

## Thermodynamic functions of para-halogenated benzaldehydes

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New measurements of the infrared ( $3650-80\text{ cm}^{-1}$ ) and Laser Raman spectra, and complete vibrational assignments available in literature for para-halogenated benzaldehydes ( $p\text{-x C}_6\text{H}_4\text{ CHO}$ ;  $\text{X} = \text{F, Cl, Br}$ ) have been utilised to compute thermodynamic functions for the ideal gases of para-fluoro, -chloro- and -bromobenzaldehydes at the pressure of one atmosphere under the rigid rotor harmonic oscillator approximation.

### 1. INTRODUCTION

Recently Green *et al* (1976) have proposed interpretation of new measurements of the infrared and laser Raman spectra of para-halogenated benzaldehydes along with benzaldehyde and its other halogenated derivatives. On the basis of the interpretation of the spectra, they have also suggested complete vibrational assignments for the above mentioned molecules. Earlier Miller *et al* (1967) made a detailed study of torsional vibrations in these molecules in the far infrared in vapour and liquid phases. Vibrational spectra of benzaldehyde and halogenated benzaldehydes have also been studied extensively by Singh *et al* (1970) in our laboratory by infrared and Raman methods. These spectroscopic data are examined and utilised to compute thermodynamic functions of halogenated benzaldehydes statistically as these are expected to be much more accurate than the direct experimental measurements. Present paper reports briefly results of the computations of thermodynamic functions in case of para-halogenated benzaldehydes on a TDC-316 computer.

### 2. CALCULATIONS AND RESULTS

Para-halogenated benzaldehydes possess a single asymmetric top ( $\text{-C}_6\text{H}_4\text{X}$ ,  $\text{X} = \text{F, Cl, Br}$ ) attached to an essentially rigid frame ( $\text{-CHO}$  group). Rotation of the top about the common C-C bond is hindered by a two-fold potential barrier. Thus the vibrational degree of freedom corresponding to hindered internal rotation has been omitted from the vibrational partition function and instead an

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appropriate term has been added. In case of completely free internal rotation, an additional factor  $Q$ , given by Herzberg (1945).

$$Q_f = \frac{(8\pi^2 I_m k T)^{1/2}}{\sigma_t h}$$

where  $I_m$  is the reduced moment of inertia of top,  $\sigma_t$  is number of potential minima per revolution and other terms having their usual meanings, appears with the overall rotational partition function. However, in case of hindered rotation as for the present molecules, the corrections to various thermodynamic functions are applied with the help of Pitzer and Gwinn's tables (1942) with the knowledge of  $Q_f$  and barrier height  $V_0$ , hindering internal rotations, given by (Miller *et al* 1967)

$$V_0 = \frac{\nu_t^2}{4F}$$

where  $F = \frac{h}{8\pi^2 C I_m}$  in  $\text{cm}^{-1}$  and  $\nu_t$  is observed torsional frequency in  $\text{cm}^{-1}$ .

Considering each molecule a planer one and having  $C_s$  symmetry, principal moments of inertia  $I_x$ ,  $I_y$  and  $I_z$  have been computed where  $X$  and  $Z$  axes are in the plane and  $Y$  axis is perpendicular to the plane of the molecule. The structure parameters of the molecules have been taken from International tables for X-ray Crystallography (1962). The reduced moments of inertia have been calculated by the formula given by Pitzer (1946) for asymmetric top attached to a rigid frame. Full programme has been developed for a TDC-316 computer reduced moments of inertia,  $F$  and potential barrier height as well as thermodynamic functions for such molecules.

Table 1 gives computed values of moments of inertia, reduced moments of inertia,  $F$ , and potential barrier heights of para-fluoro-, -chloro- and -bromobenzaldehydes. Computed values of heat capacity, enthalpy function, free energy function and entropy at various temperatures ranging between 100–1500°K for the para-fluoro-, chloro- and -bromobenzaldehydes respectively are given in

Table 1. The computed values of moments of inertia, reduced moments of inertia,  $F$ , and potential barrier heights of para-fluoro-, -chloro- and -bromo-benzaldehydes.

Compound	Principal moments of inertia ( $10^{-30}\text{gm.cm}^2$ )			Reduced moment of inertia ( $10^{-30}\text{gm.cm}^2$ )	$F$ ( $\text{cm}^{-1}$ )	Barrier height $V_0$ (Kcal/mole)
	$I_x$	$I_y$	$I_z$			
<i>p</i> -Fluorobenzaldehyde	85.98	102.37	16.39	1.6129	1.7339	3.6041
<i>p</i> -Chlorobenzaldehyde	121.63	138.18	16.56	1.7298	1.6553	2.8684
<i>p</i> -Bromobenzaldehyde	180.92	197.58	16.67	1.7467	1.6011	2.4119

Table 2. Thermodynamic functions (in cal-mole/°K) of para-halogenated benzaldehydes.

Temperature (°K)	para-Fluorobenzaldehyde			para-Chlorobenzaldehyde			para-Bromobenzaldehyde			
	$C_p^0$	$\frac{(H^0 - E_0^0) - (G^0 - E_0^0)}{T}$	$S^0$	$C_p^0$	$\frac{(H^0 - E_0^0) - (G^0 - E_0^0)}{T}$	$S^0$	$C_p^0$	$\frac{(H^0 - E_0^0) - (G^0 - E_0^0)}{T}$	$S^0$	
100-00	12.97	9.84	68.85	14.02	10.26	59.90	14.94	10.69	61.72	72.41
200-00	21.06	13.42	66.52	22.39	14.36	67.88	23.18	14.89	69.84	84.73
273-15	27.50	16.33	70.76	28.67	17.27	72.45	29.12	17.93	74.51	92.44
298-15	29.67	17.33	72.10	30.78	18.30	73.79	31.24	18.96	75.94	94.90
300-00	29.83	17.41	72.21	30.94	18.38	73.90	31.39	19.03	76.05	95.08
400-00	37.89	21.53	77.31	38.70	22.52	79.26	38.90	23.09	81.56	104.65
500-0	44.52	25.50	82.13	45.26	26.41	84.27	<del>45.14</del> 45.14	23.09	<del>86.70</del> 86.70	113.60
600-00	49.80	29.13	86.76	50.17	29.97	89.05	50.17	30.37	91.57	121.94
700-00	54.00	32.39	91.20	54.26	33.15	93.59	54.22	33.50	96.22	129.72
800-00	57.39	35.30	95.43	57.54	36.00	97.98	57.50	36.30	100.64	136.94
900-00	60.15	37.92	99.52	60.26	38.55	102.15	60.23	38.81	104.84	143.65
1000-00	62.45	40.26	103.44	62.54	40.84	106.17	62.49	41.06	108.91	149.97
1100-00	64.39	42.36	107.21	64.43	42.88	109.99	64.40	43.11	112.79	155.90
1200-00	66.01	44.28	110.83	66.05	44.75	113.67	66.01	44.95	116.50	161.45
1300-00	67.41	46.00	114.31	67.41	46.45	117.20	67.39	46.63	120.07	166.70
1400-00	68.59	47.57	117.66	68.57	47.98	120.59	68.56	48.15	123.48	171.63
1500-00	69.60	49.00	120.87	69.59	49.40	123.87	69.57	49.54	126.77	176.31

Table 2, and represented by curves in figures 1 and 2. Here  $E_0^0$  is the energy of one mole of an ideal gas at absolute zero and  $C_p^0$ ,  $H^0$ ,  $G^0$  and  $S^0$  denote heat capacity at constant pressure, enthalpy, free energy and entropy respectively.

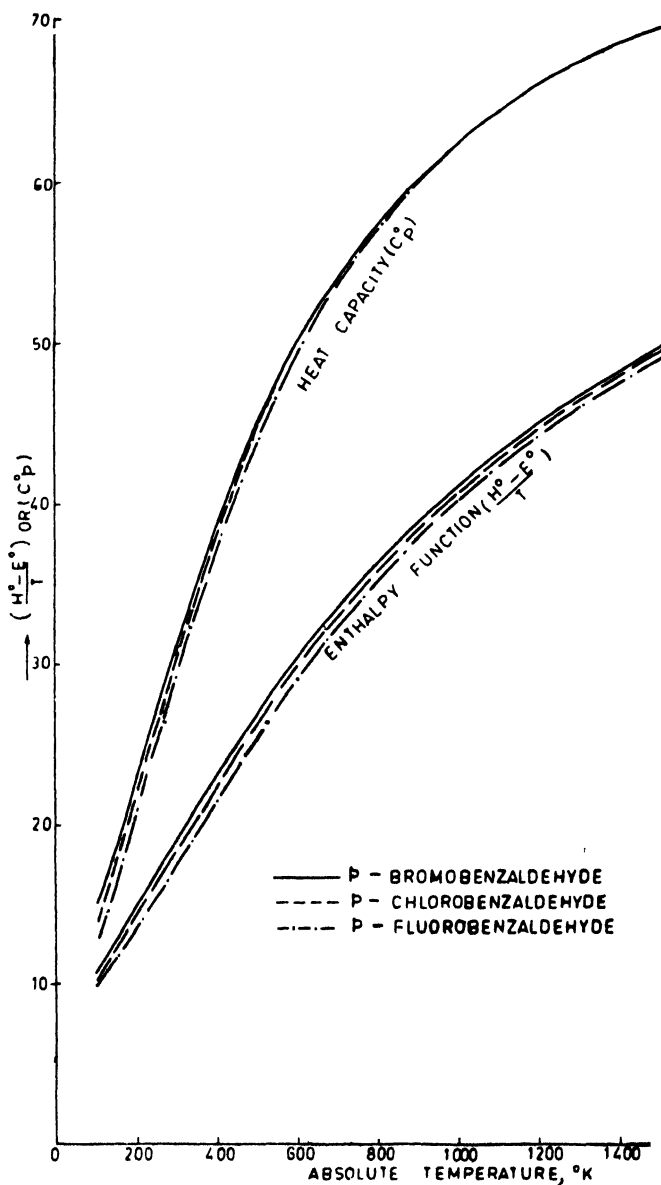


Fig. 1. Variation of enthalpy function and heat capacity with absolute temperatures for para-fluoro-, -chloro- and -bromo-benzaldehydes.

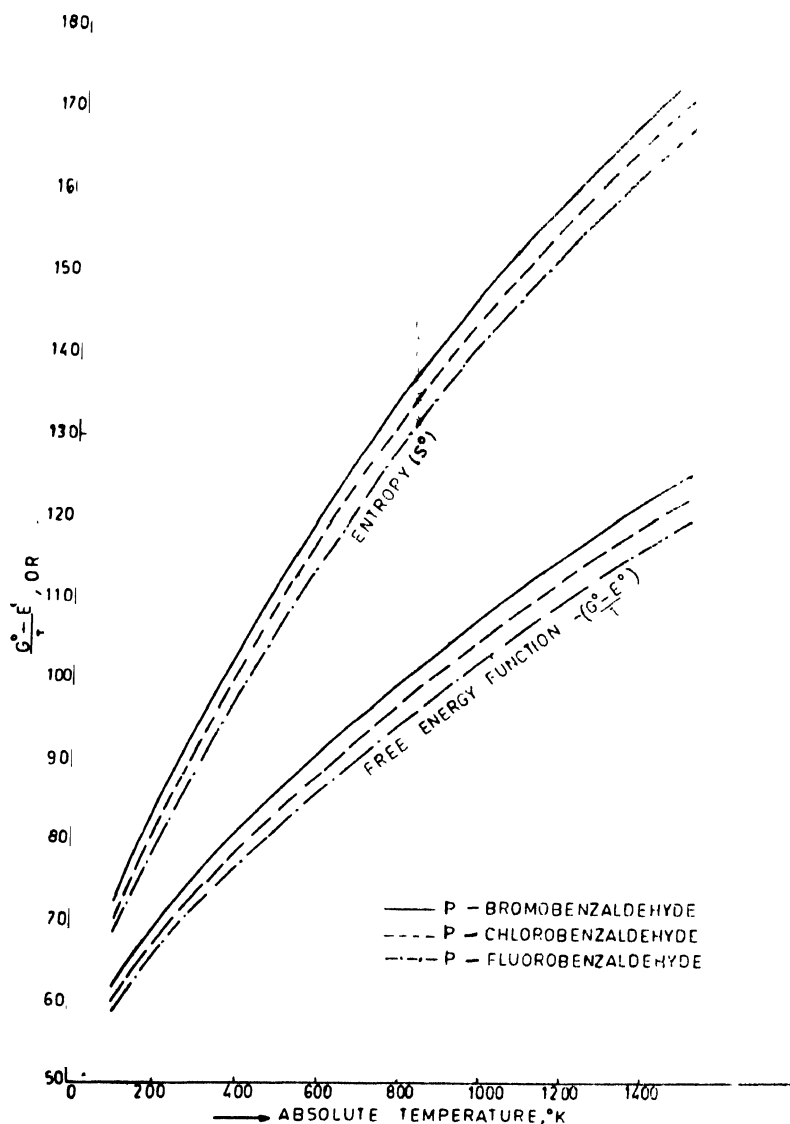


Fig. 2. Variation of free energy function and entropy with absolute temperatures for para-fluoro-, -chloro- and -bromo-benzaldehydes.

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