SOLID STATE REACTIONS BETWEEN NICKEL(II) SULPHIDE AND OXIDES OF MANGANESE AND IRON

L. GLADMAN and F. G. BUTTLER

Department of Chemistry, Teesside Polytechnic, Middlesbrough, Cleveland, U.K.

(Received February 2, 1975)

Thermogravimetry and differential thermal analysis have shown that, when nickel(II) sulphide and manganese or iron oxides are heated together, several reactions occur depending on the molar ratio of the reactants. Detailed examinations of these reactions have shown that there are a number of intermediate stages, including the formation of sulphates.

Previous workers [1] have shown that, on heating, manganese(II) sulphide reacts with oxides of manganese to give overall reactions of the type

$$\text{SOLID} + \text{SOLID} \rightarrow \text{SOLID} + \text{GAS}$$
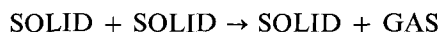
Using the basic techniques of thermogravimetry, differential thermal analysis, X-ray powder diffraction and chemical analysis, it has been possible to elucidate the reactions occurring when nickel(II) sulphide and oxides of manganese or iron are heated together, and by taking samples from the mixtures during the reactions, to study the reaction mechanisms involved.

Experimental

Reactants

(a) Manganese(IV) oxide

Samples of pyrolusite (99.5 % MnO_2) supplied by the Fisher Scientific Company Ltd were used.

(b) Manganese(III) oxide

This was prepared by heating $MnSO_4 \cdot 4H_2O$ in air at 800° for 12 hours, washing the residue with water until free from sulphate and then drying. The sample contained 99.5 % Mn_2O_3 and had the partrigetite structure.

(c) Iron(III) oxide

Samples of haematite (98.0 % Fe_2O_3) supplied by Hopkin and Williams Ltd were used.

(d) Nickel(II) sulphide

Samples of 98.9 % purity with the millerite structure were prepared, in low yield, by saturating a solution of nickel(II) chloride, at pH 3.5 [2] with hydrogen sulphide until no further precipitation occurred. The product was filtered, washed with water, ethyl alcohol and acetone and then dried. Attempts at making nickel(II) sulphide in better yield at higher pH values confirmed the results of previous workers [3] that the quality of the product deteriorated markedly.

Techniques

(a) Thermogravimetry (TG)

A Stanton massflow thermobalance was used, the balance being capable of recording an overall loss or gain in weight of 200 mg with a sensitivity of 0.1 mg. Heating rates of 200° and 400° per hour were used with a maximum temperature of 1300°. A dynamic atmosphere of nitrogen was used throughout and the exit gases were passed through a series of bubblers and the sulphur dioxide evolved titrated with 0.05 M iodine. The absorption of sulphur dioxide was found to be quite efficient and accurate determination of the volatile reaction product was therefore possible.

(b) Differential Thermal Analysis (DTA)

A Netzsch 404 DTA apparatus was used. A dynamic atmosphere of nitrogen was used and a heating rate of 600° per hour was found to give the best resolution of the reaction peaks.

(c) X-ray analysis

X-ray powder photographs were obtained using Phillips equipment and diffraction traces using Siemens equipment. Radiation from an iron target was used for the majority of the investigations.

Results and discussion

(a) *Manganese(IV) oxide — nickel(II) sulphide mixtures*

The TG results (Figs 1 and 2) showed that, depending on the molar ratio of reactants, the following reactions occur:

1. $9MnO_2 + 2NiS \rightarrow 2NiO + 3Mn_3O_4 + 2SO_2$
2. $6MnO_2 + NiS \rightarrow NiO + 2Mn_3O_4 + SO_2 + 1/2O_2$
3. $24MnO_2 + 3NiS \rightarrow 3NiO + 8Mn_3O_4 + 3SO_2 + 7/2O_2$*

* [Note: The molar ratios referred to in the text as (9 : 2) etc. are such that they represent nine moles of manganese(IV) oxide to two moles of nickel(II) sulphide. The numbering of the equations refers to the list of equations given in Table 1.]
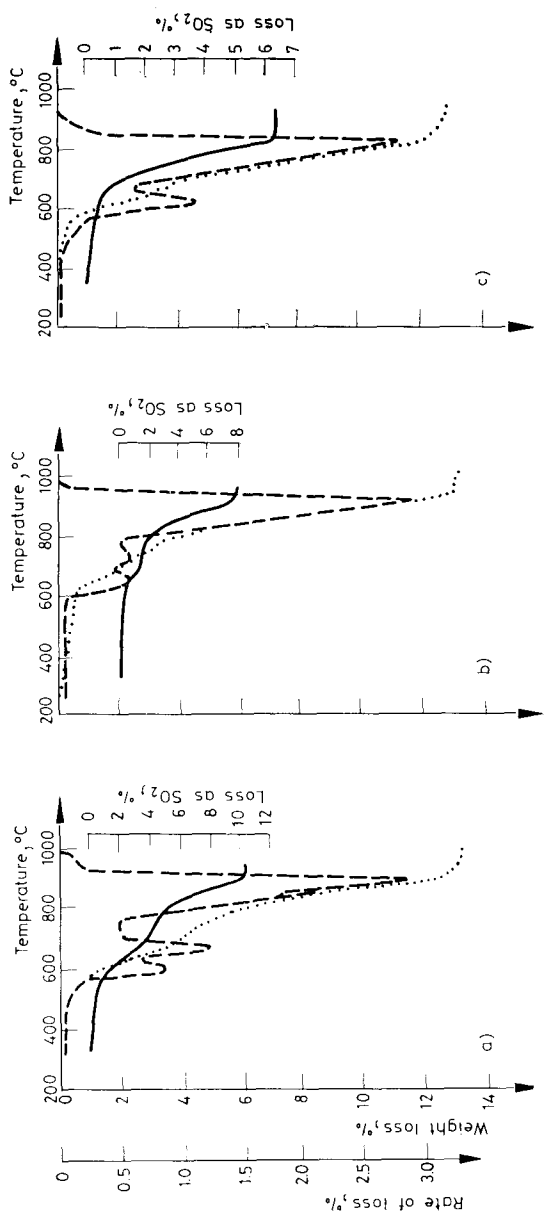
Fig. 1. TG of a mixture of manganese(IV) oxide and nickel(II) sulphide under nitrogen. a) Ratio (6 : 1), b) ratio (8 : 1), c) ratio (10 : 1). ———— % loss as SO_2, ... % weight loss, – – – – % rate of loss
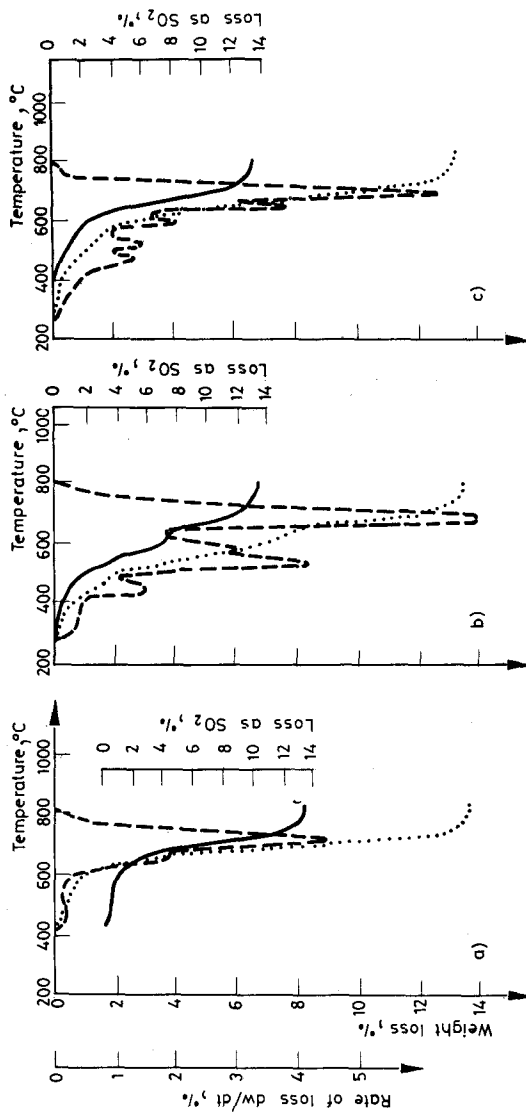
Fig. 2. TG of a mixture of manganese(IV) oxide and nickel(II) sulphide under nitrogen. Molar ratio: (9 : 2). a) heating rate 400° · hour^{-1}; b) heating rate 200° · hour^{-1}; c) heating rate 100° · hour^{-1}. ○——— % loss as SO$_2$, ... % weight loss, ------ rate of loss

For a given molar ratio of reactants the TG curve obtained changed as the heating rate was altered. For the (9 : 2) ratio, the one maximum observed in the rate graph at 400° hour^{-1} became several maxima as the heating rate was decreased. Likewise, as the molar ratio was increased for a given heating rate, there was a similar effect. The DTA results (Fig. 3) confirmed that there were a number of intermediate reactions, some exothermic and others endothermic, involved in the
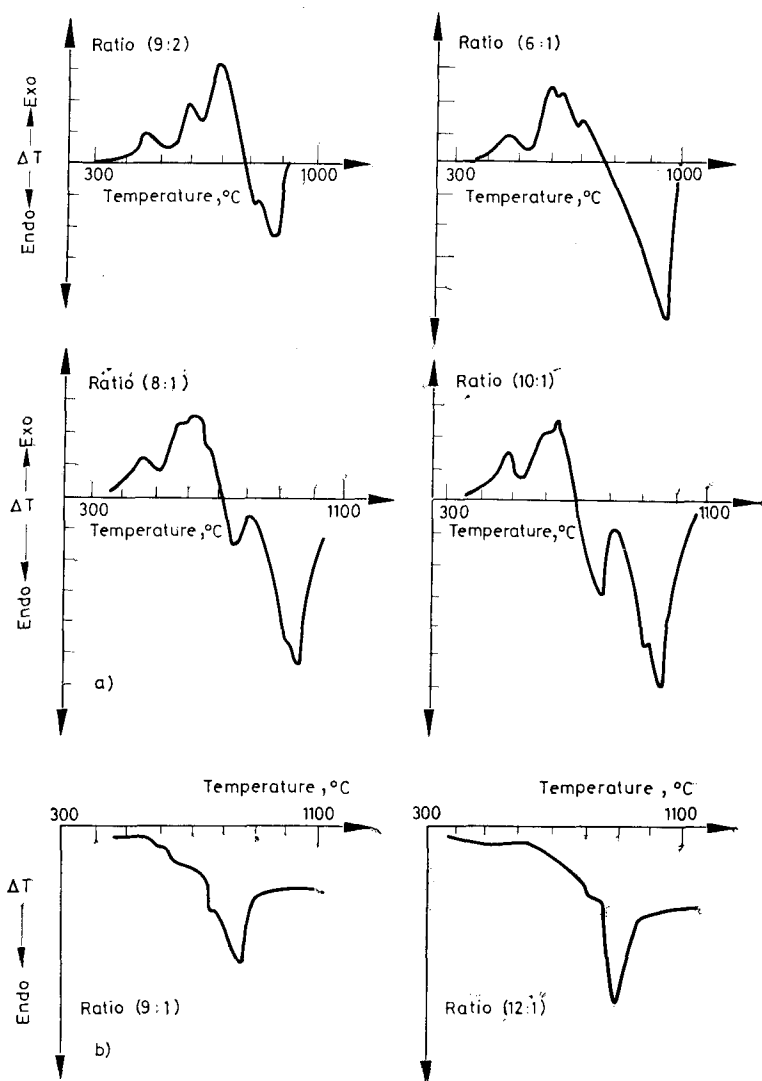

Fig. 3. DTA of a mixture of manganese(IV) oxide and nickel(II) sulphide

Fig. 3/a, b. DTA of a mixture of manganese(III) oxide and nickel(II) sulphide

overall reactions. The overall reaction tended to become more endothermic as the molar ratio of manganese(IV) oxide to nickel(II) sulphide increased, and on changing from an (8 : 1) to a (10 : 1) molar ratio there was a large increase in the size of the first endothermic peak relative to the second. The following points emerge from a comparison of the TG with the DTA results.

i) The proportion of the total loss occurring after the reaction became endothermic increased as the molar ratio manganese(IV) oxide to nickel(II) sulphide increased.

ii) The proportion of the total loss due to sulphur dioxide emission after the reaction became endothermic, increased as the molar ratio increased, and the difference between the total loss due to sulphur dioxide and the total loss for the whole reaction increased as the molar ratio increased.

iii) The appearance of cloudiness in the exit gas bubblers of the thermobalance was used as an indication of sulphur trioxide in the exit gases. During the TG experiments no sulphur trioxide was evolved with the (9 : 2) molar ratio at any stage, nor was there any with the other molar ratios during the exothermic stage. However, increasing cloudiness was observed with the (6 : 1), (8 : 1) and (10 : 1) molar ratios during the endothermic stages as the molar ratio increased.

By comparing the TG and DTA results with the general observations on the intermediate products obtained by qualitative and quantitative chemical analysis and X-ray analysis further points emerge.

iv) The percentage of water soluble sulphate increased as the molar ratio manganese(IV) oxide to nickel(II) sulphide increased and this sulphate persisted to higher temperatures as the molar ratio increased. X-ray analysis of intermediate products showed that manganese(II) sulphate was formed more readily and persisted to higher temperatures than nickel(II) sulphate.

v) No sulphides were detected in any of the intermediate samples.

vi) Similarly no sulphide was detected in any of the water insoluble portions of the products, after the reaction had become endothermic, and nickel(II) sulphide could not be identified by X-rays in any of the samples taken during the reaction.

vii) X-ray results showed that for all the molar ratios used, the change from manganese(IV) oxide to manganese(III) oxide and then to tri-manganese tetroxide followed the expected pattern.

The results show that more than one reaction occurs during the oxidation of nickel(II) sulphide by the manganese(IV) oxide. The key to these reactions lies largely with the formation of soluble sulphates as intermediates. Since sulphur dioxide is the only gaseous product during the initial stages of these reactions some of the nickel(II) sulphide must be converted into nickel(II) oxide and the manganese(IV) oxide reduced according to an equation of the type:

1. $9MnO_2 + 2NiS \rightarrow 2NiO + 2SO_2 + 3Mn_3O_4$

However, it is necessary to postulate additional reactions to account for the formation of water soluble sulphate during the early stages of the overall reaction.

One such method is the direct oxidation of sulphide according to an equation of the type:

4. $6MnO_2 + NiS \rightarrow NiSO_4 + 2Mn_3O_4$
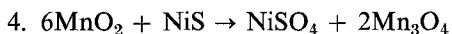
Since nickel(II) sulphate is produced at lower temperatures than that required to produce oxygen from manganese(IV) oxide, the direct oxidation of nickel(II) sulphide by oxygen can be discounted. Water soluble manganese(II) ions are produced from manganese(II) sulphate. It is possible to suggest two general routes for the formation of this compound.
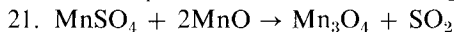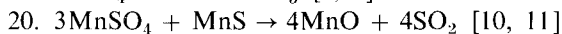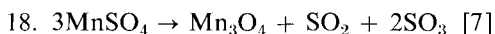
  (i) The interchange of sulphate and oxide ions

9. $NiSO_4 + MnO \rightarrow NiO + MnSO_4$
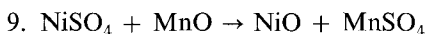
  (ii) The reaction of sulphur dioxide liberated in other reactions, either with unreacted manganese(IV) oxide, or with a lower oxide produced in another reaction, as has been shown previously [4−6].

10. $MnO_2 + SO_2 \rightarrow MnSO_4$
11. $4MnO + 4SO_2 \rightarrow 3MnSO_4 + MnS$
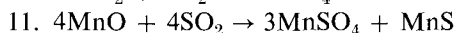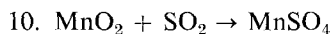
At higher temperatures in the reaction sequence the sulphate is removed. This removal can arise either by decomposition of the sulphate without reacting with another phase, or by its reaction with any remaining sulphide or with any manganese(II) oxide present.

18. $3MnSO_4 \rightarrow Mn_3O_4 + SO_2 + 2SO_3$ [7]
19. $NiSO_4 \rightarrow NiO + SO_3$ [8, 9]
20. $3MnSO_4 + MnS \rightarrow 4MnO + 4SO_2$ [10, 11]
21. $MnSO_4 + 2MnO \rightarrow Mn_3O_4 + SO_2$

Any manganese(IV) oxide which has not been reduced in earlier reactions will decompose to manganese(III) oxide and then to trimanganese tetroxide (Eqs 27 and 28).

  Since the overall reaction consists of a number of exotherms followed by one or more endotherms, it is useful to relate the possible intermediate reactions to their exo- or endothermic nature. The results of these calculations, based on thermodynamic data [12] are shown in Table 1.

  The results show that all of the reactions which involve the oxidation by manganese(IV) oxide of nickel(II) sulphide to nickel(II) oxide and sulphur dioxide are exothermic, as are most of the reactions in which sulphates are formed. Reactions 17 to 25 inclusive, which involve the decomposition of sulphates, are all endothermic, as is the decomposition of manganese(IV) oxide to lower oxides of manganese. It seems likely therefore, that the exothermic part of the overall reaction involves some of the reactions represented by equations 1 to 16 inclusive and the endothermic part to reactions represented by equations 17 to 29 inclusive. Some overlap of these is, however, extremely likely, and to a certain extent the amount of overlap will depend on the molar ratios of the individual mixtures.

Table 1

List of possible reactions

	Type of reaction
1. $9MnO_2 + 2NiS \rightarrow 2NiO + 2SO_2 + 3Mn_3O_4$	exo
2. $6MnO_2 + NiS \rightarrow NiO + SO_2 + 2Mn_3O_4 + 1/2O_2$	exo
3. $24MnO_2 + 3NiS \rightarrow 3NiO + 8Mn_3O_4 + 3SO_2 + 7/2O_2$	exo
4. $6MnO_2 + NiS \rightarrow NiSO_4 + 2Mn_3O_4$	exo
5. $6MnO_2 + NiS \rightarrow NiO + SO_2 + 3Mn_2O_3$	exo
6. $8MnO_2 + NiS \rightarrow NiSO_4 + 4Mn_2O_3$	exo
7. $3MnO_2 + NiS \rightarrow NiO + SO_2 + 3MnO$	exo
8. $4MnO_2 + NiS \rightarrow NiSO_4 + 4MnO$	exo
9. $NiSO_4 + MnO \rightarrow NiO + MnSO_4$	exo
10. $MnO_2 + SO_2 \rightarrow MnSO_4$	exo
11. $4MnO + 4SO_2 \rightarrow 3MnSO_4 + MnS$	exo
12. $Mn_2O_3 + SO_2 \rightarrow MnSO_4 + MnO$	exo
13. $Mn_3O_4 + SO_2 \rightarrow MnSO_4 + 2MnO$	exo
14. $NiS + 2O_2 \rightarrow NiSO_4$	exo
15. $4NiO + 4SO_2 \rightarrow 3NiSO_4 + NiS$	exo
16. $9Mn_2O_3 + NiS \rightarrow 6Mn_3O_4 + NiO + SO_2$	exo
17. $NiSO_4 + Mn_3O_4 \rightarrow NiO + Mn_2O_3 + MnSO_4$	endo
18. $3MnSO_4 \rightarrow Mn_3O_4 + SO_2 + 2SO_3$	endo
19. $NiSO_4 \rightarrow NiO + SO_3$	endo
20. $3MnSO_4 + MnS \rightarrow 4MnO + 4SO_2$	endo
21. $MnSO_4 + 2MnO \rightarrow Mn_3O_4 + SO_2$	endo
22. $3MnSO_4 + NiS \rightarrow 3MnO + NiO + 4SO_2$	endo
23. $3NiSO_4 + NiS \rightarrow 4NiO + 4SO_2$	endo
24. $3NiSO_4 + MnS \rightarrow 3NiO + MnO + 4SO_2$	endo
25. $9MnSO_4 + 2NiS \rightarrow 3Mn_3O_4 + 2NiO + 11SO_2$	endo
26. $MnO + NiS \rightarrow MnS + NiO$	endo
27. $4MnO_2 \rightarrow 2Mn_2O_3 + O_2$	endo
28. $6Mn_2O_3 \rightarrow 4Mn_3O_4 + O_2$	endo
29. $3Mn_3O_4 + NiS \rightarrow 9MnO + NiO + SO_2$	endo
30. $3Fe_2O_3 + NiS \rightarrow NiO + 6FeO + SO_2$	endo
31. $9Fe_2O_3 + NiS \rightarrow NiO + 6Fe_3O_4 + SO_2$	endo
32. $12Fe_2O_3 + NiS \rightarrow NiO + 8Fe_3O_4 + SO_2 + 1/2O_2$	endo
33. $12Fe_2O_3 + NiS \rightarrow NiSO_4 + 8Fe_3O_4$	endo
34. $Fe_2O_3 + SO_2 \rightarrow FeSO_4 + FeO$	exo
35. $Fe_3O_4 + SO_2 \rightarrow FeSO_4 + 2FeO$	exo
36. $4FeO + 4SO_2 \rightarrow 3FeSO_4 + FeS$	exo
37. $6Fe_2O_3 \rightarrow 4Fe_3O_4 + O_2$	endo
38. $3Fe_3O_4 + NiS \rightarrow 9FeO + NiO + SO_2$	endo

There are, therefore, at first sight, a large number of reactions which may be taking place during the exothermic part of the reactions. With the (9 : 2) molar ratios there are three well-defined peaks which become more complex as the molar ratio increased and which are somewhat shifted to lower temperatures. However

the first of these peaks remains at approximately the same temperature for all four molar ratios, and reactions 1 to 8 and 10 may tentatively be assigned to this. However, by 500° at the end of this peak, there is little evidence for the formation of tri-manganese tetroxide and no evidence for manganese(II) oxide, which would suggest a preponderance of reactions 5, 6 and 10. The involvement of reaction 10 increases as the molar ratio of manganese(IV) oxide to nickel(II) sulphide increases. According to previous work [4] the temperature range for this reaction is 320— 600° and this is in the correct region for this exothermic peak.

Several peaks are observed in the DTA experiments and it is probable that during the initial stages of the reaction the manganese(IV) oxide particles become covered with layers of manganese(III) oxide, tri-manganese tetroxide or manganese(II) oxide or even manganese(II) sulphate, whilst nickel(II) sulphate may be formed over the surface of the nickel(II) sulphide. Further reaction can then involve for any of the molar ratios taken initially, interaction of any of these phases. The second and third exothermic peaks may well involve such reactions as that given by Eq. 16, as well as those represented by Eqs 5, 6 and 10, which will occur again as fresh manganese(IV) oxide surfaces are exposed. However, reactions between manganese(III) oxide and nickel(II) sulphide have been shown to be endothermic (see section (b)) and this would tend to exclude this reaction (Eq. 16) from being largely involved in these two exothermic peaks.

Even with the higher molar ratios the oxidation of nickel(II) sulphide according to Eq. 16 is likely to occur since a much larger proportion of the sulphur dioxide produced in the early stages of reaction will have been captured with the formation of manganese(II) sulphate according to Eqs 10, 12 and 13. How important the latter reactions are depends on the conditions. Although manganese(II) oxide was not on the conditions. Although manganese(II) oxide was not detected by X-rays some phase, other than nickel(II) sulphide, which is capable of reducing manganese(II) sulphate may be present at intermediate stages, since the decomposition temperature of the manganese(II) sulphate produced is lowered. The endothermic part of the reaction shows two well-defined peaks, particularly when the molar ratio is high. The first of these is most likely due to decomposition (Eq. 27) of excess manganese(IV) oxide, required to oxidise nickel(II) sulphide to nickel(II) oxide. The DTA temperature for this peak is slightly higher than the TG temperature due to the different heating rates used. The second peak could be caused by the reduction of manganese(II) sulphate according to Eqs 21, 22 and 25 and to the decomposition of the manganese(II) sulphate according to Eq. 18. The TG results only showed cloudiness in the exit gas bubblers due to sulphur trioxide in the final stages of the reaction with the higher molar ratios, and this decomposition could probably be excluded for the lower molar ratios.

Allowing for the fact that many reactions are possible, the following sequence, which fits in with all of the results and with the thermodynamic calculations, indicates those which probably occur to the greatest extent.

Exothermic reactions

5. $6MnO_2 + NiS \rightarrow NiO + SO_2 + 3Mn_2O_3$
6. $8MnO_2 + NiS \rightarrow NiSO_4 + 4Mn_2O_3$
10. $MnO_2 + SO_2 \rightarrow MnSO_4$
12. $Mn_2O_3 + SO_2 \rightarrow MnSO_4 + MnO$

Endothermic reactions

27. $4MnO_2 \rightarrow 2Mn_2O_3 + O_2$
28. $6Mn_2O_3 \rightarrow 4Mn_3O_4 + O_2$
18. $3MnSO_4 \rightarrow Mn_3O_4 + SO_2 + 2SO_3$
21. $MnSO_4 + 2MnO \rightarrow Mn_3O_4 + SO_2$
25. $9MnSO_4 + 2NiS \rightarrow 3Mn_3O_4 + 2NiO + 11SO_2$

(b) *Manganese(III) oxide — nickel(II) sulphide mixtures*

The TG results (Fig. 4) have shown that the following overall reactions occur depending on the molar ratio of reactants:

16. $9Mn_2O_3 + NiS + NiO + 6Mn_3O_4 + SO_2$
    $24Mn_2O_3 + 2NiS \rightarrow 2NiO + 16Mn_3O_4 + 2SO_2 + O_2$

The results for the different heating rates gave essentially the same type of graph although at the lower heating rate the temperatures at which maxima occur in the
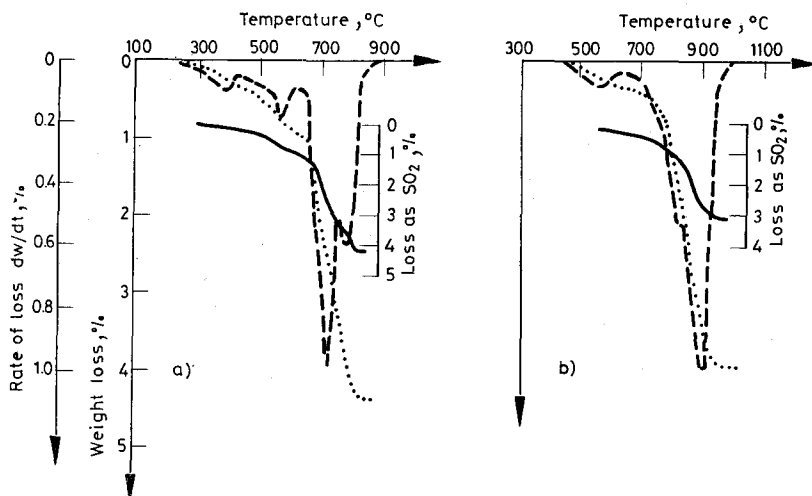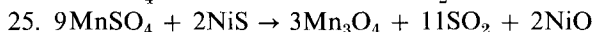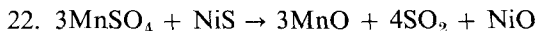

Fig. 4. TG of a mixture of manganese(III) oxide and nickel(II) sulphide under nitrogen. a) ratio (9 : 1); b) ratio (12 : 1). ——— % loss as SO_2, ... % weight loss, - - - - - - rate of loss

rate curve were lower. Peak resolution in the DTA experiments (Fig. 3) was poor due to the large weight and volume ratio of Mn_2O_3 : NiS required. Endothermic reactions were observed for both molar ratios studied, but it is possible that intermediate exothermic reactions occurred but were not detected due to base line drift and the overall endothermic nature of the reactions.

Qualitative and X-ray analysis on samples taken during the reactions showed the presence of manganese(II) sulphate together with lower oxides of manganese, and also the absence of nickel(II) sulphate and any sulphites. The absence of sulphites is easily explained since both nickel and manganese sulphites decompose at lower temperatures than those observed in this system. The absence of nickel(II) sulphate rules out reactions of the type:

$$12Mn_2O_3 + NiS \rightarrow NiSO_4 + 8Mn_3O_4$$
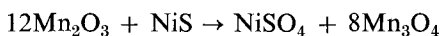
Again, as in the reactions with manganese(IV) oxide, there was "sulphur exchange" from nickel to manganese. During the TG runs no sulphur trioxide was evolved during the reactions for both molar ratios. Hence, any sulphate present must decompose by either the sulphate-sulphide or the sulphate-oxide mechanisms which have been discussed previously, and the reactions must have occurred before any surplus manganese(III) oxide decomposed. The formation of the manganese(II) sulphate occurred either by the reaction of sulphur dioxide with the oxides of manganese present, or by the sulphide ion exchange between nickel(II) sulphide and manganese(II) oxide to give manganese(II) sulphide, which was subsequently oxidized by manganese(III) oxide still present, to form manganese(II) sulphate. This latter phase was removed from the system at higher temperatures but below its usual decomposition temperature by reactions of the type:

22. $3MnSO_4 + NiS \rightarrow 3MnO + 4SO_2 + NiO$
25. $9MnSO_4 + 2NiS \rightarrow 3Mn_3O_4 + 11SO_2 + 2NiO$
21. $MnSO_4 + 2MnO \rightarrow Mn_3O_4 + SO_2$

There was no evidence from X-rays for the presence of other species e.g. manganese(II) oxide or sulphide but this could be due to the very small amounts which may be present in a large volume of material.

Thermodynamic data [12] suggest that the reaction represented by equation 16 would be exothermic whereas DTA showed that the reactions were essentially endothermic.

For the reasons already stated too much credence should not be placed on the DTA results and they probably consist of a number of exo and endotherms.

The results in total suggest a series of consecutive reactions of which the following is the most probable reaction sequence.
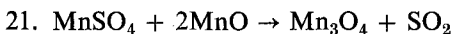

An initial reaction:

16. $9Mn_2O_3 + NiS \rightarrow 6Mn_3O_4 + NiO + SO_2$
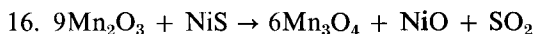
followed by interactions between the sulphur dioxide and manganese oxides:

12 $Mn_2O_3 + SO_2 \rightarrow MnSO_4 + MnO$ [4]

13. $Mn_3O_4 + SO_2 \rightarrow MnSO_4 + 2MnO$
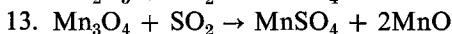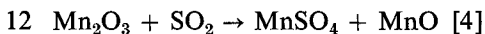
These could then be followed by:

21. $MnSO_4 + 2MnO \rightarrow Mn_3O_4 + SO_2$

and any excess oxide could then decompose:
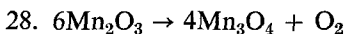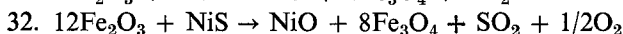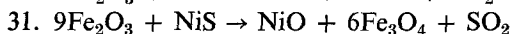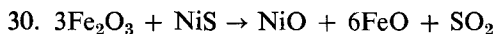
28. $6Mn_2O_3 \rightarrow 4Mn_3O_4 + O_2$

Table 1 shows that reactions 12, 13 and 16 are exothermic whereas 21 and 28 are both endothermic, in general agreement with the observed DTA and TG results. The TG results show that the bulk of the sulphur dioxide was evolved over the higher temperature range, supporting the proposed sequence of reactions. For the higher molar ratio the endothermic decomposition of the manganese(III) oxide tended to swamp the other possible peaks.

(c) *Iron(III) oxide − nickel(II) sulphide mixtures*

The TG results (Fig. 5) have shown that the following overall reactions occur depending on the molar ratio of reactants:

30. $3Fe_2O_3 + NiS \rightarrow NiO + 6FeO + SO_2$

31. $9Fe_2O_3 + NiS \rightarrow NiO + 6Fe_3O_4 + SO_2$

32. $12Fe_2O_3 + NiS \rightarrow NiO + 8Fe_3O_4 + SO_2 + 1/2O_2$

X-ray results confirmed that the residues from reaction 31 and 32 were mixtures of nickel(II) oxide and tri-iron tetroxide and that the residue from reaction 30 was the same, although weight losses suggested that iron(II) oxide was the product.

The DTA experiments were difficult, both because of the large weight and volume ratio of iron(III) oxide : nickel(II) sulphide required and also because the mixtures fluxed on reaction. However, the results showed that the reactions were essentially endothermic.

The available evidence suggests that these reactions are direct oxide-sulphide reactions and that they do not involve the intermediate stages which have been found in other systems reported here.

Observed weight losses and titres were in close agreement with calculated values. X-ray evidence and qualitative analysis did not detect any sulphates in the intermediate stages. Thermodynamic data [12] for reactions 30, 31 and 32 show that these are all endothermic in accord with the evidence from DTA experiments. This thermodynamic data also showed that the reactions between iron oxides and sulphur dioxide were exothermic and further evidence [13] showed that a temperature of $700-800°$ was required for sulphur dioxide to react slowly with iron(III) oxide.

Table 2

Qualitative and X-ray analysis on intermediate temperature samples MnO_2—NiS mixtures

Molar ratio	Temp. of sample, °	MnO_2	Mn_2O_3	Mn_3O_4	NiO	SO_4^{2-}	Ni^{2+}	Mn^{2+}
(9 : 2)	450	α			β	α	α	α
	500	α	α		β	α	α	α
	620	α	α	α	α	α	α	α
	690		α	α	α	α	α	
	790			α	α			
	850			α	α			
(6 : 1)	470	α			β	α	α	α
	520	α		β	β	α	α	α
	600		α	β	α	α	α	α
	630		α	β	α	α	β	α
	700		α	α	α	α	β	α
	950			α	α			
(8 : 1)	450	α	α		β	α	α	α
	510	β	α		α	α	α	α
	580		α	β	α	α	β	α
	620		α	β	α	α		α
	750		α	β	α	α		α
	910			α	α			
	950			α	α			
(10 . 1)	480	α	α		β	α	α	α
	520	β	α	β	α	α	β	α
	600		α	β	α	α		α
	630		α	β	α	α		α
	770		α	β	α	α		α
	910			α	α			
	960			α	α			

Mn_2O_3—NiS mixtures

Molar ratio	Temp. of sample, °	Mn_2O_3	Mn_3O_4	NiO	SO_4^{2-}	Ni^{2+}	Mn^{2+}
(9 : 1)	500	α	β	β	α		α
	800		α	α	α		α
(12 : 1)	500	α	α		α		α
	800		α	α	β		α

α indicates phase definitely present
β indicates phase probably present

Mixtures of molar ratios (9 : 1) and (12 : 1) produced one-step reactions which were essentially similar to each other except that a higher final temperature was found with the (12 : 1) ratio due to the decomposition of the excess iron(III) oxide. The mixtures of molar ratio (3 : 1) showed a distinct difference in that two separate peaks at 615° and 1200° were obtained in the rate curve. X-ray evidence showed
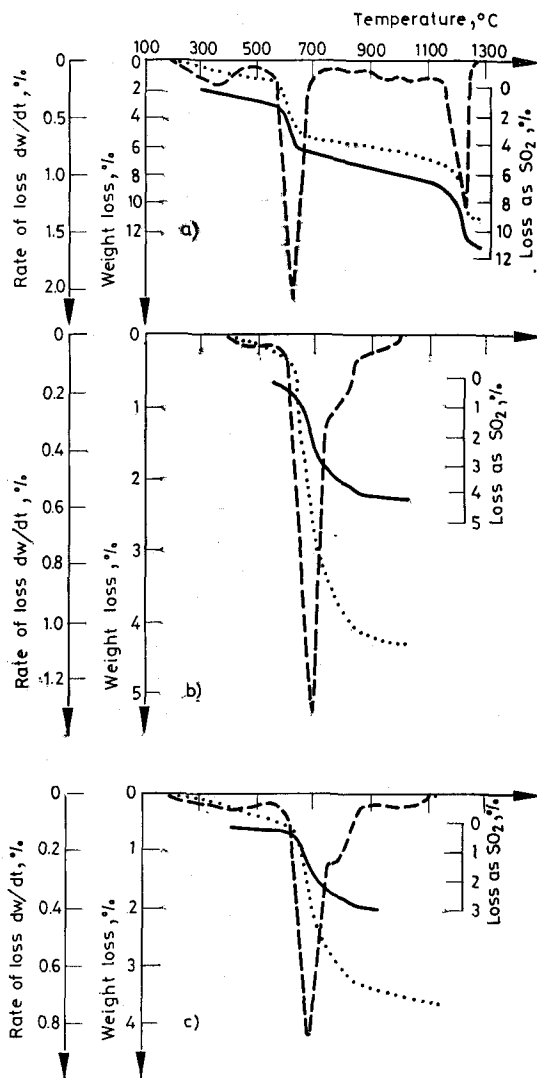

Fig. 5. TG of a mixture of iron(III) oxide and nickel(II) sulphide under nitrogen. a) ratio (3 : 1); b) ratio (9 : 1); c) ratio (12 : 1). ——— % loss as SO_2, ... % weight loss, — — — — rate of loss

that tri-iron tetroxide was present after the first peak and this was the only oxide of iron present at 800°.

Other experiments have shown that tri-iron tetroxide does react with nickel(II) sulphide according to the equation:
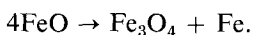
38. $3Fe_3O_4 + NiS \rightarrow 9FeO + NiO + SO_2$
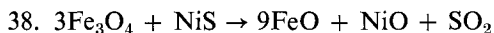
and it is therefore possible to propose the following reaction sequence for this molar ratio:

$9Fe_2O_3 + NiS \rightarrow 6Fe_3O_4 + NiO + SO_2$

followed by

$3Fe_3O_4 + NiS \rightarrow 9FeO + NiO + SO_2$
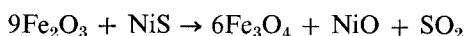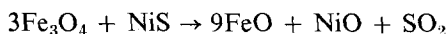
The absence of iron(II) oxide in the final product can be explained by the disproportionation [14] of iron(II) oxide which occurs on cooling slowly to room temperature:

$4FeO \rightarrow Fe_3O_4 + Fe.$

References

1. F. G. BUTTLER and A. MITCHELL, PhD Thesis and unpublished work.
2. P. J. GALMÉS and C. MATAIX, Afinidad, 27 (1950) 401.
3. E. DÖNGES, Z. Anorg. Chem., 253 (1947) 337.
4. A. MITCHELL, PhD Thesis, (1969) 66.
5. KUN LI, R. R. ROTHFUS and A. H. ADEY, Environ. Sci. Technol., 2 (1968) 619.
6. M. ATSUKAWA, Y. NISHIMOTO and K. MATSUMOTO, Tech. Rev. Mitsubishi Heavy Ind., 4 (1967), 33.
7. A. MITCHELL, PhD Thesis, (1969) 14.
8. C. MALARD, Bull. Soc. Chim. France, (1961) 2296.
9. R. FRUCHART and A. MITCHELL, Compt. Rend., 246 (1958) 1222.
10. T. V. PANTSULAYA, Tr. Gruzinsk, Politekhn. Inst., 4 (1959) 59.
11. A. MITCHELL, PhD Thesis, (1969) 42.
12. O. KUBASCHEWSKI, E. L. EVANS and C. B. ALCOCK, Metallurgical Thermochemistry, 4th edition, Pergamon Press, 1967.
13. D. L. HAMMICK, J. Chem. Soc., 111 (1917) 379.
14. F. A. COTTON and G. WILKINSON, Advanced Inorganic Chemistry, 2nd edition, Interscience, 1966. p. 850.

RÉSUMÉ — On montre par thermogravimétrie et analyse thermique différentielle que plusieurs réactions peuvent se produire suivant les rapports molaires des constituants lorsque l'on chauffe du sulfure de nickel(II) avec des oxydes de manganèse ou de fer. L'étude détaillée de ces réactions a mis en évidence un certain nombre d'étapes intermédiaires, avec formation de sulfates.

ZUSAMMENFASSUNG — Thermogravimetrie und Differentialthermoanalyse zeigen, daß bei gemeinsamer Erhitzen von Nickel(II)-Sulfid und Mangan- oder Eisenoxiden, in Abhängigkeit von dem Molarverhältnis der Reaktionspartner verschiedene Reaktionen stattfinden. Das eingehende Studium dieser Reaktionen zeigte das Auftreten einer Anzahl Zwischenstufen, darunter auch die Bildung von Sulfaten.

Резюме — С помощью термогравиметрии и дифференциального термического анализа показано, что при совместном нагревании сульфида никеля (II) с окислами магния или железа, протекает несколько реакций в зависимости от молярного соотношения реагентов. Детальное исследование этих реакций показало, что имеется ряд промежуточных стадий, включая образование сульфатов.