Thermal dehydration characteristics of hydrated salts: A critical review

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Abstract: Thermal dehydration characteristics of hydrated salts have been critically reviewed. Structural characteristics of salts, especially the nature of bonding of water molecules with the metal ion, occurrence of melting, nucleation and growth of product phase, diffusional escape of water etc. which affect the rate of dehydration have been discussed. The dehydration characteristics of CuSO₄·5H₂O, Li₂SO₄·H₂O and CaC₂O₄·H₂O have been specially discussed as typical examples of widely studied salts.

Keywords: Hydrated salts, thermal dehydration, solid state kinetics.

Hydrated crystalline salts form one of the earliest class of compounds used as models for the study of the thermally stimulated solid state reactions. The ease with which water is removed from the coordination sphere of metal ions at relatively low temperature and the distinct crystalline features of both hydrated and dehydrated salts have stimulated a large number of authors to study this class of compounds.

Water acts as a strong coordinating ligand with many positive ions not only in their aqueous solutions, but also in the crystalline structures of the salts of these positive ions. It may, however, be emphasized that water which constitutes aquo-ion may not be present in the crystalline hydrates as the limitations imposed by crystal structure allow some water molecules to be strongly bonded than others. Water molecules in the crystalline hydrates are either coordinately bonded to the cation or enter within the voids generated by anion packing and stabilized by hydrogen bonding¹. A classical example is CuSO₄·5H₂O where four water molecules are directly coordinated to Cu²⁺ and the remaining one within the anion void¹,² as illustrated in Fig. 1. In NiSO₄·7H₂O and FeSO₄·7H₂O the extra water molecule is also bonded in a similar fashion i.e. acts as a bridge between the octahedral units. Generally, cations with high charge/radius ratio tend to accommodate more water molecules in their crystalline salts. The common hydration number for the crystalline salts are 2, 4, 6 and 8, though deviations are also frequently observed, for example, Li₂SO₄·H₂O, CuSO₄·5H₂O, Na₂CO₃·10H₂O, alums with 12H₂O etc.

Nature of water in hydrated salts: Close examination of the crystal structure of many hydrated salts suggests that water molecules behave as if there were a tetrahedral distribution of two positive and two negative charges or at least one electron acceptor¹. The negative end of water

Fig. 1. (a) Schematic molecular structure of CuSO₄·5H₂O showing that the octahedral coordination of Cu consists of four H₂O molecules and two oxygen of SO₄²⁻. (b) Partial crystal structure of the salt demonstrates similar arrangement (Adapted from Ref. 1).
dipole, i.e., oxygen, is always bonded to metal ion. The two lone electron pairs of oxygen are accepted by either two monovalent cations or a divalent or a multivalent cations. The two hydrogen atoms are bonded to water molecule through hydrogen bonding (see Figs. 2a-e). This corroborates with the ice-like frame work structure of water as found in many crystalline hydrates. Therefore, the most logical way of classifying crystalline hydrates would be to group them according to the environment of water molecules in their structures and a summarized table has been provided in the monograph by Brown et al. Essentially, these are: (i) Isolated or discrete water molecules. Water molecule bonded to other water molecule to form (ii) finite and (iii) infinite structures of hydrates. In KF\(\cdot\)\(2\)\(\text{H}_2\)\(\text{O}\) there are discrete water molecules surrounded tetrahedrally by two \(\text{F}^-\) and two \(\text{K}^+\) ions. In finite structure each water molecule is surrounded by a divalent positive ion and two \(\text{Cl}^-\) e.g. in \(\text{CuCl}_2\cdot\text{H}_2\)\(\text{O}\), in \(\text{Li}_2\text{SO}_4\cdot\text{H}_2\)\(\text{O}\), each water molecule is hydrogen bonded to two others so that a chain of water molecules occur in the crystal. Similar is the case with \(\text{SrCl}_2\cdot\text{H}_2\)\(\text{O}\) where each \(\text{Sr}^{2+}\) ion is surrounded by nine water molecules. The infinite structure is identified with layer structure, where the coordination group around the metal ion consists of four \(\text{Cl}^-\) and four water molecules which form an infinite layer one above the other e.g. in \(\text{BaCl}_2\cdot\text{H}_2\)\(\text{O}\) and \(\text{SrCl}_2\cdot\text{H}_2\)\(\text{O}\). All these examples have been quoted from Wells according to whom, "...any classification of this type would be impracticable, because water molecules in many hydrates do not have the same kind of environment. Much of the complexity in structural chemistry of hydrates is due to the non-equivalence of water molecules which, in turn, is associated with the fact that so many arrangements of nearest neighbours are compatible with the tetrahedral charge distribution of water molecule".

**Characteristics of dehydration reaction**: Depending upon the nature of occurrence of water in crystalline hydrates, three different types of dehydration reactions are encountered. In the first type, the structure of the reactant has no relation with the dehydrated product. Therefore, a new product phase is nucleated and grown with the progress of dehydration. In the other case, where the product phase has the same structure as the hydrated phase, water molecules are usually trapped in large channels of the framework structure as in the case of zeolites. Such dehydration is highly reversible in nature. The intermediate type is the dehydration of those compounds where intramolecular water is sandwiched between two finite unit cells, such as clay minerals. On dehydration at low temperature the clay minerals undergo shrinkage of cell dimension usually in one direction. In the present review we shall concentrate only on the first type of dehydration which is also known as 'cryolysis'.

Dehydration reactions are generally endothermic and reversible in nature. Kinetic behavior under isothermal condition indicates that dehydration process is either interface growth or diffusion controlled process. If the elimination of water takes place at the interface this may be characterized either by (i) a rapid or perhaps complete initial nucleation on some or all the surfaces followed by the advancement of new interface thus generated, or (ii) nucleation at specific surface sites and maintained during reaction followed by growth, or (iii) elimination of water from the crystal surface without the growth of new phase, which is, however, a rare phenomenon. The effect of self-cooling in this type of endothermic reaction is considerable and allowance therefore must be made before studying the kinetics of such reaction. However, the ambient water vapour pressure has great influence on the kinetics of dehydration and also on the recrystallization of product phase.

However, it is also difficult to classify the hydrates according to the nature of dehydration (as discussed above), since there are as many mechanisms as the modes of dehydration. Broadly, the following steps are involved in the dehydration of hydrates.

(i) Thermally stimulated mobility of water molecules within the crystalline reactant. Here the occurrence of melting plays a very important role as it facilitates greater mobility.

(ii) In the case of dehydration from solid phase, water molecules diffuse to the crystal edge or reac-
tion interface.

(iii) Escape of water from the crystal edge or reaction interface.

(iv) Chemical reactions, if any, at the interface.

(v) Recrystallization of product phase results in the creation of cracks, fissure etc. due to vacancies created from the escape of water molecules from the reactant salt.

(vi) Water vapour adsorption/desorption on product phase.

(vii) Intramolecular diffusional escape of water and loss from the crystal edge.

The sequence and relative significance of the above steps vary within different dehydration reactions. Some may overlap, some may behave in an intermediate manner or some may not even occur. Where melting is extensive large deviations may take place as discussed below.

**Effect of melting of the salt:**

Among the physical phenomena which exert considerable influence on the kinetics of dehydration of the salts, melting is perhaps the most important one. It is considered that only the molten phase has the capacity to be super heated or super cooled in its reverse process. Various theories have been put forward for melting. Broadly speaking, the amplitude of vibrational displacement of the atoms in the crystal increases with temperature to such an extent that their stability in a lattice arrangement is lost. Bond redistribution is occurring in the fused material are expected to be controlled by parameters similar to those occurring in homogeneous solution, albeit in the absence of solvent. This means that concentration of reactant and therefore the frequency of reactant collisions is high. Such a situation suggests that the reaction is not truly a solid state reaction and mechanistic models proposed for heterogeneous solid phase reaction are not applicable to the molten phase.

The relaxation and increase in bond length resulting from melting of the salt facilitate the removal of water, mostly in the form of simple evaporation until the composition of the product phase is reached. Recrystallization of the product from a reactant, in many cases, requires the presence of water (liquid or vapour). When water vapour is extensively adsorbed the reaction becomes reversible; kinetic behavior will be modified and the overall rate may even increase with increase in water vapour pressure after an initial decrease. This phenomenon is commonly known as Smith-Topley effect and is generally observed for dehydration at low temperature, especially under vacuum. Many crystalline hydrates such as MnC2O4.2H2O, Li2SO4.H2O, MgSO4.4H2O, CuSO4.5H2O, CaC2O4.2H2O, β-CaSO4.1/2H2O exhibit this effect during dehydration. However, it is not an universal phenomenon applicable to all hydrates. For more details the readers may consult the original and the review articles.

Where melting is extensive at relatively lower temperature (<80 °C), water molecules escape through evaporation from the surface. But at higher temperature (~80-100 °C) fine bubbles are generated which subsequently burst near the crystal edge. Both the phenomena are in conformity with zero-order kinetics, first observed for the dehydration of UO2(NO3)2.6H2O and subsequently for the single crystals of lithium potassium tartrate hydrate (LiKC4H4O6.2H2O). In the case of latter salt zero-order kinetics was found to follow only up to 5-75% of dehydration corresponding to the loss of 1.26 mole of H2O from single crystals at 90-100 °C. The kinetics of the subsequent loss of about 0.4-0.45 mole of H2O follows first-order law. For dehydration of crushed crystals of the same salt, α-time curves are deceleratory almost from the beginning of dehydration and follows first-order law up to the loss of 1.6 mole of water. This is attributed to the decrease in the effective surface area, resulting from sintering/coalescence of particles and temporary retention of some water in the inter particle voids, increased surface tension and viscosity of molten fluid etc. It is proposed that in the zero-order regime the dehydration takes place from the surface where the mobility of water molecules is high. The high activation value (~230 kJ/mol) for dehydration in the regime has been attributed to (i) high energy required to release relatively small quantity of water (2 mole) from strong hydrogen bonded environment not only with water molecules but also with COOH groups, (ii) evaporation/desorption from hydrophilic salt surface and (iii) temperature dependent mobility of H2O molecules within the viscous salt.

Zero-order kinetics has also been observed by the present authors for the dehydration of an undried reagent grade NiCl2.xH2O (where x = 6.5-6.8) which undergoes melting at 55-60 °C. Fig. 3 shows the zero-order plot of isothermal dehydration of nickel chloride hydrate in the temperature range 60-90 °C. The apparent E value is 40.2 ± 2 kJ/mol which is close to the heat of evaporation of water at 80-85 °C (~41 kJ/mol) suggesting that the phenomenon is the simple evaporation of
released water from the molten salt. In contrast, the water released from single crystal of LiKC\textsubscript{4}H\textsubscript{4}O\textsubscript{6}.2H\textsubscript{2}O possibly is in a structured state through hydrogen bonding with its own OH groups as well as with COOH groups. However, dehydration of NiCl\textsubscript{2}.xH\textsubscript{2}O in the temperature range 100–270 °C follows different kinetic behavior (Fig. 4). Second-order rate law follows over a longer period of time i.e. higher value of \( \alpha (-0.42) \) compared to the first-order rate law which follows only up to \( \alpha = 0.22 \). Again, for both the kinetic laws the apparent \( E \) values are low (25–26 kJ/mol). Such low \( E \) value indicates large impedance to the diffusional escape of water. Guarini\textsuperscript{18} has shown that for the dehydration of NiSO\textsubscript{4}.6H\textsubscript{2}O at low temperature the rate of recrystallization of the product is either comparable or slower than the rate of evaporation of water and therefore the product layer formed is thin and discontinuous, thereby facilitating rapid escape of water. With increase in temperature rapid loss of water accelerates recrystallization of the product layer to produce an almost continuous layer thereby exerting greater impedance to the escape of water molecules and consequent pressure build up within the bulk phase. In such a situation the kinetics changes to order based law (1st and 2nd) as observed for NiSO\textsubscript{4}.6H\textsubscript{2}O.

The other examples where comprehensive melting takes place before dehydration are CoCl\textsubscript{2}.6H\textsubscript{2}O\textsuperscript{19,20}, MgCl\textsubscript{2}/MgBr\textsubscript{2}.6H\textsubscript{2}O\textsuperscript{19–24}, FeCl\textsubscript{3}.xH\textsubscript{2}O\textsuperscript{25} etc. Many nitrates undergo melting even at temperature around 40 °C. An important example is the dehydration of Mn(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O which has been extensively studied by different workers\textsuperscript{26,27}. Some sodium salts like NaOOCCH\textsubscript{3}.3H\textsubscript{2}O, Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}.5H\textsubscript{2}O and Na\textsubscript{2}HPO\textsubscript{4}.12H\textsubscript{2}O undergo melting during dehydration which takes place in single or in multiple steps\textsuperscript{28}. Due to large heat change during melting the above salts are considered as potential storage of energy as the molten salts release the absorbed energy during cooling\textsuperscript{28}.

However, the phenomenon of melting or eutectic formation of salts sometimes appear to be temporary or even localized. It may so happen that intermediate hydrates undergo transient melting before dehydration. For example, tetrahydrate, dihydrate and even anhydrous MgCl\textsubscript{2}
also exhibit melting$^{19-24}$. These are sometimes difficult to identify from thermoanalytical curves or from enhanced reactivity as revealed by autocatalytic behavior. The time data obtained from such a reaction may not be represented by rate expressions based on advancing interface models. Even if the data follow any model expression for solid state reaction, it does not preclude the involvement of liquid phase in the reaction. In such a case, other supporting evidences like microscopic observations are necessary. The presence of localized froth or bubble structure confirms the occurrence of melting of either reactant or a reaction intermediate. Where melting occurs product recrystallization takes place through rapid nucleation and growth until the formation of a reaction interface and its advancement with geometrical orientation becomes slow or rate-determining step.

**Dehydration controlled by nucleation and growth:**

If nucleation is extensive on the crystal surface the reaction interface advances from periphery to the interior of the crystal. The initiation of the reaction at the surface facilitates rapid escape of water vapour with the result that the overall rate is controlled by nucleation and growth. On the other hand, if the nucleation is random within the crystal diffusional escape of water is considerably impeded relative to nucleation and growth. In such a situation the reactant/product interface advances from inside the crystal to the periphery and is controlled by diffusion. Examples of initial ($\alpha < 0.1$) rapid nucleation and growth of reactant/product interface at preferred crystallographic sites have been observed for the dehydration of Cu(HCOO)$_2$.4H$_2$O$^{29,30}$, Mn(HCOO)$_2$.2H$_2$O$^{31}$ (above 67°C), NiSO$_4$.6H$_2$O$^{32}$ (> 40°C). In these salts, the reaction interface advances with linear or constant rate at the temperature mentioned within the parentheses.

However, the phenomenon of constant rate of progress of the reaction interface is not universally applicable since the growth of nuclei may not be uniform in all crystallographic directions or reactant surfaces. This is evident from the appearance of star-shaped nuclei during dehydration of certain hydrates$^{18}$. Anisotropic growth of nuclei has also been observed$^{33,34}$ for the dehydration of BaCl$_2$.2H$_2$O where two dimensional nuclei grow preferentially along the (010) face.

The initial spurt of rapid nucleation at certain region within the solid does not prevent further nucleation at other unreacted regions. It has been observed$^{35}$ that during the dehydration of NiSO$_4$.7H$_2$O the number of nuclei formed increase with the square of time, unlike CuSO$_4$.5H$_2$O wherein the number grows linearly with time$^{36}$. This shows that in the former, nucleation continues to take place in phased manner.

The dehydration of KAl(SO$_4$)$_2$.12H$_2$O$^{37}$ and KCr(SO$_4$)$_2$.12H$_2$O$^{38}$ also takes place at or near the reactant/product interface. The overall rate controlling step is the structural reorganization of water depleted product within the reaction zone. The process is promoted by some water retained within the subsurface nuclei or in the immediate vicinity of the reactant/product contact zone or sometimes adsorbing water from the vapour phase. Interface advance is therefore autocatalytic, a characteristic feature of nucleation and growth controlled mechanism.

**Dehydration controlled by diffusion:**

As stated above, when nucleation and growth occur within the bulk of the solid, the rate controlling step may be the migratory escape of water either through the uncrystallized product layer or through unreacted material. The diffusion controlled rate expression also include contribution from geometrical factors. However, unlike nucleation and growth controlled process it may not be necessary to establish a sharp reactant/product interface for the escape of water vapour. The kinetics of dehydration of the following salts have been found to be diffusion controlled: CaSO$_4$.2H$_2$O$^{39}$, CaSO$_4$.1/2H$_2$O$^{40}$, CaHPO$_4$.2H$_2$O$^{41}$, FeCl$_3$.xH$_2$O$^{25}$, MnCl$_2$.4H$_2$O$^{42}$, NiCl$_2$.2H$_2$O$^{43}$, Cu(acetate)$_2$.2H$_2$O$^{44}$.

**Dehydration accompanied with decomposition of the salt:**

During the decomposition of certain salts, a portion of the constituent water reacts with anions of the salts, mostly halides and nitrates, to yield hydrogen halides, NO or NO$_2$ along with water in their gaseous/vapour state. The decomposition of MgCl$_2$.2H$_2$O$^{45}$ is an ideal example in this regard:

$$\text{MgCl}_2.2\text{H}_2\text{O} (s) \rightarrow \text{MgO} (s) + 2\text{HCl} (g) + \text{H}_2\text{O} (v)$$

The process is also known as 'pyrohydrolysis'. The kinetics of the above reaction obeys the contracting area model and is identified as an interface process. Similar type of simultaneous thermal dehydration and decomposition occurs in the case of FeCl$_3$.xH$_2$O (x = 6-8)$^{25}$. However, in this case the entire salt undergoes melting (35-40°C) before decomposition. Kanungo and Mishra$^{25}$ have carried out detailed investigation including kinetics of dehydration and dehydrochlorination and the combination of both (total mass loss) of FeCl$_3$.xH$_2$O. Though
the loss of water begins even at temperature above 70 °C and is rapid at 100 °C, appreciable dehydrochlorination takes place only at 125 °C and above. Consequently, while dehydration reaches its maximum rate at temperature around 155 °C, dehydrochlorination continued up to 200 °C. In the interventing temperature range (110–150 °C) two independent parallel reactions i.e. losses of H₂O and HCl take place. Because of the molten state of the reactant no kinetic model based on progress of reaction interface is likely to follow. Therefore, kinetics of dehydration, dehydrochlorination and the combination of the two processes follow either one dimensional (surface) diffusion or order based models. There is close agreement not only in the mechanism of dehydration, but also in the apparent $E$ values derived from isothermal and non-isothermal methods.

Many hydrated crystalline nitrates also decompose in their molten state. For example, Mn(NO₃)₂·6H₂O melts completely when heated to 55–60 °C. The evaporation of water continues at temperature around 100 °C until a highly viscous molten monohydrate (according to some authors dihydrate) is formed, when decomposition begins with the liberation of NO₂ gas and deposition of MnO₂ as solid product. The kinetics of the process follow nucleation and growth controlled model ($\Delta m$ with $m = 3$). Indeed, it is very difficult to produce anhydrous nitrates of metals of oxidation states +2 and +3.

Isotope effect on the dehydration of hydrated salts:

When the H₂O molecules in a hydrated salt is replaced with its deuterium oxide (D₂O) analogue some changes in its thermal stability, thermodynamic and kinetic parameters have been observed during the dehydration reaction. The effect was observed first by Heinzinger and Rao for the different stages of the thermal dehydration of CuSO₄·5D₂O. Subsequently, it has been reported for the apparent $E$ values for the initial or first stage of dehydration of CuSO₄·5H₂O and CuSO₄·5D₂O are 79.4 and 137.9 kJ/mol respectively. Similarly, for the dehydration of trihydrate to monohydrate (second stage) the values are 125.4 and 221.5 kJ/mol for the two analogues respectively. However, the reported values of enthalphy change do not indicate any variation with D₂O. Tanaka has observed that while penta- and monohydrate CuSO₄ are thermally less stable than their deuterium analogues, trihydrate is more stable than its D₂O salt. The enthalpy changes ($\Delta H$) obtained from DSC for the different stages of dehydration indicate that deuterated sample shows slightly higher values than the hydrated sample. The difference between the two corresponding values ($\delta\Delta H$) diminishes gradually from stage 1 to 3. The author has shown that $\delta\Delta H$ is the sum of the corresponding differences of the heats of bond dissociation and heats of vapourisation of water as given below:

$$\delta\Delta H = \delta\Delta H_{\text{diss}} + \delta\Delta H_{\text{vap}}$$

Knowing $\delta\Delta H_{\text{vap}}$ values from literature and the corresponding experimental value of $\delta\Delta H$, $\delta\Delta H_{\text{diss}}$ values can be estimated. It has been observed that except for stage 1 (0.28) there is no significant difference (0.05–0.08) in the $\delta\Delta H_{\text{diss}}$ values for stages 2 and 3, though for all the three stages the values are positive.

Besides copper sulphate hydrate, the isotope effect has also been studied using various single and double salts of different metals. Dehydration of both CaC₂O₄·H₂O and its deuterium analogue were studied and it was concluded that isotope factor would at best lead to an increase of about 2 kJ/mol for the deuterated sample. Since the ratio of $p_{D²O}/p_{H₂O}$ is about 1.05 the maximum difference could be 2.2 kJ/mol in the case of diffusion controlled process as the mass ratio of D₂O/H₂O is 1.11. However, later investigators have not found any significant difference in the heats of dehydration of CaC₂O₄·H₂O (63.6 kJ/mol) and CaC₂O₄·D₂O (64.25 kJ/mol).

An extensive investigation on the thermal dehydration of a series of double sulphate hydrates and their deuterated analogues were carried out (M₁²S₂O₄·M₁¹S₂O₄·6H₂O/6D₂O where M¹ represents alkali metals including NH₄⁺ and M¹¹ represents divalent metals of Gr II and 3d transition metals) were carried out by Raychaudhuri and Pathak. The authors have observed that while certain deuterated salts, especially those containing Mg¹¹ exhibit higher stability, heats of dehydration values do not show any significant differences. Multistage dehydration of similar double salts shows isotope effect only for the 1st stage (for the loss of 1st two moles of water). Indeed, at higher temperature of dehydration isotope effect is seldom perceptible. Tanaka has briefly reviewed this aspect for at least 8 salts and found that each one behaves in its own way with respect to its stability, heats of dehydration and kinetic parameters. The authors have also suggested that enormous kinetic isotope effect reported earlier is, in fact, dubious.

Typical examples of some widely studied dehydration reactions:

More detailed discussion on the thermal dehydration of three typical hydrated salts have been provided to illustrate the nature of investigation pursued by different researchers in this field. This involves basic studies, me-
ticulous application of the available methods and even comparison of the results among different workers.

**Copper sulphate pentahydrate (CuSO₄·5H₂O)**: This is one of the oldest hydrated salt used in studying the kinetics and mechanism of dehydration reaction. At low temperature and specially under vacuum the pentahydrate loses 4 moles of water, but in the presence of moisture intermediate trihydrate is formed⁵⁵. Various aspects of the dehydration of CuSO₄·5H₂O, especially impedance to the escape of H₂O vapour at relatively low temperature have been investigated from which a model has been formulated assuming that dissociative desorption follow an activation step at the interface⁵⁶,⁵⁷. Formation of two types of nuclei, star or round shaped have been observed for the formation of monohydrate and elliptical ones for the formation of trihydrate. Each type of nuclei tends to grow at a rate different from the other. Further, elliptical nuclei do not grow when pH₂O < 0.1 Torr, whereas star or round shaped nuclei tend to grow with increase in partial pressure (pH₂O) in the region of 1 Torr. Accordingly, product composition approaches monohydrate in the region of Smith-Topley minimum and trihydrate at the maximum. The authors⁵⁹ have also observed that high ambient pH₂O has a catalytic effect on the recrystallization of product phase. Garner et al.⁶⁰,⁶¹ after an extensive study of the formation and growth of monohydrate nuclei on different crystallographic phases of pentahydrate crystals, have concluded that water elimination proceed preferentially along certain directions of which (010) is the most important.

Lallemant et al.⁶² have measured the rates of dehydration of both penta- and trihydrate and concurrently identified the phases formed at different stages using XRD method. There are many authors who have studied the kinetics of dehydration, especially under non-isothermal condition using crushed sample, Ng et al.⁶³ have studied isothermally the kinetics of dehydration of pentahydrate to trihydrate at 43–63 °C and trihydrate to monohydrate at 70.5–86 °C and have found that for both the steps the kinetics obey Arrhenius law (nucleation and growth) with m = 2 and apparent E values of 104 kJ/mol and 134 kJ/mol respectively. It has been observed⁶⁴–⁶⁹ that under the normal condition of heating in an open crucible the initial partial dehydration takes place in one step involving solid and gaseous phases. But, under the condition of self-generated atmosphere (higher pH₂O) the reaction separates into two consecutive processes. First, the sample melts in an incongruent manner, followed by the evaporation of released water (2 mol) under boiling condition. These two processes can be distinguished in a DTA curve, especially at a low heating rate. The selectivity is further increased by using quasi-isothermal heating technique. Therefore, the following endothermic processes can be observed:

\[
\begin{align*}
\text{CuSO}_4\cdot5\text{H}_2\text{O} (s) & \xrightarrow{60-70 \degree C} \text{CuSO}_4\cdot3\text{H}_2\text{O} (s) + 2\text{H}_2\text{O} (l) \\
2\text{H}_2\text{O} (l) & \xrightarrow{} 2\text{H}_2\text{O} (g) \\
\text{CuSO}_4\cdot3\text{H}_2\text{O} (s) & \xrightarrow{70-100 \degree C} \text{CuSO}_4\cdot\text{H}_2\text{O} (s) + 2\text{H}_2\text{O} (g) \\
\text{CuSO}_4\cdot\text{H}_2\text{O} (s) & \xrightarrow{100-230 \degree C} \text{CuSO}_4 (s) + \text{H}_2\text{O} (g)
\end{align*}
\]

At low partial pressure of water vapour steps 1a and 1b appear as single step because of the rapid evaporation of liquid water. Tanaka⁴⁹ has also found three steps with the losses of 2, 2 and 1 mole of water at DTA peak temperatures of 63.3, 81.3 and 211.2 °C respectively. The corresponding enthalpy changes for these three steps are 55.6, 55.4 and 55.9 kJ/mol of water respectively and the overall value is 57 kJ/mol. For deuterated samples the peak temperatures are 2–3 degrees and enthalpy values are 2.2–3.5 kJ/mol are higher than those of the hydrated salts. From DSC studies (6 °C/min) Arkhangelsky et al.⁷⁰ have found 55.8, 55.64 and 68.13 kJ/mol of water. Dei et al.⁷¹ have found ΔH₉₀ value of 312 kJ for the formation of monohydrate salt and 55.2 kJ as an average value for the individual loss of water. Marcu and Segal⁷² using first-order kinetic model have found that for the first two steps of dehydration occurring at 100 and 122 °C, the app. E values are 115 and 135 kJ/mol respectively and the corresponding log A values are 15.38 and 16.68 s⁻¹ respectively.

**Lithium sulphate monohydrate (Li₂SO₄·H₂O)**: The thermal dehydration of Li₂SO₄·H₂O was initially recommended by the Kinetics Committee of the International Confederation of Thermal Analysis (ICTA) as a model sample for the study of the kinetics of solid state reaction and to standardize the methods adopted for such studies. This is primarily because (i) the sample does not undergo any melting before and during dehydration, (ii) the dehydration takes place in a single step and (iii) the contribution from the reverse reaction is negligible over a wide range of temperature and at low water vapour pressure. Consequently, the kinetics of the reaction have been studied by many investigators and a large volume of information has already been generated. The conclusions
drawn from these studies are summarized below.

The structure of the salt provides a good example of the tetrahedral arrangement of four nearest neighbours (\(2\text{H}_{2}\text{O}, \text{Li} \text{and } \text{O of } \text{SO}_{4}^{2-}\)) around a water molecule. The water molecules, on the other hand, are bonded to form infinite chain\(^1\). It may be stated here that in this compound the dehydration reaction starts from the surface and the reactant/product interface proceeds towards the center of the particle. However, significant differences in the Arrhenius parameters have been observed among the different workers. Vasiliev and Ershova\(^73\) have found the reaction to be controlled by nucleation and growth. The app. \(E\) value decreases from 66 to 59 kJ/mol with decrease in vapour pressure of water. Subsequently, other authors\(^74\) have observed that isothermal \(\alpha\)-time curves follow contracting volume model (\(R3\)) but no \(E\) value has been reported. Okhotnikov et al.\(^75,76\) have found that the progress of nucleation is instantaneous in single crystals with app. \(E\) value of 85-87 kJ/mol. Tanaka and Koga\(^77-80\) have carried out an extensive study of the kinetics of this dehydration reaction along with microscopic observations of the reaction interface. The salient findings from their investigations are as follows:

**Microscopic observations:**

Randomly distributed product particles (~0.2–1.0 \(\mu\)m) with rounded corners and sometimes equidimensional, grow from initial nucleation site and spread as an assemblage on the original single crystals of the reactant. A significant feature in the growth of such assemblages is the development of subsurface pores or channels interconnecting the neighboring nuclei. These cracks are formed due to volume contraction and provide possible channels for the diffusion of water vapour produced at the reaction front which advances from the periphery to the center of the particles. All these phenomena occur within 5–10\% of dehydration.

In the case of crushed crystals, the surface reaction takes place at lower temperature because mechanical action during crushing produced more reactive centers in the particles. There is a positive tendency to develop fine channels extending significantly beyond the mean reaction boundary thereby facilitating the rapid progress of reaction. The advancement is characterized by nucleation and growth of product crystallites as in the case of single crystals and the overall process is controlled by bond rupture, diffusion of ions, nucleation, diffusion of product through intra and inter particle channels.

**Reaction kinetics:**

**Single crystal:** Okhotnikov et al.\(^75\) have studied the propagation of reaction interface along a selected crystallographic axes [101] and correlated the \(E\) values with the parameters for structural reorganization in the product. Subsequent studies\(^77,78\) represent the average of the rates of progress along all the possible crystallographic directions and suggest that the overall rate process can be expressed satisfactorily either by nucleation and growth (\(Am\) with \(m = 2\)) and phase boundary reaction (\(Rn\) with \(n = 2–3\)) law in accordance with the microscopic observations summarized above. The studies carried out under isothermal condition showed small but detectable variation in kinetic obedience with \(\alpha\) which was attributed to various factors such as reversibility and/or relative rates of reaction interface along different crystallographic directions.

Under non-isothermal condition (TG-DSC) in flowing nitrogen atmosphere, the app. \(E\) value, however, decreases gradually from about 123 to 65 kJ/mol with increase in \(\alpha\) or \(T\). This has been explained on the basis of change in mechanism from the \(Am\) (5–45\% dehydration) to the \(Rn\) (40–95\% dehydration) rate law. This is because the rate of escape of water vapour not only from cracks, but also from inter particle voids are high enough not to be able to control the overall kinetics.

**Crushed crystals:** Isothermal dehydration studies\(^77-79\) using \(-48 + 100\) mesh crushed crystals of \(\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}\) show that the initial and the later stages of dehydration can be described by \(A1\) and \(R3\) laws. Comparable kinetic parameters are obtained in both \(\text{N}_2\) and vacuum conditions. Non-isothermal kinetic studies\(^77,80\) carried out using the Ozawa’s method\(^81\) for three different size fractions, namely, \(-48 + 100, -100 + 170\) and \(-170 + 200\) mesh. The results show that in the early (10–50\%) and in the later (50–95\%) stages of dehydration the rate also follows \(A1\) and \(R3\) laws respectively irrespective of particle size. The average \(E\) values for the two stages are 126 and 103 kJ/mol respectively. But the \(E\) values are little higher for finer particle size (\(-170 + 200\) mesh) and sample size above 20 mg, because of the retardation in the rate of diffusion of water vapour resulting from particle compaction and narrow void spaces. However, in self-generated atmosphere the effect is not perceptible.

Despite such an extensive investigation\(^77-80,82-86\), the main problem lies in the selection of correct kinetic model as several models exhibit similar correlation coefficient. This is possibly due to the fact that TA curves for crushed samples provide information averaged over all the crystallographic directions and over the entire matrix, besides complexities arising from other usual factors involved in TA measurements, such as temperature gradi-
Brown et al. have carried out the dehydration of Li$_2$SO$_4$.H$_2$O by measuring the pressure of evolved H$_2$O vapour as function of time and temperature. The general deceleratory nature of α-time curves have been analyzed using five different methods as prescribed elsewhere. The rate constant values obtained from these methods have been critically examined for their accuracy and reproducibility. It has been found that dehydration of single crystals takes much longer time than the crushed crystal

| Experimental conditions | Kinetics of dehydration |
|-------------------------|-------------------------|
| Moles of H$_2$O lost and environment used | Isothermal method | Non-isothermal method |
| sample mass, heating rate etc. used | Mechanistic | App. E (kJ/mol) | log A (s$^{-1}$) | Method/model* | App. E (kJ/mol) | log A (s$^{-1}$) | Order |
| -1 (static air) 0.1 g, 3.45°/min | TG (reac order) 89.5 | - | 0.71 | 90 |
| " non-linear DT/m | " | 95.8 | 6.86 | 0.97 | 91 |
| -1 (N$_2$ flow) 10 °C/min | " | 104.6 | - | 0.9 | 92 |
| " 9 °/min | " | 84.5 | - | - | 93 |
| -1 (static air) 10 °C/min, 423 mg | " | 92 | - | 1 | 94 |
| -1 (air flow) Variable sample mass (1-10 mg) and heating rate (1-20 °/min), temp. range 110-195 depend upon experimental conditions, for example, 5 °/min - 5 mg, 110-167, peak temp. 156. | O-F-W method 84.2 (av) | - | - | - | - | - | - |
| -1 (N$_2$ flow) | - | 82.6 | 13.74 | 0.95 | 98 |
| " | - | 100.3 | 5.2 | 0.95 | 99 |
| " | - | 60-65 | 3 | - | 100 |
| -1 (static air) 4.7°/min, range 149-184, peak at 178 Variable heating rates $T_f = 190-220$ and $T_f$ range 280-340 | A2/R2 118.3 11.12 | $R_2$ 117.9 | 11.06 | - | 101 |
| " | $A_2$ 70.3 | 5.74 | - | - | - |
| " Variable heating rates | C-R/S-S 121.2 | 10.48 | - | - | - |
| $T_f = 190-220$ and $T_f$ range 280-340 | (R3) |
| -1 (N$_2$ flow) | C-R (reac order) 96 | 0.5 | 103 |
| -1 (static air) Variable heating rate | $a=0.1-0.9$ 108.7 12.72 | 84.3 | 90.8 | 8.62 | - | 105 |
| Isotherm range 97-137 | $R_2$ 96 9.47 | 8.62 | - | 105 |
| Am 99.1 | 10.27 | 100 |
| $Am$ 94.4 | 9.62 | 99 |
| -0.2 (static air) Variable heating rate | O-F-W (F1) 189 | 20.88 | 1 | 106 |
| -0.8 (static air) | " (R2) 86 | 9.39 |
| -0.24 (N$_2$ flow) | " (F1) 119 | 12.27 | 1 |
| -0.76 (N$_2$ flow) | " (R2) 77.5 | 8.5 |
| -1 (N$_2$ flow) Temp. range 126-196 | DSC 118 | 11.82 | - | 107 |
| 120-140, | Reaction order 86.5 | 8.27 | 0.62 | - | 108 |

$\Delta H = 52.7$ kJ/mol

*Kinetic methods used in abbreviated forms: C-R (Coats and Redfern), M-T (Maccullum and Tanner), H-M (Horowitz and Metzger), O-F-W (Ozawa, Flynn and Wall), S-S (Sakavara and Satava). For details of these methods please see: *J. Indian Chem. Soc.*, 2005, 82, 315.
or powders. It has also been observed that while the phase boundary controlled reaction (R3) fits best for single crystal, for crushed sample the first-order (F1) law fits marginally better than the R3 law. The apparent $E$ values are 106 and 91.7 kJ/mol respectively.

Subsequently, the authors have studied the kinetics of dehydration of crushed samples using various non isothermal methods. It has been observed that the advancing interface geometry (R2 and R3) models do not show better fitting than F1. The authors attributed this to the appreciable thickness of the dehydrated layer across which the geometrical models are not truly applicable. Water loss from inter nuclear surface regions during the early stage of dehydration possibly obscure the acceleratory process. As a result, the kinetic models fit the data poorly and wide variations in the values of Arrhenius parameters between different methods are observed. In conclusion, the authors failed to recommend the use of Li$_2$SO$_4$.H$_2$O as a reference material for standardization of kinetic methods.

**Calcium oxalate monohydrate (CaC$_2$O$_4$.H$_2$O)**: Thermal dehydration and decomposition of Gr II metal oxalate hydrates, especially CaC$_2$O$_4$.H$_2$O, have been extensively studied as a model reaction in solid state since the beginning of the development of thermoanalytical methods. This is due to certain excellent characteristics which have made the calcium salt as an ideal substance for carrying out thermal decomposition studies. First, it can be prepared as a very pure, well-crystallized precipitate with exactly one mole of constitutional water. It can be perfectly dried at relatively low temperature (70-80 °C) to remove extraneous moisture, if any, and stored in a dry environment over a long period of time without any change in its hydration state. It dehydrates and decomposes at relatively wide temperature gaps with distinctly characteristic features of mass loss (TG) and energy changes (DTA) as follows:

\[
\text{CaC}_2\text{O}_4\text{.H}_2\text{O} \xrightarrow{\text{H}_2\text{O (Endo)}} 135-206 °\text{C} \xrightarrow{\text{CaC}_2\text{O}_4} 396-478 °\text{C} \xrightarrow{\text{CO (Exo)}} \text{CaCO}_3 \xrightarrow{\text{CO}_2 (Endo)} 635-850 °\text{C} \rightarrow \text{CaO}
\]

Duval, in his well-known monograph on thermogravimetry, has reviewed the early literatures. During the last twenty five years scores of work have been carried out on the kinetics of dehydration and decomposition. However, there are several conflicting data on the kinetic parameters, especially regarding dehydration. These are also attributed to variations in the experimental conditions and methods adopted for data analysis. The salient information are summarized in Table 1.

**References**

1. A. F. Wells, "Structural Inorganic Chemistry", 4th ed., Clarendon Press, Oxford, 1975, pp. 542-562.
2. N. S. Akhmetov, "General and Inorganic Chemistry", 2nd ed. (Engl. Transln.), Mir Publishers, Moscow, 1983, p. 624.
3. M. Falk and O. Knop, "Water : A Comprehensive Treatise", Vol. 2, ed. F. Franks, Plenum Press, New York, 1968
4. W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids", Benjamin, New York, 1968.
5. R. Chidambaram, A. Sequiera and S. K. Sikka, *J. Chem. Phys.*, 1964, 41, 3616.
6. G. Ferraris and M. F. Angela, Acta Crystallogr., Sect. B, 1972, 28, 3572.
7. M. E. Brown, D. D. Dollimore and A. K. Galwey, "Comprehensive Chemical Kinetics", eds. C. H. Bamford and C. F. H. Tipper, Vol. 22, Elsevier. Amsterdam. 1980. p. 117.
8. A. K. Galwey and M. A. Mohamed, *J. Chem. Soc., Faraday Trans.*, 1985, 81, 2503.
9. A. K. Galwey, *J. Thermal Anal.*, 1992, 38, 99.
10. A. K. Galwey, *J. Thermal Anal.*, 1994, 41, 267.
11. B. Topley and M. L. Smith, *J. Chem. Soc.*, 1933, 321.
12. G. Bertrand, M. Lallemant and G. Watelle-Marion, *J. Inorg. Nucl. Chem.*, 1974, 36, 1303.
13. J. A. Lumpkin and D. D. Perlmutter, *Thermochim. Acta*, 1995, 249, 335.
14. W. E. Garner (ed.), "Chemistry of Solid State", Butterworths, London, 1955, p. 213.
15. M. L. Franklin and T. B. Flanagan, *J. Chem. Soc., Dalton Trans.*, 1972, 192; *J. Phys. Chem.*, 1971, 75, 1972.
16. A. K. Galwey, G. M. Lovery, V. B. Okhotnikov and J. O'Neill, *J. Thermal Anal.*, 1992, 38, 421.
17. S. B. Kanungo and S. K. Mishra, Unpublished results.
18. G. G. T. Guarini, *J. Thermal Anal.*, 1994, 41, 287.
19. E. Buzagh-Gere, S. Gal and J. Simon, Z. Anorg Allgem. Chem., 1973, 400, 37.
20. E. Buzagh-Gere, J. Sztatisz and S. Gal, *J. Thermal Anal.*, 1976, 10, 89.
21. K. Heide and H. J. Eichhorn, *J. Thermal Anal.*, 1975, 7, 397.
22. Y. Kirsh, S. Yariv and S. Shoval, *J. Thermal Anal.*, 1987, 32, 393.
23. S. Shoval, S. Yariv and Y. Kirsh, *Thermochim. Acta*, 1988, 133, 263.
24. Y. Kirsh, S. Shoval and S. Kariv, *Thermochim. Acta*, 1989, 148, 197.
25. S. B. Kanungo and S. K. Mishra. *J. Thermal Anal.*, 1996, 46, 1487; 1997, 48, 385.

26. P. K. Gallagher and D. W. Johnson. *Thermochim. Acta*, 1971, 2, 413; *J. Electrochem. Soc.*, 1971, 118, 1530.

27. T. J. W. DeBruijn, W. A. DeJong and P. J. van den Berg. *Thermochim. Acta*, 1981, 45, 265.

28. S. K. Sharma, C. K. Joshi and S. Kumar. *Thermochim. Acta*, 1991, 184, 19; R. Naumann and H.-H. Emmons, *J. Thermal Anal.*, 1989, 35, 1009.

29. P. M. Fichte and T. B. Flanagen, *Thermochim. Acta*, 1981, 45, 265.

30. T. A. Clark and J. M. Thomas. *J. Chem. Soc. (A)*, 1969, 222.

31. T. A. Clark and J. M. Thomas, *J. Chem. Soc. (A)*, 1969, 2249, 2753, 2756.

32. J. M. Thomas and G. D. Renshaw, *Proc. Roy. Soc. (London)*, 1971, 2249, 2753, 2756.

33. G. G. T. Guarini and R. Spinicci, *J. Thermal Anal.*, 1972, 4, 435.

34. R. K. Osterheld and P. R. Bloom, *J. Phys. Chem.*, 1978, 82, 1591.

35. W. E. Garner and W. R. Southon, *J. Chem. Soc.*, 1935, 1705.

36. N. F. H. Bright and W. E. Garner, *J. Chem. Soc.*, 1934, 1872.

37. A. K. Galwey, R. Spinicci and G. G. T. Guarini, *Proc. Roy. Soc. (London)*, 1981, A378, 477.

38. A. K. Galwey and M. A. Mohamed, *Thermochim. Acta*, 1987, 121, 97.

39. M. C. Ball and L. S. Norwood, *J. Chem. Soc. (A)*, 1969, 1633.

40. M. C. Ball and R. G. Urie, *J. Chem. Soc. (A)*, 1970, 528.

41. M. C. Ball and M. J. Casson, *J. Chem. Soc., Dalton Trans.*, 1973, 34.

42. S. B. Kanungo, *Indian Chem. Soc.*, 2004, 81, 644.

43. S. B. Kanungo, *Indian Chem. Soc.*, 2004, 81, 921.

44. N. Koga and H. Tanaka, *Solid State Ionics*, 1990, 44, 1.

45. A. K. Galwey and G. M. Lovetty, *Thermochim. Acta*, 1989, 138, 115.

46. T. J. W. DeBruijn, A. N. Ipekoglu, W. A. DeJong and P. J. van den Berg, *Thermochim. Acta*, 1981, 45, 293, 305.

47. K. Heinzinger and T. S. Rao, *Z. Naturforsch., Teil A*, 1967, 22, 2111.

48. H. Oki, E. Kyuno and R. Tsuchiya, *Bull. Chem. Soc. Jpn.*, 1970, 43, 3263.

49. H. Tanaka, *Thermochim. Acta*, 1981, 43, 289.

50. E. Manche and B. Carroll, *Thermochim. Acta*, 1978, 24, 1.

51. H. Tanaka and H. Negita, *Thermochim. Acta*, 1980, 41, 305.

52. N. Ray Chaudhuri and G. K. Pathak, *Thermochim. Acta*, 1975, 12, 71, 287, 397.

53. H. Tanaka, W. Yamamoto and H. Negita, *Thermochim. Acta*, 1982, 56, 65.

54. H. Tanaka, *Thermochim. Acta*, 1985, 92, 215.

55. J. Calvin and J. Hume, *Trans. Faraday Soc.*, 1938, 34, 969.

56. M. L. Smith and B. Topley, *Proc. Roy. Soc. (London)*, 1932, A134, 224.

57. B. Topley, *Proc. Roy. Soc. (London)*, 1932, A136, 413.

58. N. Z. Lyakov, A. P. Chupakhin, V. P. Isupov and V. V. Boldyrev, *Kinetic Catal.*, 1977, 19, 84.

59. A. I. Zagrag, V. V. Zyranov, N. Z. Lyakov, A. P. Chupakhin and V. V. Boldyrev, *Thermochim. Acta*, 1979, 29, 115.

60. N. Z. Lyakov and V. V. Boldyrev, *Russ. Chem. Rev.*, 1972, 41, 919.

61. W. E. Garner and H. V. Pike, *J. Chem. Soc.*, 1934, 1565.

62. M. Lallemand, N. Gerard and G. Watelle-Marion, *C. R. Acad. Sci.*, 1971, 272, 1737; 1968, 267, 1775.

63. W.-L. Ng, C. C. Ho and S. K. Ng, *J. Inorg. Nucl. Chem.*, 1978, 34, 459.

64. A. Reisman and J. Karlak, *J. Am. Chem. Soc.*, 1958, 80, 6500.

65. H. J. Borchardt and F. Daniels, *J. Phys. Chem.*, 1957, 61, 917.

66. W. W. Wendlandt, *Anal. Chim. Acta.*, 1962, 27, 309.

67. J. Paulik, F. Paulik and M. Arnold, *J. Thermal Anal.*, 1988, 34, 1455.

68. M. I. Pope and D. I. Sutton, *Thermochim. Acta*, 1978, 23, 188.

69. S. El-Haute, M. El-Sayed Ali and O. T. Sorensen, *Thermochim. Acta*, 1989, 138, 107.

70. I. V. Arkhangeskely, I. V. Sevitskaya and V. P. Rodinova, *J. Thermal Anal.*, 1986, 31, 1101.

71. L. Dei, G. G. T. Guarini and S. Piccini, *J. Thermal Anal.*, 1984, 29, 755.

72. V. Marcu and E. Segal, *Thermochim. Acta*, 1980, 36, 235.

73. V. G. Vasilev and Z. V. Ershov, *Russ. J. Phys. Chem.*, 1972, 46, 1197.

74. G. Thomas and M. Soustelle, *J. Chim. Phys.*, 1972, 69, 1776.

75. V. B. Okhotnikov, B. J. Yakobson and N. Z. Lyakov.
Kanungo et al.: Thermal dehydration characteristics of hydrated salts etc.

76. Y. A. Gopanov, B. I. Kidyarov, N. A. Kirdyashkina, N. Z. Lyakov and V. B. Okhotnikov, J. Thermal Anal., 1988, 33, 547.
77. N. Koga and H. Tanaka, J. Phys. Chem., 1989, 93, 7793.
78. A. K. Galwey, N. Koga and H. Tanaka, J. Chem. Soc., Faraday Trans. I, 1990, 86, 531.
79. N. Koga and H. Tanaka, Thermochim. Acta, 1991, 185, 135.
80. H. Tanaka, N. Koga and J. Sestak, Thermochim. Acta, 1992, 203, 203.
81. T. Ozawa, Bull. Chem. Soc. Jpn., 1965, 38, 1881; J. Thermal Anal., 1970, 2, 301.
82. N. Koga and H. Tanaka, Thermochim. Acta, 1993, 224, 141.
83. Y. Masuda, H. Takeuchi and A. Yahata, Thermochim. Acta, 1993, 228, 191.
84. H. Tanaka, Thermochim. Acta, 1982, 52, 195.
85. N. Koga and H. Tanaka, J. Thermal Anal., 1990, 36, 2601.
86. N. Koga and H. Tanaka, J. Thermal Anal., 1993, 40, 1173.
87. M. E. Brown, A. K. Galwey and A. Li Wan-Po, Thermochim. Acta, 1992, 203, 221.
88. M. E. Brown, A. K. Galwey and A. Li Wan-Po, Thermochim. Acta, 1993, 220, 131.
89. C. Duval, "Inorganic Thermogravimetric Analysis", 2nd ed., Elsevier, Amsterdam, 1963.
90. A. W. Coats and J. P. Redfern, Nature (London), 1964, 201, 68.
91. E. Segal and M. Vlad, Thermochim. Acta, 1976, 16, 115.
92. M. Subramanian, R. N. Singh and H. D. Sharma, J. Inorg. Nucl. Chem., 1969, 31, 3789.
93. H. H. Horowitz and G. Metzger, Anal. Chem., 1963, 35, 1464.
94. E. S. Freeman and B. Carroll, J. Phys. Chem., 1956, 62, 394.
95. C. G. R. Nair and K. N. Ninan, Thermochim. Acta, 1978, 23, 161; K. N. Ninan and C. G. R. Nair, Thermochim. Acta, 1979, 30, 25; 1980, 37, 161.
96. K. N. Ninan, Thermochim. Acta, 1984, 74, 143.
97. D. Dollimore, T. E. Jones and P. Spooner, J. Chem. Soc. (A), 1970, 2809.
98. R. Rock, Thermochim. Acta, 1978, 24, 182.
99. V. Marcu and E. Segal, Thermochim. Acta, 1978, 24, 178.
100. D. Dollimore and G. R. Heal, Thermochim. Acta, 1978, 24, 307.
101. H. Tanaka, S. Ohshima, S. Ichiba and H. Negita, Thermochim. Acta, 1981, 48, 137.
102. A. M. M. Gadalla, Thermochim. Acta, 1984, 74, 255.
103. P. O’Brien and S. D. Ross, Thermochim. Acta, 1982, 53, 195.
104. A. Romero-Salvadore, E. Garcia-Calvo and J. M. Navarro, Thermochim. Acta, 1985, 87, 163.
105. A. Romero-Salvadore and E. Garcia-Calvo, Thermochim. Acta, 1986, 107, 283.
106. Y. Masuda, Y. Ito, R. Ito and K. Iwata, Thermochim. Acta, 1986, 99, 205; 1986, 102, 263.
107. R. Lazano, J. Roman, F. DeJesus, A. Jerez, M. Gaitan and E. Ramos, Thermochim. Acta, 1989, 143, 93.
108. U. B. Ceipidor, R. Bucci and A. D. Magri, Thermochim. Acta, 1992, 199, 85; 1992, 203, 137.