1009. *Thermodynamic Properties of Organic Oxygen Compounds. Part I. Preparation and Physical Properties of Pure Phenol, Cresols, and Xylenols.*

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The preparation and purification of phenol, the three cresols, and the six xylenols are described. The purities of the samples have been established by freezing- and melting-point measurements. Properties which have been measured or computed are: freezing points and the depressions produced by one mole % of impurity, vapour pressure–temperature relationships, boiling points, latent heats of vaporization, second virial coefficients, densities, coefficients of expansion of the homologues which are liquid at 25°, heats of combustion and of formation.

As phenol and many of its methyl homologues are of technical interest, we have prepared very pure specimens of ten of them and measured certain physicochemical constants with precision. Although values have been recorded[1,2] for many of the properties studied by us, few measurements have been made hitherto on samples of authenticated purity. Samples of 99·9 mole % purity have now been prepared, freezing points have been determined with a standard deviation of ±0·01°, and normal boiling points have been measured with a standard deviation of ±0·003° or less. The densities of the members which are solid at 25° have been determined with a standard deviation of ±0·003 g./ml. or less,

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[1] Pardee and Weinrich, *Ind. Eng. Chem.*, 1944, **36**, 595.

[2] Karr, " Physical Properties of Low-Boiling Phenols. A Literature Survey," U.S. Department of the Interior, 1957, Information Circular 7802.

and the densities of the two compounds liquid at 25° have been found with much higher accuracy. Heats of combustion have been measured with a standard deviation of $\pm 0{\cdot}01\%$. Dissociation constants and ultraviolet absorption spectra of aqueous solutions of these highly purified samples have already been reported,[3] as have vapour pressures of some of them.[4]

EXPERIMENTAL

Purification.—All the specimens were similarly purified. Steam was passed through a boiling solution containing 1 mole of the phenol and 1·5—2·0 moles of sodium hydroxide in 5 l. of water until no further non-acidic material distilled. Except when the sterically hindered 2,6-xylenol was treated, none of the phenol distilled from the alkaline solution. The residue was cooled and acidified with 20% v/v sulphuric acid, and the liberated phenol was separated and dried over calcium sulphate. The aqueous layer was extracted with ether, and the phenol so recovered was returned for further treatment with steam. The dried phenol was distilled at ~10 mm. Hg to remove any traces of water and high-boiling materials. The phenol so obtained was fractionally distilled[5] at a pressure within the range 100—212 mm. Hg through a column equivalent to 45 theoretical plates, and the product was collected at a reflux ratio of 50 : 1. The Stedman packings for this column were made of 18/8 molybdenum stainless-steel gauze (50 mesh, 36 S.W.G.) since this steel has been found to resist attack by phenols. Batches of 1200 g. were distilled, and when the vapour temperature had become steady, separate fractions of 150 ml. were collected. A series of fractions with an overall boiling range of 0·5° was examined by infrared spectroscopy, and on the evidence obtained the best fractions were combined. In some instances the distillation through the Stedman column was repeated. Finally, the bulked material was purified either by fractional crystallization from the melt or by zone refining[6] or by a combination of both. When fractional crystallization was employed the phenol, under an atmosphere of dry nitrogen, was allowed to crystallize slowly for 2 days and a small residual liquid portion was removed. The process was repeated 6—8 times so that a total of ~50% of the material was removed as liquid during the treatment. Evacuation of the vessel held in an inverted position was found to expedite drainage of the liquid from the solid. In the later stages of purification all the samples were protected from light and were manipulated under dry nitrogen. The final colourless samples were stored in the dark under a vacuum.

Physicochemical Measurements.—The following values for the fundamental constants have been used: 0° C = 273·15° K; $\boldsymbol{R} = 1{\cdot}98725$ cal. deg.$^{-1}$ mole^{-1} = 8·31466 J deg.$^{-1}$ mole^{-1} = 0·082057 l. atm. deg.$^{-1}$ mole^{-1}; 1 cal. = 4·1840 J. The molecular weights were calculated from the 1953 Table of International Atomic Weights.

Freezing points, cryoscopic constants, and the quantitative determination of purity. The results of the measurements of these quantities are shown in Table 1. The techniques employed have been described[7,8] and the procedures used to establish the purity are listed under "Method." The initial freezing points (t_f) and the freezing-point depressions produced by adding known quantities of α-methylnaphthalene were found by means of a U-tube apparatus.[8] The statistical treatment of the data obtained from replicate experiments has previously been described.[9] In Table 1, and throughout the paper, standard deviations are those of the mean.

The values listed in Table 1 may be compared with selected freezing points quoted by Timmermans,[10] which for phenol range from 40·7° to 41°, for *o*-cresol from 30·35° to 30·94°, and for *p*-cresol from 34·4° to 34·8°, with a single value for *m*-cresol of 11·5°. Dreisbach and Martin[11] have reported that phenol of purity 99·96 mole % has f. p. 40·90°, that *o*-cresol of purity 99·90 mole % has f. p. 30·94° and that *p*-cresol of purity 99·95 mole % has f. p. 34·78°.

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[3] Herington and Kynaston, *Trans. Faraday Soc.*, 1957, **53**, 138.
[4] Biddiscombe and Martin, *Trans. Faraday Soc.*, 1958, **54**, 1316.
[5] Coulson and Herington, "Laboratory Distillation Practice," George Newnes Ltd., London, 1958.
[6] Herington, Handley, and Cook, *Chem. and Ind.*, 1956, 292.
[7] Herington, *Analyt. Chim. Acta*, 1957, **17**, 15.
[8] Handley, *Analyt. Chim. Acta*, 1957, **17**, 115.
[9] Biddiscombe, Coulson, Handley, and Herington, *J.*, 1954, 1957.
[10] Timmermans, "Physico-chemical Constants of Pure Organic Compounds," Elsevier Publ. Co. Inc., 1950, pp. 459—465.
[11] Dreisbach and Martin, *Ind. Eng. Chem.*, 1949, **41**, 2875.

Carney and Sanford [12] report f. p. 30·937° for a sample of *o*-cresol of 99·99 mole % purity, corresponding to f. p. 30·944° for the 100% pure compound; f. p. 12·20° for 100% pure *m*-cresol; and f. p. 34·734° for a sample of *p*-cresol of 99·99 mole % which corresponds to a value of 34·739° for a 100% pure specimen.

TABLE 1. *Freezing constants for ten phenols.*

Compound	Method	Purity (moles %)	Depression produced by 1 mole % of impurity	F. p. of sample (t_f)	F. p. for 100% purity ($t_{f,\,0}$)
Phenol	F. p.	99·929 ± 0·006	0·848° ± 0·004°	40·84° ± 0·01°	40·90° ± 0·01°
o-Cresol	F. p.	99·963 ± 0·002	0·596 ± 0·009	30·97 ± 0·01	30·99 ± 0·01
m-Cresol	M. p.	99·917 ± 0·020	0·749 ± 0·040	12·16 ± 0·01	12·22 ± 0·02
-Cresol	F. p.	99·963 ± 0·021	0·915 ± 0·051	34·65 ± 0·01	34·69 ± 0·02
2,3-Xylenol...	M. p.	99·928 ± 0·005	0·502 ± 0·019	72·53 ± 0·01	72·57 ± 0·02
2,4-Xylenol...	M. p.	99·972 ± 0·002	0·576 ± 0·030	24·52 ± 0·01	24·54 ± 0·01
2,5-Xylenol...	M. p.	99·896 ± 0·020	0·727 ± 0·008	74·77 ± 0·01	74·85 ± 0·02
2,6-Xylenol...	F. p.	99·886 ± 0·008	0·558 ± 0·016	45·56 ± 0·01	45·62 ± 0·01
3,4-Xylenol...	M. p.	99·971 ± 0·005	0·727 ± 0·020	65·09 ± 0·01	65·11 ± 0·01
3,5-Xylenol...	M. p.	99·960 ± 0·004	0·520 ± 0·059	63·24 ± 0·01	63·27 ± 0·02

Vapour pressure–temperature relationships, normal boiling points, values of $(\mathrm{d}t/\mathrm{d}p)_{760\ \mathrm{mm.}}$, *and latent heats of vaporization.* The vapour pressures of the liquid and solid xylenols were measured by ebulliometric and gas-saturation procedures previously described.[4,13,14] Detailed results for the six xylenols are given in Table 2.

Antoine equations [*i.e.*, equations of the form $\log_{10} P = A - B/(t + C)$] were fitted to the data for higher temperatures, and the two-constant equation $\log_{10} P = A - B/(t + 273)$ was used for the lower temperature range. Table 3 gives the constants of these equations and Table 4 shows the normal b. p.s; values of $(\mathrm{d}t/\mathrm{d}P)_{760\ \mathrm{mm.}}$ and $(\mathrm{d}t/\mathrm{d}P)_{25}$ are also listed. The standard deviations tabulated have been calculated from the standard deviations of the constants of the vapour-pressure equations. For completeness certain constants previously published [4] for phenol and the cresols are repeated in Tables 3 and 4. However, the values for the latent heat of vaporization, at 760 mm., of phenol and the cresols listed in Table 4 differ from those published previously [4] because, in the calculation of the new values by the Clapeyron equation, allowance has been made for the deviation of the vapour from the ideal-gas laws (see next section for the derivation of values employed) and for the molar volume of the liquid. The following molar volumes of the liquids at the normal boiling points were assumed: phenol 105, cresols 127, xylenols 149 cm.^{3}/mole.

The standard deviations quoted in Table 4 for the latent heats of vaporization at 760 mm. Hg were compounded from the listed standard deviations of the Antoine constants (Table 3) and from the estimated uncertainties in the virial coefficient; the larger contribution is from the latter term.

The latent heats of vaporization at 25° were calculated by the use of the Clausius–Clapeyron equation, *i.e.*, ideal-gas behaviour was assumed.

Second virial coefficients. The second virial coefficients of phenol and *o*-cresol were measured in the apparatus previously described.[15] An infrared lamp mounted above the bath provided sufficient additional heat to maintain satisfactory temperature control up to 180°. The results shown in Table 5 were obtained by using the experimental methods and calculation procedures described earlier.[15,16]

Measurements were not attempted on the other compounds of the present series because their vapour pressures were too low to enable accurate results to be obtained. Their second virial coefficients at their normal boiling points were estimated by application of an observation that for many homologous series the second virial coefficients at the normal boiling points are a smooth function of the normal boiling points. The second virial coefficients of phenol and *o*-cresol at their normal boiling points were first obtained by graphical extrapolation of the

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[12] Carney and Sanford, *Analyt. Chem.*, 1953, **25**, 1417.
[13] Herington and Martin, *Trans. Faraday Soc.*, 1953, **49**, 154.
[14] Coulson, Cox, Herington, and Martin, *J.*, 1959, 1934.
[15] Cox and Andon, *Trans. Faraday Soc.*, 1958, **54**, 1622.
[16] Cox, *Trans. Faraday Soc.*, 1960, **56**, 959.

TABLE 2. *Vapour pressures.*

t in °c; P in mm. Hg at 0° c and standard gravity.

2,3-Xylenol (solid) $\log_{10} P = 13{\cdot}1606 - 4389{\cdot}06/(t + 273)$

t	P	t	P	t	P	t	P	t	P
9·91°	$0{\cdot}0045_7$	19·70°	0·0145	29·58°	0·0432	39·54°	0·130	49·88°	0·397
14·70	$0{\cdot}0080_4$	24·71	0·0273	35·19	0·0760	44·81	0·224		

2,3-Xylenol (liquid) $\log_{10} P = 7{\cdot}04268 - 1609{\cdot}164/(t + 169{\cdot}774)$

149·346	99·79	187·374	344·43	207·544	599·68	214·768	721·19	216·987	762·16
160·940	150·35	192·094	394·33	210·612	649·12	215·091	727·03	217·323	768·59
169·634	200·30	196·778	449·43	213·454	697·75	215·646	737·18	217·928	780·14
176·314	247·24	200·752	500·88	214·137	709·89	216·144	746·41	218·467	790·54
182·500	298·37	204·000	546·36						

2,4-Xylenol (liquid, supercooled below 24·5°) $\log_{10} P = 10{\cdot}5277 - 3439{\cdot}99/(t + 273)$

9·73	0·0228	20·13	0·0621	29·91	0·151	39·41	0·328
14·94	0·0380	24·87	0·0961	35·16	0·231	44·86	0·503

2,4-Xylenol (liquid) $\log_{10} P = 7{\cdot}04694 - 1581{\cdot}391/(t + 168{\cdot}652)$

144·382	98·97	182·116	345·61	201·747	599·13	208·898	721·74	210·951	760·42
156·053	150·19	186·619	394·21	204·809	649·43	209·314	729·44	211·453	770·06
164·129	197·18	191·348	451·02	207·513	696·56	209·847	739·41	211·888	778·59
171·241	247·90	194·795	496·45	208·299	710·79	210·450	750·83	212·320	787·06
176·700	293·69	198·444	548·41						

2,5-Xylenol (solid) $\log_{10} P = 13{\cdot}3705 - 4438{\cdot}56/(t + 273)$

9·43	$0{\cdot}0045_0$	19·90	0·0164	29·83	0·0513	39·41	0·146	49·45	0·396
15·01	$0{\cdot}0091_1$	24·82	0·0296	35·33	0·0944	44·79	0·259		

2,5-Xylenol (liquid) $\log_{10} P = 7{\cdot}03684 - 1581{\cdot}906/(t + 169{\cdot}497)$

143·924	97·43	176·902	295·23	194·984	497·38	207·748	697·47	210·117	740·79
154·805	144·27	182·455	348·48	198·830	552·06	208·661	713·92	210·711	751·99
164·433	199·40	187·328	401·35	201·834	598·06	209·138	722·68	211·232	761·91
171·549	250·33	191·460	451·10	204·603	643·08	209·556	730·36	211·736	771·59

2,6-Xylenol (solid) $\log_{10} P = 12{\cdot}5036 - 3948{\cdot}27/(t + 273)$

4·75	0·0195	14·98	0·0624	24·67	0·175	34·98	0·487
9·46	0·0336	19·78	0·104	30·20	0·299	39·66	0·752

2,6-Xylenol (liquid) $\log_{10} P = 7{\cdot}05753 - 1618{\cdot}528/(t + 186{\cdot}482)$

144·798	148·61	176·276	394·26	191·754	600·37	198·937	721·38	201·059	760·56
153·385	197·43	180·369	442·14	194·810	649·67	199·432	730·36	201·616	771·12
160·624	248·11	184·792	499·01	196·676	681·38	199·983	740·47	202·519	788·44
166·759	298·92	188·694	553·93	198·414	711·94	200·450	749·17	203·525	808·10
171·831	347·08								

3,4-Xylenol (solid) $\log_{10} P = 13{\cdot}1729 - 4478{\cdot}23/(t + 273)$

9·89	$0{\cdot}0022_0$	19·98	$0{\cdot}0077_3$	29·80	0·0243	39·67	0·0704	49·36	0·191
14·78	$0{\cdot}0040_7$	24·88	0·0138	34·86	0·0422	44·76	0·121		

3,4-Xylenol (liquid) $\log_{10} P = 7{\cdot}07343 - 1617{\cdot}202/(t + 158{\cdot}778)$

171·933	152·57	202·370	393·98	217·587	597·79	224·799	720·03	226·921	759·38
180·131	200·29	207·376	453·62	220·898	651·67	225·276	728·71	227·397	768·62
186·548	245·64	211·126	502·91	223·649	699·26	225·928	740·84	228·487	789·73
193·380	302·79	214·126	545·32	224·292	710·79	226·392	749·46	228·899	797·85
197·879	346·04								

3,5-Xylenol (solid) $\log_{10} P = 12{\cdot}8271 - 4328{\cdot}13/(t + 273)$

9·57	$0{\cdot}0033_0$	20·35	0·0119	30·42	0·0365	39·94	0·0999	49·97	0·265
14·92	$0{\cdot}0061_0$	24·95	0·0197	34·85	0·0586	45·23	0·171		

3,5-Xylenol (liquid) $\log_{10} P = 7{\cdot}11745 - 1630{\cdot}124/(t + 163{\cdot}076)$

154·720	97·39	192·743	343·64	212·159	593·10	219·584	720·26	221·709	760·28
166·472	148·21	197·298	392·67	215·799	653·08	220·097	729·78	222·279	771·40
175·126	198·35	201·925	448·10	218·298	696·84	220·692	740·84	222·724	780·12
182·389	250·46	205·601	496·49	219·146	712·20	221·309	752·57	223·321	791·86
187·937	297·45	209·151	547·11						

TABLE 3. *Constants of the equations of Antoine type.*

[$\log_{10} P = A - B/(t + C)$ for the higher temperature range and $\log_{10} P = A - B/(t + 273)$ for the lower temperature range.]

Compound	Temp. range	Constants of vapour-pressure equation *A*	*B*	*C*
Phenol	9—40°	11·5638 ± 0·090	3586·36 ± 26	—
	110—200	7·13457 ± 0·0173	1516·072 ± 11·6	174·569 ± 1·29
o-Cresol	0—30	12·7778 ± 0·138	3970·17 ± 40	—
	110—200	7·07055 ± 0·0086	1542·299 ± 6·0	177·110 ± 0·68
m-Cresol	11—40	9·9653 ± 0·186	3223·45 ± 56	—
	110—200	7·15904 ± 0·0131	1603·811 ± 9·3	172·646 ± 1·02
p-Cresol	0—34	12·0298 ± 0·260	3861·98 ± 76	—
	110—200	7·11767 ± 0·0078	1566·029 ± 5·4	167·680 ± 0·60
2,3-Xylenol............	9—50	13·1606 ± 0·172	4389·06 ± 52	—
	149—218	7·04268 ± 0·0058	1609·164 ± 4·3	169·774 ± 0·49
2,4-Xylenol............	9—45	10·5277 ± 0·035	3439·99 ± 11	—
	144—212	7·04694 ± 0·0030	1581·391 ± 2·2	168·652 ± 0·25
2,5-Xylenol............	9—50	13·3705 ± 0·042	4438·56 ± 13	—
	143—212	7·03684 ± 0·0062	1581·906 ± 4·5	169·497 ± 0·51
2,6-Xylenol............	4—40	12·5036 ± 0·029	3948·27 ± 9	—
	144—203	7·05753 ± 0·0079	1618·528 ± 5·9	186·482 ± 0·68
3,4-Xylenol............	9—50	13·1729 ± 0·022	4478·23 ± 7	—
	171—229	7·07343 ± 0·0052	1617·202 ± 3·9	158·778 ± 0·44
3,5-Xylenol............	9—50	12·8271 ± 0·052	4328·13 ± 16	—
	154—224	7·11745 ± 0·0070	1630·124 ± 5·1	163·076 ± 0·58

TABLE 4. *Normal boiling points,* (dt/dP) *at* 760 *mm.* Hg *and at* 25°, *and molar latent heats of vaporization at the normal boiling point and at* 25° C.

Compound	B. p./760 mm.	$(dt/dP)_{760\text{ mm.}}$ (° C/mm.)	Heat of vaporization at 760 mm. Hg (cal./mole)	$(dt/dP)_{25}$ (° C/mm.)	Heat of vaporization at 25° C (cal./mole)
Phenol	181·839° ± 0·003°	0·04788	10,920 ± 8	31·8	16,410 ± 120 (solid)
o-Cresol	191·003 ± 0·001	0·05021	10,801 ± 14	34·1	18,170 ± 180 (solid)
m-Cresol	202·231 ± 0·002	0·05007	11,329 ± 30	85·0	14,750 ± 250 (liquid)
p-Cresol	201·940 ± 0·002	0·04985	11,365 ± 30	85·0	17,670 ± 350 (solid)
2,3-Xylenol	216·870 ± 0·001	0·05309	11,310 ± 35	325·4	20,080 ± 240 (solid)
2,4-Xylenol	210·931 ± 0·001	0·05206	11,268 ± 35	116·3	15,740 ± 50 (liquid)
2,5-Xylenol	211·132 ± 0·002	0·05233	11,219 ± 35	290·6	20,310 ± 60 (solid)
2,6-Xylenol	201·030 ± 0·001	0·05302	10,641 ± 28	54·3	18,070 ± 40 (solid)
3,4-Xylenol	226·947 ± 0·001	0·05257	11,871 ± 42	615·2	20,490 ± 30 (solid)
3,5-Xylenol	221·692 ± 0·003	0·05190	11,785 ± 42	443·3	19,800 ± 70 (solid)

TABLE 5. *Second virial coefficients of phenol and* o-*cresol.*

Compound	*t* (° C)	Max. press. (mm. Hg)	$-B_p$ * (cm.³/mole)	$-B_v$ * (cm.³/mole)
Phenol	155·3	303	1495 ± 30	1454 ± 28
	164·6	407	1373 ± 25	1338 ± 25
	180·5	577	1169 ± 18	1135 ± 16
o-Cresol	164·6	335	1748 ± 24	1693 ± 24
	180·5	433	1378 ± 35	1343 ± 31

* Defined by $PV = \boldsymbol{R}T + B_pP = \boldsymbol{R}T(1 + B_v/V)$.

experimental data, similarly shaped curves being drawn through the points for the two compounds. The values of the second virial coefficient thus obtained were then plotted against the normal boiling points and a smooth curve was drawn through the two resulting points with a shape similar to the curve found from experimental measurements on the homologous series benzene, toluene, xylenes. The following values of B_v (in cm.³/mole) were thus obtained: phenol, −1130 ± 20; *o*-cresol, −1250 ± 50; *m*-cresol, −1380 ± 100; *p*-cresol, −1380 ± 100; 2,3-xylenol, −1540 ± 120; 2,4-xylenol, −1480 ± 120; 2,5-xylenol, −1480 ± 120; 2,6-xylenol, −1370 ± 100; 3,4-xylenol, −1650 ± 140; 3,5-xylenol, −1600 ± 140.

In an earlier paper [15] from this Laboratory the second virial coefficients of benzene, toluene, pyridine, and α-picoline were calculated according to Pitzer and Curl's equation[17] and fair agreement was obtained with experimental values. Applicability of this equation to measurements of the second virial coefficients of phenol and *o*-cresol has now been examined. The ω factors were calculated[17] from published vapour pressures[4] and critical data,[18] yielding $\omega = 0{\cdot}443$ for both compounds. When this figure was substituted in Pitzer and Curl's equation,[17] a value of $BP_C/\mathbf{R}T_C$ (at $T/T_C = 0{\cdot}65$) equal to $-1{\cdot}17$ was obtained, which may be compared with experimental values of $-1{\cdot}24$ for phenol and $-1{\cdot}19$ for *o*-cresol. Having regard to uncertainties in the experimental values, the agreement can be considered satisfactory.

Densities. The results obtained by measuring the densities of *m*-cresol and 2,4-xylenol at 20° and 30° by means of a Sprengel–Ostwald pycnometer[9] are shown in Table 6.

TABLE 6. *Observed densities at* 20° *and* 30° *of* m-*cresol and* 2,4-*xylenol, and calculated densities and coefficients of cubical expansion at* 25°. [$d_{25} = 0{\cdot}5(d_{20} + d_{30})$; $\alpha_{25} = 0{\cdot}2(d_{20} - d_{30})/(d_{20} + d_{30})$.]

Compound	d_{20} (g./ml.)	d_{30} (g./ml.)	d_{25} (g./ml.)	α_{25}
m-Cresol	1·03410 ± 0·00000	1·02628 ± 0·00000	1·03019	0·000759 ± 0·00000
2,4-Xylenol	1·02017 ± 0·00000	1·01186 ± 0·00000	1·01601	0·000818 ± 0·00000

Densities of the solid phenols at 25° were measured (see Table 7) in a pycnometer, mercury (results marked Hg) or a saturated solution of the phenol in decalin (results marked D) being used as the confining liquid. Difficulties were experienced in freeing the solid in the pycnometer from gas and voids; because of this the results are of lower accuracy than those obtained for liquids. The accuracy is, however, more than sufficient for calculation of buoyancy corrections in the heat of combustion measurements.

TABLE 7. *Densities of solid phenols at* 25°.

Compound	Method	d_{25} (g./ml.)	Compound	Method	d_{25} (g./ml.)
Phenol	D	1·132 ± 0·001	2,5-Xylenol	D	1·189 ± 0·001
o-Cresol	D	1·135 ± 0·001	2,6-Xylenol	Hg	1·132 ± 0·000
p-Cresol	Hg	1·154 ± 0·000	3,4-Xylenol	D	1·138 ± 0·001
2,3-Xylenol	D	1·164 ± 0·001	3,5-Xylenol	D	1·115 ± 0·003

Considerable confusion frequently arises in the use of tabulated values[2,10,19] of the densities of phenols at temperatures near or at 25° because it is not generally appreciated that these figures all refer to the liquids and not to the solid forms of phenol, *o*-cresol, *p*-cresol, 2,5-xylenol 3,4-xylenol, and 3,5-xylenol.

Heats of combustion. The bomb calorimeter used for these measurements has been described.[20,21] The energy equivalent of the calorimeter as used in the present experiments was determined electrically[21] as 17,299·6 ± 0·8 J deg.$^{-1}$ (5 experiments). All temperature measurements were made with the aid of a platinum resistance thermometer and Smith bridge "No. 3" (Tinsley).

Each sample was sealed in a polyethylene bag to avoid aerial oxidation and contamination with moisture. All manipulations of a sample from the opening of the ampoule in which it was stored to the final sealing of the polyethylene bag were carried out in a dry box. The bags were rectangular (25 × 30 mm.) and were made from "Layflat" tubing (British Visqueen Ltd.) of 0·05 mm. film thickness, treated by the manufacturers to minimise static electrification. Use was made of one fold of the tubing to form one edge of the bag and two further edges were made by an electrically heated iron fitted with a wheel bit. The sample was introduced into a weighed bag by pipette if liquid, or in the form of a pellet, prepared in a press, if solid. The open end of the bag was then sealed by placing the bag between two sheets of Cellophane film with the lower sheet resting on a smooth metal plate. A firm stroke of the sealing iron

[17] Pitzer and Curl, *J. Amer. Chem. Soc.*, 1957, **79**, 2369.

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TABLE 8. *Heats of combustion of polyethylene, phenol, the cresols, and the xylenols.*

Compound	Mass of compound (g.)	Mass of polyethylene bag (g.)	Heat evolved (J)	q_{p} (J)	$q_{\mathrm{HNO_3}}$ (J)	$q_{\mathrm{s.a.}}$ (J)	$-\Delta U_{\mathrm{c}}^{\circ}$ (J/g.)
Polyethylene	0·79075	—	36734·3	—	11·3	11·5	46425·3
	0·80093	—	37229·2	—	11·3	11·6	46453·1
	0·80364	—	37319·7	—	6·1	11·6	46415·2
	0·70028	—	32516·4	—	1·6	10·0	46416·3
						Average	46427 ± 9
Phenol	0·86092	0·10309	32718·6	4786·3	9·1	19·4	32410·9
	0·89518	0·10130	33745·0	4703·2	9·3	20·0	32408·7
	0·87055	0·11263	33489·9	5229·2	8·6	19·8	32429·5
	0·85314	0·11171	32874·4	5186·3	4·7	19·4	32425·5
	0·83028	0·11158	32120·7	5180·4	4·6	18·9	32418·4
	0·86784	0·09419	32529·4	4373·0	4·5	19·3	32416·3
						Average	32418·2 ± 3·3
o-Cresol	0·79106	0·10875	32058·8	5049·0	4·3	17·4	34115·9
	0·84851	0·11260	34198·5	5227·5	5·4	18·6	34114·3
	0·76070	0·10817	30988·8	5022·0	4·5	16·8	34106·4
	0·80899	0·09693	32129·5	4500·3	5·0	17·5	34123·9
	0·76890	0·09861	30844·4	4578·2	5·3	16·7	34131·0
						Average	34118·3 ± 4·2
m-Cresol	0·83255	0·12676	34400·3	5885·0	10·6	18·5	34215·0
	0·70320	0·13441	30335·2	6240·3	14·1	16·2	34220·9
	0·84032	0·13342	34979·2	6194·2	13·4	18·8	34216·1
	0·73885	0·13091	31388·0	6077·9	15·1	16·8	34212·2
						Average	34216·1 ± 1·8
p-Cresol	0·81610	0·11959	33467·0	5552·1	10·1	18·1	34170·1
	0·88078	0·10987	35229·0	5101·0	13·1	19·1	34168·8
	0·74605	0·10757	30511·5	4994·1	9·2	16·5	34168·5
	0·76305	0·10835	31118·9	5030·3	8·8	16·8	34156·8
	0·85475	0·10810	34257·2	5018·7	11·0	18·6	34172·9
						Average	34167·4 ± 2·9
2,3-Xylenol...	0·68526	0·10206	29043·0	4738·2	1·6	14·2	35444·0
	0·64460	0·10098	27562·0	4688·1	2·0	13·5	35460·7
	0·63180	0·10064	27085·4	4672·3	1·6	13·3	35450·7
	0·84439	0·09841	34523·3	4568·8	2·2	17·1	35451·3
						Average	35451·7 ± 3·4
2,4-Xylenol...	0·96751	0·09222	38724·8	4281·4	11·4	19·2	35567·6
	0·63897	0·08853	26847·2	4110·0	13·8	13·2	35541·0
	0·75512	0·10422	31712·3	4838·7	11·4	15·6	35552·0
	0·70646	0·08261	28979·4	3835·4	10·9	14·3	35554·6
						Average	35553·8 ± 5·5
2,5-Xylenol...	1·00080	0·10149	40176·4	4711·9	3·2	20·0	35412·4
	0·67453	0·09883	28483·9	4588·2	3·1	14·0	35399·6
	0·76628	0·10803	32168·8	5015·5	2·4	15·8	35410·8
	0·71175	0·10097	29911·7	4687·7	2·8	14·7	35414·0
	0·68551	0·10209	29024·9	4739·9	2·7	14·3	35400·4
						Average	35407·4 ± 3·1
2,6-Xylenol...	0·71594	0·10073	30101·1	4676·5	8·3	14·8	35479·3
	0·84678	0·10114	34772·5	4695·8	2·3	17·2	35494·9
	0·79353	0·10294	32951·5	4779·2	2·8	16·2	35477·8
	0·70616	0·10233	29823·8	4751·0	2·0	14·6	35481·5
						Average	35483·4 ± 3·9
3,4-Xylenol...	0·70878	0·10129	29841·6	4702·4	4·7	14·7	35440·1
	0·84716	0·10256	34813·3	4761·4	2·5	17·2	35449·7
	0·89029	0·09994	36220·8	4640·0	2·3	17·9	35449·1
	0·88160	0·09762	35779·6	4532·1	12·4	17·7	35432·3
						Average	35442·8 ± 4·1
3,5-Xylenol...	0·71578	0·09414	29760·0	4370·4	11·9	14·7	35433·3
	0·68655	0·09656	28819·6	4483·1	9·5	14·2	35412·0
	0·72511	0·09697	30215·2	4501·8	10·7	14·9	35425·1
	0·81542	0·10028	33575·3	4655·5	10·6	16·6	35432·2
						Average	35425·7 ± 4·6

produced a strong seal without loss of molten polyethylene, as established in preliminary trials with empty bags. Finally the bag and contents were removed from the dry box and weighed.

The sealed bag containing the sample was placed in the platinum crucible within the bomb. A platinum fuse wire 0·7 cm. long, 0·1 mm. in diameter, welded to stouter platinum wires (0·5 mm. diameter) which were connected to the firing circuit, was bent so as to lie close to the top of the bag. Most of the air in the bomb was displaced by oxygen, and after the addition of 1 ml. of water the bomb head was placed in position and oxygen saturated with water vapour was passed in for one hour. The bomb was then filled with oxygen to 5 atm. and the pressure was released slowly. The bomb head was retightened and the bomb was filled to a pressure of 30·9 atm. with purified oxygen. The bag and its contents were ignited by connecting a 6 v battery to the firing circuit; a fluxmeter measured the electrical energy of ignition.

The nitric acid formed in the combustion was determined by titration of the bomb liquor with 0·1N-sodium hydroxide. The liquors from the combustion of phenol and *o*- and *m*-cresol had a very pale yellow colour, which intensified on addition of alkali. The bomb liquors from *p*-cresol and the xylenols were colourless. Spectroscopic examination suggested that the colour of the yellow solutions was due to traces of nitrophenols, but since the amount of these nitro-compounds formed never exceeded 0·014% of the phenol taken, no allowance was made for their presence in calculating the heats of combustion. It should be emphasized that there was little other evidence of partial combustion; in only a few experiments were minute patches of soot formed.

The results of the combustion experiments (including measurements on polyethylene film) are presented in Table 8. The masses listed have been corrected to a vacuum basis with the aid of the density values given in Tables 6 and 7; q_p represents the heat generated by the combustion of the polyethylene bag calculated by using the $-\Delta U_c°$ value listed (46,427 J/g.), q_{HNO_3} represents the correction for the formation of nitric acid by using a value [22] of −57·8 kJ/mole, $q_{s.s.}$ represents the standard state correction calculated by established methods; [22] $-\Delta U_c°$ is the energy of combustion in the standard state.

From the average values of $\Delta U_c°$ in Table 8, the corresponding values of $\Delta H_c°$ (the enthalpy of combustion) were derived, and these are presented in Table 9 together with values of the enthalpy of formation under standard conditions, $\Delta H_f°$. In the calculation of the values of $\Delta H_f°$, the values accepted by the National Bureau of Standards [23] for the heats of formation of carbon dioxide and of water were used. Table 9 also contains values, ΔH_f*, for the heats of formation of the compounds as gases, derived by combining the values of $\Delta H_f°$ with the values of the latent heats of vaporization at 25° given in Table 4.

TABLE 9. *Heats of combustion and formation (in kcal./mole) of phenol, the cresols, and xylenols.*

Compound	State at 25°	$-\Delta U_c°$	$-\Delta H_c°$	$-\Delta H_f°$	$-\Delta H_f$ *
Phenol	Cryst.	729·21 ± 0·08	729·80	39·46	23·05 ± 0·15
o-Cresol	Cryst.	881·83 ± 0·12	882·72	48·91	30·74 ± 0·22
m-Cresol	Liquid	884·36 ± 0·07	885·25	46·38	31·63 ± 0·26
p-Cresol	Cryst.	883·10 ± 0·08	883·99	47·64	29·97 ± 0·36
2,3-Xylenol	Cryst.	1035·15 ± 0·11	1036·33	57·67	37·59 ± 0·27
2,4-Xylenol	Liquid	1038·13 ± 0·11	1039·31	54·69	38·95 ± 0·18
2,5-Xylenol	Cryst.	1033·86 ± 0·10	1035·04	58·96	38·65 ± 0·12
2,6-Xylenol	Cryst.	1036·07 ± 0·12	1037·25	56·75	38·68 ± 0·13
3,4-Xylenol	Cryst.	1034·89 ± 0·13	1036·07	57·93	37·44 ± 0·14
3,5-Xylenol	Cryst.	1034·39 ± 0·14	1035·57	58·43	38·63 ± 0·16

Comparison may be made between the values in Table 9 and previous figures. Nineteenth-century measurements collated by Kharasch [24] have historic interest only. In the present century measurements have been made by Barker [25] on the three cresols, but his paper contains so little experimental information that detailed comparison with data in Table 9 is not fruitful. Badoche [26] gave values for the heats of combustion of phenol and *m*-cresol at 17°; when converted to 25° these values become −729·94 and −885·17 kcal./mole, respectively, in good

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[22] " Experimental Thermochemistry," edited by Rossini, Interscience Publ., Inc., New York, 1956.

[23] " Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Stand. Circular 500, 1952.

[24] Kharasch, *J. Res. Nat. Bur. Stand.*, 1929, **2**, 359.

[25] Barker, *J. Phys. Chem.*, 1925, **29**, 1345.

[26] Badoche, *Bull. Soc. chim. France*, 1941, **8**, 212.

agreement with the present values of $\Delta H_c°$. Parks, Manchester, and Vaughan's value [27] of $\Delta H_c°$ for phenol, $-730{\cdot}36$ kcal./mole, is not in good agreement with the present one, but it is just reconcilable with it if allowance is made for the " overall uncertainty " in the value due to Parks *et al.*, namely, 0·29 kcal./mole, and for the " uncertainty interval " attaching to the present value of $\Delta H_c°$, namely, 0·16 kcal./mole, equal to twice the standard deviation.

We thank Messrs. J. B. Ditcham, W. Kynaston, H. A. Gundry, and A. Sleven for technical assistance. The constants listed in Table 3 were calculated in the Mathematics Division, National Physical Laboratory, under the supervision of Mr. J. G. Hayes.

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[*Received, June 10th*, 1960.]

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