Thermochimica Acta, 224 (1993) 291–292
Elsevier Science Publishers B.V., Amsterdam

Note

ΔH–ΔS interplay in the fusion of thiourea and some alkyl-substituted thioureas

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(Received 23 December 1992; accepted 5 February 1993)

The relationship between the enthalpy and entropy changes derives from the specific coupling between the energy levels and their multiplicity. In solution chemistry, it can be used for identifying homologous (sensu latu) reaction series or for verifying homologies in the behaviour of established reaction series.

Compared with thiourea, its alkyl-substituted derivatives show lower melting temperatures and lower enthalpy changes.

Figure 1 shows a linear interdependence between the parameters ΔH and

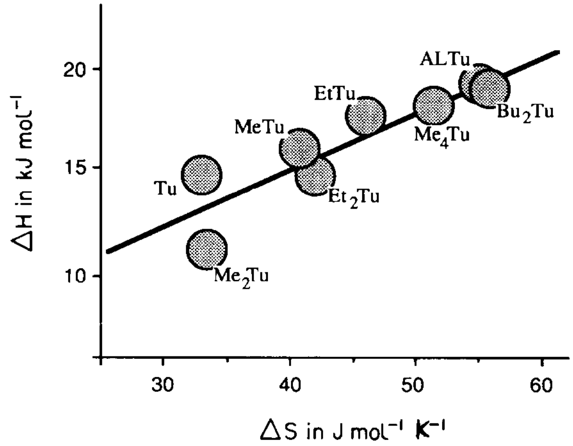

Fig. 1. The ΔH–ΔS relationship for the fusion of thiourea (Tu), *N*-methylthiourea (MeTu), *N,N'*-dimethylthiourea (Me_2Tu), *N,N,N',N'*-tetramethylthiourea (Me_4Tu), *N'*-ethylthiourea (EtTu), *N,N'*-diethylthiourea (Et_2Tu) and *N*-allylthiourea (ALTu): $\Delta H = 4.56(2.6) + 0.264(0.05)\Delta S$; $R = 0.901$. The standard deviations are reported in parentheses.

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$\Delta S = \Delta H / T$ for the fusion of thiourea and some related compounds, so that the following relationships hold

$$\Delta H\ /(\mathrm{kJ\ mol^{-1}}) = 4.56T/(T\text{-}264) \tag{1}$$

$$\Delta S\ /(\mathrm{kJ\ mol^{-1}\ K^{-1}}) = 17.29/(T\text{-}264) \tag{2}$$