

Computation of thermodynamic functions of 2- and 4-phenylpyridine from vibrational spectra

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The complete assignments of the observed frequencies are used to compute the thermodynamic functions, namely, the entropy, heat capacity, enthalpy and the free energy of 2- and 4-phenylpyridine. These functions have been calculated by using standard expressions, at one atmospheric pressure in the temperature range 100-1500 K under the rigid rotator harmonic oscillator approximation.

1 Introduction

In the study of chemical kinetics and chemical equilibria, a knowledge of the thermodynamic functions is of great importance. The direct experimental measurement of these quantities is usually tedious and may not be reliable. McCullough *et al.*¹ studied the vibrational spectra of pyridine molecule alongwith the calculation of statistical thermodynamic functions. The interpreted fundamental vibrational frequencies of 2- and 4-phenylpyridine as given by Isaq *et al.*², have been utilised to calculate the various thermodynamic functions in the temperature range 100-1500 K at one atmospheric pressure under the usual approximation of molecules being rigid rotators, harmonic oscillator model. The thermodynamic functions of the molecules under investigation, which have not been reported so far, are computed by using IBM-PC/AT computer.

2 Computation of Thermodynamic Functions

The total energy in a system (E) is given by:

$$E = \epsilon_{\text{trans}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} + \epsilon_{\text{elec}} \quad \dots(1)$$

where the subscript trans stands for translational, rot for rotational, vib for vibrational and elec for electronic respectively.

The partition function (Q) in terms of energy is given by:

$$Q = \sum g_i \exp(-\epsilon_i/kT) \\ = Q_{\text{trans}} \cdot Q_{\text{rot}} \cdot Q_{\text{vib}} \cdot Q_{\text{elec}} \quad \dots(2)$$

where g_i is the statistical weight, k the Boltzmann constant and T is the absolute temperature in Kelvin.

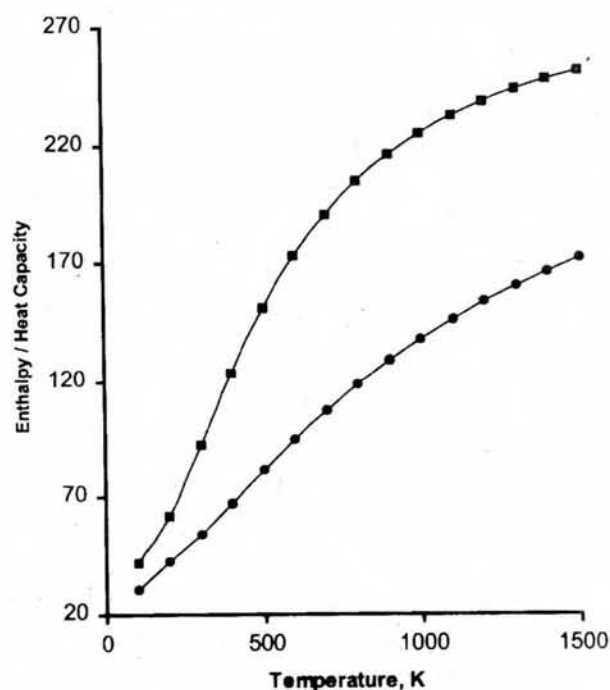


Fig. 1 — Variation of enthalpy (●)/heat capacity (◆) with temperature for 2-phenylpyridine

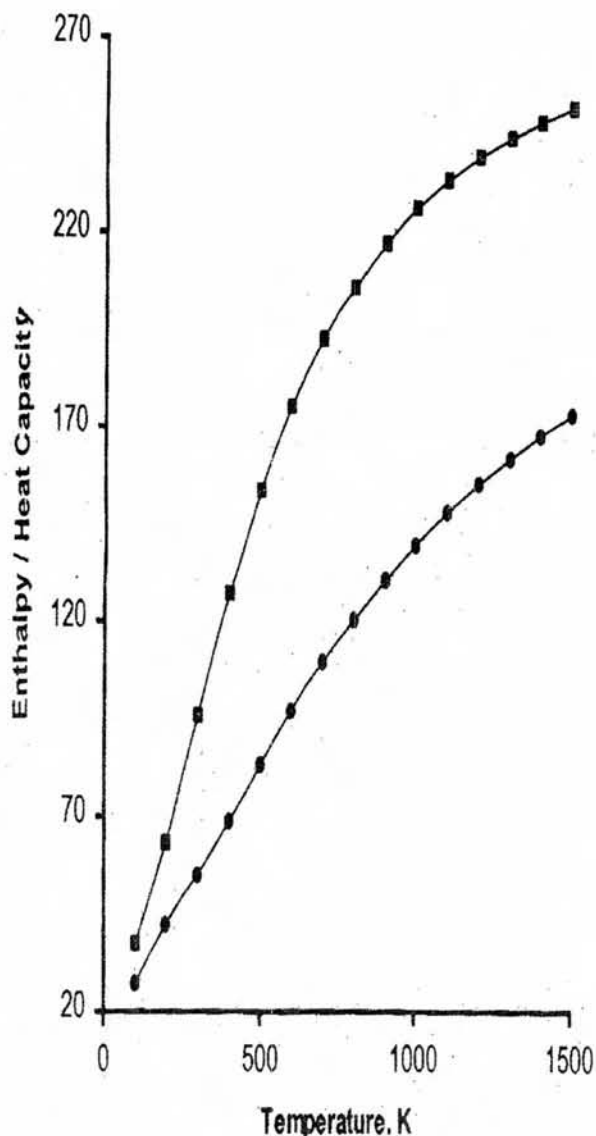


Fig. 2 — Variation of enthalpy (●)/heat capacity (◆) with temperature for 4-phenylpyridine

By using Eq. (2), each partition function may be evaluated separately and hence the corresponding thermodynamic functions are calculated. Then each contribution to the thermodynamic functions has been added to get the total value. The electronic contribution is small and hence ignored because ϵ_{elec} is large compared to kT at ordinary temperature. For the other remaining partition functions, the standard expressions as given by Colthup³ have been used and their contribution to thermodynamic functions have been calculated at various temperatures ranging from 100-1500 K.

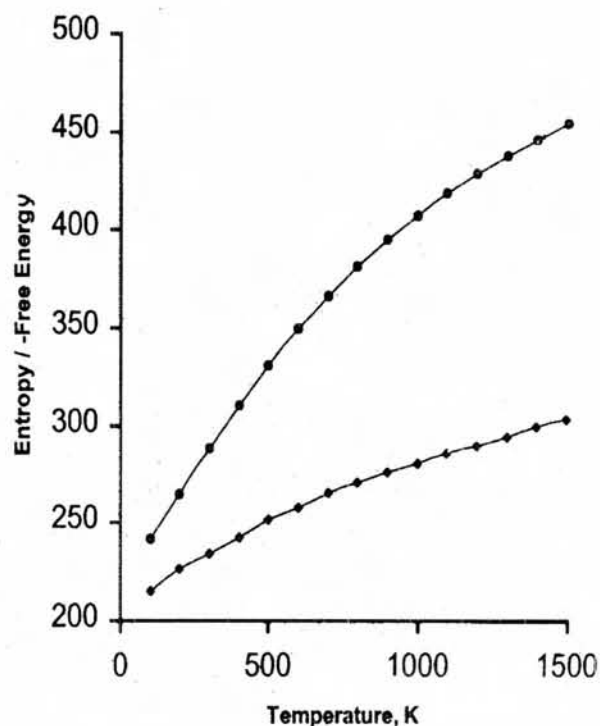


Fig. 3 — Variation of entropy (●)/free energy (◆) with temperature for 4-phenylpyridine

The thermodynamic functions, namely, the enthalpy function $(H^0 - E_0^0)/T$, heat capacity (C_P^0), the free energy function $[(-F^0 - E_0^0)/T]$ and the entropy (S_0) have been calculated by using standard expressions refined from time to time^{4,8}, by taking Y-axis perpendicular to the molecular plane and Z-axis to pass through the para positions. For determining the rotational contributions of the title molecules, the following structural parameters were used^{8,9}:

Bond length (Å)		Bond angle (°)	
2-phenylpyridine			
N ₁ -C ₂ =1.40	C ₂ -C ₃ =1.36	N ₁ C ₂ C ₃ =119	C ₂ C ₃ C ₄ =120
C ₃ -C ₄ =1.42	C ₄ -C ₅ =1.38	C ₃ C ₄ C ₅ =119	C ₄ C ₅ C ₆ =121
C ₅ -C ₆ =1.35	C ₆ -N ₁ =1.42	C ₅ C ₆ N ₁ =119	C ₆ N ₁ C ₂ =121
C ₂ -C ₇ =1.51	C ₇ -C ₈ =1.40	N ₁ C ₂ C ₇ =121	C ₃ C ₂ C ₇ =120
C ₈ -C ₉ =1.42	C ₉ -C ₁₀ =1.38	C ₂ C ₇ C ₈ =120	C ₂ C ₇ C ₁₂ =120
C ₁₀ -C ₁₁ =1.35	C ₁₁ -C ₁₂ =1.42	C ₇ C ₈ C ₉ =120	C ₈ C ₉ C ₁₀ =120
C ₁₂ -C ₇ =1.36		C ₉ C ₁₀ C ₁₁ =120	C ₁₀ C ₁₁ C ₁₂ =120
		C ₁₁ C ₁₂ C ₇ =120	C ₁₂ C ₇ C ₈ =120

where C₂ to C₆ are the carbon atoms of the pyridine ring and C₇, to C₁₂ are the carbon atoms of the phenyl group respectively. N₁ is the nitrogen atom

of the pyridine ring. Similar structural parameter are also used for 4-phenylpyridine molecule.

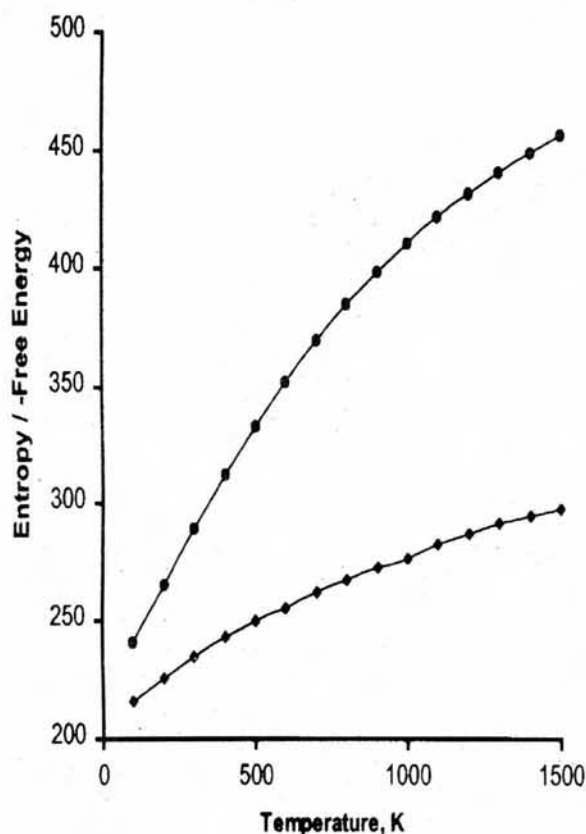


Fig. 4 — Variation of entropy (●)/free energy (◆) with temperature for 4-phenylpyridine

The symmetry number for the overall rotation has been taken as 3 and the internal rotation as 2 for the title molecules. The atomic masses used in calculations were taken from literature^{10,11} and is given as C, 12.01115 ; H, 1.00797 ; N, 14.0067.

The computed principal moments of inertia are given in Table 1.

Table 1 — Computed principal moments of inertia

2-phenylpyridine ($\times 10^{-39}$ g cm ²)	4-phenylpyridine ($\times 10^{-39}$ g cm ²)
I_x 258.91	24.70
I_y 133.98	134.89
I_z 392.49	159.59

3 Results and Discussion

The calculated values of the thermodynamic functions for 2-phenylpyridine and 4-

phenylpyridine have been shown in Tables 2 and 3, respectively. The computed thermodynamic quantities are plotted as a function of temperature and are represented in Figs 1-4.

Table 2 — Thermodynamic functions of 2-phenylpyridine (joules. K⁻¹ mol⁻¹)

Temp (K)	$(H^0 - E_0^0)/T$	C_p^0	$-(F_0^0 - E_0^0)/T$	S^0
100	30.556	41.895	214.991	242.220
200	42.453	61.904	226.809	265.078
300	53.830	92.144	234.405	288.235
400	67.380	123.506	242.808	310.188
500	81.420	150.802	251.458	330.786
600	94.900	172.978	258.104	349.657
700	107.364	190.654	265.199	366.706
800	118.689	204.752	270.864	382.022
900	128.904	216.080	276.494	395.775
1000	138.096	225.302	280.928	408.146
1100	146.374	232.794	286.040	419.310
1200	153.843	239.012	290.224	429.424
1300	160.600	244.195	294.757	438.621
1400	166.731	248.549	299.952	447.018
1500	172.312	252.231	303.741	454.714

where H^0 = enthalpy, C_p^0 = heat capacity, S^0 = entropy; F^0 = free energy; and E_0^0 = zero point energy

Table 3 — Thermodynamic functions of 4-phenylpyridine (joules. K⁻¹ mol⁻¹)

Temp (K)	$(H^0 - E_0^0)/T$	C_p^0	$-(F_0^0 - E_0^0)/T$	S^0
100	27.156	37.217	215.611	240.849
200	42.420	63.550	225.533	265.443
300	54.786	95.902	234.806	289.593
400	69.065	127.284	243.217	312.281
500	83.465	153.965	249.782	333.246
600	97.077	175.503	255.178	352.256
700	109.553	192.656	262.278	369.320
800	120.818	206.351	267.947	384.592
900	130.965	217.373	272.744	398.269
1000	140.068	226.327	276.762	410.554
1100	148.255	233.672	282.579	421.629
1200	155.634	239.750	287.318	431.655
1300	162.305	244.822	292.270	440.768
1400	168.356	249.088	294.956	449.086
1500	173.862	252.702	298.328	456.709

where H^0 = enthalpy, C_p^0 = heat capacity, S^0 = entropy; F^0 = free energy; and E_0^0 = zero point energy

The entropy is regarded as a measure of disorder of a system. The process of vapourisation is accompanied by the increase in entropy because of the increase in the disorder in the system. So, as the temperature increases, entropy increases which is shown as in Tables 2 and 3 for the title molecules. The values of entropy and other thermodynamic

functions do not differ appreciably for the two molecules which show that the change in the position of the phenyl group does not bring much changes in their thermodynamic functions. Similar trend is reported from the observed fundamentals given by Isaq *et al.*² The enthalpy function represents the total energy stored in a system. When a system is brought from solid to vapours, the enthalpy function of the system increases. Similar trend is reflected from Tables 2 and 3 for the title molecules as the temperature increases from 100-1500 K. It has also been observed that, the thermodynamic functions rise more rapidly in the low temperature range and less rapidly in the high temperature range. The calculated thermodynamic functions and their variation with temperature are in good agreement with the trend reported in the literature^{7,12-17}.

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