ZIRCONIUM SULPHATE PENTAHYDRATE: THE β PHASE*

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The formation of a zirconium sulphate pentahydrate has recently been described,[1] and it has now been found that a second phase exists; we propose designating these two forms α and β. The pentahydrates were discovered in the course of our current work on anhydrous zirconium sulphate, which can be prepared either by thermal decomposition of zirconium sulphate tetrahydrate, or by fuming the tetrahydrate with concentrated sulphuric acid. Three anhydrous sulphates, each with a characteristic X-ray diffraction pattern, have so far been identified and they have been named the α, β, and γ phases.

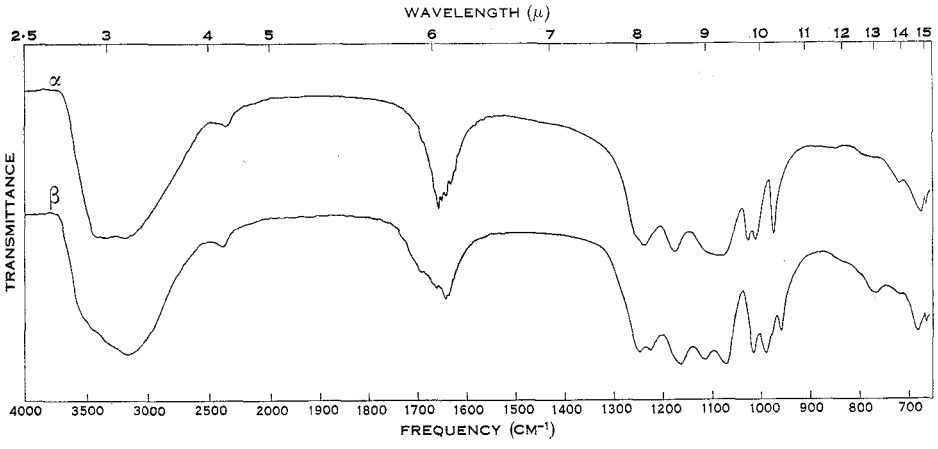

Fig. 1.—Infrared spectra of α-$Zr(SO_4)_2,5H_2O$ and β-$Zr(SO_4)_2,5H_2O$ recorded in Nujol and halocarbon mulls with a Perkin–Elmer 21 double beam prism spectrometer.

In a previous publication,[1] α-$Zr(SO_4)_2$ and its hydration to α-$Zr(SO_4)_2,5H_2O$ were described. The β-pentahydrate, which is metastable and eventually converts into $Zr(SO_4)_2,4H_2O$, is produced during the vapour phase hydration of either β- or γ-$Zr(SO_4)_2$.

The β and γ anhydrous sulphates were formed by heating well-washed, recrystallized tetrahydrate at 300–400° for 1 hr. Analyses consistently showed that the preparations had a slight deficiency of sulphate ion (about 0·03 mole)

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[1] Bear, I. J., *Aust. J. Chem.*, 1966, **19**, 357.

below the 1 : 2 mole ratio, in contrast to preparations of α-$Zr(SO_4)_2$ which always showed an excess of the same order. On exposure to air, the β- and γ-$Zr(SO_4)_2$ phases deliquesced and dissolved rapidly in their absorbed water. Provided the solution

TABLE 1

X-RAY DATA FOR β-$Zr(SO_4)_2$, γ-$Zr(SO_4)_2$, AND β-$Zr(SO_4)_2,5H_2O$

From Philips Geiger-counter diffractograms using Cu Kα radiation, recorded at 0·5°, 2θ per minute and chart speed 800 mm/hr

β-$Zr(SO_4)_2$		γ-$Zr(SO_4)_2$		β-$Zr(SO_4)_2,5H_2O$	
d (Å)	I/I_1	d (Å)	I/I_1	d (Å)	I/I_1
8·17	9	5·94	14	8·48(2)	31
		4·78	13	7·51(9)	96
5·82	12	4·61	9	7·50(0)	59
		4·16	4	6·63(2)	17
		4·02	4	6·09(5)	13
4·77	100	3·63	100	5·90(5)	11
4·60	8	3·52	3	5·67(2)	48
4·46	4	3·38	7	5·53(1)	35
		3·29	4	5·34(5)	7
4·15	20	3·01	2	5·22(9)	38
4·03–3·99	25	2·93	10	4·83(3)	95
		2·92	12	4·60(0)–4·59(7)	19
3·70	27	2·66	25	4·41(8)	73
3·67	18	2·49	20	4·229	75
3·62	24	2·14	12	4·003	12
		1·98	8	3·948	14
3·52	8	1·82	21	3·641	100
3·38–3·35	27	1·67	20	3·381	27
3·31	8			3·112	13
3·22	10			3·009	44
3·10	3			2·950	31
3·02	6			2·822	54
2·93	56			2·699–2·682	30
2·91	77			2·657	7
				2·604	12
2·76	20			2·593	20
2·72	18			2·540	12
				2·519	15
2·62	6			2·487	11
				2·436–2·415	39
				2·393	30
2·50	17			2·117	27
2·47	17				
2·38	11				

did not become too dilute and provided that a relative humidity below about 60% (i.e. below the saturated solution vapour pressure) was maintained, the β-pentahydrate crystallized out after hydration had continued for 3–4 hr.

After washing with concentrated nitric acid and drying under vacuum, samples of the β-pentahydrate had a composition in the range ZrO_2; $2 \cdot 0\ SO_3$; $5 \cdot 0 \pm 0 \cdot 1\ H_2O$. The two pentahydrates are distinguished by differences in the vapour pressures of their saturated solutions, in their crystalline habit and X-ray diffraction patterns, and in their infrared spectra. The β-form separates as tabular crystals which grow to an appreciable size ($> 0 \cdot 05$ mm) under suitable conditions of hydration, and its X-ray diffraction pattern is given, together with the patterns of β- and γ-$Zr(SO_4)_2$, in Table 1; data for the α-forms were reported previously.[1] Differences in the positions and splittings of the principal bands in the infrared spectra of the two phases can be seen in Figure 1. The vapour pressures of saturated solutions of the α- and β-pentahydrates at 25° are respectively $16 \cdot 7 \pm 0 \cdot 1$ mm and $15 \cdot 2 \pm 0 \cdot 1$ mm.