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NON-ISOTHERMAL KINETIC AND THERMODYNAMIC STUDY FOR THE DEHYDRATION OF COPPER(II) CHLORIDE DIHYDRATE AND NICKEL CHLORIDE HEXAHYDRATE

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Abstract

Non-isothermal dehydration of copper chloride dihydrate and nickel chloride hexahydrate were studied by using TG, DTG, DTA and DSC measurements. The copper chloride salt loses its two water molecules in one step while nickel chloride salt dehydrates in three consecutive steps. The first two steps involve the loss of 4 water molecules in two overlapped steps while the third step involves the dehydration of the dihydrate salt to give the anhydrous $NiCl_2$.

Activation energies (ΔE) and the frequency factor (A) were calculated from DTG and DTA results. We have also calculated the different thermodynamic parameters, e.g. enthalpy change (ΔH), heat capacity (C_p) and the entropy change (ΔS) from DSC measurements for both reactants.

The isothermal rehydration of the completely dehydrated salts was studied in air and under saturated vapour pressure of water. Anhydrous nickel chloride was found to rehydrate in three consecutive steps while the copper salt rehydrated in one step.

Keywords: copper(II) chloride dihydrate, dehydration, kinetics, nickel chloride hexahydrate, thermodynamic study, TG-DTG-DTA and DSC

Introduction

The study of thermal dehydration of crystalline hydrates have notably contributed in the theoretical foundation and understanding of solid state reactions [1]. This is due to the fact that many decomposition reactions of solids are concerned with the breakdown of previously dehydrated salts [2, 3]. Water of crystalline hydrates can vary between the weakly adsorbed water (e.g. in clays) and

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the strongly retained structural hydroxyl groups as in the natural silicates [4]. Dehydration can take place in one single step or in a number of steps. Therefore, such reactions are usually investigated by non-isothermal methods [5, 6], though sometimes not every step can easily be identified [7].

Dehydration reactions are known to proceed by nucleation and growth mechanism [8, 9]. The large, relatively perfect, crystals of many hydrates (e.g. alums) provide an insight into the factors that control the reactivities of solids. Galwey *et al.* [8–10] concluded that the nuclei developed were structures specifically capable of temporarily retaining water.

Several studies of the dehydration of metal chlorides have been reported in the literature e.g. $BaCl_2 \cdot 2H_2O$ (and $BaCl_2 \cdot H_2O$) [11], $AlCl_3 \cdot 6H_2O$ [12] and $MgCl_2 \cdot 2H_2O$ which decomposes [13] on heating. We have recently carried out a brief study [14] on the dehydration of $NiCl_2 \cdot 6H_2O$. The present non-isothermal work extends our previous study to include the kinetic and thermodynamic parameters for the dehydration of copper chloride dihydrate and nickel chloride hexahydrate. In addition, the rehydration of the two reactants are, also, discussed in air and under saturated vapour pressure of water.

Experimental

Materials used in the present study were analytical grade. Copper(II) chloride dihydrate (Cambrian chemicals) and nickel chloride hexahydrate (May and Baker chemicals) were used as received without further purification. Samples were slightly crushed prior to the dehydration study in order to avoid the effect of variation in the particle size of the reactants.

Thermal analysis experiments of both reactants were carried out using Shimadzu Stand-Alone Thermal Analyser Instruments (TGA-50H, DTA-50 and DSC-50) Japan. These instruments were equipped with a data processor chromatopac C-R4AD. The program of the data processor gives the values of temperatures, weight losses and heat involved during any thermal event.

All experiments were performed in a dynamic atmosphere of N_2 (40 $ml \cdot min^{-1}$). Highly-sintered α-Al_2O_3 powder (Shimadzu Co.) was used as a reference material for DTA measurements. The heat of transition (3.24 $kJ \cdot mol^{-1}$ [15]) of specpure Indium metal (Johnson Matthey), at 157°C was adopted for the DSC curve calibration.

The rehydration process was studied for both reactants after their complete dehydration by two methods. In one method, the rehydration process was studied in air (normal atmospheric pressure) where a known weight (ca. 2 g) of each reactant (in a small beaker) was completely dehydrated. Then each dehydrated

sample was left in air and the weight gain was measured using an electronic balance model XTA-100, Fisher Scientific (USA) at different intervals of time. In the other method, rehydration was studied under an atmosphere of air saturated with water where the rehydrated sample (in a beaker) and another beaker filled with water, both were kept in a covered glass vessel. The weight gain was also measured at different intervals of time by taking the beaker out of the glass vessel, weighed quickly and was placed back in the covered vessel.

It should be noted here that we have used a constant weight of sample for both salts (≈15 mg). This is due to the fact that sample weight does affect the shape and temperature of peaks.

Details of calculations of kinetic and thermodynamic parameters were performed as described in detail elsewhere [16].

Results and discussion

Thermogravimetric analysis

TG analysis of both reactant chlorides were carried out to completion for the dehydration process. Four different rates of heating were adopted i.e. 3, 5, 7 and 10 deg·min^{-1} (for nickel chloride reactant, we have used a slow rate of 1 deg·min^{-1} in addition to the four rates mentioned above). All these experiments were performed in a dynamic atmosphere of N_2 (40 ml/min).

Copper chloride dihydrate

Dehydration of $CuCl_2 \cdot 2H_2O$ took place in one single step. The average weight loss measured from 10 experiments, carried out at different heating rates, was found to be 21.2% of the original weight. This was in accordance with the theoretical calculations (21.14%). Figure 1 shows a collective TG curves for the dehydration of copper salt. The effect of increasing the heating rate on the dehydration process is clear from the shift, to higher values, of the T_{max} value (T_{max} is the temperature at which maximum weight loss takes place in TG or peak temperature in DTA), Table 1. These T_{max} values were measured from the DTG analysis curves given by the program of the system. The values of ln A and the correlation coefficient were calculated using a computer program.

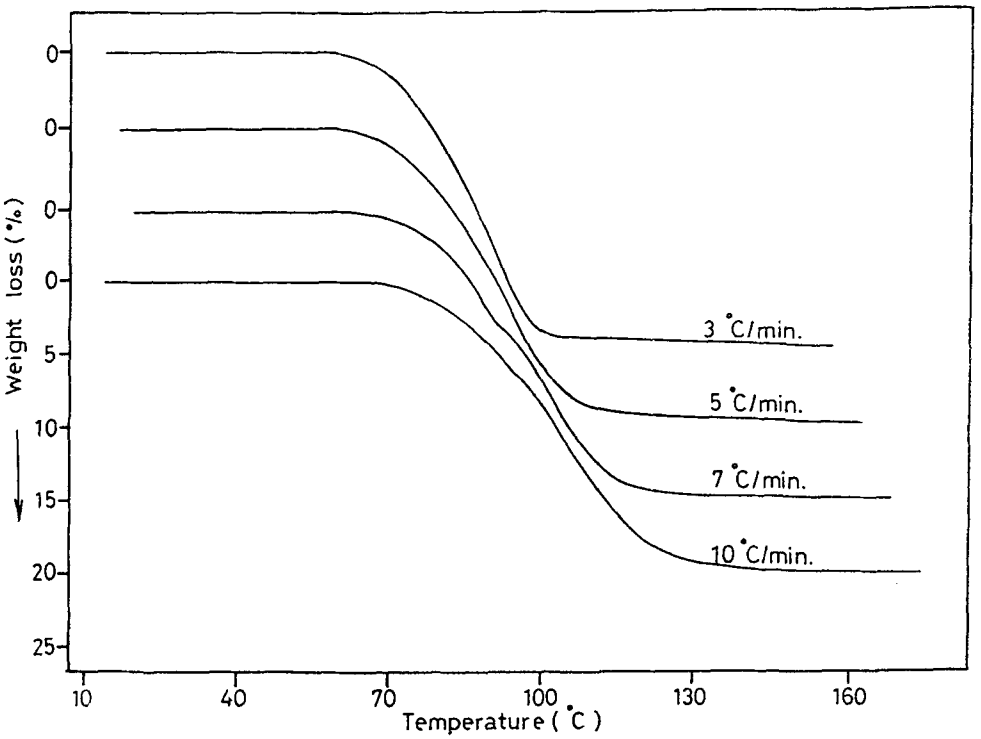

Fig. 1 TG curves for the dehydration of $CuCl_2 \cdot 2H_2O$ carried out at 4 different heating rates in a dynamic atmosphere of N_2 (40 ml·min^{-1})

Nickel chloride hexahydrate

TG analysis of $NiCl_2 \cdot 6H_2O$ showed two main weight loss steps with a total of 44.05% of the original sample weight (theoretical value is 45.48%). We have found that $NiCl_2 \cdot 6H_2O$ starts to lose weight at 22°C, this, in turn, may explain the discrepancy observed (≈1.5%) between the practical and theoretical value of weight loss. In other words, this amount of water may have been evolved before study as the ambient temperature was slightly higher than 22°C. Figure 2 shows a collective TG curves of the five heating rates used here. The first weight loss step represents about 29% (i.e. a loss of 4 molecules of water). This step, in fact, is composed of two overlapped processes as indicated from the DTG curves, where it appeared as two separated peaks and also from the break observed on the TG curves and the weight loss calculations. These two overlapped steps represent the loss of 3 water molecules followed by the loss of one molecule in case of the low rates of heating (1 and 3 deg·min^{-1}). At higher rates

Table 1 Summary of TG and DTG results for the dehydration of copper chloride and nickel chloride hydrates

Rate of heating / deg·min^{-1}	$CuCl_2 \cdot 2H_2O$			$NiCl_2 \cdot 6H_2O$				
	Temperature range / °C	Total weight loss / %	T_{max} / °C	Temperature range / °C	Total weight loss / %	$T_{1\,max}$ / °C	$T_{2\,max}$ / °C	$T_{3\,max}$ / °C
1	–	–	–	22–200	43.91	47.8	69.3	154.6
3	55–100	21.21	89.6	28–215	43.94	61.3	73.0	176.9
5	59–109	21.14	94.8	29–224	43.36	69.7	78.4	185.8
7	63–120	21.17	102.5	33–232	43.96	71.8	–	190.3
10	66–132	21.40	108.6	35–244	44.05	84.3	97.8	208.7

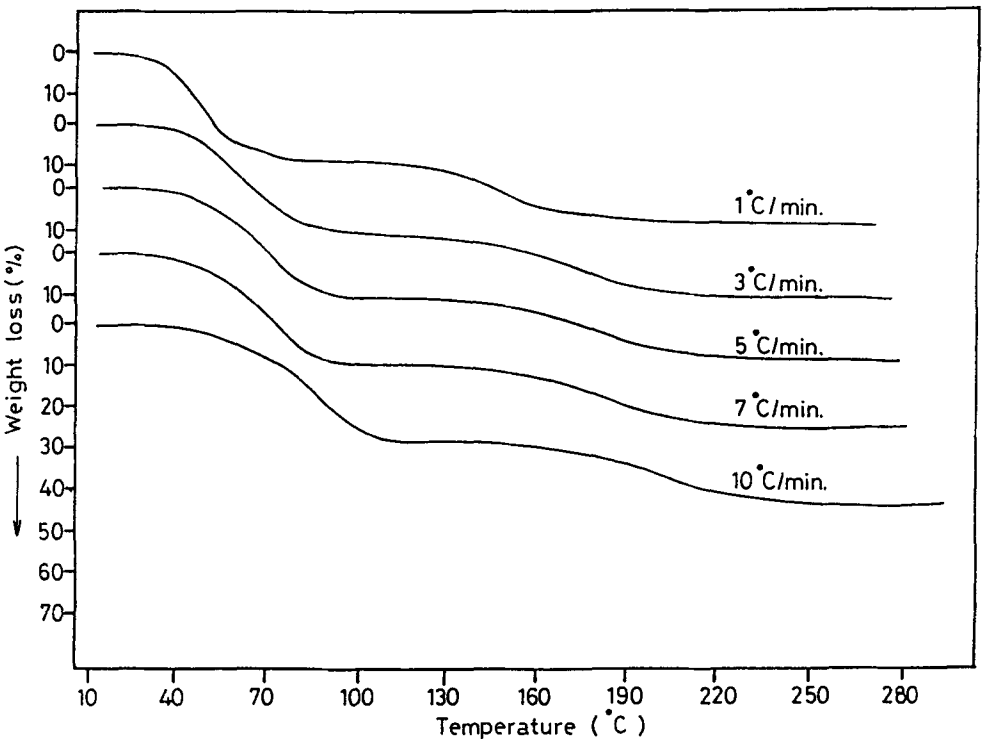

Fig. 2 TG curves for the dehydration of $NiCl_2 \cdot 6H_2O$ carried out at 5 different heating rates in a dynamic atmosphere of N_2 (40 ml·min^{-1})

of heating, however, these two steps are more likely to represent an equal loss of 2 molecules followed by a similar loss of 2 molecules of water. This is concluded from the break appears at 14.6% weight loss in the TG curve (at 10 deg·min^{-1}) which is equivalent to 2 moles of water.

The last step, above 110°C, represents the dehydration of $NiCl_2 \cdot 2H_2O$ to the anhydrous $NiCl_2$ (with a weight loss of 15% of the original weight). Table 1 summarizes the TG and DTG results of $CuCl_2 \cdot 2H_2O$ and $NiCl_2 \cdot 6H_2O$.

Differential thermal analysis (DTA)

DTA analysis was carried out for both salts under a dynamic atmosphere of N_2 (40 ml/min). Five different heating rates (5, 7, 10, 15 and 20 deg·min^{-1}) were used.

Copper chloride dihydrate

Figure 3 shows collective DTA curves for copper chloride. Each curve showed one single endothermic peak. The peak temperature increased as the heating rate grew.

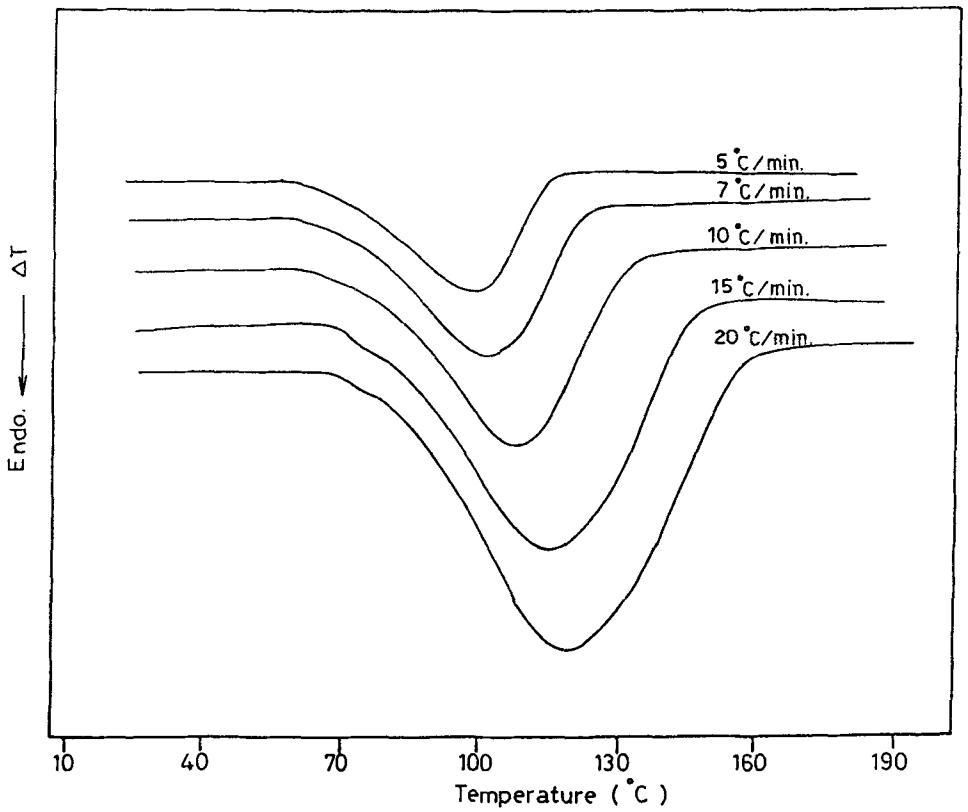

Fig. 3 DTA curves for the dehydration of $CuCl_2 \cdot 2H_2O$ carried out at 5 different heating rates in a dynamic atmosphere of N_2 (40 ml·min^{-1})

The data obtained from the DTA analysis were used to calculate the activation energy of the dehydration steps from a plot of log φ (rate of heating) against $1/T_{max}$ (where T_{max} is the peak temperature), Table 2.

The effect of weight on the DTA of copper chloride was studied, where 3 experiments were carried out at a constant rate of heating (5 deg·min^{-1}) but with different weights of sample i.e. 5, 10 and 15 mg. DTA peak temperatures for these three experiments were located at 88.3, 96.2 and 97.8°C respectively.

Table 2 Relationship between the rate of heating and temperature (T_{max}) at the peak of DTA curves for the dehydration of copper chloride and nickel chloride hydrates

Rate of heating	$CuCl_2 \cdot 2H_2O$	$NiCl_2 \cdot 6H_2O$		
deg·min^{-1}	T_{max}	T_{1max}	T_{2max}	T_{3max}
5	97.8	53.8	78.1	185.9
7	102.7	55.1	82.8	193.1
10	108.8	57.5	86.1	201.7
15	115.7	63.7	98.2	212.2
20	119.9	65.5	102.9	215.5

Nickel chloride hexahydrate

DTA of $NiCl_2 \cdot 6H_2O$ showed 3 endothermic peaks. A fourth small peak appeared between the first and second peak at low rates of heating (5 and

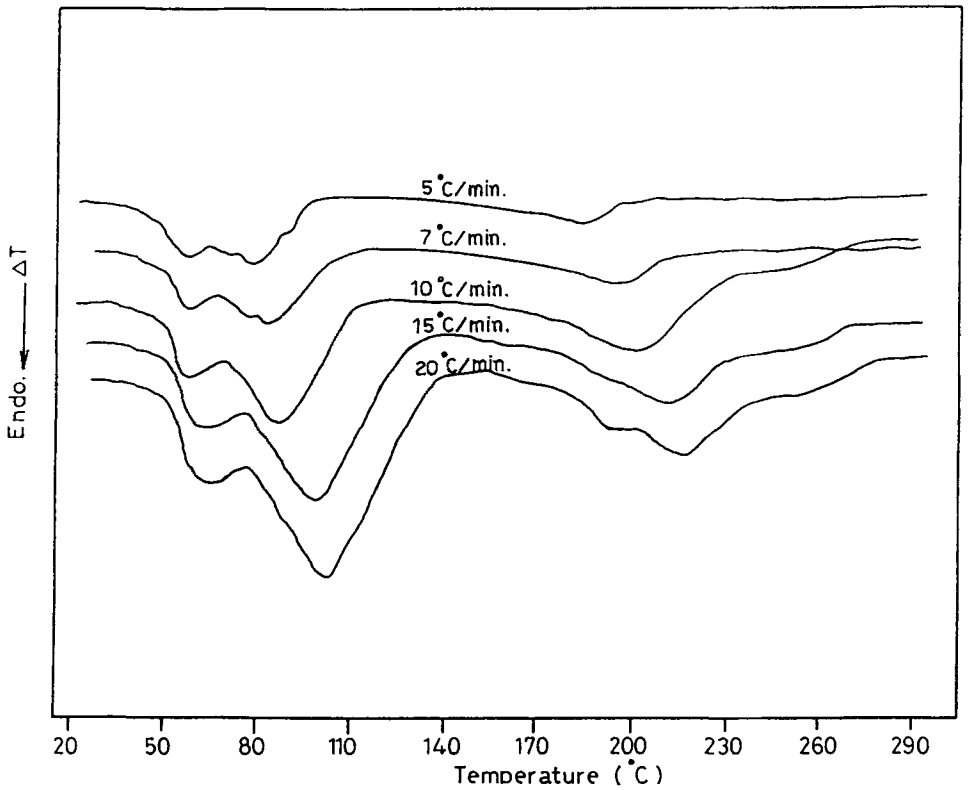

Fig. 4 DTA curves for the dehydration of $NiCl_2 \cdot 6H_2O$ carried out at 5 different heating rates in a dynamic atmosphere of N_2 (40 ml·min^{-1})

7 deg·min^{-1}). This peak vanished at higher rates (10, 15 and 20 deg·min^{-1}). This is due to the fact that the separation of the overlapping processes is better attained when low heating rates are employed [17]. Collective DTA curves for the dehydration of $NiCl_2 \cdot 6H_2O$ is shown in Fig. 4 for the five different heating rates mentioned above. Again ΔE and ln A values were calculated for the three dehydration steps. Table 2 contains the results of DTA measurements for these three steps.

Differential scanning calorimetry (DSC)

DSC measurements for both reactant hydrates were carried out at two different rates of heating, 5 and 10 deg·min^{-1}. Figure 5 shows two DSC curves of copper and nickel salts measured at 10 deg·min^{-1} under dynamic atmosphere of nitrogen.

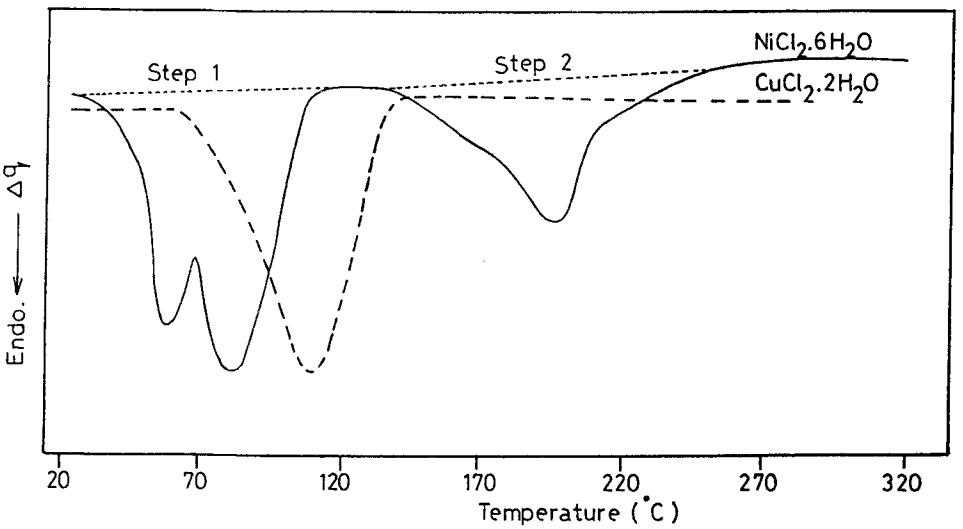

Fig. 5 DSC curves for the dehydration of $CuCl_2 \cdot 2H_2O$ and $NiCl_2 \cdot 6H_2O$, both were carried out at 10 deg·min^{-1} in a dynamic atmosphere of N_2 (40 ml·min^{-1})

These curves were used to calculate the enthalpy (ΔH), the heat capacity (C_p) and the entropy change (ΔS) for both reactants. ΔH was taken directly from the peak area measured by the program. These ΔH (kJ/mol) values were used to calculate the specific heat capacity C_p (kJ/deg·mol) using the equation:

Table 3 Non-isothermal kinetic and thermodynamic parameters of the dehydration of copper chloride and nickel chloride hydrates

Parameter	Calculated from	Copper salt	Nickel salt		
			step 1	step 2	step 3
ΔE / kJ·mol^{-1}		69.56	62.02	72.31	76.12
ln A	TG and DTG	24.25	23.36	25.94	21.49
Corr. coeff.		0.988	0.985	0.892	0.985
ΔE / kJ·mol^{-1}		74.73	75.31	57.63	83.21
ln A	DTA	25.85	29.69	21.44	23.41
Corr. coeff.		0.999	0.977	0.984	0.995
ΔH / kJ·mol^{-1}		106.54	190.16		91.51
C_p / kJ·deg^{-1}·mol^{-1}	DSC	1.32	2.23		0.79
ΔS / kJ·deg^{-1}·mol^{-1}		1.11	3.10		0.49

$$C_p = \Delta H/\Delta T$$

where $\Delta T = T_2 - T_1$ (T_1 is the temperature at which the DSC peak begins to leave the baseline, whereas T_2 is the temperature at which the peak lands [18]). Subsequently, the entropy change ΔS (kJ/deg·mol) was calculated using the relationship:

$$\Delta S = 2.303\ C_p\ \log\ (T_2/T_1)\quad [18].$$

A list of these thermodynamic parameters together with the kinetic parameters for both hydrated salts are given in Table 3.

Isothermal rehydration of both dehydrated reactants

The results of the rehydration study of both anhydrous salts (at 16±1°C) in air and under saturated vapour pressure of water are represented in Fig. 6. In air, the anhydrous $CuCl_2$ takes up two molecules of water in one single step while rehydration of $NiCl_2$ is completed in three steps. Rehydration under saturated vapour pressure of water showed two points:

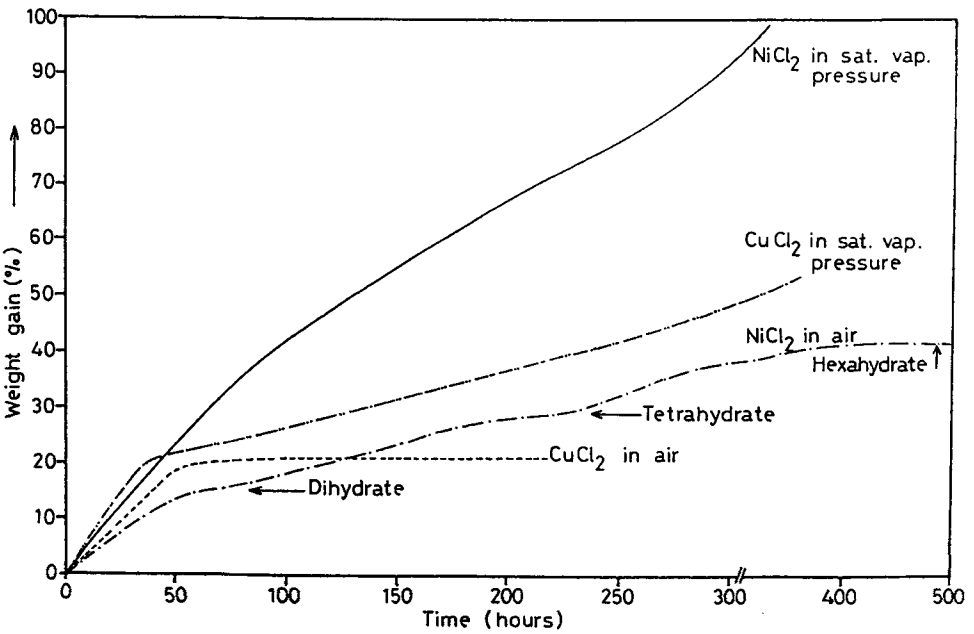

Fig. 6 Rehydration of anhydrous $CuCl_2$ and $NiCl_2$ in air and under saturated vapour pressure of water at constant temperature (16±1°C)

i) Time required to complete the rehydration was very much shorter than that recorded for rehydration in air (X 1/4 for nickel salt and X 1/2 for copper salt).

ii) Both salts continued to gain weight even after the complete uptake of the corresponding number of water molecules for each reactant salt. Both salts became wet and finally were dissolved forming aqueous solutions. This was more pronounced for the anhydrous nickel salt indicating, probably, that it is more hygroscopic than the anhydrous copper salt.

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Zusammenfassung — Mittels TG-, DTG-, DTA- und DSC-Messungen wurde die nichtisothermische Dehydratation von Kupferchlorid-Dihydrat und Nickelchlorid-Hexahydrat untersucht. Das Kupferchloridsalz setzt seine zwei Moleküle Wasser in einem Schritt frei, das Nickelchloridsalz dagegen in drei aufeinanderfolgenden Schritten. Davon umfassen die ersten zwei Schritte die Freisetzung von 4 Molekülen Wasser in zwei überlappenden Schritten, während der dritte Schritt vom Dihydratsalz zur Formung von wasserfreiem $NiCl_2$ führt.

Die Aktivierungsenergien (ΔE) und der Frequenzfaktor (A) wurden anhand von DTG- und DTA-Ergebnissen berechnet. Weiterhin berechneten wir anhand von DSC-Messungen auch thermodynamische Parameter, wie z.B. die Enthalpiedifferenz (ΔH), die Wärmekapazität (C_p) und die Entropiedifferenz (ΔS) für beide Reaktanden.

In Luft und bei Sättigungsdampfdruck für Wasser wurde die isotherme Rehydratation der vollständig dehydratierten Salze untersucht. Wasserfreies Nickelchlorid rehydratiert in drei aufeinanderfolgenden Schritten, das Kupfersalz dagegen rehydratiert nur in einem Schritt.