

Three melting points were made simultaneously. In one tube was placed a known sample of glucose penta-acetate, prepared as described in Part I; in the second tube, the plate-form crystals; and in the third, a mixture of the two. The melting points were 111.5, 110–111 and 108.5–110°, respectively.

The filtrate (R) was then examined. Evaporation at room temperature yielded plate-form crystals (S). These were removed by filtration, dissolved in ether and evaporated, giving a gum. This was taken up in alcohol and again evaporated at room temperature. Plate-form crystals (T) separated, changing in the course of two days mostly to the more usual needle-form of α -glucose penta-acetate. These were filtered off and washed with ether. Melting points of these crystals, of α -penta-acetyl glucose and a mixture of these two were taken simultaneously. The melting points were 108–110.5, 111.5 and 108–110.5°, respectively. The filtrate (U) was observed to give a further yield of needle-like crystals upon evaporation.

Summary

1. Two crystalline forms of α -glucose penta-acetate have been isolated from the chloroform extract of the precipitation liquid of the acetolysis of cellulose, without reacylation.

2. Further yields of glucose penta-acetate and of cellobiose octa-acetate have been obtained by the reacylation of the gum obtained after isolation of crystalline glucose acetate, mentioned in 1.

3. α -Glucose penta-acetate has been isolated from the mother liquors of the crystallization of crude cellobiose octa-acetate obtained in the acetolysis of cellulose.

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THERMAL DATA ON ORGANIC COMPOUNDS. VII. THE HEAT CAPACITIES, ENTROPIES AND FREE ENERGIES OF TWELVE AROMATIC HYDROCARBONS¹

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In the preceding paper⁵ the results of a study of the heat capacities, entropies and free energies of some saturated, non-benzenoid hydrocarbons were reported. The present investigation is essentially similar but deals with aromatic hydrocarbons. We shall first present heat capacity data

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⁵ Parks, Huffman and Thomas, *THIS JOURNAL*, **52**, 1032 (1930).

for the following twelve compounds: benzene, ethylbenzene, *tert.*-butylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, hexamethylbenzene, diphenyl, diphenylmethane, triphenylmethane, dibenzyl and naphthalene. We shall then utilize these data to calculate their molal entropies by the aid of the third law of thermodynamics. From the latter results, the corresponding free energy values will be derived.

Materials

Benzene.—The benzene was a very pure sample of "reagent quality" obtained from the Mallinckrodt Chemical Works. It was dried over phosphorus pentoxide and then carefully fractionated by distillation. The middle portion was next subjected to six successive fractional crystallizations. The final product gave a very sharp melting point (5.5°) during the determination of the heat of fusion, indicating a high degree of purity.

Ethylbenzene and *Tert.*-butylbenzene.—These compounds were synthesized by the Friedel-Crafts reaction in the chemical laboratory of Johns Hopkins University. They were then purified by three fractional distillations. Mr. L. M. Ellis, Jr., made the last two of these distillations, using a special still which had an eighteen-inch packed column with a heated jacket and reflux head. The ethylbenzene thus obtained boiled at 135.5 – 135.7° at 756 mm.; its specific gravity was 0.8639 at $23.4^\circ/4^\circ$. For the *tert.*-butylbenzene the boiling temperature was 168.5 to 168.8° at 758 mm.; specific gravity, 0.8636 at $23.3^\circ/4^\circ$. These compounds gave sharp melting points at 178.0 and $215.0^\circ\text{K}.$, respectively.

***o*-Xylene.**—Eastman's *o*-xylene (boiling range 0.2°) was carefully fractionated twice in a special still. The sample employed in the specific heat determinations had an almost constant boiling point of 144.5° at 760 mm.

***m*-Xylene.**—The samples of *m*-xylene which we first obtained, although supposedly quite pure, melted to give a cloudy liquid and an anomalous heat absorption a few degrees above the melting point. Presumably these phenomena were due to impurities. We finally employed a sample of Kahlbaum's "purest," which we subjected to a careful fractional distillation as well as to several fractional crystallizations. It was then dried over anhydrous copper sulfate and redistilled (b. p. 139.0° at 760 mm., range less than 0.15°). This purification process apparently lowered the temperature of the heat absorption region to a point about 50° below the melting temperature and also somewhat decreased its magnitude. While the entropy value which we have obtained for *m*-xylene is probably good to within 1%, the sample was undoubtedly the least satisfactory of any employed in this investigation, as it showed considerable premelting in addition to the peculiar heat effect just mentioned.

***p*-Xylene.**—Kahlbaum's purest material was subjected to twelve fractional crystallizations. The resulting product melted sharply at 13.2° .

Diphenylmethane.—Eastman's diphenylmethane was subjected to four fractional crystallizations. The resulting product melted sharply at 25.2° .

Hexamethylbenzene, Diphenyl, Triphenylmethane and Dibenzyl.—These were relatively pure compounds, obtained from the Eastman Kodak Co. In all cases they were subjected to two or more fractional crystallizations from ethyl alcohol. The melting points of the final materials were, respectively, hexamethylbenzene 164° , diphenyl 69.1° , triphenylmethane 92.5° and dibenzyl 51.0° . They were apparently free from inorganic impurities, as samples on ignition left no residue.

Naphthalene.—Kahlbaum's naphthalene was twice crystallized from pure benzene. It was then fractionally distilled, the entire sample coming over between 217.8 and

218.0°. The middle third was finally sublimed before use in the specific heat determinations.

Experimental Results

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and the fusion data. The apparatus and details of experimental procedure have been fully described in other places.⁶ In view of the accuracy of the various measurements involved, the error in the experimental values thereby obtained is probably less than 1%, except in so far as impurities in an hydrocarbon sample, such as that of *m*-xylene, may cause premelting or otherwise influence the results.

The specific heats and the fusion data, expressed in terms of the 15° calorie⁷ and with all weights reduced to a vacuum basis, appear in Tables I and II.

TABLE I
SPECIFIC HEATS
Benzene: Crystals

Temp., °K.	92.6	97.9	103.0	113.8	129.8	143.0	150.7	162.2
C_p per g.	0.148	0.152	0.156	0.165	0.180	0.192	0.200	0.211
Temp., °K.	178.1	195.0	201.5	218.1	229.7	239.5	250.1	259.5
C_p per g.	0.229	0.250	0.260	0.283	0.301	0.317	0.335	0.355

Liquid

Temp., °K.	281.1	282.1	286.3	289.9	294.9	300.0
C_p per g.	0.403	0.404	0.406	0.408	0.410	0.414

Ethylbenzene: Crystals

Temp., °K.	92.7	98.0	105.5	112.6	123.1	131.1
C_p per g.	0.150	0.157	0.164	0.171	0.182	0.190
Temp., °K.	140.2	149.4	156.5	162.2	167.5	172.6
C_p per g.	0.199	0.209	0.217	0.224	0.234	0.263

Liquid

Temp., °K.	185.0	188.4	194.0	210.7	220.2	230.5	239.1	254.9
C_p per g.	0.352	0.354	0.356	0.364	0.368	0.372	0.377	0.385
Temp., °K.	275.3	278.4	283.0	287.9	293.0	297.4	301.2	304.9
C_p per g.	0.396	0.398	0.402	0.404	0.407	0.409	0.412	0.414

Tert.-butylbenzene: Crystals

Temp., °K.	92.2	97.9	104.2	111.6	118.2	126.2	131.0	137.9
C_p per g.	0.140	0.148	0.155	0.164	0.173	0.178	0.188	0.197
Temp., °K.	151.3	162.7	170.8	178.4	185.9	192.9	199.8	206.0
C_p per g.	0.215	0.229	0.239	0.249	0.259	0.269	0.282	0.297

⁶ Parks, THIS JOURNAL, 47, 338 (1925); also Parks and Kelley, *J. Phys. Chem.*, 30, 47 (1926).

⁷ The factor 0.2390 has been used in converting from the joule to the 15° calorie.

TABLE I (Continued)

	Liquid							
Temp., °K.	220.4	229.6	240.0	251.4	261.9	275.2	283.0	294.3
C_p per g.	0.372	0.378	0.384	0.391	0.397	0.408	0.413	0.424
	<i>o</i> -Xylene: Crystals							
Temp., °K.	90.1	93.3	96.9	109.3	123.0	136.0	148.1	161.0
C_p per g.	0.149	0.152	0.156	0.170	0.186	0.199	0.213	0.226
Temp., °K.	177.1	194.2	199.1	204.6	210.0	212.9	217.7	223.8
C_p per g.	0.242	0.261	0.270	0.283	0.314	0.287	0.293	0.302
	Liquid							
Temp., °K.	253.3	263.0	275.2	275.3	278.5	285.3	288.7	295.1
C_p per g.	0.391	0.396	0.404	0.403	0.405	0.409	0.411	0.414
	<i>m</i> -Xylene: Crystals							
Temp., °K.	95.9	102.4	112.0	125.5	136.1	138.5	150.7	
C_p per g.	0.160	0.165	0.174	0.186	0.195	0.197	0.208	
Temp., °K.	160.8	162.0	166.1	171.0	178.6	185.3	190.2	
C_p per g.	0.224	0.250	0.282	0.242	0.248	0.267	0.357	
	Liquid							
Temp., °K.	217.0	221.1	225.0	226.9	275.0	275.3		
C_p per g.	0.359	0.363	0.364	0.364	0.396	0.395		
	<i>p</i> -Xylene: Crystals							
Temp., °K.	91.8	95.2	101.0	106.8	113.8	134.0	152.3	174.7
C_p per g.	0.159	0.163	0.170	0.176	0.184	0.204	0.221	0.241
Temp., °K.	184.3	205.1	225.3	245.1	255.4	266.1	276.4	280.1
C_p per g.	0.250	0.271	0.290	0.308	0.318	0.329	0.345	0.369
	Liquid							
Temp., °K.	290.7	292.1	294.4	299.0	299.4			
C_p per g.	0.402	0.401	0.402	0.406	0.407			
	Hexamethylbenzene: Crystals							
Temp., °K.	85.4	89.8	92.4	95.0	100.0	104.0	105.6	108.0
C_p per g.	0.155	0.164	0.170	0.176	0.190	0.248	0.342	0.50
Temp., °K.	111.8	112.6	122.4	128.8	135.6	143.0	150.7	162.9
C_p per g.	0.272	0.239	0.237	0.243	0.247	0.255	0.278	0.259
Temp., °K.	170.4	186.0	202.9	224.7	240.8	256.0	275.0	294.6
C_p per g.	0.263	0.272	0.284	0.303	0.319	0.335	0.352	0.375
	Diphenyl: Crystals							
Temp., °K.	93.0	98.4	105.0	113.3	134.2	152.1	173.6	183.9
C_p per g.	0.111	0.116	0.121	0.127	0.144	0.159	0.177	0.188
Temp., °K.	196.7	214.6	226.4	243.7	253.3	261.1	279.5	294.4
C_p per g.	0.199	0.217	0.229	0.246	0.255	0.264	0.283	0.301
	Diphenylmethane: Crystals							
Temp., °K.	89.2	93.4	99.8	107.5	122.7	129.4	136.2	150.5
C_p per g.	0.114	0.117	0.122	0.128	0.139	0.146	0.151	0.163

TABLE I (Concluded)

Temp., °K.	161.4	175.8	185.1	194.5	209.3	216.4	223.8	229.7
C_p per g.	0.172	0.186	0.196	0.205	0.222	0.229	0.237	0.244
Temp., °K.	236.3	242.7	251.2	257.1	263.0	275.6	282.5	
C_p per g.	0.251	0.259	0.269	0.277	0.285	0.304	0.318	
Liquid								
Temp., °K.	302.0	305.4	308.7	312.3				
C_p per g.	0.379	0.380	0.383	0.384				
Triphenylmethane: Crystals								
Temp., °K.	89.4	94.9	103.0	113.0	122.1	139.0	161.7	177.9
C_p per g.	0.103	0.108	0.114	0.121	0.128	0.141	0.159	0.173
Temp., °K.	196.6	202.6	229.0	238.0	248.1	275.5	283.9	294.3
C_p per g.	0.191	0.196	0.221	0.230	0.241	0.270	0.278	0.288
Dibenzyl: Crystals								
Temp., °K.	92.6	99.1	107.1	115.8	138.7	149.9	163.6	173.8
C_p per g.	0.125	0.129	0.136	0.143	0.161	0.170	0.182	0.191
Temp., °K.	196.2	205.5	215.1	227.6	240.4	254.3	275.0	293.6
C_p per g.	0.213	0.223	0.233	0.246	0.260	0.275	0.302	0.329
Naphthalene: Crystals								
Temp., °K.	91.4	92.5	96.9	108.6	122.6	129.0	136.1	151.4
C_p per g.	0.106	0.107	0.110	0.119	0.130	0.135	0.140	0.153
Temp., °K.	171.5	186.9	202.5	224.8	254.3	275.5	283.7	295.1
C_p per g.	0.171	0.186	0.202	0.224	0.254	0.278	0.289	0.305

TABLE II
FUSION DATA^a

Substance	M. p., °K.	Heat of fusion (cal. per g.)		
		1st result	2nd result	Mean
Benzene	278.6	30.11	30.06	30.09
Ethylbenzene	178.0	20.63	20.62	20.63
<i>Tert.</i> -butylbenzene	215.0	14.96	14.93	14.95
<i>o</i> -Xylene	247.8	29.35	29.35	29.35
<i>m</i> -Xylene	219.6	25.76	...	25.76
<i>p</i> -Xylene	286.3	38.07	38.16	38.12
Diphenylmethane	298.3	26.36	26.40	26.38

^a In the calculation of these fusion values, the marked rise in the specific heat of the crystals as the melting point is approached was attributed to premelting, and the heat absorbed in this region in excess of that obtained by extrapolation of the specific heat data at lower temperatures was added to the heat absorbed at the melting point.

For comparison with these values the literature contains only very meager data. Nernst⁸ in his early work studied the specific heat of crystalline benzene down to the temperature of liquid hydrogen. The curve through his experimental points lies above ours by about 4.0% at 90° and 2.4% at 200°K. More recently Maass and Waldbauer,⁹ using a method

⁸ Nernst, *Ann. Physik*, [4] **36**, 422 (1911).

⁹ Maass and Waldbauer, *THIS JOURNAL*, **47**, 7 (1925).

of mixtures, have also studied benzene down to liquid-air temperatures. Their curve is quite irregular, being 11% below ours at 90°, 5% below at 150°, 6% above at 200° and 5% above at 250°K. Our curve for liquid benzene at 293°K. is less than 1% above the value selected for the "International Critical Tables."¹⁰ In a very interesting investigation Williams and Daniels¹¹ have recently reported on the discovery of small irregularities in the specific heat curves of liquid benzene and ethylbenzene, which they attributed to superdrying of the liquids. We failed to observe these irregularities, possibly because our hydrocarbon samples had not been specially dried. Naturally there have been numerous determinations of the heat of fusion of benzene, the most recent values being 30.56 (Maass and Waldbauer), 29.92 (Stratton and Partington)¹² and 30.26 cal. per g. (Andrews, Lynn and Johnston).¹³ The "International Critical Tables" give 30.4 cal. per g. Our mean result for benzene, 30.09, is in good agreement with all these data. The heats of fusion of *p*-xylene and diphenylmethane have also been measured before. For the former Colson¹⁴ reported 39.3 cal. per g., which is 3.1% above our value. For the latter Tammann¹⁵ obtained 25.3 cal. per g. or about 4.2% below our figure.

In the case of three of the hydrocarbons the specific heat curve for the crystals shows a small maximum or "hump." Such a phenomenon has been observed for several other compounds which have been studied in this Laboratory and is undoubtedly real, although its explanation is not apparent. In some instances it may be attributed to the influence of impurities in the sample, but this interpretation hardly seems valid in all cases. For *o*-xylene the hump comes at about 208°K. and the heat effect in excess of the normal specific heat amounts to only 0.07 cal. per g. or 7.4 cal. per mole. The two parts of the heat capacity curve below and above this transition region fit together quite smoothly, indicating that the same crystalline form probably exists over the entire temperature range. A similar but larger hump was found for *m*-xylene at about 166°K. and for hexamethylbenzene at 151°K. The corresponding heat effects were 0.50 and 0.23 cal. per g., respectively.

Evidence of a definite transition was also found in the case of hexamethylbenzene at about 108°K. The portions of the heat capacity curve below and above this point possess noticeably different slopes, indicative of two crystalline forms. The heat of transition as measured amounts to 1.5 cal. per g. or 250 cal. per mole.

¹⁰ "International Critical Tables," Vol. V, p. 115.

¹¹ Williams and Daniels, *THIS JOURNAL*, **46**, 1569 (1924).

¹² Stratton and Partington, *Phil. Mag.*, [6] **48**, 1085 (1924).

¹³ Andrews, Lynn and Johnston, *THIS JOURNAL*, **48**, 1274 (1926)

¹⁴ Colson, *Compt. rend.*, **104**, 429 (1887).

¹⁵ Tammann, *Göttingen Ges. Nachr.*, 335 (1913).

Discussion

Entropies of the Compounds.—Using the data contained in Tables I and II in conjunction with the third law of thermodynamics, we have calculated the molal entropies at 298.1°K. for the twelve hydrocarbons. In these calculations we have employed the extrapolation method of Kelley, Parks and Huffman¹⁶ for estimating the entropy increases for the crystals (Col. 2 of Table III) from 0 to 90°K. The various entropy increments from 90 to 298°K., which appear in Cols. 3, 4 and 5 of the table, were obtained by the usual methods directly from the experimental data. The results for the total entropy in calories per degree appear under the heading " S_{298} experimental" in the sixth column. In the cases of the six hydrocarbons which are normally crystalline, we have roughly calculated the entropy of fusion¹⁷ at 298° so as to obtain a value for the entropy of each compound as a liquid, even though the liquid state may be unstable at this temperature.

In the preceding paper⁵ it was shown that the entropy of a liquid paraffin hydrocarbon could be calculated quite accurately by the equation, $S_{298} = 25.0 + 7.7n - 4.5r$, where n is the number of carbon atoms in the molecule and r represents the number of methyl branches on the straight chain. In the present study we have modified this equation for use with compounds containing one or more phenyl groups. It now becomes $S_{298} = 25.0 + 7.7n - 4.5r + 19.5p$, where n represents the total number of carbon atoms outside of the benzene ring and p is the number of phenyl groups in the compound. As before, r ordinarily refers to the number of methyl branches attached on the main aliphatic chain of the molecule, although in a more general sense it may be defined here as the number of hydrocarbon groups (aliphatic or aromatic), in excess of two, attached to any carbon atom in the aliphatic chain. Thus for *tert.*-butylbenzene n is 4, r is 2 and p is 1; and for triphenylmethane n is 1, r is 1 and p is 3. By this means the values of

¹⁶ Kelley, Parks and Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).

¹⁷ This approximate calculation of the entropy of fusion was made by the equation $\Delta S_{298} = (\Delta H \text{ fusion})/T_M - \Delta C_p \ln (T_M/298)$, where ΔH fusion and T_M are, respectively, the molal heat of fusion and the melting point. In all cases ΔC_p , the difference between the molal heat capacity of the liquid and crystals, was assumed to be approximately 0.05 cal. times the molecular weight. For diphenyl, dibenzyl and naphthalene we have taken the values of the heat of fusion as given in the "International Critical Tables" (Vol. V, p. 132). For triphenylmethane the value obtained by Hildebrand, Duschak, Foster and Beebe [*THIS JOURNAL*, **39**, 2293 (1917)] appears to us to be too low, owing to an inadequate allowance for premelting of the sample; and from a study of the published data we have somewhat arbitrarily increased their result to 20 cal. per g. In the absence of any data for the heat of fusion of hexamethylbenzene, we have assumed a molal entropy of fusion of 19.0 E. U. at the melting point, 437°K. This value was obtained by taking the average entropy of fusion of the xylenes, 13.0 E. U. per mole, and adding thereto 1.5 E. U. for each additional CH_3 group in the hexamethylbenzene molecule. The result is probably accurate to within 10%.

" S_{298} predicted" in the last column of Table III were obtained for all the substances except naphthalene. It will be observed that the agreement between the experimental and predicted values is very good¹⁸ except for two compounds—benzene and diphenyl.

TABLE III
ENTROPIES OF THE HYDROCARBONS PER MOLE

Substance	Crystals		Fusion	Liquid	S_{298} experi- mental	S_{298} predicted
	0-90°K.	Above 90°K.				
Benzene	11.35	20.00	8.43	2.15	41.9	44.5
Ethylbenzene	14.60	13.66	12.30	20.60	61.2	59.9
<i>Tert.</i> -butylbenzene	16.18	23.94	9.32	17.20	66.6	66.3
<i>o</i> -Xylene	14.53	23.96 ^a	12.57	8.12	59.3	59.9
<i>m</i> -Xylene	16.00	19.40 ^b	12.45	12.42	60.3	59.9
<i>p</i> -Xylene	15.58	29.06	14.13	1.71	60.5	59.9
Hexamethylbenzene (solid)	19.69	54.30 ^c	74.0	..
Hexamethylbenzene (liquid)			15.9	..	89.9	90.7
Diphenyl (solid)	15.63	33.52	49.2	..
Diphenyl (liquid)			10.6	..	59.8	64.0
Diphenylmethane (solid)	18.61	38.64	57.2	..
Diphenylmethane (liquid)			14.86	..	72.1	71.7
Triphenylmethane (solid)	23.84	50.78	74.6	..
Triphenylmethane (liquid)			10.9	..	85.5	86.7
Dibenzyl (solid)	21.60	43.00	64.6	..
Dibenzyl (liquid)			16.6	..	81.2	79.4
Naphthalene (solid)	12.69	27.21	39.9	..
Naphthalene (liquid)			11.8	..	51.7	..

^a This value includes 0.04 E. U. for the entropy of the hump at 208°K. ^b This value includes 0.30 E. U. for the entropy of a hump at 166°K. ^c This value includes 2.28 E. U. for the transition at 108° and 0.24 E. U. for the entropy of a hump at 151°K.

In the case of benzene there is a discrepancy of 2.6 E. U. or about 6%, which is undoubtedly due to the fact that this substance is somewhat unique in character. For diphenyl the discrepancy is about 7% and is largely due to a relatively low value for the entropy of fusion. This at once suggests that the experimental result for the heat of fusion of this compound may be too low, a question on which we hope soon to obtain further information through some new experimental work.

In the preceding study the entropy of *n*-hexane was found to be 71.1 E. U.; that for *n*-decane can be predicted to be about 102 E. U. Thus, compared with saturated aliphatic compounds of the same number of carbon atoms, the entropies of liquid benzene and naphthalene at 298°K. are very small. As S_{298} for cyclohexane was found to be 49.2 E. U., it is evident that this difference is primarily due to the ring structures of benzene and naph-

¹⁸ This empirical equation also gives a good check in the case of the entropy of toluene. Using it, we calculate the value of 52.2 E. U. per mole; while Kelley [THIS JOURNAL, 51, 2740 (1929)] has recently obtained 52.4 E. U. in an experimental investigation.

thalene rather than to unsaturation in the molecule or to the withdrawal of hydrogen.

The Free Energies of the Hydrocarbons

We have also calculated the free energies of these twelve hydrocarbons by means of the third law of thermodynamics and the fundamental thermodynamic equation, $\Delta F = \Delta H - T\Delta S$.

The essential data are given in Table IV. For obtaining the figures for the ΔH of formation of the first six compounds we have used the heats of

TABLE IV
THERMAL DATA AT 298.1°K.

The 15° cal. is used throughout and all weights have been reduced to a vacuum basis

Substance	Heat of combustion at constant pressure	ΔH_{298} , cal.	ΔS_{298} , E. U.	ΔF_{298}° , cal.
Benzene	782,000	+11,300	- 54.7	+ 27,600
Ethylbenzene	1,090,400	- 5,400	- 97.2	+ 23,600
<i>Ter</i> t.-butylbenzene	1,400,400	-20,700	-153.6	+ 25,100
<i>o</i> -Xylene	1,090,800	- 5,000	- 99.1	+ 24,500
<i>m</i> -Xylene	1,090,800	- 5,000	- 98.1	+ 24,200
<i>p</i> -Xylene	1,087,000	- 8,800	- 97.9	+ 20,400
Hexamethylbenzene (S)	1,711,400	-34,900	-208.0	+ 27,100
Diphenyl (S)	1,493,300	+20,400	-114.4	+ 54,500
Diphenylmethane (S)	1,654,700	+19,200	-137.3	+ 60,100
Triphenylmethane (S)	2,383,500	+45,700	-186.9	+101,400
Dibenzyl (S)	1,810,200	+12,100	-160.8	+ 60,100
Naphthalene (S)	1,231,600	+15,600	- 91.5	+ 42,900

combustion determined by Richards and his co-workers, and more recently revised by Swietoslowski and Bobinska.¹⁹ This procedure has seemed desirable, both because of the known excellence of Richards' work and the fact that all these data are then on a comparative basis. For the remaining six compounds we have taken the heats of combustion as given in the "International Critical Tables."²⁰ Except for naphthalene, these last values depend almost entirely upon Stohmann's determinations, which recent studies²¹ have shown may be in error by 0.5% in some instances. For our present purpose we have converted all the combustion data to 298.1°K. The ΔH_{298} values were then calculated by use of 68,330 and 94,270 cal.⁶ for the heats of combustion of hydrogen and graphitic carbon, respectively. Column 4 contains the entropy of formation of each compound, which is simply the difference between its S_{298} and the corresponding values for the entropies of the elements contained therein. For this purpose the respec-

¹⁹ Swietoslowski and Bobinska, *THIS JOURNAL*, **49**, 2478 (1927). The values have been increased by 0.017%, as suggested by Verkade and Coops [*Rec. trav. chim.*, **46**, 910 (1927)].

²⁰ "International Critical Tables," Vol. V, p. 163.

²¹ Verkade and Coops, *Rec. trav. chim.*, **47**, 608 (1928).

tive entropies of carbon and hydrogen were taken as 1.3 and 14.8 E. U.⁵ per gram atom.

The molal free energies appear in the last column of the table. For comparative purposes the accuracy of these values is largely limited by the accuracy of the combustion data employed. In the case of the first five compounds and naphthalene the combustion values are probably good to within a thousand calories. For the other substances, the errors may be greater, depending somewhat upon the magnitude of the heat of combustion involved. Thus the result for triphenylmethane may be uncertain to the extent of, perhaps, ten thousand calories. In a consideration of the table it also should be noted that the results for the last six compounds refer to the solid state. However, the free energy value for liquid diphenylmethane at 298.1°K. is practically identical with that for the crystalline material, since the melting point is only slightly above this temperature. In the case of the other five compounds the differences between the liquid and solid states at 298°K. can be calculated roughly (*i. e.*, to 10% or better) by the equation, $\Delta F_{298} = \Delta S_{\text{fusion}} (T_m - 298.1)$. By this means we estimate that the free energy of liquid hexamethylbenzene exceeds that of the solid by 2700 cal. In the cases of diphenyl, triphenylmethane, dibenzyl and naphthalene, the differences are 500, 800, 500 and 600 cal., respectively.

In spite of the purely qualitative character of some of the free energy data in Table IV, two interesting points are worthy of brief attention. First, the introduction of a phenyl radical into a saturated aliphatic hydrocarbon raises the free energy level by about 35,000 cal. Thus the free energy of liquid methane at 298°K. has been estimated as -9800 cal.²² and on this basis that of toluene should be about +25,200 cal., a value which is in good agreement with the result (+24,300 cal.) recently obtained by Kelley.²³ Similarly, we can predict the values +60,200, +60,800 and +95,200 cal. for diphenylmethane, dibenzyl and triphenylmethane, respectively, all in the liquid state at 298°K. These predicted quantities differ by 100, 200 and 7000 cal. from the corresponding experimental ones.

The second feature concerns the relations of benzene and its derivatives. It is apparent that the free energy level of benzene itself is somewhat above that for the simple mono- and disubstitution products. On the other hand, with the single exception of *p*-xylene, all these simple derivatives—toluene, ethylbenzene and the xylenes—have the same free energies within a thousand calories. Furthermore, it is possible that the discrepancy of over 3000 cal. in the case of *p*-xylene is partly due to an error in Richards' heat of combustion of this compound, since other investigators in thermochemistry have obtained almost identical values²⁴ in the case of such iso-

²² Parks and Kelley, *THIS JOURNAL*, **47**, 2096 (1925).

²³ Kelley, *ibid.*, **51**, 2740 (1929).

²⁴ See, for instance, Keffler and Guthrie, *J. Phys. Chem.*, **31**, 65 (1927).

mers. We, therefore, are inclined to agree with Andrews' conclusion that ortho, meta and para isomers have practically identical free energies of formation.²⁵ With the introduction of more methyl groups into the benzene ring, the free energy probably rises slightly, as our value of +29,800 cal. for hexamethylbenzene in the liquid state indicates.

The Free Energy Change in the Hydrogenation of Benzene.—The data now available permit us to study by two different methods the free energy change for the hydrogenation reaction: $C_6H_6(l) + 3H_2(g) = C_6H_{12}(l)$.

The equilibria between benzene, hydrogen and cyclohexane have been measured at 266.5 and 280° by Burrows and Lucarini.²⁶ From their results Francis²⁷ has obtained the equation $\Delta F = -46,800 + 19.75 T \ln T - 0.0115 T^2 - 34.5 T$ for the reaction in the gaseous phase. This equation, however, was derived by the use of Richards' value for the heat of combustion of benzene and that of Zubow, as revised by Swietoslawski, for cyclohexane. It is highly questionable whether Zubow was able to secure complete burning of such a volatile material. Moreover, as the heats of combustion of both substances have been determined by Richards and his co-workers and by Roth and von Auwers, we feel that it is preferable to rely solely upon the work of these two groups of investigators in a calculation of this kind. Using Richards' data,¹⁹ we obtain $\Delta H_{293} = -47,000$ cal.; Roth's results²⁸ give $\Delta H_{291} = -48,800$ cal. As a mean we have $\Delta H_{292} = -47,900$ cal., as against the figure $\Delta H_{293} = -51,600$ cal., employed by Francis. This value applies to the above reaction involving benzene and cyclohexane as liquids. For the reaction in the gaseous phase we obtain $\Delta H_{292} = -48,100$ cal., since the molal heat of vaporization of benzene exceeds that of cyclohexane by about 200 cal.²⁹ The preceding free energy equation must then be modified and we find that $\Delta F = -43,300 + 19.75 T \ln T - 0.0115 T^2 - 41.1 T$. Then at 298°K., $\Delta F = -23,030$ cal. This result is for the process at 1 atm. in the gaseous phase, but the free energy change when benzene and cyclohexane are in the liquid state will be the same, as the vapor pressures of these compounds are practically equal.

The entropy data now enable us to obtain a second result. From the ΔH_{292} value in the preceding paragraph and -16 cal. for ΔC_p we calculate $\Delta H_{293} = -48,000$ cal. for the reaction involving the liquids. Also $\Delta S_{293} = 49.2^5 - (41.9 + 88.8) = -81.5$ E. U. Hence, it follows that $\Delta F_{293} = -48,000 + (298.1)(81.5) = -23,690$ cal. Thus these two free energy changes, obtained by very different experimental methods, differ by 660 cal. or about 2.8%.

²⁵ Andrews, *THIS JOURNAL*, **48**, 1296 (1926).

²⁶ Burrows and Lucarini, *ibid.*, **49**, 1157 (1927).

²⁷ Francis, *Ind. Eng. Chem.*, **19**, 277 (1928).

²⁸ Landolt, Börnstein, Roth, Scheel, "Tabellen," **1923**, p. 1589.

²⁹ Ref. 28, p. 1483.

Summary

1. The specific heats of twelve aromatic hydrocarbons have been measured over a wide range of temperatures. The heats of fusion of seven of these compounds have also been determined.

2. The entropies of the twelve hydrocarbons have been calculated from these heat capacity data. The results thus obtained have been found to agree in most cases with the values predicted by means of a simple, empirical equation.

3. The corresponding free energies have also been calculated and certain regularities noted. The free energy change in the hydrogenation of benzene to give cyclohexane has been derived in two different ways.

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[CONTRIBUTION FROM UNIVERSITY COLLEGE, THE UNIVERSITY OF LONDON]

THE ACTION OF DIAZOMETHANE ON BENZOIC AND SUCCINIC ANHYDRIDES, AND A REPLY TO MALKIN AND NIERENSTEIN

BY W. BRADLEY AND R. ROBINSON

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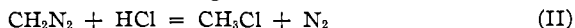
The memoir by Malkin and Nierenstein¹ contains some statements requiring comment.

(1) **The Course of the Interaction of Diazomethane and Acid Chlorides.**—The implication of these authors that the merit of experiments on the interaction of benzoyl chloride and diazomethane is directly proportional to the yield of ω -chloro-acetophenone obtained is quite unwarranted. In our work, for example, we were not trying to obtain the chloro-ketone, but rather to isolate the first stage and product of the reaction, and, with this end in view, we operated at a low temperature and, for reasons that appear in the sequel, kept the diazomethane in excess.² Under these circumstances benzoyl chloride is rapidly and completely transformed into diazo-acetophenone, and evolution of nitrogen is evident.

Therefore, we have the reaction



The resulting hydrogen chloride, reacting with the diazomethane in excess, must then give methyl chloride and nitrogen



Thus when benzoyl chloride (1 mole) is added to a cold ethereal solution of diazomethane (2 moles), the reaction is undoubtedly represented by the equation



¹ Malkin and Nierenstein, *THIS JOURNAL*, **52**, 1504 (1930).

² Bradley and Robinson, *J. Chem. Soc.*, 1317 (1928).