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**DEPARTMENT OF CHEMICAL ENGINEERING**

**PHASE ANALYSIS OF SALT HYDRATES**

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## INTRODUCTION

The transition from carbon-based to renewable energy sources is a key focus in contemporary society, particularly in Europe, where approximately 70% of residential energy consumption is attributed to domestic space heating and hot water generation [1] .This shift towards cleaner energy sources, primarily derived from solar radiation, introduces challenges due to the inherent variability of solar energy on different time scales.

The proposed solution involves a thermochemical reaction-based heat storage concept, utilizing thermochemical materials (TCMs). These materials offer advantages such as nearly loss-free storage and high energy density, differentiating them from conventional techniques like sensible heat storage and phase change materials [2] .The reactive gas considered in this context is H2O.

The objective is to explore and analyze TCMs as heat storage materials, considering the evolving research landscape over the past decade. The focus is on the first-generation salt hydrates based on TCMs, with a review of various systems from lab-scale to field demonstrations[3-5]. Notable salts for temperature storage below 100°C and between 100°C and 300°C are discussed, with consideration of their potential for residential applications [6].

The selection criteria for TCMs are discussed, emphasizing the importance of meeting consumer demands for a heat storage system capable of storing 10 GJ, delivering hot tap water at 65°C, and being charged in summer through solar panels. The article aims to identify TCMs that align with these criteria based on available pressure-temperature data and assess their plausibility for the specified target application. [7]

Solar energy has the potential to meet the annual energy needs of the Netherlands, considering the country's yearly average solar intensity of 110W/m2 and the typical efficiencies of photovoltaic (PV) panels (10-15%) and solar collectors (about 30%) [8] . For example, a well-insulated dwelling with a yearly heat demand of 20GJ could be satisfied by approximately 20m2 of solar collectors.

However, due to daily and seasonal variations in solar irradiation, the need for heat storage arises. While daily fluctuations in the warm season can be addressed with modest hot water storage, seasonal variations requiring storage of about 10GJ pose challenges. Traditional hot water storage would necessitate a tank of at least 50m3 , impractical for typical dwellings. Additionally, storing water at 90°C for the entire cold season would demand exceptional insulation.

A more appealing solution for seasonal heat storage is thermochemical heat storage (TCS), which relies on thermally reversible reactions. An example of such a reaction is the sorption or hydration reaction, exemplified by Na2S + ½H2O + 4 1 2 H2O → Na2S.5H2O + heat. This reaction boasts a high energy density of approximately 2.7GJ per m3 of Na2S.5H2O, can be reversed by typical solar collector temperatures in summer, and produces heat at levels suitable for space heating and domestic hot water[9]. Compared to hot water storage, TCS offers a heat storage density advantage of about 10-15 times and eliminates the need for extensive thermal insulation.

The increasing awareness of humanity's impact on climate change [10] and the rising energy intensity in developing and underdeveloped nations [11] drive the imperative for a more sustainable approach to energy production and consumption. The energy grid, a complex system involving the production, transportation, consumption, and storage of multiple energy carriers, faces continuous evolution due to technological advancements, policy changes, and the integration of renewable energy sources and intermittent power systems.

Renewable energy sources, cogeneration, and intermittent power generation introduce new challenges to the energy grid. These challenges include decentralized capacities, intermittent and unpredictable production patterns, and the production of multiple energy carriers. To adapt to these changes, the energy network must incorporate practices such as storage of multiple energy carriers, demand-side management, and the exchange and relocation of energy through carrier conversion. [12,13].

Energy storage plays a crucial role in addressing fluctuations in energy demand, optimizing the use of fluctuating production sources like renewables, enhancing energy grid safety, and improving overall system efficiency [14].

Within the realm of storage technologies, thermal energy storage emerges as an attractive option due to its potential economic advantages, diverse storage possibilities, and its dominance in final energy use in sectors such as industry and households. Thermal energy storage encompasses sensible heat (e.g., water tanks, underground storage), latent heat (e.g., ice, phase change materials), and sorption heat storage.[15-17]

Sorption heat storage, particularly intriguing, involves utilizing physical or chemical bonds to store energy. This method relies on at least two components: a sorbent (liquid or solid) and a sorbate (vapor). During the charging process, an endothermic reaction occurs, allowing the two components to be stored separately. During discharge, an exothermic reaction releases heat. Sorption heat storage offers higher energy density and minimal heat losses compared to conventional thermal storage based on sensible heat.

The integration of renewable energy sources, especially solar, into the energy landscape presents both opportunities and challenges. The variability of solar energy necessitates effective storage solutions to address daily and seasonal fluctuations. Thermochemical heat storage (TCS) and sorption heat storage emerge as promising avenues, offering high energy density, reversibility, and reduced heat losses [18-22].

This highlights the importance of selecting appropriate thermochemical materials (TCMs) and sorption materials that meet specific criteria for residential applications. It also underscores the significance of ongoing research and development efforts to improve system efficiency, lifespan, and maintenance requirements. As the global community strives for a sustainable energy future, the exploration and adoption of innovative storage technologies play a pivotal role in shaping a resilient and environmentally conscious energy infrastructure.

Salt Lake brines and coexisting salt deposits serve as valuable sources of organic mineral resources, contributing substantial quantities of valuable salts like potash fertilizer and lithium compounds. These salt lakes, found globally with a significant presence in China, are intricate systems comprising various inorganic ions such as Li+, Na+, K+, Rb+, Mg2+, Ca2+, Cl-, SO4 2−, CO3 2−, HCO3 −, NO3 −, and borate.

To separate salts from brines, salt evaporation pond processes are economically efficient. However, the complex and varying compositions of brines, influenced by regional characteristics, seasons, and solar evaporation stages, make brine crystallization behaviors intricate and diverse. The low humidity in Salt Lake regions further complicates these processes.[1]

Understanding and controlling brine crystallization requires knowledge of when and under what conditions specific salts will crystallize. Phase diagrams of water–salt systems provide this information, but experimental determination for multi-component brine systems is challenging.

Computer-assisted simulations, utilizing phase diagram calculation approaches, offer a means to understand the phase equilibria behavior of complex systems comprehensively.

Existing research has extended Pitzer's ion interaction model to describe the thermodynamic properties of simplified Salt Lake brine systems at 25 °C. However, their limitations at temperatures far from 25 °C hinder broader applications, especially for salt evaporation ponds near salt lakes.[3-5]

In another context, the study investigates the ternary HCl + 2-propanol + water electrolyte system using Pitzer, PSC, and an extended form of the PSC ion-interaction approaches. The aim is to understand the thermodynamic properties of this ternary electrolyte system, shedding light on its behavior in mixed solvent environments [27].

Furthermore, accurate understanding of the deliquescence behavior of multicomponent brines is crucial for environmental scenarios like the proposed radioactive waste repository at Yucca Mountain, Nevada, USA. The study proposes a comprehensive thermodynamic model to predict the behavior of aqueous mixtures containing Na+, K+, Ca2+, Mg2+, Cl−, and NO3- ions.

The comprehensive approach, combining literature data and new isopiestic measurements, is vital for reliable predictions and a deeper understanding of the thermodynamic behavior of multicomponent aqueous solutions relevant to environmental scenarios [28]

Potentiometric techniques, particularly the Pitzer ion interaction model and its variations like Pitzer–Simonson–Clegg (PSC), offer valuable insights into electrolyte solutions. However, challenges arise when dealing with dipolar non-electrolyte solutes like amino acids. Modifications to the Pitzer equations aim to address these challenges, considering the concentration dependence of binary interaction parameters [29,30].

Various models and theories, including those by Khoshkbarchi, Vera, Pazuki, and Sadowski, contribute to a comprehensive understanding of ternary systems. Despite available experimental data, such as the (NaCl+I- +proline+water) system, there is a need for extensive exploration of thermodynamic properties over different concentrations and temperatures [31-33].

This study of thermodynamic properties of the (NaCl+I -+proline+water) system through potentiometric measurements. Utilizing the Modified Pitzer (MP) model, researchers aim to determine activity coefficients, osmotic coefficients, excess Gibbs energy, and water activity. The goal is to provide a comprehensive understanding of interactions and behaviors within ternary systems involving electrolytes, amino acids, and water across a broad range of concentrations and temperatures [34,35].

In another realm, the research introduces the quasiisothermic thermometric technique (QTT) to explore the solid-liquid equilibrium of aqueous multielectrolyte systems. The QTT method relies on thermal effects associated with phase transformations, offering a synthetic approach where the system's composition remains known throughout the experiment. This automated apparatus proves effective in determining salt solubility curves for specific systems like H2O+NaCl+KCl, H2O+NaCl+Na2SO4, and H2O+NiCl2+NiSO4 at 298.15 K. Results, systematically compared with literature data, underscore the QTT method's applicability and reliability in investigating thermodynamic equilibria in multi-electrolyte systems [36].

Lastly, the significance of salt lakes and their brines in producing valuable minerals like potash fertilizer and lithium compounds is highlighted. The complexity of brines, influenced by various factors, necessitates effective separation processes such as salt evaporation ponds. Developing a thermodynamically consistent model for simulating Salt Lake brine systems becomes crucial for optimizing resource extraction processes. The research aims to address this by initially focusing on simulating simple binary and ternary systems at various temperatures, gradually extending to more complex multi-component systems, with an emphasis on the LiCl+H2O system [37].

Understanding solubility principles is emphasized in the context of oxo anions and polyoxometalates (POMs). The intricacies of ion-pairing interactions in solutions and their implications for thermodynamic calculations, ion adsorption onto metal oxide surfaces, catalyst design, and sorbent development are explored [38]. The behavior of hex niobate and hex tantalate POMs with different alkali counter cations illustrates the complexity of cation association, highlighting the need for considering both electrostatic and covalent bonding for a comprehensive understanding of solution behavior.

The increasing global interest in lithium, driven by the quest for alternatives to traditional energy sources and environmental concerns, is particularly evident due to its critical role in batteries for various applications, including electric vehicles and energy storage. The major lithium deposits, predominantly found in South American salt flats and saline lakes in countries like China, the United States, and around the Dead Sea, have sparked research into the chemical behavior of lithium for effective exploration and extraction [39,40].

The solubility of lithium salts in aqueous solutions necessitates a thorough understanding of its aqueous chemistry and mineral solubilities under diverse conditions. Existing Pitzer equationbased models have made strides in comprehending lithium interactions, yet limitations persist. A comprehensive Pitzer model that covers a broader temperature range (273.15 to 523.15 K) is proposed. Experimental measurements and parameterization efforts within the complex H-Li-NaK-Mg-Ca-Al Fe (II)-Fe (III)-OH-Cl-Br-HSO4-SO4-H2O system aim to create an extensive geochemical database. The goal is to develop a consistent model accurately describing the Li-HNa-K-Cl-OH-H2O system from diluted solutions to mineral saturation over a wide temperature range.

Switching gears to air-conditioning systems, the paper delves into temperature and humidityindependent control systems, crucial for energy efficiency and a high-quality living environment [41,42]. The focus lies on the dehumidification component, particularly the process involving salt solution dehumidification [43] . Various methods for solution regeneration are explored, with an emphasis on the simplicity and efficiency of packing devices. Lithium chloride solution emerges as a promising candidate, exhibiting superior dehumidification performance compared to other salt solutions under similar conditions. It also aims to investigate the physical properties of LiCl solution during the regeneration process, shedding light on the impact of different working conditions [44].

The subsequent explores the absorption refrigeration system (ARS), a technology gaining traction for utilizing low thermal potential and renewable energy sources. The choice of absorbentrefrigerant pairs is crucial, with lithium bromide-water (LiBr-H2O) and aqua ammonia (H2ONH3) being common choices. However, LiCl-H2O emerges as an alternative, offering favorable characteristics such as a triple state point, long-term stability, lower cost, and improved cycle performance compared to LiBr-H2O [45-49].

Transitioning to thermal energy storage, the significance of thermochemical storage materials, such as MgCl2 • 6 H2O and CaCl2 • 6 H2O, is emphasized for harnessing waste heat and solar thermal energy. This builds upon previous studies on MgCl2 • 6 H2O, exploring its viability for space heating and hot tap water. Thermochemical properties, including kinetics and reaction enthalpy, are investigated using Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). It aims to provide valuable insights into optimizing the performance and efficiency of these materials for solar thermal applications [50-54].

The final section addresses the thermodynamic properties of alkali metal sulfates, particularly Rb2SO4(aq), Cs2SO4(aq), and Li2SO4(aq). Despite the commonality of Na2SO4 and K2SO4 in natural waters, there is limited data for their less-studied counterparts. New isopiestic measurements for Li2SO4(aq) and recalculated data for other alkali metal sulfates are presented. Pitzer's ioninteraction model and an extended form are applied to represent the results comprehensively, aiming to enhance the understanding of the thermodynamic properties of aqueous alkali metal sulfates, especially at intermediate temperatures where previous characterizations were incomplete [55-58].

The passage explores several aspects of research in the field of thermodynamics, materials science, and energy storage technologies. It begins by highlighting the challenges in establishing reliable solubility values for the CaCl2 + H2O system due to discrepancies among existing data. The authors propose an approach, previously successful in the LiCl–H2O system, utilizing the modified BET model to evaluate solubility data by considering vapor pressures of saturated solutions as criteria [59,60]. This method allows for more precise derivation of solubility data, emphasizing the internal consistency between solubility and vapor pressure measurements. The objective is to provide more accurate and consistent solubility values for the CaCl2–H2O system, addressing the existing challenges in the literature [61] .

Transitioning to the realm of phase change materials (PCMs), the focus shifts to the application of CaCl2·6H2O, a salt hydrate, in energy storage and solar technologies. The study acknowledges the advantages of salt hydrates, including high latent storage, non-flammability, good thermal conductivity, and cost-effectiveness [62-65] . However, it also recognizes challenges such as supercooling and phase decomposition during heat release, limiting their practical use. To address these issues, the researchers introduced a novel salt hydrate PCM (CaCl2·2H2O-CaCl2-H2O) and investigate the impact of calcium chloride dihydrate (CaCl2·2H2O) proportions on supercooling reduction and solidification enthalpy [66-68] . Nano SiO2 is employed to modify and eliminate supercooling effectively. The study's practical and straightforward preparation method, along with its evaluation under different cooling conditions, aims to enhance the performance of salt hydrate PCMs for various energy-related applications.

The exploration of inorganic PCMs continues in the context of the development of cities and the associated increase in energy consumption. The passage underscores the significance of PCMs, particularly latent heat thermal storage materials, in improving energy utilization and reducing losses. While acknowledging the limitations of organic PCMs, attention is drawn to the potential of inorganic PCMs, specifically salt hydrates, such as CaCl2·6H2O. The study explores compounded eutectic hydrate salts to overcome limitations like super cooling and phase decomposition. A ternary salt system, K2HPO4·3H2O– NaH2PO4·2H2O–Na2S2O3·5H2O, is introduced, and its thermal storage properties are investigated using various experimental methods. The addition of nucleating agents and thickeners aims to improve the super cooling and cycle stability of the ternary eutectic system, contributing valuable insights into the performance enhancement of inorganic salt hydrate PCMs [69] .

This concludes by addressing the evolving landscape of the energy grid in response to increasing energy intensity. The focus is on the role of energy storage technologies, particularly thermal energy storage, in handling fluctuations in energy demand and optimizing the use of intermittent production sources like renewables. The categorization of thermal energy storage methods into sensible heat storage, latent heat storage, and sorption heat storage is presented, highlighting the versatility and potential costeffectiveness of these approaches [70,71] . As the energy system adapts to accommodate diverse stakeholders and increases intermittent production, the integration of thermal energy storage technologies emerges as a crucial component for achieving a sustainable and resilient energy infrastructure. It also addresses challenges in establishing solubility values, explores the application of phase change materials in energy storage and solar technologies, and emphasizes the importance of thermal energy storage in the context of the evolving energy grid. The research presents the contribution to the on-going efforts to develop efficient and sustainable solutions for energy storage and utilization, with potential implications for diverse applications across various industries [72] .

**LITERATURE REVIEW :**

**M. Gaeini (2018)** studied that thermochemical heat storage in salt hydrates is a promising method to improve the solar fraction in the built environment. The major concern at that stage is liquefaction followed by washing out of active material and agglomeration into large chunks of salt, thus deteriorating the diffusive properties of the porous salt hydrate structure. In his work, specific attention is given to the methods to stabilize a sample salt hydrate. Attempts have been made to stabilize calcium chloride by impregnation in expanded natural graphite and vermiculite, and by microencapsulation with ethyl cellulose. The effect of these stabilization methods on the performance of the material, such as kinetics and energy density, has investigated. Characterization of the materials is carried out with combined Thermo-Gravitational Analysis (TGA) and Differential Scanning Calorimetry (DSC) methods and microscopic observation, in order to evaluate the improvements on the basis of three subjects: reaction kinetics, heat storage density and stability

Calcium chloride is found to be one of the promising salt hydrates for thermochemical heat storage for common building applications. A reversible chemical gas-solid reaction can be employed that involves CaCl2, according to the de/re-hydration reaction of

The interest for calcium chloride has been triggered by: easy availability and subsequently low price, high capacity for water uptake and energy storage density, relatively better chemical stability than other salt hydrates, low corrosiveness and non toxicity. Furthermore, the material dehydrates at low temperature (below 100 °C), which makes it suitable for the applications.

The energy storage density is studied for the four calcium chloride based materials. The energy release for each sample during hydration from anhydrous to hexahydrous state was studied. The simultaneous thermal analysis method allows the estimation of the energy per mole of calcium chloride and per mole of absorbed water. Microencapsulated calcium chloride showed high multicyclic stability, compared with pure and impregnated materials, that liquefy upon hydration under the given conditions. Microencapsulated material remains stable over multiple cycles and shows the fastest kinetics. The only disadvantage of the encapsulation methodology used in paper is the resulting low energy storage density.

**Ard-Jan de Jong (2016)** observed that long-term and compact storage of solar energy is crucial for the eventual transition to a 100% renewable energy economy. For that, thermochemical materials provided a promising solution. The compactness of a long-term storage system was determined by the thermochemical reaction, operating conditions, and system implementation with the necessary additional system components. Within the prototype project a thermochemical storage system is being demonstrated using evacuated, closed thermochemical storage modules containing Na2S as active material.

A significant part of energy to be stored is for space heating and domestic hot water for buildings. Daily storage can be arranged by mature boiler technology, but seasonal storage for at least half a year will require considerably lower heat losses. Besides, seasonal heat storage will usually imply storing very large amounts of heat, so that heat storage should be compact, with high storage density. Energy storage by using solar heat (e.g. at 60-1400C) to reverse chemical reactions is an attractive solution, as the reaction products can be stored virtually loss-free.

Thermochemical storage offers the potential of loss-free storage with a heat storage density higher than water. The first lab results of the prototype used in this project showed that a storage density of 0.14GJ/m3 was achieved and they observed that it can expect to reach 0.18GJ/m3 for coming field tests. In this paper identified and apourn several possible improvements and show that by mere optimization of the prototype fixed-bed reactor concept using Na2S, a heat storage density of approximately 1GJ/m3 can already be achieved.

**Michael Graham(2016)** studied that thermal energy storage has many important applications, and is most efficiently achieved by latent heat storage using phase change materials (PCMs). Salt hydrates have advantages such as high energy storage density, high latent heat and apourngbility. However, they suffer from drawbacks such as incongruent melting and corrosion of metallic container materials. By encapsulating them in a polymer shell, problems can be eliminated. Here we demonstrate a simple method to nanoencapsulate magnesium nitrate hexhydrate, employing an in situ mini emulsion polymerisation with ethyl-2- cyanoacrylate as monomer. Using sonication to prepare mini emulsions improved the synthesis by reducing the amount of surfactant required as stabiliser. Thermal properties were analysed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Fourier transform infrared spectroscopy (FTIR) was employed to prove the presence of salt hydrate within the nanocapsules. Results showed the capsules are 100-200nm in size, have salt hydrate located in the core and are stable over at least 100 thermal cycles with only a 3% reduction in latent heat. Supercooling is also drastically reduced

DSC results demonstrated for the first time high thermal stability of the nanoencapsulated salt hydrates, which remained unchanged after 100 thermal cycles with a latent heat of 83.2Jg-1. Chemical and macroscale stability of the nanoencapsulated salt hydrates were also proven by FTIR and visual observations after heating/cooling cycles. The thermal properties of the nanocapsules are a great improvement over the bulk Mg(NO3)2⋅6H2O, which loses its structural integrity and chemical composition after only 5 cycles.

Salt hydrate PCMs with long lifetimes are important for future energy storage applications, due to their high heat capacity and cost effectiveness compared to commonly used paraffin wax PCMs. Efficient energy storage has the potential to greatly reduce global energy demand, providing a sustainable future

**Lin Liang (2017)** studied that a new cold storage phase change material eutectic hydrate salt (K2HPO4·3H2O–NaH2PO4·2H2O–Na2S2O3·5H2O) was prepared, modified, and tested. The modification was performed by adding a nucleating agent and thickener. The physical properties such as viscosity, surface tension, cold storage characteristics, supercooling, and the stability during freeze-thaw cycles were studied. Results showed that the use of nucleating agents, such as sodium tetraborate, sodium fluoride, and nanoparticles, are effective. The solidification temperature and latent heat of these materials which was added with 0, 3, and 5 wt% thickeners were −11.9, −10.6, and −14.8° C and 127.2, 118.6, 82.56 J/g, respectively. Adding a nucleating agent can effectively improve the nucleation rate and nucleation stability. Furthermore, increasing viscosity has a positive impact on the solidification rate, supercooling, and the stability during freeze-thaw cycles.

**Luca Scapino (2017)** studied thatsorption heat storage has the potential to store large amounts of thermal energy from renewables and other distributed energy sources. This article provides an overview on the recent advancements on long-term sorption heat storage at material- and prototype- scales. The focus is on applications requiring heat within a temperature range of 30–1500C such as space heating, domestic hot water production, and some industrial processes.

Thermal energy storage is an attractive storage category because in principle it can be more economical than other technologies, it has a wide range of storage possibilities with storage periods ranging from minutes to months, and finally because thermal energy dominates the final energy use in sectors such as industry or household .Thermal energy storage can be divided into three main categories according to how energy is stored: sensible heat (e.g. water tanks, underground storage) latent heat (e.g. ice, phase change materials) , and sorption heat storage

Currently, composite materials are investigated because they have the potential to overcome the disadvantages of pure salt hydrates by increasing their hydrothermal stability. This is done by mixing or impregnating salt hydrates with highly porous host matrices or powders. However, problems in heat and mass transport still can arise due to the reduction of empty pores, possible deliquescence and leakage of the salt from the composite, and degradation. To this regard, further research is needed to overcome these problems and to understand extensively the kinetics of a composite material, which does not follow a typical apourng of a salt hydrate nor of an adsorbent. Various prototype reactors and systems were developed by the scientific community to study the performances of sorption materials at macro-scale. Open and closed solid sorption systems have been apourn and compared. Among the reviewed prototypes, mostly systems based on zeolites were able to achieve temperatures suitable for space heating or DHW production. For these systems, relatively high desorption temperatures were required, unachievable, for example, by conventional solar thermal collectors.

**Dongdong Li (2018)** studied on the development of a multi-temperature thermodynamically consistent model for salt lake brine systems. Under the comprehensive thermodynamic framework proposed in his previous work, the thermodynamic and phase equilibria properties of the apourn binary systems (i.e., Li2SO4 + H2O, Na2SO4 + H2O, K2SO4 + H2O, MgSO4 + H2O and CaSO4 + H2O) were simulated using the Pitzer-Simonson Clegg (PSC) model. Various type of thermodynamic properties (i.e., water activity, osmotic coefficient, mean ionic activity coefficient, enthalpy of dilution and solution, relative apparent molar enthalpy, heat capacity of aqueous phase and solid phases) were collected and fitted to the model equations. The thermodynamic properties of these systems can be well reproduced or predicted using the obtained model parameters.

**Farzad Deyhimi (2009)** studied the use of Pitzer, PSC as well as an extended PSC ion-interaction approaches for modelling the non-ideal apourng of the ternary HCl + water + 1- propanol systems. These modelling purposes were achieved based on the experimental potentiometric data of a galvanic cell containing a Ph glass membrane and Ag/AgCl electrodes. The measurements were performed over the HCl electrolyte molality ranging from 0.01 up to 4.5 mol kg−1 system with different alcohol percent mass fractions (x% = 10, 20, 30, 40 and 50%), at 298.15 ± 0.05 K

Pitzer semi-empirical virial coefficient approach has been remarkably successful in apourng the thermodynamic properties of aqueous electrolyte solutions. Although this approach proved to be also a valuable method for correlation and prediction of thermodynamic properties of electrolytes in mixed solvent media, there is still only a limited number of reported studies concerning its application for apourng such systems. Pitzer and Simonson (PS) developed a newer model as well that is applicable over the entire concentration range for the investigation of mixtures containing ions of symmetrical charge type.

Both experimental potentiometric data along with the related model parameters associated with Pitzer, PSC, and an extended PSC approaches concerning the investigation of the ternary HCl + 1- PrOH + water electrolyte system, are for the first time reported in his work.

**Edilson C. Tavares (1999)** studied the solid-liquid equilibrium in aqueous multi-electrolyte systems using the quasiisothermic thermometric technique (QTT). The principle of the QTT is based on thermal effects associated with the phase transformations that occur in the system. In order to test the apparatus, salt solubility data at 298.15 K for the aqueous systems H2O+NaCl+KCl, H2O+NaCl+Na2SO4, H2O+NiCl2+NiSO4 are presented. The data obtained for the three systems are in good agreement with the literature, including solid phase boundaries due to hydration. This agreement indicates the accuracy of the proposed method.

The QTT has been properly tested for the measurement of salt solubilities and solid phase transitions. The apparatus is simple construction and can be operated with the aid of the computer interface, giving accurate data. The burette should be monitored via interface and computer. The QTT has been applied for the measurement of new salt solubility and solid phase transition data for the system NiCl2+NiSO4+H2O at 298.15 K.

**Huinan Wang (2020)** Vapor–liquid equilibrium (VLE) data and apourng for LiBr + H2O and LiBr + CaCl2 + H2O are reported in this paper. This work focuses on the experimental determination of the boiling point of LiBr + H2O and LiBr + CaCl2 + H2O solutions with apour pressures between 6 and 101.3 kPa and the total molality of salt ranging from 0 to 21.05 molkg−1 . The procedures were carried out in a computer-controlled glass apparatus. The relationship between the boiling point and saturated apour pressure is obtained, and Xu’s model is used to correlate and predict the VLE. By correlation of the data (literature and experimental) for LiBr + H2O and LiBr + CaCl2 + H2O, the parameters are obtained. E compared the results with the ElecNRTL model and Pitzer model. The parameters for the LiBr + H2O, CaCl2 + H2O, and LiBr + CaCl2 + H2O systems can be successfully used to calculate and predict the VLE data

**Christoph Rathgeber (2019)** In this work, the modified BET equations are extended in order to calculate solubility phase diagrams of concentrated salt solutions with relatively high water activities within the range of undersaturation. Predicting solubility phase diagrams of mixtures of salts and water is of interest in various application fields, e.g. in the process of extracting salts or salt hydrates from natural salt brines to develop working fluids in absorption refrigeration systems, or to develop phase change materials for thermal energy storage . As an example, BET parameters of NaCl are determined and applied to calculate solubility phase diagrams of NaCl + H2O, NaCl + LiCl + H2O, and NaCl + CaCl2 + H2O within the temperature range of around 250–500 K. In the ternary systems, the best agreement with solubility data from literature is obtained using constant BET parameters of NaCl and an additional temperature-dependent regular solution parameter to account for salt-salt interaction.

**RESEARCH GAP:**

There is wide research gap in the Salt hydrates such as

1. Lack of experimental data at high temperature and pressure and validation,

2.Model accounting for salt hydrates at elevated temperature, pressure, and concentration

3. Accounting of unstable chemical reactions

4. Accounting of complex phase equilibria (vapor: liquid: solid).

**OBJECTIVES OF STUDY :**

The main objectives include:

1. Study of Charging and Discharging cycles
2. Study of Capacity of batteries
3. Study of thermal management in batteries

# METHODOLOGY

## Model 1

In this work, Gibbs free energy term is given by long range (Lr) electrostatic contributions b/w ions and short range (Sr) interaction b/w all species.

Using Pitzer`s form of the Debye- Huckle (PDH) function as the electrostatic contribution to the free energy. So

Where nw, ns = no. of moles of water, salt respectively

vs, vw = partial molar volume (m3/mole) of salt, solvent respectively

b = the closest approach parameter

Total no. of ions per salt

Debye Huckel type constant

Where Mw = molecular weight of solvent i.e., water in gram/mol,

NA = Avogadro number,

K = Boltzmann constant, ε = permittivity of vacuum, e = electronic charge,

DS = dielectric constant of water, VS = the molar volume of water

I = the ionic strength or

The expression for the short-range interaction contribution of aqueous salt solution is obtained from Flory- Huggins theory as given below,

Where χsw = salt-water interaction parameter, which dependent on the salt concentration and temperature

where and represent the moles of salt hydrate and water in salt hydrate solution, respectively. is the number of Kuhn segments in Salt hydrate chain.

The term is the generalized Flory-Huggins parameter and considered as the function of the volume fraction of the salt hydrate, , and temperature, .

is temperature dependent coefficient and as expressed as:

and are constants.

is temperature dependent coefficient are calculated using non linear regression method

Derivative of Equation (1) w.r.t. moles of water and salt gives us chemical potential of water and salt hydrate respectively.

The condition for the phase equilibrium between two separate phases (Phase-1 and Phase-2) are given by

And

By solving equation simultaneously, phase diagram can be obtained.

The critical point is given by the following conditions:

## Model 2

We assume that the molar gibbs energy of mixing contains an electrostatic contribution given by a Deybe Huckel-type function and a contribution from extended Flory-Huggins theory, as follows:

Where superscripts DH and FH denote Deybe Huckel and Flory Huggins Contribution, respectively.

Pizer’s form of the Deybe-Huckel type function as the electrostatic contribution to the molar Gibbs energy of mixing is given by

Where

The electrostatic contribution does not contain adjustable parameters.

The Flory-Huggins contribution to the molar Gibbs energy of mixing is given by the following

Where the first two terms and the last term on the right hand side of equation represent, respectively, the configurational entropy of mixing and the residual free-energy, mostly enthalpic, interaction between water and salt ion.

refers the interaction between water and ion. It is interaction parameter.

For a binary saltwater system Deybe Huckel and Flory Huggins contribution are combined to give the molar Gibbs energy of mixing given by

The condition for the phase equilibrium between two separate phases (Phase-1 and Phase-2) are given by

And By solving equation and simultaneously, phase diagram can be obtained.

Phase Diagram equations

Critical Point equations