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Note

Thermodynamic properties of oxygen compounds
III. Benzaldehyde and furfural (2-furaldehyde)

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This is the third part of a series on the thermodynamic properties of oxygen compounds[1,2]. Ideal gas thermodynamic properties for benzaldehyde and furfural have not been reported in the literature so far.

MOLECULAR STRUCTURE AND VIBRATIONAL FREQUENCIES FOR BENZALDEHYDE

No molecular parameters are available in the literature for benzaldehyde. Zwarich et al.[3] have estimated them from similar molecules and we have adopted these data in this work for calculating the moments of inertia which are reported in Table 1.

TABLE 1
MOLECULAR PARAMETERS FOR BENZALDEHYDE AND FURFURAL

	Benzaldehyde	*Furfural*
I_a (amu Å^2)	96.380	61.7067
I_b (amu Å^2)	325.983	247.0919
I_c (amu Å^2)	422.363	308.7810
I_r (amu Å^2)	8.913	8.498
ν_{tors} (cm^{-1})	111.0	145.0
V_1 (kcal mol^{-1})	—	2.03
V_2 (kcal mol^{-1})	4.66	7.07

Zwarich et al.[3] have reported complete assignments for benzaldehyde from their infrared and Raman spectral measurements in the liquid state and from the normal coordinate analysis. We have adopted the same except for the torsional frequency. Miller et al.[4] have reported torsional frequency from the measurements in the far infrared region for the gaseous state which is adopted here. The adopted vibrational frequencies are given in Table 2.

TABLE 2

ADOPTED VIBRATIONAL FREQUENCIES (cm^{-1}) FOR BENZALDEHYDE AND FURFURAL

Benzaldehyde		*Furfural*	
In-plane (A′)		*In-plane (A′)*	
3088	1298	3164	1008
3065	1206	3145	946
3052	1170	3141	888
3045	1164	2801	746
3035	1074	1718	501
2820	1025	1577	214[b]
1707	1003	1472	
1600	834	1395	
1588	650	1364	
1496	616	1275	
1458	442	1240	
1394	221	1162	
1314		1084	
Out-of-plane (A″)		*Out-of-plane (A″)*	
1010	688	882	250[b]
992	449	829	145[a]
960	410	799	
925	245	756.5	
814	111[a]	630	
746		594	

[a]Ref. 4. [b]Ref. 7.

MOLECULAR STRUCTURE AND VIBRATIONAL FREQUENCIES FOR FURFURAL

Furfural exists as two isomers, O–O-*trans* and O–O-*cis*. Monnig et al.[5] have unequivocally determined from their microwave measurements that the most abundant isomer in the gas phase is the O–O-*trans* isomer. Miller et al.[4] have reported that the *trans* isomer is more stable by 2 kcal mol^{-1} than the *cis* isomer. As reliable vibrational data are available only for the *trans* isomer we have here dealt with the *trans* isomer only.

Monnig et al.[5] have reported the molecular structure and moments of inertia for the *trans* and the *cis* isomers. The same are adopted here and are given in Table 1.

Recently Adamek et al.[6] studied the infrared spectra in the gaseous, liquid and solution states and Raman spectra in the liquid state. They have calculated in-plane and out-of-plane frequencies from normal coordinate analysis but have assigned only in-plane frequencies of the *trans* form. From eight out-of-plane frequencies six were adopted by us from Adamek et al.'s work comparing their observed and calculated frequencies. The torsional frequency was adopted from Miller et al.'s far infrared measurements and the eighth frequency was taken from Monnig et al.'s measurements[7] of rotational spectra. Complete vibrational frequencies for the O–O-*trans* isomer are given in Table 2.

TABLE 3

IDEAL GAS THERMODYNAMIC PROPERTIES OF BENZALDEHYDE

Temp. (*K*)	C_p^0	S^0 *cal deg⁻¹ mol⁻¹*	$-(G^0 - H_0^0)/T$ *cal deg⁻¹ mol⁻¹*	$(H^0 - H_0^0)$ *kcal mol⁻¹*	ΔH_f^0 *kcal mol⁻¹*	ΔG_f^0 *kcal mol⁻¹*	*Log* K_f
100.00	10.700	59.272	50.193	0.908	−4.585	−0.967	2.11383
150.00	12.180	63.887	54.024	1.479	−5.251	0.979	−1.42663
200.00	13.872	67.615	56.968	2.129	−6.064	3.180	−3.47503
273.15	16.829	72.364	60.468	3.250	−7.447	6.776	−5.42151
298.15	17.915	73.885	61.529	3.684	−7.950	8.103	−5.93944
300.00	17.996	73.996	61.606	3.717	−7.988	8.206	−5.97805
400.00	22.197	79.760	65.433	5.731	−10.097	13.929	−7.61042
500.00	25.658	85.101	68.840	8.131	−12.436	20.200	−8.82949
600.00	28.252	90.021	71.966	10.833	−14.850	26.952	−9.81715
700.00	30.138	94.525	74.872	13.758	−17.389	34.123	−10.65353
800.00	31.510	98.644	77.590	16.844	−20.038	41.665	−11.38220
900.00	32.521	102.417	80.142	20.048	−22.783	49.541	−12.03026
1000.00	33.278	105.884	82.545	23.340	−25.595	57.765	−12.62453
1100.00	33.855	109.084	84.814	26.697	−28.482	66.148	−13.14236
1200.00	34.304	112.050	86.962	30.106	−31.463	74.950	−13.65016
1300.00	34.658	114.811	88.999	33.555	−34.529	83.926	−14.10913
1400.00	34.942	117.390	90.936	37.036	−37.670	93.234	−14.55447
1500.00	35.173	119.809	92.781	40.542	−40.876	102.664	−14.95807

TABLE 4

IDEAL GAS THERMODYNAMIC PROPERTIES OF FURFURAL

Temp. (K)	C_p^0	S^0 *cal deg⁻¹ mol⁻¹*	$-(G^0-H_0^0)/T$ *cal deg⁻¹ mol⁻¹*	$H^0-H_0^0$ *kcal mol⁻¹*	ΔH_f^0 *kcal mol⁻¹*	ΔG_f^0 *kcal mol⁻¹*	*Log* K_f
100.00	11.221	62.483	53.419	0.906	−34.338	−31.455	68.74547
150.00	13.604	67.471	57.302	1.525	−34.785	−29.919	43.59214
200.00	16.576	71.777	60.390	2.277	−35.257	−28.223	30.84020
273.15	21.672	77.685	64.236	3.674	−35.906	−25.544	20.43809
298.15	23.443	79.660	65.447	4.238	−36.100	−24.586	18.02221
300.00	23.573	79.805	65.535	4.281	−36.114	−24.512	17.85707
400.00	30.100	87.507	70.072	6.974	−36.665	−20.538	11.22167
500.00	35.400	94.816	74.297	10.259	−37.193	−16.437	7.18452
600.00	39.555	101.653	78.294	14.016	−37.477	−12.257	4.46463
700.00	42.818	108.005	82.090	18.141	−37.654	−8.035	2.50860
800.00	45.415	113.899	85.703	22.557	−37.746	−3.794	1.03638
900.00	47.513	119.373	89.143	27.207	−37.767	0.453	−0.10990
1000.00	49.228	124.471	92.424	32.047	−37.716	4.724	−1.03247
1100.00	50.648	129.232	95.556	37.043	−37.617	8.897	−1.76770
1200.00	51.832	133.691	98.550	42.169	−37.495	13.169	−2.39841
1300.00	52.830	137.880	101.416	47.403	−37.359	17.375	−2.92094
1400.00	53.675	141.827	104.163	52.730	−37.209	21.636	−3.37751
1500.00	54.397	145.556	106.800	58.134	−37.049	25.811	−3.76066

THERMODYNAMIC PROPERTIES

Benzaldehyde and furfural are planar molecules[3,5] with the overall symmetry number one. The translational, rotational and vibrational contributions to the ideal gas thermodynamic properties (C_p°, $(H^\circ-H_0^\circ)$, S° and $-(G^\circ-H_0^\circ)/T$) were calculated by the usual statistical formulas using the moments of inretia and the vibrational frequencies as given in Table 1 and 2, respectively.

The internal rotational contributions to the thermodynamic properties due to the presence of an OH asymmetric rotating top in these molecules were derived by the use of the internal rotational partition function given below:

$$Q=\left[\frac{(2\pi I_{\text{red}}kT)^{\frac{1}{2}}}{nh}\int_0^{2\pi} e^{-V/2kT}\,\mathrm{d}\phi\right]\frac{hC\nu_{\text{tors}}}{kT}\cdot\frac{1}{(1-e^{-hC\nu_{\text{tors}}/kT})} \qquad (1)$$

where all the symbols have usual meaning.

The following potential energy functions reported by Miller et al.[4] for internal rotation were used: Benzaldehyde: $V(\alpha)(\text{kcal mol}^{-1}) = 4.66(1-\cos 2\alpha)/2$; furfural: $V(\alpha)(\text{kcal mol}^{-1}) = 2.03(1-\cos\alpha)/2+7.07(1-\cos 2\alpha)/2$. To be consistent the reduced moments of inertia required in the calculations were obtained from the F values of Miller et al. and are given in Table 1.

In the case of furfural as mentioned earlier two rotational isomers are present. The term $R\ln 2$ was added to entropy, and Gibbs energy function $(G^\circ-H_0^\circ/T)$ to make corrections for the presence of two isomers. Heat capacity and enthalpy are not affected.

The enthalpy of formation, Gibbs energy of formation and logarithm of equilibrium constant of formation as a function of temperature were calculated by the usual procedure. The adopted enthalpies of formation[8,9] at 298.15 K for the gaseous states for the two molecules are: benzaldehyde: $\Delta H_f^\circ(g) = -7.95\pm0.4$ kcal mol^{-1}; furfural: $\Delta H_f^\circ(g) = -36.1\pm1.2$ kcal mol^{-1}. The values of the enthalpy and Gibbs energy functions for the elements in their reference states were used[1]. The calculated thermodynamic properties are given in Tables 3 and 4.

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