THE DEAQUATION REACTIONS OF SOME METAL SALT HYDRATES AT ELEVATED PRESSURES*

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ABSTRACT

The deaquation reactions of $BaCl_2 \cdot 2H_2O$, $BaBr_2 \cdot 2H_2O$ and $CoCl_2 \cdot 6H_2O$ were studied by the thermal analysis techniques of thermogravimetry, differential thermal analysis (DTA), and electrical conductivity in the pressure range from one to 170 atm. In general, the effect of pressure on the TG curves increased the T_i and T_f values and also the reaction interval, $(T_f - T_i)$. The DTA curves exhibited splittings into multiple peaks as a result of the increased pressure. These splittings were interpreted as due to the evolution of a liquid water phase followed by its subsequent vaporization.

INTRODUCTION

There have been numerous thermal analysis investigations of the deaquation reactions of metal salt hydrate systems at atmospheric or sub-atmospheric pressures. From these studies, the nature of the deaquation reactions has been elucidated such as the thermal stability temperatures, the existence of intermediate hydrates, and the composition of the anhydrous products. However, very few of these studies have been carried out at supra-atmospheric pressures.

Garn[1] reported the differential thermal analysis curves of $BaCl_2 \cdot 2H_2O$ in a self-generated atmosphere at pressures up to four atm. Several new endothermic peaks were observed during the deaquation reaction but no effort was made to interpret their origin. The DTA curves of this compound at elevated pressures were also reported by Kessis[2]. Locke[3,4] reported the DTA curves of $MgSO_4 \cdot 7H_2O$ at pressures up to 150 atm. At the higher pressures single endothermic peaks, which were observed at one atmosphere, were split into two or more peaks. Unfortunately, the origin of these peaks and the effect of pressure on them was not discussed. It was stated that the deaquation reaction was quite complex and that it was influenced by the presence of water vapor and sample particle size.

A simple method for the study of deaquation reactions of metal salt hydrates at elevated pressures is by the use of a sealed tube sample holder. Such an approach was used by Wendlandt[5] to investigate the deaquation of $CuSO_4 \cdot 5H_2O$. Using this technique, only two endothermic peaks were observed rather than three for the loss of the first four moles of water per mole of metal salt. It was possible to separate the deaquation reaction from the large heat of vaporization of water reaction. The sealed tube technique was applied to other systems also, such as: $BaCl_2 \cdot 2H_2O$ and $BaBr_2 \cdot 2H_2O$[6]; $CoCl_2 \cdot 6H_2O$[7]; $[Cr(NH_3)_5H_2O]X_3$[8]; and others.

The purpose of this investigation is to report the deaquation reactions of certain metal salt hydrates at pressures up to 170 atm using the thermal analysis techniques of thermogravimetry (TG), differential thermal analysis (DTA), and electrical conductivity (EC).

EXPERIMENTAL

Compounds

The metal salt hydrates, $BaCl_2 \cdot 2H_2O$, $BaBr_2 \cdot 2H_2O$ and $CoCl_2 \cdot 6H_2O$, were all of reagent grade quality. After grinding in a mortar and pestle, the 200 mesh particle size fractions were used in all of the measurements.

High pressure thermal analysis equipment

The high pressure thermobalance[9], differential thermal analysis[10], and electrical conductivity[11] instruments used have all been previously described. Operational procedures, sample size and furnace heating rates were the same as previously employed.

RESULTS AND DISCUSSION

$BaCl_2 \cdot 2H_2O$ system

The TG curves for this compound are shown in Fig. 1. The curve recorded at one atm pressure (curve A) indicates a mass-loss in the temperature range from 80 to 115 °C which corresponds to the loss of one mole of water per mole of metal salt, according to the reaction:

$$BaCl_2 \cdot 2H_2O(s) \rightarrow BaCl_2 \cdot H_2O(s) + H_2O(g)$$

This agrees with previous TG studies[6]. A second mass-loss takes place between 125 and 160 °C which again corresponds to the loss of one mole of water per mole of metal salt, or

$$BaCl_2 \cdot H_2O(s) \rightarrow BaCl_2(s) + H_2O(g)$$
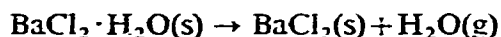
As the pressure of the system is increased, the most obvious change in the TG curves is that the initial deaquation temperatures, T_i, increase. Also, the mass plateau corresponding to the composition, $BaCl_2 \cdot H_2O$, disappears completely or is

indicated only by a curve inflection point. The rate of the deaquation reaction is also affected by the pressure increase, as indicated by the slopes of the curves. At a pressure of 69 atm (curve E), the mass-loss is continuous from about 110°C to a maximum temperature of 300°C. As seen from the curves. the final dehydration temperature, T_f, increases by 140°C on going from one to 69 atm.
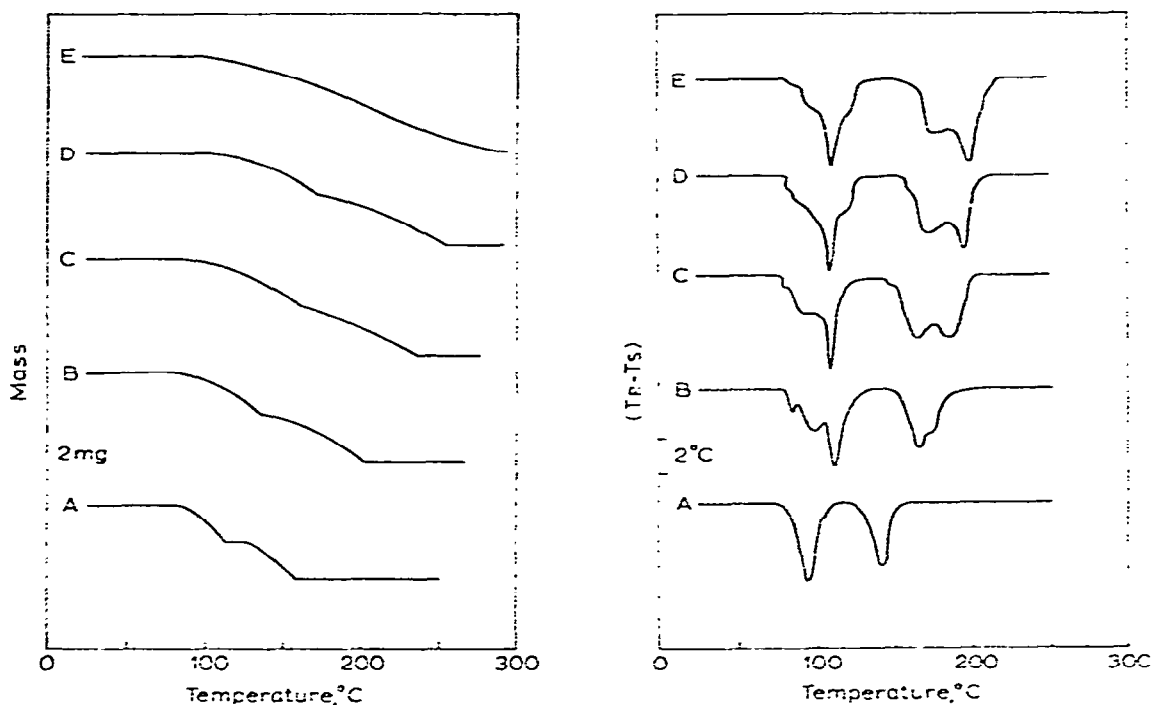

Fig. 1 (left). Thermogravimetric curves of $BaCl_2·2H_2O$. A. 1 atm; B, 15 atm; C, 27 atm; D, 42 atm; E, 69 atm.

Fig. 2 (right). Differential thermal analysis curves of $BaCl_2·2H_2O$. A, 1 atm; B, 27 atm; C, 42 atm; D, 69 atm; E, 137 atm.

The DTA curves at various pressures are shown in Fig. 2. At one atmosphere of pressure, the curve consists of two endothermic peaks; the first peak temperature minimum occurs at 95°C while the second minimum is at 142°C (curve A). These two peaks are due, of course, to the two dehydration reactions previously discussed. As the pressure is increased, the most obvious change observed is the formation and consequent disappearance of new shoulder peaks on the two main peaks. The initial peak temperatures did not change with change in pressure which indicates that the first peak is due to the sum of the two reactions,

$$BaCl_2·2H_2O(s) \rightarrow BaCl_2·H_2O(s) + H_2O(l)$$

and

$$H_2O(l) \rightarrow H_2O(g)$$
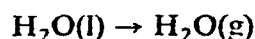
This behavior has previously been shown to exist by both electrical conductivity[12] and DTA measurements[13]. The evolution of liquid water in the first step of the reaction should not be pressure dependent while the vaporization step is. The first reaction also shows up as the initial shoulder peaks in curves B and C and does not change as the pressure is increased from 27 to 137 atm. The reason for this is not clearly understood. The curve peak minimum for the second stage of the dehydration reaction, at a pressure of 42 atm (curve C), splits into two poorly resolved peaks suggesting that perhaps the compound, $BaCl_2 \cdot 0.5H_2O$, exists. The two peaks appear even at the highest pressure employed, 137 atm (curve E).
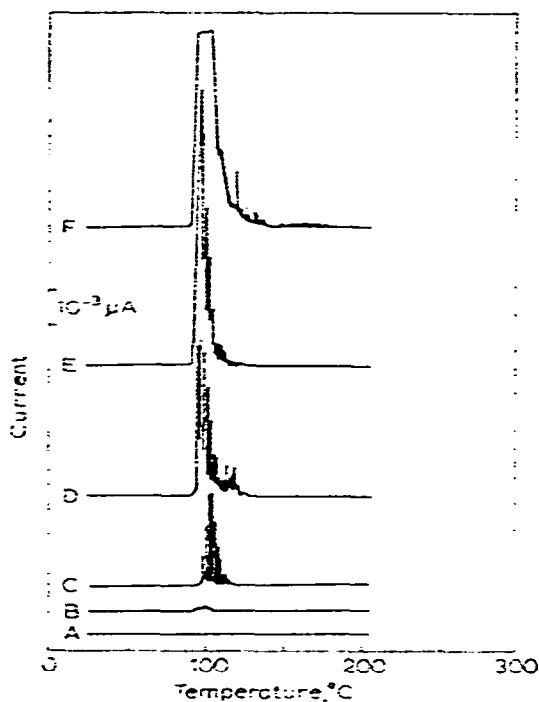

Fig. 3. Electrical conductivity curves of $BaCl_2 \cdot 2H_2O$. A, 1 atm; B, 7 atm; C, 15 atm; D, 27 atm; E, 42 atm; F, 170 atm.

The fact that the pressure of the system alters the diffusivity of the liberated water through the solid sample and thus the amount of water vapor present is illustrated by the electrical conductivity curves shown in Fig. 3. In curve A, it is seen that no deviation from the baseline is detected even though water is evolved. The reason for this appears to be that the rate of diffusion of water vapor from the thin layer of sample is so rapid that no liquid water can exist and no electrical conductivity is possible. As the system pressure is increased (curve B), a slight change in the baseline at the predicted temperature for the first dehydration step is observed. The second dehydration reaction is not detected since at the higher temperature, the water is vaporized as rapidly as it is liberated and the diffusion is rapid enough to prevent

the presence of a liquid water phase. As the pressure is increased, the effects previously mentioned increase, as indicated by the amplitude of the EC peak and the temperature range of the peak. At a pressure of 170 atm, the second dehydration reaction is observed, as noted by a slight change in the base line at the expected temperature.
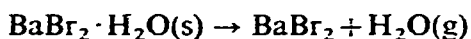
$BaBr_2 \cdot 2H_2O$ system

The TG curves of this compound are shown in Fig. 4.

As expected, the dehydration reactions were similar to those for the $BaCl_2 \cdot 2H_2O$ system, and indicates that the first dehydration reaction proceeds according to:

$$BaBr_2 \cdot 2H_2O(s) \rightarrow BaBr_2 \cdot H_2O(s) + H_2O(g)$$

and occurs over the temperature range from 70 to 110°C, at one atm. A well defined mass plateau extends from 110 to 160°C, where the second dehydration raaction.

$$BaBr_2 \cdot H_2O(s) \rightarrow BaBr_2 + H_2O(g)$$

takes place and is completed by about 200°C. With increasing pressure. the same behavior was observed as was found for the $BaCl_2 \cdot 2H_2O$ systems in that the T_i and T_f temperatures increased while the mass plateau decreased, yielding only an inflection point in the curves.
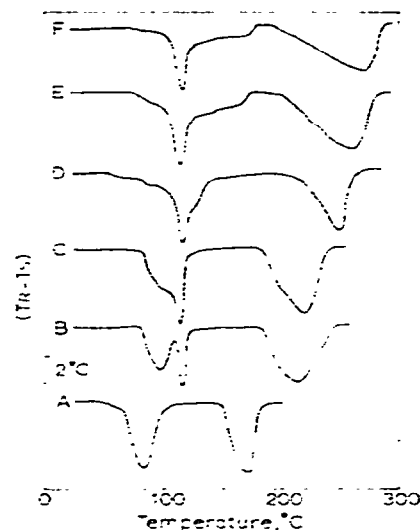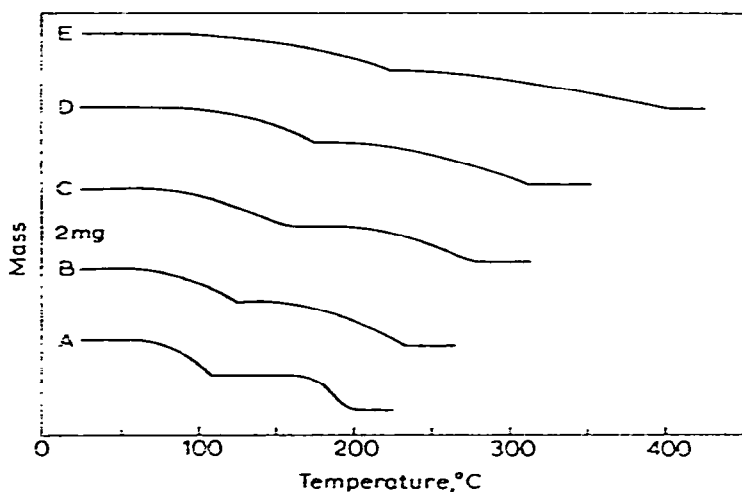

Fig. 4 (left). Thermogravimetric curves of $BaBr_2 \cdot 2H_2O$. A, 1 atm; B, 15 atm; C, 27 atm; D, 42 atm; E, 69 atm.

Fig. 5 (right). Differential thermal analysis curves of $BaBr_2 \cdot 2H_2O$. A, 1 atm; B, 18 atm; C, 35 atm; D, 69 atm; E, 103 atm; F, 137 atm.

The DTA curves for this system are shown in Fig. 5. The curve at one atmosphere (curve A) of pressure contains two endothermic peaks due to the two dehydration reactions previously described. The peaks are well separated. with peak minima temperatures of 90 and 175°C, respectively. At elevated pressures, 18 and 35 atm.

the liberation of liquid water is observed as evidenced by the splitting of the peak into two peaks (one main peak and a shoulder peak). Thus, as in the case of $BaCl_2 \cdot 2H_2O$, the first peak is made up of the two reactions: (a) the liberation of a liquid water phase; and (b) the vaporization of the liquid water. The second dehydration peak minima temperatures shift to higher temperatures as the pressure is increased, changing from 175°C at one atm to 275°C at 170 atm. This change occurs in a regular manner, as shown by the plot of pressure *versus* temperature in Fig. 6.
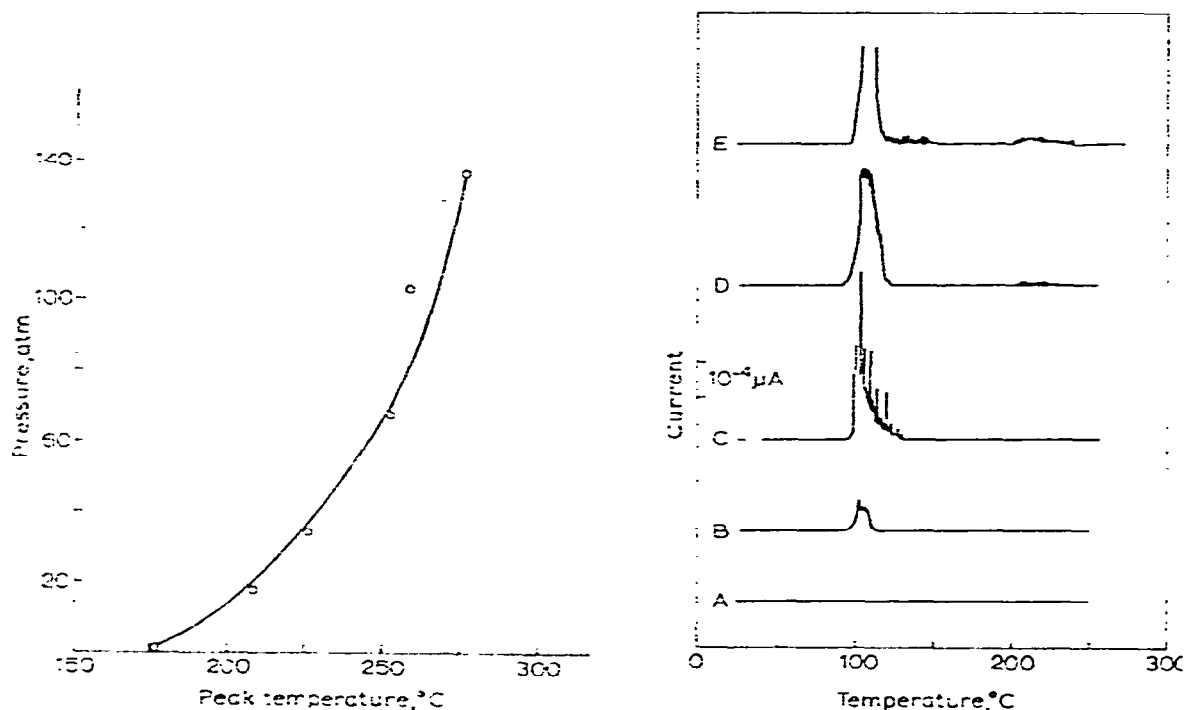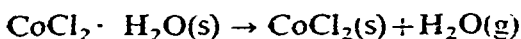

Fig. 6 (left). Change in peak minimum temperature with pressure for the $BaBr_2 \cdot H_2O \rightarrow BaBr_2$ transition.

Fig. 7 (right). Electrical conductivity curves of $BaBr_2 \cdot 2H_2O$. A, 1 atm; B, 15 atm; C, 35 atm; D, 69 atm; E, 170 atm.

The EC curves for this compound at various pressures are shown in Fig. 7. At one atmosphere of pressure, no conductivity is observed indicating that the water vaporization rate is equal to the rate of evolution from the solid phase. As the system pressure increases (15 atm), the EC curves increase in magnitude. There was even some indication of a conducting phase for the second dehydration reaction at 170 atm.

$CoCl_2 \cdot 6H_2O$ *system*

The TG curves for this compound are shown in Fig. 8. In agreement with earlier studies[7], the dehydration reactions take place in three steps, according to the equations:

$$CoCl_2 \cdot 6H_2O(s) \rightarrow CoCl_2 \cdot 2H_2O(s) + 4H_2O(l)$$

$$CoCl_2 \cdot 2H_2O(s) \rightarrow CoCi_2 \cdot H_2O(s) + H_2O(g)$$

$$CoCl_2 \cdot H_2O(s) \rightarrow CoCl_2(s) + H_2O(g)$$

There is no evidence from the TG curves concerning the physical state of the first water evolution but previous DTA and melting point studies indicate that it is in the liquid phase. More will be discussed about this reaction later on.
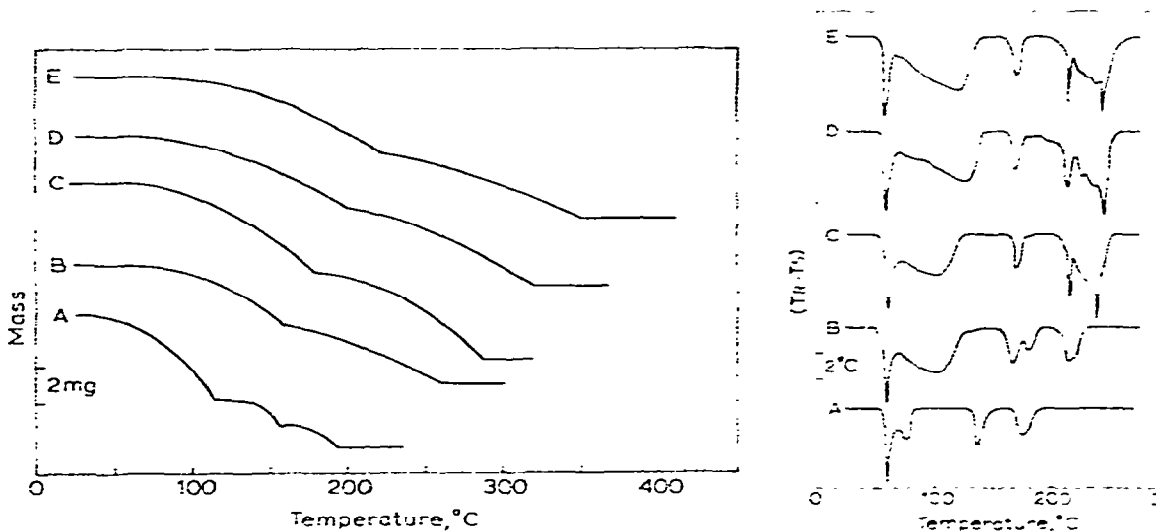

Fig. 8 (left). Thermogravimetric curves of $CoCl_2 \cdot 6H_2O$. A, 1 atm; B, 15 atm; C, 27 atm; D, 42 atm; E, 69 atm.

Fig. 9 (right). Differential thermal analysis curves of $CoCl_2 \cdot 6H_2O$. A, 1 atm; B, 15 atm; C, 21 atm; D, 35 atm; E, 69 atm.

At one atmosphere of pressure, the first mass-loss occurs at about 40 °C giving a mass plateau starting at about 115 °C. From 135 to 155 °C, the $CoCl_2 \cdot 2H_2O$ loses water to give the monohydrate, $CoCl_2 \cdot H_2O$, while above 175 °C, the anhydrous salt, $CoCl_2$, is formed. As the system pressure is increased, an inflection point is still evident in the curve for the 2-hydrate, $CoCl_2 \cdot 2H_2O$, but no curve inflection point is present for the existence of the monohydrate. The reaction interval, $T_f - T_i$, increases as the pressure increases, as was observed for the other metal salt hydrate systems.

Perhaps the most interesting aspect of this system is shown in the DTA curves, as illustrated in Fig. 9. The narrow endothermic peak at a peak minimum temperature of about 50 °C is due to the evolution of the four moles of liquid water per mole of compound and is independent of pressure up to 69 atm. Thus, the first peak (plus the shoulder peak) at one atm of pressure (curve A) is due to the two reactions:

$$CoCl_2 \cdot 6H_2O(s) \rightarrow CoCl_2 \cdot 2H_2O(soln.) + 4H_2O(l)$$

$$4H_2O(l) \rightarrow 4H_2O(g)$$
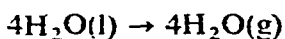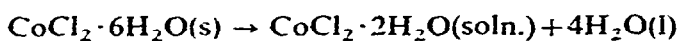
As the pressure is increased, the second endothermic peak shifts to higher peak minimum temperatures due to the pressure dependence of the vaporization of the water.

No simple explanation can be used to explain the multiple peaks occurring above 150 °C at pressures greater than 15 atm. The narrow peaks must be related to dezquation transitions, with the 2-hydrate → 1-hydrate peak at a ΔT minimum peak temperature of 175 °C as the most prominent feature. This temperature did not shift with an increase in system pressure. Using the same type of explanation as before, the narrow peak with a ΔT peak minimum at 210 °C is probably due to the 1-hydrate→ $CoCl_2$ transition; it also is independent of pressure. This narrow peak is a shoulder peak on a broader endothermic peak, the latter of which must certainly be due to the vaporization of the liquid water.
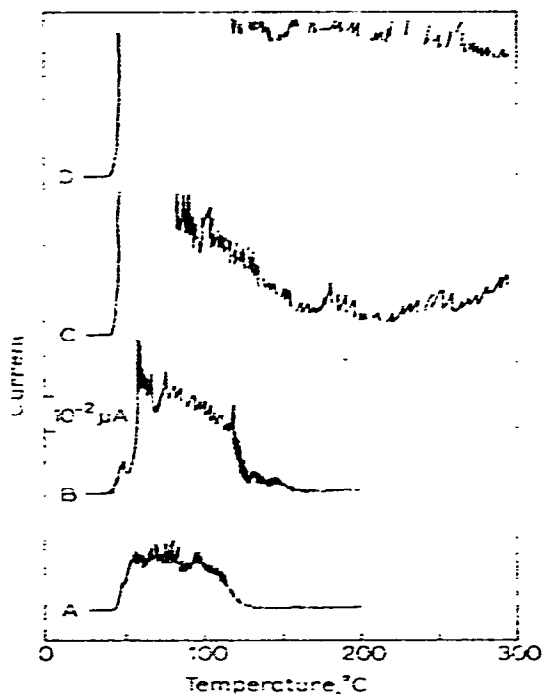

Fig. 10. Electrical conductivity curves of $CoCl_2 \cdot 6H_2O$. A, 1 atm; B, 7 atm; C, 27 atm; D, 69 atm.

The electrical conductivity curves are shown in Fig. 10. At one atmosphere of pressure (curve A), the conductivity increases very rapidly at about 50 °C, due to the liberation of liquid water and the formation of a saturated solution of $CoCl_2 \cdot 2H_2O$ or some similar ionic species. As the pressure in the system increases, the temperature interval at which electrical conductivity occurs also increases. At a pressure of 69 atm, the conductivity continues over the temperature range from 50 to 300 °C, indicating the presence of a liquid conducting phase.

GENERAL

Thermodynamic considerations

There are two primary deaquation reaction considerations which may be approached thermodynamically: (a) the temperature at which the reaction is initiated, T_i: and (b) the reaction interval. $T_f - T_i$. The effect of pressure on these two parameters can be determined qualitatively through the following considerations.

Deaquation reactions for metal salt hydrates can be represented by the equations

$$MX \cdot nH_2O \rightleftarrows [MX \cdot nH_2O]^+ \rightarrow MX + nH_2O(l) \tag{1}$$

and

$$nH_2O(l) \rightarrow nH_2O(g) \tag{2}$$
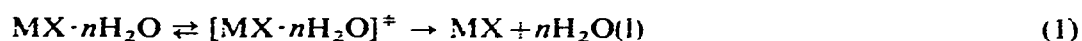
where $MX \cdot nH_2O$ is the initial metal salt hydrate; $[MX \cdot nH_2O]^+$ is the activated complex; MX is the metal salt; and (l) and (g) refer to the liquid and gaseous state, respectively. For a reaction to occur, the free energy change to form the activated complex, ΔG^+, must be negative. Therefore, at the temperature at which the reaction just begins.

$$\Delta G^+ \cong 0 \tag{3}$$

and

$$\Delta H^+ - T_i \Delta S^+ = \Delta G^+ \cong 0 \tag{4}$$

where ΔH^+ is the enthalpy of activation and ΔS^+ is the entropy of activation. Since both $MX \cdot nH_2O$ and $[MX \cdot nH_2O]^+$ are solids, neither ΔS^+ nor ΔH^+ should be pressure dependent. Hence, from eqn (1).

$$T_i \cong \Delta H^+ / \Delta S^+ \cong \text{constant} \tag{5}$$

which indicates that T_i should be almost independent of pressure. The free energy change, ΔG, for the overall reaction is

$$\Delta G = \Delta H - T \Delta S \tag{6}$$

where ΔH and ΔS are the reaction enthalpy and entropy, respectively, and T the absolute temperature. This equation can only be considered in a very qualitative manner since during the reaction, T is not constant but varies with time. The enthalpy and entropy changes are the sum of those for both steps of the reaction shown in eqns (1) and (2). or

$$\Delta H = \Delta H_1 + \Delta H_v \tag{7}$$

and

$$\Delta S = \Delta S_1 + \Delta S_v \tag{8}$$

where the subscript, (1), refers to the overall reaction given in eqn (1) and the subscript,

(v), refers to the vaporization step in eqn (2). Since the reactions in eqn (1) involve no gaseous species, the entropy change would be expected to be less than ΔS_v, or

$$\Delta S_v > \Delta S_1 \tag{9}$$

further, it is known from previous investigations[11] that generally

$$\Delta H_v > \Delta H_1 \tag{10}$$

hence,

$$\Delta G \cong \Delta G_v = \Delta H_v - T\Delta S_v \tag{11}$$

where thermodynamic parameters are controlled predominantly by the vaporization step. But, for vaporization (liquid and gaseous phase in equilibrium),

$$\Delta G_v = 0 \tag{12}$$

and eqn (11) may therefore be written as

$$\Delta H_v = T\Delta S_v \tag{13}$$

which is simply a special form of the Clapeyron equation. Since the enthalpy of vaporization varies only slightly with pressure changes,

$$\Delta H_v = T\Delta S_v \cong C \tag{14}$$

where C is a constant independent of pressure. Thus, increasing the pressure decreases ΔS_v so T must increase in order for ΔH_v to remain constant. Hence, increasing the pressure of the system should increase T_i and also the reaction interval, $T_f - T_i$.

Kinetics considerations

Nonisothermal deaquation reactions may be conveniently classified into three general categories: reactions in which the water is released (i) below the boiling point; (ii) above its boiling point; and (iii) at or near its boiling point. The mass-loss kinetics of reactions of type (i) are controlled by the vaporization of water below its boiling point, while for reactions of type (ii), in which the water is vaporized as quickly as it is released, the mass-loss kinetics are controlled by the actual deaquation reaction. In both cases, the usual non-isothermal kinetic equations are probably applicable. As is well known, most of the non-isothermal kinetics methods are based on the three equations:

$$dc/dt = kc^n \tag{15}$$

$$k = Ae^{-E/R} \tag{16}$$

and

$$dT/dt = \beta \tag{17}$$

where c is the concentration of the reactant at time, t; k the rate constant; n the reaction order; E the activation energy; A the preexponential factor; T the absolute temperature; and β the heating rate.

These methods are probably not valid, however, for reactions of type (iii). In this case, the water is released at or near its boiling point and its enthalpy of vaporization tends to keep the sample temperature constant throughout the vaporization step. Reactions of this type possess quadruple points in which gaseous and liquid water and hydrated and dehydrated salts in equilibrium. The mass-loss kinetics of type (iii) reactions have been analyzed[14] by balancing the rate of heat loss of the sample due to water vaporization by that of the heat gain due to heat transfer from the furnace; the equation employed is

$$\frac{dc}{dt} = \frac{C\beta t\gamma}{C_p T_B - \Delta H_v} \tag{18}$$

where γ is a proportionality constant (a type of heat transfer coefficient); C_p the heat capacity of water at constant pressure at its boiling point, T_B; and ΔH_v the heat of vaporization of water.

The brief kinetic considerations given above allow a qualitative description of some of the effects of pressure on deaquation reactions. First, it is apparent that an increase in pressure may change a deaquation reaction from one type to another. Specifically, a pressure increase may change a reaction of type (iii) to reaction (i) or a reaction of type (ii) to reaction (i) or (iii), and so on. Hence, a pressure increase may change completely the type of kinetics which describe the mass-loss during the deaquation reaction. A well known example of this behavior is the deaquation reaction of $BaCl_2 \cdot 2H_2O$ which at ambient atmosphere pressure is a type (iii) reaction but becomes a type (i) reaction on increasing the pressure.

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