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Calorimetric and spectroscopic measurements on the SO_2 oxidation catalyst model system $M_2S_2O_7$–M_2SO_4–V_2O_5/SO_2(g) or Ar(g) (M = K or Cs) at 430–470°C

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Abstract

Calorimetric measurements have been performed on the melt–gas systems $M_2S_2O_7$–V_2O_5 and $M_2S_2O_7$–M_2SO_4(sat)–V_2O_5 (M = K and Cs) in SO_2(g) and Ar(g) at 430–480°C and for mole fractions $X_{V_2O_5} = 0$–0.1. Enthalpies have been obtained for complex formation reactions as $(VO)_2O(SO_4)_4^{4-} + SO_4^{2-} \rightleftarrows 2VO_2(SO_4)_2^{3-} + S_2O_7^{2-}$ for V(V) and $2VO(SO_4)_2^{2-} + 3SO_4^{2-} + SO_3 \rightleftarrows 2VO(SO_4)_3^{4-} + S_2O_7^{2-}$ for V(IV). Similarly enthalpies of the V(V)–V(IV) redox reactions $(VO)_2O(SO_4)_4^{4-} + SO_2 \rightleftarrows 2VO(SO_4)_2^{2-} + SO_3$ and $2VO_2(SO_4)_2^{3-} + SO_4^{2-} + SO_2 \rightleftarrows 2VO(SO_4)_3^{4-}$ could be calculated. These enthalpies of reduction compare well with those obtained by spectrophotometric measurements in the same temperature range. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: SO_2 oxidation catalysts; Vanadium Oxo sulfato complexes; Redox reactions; Calorimetric measurements

1. Introduction

The molten salt–gas system $M_2S_2O_7$–V_2O_5/SO_2–O_2–N_2 (M = alkali mixture) at 400–500°C is considered [1,2] a realistic model for the industrial SO_2 oxidation catalyst used in sulfuric acid production. Usually, the alkali mixture consists of 20% Na and 80% K, but in the latest years also Cs has been added as copromoter in some catalysts. The catalytic active species seem to be [3] oxo sulfato complexes of V(V), e.g. the dimer $(VO)_2O(SO_4)_4^{4-}$ complex formed by the dissolution process $V_2O_5 + 2S_2O_7^{2-} \rightarrow (VO)_2O(SO_4)_4^{4-}$. Previously [4–6], we have carried out calorimetric investigations on the $M_2S_2O_7$–V_2O_5 (M = K or Cs) systems and these systems added M_2SO_4 in O_2(g) or inert gas atmospheres and obtained the heat of liquid–liquid mixing. However, only $M_2S_2O_7$ melts with very high content of V_2O_5, i.e. $X_{V_2O_5} = 0.25$, 0.33 and 0.50 were investigated with respect to the addition of M_2SO_4. In the present work the heat of mixing in reducing atmospheres, like SO_2(g), of these systems is measured for the first time in order to study the heat of reaction for V(V)–V(IV) redox and sulfato complex formation processes relevant for the chemistry of the working industrial catalyst. However, at high partial pressures of SO_2, i.e. around 1 atm, precipitation of V(IV) (and possibly

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V(III)) salts occur [3,7,8] below ca. 430°C at mole fractions $X_{V_2O_5}$ greater than ca. 0.1. Therefore, the present investigation is carried out in rather dilute melts, i.e. $X_{V_2O_5} < 0.1$, whereby it also is possible to compare with earlier spectroscopic [9] and electrochemical [10] work performed in dilute solutions of V_2O_5 in alkali pyrosulfate melts.

2. Experimental

2.1. Materials

Pure and dry alkali pyrosulfates are not commercially available. Thus, $K_2S_2O_7$ was prepared by thermal decomposition of $K_2S_2O_8$ (Merck, pro analysi) [11] and $Cs_2S_2O_7$ prepared from $Cs_2S_2O_8$ synthesized in the laboratory as earlier described [12]. All handling of these hygroscopic salts was performed in a glove box and thereafter kept into sealed ampules. M_2SO_4 was from Merck (pro analysi, >99.5%). Commercial gases, O_2, N_2, Ar and SO_2 were used. V_2O_5 was from Cerac (pure, 99.9%).

The non-hygroscopic compounds M_2SO_4 and V_2O_5 could be stored and handled outside the glove box.

2.2. Calorimetric measurements

The heat of mixing of the investigated systems was measured in a Calvet microcalorimeter which has been described earlier [13] in detail. It contains two thermopiles of several hundred thermocouples (Pt/Pt–10% Rh) each surrounding a cavity (calorimetric cell). Two methods were used: the direct drop and the indirect drop method.

The device used for the indirect drop method is shown in Fig. 1. By this method the added crystals of V_2O_5 were thermally equilibrated just above and at the same temperature as the melt. Then, by applying current to coil (1), the crystal dropped into the melt and the exchanged heat was recorded and integrated graphically or by a connected data acquisition computer.

Alternatively the experiments were carried out by the direct drop method essentially performed by a set-up as shown in Fig. 1, but omitting the intermediate tube.

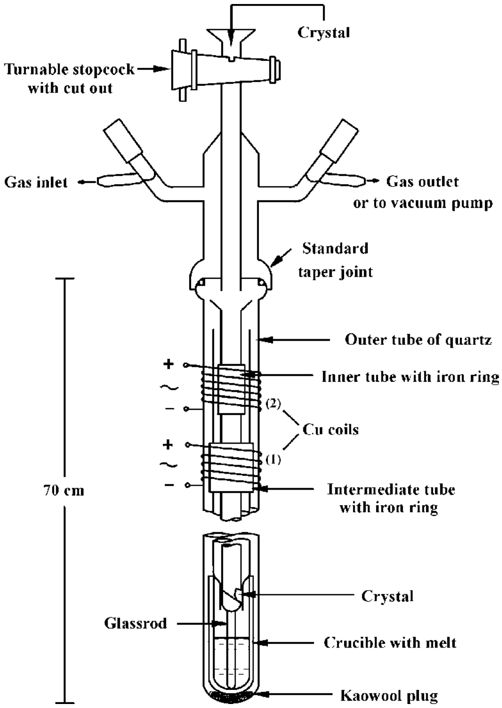

Fig. 1. Calorimetric device allowing indirect addition in a controlled atmosphere and agitation of the melt. Onset of current to coil (1) elevates the intermediate tube and the thermal equilibrated crystal drops into the melt at the same temperature. By varying the current to coil (2) the inner tube moves up and down whereby the glass rod agitates the melt.

The calorimeter was calibrated at the end of each experimental series by direct drop of preweighted gold bullets to the melt.

2.3. UV–VIS spectrophotometry

The absorption spectra were obtained on melts contained in cuvettes of silica (Ultrasil, Helma (Germany)), either in a closed system under $SO_2(g)$–$N_2(g)$ atmospheres, where the equilibrium partial pressure of SO_2 could be measured spectrophotometrically by use of a connected cuvette, or in the case of mixed $SO_2(g)$–$SO_3(g)$ atmospheres by leading the gas through a capillary tube immersed into the melt whereby equilibrium could be obtained rather fast. Home made two-windows furnaces which fitted to the compartments of the spectrophotometers (Hitachi 200S or Cary 14R) were used for recording the spectra at 430–470°C. The experimental details of the spectrophotometric investigations have been given previously [9,10]

3. General considerations

3.1. Calorimetry

The partial enthalpy of liquid–liquid mixing, $\Delta H_{\mathrm{part}}(\mathrm{A})$, when a solid (A) is dropped from room temperature, T_{amb}, into a liquid at temperature T and at constant pressure, is given by Eq. (1):

$$\Delta H_{\mathrm{part}}(\mathrm{A}) = \frac{\Delta h_{\mathrm{exp}} - n_{\mathrm{A}}\int_{T_{\mathrm{amb}}}^{T} C_P(\mathrm{A})\,\mathrm{d}T - n_{\mathrm{A}}[\Delta H_{\mathrm{f}}(\mathrm{A},T)]}{n_{\mathrm{A}}} \quad (1)$$

where Δh_{exp} is the experimentally measured heat, n_{A} the number of moles of component A added by each experiment, $C_P(\mathrm{A})$ the heat capacity of A and $\Delta H_{\mathrm{f}}(\mathrm{A}, T)$ is the molar enthalpy of fusion of A extrapolated to the experimental temperature T. The molar heat of fusion of V_2O_5 (mp 670°C), was found to be 61.65 and 62.16 kJ/mol, respectively at 430 and 470°C, by extrapolation of the data in [14].

3.2. Spectrophotometry

In the case of two species redox equilibria involving V(IV) and V(V) complexes the application of Beer's law on the absorbance at a fixed wave length (e.g. 730 nm) leads to the equation $A/l = C_{\mathrm{V(IV)}}\varepsilon_{\mathrm{V(IV)}} + C_{\mathrm{V(V)}}\varepsilon_{\mathrm{V(V)}}$, where l is the optical path length (cm), $C_{\mathrm{V(IV)}}$ and $C_{\mathrm{V(V)}}$ are the equilibrium concentrations (mol/l) of the V(IV) and V(V) complexes and $\varepsilon_{\mathrm{V(IV)}}$ and $\varepsilon_{\mathrm{V(V)}}$ their molar absorptivities in l/mol cm. The initial concentration of vanadium is given by $C^0_{\mathrm{V(V)}} = C_{\mathrm{V(V)}} + C_{\mathrm{V(IV)}}$ and the temperature dependency of $\varepsilon_{\mathrm{V(V)}}$ at 730 nm by $\varepsilon_{\mathrm{V(V)}} = 0.009307T - 2.326$ l/mol cm in $K_2S_2O_7$–K_2SO_4(sat) melts and by $\varepsilon_{\mathrm{V(V)}} = 0.00948\,T - 2.70$ l/mol cm in $K_2S_2O_7$ melts [9].

4. Results and discussion

4.1. $M_2S_2O_7$–M_2SO_4(sat)–V_2O_5 (M = K and Cs)

Initial measurements of the partial enthalpy of liquid–liquid mixing of V_2O_5 in molten $K_2S_2O_7$ and $Cs_2S_2O_7$ were carried out by the indirect drop method in Ar. Prior to the addition of V_2O_5, the molten pyrosulfates were saturated with sulfate in the calorimeter by addition of solid M_2SO_4 in excess, i.e. a precipitate of solid M_2SO_4 was present in the melt. However, earlier calorimetric [4–6] and recent potentiometric [10] measurements point to an enhanced solubility of M_2SO_4 in molten $M_2S_2O_7$ by addition of V_2O_5 due to the reactions

$$V_2O_5 + 2S_2O_7{}^{2-} \rightarrow (VO)_2O(SO_4)_4{}^{4-} \quad \text{(dissolution)} \quad (2)$$

and

$$(VO)_2O(SO_4)_4{}^{4-} + 2SO_4{}^{2-} \rightleftarrows 2VO_2(SO_4)_2{}^{3-} + S_2O_7{}^{2-} \quad \text{(complex reaction)} \quad (3)$$

Therefore, the heat observed by the calorimetric measurements should be corrected for the heat involved in the dissolution of the solid sulfate that dissolves in order to maintain saturation of the melt. However, close to saturation of the melt this process is probably very slow compared to the rapid dissolution of V_2O_5 in the melt (thermal equilibrium is apparently obtained after around 15 min). Therefore, the thermal effect of sulfate dissolution could not be detected sufficiently accurate within reasonably experimental times. Rather large scattering of the data and large deviation between the two alkali pyrosulfate systems were observed.

Due to these observations, an alternative procedure was followed, where molten $M_2S_2O_7$ (M = K and Cs) was presaturated by powder M_2SO_4 in sealed pyrex ampules during 4 days in a separate aluminum block furnace regulated to within ±0.1°C [10]. During this period the melt was gently agitated by tilting the furnace. Finally, the saturated melt was separated from excess solid M_2SO_4 by carefully decanting the melt. The melts were saturated with M_2SO_4 at 430 and 470°C for M = K and Cs, respectively. The solidified presaturated melts were loaded into the crucible in the glove box and transferred to the calorimeter.

The results of the addition (direct drop method) of V_2O_5 to the $K_2S_2O_7$–K_2SO_4(sat) system are shown in Fig. 2. The measured heat has been corrected for the heat exchanged with the melt due to heating of the

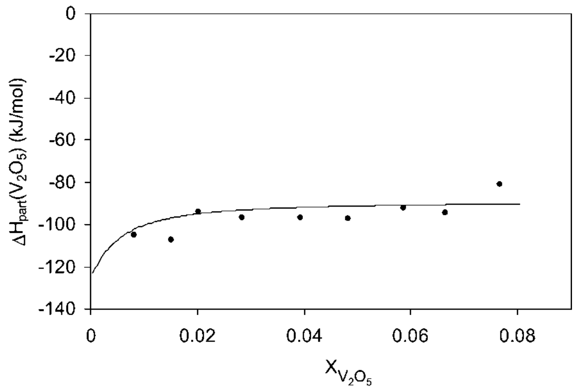

Fig. 2. Partial enthalpy of liquid–liquid mixing for the ternary (or pseudo-binary) system $K_2S_2O_7$–K_2SO_4(sat)–V_2O_5 in Ar (1 atm) at 437°C.

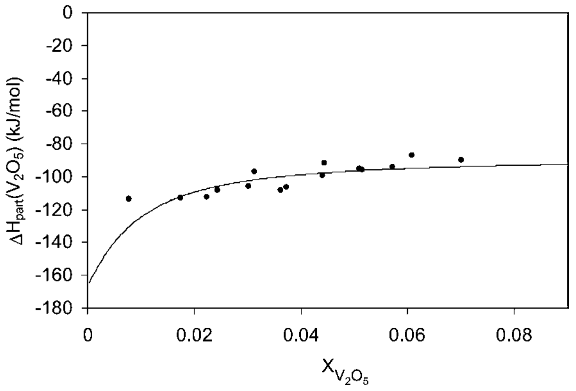

Fig. 3. Partial enthalpy of liquid–liquid mixing for the ternary (or pseudo-binary) system $Cs_2S_2O_7$–Cs_2SO_4(sat)–V_2O_5 in Ar (1 atm) at 465–477°C.

V_2O_5 crystalline sample from ambient temperature to the experimental temperature and for the heat of fusion of V_2O_5 at the experimental temperature using Eq. (1) and the data in [14]. From Fig. 2 it appears that the partial molar enthalpy of liquid–liquid mixing rises from below −110 kJ/(mol V_2O_5) to around −89 kJ/mol (at $X_{V_2O_5} = 0.08$). The value of −89.2 kJ/mol is equal to the limiting enthalpy of mixing of V_2O_5(l) in $K_2S_2O_7$(l) at 437°C (i.e. the sulfate-free system) found by interpolation of our previously [5] measured values at 430 and 450°C. Thus, it seems that at low mole fractions, V_2O_5 dissolves to form the dimer anion $(VO)_2O(SO_4)_4{}^{4-}$ (Eq. (2)) which at the large excess of sulfate ($X_{K_2SO_4} = 0.04249$ at 430°C in the $K_2S_2O_7$–K_2SO_4(sat) system [11]) reacts to form the monomeric sulfate complex $VO_2(SO_4)_2{}^{3-}$ (Eq. (3)). By further addition of V_2O_5, sulfate is consumed due to Eq. (3), whereby the solvent approaches the properties of the pure molten $K_2S_2O_7$ and the partial enthalpy of mixing approaches the value expected for mixing of V_2O_5(l) with $K_2S_2O_7$(l), i.e. −89.2 kJ/mol. The equilibrium constant, K, for Eq. (3) has previously [10] been found to be 3.53 based on our potentiometric measurements at 450°C. Applying this constant on the data in Fig. 2 and calculating the densities of the molten mixtures as described earlier [10], the molar concentrations of the two species, $(VO)_2O(SO_4)_4{}^{4-}$ and $VO_2(SO_4)_2{}^{3-}$, can be calculated in the whole composition range $X_{V_2O_5} = 0$–0.1. Then, using the value of −89.2 kJ/mol for the enthalpy of formation of $(VO)_2O(SO_4)_4{}^{4-}$, (Eq. (2)), the liquid–liquid enthalpy of formation of $VO_2(SO_4)_2{}^{3-}$ according to the reaction

$$V_2O_5 + S_2O_7{}^{2-} + 2SO_4{}^{2-} \rightarrow 2VO_2(SO_4)_2{}^{3-} \qquad (4)$$

can be calculated by an iterative procedure (least squares fit to the data shown in Fig. 2). A very good agreement between calculated and measured partial enthalpies is seen by the curve displayed in Fig. 2, obtained for a value of -62 ± 6 kJ/mol for the formation of $VO_2(SO_4)_2{}^{3-}$.

The measurements of two series of additions of V_2O_5 to the molten $Cs_2S_2O_7$–Cs_2SO_4(sat) system at 465 and 477°C are given in Fig. 3. As for the K-system a gradually increase (from around −114 to −89 kJ/mol) in the partial enthalpy of liquid–liquid mixing is observed by increase of $X_{V_2O_5}$ (three measurements of around −60 kJ/mol at very low $X_{V_2O_5}$ have been considered in error and are omitted). As for the K-system the partial enthalpy of liquid–liquid mixing of −89.1 kJ/mol at high $X_{V_2O_5}$ is equal to the value found previously [6] for the sulfate-free $Cs_2S_2O_7$–V_2O_5 system at 470°C. Both the recent potentiometric work [10] and the present very similar values for the partial enthalpies of mixing found here for both the K- and the Cs-system indicates strongly that the same complex reactions, i.e. Eqs. (2)–(4), are present. Applying the equilibrium constant of $K = 2.88$ for Eq. (3) and the density calculations outlined in [10] together with the previously [6] measured mole fraction $X_{Cs_2SO_4} = 0.06844$ for the molten system $Cs_2S_2O_7$–Cs_2SO_4(sat) at 470°C, the concentration of the

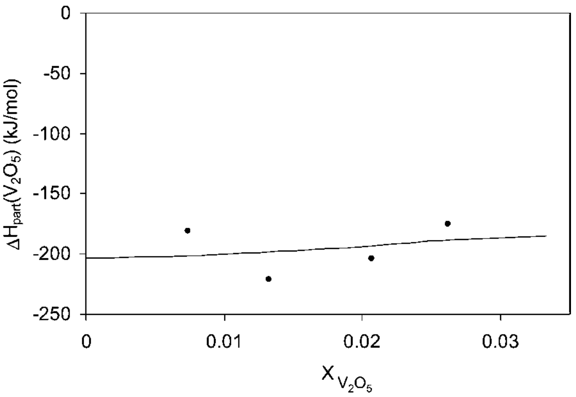

Fig. 4. Partial enthalpy of liquid–liquid mixing for the ternary (or pseudo-binary) system $K_2S_2O_7$–K_2SO_4(sat)–V_2O_5 in SO_2 (1 atm) at 437°C.

complex species $(VO)_2O(SO_4)_4^{4-}$ and $VO_2(SO_4)_2^{3-}$ can be calculated for $X_{V_2O_5} = 0$–0.1. Then, using the previously [6] measured value of −89.1 kJ/mol for the liquid–liquid enthalpy of formation of $(VO)_2O(SO_4)_4^{4-}$ (Eq. (2)), the enthalpy of formation of $VO_2(SO_4)_2^{3-}$, (Eq. (4)), that makes the best (least squares) fit to the measured enthalpies (curve in Fig. 3), can be calculated to be -83 ± 6 kJ/mol.

4.2. $M_2S_2O_7$–M_2SO_4(sat)–V_2O_5/SO_2 (1 atm) (M = K and Cs)

Four additions of V_2O_5 by the direct drop method were done to the liquid–gas system $K_2S_2O_7$–K_2SO_4(sat)/SO_2 (1 atm) at 437°C. A strong exothermic reaction was observed as indicated by the very high negative experimental enthalpies of mixing given in Fig. 4. By previous potentiometric and spectrophotometric investigations [10] it was shown that V(V) is almost completely reduced (97%) in this system to two monomeric V(IV) complexes expressed by the equilibrium

$$VO(SO_4)_2^{2-} + SO_4^{2-} \rightleftarrows VO(SO_4)_3^{4-} \qquad (5)$$

with the equilibrium constant $K = 12.76$ at 430°C.

Thus, essentially the following two reactions take place at low sulfate concentration (SO_3 is probably solvated by $S_2O_7^{2-}$ to form $S_3O_{10}^{2-}$)

$$V_2O_5 + 2S_2O_7^{2-} + SO_2 \rightleftarrows 2VO(SO_4)_2^{2-} + SO_3 \qquad (6)$$

and at high sulfate concentration, respectively.

$$V_2O_5 + S_2O_7^{2-} + 3SO_4^{2-} + SO_2 \rightleftarrows 2VO(SO_4)_3^{4-} \qquad (7)$$

As in the systems without SO_2 we have fitted the data in Fig. 4 to the distribution of the two monomeric V(IV) complexes in the investigated mole fraction range $X_{V_2O_5} = 0$–0.026, calculated from the equilibrium constant and the density as outlined in [10]. By this procedure the best fit (curve in Fig. 4) was found for -90 ± 10 kJ/mol for the formation of $VO(SO_4)_2^{2-}$ (Eq. (6)) and -104 ± 10 kJ/mol for $VO(SO_4)_3^{4-}$ (Eq. (7)), respectively, taking into account the correction (3%) for the complete reduction to V(IV). By the indirect drop method we have measured around −180 kJ/mol for $\Delta H_{part}(V_2O_5)$ in the same system, but with a crystalline precipitate of K_2SO_4 in the cell. This value is, therefore, lower than found in Fig. 4 due to the slow endothermic dissolution process of K_2SO_4(s) going on during the experiment. By these measurements we also note very high negative scattered values in the range −200 to −350 kJ/mol by additions of V_2O_5 above $X_{V_2O_5}$ around 0.08. This is most probably due to precipitation of V(IV) and/or V(III) salts like $K_4(VO)_3(SO_4)_5$ and $KV(SO_4)_2$, respectively, as found earlier [7,8] in this type of systems. This leads to the liberation of the usually large enthalpy of crystallization in addition to the heat of liquid–liquid mixing observed.

Also to the $Cs_2S_2O_7$–Cs_2SO_4(sat)/SO_2(1 atm) system at 477°C four additions of V_2O_5 were made by the direct drop method, and the obtained partial enthalpies of mixing, $\Delta H_{part}(V_2O_5)$, are displayed in Fig. 5. In this case too, based on the equilibrium constant for Eq. (5), $K = 7.01$ and the density of the system [10], a least squares fit to the data in Fig. 5 could be made. Thus, the best fit (curve in Fig. 5) was found for -88 ± 4 kJ/mol for the formation of $VO(SO_4)_2^{2-}$ (Eq. (6)) and -114 ± 4 kJ/mol for $VO(SO_4)_3^{4-}$ (Eq. (7)), assuming the same degree of reduction (97%) as for the M = K system. In summary the most probable reactions and their molar enthalpies are given in Table 1.

From the enthalpies given in Table 1 we can now combine the reactions, e.g. to obtain the reaction enthalpy for the V(V) oxo sulfato complex formation:

$$(VO)_2O(SO_4)_4^{4-} + 2SO_4^{2-} \rightarrow 2VO_2(SO_4)_2^{3-} + S_2O_7^{2-} \qquad (8)$$

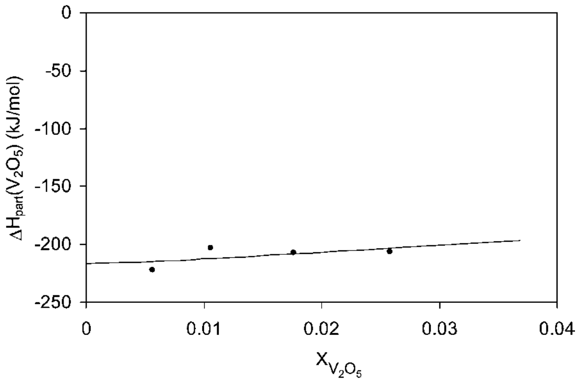

Fig. 5. Partial enthalpy of liquid–liquid mixing for the ternary (or pseudo-binary) system $Cs_2S_2O_7$–Cs_2SO_4(sat)–V_2O_5 in SO_2 (1 atm) at 477°C.

for which the enthalpies are $\Delta H = -124 - (-89.2) = -35 \pm 12$ kJ/mol (M = K, 430°C) and $\Delta H = -166 - (-89.1) = -77 \pm 12$ kJ/mol (M = Cs, 470°C). Similarly, we find for the V(IV) oxo sulfato complex reaction:

$$2VO(SO_4)_2^{2-} + 3SO_4^{2-} + SO_3 \rightarrow 2VO(SO_4)_3^{4-} + S_2O_7^{2-} \quad (9)$$

$\Delta H = -208 - (-180) = -28 \pm 28$ kJ/mol (M = K, 430°C) and $\Delta H = -228 - (-176) = -52 \pm 10$ kJ/mol (M = Cs, 470°C). It is now possible to calculate the enthalpy of the V(IV)–V(V) redox reaction:

$$2VO_2(SO_4)_2^{3-} + SO_4^{2-} + SO_2 \rightarrow 2VO(SO_4)_3^{4-} \quad (10)$$

to be $\Delta H = -208 - (-124) = -84 \pm 23$ kJ/mol (M = K, 430°C) and $\Delta H = -228 - (-166) = -62 \pm 10$ kJ/mol (M = Cs, 470°C). For the V(V)–V(IV) redox reaction (SO_3 is probably solvated by $S_2O_7^{2-}$ to form $S_3O_{10}^{2-}$):

$$(VO)_2O(SO_4)_4^{4-} + SO_2 \rightarrow 2VO(SO_4)_2^{2-} + SO_3 \quad (11)$$

we find $\Delta H = -180 - (-89.2) = -91 \pm 20$ kJ/mol (M = K, 430°C) and $\Delta H = -176 - (-89.1) = -87 \pm 7$ kJ/mol (M = Cs, 470°C).

4.3. Spectrophotometric measurements

The above-mentioned values for the enthalpies of the V(V)–V(IV) redox reactions can be compared to those found from spectrophotometric measurements. For the $M_2S_2O_7$–M_2SO_4(sat)–V_2O_5/SO_2(g) system, where M = 20% Na + 80% K reflects the composition of a widely used SO_2 oxidation catalyst [15], five series of UV–VIS spectra have been obtained [10,16] in the temperature range 430–460°C. The series at 430°C is shown as an example in Fig. 6, where the isosbestic point clearly indicates a two species redox equilibrium like Eq. (10). By systematic variation of the equilibrium constant for Eq. (10) and using the experimental molar absorptivities at 730 nm (Fig. 6) and the information given under General Considerations, optimal values of $\varepsilon_{V(IV)} = 18.89$ and $K = 3.2 \times 10^3$ were found. Similar calculations for the other series [10,16] gave five values of the equilibrium constant K in the range 430–460°C. From the rather scattered variation of K versus $1/T$ the enthalpy of Eq. (10) was obtained to be in the wide range 120–340 kJ/mol, but the lower limit is not far from -84 ± 23 kJ/mol found for the calorimetric measurements at 430°C in the present work on the M = K system.

For the previous [9] spectrophotometric measurements performed on the melt–gas system $K_2S_2O_7$–

Table 1
Possible reactions and reaction enthalpies of the molten system $M_2S_2O_7$–V_2O_5 and $M_2S_2O_7$–M_2SO_4(sat)–V_2O_5 (M = K and Cs) in Ar or SO_2 gas atmospheres[a]

Liquid–liquid reaction	K (kJ/mol)	Cs (kJ/mol)
$V_2O_5 + 2S_2O_7^{2-} \rightarrow (VO)_2O(SO_4)_4^{4-}$	−89.2 ± 1	−89.1 ± 1
$V_2O_5 + S_2O_7^{2-} + 2SO_4^{2-} \rightarrow 2VO_2(SO_4)_2^{3-}$	−124 ± 12	−166 ± 12
$V_2O_5 + 2S_2O_7^{2-} + SO_2 \rightleftarrows 2VO(SO_4)_2^{2-} + SO_3$	−180 ± 20	−176 ± 7
$V_2O_5 + S_2O_7^{2-} + 3SO_4^{2-} + SO_2 \rightleftarrows 2VO(SO_4)_3^{4-}$	−208 ± 20	−228 ± 7

[a] Reaction temperatures: 430°C (K) and 470°C (Cs); pressure: 1 atm.

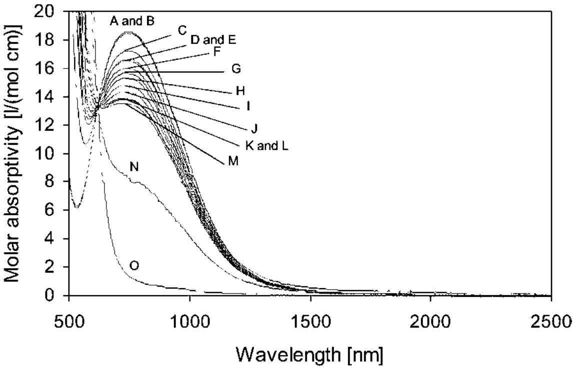

Fig. 6. VIS–NIR spectra of the mixture $M_2S_2O_7$ ($M = 20\%$ Na + 80% K)–K_2SO_4(sat)–V_2O_5/SO_2(g) at 430°C, $C^0_{V(V)} = 0.2$ M (i.e. $X_{V_2O_5} = 0.012$), equilibrated at different partial pressures (atm): A, 1.72; B, 1.54; C, 0.0805; D, 0.0368; E, 0.0287; F, 0.0188; G, 0.0227; H, 0.0150; I, 0.0106; J, 0.0069; K, 0.0051; L, 0.0055; M, 0.0041; N, <0.004; O, 0 (1.5 atm O_2).

$V_2O_5/SO_2(g)–SO_3(g)–N_2(g)$ at four different temperatures in the range 435–480°C the reaction expressed by Eq. (11) was fitted to the spectra. From the obtained values of the equilibrium constants for Eq. (11) versus $1/T$ a reaction enthalpy of -107 ± 4 kJ/mol could be calculated [9]. This value fits well with -91 ± 20 kJ/mol found by the present calorimetric measurements.

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