

CATALYTIC EFFECTS OF COPPER(II) OXIDE AND ZINC(II) OXIDE ON THE THERMAL TRANSITIONS OF SODIUM AND POTASSIUM PERSULFATES

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The thermal transitions of $\text{Na}_2\text{S}_2\text{O}_8$ and $\text{K}_2\text{S}_2\text{O}_8$ have been studied by means of a derivatograph in the presence of CuO or ZnO at various molar mixtures. A slight shift in the DTG peak of the first decomposition stage (persulfate into pyrosulfate) to higher temperature was noticed as the amount of oxide increases.

The second decomposition stage (pyrosulfate into sulfate) was shown to proceed via the formation of double salts of alkali metal copper(II) sulfates and alkali metal zinc(II) sulfates, namely, $\text{Na}_2\text{Cu}(\text{SO}_4)_2$, $\text{K}_2\text{Cu}(\text{SO}_4)_2$, $\text{Na}_2\text{Zn}(\text{SO}_4)_2$ and $\text{K}_2\text{Zn}(\text{SO}_4)_2$. The reaction has a close relation to the semiconductivity of both oxides. The melting points recorded for these double salts were respectively 532, 634, 467 and 462°.

The results were confirmed by the IR spectra of the reaction products.

The double salts slowly decompose into the metal oxide, alkali metal sulfates, and sulfur trioxide.

In a study of the interaction of metal oxides with the alkali metal persulfates and their decomposition products, it was shown [1] that nickel(II) oxide catalyzes the thermal decomposition of alkali metal pyrosulfates into the sulfates, and a mechanism was proposed for this catalytic decomposition. The mechanism was based essentially on the semiconductive behaviour of this oxide and its adsorptive characteristics towards the pyrosulfate anions. Titanium (IV) oxide, on the other hand, was shown to react with the persulfates and the pyrosulfates at high temperatures, forming products of a complex nature [2].

In the present work, the derivatograph (TG, DTG and DTA) is applied to the study of the thermal behaviour of alkali metal persulfates in the presence of copper (II) oxide or zinc(II) oxide at various molar ratios within the temperature range 20–1000°. The possibility of double salt formation is also discussed.

Experimental

Materials

All the chemicals used were analytical grade $\text{Na}_2\text{S}_2\text{O}_8$ and $\text{K}_2\text{S}_2\text{O}_8$ were Hopkin and Williams AnalaR; CuO and ZnO were BDH AnalaR products.

Apparatus and methods

The present investigation comprised experiments on TG, DTG and DTA methods. The apparatus and techniques were described earlier [1].

The infrared spectra were obtained using the Pye-Unicam SP-1100 I.R. spectrophotometer. The samples were analyzed as KBr discs.

Results and discussion

$CuO + M_2S_2O_8$ mixtures

In Figs 1 and 2 the TG and DTA curves are plotted against temperature for sodium and potassium persulfates in intimate admixtures with copper(II) oxide, in oxide to persulfate molar ratios of 1 : 4, 1 : 2, 1 : 1, 2 : 1 and 4 : 1.

A slight shift in the DTG peak temperatures of the decomposition of the alkali metal persulfates to higher values is obtained with the increased proportion of the oxide in the mixture. This may be due mainly to dilution effects [3] since the persulfate decomposition reactions are second-order reactions [4, 5].

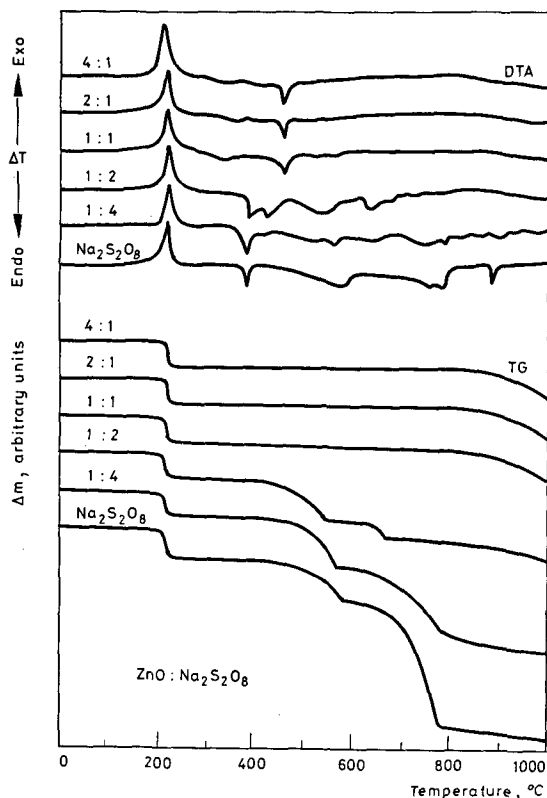


Fig. 1. TG and DTA curves of $CuO : Na_2S_2O_8$ mixtures at mole ratios 1 : 4, 1 : 2, 1 : 1, 2 : 1 and 4 : 1 respectively

The melting of the sodium and potassium pyrosulfates produced occurs in temperature ranges very close to those of the individual salts, as indicated from the DTA curves (Figs 1 and 2).

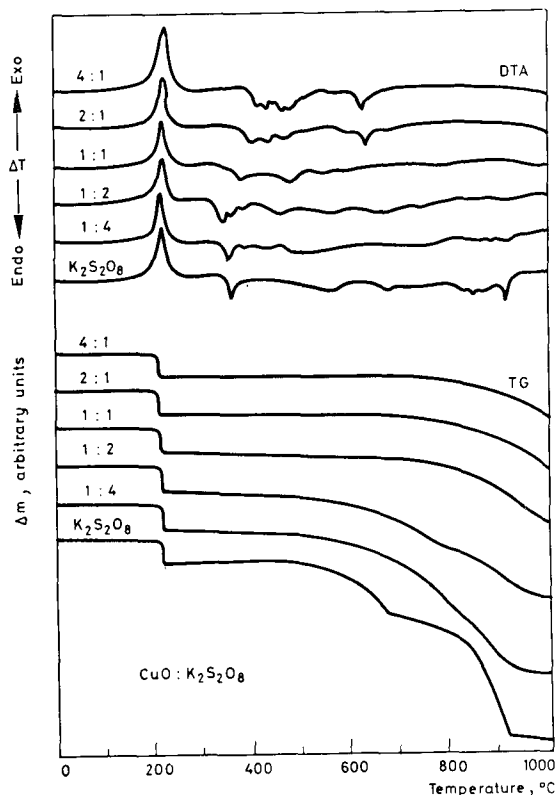
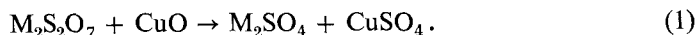


Fig. 2. TG and DTA curves of $\text{CuO} : \text{K}_2\text{S}_2\text{O}_8$ mixtures at mole ratios 1 : 4, 1 : 2, 1 : 1, 2 : 1 and 4 : 1 respectively

The DTA curves also indicate other endothermic processes following the melting for the mole ratios studied. The complication of the DTA curves is expected, since they describe the overall sum of the effects occurring in the heterogeneous equilibrated system of solid CuO , liquid $\text{M}_2\text{S}_2\text{O}_7$ and the gaseous SO_3 locally produced. The overall reaction can be expressed as follows:



This reaction, however, has a close relationship with the semiconductivity of the copper(II) oxide, since for the 1 : 1 molar ratio the TG curve (Fig. 2) shows a weight loss of about 4.0% up to a temperature of 514°. At any temperature lower

than this, CuO behaves as an insulator [6], and so part of the stoichiometric amount of the $\text{Na}_2\text{S}_2\text{O}_7$ undergoes decomposition over the range 380–514°.

In the case of $\text{K}_2\text{S}_2\text{O}_7$, the TG curve of the 1 : 1 molar ratio mixture does not show a corresponding appreciable weight loss since the potassium pyrosulfate decomposition proceeds slowly up to this temperature [4].

Equation (1) suggests that potassium sulfate may be produced as a result of such treatment. However, DTA plots (Fig. 2) do not show the endothermic peak accompanying the α – β phase transition of potassium sulfate [7], which has already been observed in a similar treatment of NiO with $\text{K}_2\text{S}_2\text{O}_7$ [1]. This indicates that K_2SO_4 is not present as such, but most likely in the form of a double salt with the copper(II) sulfate, namely, $\text{K}_2\text{Cu}(\text{SO}_4)_2$. The melting point found for this double salt is 634° (noticed in the 2 : 1 and 4 : 1 CuO : $\text{K}_2\text{S}_2\text{O}_8$ molar mixtures), in comparison with that for the corresponding sodium copper(II) sulfate, $\text{Na}_2\text{Cu}(\text{SO}_4)_2$, which is 532°. These melting points are indicated by sharp, highly-reproducible endotherms.

The IR spectra, however, confirm the latter observations, since the peaks and bands characteristic of the individual species do not show up in all of the examined reaction products. The spectrum of the 1 : 1 molar mixture of CuO : $\text{Na}_2\text{S}_2\text{O}_8$ after being heated to 600° shows the following absorption bands: 565, 607, 645, 675, 1050, 1130 and 1245 cm^{-1} . The spectrum corresponding to the 1 : 1 molar mixture of CuO : $\text{K}_2\text{S}_2\text{O}_8$ after being heated to the same temperature shows the following absorption bands: 610, 662, 990, 1060, 1135 and 1212 cm^{-1} . None of the bands in either of the two spectra correspond to CuO, CuSO_4 , Na_2SO_4 or K_2SO_4 as compared with the individual spectra [8].

The existence of the reaction products as faint blue crystals may be attributed to the coordination of the cupric ion with two bidentate sulfate groups to satisfy the tetrahedral structure. A similar product has been detected in the Li_2SO_4 (Na_2SO_4) K_2SO_4 eutectic at 600° [9].

Beyond 700° decomposition of these double salts starts, with subsequent formation of copper(II) oxide, alkali metal sulfates, and sulfur trioxide. The decomposition proceeds at a rate lower than that if there were pure copper(II) sulfate alone [10], since the process involves the splitting of the double salt into CuSO_4 and M_2SO_4 and the subsequent decomposition of the CuSO_4 into CuO and SO_3 . Moreover, the sulfur trioxide evolution requires the penetration of the gas through a thick melt, a state which causes some relaxation [11].

ZnO + $\text{M}_2\text{S}_2\text{O}_8$ mixtures

In Figs 3 and 4 the TG and DTA curves are plotted against temperature for sodium and potassium persulfates in intimate admixtures with zinc(II) oxide in oxide to persulfate molar ratios of 1 : 4, 1 : 2, 1 : 1, 2 : 1 and 4 : 1.

A similar shift in the DTG peak temperature is noted for these heated mixtures, corresponding to the persulfate decomposition, which is also due to dilution effects [3].

It has been proved that zinc(II) oxide is a semiconductor at all temperatures [6]. This effect is reflected in the behaviour of the oxide towards the molten alkali metal pyrosulfates. With increasing proportions of the oxide, the melting endotherm diminishes in relative area. This observation can be attributed to the thermoneutrality of the system due to exothermic reactions of ZnO with the molten pyrosulfates:

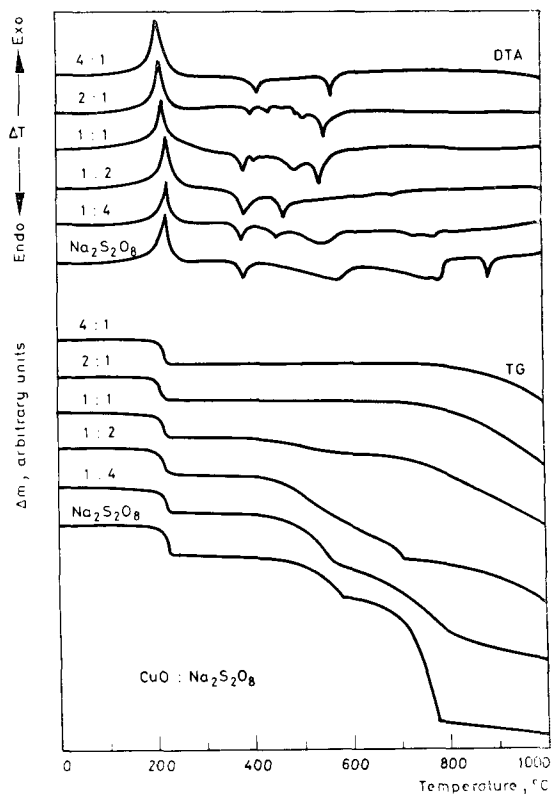


Fig. 3. TG and DTA curves of ZnO : Na₂S₂O₈ mixtures at mole ratios 1 : 4, 1 : 2, 1 : 1, 2 : 1, and 4 : 1 respectively

For the 1 : 1, 2 : 1 and 4 : 1 molar ratios the DTA curves (Figs 3 and 4) show sharp, reproducible endotherms that correspond to the melting process of the reaction products. The melting temperatures recorded are 467 and 462° for the sodium and potassium sulfate mixtures, respectively.

However, it can not be concluded from the DTA curves whether potassium sulfate is present as an individual species or a double salt with zinc(II) sulfate, because

the mixtures are present in the molten phase prior to the phase change temperature of the potassium sulfate.

Strong evidence as to the existence of the reaction products as double salts, $\text{Na}_2\text{Zn}(\text{SO}_4)_2$ and $\text{K}_2\text{Zn}(\text{SO}_4)_2$, and not as individual sulfates, is the reproducibility of the melting points for the varying compositions of the mixtures. In contrast, the individual sulfates, if present, must have a definite eutectic temperature which varies with the type of the mixture composition.

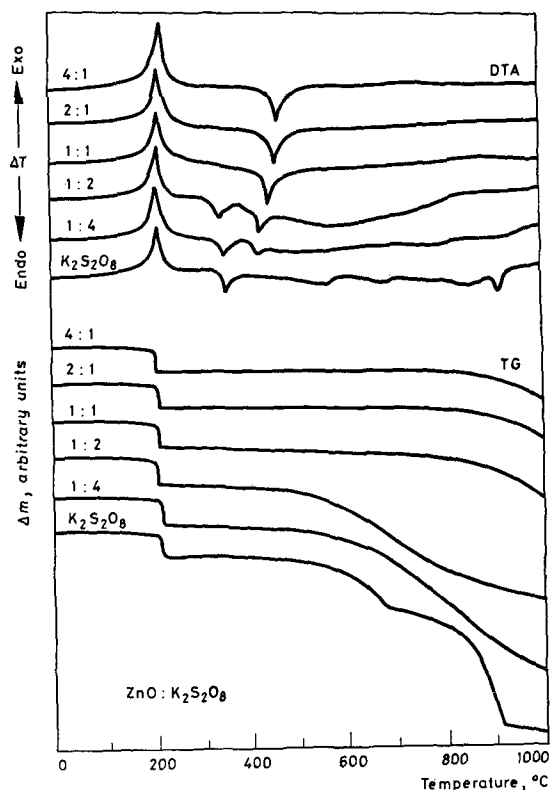


Fig. 4. TG and DTA curves of $\text{ZnO} : \text{K}_2\text{S}_2\text{O}_8$ mixtures at mole ratios 1 : 4, 1 : 2, 1 : 1, 2 : 1, and 4 : 1 respectively

However, zinc is known to form double sulfates with alkali metals, e.g. $\text{K}_2\text{Zn}_2(\text{SO}_4)_3$ [12] and $\text{Na}_2\text{Zn}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ [13], prepared under different experimental conditions. In the present investigation, a compound like $\text{K}_2\text{Zn}_2(\text{SO}_4)_3$ is not likely to be formed as a result of the reaction of ZnO with $\text{K}_2\text{S}_2\text{O}_8$, because (as indicated from the TG curves of Fig. 4) the first stoichiometric molar mixture noticed is the 1 : 1 and not the 2 : 1 ($\text{ZnO} : \text{K}_2\text{S}_2\text{O}_8$).

Again the IR spectra indicated the absence of the individual species ZnO, ZnSO₄, Na₂SO₄ and K₂SO₄, reference being made to the spectra of each substance available in the literature [8]. The absorption bands displayed by the reaction products of the ZnO and Na₂S₂O₈ 1 : 1 molar mixture after being heated to 450° are 507, 625, 662, 677, 987, 1007, 1120 and 1167 cm⁻¹. The absorption bands displayed by the ZnO : K₂S₂O₈ 1 : 1 molar mixture heated to 450° are 475, 610, 620, 645, 985, 1005, 1050, 1130 and 1175 cm⁻¹.

Similarly, the decomposition of the molten products into zinc(II) oxide, alkali metal sulfates and sulfur trioxide occurs above 830°. The decomposition reactions proceed as expected, slowly due to the reasons mentioned above.

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RÉSUMÉ — Les transitions thermiques de Na₂S₂O₈ et K₂S₂O₈ en présence de CuO et de ZnO ont été étudiées à l'aide d'un Derivatograph pour diverses compositions molaires des mélanges. L'augmentation de la teneur en oxyde provoque un faible déplacement vers les températures plus élevées du pic TGD de la première étape de décomposition (persulfate → pyrosulfate).

La deuxième étape de la décomposition (pyrosulfate → sulfate) s'effectue avec formation de sels doubles entre le sulfate du métal alcalin et le sulfate de cuivre(II) ou le sulfate de zinc(II), notamment Na₂Cu(SO₄)₂, K₂Cu(SO₄)₂, Na₂Zn(SO₄)₂ et K₂Zn(SO₄)₂. La relation est en étroit rapport avec le caractère semi-conducteur des deux oxydes. Les points de fusion enregistrés pour ces sels doubles s'élèvent respectivement à 532, 634, 467 et 462°.

Les résultats sont confirmés par les spectres d'absorption infrarouge des produits de réaction.

Les sels doubles se décomposent lentement avec formation de l'oxyde métallique, du sulfate du métal alcalin et de trioxyde de soufre.

ZUSAMMENFASSUNG — Die Wärmeübergänge von $\text{Na}_2\text{S}_2\text{O}_8$ und $\text{K}_2\text{S}_2\text{O}_8$ wurden in Gegenwart von CuO und ZnO in verschiedenen molaren Gemischen mittels eines Derivatographen untersucht. Mit steigendem Oxidanteil wurde eine kleine Verschiebung des DTG-Peaks der ersten Zersetzungsstufe (Persulfat zu Pyrosulfat) in Richtung der höheren Temperaturen beobachtet.

Es wurde gezeigt, daß die zweite Zersetzungsstufe (Pyrosulfat zu Sulfat) über die Bildung von Doppelsalzen des Alkalimetall-Kupfer(II) Sulfats und Alkalimetall-Zink(II)Sulfats, d.h. $\text{Na}_2\text{Cu}(\text{SO}_4)_2$, $\text{K}_2\text{Cu}(\text{SO}_4)_2$, $\text{Na}_2\text{Zn}(\text{SO}_4)_2$ und $\text{K}_2\text{Zn}(\text{SO}_4)_2$ verläuft. Die Reaktion ist eng mit dem Halbleiterverhalten beider Oxide verbunden. Die aufgezeichneten Schmelzpunkte dieser Doppelsalze waren in obiger Reihenfolge 532, 634, 467 und 462°.

Die Ergebnisse wurden durch IR-Spektren der Reaktionsprodukte bestätigt.

Die Doppelsalze werden langsam in Metalloxide, Alkalisulfate und Schwefeltrioxid zersetzt.

Резюме С помощью дериватографа были изучены термические переходы $\text{Na}_2\text{S}_2\text{O}_8$ и $\text{K}_2\text{S}_2\text{O}_8$ в присутствии CuO и ZnO при различных молярных соотношениях. На первой стадии разложения персульфата до пиросульфата был замечен небольшой сдвиг ДТГ пиков в сторону более высоких температур при увеличении молярного количества окислов. Показано, что вторая стадия разложения — пиросульфат до сульфата протекает через образование двойных солей сульфатов щелочной металл — медь(II) и щелочной металл — цинк(II), а именно: $\text{Na}_2\text{Cu}(\text{SO}_4)_2$, $\text{K}_2\text{Cu}(\text{SO}_4)_2$, $\text{Na}_2\text{Zn}(\text{SO}_4)_2$ и $\text{K}_2\text{Zn}(\text{SO}_4)_2$. Измеренные температуры плавления этих двойных солей соответственно были равны 532, 634, 467 и 462°. Результаты были подтверждены инфракрасными спектрами продуктов реакции. Двойные соли медленно разлагаются на окись металла, сульфаты щелочных металлов и трехокись серы.