

Thermal Analysis, calorimetry and molten salts

A salt which is solid under standard temperature and pressure conditions and liquid at elevated temperatures can be designated as a molten salt. There is a growing interest for molten salts in different fields, including thermal energy storage, heat transfer, catalysis or chemistry. While for the two first cases, their interesting thermodynamic properties (heat capacity and thermal conductivity) are applied, in the two other cases they are used for their ability to dissolve substances (especially oxides, carbides, nitrides and metals).

High temperature calorimetry can bring key information on the thermal properties of pure or blends of salts, like melting / crystallization temperatures, heat of melting, heat capacity and heat of mixing and / or dissolution.

1. Molten salts in the nuclear industry and High Temperature Calorimetry

INTRODUCTION

Molten Salts are believed to be a good solution to replace water as a heat transfer medium in nuclear reactors. Their potential use in 4th generation nuclear power plants has renewed interest of the nuclear science community since ORNL (USA) recently started again project kept dormant since the 1960s. This move forward was accelerated by the Fukushima accident in Japan, as the power failure of the cooling circuit pumps of the reactors, lead to extreme water temperature, hydrogen formation and its subsequent explosion.

It isn't likely to happen in a so called fluoride salt high temperature reactor (FHR) because the molten salts have extremely high boiling point and extremely low vapor pressure. Moreover, new concepts of reactors employing liquid uranium fluoride based fuels instead of solid fuel are under study. In case of loss of control of the reactor, it leads to a stop of the reaction, so a stop of the heat production. It is thus qualified as "inherently safe" reactors.

But it makes then clear that there is a need to study complex molten salts phase diagrams, conduct a lot of dissolution experiments and measure the heat capacity of all of these materials and blends of materials.

EXPRIMENT

Some labs have already started producing experimental thermodynamic databases like the Joint Research Center (Institute of Transuranium Elements) where CALVET DC with HFDSC and Drop sensor are used by Dr Ondrej BENES and his team. They worked on the thermodynamic properties of the LiF–ThF₄ system potentially meant to be used together with ²³⁵U or ²³⁹Pu in the form of fluorides serving as startup fissile material [1].

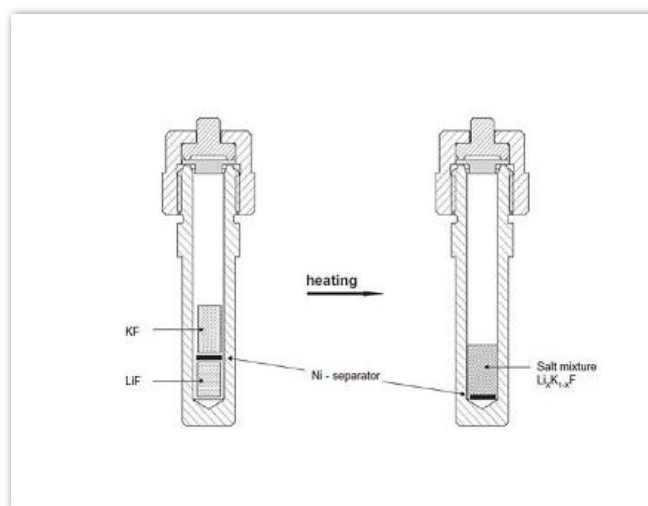


Figure 1 – special cell for determination of enthalpies of mixing involving a nickel based separator that melts before letting the two samples mix. From [1].

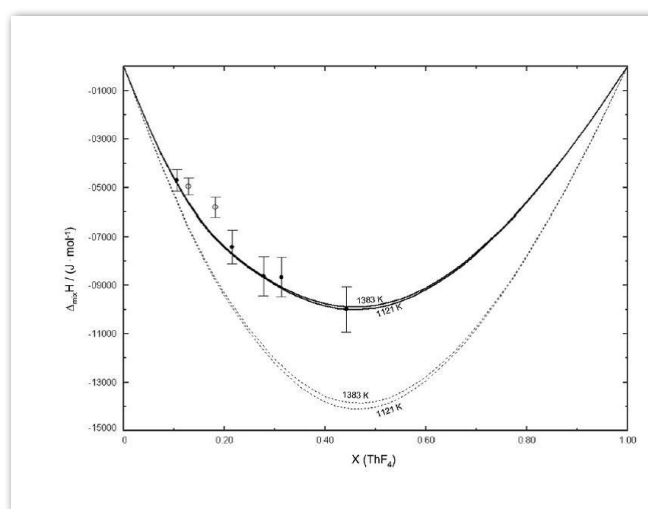


Figure 2 – Measured and simulated variations of enthalpies of mixing the LiF-ThF₄ system. From [1]

RESULTS AND CONCLUSION

The enthalpy of mixing of the LiF-KF and LiF-ThF₄ systems have been measured using an innovative temperature scanning method based on a CALVET DSC calorimeter and purposely designed closed cells including a nickel separator. CALVET DC is an isothermal or temperature scanning differential calorimeter with operating temperatures up to 1600°C and drop calorimetry capacities.

INSTRUMENT

CALVET DC

20°C to 1500°C



IMPROVED HEAT CAPACITY AND HEAT MEASUREMENTS WITH THE CALVET DC

- heat flux DSC up to 1600°C – for accurate heat capacity, heat, and glass transition measurements
- drop calorimetry up to 1500°C – for accurate heat capacity, heat of dissolution and heat of formation measurements

VARIETY OF ATMOSPHERE CONDITIONS

possible with multiple carrier and reactive gas options

CONVENIENCE AND ECONOMY

with one instrument and furnace for TGA, TG-DSC, TGDTA, DSC, DTA, and TMA up to 1600°C

2. Molten salts for solar power plants and Thermogravimetry

INTRODUCTION

Concentrated solar power plants use mirrors to concentrate sunlight on a target (receiver) which is subsequently intensely heated. This heat is then used to drive a heat engine (like a steam turbine) connected to an electrical power generator. Large amounts of heat need to be transferred and stored, due to the intermittent nature of this type of energy production. Today, thermal energy storage is thus a key issue for concentrated solar power plants. Molten salts are involved as heat transfer fluids in order to either directly transport the heat to the heat engine or to a heat storage system (for instance Phase Change Materials).

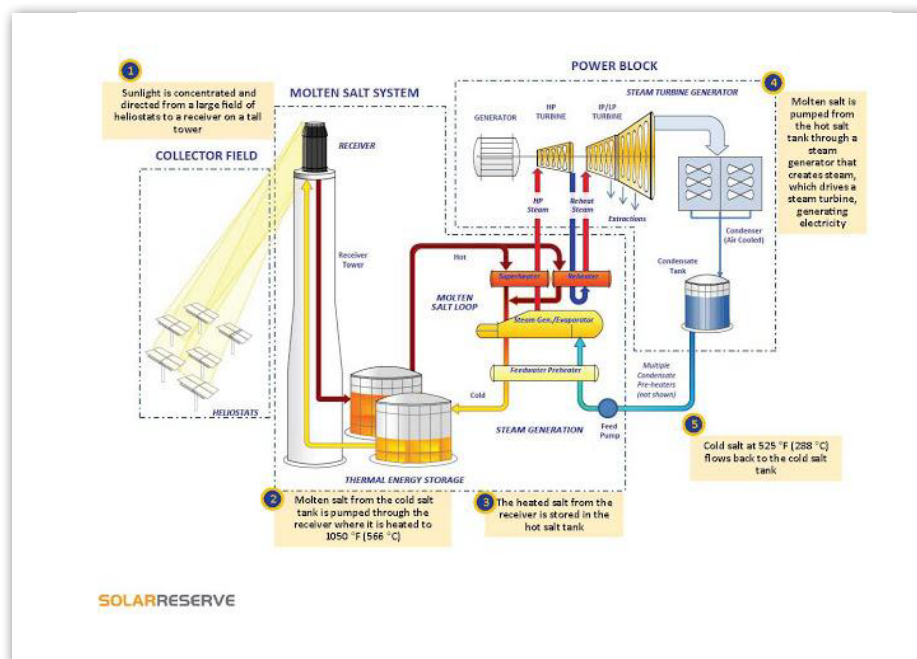


Figure 3 – Process diagram of Concentrated Solar Plant Technology (<http://www.solarreserve.com/>)

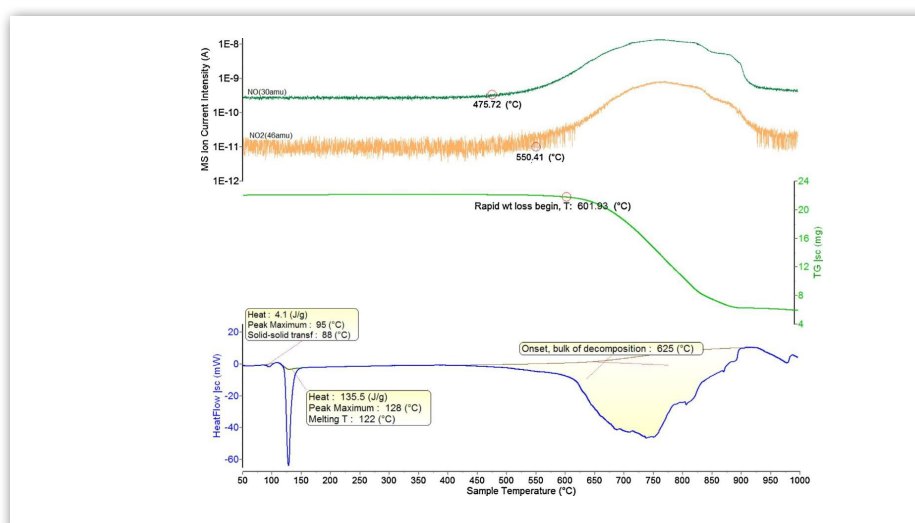


Figure 4 – TG, DSC and MS data for the decomposition of the $\text{LiNO}_3\text{-NaNO}_3\text{-KNO}_3$ salt in air atmosphere. From bottom to top: DSC, Mass Loss, Ion Current Intensity signals for NO_2 and NO as a function of temperature – From [2]

EXPERIMENT, RESULTS AND CONCLUSION

Rene I. Olivares from CSIRO in Australia studied the thermal stability of commercially available molten nitrite/nitrates salt for solar thermal energy storage in different atmospheres using the TG/DSC+MS coupled technique [2]. Temperature scanning experiments up to 1000 °C in atmospheres of argon, nitrogen, air and oxygen were conducted and allowed concluding that the thermal stability of the salt can be significantly enhanced by controlling the atmosphere. The maximum temperature of use of the salt was shifted up to between 650°C and 700°C under oxidizing atmosphere.

Reference: [1] E. Capelli et al., J. Chem. Thermodynamics 58 (2013) 110–116
[2] R.I. Olivares, W. Edwards / Thermochemica Acta 560 (2013) 34– 42

INSTRUMENT

THEMYS TGA

