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Note

SUBLIMATION ENTHALPY OF MONO-BUTYLUREA

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As part of a program concerning the investigation of urea derivatives [1], the mono-butylurea (MBU) was studied because apparently no thermodynamic data are reported in literature.

The vapor pressure of this compound was measured by the torsion effusion technique. The method and assembly were described in detail in a previous work [2]. Three graphite cells with effusion holes of different diameters (0.5, 1.0 and 1.6 mm, cells A, B and C, respectively) were employed and the corresponding instrument constants were determined by vaporizing pure naphthalene as a standard. Naphthalene was used as its vapor pressure [3] is comparable with MBU.

The MBU used in this study was first-grade purity (> 98%) commercial product from Aldrich-Chemie and purified by crystallization from methylacetate solution.

The calorimetric analysis [4] of MBU showed two phase transitions: $\alpha \rightarrow \beta$ (315 K) $\Delta H^0_T = 7.00 \pm 0.14$ kJ mol^{-1}; and $\beta \rightarrow \gamma$ (346 K) $\Delta H^0_T = 0.87 \pm 0.06$ kJ mol^{-1}.

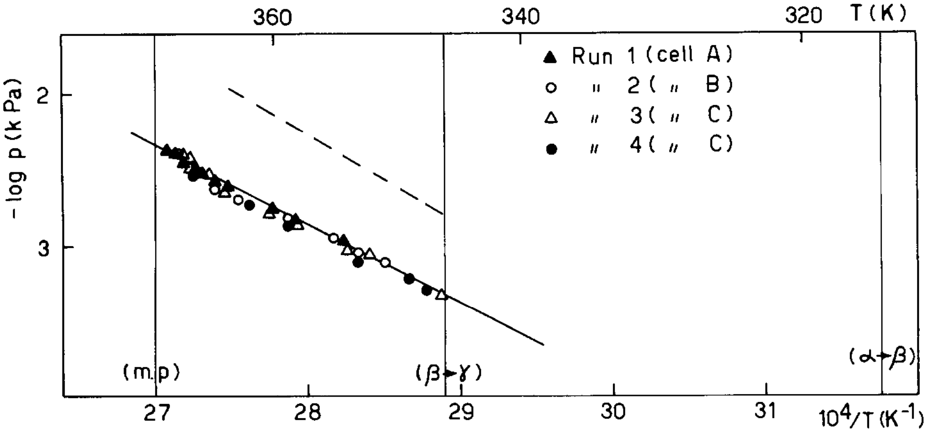

Fig. 1. Vapor pressure of MBU determined in the second stage of the sublimation process (dotted line refers to the first stage).

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In the first stage of vaporization of this compound, the vapor pressures fit reasonably well on a log p vs. $1/T$ line but as the vaporization proceeds further, the values are not reproducible and tend to decrease, fitting on a second line. In this second stage the vapour pressure values are decidedly more reproducible.

The X-ray analysis of the vapour opportunely condensed and the residues of both stages showed that MBU vaporizes congruently without decomposing. We believe, therefore, that the behaviour in the first vaporization stage is probably due to a strong metastability of the phases of the condensed system.

Figure 1 gives a rough sketch of the vaporization behavior in the first stage (dotted line) together with the vapor pressure values determined in the second stage in detail. Table 1 gives the pressure–temperature equations derived from the least squares treatment of the results of each experimental run. Weighing the slopes and intercepts proportionally to the number of experimental points, the following pressure–temperature equation was derived:

$$\log p(\text{kPa}) = 11.56 \pm 0.25 - (5160 \pm 100)/T \qquad (1)$$

where the errors were estimated considering the uncertainties on the temperature measurements and the instrument constant value. This equation is drawn as a continuous line in Fig. 1. The sublimation enthalpy $\Delta H^0_{358} = 99$

TABLE 1

Vapor pressure of mono-butylurea

Run	ΔT (K)	No. of points	$-\log p(\text{kPa}) = A - B/T$	
			A	B
1	354–369	10	11.88±0.35	5266±129
2	351–368	8	11.53±0.37	5151±142
3	346–369	10	11.55±0.40	5153±146
4	348–362	7	11.15±0.24	5027± 84

TABLE 2

Sublimation enthalpy and entropy changes of urea and its monoderivatives

Compound	$\bar{T}$ (K)	ΔH^0_T (kJ mol^{-1})	ΔS^0_T (J mol^{-1} K^{-1})
Urea	381	90.9±1.9	159.0±5.7
MMU	348	87.3±1.9	167.0±3.4
MEU	346	86.0±1.9	156.0±3.4
MPU	351	88.2±1.9	169.0±3.4
MBU	358	99 ±4	183 ±5

$\pm$ 4 kJ mol^{-1}, and $\Delta S^0_{358} = 183 \pm 5$ kJ mol^{-1} of γ-MBU were derived from the slope and intercept of eqn. (1).

By using the heats of the transition phases [4] and considering the heat capacities of the gaseous and condensed phases to be the standard sublimation enthalpy of α-MBU $\Delta H^0_{298} = 107$ kJ mol^{-1} was estimated. This value is surprisingly higher than those found for the compounds of the homologous series (see Table 2) in the previous work [1].

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