# Dehydration of Ammonium Magnesium Chloride Hexahydrate (Ammonium Carnallite)

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The dehydration of ammonium carnallite ($NH_4MgCl_3{\cdot}6H_2O$) has been studied in the temperature range 373—453 K under partial pressures of water vapour between $1 \times 10^{-3}$ N m$^{-2}$ and 2.7 kN m$^{-2}$. At lower temperatures a dihydrate is formed by a phase-boundary controlled process, having an activation energy varying with water-vapour pressure between 65 and 125 kJ mol$^{-1}$. At higher temperatures and low water-vapour pressures the anhydrous chloride is formed in a single stage following first-order kinetics with an activation energy close to 40 kJ mol$^{-1}$. Intermediate temperatures and vapour pressures cause the reaction to proceed in two stages, both of which are controlled by phase-boundary processes; Arrhenius parameters have been derived for these also. Enthalpy data are given for the reactions as well as provisional $X$-ray diffraction data for the products.

It has been known for many years that the thermal decomposition of ammonium magnesium chloride hexahydrate (ammonium carnallite, $NH_4MgCl_3{\cdot}6H_2O$) provides a useful method for the preparation of anhydrous magnesium chloride.[1] This method was used in the study of the reaction between magnesium chloride and oxygen,[2] and some preliminary results obtained for the dehydration led to the present work. The dehydration has not been studied recently, although earlier work [3] suggests the formation of a dihydrate as an intermediate together with some evidence of a higher hydrate with 4.5 $H_2O$.

Ammonium carnallite is isomorphous with bromocarnallite, $KMg(Cl,Br){\cdot}6H_2O$ (20—75 atom % Br) and the crystal structure of the latter has been determined.[4] The unit cell of ammonium carnallite is tetragonal ($a_0 = 13.3$, $b_0 = 6.66$, and $c_0 = 6.68$ Å) and the water molecules are octahedrally co-ordinated to the Mg.

The dehydration of carnallite ($KMgCl_3{\cdot}6H_2O$) does not appear to have been studied directly, although it has been suggested that 1.5 mol of water are lost on heating.[5]

## EXPERIMENTAL

*Starting Material.*—The material used throughout was AnalaR $NH_4MgCl_3{\cdot}6H_2O$ which had been recrystallised from deionised water. After vacuum drying, the compound was analysed for chloride by standard methods [6] (Found: Cl, 41.2. Calc.: Cl, 41.4%). These results indicated that no hydrolysis had occurred. $X$-Ray diffraction using Cu-$K_\alpha$ radiation gave a pattern in excellent agreement with that published.[7] Optical examination showed the recrystallised material to consist of rhombohedra varying in size between 40 and 200 μm with 80% of the material between 90 and 140 μm. All the samples were taken from a single batch which was stored over uncrystallised material so that deliquescence would not occur.

*Thermal Decomposition.*—Samples weighing 60 ± 6 mg were heated at various constant temperatures under flowing nitrogen (70 cm$^3$ min$^{-1}$) containing constant partial pressures of water vapour which were obtained by passing the gas over drying agents or through saturated salt solutions held in a thermostat. The weight losses were recorded automatically using an electrobalance and recorder (CI Microforce balance, Mark 11C, sensitivity 25 mg full scale deflection). Variations in sample weight between 40 and 100 mg had no effect on the results when these were plotted on reduced axes; gas flow rates greater than 30 cm$^3$ min$^{-1}$ also had no effect. At temperatures greater than *ca.* 500 K sublimation of ammonium chloride gave variable weight losses, but these were easily recognised. The temperatures quoted in the present work all lie well below such sublimation temperatures.

Some runs were carried out using $MgCl_2{\cdot}6H_2O$ and anhydrous $MgCl_2$ for comparison purposes.

*Enthalpimetric Measurements.*—The calorimeter module of a Du Pont 900 Thermal Analyser was used, with sample weights of 2 mg and a heating rate of 15 K min$^{-1}$. Sapphire was used as the calibration standard [8] and results were averaged over three runs.

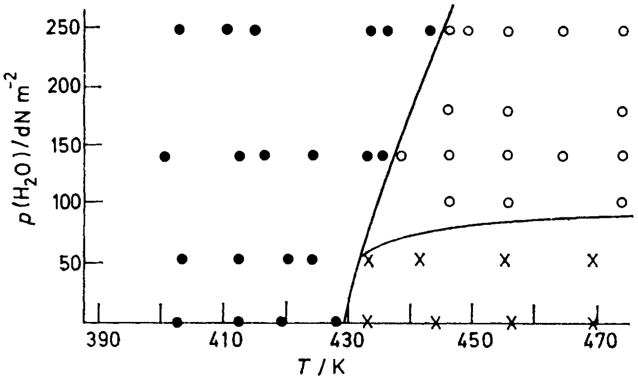

FIGURE 1 Temperature–pressure diagram for decomposition of ammonium carnallite: (●) dihydrate product; (○) two-stage dehydration; (×) anhydrous product

*Infrared Spectroscopy.*—Samples at various stages of decomposition were examined on a Perkin-Elmer 457 instrument using a Nujol-mull technique.

## RESULTS

*Products.*—Figure 1 summarises the experimental results, as a function of temperature and partial pressure of water vapour. Two products were formed, with weight losses corresponding to a dihydrate and the anhydrous compound. Analytical results [6] for these are given in Table 1 and provisional $X$-ray diffraction data in Table 2. The dihydrate is delinquescent and rehydrates easily to the hexahydrate with no obvious intermediates. The anhydrous material does not have the diffraction pattern expected from a mixture of $NH_4Cl$ and $MgCl_2$.

The pressure–temperature conditions for the formation of these products were as expected, with low temperatures and/or high partial pressures favouring the dihydrate and high temperatures favouring the anhydrous compound. Over a large range of temperatures and pressures the decomposition occurred in two stages with the anhydrous compound as final product.

TABLE 1

Analytical results for reaction products

| | Dihydrate | | Anhydrous | |
|---|---|---|---|---|
| | Obs. | Theory | Obs. | Theory |
| % Mg | 12.96 | 13.16 | 16.24 | 16.35 |
| % Cl | 57.38 | 57.56 | 71.41 | 71.49 |
| % Weight loss from $NH_4MgCl_3{\cdot}6H_2O$ | 28.3 | 28.22 | 42.0 | 42.32 |

TABLE 2

*X*-Ray diffraction data for reaction products

| Dihydrate | $MgCl_2{\cdot}2H_2O$* | | $NH_4Cl$* | | Anhydrous | $MgCl_2$* | |
|---|---|---|---|---|---|---|---|
| | *d* | *I* | *d* | *I* | | *d* | *I* |
| | 5.55 | 30 | | | | 5.85 | 29 |
| 4.5vw | | | | | | | |
| | 4.28 | 30 | | | | | |
| | | | | | 4.0s | | |
| | 3.95 | 4 | 3.87 | 23 | | | |
| | | | | | 3.45s | | |
| | | | | | 3.10s | 3.10 | 10 |
| 2.95vs | 2.86 | 13 | | | 2.9vs | 2.96 | 57 |
| | 2.76 | 100 | 2.74 | 100 | | | |
| | | | | | 2.7vs | | |
| 2.65w | 2.64 | 4 | | | | | |
| | | | | | | 2.65 | 100 |
| | | | | | 2.45w | | |
| | 2.37 | 40 | | | | 2.35 | 1 |
| | 2.32 | 5 | | | | | |
| 2.25vw | | | 2.24 | 4 | | | |
| 2.18w | 2.12 | 25 | | | | | |
| | 2.07 | 13 | | | 2.05ms | | |
| | | | | | | 1.98 | 9 |
| 1.92w | | | 1.94 | 7 | | | |
| | 1.82 | 10 | | | | 1.82 | 63 |
| | 1.80 | 9 | | | 1.80ms | | |
| 1.75vw | 1.77 | 10 | | | | | |
| | | | | | | 1.74 | 10 |
| | 1.73 | 4 | 1.73 | 5 | | | |
| 1.70vw | 1.69 | 9 | | | | | |
| 1.675ms | 1.66 | 4 | | | | | |
| | 1.59 | 15 | 1.58 | 23 | 1.5w | 1.55 | 11 |
| | | | | | | 1.48 | 23 |
| | | | | | | 1.43 | 3 |
| 1.40w | | | | | | | |
| | | | 1.37 | 5 | 1.38vw | 1.34 | 2 |
| | | | 1.29 | 3 | | 1.28 | 9 |
| | | | 1.225 | 5 | | | |
| | | | | | 1.14vw | 1.18 | 3 |
| | | | | | | 1.15 | 14 |
| | | | | | | 1.12 | 1 |
| | | | | | | 1.08 | 2 |
| | | | | | | 1.05 | 10 |
| | | | 0.968 | 1 | | | |
| | | | 0.889 | 1 | | | |

* Data from ASTM Index.

*Kinetics and Mechanisms.*—The decomposition curves ($\alpha$ against $t$, where $\alpha$ = proportion decomposed) were mainly sigmoid in shape, with short initiation periods. The results were interpreted in terms of models based on nucleation control, phase-boundary control, or diffusion control of the dehydration reaction and the data of Sharp *et al.*[9] were used. Experimental reduced-time plots were constructed and compared with those for various model systems. This comparison was carried out for the single-stage reactions and for each of the two stages in the high-pressure runs, since the inflection was very marked. This comparison easily decided the best fit between experimental and calculated plots.

At temperatures below 406 K and at all the partial pressures studied, *i.e.* in the region of dihydrate stability, a phase-boundary process was rate controlling. This followed the contracting-disc equation (1). At temperatures above 406 K and vapour pressures less than 100 dN m$^{-2}$, *i.e.* in the area in which the anhydrous compound is formed directly, the best fit between experimental and calculated plots was in terms of first-order kinetics, following equation (2).

$$[1 - (1 - \alpha)^{\frac{1}{2}}] = kt \qquad (1)$$

$$- \ln(1 - \alpha) = kt \qquad (2)$$

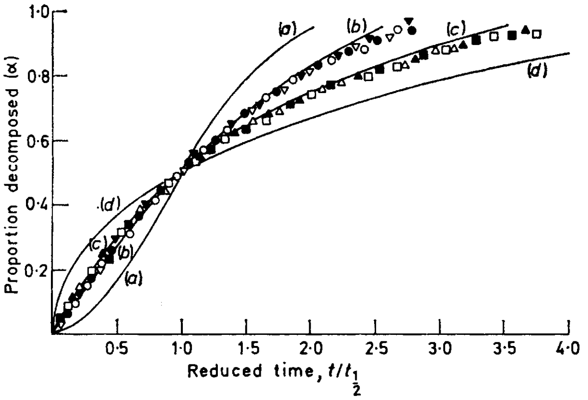

FIGURE 2 Reduced-time plots for formation of the dihydrate and anhydrous compound: dihydrate (▼) 378, 250; (▽) 388, 141; (●)400, 53; (○)404 K, 0.03 dN m$^{-2}$; anhydrous (▲) 417, 53; (△) 445, 53; (■) 409, 0.03; (□) 432 K, 0.03 dN m$^{-2}$

Curves: (*a*) Avrami–Erofeyev equation ($n = 2$), $[-\ln(1 - \alpha)]^{\frac{1}{2}} = kt$; (*b*) contracting-disc equation (1); (*c*) first-order equation (2); (*d*) Cylindrical-diffusion equation, $[(1 - \alpha)\ln(1 - \alpha) + \alpha] = kt$

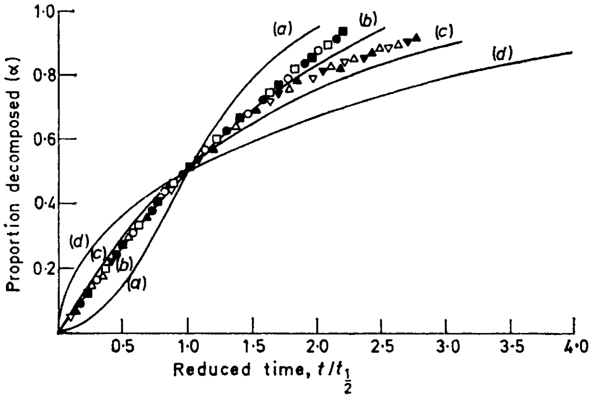

FIGURE 3 Reduced-time plots for the two-stage process: first stage (■) 431, 250; (□) 422, 180; (●) 422, 141; (○) 440 K, 106 dN m$^{-2}$; second stage (▲) 450, 250; (△) 422, 180; (▼) 414, 141; (▽) 450 K, 106 dN m$^{-2}$. Curves as in Figure 2

In the high-temperature–high-pressure region, corresponding generally to the two-stage decomposition, each stage followed the contracting-disc equation over the whole range of conditions used. Figures 2 and 3 show comparisons between experimental data and models for various stages in the decomposition. In the two-stage process there is some overlap between the two stages and this is reflected in the apparent high values of $\alpha$ for the first stage (Figure 3).

Rate constants were calculated from the gradients of the curves of $f(\alpha)$ against $t$, and these were used to calculate the activation energies and frequency factors given in Table 3.

TABLE 3

Arrhenius parameters

| $p(H_2O)$ | Dihydrate | | Two-stage reaction: First-stage | | Two-stage reaction: Second stage | | Anhydrous | |
|---|---|---|---|---|---|---|---|---|
| dN $m^{-2}$ | $E$/kJ $mol^{-1}$ | log ($A/s^{-1}$) | $E$/(kJ $mol^{-1}$) | log ($A/s^{-1}$) | $E$/kJ $mol^{-1}$ | log ($A/s^{-1}$) | $E$/kJ $mol^{-1}$ | log ($A/s^{-1}$) |
| 0.03 | 101 ± 10 | 26 | | | | | 37 ± 5 | 7.6 |
| 53 | 103 ± 10 | 25.5 | | | | | 40 ± 5 | 8.3 |
| 106 | | | 67 ± 5 | 11.1 | 95 ± 10 | 8.8 | | |
| 141 | 65 ± 8 | 18 | 48 ± 5 | 10.6 | 88 ± 10 | 9.8 | | |
| 180 | | | 42 ± 5 | 8.5 | 84 ± 8 | 7.6 | | |
| 250 | 125 ± 15 | 16.5 | 35 ± 4 | 10.2 | 79 ± 8 | 8.8 | | |

*Enthalpy Measurements*.—The enthalpy of decomposition was calculated to be 240 ± 20 kJ for the loss of four water molecules and 114 ± 10 kJ for the subsequent formation of the anhydrous compound.

*Infrared Spectroscopy*.—The results are given in Table 4; assignments given are those suggested by Gamo.[10]

TABLE 4

Infrared data ($cm^{-1}$) for reactants and products

| Hexahydrate | Dihydrate | Anhydrous | Assignment |
|---|---|---|---|
| 3 400 | 3 400 | | $\nu(H_2O)$ str. |
| | 3 150 | | |
| 2 225 | | | $\nu_2 + \nu_R$ (bend + wag) |
| 1 860 | | | |
| 1 648 | 1 610 | | $\nu_2(H_2O)$ bend |
| | 600 | 608 | $H_2O$ rock, wag |
| | 450 | | |
| 350 | | 300 | M–Cl |

## DISCUSSION

*Products*.—As mentioned previously, the general fields of stability of the dihydrate and anhydrous compounds are as might be expected, with higher temperatures favouring the anhydrous material and higher partial pressures of water vapour favouring the dihydrate.

The evidence presented suggests that the dihydrate and the anhydrous chloride are single compounds rather than mixtures of ammonium chloride and magnesium chloride. The $X$-ray diffraction data and the behaviour in the second stage of dehydration and on rehydration are not compatible with the latter formulation. Magnesium chloride hexahydrate dehydrates through intermediates with four, two, and one molecules of water.[11] No evidence for either the tetra- or mono-hydrates was obtained on either dehydration or rehydration, whereas using the same equipment and the hexahydrate or anhydrous $MgCl_2$, both the tetra- and di-hydrates could be formed easily, and some additional evidence was obtained for the monohydrate.

The i.r. data show a lowering in frequency for the water molecules which reflects tighter co-ordination in the dihydrate than in the starting material. The occurrence of a stretching band at 3 150 $cm^{-1}$ suggests that two types of water molecule are present.

*Kinetics and Mechanisms*.—There is a close relationship between reaction stoicheiometry and mechanisms. It is not possible to generalise such relationships since few studies have been made on multistage reactions. Previous work[12] on the dehydration of $CaSO_4 \cdot 2H_2O$ suggests a similar close relationship between the two.

The high-temperature-low-pressure loss of $6H_2O$ in a single stage follows linear (first-order) kinetics. There are two possible mechanistic interpretations of such behaviour: that each crystal of ammonium carnallite produces a single nucleus of product which then grows uniformly,[13] or that a constant number of one-dimensional nuclei exist. The latter is equivalent to Avrami–Erofyev kinetics[14] with $n = 1$. The main difference between these interpretations is obviously in the number of nuclei existing in each crystal. Attempts to determine the number of dehydration nuclei were difficult but microscopic examination using a hot stage always revealed very rapid surface nucleation producing opaque material. This suggests a large number of nuclei rather than anything which could be interpreted as a single dehydration nucleus per crystal.

The dihydrate is formed by a phase-boundary process over the range of temperatures studied and the loss of water from this compound follows the same mechanism although the activation energies for the two processes are different. This type of rate-controlling step is generally taken to refer to bond-making or -breaking processes and it seems reasonable to suppose that in the slowest step $Mg-OH_2$ bonds are being broken or Mg–Cl bonds are being formed. There is obviously a difference in activation energy between the apparently similar processes occurring in the hexahydrate and the dihydrate. These are discussed in the next section.

*Enthalpy Changes*.—As part of a study on the dehydration of cobalt(II) chloride hexahydrate, Grindstaff and Fogel[15] correlated the enthalpy changes on dehydration of some 200 hydrates. They suggested that simple replacement of water by chloride ion in the co-ordination sphere of a bivalent cation led to changes in enthalpy of *ca.* 55 kJ per mole of water; this value is close to the enthalpy of vaporisation of ice. If the mechanism is more complex than this simple replacement, *e.g.* formation or replacement of bridging groups, then very different values are obtained, although these could be larger or smaller than 55 kJ $mol^{-1}$. On this basis the present results appear normal, in that the overall enthalpy changes are close to (4 × 55) kJ for the first stage of dehydration and (2 × 55) kJ for the second stage.

However, comparison of the data shows that for each stage in the decomposition the activation energy is less than the enthalpy change. This indicates that each decomposition consists of more than a single step. The slowest of these is the true rate-controlling step and the observed activation energy establishes the maximum enthalpy change possible in any step. The difference between the activation energy and the overall enthalpy change establishes a minimum value for the enthalpy change in the individual steps.

Applying this reasoning to all the stages in the decomposition gives the results in Table 5. Since there is a maximum number of water molecules to be lost per mol of reactant at each stage, some of the higher numbers of stages are less likely to reflect real processes.

TABLE 5

Activation energy–enthalpy comparison

| Reaction | Activation energy (kJ) | Enthalpy change (kJ) | $\Delta$ | Range of energy (kJ) | No. of stages Min. | Max. |
|---|---|---|---|---|---|---|
| Loss of $4H_2O$ low $T$ | 125 | 240 | 115 | 115—125 | 2 | 2 |
| Loss of $4H_2O$ high $T/p$ | 35 | 240 | 205 | 35—205 | 2 | 7 |
| Loss of $2H_2O$ | 80 | 114 | 34 | 34—80 | 2 | 3 |
| Loss of $6H_2O$ | 40 | 354 | 314 | 40—314 | 2 | 9 |

*Frequency Factors and Mechanisms.*—If the steps in the reaction are (*a*) loss of water from the $Mg^{2+}$ co-ordination sphere, followed by, or coincidental with, (*b*) entry of $Cl^-$ into the co-ordination sphere, then this could occur by either an $S1$ mechanism where the second of these steps is rate controlling or by an $S2$ mechanism if the rates of migration of $H_2O$ and $Cl^-$ are sufficiently similar. The former, $S1$, process would produce a lowered co-ordination round $Mg^{2+}$ and a transition state with fewer degrees of freedom than the reactant or product. This would indicate [16] a frequency factor lower than an isolated gaseous molecule ($A = 10^{13}$). Conversely, the $S2$ mechanism would produce a higher co-ordination number round the $Mg^{2+}$, more degrees of freedom in the transition state, and hence high frequency factors.

Inspection of Table 3 shows that the low-temperature formation of dihydrate produces high values of $A$ while all the other reactions have low frequency factors. It seems possible therefore that at low temperatures the dihydrate is produced by an $S2$ mechanism. One effect of temperature would seem to be to increase preferentially the rate of migration of water, so that attack by chlorine becomes the slow step. The observed reduction in frequency factor with increasing partial pressure of water vapour for this stage perhaps lends weight to this suggestion.

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