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THERMODYNAMIC FUNCTIONS FOR ACRYLAMIDE

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ABSTRACT

Thermodynamic functions (heat capacity, enthalpy, entropy, and free energy) have been calculated for acrylamide in the ideal gas state from 273.15 K to 1400 K at 1 atm pressure. All the functions were obtained by statistical mechanical means.

INTRODUCTION

The recent availability of molecular structural and spectroscopic data [1–6] has enabled the calculation of thermodynamic functions (heat capacity, enthalpy, entropy and free energy) for acrylamide in the ideal gas state from 273.15 K to 1400 K at 1 atm pressure. All the functions were calculated by statistical mechanical methods. The calculated results are found in Table 1. The functions have all been fitted to a four constant polynomial of the form

$$\Lambda = a + bT + cT^2 + dT^3 \qquad (1)$$

where Λ is any thermodynamic function at temperature T(K). The constants a, b, c and d [eqn. (1)] have been obtained using linear least squares curve fitting techniques [7], and are found in Table 2. The molecular structural data needed for the thermodynamic functions are found in Tables 3 and 4. Table 5 gives the possible uncertainties in the calculated final function values.

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TABLE 1

Heat capacity, entropy, free energy function and enthalpy function for acrylamide

Temp. (K)	C_p^0 (cal g^{-1} mole^{-1} K^{-1})	S^0 (cal g^{-1} mole^{-1} K^{-1})	$-(F^0-H_0^0)/T$ (cal g^{-1} mole^{-1} K^{-1})	$(H^0-H_0^0)/T$ (cal g^{-1} mole^{-1} K^{-1})
273.15	18.00	70.33	58.26	12.07
298.15	19.32	71.96	59.34	12.62
300.00	19.42	72.08	59.42	12.66
350.00	22.03	75.27	61.46	13.82
400.00	24.49	78.38	63.38	15.00
450.00	26.77	81.39	65.21	16.18
500.00	28.84	84.32	66.98	17.35
550.00	30.73	87.16	68.69	18.48
600.00	32.43	89.91	70.34	19.57
650.00	33.98	92.57	71.95	20.62
700.00	35.40	95.14	73.51	21.63
750.00	36.69	97.63	75.04	22.59
800.00	37.88	100.03	76.53	23.51
850.00	38.97	102.36	77.98	24.39
900.00	39.98	104.62	79.40	25.22
950.00	40.92	106.81	80.78	26.03
1000.00	41.78	108.93	82.14	26.79
1100.00	43.32	112.98	84.76	28.23
1200.00	44.64	116.81	87.27	29.54
1300.00	45.79	120.43	89.68	30.75
1400.00	46.78	123.86	92.00	31.86

TABLE 2

Calculated[a] constants *a*, *b*, *c* and *d* in eqn. (1)

Function	a	$b \times 10^2$	$c \times 10^5$	$d \times 10^8$	Sum of squares × 10^2
C_p^0	−0.88737	8.2573	−5.3127	1.3223	5.9681
$(H^0-H_0^0)/T$	4.4956	2.9212	−0.67993	−0.0099312	4.9340
$-(F^0-H_0^0)/T$	46.036	4.9454	−1.7154	0.37884	2.8924
S^0	50.536	7.8636	−2.3918	0.36814	0.34937

[a] All values of constants in cal g^{-1} mole^{-1} K^{-1}.

TABLE 3

Summary of frequencies (in cm^{-1}) as suggested by several investigators

Assignment	Jonathan [1]	Rao et al. [2]	Rao and Ramiah [3]	This work
NH_2 asym. stretch	3331(IR)[a]	3340(R),3331(IR)	3340	3331
NH_2 sym. stretch	3175(IR)	3163(R),3175(IR)	3165	3175
C=0 stretch	1681(IR)	1685(R),1681(IR)	1675	1681
NH_2 deform.	1613(IR)	1590(R),1613(IR)	1610	1613
C–N stretch	1280(IR)	1285(R),1280(IR)	1278	1280
NH_2 rock.	1138(IR)	1146(R),1138(IR)	1134	1138
C–C stretch	984(IR)	962(R), 984(IR)	988	984
O=C–N deform.			615	621
C–C rock.		495(R)	495	495
CH_2 asym. stretch	3119(R)[b]	3103(R),3102(IR)	3103	3102
CH_2 sym. stretch	3021(IR)	3030(R),3021(IR)	3030	3021
C–H stretch	2807(IR)	2807(IR)	2800	2807
C=C stretch	1645(IR)	1637(R),1645(IR)	1650	1645
CH_2 deform.	1429(IR)	1435(R),1429(IR)	1425	1429
C–H deform.	1351(IR)	1351(IR)	1344	1351
CH_2 rock.	1050(IR)	1054(R),1050(IR)	1048	1050
C–C=C deform.	308(R)	305(R)	305	305
C=O out of plane deform.			1048	1048
C–N tors.			959	961
NH_2 wagging	843(IR)		838	843
C–H out-of-plane deform.			815	819
CH_2 wagging			695	695
CH_2 tors.		509(R)	509	509
C–C tors.			88	88

[a] IR = Infrared; [b] R = Raman.

TABLE 4

Molecular parameters for acrylamide

Molecular weight: 71.080 g g-$mole^{-1}$
External symmetry number: 1
Principal moments of inertia [5,6]:
$I_A = 47.087$ a.m.u. Å^2
$I_B = 119.795$ a.m.u. Å^2
$I_C = 166.750$ a.m.u.·Å^2
Principal moment of inertia product [5,6]:
$I_{ABC} = 940601.25$ a.m.u.^{3} A^6
Physical constants: ref. 8

TABLE 5

Uncertainties [a] at final function values at 298.15 K (% error)

Function	Allotted [a] frequency change (principal moment of inertia product fixed)		Allotted [a] principal moment of inertia product change (frequencies kept fixed)	
	10% Increase	10% Decrease	10% Increase	10% Decrease
C_p^0	−1.50%	1.50%	0	0
$(H^0-H_0^0)/T$	−2.06%	2.30%	0	0
$-(F^0-H_0^0)/T$	−0.54%	0.64%	0.15%	−0.18%
S^0	−0.79%	0.93%	0.14%	−0.14%

[a] ±10% Uncertainty made in the principal moment of inertia product value (Table 4) and similarly, ±10% uncertainty assumed in four smaller frequency values, this work (Table 3).

DISCUSSION

Structure and frequency assignments

Mono-crystalline acrylamide, $CH_2:CH\cdot CO\cdot NH_2$, forms a monoclinic lattice possessing a space group of $P2_{1/c}(C_{2h}^5)$ [5]. The recent far-IR vapour phase spectra work of Kydd and Dunham [4] reaffirms the finding of Jonathan [1] that the entire acrylamide molecule is planar; and that in the case of the presumed rotation about the single C–C bond, the *cis*-orientation of the two double bonds of the acrylamide structure is the dominant orientation. No evidence of the *trans*-conformer was found. As cited by Kydd and Dunham [4], the independent microwave work of Davis and Gerry [6] further supports the existence of this proposed planar, *cis*-structure for acrylamide. The microwave data of Davis and Gerry [6] were also used to calculate the product of principal moments of inertia (Table 4).

The frequency assignments used (Table 3) were chiefly taken from the IR spectra of the solid state (between 4000 and 450 cm^{-1}) and Raman spectra of acrylamide–water solutions (between 250 and 3200 cm^{-1}) from the work of Jonathan [1]. Additional solid state vibrational frequency assignments and/or corrections were made considering the work of Rao et al. [2] and Rao and Ramiah [3].

Accuracy and range of reliability

In this work all values are in cal g^{-1} $mole^{-1}$ K^{-1} units and apply to the ideal gas state at 1 atm pressure, tabulated values given to ±0.1 cal g^{-1} $mole^{-1}$ K^{-1}. However, probable errors may be larger than this uncertainty. The percentage errors (uncertainties) assigned to the calculated thermodynamic functions (Tables 1 and 2) are really estimates. These estimates were obtained accounting for two main sources of uncertainties: the uncertainties in input parameters, and uncertainties in the assumptions.

Input data uncertainties

In this work the frequency assignments for acrylamide (Table 3), because they are all solid state or acrylamide–water solution (liquid state) values, should be considered the least certain. Table 5 considers this (first column, at fixed product of principal moments of inertia), showing the effect in % change that could be expected in thermodynamic functions assuming ±10% uncertainty in the four lowest frequency values of this work (Table 3). The introduction of a possible change in the principal moment of inertia product value of an amount of ±10% causes very small deviation in the calculated thermodynamic function values (Table 5, second column).

Calculation assumption errors

In view of the implied rigidity of the planar structure of acrylamide [1,4,6], it should be plausible to expect that this molecule may well behave as a harmonic oscillator. Consequently, the errors introduced through the subsequent neglect of the various anharmonicity aspects such as vibrational cross-product terms, electronic transitions, internal rotational barrier over the low temperature range (273.15–1400 K) become small and do not affect in any meaningful way the values of the calculated thermodynamic functions. This discussion indicates that, barring major errors in frequency assignments, the expected overall error should be within 0.5–2.0% range. This expectation is strongly supported by Table 5 which indicates that even if frequency assignments are those of solid and liquid phases (Table 3), uncertainties in the calculated values of thermodynamic functions will still be low.

NOMENCLATURE

Å	Angstrom
C_P^0	Heat capacity, cal g^{-1} mole^{-1} K^{-1}
$-(F^0 - H_0^0)/T$	Free energy function, cal g^{-1} mole^{-1} K^{-1}
$(H^0 - H_0^0)/T$	Enthalpy function, where $H_0^0 = H^0$ at 0 kcal g^{-1} mole^{-1} K^{-1}
I_{ABC}	Product of principal moments of inertia, a.m.u.^{3} Å^6
IR	Infrared spectra
R	Raman spectra
S^0	Entropy, cal g^{-1} mole^{-1} K^{-1}

Superscript

^{0}	Reference state referring to the hypothetical state of an ideal gas at 1 atm

Subscript

p	Pressure

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