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Calorimetric and conductometric investigations of the systems $K_2S_2O_7$–V_2O_5 and $K_2S_2O_7$–K_2SO_4–V_2O_5 in the range 390–500°C

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Abstract

The systems $K_2S_2O_7$–V_2O_5 and $K_2S_2O_7$–K_2SO_4–V_2O_5 are important for the catalytic oxidation of SO_2 to SO_3. The enthalpies of mixing of solid V_2O_5 and liquid $K_2S_2O_7$ have been measured in the whole liquidus range, i.e. up to a mole fraction of around $X_{V_2O_5} = 0.5$, at 400 and 450°C. The enthalpy of liquid–liquid mixing could then be calculated and ΔH_{mix} was found to be strongly exothermic, the partial enthalpy at infinite dilution in $K_2S_2O_7$, $\Delta\bar{H}^{\infty}_{V_2O_5}$, being -85.0 kJ mol^{-1} at 450°C. The local minimum for ΔH_{mix} found at $X_{V_2O_5} = 0.33$ indicates the formation of a dimeric complex $(VO_2)_2(SO_4)_2S_2O_7^{4-}$ (or possibly formulated as $(VO)_2O(SO_4)_4^{4-}$) over the whole temperature range 400–450°C. However, lowering the temperature in this range apparently increases the formation of polymeric complexes such as $(VO_2SO_4)_n^{n-}$. The enthalpy of liquid–liquid mixing at 400 and 450°C has also been obtained for K_2SO_4 as well as for the three cross-sections $K_2S_2O_7 \cdot V_2O_5$, $2K_2S_2O_7 \cdot V_2O_5$ and $3K_2S_2O_7 \cdot V_2O_5$ of the binary system. In these pseudo-binary systems dimeric and polymeric complexes such as $(VO_2)_2(SO_4)_3^{4-}$ and $(VO_2(SO_4)_2)_n^{3n-}$ are also probably formed in which polymerization seems to increase at lower temperatures. With increased addition of K_2SO_4, a compound, probably $K_3VO_2(SO_4)_2$, precipitates. Finally, the conductivities of the same three pseudo-binary cross-sections have been measured in the temperature range 390–500°C and at 20 totally different compositions in the range $X_{K_2SO_4} = 0$–0.55. For each composition and temperature T in the measured range, the conductivity can be expressed by an equation of the form $\kappa = A(X) + B(X)(T-450) + C(X)(T-450)^2 + D(X)(T-450)^3$. The calculated molar conductivities exhibit a large deviation from ideality, supporting the concept of strong interaction between the components of the melts.

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1. Introduction

This series of investigations is concerned with the formation of vanadium complexes in the molten system $M_2S_2O_7$–M_2SO_4–V_2O_5 (M is Na, K and Cs, the so-called catalyst promoters) which are related to the catalyst used for the production of sulphuric acid and the cleaning of flue gases.

Our investigations so far on K-promoted catalyst systems $K_2S_2O_7$–V_2O_5 and $K_2S_2O_7$–K_2SO_4–V_2O_5 that are dilute in V_2O_5, i.e. $X_{V_2O_5} < 0.05$, has been carried out by spectrophotometric, potentiometric and cryoscopic methods [1]. However, in systems much more concentrated in V_2O_5, as found for industrial catalysts, i.e. $X_{V_2O_5} = 0.2$–0.4, the melts are very dark, viscous and hygroscopic, and only methods such as calorimetry, conductivity and densitometry can be applied [2,3]. These investigations revealed that in the dilute solutions, monomeric V(V) complexes such as $VO_2SO_4^-$, $VO_2SO_4S_2O_7^{3-}$ and $VO_2(SO_4)_2^{3-}$ are most probably formed, while at higher concentrations of V_2O_5, dimeric and polymeric complexes such as $(VO_2)_2(SO_4)_2S_2O_7^{3-}$, $(VO_2)_2(SO_4)_3^{3-}$, $(VO_2SO_4)_n^{n-}$ and $(VO_2(SO_4)_2)_n^{3n-}$ seem to be stabilized. The previous calorimetric investigation [2] was carried out at one temperature only, 430°C, whereas a temperature range of 400–600°C is found in the working sulphuric acid catalyst in an industrial 4-bed converter. The present calorimetric investigation is carried out at 400 and 450°C and the conductometric investigation covers the range 390–500°C. No comparative data could be found in the literature.

2. Experimental

2.1. Materials

Pure, dry $K_2S_2O_7$ was obtained by thermal decomposition of $K_2S_2O_8$ (Merck, Pro Analysi) as described earlier [1]. The V_2O_5 used was from Cerac (Pure, 99.9%) and the K_2SO_4 was from Merck (Suprapur, >99%). All handling of the hygroscopic $K_2S_2O_7$ took place in glove boxes with nitrogen or argon, dried continuously to around 5 ppm H_2O [1,2]. The non-hygroscopic compounds V_2O_5 and K_2SO_4 could be stored and handled outside the glove box.

2.2. Calorimetric measurements

The Calvet microcalorimeter used has been described in detail earlier [4]. It contains two cavities (calorimetric cells) each surrounded by a thermopile consisting of several hundred thermocouples (Pt/Pt–10%Rh).

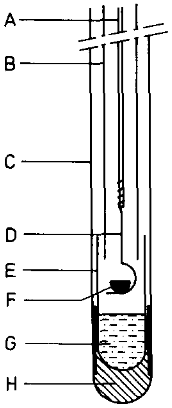

Fig. 1. Microcalorimetric device used for the modified "indirect drop method": A, glass rod; B, inner glass tube; C, outer quartz tube; D, gold support; E, glass crucible; F, gold container; G, melt; H, kaowool plug.

Previous measurements [2] of the heat of mixing in the $K_2S_2O_7$–K_2SO_4–V_2O_5 system have been performed by addition of solid K_2SO_4 to the liquid mixture in a quartz container under inert atmosphere (Ar) in the sample cavity of the calorimeter.

However, the dissolution time for the compact K_2SO_4 crystals was long and the low rate of heat exchanged increased the experimental error, especially at compositions $X_{K_2SO_4}$ close to the saturation of the melt. In this work, the method has been modified (Fig. 1). A finely ground powder (20–30 mg) of K_2SO_4 was placed in a small gold container (F) (diameter 3–4 mm, height 2–3 mm) on a gold support (D) just above the surface of the melt (G) in the crucible (E) in the calorimeter cavity at uniform temperature. Gold is thought to be the only metal resistant to the melt [1]. By rotating the glass rod (A) the gold container dropped into the melt and the K_2SO_4 powder then dissolved relatively quickly. No thermal effect was detected when an empty container was dropped into the melt. This modified method has the disadvantage compared to the earlier one [2] that there is only space for 5–7 containers to be dropped into the melt. Therefore, a greater number of series of experiments than before [2], with premixed components of the $K_2S_2O_7$–K_2SO_4–V_2O_5 system, had to be carried out. The indirect drop method could be used as before for measurements on the $K_2S_2O_7$–V_2O_5 system, where solid V_2O_5 is dropped into the melt.

2.3. Conductivity measurements

The borosilicate cell used for measuring the conductivity has been described previously [3]. The cell was filled in the glove box, evacuated, and closed by sealing the stem. For control of a possible reduction of V(V) to V(IV) the cell was in some cases closed under oxygen atmosphere (≈ 0.7 atm) but no variation in the conductivity was ever observed. Up to seven different compositions could be measured with each cell by addition of chemicals through the stem which was cut open in the glove box and sealed again.

The resistance was measured at 2 kHz with an accuracy better than 0.1% by using a Wheatstone bridge [3]. Cell constants of the order of 300 cm^{-1} (relative accuracy ±0.5%) were determined in a thermostat at room temperature by using 0.1 Demal KCl standard solution as described in the literature [5].

The metal block furnace was regulated to within ±0.1°C and the temperature of the melt was measured by a controlled chromel–alumel thermocouple placed at the capillary tube.

3. General considerations

3.1. Calorimetry

When a solid (B) is dropped into a liquid (A), both at the same temperature T, the molar enthalpy of liquid–liquid mixing ΔH_{mix} (at the temperature T) is given by

$$\Delta H_{\mathrm{mix}} = \Delta H_{\mathrm{exptl}} - X_{\mathrm{B}}(H_{\mathrm{B(l)},T} - H_{\mathrm{B(s)},T}) \tag{1}$$

where $\Delta H_{\mathrm{exptl}}$ is the molar heat evolved at constant pressure during the experiment, X_{B} is the mole fraction of the solid, and the term $H_{\mathrm{B(l)},T} - H_{\mathrm{B(s)},T}$ is the molar heat of fusion of the solid at the temperature T. The molar heats of fusion at 400 and 450°C were found by extrapolation to be 60.8 and 61.8 kJ mol^{-1}, respectively for V_2O_5 (m.p. 670°C), on the basis of the data in the tables in ref. 6.

In the case of the ternary system $K_2S_2O_7$–K_2SO_4–V_2O_5, where the liquid (A) has the composition V_2O_5–$nK_2S_2O_7$ ($n = 1$, 2 or 3), the molar enthalpy of liquid–liquid mixing ΔH_{mix} at the temperature T is given by

$$\Delta H_{\mathrm{mix}} = \Delta H_{\mathrm{exptl}} + (1 - X_{\mathrm{B}})\,\Delta H_{\mathrm{premix}} - X_{\mathrm{B}}(H_{\mathrm{B(l)},T} - H_{\mathrm{B(s)},T}) \tag{2}$$

where the term $\Delta H_{\mathrm{premix}}$ is the enthalpy of mixing found for $n = 1$, 2 or 3 in the binary system $K_2S_2O_7$–V_2O_5. The spread (uncertainty) in the values of the heat of mixing for a particular drop was around ±2%. However, the deviation between the measured value and the true value is probably ±5% [7]. The uncertainty in the temperatures is ±1°C.

3.2. Conductometry

For each value of the molar ratio $K_2S_2O_7/V_2O_5 = \theta$, we can consider the mixtures as binary systems in which one component is $(K_2S_2O_7)_\theta \cdot V_2O_5$ and the other one is K_2SO_4. The mole fraction X_{b} of K_2SO_4 in this system is given by the equation

$$X_{\mathrm{b}} = \frac{(\theta + 1)X}{\theta X + 1} \tag{3}$$

where X is the mole fraction of K_2SO_4 in the ternary system.

Considering the binary system as ideal, the molar volume V^{M} is given by

$$V^{\mathrm{M}} = (1 - X_{\mathrm{b}})V_1 + X_{\mathrm{b}}V_2 \tag{4}$$

where V_1 and V_2 are the molar volumes of the components $(K_2S_2O_7)_\theta \cdot V_2O_5$ and K_2SO_4, respectively.

From the measured conductivity κ, the experimental molar conductivity Λ_{exptl} at a given composition and temperature can be expressed by

$$\Lambda_{\mathrm{exptl}} = \kappa V_{\mathrm{M}} \tag{5}$$

In order to discuss possible complex formation in molten salts, Λ_{exptl} is compared with Λ_{calcd} according to Delimarskii and Markov [8]

$$\Lambda_{\mathrm{calcd}} = (1 - X_{\mathrm{b}})\Lambda_1 + X_{\mathrm{b}}\Lambda_2 + 2X_{\mathrm{b}}(1 - X_{\mathrm{b}})\Lambda_1 \qquad (\Lambda_1 < \Lambda_2) \tag{6}$$

where Λ_1 and Λ_2 are the molar conductivities of $(K_2S_2O_7)_\theta \cdot V_2O_5$ and $K_2S_2O_4$, respectively and X_{b} represents the mole fraction of K_2SO_4 in the binary system.

4. Results and discussion

4.1. Calorimetric measurements of the binary system $K_2S_2O_7$–V_2O_5

The enthalpies of mixing of V_2O_5 with liquid $K_2S_2O_7$ have been measured at 24 and 32 different compositions at 400 and 450°C, respectively. The data have been corrected for the calculated heat of fusion of V_2O_5 in order to obtain the enthalpy of liquid–liquid mixing. In Fig. 2, the data are displayed together with the previously [2] obtained data at 430°C for comparison. At 400 and 450°C, two

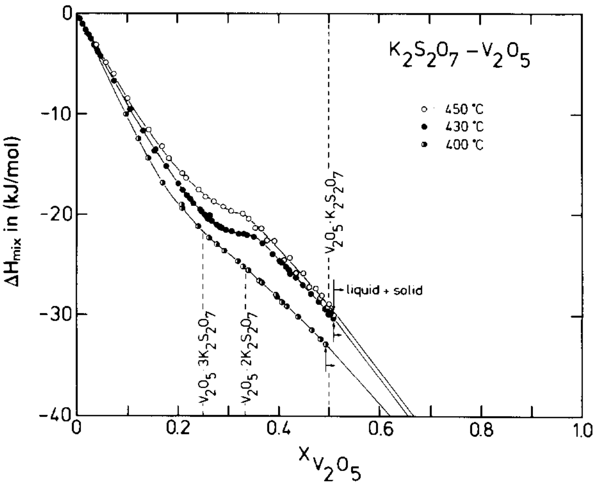

Fig. 2. Molar enthalpy of liquid–liquid mixing for the binary system $K_2S_2O_7$–V_2O_5 at 400–450°C. The data for 430°C are taken from ref. 2. The indicated compounds are proposed in ref. 10.

different series of measurements have been carried out. In both cases a good reproducibility is observed. $K_2S_2O_7$ is not molten at 400°C (m.p. 418.8°C [1]) but the binary system is liquid in the composition range $X_{V_2O_5} = 0.05-0.45$ according to the most reliable phase diagram published [9]. Thus measurements at 400°C have been obtained from premixed components with the composition $X_{V_2O_5} = 0.05$. The heats of mixing for these initial melts were therefore obtained by linear extrapolation from the first experimental enthalpies observed in each series. For all three experimental temperatures, no thermal effects were observed at mole fractions higher than those indicated by the arrows in Fig. 2; the added granules of V_2O_5 could be recovered by crushing the solidified melts after the experiments. This is in good accordance with the phase diagram [9] that shows a steep increase of the liquidus temperature at around $X_{V_2O_5} = 0.5$ (liquidus temperature $\approx$430°C). For all three temperatures, a strong, increasingly negative molar enthalpy of mixing is found with increased addition of V_2O_5 to the molten $K_2S_2O_7$. The partial enthalpy of V_2O_5 at infinite dilution in $K_2S_2O_7$ could be calculated. In the composition range $X_{V_2O_5} = 0-0.05$ and at 450°C, it was found to be $\Delta \bar{H}^{\infty}_{V_2O_5} = -85.0\ \mathrm{kJ\ mol^{-1}}$. Previously [2], a value of $-91.5\ \mathrm{kJ\ mol^{-1}}$ was found at 430°C. No value can be calculated at 400°C because a two-phase liquid–solid system is found in this composition range. These high negative enthalpies support the impression that a rigorous reaction takes place between the two components at all temperatures. The compounds indicated in Fig. 2 are in accordance with the phase diagram studies [9,10]. From these studies and our recent study [11] of the phase diagram of the analogous Cs system, $Cs_2S_2O_7-V_2O_5$, the compounds $K_2S_2O_7 \cdot V_2O_5$, $2K_2S_2O_7 \cdot V_2O_5$ and $3K_2S_2O_7 \cdot V_2O_5$ might be formulated as KVO_2SO_4, $K_4(VO_2)_2(SO_4)_2S_2O_7$ (or as $K_4(VO_2)_2O(SO_4)_4$ [12]) and $K_3VO_2SO_4S_2O_7$, respectively. In the melt, complexes corresponding to the anionic part of these salts, i.e. $VO_2SO_4^-$, $(VO_2)_2(SO_4)_2S_2O_7^{4-}$ (or $(VO_2)_2O(SO_4)_4^{4-}$) and $VO_2SO_4S_2O_7^{3-}$, are probably formed. The measurements performed at 450°C show close analogy with the previous measurements at 430°C as can be seen in Fig. 2. The interpretation is therefore also analogous. At low mole fractions $X_{V_2O_5}$, the monomeric complexes $VO_2SO_4^-$ and $VO_2SO_4S_2O_7^{3-}$ seem to be formed, based on previous spectrophotometric, potentiometric and cryoscopic measurements [1]. At increasing mole fractions $X_{V_2O_5}$, dimerization of the complexes probably takes place in accordance with the equation

$$VO_2SO_4^- + VO_2SO_4S_2O_7^{3-} \rightleftharpoons (VO_2)_2(SO_4)_2S_2O_7^{4-} \qquad (7)$$

The dimer can possibly be formulated as the stoichiometric analogue, $(VO)_2O(SO_4)_4^{3-}$, because the compound $Cs_4(VO)_2O(SO_4)_4$ has been determined by a recent X-ray investigation [12]. The dimer is expected to reach the maximum concentration at the molar ratio $V_2O_5:K_2S_2O_7 = 1:2$ or $X_{V_2O_5} = 0.33$. A local minimum for ΔH_{mix} is indeed found at $X_{V_2O_5} = 0.33$, supporting this interpretation. At higher mole fractions, the increased heat of mixing indicates a lowering of the entropy of the system. Together with the observed increase in the viscosity, this points to the formation of polymeric complexes according to the reaction

$$0.25nV_2O_5 + 0.25n(VO_2)_2(SO_4)_2S_2O_7^{4-} \rightarrow (VO_2SO_4)_n^{n-} \qquad (8)$$

Around $X_{V_2O_5} = 0.5$, i.e. V_2O_5:$K_2S_2O_7$ = 1:1, the solubility limit is reached. The absence of a break in Fig. 2 at $X_{V_2O_5} = 0.25$, i.e. V_2O_5:$K_2S_2O_7$ = 1:3, corresponding to the formation of the compound $K_3VO_2SO_4S_2O_7$, indicates that the monomeric complex $VO_2SO_4S_2O_7^{3-}$ is possibly formed only to a small extent at this composition.

Compared to the other temperatures of investigation, the highest heat of mixing is found at 400°C for all compositions. In addition, the minimum at $X_{V_2O_5} = 0.33$ is smeared out at 400°C. These effects are probably due to increased polymerization ($n VO_2SO_4^- \rightleftharpoons (VO_2SO_4)_n^{n-}$) as the temperature is lowered.

The calculated solid straight lines in Fig. 2 in the two-phase region above the value $X_{V_2O_5}$ of the saturated melts will, consequently, be followed up to $X_{V_2O_5} = 1$, where the lines end up at the extrapolated heat of fusion of V_2O_5 at the different temperatures.

4.2. Calorimetric measurements of the ternary $K_2S_2O_7$–K_2SO_4–V_2O_5 system

The possible formation of sulfato complexes by the addition of K_2SO_4 to the above-mentioned V(V) complexes of the binary $K_2S_2O_7$–V_2O_5 system has also been investigated. As before [2], three pseudo-binary cross-sections of the ternary systems, i.e. $K_2S_2O_7 \cdot V_2O_5$, $2K_2S_2O_7 \cdot V_2O_5$ and $3K_2S_2O_7 \cdot V_2O_5$, were added to solid K_2SO_4 at 400 and 450°C. These compositions correspond to the compounds claimed [10] to be formed in the $K_2S_2O_7$–V_2O_5 system. The extrapolated heat of fusion of K_2SO_4 was found [6] to be approximately 49.2 kJ mol^{-1} in the range 400–450°C. From the experimentally observed heats of reaction and the molar heat of liquid–liquid mixing obtained above for the three compositions of the binary $K_2S_2O_7$–V_2O_5 system, the molar heat of liquid–liquid mixing in the ternary systems could then be calculated. The results are displayed on Figs. 3–5. For

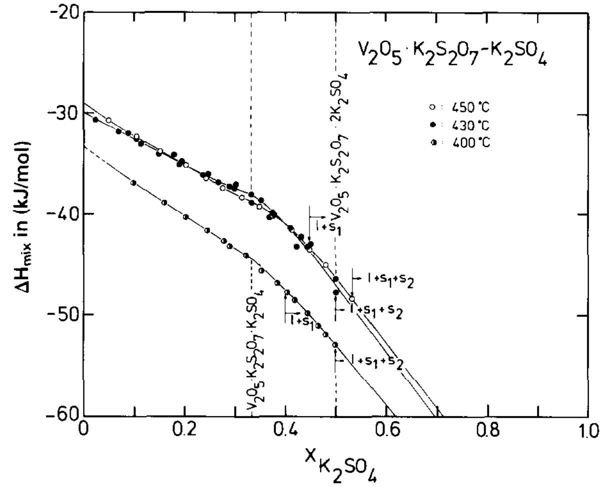

Fig. 3. Molar enthalpy of liquid–liquid mixing for the ternary (or pseudo-binary) system $V_2O_5 \cdot K_2S_2O_7$–K_2SO_4 at 400–450°C. The data for 430°C are taken from ref. 2. The broken lines indicate the composition of possible compounds.

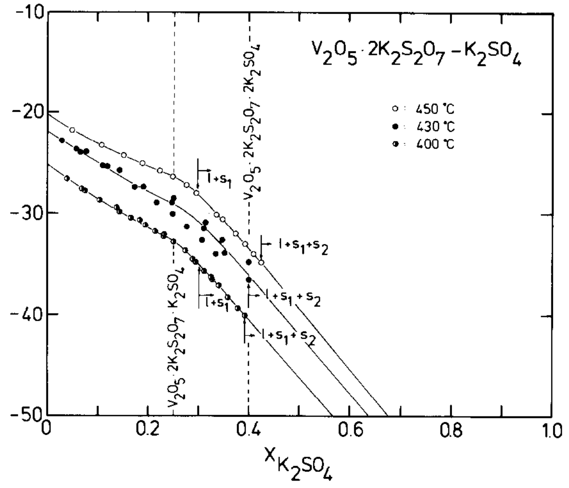

Fig. 4. Molar enthalpy of liquid–liquid mixing for the ternary (or pseudo-binary) system $V_2O_5 \cdot 2K_2S_2O_7$–K_2SO_4 at 400–450°C. The data for 430°C are taken from ref. 2. The broken lines indicate the composition of possible compounds.

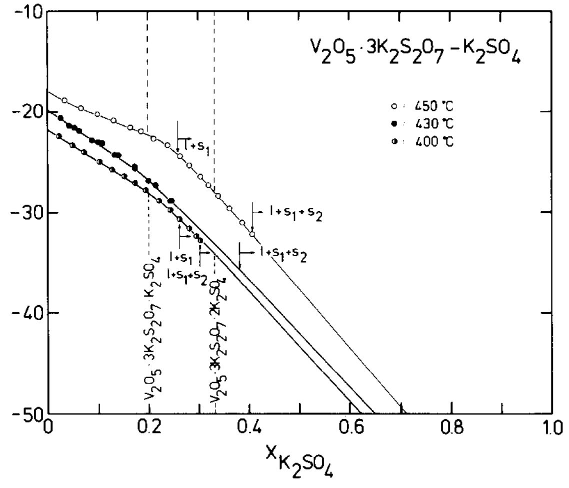

Fig. 5. Molar enthalpy of liquid–liquid mixing for the ternary (or pseudo-binary) system $V_2O_5 \cdot 3K_2S_2O_7$–K_2SO_4 at 400–450°C. The data for 430°C are taken from ref. 2. The broken lines indicate the composition of possible compounds.

comparison, the data obtained previously [2] at 430°C are also included. It can be seen that the scattering of the measurements is considerably higher at 430°C, most probably due to the reasons discussed in the Experimental Section.

According to the phase diagram [9], the mixture $K_2S_2O_7 \cdot V_2O_5$ is not molten at 400°C and the mixture was premixed with K_2SO_4 at $X_{K_2SO_4} = 0.0540$ in order to be molten. The heat of mixing of this composition was obtained by extrapolation of the heat observed from the addition of K_2SO_4.

For the pseudo-binary compositions and temperatures investigated, an increasingly exothermic heat of mixing was found with increased addition of K_2SO_4. In addition, a much higher solubility of K_2SO_4 was found in these systems containing vanadium, compared to the $K_2S_2O_7$–K_2SO_4 system where the solubility was found to be in the range $X_{K_2SO_4} = 0.04–0.05$ at 420–450°C [1]. Thus a strong interaction of the components is taking place, most probably due to complex formation in the melts.

In Figs. 3–5, a "break" in ΔH_{mix} seems to be present at the molar ratio $K_2SO_4/V_2O_5 = 0.5$. The corresponding compositions of the ternary systems are indicated on the figures. The compositions corresponding to the molar ratios $K_2SO_4/V_2O_5 = 1.0$ are also included.

In between, the first vertical arrow indicates the composition where a solid, S_1, is formed, according to the conductivity measurements to be discussed in the next section. These findings can be interpreted as follows.

On addition of K_2SO_4 up to the break, the dimer vanadium oxo sulfato complex $(VO_2)_2(SO_4)_3^{4-}$ is increasingly formed from the V(V) complexes present in the $nK_2S_2O_7 \cdot V_2O_5$ (n = 1, 2 or 3) melts, e.g. by the reactions

$$(VO_2)_2(SO_4)_2S_2O_7^{4-} + SO_4^{2-} \rightleftharpoons (VO_2)_2(SO_4)_3^{4-} + S_2O_7^{2-} \quad (9)$$

and

$$(VO_2SO_4)_n^{n-} + SO_4^{2-} \rightleftharpoons (VO_2)_2(SO_4)_3^{4-} + (VO_2SO_4)_{n-2}^{(n-2)-} \quad (10)$$

The polymerization

$$0.5n(VO_2)_2(SO_4)_3^{4-} + 0.5nSO_4^{2-} \rightleftharpoons (VO_2(SO_4)_2)_n^{3n-} \quad (11)$$

is probably [2] also important in this composition range and, to an increasing extent, at 400°C, where the largest negative heat of mixing is observed.

At somewhat higher mole fractions $X_{K_2SO_4}$, the solubility limit of a vanadium oxo sulfato compound S_1 is crossed. This compound is probably $K_3VO_2(SO_4)_2$ which has been isolated from the $K_2S_2O_7$–K_2SO_4–V_2O_5 system [13]. Increasing the addition of finely ground K_2SO_4 with a large surface area leads to further precipitation of $K_3VO_2(SO_4)_2$.

Finally no thermal effect is observed and the solubility limit of K_2SO_4 is crossed as indicated by the second vertical arrow in Figs. 3–5, where the solid (S_2), K_2SO_4, is precipitated.

4.3. Conductivity measurements of the ternary $K_2S_2O_7$–K_2SO_4–V_2O_5 system

The conductivity of the $K_2S_2O_7$–K_2SO_4–V_2O_5 molten salt system has been measured for the same above-mentioned pseudo-binary cross-sections of the ternary system $K_2S_2O_7$–V_2O_5–K_2SO_4, $2K_2S_2O_7 \cdot V_2O_5$–K_2SO_4 and $3K_2S_2O_7 \cdot V_2O_5$–K_2SO_4. For each pseudo-binary system, measurements were made at several compositions in the mole fraction range $X_{K_2SO_4} = 0–0.55$ and in the range 390–

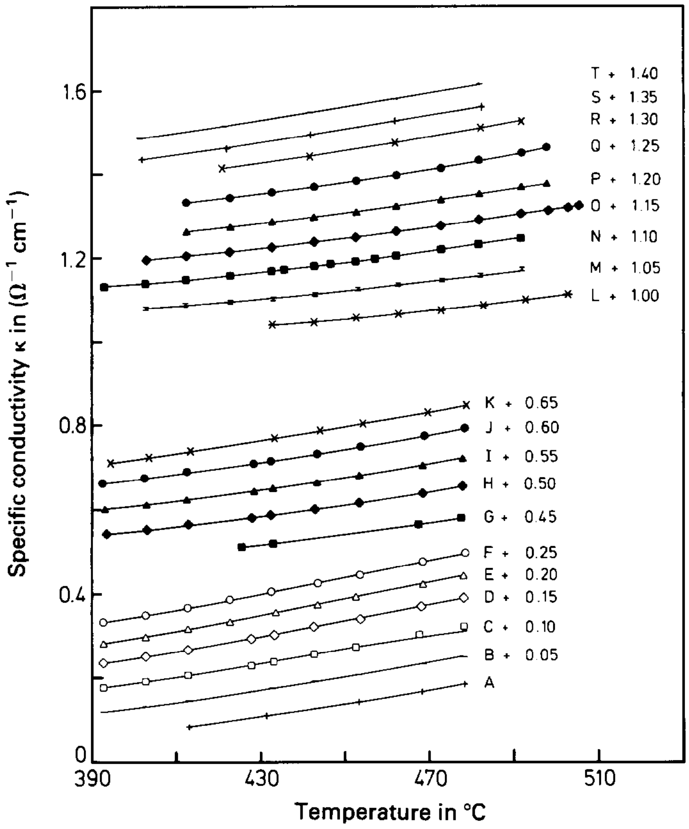

Fig. 6. Conductivity of the systems $V_2O_5 \cdot 3K_2S_2O_7$–K_2SO_4 (A–F), $V_2O_5 \cdot 2K_2S_2O_7$–K_2SO_4 (G–K) and $K_2S_2O_7 \cdot V_2O_5$–K_2SO_4 (L–T). For clarity, the data are offset on the ordinate by the specified value. See Table 1 for the compositions $X_{K_2SO_4}$ for the melts A–T.

500°C. All measured values of the conductivity for each composition investigated are shown in Fig. 6 where the specific conductivity κ is plotted versus T. As expected, the conductivity increases with increasing temperature. For each pseudo-binary system and for each value of $X_{K_2SO_4}$, the experimental data can be expressed by the polynomial

$$\kappa = A(X) + B(X)(T-450) + C(X)(T-450)^2 + D(X)(T-450)^3$$

where κ is the conductivity in Ω^{-1} cm^{-1} and T is the temperature in °C. In Table 1, the coefficients are given for the different compositions along with the standard deviations. Another way of presenting the data is shown in Figs. 7–9, where the conductivity is plotted for each pseudo-binary mixture versus $X_{K_2SO_4}$. For simplicity only two curves are shown, representing the conductivities at 430 and 475°C.

The conductivity increases with increasing the amount of K_2SO_4 added to the melt. When the solubility limit of $K_3VO_2(SO_4)_2$ in the melt is reached, the

Table 1
Coefficients of the empirical equations[a] for the specific conductivity for different compositions $X_{K_2SO_4}$ of the $3K_2S_2O_7 \cdot V_2O_5$–K_2SO_4, $2K_2S_2O_7 \cdot V_2O_5$–K_2SO_4 and $K_2S_2O_7 \cdot V_2O_5$–K_2SO_4 systems[b]

Mole fraction, $X_{K_2SO_4}$	$A(X)$/ $(\Omega^{-1}\,cm^{-1})$	$10^3B(X)$/ $(\Omega^{-1}\,cm^{-1}\,deg^{-1})$	$10^6C(X)$/ $(\Omega^{-1}\,cm^{-1}\,deg^{-2})$	$10^8D(X)$/ $(\Omega^{-1}\,cm^{-1}\,deg^{-3})$	SD/$(\Omega^{-1}\,cm^{-1})$
$3K_2S_2O_7 \cdot V_2O_5$					
A, 0.0000	0.137458	1.50540	4.229	5.624	9.23×10^{-5}
B, 0.0877	0.153651	1.701759	1.97	−3.55	0.000434
C, 0.1829	0.169300	1.640092	−4.6	−9.42	0.001587
D, 0.2590	0.184135	1.88449	2.11	−1.6	0.000278
E, 0.3357	0.186940	1.985166	24.8	−4.5	0.000224
F, 0.4030	0.186940	1.985166	24.8	−4.5	0.000481
$2K_2S_2O_7 \cdot V_2O_5$					
G, 0.0000	0,088755	1.302551	4.87	−4.3	9.02×10^{-6}
H, 0.0890	0.109289	1.41451	4.39	0.847	0.000164
I, 0.2013	0.1240151	1.503318	4.22	0.629	9×10^{-5}
J, 0.2966	0.14038411	1.579535	4.65	2.27	0.00029
K, 0.3570	0.1449920	1.666373	1.88	−0.58	0.000176
$K_2S_2O_7 \cdot V_2O_5$					
L, 0.0000	0.058838	0.972172	4.695	−1.464	6.12×10^{-5}
M, 0.0480	0.0761709	1.145398	2.649	−3.248	0.000242
N, 0.1060	0.092605	1.304159	3.771	−1.244	8.1×10^{-5}
O, 0.2005	0.099714	1.330849	3.607	−1.228	4.9×10^{-5}
P, 0.2618	0.110355	1.409914	4.15	−1.8	9.71×10^{-5}
Q, 0.3736	0.1322566	1.517798	5.23	1.67	0.000275
R, 0.4500	0.1601516	1.681115	3.46	−5.5	0.000437
S, 0.5000	0.1611606	1.700222	1.31	−4.7	0.000611
T, 0.5500	0.1635791	1.745209	1.01	−3.2	0.0003

[a] $\kappa = A(X) + B(X)(T-450) + C(X)(T-450)^2 + D(X)(T-450)^3$. [b] For the measured temperature range, see Fig. 6.

conductivity becomes invariable because the composition of the melt is not changed. This seems in contradiction to the calorimetric measurements, where a heat of mixing was obtained beyond this composition. However, the larger crystals of K_2SO_4 added here, having a relatively small surface area, may cause a very small transfer to the solid oxo sulfato compound $K_3VO_2(SO_4)_2$, covering the surface of the K_2SO_4 crystal. Therefore, from Figs. 7–9, the solidi of the systems at 430 and 475°C can be deduced.

In previous papers [3,14], we have shown that in the binary system $M_2S_2O_7$–V_2O_5 (M is K, Cs), the cation carries the major part of the current. Consequently, when K_2SO_4 is added to the binary systems $K_2S_2O_7 \cdot V_2O_5$, $2K_2S_2O_7 \cdot V_2O_5$ or $3K_2S_2O_7 \cdot V_2O_5$, the conductivity is expected to increase with increasing mole fraction of $X_{K_2SO_4}$ as seen in Figs. 7–9.

In Figs. 7 and 8, it is seen that an inflexion point for κ seems to be present at a low mole fraction of K_2SO_4, i.e. $X_{K_2SO_4} \approx 0.15$. This variation of κ with $X_{K_2SO_4}$ can be explained by a change in the structure of the liquid. Indeed the mobility of the potassium ion is influenced by the strength of interaction between the cation (K^+)

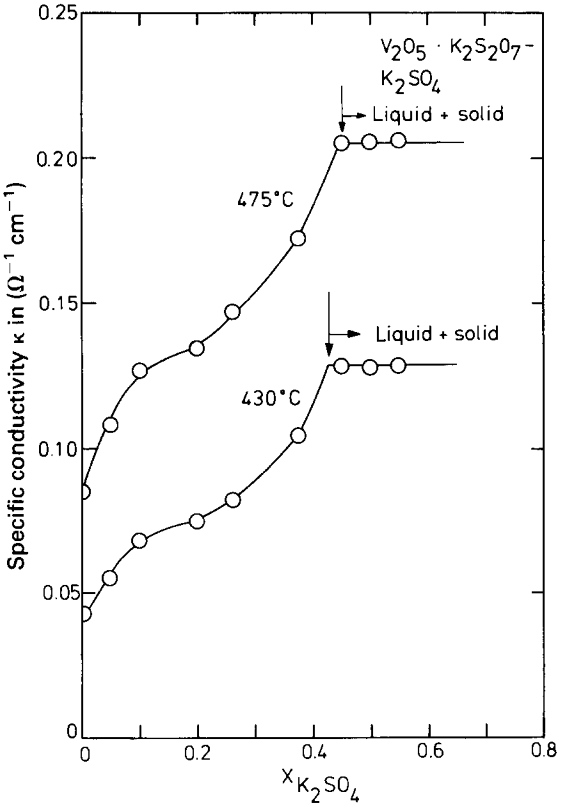

Fig. 7. Conductivity isotherms for the system $V_2O_5 \cdot K_2S_2O_7$–K_2SO_4.

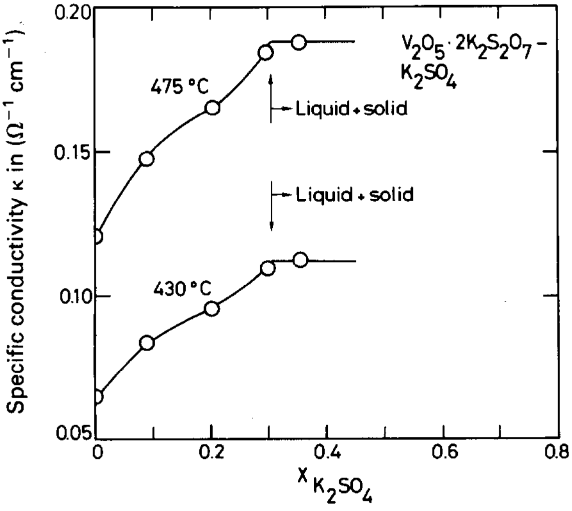

Fig. 8. Conductivity isotherms for the system $V_2O_5 \cdot 2K_2S_2O_7$–K_2SO_4.

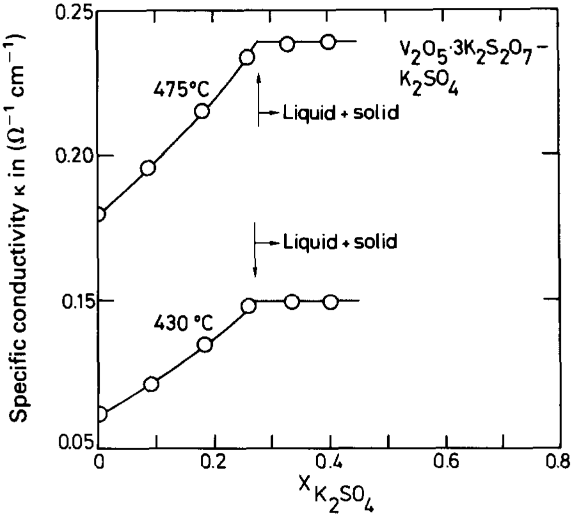

Fig. 9. Conductivity isotherms for the system $V_2O_5 \cdot 3K_2S_2O_7$–K_2SO_4.

and the anions formed in the liquid. According to the above-mentioned reactions Eqs. (9) and (10), the nature and the amount of vanadium oxo sulfato complexes formed in the liquid vary with $X_{K_2SO_4}$. For example in the pseudo-binary system $K_2S_2O_7 \cdot V_2O_5$ at $X_{K_2SO_4} = 0$, the main complexes formed are polymer $(VO_2SO_4)_n^{n-}$. When K_2SO_4 is added, the polymer is broken into $(VO_2)_2(SO_4)_3^{4-}$ and $(VO_2SO_4)_{n-2}^{(n-2)-}$.

On the basis of the measured conductivities and the calculated molar volume from Eq. (4), the experimental molar conductivity, Λ_{exptl} can be calculated by applying Eq. (5). This has been done at 430°C for each pseudo-binary system and for each composition in the composition range $X_{K_2SO_4}$ at which the mixtures are liquid. In addition, the ideal values of the molar conductivities Λ_{calcd} have been calculated by applying Eq. (6). In the calculations for Λ_{exptl} and Λ_{calcd} the values of Λ_1, V_1 and Λ_2, V_2 are taken respectively from our previous work [3] and the NBS tables [15]. The deviation $((\Lambda_{\text{exptl}} - \Lambda_{\text{calcd}})/\Lambda_{\text{calcd}})$ in % is plotted against $X_{K_2SO_4}$ in Fig. 10. The very large positive and negative deviations from ideality suggest, as mentioned above, that most probably complexes are broken and new complexes are formed on addition of K_2SO_4 to the system.

4.4. Relation to catalyst activity

It is in general considered [16–18] that dimeric V(V) complexes play an essential role in the catalytic conversion of SO_2 to SO_3 by O_2 in the sulfuric acid and in the flue gas cleaning process. Indeed the results presented here support the presence of dimeric V(V) complexes in the catalyst model melts at conditions of industrial operation. Furthermore this investigation points to an increased polymerization of V(V) on lowering the temperature, at the expense of the highly active dimeric V(V)

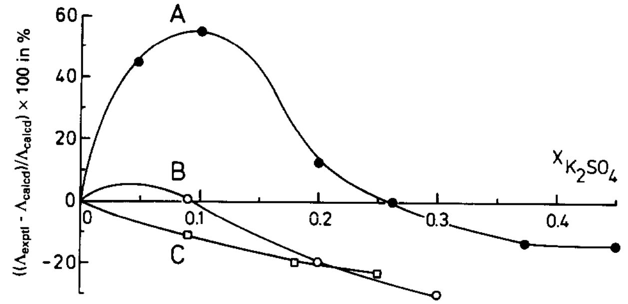

Fig. 10. Deviation (%) between the experimental and calculated molar conductivities at 430°C for the molten systems: A, $V_2O_5 \cdot K_2SO_7$–K_2SO_4; B, $V_2O_5 \cdot 2K_2S_2O_7$–K_2SO_4; C, $V_2O_5 \cdot 3K_2S_2O_7$–K_2SO_4.

complexes. This is in accordance with the observed decrease in the activity of commercial catalysts and model melts [16–19] by decreasing the temperature in the range 400–500°C, i.e. at temperatures above the deactivation temperature where V(III) or V(IV) compounds precipitate [19] and deplete the catalyst for the active species.

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Supplementary material

All measured molar enthalpies and conductivities of the investigated systems can be obtained on request from the authors.

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