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ENTHALPIES OF POLYMERISATION OF SbF_5, NbF_5 and TaF_5

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SUMMARY

The enthalpies of polymerisation of $SbF_{5(g)}$, $NbF_{5(g)}$ and $TaF_{5(g)}$ have been estimated from molecular weight data to be -18.5, -25.9 and -25.7 kJ mol^{-1} respectively assuming mixtures of monomer and tetramer. Estimates of the entropy changes have also been made.

INTRODUCTION

Several pentafluorides are known to be associated in the vapour phase as well as in the solid and liquid phases, and recently two of us were involved in vapour density measurements (Dumas method) with SbF_5, NbF_5, and TaF_5.[1] In this communication we use a simple model to estimate the enthalpies of polymerisation of these compounds from the earlier data.

RESULTS AND CALCULATIONS

The data given in Table 1 were obtained by replotting the results obtained by Fawcett et al. [1] and reading off the degrees of association from best fit curves. In the present model it is assumed that the monomeric pentafluoride is in equilibrium with either trimer or tetramer only. In the former case,

$$M \overset{k_3}{\rightleftharpoons} \tfrac{1}{3}M_3 \quad \text{and} \quad \frac{P_3^{\frac{1}{3}}}{P_1} = k_3$$

since $P_1 + P_3 = 1$, and $\alpha = \dfrac{P_1 + 3P_3}{P_1 + P_3}$

$$\text{we obtain } k_3 = \frac{[\frac{1}{2}(\alpha - 1)]^{\frac{1}{3}}}{[1 - \frac{1}{2}(\alpha - 1]}$$

TABLE 1

Degrees of Association of Pentafluorides

Temperature (C)	(K)	Compound		
		NbF_5	TaF_5	SbF_5
150	423			3.00
175	448			2.64
200	473			2.39
225	498			2.10
250	523	2.60	2.95	1.83
275	548	2.10	2.45	1.58
300	573	1.75	2.05	1.39
325	598	1.53	1.73	
350	623	1.32	1.48	
375	648	1.17	1.30	
400	673	1.10	1.20	

Similarly, in the case of tetramer only, we obtain

$$k_4 = \frac{[\frac{1}{3}(\alpha - 1)]^{\frac{1}{4}}}{[1 - \frac{1}{3}(\alpha - 1)]}$$

A plot of $\ell n\, k_3$ or $\ell n\, k_4$ against $^1/T$ should yield a straight line for the correct model, and the slope yields a value for the enthalpy of polymerisation. This model assumes that both ΔH and ΔS are constant over the temperature ranges of the investigation. Entropies of polymerisation are estimated from the equation $\Delta G = \Delta H - T\Delta S$, ΔG being obtained from the equilibrium constants.

Results are listed in Table 2. Our model suggests that these pentafluorides are composed mainly of tetramers and monomers at atmospheric pressure in the vapour state, though there is one point for TaF_5 (at the lowest temperature) which does not fit, either because of experimental error (it is difficult to get equilibrium conditions just above the boiling point) or the presence of higher oligomers. We note that under other conditions NbF_5, WF_5, and other pentafluorides have been shown to form trimers and tetramers, and that sometimes evidence for higher oligomers has been obtained [2-5]. So far as enthalpies of polymerisation are concerned, there are no literature values for our three compounds. For WF_5, values of -130.3 [7] and -26.2 kJ mol^{-1} [6,8] have been estimated by difference between the enthalpies of formation of the various species involved. For VF_5, which forms a polymeric liquid and a monomeric vapour, [9,10] a rough value of -16 kJ mol^{-1} may be estimated from the Trouton constants [11], and the related oxide tetrafluorides have values similarly calculated, ranging from -8.5 ($CrOF_4$) to -20.8 kJ mol^{-1} ($ReOF_4$) [12].

It is clear that further work remains to be done in this area of chemistry, both in respect of experimental data and of improved models for calculating the results. It would also be interesting to see whether measurements could be obtained for more reactive compounds such as RuF_5.

TABLE 2

Calculated Enthalpies (kJ mol^{-1}) and Entropies (J K^{-1}) of Polymerisation for SbF_5, NbF_5, and TaF_5

		ΔH	ΔS
SbF_5	Tetramer	-18.5	-35.5
NbF_5	Tetramer	-25.9	-44.8
TaF_5	Tetramer	-25.7	-43.4

REFERENCES

1 J. Fawcett, A. J. Hewitt, J. H. Holloway and M. A. Stephen, J. Chem. Soc. Dalton (1976) 2422.

2 J. Brunvoll, A. A. Ischenko, I. N. Miakshin, G. V. Romanov, V. B. Sokdov, V. P. Spiridonov and T. G. Strand, Acta Chem. Scand. A33 (1979) 775.

3 A. V. Gusarov, V. S. Pervov, I. S. Gotkis, L. I. Klyuev and V. D. Butskii, Dokl. Akad. Nauk. S.S.S.R., 216 (1974) 1296; English trans. p.445.

4 A. V. Gusarov, L. N. Gorokhov and I. S. Gotkis, Adv. Mass Spectrometr. 7A (1978) 666.

5 W. E. Falconer, G. R. Jones, W. A. Sunder, M. J. Vasile, A. A. Muenter, T. R. Dyke and W. Klemperer, J. Fluorine Chem. 4 (1974) 213.

6 G. Dittmer, A. Klopper, D. S. Ross and J. Schröder, J. Chem. Soc. Chem. Comm. (1973) 846.

7 D. L. Hildenbrand, J. Chem. Phys., 62 (1975) 3074.

8 G. Dittmer, A. Klopfer and J. Schröder, Phillips Res. Repts., 32 (1977) 341.

9 L. E. Trevorrow, J. Fischer and R. D. Steunenberg, J. Amer. Chem. Soc., 79 (1957) 5167.

10 H. H. Claassen and H. Selig, J. Chem. Phys., 44 (1966) 4039.

11 H. J. Emeléus and H. C. Clark, J. Chem. Soc., (1957) 2119.

12 R. D. Peacock, Adv. Fluorine Chem., 7 (1973) 134, 136.