

Vapour pressures and vaporization enthalpies of thiourea and a homologous series of its 1,3-dialkyl derivatives

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Abstract

Second-law vaporization enthalpies of thiourea and four of its dialkyl derivatives (1,3-dimethyl-, 1,3-diethyl-, 1,3-di-*n*-propyl-, and 1,3-di-*n*-butylthiourea) were determined from the temperature dependence of their vapour pressures. The pressures were measured by torsion and Knudsen methods.

INTRODUCTION

This paper is the last in a series of works in a study of the vaporization of urea [1–3], thiourea [4], selenurea [5] and some of their derivatives. In particular, in this work we have determined the vaporization enthalpies of thiourea and of some of the homologous series of its dialkyl derivatives, 1,3-dimethyl-, 1,3-diethyl-, 1,3-di-*n*-propyl-, and 1,3-di-*n*-butylthiourea (hereafter referred to as TU, 1,3-DMTU, 1,3-DETU, 1,3-DPTU and 1,3-DBTU). To our knowledge, apart from some vapour pressure values of TU obtained by de Wit et al. [6] employing a simultaneous torsion–Knudsen effusion apparatus, one value reported by Gomez and Sabbah [7] (1.1×10^{-3} kPa at 404 K), and our previous torsion data measured above TU and 1,3-DMTU [4], no other pressure data for TU and its 1,3-dialkyl derivatives are available in the literature. Moreover, the only data available for the sublimation enthalpies of these compounds are those of TU determined calorimetrically [7] and calculated from the temperature dependence of the vapour pressure by de Wit et al. [6]. The vaporization enthalpies reported in the present work were determined from the temperature dependence of the vapour pressure measured by two different techniques, the torsion and Knudsen effusion methods.

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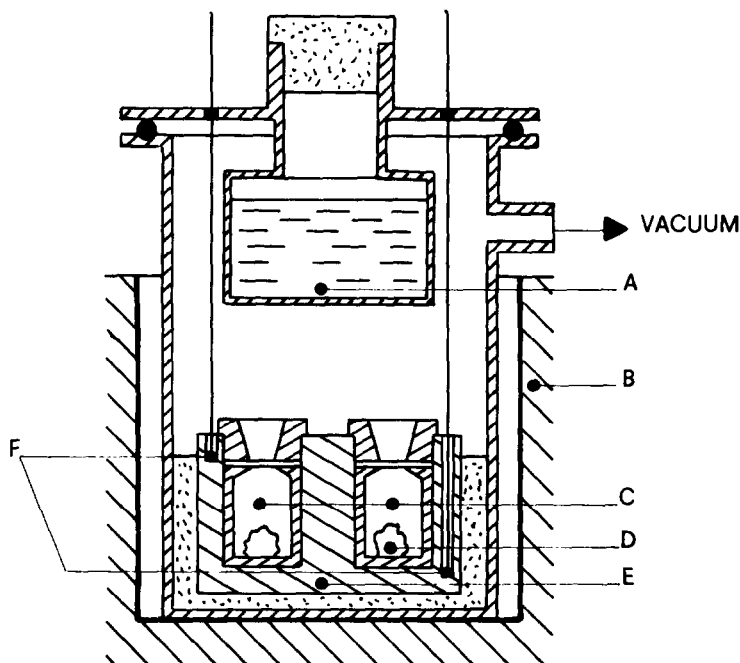


Fig. 1. Section through the multiple Knudsen cell apparatus: A, liquid nitrogen; B, furnace; C, aluminium Knudsen cells; D, sample; E, copper block; F, thermocouples.

EXPERIMENTAL

The TU and its derivatives employed in this study, designated pure, were repurified by recrystallization. The torsion assembly used to measure the vapour pressure was the same as described previously [8]. Two conventional aluminium cells, with different diameter effusion holes (1.0 and 1.6 mm for cells A and B, respectively), were used. In order to verify the reliability of the apparatus and to determine the torsion constants associated with the cells used, standards with well-known vapour pressures (urea [1] and benzoic acid [9]) were vaporized. The vapour pressure measurements of the derivatives were also carried out, using the Knudsen apparatus drawn in Fig. 1. Because of differences in the vapour pressure, in order to vaporize comparable amounts of the samples the diameters of the effusion holes of the four Knudsen cells are different. With this assembly at fixed temperature, the vapour pressure of each compound can be measured simultaneously from the rate of weight loss of the sample. However, we used this set-up to determine accurate ratios of the pressures of the compounds studied, from the ratios of the weight losses of the samples at the end of the experiment. The weight losses were corrected accordingly for calibration factors due to the differences in the diameters of the effusion holes and in

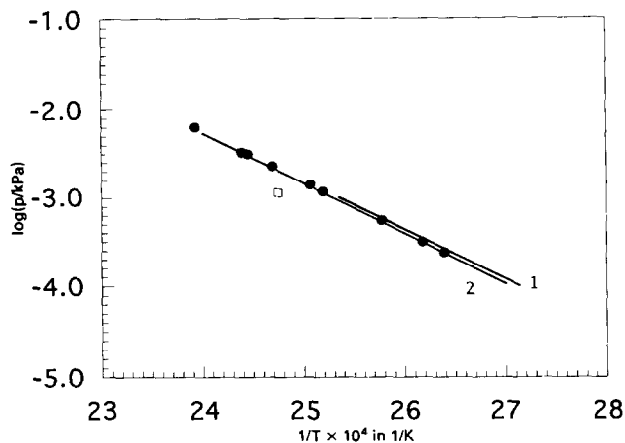


Fig. 2. Vapour pressure of thiourea: ●, present work; □, ref. 7; 1, ref. 6; 2, our previous equation [4].

the molecular weights of the vapours. In this way, the pressure ratios of the studied derivatives, with reference to one of them (1,3-DBTU in this work), are not affected by uncertainties associated with the small temperature variations that occur during the experiments or by the vaporization times. In order to evaluate the cell calibration factors, several preliminary experiments were carried out, loading the four cells with a pure compound.

RESULTS AND CONCLUSIONS

Figure 2 shows the torsion pressures measured over TU, together with the literature data. Table 1 reports the temperature–pressure equation of this compound as obtained from the least-squares treatment of data determined in one run, together with those determined in our previous work and derived from the pressure data reported by de Wit et al. [6]. In practice, the pressures agree very well with each other; therefore, we believe that the temperature dependence of the vapour pressure of TU follows the equation proposed in our previous work (see Table 1). Table 1 reports the temperature–pressure equations for the derivatives, as obtained from least-squares treatment of the results of each run. From the equations, the following equations are selected

$$1,3\text{-DMTU} \quad \lg(p/\text{kPa}) = (10.88 \pm 0.50) - (4866 \pm 200)/T$$

$$1,3\text{-DETU} \quad \lg(p/\text{kPa}) = (12.03 \pm 0.30) - (5267 \pm 150)/T$$

$$1,3\text{-DPTU} \quad \lg(p/\text{kPa}) = (12.52 \pm 0.20) - (5612 \pm 150)/T$$

$$1,3\text{-DBTU} \quad \lg(p/\text{kPa}) = (11.69 \pm 0.20) - (5505 \pm 100)/T$$

TABLE 1
Vapour pressure of TU and its 1,3-dialkyl derivatives

Compounds	Source	Temperature range/K	Number of points	$\lg[p/(\text{kPa})] = A - B/T$	
				A^a	B^a
TU	Previous work	377–340	5 runs	11.94 ± 0.25	5711 ± 98
	de Wit [6]	369–395	–	11.09	5561^b
	This work	379–418	9	11.53 ± 0.06	5741 ± 24
1,3-DMTU	Previous work [4]	350–372	4 runs	11.33 ± 0.50	4971 ± 150
	This work, cell A	347–375	12	10.57 ± 0.27	4762 ± 97
	This work, cell A	342–365	8	10.22 ± 0.25	4635 ± 90
1,3-DETU	This work, cell B	348–360	11	11.70 ± 0.10	5149 ± 68
	This work, cell A	351–384	9	12.32 ± 0.39	5382 ± 143
	This work, cell A	356–382	9	12.14 ± 0.16	5304 ± 59
1,3-DPTU	This work, cell B	352–375	10	11.66 ± 0.31	5131 ± 114
	This work, cell A	361–394	11	12.93 ± 0.16	5792 ± 62
	This work, cell A	355–389	12	12.52 ± 0.24	5594 ± 91
1,3-DBTU	This work, cell B	346–381	11	12.24 ± 0.35	5498 ± 128
	This work, cell B	349–379	8	12.33 ± 0.39	5552 ± 144
	This work, cell A	368–403	10	11.55 ± 0.38	5453 ± 147
1,3-DBTU	This work, cell A	374–389	8	11.84 ± 0.16	5569 ± 60
	This work, cell B	369–389	7	11.73 ± 0.36	5506 ± 137

^a The quoted errors are standard deviations. ^b Calculated from the data reported in ref. 6.

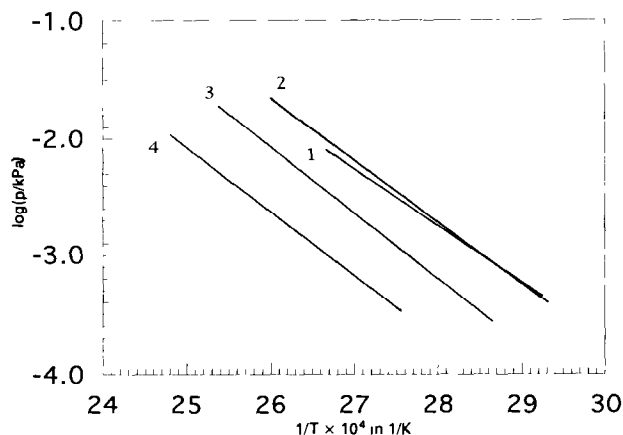


Fig. 3. Vapour pressure of thiourea 1,3-derivatives: 1, 1,3-di-methylthiourea; 2, 1,3-di-ethylthiourea; 3, 1,3-di-*n*-propylthiourea; 4, 1,3-di-*n*-butylthiourea.

TABLE 2

Differences in the vapour pressures of the studied TU 1,3-dialkyl derivatives measured by the Knudsen method and calculated from the torsion vapour pressure–temperature equations

Compounds	Time (± 1 min) [$T(\pm 0.5$ K)]	Mass loss (± 0.01 mg)	$\lg(p(\text{compounds})/p(\text{DBTU}))$	
			Knudsen	Torsion
1,3-DMTU	2610 [353]	24.39	1.03	1.00
1,3-DETU		29.80	1.08	1.01
1,3-DPTU		29.21	0.57	0.53
1,3-DBTU		22.40	–	–
1,3-DMTU	363 [357]	4.83	0.90	0.98
1,3-DETU		5.71	1.01	1.01
1,3-DPTU		6.55	0.56	0.53
1,3-DBTU		5.10	–	–
1,3-DMTU	326 [359]	4.74	0.99	0.97
1,3-DETU		5.74	1.04	1.00
1,3-DPTU		6.25	0.57	0.53
1,3-DBTU		4.65	–	–
1,3-DMTU	347 [360]	5.59	0.97	0.97
1,3-DETU		6.76	1.03	1.00
1,3-DPTU		7.79	0.58	0.53
1,3-DBTU		5.70	–	–
1,3-DMTU	791 [360.5]	13.84	1.00	0.96
1,3-DETU		16.79	1.05	1.00
1,3-DPTU		18.60	0.59	0.53
1,3-DBTU		13.40	–	–

The associated errors are estimated from the corresponding standard deviations in each equation and the uncertainties in the torsion angles measured in the first steps of the vaporizations. These equations are drawn in Fig. 3.

Employing the multiple Knudsen cells, the ratios between the vapour pressure of each derivative and of 1,3-DBTU were measured as ratios of weight loss of the cell containing the derivative and that loaded with 1,3-DBTU, corrected for the calibration factors. The ratios thus obtained and those calculated from the pressures derived from the selected torsion equations are summarized in Table 2. The agreement is satisfactory.

It is interesting to note that though 1,3-DETU, 1,3-DPTU and 1,3-DBTU present vapour pressures that decrease with decreasing molecular weight, those of 1,3-DMTU are comparable within experimental uncertainty with those of 1,3-DETU, and, particularly at high temperatures (as confirmed in the Knudsen experiments), are slightly lower (see Fig. 3). The vaporization enthalpies of the derivatives at the experimental mid-point

TABLE 3

Thermodynamic parameters of 1,3-dialkylthioureas

Compound	\bar{T} in K	$\Delta_{\text{vap}}H_m^\circ(\bar{T})$ in kJ mol ⁻¹	$C_p/(J \text{ mol}^{-1}) = A - B(T/K)^a$				T_{fus} in K ^a	$\Delta_{\text{fus}}H_m^\circ(T_{\text{fus}})$ in kJ mol ⁻¹	$\Delta_{\text{sub}}H_m^\circ(298)$ in kJ mol ⁻¹
			Solid		Gaseous				
			A	B	A	B			
1,3-DMTU	358.5	93 ± 4	36.070	0.385	78.350	0.174	337.0	12.7 ± 0.4	107.3 ± 4
1,3-DETU	367.5	101 ± 3	52.200	0.500	76.030	0.314	350.6	16.6 ± 0.5	120.2 ± 3
1,3-DPTU	370.0	107 ± 3	54.500	0.650	88.770	0.426	342.7	22.6 ± 0.2	132.5 ± 3
1,3-DBTU	385.5	105 ± 2	65.770	0.783	101.510	0.538	337.5	27.8 ± 0.4	137.0 ± 3

^a See ref. 10.

temperatures were calculated from the slopes of the selected vapour pressure–temperature equations and are reported in Table 3. Using the heat capacities of the solid and liquid phases and the enthalpies of fusion of these compounds, both measured calorimetrically by Della Gatta et al. [10], we have calculated their standard sublimation enthalpies (see Table 3). In this calculation we have considered that the heat capacities of the liquid phases are equal to those of the solid ones. This approximation should not influence the final $\Delta_{\text{sub}}H_m^\circ(298)$ values, because the experimental temperatures are very near to the melting points. The standard sublimation enthalpies thus obtained show an interesting trend with the molecular weight of the alkanes in the TU derivatives. The increase in the standard sublimation enthalpies is not surprising, considering that an increase in the length of the chain favours the stability of the solid compounds.

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