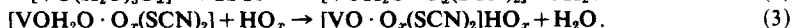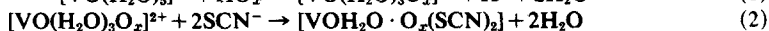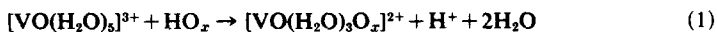assumed to exist mainly as VO^{3+} in a six coordinated state[8]. The following reactions explain the probable mechanism of formation of the final extracting species. (HO_x represents oxine)

$$[VO(H_2O)_5]^{3+} + HO_x \rightarrow [VO(H_2O)_3O_x]^{2+} + H^+ + 2H_2O \qquad (1)$$
$$[VO(H_2O)_3O_x]^{2+} + 2SCN^- \rightarrow [VOH_2O \cdot O_x(SCN)_2] + 2H_2O \qquad (2)$$
$$[VOH_2O \cdot O_x(SCN)_2] + HO_x \rightarrow [VO \cdot O_x(SCN)_2]HO_x + H_2O. \qquad (3)$$

In Reaction (3) a further oxine molecule adds. This adduct may also coordinate with vanadium(V) in the sixth position replacing the last water molecule as a monodentate ligand as believed by Freiser *et al.*[9]. In the presence of oxine and thiocyanate a single extraction recovers vanadium quantitatively since it is rendered hydrophobic as shown in the equations. This explains the synergic effect, although it is not very marked.

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8. Dyrssen D, and T. Sekine, *J. inorg. nucl. Chem.* **26**, 981 (1964).
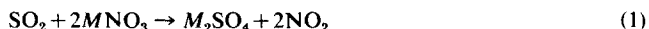9. Fa. Chunchou, Q. Fernando and H. Freiser. *Analyt. Chem.* **37**, 361 (1965).

Reactions between acidic gases and molten alkali metal hydroxides

REACTIONS between acidic gases and molten salts[1] showed that $SO_2(g)$ and molten nitrates react in the following manner,

$$SO_2 + 2MNO_3 \rightarrow M_2SO_4 + 2NO_2 \qquad (1)$$

where M is Na^+ or K^+. This reaction is extremely rapid at temperatures greater than 350°C. As part of a continuing program we investigated the reaction between NO_2 or SO_2 and alkali metal hydroxide melts.

Pure hydroxide melts were fused in a zirconium crucible, in a dry argon (CO_2 free) atmosphere. The crucible plus solid hydroxide were placed on a bed of sand at the bottom of a glass reaction vessel. A close fitting transite cap with three holes in it was used to cover the top of the reaction vessel. The system was continuously flushed through one hole with argon even before the hydroxide was melted. A nickel tube which could be lowered in and out of the melt was placed in the center hole. Through this tube, NO_2–argon mixture or SO_2 were passed through the melt. The flow rate of the reactive gases was monitored by using a flow system described elsewhere[2]. The effluent gases were led out of the reaction vessel through the third outlet, which was connected to a vacuum rack. As a pressure

1. T. R. Kozlowski, R. F. Bartholomew and H. M. Garfinkel, *J. inorg. nucl. Chem.* **32**, 401 (1970).
2. R. F. Bartholomew and D. W. Donnigan, *J. phys. Chem.* **72**, 3545 (1968).

slightly greater than atmospheric was maintained in the system at all times, the rack was left open to the atmosphere most of the time. Samples of the effluent gases were taken from time to time and analysed by using a mass spectrophotometer. The temperature of the reaction vessel was controlled to $\pm 1°C$.

The reaction between NO_2 and hydroxide was very rapid as shown by the lack of brown coloration in the effluent gases when NO_2 was passed through molten KOH at 440°C. A considerable quantity of water vapor condensed on the cooler parts of the vacuum rack. After the gas had been passed through the melt for 2 hr, the effluent gases suddenly indicated copious quantities of NO_2 by their brown color. An aqueous solution of the immediately quenched melt gave a pH of about seven suggesting that all the hydroxide had reacted. In this particular run the flow rate of the NO_2–Argon mixture was 130 cm³ min⁻¹ at room temperature, and the partial pressure of the NO_2 was 0·94 atm so that 8×10^{-3} moles of NO_2 entered the melt each minute. Thus, 0·96 moles of NO_2 were required to react completely with the 50 g melt (0·9 moles) of KOH. The products in the melt after completion of the reaction were identified by i.r. analysis (KBr technique) to be nitrite and nitrate as shown in Fig. 1(a). These facts can be explained by the equation:

$$2NO_2 + 2KOH \rightarrow KNO_2 + KNO_3 + H_2O. \tag{2}$$
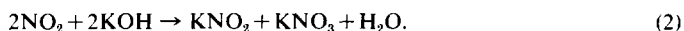
This predicts one mole of NO_2 reacts with one mole of KOH. The above calculation indicated more NO_2 reacted than accounted for by Equation (2). The extra NO_2 consumed can be accounted for by the side Reaction[3]

$$NO_2 + KNO_2 \rightarrow KNO_3 + NO. \tag{3}$$

This reaction predicts NO in the gas byproducts. If NO were produced in large quantities, then as soon as the gas came in contact with the air, brown fumes of NO_2 should be visible; no such brown fumes were seen. Additional evidence for the fact that most of the nitrite does not react according to Reaction (3) is given in Fig. 1(a). Here the i.r. spectrum of the quenched melt after complete reaction
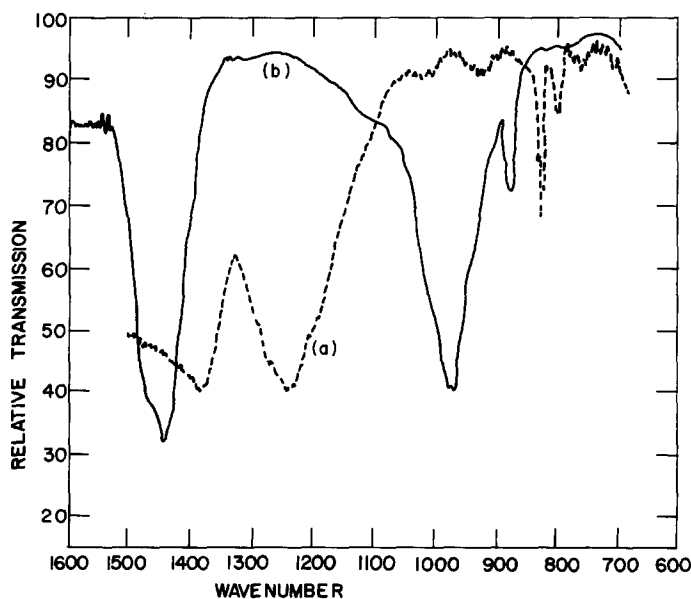

Fig. 1. (a). I.R. spectrum of the quenched melt after passing NO_2 through molten KOH at 440°C: (b). I.R. spectrum of the quenched melt after passing SO_2 for 20 min through molten NaOH at 380°C.

3. L. E. Topol, R. A. Osteryoung and J. H. Christie, *J. phys. Chem.* **70**, 2857 (1966).

shows the presence of KNO_3 (828, 1380 cm^{-1}) and KNO_2 (805, 1245 cm^{-1}). The spectrum indicates approximately similar amounts of the two compounds. However, some side reactions involving NO_2 must have taken place to account for the greater amount of NO_2 consumed during the reaction compared with that required by Equation (2). The presence of water in the gaseous products was confirmed by mass spectrographic analysis.

The reaction between SO_2 and molten alkali metal hydroxide is also rapid. The overall reaction in molten hydroxide can be described by:

$$SO_2 + 2MOH \rightarrow M_2SO_3 + H_2O. \tag{4}$$

The presence of sulphite was demonstrated by qualitative chemical tests, as well as by i.r. analysis of the quenched melt (see Fig. 1b). The very strong peak at 965 cm^{-1} arises from sulphite[4], and is present in samples only one minute after bubbling of SO_2 had been started. The bands at 1440 cm^{-1} and 880 cm^{-1} arise from carbonate present in the hydroxide melt. These bands were present in the NaOH taken from the bottle, and despite very careful handling, even in a dry box, they were always present. However, it should be noticed in Fig. 1(a) that there is no evidence for the presence of carbonate. This suggests that NO_2 will replace CO_2 in a hydroxide melt. The absence of a band at 1110 cm^{-1} rules out sulphate as a product, and other sulphur containing sodium salts can also be ruled out on the grounds that their strong bands were not present in this spectrum.

The rapid reaction between NO_2 and molten hydroxides led us to investigate the reaction between SO_2 and nitrate–hydroxide melts. In the absence of hydroxide, NO_2 is evolved as described by Equation (1). An equimolar NaNO$_3$–NaOH melt was used to determine the efficiency of reacting with SO_2 in a gas stream without production of NO_2. At 400°C no brown fumes were observed above such a melt until sufficient sulphate had been produced to cause the mixture to freeze. Moreover, the i.r. spectrum of a quenched sample showed NO_2^- and SO_4^{2-} to be present. These facts suggest the overall reaction is given by:

$$SO_2 + MNO_3 + 2MOH \rightarrow M_2SO_4 + MNO_2 + H_2O.$$
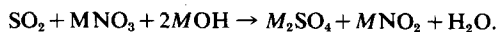
This reaction could result from Reaction (1) followed by Reaction (2), or by Reaction (4) followed by the reaction between sulphite and nitrate, which has been described elsewhere[1]. There are several possible side reactions which can take place in such a melt; most of them involve the oxidation of the nitrite produced. However, the fact that no brown fumes of NO_2 were observed above the melt suggests that these reactions are not taking place to any appreciable extent. Additional work is needed to elucidate the exact mechanisms involved.

The recent interest in methods of removal of toxic gases from flue stacks has resulted in the proposal of many schemes including the use of molten carbonates for pollution control. The rapid reactions discussed in this paper with water as the only gaseous product suggest that molten hydroxides could be used for the removal of SO_2 from flue gases.

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4. F. A. Miller and C. H. Wilkins, *Analyt. Chem.* **24**, 1253 (1952).

Mercury(II) bridged intermediates in the catalyzed aquation of dichloro complexes of cobalt(III)

RECENT synthesis of various new quadridentate ligands has resulted in the preparation and isolation of