

## The Acidic and Basic Properties of Oxides

### II. The Thermal Decomposition of Pyrosulphates

H. FLOOD and T. FÖRLAND

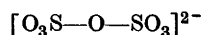
*Institutt for Uorganisk Kjemi, Norges Tekniske Högskole, Trondheim, Norway*

In a previous communication <sup>1</sup> dealing with the acid-base properties of the oxides, the influence of the cations on the oxygen bridges of the polyacids was discussed.

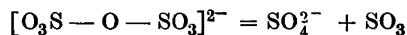
It was stated as a general rule that the stability of the oxygen bridges decreases with increasing polarizing power of the cation.

A particularly simple type of reaction which clearly demonstrates this rule is the thermal decomposition of pyrosulphates.

In the pyrosulphate ion two SO<sub>3</sub>-groups are connected by a single oxygen bridge



and the thermal decomposition consists in a breaking of the bridge



An account will now be given of some experimental investigations concerning the influence of the cations on the decomposition equilibrium.

The data on pyrosulphates in the literature are rather scarce.

Weber <sup>2</sup> prepared the pyrosulphates of Na, K, Rb, Cs, Ag and Tl. The pyrosulphates of Na and Ag are obtained directly by heating the sulphate with SO<sub>3</sub> in sealed tubes at 100—150° C. By heating K, Rb, Cs and Tl-sulphates with SO<sub>3</sub> to 100° C, compounds were formed to which were ascribed the formula Me<sub>2</sub>O · 8SO<sub>3</sub>. By heating these compounds further, the normal pyrosulphates were formed.

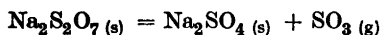
Baumgarten and Thilo <sup>3</sup> have also prepared a tripyrosulphate K<sub>3</sub>S<sub>3</sub>O<sub>10</sub>, which is stable in SO<sub>3</sub>-atmosphere in the interval 100—150° C.

The data on the thermal decomposition of the pyrosulphates are mainly of a qualitative nature. It is stated that they decompose at temperatures of about red heat.

The equilibrium data of Ishikawa, Masuda and Hagusawa<sup>4</sup> for the reaction



should permit a computation of the change in free energy and the heat of reaction for the decomposition



We find

$$\begin{aligned} \Delta F_{298} &= 20.0 \text{ kcal} \\ \Delta H &= 30.5 \text{ kcal} \end{aligned}$$

For the reaction

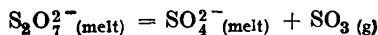


Berthelot's calorimetric measurements<sup>5</sup> give, however, the value

$$\Delta H = 37,900 \text{ kcal}$$

#### EXPERIMENTS

For the reaction



we have

$$K = \frac{a_{\text{SO}_4^{2-}} P_{\text{SO}_3}}{a_{\text{S}_2\text{O}_7^{2-}}}$$

Values of

$$K' = \frac{N_{\text{SO}_4^{2-}} P_{\text{SO}_3}}{N_{\text{S}_2\text{O}_7^{2-}}}$$

( $N$  = mole fraction) are found by determining the ratio  $N_{\text{SO}_4^{2-}}/N_{\text{S}_2\text{O}_7^{2-}}$  in melts in equilibrium with a known  $\text{SO}_3$ -tension.

The composition of the melt was found by a simple gravimetric method. Starting with a weighed charge of known composition (preferably pure sulphate), the amount of  $\text{SO}_3$  expelled or absorbed during adjustment of the equilibrium could be determined by weighing after quick cooling.

During the experiments  $\text{SO}_3$ -gas of 1 atm was conveyed upwards through a vertical furnace past a platinum crucible containing the weighed sulphate-pyrosulphate charge (Fig. 1). As the experiments were carried out at temperatures where  $\text{SO}_3$  is partly decomposed, it must be secured that the decomposition

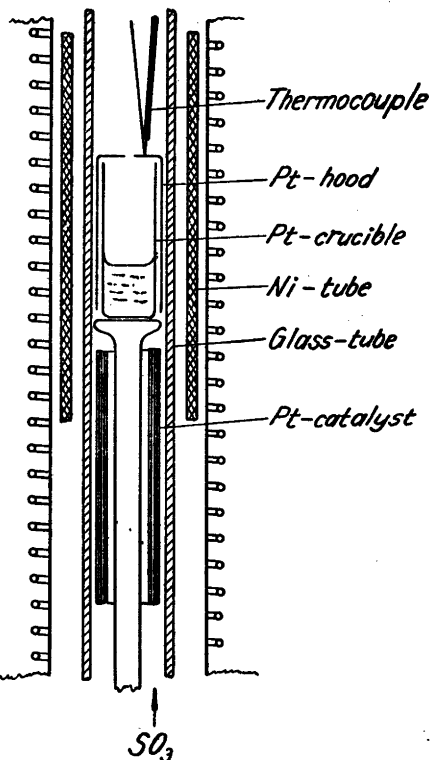
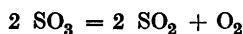


Fig. 1. Apparatus.



is carried to completion. A platinum catalyst was therefore placed in the heating zone immediately beneath the platinum crucible, which was moreover placed under a platinum hood. The flow velocity of  $\text{SO}_3$  was kept low. In calculating the  $\text{SO}_3$ -tension the well known data of Bodenstein and Pohl, Tayler and Lehner, Kapustinsky and Shamovsky were used<sup>6, 7, 8</sup>.

Our investigations included the decomposition equilibria for Li, Na, K, Ag and Tl-pyrosulphates. Moreover, a few experiments were carried out in which  $\text{Na}_2\text{SO}_4$ ,  $\text{Li}_2\text{SO}_4$  and  $\text{PbSO}_4$  were added to the K-system. The results of the former experiments are given in Table 1.

By plotting  $\log K'$  against  $1/T$  we get straight lines within the limits of error. Hence, if the melts may be regarded as ideal mixtures, the slope would represent the heats of decomposition of the pyrosulphates. This assumption is, however, presumably not permissible, and

$$R \frac{d \log K'}{d 1/T}$$

Table 1. The equilibrium between  $SO_3$  gas and sulphat-pyrosulphate melts.

System	$t^\circ C$	mol % $Me_2S_2O_7$	$P_{SO_3(atm)}$	$\log K'$
$Ag_2SO_4$ — $Ag_2S_2O_7$	347	97.72	1	— 1.63
»	395	91.43	1	— 1.03
»	423	82.21	1	— 0.66
»	442	67.05	0.95	— 0.33
»	491	48.93	0.89	— 0.03
$Li_2SO_4$ — $Li_2S_2O_7$	371	99.24	1	— 2.12
»	401	96.85	1	— 1.49
»	417	96.63	1	— 1.46
»	427	94.58	1	— 1.24
$Tl_2SO_4$ — $Tl_2S_2O_7$	554	96.01	0.80	— 1.48
»	585	89.80	0.72	— 1.09
»	623	76.14	0.65	— 0.69
»	661	59.75	0.53	— 0.45
$Na_2SO_4$ — $Na_2S_2O_7$	555	96.10	0.79	— 1.50
»	582	90.61	0.73	— 1.11
»	603	87.28	0.68	— 1.01
»	618	81.62	0.63	— 0.85
»	635	73.33	0.60	— 0.67
»	645	64.80	0.56	— 0.52
»	655	59.39	0.55	— 0.43
$K_2SO_4$ — $K_2S_2O_7$	653	98.77	0.56	— 2.16
»	669	98.26	0.503	— 2.05
»	698	95.76	0.430	— 1.72
»	727	92.12	0.366	— 1.50

may therefore only be taken as a rough measure for  $\Delta H$

[Li	32] kcal
Na	40 »
K	40 »
Ag	26 »
Tl	38 »

The value for Na differs remarkably from the value computed from the data of Ishikawa, Masuda and Hagiwara (30.5 kcal). The value for K however agrees with Berthelot's calorimetric measurement (37.9 kcal).

The experiments with addition of  $Li_2SO_4$ ,  $Na_2SO_4$  and  $PbSO_4$  to  $K_2S_2O_7$ .  $K_2SO_4$  were carried out at different temperatures, *viz* 662—87° C, corresponding to an original equilibrium ratio  $N_{SO_3}/N_{S_2O_7} = 0.015$ —30, and at 779° C,

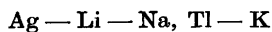
Table 2. The effect of  $\text{Na}^+$ ,  $\text{Li}^+$  or  $\text{Pb}^{2+}$  on the equilibrium between  $\text{SO}_3$  gas and melts of  $\text{K}_2\text{SO}_4$ — $\text{K}_2\text{S}_2\text{O}_7$ .

System	Mol % $\text{Li}^+$ $\text{Na}^+$ , $\text{Pb}^{2+}/2$	$t^\circ\text{C}$	$N_{\text{SO}_4^{2-}} = \frac{N_{\text{SO}_4^{2-}}}{N_{\text{SO}_4^{2-}} + N_{\text{S}_2\text{O}_7^{2-}}}$
$\text{Na}^+ - \text{K}^+ - \text{SO}_4^{2-} - \text{S}_2\text{O}_7^{2-}$	0	662	1.5
»	7.1	»	2.6
»	17.0	»	6.7
$\text{Li}^+ - \text{K}^+ - \text{SO}_4^{2-} - \text{S}_2\text{O}_7^{2-}$	0	687	2.9
»	12.3	»	11.6
»	18.1	»	18.2
»	28.0	»	26.2
»	0	779	25.0
»	9.8	»	36.6
»	17.0	»	56.0
»	23.4	»	71.7
$\text{Pb}^{2+} - \text{K}^+ - \text{SO}_4^{2-} - \text{S}_2\text{O}_7^{2-}$	0	687	2.9
»	3.1	»	7.3
»	8.4	»	18.9

corresponding to an original equilibrium ratio  $N_{\text{SO}_4^{2-}}/N_{\text{S}_2\text{O}_7^{2-}} = 0.3$ . The results of these experiments are shown in Table 2.

#### DISCUSSION

In Fig. 2  $\log K'$  is plotted against  $T$ . It appears from the curve that the stability of the pyrosulphates increases strongly in the order



For the inert gas ions the stability increases with the radius of the cation ( $\text{Li} - \text{Na} - \text{K}$ ). The pyrosulphates of  $\text{Ag}$  and  $\text{Tl}$  show, however, that this is not the only factor of importance.  $\text{Ag}_2\text{S}_2\text{O}_7$  is far more easily decomposed than  $\text{Na}_2\text{S}_2\text{O}_7$ , and similarly  $\text{Tl}_2\text{S}_2\text{O}_7$  decomposes more easily than  $\text{K}_2\text{S}_2\text{O}_7$ , despite the fact that the inert gas ions in both cases have the smaller ionic radii. Hence it seems that the polarizing power of the cation is an important factor determining the stability of the oxygen bridge of the pyrosulphate ion. As is well known, the polarizing power is stronger for ions with 18 or 20 outer electrons than for ions with inert gas configuration (octet) of the same radius.

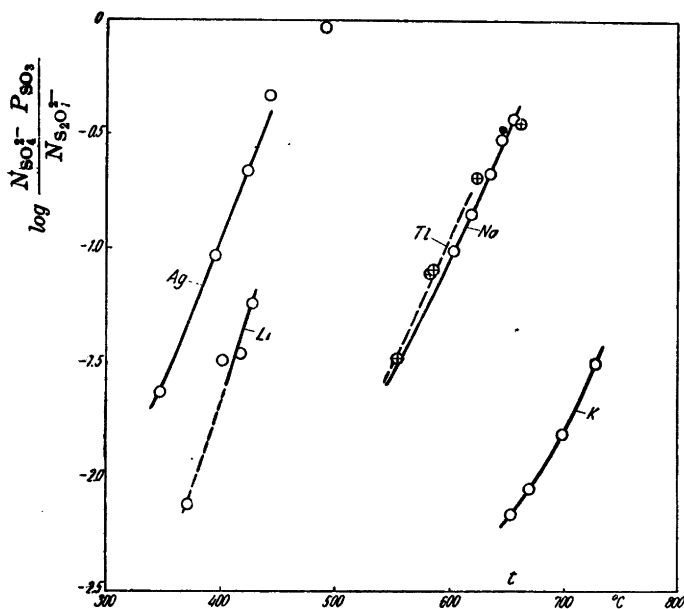


Fig. 2. The variation of  $\log K'$  with the temperature.

The preparation of Li-pyrosulphate does not seem to be mentioned in the literature previously. It is, however, readily formed by sulphate in  $\text{SO}_3$ -atmosphere at temperatures approaching  $300^\circ\text{C}$ , and may after cooling be kept unchanged in dry air.

As mentioned above some experiments were carried out in which  $\text{Na}_2\text{SO}_4$ ,  $\text{Li}_2\text{SO}_4$  and  $\text{PbSO}_4$  were added to the  $\text{K}_2\text{SO}_4$ — $\text{K}_2\text{S}_2\text{O}_7$  mixture, in order to get closer information as to the relations which determine the stability of the pyroion bridge. Fig. 3 shows how the mole fraction of sulphate at equilibrium is increased by the addition (at constant  $\text{SO}_3$ -tension and at constant temperature). It appears that an addition of Li-, Na- or  $\text{PbSO}_4$  (beyond a certain limit) causes an increase in the mole fraction of sulphate proportional to the mole fraction of the cation added. The effect increases in the order Na, Li, Pb.

This change corresponds at  $687^\circ\text{C}$  to an expulsion of approximately 0.5 mole  $\text{SO}_3$  per mole Li and approx. 2 moles  $\text{SO}_3$  per mole Pb replacing K in the melt. (At  $662^\circ\text{C}$  the corresponding expulsion by exchange of K by Na amounts to 0.2 mole  $\text{SO}_3/\text{Na}$ ). The formal explanation of this must be, that each  $\text{Li}^+$  takes hold of  $\frac{1}{2}$ , and each  $\text{Pb}^{2+}$  of 2  $\text{SO}_4^{2-}$  ions, which have to be formed by decomposition of  $\text{S}_2\text{O}_7^{2-}$  whereby  $\text{SO}_3$  is expelled. An explanation for this might be, for example, that Pb coordinates 6 oxygen ions from 2  $\text{SO}_4^{2-}$ -groups as schematically represented by

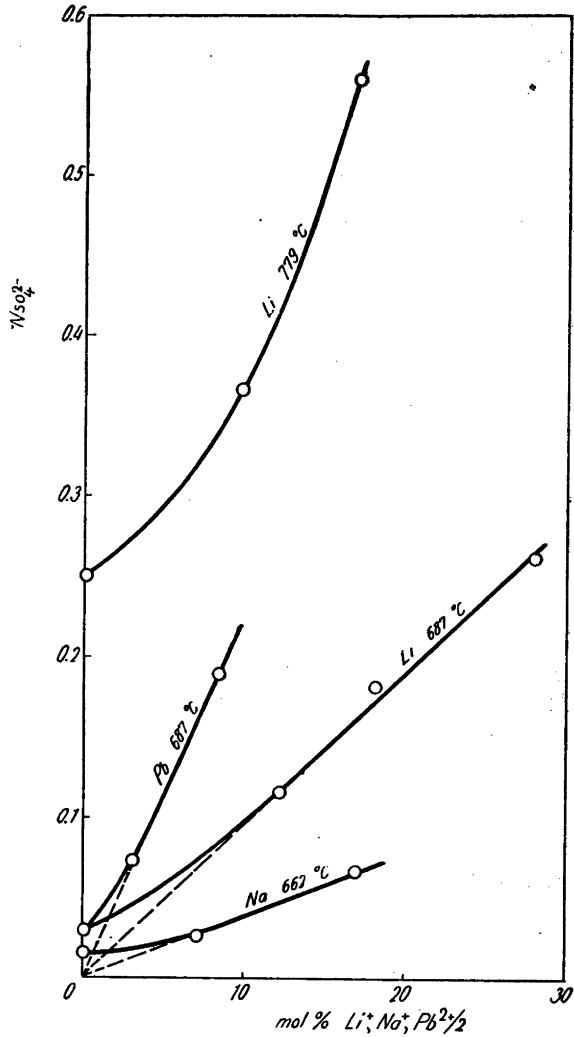
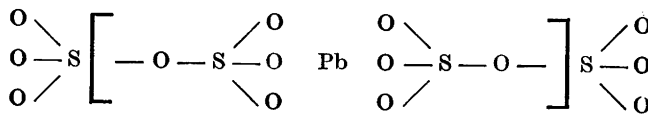


Fig. 3. The variation of the mole fraction of sulphate with addition of  $Li_2$ ,  $Na_2$ - or  $PbSO_4$  to equilibrium melts of  $K_2SO_4-K_2S_2O_7$ .



The  $SO_3$ -group is polarized to such an extent that it can no longer maintain the oxygen bridge. At temperatures a  $100^\circ$  higher ( $775-780^\circ$ ) the effect of Li is increased to ca. 1  $SO_3/Li$ . This indicates that the coordination effect of  $Li^+$  is a statistical phenomenon.

Lux and Rogler<sup>9</sup> have shown by means of the chromate indicator that the acid character of boron oxide in Na borate melts at 1100° C is strongly increased by addition of various oxides, among others Pb and Li. These effects are undoubtedly of a similar nature to those described in this paper, though their method of investigation lends itself less to quantitative conclusions. Thus it is uncertain to what extent the indicator-acid-base-equilibrium itself is influenced by the cations present. But it seems as if in their case each Pb<sup>2+</sup>-ion is able to break ca. 6 B-O-B-bridges, while each Li<sup>+</sup>-ion does not break more than 1—2 bridges. The systems concerned had a high boron oxide content, each BO<sub>3</sub>-group was sharing 2—3 oxygen bridges. Hence the primary phenomenon in this case as well appears to be that the Pb<sup>2+</sup>-ion coordinates 6 oxygen ions (*i. g.* from 2 BO<sub>3</sub>-groups which are thereby so strongly polarized that they are unable to form B-O-B-bridges).

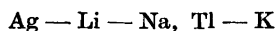
The measurements of Lux and Rogler seem to indicate that the number of bridges which are broken per cation added (additions below 20 %) decreases in the sequence Ba<sup>2+</sup> ≥ Mg<sup>2+</sup> >> Be<sup>2+</sup>. This shows clearly that the size of the cation is the decisive factor for the *number* of oxygen bridges to be broken per cation (provided the polarizing power of the cation exceeds a certain amount). The Ba<sup>2+</sup>-ion is sufficiently large to coordinate 12 oxygen ions, and should therefore be able in principle to break 12 oxygen bridges. The smaller Mg<sup>2+</sup>-ion can coordinate a maximum of 6, while the Be<sup>2+</sup>-ion is only able to coordinate 4 oxygen ions.

#### SUMMARY

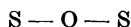
1. The equilibrium between SO<sub>4</sub><sup>2-</sup>—S<sub>2</sub>O<sub>7</sub><sup>2-</sup> melts and SO<sub>3</sub>-gas shows that the stability of the pyrosulphates on thermal decomposition according to the equation



increases in the order



This shows that the stability of the oxygen bridge



is highly influenced by the polarizing power of the cation. This effect is also examined by addition of Na<sub>2</sub>SO<sub>4</sub>, Li<sub>2</sub>SO<sub>4</sub> or PbSO<sub>4</sub> to K<sub>2</sub>SO<sub>4</sub>—K<sub>2</sub>S<sub>2</sub>O<sub>7</sub>-melts. The results are discussed.

2. The compound Li<sub>2</sub>S<sub>2</sub>O<sub>7</sub> has been prepared. It is formed by heating Li<sub>2</sub>SO<sub>4</sub> in SO<sub>3</sub>-atmosphere at temperatures below 300° C. The crystals may be kept unchanged in dry air.



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