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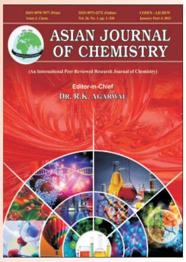

Thermodynamics and Kinetics of Reaction Between NaCl and KF

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Thermodynamics and kinetics of reaction between NaCl and KF were investigated. The negative Gibbs free energy change for the reaction indicated that the reaction was thermodynamically possible. Differential thermal analysis was used to study the reaction. Differential thermal analysis analysis revealed that the reaction between NaCl and KF occurred at 595 °C after a eutectic liquid formation at 582 °C and its activation energy was calculated to be 805 KJ/mol using Kissinger differential method. Moreover, powder X-ray diffraction measurement further confirmed the formation of NaF and KCl.

Keywords: Thermodynamics, Kinetics, Reaction, NaCl and KF.

INTRODUCTION

Molten salts exhibit excellent properties and have received a great deal of attention as their ever increasing industrial applications. Molten salts have unusual solvent properties which have led to their use in electrochemistry and metallurgical electrolysis. Metals belong to the group with very negative electrode potentials cannot be electrochemical deposited from any aqueous media owing to the hydrogen evolution at the cathode. Consequently, molten salts are required for electrolytic production, refining and plating of this kind of metal[1]. Alkali metal halides form the basis of molten electrolytes for a number of electrochemical processes because of a unique combination of their physicochemical properties (high decomposition voltage, conductivity and thermal stability, low vapor pressure and viscosity). Sodium and potassium fluorides and chlorides (NaCl, KCl, NaF, KF) are usually used as solvents for salts of multivalent metals, which are deposited on electrolysis at the cathode[2]. At present, the thermodynamic data of pure sodium and potassium fluorides and chlorides are of good quality. The interaction between the two salts is of interest for the overall understanding of chemical-physical properties of the molten salt. The interaction between NaCl and KF has not been reported in the literature. Therefore, the aim of this study is to investigate the interaction between NaCl and KF.

Thermal analysis includes several techniques that enable to evaluate some physical and chemical properties of a sample after a temperature cycle. Parameters measured by means of a differential thermal analysis (DTA) are the transition and reaction temperatures and it is employed in phase diagrams and thermal stability. It is also used to determine kinetics of the reactions. By means of DTA, reaction mechanisms were also studied. In addition, DTA, along with other techniques, is used to characterize product. In the present study, the interaction between NaCl and KF was investigated by means of DTA and XRD.

EXPERIMENTAL

NaCl (99.5 mass % min.) and anhydrous KF (99.5 mass % min) provided by Sinopharm Chemical Reagent Co. Ltd. were all analytical grade and dried at 200 °C for 8 h to remove excess water. All handling of the salts was done under high purity argon atmosphere in a glove box.

A simultaneous TG/DTA instrument (model HCT-3, Beijing Henven Scientific Instrument, China) was used to measure the heat evolved from reaction of NaCl and KF. The HCT-3 was capable of heating a sample from 0.1 to 80 °C/min. The TG/DTA furnace assembly was continuously flushed with high purity argon at a flow rate of 50 mL/min. Equimolar NaCl-KF powders of 30 mg were placed in high purity graphite crucible of 8 mm in diameter and 8 mm in height. The reference standard was empty high purity graphite crucible. The heating schedules for the samples were programmed using the software delivered with the TG/DTA apparatus. Temperatures were measured with Pt/(Pt + 10 % Rh) thermocouples. The thermocouples were calibrated using the following structure change or melting temperatures: 154 °C (ln), 571 °C (SiO_2) and 928 °C ($SrCO_3$).

X-ray powder diffraction (XRD D/MAX2500PC, Rigaku, Japan) with CuKα line at 40 kV and 100 mA was used to determine phase composition of the reaction products between NaCl and KF.

RESULTS AND DISCUSSION

In KF and NaCl system, the following reaction is considered:

$$NaCl + KF = NaF + KCl \quad (1)$$

Thermodynamic investigation is essential to determine whether or not the reaction is spontaneous. The Gibbs free energy change (ΔG) indicates if the reaction occurs spontaneously, *i.e.*, the value of ΔG is negative. The Gibbs free energy change (ΔG) was calculated for the eqn. (1) in the temperature range 25 to 750 °C using Factsage version 6.4 software. Fig. 1 showed how the Gibbs free energy change (ΔG) calculated for the reaction (1) varied with the temperature. It was noted that the free energy change for this reaction from 25 to 750 °C was negative which indicated that chemical reaction of NaCl with KF may occured spontaneously.

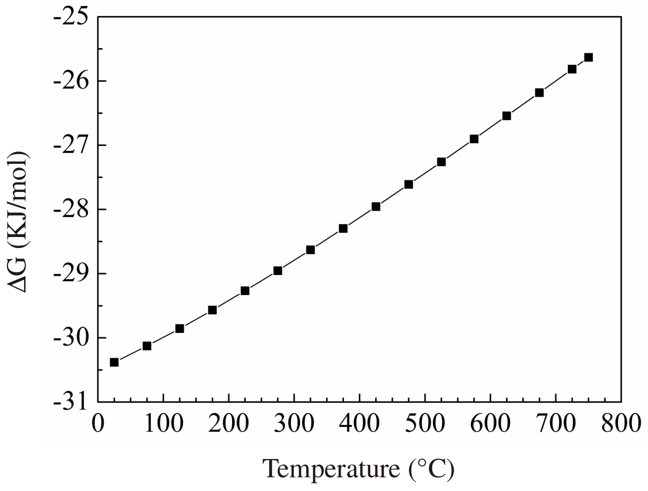

Fig. 1. Gibbs free energy change with temperature

Contrarily to the calculation results, NaCl with KF did not show the formation of NaF and KCl at ambient temperature. This can be due to when calculating thermodynamic by the Gibbs free energy; all reactions are considered to reach equilibrium. However, if the kinetic of one reaction is slow, then the equilibrium is limited by the rate of that particular reaction[3]. In other words, the Gibbs free energy is constrained by the kinetics.

Differential thermal analysis: Equimolar NaCl-KF mixture was subjected to differential thermal analysis for tracing the reaction processes. The thermal analysis was carried out in the temperature range of 25 to 750 °C with a heating rate of 10 °C/min. The DTA curve was shown in Fig. 2. It can be seen that there were three peaks in Fig. 2, one exothermic peak at 595 °C after an endothermic valley at 582 °C and another endothermic peak at 658 °C.

The first endothermic peak which occurs at 582 °C in the DTA curve should correspond to eutectic point between NaCl and KF. Two samples containing NaCl with different mole

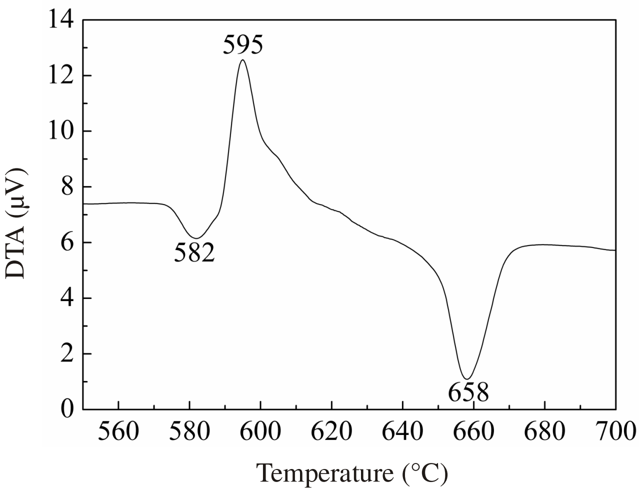

Fig. 2. DTA curve for equimolar NaCl-KF mixture

percent of KF (20 and 40 %) were prepared and the differential thermal analyses were carried out. As a result, the endothermic peaks at about 582 °C for the two samples were shown in Fig. 3 and this indicated that 582 °C should be eutectic point between NaCl and KF.

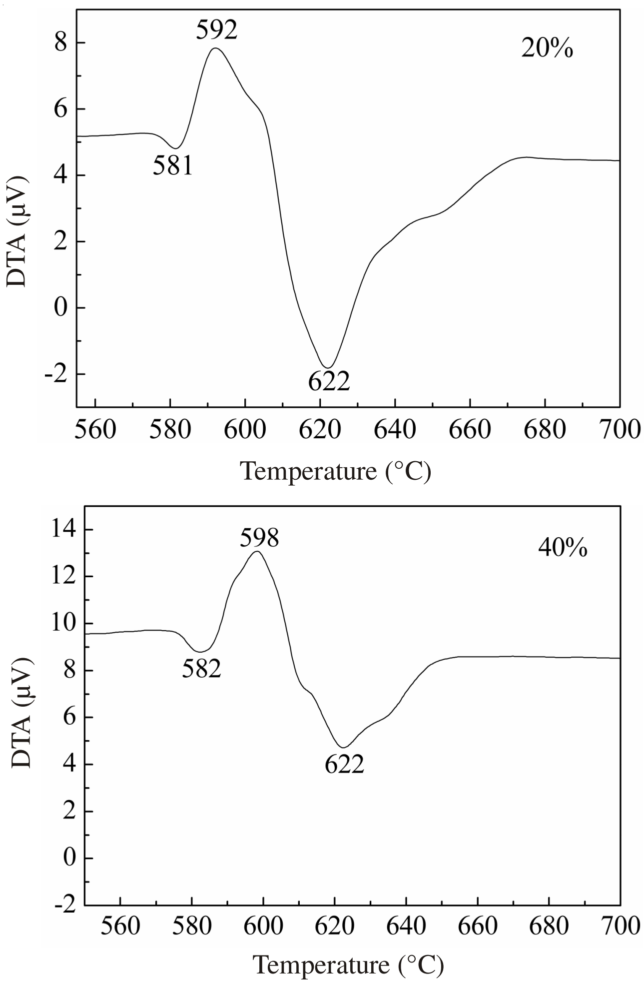

Fig. 3. DTA curves for NaCl with different mole percent of KF (20 and 40 %)

The exothermic peak at 595 °C was due to the reaction that took place between NaCl and KF. The reaction enthalpy of eqn. (1) was theoretically calculated using Factsage version 6.4 software and the result was shown in Fig. 4. As can be seen, the reaction enthalpy was negative which reflected that the reaction was exothermic.

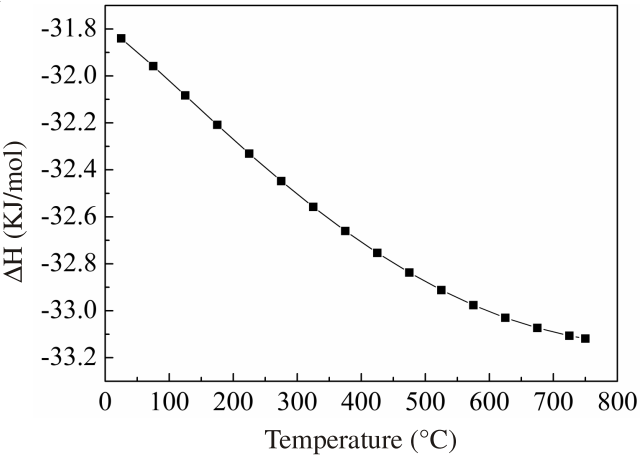

Fig. 4. Reaction enthalpy of NaCl with KF as a function of temperature

There was partial liquid after a eutectic reaction between NaCl and KF occurred at 582 °C. The appearance of liquid phase made the reaction rate increased greatly due to atom diffusion can be accelerated. Additionally, since the reaction between NaCl and KF was an exothermic reaction as described above, much heat was released to accelerate the process. As a result, the reaction between NaCl and KF occured rapidly. These conclusions were consistent with Galwey's work[4]. Galwey[4] discussed reasons for the enhancement of reactivity on fusion and contrasted the rate characteristics of heterogeneous (solid state) with homogeneous reactions. It was demonstrated that there was the essential participation of perhaps local and temporary fusion or liquid intermediate formation during chemical changes that had initially appeared to proceed in the solid state. The partial, local and/or temporary liquids or molten eutectic that had previously been regarded as proceeding in the solid state may themselves be present as the active participants. The reactions may proceed more rapidly in the fused phase. This could be represented as an autocatalytic process, involving a 'liquid nucleus'. After fusion, the intracrystalline stabilizing forces were relaxed and the stereochemical constraints, capable of opposing the adoption of the most effective precursor molecular disposition for chemical change (activated complex formation), may be significantly diminished[5].

After reaction, the products should be NaF and KCl, so the endothermic peak at 658 °C would be eutectic point between NaF and KCl. This was studied by carrying out DTA for the samples KCl with different mole percent of NaF (20 and 50 %). As it can be observed in Fig. 5, the endothermic peak at 658 °C for all the samples indicated that 658 °C should be eutectic point between KCl and NaF.

X-ray diffraction analysis: XRD analysis was applied for further confirmation of NaF and KCl formation. The DTA products of equimolar NaCl-KF mixture were ground into powder and further analyzed by XRD to investigate the phase. The pattern was given in Fig. 6. The pattern was analyzed and the peaks were identified using ICSD data file. It can be seen from the Fig. 6, that all the peaks belonged to KCl (ICSD, 75-0296) and NaF (ICSD, 36-1455), no NaCl and KF diffraction peaks were found. This further comfirmed that NaCl reacted with KF to form KCl and NaF.

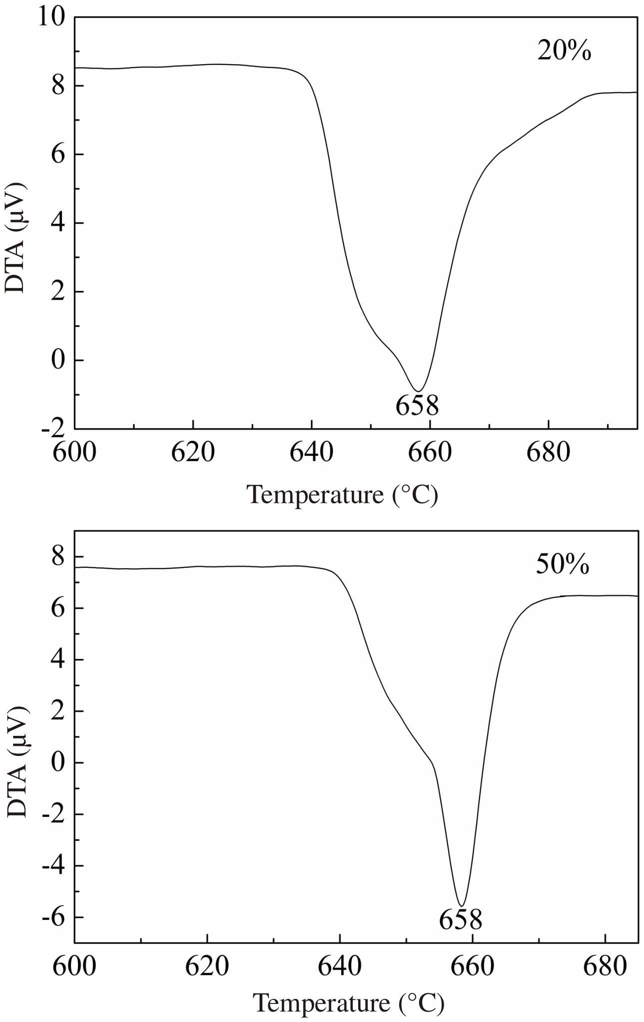

Fig. 5. DTA curves for KCl with different mole percent of NaF (20 and 50 %)

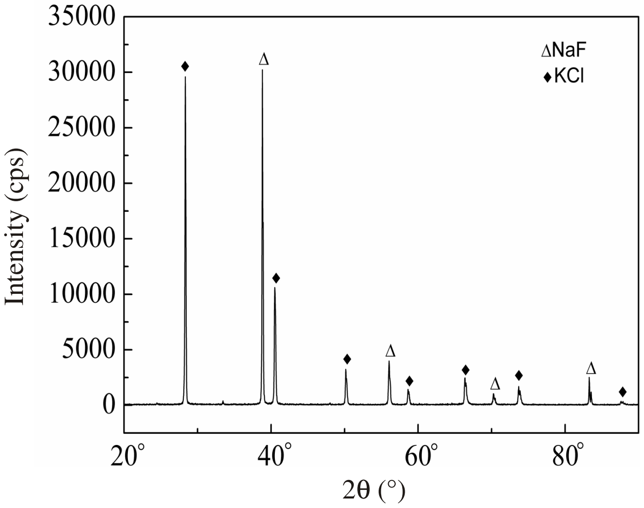

Fig. 6. XRD pattern of equimolar NaCl-KF reaction product

Reaction dynamics: The Kissinger differential method has been widely utilized to estimate the activation energy of reaction with its advantage not requiring any detailed information on the reaction mechanism[6]. The reaction activation energy (E) can be calculated by Kissinger equation[7]:

$$\ln\left(\frac{\beta}{T_m^2}\right) = \text{Const} - \frac{E}{RT_m} \qquad (2)$$

where T_m is the temperature peak of the DTA curve (K), β is the heating rate (K/min), Const is a constant, E is the reaction activation energy (KJ/mol), R is the air constant (8.314 J/mol). The Kissinger eqn. (2) is based on the shift of the DTA curves with respect to different heating rates. Fig. 7 showed the exothermic peaks on DTA curves of equimolar NaCl-KF mixture generated at different heating rates of 5, 10, 15 and 20 K/min, respectively, in high purity argon protective atmosphere. These exothermic peaks were located at around 592, 595, 599 and 602 °C, respectively.

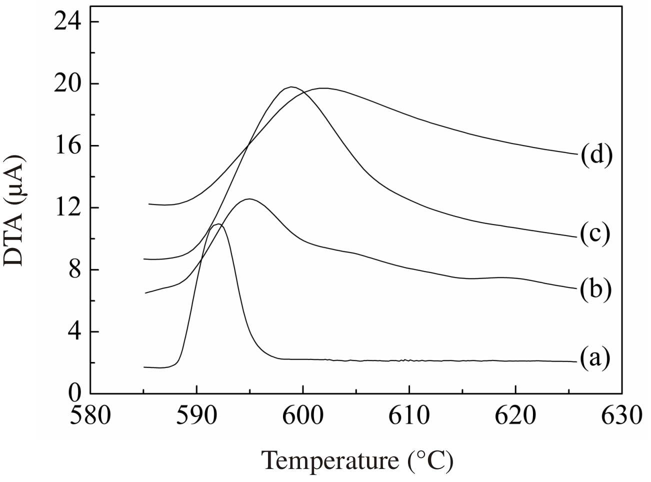

Fig. 7. DTA curves of equimolar NaCl-KF mixture obtained at different heating rates of (a) 5 K/min, (b) 10 K/min, (c) 15 K/min and (d) 20 K/min

Then $\ln(\beta/T_m^2)$-$1/T_m$ can be plotted (Fig. 8). By fitting four points using a straight line and setting its slope equal to -E/R, the activation energy of the reaction can be calculated. The reaction activation energy for the formation of NaF and KCl was 805 KJ/mol. Such a large value indicated that the solid state reaction between NaCl and KF was not easy. Therefore, the reaction would not take place until the eutectic liquid formed at 582 °C. In this case, liquid probably triggered the reaction.

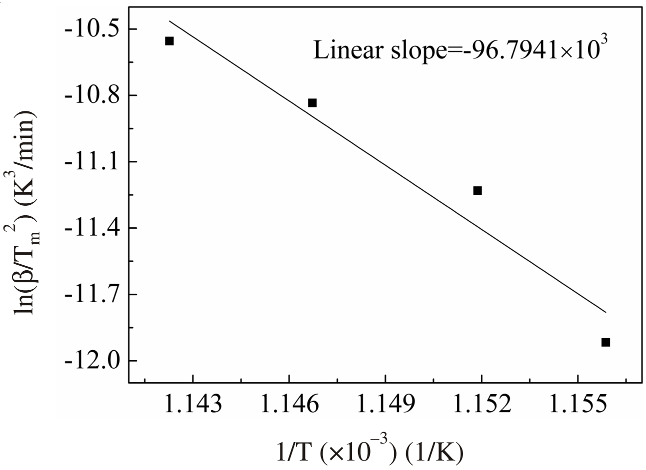

Fig. 8. Plot of $\ln(\beta/T_m^2)$-$1/T_m$ for the reaction as eqn. (2)

Conclusions

In the present study, the reaction between NaCl and KF was studied by thermodynamic calculation, DTA and XRD. The following conclusions can be drawn:

(1) Possible chemical reaction of NaCl with KF to form NaF and KCl from 25 to 750 °C was considered and the Gibbs free energy change ΔG was calculated. The negative ΔG indicates that chemical reaction of NaCl with KF may occur spontaneously.

(2) DTA results showed that the reaction between NaCl and KF should be occurred at 595 °C after a eutectic liquid formation at 582 °C. By Kissinger differential method, the activation energy of the reaction was calculated to be 805 KJ/mol. The appearance of liquid phase made the reaction rate increased greatly due to atom diffusion can be accelerated and triggered the reaction.

(3) X-ray diffraction observation for the products provided confirmation of the reaction between NaCl and KF. The diffraction pattern obtained gave good matches with NaF and KCl.

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