

## MOLTEN LITHIUM SULPHATE–SODIUM SULPHATE–POTASSIUM SULPHATE EUTECTIC. THE REACTIONS OF SIX VANADIUM COMPOUNDS

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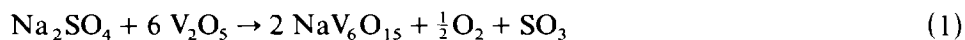
### ABSTRACT

The solubilities and thermal stability of six vanadium compounds of oxidation states V, IV and III [i.e.,  $V_2O_5$ ,  $NaVO_3$ ,  $Na_3VO_4$ ,  $VOSO_4$ ,  $VO_2$  and  $KV(SO_4)_2$ ] have been studied in the ternary eutectic (78 mole %  $Li_2SO_4$ , 8.5 mole %  $Na_2SO_4$ , 13.5 mole %  $K_2SO_4$ ) and the products of their reactions with basic, acidic, oxidising and reducing reagents have been identified.

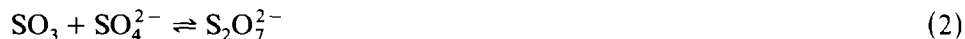
### INTRODUCTION

Vanadium solutions in molten sulphates are the basis of all the catalysts used in sulphuric acid manufacture by aerial oxidation of sulphur dioxide. Despite this importance there has been no systematic study of vanadium chemistry in these melts, though Johnson and Laitinen [1] have reported that vanadium pentoxide dissolved in lithium sulphate–sodium sulphate–potassium sulphate eutectic at 550°C to give a brown solution which could be reduced to insoluble vanadium dioxide by addition of magnesium or thallium. Conversely, in a potassium sulphate–zinc sulphate melt at 600°C, Duffy and Macdonald [2] found that vanadium(III) was quickly oxidised to vanadium(IV) but more slowly to vanadium(V).

Several phase diagram studies of vanadium pentoxide with alkali metal sulphates have also been reported, though on heating such mixtures the first reaction occurs in the solid state when oxygen is released and the vanadium is partially reduced [3]. A typical reaction would be



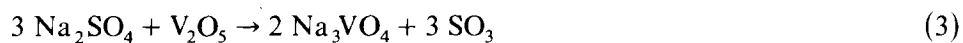
though the sulphur trioxide remains absorbed, possibly as pyrosulphate if excess sulphate is present



The solid product of eqn. (1), termed a ‘vanadium bronze’, differs from

vanadium pentoxide in having a more open structure of "tunnels" in which the alkali metal cations are located [4].

All the alkali metal sulphate–vanadium pentoxide phase diagrams were found to be of the eutectic type (e.g., the minimum melting point was 630°C with 12.1 mole % Na<sub>2</sub>SO<sub>4</sub> [5], and 455°C with 55 mole % K<sub>2</sub>SO<sub>4</sub> [6]) and on melting the bronzes reabsorb oxygen from the air (a process which is reversed again on solidification). On further heating sulphur trioxide is lost and vanadates are formed stepwise, ultimately giving *ortho*-vanadate after prolonged heating at 1300°C [3,7].



These studies naturally have not been focussed on the chemistry of the molten sulphate system and thus the comparative studies reported here were undertaken.

## EXPERIMENTAL

### Materials

The ternary eutectic, sodium carbonate and potassium pyrosulphate were prepared as previously reported [8]. Vanadium pentoxide and sodium *meta*-vanadate (reagent grades) were dried for 2 h at 110°C and analysed (found: V, 55.5 and 41.0; calcd. for V<sub>2</sub>O<sub>5</sub> and NaVO<sub>3</sub>: V, 56.0 and 41.8%, respectively). Hydrated sodium *ortho*-vanadate, reagent grade, was heated at 250°C for 2 h (found: V, 27.8; calcd. for Na<sub>3</sub>VO<sub>4</sub>: V, 27.7%). Oxovanadium(IV) sulphate (found: V, 31.8; SO<sub>4</sub>, 58.8; calcd. for VOSO<sub>4</sub>: V, 31.3; SO<sub>4</sub>, 58.9%) and potassium vanadium(III) sulphate (found: V, 17.9; calcd. for KV(SO<sub>4</sub>)<sub>2</sub>: V, 18.1%) were prepared by the methods of Sieverts and Muller [9]. Vanadium dioxide was made by Tandy's method [10] (found: V, 61.3; calcd. for VO<sub>2</sub>, 61.4%).

### Procedure

Reactions were carried out as described earlier [8] and the products identified by standard qualitative and quantitative methods. Vanadium(IV) was determined by titration with standard permanganate solution using ferroin as indicator where necessary, and total vanadium by the same method after reducing all vanadium with sulphur dioxide. Vanadium(V) was also titrated with standard iron(II) solution using diphenylamine as indicator.

Solubilities were determined by analysing samples taken from saturated solutions containing excess solid solute, by suction into glass tubes equipped with glass wool filter plugs at their lower ends. Thermogravimetric analysis

was carried out on a Stanton TR-1 thermobalance using 10 ml silica crucibles and a heating rate of  $2^{\circ}\text{C min}^{-1}$ . Weight changes, the average of three or more determinations, are reported as a percentage of the weight of the initial reactant, or as grams per mole of initial reactant where this is more helpful in interpretation of reaction stoichiometries.

## RESULTS AND DISCUSSION

### *Vanadium(V) reactants*

Mixtures of vanadium pentoxide and powdered solid ternary sulphate eutectic when heated in air were observed to become slightly greenish in colour near  $500^{\circ}\text{C}$  before melting at  $512^{\circ}\text{C}$ . After fusion the solutions were yellow-brown when dilute but became reddish-brown as more vanadium dissolved. Analysis of samples held at  $580^{\circ}\text{C}$  showed some reduction to vanadium(IV) which diminished slowly with time (Fig. 1) and an almost equally slow approach to equilibrium solubility ( $0.049 \pm 0.001$  m at  $580^{\circ}\text{C}$ ).

However, when vanadium pentoxide was dropped onto eutectic held at  $580^{\circ}\text{C}$  it initially turned red (the colour of  $\text{V}_2\text{O}_5$  at this temperature) and then dissolved (an amount of  $\text{V}_2\text{O}_5$  equivalent to 0.030 m dissolving in 10 min). The latter solution contained less than 1% vanadium(IV) and was stable at  $580^{\circ}\text{C}$ , though after heating at  $610^{\circ}\text{C}$  for several days sulphur trioxide was slowly evolved and *meta*-vanadate was present in the melt. Thermogravimetric analysis (Fig. 2) of a more concentrated (0.5 m) solution showed the main weight loss to occur above  $670^{\circ}\text{C}$  though small bubbles of sulphur trioxide were observed to be trapped in the quite viscous melt at  $600^{\circ}\text{C}$ . The overall weight loss to  $840^{\circ}\text{C}$  when some *meta*-vanadate was

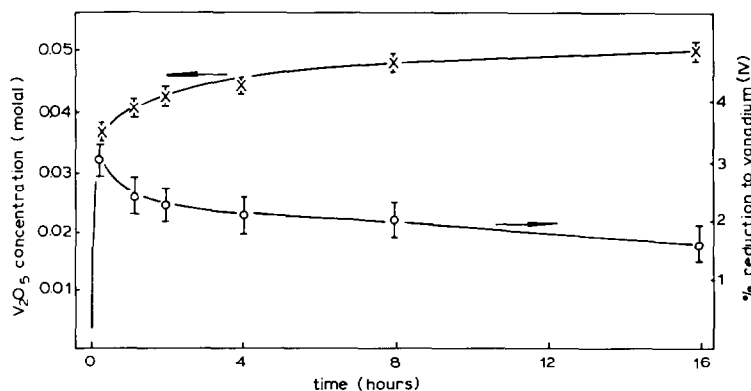


Fig. 1. Solubility and percentage reduction of vanadium pentoxide in ternary sulphate eutectic (initially containing the equivalent of 0.060 m  $\text{V}_2\text{O}_5$ ) as a function of time at  $580^{\circ}\text{C}$ .

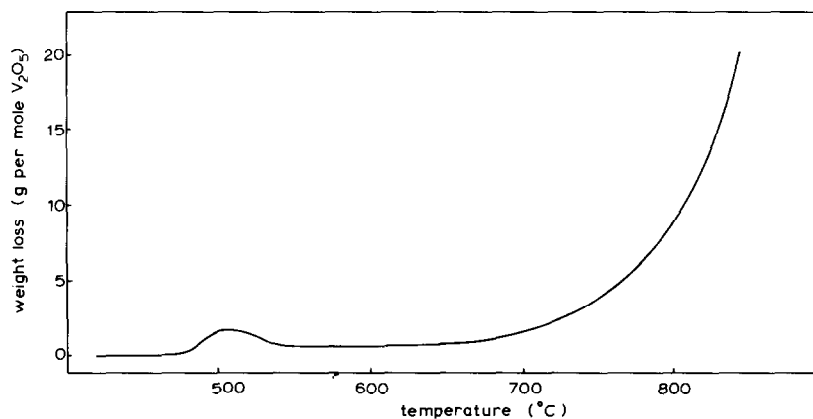


Fig. 2. Thermogravimetric analysis of vanadium pentoxide (1 mmole) in ternary sulphate eutectic (2 g).

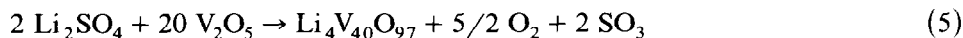
present was 9.9%, only some 22% of that expected for the reaction



(calcd. weight loss 44.0%)

which was shown by Fotiev [3] to be the eventual reaction up to 900°C.

The small initial weight loss (0.8%) beginning at 470°C and followed by a nearly equivalent weight gain above the fusion temperature may be correlated with the known formation of vanadium bronzes in the solid state ( $\text{Li}_4\text{V}_{40}\text{O}_{97}$  forms from  $\text{Li}_2\text{O}$  and  $\text{V}_2\text{O}_5$  at 480°C [11],  $\text{NaV}_6\text{O}_{15}$  at 526°C [5,7],  $\text{K}_5\text{V}_{20}\text{O}_{52}$  [3], etc.), though the expected weight losses suggests that reaction may be incomplete, e.g.



(calcd. for loss of  $1/8 \text{O}_2 + 1/10 \text{SO}_3$  per  $\text{V}_2\text{O}_5$  6.6%; calcd. for loss of  $1/8 \text{O}_2$  per  $\text{V}_2\text{O}_5$  2.2%.)

even if the sulphur trioxide was absorbed and not evolved [cf. eqn. (2)]. Bronze formation appeared to cease on melting, when some vanadium(IV) could dissolve giving the observed green colour, though the majority of the bronze reoxidised, largely when a high surface area was exposed, since the solubility of oxygen in sulphate melt is known to be very low [12]. The slow reoxidation of residual vanadium(IV) (Fig. 1) supports this and might also explain the very slow approach to equilibrium solubility if the bronze was much less readily soluble than vanadium pentoxide itself.

Sodium *meta*-vanadate added directly to sulphate eutectic dissolved to give a pale yellow solution when dilute but a more reddish-brown when concentrated [analysis showed < 1% V(IV)]. At 580°C the solubility was  $0.157 \pm 0.001$  m, and the excess solute melted to form to a dark viscous

immiscible lower layer. These solutions were stable showing no weight loss on the thermobalance to 900°C. Sodium *ortho*-vanadate dissolved to form colourless solutions at 580°C which were also stable.

Acidic reactions of vanadium pentoxide [e.g., eqn. (4)] were found to occur at much lower temperatures in the presence of sodium carbonate, a Lux-Flood base. A brisk reaction took place at 580°C, carbon dioxide being evolved, and the solution became colourless when dissolved *ortho*-vanadate was detected. (The yellow-brown colour was reformed on addition of excess potassium pyrosulphate to this solution or when it was added to solutions of *meta*- or *ortho*-vanadate.) Quantitatively the reaction began at 450°C (Fig. 3), reacted a maximum rate at 470°C when some melting or sintering was apparent and ended at 500°C when complete melting had occurred. No further weight loss was observed except when high ratios of carbonate were used (Fig. 3, curve D). A sulphate melt containing only sodium carbonate lost weight at a similar slow rate (Fig. 3, curve E, 3.8% weight loss at 700°C), in both cases due to attack on the surface of the silica crucible which was visibly heavily etched, though the reaction



was evidently incomplete (calcd. weight loss of CO<sub>2</sub> per Na<sub>2</sub>CO<sub>3</sub> 41.5%). The other weight losses were completely in accordance with the formation of *ortho*-, *pyro*- and *meta*-vanadates (Fig. 3). Only when carbonate was present in excess of the ratio required to form *ortho*-vanadate (Fig. 3, curve D) was there unreacted carbonate at 500°C which slowly decomposed with increasing temperature as when carbonate was the sole solute (Fig. 3, curve E). These reactions were considerably facilitated when sulphate was present, as

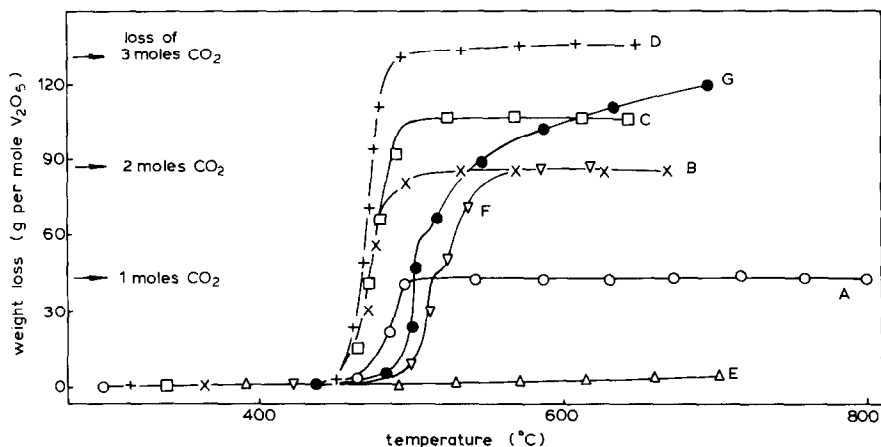


Fig. 3. Thermogravimetric analysis of sodium carbonate and vanadium pentoxide. Reactant compositions, in mmoles of Na<sub>2</sub>CO<sub>3</sub>: V<sub>2</sub>O<sub>5</sub>, were: curve A, 1:1; curve B, 2:1; curve C, 2.5:1; curve D, 4:1; curve F, 2:1; and curve G, 3:1 respectively. Curve E is of Na<sub>2</sub>CO<sub>3</sub> alone. Curves A–E in 2 g ternary sulphate eutectic. Curves F and G without eutectic.

can be seen by comparison with the reactants heated without eutectic (cf. curves B and F, also curves D and G of Fig. 3); this is likely to be due in part to the presence of some liquid phase since the melting point of the sulphate eutectic is most probably lowered by the presence of vanadium pentoxide, sodium carbonate and their reaction products. The presence of potassium may also be helpful since Fotiev [3] has reported that reaction temperatures with vanadium pentoxide decrease with increasing size of alkali metal cation. For example, the temperature of maximum rate of removal of carbon dioxide from 1 : 1 mole ratios were 580, 520 and 400°C for lithium, sodium and potassium carbonates, respectively, which correlate with 465°C (curve A) and 510°C (curve F) when sulphate eutectic was and was not present respectively, and suggest that even the small ratio of potassium present in the ternary eutectic could be effective.

#### *Vanadium(IV) reactants*

Oxovanadium(IV) sulphate dissolved quickly in the ternary eutectic at 580°C to form a turquoise solution, the solubility being  $0.470 \pm 0.001$  m. In air the solution was slowly oxidised to soluble yellow-brown vanadium(V) species. For example, though immediately after solution only  $0.7 \pm 0.5\%$  vanadium(V) was present, a 0.03 m solution was completely oxidised in 36 h at 580°C, sulphur trioxide being evolved and the pyrex tube being heavily etched especially at the air-melt interface. Under nitrogen the solution was much more stable though some vanadium(V) was present after 8 days.

Thermogravimetry also showed the reaction to proceed slowly in air

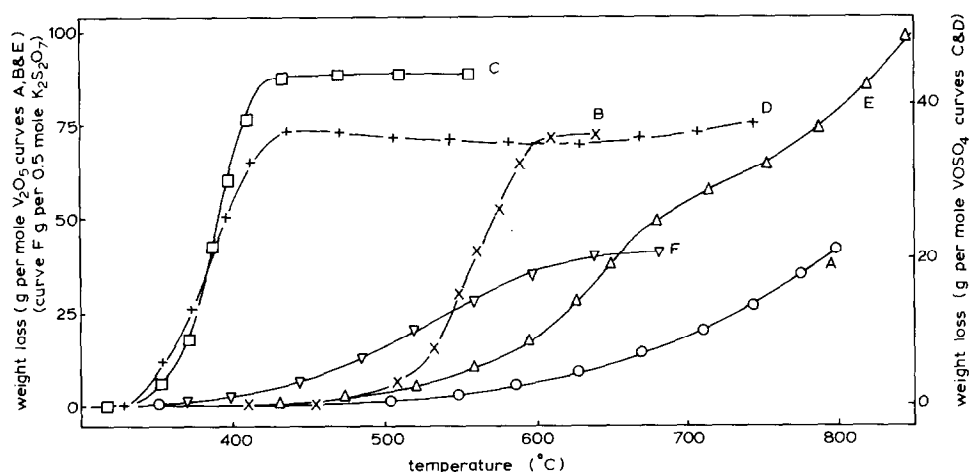


Fig. 4. Thermogravimetric analysis of oxovanadium(IV) sulphate in ternary sulphate eutectic (2 g) in air (except for curve C in nitrogen). Curve B, without eutectic. Reactant compositions: 2 mmoles  $VOSO_4$ , curves A, B, C, D and E; 2 mmoles  $Na_2CO_3$ , curves C and D; 1 mmole  $K_2S_2O_7$ , curves E and F.

(Fig. 4, curve A) and not to have reached equilibrium at 800°C where the weight loss was approximately half that obtained for oxovanadium(IV) sulphate heated alone. Without sulphate eutectic, under either air or nitrogen, decomposition again began at 450°C but proceeded much more rapidly (Fig. 4, curve B). The weight loss at equilibrium (43.8%) was close to that expected, i.e.



(calcd. weight loss 44.2%)

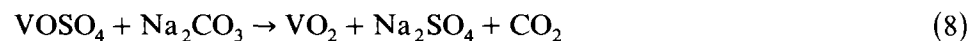
The solid product was confirmed by analysis (found: V, 55.9%; calcd. for  $\text{V}_2\text{O}_5$ ; V, 56.1%) and had also been obtained by the thermal decomposition of hydrated oxovanadium(IV) sulphates [13].

The considerable stabilisation of oxovanadium(IV) sulphate in molten sulphate solution is similar to that generally found with transition metal cations [14] and is considered to be largely caused by solvation to form a (probably) anionic complex. A further point is that sulphate anions have a lower Lux-Flood basicity (and hence lower reactivity) in the presence of alkali metal cations, and sulphate would also tend to combine with the sulphur trioxide formed, thus facilitating the back reaction of pyrosulphate and transition metal oxide.

In view of the considerably slower oxidation under nitrogen it is thought that reaction in melt is largely with oxygen, and the low solubility of the latter [12] would then be the cause of the relatively slow reaction under an air atmosphere. The ultimate reduction product of oxygen is presumed to be oxide which caused the etching of the pyrex tube and thus most heavily at the air interface.

Addition of sodium carbonate to a turquoise solution of oxovanadium(IV) sulphate at 580°C caused an immediate evolution of carbon dioxide and formation of a blue-black precipitate which could be redissolved by addition of excess potassium pyrosulphate, the turquoise solution being reformed. The precipitate isolated after quenching, by extracting the melt with water and drying, was shown to be vanadium(IV) oxide by analysis (found: V, 61.0%; calcd. for  $\text{VO}_2$ ; V, 61.4%) and by X-ray diffraction [ $d$  values 3.21(100), 2.66(35) and 2.41(50); ASTM Index for  $\text{VO}_2$  3.20(100), 2.68(30) and 2.43(60)].

Thermogravimetry showed this reaction to begin in the solid state at 330°C (Fig. 4, curve C) with a weight loss under nitrogen of 44.0 g mole<sup>-1</sup>  $\text{VOSO}_4$  corresponding to the Lux-Flood acid-base reaction



(calcd. weight loss 44.0 g mole<sup>-1</sup>  $\text{VOSO}_4$ )

However, under air a weight gain became evident at 440°C (Fig. 4, curve D), when the mixture was still a powdered solid which oxygen could readily

permeate, giving an overall weight loss to 600°C of 35.5 g mole<sup>-1</sup> VOSO<sub>4</sub>. An additional oxidation



(calcd. weight gain 8 g mole<sup>-1</sup> VO<sub>2</sub>)

is considered to have occurred giving an overall weight loss [i.e., eqn. (8) plus (9)] of 36.0 g mole<sup>-1</sup> VOSO<sub>4</sub>. The further weight loss above 670°C was attributed to the slow acidic reaction of the vanadium pentoxide thus formed with the sulphate melt as had already been observed (Fig. 2).

When vanadium(IV) oxide was added directly to a sulphate melt in air at 550°C it was found to be insoluble and unreactive in the short term. However, over several days it oxidised and dissolved slowly forming a brown solution of vanadium(V) without evolution of sulphur oxides or etching of the tube. This slow reaction (as compared to Fig. 4, curve D) is also attributed to eqn. (9), with the great difference in rate again being caused by the low solubility of oxygen in molten sulphate.

Addition of potassium pyrosulphate to a vanadium(IV) oxide suspension caused it to dissolve to form a turquoise vanadium(IV) solution, i.e.



Any excess pyrosulphate, or pyrosulphate added directly to oxovanadium(IV) sulphate solutions, decomposed slowly, particularly below 600°C (Fig. 4, curve E). Moreover, the rate was much less than that of pyrosulphate heated alone (Fig. 4, curve F), suggesting that the latter is stabilised by some interaction with vanadium(IV) species, as also occurs by interaction with vanadium(V) species [15].

#### *Lower oxidation state reactants*

Potassium vanadium(III) sulphate dissolved in sulphate eutectic at 580°C to give a blue solution, which was unstable and oxidised under an air atmosphere to a turquoise vanadium(IV) solution within 30 min. A similar blue solution was obtained by adding powdered zinc and potassium pyrosulphate to a brown vanadium pentoxide solution. But when these reactants were added to oxovanadium(IV) sulphate solution much gas was evolved and the turquoise solution became a pale lilac colour, which was equally easily oxidised. A lower oxidation state of vanadium may have been formed. Vanadium(II) is lilac coloured in acidic aqueous solutions.

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