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Title: Computational Investigatio of Mixed $MgCl_2$/ $CaCl_2$/$MgSO_4$ hydrated Materials for Thermochemical Energy Storage Applications

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I.

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Abstract

Because of their excellent thermal energy storage, renewable nature, and sustainability, magnesium chloride hydrates have gained a lot of attention as potential energy storage materials.The processes of hydration and dehydration result in the discharge or charging of the $MgCl_2$ salt substance.A magnesium chloride cluster has a higher energy than a $MgCl_2$ formula unit.An effective approach for creating $MgCl_2$ clusters was the computationally artificial bee colony algorithm. In addition, we optimized $(MgCl_2)_n.mH_2O$ and $(MgCl_2)_n$ to obtain low lyining cluster structure using the VASP software.

However, the side reaction known as hydrolysis impedes the cyclic kinetics response that occurs between the dehydration and hydration phases. The hydrolysis reaction and the dehydration reaction occur at different temperature intervals for different clusters.

1.Introduction

Magnesium chloride hydrates have gained recognition as promising energy storage materials in the built environment[1]. These materials offer several advantages for energy storage applications due to good thermal energy storage and renewability and sustainability[2].

The small cluster $(MgCl_2)_{n,}$ n=1-4, and hydrated $(MgCl_2)_n$ generation was carried out by using the Artificial Bee Colony Algorithm and Charmm force fields [[3]. Geometry optimization of generated structure was proceeded by using DFT after input preparation. We used VASP for further optimization to obtain a low-lying structure. Binding energy, formation energy, dehydration energy, and hydrolysis energy at T =0K and after frequency calculation and ZPE correction were calculated and discussed. Different graphs of dehydration and hydrolysis of partial pressure versus temperature at P = 1atm were plotted by different temperature intervals [4].

1.1 Survey of the field/Background of study

The small clusters $(MgCl_2)$ were reported using second-order Moller and Plesset perturbation theory \MP2!, as well as Self-consistent-field \SCF! computations [6]. The study shows that the structural properties of solid MgCl2 and tiny clusters are incompatible, which is the drove the formation of $MgCl_2$ clusters. $MgCl_2$ is a linear molecule, and the small clusters $(MgCl_2)_n$, n = 2-5 are reasonably assumed to form chains of edge connected $MgCl_2$ tetrahedra [6]. Furthermore, various studies have indicated that hydrated magnesium chloride was discovered as a potentially effective material for energy storage in the built environment [1]; because of their high thermal energy storage capacity, sustainability, and renewability. These materials have several benefits for energy storage applications. For example, $(MgCl_2.6H_2O)$, hexahydrates of magnesium Chloride have been proposed as a suitable option for solar thermal storage. Solar energy collected in summer can be stored as the energy of dehydration, and in winter, the system is hydrated to retrieve the stored energy [[7]. Many hydrated crystalline salts undergo a reaction that often occurs at the reactant-product contact when heated, evolving water to produce a lower hydrate, or anhydrous salt.

Dehydration and hydrolysis are fundamental processes that occur in hydrates of ($MgCl_2$), where the number of water molecules (n) associated with the compound can vary[8]. In energy storage systems, hydrolysis reactions possess a challenge due to the release of harmful HCl gas, to the salt hydrates as well as to the equipment. Many studies have been carried out to understand the process of hydrolysis during the dehydration step[9]. Many studies focused on how to improve the thermochemical performance and properties of hydrate salts, as well as their potential applications in various fields by ignoring formation of HCl gas [3]. In this work, we focused on the dehydration and hydrolysis pathways of hydrated $(MgCl_2)_n$ cluster to propose improvements [[10].

1.2.Objective

The aim of this study is to know the dehydrations and Hydrolysis eqiulibrium curve of reaction.

To prepare thermally stable hydrated clusters of $(MgCl_2)_n$

To study dehydration reaction process of hydrated $(MgCl_2)_n$

2. Computational details

2.1. Cluster preparation

2.1.1 Cluster generation with Artificial Bee Colony Algorithm and Charm force-field

The small cluster $(MgCl_2)_n$, n=1-4, $(MgCl_2)_n.mH_2O)$, n=1-4, m=1-4 for modelling $(MgCl_2)_n.mH_2O$ and n =1,2,3,4 & m= 2, 4, 6, 8 for modeling $MgCl_2.2H_2O$, $(MgOHCl)_n$, n= 1-4 , $(MgOHCl)_n.mH_2O$, $(MgCl_2)_n(MgOHCl)_m$ and $(MgCl_2)_n(MgOHCl)_m$.yH2O m =1,2,3,4 y =1,2,3,4 generation process was carried out using Artificial Bee Colony Algorithm and Charmm force-field[3]. The algorithm is used to explore different structural arrangements and conformations to find energetically favorable configuration[[11].

An Artificial Bee Colony Algorithm and Charmm force-field typically provides output files that contain information about the generated clusters, including their coordinates, energies, and other relevant properties[12]. We have stored around the 30 LMs cluster and we have manuauuly selected 5 LMs from each cluster structure for DFT electronic calculations[13].

2.1.2 DFT geometry optimization

We used DFT; which is a computational quantum mechanical modeling method used to study the electronic structure and geometry optimization of atoms, molecules, and materials [[14].

DFT calculations would typically minimize the forces on the atoms within the clusters, iteratively adjusting their positions until reaching a converged state[15]. The resulting optimized structures would provide information on the positions of the atoms, bond lengths, bond angles, and other geometric properties of the clusters.

Our aim here is to obtian optimized structure and to select the low-lying geometry for further analysis. The selected geometry form 2.1.1 were optimized with VASP again. This approach is successfully used to investigate molecular systems, including hydrogen bonds, magnesium, and chlorides interactions[16]. [Once the VASP optimization calculation is completed, we analyze the optimized structure by Comparing the energy and the possible low-lying structural isomers. The obtained structures will be discussed in the result and discussion part in chapter 3. We also visualized the structure using visualization software such as ASE (atomic simulation Environment) to visually inspect its geometry[17].

These calculations aim to find the most energetically favorable arrangement of atoms by minimizing the forces on the atoms and iteratively adjusting their position.

Based on this; $MgCl_2$,$(MgCl_2)_2$, $(MgCl_2)_3$ and $(MgCl_2)_4$ $(MgOHCl)_n$, n=1-4 , $(MgOHCl)_n.mH_2O$, $(MgCl_2)_n(MgOHCl)_m$ and $(MgCl_2)_n(MgOHCl)_m.yH_2O$ m =1,2,3,4 y =1,2,3,4 cluster with low energy was selected fom different isomers; Consider figure below:1 and2

2.2 Energetics at T=0K

2.2.1 Formation energy and Binding energy

We calculated the binding energy and formation energy of a $(MgCl_2)_{n,}$ $(MgCl_2)_{n.}mH_2O$ $(MgOHCl)_n$, n=4 , $(MgOHCl)_n.mH_2O$, $(MgCl_2)_n(MgOHCl)_m$ and $(MgCl_2)_n(MgOHCl)_m.yH_2O$ cluster[24]. The binding energy is a measure of the strength of the attractive forces holding the cluster together [[18] . To calculate the binding energy, we performed a theoretical calculation using appropriate computational method [[5]. The binding energy of the different $(MgCl_2)_n$ cluster is given by the difference in energy between the optimized cluster and the sum of the energies of the isolated fragments. It can be calculated using the equation (1,3).The formation energy of a compound represents the energy change associated with the formation of that compound from its constituent elements [[19]. In the case of $(MgCl_2)_n$, where n represents the number of $MgCl_2$ units, we calculated the formation energy for different values of n using equation (2,4)

$$Mg + Cl_2 \rightarrow (MgCl_2)n$$

$$(MgCl_2)_n + mH_2O => (MgCl_2)_n.mH_2O$$

$$BE = \frac{nE(Mg) + nE(Cl) - E(MgCl2)}{3n}(\text{per formula unit}) \quad ....(1)$$

$$FE = nE(MgCl_2)n - nE(Mg) + nE(Cl) \quad ......(2)$$

$$BE = \frac{nE(MgCl2)n + nE(H2O) - E(MgCl2)n.mH2O)n}{4n} \quad (\text{per formula unit}) \quad ....(3)$$

$$FE = E_{(MgCl2)n.mH2O} - nE_{(MgCl2)} + nE_{(H2O)} \quad ......(4)$$

In general, the binding energy of $(MgCl_2)_n$ will increase as the number of $MgCl_2$ units (n) increases. This is because the compound becomes more stable as the number of bonds between Mg and Cl atoms increases,it was disussed else where.

2.3 Dehydration energy and hydrolysis energy At T =0

Dehydration energy is the energy required to remove water molecules from a hydrated compound[12]. In the case of hydrated magnesium chloride, the dehydration energy would represent the energy required to remove water molecules from the compound $(MgCl_2)_n \cdot mH_2O$ to form water gas and anhydrous $(MgCl_2)_{n.}$

$(MgCl_2)n.mH_2O$ +Heat <=> $(MgCl_2)n.(m-yH_2O)$ + (xH_2O).

$E_{Dehy} = \frac{1}{x}[E_{(MgCl2)n.(m-yH2O)} + xE_{H2O}\ ] - \frac{1}{x}[E_{(MgCl2)n\cdot mH2O}]$. Where n= 1-4 and m =1,2,3,4,6 and x =1,2,3,4,6 where x is the number of mole of water released, y is the number of mole of water remianed in cluster

$(MgCl_2)_3.6H_2O$ +Heat <=> $MgCl_2 + 6H_2O$.

$E_{Dehy} = \frac{1}{6}[E(MgCl_2)_2 + 6xE_{H2O}] - \frac{1}{6}[E(MgCl_2)3\cdot 6H2O] = 18.495$Kcal/mol

For 1Mol of water per formula units

$(MgCl_2)_4.4H_2O$ +Heat <=> $MgCl_2)_3 + 4H_2O$.

$E_{Dehy} = \frac{1}{4}[E(MgCl2)4 + 4xE_{H2O}] - \frac{1}{4}[E(MgCl_2)4\cdot 4H_2O] = 17.3673$Kcal/mol

$(MgCl_2)_3.3H_2O$ +Heat <=> $(MgCl_2)_3 + 3H_2O$.

$E_{Dehy} = \frac{1}{3}[E(MgCl_2)_2 + 3xE_{H2O}] - \frac{1}{3}[E(MgCl_2)_3\cdot 3H_2O] = 21.356$Kcal/mol

$(MgCl_2)_2.2H_2O$ +Heat <=> $MgCl_2 + 2H_2O$.

$E_{Dehy} = \frac{1}{2}[E(MgCl_2)_2 + 2xE_{H2O}] - \frac{1}{2}[E(MgCl_2)\cdot 2H_2O] = 22.8532$Kcal/mol

$MgCl_2.H_2O$ +Heat <=> $MgCl_2 + 1H_2O$.

$E_{Dehy} = \frac{1}{1}[E_{(MgCl2).1H2O)}] + 1xE_{H2O} - \frac{1}{1}[E_{(MgCl2)\cdot 1H2O}] = 23.788$Kcal/mol

Hydrolysis energy on other hands , the energy needed for the cleavage of Mg-Cl,Mg-O and O-H bonds in hydrated materials,simaltineously resulting in the formation of new chemical bonds (MgOHCl) and HCl gas. In the case of hydrated magnesium chloride, the hydrolysis energy would represent the energy added or released to or from the system . Hydrolysis energy calculated for the following reaction as follows;

$(MgCl_2)_n.mH_2O$ +Heat =>$(MgOHCl)n.(m-yH_2O)$ (aq) + (xH_2O)(g) + zHCl (g).

$E_{hydro} = \frac{1.}{x.}[E_{(MgOHCl)n.(m-yH2O)} + E_{(zHCl)} + xE_{H2O}] - \frac{1}{x.}[E_{(MgOHCl)n\cdot mH2O}]$. Where n= 1-4 and m = 1,2,3,4,6 and m = 1,2,3,4,6,Where n= 1-4 and m =1,2,3,4,6 and z, x =1,2,3,4,6 where z and x is the number of mole of water released, y is the number of mole of water remianed in cluster.
$MgCl_2.1H_2O$ +Heat <=>$(MgOHCl)n.(m-yH_2O)$ (aq) +(xH_2O) (g) + zHCl (g).

2.4 Gibbs free energy and modeling the PT equilibrium line

2.4.1 Theoratical Background

The dehydration of $(MgCl_2)_n{\cdot}mH_2O$; the compounds involve the removal of water molecules from the hydrated $(MgCl_2)_n$ structures, resulting in anhydrous forms of $(MgCl_2)_n$ and water gas. This process was studied by optimizing the hydrated structures using VASP and subsequently removing the water molecules. For the free energy calculation, the ideal poly-atomic gas assumption was reported [13]. The free energy change associated with this process was determined by performing thermodynamic integration calculations in VASP. To calculate the free energy difference between the hydrated and dehydrated states, the reaction coordinates were defined as the gradual removal of water molecules [[20].

This can be achieved by considering a series of intermediate states, where one or more water molecules are successively removed [10]. The relationship between dehydration energy and the free Gibbs energy can be described using the equation:

$\Delta G = \Delta H - T\Delta S$ where ΔG is the change in free Gibbs energy, ΔH is the change in enthalpy, T is the temperature in Kelvin, and ΔS is the change in entropy. During dehydration, the enthalpy change (ΔH) would be positive because energy is required to break the bonds between the water molecules and the compound [[21]. The entropy change (ΔS) would typically be negative as the removal of water molecules reduces the disorder of the system. Therefore, the overall change in free Gibbs energy (ΔG) for dehydration would be positive or zero, indicating that the process is not thermodynamically favorable. The magnitude of ΔG would depend on the specific values of ΔH and ΔS. The some of the dehydration reactions considered for analysis are as follows [[22];

$MgCl_2.2H_2O <=> MgCl_2.2H_2O$ (aq) + $1H_2O$ (g)
$(MgCl_2)_2.4H_2O <=> (MgCl2)2.2H_2O$(aq) + $2H_2O$(g)
$(MgCl_2)4.4H_2O <=> 4MgCl_2.2H_2O$(aq) + $2H_2O$ (g)
$(MgCl_2)_3.3H_2O <=> (MgCl_2)_3$ (s) + $3H_2O$(g)
$(MgCl_2)_3.6H_2O <=> 3MgCl2.3H_2O$ (aq) + $3H_2O$(g)

The dehydration of $(MgCl_2)n{\cdot}mH_2O$, where m = 2, 3, 4, or 6, May be complete dehydration, or stepwise dehydration. The resulting compounds are anhydrous forms of magnesium chloride or intermediate state with water. VASP calculations are performed to optimize the structure and determine the total energy. The total energy of each intermediate state is used to compute the Gibbs free energy changes of reactions.[23]

$(MgCl_2)_n.mH_2O$ + Heat <=> $(MgCl_2)_n(s)$ + $mH_2O(g)$,n = 1,2,3,4& m = 2, 3,4,&6. To investigate the equilibrium condition of the above reactions, it is essential to obtain the Gibbs free energy (G) of each component at constant pressure P (1atm) and varied temperature (T). The Gibbs free energy changes of molecule reactions is defined as

$\Delta rG = \sum Gp - \sum Gr$ .....(1)

$\Delta H = \Delta U + \Delta PV$ ...(2)

$G(T,P) = \Delta H - T\Delta S$ ....(3)

$U(T) = Utrans + Urot + Uvib + UZPE + Uelec$ .....(4)

$U_{trans} = \frac{3}{2}RT$......(5)

$U_{rot} = \frac{3}{2}RT$ .....(6)

$U^{rot}_{linear} = RT$ ...(7)

$U_{vib} = R\sum_{i=1}^{3N-6}\left[\frac{hvib/KB}{\exp(hvib/KB)-1)}\right]$ ....(8)

$pV = nRT$ ....(9)

$\Delta_rG = \Delta G + RTlnQrxn$ ....(10)

At equilibruim position in the given reaction Keq. constant calculated

$Qrxn = Keq = [H2O]$, $\Delta_rG = 0$ ....(11)

$Log(PH2O)m = \frac{-\Delta G}{2.303mRT}$ ....(12) where m is number of mole of water gas released at different temperature interval.Thermal correction to G(T) is also calculated as

$G(T) = \sum ZPE + G(T => 0$ Zero-point energy = $R\sum_{i=1}^{3N-6}\frac{[hvi]}{2Kb}$ ...(13)

2.4.2 Vibrational Frequency calculation

The specific frequencies of vibrational modes was obtained through frequency calculations using density functional theory (DFT) calculation.

In hydrated magnesium chloride,$(MgCl_2)_n.mH_2O$ n =1-4 and m =1,2,3,4,6 there are several types of vibrational modes and some of them are except imaginary frequency;Stretching mode,and Bending mode. These vibrations involve the stretching,bending and rocking of chemical bonds. In hydrated magnesium chloride, we expect stretching vibrations of the Mg-Cl bonds and the O-H bonds in water molecules,bending vibrations of the water molecules around the $MgCl_2$ complex, such as the bending of the H-O-H bonds. Rotational vibrations occur when a molecule rotates.

2.4.3 enthalpy and Gibbs free energy of dehydration and hydrolysis

The enthalpy (ΔH) and Gibbs free energy (ΔG) of dehydration and hydrolysis reactions depend on the specific reaction [[24] (3), it is understood that the change in Gibbs free energy ΔG for a reaction is a function of temperature T and pressure p, i.e. $\Delta G = \Delta G\ (T,\ P)$.

At equilibrium, $\Delta G = 0$ which implies that we calculated the equilibrium partial pressure of the reactants and products as a function of temperature, i.e., $p = p(T)$.

The enthalpy change (ΔH) of dehydration represents the heat energy absorbed or released during the dehydration process. It can be either endothermic (positive ΔH) if heat is absorbed or exothermic (negative ΔH) if heat is released. The Gibbs free energy change (ΔG) of dehydration indicates the spontaneity of the reaction. If ΔG is negative, the dehydration reaction is thermodynamically favorable and tends to occur spontaneously. If ΔG is positive, the reaction is non-spontaneous under standard conditions and requires an input of energy to proceed.

Hydrolysis, on the other hand, involves the reaction of a compound with water, resulting in the cleavage of chemical bonds and the formation of new compounds. In this work Hydrolysis is taken as side reaction that leads to formation of unwanted products HCl and Various MgOHCl.[25]

The enthalpy change (ΔH) of hydrolysis represents the heat energy absorbed or released during the hydrolysis process. It can be either endothermic (positive ΔH) if heat is absorbed or exothermic (negative ΔH) [2] heat is released. The Gibbs free energy change (ΔG) of hydrolysis determines the spontaneity of the reaction. If ΔG is negative, the hydrolysis reaction is thermodynamically favorable and tends to occur spontaneously. If ΔG is positive, the reaction is non-spontaneous under standard conditions and requires an input of energy to proceed. In this case we calculated thermal energy correction using equation(9).

2.4.4. PT lines for dehydration, hydrolysis and combination.

Comparing Figures 9 , 11 and 15, it can be seen that at a given water vapor pressure and HCl pressure, the equilibrium temperatures for the hydrolysis reactions are higher than those for the dehydration reactions[4].Similarly; comparing Figures 9 and 16 for Hydrolysis of $(MgCl_2)_4.4H_2O$ to $(MgOHCl)_2$ + nHCl; it can be seen that at a given water vapor pressure and HCl pressure, the equilibrium temperatures for the hydrolysis reactions are higher than those for the dehydration reactions.

3.Results and discussion

3.1 structures of clusters

We obtained some of the best stable isomers from five selected structures based on their electronic energy anhydrous (MgCl2)n, where n = 1-4.The total energy of the system obtained from VASP output indicated the stability of the compounds,with lower energy values corresponding to more stable structure [27].

3.1.1 $(MgCl_2)_n$ clusters

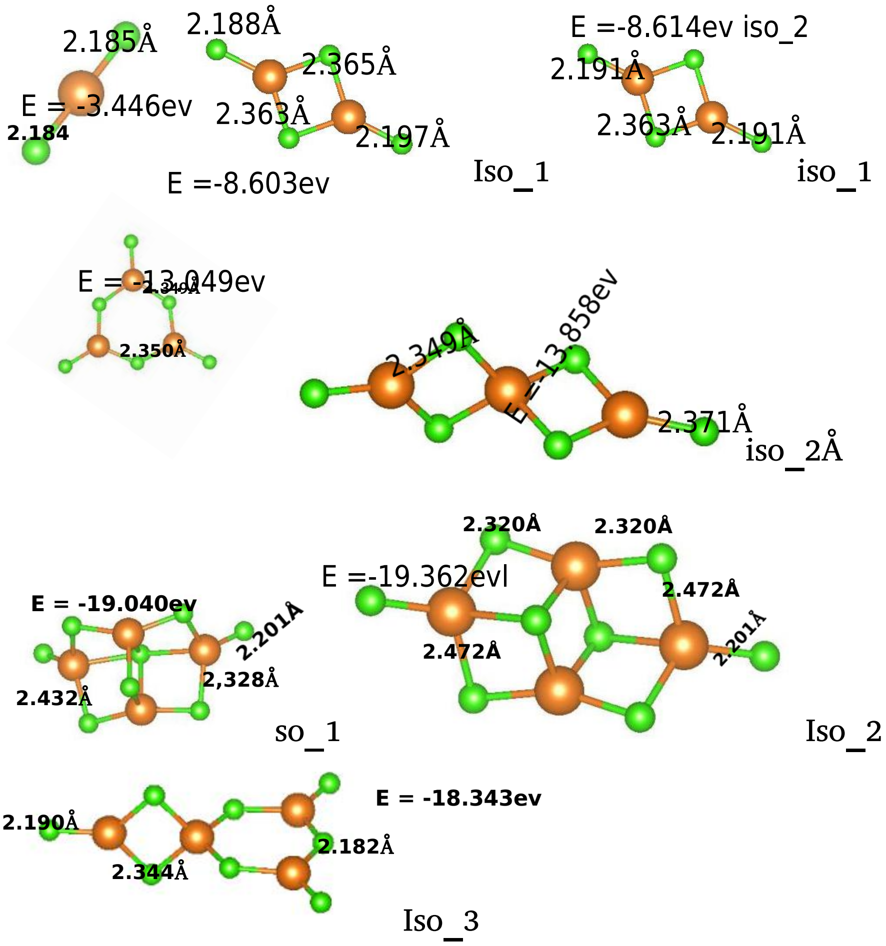
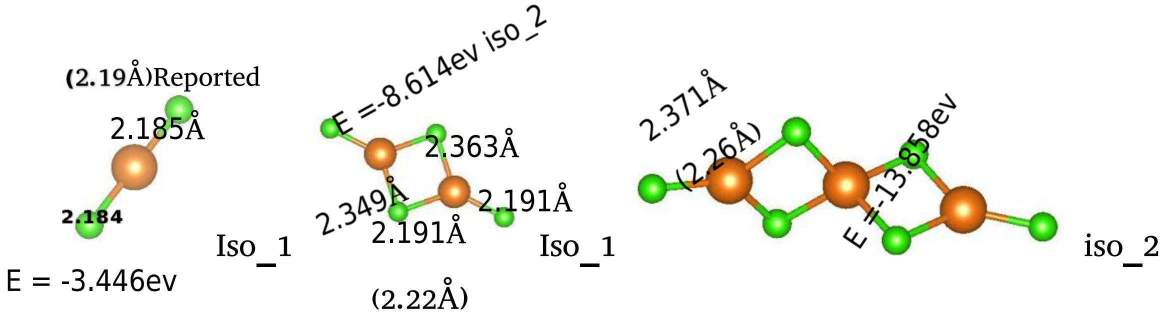
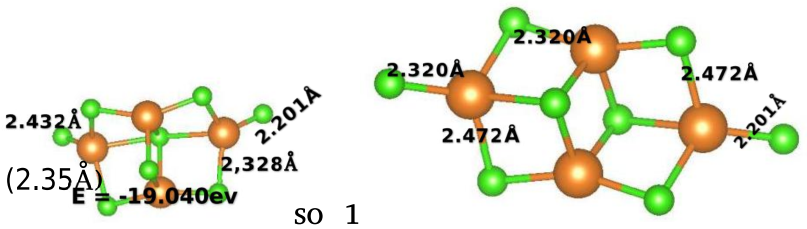


Figure 1:Optimized structure of $(MgCl_2)_n$





so_1 iso_2

E =-19.362evl

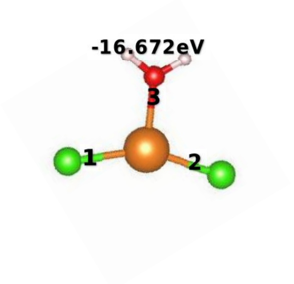
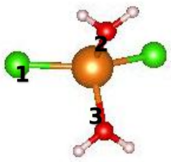
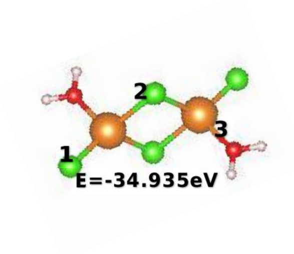
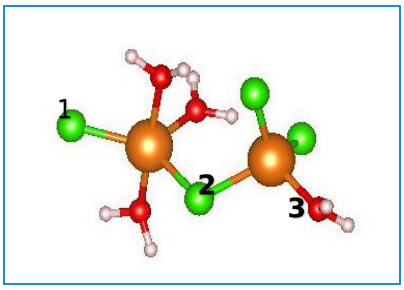
Figure 2:The selected cluster structure from different isomers of $MgCl_2$, $(MgCl_2)_2$,$(MgCl_2)_3$ and $(MgCl_2)_4$.

In anhydrous $(MgCl_2)_n$ (without water molecules), the bond length between Mg and Cl is relatively short and typically around 2.184-2.332Å when comparing with hydrated $(MgCl_2)_n$[6].

When $MgCl_2$ is hydrated, the presence of water molecules can significantly affect the bond lengths. The water molecules interact with the $MgCl_2$ units through electrostatic forces and hydrogen bonding. These interactions can cause a slight expansion(either bending or stretching) of the Mg-Cl bond length. The extended bond length is typically around 2.201-2.383Å Table 3. This is the same as reported in [[20]. In all cases, the bond lengths and angles may change due to the interactions between the water molecules and the $(MgCl_2)$ units. The presence of water can lead to the formation of hydrogen bonds, which can influence the geometry of the system. The total energy of the system can indicate the stability of the hydrated compounds, with lower energy values corresponding to more stable structure. Figure 2&3

3.1.2 $(MgCl_2)_n.mH_2O$ clusters

Table3.Comporision of bond distances with past reported one

		This Work	Reported[1]	
	Mg-Cl(1) Mg-Cl(2) Mg-O(3) O-H	2.217Å 2.217Å 2.049Å 0.973Å	2.208Å 2.211Å 2.037Å 0.972Å	
	Mg-Cl(1) Mg-Cl(2) Mg-O(3)	2.260Å 2.260Å 2.076Å	2.255Å 2.211Å 2.061Å	
	Mg-Cl(1) Mg-Cl(2) Mg-O(3) O-H	2.228Å 2.380Å 2.064Å 0.973Å	2.27Å 2.26Å 2.08Å 0.973Å	
	Mg-Cl(1) Mg-Cl(2) Mg-O(3)	2.305Å 2.375Å 2.063Å		

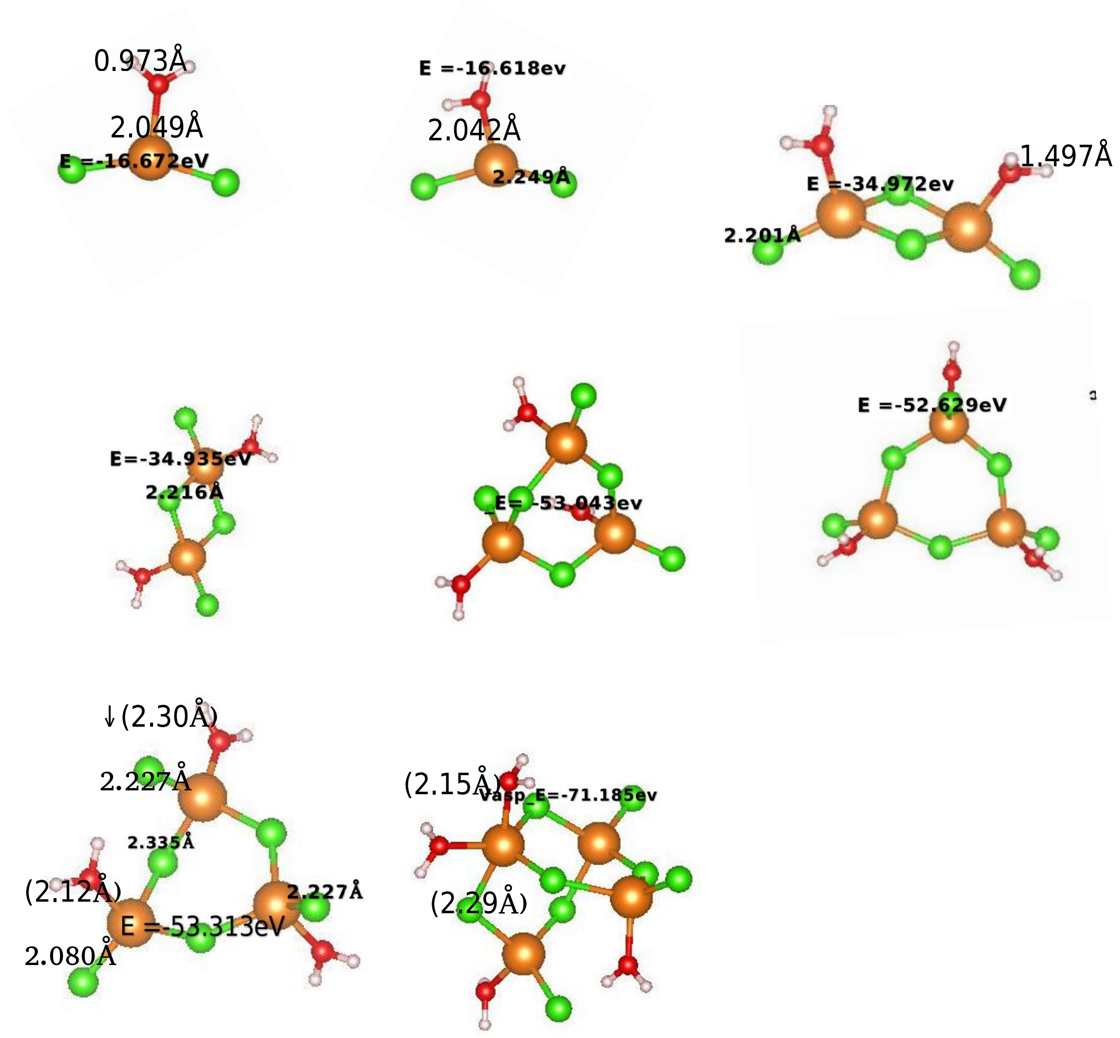


Figure 3:Hydrated $(MgCl_2)_n$ whith 1mol of water

$(MgCl_2)_n$ +mH_2O <=> $(MgCl_2)_n$.mH_2O is Hydration reactions.

The coordination of hydrated $MgCl_2$ with water molecules is influenced by the electrostatic attraction between the positively charged magnesium ion and the negatively charged oxygen atoms in the water molecules. The coordination number and geometry play a significant role in determining the physical and chemical properties of the hydrated compound, such as its stability, solubility, and reactivity as well as kenitics of hydration and dehydration reaction. The bond length of Mg-Cl before and after hydration is completely different.

$(MgCl_2)_2 \cdot 2H_2O$: When one mole of water is added to a single $(MgCl2)_2$ unit, the resulting compound is $(MgCl_2)_2 \cdot 2H_2O$. The optimized structure of $(MgCl_2)_2 \cdot 2H_2O$ obtained using VASP would give information about the bond lengths and angles in the system. For example, the bond lengths between magnesium (Mg) and chlorine (Cl) atoms, as well as the bond lengths between hydrogen (H) and oxygen (O) atoms, already determined. The bond angles involving these atoms was also analyzed. Additionally, the total energy of the system, which is obtained through VASP calculations, can provide insights into the stability of the hydrated compound.

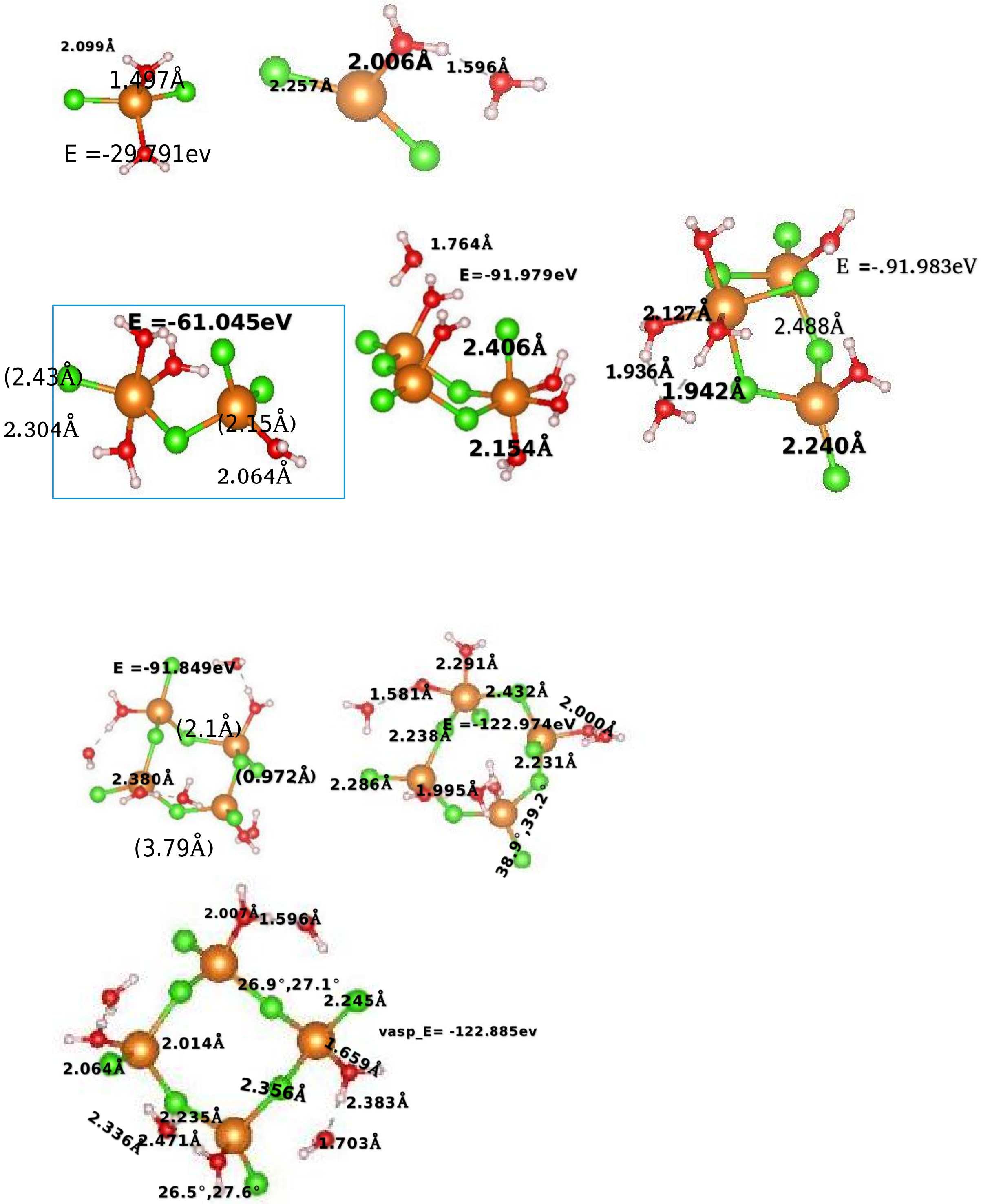


Figure 4:Hydrated $(MgCl_2)_n$ whith 2mol of water

$(MgCl_2)_n \cdot mH_2O$: When two moles of water are added to diffrernt $(MgCl_2)_n$ formula units, the resulting compound is $(MgCl_2)_2 \cdot 4H_2O$,$(MgCl_2)_3 \cdot 6H_2O$, and $(MgCl_2)_4 \cdot 8H_2O$. Similar to the previous case, the optimized structure of $(MgCl_2)_n \cdot mH_2O$ obtained using VASP would provide information about the bond lengths and angles in the system. The bond lengths between Mg, Cl, H, and O atoms, as well as the bond angles involving these atoms, already analyzed. The total energy of the system can also be obtained, which reflects the stability of the hydrated compound.

Dehydration and Hydrolysis Reactions

The dehydration process of the hydrated $(MgCl_2)_n$ cluster can be influenced by various factors, including the number of water molecules in the cluster (n), the size and structure of the cluster, and the strength of the interactions between the water molecules and the cluster.

Figure.9: Within the temperature range of 250-500K, the dehydration process may be relatively slow. The thermal energy at these temperatures is not sufficient to fully overcome the binding forces, so some water molecules may still remain in the cluster, resulting in partially dehydrated structures.

$MgCl_2.2H_2O$ + Heat <=> $MgCl_2.2H_2O$ (aq) + $1H_2O$ (g) ...(1)

$(MgCl_2)_2.4H_2O$ + Heat<=> $(MgCl_2)_2.2H_2O$(aq) + $2H_2O$(g)....(2)
$(MgCl_2)4.4H_2O$ +Heat <=> $4MgCl_2.2H_2O$(aq) + $2H_2O$ (g)...(3)
$(MgCl_2)_3.3H_2O$ +Heat <=> $(MgCl_2)_3$ (s) + $3H_2O$(g) ....(4)
$(MgCl_2)_3.6H_2O$ + Heat <=> $3MgCl_2.3H_2O$ (aq) + $3H_2O$(g) ....(5)

The $(MgCl_2)_4.4H_2O$ cluster consists of four magnesium chloride molecules with 4 water molecules attached to it (reaction(4)). If we consider the removal of 2 moles of water, it implies the removal of 1/2 of the water molecules present in the cluster. Similarly, the removal of 1 mole of water implies the removal of 1/4th of the water molecules.The exact temperature interval at which 2 moles and 1 mole of water are released is 520K-995K.Figure13. Within the temperature range of 200-995K, the thermal energy becomes more significant, allowing the water molecules to overcome the binding forces more effectively. As a result, one water molecule gradually desorbs from the cluster, leading to the release of 1 mole of water. Figure 11.

DEHYDRATION OF $(MgCl_2)_2.4H_2O$

A. Release $2H_2O$, the fraction of dehydration is 50%.
At lower temperatures,from reaction (2) below 300K, the $(MgCl_2)_2.4H_2O$ cluster would likely exist in a hydrated form, with the water molecules coordinated around the magnesium and chloride ions. As the temperature increases, the thermal energy provided to the system enables the water molecules to overcome the binding forces holding them to the cluster, causing them to evaporate or desorb from the surface. figure 12
The $(MgCl_2)_3.6H_2O$ cluster consists of three magnesium chloride molecules with 6 water molecules attached to it. If we consider 3moles of water being released, it implies the removal of 3/6th or 1/2 of the water molecules present in the cluster.
The $(MgCl_2)_3.6H_2O$ cluster consists of three magnesium chloride molecules with 6 water molecules attached to it. If we consider 3moles of water being released, it implies the removal of 3/6th or 1/2 of the water molecules present in the cluster.
Within the temperature range of 250-900K, the thermal energy becomes more significant, allowing the water molecules to overcome the binding forces more effectively. As a result, the water molecules gradually desorb from the cluster, leading to the release of 3moles of water at 250-600K temperature interval Figure14.

3.1.3 $(MgOClH)_n$ and $(MgCl_{2)n}(MgOHCl)_n$ clusters

The rate and extent of hydrolysis depend on various factors, including the strength of the water cluster interactions and the energy barriers associated with the hydrolysis reaction. The hydrolysis process may occur in a stepwise manner, with water molecules reacting with the cluster to form hydroxide ions and hydrogen chloride. The reaction is irreversible reaction.Figure 13-16. The following reactions were carried out for the investigation of HCl and different MgOHCl cluster formation at temperature range of 250...995K interval and at constant Pressure(1atm).

$(MgCl_2)2.2H_2O$ => $MgOHCl.1H_2O + 1HCl$ 6
-$(MgCl_2)_2.2H_2O$ => $MgCl_2.MgOHCl + 2HCl$ 7
-$(MgCl_2)_3.3H_2O$ => $MgOHCl$+($MgCl_2)_2.2H_2O$ +1HCl ...8
-$(MgCl_2)_3.3H_2O$ => $MgCl_2.MgOHCl.2H_2O$ + MgCl2+1HCl 9
-$(MgCl_2)_3.3H_2O$ => $MgCl_2.MgOHCl + MgCl_2$ +1HCl + $2H_2O$ 10
-$(MgCl_2)_3.3H_2O$ => $(MgOHCl)_3 + 1H_2O$+2HCl 11

-$(MgCl2)_3.3H_2O$ => $MgCl_2.(MgOHCl)_2$ + $2H_2O$+ 1HCl 12

$(MgCl2)_3.6H_2O$ => $(MgOHCl)_3.3H_2O$ + 3HCl 13

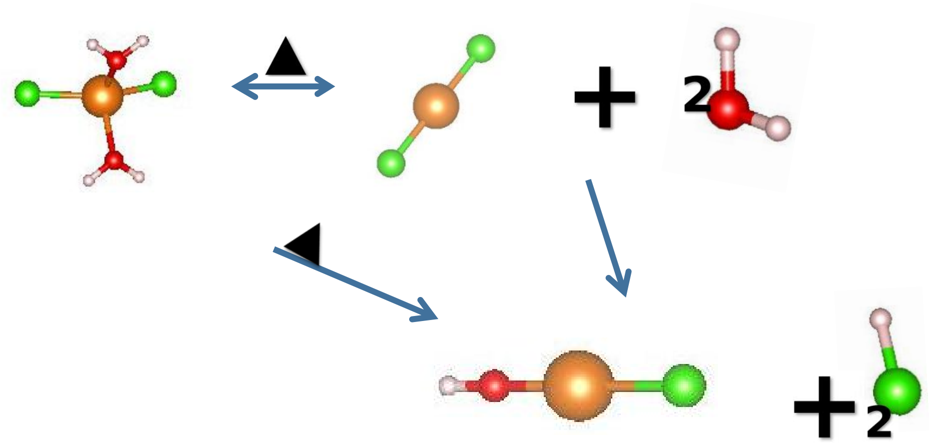
$(MgCl2)_3.6H_2O$ => MgOHCl + $(MgOHCl)_2$ + 3H2O + 3HCl 14

$(MgCl2)_3.6H_2O$ => $(MgOHCl)_3$ + $3H_2O$ + 3HCl 15

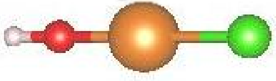
$(MgCl_2)_3.6H_2O$ => $(MgCl_2)_2.2MgOHCl.1H_2O$ + 2HCl + 3H2O ...16

$MgCl_2)_4.4H_2O$ => $MgOHCl.(MgCl_2)_3$ + 1HCl + 3H2O 17
$(MgCl2)_4.4H_2O$ => $MgCl_2.MgOHCl.3H_2O$ + 2MgCl + 1HCl 18
$(MgCl2)_4.4H_2O$ => $(MgCl_2)_2.MgOHCl.3H_2O$ + MgCl + 1HCl 19

$MgCl_2)_4.4H_2O$ => $MgOHCl.1H_2O$ + $(MgCl_2)_3.2H2O$ + 1HCl 20
$(MgCl_2)_4.4H_2O$ => $(MgCl_2)_2.MgOHCl.2H_2O$ + $(MgCl_2).1H_2O$ + 1HCl 21



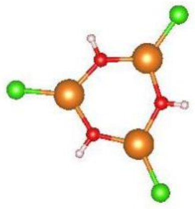
MgOHCl



(MgOHCl)₂

Iso_1

(MgOHCl)₃ **Iso_2**



Iso_Is

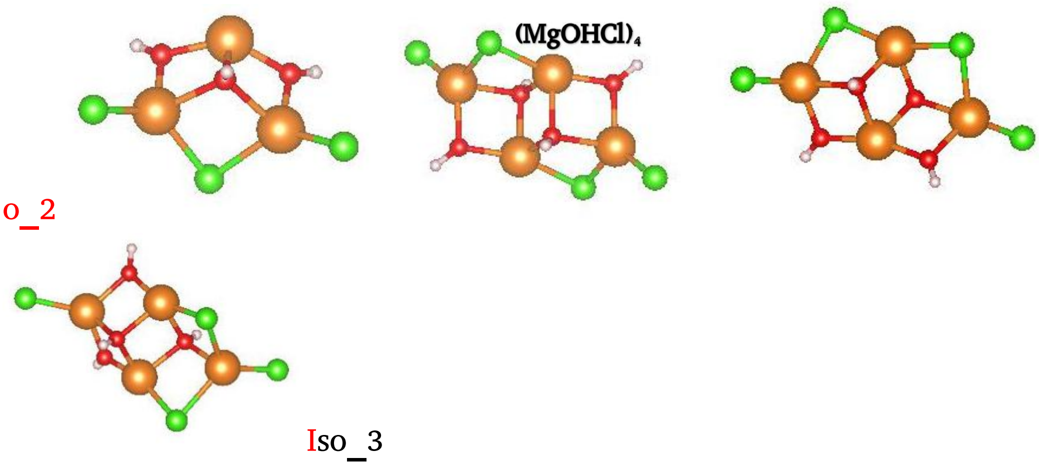


Figure 5: shows the optimized structure of the isomers (MgOHCl)n n =1-4

Figure 5 shows the optimized structure of the isomers $(MgOHCl)_n$ n =1-4 molecule along with its bond lengths and energy. TheMg–Cl bond length and the energy of the clusters are close to those in the structure of $MgCl_2$. On the other side of the Mg atom, the OH fragment is bonded with an Mg–O bond length of 1.78 Å. The magnitude of energy of the $(MgOHCl)_n$ n = 1-4 atom and the O atom are larger than is seen for the $MgCl_2$ hydrates, resulting in a smaller Mg–O bond length. Due tothe low crystallinity of this material, the crystal structure of MgOHCl could not be determined experimentally.

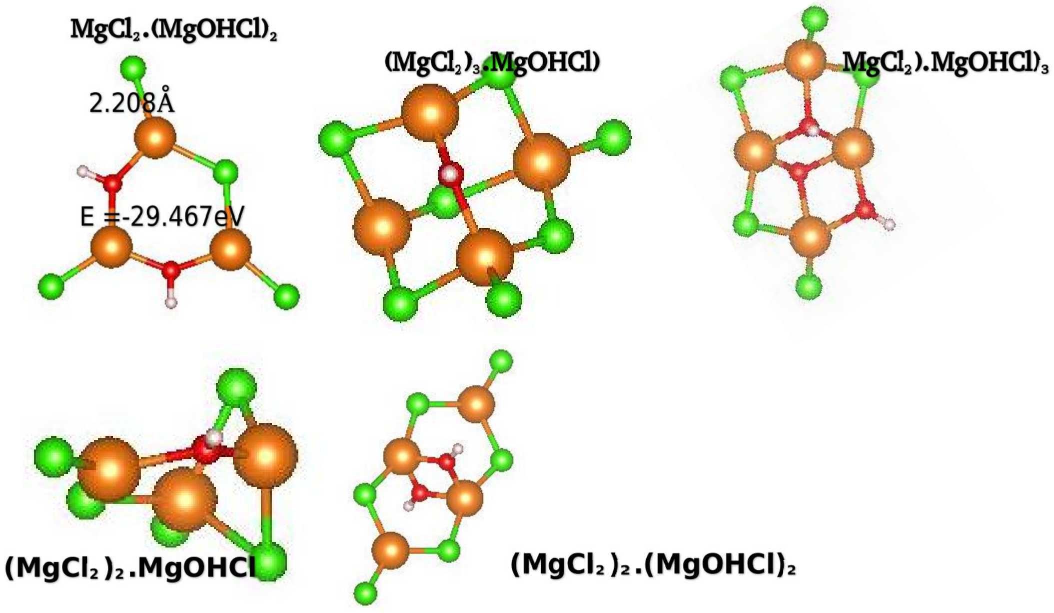


Figure 6:OPtimized Structure of $(MgCl_2)_n.(MgOHCl)_n$

The structure transitions of $(MgCl_2)_n.(MgOHCl)_n$ under dehydration and hydrolysis pathways were quite similar. In dehydration, Cl atom replaces O atom vacancy which makes Mg atom in the center with all Cl atom in corner in $MgCl_2$ structure. In hydrolysis, O atom replaces Cl atom vacancy which also makes Mg atom in the center with Cl and O

atom central symmetry in corner in MgOHCl structure in the determined structure of MgOHCl in our present work, and MgOHCl molecules possess different kinds of arrangement patterns. MgOHCl molecules are syntropy but cis-opposite or trans-opposite pattern on the planes alternately.

3.1.4 (MgClOH)n.nW   MgCl2(MgClOH)n.nW clusters

A.(MgClOH)n.nW

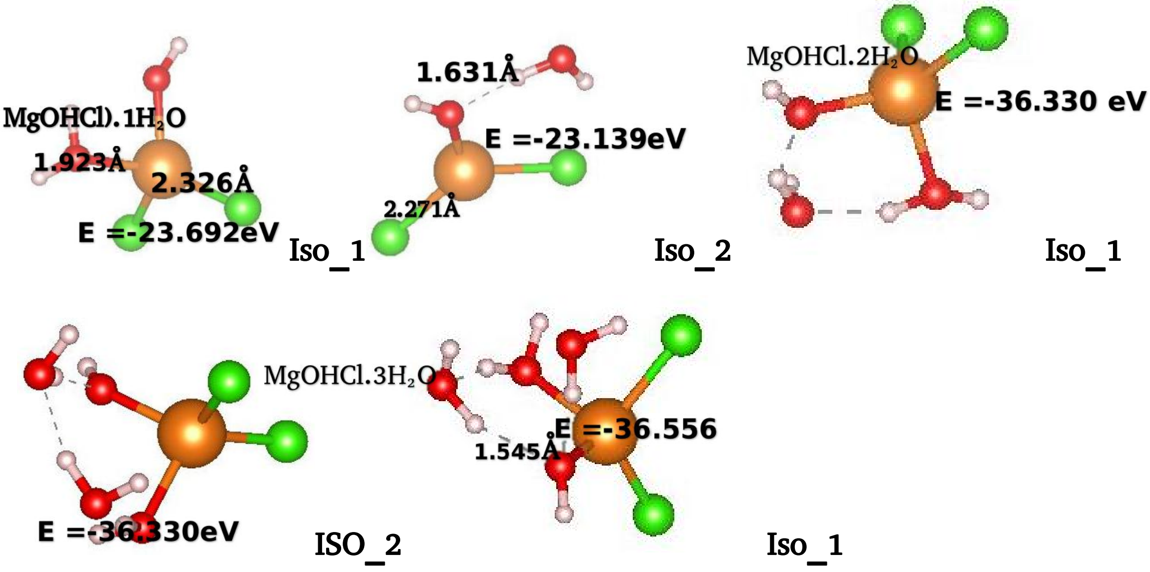


Figure 7: Optimized Structure of (MgClOH)n.nW

During hydrolysis, water molecules react with (MgCl2)$_n$., leading to the formation of (MgOHCl).1H2O with bond lenght of Mg-Cl average 2.271-2.323Å and O-H bond 1.631Å,1.545Å. This is almost similar bond length of hydrated compounds[2].Click here to enter text.This compound consists of a single magnesium hydroxy chloride unit (MgOHCl) bonded to one water molecule (H_2O). The hydrolysis reaction replaces some of the chloride ions (Cl-) in $(MgCl2)_3.3H_2O$ with hydroxide ions (OH-), resulting in the formation of the hydroxychloride moiety (MgOHCl). The compound contains one water molecule per unit of (MgOHCl). [27]

(MgOHCl).$2H_2O$:

Another product that can be formed during hydrolysis is (MgOHCl).$2H_2O$. This compound consists of a single magnesium hydroxychloride unit

(MgOHCl) bonded to two water molecules ($2H_2O$). The hydrolysis reaction incorporates additional water molecules into the crystal lattice of the magnesium hydroxychloride compound.

B.$MgCl_2(MgClOH)_n.nW$

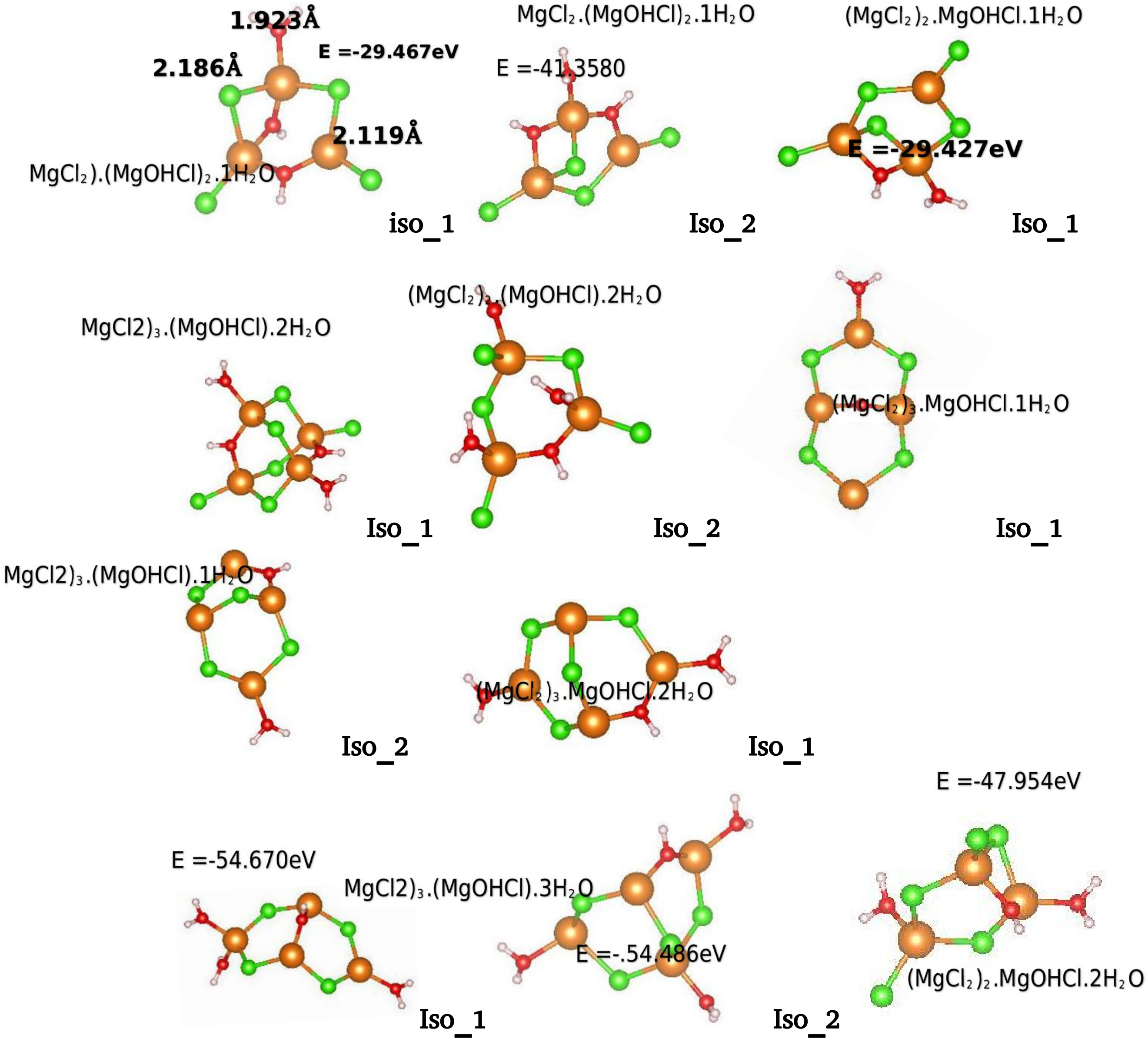


Figure 8:OPtimized Structure of $MgCl_2(MgClOH)_n.nW$.

The hydrolysis of magnesium chloride hexahydrate, tetrahydrate and dihydrate can result in the formation of various magnesium hydroxy chloride compounds, such as $(MgOHCl)_4$,$(MgOHCl)_3$ and $(MgOHCl)_2$ and (MgOHCl)[28]. During hydrolysis, water molecules react with the magnesium chloride hexahydrate, leading to the formation of magnesium hydroxy chloride, $(MgOHCl)_3$,HCl and Water gas. This compound consists of three magnesium cations (Mg^{2+}) bonded to three hydroxide ions (OH-)

and three chloride ions (Cl-)[29]. The resulting compound is a white solid with a complex crystal structure[1] figure 7.

In addition to $(MgOHCl)_n$, n= 1-4, another product that can be formed during the hydrolysis of magnesium chloride hexahydrate is $MgCl_2.(MgOHCl)_2.2H_2O$,$MgCl_2.(MgOHCl)_2.2H_2O$,$(MgCl_2)_2.MgOHCl.1H_2O$,with bond length Mg-O 1.908Å and Mg-Cl at egde 2.093Å at the center Mg-Cl 2.219Å. $(MgCl_2)_2.MgOHCl.2H_2O$, $(MgCl_2)_2.MgOHCl.3H_2O$ etc. This compound contains one magnesium chloride unit ($MgCl_2$) bonded to two magnesium hydroxychloride units $(MgOHCl)_2$, along with two water molecules ($2H_2O$). The compound possesses a hydrated structure with water molecules trapped within its crystal lattice[30].

Another product that can form during the hydrolysis process is $(MgCl_2)_3.(MgOHCl)_2.2H_2O$. This compound consists of three magnesium chloride units ($MgCl_2$) bonded to two magnesiumhydroxy chloride units (MgOHCl), along with two water molecules ($2H_2O$). The compound has a hydrated structure with water molecules incorporated within its crystal lattice [[31].

3.2 Cluster energetics, dehydration and hydrolyis

3.2.1 Formation energy and Binding Energy

Table 1:Calculated Binding energy and formation enegy of low lyining stucture

Cluster	BE(eV)	FE (eV)
$MgCl_2$	4.435	- 6.853
$(MgCl_2)_2$	4.650	-15.428
$(MgCl2)_3$	4.715	- 24.079
$(MgCl_2)_4$	4.835	-33.065

The binding energy is a measure of the strength of the attractive forces holding the cluster together [[18] . To calculate the binding energy, we performed a theoretical calculation using appropriate computational method [[5]. The binding energy of the different $(MgCl_2)_n$ cluster is given by the difference in energy between the optimized cluster and the sum of the energies of the isolated fragments. It can be calculated using the equation (1,3).Table 2:Calculated Binding energy and formation enegy of Hydrated $(MgCl2)n$ low lyining stuctures.

Structure	BE	FE
$MgCl_{2.}1H_2O$	1.005	-25.439
$(MgCl_2)_{2.}2H_2O$	3.646	-52.513
$(MgCl2)_{3.}3H_2O$	6.192	-79.500
$(MgCl_2)_{4.}4H_2O$	8.523	-106.257
$MgCl_2.2H_2O$	1.946	-50.813
$(MgCl_2)_2.4H_2O$	5.277	-103.013
$(MgCl2)_3.6H_2O$	8.328	-154.930

The formation energy of a compound represents the energy change associated with the formation of that compound from its constituent elements [[19]. In the case of $(MgCl_2)_n$, where n represents the number of $MgCl_2$ units, we calculated the formation energy for different values of n using equation (2,4)

3.2.2 Dehydration and Hrdrolysis energy at T =0 ,300K, 500 and 600 K.

Table 3:Calculated Dehydrolysis and hydroysis energy of low lyining stuctures at T =0

Cluster	Hydrolysis Energy(eV)	Dehydration Energy
$MgCl_{2.}1H_2O$	1.766 eV	1.034eV
$MgCl_2.2H_2O$	7.451	0.993
$(MgCl_2)_{2.}2H_2O$	1.027	0.932
$(MgCl2)_{3.}3H_2O$	1.109	0.928
$(MgCl_2)_{4.}4H_2O$	9.861	0.755
$(MgCl_2)_2.4H_2O$	1.748	0.733
$(MgCl_2)_3.6H_2O$	6.577	0.804

Table 4:Calculated Dehydrolysis and hydroysis energy of low lyining stuctures at T **= 300K, 500 and 600 K(after addition of ZPE)**

Cluster	DehydrationEnergy(eV)	Hydrolyis energy(eV
$MgCl_2.1H_2O$	13.993829ev	17.739
$MgCl_2.2H_2O$	15.938	17.253
$(MgCl_2)_2.2H2O$	27.441	33.455
$(MgCl_2)_2.4H_2O$	28.487	31.432
$(MgCl_2)_3.3H_2O$	37.704	39.474
$(MgCl_2)_4.4H_2O$	41.087	47.234
$(MgCl_2)_3.6H_2O$	60.774	75.361

3.3 P-T for dehydration

As the temperature continues to increase within the range of 500-900K, and 250-500K the thermal energy becomes more significant. This allows the water molecules to overcome the binding forces more effectively, leading to a more efficient removal of water molecules from the cluster figure 9 and 10. The interactions between the water molecules and the cluster weaken, facilitating the evaporation or desorption of the remaining water molecules. At higher temperatures, closer to 1000K, the dehydration process is expected to be nearly complete, resulting in the formation of a fully dehydrated $(MgCl_2)_n$ cluster figure 9.

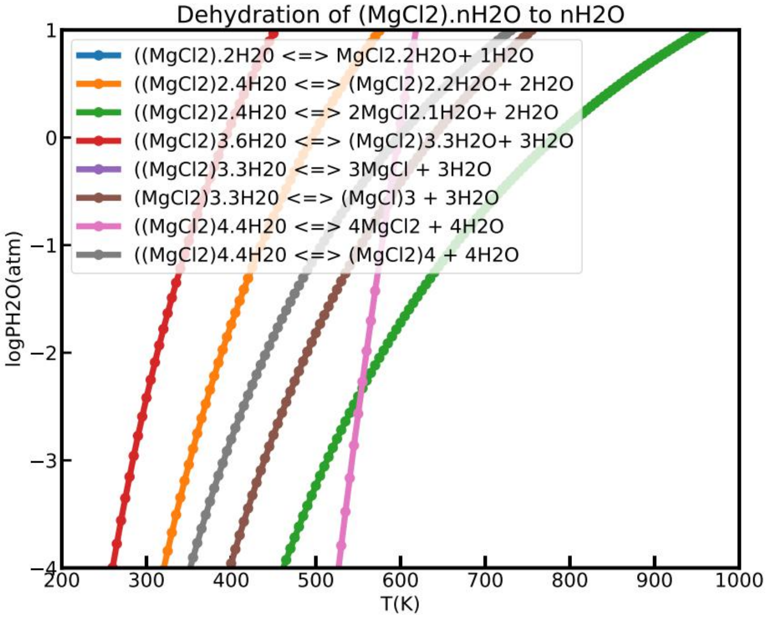


Figure 9:Complete Dehydration of $(MgCl_2)_n.mH_2O$ to nH_2O, n = 1,2,3,4

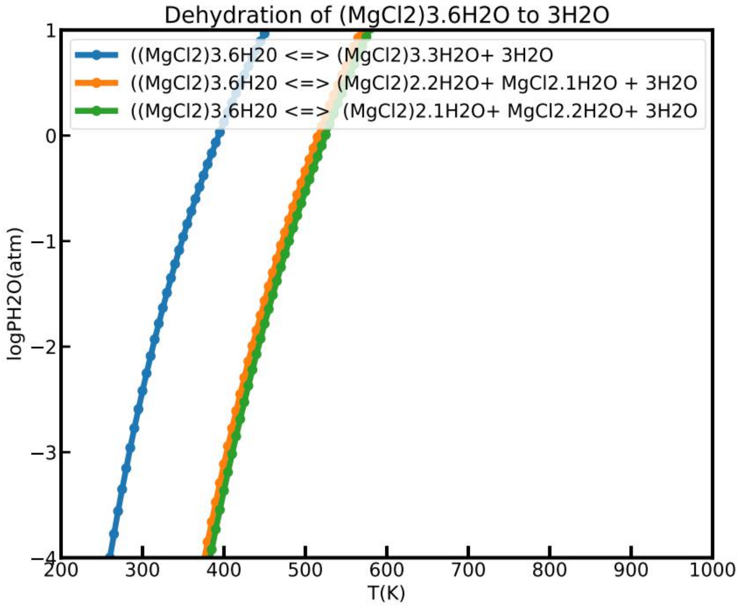


Figure 10:Dehydration of $(MgCl_2)_3.6H_2O$ to $3H_2O$ + $(MgCl_2)_3.H_2O$

The $(MgCl_2)_4.4H_2O$ cluster consists of four magnesium chloride molecules with 4 water molecules attached to it. If we consider the removal of 2 moles of water, it implies the removal of 1/2 of the water molecules present in the cluster. Similarly, the removal of 1 mole of water implies the removal of 1/4th of the water molecules.The exact temperature interval at which 2 moles and 1 mole of water are released is 520K-

995K.Figure13. Within the temperature range of 200-995K, the thermal energy becomes more significant, allowing the water molecules to overcome the binding forces more effectively. As a result, one water molecule gradually desorbs from the cluster, leading to the release of 1 mole of water. Figure 11.

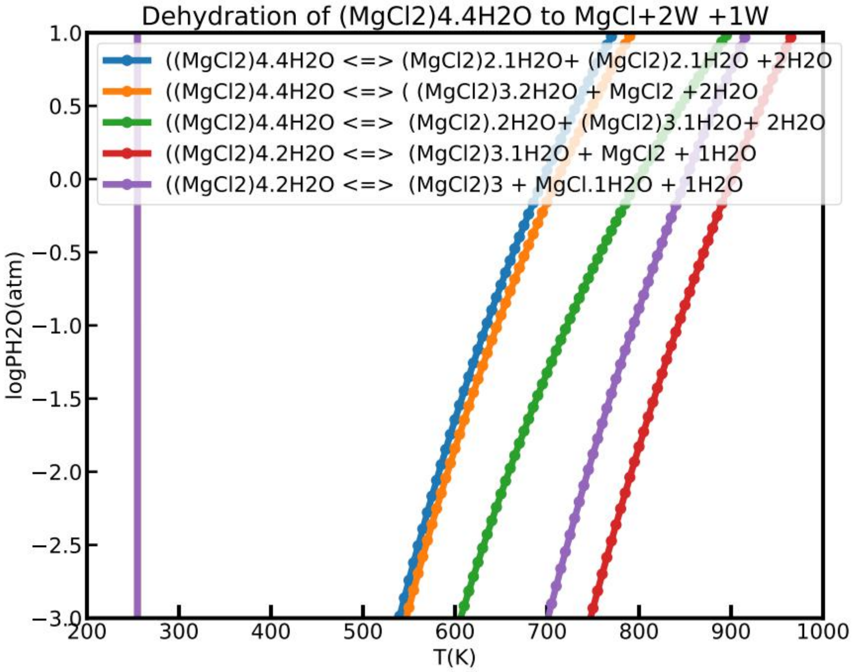


Figure 11:Dehydration of $(MgCl_2)_4.4H_2O$ to $2H_2O$ + $(MgCl_2)_n$

At lower temperatures, below the dehydration temperature 300K, the $(MgCl_2)_2.4H_2O$ cluster would be fully hydrated with all 4 water molecules attached. As the temperature increases within the range of 320-900K, the thermal energy provided to the system enables the water molecules to overcome the binding forces holding them to the cluster

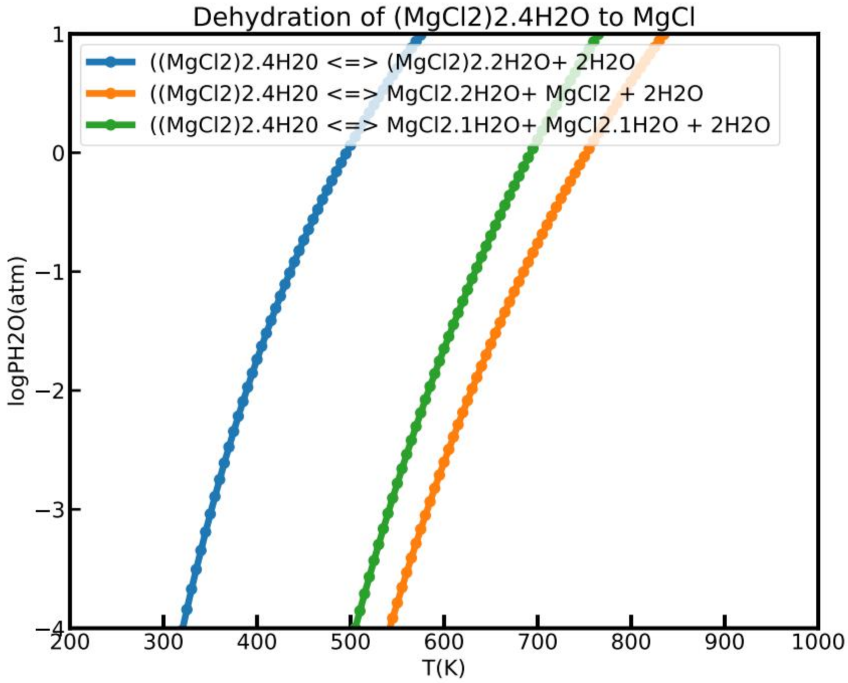


Figure 12:Dehydration of $(MgCl_2)_2.4H_2O$ to $(MgCl_2)_2.nH_2O$ (s) + $2H_2O$ (g)

3.4 P-T for hydrolysis

Within the temperature range of 400-1000K, the thermal energy becomes more significant, allowing the water molecules to overcome the energy barriers and react with the cluster more effectively. As a result, 1,2 and 3 mole of water reacts with the cluster, leading to the formation of magnesium hydroxychloride and hydrogen chloride gas at 400K-1000K temperature interval.Figure 13

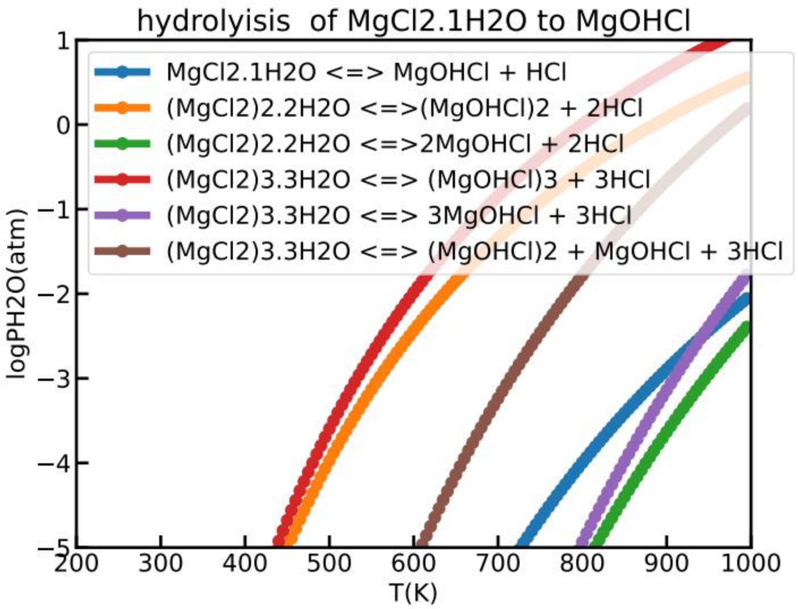


Figure 13:Hydrolysis of $(MgCl_2)_n.mH_2O$ to (MgOHCl)n **+**nHCl

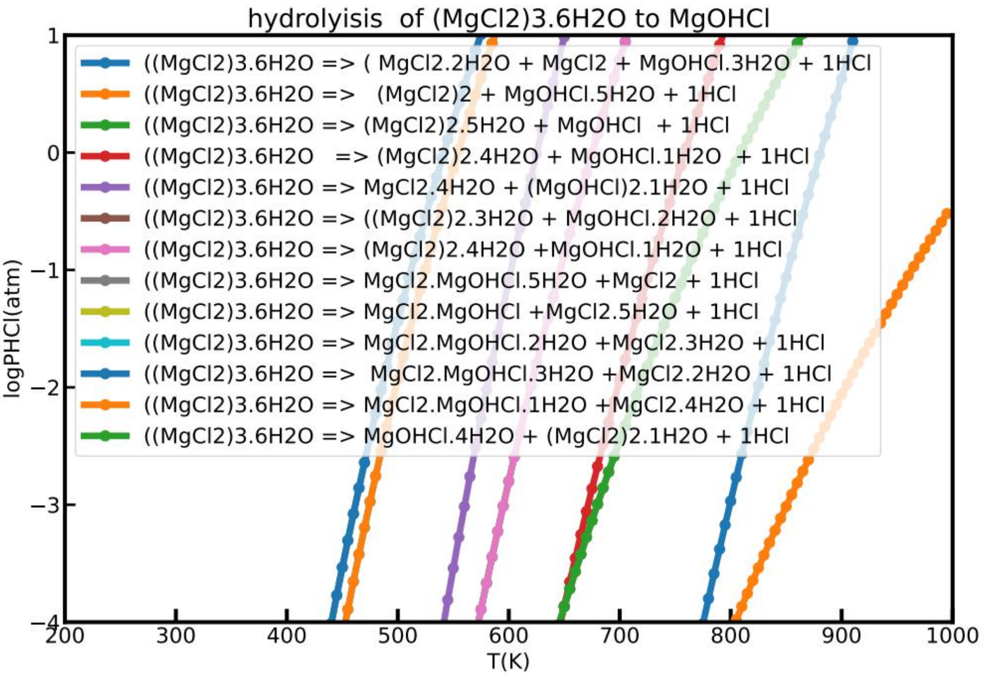


Figure 14:Hydrolysis of $(MgCl_2)_3.6H_2O$ to 2HCl

The hydrolysis process may occur in a stepwise manner, with the HCl molecule reacting with the cluster to form a hydroxide ion and release Hdrogen chloride gas.Within the temperature range of 430-1000K, the thermal energy becomes more significant, allowing the HCl molecule to overcome the energy barriers and react with the cluster more effectively.

As a result, 2mole of HCl reacts with the cluster, leading to the formation of 2HCl. Figure 14.

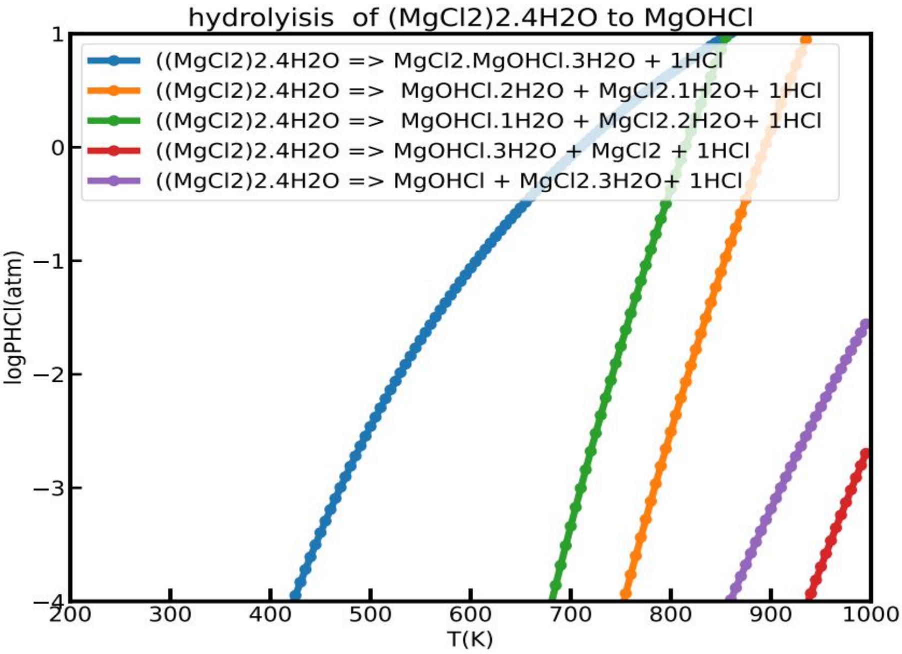


Figure 15:Hydrolysis of $(MgCl2)_3.3H_2O$ to 2HCl + 1HCl

Comparing Figures 9 , 11 and 15, it can be seen that at a given water vapor pressure and HCl pressure, the equilibrium temperatures for the hydrolysis reactions are higher than those for the dehydration reactions[4]. n similar ways for each $MgCl_2)_4.4H_2O$ + heat => $MgOCl.mH_2O$ + $(MgCl_2)n.1H_2O$ +1HCl is formed at 520K-700K temperature interval at the begining.Figure 15.

Hydrolysis of $(MgCl_2)_2.4H_2O$ and $(MgCl_2)_4.4H_2O$ to 1HCl depending on the strength of the HCl-cluster interactions and the energy barriers associated with the hydrolysis reaction. The hydrolysis process may occur in a stepwise manner, with HCl molecules reacting with the cluster to form hydroxide group compounds and release Hydogen chloride gas.

Within the temperature range of 500-1000K, for $(MgCl_2)_2.4H_2O$, the thermal energy becomes more significant, allowing the HCl molecules to overcome the energy barriers and react with the cluster more effectively.As a result, 1moles of HCl gas release from reaction. consider the figure 15

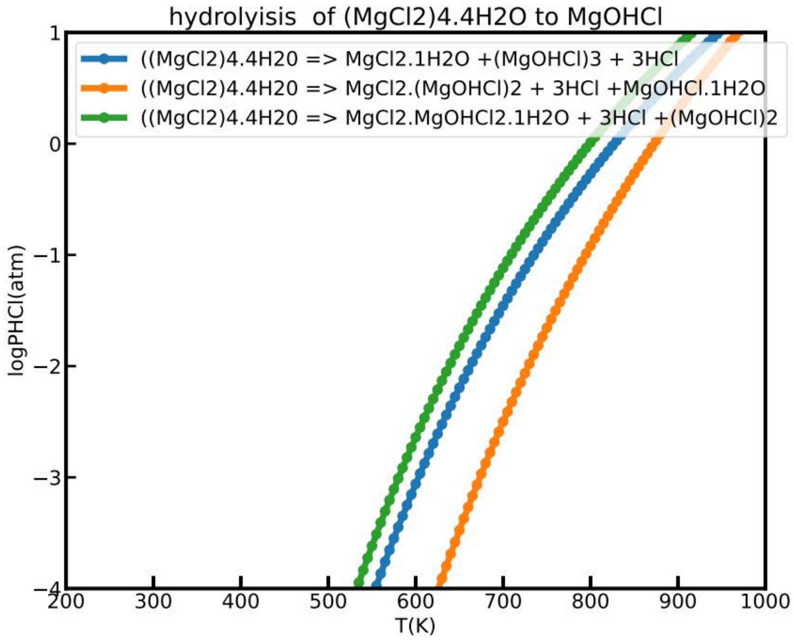


Figure 16:Hydrolysis of $(MgCl_2)_4.4H_2O$ to $(MgOHCl)_2$ + 3HC

Comparing Figures 9 and 16 for Hydrolysis of $(MgCl_2)_4.4H_2O$ to $(MgOHCl)_2$ + nHCl; it can be seen that at a given water vapor pressure and HCl pressure, the equilibrium temperatures for the hydrolysis reactions are higher than those for the dehydration reactions.

3.5 P-T for combinations

Figure 17-22 shows the changes in the equilibrium HCl

pressure as a function of temperature for the hydrolysis reactions with the H_2O pressure kept constant at $p_{H2O} = 10^{-7}$atm - 0.5atm and also HCl pressure kept constant at $p_{HCl} = 10^{-7}$atm - 0.5atm[4]. A comparison between the hydrolysis reaction and the dehydration reaction, to understand the preference of one over the other for different combinations of HCl and H_2O Over pressures, is shown here[20].

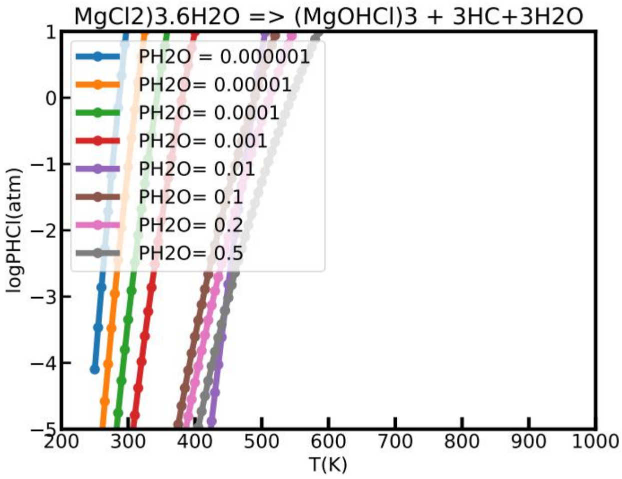


Figure 17:A.Hydrolysis of $(MgCl_2)_3.6H_2O$ to $(MgOHCl)_2$ + 3HC +$3H_2O$

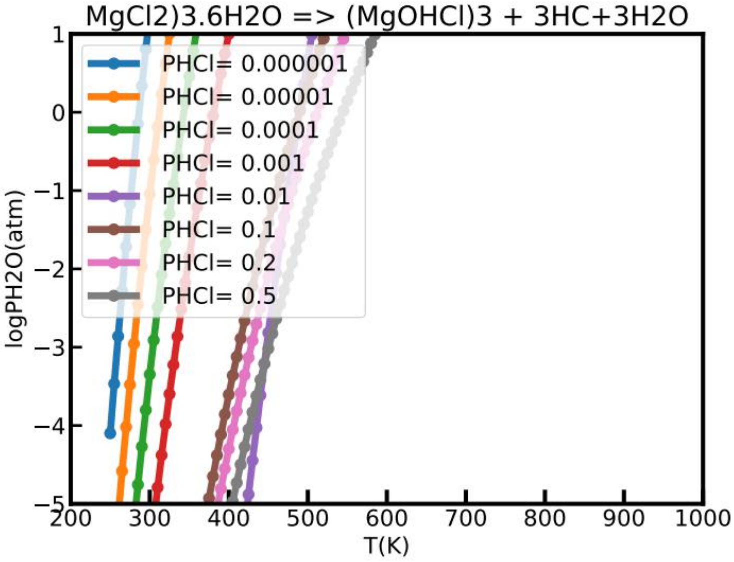


Figure 18:B.Hydrolysis of $(MgCl_2)_3.6H_2O$ to $(MgOHCl)_3$ + 3HCl + $3H_2O$

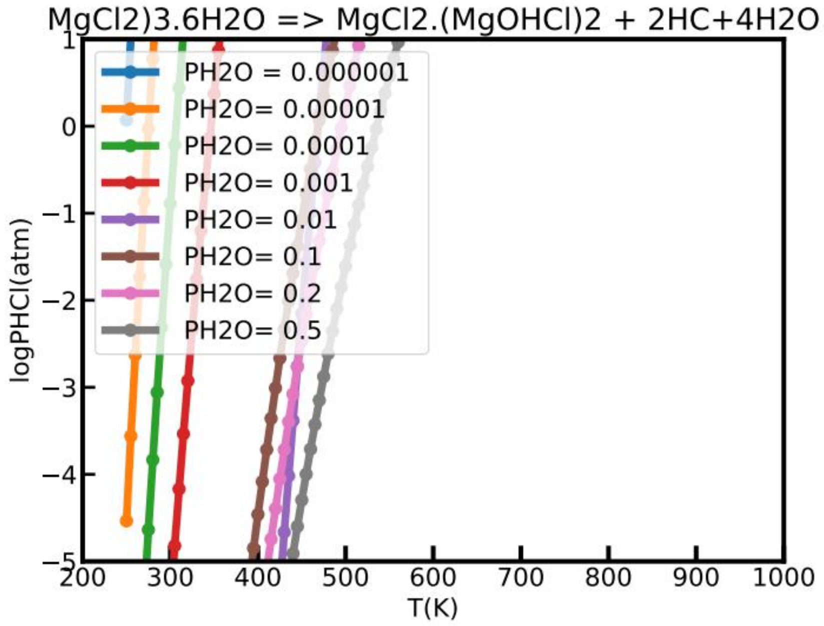


Figure 19:A.Hydrolysis of $(MgCl_2)_3.6H_2O$ to $MgCl_2.(MgOHCl)_2$ + 2HCl +$4H_2O$

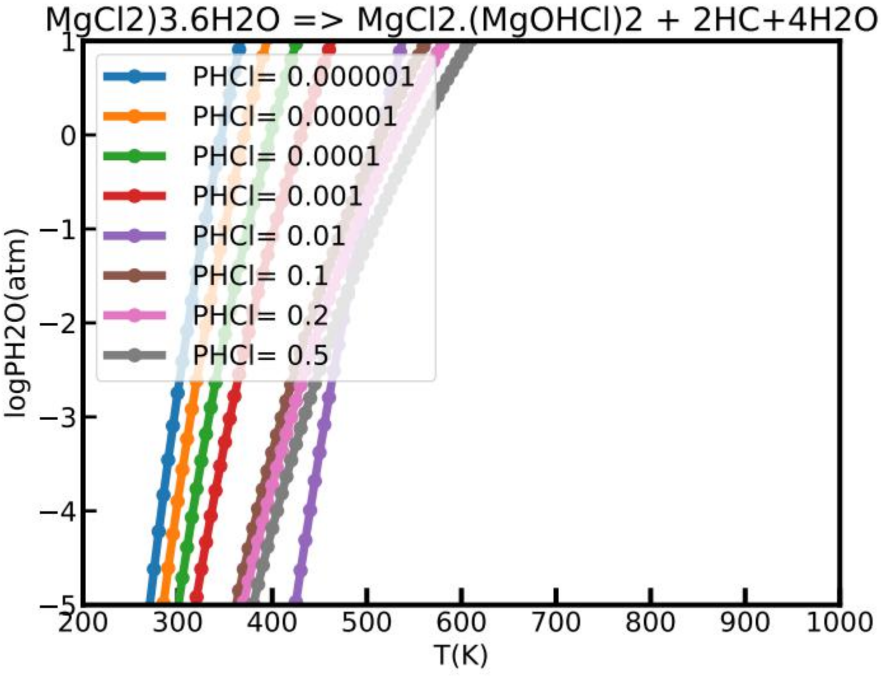


Figure 20:B.Hydrolysis of $(MgCl2)_3.6H_2O$ to $MgCl_2.(MgOHCl)_2$ + 2HC +$4H_2O$

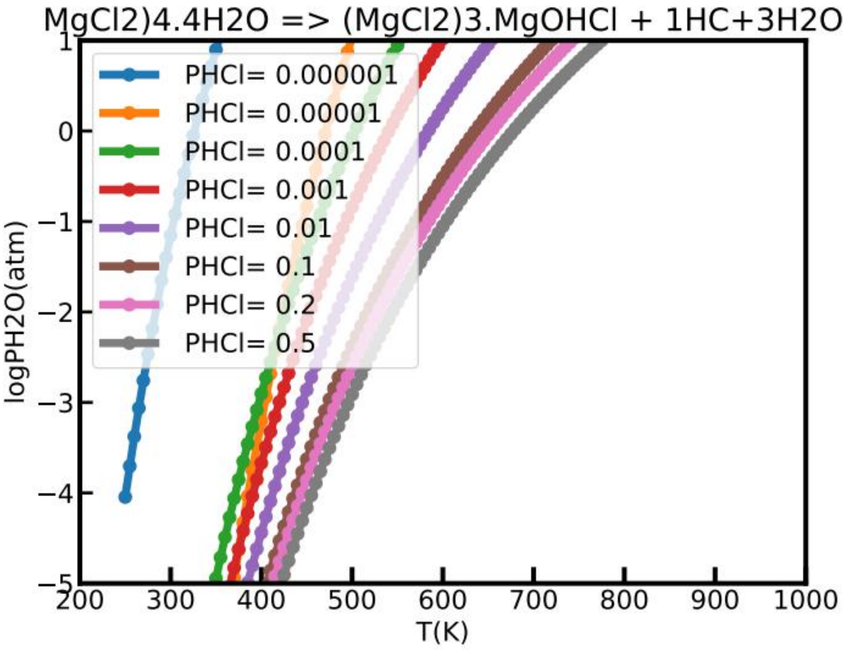


Figure 21:A.Hydrolysis of $(MgCl_2)_4.4H_2O$ to $(MgCl_2)_3.MgOHCl$ + 1HC $+3H_2O$

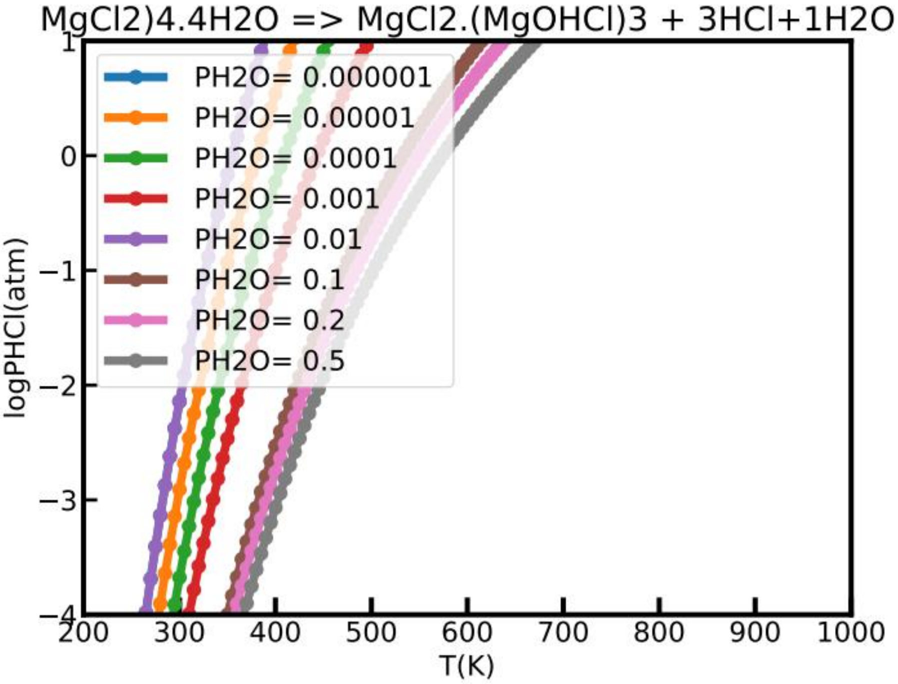


Figure 22:B.Hydrolysis of $(MgCl_2)_4.4H_2O$ to $(MgCl_2).(MgOHCl)_3$ + 3HC $+1H_2O$

6.Dehydration and Hydrolysis of Mixed Compound

Properly capturing the water adsorption/desorption behavior and the formation/dissociation of hydrated phases is crucial for modeling the thermodynamicsand kinetics. Identifying the stable crystalline phases and their relative stabilities,as well as the phase transformation pathways during hydration/dehydration, isessential for TCES modeling. Accurately predicting phase diagrams and phase transition temperatures for mixed hydrated materials is computationally demanding. The initial geometry of the hydrated mixture of ($CaCl_2$. $MgCl_2$),($CaCl_2 \cdot MgSO_4$),($MgCl_2 \cdot MgSO_4$), and ($MgCl_2 \cdot CaCl_2 \cdot MgSO_4$) with mixed ratio of 1:1,1:2 or 2:1 wt using similar methodology i.e artificial bee colony algorithm and Charmm force field.The goal of this project was to create a tool that could offer information on the process by which complex (new) materials hydrate in order to forecast equilibrium conditions at a specific pressure and temperature for thermochemical heat storage applications. When it comes to their utilization as TCM, the majority of common salts have disadvantages when they are pure. These include the occurrence of undesired salt melting or deliquescence that forms blocking agglomerates in the storage system,slow kinetics and low thermal conductivities that reduce thermal input and output power, and undesired irreversible side reactions that reduce storage capacity. They can also include a metastable zone surrounding equilibrium conditions. Deliquescence is the term for the phenomenon that occurs when a substance dissolves in water andabsorbs so much water vapor from the surrounding water that it dissolves in the water. These flaws make the TCM less cyclable and stable, which affects the storage 39 system [25]. To hydrate the mixtures, one or two moles of water were added at atime (Figure 23). The average distance between Mg and Cl in the mixtures varies from 2.28 to 3.86, as n varies from 0 to 6, depending on hydration (see Figures 2). The average interatomic distance between Mg and Cl rises more significantlyby increasing n from 2 to 6. The higher numbers of hydrations in the mixtures (n =6) push the Cl atoms further apart from the Mg atom.

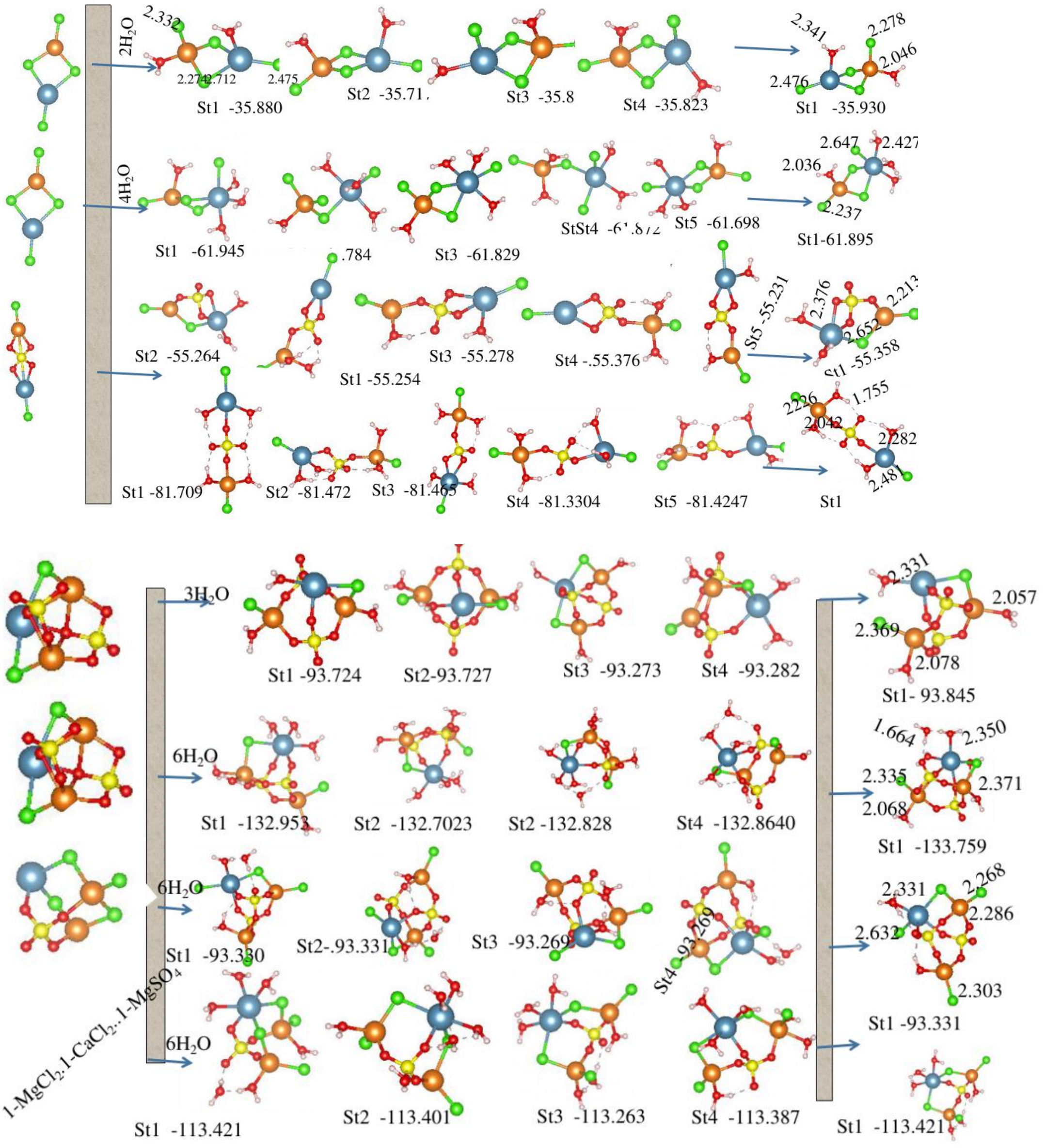


Figure: 23 Hydrated mixtures

Hydrolysis of Hydrated Mixture

In the thermolysis of chloride-based salts, which yields HCl and H2O, hydrolysis is an undesirable product. Hydrolysis begins at a temperature higher than dehydration, as the enthalpy change in hydrolysis is substantially greater than the enthalpy change in dehydration. Under comparable DFT formalism, the hydrolysis characteristics of the elementary salt hydrates of MgCl2 have been studied previously and shown to be in good agreement with the experiments.We have adjusted the partial pressures vs. temperature of one of the reaction products while keeping the partial pressure of the other product constant in order to comprehend the impact of temperature and partial pressure of the products (pHCl , pH2O) on hydrolysis. Chemical mixing can greatly minimize hydrolysis in (MgCl2)n hydrates within the working range of the TCM for solar applications.

7. Conclusion

$(MgCl_2)_n$ hydrates are thought to be highly promising materials for seasonal heat storage. The Artificial Bee Colony Algorithm was utilized to generate the tiny clusters $(MgCl_2)_n$ and $(MgCl_2)_n.mH_2O$.These substances have quick dehydration kinetics and a large storage capacity. Next, we optimized the structure for more research by creating a file for Vasp.From the VASP output, a stable or low lining energy structure was chosen.The bond length and energy of the optimized structure differ from the previously optimized structures of $(MgCl_2)_n$ and $(MgCl_2)_n.mH_2O$. A variety of temperature intervals were tested to determine the ideal storage interval for dehydration. Nevertheless, hydrolysis may happen at various temperature intervals as a side reaction to dehydration.One very promising material for seasonal heat storage is regarded to be magnesium chloride hydrates.In general, the examination of the characteristics, stability, and hydrolysis of hydrated $(MgCl_2)$ clusters is crucial and to get sustianable energy storage Materials.The study identified both(MgCl2)n cluster and binary and ternary mixtures of the most stable isomers from five structures based on their electronic energy,with lower energy values indicating more stability. The most stable isomers wereselected for the hydration process, and we understood that the bond lengths canbe significantly affected when combining with water. The bond length between Mgand Cl is relatively short compared to hydrated MgCl2.This increased bond length typically falls within the range of 2.201–2.383Å

8.Reference

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