Ideal Gas Thermodynamic Properties of Phenol and Cresols

S.A. Kudchadker, A.P. Kudchadker, R.C. Wilhoit, and B.J. Zwolinski

Thermodynamics Research Center, Texas Engineering Experiment Station, Texas A&M University, College Station, Texas 77843

The standard chemical thermodynamic properties of phenol, *o*-cresol, *m*-cresol, and *p*-cresol were calculated by use of the rigid rotor harmonic oscillator approximation. The partition functions for internal rotation of -OH and $-CH_3$ groups were calculated as a direct sum over the internal rotation energy levels. It was assumed that *o*-cresol is a mixture of two rotational isomers. Values of molecular parameters, fundamental frequencies, potential barriers to internal rotation and enthalpies of formation were selected from among those reported in the literature and from some additional molecular orbital calculations.

Key words: Ideal gas thermodynamic properties; internal rotation; *m*-cresol; *o*-cresol; *p*-cresol; phenol; potential barrier heights; rotational isomers; torsional frequencies.

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1. Introduction

This study involves the calculation of ideal gas thermodynamic properties of phenol and the three cresols. A survey of the literature revealed that information regarding values of molecular parameters and barriers to methyl group rotation in the cresols was incomplete, particularly in the *o*-cresol. The additional information needed in this study was obtained from molecular orbital calculations carried out on *o*-cresol, *m*-cresol and *p*-cresol by the authors [1].[1] The ideal gas thermodynamic properties, heat capacity (C_p°), entropy (S°), enthalpy ($H^\circ-H_0^\circ$), Gibbs energy function [$-(G^\circ-H_0^\circ)/T$], enthalpy of formation (ΔHf°), Gibbs energy of formation (ΔGf°), and the logarithm of the equilibrium constant of formation ($\log Kf$), have been obtained for phenol and the three cresols. Values for these properties were computed at the pressure of one atmosphere (101325 Pa) and temperatures from 0-1500 K, using selected values of molecular parameters, vibrational frequencies, and potential barrier heights and assuming a rigid-rotor harmonic oscillator approximation. The internal rotation contributions to the thermodynamic properties for each compound were calculated by the use of a partition function formed by summation of the calculated internal rotation energy levels. These energy levels were obtained from an approximate solution of the Schroedinger equation using the potential functions

$$V_{OH}=\tfrac{1}{2}V_2(1-\cos 2\theta) \tag{1}$$

and

$$V_{CH_3}=\tfrac{1}{2}V_3(1-\cos 3\theta) \tag{2}$$

for $-OH$ and $-CH_3$ groups, respectively, where V_2 and V_3 are potential barrier heights and θ is the angle of internal rotation.

In these calculations, recent values of physical constants [2] and atomic weights [3] were used. The values of enthalpy and Gibbs energy function of elements C [4], H [5], and O [5] in their standard reference state were used.

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[1] Figures in brackets indicate the literature references.

The uncertainties in the calculated thermodynamic properties due to the uncertainties in the various molecular parameters are given below.

Molecular parameter	Uncertainty	Property	Average effect at 200–1000 K
Structural parameter	±0.05 Å ± 2.0°	S° $-(G^\circ-H_0^\circ)/T$	± 0.8 J K^{-1} mol^{-1} ± 0.8 J K^{-1} mol^{-1}
Vibrational frequencies	± 10 cm^{-1}	C_p° S° $-(G^\circ-H_0^\circ)/T$ $H^\circ-H_0^\circ$	± 0.8 J K^{-1} mol^{-1} ± 1.6 J K^{-1} mol^{-1} ± 0.8 J K^{-1} mol^{-1} ± 0.4 kJ mol^{-1}
OH potential barrier	± 1000 J mol^{-1}	C_p° S° $-(G^\circ-H_0^\circ)/T$ $H^\circ-H_0^\circ$	± 0.6 J K^{-1} mol^{-1} ± 1.4 J K^{-1} mol^{-1} ± 0.8 J K^{-1} mol^{-1} ± 0.4 kJ mol^{-1}
CH_3 potential barrier	± 1000 J mol^{-1}	C_p° S° $-(G^\circ-H_0^\circ)/T$ $H^\circ-H_0^\circ$	± 0.6 J K^{-1} mol^{-1} ± 0.6 J K^{-1} mol^{-1} ± 0.4 J K^{-1} mol^{-1} ± 0.4 kJ mol^{-1}

2. Phenol

Kojima [6], Forest and Dailey [7], and Pedersen et al. [8] reported the molecular parameters for phenol from their microwave measurements. Pedersen et al. have now concluded with certainty that phenol is planar in its equilibrium configuration. We have adopted their values of molecular parameters and moments of inertia in these calculations, and they are presented in table 1.

The vibrational frequencies were reported by Evans [9], Green [10], and Bist et al. [11]. Bist et al. obtained their values from an infrared and an electronic spectrum in the vapor phase. We adopted their values of the fundamental frequencies except for the following two frequencies: 958 cm^{-1} instead of 995 cm^{-1} [12] and 225 cm^{-1} instead of 244 cm^{-1} [13] (table 2).

TABLE 1. Molecular parameters for phenol (1 Å=10^{-8}m)

C-C =1.397 Å C_1-O=1.364 Å C_2-H=1.084 Å C_3-H=1.076 Å C_4-H=1.082 Å O-H =0.956 Å	∠ COH=109.0° ∠ between CO and rotation axis=2.2° all ∠ CCC and ∠ CCH=120°

I_a = 89.4667 amu $Å^2$
I_b =193.0073 amu $Å^2$
I_c =282.4440 amu $Å^2$
I_r = 0.7370 amu $Å^2$
V_2(OH)= 14.510 kJ mol^{-1}
σ =1 (overall)
σ =2 (OH rotor)

TABLE 2. Vibrational frequencies (cm^{-1}) for phenol and cresols

Phenol		o-Cresol		m-Cresol		p-Cresol	
a_1	3656	a'	3073	a'	3080	a_1	3062
	3087		3060		3060[c]		3030
	3063		3049		3042		1615
	3027		3028		3028[c]		1515
	1603		1608		1614		1252
	1501		1587		1600		1213
	1261		1492		1490		1170
	1176		1462		1462		1018
	1168		1324		1306		843
	1025		1300		1281		738
	999		1255		1268		462
	823		1207		1163	a_2	949
	526		1149		1151		810
a_2	958[a]		1102		1082		407
	817		1043		1000	b_1	922
	409		842		930		817
b_1	973		748		733		699
	881		586		536		507
	751		529		518		320
	686		429		443		178
	503		275		297	b_2	3062
	309	a''	967	a''	962		3030
	225[b]		928		880		1598
b_2	3070		844		848		1428
	3049		749		771		1328
	1610		711		685		1291
	1472		542		560		1102
	1343		442		443		643
	1277		315		246		426
	1150		191		211		282[f]
	1070	OH	3600	OH	3614		3608
	619		1164		1182		1170
	403	ν_τ	322[d]		311		298
			297[e]				
		CH_3	2974	CH_3	2980	CH_3	2970
			2944		2951		2945
			2916		2924		2922
			1441		1439		1458
			1441		1439		1458
			1381		1380		1379
			1039		1038		1043
			986		1008		985
		ν_τ	173[c] *cis*		free		free
			free rotation } *trans*		rotation		rotation

[a] Ref [12].
[b] Ref [13].
[c] Estimated.
[d] *cis*.
[e] *trans*.
[f] See text.

The literature gives various values of potential barrier heights as follows: 1100 [14], 1190 [15], 1207 [16], 1213 [13], 1215 [11], 1244 [17], and 1266 cm^{-1} [18]. These values correspond to a torsional frequency 309–310 cm^{-1} and various values of reduced moments of inertia of the OH top obtained by assuming different molecular parameters for phenol. We have adopted here the value reported by Larsen and Nicolaisen [13], as it is obtained from a combination of far infrared [11] and microwave data [8].

Cox and Pilcher [19] critically reviewed the enthalpies of formation for phenol and recommended the value reported by Andon et al. [20]. We adopted the same value in this work.

Ideal gas thermal functions were calculated using the data from tables 1 and 2 and are presented in table 3. For comparison, the third law entropies were obtained as follows. The ex-

TABLE 3. Ideal gas thermodynamic functions of phenol

T	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔHf°	ΔGf°	log Kf
K	J K⁻¹ mol⁻¹			kJ mol⁻¹			
0	0.000	0.000	0.000	0.000	—77.804	—77.804	Infinite
50.00	33.909	218.686	185.333	1.668	—83.215	—77.161	80.609
100.00	41.384	244.047	208.865	3.518	—85.630	—70.193	36.665
150.00	54.189	263.131	223.843	5.893	—88.310	—61.907	21.558
200.00	69.651	280.789	235.886	8.981	—91.142	—52.719	13.769
273.15	94.609	306.152	251.310	14.980	—95.134	—37.866	7.241
298.15	103.223	314.810	256.271	17.453	—96.399	—32.631	5.717
300.00	103.855	315.451	256.634	17.645	—96.491	—32.229	5.611
400.00	135.794	349.823	275.649	29.670	—100.869	—10.180	1.329
500.00	161.907	383.042	293.832	44.605	—104.237	12.967	—1.355
600.00	182.480	414.454	311.345	61.865	—106.809	36.652	—3.191
700.00	198.839	443.858	328.199	80.961	—108.797	60.753	—4.533
800.00	212.142	471.307	344.392	101.532	—110.297	85.025	—5.552
900.00	223.185	496.950	359.934	123.314	—111.367	109.586	—6.360
1000.00	232.490	520.960	374.849	146.111	—111.992	134.282	—7.014
1100.00	240.411	543.500	389.167	169.767	—112.283	158.625	—7.532
1200.00	247.202	564.718	402.921	194.156	—112.388	183.351	—7.981
1300.00	253.055	584.741	416.144	219.176	—112.331	208.070	—8.360
1400.00	258.121	603.684	428.870	244.741	—112.125	233.051	—8.695
1500.00	262.523	621.646	441.128	270.778	—111.779	257.541	—8.968

perimental heat capacity data for solid and liquid [21] were fitted to the equations and the following values of entropy were obtained. S(s, 298.15 K)=143.43±0.42 J K⁻¹ mol⁻¹ and S(1, 400 K)=238.86±0.84 J K⁻¹ mol⁻¹. Using these values plus vapor pressure data [22] and enthalpy of sublimation [20], ideal gas entropies were obtained (table 4). As seen from table 4, the statistically calculated entropy value agreed well with the third law entropy at 400 K but not at 298.15. The discrepency at 298.15 K, as pointed by Andon et al., lies in the lack of good vapor pressure data at 298.15 and in the uncertainty in the enthalpy of sublimation and not in the heat capacity measurements. Recently, Nichols and Wadso [22a] obtained C_p(s, 298.15)=127.21 J K⁻¹ mol⁻¹ which agrees well with that obtained from the measurements of Andon et al. (126.78 J K⁻¹ mol⁻¹). Previous calculations of ideal gas thermodynamic properties of phenol [9,10,23,24] were based on less complete data than are now available. They are compared with our values at 298.15 and 400 K in table 4.

3. *o*-Cresol

No microwave measurements are reported in the literature for *o*-cresol. Bois [25] reported the crystal structure for *o*-cresol with three sets of molecular parameters for the hydrogen bonded molecules. Hence, we obtained the best set of molecular parameters for the free molecule from the molecular orbital calculations (M.O.) [1] which are presented in table 5.

Jha and Chattopadhyay [26] reviewed the spectral work of various workers [27,28,29] and also reported the partial assignments for *o*-cresol. Green et al. [12] reported all the vibrational frequencies except CH_3 torsion from their infrared and Raman spectral measurements. They observed a doublet for δ (OH) which they attributed to the two isomers of *o*-cresol. Recently, Carlson and Fateley [30] studied the low frequency spectra of *o*-cresol and deuterated *o*-cresol (OD). They found that in dilute cyclohexane solution, the torsional region is more complex than for any other substituted phenol. It contained three bands of equal intensity. However, they observed only one torsional band for deuterated o-cresol and hence could not conclude whether there is only one, two or three isomers for *o*-cresol.

From our M.O. calculations [1,31] it has been shown that the strong interactions between the rotation of the OH and CH_3 groups result in two identifiable rotational isomers, and the two OH torsional bands, 322 and 297 cm⁻¹ observed by

TABLE 4. Comparison of calculated and experimental entropies (J K⁻¹ mol⁻¹) at 298.15 and 400 K

Authors	Phenol		*o*-Cresol		*m*-Cresol		*p*-Cresol	
	298.15 K	400 K	298.15 K	400 K	298.15 K	400 K	298.15 K	400 K
Evans [9]	314.30	349.24						
Green [10]	315.60	350.62	357.61	401.20	356.77	398.94	347.65	393.92
Ramaswamy [23]	298.44	307.94	346.02	363.34	346.02	363.34	346.02	363.34
Sarin [24]	309.28	345.05						
This work	314.80	349.82	352.59	395.27	356.06	398.15	350.74	392.88
Experimental	309.66	350.83	354.80	397.35	348.11	399.40	342.33	394.09
	±2.51	±0.92	±2.93	±1.67	±3.77	±0.84	±5.44	±0.84
Exp.—this work	−5.14	+1.01	+2.21	+2.08	−7.95	+1.25	−8.41	+1.21

TABLE 5. Molecular parameters for *o*-cresol

C-C	=1.40 Å	∠ COH=109°	
C-H	=1.08 Å	all ∠ CCC and ∠ CCH=120°	
C-O	=1.38 Å	∠ CCH and ∠ HCH=tetrahedral	
O-H	=1.00 Å		
$C-CH_3$	=1.51 Å		
$C-H(CH_3)$	=1.10 Å		
cis		*trans*	
I_a	=153.897 amu Å^2	I_a	=159.028 amu Å^2
I_b	=231.711 amu Å^2	I_b	=227.873 amu Å^2
I_c	=382.355 amu Å^2	I_c	=383.648 amu Å^2
$I_r(OH)$	= 0.8656 amu Å^2	$I_r(OH)$	= 0.8519 amu Å^2
$I_r(CH_3)$	= 3.1888 amu Å^2	$I_r(CH_3)$	= 3.1908 amu Å^2
$V_a(OH)$	= 18.046 kJ mol^{-1}	$V_b(OH)$	= 15.769 kJ mol^{-1}
$V_3(CH_3)$	= 8.673 kJ mol^{-1}	$V_3(CH_3)$	=free rotor
σ	=1 (overall)	σ	=1 (overall)
σ	=3 (CH_3 rotor)	σ	=3 (CH_3 rotor)
cis + trans		V_1	= 2.276 kJ mol^{-1}
		V_2	=16.907 kJ mol^{-1}

Carlson and Fateley [30] are accordingly assigned to the *cis* and the *trans* isomer, respectively. The band at 266 cm^{-1} is assumed to be present due to some unidentified splitting. Green et al. [12] assigned it to ν_{21}.

The M.O. calculations obtained the potential barrier height of 8.673 kJ mol^{-1} for the CH_3 rotor of the *cis* isomer and 0.360 kJ mol^{-1} for the *trans*. Here the methyl group of the *trans* is considered to be a free rotor as the potential barrier is very low.

The other fundamentals for *o*-cresol are listed in table 2 and were assumed to apply to both isomers. These are the same as given by Green et al., [12] except that 266 cm^{-1} was replaced by 275 cm^{-1} as recommended by Carlson and Fateley [30].

The enthalpy of formation at 298.15 K reported by Andon et al., [20] and recommended by Cox and Pilcher [19] was adopted by us.

The ideal gas thermodynamic properties based on the above model (two rotational isomers) were calculated using the data given in tables 2 and 5. The potential barrier heights of the OH rotor for the two isomers were obtained by the usual procedure [32]. The internal rotation energy levels for the OH rotor were calculated from the potential function

$$V=\tfrac{1}{2}V_1(1-\cos\theta)+\tfrac{1}{2}V_2(1-\cos 2\theta),\ \sigma=1 \tag{3}$$

where θ and σ are the rotational angle and symmetry number respectively. V_1 and V_2 were calculated from the following relationships

$$V_1=\Delta E \tag{4}$$

$$V_2=V_a-\tfrac{1}{2}V_1 \tag{5}$$

where ΔE=energy difference between the two isomers, and V_a is the barrier height of the *cis* isomer. The energy levels obtained from equation (3) were separated into subsets for the two isomers. The energy levels for the CH_3 rotor were obtained from equation 2. The calculated thermodynamic properties for the equilibrium mixture of two isomers are presented in table 6 and the composition of the equilibrium mixture at various temperatures is presented in table 7.

The comparison of observed and calculated entropy is shown in table 4. The discrepancy is close to the experimental uncertainty. The vibrational assignments are less well-determined and though the agreement of the computed and experimental entropy is satisfactory, it is not a sufficient argument for the proposed assignment. Green's [10a] values are higher than ours though he considered only one rotational isomer for *o*-cresol. This is because he used one extra low vibrational frequency (190 cm^{-1}) and lower potential barrier height (3100 cal mol^{-1}) for the OH rotor.

4. *m*-Cresol

No microwave measurements are reported in the literature for *m*-cresol. Bois [34] reported the crystal structure with six sets of molecular parameters. As in case of *o*-cresol, molecular orbital calculations were carried out and the molecular parameters obtained are given in table 8.

Partial vibrational assignments were made by several workers [26,27,28,35]. Green et al. [12] reported complete vibrational assignments except for the CH_3 torsion. They observed some doublets which they attributed to the presence of two isomers. Manocha et al. [36] studied the far infrared spectrum of *m*-cresol in the vapor phase and observed two torsional transitions, 311 cm^{-1} ($0\leftarrow1$) and 279 cm^{-1} ($1\leftarrow2$). They assumed very small difference between the *trans* and the *cis* isomer, which seems to be true from our molecular orbital calculations. Hence we have adopted the vibrational frequencies of Green et al., and ν_τ=311 cm^{-1} (table 2).

The potential barrier height for the OH rotor was obtained using ν_τ=311 cm^{-1} [32]. No torsional frequency for the CH_3 rotor is reported. From the molecular orbital calculations [1], it was found that in *m*-cresol the CH_3 rotor behaves as a free rotor and hence we have assumed it to be so.

The enthalpy of formation at 298.15 K reported by Andon et al. [20] and recommended by Cox and Pilcher [19] was adopted by us.

The ideal gas thermodynamic properties were calculated using the data given in tables 2 and 8 and presented in table 9. The contribution to the thermodynamic properties of two isomers was obtained by adding $R\ln2$ to $S°$ and $-(G°-H^\circ_0)/T$.

As in phenol, the calculated entropy value agrees well with the third law entropy value [33] at 400 K but not at 298.15 K (table 4). The same justification proposed by the authors for phenol applies here. However, this is not conclusive proof that the vibrational assignments are well determined.

5. *p*-Cresol

No microwave measurements are reported for *p*-cresol. Bois [37] reported the crystal structure with two sets of molecular parameters. As in the case of *o*- and *m*-cresol, a set of molecular parameters was obtained from molecular orbital calculations [1] and is given in table 10.

TABLE 6. Ideal gas thermodynamic functions for *o*-cresol

T	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔHf°	ΔGf°	log *Kf*
K	$J\ K^{-1}\ mol^{-1}$			$kJ\ mol^{-1}$			
0	0.000	0.000	0.000	0.000	—106.285	—106.285	Infinite
50.00	38.217	225.631	191.489	1.707	—111.391	—101.656	106.198
100.00	59.181	258.691	217.154	4.154	—114.586	—90.699	47.376
150.00	75.094	285.778	235.641	7.521	—118.034	—78.023	27.170
200.00	91.259	309.553	251.193	11.672	—121.673	—64.189	16.764
273.15	117.844	341.859	271.187	19.304	—126.890	—42.136	8.058
298.15	127.301	352.587	277.564	22.368	—128.574	—34.378	6.023
300.00	128.000	353.377	278.029	22.605	—128.696	—33.785	5.882
400.00	164.312	395.267	302.135	37.253	—134.659	—1.287	0.168
500.00	195.289	435.373	324.805	55.284	—139.380	32.705	—3.417
600.00	220.432	473.283	346.425	76.115	—143.036	67.470	—5.874
700.00	240.845	508.848	367.116	99.213	—145.855	102.822	—7.673
800.00	257.677	542.142	386.936	124.165	—147.951	138.419	—9.038
900.00	271.768	573.329	405.932	150.657	—149.410	174.410	—10.122
1000.00	283.696	602.597	424.151	178.447	—150.232	210.561	—10.998
1100.00	293.871	630.126	441.637	207.338	—150.567	246.315	—11.696
1200.00	302.597	656.080	458.436	237.173	—150.607	282.482	—12.296
1300.00	310.113	680.604	474.591	267.817	—150.395	318.677	—12.804
1400.00	316.611	703.830	490.143	299.161	—149.956	355.155	—13.251
1500.00	322.250	725.870	505.130	331.111	—149.315	391.024	—13.617

TABLE 7. Composition of equilibrium mixture of *o*-cresol

Temp	Mole fraction	
K	*cis*	*trans*
50	0.99	0.01
100	0.88	0.12
150	0.73	0.27
200	0.64	0.36
273.15	0.56	0.44
298.15	0.55	0.45
300	0.55	0.45
400	0.51	0.49
500	0.49	0.51
600-1500	0.48	0.52

TABLE 8. Molecular parameters for *m*-cresol

C-C =1.40 Å
C-H =1.08 Å
C-O =1.38 Å
O-H =1.00 Å
$C-CH_3$ =1.51 Å
$C-H(CH_3)$ =1.10 Å

∠COH=109°
all ∠CCC and ∠CCH=120°
∠CCH and ∠HCH=tetrahedral

I_a =136.873 amu $Å^2$
I_b =285.368 amu $Å^2$
I_c =418.988 amu $Å^2$
$I_r(OH)$ = 0.8605 amu $Å^2$
$I_r(CH_3)$ = 3.1844 amu $Å^2$

$V_2(OH)$ = 16.803 kJ mol^{-1}
$V_2(CH_3)$ =free rotor

σ =1 (overall)
σ =2 (OH rotor, two isomers)
σ =3 (CH_3 rotor)

TABLE 9. Ideal gas thermodynamic functions for *m*-cresol

T	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔHf°	ΔGf°	log Kf
K	J K^{-1} mol^{-1}			kJ mol^{-1}			
0	0.000	0.000	0.000	0.000	—107.919	—107.919	Infinite
50.00	38.690	238.932	201.327	1.880	—115.228	—105.812	110.540
100.00	50.748	268.919	228.139	4.078	—118.421	—95.173	49.713
150.00	67.590	292.610	245.758	7.028	—121.849	—82.821	28.841
200.00	85.999	314.545	260.234	10.862	—125.460	—69.319	18.104
273.15	114.726	345.561	278.947	18.195	—130.631	—47.764	9.134
298.15	124.675	356.038	284.972	21.188	—132.298	—40.179	7.039
300.00	125.408	356.812	285.413	21.420	—132.419	—39.600	6.895
400.00	162.970	398.148	308.452	35.879	—138.301	—7.810	1.020
500.00	194.537	438.027	330.410	53.809	—142.932	25.451	—2.659
600.00	219.937	475.826	351.527	74.579	—146.500	59.467	—5.177
700.00	240.449	511.324	371.847	97.634	—149.241	94.055	—7.018
800.00	257.311	544.567	391.382	122.548	—151.274	128.880	—8.415
900.00	271.408	575.712	410.152	149.004	—152.683	164.091	—9.523
1000.00	283.336	604.942	428.185	176.758	—153.467	199.456	—10.418
1100.00	293.512	632.437	445.516	205.613	—153.776	234.422	—11.132
1200.00	302.244	658.359	462.183	235.411	—152.798	269.799	—11.744
1300.00	309.769	682.856	478.224	266.021	—153.574	305.202	—12.263
1400.00	316.280	706.055	493.676	297.331	—153.129	340.888	—12.719
1500.00	321.935	728.074	508.575	329.249	—152.484	375.965	—13.092

TABLE 10. Molecular parameters for *p*-cresol

C-C	=1.40 Å	∠ COH=109°
C-H	=1.08 Å	all ∠ CCC and ∠ CCH=120°
C-O	=1.36 Å	∠ CCH and ∠ HCH=tetrahedral
O-H	=1.00 Å	
C-CH_3	=1.51 Å	
C-H(CH_3)	=1.10 Å	

I_a	= 93.305 amu Å^2
I_b	=344.076 amu Å^2
I_c	=434.128 amu Å^2
I_r(OH)	= 0.8592 amu Å^2
I_r(CH_3)	= 3.1389 amu Å^2
V_2(OH)	= 15.493 kJ mol^{-1}
V_3(CH_3)	=free rotor
σ	=1 (overall)
σ	=2 (OH rotor)
σ	=3 (CH_3 rotor)

Partial vibrational assignments are reported in the literature [26,27,28,38,39]. Green et al. [12] reported complete vibrational assignments except for the CH_3 torsion. Fateley et al. [40] reported 298 cm^{-1} for the OH torsional frequency in cyclohexane solution, while Green et al. observed it at 295 cm^{-1} in vapor phase. When the lowest three frequencies of *o*-, *m*-, and *p*-cresols, excluding OH torsion, were compared, the ν_{30} (338 cm^{-1}) was suspect and we feel it should be 282 cm^{-1} which was observed by Biswas [28] in the Raman spectrum. The better agreement between the experimental and calculated entropies with the use of 282 cm^{-1} has made us adopt this fundamental. However, this should be studied further. The adopted frequencies are given in table 2.

The potential barrier height for OH rotor was obtained [32] from ν_r=298 cm^{-1}. As expected the CH_3 rotor is found to behave as a free rotor from the M.O. calculations.

Andon et al., [20] reported the enthalpy of formation at 298.15 which is recommended by Cox and Pilcher. We have adopted the same value.

Ideal gas thermodynamic properties were calculated using the data from table 2 and 10 and are reported in table 11. The internal rotation contribution was obtained by the procedure mentioned earlier using the symmetry number two for the OH rotor and three for the free CH_3 rotor.

As in the case of phenol and *m*-cresol, the calculated entropy of *p*-cresol agrees well with the third law entropy at 400 K but not at 298.15. Even for *p*-cresol the agreement at 400 K is not a sufficient argument for the proposed vibrational assignments.

TABLE 11. Ideal gas thermodynamic functions for *p*-cresol

T	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔHf°	ΔGf°	log Kf
K	J K^{-1} mol^{-1}			kJ mol^{-1}			
0.	0.000	0.000	0.000	0.000	—101.131	—101.131	Infinite
50.00	39.108	232.576	194.862	1.886	—108.434	—98.701	103.111
100.00	51.307	262.895	221.819	4.108	—111.603	—87.753	45.837
150.00	68.393	286.868	239.584	7.093	—114.996	—75.107	26.154
200.00	86.746	309.032	254.198	10.967	—118.567	—61.324	16.016
273.15	115.153	340.237	273.081	18.344	—123.695	—39.374	7.529
298.15	124.972	350.746	279.153	21.346	—125.353	—31.656	5.546
300.00	125.694	351.521	279.596	21.577	—125.473	—31.067	5.409
400.00	162.770	392.871	302.771	36.040	—131.352	—1.250	—0.163
500.00	194.020	432.668	324.802	53.933	—136.020	35.042	—3.661
600.00	219.281	470.358	345.953	74.643	—139.648	69.600	—6.059
700.00	239.772	505.752	366.280	97.630	—142.457	104.740	—7.816
800.00	256.675	538.907	385.809	122.478	—144.555	140.127	—9.149
900.00	270.837	569.980	404.565	148.874	—146.025	175.907	—10.209
1000.00	282.836	599.154	422.580	176.574	—146.863	211.849	—11.066
1100.00	293.080	626.604	439.892	205.383	—147.218	247.396	—11.748
1200.00	301.871	652.492	456.541	235.142	—147.280	283.357	—12.334
1300.00	309.447	676.961	472.563	265.716	—147.090	319.349	—12.831
1400.00	316.002	700.138	487.998	296.997	—146.676	355.625	—13.268
1500.00	321.693	722.139	502.881	328.888	—146.057	391.294	—13.626

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