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THERMAL DECOMPOSITION OF IRON(II) SULPHATE IN AIR. IV

HEATS OF REACTION AND HEATS OF FORMATION

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Heats of decomposition and formation of various hydrates of iron(II) sulphate have been presented and discussed. The heat of dehydration of the monohydrate calculated from the DTA curves (50.2 kJ/mole) appears to be lower than the expected value. The value calculated from the heats of formation (79.4 kJ/mole) is therefore taken as the more accurate value.

In our previous communications, we presented our results for the thermal decomposition of iron(II) sulphate heptahydrate [1] and other hydrates of iron(II) sulphate [2]. It was observed that the thermal decomposition of iron(II) sulphate hydrates proceeds in a stepwise fashion, with considerable oxidation to oxysulphate directly or through hydroxy sulphate, depending on the experimental conditions. The oxysulphate thus formed decomposes to iron(III) oxide and sulphur oxides either directly or through intermediate iron(III) sulphate. In this communication we present our results on some thermochemical aspects of the decomposition processes.

Experimental

Materials: Iron(II) sulphate heptahydrate and other hydrates were prepared by the procedures described earlier [2, 3].

Apparatus: As described in our previous communication [1].

Methods: The DTA peak areas were used to calculate the heats of reactions. The heat of fusion of sodium nitrate and the heat of decomposition of calcium carbonate were used for the calibration of the apparatus. For this purpose, the area under a peak was traced on high quality tracing paper, and the portion representing the area was cut out carefully and weighed. The accuracy expected from the DTA method is estimated to be about $\pm 20-40$ kJ. From the heats of reactions, the heats of formation of the various hydrates were calculated. In calculating the heats of formation, it is assumed that the ΔH value calculated from the DTA curves holds approximately at 298 K.

Results and discussion

The heats of dehydration of the various hydrates of iron(II) sulphate are given in Table 1. The heats of decomposition of the various hydrates to sulphur oxides,

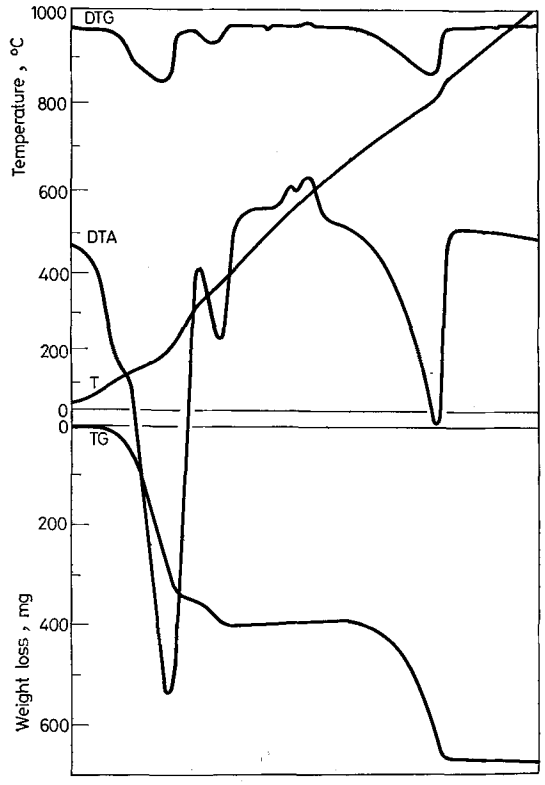

Fig. 1. TG, DTG and DTA curves of $FeSO_4 \cdot 7\,H_2O$ in air

Table 1

Heats of dehydration of iron(II) sulphate hydrates to anhydrous iron(II) sulphate

Dehydration reaction	Heat of dehydration ΔH, kJ/mole	Heat of dehydration per mol of water, kJ
$FeSO_4 \cdot 7\,H_2O = FeSO_4 + 7\,H_2O$	443.1* (397)	63
$FeSO_4 \cdot 6\,H_2O = FeSO_4 + 6\,H_2O$	364	63
$FeSO_4 \cdot 5\,H_2O = FeSO_4 + 5\,H_2O$	309	63
$FeSO_4 \cdot 4\,H_2O = FeSO_4 + 4\,H_2O$	251	63
$FeSO_4 \cdot 3\,H_2O = FeSO_4 + 3\,H_2O$	175	58.5
$FeSO_4 \cdot 2\,H_2O = FeSO_4 + 2\,H_2O$	121	63
$FeSO_4 \cdot H_2O = FeSO_4 + H_2O$	50.2 (79.4)*	50.2

* Literature values [4].

together with their heats of formation, are presented in Table 2. In calculation of the heats of decomposition, the endothermic peak following the exothermic one (see Figs 1 and 2) was taken into consideration.

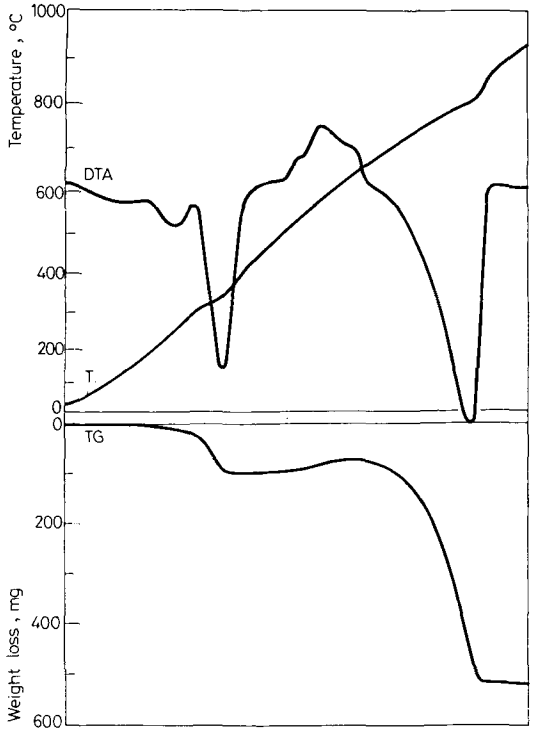

Fig. 2. TG, DTG and DTA curves of $FeSO_4 \cdot H_2O$ in air

Table 2

Heats of decomposition of iron(II) sulphate hydrates to sulphur oxides, and heats of formation

Hydrate	Heat of decomposition, ΔH, kJ/mole of $Fe_2O(SO_4)_2$	Heat of formation, $\Delta H_{f_{298}}$, kJ/mole
$FeSO_4 \cdot 7\,H_2O$	506	−3505 (−3009.5)*
$FeSO_4 \cdot 6\,H_2O$	497	−2733
$FeSO_4 \cdot 5\,H_2O$	493	−2437
$FeSO_4 \cdot 4\,H_2O$	493	−2136
$FeSO_4 \cdot 3\,H_2O$	493	−1822
$FeSO_4 \cdot 2\,H_2O$	485	−1526
$FeSO_4 \cdot H_2O$	485	−1212 (−1240.6)*

* Literature values [4]

As can be seen from the data presented in Table 1, the heats of dehydration decrease in the decreasing order of the number of water molecules. However, the heat of dehydration per water molecule remains constant at around 63 kJ/mole, except in the case of the monohydrate, where the value appears to be low. The heats of dehydration calculated from the literature values of heats of formation have been found to be 397 and 79.4 kJ/mole, respectively, for the heptahydrate and monohydrate. From these values, the heat of dissociation per water molecule may be calculated to be 56.8 and 79.4 kJ/mole, respectively, for the hepta- and monohydrate. While the value of 56.8 kJ/mole compares favourably with the experimental value of 63 kJ/mole, the value of 79.4 kJ/mole does not compare well with the value of 50.2 kJ/mole. As it is expected that more energy is required to drive away the last water molecule, we may take the value 79.4 kJ/mole as the more accurate figure for the monohydrate.

The heats of decomposition of various hydrates to iron(III) oxide and sulphur oxides are nearly the same (cf. Table 2): 493 ± 12 kJ/mole. This is because the compound that decomposes to iron(III) oxide and sulphur oxides is the same, irrespective of the hydrate taken. It has been shown earlier [1, 2] that all hydrates give rise to an intermediate oxidation product, $Fe_2O(SO_4)_2$, which decomposes to iron(III) oxide and oxides of sulphur. The heats of decomposition obtained from the DTA study were utilised to calculated the heats of formation of various hydrates (Table 2). It can be seen that the values obtained for the monohydrate and the heptahydrate agree fairly well with the literature values. It may therefore be said that the heats of formation obtained for the other hydrates are also accurate enough.

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References

1. M. S. R. SWAMY, T. P. PRASAD and B. R. SANT, J. Thermal Anal., 16 (1979) 471.
2. M. S. R. SWAMY and T. P. PRASAD, J. Thermal Anal., 19 (1980) 297.
3. M. S. R. SWAMY, T. P. PRASAD and B. R. SANT, J. Thermal Anal., 15 (1979) 307.
4. M. KH. KARPETYANTS and M. L. KARPETYANTS, Thermodynamic constants of Inorganic and Organic compounds, Ann Arbor-Humphrey Science Publishers, Ann. Arbor, 1970.

RÉSUMÉ — On présente et discute les valeurs des chaleurs de décomposition et de formation de divers hydrates du sulfate de fer(II). La chaleur de déshydratation du monohydrate, calculée à partir des courbes d'ATD (50.2 kJ) paraît être plus faible que la valeur attendus. C'est pourquoi la valeur calculée à partir des chaleurs de formation (80.1 kJ) est considérée comme plus exacte.

ZUSAMMENFASSUNG — Die Zersetzungs- und Bildungswärmen verschiedener Hydrate der Eisen(II)sulfate wurden aufgeführt und diskutiert. Die aus den DTA-Kurven berechnete Dehydratisierungswärme (50.2 kJ) des Monohydrats scheint niedriger zu sein als der erwartete Wert. Der aus den Bildungswärmen berechnete Wert (80.1) kJ) wird deshalb als der exaktere Wert angenommen.

Резюме — Представлены и обсуждены теплоты разложения и образования различных гидратов сульфата железа(II). Очевидно, что теплота дегидратации моногидрата, вычисленная из кривых ДТА (50.2 кдж), ниже ожидаемого значения. В свяси с этим, значение теплоты, вычисленное из данных по теплотам образования, равное 79.4 кдж и принято как более точное.