

Paper 1:

Currently society is moving from carbon-based to more renewable energy sources to become less dependent on fossil fuels. A dominant part of the energy consumption of European residential sector (around 70% of the total consumption [1]) is related to domestic space heating and hot tap water generation. A cleaner sourcing of this part of the energy sector will have a large impact on the carbon production. For generation of carbon-free heat, new energy production techniques must be implemented, the majority of which are based on capturing solar radiation. However, solar radiation fluctuates on different time scales, i.e., hourly, daily and seasonally. The power generated fluctuates, resulting in a variable and unpredictable supply of heat. For matching heat demand and supply, heat storage systems that account for the timescale of radiation fluctuations are required. In this article, the focus is on seasonal storage in the built environment in the future, requiring a storage capacity of about 7–12 GJ in a typical West European dwelling based on the passive house standard (<http://www.passivehouse.com/>). This storage capacity is based on an average dwelling in the Netherlands with a floor area of 120 m², with the passive house standard of 15 kWh/m² for newly built houses and 28 kWh/m² in renovated houses [2,3]. A promising heat storage concept is based on a thermochemical reaction, which was suggested by Goldstein [4] in the sixties and gained interest in the last decade [5–7]. The solid materials involved in these reactions are called thermochemical materials (TCMs). Key advantages with respect to techniques like sensible heat storage and phase change materials (PCM) include nearly loss-free storage period and high energy density. In the current literature reactive gas L is considered to be H₂O, NH₃ or CH₃OH. As the targeted heat storage system should be used in residential areas, NH₃ and CH₃OH are not considered because of currently strict Dutch safety regulation [8]. As a result, H₂O is considered a reactive gas in this article. The amount of reactive gas L inside salt complex MX is called the loading of the salt. This happens during summer heat storage periods. The equilibrium reaction in Eq. (1) implies that the maximum loading of a salt MX at a temperature T is determined by the vapor pressure of L(g).

1.2. Aim During the past decade, many researchers have investigated TCM's as heat storage materials. The first generation of salt hydrates based on TCMs have already been developed, varying from lab scale [9–11] to field demonstrations [12–14]. A complete overview of the systems constructed in the last decade is given by Scapino et al. [6]. A great body of research is also available on high potential salts for temperature storage below 100 C, such as MgSO₄ [15–19], MgCl₂ [19–22], SrBr₂ [7,23], Na₂S [12,24] and CaCl₂ [22,25,26] which have been studied in detail. Storage of heat for temperature applications between 100 and 300 C already shows some promising results with salts based on CaO/Ca(OH)₂ [27] and CaC₂O₄/CaC₂O₄H₂O [28]. Furthermore, some reviews have been published on TCM's [5,29–34], that use the energy density as selection criterion, with one exception focusing on applied working conditions [5] during hydration/dehydration. In the latter study three salts were selected: MgSO₄, LaCl₃ and SrBr₂ based on dehydration below 105 C and rehydration at 20 mbar vapor pressure at 25 C, which corresponds to the saturated vapor pressure in equilibrium with a water reservoir at 17 C. However, the missing parameter for selection in this review is the generated temperature T_h during the hydration reaction, since this temperature is the highest output temperature the heat battery can deliver. For introduction of TCMs on the market, it is important that TCMs are able to match the demands of the customers. As a first indication it is therefore necessary to determine if TCMs can theoretically match such demands. In the present work, we attempted to analyze and extend the search for pressure-temperature (pT) data on the basis of demanded working conditions of a TCM reactor in the built environment, i.e. a system that can store 10 GJ, deliver hot tap water at 65 C and can be charged in summer with the help of solar panels. The goal is to select TCM's which fulfil the temperature demand and energy density of the consumer, with the help of available pT data, and analyse the plausibility of using these TCM's.

Firstly, the process of data collection will be summarized, secondly the selection criteria are explained. Based on these criteria a short list of the most promising salts will be generated and discussed in view of the target application.

Paper 2:

The yearly energy needs of the Netherlands could be satisfied by solar energy, as can be verified from the yearly average solar intensity of 110W/m² for the Netherlands (cf. [1]), and typical efficiencies of 10-15% for PV panels and about 30% for solar collectors. For instance, the yearly heat demand of 20GJ for a typical, well-insulated dwelling can be delivered by about 20m² of solar collectors. This is illustrated by Figure 1, showing the balance of heat demand and collector supply. As these do not overlap in time due to daily and seasonal fluctuations of solar irradiation, heat must be stored. Daily fluctuations during the warm season could be countered by a relatively modest hot water storage, e.g. at 90 C. But for seasonal fluctuations where about 10GJ must be stored, hot water storage would require a tank of at least 50m³, which is large compared to a typical dwelling. Besides, storage of 90 C water for the whole cold season would require exceptional insulation. An attractive alternative solution for seasonal heat storage is thermochemical heat storage (TCS), which is based on thermally reversible reactions such as: $\text{Na}_2\text{S} \cdot \frac{1}{2}\text{H}_2\text{O} + 4\frac{1}{2}\text{H}_2\text{O} \rightarrow \text{Na}_2\text{S} \cdot 5\text{H}_2\text{O} + \text{heat}$. This sorption or hydration reaction is an attractive example as it comes with a high energy density of about 2.7GJ per m³ of Na₂S · 5H₂O [2], because it can be reversed by typical temperatures of solar collectors in summer and because it can produce heat at temperature levels of space heating (SH) and domestic hot water (DHW), as we will discuss later. Compared to hot water storage, TCS not only has the advantages of a higher heat storage density by about a factor 10-15, but also does not require thermal insulation. One only needs to keep chemical components separate, in the above case dried sodium sulfide and water, which is ideal for seasonal storage. For this paper, seasonal storage of 10GJ for a typical dwelling serves as a business case and we discuss challenges for designing a TCS system which can operate for 20-30 years with minimum maintenance. Chapter 2 is on system operation and required system components, Chapter 3 is on components and Chapter 4 on material challenges. Our observations are summarized in Chapter 5. Throughout this paper, we refer to our activities in the EU FP7-projects E-hub and Einstein, where we work on reactor modeling and development, and realized an operational TCS system with a storage capacity of about 1kWh and up to 12kW of output power using 40kg of zeolite 5A as thermochemical material (TCM) [3]. In the EU FP7-project MERITS, we focus on a reactor with higher storage density TCM. Our work is also supported by internally funded research on composite TCM for improving physical and chemical stability [4]. With this paper, we hope to provide directions for designing and modeling future TCS systems.

Paper 3:

The awareness of humankind's role into climate change [1] and the increasing energy intensity in developing and underdeveloped countries [2] are among the main drivers for a more sustainable production and use of energy. The energy grid consists of a system in which multiple carriers are produced, transported, consumed, and stored. The level of complexity of this system is constantly increasing due to technological advancements such as energy production systems with new requirements, transportation and storage methods that are more efficient, new policies, and new types of consumers and other stakeholders. The advance of renewable energy sources, cogeneration,

and intermittent power sources in general, is drastically changing the requirements on the energy grid. Some of the new energy production units are characterized by relatively low and decentralized installed capacities, intermittent and often unpredictable production patterns frequently driven by the owner's needs or by the source availability, and production of multiple energy carriers. Therefore, the energy network is constantly evolving [3,4] to cope with new types of stakeholders and an increasing penetration of intermittent distributed production sources. Storage of multiple energy carriers, demand side management, exchange and relocation through conversion of energy carriers are among the main practices that the future system will have to incorporate to gain the needed flexibility [5]. Energy storage is useful to handle fluctuations in energy demand to spread the production of energy needed during demand peaks over a different time period and to make efficient use of fluctuating production sources such as renewables, increase energy grid safety, and improve the overall system efficiency [6]. In Table 1-1, an overview of the main storage technologies, their costs, efficiencies, and typical response times is displayed. 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 (Fig. 1-1 left). Thermal energy storage can be divided into three main categories according to how energy is stored: sensible heat (e.g. water tanks, underground storage) [11–13], latent heat (e.g. ice, phase change materials) [14–16], and sorption heat storage. 1.1. Sorption heat storage Sorption heat storage implies the use of physical or chemical bonds to store energy. The principle of sorption occurs during a reaction, and in order to take place, at least two components are needed: a sorbent, which is typically a liquid or solid, and a sorbate, which is typically a vapor. During the charging process (Fig. 1-1 right), an endothermic reaction occurs, and the sorbent and sorbate are separated. The two components can then be stored separately, ideally without energy losses. During the discharging process, sorbent and sorbate react producing an exothermic reaction that releases heat. The main advantages of sorption heat storage are higher energy density and negligible heat losses compared to a conventional thermal storage based on sensible heat. A conventional water storage needs to be approximately five to ten times larger than a sorption heat storage system for storing the same energy. Since many years, the use of sorption heat storage systems for long-term storage applications is being investigated [18–22]. Previous review works on the topic are from N'Tsoukpoe et al. [23], who reviewed long-term sorption energy storage technologies; Yu et al. [18], who reviewed solid and liquid sorption materials and reactors; Solé et al. [24], who focused in particular on reactors and systems for building applications; and Xu et al. [19], who reviewed sensible, latent and chemical heat storage systems for seasonal storage applications. The aim of this work is to provide an overview on the last advancements on sorption heat storage technologies for long-term low-temperature applications based on solid/gas reactions with water as sorbate. The focus of this article is on the state of the research at material- and prototype-scale. The current work is divided into two main sections. In Section 2, the focus is on sorption materials and current advancements on their research. In Section 3, a review on the state-of-the-art research on solid sorption storage systems is carried out, and their performances are discussed and compared.

Paper 4:

Salt lake brine and coexisting salt deposits are important inorganic mineral resources, from which a huge amount of valuable salts, i.e., potash fertilizer and lithium compounds, can be produced. Many salt lakes exist on Earth, and over thousands of them are located in China. Salt lake brines are complex multi-component electrolyte aqueous systems, which consist of many inorganic ions, e.g.,

Li⁺, Na⁺, K⁺, Rb⁺, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻, CO₃²⁻, HCO₃⁻, NO₃⁻, and borate. From these brines, dozens of solid salts can be crystallized under certain natural or artificial conditions. Depending on the chemical components of the brine, the salt lakes can be classified into chloride, chloride–sulfate, carbonate, and nitrate types. Because the brine compositions vary with regional characteristics, seasons, and solar evaporation stages, brine crystallization behaviors are very complex and differ from each other. Usually, the humidity is very low in the regions where a salt lake is located. Salt evaporation pond process is one of the most economical tools to separate the salts from the brine. By adjusting the brine compositions in fractional crystallization processes, effective separation can be achieved. To obtain the desired salts, it is essential to know when and under what conditions (compositions and temperature) a specific type of salt will crystallize. Phase diagrams of the water–salt systems, if we have, can answer these questions. For decades, many authors have studied solid–liquid equilibria of simple binary, ternary and quaternary systems of salt lake brines at a scattered variety of temperatures. However, the exact crystallization sequence of salts and the appearance nodes of the salts cannot be determined from these scattered and limited experimental data alone. For a multi-component brine system, experimental determination of the phase diagram at a certain temperature is strenuous and time consuming work. Therefore, only the phase boundary, rather than a full characterization of the solid–liquid equilibria, is known for a given brine composition. Fortunately, phase diagram calculation approaches make it possible to reveal the phase equilibria behavior of a complex multi component system over the entire composition field using computer assisted simulation. Song and Yao [1] have extended the Pitzer's ion interaction model [2] to describe the excess thermodynamic properties of the simplified salt lake brine system of Li⁺, Na⁺, K⁺, Mg²⁺, Cl⁻, SO₄²⁻–H₂O at 25 °C. Applying the model with new model parameters, they have not only simulated the phase diagrams of this complicated system and its lower-order systems, but they have also predicted the salts crystallization sequence of any brine with a specific composition under isothermal evaporation conditions at 25 °C [3–5]. Kwok et al. [6] have also described the thermodynamic and phase equilibrium properties of the simplified salt lake brine system of Li⁺, Na⁺, K⁺, Mg²⁺, Cl⁻, SO₄²⁻–H₂O at 25 °C with an extended UNIQUAC equations [7]. Unfortunately, the validity of these models are limited to 25 °C, and cannot be used to predict the phase equilibria of this brine system at temperatures far away from 25 °C. Most salt evaporation ponds are constructed near salt lakes, and the pond temperatures change with the local environment and seasons. The crystallization route of any brine with a specific composition can change with temperature. For example, halite usually precipitates from a chloride–sulfate type brine during evaporation processes in the summer, while mirabilite precipitates in the winter. Based on the fact that Li₂CO₃ solubility decreases with increasing temperature, a novel Li-extraction approach has been proposed to precipitate Li₂CO₃ from a carbonate-type brine at high temperatures [8]. In these cases, the influence of temperature on the crystallization route of brine can be significant. To understand the crystallization route of a brine at various temperatures, its solid–liquid phase diagram at various temperatures must be known. However, known thermodynamic models cannot represent the phase equilibria behavior of brine at various temperatures, especially for systems containing Li-salts. Some research groups [9–14] have extended the primitive Pitzer model to represent the solid–liquid phase diagram of oceanic salt systems, where Li-salts are absent, at multiple temperatures. For salt lake brine systems where Li-salts are present, the phase diagram simulation becomes challenging. Because Li-salts, such as LiCl, are very soluble, e.g., nearly 20 mol kg⁻¹ at 25 °C and more than 30 mol kg⁻¹ at 100 °C for LiCl, the primitive Pitzer model cannot successfully simulate the thermodynamic properties of the system [15]. A proper thermodynamic model should be chosen to simulate the salt lake brine containing Li-salts. Based on the above considerations, we intend to develop a thermodynamically consistent model for the simulation of salt lake brine systems. This simulation will aid in the design of evaporation crystallization processes and optimization of salt lake brine. This

series of work will begin with the simulation of simple binary and ternary systems at multiple temperatures, and it will gradually extend to more complex multi-component systems. In the first part of the series papers, the LiCl/H₂O system will be simulated, and the model selection and parameter determination methodology will be established

Paper 5:

Although the semi-empirical virial coefficient approach of Pitzer [1–4] has been considered as a very successful approach for describing the thermodynamic properties of aqueous electrolyte systems up to ionic strength values of about 6 mol·kg⁻¹ [5–9], its application to investigate electrolytes in nonaqueous or in mixed solvent media are still very scarce [10, and references cited therein]. On the other hand, Pitzer and Simonson (PS) presented a more elaborated model for the investigation of mixtures containing ions of symmetrical charge type that is applicable over the entire concentration range [11, 12]. Later, Clegg, Pitzer and Brimblecombe further extended this model in order to take into account the presence of arbitrary charge type electrolytes and an indefinite number of ionic and neutral species [13]. This model uses an extended Debye–Hückel (DH) expression for long-range forces (including composition-dependent terms), a four-suffix Margules expansion for representing short-range forces, along with additional parameters which take into consideration the interaction between solvent molecules and involved ions in concentrated solutions. Nevertheless, a review of the literature shows that only two research groups [15–17] have used a complete form of the PSC equations for the investigation of electrolytes in mixed solvent systems. Probably, the apparent complexity and the number of involved ion-interaction parameters in the PSC model would explain both its limited applications and the reason why simplified versions of this model were more frequently used [18–24]. The present work reports the investigation of the ternary HCl + 2-propanol + water electrolyte system by the Pitzer, PSC and an extended form of the PSC ion-interaction approaches, using the experimental potentiometric data of a cell containing pH glass membrane and Ag/AgCl electrodes. The concentration of HCl was varied from 0.01 to about 4.5 mol·kg⁻¹ in mixed 2-propanol (x%) + water (100 – x%) solvent systems, with different solvent mass fractions (x = 10, 20, 30, 40 and 50%), at 298.15 ± 0.05 K. Previously, Harned and Calmon [25] reported potentiometric data for HCl in a mixed 2-propanol + water solvent, but only for x = 10%, with a range of hydrochloric acid molalities from 0.001 to 0.1 mol·kg⁻¹, at 298 K. In addition, these authors did not report the HCl activity coefficient values but only a formula to calculate them in the range studied. Roy et al. [26] also reported the results of emf measurements on HCl in water + 2-propanol with alcohol mass fractions x = 8.03, 20.76, 44.04, 70.28, and 87.71%, at different temperatures. The HCl molality used by these authors was in the range 0.001 to < 0.125 mol·kg⁻¹. Therefore, the reported Roy et al. [26] data correspond to low concentrations, and the mass fraction percents of 2-propanol do not correspond to those used in this work. However, there is no previous investigation of HCl in 2-propanol + H₂O mixed solvents using the Pitzer or PSC approaches.

Paper 6:

Accurate knowledge of the deliquescence behavior of multicomponent brines is expected to enhance the understanding of the evolution of the chemical environment in contact with metal surfaces at the proposed radioactive waste repository at Yucca Mountain, Nevada, USA. It is anticipated that a layer of dust containing volcanic tuff and a mixture of salts originating from evaporation of seepage waters will tend to accumulate over time on all surfaces. The air inside the

placement drifts will be relatively dry after final closure due to the temperature remaining well above the boiling point of water. As the temperature slowly decreases for several centuries due to radioactive decay, the relative humidity may reach sufficiently high levels for the mixture of initially dry salts to form concentrated brines through deliquescence. The concentrations of ions present in solutions contacting metal surfaces affect corrosion processes as, for example, the $\text{Cl}^-/\text{NO}_3^-$ ratio is an important consideration in corrosion calculations. Hence, thermodynamic properties of mixed aqueous solutions are needed for reliable predictions of the composition of the brines formed under the expected scenarios of in-drift temperature and humidity evolution. Complete phase diagrams, showing relative humidity (or water activity) as a function of composition, are scarce even for solutions containing two salts. There are very few accurate experimental data sets available on deliquescence behavior of multicomponent aqueous salt solutions at elevated temperatures. This underscores the importance of having an accurate thermodynamic model that would be capable of predicting the behavior of multicomponent systems in a wide temperature range using parameters determined from limited experimental data. While the well-known Pitzer ion-interaction model provides a useful framework for the prediction of solubilities in multicomponent solutions using activity data on binary systems with a common ion, the temperature dependence of solute-specific parameters is often not available with sufficient accuracy. Also, the molality-based Pitzer model is applicable for concentrations typically up to ca. $6 \text{ mol}\cdot\text{kg}^{-1}$, which is often insufficient for highly concentrated systems that contain nitrates. Thus, it is necessary to develop a model that would be applicable to multicomponent, concentrated solutions up to solid saturation or, under some conditions, even the fused salt limit. Further, it is desirable to verify model results against measurements made in the temperature range that is of direct interest for studying deliquescence phenomena. The main purpose of the measurements described here is to demonstrate that the unique ORNL high-temperature isopiestic apparatus can be used to investigate the relationship between deliquescence, relative humidity (RH) and temperature for multicomponent aqueous solutions. The points where a new phase appears or disappears can be detected when a series of measurements of solvent mass and the corresponding vapor pressure are made as water is added or withdrawn. When the relative humidity over a mixture of solid salts increases, the solution first appears at the eutonic point of the mixture where the solution is simultaneously saturated with respect to all components. The relative humidity at the eutonic point, the mixture deliquescence RH, is the lowest relative humidity coexisting with a liquid solution. The tendency to deliquesce (the hygroscopic character) of solutes depends mainly on their solubility, but also on the particular character of solute-solvent interactions, described also as nonideality, or vapor-pressure lowering ability. Because an addition of a new electrolyte to a saturated solution initially lowers its vapor pressure without causing precipitation, the deliquescence RH of multicomponent solutions decreases as the number of solutes increases. The second objective of this paper is to develop a comprehensive thermodynamic model for predicting the thermodynamic behavior of aqueous mixtures containing the Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- and NO_3^- ions. These are the key ionic components in natural environments that may give rise to the formation of concentrated solutions through deliquescence phenomena. Comprehensive modeling of such mixtures requires calibrating the model to match the properties of the constituent binary (i.e., salt–water), ternary (i.e., salt 1–salt 2–water) and higher-order subsystems. For all such systems, the primary requirement for the model is to reproduce the solid–liquid equilibria and vapor pressures as a function of temperature and composition. In the development of the model, both literature data and the new isopiestic measurements are used. Whereas literature data are primarily used to ensure the correct representation of the properties of simpler (i.e., binary and ternary) subsystems, the new isopiestic data are essential for verifying the performance of the model for concentrated multicomponent mixtures at high temperatures.

Paper 7:

Over many years, the use of amino acids has increased in various fields, of industry such as the chemical, pharmaceutical, food additives, acidulants, cosmetics, antibacterial agents, and biodegradable plastics [1, 2]. Besides, the accurate study of the effect of electrolytes on amino acid solutions is important because amino acids play a central role in the structure, function and conformation of proteins in aqueous solution [3]. They are regarded as model compounds for more complex molecules because their phase behaviors represent similarities with more complex molecules, such as proteins, which are closely related to the biological processes [4]. Hence, the thermodynamic properties of ternary (electrolyte+amino acid+water) systems have been correlated, measured, and calculated [5–12]. The literature data does not cover the thermodynamic properties of all ternary (electrolyte+amino acids+water) systems. Proline as a non-essential amino acid has an important role in enzymes, proteins, and peptide hormones and this molecule shows cis–trans isomerism [13, 14]. Proline has a medicinal effect on high blood pressure and it helps to release already deposited fat globules from the blood vessel wall into the bloodstream. Among the various methods for measuring the thermodynamic properties of electrolyte solutions [15–18], the potentiometric technique is one of the most common, because of benefits such as rapidity and relative simplicity compared to other techniques [19]. The most common models for determining the thermodynamic properties of electrolyte solutions are the specific ion interaction theory (SIT) [20], Pitzer ion interaction model [21], extended ion interaction Pitzer (Pitzer–Archer) model [22], Non-Random-Two-Liquid (NRTL) [23], and the Universal QUasi-Chemical (UNIQUAC) [24]. These models include a number of adjustable parameters that are obtained from fitting experimental data over composition and temperature ranges. Considering the importance of ternary (electrolyte+amino acids+water) systems, some authors have developed thermodynamic models for determining the thermodynamic properties of these systems. Two models were qualitatively developed to describe the interactions between amino acids and ions based purely on electrostatic interactions at low concentrations by Kirkwood [25, 26]. Chen et al. presented a molecular thermodynamics framework to investigate the solubility behavior of amino acids by employing their own version of the electrolyte NRTL model [27] and the chemical theory [28]. The Pitzer ion interaction model is one of the most famous and useful models to determine the thermodynamic properties of electrolyte solutions, not only because it fits data well with the use of just a few adjustable parameters but also since these parameters represent the interactions in the system [21, 29, 30]. Pitzer and Simonson [31, 32] developed a mole-fraction based model for the investigation of symmetrical electrolyte mixtures such as Na^+Cl^- , or $\text{Mg}^{2+}\text{SO}_4^{2-}$ over the entire concentration range. This model included a Debye–Hückel (DH) long-range force term and three-suffix Margules expansion for the short-range forces. Clegg et al. [33, 34] extended the Pitzer and Simonson model by introducing additional composition-dependent terms into the Debye–Hückel expression and an additional short-range parameter for the interaction between the neutral species and a single ionic species in highly concentrated solutions; this is known as the Pitzer–Simonson–Clegg (PSC) model. Thermodynamic investigation of ($\text{KCl}+\text{L-proline}+\text{water}$), ($\text{NaCl}+\text{L-serine}+\text{water}$), and ($\text{CaCl}_2+\text{L-alanine}+\text{water}$) systems was carried out based on the Pitzer and PSC models by our research group [6, 7, 9]. Despite the advantages of the Pitzer model, it does not provide explicit analysis when the non-electrolyte solute has a dipolar structure (zwitterion). Therefore, Estes et al. presented modified Pitzer equations including the dependence of the binary interaction parameters (containing the nonelectrolyte) on the concentration of both the electrolyte and the non-electrolyte [35] and used their own modified Pitzer equations to fit the activity coefficients in ternary (electrolyte+amino acid+water) systems at 298.15 K [12, 36, 37]. Khoshkbarchi and Vera developed a perturbation theory thermodynamics model for ternary (electrolyte+amino acid+water) systems. Their model correlates the experimental

activity coefficients of amino acids in aqueous solutions with acceptable deviations. However, it needs the experimental data to calculate the binary and ternary interaction parameters [38]. Khoshkbarchi's group [11, 39–43] measured activity coefficients for different ternary (electrolyte+amino acid+water) systems and fitted them to a virial expansion series similar to that suggested by Scatchard and Prentiss [44]. Pazuki et al. [45] proposed a model containing long-range interaction and short-range interaction terms. They used the Khoshkbarchi–Vera model [38] for long-range interactions and one of the models: Wilson [46], NRTL [23] or the non-random two liquid non-random factor (NRTL–NRF) [47, 48] for short-range interactions. Sadowski et al. measured and modeled aqueous electrolyte and amino acid (glycine, L-/D-alanine, L-/D-valine, and L-proline) solutions using the electrolyte perturbed-chain statistical associating fluid theory (ePCSAFT) equation [49]. The only available experimental potentiometric data for ternary (NaCl+L-proline+water) system are those reported by Kim et al. [50] up to 1.0 mol·kg⁻¹ NaCl at 298.2 K. In this work, we report thermodynamic properties of the ternary (NaCl+L-proline+water) system over a wide range of concentrations and temperatures. To this aim, we measured the activity coefficient of NaCl, based on potentiometric measurements, and then utilized the thermodynamic models to obtain the L-proline activity coefficient and NaCl effect on the thermodynamic behavior. The potentiometric measurements were carried out on galvanic cells containing ion selective electrodes (Na-ISE) and Ag/AgCl electrodes in various aqueous solutions (0.0000, 0.2227, 0.4571, 0.7043 and 0.9651) mol·kg⁻¹ of L-proline, over ionic strength ranging from (0.0100 to 4.0000) mol·kg⁻¹ at T=(293.2, 303.2 and 313.2) K and p=101.3 kPa. These experimental results were interpreted based on the MP model. The adjustable parameters were determined from experimental data correlation. Then, the resulting values of the natural logarithm of ratio of the L-proline activity coefficients in NaCl and water mixture to L-proline activity coefficients in water ($\ln(\frac{\gamma_A}{\gamma_0 A})$), osmotic coefficients (ϕ), excess Gibbs energy (GE/RT) and water activity (a_w) were obtained with MP model. Finally, the NaCl transfer Gibbs energy was calculated.

Paper 8:

In the thermodynamic equilibria of polyphase systems, the appearance and disappearance of the phases are related with the change of the mixture composition. These phenomena have been previously used [1± 3] to determine solid-liquid diagrams. Among the physical properties, density and conductivity have usually been exploited. In the present work, an automatic device to study the solid-liquid equilibrium of aqueous multi-electrolyte systems was developed. The technique, known as quasiisothermic thermometric technique (QTT), is based on the thermal effects associated with the phase transformations that occur in the mixture. The QTT is classified as a synthetic method, in which the composition of the system is known during the experiment and temperature is utilized to detect phase equilibrium data. In order to test this technique, salt solubility curves at 298.15 K for the systems H₂O+NaCl+KCl, H₂O+NaCl+Na₂SO₄ and H₂O+NiCl₂+NiSO₄ were determined and compared with the available literature data.

Paper 11:

Salt lake brine and coexisting salt deposits are important inorganic mineral resources, from which a huge amount of valuable salts, i.e., potash fertilizer and lithium compounds, can be produced. Many salt lakes exist on Earth, and over thousands of them are located in China. Salt lake brines are complex multi-component electrolyte aqueous systems, which consist of many inorganic ions, e.g.,

Li^+ , Na^+ , K^+ , Rb^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , CO_3^{2-} , HCO_3^- , NO_3^- , and borate. From these brines, dozens of solid salts can be crystallized under certain natural or artificial conditions. Depending on the chemical components of the brine, the salt lakes can be classified into chloride, chloride–sulfate, carbonate, and nitrate types. Because the brine compositions vary with regional characteristics, seasons, and solar evaporation stages, brine crystallization behaviors are very complex and differ from each other. Usually, the humidity is very low in the regions where a salt lake is located. Salt evaporation pond process is one of the most economical tools to separate the salts from the brine. By adjusting the brine compositions in fractional crystallization processes, effective separation can be achieved. To obtain the desired salts, it is essential to know when and under what conditions (compositions and temperature) a specific type of salt will crystallize. Phase diagrams of the water–salt systems, if we have, can answer these questions. For decades, many authors have studied solid–liquid equilibria of simple binary, ternary and quaternary systems of salt lake brines at a scattered variety of temperatures. However, the exact crystallization sequence of salts and the appearance nodes of the salts cannot be determined from these scattered and limited experimental data alone. For a multi-component brine system, experimental determination of the phase diagram at a certain temperature is strenuous and time consuming work. Therefore, only the phase boundary, rather than a full characterization of the solid–liquid equilibria, is known for a given brine composition. Fortunately, phase diagram calculation approaches make it possible to reveal the phase equilibria behavior of a complex multi-component system over the entire composition field using computer assisted simulation. Song and Yao [1] have extended the Pitzer's ion interaction model [2] to describe the excess thermodynamic properties of the simplified salt lake brine system of Li_p , Na_p , K_p , Mg_2p , Cl , SO_4^{2-} – H_2O at 25 °C. Applying the model with new model parameters, they have not only simulated the phase diagrams of this complicated system and its lower-order systems, but they have also predicted the salts crystallization sequence of any brine with a specific composition under isothermal evaporation conditions at 25 °C [3–5]. Kwok et al. [6] have also described the thermodynamic and phase equilibrium properties of the simplified salt lake brine system of Li_p , Na_p , K_p , Mg_2p , Cl , SO_4^{2-} – H_2O at 25 °C with an extended UNIQUAC equations [7]. Unfortunately, the validity of these models are limited to 25 °C, and cannot be used to predict the phase equilibria of this brine system at temperatures far away from 25 °C. Most salt evaporation ponds are constructed near salt lakes, and the pond temperatures change with the local environment and seasons. The crystallization route of any brine with a specific composition can change with temperature. For example, halite usually precipitates from a chloride–sulfate type brine during evaporation processes in the summer, while mirabilite precipitates in the winter. Based on the fact that Li_2CO_3 solubility decreases with increasing temperature, a novel Li-extraction approach has been proposed to precipitate Li_2CO_3 from a carbonate-type brine at high temperatures [8]. In these cases, the influence of temperature on the crystallization route of brine can be significant. To understand the crystallization route of a brine at various temperatures, its solid–liquid phase diagram at various temperatures must be known. However, known thermodynamic models cannot represent the phase equilibria behavior of brine at various temperatures, especially for systems containing Li-salts. Some research groups [9–14] have extended the primitive Pitzer model to represent the solid–liquid phase diagram of oceanic salt systems, where Li-salts are absent, at multiple temperatures. For salt lake brine systems where Li-salts are present, the phase diagram simulation becomes challenging. Because Li-salts, such as LiCl , are very soluble, e.g., nearly 20 mol kg⁻¹ at 25 °C and more than 30 mol kg⁻¹ at 100 °C for LiCl , the primitive Pitzer model cannot successfully simulate the thermodynamic properties of the system [15]. A proper thermodynamic model should be chosen to simulate the salt lake brine containing Li-salts. Based on the above considerations, we intend to develop a thermodynamically consistent model for the simulation of salt lake brine systems. This simulation will aid in the design of evaporation crystallization processes and optimization of salt lake brine. This

series of work will begin with the simulation of simple binary and ternary systems at multiple temperatures, and it will gradually extend to more complex multi-component systems. In the first part of the series papers, the LiClpH₂O system will be simulated, and the model selection and parameter determination methodology will be established

Paper 19:

Aqueous ion behavior is driven by many fundamental and interrelated physical processes. The solubility of ionic salts in water is predictable to some degree by the “hardness” or “softness” of the component cations and anions, which arises from their degrees of hydration upon dissolution, electron count in the frontier molecular orbitals, overall charge, and charge density [1–4]. Typically, close interactions between cations and anions (ion-pairing) in solutions predates precipitation, with larger hydration spheres from more charge-dense species (i.e., Li⁺) maintaining solubility, according to the Hoffmeister series [5]. This factor competes with lattice energy, which is a sum of energies of all the bonds present in the lattice. For simple monoatomic ions such as alkali halides, similarly sized cations and anions stabilize each other to the greatest degree, decreasing solubility. The relationship between lattice energy and solubility is less well defined for alkali salts of oxoanions; in particular, the anomalous solubilities of some highly charged oxoanions including carbonate [6,7], which is further complicated by protonation in solution. We define anomalous solubility as increased solubility with increased ion-pairing, while normal solubility is the opposite. As an initial approximation, oxoanions and POMs with low charge density exhibit the typical solubility trend (less soluble with increasing alkali counter-cation size), whereas those with high charge densities exhibit the reversed, atypical solubility trend. Some common POMs and simple oxoanions, their charge densities (described here as cluster charge divided by number of cluster atoms), and observed solubility trends as alkali salts are summarized in Table 1 and below we provide a qualitative explanation of these opposite solubility trends. We surmise that oxo species with higher charge densities exhibit this atypical trend due to their ability to disrupt the relatively weakly bound hydration spheres of larger alkali cations (i.e., Rb⁺ and Cs⁺), allowing for contact ion pairing. Because of the high POM/oxoanion charge, the alkali is strongly associated and therefore does not bridge to other oxoanions, suppressing aggregation and precipitation [8]. On the other hand, the high charge density of the same POMs/oxoanions does not completely satisfy bonding of the smaller and more charge-dense alkali cations (i.e., Li⁺ and Na⁺), therefore these alkalis bridge POM/oxoanions in solution, initiating precipitation. Considering the low-charge density POMs, they may also form contact ion-pairs with larger alkalis, but these alkalis are not as strongly associated to a single POM/oxoanion. Rather they bridged two or more of these anions in solution, initiating precipitation. Finally the low-charge density POMs likely cannot penetrate the large hydration sphere of the charge-dense alkalis (Li⁺, Na⁺), so there is no interaction in solution and solubility is retained. Understanding the governing principles of solubility is important because it yields more complete models for thermodynamic calculations of aqueous speciation and ion association. Additionally, the solubility and association of ions in water affects their adsorption onto metal oxide surfaces [9], and knowledge of ion association can be used to fine-tune the electronic properties and chemical reactivities of catalysts, as well as design ion-specific sorbents Polyoxometalates (POMs), nanoscale molecular oxoanions of Group V and VI metals in their highest oxidation states, can generally be synthesized with any alkali cation, thus providing an excellent model for ion-pairing in water and at metal oxide surfaces [15,22]. These “molecular metal oxides” exhibit a wide range of aqueous behaviors that depend on their metal centers and, crucially, their counter-cations [23]. The isostructural and isovalent hexaniobate ([Nb₆O₁₉]⁸⁻, Nb₆) and hexatantalate ([Ta₆O₁₉]⁸⁻, Ta₆) POMs exhibit very similar pH stabilities,

and aqueous solubilities with respect to alkali counteranions [16,24,25]. In particular, Cs^+ undergoes significant ion-pairing with these POMs, which increases their solubilities due to each Cs^+ more favorably interacting with a single cluster rather than coordinating to multiple clusters, wherein binding to a single cluster inhibits aggregation and precipitation, even at high concentration [8]. However, subtle differences have been found in their degrees of ion association with Cs^+ . For example, Ta6 undergoes greater ion-pairing than Nb6 with Cs^+ in dilute solutions in neat water, even at low concentration. This was attributed to the presence of relativistic effects in Ta6, which results in the orbital interaction term having a larger contribution to the total bonding energy [8]. In other words, electrostatics alone are insufficient to describe cation association in the presence of Group V POMs, and covalent bonding between the alkalis and oxo ligands may also be considered, in order to arrive at a complete description of solution behavior

Paper 26:

The interest in lithium is increasing because of the difficulties involved in finding oil substitutes for the world's energy supply, taking into account environmental constraints. It is used, in particular, in batteries (including vehicle batteries and energy storage devices) and the demand for lithium is expected to increase greatly in the coming years (Ebensperger and others, 2005; Grosjean and others, 2012; Kushnir and Sande'n, 2012). Large amounts of lithium are found in the salt flats (salars) of the Altiplanos in South America, mostly in Chile, Argentina and Bolivia (Garrett, 2004; Risacher and Fritz, 2009), in saline lakes in China (Song and Yao, 2001) and the United States, and in the Dead Sea (Warren, 2010). There may be other sources of lithium in other countries and hydrosystems, such as in some geothermal waters (Pauwels and others, 1993, 1995) and oil brines (Gruber and others, 2011). Regardless of the source and geochemical cycle of lithium, an understanding of its chemical behavior is a prerequisite for its exploration, extraction and exploitation, in particular because of the very high concentrations it can reach in aqueous solutions due to the very high solubility of the lithium salts. Part of this understanding relies on the development of comprehensive thermodynamic models that accurately predict lithium aqueous chemistry and lithium mineral solubilities as a function of the composition of precipitates and solution concentration at high temperature. For example, the study of lithium salt solubility diagrams is of practical importance with a view to explaining the distribution of lithium ions in natural evaporate deposits during crystallization of salts as a result of sea water evaporation and during treatment of natural deposits (Song and Yao, 2001, 2003). Several authors (Pitzer and Mayorga, 1973; Kim and Frederick, 1988a; Christov and others, 1994; Ojkova and others, 1998; Song and Yao, 2001; El Guendouzi and others, 2003, 2004; Nasirzadeh and others, 2005) have developed 298.15 K Pitzer equation-based models for Li interactions in binary and mixed sea-type systems. The standard temperature Pitzer models of Christov and others (1994, 2000) for the Li-Mg-Ca-Cl-Br-H₂O system, of Song and Yao (2001) for Li chloride ternary sub-systems within the Li-K-Mg-Cl-SO₄-H₂O system, of Song and Yao (2003) for the Li-Na-K-Mg-ClSO₄-H₂O system, and of Christov (1995) for Li-Mg-Br-H₂O at 343.15 K consider precipitation of lithium minerals. On the basis of their own high temperature osmotic coefficient data and reference activity data at lower temperature, Holmes and Mesmer (HM) developed temperature variable models for binary systems LiCl-H₂O (Holmes and Mesmer, 1981, 1983) and LiOH-H₂O (Holmes and Mesmer, 1998a). The models of HM are valid only up to low molality ($m_{\text{max}} \leq 6 \text{ mol.kg}^{-1}$ for chloride and hydroxide systems) and therefore cannot be used for solid-liquid equilibrium calculations. With only one exception (Li₂SeO₄-H₂O model), all of the Pitzer models described in the literature for Li binary systems (LiCl-H₂O, LiBr-H₂O, LiI-H₂O, LiOH-H₂O, LiClO₄-H₂O, LiNO₃-H₂O, Li₂SO₄-H₂O) have used a standard molality-based Pitzer approach for 1-1 and 1-2 types of

electrolytes with three ion interaction pure electrolyte parameters (β (0), β (1), and C). Ojkova and others (1998) include in their model for the $\text{Li}_2\text{SeO}_4\text{-H}_2\text{O}$ system a fourth interaction parameter (β (2)) from basic Pitzer equations. Only two temperature variable solid-liquid equilibrium models are available in the literature for lithium chloride systems: the one from Monnin and others (2002) for the $\text{LiCl-H}_2\text{O}$ system, which is based on the Pitzer equations for subzero temperatures (up to about 200 K) and on the mean spherical approximation (MSA) model for temperatures up to 433 K, and the one from Zeng and others (2007) for the $\text{H-Li-Mg-Cl-H}_2\text{O}$ system who used the BET model over the temperature range from 273 to 473 K. There is no model available in the framework of the Pitzer formulation for temperatures comprised between 273.15 and 523.15 K. The construction of a comprehensive Pitzer model has, however, been initiated through a series of experimental measurements and parameterization of XTP- and pH-variable thermodynamic solid-liquid equilibrium models of highly soluble chloride, hydroxide, and bromide minerals precipitating within the $\text{H-Li-Na-K-Mg-Ca-AlFe(II)-Fe(III)-OH-Cl-Br-HSO}_4\text{-SO}_4\text{-H}_2\text{O}$ system (Christov and others, 2000; Christov, 2004, 2012; Christov and Møller, 2004a, 2004b; Christov and others, 2007). The resulting consistent and extensible geochemical databases are able to describe complex systems that can be applied to natural and industrial contexts. The objective of the present work is to continue the development of such a database, providing the Pitzer parameters that enable the accurate description of the $\text{Li-H-Na-K-Cl-OH-H}_2\text{O}$ system from diluted aqueous solutions up to saturation with respect to minerals, and from low (273.15 K) to high temperatures (up to 523.15 K).

Paper 30:

In recent years, with the energy crisis and people's demand for high-quality living environment, temperature and humidity independent control air-conditioning system has attracted much attention from domestic and foreign researchers[1-2]. The temperature and humidity independent control air conditioning system is divided into two parts as a whole, one is the cooling part; the other is the dehumidification part[3]. Solution dehumidification is a process of adjusting the humidity of air using a salt solution having a humidity control function. The pressure difference between the partial pressure of water vapor of the treated air and the vapor pressure of the surface of the moisture absorption solution is used as the driving force for moisture transfer [4-5]. After desiccation agent by absorbing moisture in the air, reduce the concentration of, dehumidifying diminished capacity, we must return to the regenerator for regeneration solution[6-8]. At present, solution regeneration methods include electrodialysis [9-10], membrane regeneration [11] and packing regeneration. Electrodialysis and membrane regeneration require more complex processes and cost, so they have not been widely used. Packing device can be used for solution regeneration and dehumidification. It has simple structure and high performance. At present, its common form is: spraying the solution on the filler at atmospheric pressure, heating the solution, evaporating the water in the solution and increasing the solution concentration[12]. Because the dehumidification and regeneration process of the solution depend on the surface vapor pressure of the solution, the physical and chemical properties of the solution dehumidifier determine whether the dehumidification and regeneration process can be carried out and the efficiency of the process. Studies have shown that [13] salt solution is less corrosive to pipelines and other equipment, and is not easily volatilized into the air to cause indoor air pollution, it is a better dehumidification solution. Zhao Yun et al. showed that[14] at the same solution temperature and concentration, the lithium chloride solution has a lower vapor partial pressure than the lithium bromide solution and the calcium chloride solution, and the

dehumidification performance is better. Therefore, the study of the properties of LiCl solution is particularly important. In this paper, the physical properties of the solution during the regeneration of LiCl solution and the effects of different working conditions on the physical properties of the solution were studied.

Paper 32:

As a promising technology to use low thermal potential energy and renewable energy, an absorption refrigeration system (ARS) is getting significant attention nowadays because it can be driven by waste heat [1], biomass [2], solar [3], geothermal energy [4], etc., instead of conventional compression-work-driven chillers. Furthermore, the ARS typically uses water as a refrigerant and the working fluids of system operation are environmentally friendly with zero global warming potential (GWP) and ozone depletion potential (ODP) [5]. In the ARS, the type of absorbent–refrigerant pair selected plays a major role in the performance. Sun et al. [6] has presented a complete review of working pairs of absorption cycles by dividing them into five general series according to the kinds of refrigerant. However, there are limited pairs commercially available from very large to small capacities. Among them, the most commonly used pairs are lithium bromide–water (LiBr-H₂O) for a higher coefficient of performance (COP) and aqua ammonia (H₂O-NH₃) for producing cold at a lower temperature level [7]. A H₂O-NH₃ ARS is more complicated as it requires a rectifier mechanism to separate water vapor from ammonia, whereas the main problem for LiBr-H₂O ARS is the crystallization, which is also present for other salt-based aqueous solutions [8]. In recent years, numerous analyses have been undertaken to find better alternative working pairs of ARS, mostly using H₂O and NH₃ as refrigerants [9–12]. According to these studies, LiCl-H₂O seems to be one of the satisfying options as an absorption cycle working fluid for its advantages regarding the triple state point, long-term stability, comparatively lower cost, and better cycle performance, compared to LiBr-H₂O [13]. Numerous experimental studies on the properties of LiBr-H₂O and LiCl-H₂O solutions have been conducted and empirical formulations with reasonable accuracy are developed through curve fitting of the experimental data [14–18], which are helpful for researchers carrying out theoretical analyses of ARS using these working fluids. However, most of the studies focus on the evaluation of the LiBr-H₂O working pair and few studies are available on the analysis of LiCl-H₂O ARS. Parham et al. [19] stated that an absorption chiller using LiCl-H₂O has a $\approx 5\text{--}6\%$ higher exergetic efficiency when the condensation temperature is 40 °C and absorber temperature is 35 °C, but a LiBr-H₂O working pair has a $\approx 0.6\text{--}0.8\%$ higher COP under the same working conditions and even a $\approx 1.5\text{--}2\%$ greater COP under the optimum conditions. Patel et al. [20] theoretically investigated a 1 RT (United States refrigeration ton) single effect LiCl-H₂O ARS on the basis of the first and second law of thermodynamics, and found that the COP of a LiCl-H₂O system is $\approx 4\text{--}9\%$ higher, while the exergetic efficiency is $\approx 3\text{--}6\%$ higher than that of LiBr-H₂O. Bellos et al. [21] parametrically examined the performance of a solar absorption cooling system under various heat sources and three ambient temperature levels and proved that the usage of the LiCl-H₂O pair performs better than LiBr-H₂O in terms of energetic and exergetic analysis for all the examined cases. Gogoi et al. [22] obtained a total of 34 different combinations of operating temperatures of single effect LiCl-H₂O ARS by using an inverse technique and specific optimization method. They found that LiCl-H₂O ARS is better than LiBr-H₂O ARS under the same conditions and the performance variation with the generator temperature in both systems solely depends on the operating temperatures of the condenser and absorber. Almost all the cycles mentioned above contain just a single working pair and can only make use of partial energy in heat sources. For the effective utilization of the low-temperature thermal energy, She et al. [23] proposed a low grade heat-driven ARS combined with LiCl-H₂O and LiBr-H₂O

working pairs in different pressure levels. Results show that the two parallel modes have much higher COP than the conventional double-stage LiBr-H₂O ARS in the specific operating ranges and the maximum COP improves by about 26.7% and 35%, respectively. What is common with all the above studies is that the LiCl-H₂O is more desirable than LiBr-H₂O at a lower generator temperature and this is also confirmed in this paper. Besides, studies about LiCl-H₂O ARS are far from enough and many situations have not been examined yet. Meanwhile, in the parametric study of the absorption system, most studies simply focus on the influence of temperature on the main components of the thermodynamics performance, but rarely consider the actual heat transfer process between the pure water and the LiBr-H₂O or LiCl-H₂O solution. According to the studies, the temperature of each state point is given by assuming a constant increment or decrement with parameters of internal or external circuit flows in the whole process, such as a fixed temperature difference between the heat resource and generator, cooling water and condenser or absorber, chilled water and evaporator, as well as the hot and cold side, in the solution heat exchanger. Though it is a rational and convenient way, they do not accord with the actual situations very well. In the practical application, the operation of an absorption chiller will change with the environment conditions, resulting in deviations from the design parameters. By considering the internal heat transfer process in each component, the off-design performance of the absorption chiller could be predicted. In contrast to the above studies, parameters of all the state points will change as a whole in the absorption system to exhibit the influence of the outside environment on system operation. For more precise models, a number of works have been carried out to explore the dynamic performance of absorption chillers. Ochoa [24,25] developed a mathematical model to conduct the dynamic analysis of a single-effect LiBr-H₂O absorption chiller by considering the correlations of the convective coefficients of absorption refrigeration processes and results showed the relative errors between experimental and numerical values were approximately 5% and 0.3% in the chilled and cold water circuits, respectively, when the variable overall coefficients were considered. Similarly, Olivier [26] presented the dynamic modeling of a 30 kW single effect LiBr-H₂O absorption chiller considering both the transient and steady state phases. The simulation results agreed very well with the experimental measurements with the mean absolute errors lower than 1 °C for the outlet temperatures of external water circuits in the components. In addition, Kohlenbach and Ziegler [27,28] built a dynamic model of absorption chiller based on internal and external steady-state enthalpy balances and took into account the mass and thermal storage terms as well as the solution transport delay in the components of the chiller. Results indicate that the deviations between the simulation and experimental data were approximately 1–3% in magnitude for the dynamic state and 0.7–3.5 K in temperature for steady state. The above dynamic models with different approaches are applied to predict the reaction of the absorption chiller to the change of external conditions. However, the above studies created whole dynamic models that require specific information on the physical configurations of vessels for the heat exchanger surface area and characteristics of the inner and outer fluids in each component to calculate the heat transfer coefficient, which are hardly obtained from a commercial absorption chiller or supplied by manufacturers. In fact, the basic heat transfer characteristics in the components could be obtained from the design parameters. Different with the dynamic model, the observation of chiller's behaviors varying with time is not the aim of our work. The intention of the present study is to conduct a quick prediction of the off-design performance of the chiller under a steady state and examine the effects of external fluids on the system's operation. This is much easier to achieve by the new method with no need of detailed information or a complex mathematical model. More importantly, the dynamic models developed above are used only for conventional LiBr-H₂O absorption chillers, not for other alternative working pairs like LiCl-H₂O. In another field of investigations, different methodologies have been proposed to analyze such commercial equipment by adding all operating characteristics of the chiller into a set of simple algebraic equations, which

avoids the extensive information of the machine and complex numerical simulations. Hellmann et al. [29] developed a method using a so-called characteristic equation, which is able to approximate the part load behavior of single effect absorption chillers and heat pumps. In the following research, Puig [30] extended the adaptation of the characteristic equation method to double-effect commercial chillers. Gutiérrez-Urueta [31] obtained an extension of the characteristic equation method for adiabatic absorption based on a characteristic temperature difference, taking into account the facility features. However, these models use a multiple linear regression algorithm, where the accuracy relies on experimental or the manufacturer's data. Though the method requires less information about the chiller, it is limited to predictive the heat flow variation with temperature in a specific machine. The operating parameters of state points in the internal and external fluids are unable to be observed, which is available in our model. Furthermore, it is necessary to select the recorded data from the manufacturer's catalogue or measurements first, which have a great influence on the results. Thus, the characteristic equation method is merely appropriate for the existing commercial equipment and scarcely applied to LiCl-H₂O or other alternative working pairs, the same as the above dynamic model. Also, it hardly provides advice on the parameter or structure optimization of the chiller in the design. The commonality between this method and ours is that the simulations are based on steady-state conditions in the process. This study developed a novel calculation method of ARS rarely used in other literatures. The model is based on energy and mass balances and the Dühring equation to describe the primary absorption cycle, and it is reliable and validated in the study of the LiCl-H₂O and LiBr-H₂O ARS simulations. Furthermore, the performance of LiCl-H₂O ARS has been examined comprehensively to complement the previous studies. Furthermore, this study is worthwhile because the variations of LiCl-H₂O absorption chiller with different operating conditions of external circuit flows (hot, cold, and chilled water) under design features have not been examined in detail before. A new computational procedure considering heat transfer characteristics of components has been created for comparative analysis of the whole LiCl-H₂O and LiBr-H₂O absorption chiller, something that is not well established for general application. The computation work in the absorption cycle will be greatly reduced by combining a new method with a computational procedure because it avoids complex iterative calculations of solution properties. In addition, the developed model in this paper can be extended to more absorption cycles using other working pairs to predict their performances with high accuracy and efficiency.

Paper 34:

Thermal energy storage drives the change towards the use of renewable energy resources and energy efficiency. It can be applied for the use of waste heat and solar thermal. Solar thermal systems work at temperatures between 120°C (space heating and hot tap water) and up to 600°C (CSP plants), where thermal energy storage is a key component [1]. In comparison to most commonly used water or molten salt storage, thermochemical storage materials provide ten times or higher storage capacities per mass or volume and the ability to store heat for longer times without the need of insulation [2]. Recently published results state MgCl₂ • 6 H₂O and CaCl₂ • 6 H₂O to be useful for space heating and hot tap water [3] and Ca(OH)₂ for higher temperature levels [4]. We reported earlier about our studies in MgCl₂ • 6 H₂O as pure and composite materials [5] and about our cycle stability measurements with MgCl₂ • 6 H₂O, CaCl₂ • 6 H₂O and Ca(OH)₂ [6]. In this paper we discuss detailed TGA/DSC investigations of hydration and dehydration reaction of salt hydrates and hydroxides. The main issues addressed in this paper are the kinetics and the reaction enthalpy of water release and uptake as well as the released power in dependence on water vapor pressure and temperature.

Paper 35:

Both Na_2SO_4 and K_2SO_4 occur widely in natural waters and are found in many evaporite deposits. Consequently, their thermodynamic properties have been widely studied and models are available that represent these thermodynamic properties over wide ranges of molality and temperature [1–3]. Thermodynamic data for the more rare alkali metal sulfates $\text{Rb}_2\text{SO}_4(\text{aq})$ and $\text{Cs}_2\text{SO}_4(\text{aq})$ are much less extensive. Isopiestic data are available only at 298.15 and 323.15 K for $\text{Rb}_2\text{SO}_4(\text{aq})$ and enthalpies of dilution are limited to 298.15 K and are incomplete [4]. The available thermodynamic data for $\text{Cs}_2\text{SO}_4(\text{aq})$ include isopiestic results at 298.15 and 323.15 K [4] and from 383.14 to 498.19 K [5]. However, the enthalpies of dilution for $\text{Cs}_2\text{SO}_4(\text{aq})$ are very limited in extent and quality and there is an absence of heat capacities. Thus the thermodynamic properties in the region between the high temperature and low temperature isopiestic measurements have not been characterized. A similar situation exists for $\text{Li}_2\text{SO}_4(\text{aq})$ where there is a gap between the low-temperature thermodynamic measurements, summarized in reference [3], and the high-temperature isopiestic measurements of Holmes and Mesmer [5]. Because of the incomplete characterization of the thermodynamic properties of most of the aqueous alkali metal sulfates at intermediate temperatures, an extensive series of isopiestic measurements was made at Oak Ridge National Laboratory between 1985 and 1997 at temperatures of 298.15 and 323.15 K. There were no isopiestic data available for the alkali metal sulfates at 323.15 K prior to these measurements. The results for $\text{Na}_2\text{SO}_4(\text{aq})$ [1], $\text{K}_2\text{SO}_4(\text{aq})$ [2], $\text{Rb}_2\text{SO}_4(\text{aq})$ and $\text{Cs}_2\text{SO}_4(\text{aq})$ [4] have already been published. In the present report new isopiestic data for $\text{Li}_2\text{SO}_4(\text{aq})$ are presented, published thermodynamic data are recalculated consistently and critically assessed, and the more reliable of these results are represented with Pitzer's ion-interaction model [6] and with an extended form that has an ionic-strength dependent C-term as described by Archer [7].

Paper 41:

A large number of experimental data of solubility for the binary system $\text{CaCl}_2 + \text{H}_2\text{O}$ have been determined so far. However, experimental data reported by different authors at different time usually do not agree with each other, and the differences between them are even larger than 2 mass percent at some temperatures. In this case, Linke and Seidell [1] and Smith-Magovan et al. [2] compiled different sets of solubility values of this system from a large number of experimental data, respectively. Linke and Seidell's data are averages read from a plot of the different experimental results, while Smith-Magovan et al. has given most emphasis on the more recently published experimental data [3–9] in their evaluation. It seems that Smith-Magovan et al. preferred the lower solubility data determined by a visual method. However, large differences still exist among the experimental data determined by a visual method. In our previous work [10], we have evaluated the solubility data of the system $\text{LiCl}-\text{H}_2\text{O}$ with the Stokes and Robinson's modified BET model [11] using experimental vapor pressures of saturated solutions as criteria. The philosophy of the method is concluded as the following: A solubility datum and a vapor pressure above the corresponding salt-saturated aqueous solution must show internal consistency. Because that vapor pressures above concentrated saturated salt solutions can be determined more accurate than chemical composition analysis, thus, with a thermodynamic model, more accurate solubility data can be derived from corresponding vapor pressure measurements. In this paper the same method will be used to treat the $\text{CaCl}_2-\text{H}_2\text{O}$ system. At first, we will discuss prediction ability of various thermodynamic models and choose suitable one to treat the most recently published experimental osmotic coefficients.

Then, the vapor pressure above the saturated solutions will be critically evaluated. After that, a set of solubility data and their limits of uncertainty will be predicted applying the BET model and the vapor pressures above the saturated solutions. At last, the predicted solubility data will be compared with various experimental data and causes for differences will be discussed.

Paper 42:

Phase change materials (PCMs), which are widely being used in many fields including buildings and solar applications, have attracted the research community due to their high energy storage and small temperature change from storage to retrieval [1,2]. In comparison to organic PCMs, inorganic PCMs such as salt hydrates are more preferred due to their high latent storage, non-flammability, good thermal conductivity, and low cost [3]. However, many salt hydrate PCMs undergo serious supercooling and phase decomposition during the process of releasing latent heat, which limits their utilization in practical applications. Extremely tiny nucleation agents have been used to influence the supercooling of hydrate salt PCMs. These nucleation agents when added to the melted PCM will stimulate crystallization during freezing [4–7]. The $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ PCM has high latent heat, a low phase-transition temperature (29.5°C), and is more suitable for utilization in building for energy conservation or power saving in summer [8]. It is a by-product (waste) commonly obtained from many chemical processes such as the production of soda ash. The formation of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ usually depends on water loss from $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ by heating it to 175.5°C . In addition, it is convenient to develop $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ from $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. However, high purity $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ has serious supercooling during freezing, which restricts its practical application as a phase change material and needs to be avoided. Lane [4] introduced different kinds of inorganic salt (as additive) having a similar crystal structure to that of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ to reduce the supercooling degree of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. During the past decades, investigators have provided some explanation, reasons, and instructions for further research. Fellchenfeld and Sarig [9] hold a view that a specific nucleation agent should have a structure similar to that of the crystal it is going to nucleate. While investigating $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, the authors concluded that the purpose of a nucleation agent is to ensure that the hexahydrate crystallizes and makes the system more stable. Agron and Busing [10] compared $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ with $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and found that the interatomic distances, bond angles, and dihedral angles between planes are all similar. The crystal structure similarity helps liquid $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ easily adhere to the surface of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and to crystallize when the temperature of the liquid falls below the phase-transition point. Hence, the researchers commonly utilized inorganic salts or some hydrate salts with the goal to reduce the supercooling of PCMs, and effective results were obtained. Nano additives have been used to eliminate the supercooling of different PCM systems [11–13]. It is known that the shape and size of nanoparticles could have positive effects on nucleation during the crystal growth process of a PCM. He et al. [12] used TiO_2 nanoparticles in a BaCl_2 aqueous solution, and reduced the supercooling degree of a PCM system by 84.92%. Ma et al. [13] reported that nano- TiO_2 reduced the supercooling of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ by 88.39%. Metal nanoparticles, metallic oxide nanoparticles, and metal nitride nanoparticles (Cu , Al_2O_3 , and AlN) added into a PCM can also stimulate and ensure a timely crystallization so as to reduce the supercooling that occurs during solidification [14–16]. Zhang et al. [17] dispersed hydrophobic SiO_2 nanoparticles as nucleating agents into n-Octacosane emulsions, and found that the composite with a 0.3 wt % concentration of SiO_2 nanoparticles was most effective in eliminating supercooling. Li et al. [18] evaluated the performance of graphene, SiO_2 nanofluids, and TiO_2 nanofluids (with different additive volumes) in reducing the supercooling degree of pure water. The authors found that graphene was the most effective,

and with a small dosage ($0.02 \text{ wt } \% \pm 0.001$) can entirely eliminate the supercooling degree of pure water. Hence, in recent years, nano materials, which use salt or hydrate salt, are more preferred due to its lower additive volume and higher efficiency. However, the literature evaluating the performance of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and similar PCMs based on CaCl_2 with nano particles is scarce. According to the researchers in Ref. [19], $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is a promising PCM for heating and cooling processes in building applications. However, in their research [19], the data of DSC (Differential Scanning Calorimetry) measurements under different cycles seemed to be random and instable. Some researchers insisted that adding additives can suppress the formation of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, which leads to the segregation of a PCM [20,21]. Chmit et al. [21] investigated the relationships between the volume of CaCl_2 and H_2O for the preparation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. They found that the maximum enthalpy was obtained with a 50.66 wt % of CaCl_2 . However, they also found that the formation of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ as well as the sample volume would result in the instability of DSC data. It is pertinent to mention here that in the existing studies, the authors have seldom discussed the preparation method of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. Moreover, as per the authors' knowledge, no researchers have explored the relationships between the additive volumes of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and CaCl_2 . Hence, in this paper, a novel salt hydrate PCM ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ - CaCl_2 - H_2O) was prepared to reduce supercooling by evaluating the relationship between the proportion of calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) and calcium chloride anhydrous (CaCl_2). The role of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in reducing supercooling as well as its effect on adjusting the solidification enthalpy was investigated. Nano SiO_2 was selected to modify and eliminate the supercooling of the PCM system to less than a degree. The method applied in this research to prepare the salt hydrate PCM was relatively uncomplicated and easy to use. Finally, the effect of the different cooling conditions, including frozen storage (-20°C) and cold storage (5°C), that were used to prepare the salt hydrate PCM was considered.

Paper 49:

The development of cities is accompanied by huge energy consumption; people have gradually realized that the energy storage technology has very good ability to improve this situation, which can effectively improve the energy utilization ratio and reduce losses. Phase change material (PCM) is an effective latent heat thermal storage material. It has been widely used as a thermal functional material in thermal and cold energy storage fields, like solar energy storage [1], industrial waste heat utilization [2], building heating and air conditioning [3], thermal management of mobile devices [4], and so on. All of these are aimed at realizing the conversion of energy beyond the restriction of time and space. Thus, the study of PCM is of great significance for energy storage [5]. PCM can be mainly divided into two categories of organic and inorganic. However, organic PCMs such as paraffin wax [6] and some organic compounds [7] are poor in low thermal conductivity and have flammability, which greatly limits the application of PCMs [8]. Therefore, the study of inorganic PCM has attracted much attention of researchers. Salt hydrates [8] as an inorganic PCM have an advantage in higher heat storage capacity, suitable cold storage temperature [9], nonflammable, and so on. Thus, it would be more suitable and safer than organic PCM in energy storage application especially cryogenic storage. The traditional ice storage and water storage cannot reach the temperature of low-temperature cold storage. The temperature requirement of low cold storage is between -20 and -30°C , and the high-temperature cold storage is between 0 and 4°C . However, the ice storage and water storage systems can only reach 0°C , which cannot meet requirements of low-temperature application. Adding inorganic salts in the water can ensure that the amount of phase change latent heat almost unchanged and reduce the phase change temperature of cool storage material at the same time. Compound salts can not only further reduce the melting point of solidification but also optimize and

modify the overall physical properties of certain materials. Many researchers have studied the compounded eutectic hydrate salt to achieve more suitable phase change temperature and better cold storage performance. Li et al. [10] have studied the preparation, characterization, and modification of a new phase change material $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ – $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ eutectic hydrate salt. As a result, its phase change temperature and latent heat are 21.4°C and 102.3 J/g , respectively. Liu et al. [11] studied the energy storage characteristics of a novel binary hydrated salt by means of SEM, XRD, and DSC techniques. It was concluded that the phase transition temperature was 27.3°C , the degree of supercooling was 3.67°C , and the enthalpy of phase transition was 220.2 J/g . Efimova et al. [12] proposed a ternary hydrated salt mixture suitable for use in air conditioning systems and carried out the thermal analysis. It was concluded that the material has a melting temperature of $18\text{--}21^\circ\text{C}$ and an enthalpy of fusion of 110 kJ/kg . However, different from organic PCM [13], inorganic PCM such as salt hydrates has a significant supercooling [14, 15] and relatively poor stability, which greatly limit the life of phase change material and energy storage performance. In general, methods that can be used to effectively enhance the stability of the material are additions of the thickener [16], nucleating agent [17, 18], microencapsulation [19] or nanocomposite modification [20], and so on. Tyagi [21] et al. studied the supercooling behavior of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and the effect of pH value, which indicates that the supercooling of PCM can be removed or decreased by adjusting the pH value. Bilen et al. [22] studied the modification of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ PCM system and selected different nucleating agents. Pilar et al. [23] used SrCO_3 and $\text{Sr}(\text{OH})_2$ as nucleating agents for $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; the results show that the addition of 1 wt% SrCO_3 and 0.5 wt% $\text{Sr}(\text{OH})_2$ almost fully suppress the supercooling and improve the performance of this PCM system. For phase separation, Wang et al. [24] studied the thermal stability of a novel eutectic ternary system by placing the salt mixture in an argon atmosphere with a constant heating rate. In order to determine the accurate upper limit of the working temperature of the ternary salt, Sharma et al. [25] used a differential scanning calorimeter to carry out 1500 times melting and freezing cycles to study the changes in thermal properties of thermal energy storage materials. At present, the inorganic salt hydrate phase change cold storage materials have a good application prospect in refrigerator energy-saving field. It can be seen above that most of the research on hydrated salt cold storage has focused on the development of energy storage materials for air conditioning. There is a lack of research on the energy storage materials with phase change temperature below 0°C . Otherwise, it is a meaningful attempt to study the improvement of supercooling and cycle stability of ternary eutectic system from the point of fluid viscosity and different nucleating agents added. In this paper, firstly, a $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ – $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ – $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ternary salt system was prepared, modified, and synthesized. Then the contrast experimental method, step cooling method, and DSC technology were proceeded to investigate the thermal storage property and solidification behavior of eutectic hydrate when adding different amounts of nucleating agent and thickener.

Paper 50:

The awareness of humankind's role into climate change [1] and the increasing energy intensity in developing and underdeveloped countries [2] are among the main drivers for a more sustainable production and use of energy. The energy grid consists of a system in which multiple carriers are produced, transported, consumed, and stored. The level of complexity of this system is constantly increasing due to technological advancements such as energy production systems with new requirements, transportation and storage methods that are more efficient, new policies, and new types of consumers and other stakeholders. The advance of renewable energy sources, cogeneration, and intermittent power sources in general, is drastically changing the requirements on the energy

grid. Some of the new energy production units are characterized by relatively low and decentralized installed capacities, intermittent and often unpredictable production patterns frequently driven by the owner's needs or by the source availability, and production of multiple energy carriers. Therefore, the energy network is constantly evolving [3,4] to cope with new types of stakeholders and an increasing penetration of intermittent distributed production sources. Storage of multiple energy carriers, demand side management, exchange and relocation through conversion of energy carriers are among the main practices that the future system will have to incorporate to gain the needed flexibility [5]. Energy storage is useful to handle fluctuations in energy demand to spread the production of energy needed during demand peaks over a different time period and to make efficient use of fluctuating production sources such as renewables, increase energy grid safety, and improve the overall system efficiency [6]. In Table 1-1, an overview of the main storage technologies, their costs, efficiencies, and typical response times is displayed. 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 (Fig. 1-1 left). Thermal energy storage can be divided into three main categories according to how energy is stored: sensible heat (e.g. water tanks, underground storage) [11–13], latent heat (e.g. ice, phase change materials) [14–16], and sorption heat storage.

Paper 53:

Sustainable, safe energy storage will be key to fully utilizing renewable power sources and enabling new classes of technology. One significant limitation of electrochemical energy storage is performance loss or failure at low ($< -20\text{ }^{\circ}\text{C}$) temperatures. This shortcoming impacts the efficiency of mature technologies such as electric vehicles in cold climates.¹ In more extreme environments, such as polar regions, aerospace, and other potentially habitable planets, the development of certain novel technologies which demand power delivery at $-70\text{ }^{\circ}\text{C}$ and colder are even more severely limited. Clearly, a means of low-temperature energy storage is needed. The lower limit of commercial energy storage devices ranges from about -20 to $-40\text{ }^{\circ}\text{C}$, with supercapacitors being generally more tolerant than lithium-ion batteries.² Below these limits, issues arise in the ion-conducting electrolyte where increased viscosity and freezing hamper the mobility of charges. This manifests as an increased ionic resistance which either hurts the efficiency of the device or completely arrests device operation. For most electrochemical devices, the electrolyte is comprised of organic solvents and salts; therefore, much of the work on low-temperature energy storage has focused on these materials.^{3–5} Propylene carbonate and acetonitrile are some commonly used examples, with low freezing points around $-50\text{ }^{\circ}\text{C}$. A common approach to extend the temperature range of the electrolyte is to add the lowfreezing solvent dioxolane. However, this is a poor electrolyte solvent (having a high viscosity and low dielectric); therefore, custom electrode materials must be engineered to pair with it.⁴ Other efforts include developing low-freezing ionic liquid mixtures matched to activated carbons with, again, specially engineered pore distributions to accommodate bulky ions.^{6,7} Such ionic liquids enable energy storage down to $-70\text{ }^{\circ}\text{C}$, but these exotic chemicals have a correspondingly high cost. Aqueous electrolytes are perhaps an unlikely candidate for low-temperature energy storage. Despite the growing interest in safe and low-cost alternatives to organic electrolytes,^{8–10} these materials are little considered in the context of lowtemperature energy storage, likely due to the high freezing point of pure water. Here, we demonstrate that a mixture of the commodity salt lithium chloride (LiCl) and water forms an excellent low-temperature electrolyte, supporting energy storage in supercapacitors as low as $-80\text{ }^{\circ}\text{C}$. The electrolyte used is a eutectic

mixture of LiCl (24.8 wt %) in water with a greatly depressed freezing point of $-74\text{ }^{\circ}\text{C}$, allowing for remarkably high conductivity (1.83 mS/cm) even at $-70\text{ }^{\circ}\text{C}$. Efficient charging of an off-the-shelf activated carbon (Kuraray) at low temperatures demonstrates the practical nature of the aqueous electrolyte which outperforms a conventional organic electrolyte below $-40\text{ }^{\circ}\text{C}$. Not only does this aqueous electrolyte support exceptional low-temperature charging kinetics, but its stability window also widens from about two to three volts when cooled from room temperature to $-70\text{ }^{\circ}\text{C}$. This aqueous electrolyte is a low-cost, competitive alternative to organic electrolytes for energy storage in extreme environments.

Paper 73:

Understanding the physico-chemical behaviour of natural and synthetic saline aqueous systems is very important for environmental and industrial purposes. Various models have been developed to describe such systems [1–5]. Pitzer [6] developed one of the most promising and frequently used models. Indeed, researchers have shown that it can represent the physico-chemical solution properties of very low to very high salinities [7] in complex systems [8], and at high temperatures [7], and it has been applied to many different chemical systems ([9], and references therein). The semi-empirical Pitzer approach considers specific interactions between dissolved species and uses interaction parameters, thermodynamic constants for aqueous complexation reactions, and mineral (respectively gas) solubility products for dissolution/precipitation (respectively dissolution/degassing) reactions. All of these parameters are included in thermodynamic databases that can be used by geochemical codes. However, extending these databases to include new species might be problematic in terms of numerical stability and/or model consistency, especially when the previously tabulated parameters are limited by their salinity range of validity. Fundamental systems should therefore be reviewed and updated to extend their thermodynamic characterisation to very high salinities and high temperatures. Here, we consider the NaOH-H₂O binary system because of the very high solubility of NaOH salts [10]. This electrolyte has been widely studied both in the binary system NaOH-H₂O and in mixtures. Pitzer and Mayorga [11] worked on this binary system up to $6\text{ mol}\cdot\text{kgw}^{-1}$ at 298.15 K . Harvie et al. [8] predicted solid-liquid equilibria in the Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-CO₂-H₂O systems at 298.15 K up to $6\text{ mol}\cdot\text{kgw}^{-1}$. Pabalan and Pitzer [12] predicted solid-liquid equilibria in the Na-K-Mg-Cl-SO₄-OH-H₂O at high temperature. Pabalan and Pitzer [13] provided parameters for the binary system NaOH-H₂O between 273.15 – 623.15 K and up to $10\text{ mol}\cdot\text{kgw}^{-1}$ using both osmotic coefficient data and volumetric data such as apparent molar volumes. Simonson et al. [14] deduced, from heat capacity and dilution enthalpy measurements in the NaOH-H₂O system, the osmotic coefficient between 273.15 K and 523.15 K and up to $6\text{ mol}\cdot\text{kgw}^{-1}$. They represented these data with Pitzer's model and introduced the interaction parameter $\beta(2)$ in order to improve their fit. Petrenko and Pitzer [15] measured vapor pressure and deduced water activity values. Using a modified version of the original Pitzer model, based on a mole fraction scale instead of a molality scale, they modeled these data between 273.15 and 523.15 K and for molalities ranging from 0 to $249.786\text{ mol}\cdot\text{kgw}^{-1}$. Christov and Møller [16] worked on the H-Na-K-OH-Cl-HSO₄-SO₄-H₂O system at high temperature (523.15 K). The parameters for the NaOH-H₂O system are valid up to $6\text{ mol}\cdot\text{kgw}^{-1}$. The excess properties of NaOH solutions are described with accuracy up to this concentration limit. In this paper, the authors also underline the non validity of their parameters at higher concentration. However these authors tested with success their parameters to determine the solubility of some hydrated salts up to about 60°C and $50\text{ mol}\cdot\text{kgw}^{-1}$. The work described here goes further and aims to develop a set of parameters able to represent both the excess properties (e.g. osmotic coefficient, activity coefficient) and the mineral solubility in the NaOH-H₂O binary system to

very high salinities, from 273.15 to 523.15 K, using the Pitzer approach. The originality of this study is to propose a model valid up to salt saturation between 273.15 and 523.15 K. Up to our knowledge, no Pitzer model exists on a such system up to so high concentrations (higher than 30 mol·kgw⁻¹). Its compatibility with more complex systems is checked on the LiOH-NaOH-H₂O and NaOHNaCl-H₂O ternary systems.

Paper 86:

With the growing consumption of fossil fuels and increasing emission of carbon dioxide, thermal energy storage (TES) has received a great deal of attention. Latent heat storage and sensible heat storage are two main forms of TES. Using phase change materials (PCMs) for latent heat storage, which can storage and release energy by melting and solidification, is becoming an effective way to solve the contradiction of supply and demand of energy, such as peak difference of power load and gap of solar energy [1,2]. High storage density, stable performance, wide phase change temperature range and reasonable price make PCMs play a significant role in energy conserving areas. In the field of phase change energy storage technology, it is a fundamental step to develop high latent heat, stable, and cost-effective materials. Different types of PCMs have been studied after petroleum crisis in 1970s, including solid-solid PCMs (polyalcohols and other polymers), solid-gas PCMs and solid-liquid PCMs (salt and salt hydrates, clathrate hydrates, paraffins, fatty acids and their mixtures, alloys and ect) [3,4]. Among these, salt hydrates, which account for a large proportion in inorganic PCMs, have always been attracted attention owing to their reasonable price, wide sources, good thermal conductivity and high volumetric energy storage density. However, some defects, such as leakage, causticity, supercooling and phase separation impose restrictions on their practical applications [5–7]. In order to reduce such adverse effects, form-stable PCMs are studied recent years by incorporating PCMs into porous materials or through the method of microencapsulation to prevent leakage and phase separation [8–10]. Moreover, different kinds of nucleating agents have also been developed to reduce supercooling degree. It is a promising direction to apply low-cost inorganic PCMs to energy conservation areas such as electric peak-shaving, industrial waste heat utilization, aerospace field, air conditioning cold storage and so on. This paper reviews the research progress of salt hydrates for TES including properties, improvements as well as their specific characteristics, which are suitable for practical application in different fields in recent years. Research trends and potentials of these PCMs are also prospected.

Paper 92:

One line of development in solar-energy research concerns the construction of buildings where surplus heat on sunny days can be stored for later use in concrete or other materials with high heat capacity. (1) Far more energy per unit mass or volume may, however, be stored in materials which undergo reversible phase changes or chemical reactions just above room temperature. Heat-storage materials which melt around 290 K with high enthalpies of fusion are available with for instance CaCl₂·6H₂O as the main component. (2) Such materials have recently been installed in a number of experimental solar houses, (2-7' with promising results. The properties of CaCl₂·6H₂O have been extensively studied. i.e. by measurements of thermal conductivity, "–" rate of crystallization, 's-' O) compatibility with containers of various materials, "0-12' and performance in various types of energy-storage systems. (2-8*13*14) The specific enthalpy of crystallization of CaCl₂·6H₂O was found to be 170 J·g⁻¹ by Person's in 1849 (drop calorimetry). Recent values for the specific and volumetric

enthalpy of fusion have been given by Lane: (') 190.8 J . g⁻¹. by Schroder and Gawron: " 01 173.0 J g⁻¹. and by Achard et al.: (r6' 281 MJ. mp3, but without exact reference to the method of determination. Due to the large discrepancies among the literature values, further measurements with more exact control of the crystal-water content seem needed." ') Values for the specific enthalpy of fusion of FeCl₂ . 6H₂O have been given by Telkes: " " 223 J. g⁻¹, and by Hale et al.: " " 226 J. g⁻¹, also without reference to the method of determination. The use of FeCl₂ . 6H₂O as an energy-storage material has been prevented by its extremely low rate of crystallization. " " Less attention has been paid to CaCl₂ . 4H₂O, in spite of the fact that its melting temperature is suitable for storage of solar energy for domestic-heating purposes. '20' Here we report heat capacities and phase-transition enthalpies for CaCl₂ . 6H₂O, CaCl₂ . 4H₂O, CaCl₂ . 2H₂O, and FeCl₂ . 6H₂O between 270 and 400 K.

Paper 99:

Currently society is transitioning, from a carbon based economy to a renewable one. To transform the domestic heat demand from carbon consumption to renewable energy, various techniques are developed to generate heat like solar collectors, parabolic solar collectors, solar ponds and solar concentrators. One of the major drawbacks of these techniques is of course that sunlight is needed for the process. This makes the production of heat uncertain overtime, which could be solved by heat storage. A storage option with a promising potential is thermochemical heat storage utilizing salt hydrates, by which heat can be stored almost lossfree over long time. Several papers have been written about requirements to consider when choosing a thermochemical heat storage material [1–5]. The publication of Goldstein [6] marks the beginning of the renewed interest in these hydrates as heat storage materials. Salt hydrates can include water in a newly formed crystal structure by which chemical energy can be stored. The basic reaction behind this process can be represented as: $AxH_2O \rightleftharpoons A + xH_2O$; DH; (1) wherein AxH₂O is a solid salt complex produced from solid A and solvent H₂O. The amount of mol water inside product A is called the loading of the salt. For the decomposition of AxH₂O energy (DH) has to be added, where as in the formation of AxH₂O the same reaction energy (DH) is produced. While Eq. (1) is an equilibrium reaction, the state of the system can be modified by the vapor pressure and temperature of the system. This study focusses on hydrates, which (partially) dehydrate at temperatures below 150 °C. Previous studies focussed on a single hydration or dehydration step either induced by temperature changes, i.e. using thermal gravimetric analysis (TGA) [7–9], differential scanning calorimetry (DSC) [10–12], XRD [10,13], Raman [14] and neutron diffraction [15] or by vapor pressure; i.e. using gravimetric analysis [16,17] and Raman [18–20]. Reviews on the selection of hydrates that are suitable for heat storage [5,21–23] are mainly based on single dehydration or hydration steps or are based purely on theoretical energy densities and dehydration temperatures. This selection procedure is insufficient, as it does not take account of multicyclic stability. It has been observed that the salt grains are not stable (physically, mechanically and/or chemically) over several cycles of repeated hydration and dehydration, e.g., considering changes in the rehydration/dehydration rates and/or grain sizes [24–27]. For example, during dehydration a pseudomorphic structure may appear [28,29] due to volume changes, which facilitates vapor transport through the crystal, thereby influencing the transport in time [25]. Such observations are mainly based on mass measurements and information on the crystal structure or water transport inside the grains is missing. Furthermore, a drawback of most of the techniques used in these studies is that during the dehydration or rehydration the moist air supply is from one side of the sample only, i.e. single-sided induced hydration/dehydration. As a result most experiments are performed on sample mass below 10 mg, because in larger samples diffusion of air through the bed of grains limits the dehydration and (re)hydration processes. In this paper, the cyclability of several hydrates is

studied, which were selected on the basis of their theoretical volume variation during a hydration/dehydration reaction. Using Nuclear Magnetic Resonance (NMR), the water transport in these hydrates is studied in larger beds of grains where the moist air is blown through the bed itself. This is in contrast with techniques like TGA or DSC, where moist air can only be blown along the top of the sample. In such experiments, the number of layers of grains will affect the dehydration process as a result of vapor diffusion through the bed of grains. In the NMR experiments, this effect can be avoided as long as the moist air flow through the bed is high compared to the vapor production or consumption of the grains in the bed.