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Thermal stability and related thermodynamic properties of *N*-ethylthiourea

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Abstract

The enthalpy and entropy of sublimation of *N*-ethylthiourea were obtained from the temperature dependence of its vapour pressure measured by both the torsion–effusion and the Knudsen effusion method in the temperature range 360–380 K. The compound undergoes no solid-to-solid phase transition or decomposition below 380 K. The pressure against reciprocal temperature resulted in $\lg(p,\ \mathrm{kPa}) = (13.40 \pm 0.27) - (6067 \pm 102)/T(\mathrm{K})$. The molar sublimation enthalpy and entropy at the mid interval temperature were $\Delta_{\mathrm{sub}}H_{\mathrm{m}}(370\ \mathrm{K}) = (116.1 \pm 2.0)\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_{\mathrm{sub}}S_{\mathrm{m}}(370\ \mathrm{K}) = (218.0 \pm 5.2)\ \mathrm{J\ mol^{-1}\ K^{-1}}$, respectively. The same quantities derived at 298.15 K were $(118.8 \pm 2.1)\ \mathrm{kJ\ mol^{-1}}$ and $(226.1 \pm 5.5)\ \mathrm{J\ mol^{-1}\ K^{-1}}$, respectively.

Keywords: *N*-Ethylthiourea; Sublimation thermodynamics; Torsion–effusion method; Knudsen method

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1. Introduction

The knowledge of the changes in thermodynamic quantities during sublimation is of great importance in the study of the stability of organic compounds as well as in many thermodynamic calculations. The present paper reports the experimental vapour pressures of *N*-ethylthiourea and its derived sublimation thermodynamic parameters. These measurements were performed as a part of our research programme on the thermodynamic properties of urea and thiourea, and some of their *N*-alkylderivatives, concerning fusion [1–3], vaporisation [4,5], sublimation [3,6,7], as well as their heat capacities [8,9] and solvation in water at infinite dilution behaviour [10,11]. The vapour pressure data as a function of temperature obtained by the torsion–effusion method [12–14] of thiourea and some of its derivatives, namely methylthiourea, 1,3-dimethylthiourea and 1,1,3,3-tetramethylthiourea, and 1,3 diethylthiourea, 1,3 dipropylthiourea and 1,3 dibutylthiourea were reported in [7,3]. For *N*-ethylthiourea, the values of enthalpy and entropy of sublimation at mid interval temperature, T_{av}, and at 298.15 K were reported in [3] (Tables 6 and 8) based on a limited number of experimental values available at that time. Recently, further torsion–effusion measurements were performed on *N*-ethylthiourea (Table 1) which practically confirmed the previous values of both enthalpy and entropy of sublimation at T_{av}. The Knudsen method [5] was also employed to confirm the torsion–effusion results.

2. Experimental

N-Ethylthiourea was supplied by Aldrich (commercial purity 99%) and purified by several successive crystallisations from absolute ethanol and dried under reduced pressure. A series of fusion cycles showed neither solid-to-solid transitions nor decomposition from room temperature to the melting point 380.9 K [3].

Our tensimetric measurements were obtained with both the torsion–effusion and the Knudsen method at $T = 360$–380 and 360.5–367.5 K, respectively.

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Table 1
Vapour pressure data obtained with the torsion–effusion method

Run 1 (cell A)		Run 2 (cell A)		Run 3 (cell C)		Run 4 (cell B)		Run 5 (cell C)	
T (K)	$-\lg(p, \text{kPa})$	T (K)	$-\lg(p, \text{kPa})$	T (K)	$-\lg(p, \text{kPa})$	T (K)	$-\lg(p, \text{kPa})$	T (K)	$-\lg(p, \text{kPa})$
360	3.48	361	3.36	368	3.04	364	3.26	368	3.19
367	3.13	363	3.35	369.5	2.93	366	3.20	370	3.06
369	3.05	365	3.18	371	2.89	371	2.96	372	3.01
370	2.98	366.5	3.09	375	2.70	373	2.89	374.5	2.87
374	2.86	368.5	3.10	370.5	2.93	375	2.78	376	2.83
375	2.82	371	2.98	376	2.64	376	2.75	377	2.77
378	2.65	374	2.76	378	2.61	378	2.65	378	2.75
		375	2.73	379	2.54	378	2.67	380	2.66
		376	2.76	380	2.53	379.5	2.58	380.5	2.64
		377	2.72						
		379	2.57						
		380	2.53						

The torsion–effusion method and employed experimental assembly have been described in [4,6]. Vapour pressure was determined by measurement of the torsion angle α of the tungsten wire (30 μm in diameter) from which the effusion cell is suspended. This is connected to the vapour pressure through the simple relation $p = K\alpha$, were K is a constant that takes into account the geometrical constants of the effusion cell and of the torsion wire. The constant K was determined experimentally by vaporising standard compounds (urea, naphthalene and benzoic acid). Three aluminium cells A, B and C with 1.0, 1.4, and 1.6 mm effusion orifices, respectively, were used.

To confirm the thermodynamic parameters of sublimation of *N*-ethylthiourea a run was also performed by the Knudsen method [15]:

$$p = K' \frac{\mathrm{d}m}{\mathrm{d}t} \left(\frac{T}{M}\right)^{1/2}, \tag{1}$$

where d*m*/d*t* is the mass loss rate, M the molar mass of the effusing species, T the experimental temperature and K' is the Clausing probability factor which takes into account the area of the effusion cell orifice [16]. Its value was determined by using naphthalene as a reference material [17].

For both methods, aluminium cells were used to avoid any chemical interaction with samples. The temperature measurements were performed with a calibrated chromel–alumel thermocouple with an accuracy of ±0.5 K, placed below the effusion cell.

Table 2
Temperature dependence of the vapour pressure of *N*-ethylthiourea obtained with the torsion–effusion method

Run	Cell[a]	ΔT (K)	N[b]	$\lg(p, \text{kPa}) = A - B/T(\text{K})$	
				A[c]	B[c]
1	A	360–378	7	13.36 ± 0.61	6055 ± 227
2	A	361–380	12	13.43 ± 0.76	6072 ± 280
3	C	368–380	9	13.41 ± 0.71	6047 ± 265
4	B	364–380	9	13.56 ± 0.31	6128 ± 118
5	C	368–380	9	13.21 ± 0.49	6029 ± 187

[a] See text.
[b] Number of experimental points.
[c] Uncertainties at 95% confidence limits.

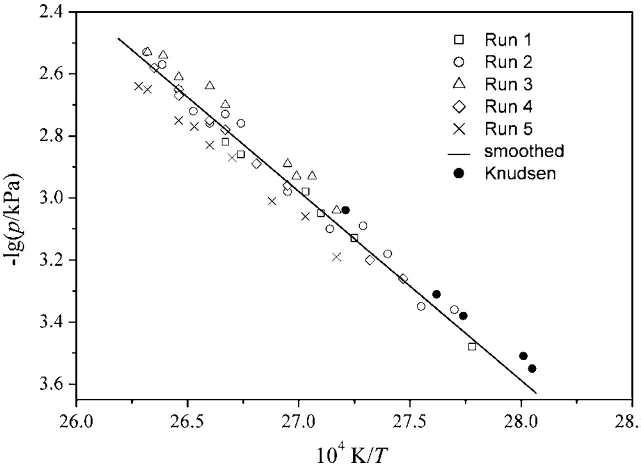

Fig. 1. Temperature dependence of the vapour pressure of *N*-ethylthiourea obtained with the torsion–effusion (runs 1–5) and Knudsen effusion methods. Smoothed curve only refers to the torsion–effusion data.

3. Results and discussion

Vapour pressures obtained with the torsion–effusion method are listed in Table 1. Table 2 presents the lg *p* versus 1/*T* equations obtained by the least-squares treatment of the data from each torsion–effusion run. Our results showed good reproducibility with different orifice cell sizes. By weighting the slopes and intercepts of these equations according to the number of

Table 3
Temperature dependence of the vapour pressure of *N*-ethylthiourea obtained with the Knudsen method

T (K)	Mass loss (10^3) (g)	$10^{-3}\Delta t$ (s)	p (Pa)
367.5	19.47	22.08	0.912
362.0	23.28	48.96	0.490
357.0	25.16	82.74	0.309
356.5	22.76	82.00	0.282
360.5	30.82	75.90	0.417

Table 4
Molar heat capacity of solid and gaseous *N*-ethylthiourea as a function of temperature from the equation: $C_{p,\mathrm{m}}(\mathrm{J\,K^{-1}\,mol^{-1}}) = A + B(T(\mathrm{K}) - 298.15)$, where $A = C_{p,\mathrm{m}}(298.15\,\mathrm{K})$

T range	Solid[a]		*T* range	Gaseous[b]	
	A	*B*		*A*	*B*
313–363	150.4 ± 0.70	0.475 ± 0.02	300–600	122.2 ± 2.0	0.212 ± 0.01

[a] Reference [9].
[b] Calculated with the Benson group additivity scheme [18].

Table 5
Molar enthalpy of sublimation of *N*-ethylthiourea at experimental $T_{\mathrm{av}} = 370\,\mathrm{K}$ and value derived at $T = 298.15\,\mathrm{K}$

$\Delta_{\mathrm{sub}}H_{\mathrm{m}}(T_{\mathrm{av}})$	$H_{\mathrm{m}}(T_{\mathrm{av}}) - H_{\mathrm{m}}(298.15\,\mathrm{K})$		$\Delta_{\mathrm{sub}}H_{\mathrm{m}}(298.15\,\mathrm{K})$
	g	cr	
116.1 ± 2.0	9.33 ± 0.35	12.03 ± 0.49	118.8 ± 2.1

Units: $\mathrm{kJ\,mol^{-1}}$; uncertainties calculated by the error propagation rule.

Table 6
Molar entropy of sublimation of *N*-ethylthiourea at experimental $T_{\mathrm{av}} = 370\,\mathrm{K}$ and value derived at $T = 298.15\,\mathrm{K}$

$\Delta_{\mathrm{sub}}S_{\mathrm{m}}(T_{\mathrm{av}})$	$S_{\mathrm{m}}(T_{\mathrm{av}}) - S_{\mathrm{m}}(298.15\,\mathrm{K})$		$\Delta_{\mathrm{sub}}S_{\mathrm{m}}(298.15\,\mathrm{K})$
	g	cr	
218.0 ± 5.2	27.97 ± 1.07	36.02 ± 1.45	226.1 ± 5.5

Units: $\mathrm{J\,mol^{-1}\,K^{-1}}$; uncertainties calculated by the error propagation rule.

the experimental points, the following smoothed equation was obtained:

$$\lg(p, \mathrm{kPa}) = (13.40 \pm 0.27) - (6067 \pm 102)/T\,(\mathrm{K}) \tag{2}$$

in which uncertainties were calculated by the error propagation rule. This equation is drawn in Fig. 1 together with the experimental points. Vapour pressure values obtained by the Knudsen method are also reported in Fig. 1. These data were not considered when deriving Eq. (2) due to their relatively small number (Table 3) and not negligible scatter of intercepts. From the slope and the intercept of Eq. (2), the second-law molar sublimation enthalpy and entropy of *N*-ethylthiourea were calculated at the mid-interval temperature $T_{\mathrm{av}} = 370\,\mathrm{K}$, giving rise to $\Delta_{\mathrm{sub}}H_{\mathrm{m}}(T_{\mathrm{av}}) = (116.1 \pm 2.0)\,\mathrm{kJ\,mol^{-1}}$ and $\Delta_{\mathrm{sub}}S_{\mathrm{m}}(T_{\mathrm{av}}) = (218.0 \pm 5.2)\,\mathrm{J\,mol^{-1}\,K^{-1}}$.

The molar enthalpy of sublimation at 298.15 K was derived from the experimental value at T_{av} and corresponding enthalpy changes from T_{av} to 298.15 K of both gaseous and solid phases according to the equation:

$$\Delta_{\mathrm{sub}}H_{\mathrm{m}}(298.15\,\mathrm{K}) = \Delta_{\mathrm{sub}}H_{\mathrm{m}}(T_{\mathrm{av}}) - \int_{T=298.15\,\mathrm{K}}^{T_{\mathrm{av}}} [C_{p,\mathrm{m}}(\mathrm{g}) - C_{p,\mathrm{m}}(\mathrm{cr})]\,\mathrm{d}T \tag{3}$$

Heat capacity as a function of temperature for gaseous *N*-ethylthiourea was calculated through the Benson additivity group scheme [18] and its solid state value was taken from reference [9]. The slopes and intercepts of the equation $C_{p,\mathrm{m}}(\mathrm{J\,K^{-1}\,mol^{-1}}) = A + B(T(\mathrm{K}) - 298.15)$ for both gaseous and solid state are given in Table 4. The same procedure was applied to calculate the molar entropy of sublimation at 298.15 K. The molar values of enthalpy and entropy of sublimation derived at 298.15 K (Tables 5 and 6) were $\Delta_{\mathrm{sub}}H_{\mathrm{m}}(298.15\,\mathrm{K}) = (118.8 \pm 2.1)\,\mathrm{kJ\,mol^{-1}}$ and $\Delta_{\mathrm{sub}}S_{\mathrm{m}}(298.15\,\mathrm{K}) = (226.1 \pm 5.5)\,\mathrm{J\,mol^{-1}\,K^{-1}}$.

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