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SEALED TUBE DIFFERENTIAL THERMAL ANALYSIS STUDIES OF SOME NICKEL(II) SALT HYDRATES

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ABSTRACT

Sealed and open tube DTA curves are reported for nickel sulfate, nitrate, ammonium sulfate, chloride, acetate, formate and perchlorate hydrates. The endothermic peaks for the sealed tube reactions were smaller than those found for the open tubes, due to the lack of water vaporization in the former. With the exception of $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, the peaks for the sealed and open tube reactions appeared at about the same initial peak temperature. The sealed tube reaction intervals $(T_f - T_i)$ were shorter than those found for the open tube.

INTRODUCTION

The thermal analysis of nickel(II) salt hydrates has been the subject of numerous investigations during the past twenty years. Compounds studied include the hydrated nickel(II) halides, sulfate, nitrate, perchlorate, acetate, formate and other salts. Most of the investigations have been concerned with the DTA and TG parameters of these compounds and their use in the elucidation of the thermochemical and kinetics of the deaquation processes. There have been no studies using the sealed tube DTA[1,2] technique to examine the dehydration reactions. This technique is useful for the detection of dehydration processes because the large endothermic peaks due to the vaporization of water are not present[1]. Hence, only the cation–water bond breaking reactions, water–cation bond making reactions, and crystalline structure changes are observed. These reactions generally have a much smaller ΔH and are easily obscured by the large heat of vaporization of water. Both sealed and open tube DTA curves are reported here, the latter for comparison purposes only.

EXPERIMENTAL

Nickel(II) salt hydrates

The nickel(II) salt hydrates were of C.P. quality and were obtained from various commercial sources. Particle size of the salts was about 100 mesh.

Sealed tube DTA apparatus

This technique has been previously described[1]. A Deltatherm III furnace and sample holder was modified to accept the aluminum metal sleeves and the 1.6–1.8 mm diameter capillary tubes. Sample size ranged from 8 to 20 mg; the sealed tube samples, because of the smaller ΔH involved, were somewhat larger than the open tube samples. A heating rate of about 5°C min^{-1} was employed over the temperature range from 25 to 250°C. The sample temperature, as detected by a Chromel–Alumel thermocouple, was recorded on the X-axis. A static air atmosphere was present in the furnace chamber.

RESULTS AND DISCUSSION

General

The DTA curves for the nickel(II) salt hydrates, in both open and sealed tubes, are given in Figs. 1–3. As expected, only endothermic peaks were observed for the sealed tube reactions and they were smaller, in general, than those found for the open tube studies. The open tube curve peaks, as discussed earlier, are larger due to the large contribution of the ΔH_v of water. No attempt was made to obtain the heats of dehydration for the dehydration processes for either the sealed or open tube studies because most of these values (for open systems at least) are known.

With the exception of $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, the curve peaks for the sealed tube reactions appeared at approximately the same initial peak temperature

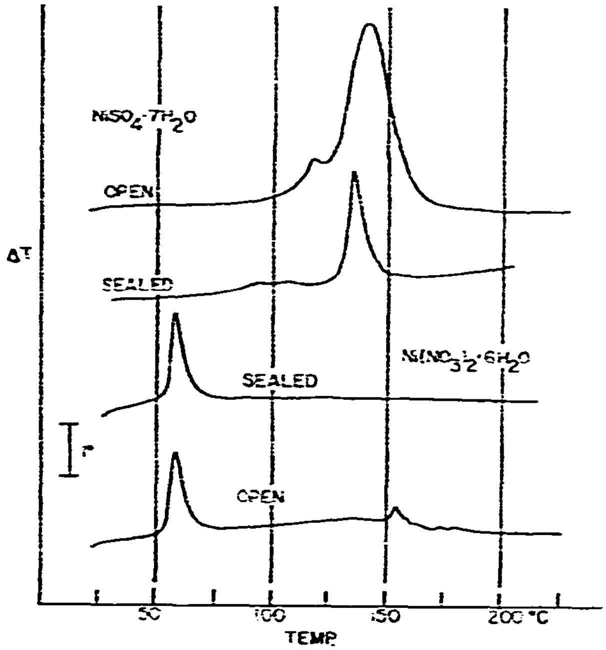

Fig. 1. Sealed and open tube DTA curves of some nickel(II) salt hydrates. (Upward peak direction indicates endothermic reaction.)

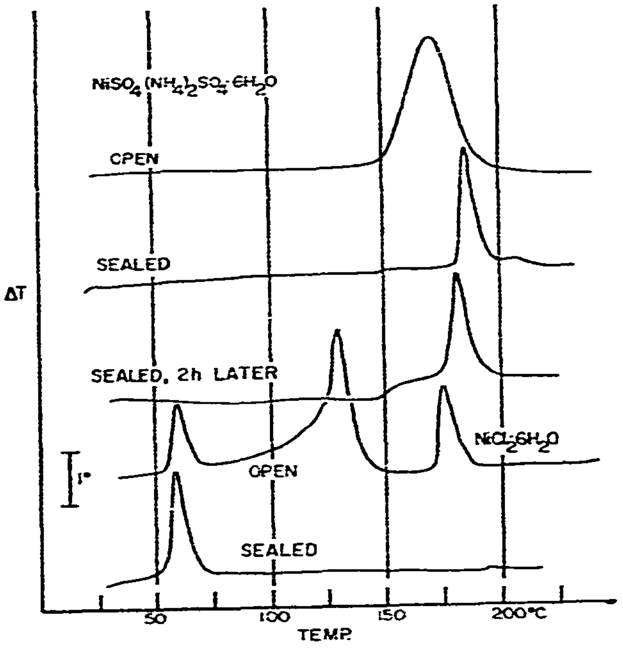

Fig. 2. Sealed and open tube DTA curves of some nickel(II) salt hydrates.

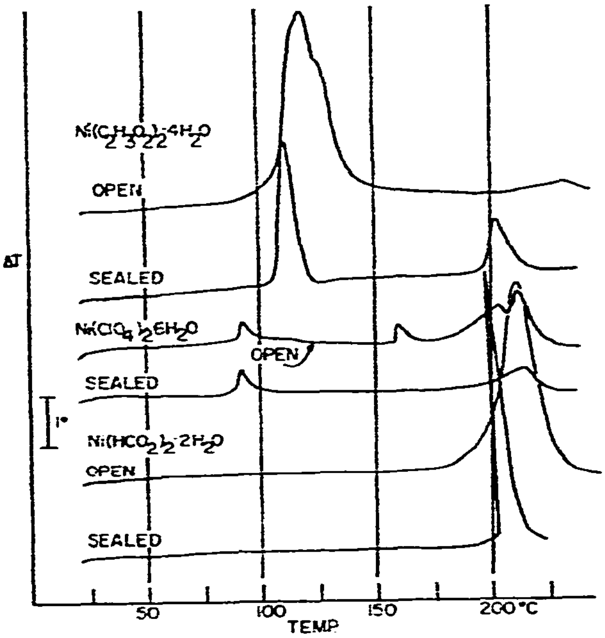

Fig 3. Sealed and open tube DTA curves of some nickel(II) salt hydrates.

(T_i) as the open tube reactions for all of the compounds studied. However, the final peak temperature (T_f) and the maximum peak temperature (ΔT_m) differed. The reaction interval ($T_f - T_i$) was generally shorter for the sealed tube reactions, which resulted in narrower peaks that terminated at lower T_f values. In some cases, the sealed and open tube DTA curve peaks were identical which indicates that the dehydration processes involved were the same. These processes may be due to a *solid → solid* phase transition or to the evolution of a liquid water phase resulting in the formation of a quadruple point where the initial salt hydrate, the next lower hydrate, and liquid and gaseous water, exist in equilibrium. Quadruple points in metal salt hydrate systems have been discussed in detail by Borchardt and Daniels[3].

In some of the nickel(II) salt hydrate systems, no sealed tube curve peaks were found in the temperature regions where open tube peaks were observed. This is perhaps due to the very small heat of reaction present or to the fact that only vaporization phenomena are occurring. In the latter case, no heat of reaction would be detected by the sealed tube technique.

Nickel(II) salt hydrates

$NiSO_4 \cdot 7H_2O$. The dehydration of this compound has recently been studied by TG by Lumme and Peltonen[4] who discussed the previous thermal studies on this compound and also the 6-hydrate. They found that the 6-hydrate lost five moles of water between 76 and 296 °C and that the anhydrous salt was obtained at about 533 °C. These results were in agreement with other investigations[5–7].

The open tube DTA curve (Fig. 1) indicates a broad peak from 80 to 185 °C with a ΔT_m of 140 °C and a shoulder peak at a ΔT_m of 118 °C. The sealed tube curve consists of a narrow peak from about 120 to 160 °C, with a ΔT_m of 135 °C. These peaks are due to the transition, 7-hydrate → 1-hydrate, as reported previously. It is of interest to note that the ΔT_m temperatures found were similar to those reported for the evolved gas detection (EGD) by Cabicar and Einhorn[8]. The 6-hydrate → 1-hydrate transition had a maximum peak temperature of 143 °C.

$Ni(NO_3)_2 \cdot 6H_2O$. According to the TG curve[4], no intermediate hydrates could be detected for this compound although dehydration was said to begin at about 30 °C. At the 5.5 °C min^{-1} heating rate employed, a curve break was observed at about 282 °C which corresponded to a compound having the approximate composition, $Ni(NO_3)_{1.33}(OH)_{0.67}$. Kalinichenko and Purtov[9] reported that the 6-hydrate melts at 55 °C, loses 0.2 moles of water at 100 °C, forms the 4-hydrate at 164 °C, and the 3-hydrate at 170 °C. At 257 °C, $Ni(NO_3)_2 \cdot 1.16H_2O$ is formed and on further heating to 310–337 °C, decomposition to NiO occurs. The enthalpy of dehydration of the 6-hydrate → 4-hydrate reaction has been reported by Auffredic et al.[10] to be 26,330 cal/mole.

The first peaks in the sealed and open tube curves for this compound (Fig. 1) are identical, indicating a similar transition. The peaks begin at about 50 °C and end at 80 °C with a ΔT_m at 59 °C. The transition observed is probably that of the reaction:

$$Ni(NO_3)_2 \cdot 6H_2O(s) \rightarrow Ni(NO_3)_2 \cdot 4H_2O + 2H_2O(l)$$

where the 4-hydrate dissolves in the evolved water. This is the "melting" transition previously reported[9]. In the open tube there are some small peaks in the temperature range from 125 to 175 °C, which are due to the decomposition of the lower hydrates. Curve peak resolution is poor because the sample is ejected from the capillary tube and hence is not in contact with the heat transfer sleeve.

$NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$. The dehydration process for this compound occurs between 140 and 210 °C in both the sealed and open tube techniques (Fig. 2). For the open tube DTA curve peak, which is much broader than that for the sealed tube, dehydration occurs in the temperature range of 140 to 210 °C with a ΔT_m of 170 °C. In the sealed tube curve, the reaction interval is from 175 to 200 °C with a ΔT_m of 185 °C. There is also some evidence from the change in the curve baseline that dehydration begins at about 150 °C. On reheating the same sample in the sealed tube 2 h later, the curve peak was found to be shifted to a slightly lower temperature, with a $\Delta T_m = 182\,^\circ C$, and there was also a greater pre-peak baseline change at 150 °C. It is obvious from the sealed tube curves that the heat of dehydration was much less for the sealed tube reaction.

$NiCl_2 \cdot 6H_2O$. According to Lumme and Peltonen[4], TG studies indicate that the 6-hydrate → 2-hydrate transition occurs between 30 and 139 °C and that the remaining water of hydration is evolved from 139 to 274 °C. This is essentially in agreement with Van My et al.[11] who reported lower transition temperatures and also the DTA curve. They stated that transition from the 6-hydrate → 4-hydrate occurs at 35–40 °C. Although it was found[4] that the last mole of water was lost with great difficulty, Shen and Chang[12] reported that the 1-hydrate → anhydrous transition took place at 166 °C.

The open tube DTA curve (Fig. 2) shows three endothermic peaks, with ΔT_m values of 60, 130 and 175 °C, respectively. These peaks are due to the transitions:

$$60\,^\circ\text{C:}\quad \text{NiCl}_2\cdot 6\text{H}_2\text{O(s)} \rightarrow \text{NiCl}_2\cdot 2\text{H}_2\text{O(soln.)} + 4\text{H}_2\text{O(l)}$$

$$130\,^\circ\text{C:}\quad \text{NiCl}_2\cdot 2\text{H}_2\text{O(soln.)} + 4\text{H}_2\text{O(l)} \rightarrow \text{NiCl}_2\cdot 2\text{H}_2\text{O(s)} + 4\text{H}_2\text{O(g)}$$

$$175\,^\circ\text{C:}\quad \text{NiCl}_2\cdot 2\text{H}_2\text{O(s)} \rightarrow \text{NiCl}_2\text{(s)} + 2\text{H}_2\text{O(g)}$$

In the case of the sealed tube reaction, only the first peak is observed, with a ΔT_m of 60 °C, as expected. The other peaks are not present due to $H_2O(l) \rightarrow H_2O(g)$ transitions which cannot be observed by this technique.

$Ni(C_2H_3O_2)_2 \cdot 4H_2O$. Most of the thermal analysis (DTA, TG, etc.) studies on this compound have been concerned with the dissociation of anhydrous $Ni(C_2H_3O_2)_2$. Manabe and Kubo[13] showed that for thin-layered (<4 mm thick) samples, the initial decomposition reaction is:

$$13\text{Ni(C}_2\text{H}_3\text{O}_2)_2 \rightarrow 10\text{Ni(C}_2\text{H}_3\text{O}_2)_2\cdot 3\text{NiO} + 3(\text{CH}_3)_2\text{CO} + 3\text{CO}_2$$

The composition of the residue dependend on the type of atmosphere employed—high vacuum gave a large amount of nickel and a small amount of nickel oxide; low vacuum gave a large amount of nickel oxide. Doremieux[14,15] reported that between

256 and 346°C, three decomposition mechanisms occurred. At <320°C, the reaction,

$$Ni(C_2H_3O_2)_2 \rightarrow NiO+(CH_3)_2CO+CO_2$$

took place without an induction period. During this reaction, nickel nuclei result spontaneously or by reduction and initiate the autocatalytic reaction,

$$Ni(C_2H_3O_2)_2 \rightarrow Ni+2[C_2H_3O^-]$$

Further reaction then takes place between the nickel and nickel oxide and the other reaction products to form nickel carbide (Ni_3C), acetic acid and acetic anhydride.

The open tube DTA curve (Fig. 3) indicates a large endothermic peak in the temperature range from 90 to 160°C with a ΔT_m of 120°C. This peak is probably due to several competing reactions, as indicated by the shoulder peak at 125°C. Two endothermic peaks are indicated in the sealed tube curve, with ΔT_m values of 110 and 205°C, respectively. The first peak is due to the dehydration reaction while the second peak is probably caused by a hydrolysis reaction of some type due to the presence of water in contact with the anhydrous nickel acetate. The nature of this reaction was not determined.

$Ni(HCO_2)_2 \cdot 2H_2O$. The thermal decomposition of nickel formate both in the hydrated and anhydrous forms, has been the subject of numerous investigations. Rao et al.[16], on the basis of TG and DTA curves, stated that the anhydrous compound dissociated according to the reaction:

$$Ni(HCO_2)_2 \rightarrow Ni+NiO+2CO+2CO_2+H_2O+H_2$$

Van My[17] reported a heat of decomposition for the anhydrous salt of 15.6 kcal mol^{-1} in argon and 17.8 kcal mol^{-1} in vacuum. The activation energy for the decomposition reaction was given as 19 kcal by Criado et al.[18] with a frequency factor of 1.7×10^7. At <310°C, the reactions were diffusion controlled with $\alpha = (k_1 t + k_2)^{\frac{1}{2}}$, where k_1 and k_2 are constants. TG curves have been reported by Rienacker and Toursel[19], Liptay[20], and others.

Only one endothermic peak is found in both the sealed and open tube DTA curves (Fig. 3). In the open tube curve, the peak has a reaction interval of 170 to 250°C with $\Delta T_m = 210$°C. The sealed tube curve peak covers a much narrower reaction interval, 190 to 225°C, with $\Delta T_m = 195$°C. This single peak is due to the 2-hydrate → anhydrous transition.

$Ni(ClO_4)_2 \cdot 6H_2O$. The open tube DTA curve indicates four small endothermic peaks with ΔT_m values of 95, 160, 205 and 210°C, respectively. Due to the evolution of liquid water, the sample was forced out of the sample tube holder at the higher temperatures, which resulted in fewer curve peaks as was the case with $Ni(NO_3)_2 \cdot 6H_2O$. The sealed tube curve contained two endothermic peaks with ΔT_m values of 93 and 215°C, respectively. Since a thermal transition was not found in the TG curve for this compound in the temperature range of 90 to 100°C, it is concluded that the first peak is due to some type of a phase transition which does not involve a mass loss. The second peak, at $\Delta T_m = 215$°C, is due to the dehydration process

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