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Note

An investigation into the sublimation of selenourea

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The vaporization behaviour of selenourea has apparently not yet been investigated. In previous related studies, the vapour pressures of urea [1] and thiourea [2] were measured: therefore we considered it interesting to compare their vaporization behaviour with that of selenourea.

The vapour pressure of selenourea, (Aldrich Chem. Co., about 99.8% pure) was measured by the torsion-effusion [3] and Knudsen-effusion [4] methods using the assembly described in a previous paper [5]. Accurate determinations of the torsion and Knudsen constants of the employed cells (having different effusion holes) were obtained by vaporizing very pure urea [1] benzoic acid [6] and cadmium [7] as standards.

Two preliminary experiments were carried out by heating simultaneously under vacuum at fixed temperatures five selenourea samples from five conventional Knudsen cells placed in an isothermal copper block and closed with lids having effusion holes of different diameters. Table 1 reports the percentage of the sample vaporized in about 40 hours. It is interesting to note that when the cell is open, or closed with a lid that has a large effusion hole (the approximate Langmuir condition), the sample vaporizes completely, while when the vaporization is carried out from cells with a small effusion hole, at the end of the experiment a stable black residue is found in the cell. Vapour pressure measurements of these residues at higher temperatures and X-ray analysis showed that they consist of practically pure selenium, but their amounts are definitely smaller than those derivable from stoichiometric considerations.

In addition, the vapour pressure values measured by the torsion-effusion method depend on the diameter of the effusion holes in the cell used. In fact, with small orifices (≈0.3 mm in diameter), after the first few values measured in the very first step of the experiment were fitted to an approximate $\log p$ versus $1/T$ line, the pressure increases rapidly and follows a second line (see Fig. 1).

When a cell with large holes (≈3 mm in diameter) is used, the vapour

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TABLE 1

Weight loss (%) of $SeC(NH_2)_2$ vaporized from cells A, B, C, D which effusion holes 0.30, 1.01, 1.00, 2.32 mm in diameter respectively; cell E was open

Run	T (K)	Cell A	Cell B	Cell C	Cell D	Cell E
1	429	75	91	90	98	100
2	437	73	90	81 [a]	99	100

[a] This sample was in one large piece.

pressure points lie in a reproducible way on the first line as drawn in Fig. 1. Of course additionally in these pressure measurements, a residue of pure selenium was observed when the cell with small effusion holes was used.

At a fixed temperature, if the vapour pressure (p_t) is measured by the torsion method and the weight-loss rate of the sample (dm/dt) is measured simultaneously by a thermobalance coupled with the torsion assembly (see ref. 5), the molecular weight of the effusing vapour can be

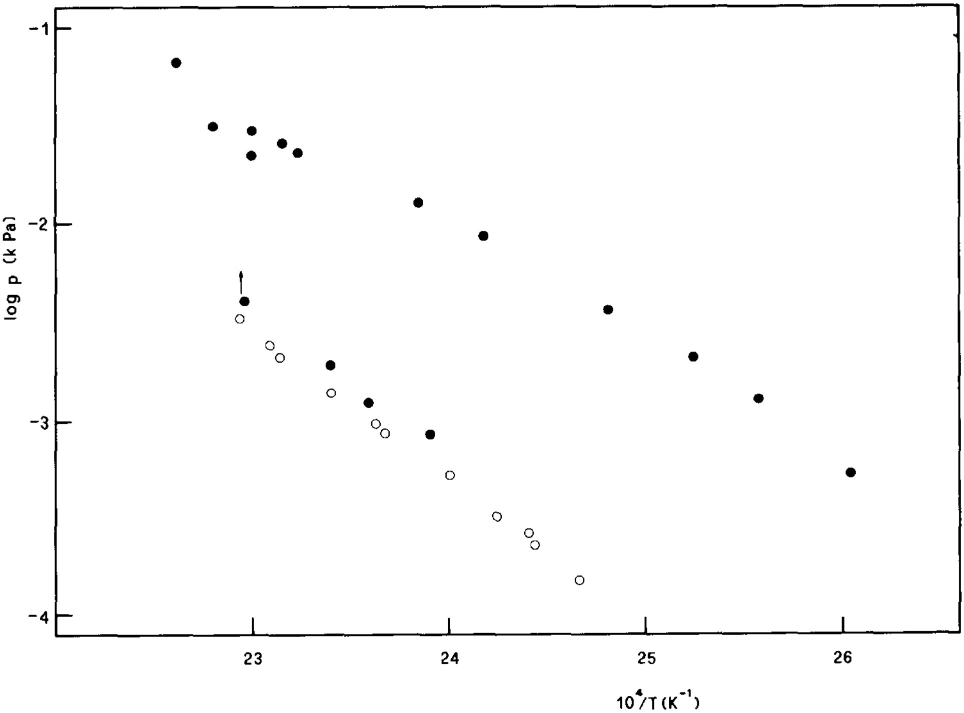

Fig. 1. Some vapour pressure values of selenourea measured using cells with different effusion holes: ○, 3.0 mm; ●, 0.3 mm in diameter.

calculated by the well-known Knudsen equation [4]

$$M = T[(\mathrm{d}m/\mathrm{d}t)(K_\mathrm{K}/p_\mathrm{t})]^2$$

where K_K is the Knudsen constant of the torsion cell used.

It is interesting to note that when the cell with large effusion holes was used (with which low vapour pressure values were measured and the sample vaporized completely), the molecular weight of the vapour is reproducible and equal to about 120 ± 5 m.u., very close to the molecular weight of selenourea (122). When the vaporization occurs from small effusion holes (high vapour pressure value and selenium residue), the molecular weight value is smaller, ranging from 40 to 60 m.u.

These observations suggest that in addition to the sublimation process, the surface of the compound also decomposes into pure selenium and an organic compound (with a molecular weight lower than that of selenourea). This surface decomposition could be governed by a kinetic process so that in the experiment carried out in cells with large effusion holes, the rate of sublimation necessary to maintain the vapour-condensed phase equilibrium is more important than the decomposition phenomenon. But when cells with small effusion holes are used, in addition to the sublimation, the partial decomposition of the sample surface also occurs, probably according to the reaction

$$\mathrm{SeC(NH_2)_2(s)} \rightarrow \mathrm{Se(s)} + \mathrm{H_2NCN(g)} + \mathrm{H_2(g)}$$

Considering the non-stoichiometric amount of selenium residue, some of the hydrogen probably reacts with selenium to give $\mathrm{SeH_2(g)}$ so that the vapour effusing from the cell with small effusion holes is a mixture of selenourea, cyanamide, hydrogen and selenium hydride, their relative amounts depending on different parameters such as the diameter of the effusion hole, the vaporization time, the temperature, and also the particle size of the sample; this last parameter was observed in the Knudsen experiment carried out in cells with equal effusion holes (see run 2 in Table 1) but using powder and one large piece of the sample in the cells C and B respectively.

The vapour pressure values measured using cells with large effusion holes are plotted as $\log p$ versus $1/T$ in Fig. 2: the data do not lie on a line but on a curve. At present we are not able to determine if this behaviour is due to the temperature dependence of the ΔC_p, to these vapour pressure points following a probable Antoine's equation, or to a small contribution of the surface decomposition to the vaporization process.

It is, however, interesting to compare the results obtained in the present experiments for selenourea with the vapour pressures of urea and thiourea (see Fig. 2) reported in the literature [1, 2]. The comparison shows an evident increase in the chemical stability of selenourea with respect to the other compounds.

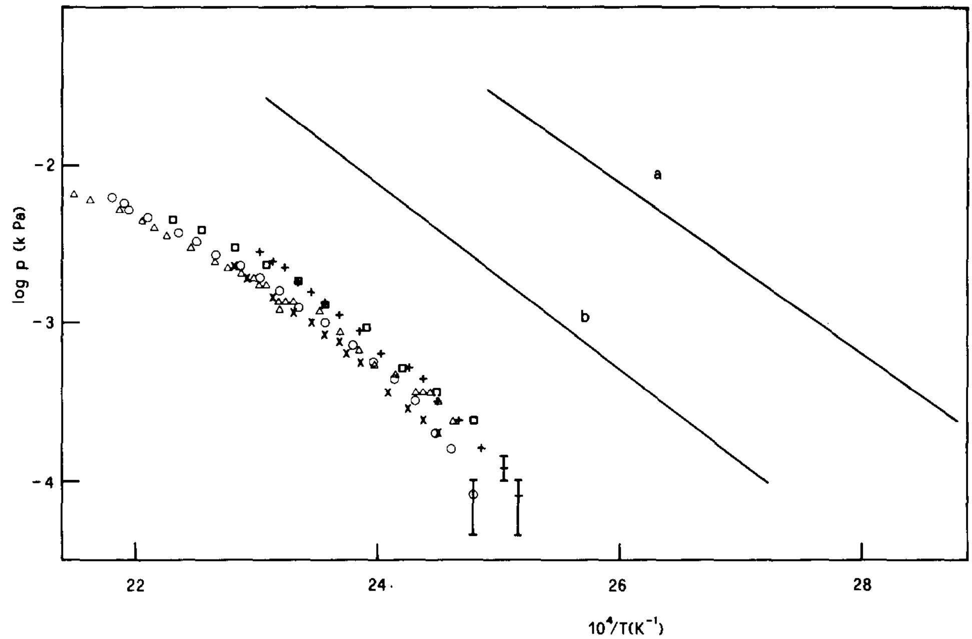

Fig. 2. Vapour pressure of selenourea compared with those of urea (a) [1], and thiourea (b) [2].

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