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THERMODYNAMIC STUDY OF THE VAPORIZATION OF URACIL

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ABSTRACT

The vapour pressure of uracil was measured in the temperature range 452—587 K using different techniques and the pressure—temperature equation $\log P(\text{kPa}) = 12.13 \pm 0.50 - (6823 \pm 210)/T$ was derived. The thermodynamic functions of gaseous and solid uracil were also evaluated through spectroscopic and calorimetric measurements. The sublimation enthalpy of uracil, $\Delta H^0_{298} = 131 \pm 5$ kJ mole^{-1}, was derived from second and third law treatment of the vapour data.

INTRODUCTION

The biological importance of uracil has prompted several scientific investigations as spectroscopic [1—4] and mass spectrometric studies [5,6]. At present, apparently, no vapour pressure data are reported in the literature except a few data obtained from spectroscopic measurements carried out by Clark et al. [7].

In order to obtain the vapour pressure of uracil over a wide range of temperature, vapour pressure measurements were carried out by means of three different methods: torsion-effusion, thermogravimetry and transpiration. An infrared study on gaseous uracil was performed in order to evaluate its thermodynamic functions and to derive the third-law sublimation enthalpy. Calorimetric techniques provided the heat capacity values of the solid phase.

EXPERIMENTAL AND RESULTS

High purity uracil (99.99%) samples were purchased from Koch—Light Laboratories. A check of its purity was made by comparing the melting point of the sample (612 ± 1 K) with the value reported in the literature (611 K) [8].

Part A. Vapor pressure measurements

Torsion-effusion method

The basis of the method and the experimental apparatus have been

TABLE 1

Constants of the torsion-effusion cells

Cell	Orifice area (10^3 cm^2)		Moment arm (cm)		Freeman's factor	
	a_1	a_2	l_1	l_2	f_1	f_2
A Pyrophillite	0.71	0.71	0.73 ± 0.05	0.76 ± 0.05	0.168	0.168
B Pyrophillite	3.80	3.80	0.75 ± 0.05	0.74 ± 0.05	0.371	0.351
C Graphite	7.09	7.09	0.86 ± 0.05	0.85 ± 0.05	0.926	0.916

described elsewhere [9,10]. From the torsion angle α of the effusion cell, the vapor pressure of uracil is derived from the equation

$$P = \frac{2\alpha K}{a_1 l_1 f_1 + a_2 l_2 f_2}$$

where K is the torsion constant of the tungsten wire from which the Knudsen cell is suspended, a_1 and a_2 are the areas of the two effusion holes, l_1 and l_2 are the distances from the rotation axis and f_1 and f_2 are the corresponding geometrical correction factors [11]. The constants of the cells used in our experiments are given in Table 1. During vaporization, the temperature of the cell was measured by a calibrated chromel—alumel thermocouple placed in a second cell beneath it.

The vapor pressures were determined in four runs in the temperature range 455—575 K.

A check of the geometrical factors of the cells was performed with pure sulfur and the obtained results were in good agreement with those reported in the literature [12].

The experimental data reported in Table 2 were treated by using the least

TABLE 2

Vapour pressure of uracil determined by torsion-effusion method

T (K)	α (degree)	P (kPa)	$-\Delta(G^0_T - H^0_{298})/T$ (J mole^{-1} K^{-1})	ΔH^0_{298} (kJ mole^{-1})
Run 1. Cell C				
455	8	8.69×10^{-4}	194.4	132.6
468	20	2.17×10^{-3}	194.4	132.6
483	53	5.75×10^{-3}	194.5	133.0
492	97	1.05×10^{-2}	194.5	133.0
501	158	1.72×10^{-2}	194.6	133.5
503	188	2.04×10^{-2}	194.6	133.5
506	220	2.39×10^{-2}	194.6	133.5
510	254	2.76×10^{-2}	194.6	133.9
514	352	3.83×10^{-2}	194.6	133.5
518	464	5.05×10^{-2}	194.6	133.5

Average 133.3 ± 0.4 [a]

TABLE 2 (continued)

T (K)	α (degree)	P (kPa)	$-\Delta(G^0_T - H^0_{298})/T$ (J mole^{-1} K^{-1})	ΔH^0_{298} (kJ mole^{-1})
Run 2. Cell A				
499	9	2.56×10^{-2}	194.6	131.4
503	11	3.28×10^{-2}	194.6	131.4
515	25	7.13×10^{-2}	194.6	131.4
518	30	8.57×10^{-2}	194.6	131.4
523	43	1.23×10^{-1}	194.6	131.0
525	52	1.48×10^{-1}	194.7	130.5
530	67	1.91×10^{-1}	194.7	130.5
539	109	3.10×10^{-1}	194.7	131.0
542	115	3.28×10^{-1}	194.7	131.4
547	133	3.79×10^{-1}	194.7	131.8
			Average	131.2 ± 0.4 [a]
Run 3. Cell A				
509	13	3.71×10^{-2}	194.6	131.4
512	15	4.28×10^{-2}	194.6	132.6
514	17	4.85×10^{-2}	194.6	132.6
516	19	5.42×10^{-2}	194.6	132.6
518	23	6.56×10^{-2}	194.6	132.2
520	26	7.41×10^{-2}	194.6	132.2
525	37	1.05×10^{-1}	194.7	132.2
528	47	1.34×10^{-1}	194.7	131.8
558	282	7.24×10^{-1}	194.8	131.4
560	305	7.93×10^{-1}	194.8	131.8
565	343	8.91×10^{-1}	194.8	132.2
571	397	1.13	194.85	132.6
575	415	1.20	194.9	132.6
			Average	132.2 ± 0.4 [a]
Run 4. Cell B				
483	10	6.30×10^{-3}	194.5	132.6
490	13	1.00×10^{-2}	194.5	133.5
498	20	1.26×10^{-2}	194.5	133.9
503	28	1.76×10^{-2}	194.6	133.9
506	40	2.51×10^{-2}	194.6	133.5
511	53	3.31×10^{-2}	194.6	133.0
514	73	4.60×10^{-2}	194.6	133.0
517	94	5.92×10^{-2}	194.6	132.6
519	106	6.67×10^{-2}	194.6	132.6
521	128	8.05×10^{-2}	194.6	132.2
523	153	9.64×10^{-2}	194.65	131.8
524	170	1.12×10^{-1}	194.7	131.8
525	175	1.10×10^{-1}	194.7	131.8
526	200	1.26×10^{-1}	194.7	131.4
528	208	1.31×10^{-1}	194.7	132.2
537	334	2.10×10^{-1}	194.7	132.2
540	394	2.51×10^{-1}	194.7	132.2
			Average	132.6 ± 0.7 [a]

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[a] The error is the standard deviation.

squares method and the equations

$$\log P(\text{kPa}) = 11.23 \pm 0.09 - \frac{6504 \pm 47}{T}$$

$$\log P(\text{kPa}) = 12.72 \pm 0.32 - \frac{6964 \pm 169}{T}$$

$$\log P(\text{kPa}) = 12.44 \pm 0.19 - \frac{7057 \pm 103}{T}$$

$$\log P(\text{kPa}) = 11.53 \pm 0.80 - \frac{6617 \pm 433}{T}$$

were obtained where the associated errors are the standard deviations.

Thermogravimetry

Thermogravimetric measurements were carried out with a Setaram Model 1360 Ugyne Eyraud null thermobalance coupled with a Knudsen cell suspended by means of a platinum chain in the isothermal zone of the reaction chamber. The assembly and the method have been described previously [13]. The temperature was measured with a Pt—Pt/10% Rh thermocouple fitted snugly into a fixed cell identical to the effusion cell and placed immediately below it.

The vaporization of uracil was carried out in two graphite cells and the measurements were made in the temperature range 452—521 K. The values of the pressure at temperature T were derived from the rate of mass loss ($\mathrm{d}m/\mathrm{d}t$) of the sample, by the well-known Knudsen equation

$$P(\text{kPa}) = \frac{2.29}{K'}\frac{\mathrm{d}m}{\mathrm{d}t}A\left(\frac{T}{M}\right)^{1/2}$$

where M is the molar mass of the vapour assuming that the sample vaporizes in monomeric form [5,6], A is the area of the effusion hole and K' is the Clausing correction factor [14]. The experimental vapour pressures are reported in Table 3 and from these data the equation

$$\log P(\text{kPa}) = 12.31 \pm 0.23 - \frac{6634 \pm 112}{T}$$

where the associated errors are the standard deviations, was derived.

Transpiration

Measurements were obtained by utilizing an apparatus described in detail in a preceding paper [15]. Helium was employed as carrier gas and its purification was carried out by means of a procedure proposed by Bourke et al. [16].

The vapour pressure, P_i, was derived from the sample of mass m_i transported and condensed during the time Δt in a cooled quartz collector using the relation

$$P_i = \frac{m_i}{[m_i + (P_0\Phi\ \Delta t M_i/RT)]}$$

TABLE 3

Vapour pressure determined by the thermogravimetric technique

T (K)	dm/dt (g s^{-1})	P (kPa)	$-\Delta(G_T^0 - H_{298}^0)/T$ (J mole^{-1} K^{-1})	ΔH_{298}^0 (kJ mole^{-1})
Cell 1 [a]				
452	1.72×10^{-6}	4.57×10^{-3}	194.4	125.5
459	2.85×10^{-6}	7.59×10^{-3}	194.4	125.5
469	5.00×10^{-6}	1.35×10^{-2}	194.4	125.9
477	8.33×10^{-6}	2.29×10^{-2}	194.5	125.9
485	1.40×10^{-5}	3.80×10^{-2}	194.5	125.9
493	2.19×10^{-5}	6.17×10^{-2}	194.5	125.4
			Average	125.7 ± 0.2 [c]
Cell 2 [b]				
475	1.28×10^{-6}	2.19×10^{-2}	194.4	125.5
479	1.67×10^{-6}	2.95×10^{-2}	194.5	125.5
487	2.69×10^{-6}	4.79×10^{-2}	194.5	125.5
493	3.87×10^{-6}	6.92×10^{-2}	194.5	125.5
498	5.69×10^{-6}	1.02×10^{-1}	194.5	125.5
506	9.52×10^{-6}	1.74×10^{-1}	194.6	125.1
513	1.44×10^{-5}	2.63×10^{-1}	194.6	125.1
521	2.14×10^{-5}	3.89×10^{-1}	194.6	125.5
			Average	125.3 ± 0.2 [c]

[a] Cell 1. Effusion hole diameter 0.6 mm; thickness of edge 0.4 mm.

[b] Cell 2. Effusion hole diameter 0.3 mm; thickness of edge 0.5 mm.

[c] The error is the standard deviation.

TABLE 4

Vapour pressure determined by transpiration method

T (K)	Φ (ml min^{-1})	Condensed sample mg)	Time (min)	P (kPa)	$-\Delta(G_T^0 - H_{298}^0)/T$ (J mole^{-1} K^{-1})	ΔH_{296}^0 (kJ mole^{-1})
509	151	18.0	12	2.14×10^{-1}	194.6	135.1
519	150	4.4	12	4.41×10^{-2}	194.6	134.3
526	154	6.0	14	5.37×10^{-2}	194.7	135.1
533	144	8.0	16	8.32×10^{-2}	194.7	135.1
533	145	7.6	15	7.62×10^{-2}	194.7	135.6
534	137	10.1	15	1.05×10^{-1}	194.7	134.3
534	146	9.3	13	1.07×10^{-1}	194.7	134.3
537	137	18.7	25	1.20×10^{-1}	194.7	134.7
537	140	15.0	20	1.17×10^{-1}	194.7	134.7
544	158	7.0	6	1.61×10^{-1}	194.7	135.0
544	159	5.9	6	1.39×10^{-1}	194.7	135.7
					Average	134.9 ± 0.5 [a]

[a] The error is the standard deviation.

where M_i is the molar mass of the sample, R is the gas constant, Φ is the flow rate of the carrier gas measured by a flowmeter placed at the inlet of a furnace, and P_0 and T are its pressure and temperature where the flow was measured. The geometry of the apparatus ensured the saturation of the carrier gas with the uracil vapour in the flow rate range 1.2—1.6 l min^{-1}. Under these conditions, diffusion effects were considered negligible. The amount of the condensate phase was determined by varying, at each experimental temperature, the flow rate of the carrier gas and/or the time of the transpiration experiment. The vapour pressure data are summarized in Table 4. The least-squares treatment of the experimental data over the temperature range 509—587 K yielded the equation

$$\log P(\mathrm{kPa}) = 12.54 \pm 1.10 - \frac{7111 \pm 572}{T}$$

where the associated errors are standard deviations.

Part B. Spectroscopic and calorimetric measurements

The infrared spectra of gaseous uracil were recorded in the range 100—4000 cm^{-1} by using a Perkin-Elmer 180 IR grating spectrophotometer and a Laser Analitics' Model LS-3 laser source spectrometer. Stainless steel spectroscopic cells with 30 cm pathlength and equipped with suitable optical windows were used. The cell was kept at a temperature of about 425 K, measured with calibrated iron-constantan thermocouples. Nitrogen at 1 atm was employed as a diffusion barrier. Various scans were made before and after each experiment in order to distinguish between the background, the vapours condensed on the optical windows and the absorption due to the uracil.

The assignment of the thirty fundamental vibrations of uracil is reported elsewhere in a detailed spectroscopic study [1]. The vibrational contribution to the partition function was computed employing the spectroscopic results carried out in the frequency range 200—4000 cm^{-1} by means of the matrix isolation technique and from 100 to 4000 cm^{-1} in the gas phase. One of the fundamentals (an out-of-plane ring torsion) expected below 100 cm^{-1} was calculated on the basis of a theoretical calculation CNDO [17]. The rotational contribution to the thermodynamic functions of the gaseous uracil is

TABLE 5

Thermodynamic functions of gaseous uracil

T (K)	S^0_T (J mole^{-1} K^{-1})	$-(G^0_T - H^0_{298})/T$ (J mole^{-1} K^{-1})	$(H^0_T - H^0_{298})$ (kJ mole^{-1})
298.15	333.6	333.6	0.0
400	367.3	335.5	12.7
450	382.8	339.3	19.6
500	399.1	343.9	27.6
550	414.2	348.9	35.9
600	429.3	354.8	44.7

TABLE 6

Thermodynamic functions of solid uracil

T (K)	C^0_p ($\mathrm{J\ mole^{-1}\ K^{-1}}$)	S^0_T ($\mathrm{J\ mole^{-1}\ K^{-1}}$)	$-(G^0_T - H^0_{298})/T$ ($\mathrm{J\ mole^{-1}\ K^{-1}}$)	$(H^0_T - H^0_{298})$ ($\mathrm{kJ\ mole^{-1}}$)
400	152.7	183.2	140.6	17.0
450	158.0	197.0	145.1	23.3
500	163.2	210.9	149.8	30.5
550	168.0	225.9	155.0	38.9
600	171.8	139.7	160.2	47.7

evaluated employing the available structural data [18]. The values of the computed thermodynamic functions of uracil in its gaseous phase are reported in Table 5.

As far as the evaluation of the thermodynamic functions of solid uracil is concerned, the necessary heat capacity values [19] were measured using a Perkin-Elmer D5C-2 differential calorimeter in the temperature range 400—600 K. In Table 6, we report the heat capacity data and the derived thermodynamic functions of the solid phase.

CONCLUSIONS

Considering the sets of measurements obtained by the torsion, transpiration and thermogravimetric techniques, we propose the following vapour pressure equation for uracil.

$$\log P(\mathrm{kPa}) = 12.13 \pm 0.50 - \frac{(6823 \pm 210)}{T}$$

The constants were evaluated by weighting the corresponding values yielded by each technique and their errors were estimated taking into account the uncertainties in the temperature measurements and in the calibration factors. From the slope of the $\log P$ vs. $1/T$ linear least-squares equation, the second-law sublimation enthalpy $\Delta H^0_{520} = 130.6 \pm 4.0$ kJ $\mathrm{mole^{-1}}$ was derived. In Tables 2—4, the third-law ΔH^0_{298} values are reported at each experimental temperature. The free energy functions of both gaseous and solid phases are those reported in Table 5 and 6.

The third-law $\Delta H^0_{298} = 131 \pm 5$ kJ $\mathrm{mole^{-1}}$ was obtained from torsion and transpiration techniques data. This value is higher than that derived from the thermogravimetric method (third-law $\Delta H^0_{298} = 125 \pm 0.04$ kJ $\mathrm{mole^{-1}}$) but taking into account the systematic errors in the temperature readings and the evaluation of the instrumental constants and considering the second-law $\Delta H^0_{298} = 133.0 \pm 2.0$ kJ $\mathrm{mole^{-1}}$, we propose as ΔH^0_{298} the value 131 ± 5 kJ $\mathrm{mole^{-1}}$ for the sublimation process of uracil. The error associated to this value is estimated.

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