Thermochimica Acta, 6 (1973) 39–46

THERMODYNAMIC PROPERTIES IN THE GASEOUS STATE OF CERTAIN MONOSUBSTITUTED BENZENES

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(Received 1 September 1972)

ABSTRACT

The vibrational vapour-phase frequencies and recently reported moments of inertia have been used for computing thermodynamic properties of one mole gas of both benzaldehyde and the two deuterated species of phenol (C_6H_5OD and C_6D_5OH) at 1 atmosphere pressure in the temperature range 200–1000 K for the first time. The earlier similar data for chlorobenzene and phenol have been revised. The gas imperfection correction has been applied to the calculated thermodynamic properties of all the molecules. The effect of hindered rotation in benzaldehyde and the three species of phenol has also been taken into account. The correction for isotopic mixing of ^{35}Cl and ^{37}Cl in chlorobenzene has been applied to improve upon the earlier results. Good agreement between the observed (where data is available) and computed values is obtained.

NOMENCLATURE

C_p°	Ideal gas heat capacity at constant pressure (cal/mole K).
$-\frac{G_0^\circ - H_0^\circ}{T}$	Ideal gas free energy function (cal/mole K).
$\frac{H^\circ - H_0^\circ}{T}$	Ideal gas enthalpy function (cal/mole K).

INTRODUCTION

Using the data obtained from molecular spectroscopy the values of the useful thermodynamic quantities *i.e.* Gibb's energy G°, enthalpy H°, specific heat at constant pressure C_p° and entropy S° have been computed with great precision for benzaldehyde, phenol-d_1 and phenol-d_5 for the first time and the earlier values for phenol-h_6 and chlorobenzene have been revised. Further, these calculated values, the experimental heat of formation $\Delta H_{298.16}^\circ$ of these molecules and the thermodynamic quantities of C (graphite), H_2 (gas), O_2 (gas) and Cl_2 (gas)[1] have been used to compute the values of ΔH°_{fT}, ΔG°_{fT} (Gibbs energy of formation) and $\log_{10} K_p$ (equilibrium constant in terms of pressure) for all the molecules except the two deuterated species of phenol for which the experimental values of heat of formation are not known. Well-known formulae given in the text books[2,3] have been used to calculate the above mentioned quantities for one mole of a gas, at 1 atmosphere pressure in the temperature range 200–1000 K. The necessary correction due to hindered rotation[3] (in benzaldehyde, phenol and its deuterated species) and correction for isotopic mixing[3] (of ^{35}Cl and ^{37}Cl in chlorobenzene) have been applied to obtain improved results. Details for each molecule have been discussed separately.

EXPERIMENTAL

The vapour-phase spectra of the samples were recorded on a Perkin–Elmer Model 621 spectrophotometer using a multiple reflection cell with an adjustable path length from 1.25 to 10 meters in steps of 1.25 meters. The frequency marker accessory provided exact measurement of band positions. The pressure of the sample and the path length of the cell were adjusted to obtain a good spectrum. As far as possible low pressures and full 10 meter path lengths were used to obtain the resolved band contours. The instrument was purged with dry air obtained from a high pressure line, after drying with a pneumatic air dryer; this is to avoid the unwanted atmospheric water vapour and CO_2 absorption bands, spectroscopic data thus obtained has been recorded in Appendix I, and used for all the computations. The rotational constant have been listed in Appendix II, while the thermodynamic quantities for individual molecule are listed in Tables 1, 2, 3, 4 and 5.

CHLOROBENZENE

Whiffen[4] used fundamental frequencies of liquid phase and moments of inertia determined by Erlandsson[5] to calculate the thermodynamic properties of chlorobenzene. The isotopic mixing terms and gas imperfection correction were excluded in the computation. So it is worthwhile to recalculate the thermodynamic quantities using precisely determined vapour-phase fundamental frequencies (*cf.* Appendix I), the moments of inertia from the rotational constants (*cf.* Appendix II) determined by Poynter[6] and applying the corrections for isotopic mixing and gas imperfections.

For isotopic mixing the presence of two isotopes of chlorine ^{35}Cl and ^{37}Cl have been taken in the ratio 3:1. The gas imperfection correction has been estimated using the critical temperature and pressure data as reported in the literature[3]. The symmetry number for over all rotation of the molecule is 2. Thus, the values computed for 1 mole of gas at 1 atmosphere pressure in the temperature range 200–1000 K have been listed in Table 1.

The values given in columns 3 and 5 of Table 1 together with those[1] for C (graphite), H_2 (gas), Cl_2 (gas) and the experimental value of heat of formation of

TABLE 1

THE MOLAL THERMODYNAMIC PROPERTIES OF CHLOROBENZENE IN THE IDEAL GAS STATE

$T(K)$	$C_p^{\circ a}$	$(H^\circ - H_0^\circ)/T^a$	$(G^\circ - H_0^\circ)/T^a$	$S^{\circ a}$	$\Delta H_{fT}^{\circ\, b}$	$\Delta G_{fT}^{\circ\, b}$	$\log_{10} K_p$
200	17.15	10.15	56.13	66.28	13.39	20.27	−22.148
298.16	23.77	13.53	61.46	74.99	12.39	23.68	−17.357
400	30.75	17.04	66.07	83.11	11.48	27.62	−15.090
500	36.53	20.38	70.28	90.66	10.77	31.73	−13.869
600	41.45	23.47	74.30	97.77	10.21	35.94	−13.091
700	44.86	26.27	78.14	104.41	9.76	40.25	−12.566
800	47.87	28.79	81.82	110.61	9.46	44.64	−12.194
900	50.35	31.05	85.35	116.40	9.30	49.13	−11.930
1000	52.44	33.09	88.73	121.82	9.10	53.49	−11.690

[a] Units: cal/mole K. [b] Units: kcal/mole.

chlorobenzene gas[7] have been used to calculate ΔH_{fT}° and $\log_{10} K_p$ for the reaction

$$6\text{C (graphite)} + \tfrac{5}{2}\text{H}_2\text{ (gas)} + \tfrac{1}{2}\text{Cl}_2\text{ (gas)} = \text{C}_6\text{H}_5\text{Cl (gas)}$$

However the present computations may be considered more reliable because we have applied more important corrections and used accurate spectroscopic data.

Whiffen[4] used Stull's[8] calorimetric values of liquid phase entropies, Jones and Bowden's[9] values of latent heats of vapourization and values of vapour pressures from Stull's data[7] to calculate the gas-state entropies for PhCl. The reported gas-state calorimetric and calculated entropies are 71.8 cal/mole K and 74.92 cal/mole K, respectively, while the present computed value is 74.99 cal/mole K. Whiffen's suggestions, that the Stull's[8] extrapolation for entropy change 0–91 K and the errors in the values of vapour pressure and latent heats are responsible for this large difference between calculated and experimental values, gets further support from the present computations; and a direct determination of specific heats below 91 K would be desirable.

PHENOL-h_6

With the availability of precise values of vapour-phase fundamental vibrational frequencies of phenol, the barrier height for free rotation of the OH group[10,11] and the moments of inertia[12], it is worthwhile to recalculate the thermodynamic quantities and compare them with the earlier results[13] reported on the basis of solution-phase spectral data and speculated geometry of the molecule. The thermodynamic quantities have been calculated for 1 mole of gas at 1 atmosphere pressure in the temperature range 200–1000 K and corrected for gas imperfections and restricted rotation. The symmetry numbers are "one" for overall rotation and "two" for internal rotation. The thermodynamic functions thus computed have been listed in Table 2A.

TABLE 2

A. THE MOLAL THERMODYNAMIC PROPERTIES OF PHENOL IN THE IDEAL GAS STATE

$T(K)$	$C_p^{\circ a}$	$(H^\circ - H_0^\circ)/T^a$	$(G^\circ - H_0^\circ)/T^a$	$S^{\circ a}$	$\Delta H_{fT}^{\circ b}$	$\Delta G_{fT}^{\circ b}$	$\log_{10} K_p$
200	17.71	10.10	54.83	64.93	−21.82	−12.21	13.342
298.16	24.94	13.75	60.17	73.92	−23.03	−7.41	5.431
400	32.52	17.58	64.89	82.47	−24.09	−1.97	+1.076
500	38.71	21.21	69.26	90.47	−24.88	3.65	−1.595
600	43.60	24.59	73.41	98.00	−25.49	9.40	−3.424
700	47.51	27.59	77.43	105.02	−25.96	15.26	−4.764
800	50.68	30.26	81.33	111.59	−26.34	21.15	−5.775
900	53.32	32.68	85.04	117.72	−26.60	27.09	−6.578
1000	55.55	34.85	88.60	123.45	−26.76	33.08	−7.229

B. VAPOUR-PHASE ENTROPY OF PHENOL AT 298.16 K

calorimetric	73.81 ± 0.64	cal/mole K
spectroscopic (present)	73.92	cal/mole K
spectroscopic (ref. 16)	75.43	cal/mole K

[a] Units: cal/mole K. [b] Units: kcal/mole.

From the quantities given in columns 3 and 5 of Table 2A together with those[1] for C (graphite), H_2 (gas), and O_2 (gas) and the experimental values of heat of formation of phenol gas[14] the values of ΔH_{fT}°, ΔG_{fT}° and $\log_{10} K_p$ have been calculated for the reaction

$$6C\text{ (graphite)} + 3H_2\text{ (gas)} + \tfrac{1}{2}O_2\text{ (gas)} = C_6H_5OH\text{ (gas)}$$

In comparison to the entropy calculated by Green[13] the present value is found to be in better agreement with the experimental (*cf.* Table 2B) value.

BENZALDEHYDE

The thermodynamic properties for benzaldehyde vapour have been computed for the first time using (a) the precise vapour-phase fundamental frequencies for the compound (*cf.* Appendix I), (b) the three moments of inertia from the rotational constants determined by Kojima* *et al.*[15], (c) the reduced moment of inertia for internal rotation[16], and (d) the symmetry numbers 1 for overall rotation and 2 for internal rotation. The thermodynamic quantities have been found for different temperatures in the range 200–1000 K for 1 mole of perfect gas at 1 atmosphere

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*T. Kojima, personal communication (Aug. 1969) to Dr. H. D. Bist in which the rotational constants in the rotational states of benzaldehyde were given: for the lower level $A = 5235.2$, $B = 1564.3$ and $C = 1204.7$ Mc/sec and for the higher level $A = 5213.9$, $B = 1564.9$ and $C = 1206.5$ Mc/sec.

pressure. The gas imperfection correction has been applied using the reported values[17] of critical temperature and pressure. The contribution of restricted rotation has been evaluated from the tables of Pitzer and Gwinn[18] by interpolation. The corrected quantities are listed in Table 3.

TABLE 3

THE MOLAL THERMODYNAMIC PROPERTIES OF BENZALDEHYDE IN THE IDEAL GAS STATE

$T(K)$	$C_p^{\circ a}$	$(H^\circ - H_0^\circ)/T^a$	$(G^\circ - H_0^\circ)/T^a$	$S^{\circ a}$	$\Delta H_{fT}^{\circ b}$	$\Delta G_{fT}^{\circ b}$	$\log_{10} K_p$
200	20.93	11.09	56.52	67.61	−14.44	−5.23	5.715
298.16	7.40	15.28	63.43	78.71	−15.55	−0.96	0.704
400	35.30	19.38	68.80	88.18	−16.60	4.08	−2.229
500	42.05	23.26	73.66	96.92	−17.40	9.28	−4.057
600	47.54	26.87	78.25	105.12	−18.04	14.65	−5.336
700	51.94	30.15	82.66	112.81	−18.56	20.15	−6.291
800	55.52	33.10	86.90	120.00	−18.88	25.66	−7.010
900	58.47	35.76	90.95	126.71	−19.13	31.26	−7.591
1000	60.93	38.15	94.86	133.01	−19.26	36.87	−8.058

[a] Units: cal/mole K. [b] Units: kcal/mole.

The values listed in columns 3 and 5 of Table 3 together with those[1] for C (graphite), H_2 (gas), O_2 (gas) and the estimated heat of formation of benzaldehyde (gas) *i.e.* −15.45 kcal/mole* have been used to calculate ΔH_{fT}°, ΔG_{fT}° and $\log_{10} K_p$ for the reaction:

$$7\text{C (graphite)} + 3\text{H}_2\text{ (gas)} + \tfrac{1}{2}\text{O}_2\text{ (gas)} = \text{C}_6\text{H}_5\text{CHO (gas)}$$

From the approximate value of the liquid-state entropy[14] of benzaldehyde, the gaseous-state value has been estimated by using its heat of vapourization. So we do not expect exact agreement between the estimated vapour-phase entropy 82.47 cal/mole K and the computed value from the spectroscopic data 78.71 cal/mole K.

PHENOL-d_1 AND PHENOL-d_5

The thermodynamic properties of phenol-d_1 and phenol-d_5 have neither been determined experimentally nor computed from the spectroscopic data in the past. So these quantities have been computed for the first time using (a) the precise vapour-phase fundamental frequencies (*cf.* Appendix I) obtained by us, (b) the three moments

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*Gibbs energy of formation ΔG_{fT}° of benzaldehyde (gas) at 298 K is −1.07 kcal/mole and change in entropy for the formation of benzaldehyde (gas) at 298 K *i.e.* $\Delta S_{fT}^\circ = -48.222$ cal/mole K. Using these values in the relation

$$\Delta H_{fT}^\circ = \Delta G_{fT}^\circ - T\Delta S_{fT}^\circ$$

the value of ΔH_{fT}° is found to be −15.45 kcal/mole at 298 K.

of inertia from the rotational constants (*cf.* Appendix II), (c) the reduced moments of inertia[12] for internal rotation, and (d) the symmetry number "one" for over all rotation and "two" for internal rotation. The gas imperfection corrections have been applied assuming the same critical temperature and pressure as for phenol-h_6. The restricted rotation has been taken into account and its contribution has been evaluated from the tables of Pitzer and Gwinn[18] by interpolation. These corrected values have been listed in Tables 4 and 5.

TABLE 4

THE MOLAL THERMODYNAMIC PROPERTIES OF PHENOL-d_1 IN THE IDEAL GAS STATE

$T(K)$	$C_p^{\circ a}$	$(H^\circ - H_0^\circ)/T^a$	$-(G^\circ - H_0^\circ)/T^a$	$S^{\circ a}$
200	18.18	10.39	55.15	65.54
298.16	25.48	14.25	60.52	74.77
400	33.09	18.00	65.45	83.45
500	39.26	21.66	69.91	91.57
600	44.14	25.01	73.98	98.99
700	48.06	28.04	78.28	106.32
800	51.24	30.74	82.22	112.96
900	53.92	33.17	85.99	119.16
1000	56.13	35.35	89.60	124.95

[a] Units: cal/mole K.

TABLE 5

THE MOLAL THERMODYNAMIC PROPERTIES OF PHENOL-d_5 IN THE IDEAL GAS STATE

$T(K)$	$C_p^{\circ a}$	$(H^\circ - H_0^\circ)/T^a$	$-(G^\circ - H_0^\circ)/T^a$	$S^{\circ a}$
200	19.19	10.75	55.59	66.34
298.16	28.63	15.21	61.36	76.57
400	36.56	19.67	66.62	86.29
500	42.70	23.69	71.48	95.17
600	47.50	27.27	75.78	103.05
700	51.33	30.45	80.59	111.04
800	54.40	33.25	84.87	118.12
900	56.90	35.75	88.93	124.68
1000	58.96	37.96	92.82	130.78

[a] Units: cal/mole K.

The values of ΔH_{fT}°, ΔG_{fT}° and $\log_{10} K_p$ could not be determined for phenol-d_1 and phenol-d_5 because the experimental values of heats of formation of these compounds are not known.

REFERENCES

1 D. R. Stull, I. Carr, J. Chao, T. E. Dergazarian, L. A. du Plessis, R. E. Josted, S. Levine, F. L. Oetting, R. V. Petrella, H. Prophet and G. C. Sinke, *JANAF Thermodynamical Tables*, Clearing House For Federal Scientific and Technical Information, Spring Field, Va., 1966.
2 G. Herzberg, *Molecular Spectra and Molecular Structure*, Vol. II, Van Nostrand, Princeton, N.J., 1945.
3 K. S. Pitzer and L. Brewer, in G. M. Lewis and M. Randell (eds.), *Thermodynamics*, McGraw-Hill, New York, 1961.
4 D. H. Whiffen, *J. Chem. Soc.*, (1956) 1350.
5 G. E. Erlandsson, *Ark. Fys.*, 7 (1953) 189, 8 (1954) 341.
6 R. L. Poynter, *J. Chem. Phys.*, 39 (1963) 1962.
7 D. R. Stull, *Ind. Eng. Chem.*, 39 (1947) 517.
8 D. R. Stull, *J. Amer. Chem. Soc.*, 59 (1937) 2726.
9 W. J. Jones and S. T. Bowden, *Phil. Mag.*, 37 (1946) 480.
10 H. D. Bist, J. C. D. Brand and D. R. Williams, *J. Mol. Spectrosc.*, 24 (1967) 402.
11 H. D. Bist, J. C. D. Brand and D. R. Williams, *J. Mol. Spectrosc.*, 24 (1967) 413.
12 H. Forest and B. P. Daily, *J. Chem. Soc.*, (1966) 1736.
13 J. H. S. Green, *J. Chem. Soc.*, (1961) 2236.
14 D. R. Stull, E. F. Westrum Jr. and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, Wiley, New York, 1969, p. 454.
15 T. Kojima, C. R. Quade and C. C. Lin, *Bull. Amer. Phys. Soc.*, 7 (1962) 44 (as given in *Landolt-Bornstein Molecular Constants from Microwave Spectroscopy* by B. Starck, Springer-Verlag Berlin, 1967).
16 W. G. Fateley, R. K. Harris, F. A. Miller and R. E. Witkowski, *Spectrochim Acta*, 21 (1965) 231.
17 F. Glasser and H. Ruland, *Chem. Ing. Tech.*, 29 (1957) 772.
18 K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, 10 (1942) 428.

APPENDIX I

VAPOUR-PHASE FUNDAMENTAL VIBRATIONAL FREQUENCIES

	$^{35}ClC_6H_5$	OHC_6H_5	ODC_6H_5	OHC_6D_5	$CHOC_6H_5$
6a	416.8 (410.0)*	526.6	521.7	512.6	437
12	706.5 (704.6)*	823.2	805.5	754.4	825.3
1	1003.7	999.3	999.1	960.2	1002.3
18a	1025.7	1025.9	1025.8	840.0	1024.8
7a	1092.6 (1090.5)*	1261.5	1258.1	1187	1202.0
9a	1153.0	1168.9	1168	879.1	1167.0
19a	1482.3	1501	1500	1405	1489
8a	1586.4	1603	1603	1572	1610
13	3031	3027	3024	2262	3011
2	3054	3063	3060	2295	3062
20a	3082	3087	3087	2313	3110
18b	294.7 (290.8)*	403.1	381.0	384.8	233.8
6b	614.9	618.7	616.8	594.9	530
15	1067.6	1072.4	1064.7	810.9	1071
9b	1167.1	1150.7	1149.7	831.2	1188.5
3	1271.8	1277.4	1277.4	1021.3	1284
14	1326.6	1343	1309	1300	1313
19b	1447.2	1472	1465	1372	1460
8b	1598.2	1610	1609	1578	1590.8
7b	3067	3049	3051	2283	3041.0
20b	3096	3070	3070	2302	3082.8
11	197.5†	244.5	232.4	231.8	223.4
16b	467.1	502.8	501.7	431.0	449.1

APPENDIX I: *continued*

	$^{35}ClC_6H_5$	OHC_6H_5	ODC_6H_5	OHC_6D_5	$CHOC_6H_5$
4	683.9	685.9	686.2	551.2	688.0
10b	741.4	750.6	751.3	625.5	739.5
17b	902.5	881.0	880.0	720.0	918.0
5	981.5	972.5	970.7	825.1	(973.0)[†]
16a	403.4	408.5	408.5	357.4	980.3
10a	831.2	817.2	807.3	694.0	848.2
17a	961.7	999.52	998.2	765.9	403.2
O–H	—	3656	2699	3656	—
O–H	—	1176.5	917	1179	—
O–H	—	309.2	246	306.9	—
C–H	—	—	—	—	2731
C–O	—	—	—	—	1727
HCO	—	—	—	—	1386.6
CHO	—	—	—	—	650.0
CHO	—	—	—	—	1003.5
CHO	—	—	—	—	(111)[*]

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[*] Values are from ultraviolet absorption data of H. D. Bist, V. N. Sarin, A. Ojha and Y. S. Jain, *Spectrochim. Acta*, 26A (1970) 841.

[‡] Has not been observed directly in the infrared.

[†] Values taken from C. Garrigou-Lagrange, N. Claverie, J. M. Lebas and M. L. Josien, *J. Chem. Phys.*, 58 (1961) 559.

APPENDIX II

ROTATIONAL CONSTANTS OF THE MOLECULES

Molecule	*Principal moments of inertia (amu Å²)*			*Molecular weight (amu)*
	I_A	I_B	I_C	
benzaldehyde	96.760	323.106	419.319	106.12527
phenol-d_1	90.1245	199.938	290.010	95.12025
phenol-d_5	107.985	208.654	316.564	99.14477
phenol-h_6	89.467	193.010	282.444	94.11412
$^{35}ClC_6H_5$	89.113	320.611	409.7775	112.07560
$^{37}ClC_6H_5$	89.119	329.811	418.9816	114.07265