

# STUDY OF THERMAL DECOMPOSITION OF Ni(II) AND Fe(III) NITRATES AND THEIR MIXTURE

**Rabindra Kumar Ambasta**

Assistant Professor Chemistry  
31, Kautilya Nagar, P.O.- B.V. College  
Distt.- Patna-800014, Bihar

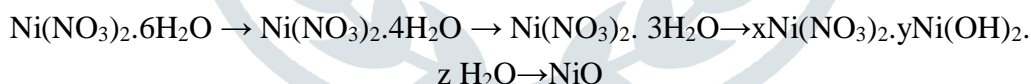
**Abstract :** In the present paper study of the thermal decomposition of Nickel (II) nitrates hexahydrate and iron (III) nitrate nonhydrate were followed. It was found that final decomposition products were NiO at 623 K and at 523 K, respectively. The two salts exhibited only endothermic peaks and a loss in per until constant mass was attained. The decomposition reactions and the compounds coordinating to each reaction were established. A heating rate of 1 K min<sup>-1</sup> revealed several immediate; higher heating rates shifted the peaks to higher temperatures. The use of an air during decomposition shifted the reactions to lower temperatures.

The DTA for the mixed salts was found to e an overlap and the TG a summation of the reaction for the two individual salts. AT 773 K, the decomposition products were composed of the phases: NiO, Fe<sub>2</sub>O<sub>3</sub> and NiFe<sub>2</sub>O<sub>4</sub>.

**Keywords:** Fe (III) nitrate, nickel ferrite, nickel nitrate, thermal decomposition.

## I. Introduction

In the 1958, V. W. Wendlandt reported the study of thermal decomposition of nickel(II) nickel hexahydrate and iron(III) nitrate nonhydrate. Several intermediate compounds were reported to appear during the thermal decomposition of nickel nitrate hexahydrate, but there is no agreement regarding the type of these intermediates. At linear heating rate of 5.4 min<sup>-1</sup> in flowing air, the salt was stated to water of hydration at 323K. At 478K, anhydrous Ni(NO<sub>3</sub>)<sub>2</sub> was obtained; at K, the end product was NiO. In the 1985 and 1986 reported by D. Dollimore in stationary air, basic nickel was reported as the only intermediate. In a water vapour- air atmosphere at heating rates of 5-7 K min<sup>-1</sup>, the following steps were suggested



y ~1.16, x and z unspecified constants.

In the 1958, V. W. Wendlandt<sup>(1)</sup> reported that in flowing air at a heating rate of 5.4 K min<sup>-1</sup> iron(III) nitrate nonhydrate loses its water of hydration at 307K. At 718 K, Fe<sub>2</sub>O<sub>3</sub> was obtained. On the other hand, in flowing nitrogen and at 553 K, Fe<sub>2</sub>O<sub>3</sub> was obtained while anhydrous iron nitrate was reported to exist as an intermediate by J. Mu.<sup>(6)</sup> in the 1982. No experimental work has been reported on the thermal decomposition of mixed Ni(II) and Fe(III) nitrates. Thus, it was the aim of the present work to study the thermal decomposition of the mixed salt as concerns the production of pure NiFe<sub>2</sub>O<sub>4</sub>, which is a very important material as a magnetic ceramic used in the electronics industry reported by V. D. Kingery<sup>(7)</sup> in the 1986.

## II. Experimental techniques:

In the present study, the behaviour of these salts was followed as a function of temperature. A Netzsch STA 409 simultaneous thermal analyser was used. Calcined kaolin was used as reference material and an alumina crucible (99.5% purity) as sample holder. Heating rates in the range 1-20 K min<sup>-1</sup> were applied while the atmosphere in the furnace was either stationary or flowing air reported by R. F. Speyer<sup>(8)</sup> in the 1984.

In order to conform the thermal analysis results, the powder resulting from the DTA was established the degrees of crystalline of the starting materials and their intermediates.

### III. Results and Discussion:

Thermal decomposition of nickel nitrate hexahydrate

#### In stationary air

The DTA and TG curves of nickel nitrate hexahydrate at a heating rate of  $1 \text{ K min}^{-1}$  in stationary air were recorded in the temperature range 300-873 K. The thermo grams reveal several endothermic peaks accompanied by a loss in mass; constant mass was achieved above 623 K, after the loss of 73.33% of the original mass, which indicates that NiO is the final product. Back-calculations based on these results indicates that the formula of the original salts was  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . The resulting loss may have occurred during transportation and/or storage of the salt. Accordingly, at a heating rate of  $1 \text{ K min}^{-1}$  in stationary air, according to the TG curve in fig. 1, the following decomposition mechanism is postulated:

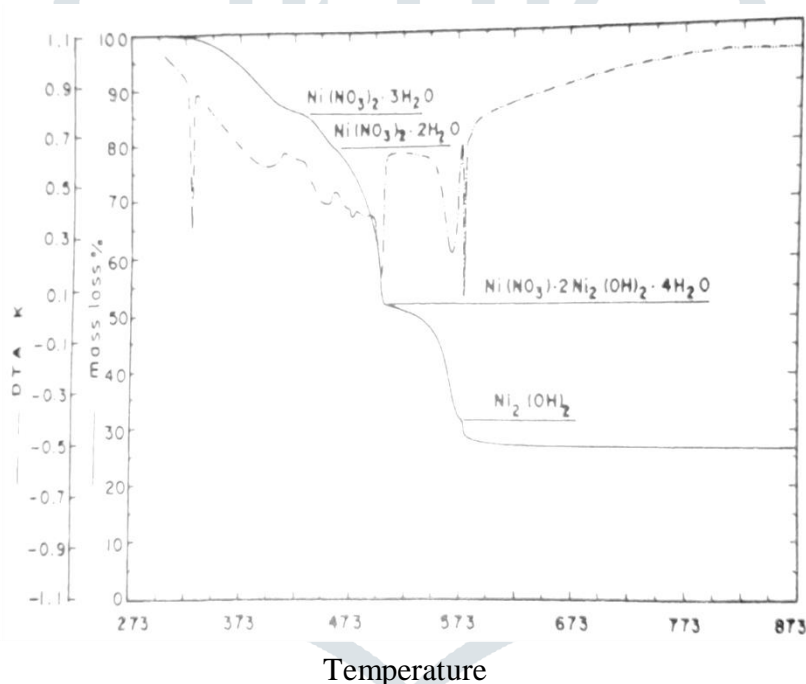
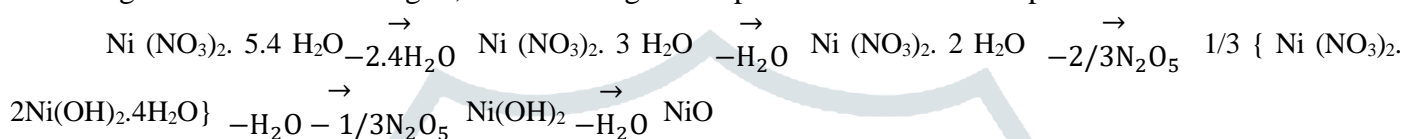


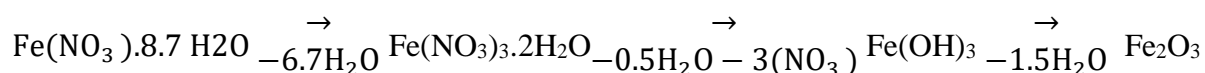
Fig.1 DTA and TG curves of nickel nitrate hexahydrate in stagnant air,  $1 \text{ K min}^{-1}$

#### In flowing air

The effects of flowing air and the heating rate on the thermal decomposition nickel nitrate hexahydrate were investigated. DTA and TG curves were related for nickel nitrate hexahydrate at heating rates of 5, 10 and  $20 \text{ K min}^{-1}$  in and at  $10 \text{ K min}^{-1}$  in air following at  $10.9 \text{ ml min}^{-1}$ . In the flowing air, all the decomposition reactions occurred at lower temperatures, due to the enhanced removal the gaseous products by air stream. A similar effect was observed at lower heating rates. It was also interesting that all the curves obtained at heating rates  $5 \text{ K min}^{-1}$  and above were similar, but the decomposition reactions were heated towards higher temperatures for higher heating rates. A heating rate of  $6 \text{ K min}^{-1}$  revealed several intermediates, while higher rates caused the overlap the corresponding decomposition reactions, revealing only the anhydrous banitrate, which was not detected at the lowest rate investigated.

### Thermal decomposition of iron (III) nitrate nonahydrate

DTA and TG curves were recorded for iron (III) nitrate nonahydrate at heating of 1,5,10 and 20 K min<sup>-1</sup> in stationary air and at 10 K min<sup>-1</sup> in stationary air and at 10 K min<sup>-1</sup> in flowing air (10.9 ml min<sup>-1</sup>). From the results, it was obvious that a flow of air or lower heating rates shifted the decomposition temperature to lower values. All the DTA curves indicated an endothermic peak starting at 323 K. Above this temperature, water was rapidly lost until a break corresponding to iron (III) nitrate dehydrate was reached. Fe(NO<sub>3</sub>)<sub>3</sub>.2H<sub>2</sub>O decomposed rapidly to Fe(OH)<sub>3</sub>. Gradual decomposition of the latter compound occurred on increase of the temperature, and finally Fe<sub>2</sub>O<sub>3</sub> was formed, the TG curves indicating a constant mass. From these results, the decomposition of the salt proceeds in the following steps:



On heating from 573 up to 1773 K, a small endothermic peak was obtained between 1645 and 1673 K. This is due to the decomposition of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4,09</sub>. This result is supported by the phase diagram of FeO-Fe<sub>2</sub>O<sub>3</sub>, which indicates that in air Fe<sub>2</sub>O<sub>3</sub> decomposes to a non-stoichiometric magnetite rich in oxygen reported by I. Levin<sup>(9)</sup> in the 1959.

### Thermal decomposition of mixed nitrates:

Study the final results of the thermal analyses of mixture of Ni(II) and Fe(III) nitrates, prepared in a ratio corresponding to NiFe<sub>2</sub>O<sub>4</sub>, carried out in stationary air at different heating rates, are shown in Fig 2. On heating the mixture up to 773 K in a muffle furnace, a total mass loss of 78% was observed, a value close to the theoretical loss of 78.27% for the formation of NiFe<sub>2</sub>O<sub>4</sub>. From the thermal decomposition of the individual salts and the thermal decomposition of the mixed salt at a heating rate of 1 K min<sup>-1</sup>, it was concluded that the DTA curve for the mixed salt is an overlap of those for the individual salts. The first double peak, between 303 and 330 K reflects the decomposition of the two hydrates, giving liquid water. In the temperature range from 330 to 387 K, an accelerated mass loss, giving an endothermic peak, was observed. In the temperature range 388-433 K, the nitrate began to decompose, giving nitrogen oxides. This decomposition was accompanied by a sharp endothermic peak in the DTA curve and a rapid mass loss in the TG curve. Above 648 K, no mass loss was observed, and at 773 K the material had a weak magnetic character, as indicated by a Gouy magnetic balance.

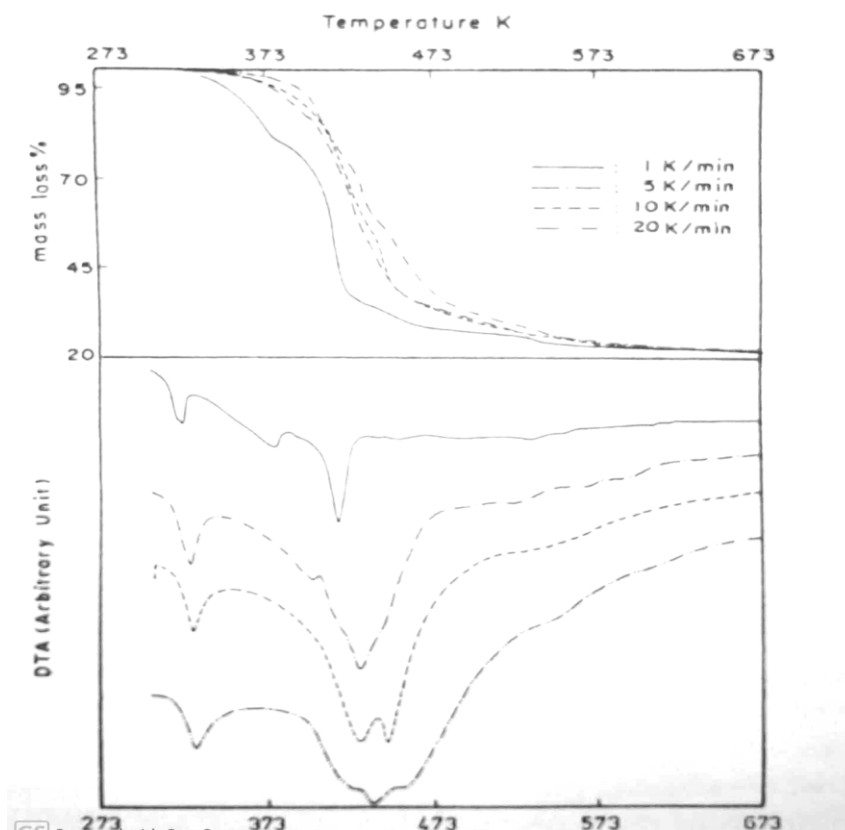


Fig. 2 Effect of heating rate on the thermal behaviour of the mixed Ni(II) and Fe(III) nitrates in stagnant air

In the final confirm the concluding remarks that the behaviour of mixed nitrates is an overlap of the mass losses of the individual components, the values of the losses in masses at different temperatures were calculated for the individual salts, added together and compared with those for the mixed salts. IT was concluded that the mixed nitrates tend to decompose earlier than the individual nitrates. This phenomenon indicates a fine particle size for the intermediates obtained from the mixture. When the analysis was carried with a  $20 \text{ K min}^{-1}$  heating rate in flowing air ( $10.9 \text{ ml min}^{-1}$ ), better agreement was obtained between the calculated and experimental results.

### III. Concluding Remarks:

From the above present study, it can be concluded remarks that:

1. NiO is the final product of thermal decomposition of nickel(II) nitrate hexahydrate above 623 K.
2. FeO is the final product of thermal decomposition of iron(III) nitrate nonahydrate above 523 K.
3. The initial composition of the nickel nitrate hexahydrate was  $\text{Ni}(\text{NO}_3)_2 \cdot 5.4\text{H}_2\text{O}$  and not  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .
4. The initial composition of the iron(III) nitrate nonahydrate was  $\text{Ni}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$  and not  $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ .
5. A heating rate of  $1 \text{ K min}^{-1}$  revealed several intermediates; higher rates used an overlap of the peaks and shifted them to higher temperatures.
6. The DTA curve is the mixed salt is an overlap of those of the two individual salts, and the TG curve is the summation of the two curves.
7. The decomposition of the mixed salts is completed at 648 K, since no mass was observed above that temperature.
8. No peaks in the DTA curve correspond to the formation of  $\text{NiFe}_2\text{O}_4$ .

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