of Tables XXV and XXVIII

TABLE XXVIII

HEAT CONTENT DIFFERENCES OF GASES AT THE ABSOLUTE ZERO

Reaction	ΔH^0_0, kcal./mole
m-xylene = *p*-xylene	0.43 ± 0.2
m-xylene = *o*-xylene	.62 ± 0.2
p-xylene = *o*-xylene	.19 ± 0.3
2 toluene = benzene + *m*-xylene	.23 ± 0.3
elements = benzene	48.6 ± 1.0
elements = toluene	51.6 ± 1.5
elements = *m*-xylene	54.8 ± 2.0

TABLE XXIX

EQUILIBRIA AMONG THE XYLENES AND BETWEEN TOLUENE, BENZENE, AND XYLENE AT VARIOUS TEMPERATURES IN THE GAS STATE

$$K_m = \frac{P_{\text{benzene}}\, P_{m\text{-xylene}}}{P^2_{\text{toluene}}}, \qquad K_t = \frac{P_{\text{benzene}}\, P_{\text{total xylene}}}{P^2_{\text{toluene}}}$$

T	Equil., % ortho	Equil., % meta	Equil., % para	K_m	K_t
298.16	9	74	17	0.12	0.16
400	12	68	20	.13	.19
500	15	64	21	.15	.23
600	17	62	21	.16	.26
800	21	58	21	.17	.30
1000	24	55	21	.19	.34
1500	27	52	21	.20	.39

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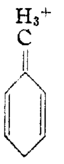
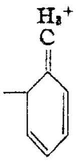
(45) (a) Richards and Jesse, THIS JOURNAL, **32**, 268 (1910); (b) Richards and Barry, *ibid.*, **37**, 993 (1915); (c) Richards and Davis, *ibid.*, **42**, 1599 (1920); (d) Swietoslawski and Bobinska, *ibid.*, **49**, 2476 (1927).

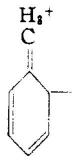
(46) Roth and von Auwers, *Ann. chim.*, **407**, 109 (1914).

the equilibrium composition of the xylenes was computed for various temperatures. The equilibrium constants for the benzene—toluene—xylene reaction were also obtained. These are given in Table XXIX. It is interesting to note that the percentage of para stays almost constant while ortho increases in abundance threefold. The restriction of internal rotation and higher energy content of ortho are the factors causing this.

Discussion.—It is now interesting to see what explanation may be offered for the energy differences among the xylenes. Toluene has a small but definite dipole moment, the methyl group (particularly the hydrogen atoms) being positive with respect to the ring. This might be formulated in terms of hyperconjugation[47] or resonance[48] structures such as





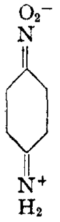


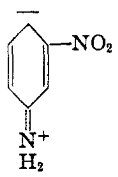
It is apparent that the negative charge appears only in ortho and para positions. Such resonance forms are of course connected to the ortho–para orienting effect of a methyl group with respect to substitution reactions.

Now in *m*-xylene the two methyl groups lead to resonance forms placing the negative charges in the same places on the ring. In *o*- or *p*-xylene on the contrary the two methyl groups give resonance forms which place the negative charges on different sets of atoms in the ring. According to the experimental results the former is the preferred form, *i. e.*, of lower energy. Although it is not difficult to suggest "theories" in accord with this, now that the facts are known, the writers are not aware of any well defined theory that clearly predicts this result. Rather we prefer now to predict from this result that in other situations of this type the meta form will be more stable.

Among the trimethylbenzenes 1,3,5 should have lowest energy being "all meta" with 1,2,4 and 1,2,3 about equal. It is likely, however, that the 1,2,3 isomer is subject to some steric repulsion among the methyl groups so that it would be definitely less stable than 1,2,4.

Similar reasoning would apply to other di- and tri-substituted benzenes so long as either identical or similar groups are present. However, in a case such as nitroaniline when the groups have resonance effects of opposite sign the ortho–para orientation would be preferable since both substituents





can enter into the same resonance form.

Summary

1. **Thermodynamic Data.**—The following thermodynamic quantities were measured, calculated, or taken from the literature for each of the substances, benzene, toluene, *o*-, *m*- and *p*-xylene: the heat capacity of solid, liquid and gas in appropriate ranges from 15 to 470°K.; the heats of fusion and vaporization; the melting points and vapor pressures; the entropies of liquid and gas; and the free energy function $(H^0_0 - F^0_T)/T$, the heat content, and the heat capacity over the range 298–1500°K.

The freezing point diagram for the ternary system *o*-, *m*- and *p*-xylene was calculated and certain points experimentally verified.

The direct isomerization reaction of the xylenes, catalyzed by aluminum bromide and hydrogen bromide, led to a direct measure of the equilibrium composition. Using the same catalyst, the equilibrium constant for the reaction 2 toluene = benzene + xylene (equil.) was found to be between 0.15 and 0.22 at 323°K. From these data the various thermodynamic constants for the isomerization and the toluene, benzene, xylene reactions were calcuated.

A few of the most important values for the xylenes are listed in the following table.

MISCELLANEOUS THERMODYNAMIC CONSTANTS FOR THE XYLENES

	Ortho	Meta	Para
Melting point, °K.	247.82	225.27	286.39
Heat of fusion, cal./mole	3250	2765	4047
Heat of vapn. (298°K.), cal./mole	10470	10160	10110

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(47) Mulliken, Rieke and Brown, THIS JOURNAL, 63, 41 (1941).

(48) See, for example, Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, or Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall, New York, N. Y., 1941.

	Ortho	Meta	Para
Vapor press. (298°K.), mm.	6.64	8.39	8.87
Entropy of vap. (298°K.) (liq. to hypoth. gas 1 atm.), cal./deg.	25.70	25.13	25.07
Entropy of the gas (298°K.), cal./deg.	84.50	85.60	84.27
Equil. comp. (323°K.), %	10	72	18

Various thermodynamic functions were calculated for mesitylene from molecular structure data, the gas entropy at 298°K. being 92.34 cal. per degree. The entropies of pseudocumene (1,2,4-trimethylbenzene) and durene (1,2,4,5-tetramethylbenzene) were estimated to be 94.2 and 98.5 cal. per degree, respectively, in the gas state at 298°K.

2. **Molecular Structure Data.**—By consideration of the lines appearing in the infrared and Raman spectra of liquid benzene (but not of gaseous benzene) in violation of the simple selection rules, it was possible to complete the assignment of fundamental vibration frequencies. Although a few values are not completely certain, all are reasonable from the point of view of the force constants of the benzene molecule. The spectra of the simpler deuterated benzenes were also considered.

The fundamental vibration frequencies were selected for toluene, all three xylenes, and mesitylene using Raman and infrared spectra from the literature. A modification of the Teller–Redlich product rule appropriate for methyl substitution was of great assistance in these assignments. The results vary from reasonably certain selections for some substances to somewhat arbitrary ones for others.

Attention is called to the striking behavior of the 1000 cm.$^{-1}$ line in benzene derivatives which are substituted in only 1,3,5-positions. Corresponding effects are observed where the trigonal positions are all similarly substituted. It is suggested that the Raman spectra might be used to determine the position of substituents in favorable cases.

Using these frequencies the vibrational entropy and heat capacity contributions can be calculated and the corresponding quantities for internal rotation of methyl groups obtained. The results indicate relatively free rotation of methyl groups in toluene, *m*- and *p*-xylene but about a 2000 cal. potential barrier for *o*-xylene. These results are shown to be reasonable in terms of steric effects.

The xylene equilibrium data show the meta compound to have lowest energy and suggest that meta orientation of identical or similar groups may be generally the most stable.

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[CONTRIBUTION FROM THE EASTMAN KODAK COMPANY]

Carbamates of Cellulose and Cellulose Acetate. I. Preparation[1]

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Reactions of cellulosic materials with isocyanates have been described in the patent literature. According to a U. S. patent,[2] cellulose or its derivatives containing free hydroxyl groups react with aliphatic or aromatic isocyanates in the presence of tertiary organic bases. A Swiss patent[3] describes the treatment of cellulose with phenyl isocyanate with or without the addition of a small amount of pyridine. The cellulosic structure was not changed but the material increased in weight and the product contained nitrogen. Another U. S. patent[4] covers the production of acetone-soluble organic acid esters of cellulose containing carbamyl groups. Examples in all of these patents include only phenyl isocyanate for preparing derivatives, although the claims in several cases are of a general nature.

In addition to the chemical nature of the isocyanate, several other factors must be considered in the preparation of carbamates of cellulose. Among these are the nature of the cellulosic material, the reaction solvent, concentration of reagent and the time and temperature of reaction. This paper reports a study of the reaction of both aliphatic and aromatic isocyanates on cellulosic

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[1] Presented before the Division of Cellulose Chemistry at the 104th meeting of the American Chemical Society at Buffalo, New York.

[2] P. E. C. Goissedet, U. S. Patent 1,357,450 (November 2, 1920).

[3] Gesellschaft für Chemische Industrie, Basel, Swiss Patent 142,749 (December 16, 1930).

[4] C. J. Malm and G. F. Nadeau, U. S. Patent 1,991,107 (February 12, 1935).