# B. TECH PROJECT REPORT On Thermodynamic Properties Measurement using Knudsen Effusion Mass Spectroscopy

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# THERMODYNAMIC PROPERTIES MEASUREMENT USING KNUDSEN EFFUSION MASS SPECTROSCOPY

## A PROJECT REPORT

Submitted in partial fulfillment of the requirements for the award of the degrees

of

# **BACHELOR OF TECHNOLOGY**

in

Metallurgical Engineering and Materials Science Submitted by:

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# INDIAN INSTITUTE OF TECHNOLOGY INDORE DECEMBER 2019

#### **CANDIDATE'S DECLARATION**

I hereby declare that the project entitled **Thermodynamic Properties Measurement Using Knudsen Effusion Mass Spectroscopy** submitted in partial fulfillment for the award of the degree of Bachelor of Technology in Metallurgical Engineering and Materials Science completed under the supervision of **Dr. Sumanta Samal, Assistant professor, Metallurgical Engineering and Materials Science, IIT Indore and Shri. Uttam Jain, Scientific Officer – E, Material science division, BARC Mumbai** is an authentic work.

Further, I declare that I have not submitted this work for the award of any other degree elsewhere.

20/11/2019

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## **CERTIFICATE BY BTP GUIDES**

It is certified that the above statement made by the students is correct to the best of our knowledge.

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# PREFACE

This report on Thermodynamic Properties Measurement Using Knudsen Effusion Mass Spectroscopy is prepared under the guidance of Dr Sumanta Samal, Assistant professor, Discipline of Metallurgical Engineering and Materials Science, IIT Indore and Shri Uttam Jain, Scientific officer-E, BARC Mumbai

In this report I have measured the partial pressures and calculated the thermodynamic properties like enthalpy of vaporization, thermodynamic activities partial molar enthalpy of mixing and other thermodynamic properties of fluoride salts, Ni-Cr-Mo alloys which can be used in molten salt reactor and borosilicate glasses which are used in nuclear waste immobilization by using Knudsen effusion mass spectroscopy.

I have tried to the best of our abilities and knowledge to explain the content in a lucid manner. I have also detailed graphs and figures to make it more illustrative.

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#### ABSTRACT

In the field of Indian nuclear power, thorium has always had a prominent place due to large thorium deposits and limited uranium resources in India. To efficiently utilize the available resources in a sustainable manner A three-stage program (India's Three-Stage Nuclear Power Program) has been designed. Department of Atomic Energy (DAE) India has been focused in the field of utilization of thorium in the third stage of the nuclear power program. The most efficient method of fuel utilization in the third stage is by the molten salt reactor. BARC (Bhabha Atomic Research Centre) has designed an 850 MWe IMSBR (Indian molten salt breeder reactor) which has excellent safety and efficient fuel utilization. FLiNaK (Eutectic mixture of LiF-KF-NaF) and FLiBe (a mixture of LiF BeF<sub>2</sub> in the ratio of 2:1) are the best candidates for molten salt reactors which are used as a coolant. Hastelloys (Ni-Cr-Mo alloys) can be used for structural material for molten salts because of its high corrosion resistant from molten fluoride. Better understanding of the thermal properties of molten salt coolant and Hastelloys are required for design and analysis of the nuclear facilities. Apart from these, in nuclear industry, nuclear waste disposal is one of the major challenges. Glass vitrification is one of the best disposal methods used by many nuclear industries. For better safety and efficiency, it is essential to choose proper composition and processing route on the basis of thermodynamic stability.

In this study, vaporization behaviours of molten salt fluorides were done by Knudsen effusion mass spectroscopy (KEMS) in temperature range from 900-1000K. Hastelloys measurement were taken in the temperature range 1400-1500K and for borosilicate glasses 950-1050k. Vapor pressure and thermodynamic activities were computed by mass spectroscopy relations. From these thermodynamic parameters, the materials thermal stabilities were discussed. Knudsen effusion mass spectroscopy is most efficient method for analysing vapour species in equilibrium with condensed phase at very high temperature. This method enables identification of gaseous species and determination of individual partial pressures. Once partial pressure and its dependency with temperature is determined one can obtain vaporization behaviour, thermodynamic parameters like activity, enthalpy of vaporization, partial molar/molar quantities of enthalpy of mixing, free energy of formation, excess free energy and other thermodynamic functions which are essential for developing CALPHAD type thermodynamic descriptions.

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#### **CHAPTER 1**

#### **1 INTRODUCTION**

Material selection is an essential application of material science. Materials selection is made based on their properties, cost, availability among other characteristics. Most of the materials in engineering applications are to have better mechanical and physical properties. But in the case of high-temperature applications, it is required to know the material's thermal stability as well. High-temperature materials are used in different areas like aerospace, nuclear reactor, thermal power plant, etc.

Thermodynamic properties like thermodynamic activities, enthalpies, free energy, specific heat, and other partial molar properties will decide the stability of materials at high-temperature conditions. These thermodynamic properties are the basic criteria for selecting any material or any alloy for the use in high temperatures. There are electrochemical and calorimetric techniques to measure the thermodynamic properties, but these instruments are unable to work at high temperatures. Knudsen effusion mass spectrometer (KEMS) also known as high-temperature mass spectrometry can go as high as 2000°C via the electron bombardment furnace. There are mainly two techniques to study high-temperature vapor pressures: (1) Mass spectrometer combines with Knudsen cell or some other source of equilibrium vapor (2) Mass spectrometer combines with Langmuir or under non-equilibrium conditions. In the case of Knudsen cell mass spectroscopy (KEMS/KCMS), we can efficiently measure vapor pressure of the condensed phase at temperature as high as 2000°C with more accuracy. It is one of the most innovative methods for this use, which able to obtain information on vaporization processes and partial thermodynamic properties of components of the multi-component system at high temperatures.

In databases like JANAF SGTE, most of vapor pressure data are recorded using Knudsen effusion mass spectrometer. For developing CALPHAD (Calculation of Phase Diagrams) type thermodynamic descriptions, it is essential to know the thermodynamic functions, especially the activity of the elements [1]. It is crucial to know the activity or partial pressure of highly volatile species like Cr and Mn. These elements in the alloy for long periods at high temperatures can result in a change in its composition which could result in a change in its mechanical properties. By Knudsen effusion mass spectroscopy technique vapor pressure in the

order of 10-10<sup>-8</sup> Pa can be measured. Today several groups are applying KEMS to measure thermodynamic functions in multicomponent metallic and ceramic systems.

# **1.1 EFFUSION AND DIFFUSION**

The movements of gas molecules from one chamber to another can be divided into two. Effusion is defined as the movement of gas molecules from one chamber to another through a tiny hole where the mean free path of the molecule is larger than the hole diameter. Whereas in diffusion, it is the movement of gas molecules through one or more additional types of gas via random molecular motion. In diffusion, the movement of molecules are much more complicated as collisions occur between molecules that change the direction and speed of the molecules and can cause back diffusion. As a result of these collisions, the path a molecule travels in diffusion is made up of random straight, short segments.



Figure 1.1 (a) diffusion, (b) effusion

# **1.2 A HISTORICAL PERSPECTIVE OF KNUDSEN EFFUSION**

In the early 1900s, Martin Knudsen developed the Knudsen effusion method for vapor-pressure determination [2]. He studied the effusion through the near-ideal round and cylindrical orifices and using the kinetic theory of gases, he found that too much sample effused through the orifice when the pressure of the effusing vapor was high. He correlated these results with the mean-free path for the gaseous molecules and found that the orifice transmission probability increased when the ratio of mean-free path length to the orifice diameter (Knudsen number) was more than 10. This is used as a criterion for the distinction between molecular flow and the hydrodynamic flow. Thus, In the Knudsen effusion technique, molecular flow takes place and effusing species are in equilibrium with condensed phases in the Knudsen cell and outside the

cell vacuum is maintained.

In 1948 Ionov developed the mass spectrometer combined with the Knudsen effusion method to find the partial pressures of alkali metal halides [3]. This study was followed by Chupka and Inghram [4] as well as by Honig [5] to study the free evaporation behavior of carbon. Since that time, Knudsen effusion mass spectrometry, with its attractive features of high sensitivity and resolution under high vacuum conditions, has become a useful tool for the qualitative and quantitative detection of gaseous species effusing from the Knudsen cell. Almost all groups of inorganic materials were taken into investigations, such as borides, carbides, fullerenes, nitrates, sulphates, halides, metals, alloys, oxides, glasses, ceramics. taken from [6]

## **1.3 KNUDSEN AND LANGMUIR METHOD**

Knudsen and Langmuir method are similar methods to find vapour pressure. Langmuir calculated the vapour pressure of high melting metals from measurements of weight loss from the filament metal having a known area [7]. If the metal is at T<sup>o</sup>K and surrounded by its equilibrium vapour at P atm, the number of molecules striking a unit surface area is given by

$$v = \frac{Pc}{4KT} \tag{1.1}$$

Where c is the average molecular velocity. At equilibrium, the number of molecules striking the surface and sticking must be equal the number of leaving. The fraction of the molecules striking which stick is  $\alpha$ , the condensation coefficient. The number of molecules striking unit area is proportional to the equilibrium vapour pressure thus

$$v_{Sticking} = v_{escaping} = \alpha v_{Striking} = \frac{\alpha Pc}{4KT}$$
(1.2)

If m is the rate of weight loss per unit area then

$$P_{\text{equilibrium}} = \frac{m}{\alpha} \left(\frac{2\pi RT}{M}\right)^{\frac{1}{2}}$$
(1.3)

There are difficulties in obtaining satisfactory result by Langmuir method since one needs a surface of known area, an independent method for evaluating  $\alpha$  if equilibrium vapour pressure is desired. The ratio  $P_L/P_K$  can be used to obtain an independent value of  $\alpha$  where  $P_L$  is the Langmuir vapour pressure =  $\alpha P_{equilibrium}$  and  $P_K$  is the Knudsen vapour pressure.

In Knudsen method, the effusion of a gas through a hole of small diameter and infinitely small thickness is desired for equilibrium vapour pressure measurement. If the region into which the molecules escape is filled with gas of high density, collision may occur in the orifice or back-diffusion may return the molecule into the system. If the region is evacuated, re-entry is negligible. The number of molecules striking unit surface area in unit time is given by equation (1). With low pressure P<sub>1</sub> on one side of the hole and P<sub>2</sub> on the other, the pressures being such that the means free paths are at least ten times the diameter of the hole, the net rate of transfer of molecules is  $v_{1-2} - v_{2-1} = (P_1 - P_2) * c/4KT$  (1.4) If P<sub>2</sub> is equal to 0, the vapor pressure is given by

$$P_{\text{equilibrium}} = m \left(\frac{2\pi RT}{M}\right)^{\frac{1}{2}}$$
(1.5)

At pressure lower than 10<sup>-3</sup> atm, almost all molecules striking the hole escape. Interference can arise from the edge of the hole because of the thickness of the hole walls. In ideal Knudsen equation a hole with infinitely thin edge is assumed.

A difficulty in the Knudsen and Langmuir method is that of unequivocal identification of vapour species involved. In mass spectrometer combined with Knudsen/Langmuir system, identification can made of all molecules in vapour as long as they may be ionized to +1 ions by electron bombardment without spontaneous dissociation. The absolute vapour pressures can be calculated by comparing the intensity of substance under study with that of for a calibrating substance eg: Ag, Cu for which the vapour pressure is well known.

## **1.4 OBJECTIVES OF THIS PROJECT**

- Identify all gaseous species which are in equilibrium with the materials: Fluorides, Hastelloys, and borosilicate glasses.
- Measure the equilibrium partial vapor pressures and total vapor pressure of these materials by Knudsen effusion mass spectroscopy.
- Calculate the thermodynamic properties of gaseous molecules and condensed phases from the partial pressures and their temperature dependencies, for example, enthalpies and entropies of vaporization, thermodynamic activity partial Gibbs free energy of formation and analyze the results.

## **CHAPTER 2**

## LITERATURE REVIEW

#### 2.1 MATERIALS IN MOLTEN SALT REACTOR

India's three-stage nuclear power program is aimed at the optimum utilization of India's nuclear resource thorium. The three stages are (i) natural uranium-fuelled pressurized heavy water reactors (PHWRs), (ii) plutonium-fuelled fast breeder reactors (FBRs), including metallic fuelled ones and (iii) <sup>233</sup>U-fuelled systems [8]. The spent fuel of one stage is used as a resource for the subsequent stages. When the spent fuel is reprocessed to produce fuel for the next stage, it multiplies the energy potential of the fuel many-fold and greatly reduces the quantity of waste. As a long-term program, and to effectively utilize thorium for the third stage of its nuclear power program, India is working on the development of technologies for the molten salt breeder reactor (MSBR) [8], which can breed fissile material effectively. Molten salt reactor is a fission reactor where the fuel and coolant in molten salt form.

the coolants must have the following characteristics:

- Chemical stability at operating temperature (500–800°C).
- stability in a high radiation environment (for primary coolant only).
- Melting point as low as possible, preferably lower than 525°C.
- Large specific heat and thermal conductivity.
- Low vapor pressures that are substantially less than one atmosphere at operating temperatures and are thus not volatile.
- Compatible with high-temperature structural materials.

Several types of molten salts, including LiF-NaF-KF (46.5, 11.5, and 52 mol%, respectively; also known as FLiNaK), LiF-BeF2 (67 and 33 mol%, respectively; also known as FLiBe), and KCl-MgCl2 (67 and 33 mol%, respectively), have been suggested for molten salt reactor out of that FLiBe and FLiNaK has excellent properties discussed by [9-10]. FLiBe is been avoided due to its toxicity, so in this study, FLiNaK vaporization behavior has been studied.

Eutectic mixture (low melting point) is chosen so that salt will not solidify as it cooled in the heat exchanger. It is necessary to know the coolant salt vapors pressure and thermal stability at operating temperature since the reactor is designed to work at low pressure (latm pressure)

compare with conventional heavy water reactors. In this work vaporization behavior of FLiNaK was done by Knudsen effusion mass spectroscopy and calculated its vapor pressure, activity and other thermodynamic parameters. It is required to know if there is any selective vaporization of more volatile species resulting which can cause composition change thereby increase in the melting point (shift from eutectic composition) so chances of failure by solidification will be more.

# **2.1.1 HASTELLOYS**

Hastelloys are a group of corrosion-resistant nickel alloys, namely the Ni-Mo and the Ni-Cr-Mo alloys. Hastelloys contain varying amounts of Mo (up to 30 percent), Cr (up to 23 percent), Fe (up to 29 percent), and C (up to 0.15 percent). Some are alloyed with W, Si, Co, or Cu, V, Ta, Nb, and other elements [22]. Hastelloys have a unique combination of properties that provide them with significantly stronger corrosion resistance capabilities compared to traditional alloys. The stability of the molten salts with structural alloys was studied in [11]. Nickel and high-temperature alloys with dense Ni coatings are effectively inert to corrosion in fluorides. In chromium-containing alloys like Hastelloy N, Haynes 230, Hastelloy N shows the best corrosion resistance in fluorides, while Haynes 230 was the most resistant in chloride. In general, alloys with increasing carbon and chromium content are increasingly subject to corrosion by the fluoride salts FLiBe and FLiNaK due to the attack and dissolution of the intergranular chromium carbide[11].

In this work vaporization behavior of three alloys containing Ni-Cr-Mo was done by Knudsen effusion mass spectroscopy. Partial pressure, activity, and other partial thermodynamic properties were calculated to check the thermal stability of the alloy and to select the best composition of Hastelloy. It is important to know the effect of the composition of Ni and Mo on the activity of Cr since Cr is a more volatile compound also it can cause intergranular corrosion.

# 2.2 GLASSES FOR NUCLEAR WASTE VITRIFICATION

Nuclear waste immobilization is defined as the conversion of nuclear waste into a waste form by vitrification, embedding or encapsulation. It helps in handling the wastes, transporting, storage and disposal of radioactive wastes. The two main glass types that have been accepted for nuclear waste immobilization are Borosilicates and Phosphates. Vitrification involves the melting of waste materials with glassforming additives so that the final product incorporates the waste materials in a stable form. Vitrification should be performed at temperatures below 1200°C because of the volatility of fission products. In contrast to borosilicate melts molten phosphate glasses are highly corrosive to refractory linings, because of this behavior it is not widely used. The processing of vitrification can be seen from the figure (2.1)

In this work two sodium borosilicate glasses, one containing Ba another containing Ca were tested by using Knudsen effusion mass spectroscopy. It is necessary to know the total vapor pressure because of volatile loss of oxides can lead to composition change while processing in the molten state. Vaporization behaviors of both sodium borosilicate glasses and volatile fission products, which are incorporated into the glasses, are related to the safety requirements for the design of off-gas systems in the vitrification processes and the storage facilities. Also, it is essential to accumulate the knowledge of the chemical forms of vapors and the compositional dependence of their partial pressures over various sodium borosilicate glasses



Figure 2.1 Flow chart of glass vitrification

# **2.3 INTERPRETATION OF VAPOUR PRESSURE DATA**

If the effusion of vapor species from an orifice of the Knudsen cell satisfies the molecular flow condition, the partial vapor pressure p; of the vapor species i can be related with the measured Intensity as follows:

$$p_i = \frac{\kappa I_i T}{\sigma_i A_i} \tag{2.1}$$

Where K is a constant which depends on the Knudsen cell orifice size, volume, and position.  $I_i$  is the current(intensity) of the ion formed from the vapor species i alone, a is the ionization cross-section to form this ion, *T* the absolute temperature of the sample, and  $A_i$  is the natural isotopic abundance of Vapour species that measured.

The Ionization cross sections and Isotopic abundance of ions are listed in the table (2.1) in which ionization cross-sections are taken from [12] For compounds it is calculated by .75 multiplied by sum atomic cross-sections of atoms as proposed by Miller [13]

Ions	Ionization cross sections A <sup>o2</sup> (35eV)	Isotopic abundance	Ions	Ionization cross sections A <sup>o2</sup> (35eV)	Isotopic abundance
$Ag^+$	5.04	0.51839	Cu <sup>+</sup>	3.77	0.6917
Cr <sup>+</sup>	4.89	0.83789	K <sup>+</sup>	5.80	0.9325
Li <sup>+</sup>	2.57	0.9241	$KF^+$	4.91	0.9325
LiF <sup>+</sup>	2.49	.9241	$K_2F^+$	9.26	0.8695
$Li_2F^+$	4.42	0.8539	$K_3F_2^+$	14.18	0.8108
Li <sub>3</sub> F <sub>2</sub> <sup>+</sup>	6.92	0.7891	KLiF <sup>+</sup>	6.84	0.8617
Na <sup>+</sup>	3.07	1	NaLiF <sup>+</sup>	4.79925	0.9241
NaF <sup>+</sup>	2.87	1	NaKF <sup>+</sup>	7.22	0.9325
Na <sub>2</sub> F <sup>+</sup>	5.17	1	Ni <sup>+</sup>	5.46	0.6807
Na <sub>3</sub> F <sub>2</sub> <sup>+</sup>	8.04	1	NaO <sup>+</sup>	3.08	0.9975
NaBO <sub>2</sub> <sup>+</sup>	5.79	0.7966	$B^+$	2.58	0.8010
Na <sub>2</sub> BO2 <sup>+</sup>	8.104	0.7966	Ca <sup>+</sup>	10.04	0.9694

Table 2.1 Electron ionization cross section and isotopic abundance of ions

For the reaction at T°K,

$$M(s \text{ or } l) \rightleftharpoons M(g) \tag{2.2}$$

$$\Delta G_T^o = \Delta H_T^o - T \Delta S_T^o = -RT ln(P_M)$$
(2.3)

If  $\Delta C_p \approx constant$  for the reaction,

$$\Delta H_T^o = \Delta H' + \int_{T'}^T \Delta C_p dT = \Delta H' + \Delta C_p (T - T')$$
(2.4)

Similarly,

$$\Delta S_T^o = \Delta S' + \int_{T'}^T \frac{\Delta C_p dT}{T} = \Delta S' + \Delta C_p ln(\frac{T}{T'})$$
(2.5)

Where T' is a reference temperature, usually 298K.

$$ln(P_M) = -\frac{\Delta G_T}{RT} = -\frac{\Delta H_T}{RT} + \frac{\Delta S_T}{R}$$
(2.6)

For the reaction (2.2)  $\Delta H_T$  and  $\Delta S_T$  will be enthalpy and entropy of sublimation/vaporization.

#### 2.3.1 Thermodynamic Activity of a component in a solution:

At temperature T<sup>o</sup>K, the thermodynamic activity of a component/element in a state is defined as the ratio of fugacity of the substance in that state to its fugacity in standard state,

Activity of 
$$i = a_i = \frac{f_i}{f_i^o}$$
 (2.7)

In a condensed solution,  $f_i$  is the fugacity of the component i in the solution at the temperature T, and  $f_i^o$  is the fugacity of pure i (the standard state) at the temperature T. If the vapor in equilibrium with the condensed solution is assume to be ideal, then  $f_i = p_i$ , in which case

$$a_i = \frac{p_i}{p_i^o} \tag{2.8}$$

If component i exhibit Raoultian behavior, then

$$a_i = X_i \tag{2.9}$$

A non-ideal solution is one which the activities of components are not equal to their mole fractions. The activity coefficient of a component is defined as the ratio of the activity of the component to its mole fraction i.e., for the component i

$$a_i = \gamma_i X_i \tag{2.10}$$

If The value of  $\gamma_i$  is greater than unity, then the component i is said to exhibit a positive deviation from Raoultian ideal behavior, and, if  $\gamma_i < 1$ , then the component I is said to exhibit a negative deviation from Raoult's law

# 2.3.2 Partial Molar Gibbs free energies of Components

The molar Gibbs free energy of the solution for a binary A-B solution at fixed temperature and pressure, is

$$G = X_A \bar{G}_A + X_B \bar{G}_B \tag{2.11}$$

Where  $\bar{G}_A$ ,  $\bar{G}_B$  are, respectively, the partial molar Gibbs free energies of A and B in the solution. The change in Gibbs free energy accompanying the solution of 1 mole of A in the solution is

$$\Delta \bar{G}_A^M = \Delta \mu_A = \bar{G}_A - \bar{G}_A^o = RT \ln(a_A) = \Delta H_{mix} - T \Delta S_{mix}$$
(2.12)

Since  $G = G^{ideal} - G^{excess}$ , the excess partial Gibbs free energy of A in solution is given by

$$\Delta \bar{G}_A^{Excess} = \Delta \mu_A^E = RTln(a_A) - RTln(X_A) = RTln(\gamma_A)$$
(2.13)

The molar Gibbs free energy of mixing and excess free energy of solution is given by,

$$\Delta G = X_A \Delta \bar{G}_A + X_B \Delta \bar{G}_B = RT(X_B \ln(a_B) + X_A \ln(a_A))$$
(2.14)

$$\Delta G^{excess} = X_A \Delta \bar{G}_A^{Excess} + X_B \Delta \bar{G}_B^{Excess}$$
(2.15)

## **CHAPTER 3**

## **3.1 KEMS COMPONENTS**

## 3.1.1 Two Ultrahigh Vacuum Chambers

KEMS consists of two chambers; one is the Knudsen cell chamber and another is the ion chamber consist of a mass spectrometer. Both kept under ultrahigh vacuum (10<sup>-10</sup> mbar in ion chamber, 10<sup>-7</sup> mbar in Knudsen chamber) and are separated by a metallic shutter which is used for opening the Knudsen chamber while the ion chamber is still in ultrahigh vacuum. These chambers are made of Stainless Steel which works under 1100°C, and for protection, water-cooling is provided in the annular space of the Knudsen cell chamber and also for the Knudsen cell furnace assembly. The Knudsen cell furnace assembly kept on a small platform attached to a X-Y. The X-Y positioner used to align the Knudsen cell with the ion chamber of the mass spectrometer. Both the chambers connected to the high vacuum pumps. To be able to distinguish the ions that are formed due to ionization of effusing vapor species from those in the background, a shutter for the molecular beam is provided just above the cell assembly. The closed, and when open, it will let the effusing beam enter the ion-source. Figure 3.1 shows the schematic of KEMS instrument.

#### 3.1.2 Knudsen Cell Furnace

There are techniques like resistance heating, induction heating and electron bombardment heating for attainment and control of high temperature. Here we are using the EB mode of heating based on the following considerations: relatively more precise heating of the cell and attainment of the desired high temperatures at relatively faster heating rates are possible; open and compact structure of EB furnace makes it more readily compatible with the vacuum systems; and good heat shielding can be provided which can aid better temperature control. The Knudsen cell is placed in an outer cup, which has three holes at the bottom such that the cup could be slid onto a tripod of tungsten legs. The cup is heated by radiation and by the emission of electrons from two tungsten filaments encircling it. It also has Ta heat shields all around. While the support rods in the EB are all mainly of Ta, some components which would see T  $\leq$  1000 K are made of Stainless Steel (SS). The power supply for the EB furnace was made by

BARC itself. AC power supply is used to heat the filaments, and the electron bombardment of the Knudsen cell is achieved by keeping the latter at varying DC voltages depending upon the temperature requirement. DC power supply (Ionix, BARC) which has one unit for Voltage Regulation and another unit for current regulation. The heat shields help in maintaining the temperature of the Knudsen cell uniform, keeping the power requirement less, in reducing the out-gassing that would result from the heating of the surroundings otherwise, and in protecting the inner wall of the vacuum chamber from excessively heated. For further protection to the vacuum vessel, water-cooling is provided in the annular space of the Knudsen cell chamber and also for the Knudsen cell furnace assembly flange. The furnace could be safely heated to and maintained at T as high as ~ 2600 K. A platform is made under the furnace for keeping a prism having an incident angle of 90 degrees which allows the infrared beam to the pyrometer. Pyrometer is set by moving in 3 axes and one tilting axis such that temperature will be maximum (set to the center of the beam).

Since EB mode of heating required that the Knudsen cell is kept at some positive potential relative to the two filaments that heat the Knudsen cell and since the experiments that will be carried out in this system will mostly correspond to high temperatures (T > 1200 K), a non-contact method, optical pyrometry was sought to be employed for temperature measurements. Two important requirements exist 1) provision of a blackbody hole at a suitable location in the sample holder; and 2) provision of suitable arrangements to view the blackbody hole conveniently from outside the Knudsen assembly. a black body hole provided at the bottom of the cell will eliminate most of the difficulties associated with top- and side-viewing.



Figure 3.1 schematic of KEMS Figure 3.2 Electron bombardment Furnace Assembly [14]

# 3.1.3 Vacuum pumps

The ultrahigh vacuum is used to prevent the loss of ions through collisions with gas molecules present in air and helps to reduce background ions in spectrometer. The vacuum is established through Scroll pumps and Turbo molecular pumps. Scroll pumps are used to minimize the pressure low up to 1mbar, so that the turbo molecular pump can start also it removes the exhaust from turbo pump during normal operations.

# Scroll Pump:

The two main components of this scroll pump are a stationary scroll and an identical moving scroll. The moving scroll is mounted on a spigot, so that the rotation of the shaft produces an orbital motion of this member. The moving scroll is constrained from rotating by an arrangement which ensures that it maintains the same angular position during the orbiting motion. The arrangement is shown in Fig3.2, which indicates how gas is taken in at the inlet and transferred to the outlet. The main problem in achieving a good vacuum is leakage across the edge of the moving scroll and the stationary scroll. A spring-loaded gasket is normally fitted to ensure good sealing along the moving scroll to overcome this problem.

Turbo-molecular Pump:

These pumps work on the principle that gas molecules can be given momentum in a desired direction by repeated collision with a moving solid surface. In a turbo-molecular pump, a rapidly spinning fan rotor 'hits' gas molecules from the inlet of the pump towards the exhaust in order to create or maintain a vacuum. It consisting of a quickly rotating rotor blade and stationary stator blade pair. As the gas molecules enter through the inlet, the rotor, which has a number of angled blades, hits the molecules. Thus, the mechanical energy of the blades is transferred to the gas molecules. With this newly acquired momentum, the gas molecules enter into the gas transfer holes in the stator. This leads them to the next stage where they again collide with the rotor surface, and this process is continued, finally leading them outwards

through the exhaust.





Figure 3.3 Transport of gas in a scroll mechanism

Figure 3.4 Schematic of Turbopump

#### 3.1.4 Quadrupole Mass Analyzer:

In Ion chamber the vapor species are ionized by electron bombardment (having energy 35eV), These ions will accelerate towards Quadrupole analyzer. The quadrupole mass spectrometer (QMS) is the most popular mass analyzer used for vacuum partial pressure measurements because of its rapid scanning capability compact size, linear mass scale and relatively low cost. The quadrupole analyzer is a device which uses the stability of the trajectories in oscillating electric fields to separate ions according to their m/z ratios. The QMS uses a mass filter that consists of four parallel conductive rods arranged in a square array with opposite rods connected electrically in parallel Ions from a source enter an end of the quadrupole mass filter near the axis drifting parallel to the rods (defined as the z-axis) with a kinetic energy of 315 eV. The combination of a direct-current (dc) potential and radio-frequency (rf) potential applied to the rods accelerates the ions perpendicular to the z-axis; transmission through the quadrupole potential field of the rod assembly occurs for ions in a narrow mass range. Low M/e ions move nearly in phase with the applied RF voltage and are accelerated to large x and y displacements. These light ions collide with the rods and are neutralized and lost from the beam. High M/e ions do not gather sufficient x or y velocity during the rf cycle to achieve much displacement, but the dc potentials give a constant acceleration that centers the ions between the rods with positive potential and attracts the ions to the rods with negative potential where the ions collide with the rods and are neutralized. Between the high mass and low mass extremes, there is a range of M/e ions that can oscillate with small amplitudes and drift through the rod structure without striking the rods. These ions are transmitted to the detector. The value of M/e that is transmitted depends on the amplitude of the rf voltage

#### 3.1.5 Ion current Detector:

After the separation according to their m/z ratio soothe task is to be further detection then results to amplify the produced electron pulses after that these pulses are need to be stored in a database of the computer. An electron multiplier is used here to detect the ions. The collected ions hit the surface of the electron multiplier material and produce electrons further these electrons get accelerate towards a secondary surface from which the avalanche of the electrons are released. The production of this cascade of electrons results in electron current pulses which further amplified and recorded in database system. The induced sinusoidal current having a frequency

which is proportional to m/z ratio of the ions while the intensity of signal reflects concentration of sample. These induced current frequencies further result in an image current and then converted mathematically by Fourier transformation to obtain spectrum in computer.

# **3.1.6 Ionization Gauges:**

Two BA ionization pressure gauges are used to measure the pressure in both chambers. Ionizing particles enter the ionizing space containing gas molecules at reduced pressure from a thermionic source. Inelastic collisions of the electrons with gas molecules produce ion/electron pairs these ions are collected by the suitably biased lower electrode. The electrometer in the external circuit measures the ion current as an indirect measure of gas pressure.

Some contents are taken from Raj [14]. Figure 3.4 shows the instrument used for this project



Figure 3.5 KEMS instrument

# **3.2 EXPERIMENTAL METHODOLOGY:**

For each measurement, The Knudsen chamber is opened to insert the sample (before opening the chamber, both chambers are isolated by a shutter (only after furnace cooldown) and vacuum is removed from the Knudsen chamber) and carefully remove the Ta shields and replace the

cell. After closing the furnace, the vacuum system can be turned on and the isolation shutter can be opened once vacuum in the furnace chamber reaches 10<sup>-5</sup>mbar or less. EB furnace heating can be achieved by applying a voltage and current to the W wire after the water-cooling system turned on. When heating started, a lot of foreign particles gets evaporated and reduce the vacuum, so keep furnace at low temperature (100-200°C) by turning off and on the current supply and let the volatile gases to escape. Once the vacuum in the Knudsen chamber reaches 10<sup>-6</sup>mbar and in ion chamber 10<sup>-9</sup> mbar, the mass spectrometer can turn on for measurement. This mass spectrometer has two modes of measurements which are profile mode and MIB. The profile mode is a plot between intensity and m/z which used to find the accurate mass value of the sample for the measurement. MID is the plot between Intensity and time for selective masses that we are interested in, which is used here for measuring intensity at different temperatures in open and closed conditions of molecular beam shutter. For each measurement samples were taken in powder or small pieces (to have large surface area). Knudsen cell material is chosen to be one that doesn't react with the sample (usually oxides for metal samples/ metals for oxides samples). The cell dimensions are inner diameter 7.5 mm, outer diameter 10.0 mm, height: 10.0 mm with lid having knife-edged orifice with diameter .2/.1 mm. Pyrometer calibration is done by finding the melting point of pure metals. Instrument calibration is done by pure Silver, Cr or other pure metals whose partial pressures are well defined. From the pressure calibration constant of the Knudsen cell, one can calculate the partial pressure of any samples. Measurements are done once the vacuum is stabilized and reached to less than 10<sup>-6</sup>mbar in the Knudsen chamber and 10<sup>-9</sup> mbar in the mass spectroscopy chamber in heated condition for better results. After each experiment furnace is heated to high temperature (1600-1700°C) in an empty cell so that residuals that are deposited from the previous experiment will evaporate off which will take around 5-6 hrs.

## **CHAPTER 4**

## 4 RESULTS AND DISCUSSION

## 4.1 Temperature calibration of radiation pyrometer

The temperature calibration was done by measuring the melting point of silver and Ni. It was found that silver melts at temperature 65°C more than the actual melting point and in the case of Ni it was found that melting occurs at temperature 74°C more than the actual melting point. So, a straight-line plot has been made for the remaining temperature range to find the actual temperature. These measurements were repeated 3-4 times for more confidence in the results.

## 4.2 Setting Mass Spectroscopy parameters

Silver measurements were done at different values of parameters like electron energy, multiplier voltage, emission current and set the values which can give enough counts and least error. The electron energy was set to 35eV for ionizing the vapors and emission current set to  $100\mu$ A. The secondary electron detector's multiplier voltage was found by plotting ion count of H<sub>2</sub>O vs. multiplier voltage and finding the Knee of the plateau scan (multiplier voltage is 200V passed the knee of the plateau scan) which is 2350V (from figure 4.1).



Figure 4.1 Plateau scan of multiplier voltage

## 4.3 VAPORIZATION STUDY OF Ag AND FINDING CELL CONSTANT

Pure Silver (99.999%) taken in graphite cell with Ta lid was studied in KEMS in the temperature range of 1000-1100K. In the course of the measurement, the temperature of the Knudsen cell was decreased step-by-step between 1000K and 1100 K. The mass spectrometer data at different temperatures in the open and closed conditions of the beam shutter is plotted with respect to time. The intensity was chosen by taking the average in that region.



Figure 4.2 Mass spectrometer data of Silver

Figure 4.2 shows the intensity of Ag+ ion of mass/charge ratio 106.8 m/z (taken the peak intensity in that value range by profile mode in mass spectrometer) which corresponds to isotope 107 also the temperature during the measurement shown in the figure. It can be seen that the intensities are decreasing while decreasing the temperature.





From the equation (2.1), partial pressure is directly related to IT, and from equation (2.6), ln (P) vs 1/T gives a straight line. Figure 4.3 which is the plot between Ln (IT) vs reciprocal of temperature gives a straight-line and slope will be equal to the  $-\Delta H_{vaporization}/R$  (The constant in Pressure IT relation won't affect the slope but just shift the graph).

From the graph, the enthalpy of vaporization of Ag at temperature range 1000-1100K was found to be 279.6+2.8KJ/mol (By multiplying slope with negative of the gas constant, From equation (2.6)) which is matches with literature value [15-16] (278.5KJ/Mol). The K<sub>cell</sub> (Pressure calibration constant) is equal to  $2.5X10^{-14}$  barA<sup>o2</sup>/counts\*Kelvin.

# 4.4 Vaporization study of Cr and finding cell constant

Similar Method of Ag was done for Cr in alumina and yttria coated Ta Knudsen cell with tantalum lid in the temperature range of 1320-1520K. In the course of the measurement, the temperature of the Knudsen cell was decreased step-by-step between 1520K and 1320K. The mass spectrometer data is given in figure (4.4) also the Plot between Ln (IT) and reciprocal of Temperature is given in figure (4.5).





Figure 4.4 shows the intensity of Cr+ which has a mass to charge ratio 51.70 which corresponds to its isotope 52. 13 readings have been done for getting a better result.



Figure 4.5 Logarithm of (Cr+ ion intensity x temperature) vs reciprocal of temperature

Figure 4.8 is plotted by the same method in case of Ag, and the graph doesn't show any variation from the straight line

From figure (4.5) the enthalpy of vaporization is calculated as  $379.3\pm2.3$ KJ/Mol which is close to literature data [15,16] (384KJ/mol), also pressure calibration constant calculated is 2.41E-14 barA<sup>o2</sup>/counts\*Kelvin which is matching with silver pressure calibration constant value.

# 4.5 VAPORIZATION STUDY OF FLURIDES

Fluorides include pure salts NaF, KF, LiF all have purity 99.99% and their ternary eutectic mixture FLiNaK which has a composition (46.5, 11.5, and 52 mol%, for LiF, NaF and KF respectively). Pure salt's partial pressures were calculated to measure the activity and other thermodynamic properties also to check the vaporization behavior of fluorides.

## 4.5.1 VAPORIZATION STUDY OF PURE LiF

Pure LiF (99.99%) sample taken in the platinum cell which was kept inside graphite Knudsen cell (Cell volume is same as that of alumina cell) and tantalum lid (Pt was used because of fluoride reaction with graphite). In the course of measurement, the temperature was decreased in step by step between 1029-954K. Ions of  $Li_3F_2^+$ ,  $Li_2F^+$ ,  $Li^+$ ,  $LiF^+$  were observed in the mass spectrometer. There were no other ions detected which were coming from the sample. The intensity time plots of these ions are given in figure 4.6 also the temperature during the measurement shown in the figure.



Figure 4.6 Mass spectrometer data of LiF

From the figure the intensity is in order of  $Li^+>Li_2F^+>LiF^+>Li_3F_2^+$ . In these studies, it assumed that  $Li^+$  ions are formed mostly from monomer LiF (Fragmentation  $LiF + e^- => Li^+ + F^- + e^-$ ) and small amount from dimer ( $Li_2F_2+e^-=>Li^++LiF_2^-+e^-$ ). In case of  $LiF^+$  the most contribution is from by monomer (ionization  $LiF + e^- => LiF^+ + 2e^-$ ) followed by small amount from dimer ( $Li_2F_2+e^-=>LiF^++LiF^-+e^-$ ). In  $Li_2F^+$  contribution is by dimer ( $Li_2F_2+e^-=>Li_2F^++F^-+e^-$ ) and in  $Li_3F_2^+$  contribution is by trimer ( $Li_3F_3+e^-=>Li_3F_2^++F^-+e^-$ ). These reactions are discussed in [17]. Ions that are detected are only coming from monomer, dimer and trimer. These assumptions were made based on the ions appearance potential curve obtained for pure LiF.



Figure 4.7 partial pressure in bar (logarithmic scale) vs reciprocal of temperature of LiF sample

Partial pressures were calculated from equation (2.1), ionization cross sections at 35eV were taken from the table (2.1) and the plot between partial pressure (in logarithmic scale) and reciprocal of Temperature is given in figure (4.7). since the percentage of contribution from different molecules for the ions are unknown the vapor pressures of monomer, dimer, and trimer cannot calculate separately but the partial pressure of ions can be calculated which may be

contributed by two or more types of gaseous molecules (in case of Li+ monomer and dimer) and the total vapor pressure shown in the same graph (by adding all partial pressure of ions) which is in range of 10<sup>-6</sup>-10<sup>-7</sup>Bar in temperature range 954-1029K. The enthalpy of vaporization calculated from the slope of total vapor pressure is 290.45+1.304KJ/Mol.

# 4.5.2 VAPORIZATION STUDY OF PURE NaF

Pure NaF (99.99%) sample taken in the platinum cell which was kept inside graphite Knudsen cell and tantalum lid was measured in the temperature range of 900-1000K. In the course of measurement, the temperature was decreased in step by step between 1000-900K. Ions of Na<sub>3</sub>F<sub>2</sub><sup>+</sup>, Na<sub>2</sub>F<sup>+</sup>, Na<sup>+</sup>, NaF<sup>+</sup> were observed in mass spectrometer. But the counts of Na<sub>3</sub>F<sub>2</sub><sup>+</sup> is so low that variation with respected to temperature cannot be determined. Ions are formed the same reactions as that in LiF discussed above. The mass spectrometer data is given in figure (4.8) also the Plot between partial pressure (in logarithmic scale) and reciprocal of Temperature is given in figure (4.9).





Figure 4.8 shows the intensity of ions when the shutter closed and open conditions also the temperature with respect to time. It can be seen that the ions intensities are in the order of  $Na^+>Na_2F^+>NaF^+>Na_3F_2^+$  which is the same as that of LiF.



Figure 4.9 Partial pressure in bar (logarithmic scale) vs reciprocal of temperature of NaF sample

From figure 4.9, the partial pressure from Na+ is highest followed by Na2F+ and NaF. It can be seen that the plot of NaF+ shows some deviation from straight at low temperatures because of low counts. The enthalpy of vaporization calculated from the slope of total vapor pressure is  $275.31 \pm 2.751$ KJ/Mol.

## 4.5.3 VAPORIZATION STUDY OF PURE KF

Pure KF (99.99%) sample taken in the platinum cell which was kept inside graphite Knudsen cell and tantalum lid was measured in the temperature range of 953-985K. In the course of measurement, the temperature was decreased in step by step between 985-953K. Ions of  $K_3F_2^+$ ,  $K_2F^+$ ,  $K^+$ ,  $KF^+$  were observed in the mass spectrometer. Ions are formed the same reactions as that in LiF and NaF which was discussed above. The mass spectrometer data is given in figure

(4.10) also the Plot between partial pressure (in logarithmic scale) and reciprocal of Temperature is given in figure (4.11).



Figure 4.10 Mass spectrometer data of KF

From figure 4.10 the intensities of ions are in the order of  $K^+>K_2F^+>KF^+>K_3F_2^+$  ( $K_3F_2^+$  is not included here because of its low counts compare with other ions) which is same as that of previous fluoride behavior. It can be seen that the counts are much higher than that of pure NaF and LiF samples at similar temperatures.



Figure 4.11 Partial pressure in bar (logarithmic scale) vs reciprocal of temperature of KF sample

From figure 4.11, the partial pressure from  $K^+$  is highest followed by  $K_2F^+$  and  $KF^+$ . The enthalpy of vaporization calculated from the slope of total vapor pressure is 205.713+13.26KJ/Mol and it shows larger vapor pressure compare with NaF and LiF. Here the K3F2+ is excluded from the figure.

# 4.5.4 Vaporization study of FLiNaK

FLiNaK (46.5-11.5-42 mol %) sample taken in the platinum cell which was kept inside graphite Knudsen cell and tantalum lid was measured in the temperature range of 900-1010K. In the course of measurement, the temperature was increased in step by step between 900-1010K.



Figure 4.124 mass spectrometer data of effective ion intensities (removed the background intensity) for FLiNaK sample

Ions of Li<sub>3</sub>F<sub>2</sub><sup>+</sup>, Li<sub>2</sub>F<sup>+</sup>, Li<sup>+</sup>, LiF<sup>+</sup>, K<sub>3</sub>F<sub>2</sub><sup>+</sup>, K<sub>2</sub>F<sup>+</sup>, K<sup>+</sup>, KF<sup>+</sup>, Na<sub>3</sub>F<sub>2</sub><sup>+</sup>, Na<sub>2</sub>F<sup>+</sup>, Na<sup>+</sup>, NaF<sup>+</sup>, NaKF<sup>+</sup>, KLiF<sup>+</sup>, NaKF<sup>+</sup> were observed in mass spectrometer which can be seen from the figure (4.12). NaKF<sup>+</sup>, KLiF<sup>+</sup>, NaKF<sup>+</sup>, NaKF<sup>+</sup> were formed from fragmentation of NaKF<sub>2</sub> KLiF<sub>2</sub> NaKF<sub>2</sub> respectively (e.g. NaKF<sub>2</sub>+e<sup>-</sup>=>NaKF<sup>+</sup>+F<sup>-</sup>+e<sup>-</sup>). Since both <sup>23</sup>Na<sub>2</sub>F<sup>+</sup> and <sup>39</sup>K<sup>7</sup>LiF<sup>+</sup> m/z values are matching, <sup>40</sup>K<sup>7</sup>LiF intensity was measured and from that the intensity of <sup>39</sup>K<sup>7</sup>LiF obtained (from vapor pressure of

KLiF<sub>2</sub>) and subtracted from total intensity which corresponded to both  ${}^{23}Na_2F^+$  and  ${}^{39}K^7LiF^+$ and calculated intensity from  $Na_2F^+$ . The mass spectrometer data is given in figure (4.13). The first four graphs show the intensities of all the ions (different scales for different graphs) and the last graph shows the temperature during the measurement.





The Plot between partial pressure (in logarithmic scale) and reciprocal of Temperature is given in figure (4.14). from the figure it can be seen that most of the pressure is coming from K<sup>+</sup> (in the range of  $10^{-6}$ bar) then KLiF<sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, K<sub>2</sub>F<sup>+</sup>, etc. Here the straight line shows some deviation in NaF<sup>+</sup>, Li<sub>3</sub>F<sub>2</sub><sup>+</sup>, K<sub>3</sub>F<sub>2</sub><sup>+</sup>, Na<sub>3</sub>F<sub>2</sub><sup>+</sup> which are because of high residual counts in case of NaF<sup>+</sup> and very low counts of trimer ions.



Figure 4.14 Partial pressure in bar (logarithmic scale) vs reciprocal of temperature of FLiNaK sample

The activity of LiF, KF and NaF were calculated using equation (2.8) and plotted with respect to reciprocal of temperature in logarithmic scale is given in figure (4.14). For calculating the partial pressure of LiF in FLiNaK, all the ions which contains Li+ are considered (Li<sup>+</sup>, NaLiF<sup>+</sup>, KLiF<sup>+</sup>, Li<sub>2</sub>F<sup>+</sup>, LiF<sup>+</sup>, Li<sub>3</sub>F<sub>2</sub><sup>+</sup>), similar for remaining NaF and KF. from the figure it can be seen that the slopes are positive which means that the partial molar enthalpy of formation of all components are positive (consist of partial molar enthalpy of mixing and enthalpy of melting since FLiNaK is in liquid-state whereas pure LiF NaF and KF are in solid-state in the measured temperature) and the slope is highest for NaF followed by LiF and KF also from activity point of view NaF shows positive deviation whereas LiF and KF shows negative deviation.



Figure 4.15 Activity of fluorides (logarithmic scale) vs reciprocal of temperature

## 4.5.5 Discussion

By Knudsen effusion mass spectroscopy study the vapor species present on LiF, NaF, KF and FLiNaK were identified and partial pressures of these fluorides were calculated which are given in table (4.1). It was found that the vapour pressures are in the order of NaF<LiF<KF at the temperature range 900-1000K. For all three pure salts, it is found that the partial pressures of monomer, dimer, and trimer are in the order of Monomer>dimer>Trimer. The enthalpies of vaporization of salts are in the order of LiF>NaF>KF. In the case of FLiNaK sample, from the figure (4.14), partial pressure is highest for KF followed by KNaF<sub>2</sub>, LiF and NaF. The graphs of Li<sub>3</sub>F<sub>2</sub><sup>+</sup> Na<sub>3</sub>F<sub>2</sub><sup>+</sup> Li<sub>3</sub>F<sub>2</sub><sup>+</sup> were showing deviation because of low counts from mass spectroscopy. Also due to a lot of background intensity the graph of NaF<sup>+</sup> was showing some deviation. The total vapor pressure of FLiNaK is in the order of  $10^{-6}$  bar which is less than the vapor pressure of pure KF (of the order of  $10^{-5}$  bar) at temperature 1000K. The partial pressure of salts in FLiNaK are listed in the table (4.1). Figure (4.18) is obtained from finding the activity by using equation (2.12). The activity calculated for NaF shows positive deviation from Raoultian ideal

behavior whereas in LiF and KF it showing negative deviation from Raoultian behavior. Even though the activities are negatively deviating from Raoultian ideal behavior, the slope is showing large positive value (according to equation 2.12 it should show negative value since enthalpy of mixing is negative for salt that showing negative deviation in activity) which due to the slope is partial molar enthalpy of formation of that composition which is composed of two enthalpies which are partial molar enthalpy of mixing and enthalpy of melting since the FLiNaK at measuring temperature is in liquid state whereas pure fluoride salts are in solid-state. So, to find the partial molar enthalpy of mixing one needs to subtract enthalpy of melting of pure fluoride salt from the partial molar enthalpy of formation at that temperature. The Raoultian activity coefficient at temperature 1000K calculated using equation (2.10) are 0.495, 1.968 and 0.395 for LiF, NaF, KF respectively. Thermodynamic activity shows negative deviating which means that thermodynamically KF/LiF as pure in the condensed phase is less stable than KF/LiF in FLiNaK at the same temperature. The partial molar Gibbs free energy of formation Gibbs free energy of vaporization can be calculated by using equations (2.12), (2.13), (2.3), respectively.

 Table 4.1 thermodynamic parameters of Fluoride salts

Compoun	Vapor pressure curve (P in bar, Tin K)	Temperatu	Vapor	Activity/Enth
ds		re	Pressure	alpy of
		range (K)	(bar) at	vaporization
			1000K	at 1000K
LiF(99.99	$Log P_{LiF} = -(1.51 \pm 0.0068) \ 10^4/\text{T} + (9.27 \pm 0.068)$	954-1028	1.2682E-06	290.45+1.30
%)		К		4KJ/Mol
NaF(99.9	$Log P_{NaF} = -(1.438 \pm 0.0143) \ 10^4/\text{T} + (8.336 \pm 0.014$	907-1005	9.0219E-07	275.31+2.75
9%)	0.15)	Κ		1KJ/Mol
KF(99.99	$Log P_{KF} = -(1.0746 \pm 0.692) \ 10^4/\text{T} + (5.841 \pm 0.72)$	953-985 K	1.24E-05	205.713+13.
%)				26KJ/Mol
FLiNaK	$Log P_{LiF} = -(1.121 \pm 0.009) \ 10^4/\text{T} + (4.6 \pm 0.10)$	950-1006	2.9865E-07	0.2354
		K		
	$Ln(a_{LiF}) = (3958.7 \pm 99.39)/T - (4.59 \pm 0.1)$			

$Log P_{KF} = -(7.659 \pm 0.0114) \ 10^{4}/\text{T} + (1.9 \pm 0.11)$ $Ln(a_{KF}) = (3086.9 \pm 114.68)/\text{T} - (3.68 \pm 0.11)$	2.0136E-06	0.1618
$Log P_{NaF} = -(8.732 \pm 0.0183) \ 10^{4}/\text{T} + (2.04 \pm 0.18)$ $Ln(a_{NaF}) = (5648.6 \pm 183.8)/\text{T} - (6.2 \pm 0.18)$	2.0589E-07	0.2282

# 4.6 Vaporization Study of Hastelloys and Pure Ni, Cr, Mo:

The compositions of Hastelloys that have been tested using Knudsen effusion mass spectrometer are given in table 4.2 at all these compositions the alloy contains  $\gamma$  phase.

Table 4.2 Composition of Hastelloys

Alloys	Ni (at%)	Cr (at%)	Mo (at%)
Alloy1	77	23	0
Alloy2	71	23	6
Alloy3	74	13	13

# 4.6.1 Vaporization study of Pure Ni:

Pure Ni (99.99%) sample taken in yttria coated Ta Knudsen cell with tantalum lid was measured in the temperature range of 1495-1586K. In the course of measurement, the temperature was increased in step by step between 1495-1586K.



Figure 4.16 Mass spectrometer data of Ni

Figure 4.16 shows the intensity of Ni with respect to time also the temperature during the measurement shown in the same figure. The counts of Ni are quite low compared with Cr and Ag.



Figure 4.17 Partial pressure in bar (logarithmic scale) vs reciprocal of temperature of Ni sample

Figure 4.17 shows the partial pressure calculated by using equation (2.1) with respect to the reciprocal of temperature. The enthalpy of vaporization of Ni at this temperature range calculated by using equation (2.6) is 411.03±8.70KJ/Mol.

# 4.6.2 Vaporization Study of Mo:

Pure Mo (99.99%) sample taken in yttria coated Ta Knudsen cell with tantalum lid was measured in the temperature range of 2092-2211K. In the course of measurement, the temperature was increased in step by step between 2092-2211K.

Figure 4.18 shows the intensity of Mo with mass/charge ratio 94.87m/z which corresponds to <sup>95</sup>Mo isotope (abundance 15.87%). Since there was a lot of residual in the mass range 98, <sup>98</sup>Mo (abundance 24.29%) was avoided from the measurement. The temperature during the measurement also shown in the same figure. It can be seen that the ions counts are in the range

of 10-50 counts/sec even at a temperature as high as 2200K which due to its low vapor pressure also its low isotopic abundance (15.87%).







Figure 4.19 Partial pressure in bar (logarithmic scale) vs reciprocal of temperature of Mo sample

Figure 4.19 shows the partial pressure calculated by using equation (2.1) with respect to the reciprocal of temperature. The enthalpy of vaporization of Ni at this temperature range calculated by using equation (2.6) is 696.84+44.55 KJ/Mol.

# 4.6.3 Vaporization study of Hastelloy 1:

Hastelloy 1 sample (prepared by vacuum arc melting unit and composition measured by EDS, The sample cut to small pieced by using diamond cutter) taken in alumina Knudsen cell with new tantalum lid (pressure calibration constant is calculated by using pure silver and found out to be 1.00E-12 barA<sup>o2</sup>/counts\*Kelvin) was measured in the temperature range of 1475-1529K. In the course of measurement, the temperature was decreased in step by step between 1529-1475K.



Figure 4.20 Mass spectrometer data of Hastelloy 1

Figure 4.20 shows the intensities of Ni and Cr in alloy 1, also the temperate during the measurement shown in the same figure. The intensity of Cr is comparatively higher than that of

Ni even though the alloy contains more Ni than Cr it is because of the partial pressure of Cr is larger than that of Ni in the same temperature



Figure 4.21 Partial pressure in bar (logarithmic scale) vs reciprocal of temperature of Hastelloy 1 sample

Figure 4.21 shows the partial pressure calculated by using equation (2.1) with respect to the reciprocal of temperature. Also, the partial pressure of pure Cr and Ni are shown in the same figure for comparing the partial pressures. For both Cr and Ni, the partial pressures are lower than that of their pure states. The difference in the slope of the partial pressure of element in alloy and standard state is the partial molar enthalpy of formation in here it is partial molar enthalpy of mixing. It can be seen that the slope of P<sub>cr</sub> in the alloy is lesser than that of P<sup>o</sup><sub>cr</sub> pure which means that it requires lesser enthalpy to vaporize compare with pure means the stability of Cr in the alloy (condensed phase) is less compared to the pure state. similarly, for Ni in alloy shows a larger slope compare with pure which means Ni is stable in alloy compare with pure state

The calculated activity is plotted in figure 4.22 with respect to reciprocal of temperature also the activity coefficient calculated using equation (2.10) plotted in the second graph. From the graph, it can be seen that activity shows a slight positive deviation in the case of Cr and a negative deviation in the case of Ni. The partial molar enthalpy of mixing of Ni and Cr are  $-23.18\pm5.7$ ,  $13.87\pm8.12$  KJ/mol respectively.



Figure 4.22 Activity and activity coefficient of Ni and Cr (in logarithmic scale) vs reciprocal of temperature

## 4.6.4 Vaporization study of Hastelloy 2:

Hastelloy 2 sample (cut by using diamond cutter) taken in alumina Knudsen cell with new tantalum lid was measured in the temperature range of 1427-1470K. In the course of measurement, the temperature was increased in step by step between 1427-1470K.

Figure 4.23 shows the intensities of Ni and Cr and Mo in alloy 2 also the temperate during the measurement shown in the same figure. The intensity of Cr is comparatively higher than that of Ni even though the alloy contains more Ni than Cr. There is no evident change in the counts of Mo when there is any change in the temperature which means that the partial pressure of Mo is

negligibly small compared with Cr and Ni. Only four readings have been done due to fault in the voltage supply to the electron bombardment furnace which was because of failure in the W filament.



Figure 4.23 Mass spectrometer data of Hastelloy 2



Figure 4.24 Partial pressure in bar (logarithmic scale) vs reciprocal of temperature of Hastelloy 2 sample

Figure 4.24 shows the partial pressure calculated by using equation (2.1) with respect to the reciprocal of temperature. Also, the partial pressure of pure Cr and Ni are shown in the same figure for comparing the vapor pressures. For both Cr and Ni, the partial pressures are lower than that of their pure states. It can be seen that the slope difference is more evident than in alloy 1.



Figure 4.25 Activity and activity coefficient of Ni and Cr (in logarithmic scale) vs reciprocal of temperature

The calculated activity is plotted in figure 4.25 with respect to reciprocal of temperature also the activity coefficient calculated using equation (2.10) plotted in the second graph. From the graph, it can be seen that activity shows positive deviation in case of Cr and negative deviation in the case of Ni. The partial molar enthalpy of mixing of Ni and Cr are  $-106\pm7.9$ ,  $45.718\pm4.2$ KJ/mol respectively. Yaqoob et al [18] showed that in Ni-Mo system, Ni shows large negative deviation and Jindal [19-20] et al showed that in Cr- Mo system, Cr shows positive deviation which is consistent with the result from Hastelloy 1 and 2 where the addition of Mo increases the activity of Cr and decreases the activity of Ni. The partial molar enthalpy of mixing also increased with the addition of Mo (in magnitude).

# 4.6.5 Vaporization study of Hastalloy3

Hastelloy 1 (99.99%) sample (cut by using diamond cutter) taken in alumina Knudsen cell with new tantalum lid was measured in the temperature range of 1447-1532K. In the course of

measurement, the temperature was increased in step by step between 1447-1532K.

Figure 4.26 shows the intensities of Ni and Cr and Mo in alloy 3 also the temperate during the measurement shown in the same figure. There is no evident change in the counts of Mo when there is any change in the temperature



Figure 4.26 Mass spectrometer data of Hastelloy 3



Figure 4.27 Partial pressure in bar (logarithmic scale) vs reciprocal of temperature of Hastelloy 3 sample

Figure 4.27 shows the partial pressure calculated by using equation (2.1) with respect to the reciprocal of temperature. Also, the partial pressure of pure Cr and Ni are shown in the same figure for comparing the vapor pressures. For both Cr and Ni, the partial pressures are lower than that of their pure states. The slope differences are increased compares with the previous two alloys.



Figure 4.28 Activity and activity coefficient of Ni and Cr (in logarithmic scale) vs reciprocal of temperature

The calculated activity is plotted in figure 4.28 with respect to reciprocal of temperature also the activity coefficient calculated using equation (2.10) plotted in the second graph. From the graph, it can be seen that activity shows a positive deviation in the case of Cr and negative deviation in the case of Ni. The partial molar enthalpy of mixing of Ni and Cr are -110.15 $\pm$ 12.6, 52.16 $\pm$ 1.603 KJ/mol respectively. As discussed before the addition of Mo increased the activity of Cr and decreased the activity of Ni. The partial molar enthalpy of mixing also increased with the addition of Mo (in magnitude).

#### 4.6.6 Discussion

By Knudsen effusion mass spectroscopy study of vaporization was done for three Hastelloys and pure Ni, Cr, Mo materials. The partial pressure and thermodynamic activities of Ni and Cr are listed in the table (4.3). For pure Ni, Cr, Mo the vapor pressures are in the order of Cr > Ni> Mo. The enthalpy of vaporization of Ni, Cr, Mo are in the order of Cr<Ni<Mo (not considered temperature dependence). It was found that for alloy 1 (Ni-23Cr), Ni shows a negative deviation from Raoult's ideal behavior whereas Cr shows a positive deviation from ideal behavior. For Hastelloy 2 (Ni-23Cr-6Mo), Ni activity (also activity coefficient) decreased compared with alloy 1 whereas in the case of Cr the activity (also activity coefficient) got increased. Since Mo partial pressure cannot be determined at this temperature, activity or partial enthalpy of mixing cannot calculate for Mo. From the figures (4.28,4.25) It shows that the activity/activity coefficient of Cr is increased with Mo content and Ni activity/coefficient is decreased. In Alloy 3, similar to Alloy2 it shows a large negative deviation for Ni and positive deviation for Cr. From alloy 2 and 3 the enthalpy of mixing of Cr and Ni got increased with the addition of Mo. From these results, it shows that Hastelloys with less Cr is suitable for molten salt reactor also it is better to add alloys elements that can reduce Cr activity since Mo cannot be avoided for this system. The calculated data are given in the table 4.3

Metals/Al	Vapor pressure curve (P in bar, T in K)	Temperatur	Partial pressure	Enthalpy of
lovs		e	(bar)/ Enthalpy of	vaporization in
5				the temperature
		range (K)	mixing at 1470K	range /Activity
				at 1470K
Cr	$Log P_{Cr} = -(1.98 \pm 0.0125) \ 10^4/\text{T} + (6.94 \pm 0.088)$	1316-1514	2.96224E-07	379.3±2.3KJ/
		K		Mol
Ni	$Log P_{Ni} = -(2.14 \pm 0.045) \ 10^4/\text{T} + (7.09 \pm 0.29)$	1495-	2.57261E-08	411.03+8.70
		1586K		KJ/Mol
Мо	$Log P_{Mo} = -(3.64 \pm 0.23) \ 10^4/\text{T} + (7.84 \pm 1.07)$	2092-	1.197E-17	696.84+44.55
		2211K		KJ/Mol
Hastello	$Log P_{Ni} = -(2.32 \pm 0.027) \ 10^4/\text{T} + (7.9 \pm 0.19)$	1475-	-23.18±5.7KJ/mol	0.58
v 1	$L_{7} D = (1.027 \pm 0.0429) 10^{4} / T \pm ((.15 \pm 0.29))$	1529K	12 07 10 12 1/	0.21
	$Log P_{Cr} = -(1.93 / \pm 0.0428) 10^{-7} / 1 + (6.15 \pm 0.28)$		13.8/±8.12 KJ/mol	0.31
1				

Table 4.3 Thermodynamic parameters of Hastelloys

Hastello	$Log P_{Ni} = -(2.7 \pm 0.0409) \ 10^4/\text{T} + (10.51 \pm 0.2)$	1427-	-106±7.9KJ	0.52
y 2		1470K	KJ/mol	
	$Log P_{Cr} = -(1.77 \pm 0.0223) \ 10^{4}/\text{T} + (5.09 \pm 0.15)$		45.718±4.2KJ	0.3357
			KJ/mol	
Hastello	$Log P_{Ni} = -(2.77 \pm 0.065) \ 10^4/\text{T} + (10.89 \pm 0.44)$	1447-	-110.15±12.6KJ	0.4078
у 3		1532K	KJ/mol	
	$LogP_{Cr} = -(1.73 \pm 0.0083) \ 10^{4}/\text{T} + (4.84 \pm 0.056)$		52.16±1.603	0.248
			KJ/mol	0.340

# 4.7 VAPORIZATION STUDY OF SODIUM BORO-SILICATE GLASSES:

Composition of Borosilicate glasses that were tested are given in the table 4.4

Glasses	SiO <sub>2</sub> (at%)	B <sub>2</sub> O <sub>3</sub> (at%)	Na <sub>2</sub> O(at%)	BaO/CaO(at%)	TiO <sub>2</sub> (at%)	Al <sub>2</sub> O <sub>3</sub> (at%)
Barium-Glass	35	25	25	10 (BaO)	2	3
Calcium-Glass	35	25	30	5 (CaO)	2	3

Table 4.4 Composition of Sodium Borosilicate glasses

# 4.7.1 Vaporization study of Barium glass:

The barium glass sample taken in platinum cell which kept in yttria coated Ta Knudsen cell with tantalum lid was measured in the temperature range of 1004-1103K. In the course of measurement, the temperature was decreased in step by step between 1103-1004K. The ions observed were  $Na^+ NaBO_2^+$ ,  $NaO^+$ ,  $B^+$ ,  $Na_2BO_2^+$  there was no sign of other ions like  $Ba^+$  or other Ba oxide compounds. These ions are coming from ionization of sodium metaborate (NaBO<sub>2</sub>) or its dimer (Na<sub>2</sub>B<sub>2</sub>O<sub>4</sub>).

Figure 4.29 shows the intensities of ions also the temperature during the measurement. It can be seen that the intensities are in the order of  $Na^+>NaO^+>NaBO_2^+>Na_2BO_2^+>B^+$ . The ions observed here are coming from  $NaBO_2$  and  $Na_2(BO_2)_2$  which already discussed by [21].



Figure 4.29 Mass spectrometer data of Barium glass



Figure 4.30 Partial pressure in bar (logarithmic scale) vs reciprocal of temperature of Ba-Glass sample

Figure 4.30 shows the partial pressure of ions, it can be seen that partial pressure are in order of  $Na^+>NaO^+>NaBO_2^+>B^+>Na_2BO_2^+$  here B+ shows higher partial pressure than  $Na_2BO_2^+$  even though intensities are large because of high ionization cross-section (the probability of ionizing the molecule) of  $Na_2BO_2^+$ 

#### 4.7.2 Vaporization study of Ca borosilicate:

The calcium glass sample taken in platinum cell which kept in graphite coated Ta Knudsen cell with new tantalum lid was measured in the temperature range of 946-1011K. In the course of measurement, the temperature was increased in step by step between 946-1011K. The ions observed were Na<sup>+</sup> NaBO<sub>2</sub><sup>+</sup>, NaO<sup>+</sup>, B<sup>+</sup>, Na<sub>2</sub>BO<sub>2</sub><sup>+</sup> and Ca<sup>+</sup> there was no sign of other ions like CaO<sup>+</sup> or other Ca oxide mixture or any silica compounds. These ions are coming from ionization of sodium metaborate (NaBO<sub>2</sub>) or its dimer (Na<sub>2</sub>B<sub>2</sub>O<sub>4</sub>) except Ca<sup>+</sup>, which is formed by ionizing CaO.

The mass spectrometer data is given in figure (4.31).it shows that the ion intensities are in the order  $Na^+>NaO^+>NaBO_2^+>Na_2BO_2^+>B^+$ 



Figure 4.31 Mass spectrometer data of Ca-Glass

Figure 4.32 shows the partial pressure of ions, it can be seen that partial pressure are in order of  $Na^+>NaO^+>NaBO_2^+>Ca^+>B^+>Na_2BO_2^+$  here B+ shows higher partial pressure than  $Na_2BO_2^+$  even though intensities are large because of high ionization cross-section (measure of probability of ionizing the molecule) of  $Na_2BO_2^+$ . Here Ca shows deviation from the straight line because of its least intensity and large ionization cross-sections or may due to excessive evaporation during measurement.



Figure 4.32 Partial pressure in bar (logarithmic scale) vs reciprocal of temperature of Ca-Glass sample

## 4.7.3 Discussion

By Knudsen effusion mass spectroscopy vaporization study was done for two borosilicate glasses. The vapour pressures and enthalpy of vaporizations of both glasses are given in the table (4.5). It is found that the vapor pressure of Ca-borosilicate shows high compare to Ba-borosilicate even though Ba is easily evaporating compare with Ca. The enthalpy of vaporization of Ba-glass is more compare with Ca glass. The vapor species observed are

monomer and dimer of sodium metaborate. In the case of Ca glass, a small amount of Ca+ observed which may from CaO or other Ca compounds whereas in Ba glass there weren't any Ba ions or any ions that contain Ba observed which means that Ba is quite stable in borosilicate matrix. So, from these analyses, Ba glass shows better stability of oxides compared with Caglass at this composition. The high vapor pressure in Ca glass due to more Na<sub>2</sub>O in the system compare to Ba glass also due to less stability because of CaO. Ba as radioactive isotope can be incorporated into the glass with this composition since there was no evaporation of Ba or its oxide observed. The partial pressure calculated by using this instrument can be used to compute the vaporization loss of the volatile species like sodium metaborate while glass processing which is important to get the desired composition of glass after the vitrification also for designing off-gas systems.

Compoun	Vapor pressure curve (P in bar, Tin	Temperatur	Vapor	Enthalpy of
d	K)	e	Pressur	vaporization
		range (K)	e at	(KJ/mol)
			1000K	
Ba-Glass	$LogP = -(1.417 \pm 0.0327) \ 10^{4}/\text{T} +$	1000-1103	2.187E-	
	(7.51±	Κ	07	271.36±6.26
	0.30)			
Ca-Glass	$LogP = -(0.9025 \pm 0.0304) \ 10^4/\text{T} +$	946-1011K	5.308E-	
	$(3.75 \pm 0.30)$		06	172.78±5.81
				9

Table 4.5 Thermodynamic parameters of borosilicate glasses

#### **CHAPTER 5**

#### **5.1 CONCLUSION**

Vaporization behavior, partial pressures and thermodynamic activities of fluorides in FLiNaK have been determined with particularly high accuracy and precision by using Knudsen effusion mass spectrometer. The measurements were performed in the temperature range 900-1000K using Knudsen Cell Mass Spectrometry. Pressure calibrations were done by using pure silver (in the temperature range of 900-1000K) and chromium (in the temperature range of 1300-1400K) and other pure metals for better results.

From Knudsen effusion mass spectroscopy studies of LiF, KF, NaF, it was found that the vapor pressures of pure salts are in the order of KF>LiF>NaF. In Pure Fluoride salts ions of M+, MF+, M2F+, M3F2+ are detected by the mass spectrometer (where M=Na, K, Li). These ions are corresponding to its monomer, dimer, and trimer which are in the gaseous state. The dimer and trimer are formed from a gaseous monomer reaction. M+ ions can be contributed by mostly monomer and a small amount by dimer and trimer. The vapor pressure of Monomer is highest and followed by dimer and least for trimer. There is no sign of other gaseous species that are coming from the sample. Apart from monomer, dimer, and trimer of the constituent of FLiNaK vapors of NaKF<sub>2</sub>, LiKF<sub>2</sub>, and NaLiF<sub>2</sub> were observed from mass spectroscopy which are formed by gaseous monomers reaction. The vapor pressure of FLiNaK is very low (order of 10<sup>-6</sup>bar at 1000K) compare to the molten salt reactor pressure (1atm) and other salts like FLiBe. So, by vapor pressure, it is evident that FLiNaK is suitable for the molten salt reactor. From the activity point of view, NaF is showing positive deviation from Raoultian behavior but KF and LiF are showing negative deviation in the temperature range 900-1000K. This implies that the NaF has more tendency to evaporate in FLiNaK than in pure NaF sample. Since both LiF and KF have very low activity and total vapor pressure of FLiNaK is quite low, this material is the best candidate for the molten salt reactor from a thermodynamic point of view.

Vaporization study of three Hastelloys samples have been done in the temperature range 1400-1500K. Partial pressure, activity, and other thermodynamic parameters have been calculated using standard thermodynamic equations. For calculating thermodynamic activity, the partial pressures of pure samples were also measured. It is found that in Ni-23Cr alloy Ni shows negative deviation and Cr shows positive deviation from Raoult's ideal behavior. With addition of Mo, the Cr activity got increased and Ni activity reduced (in alloy 2). The partial molar enthalpy of mixing of Cr (+ve value) and Ni (-ve value) also increased (magnitude) with the addition of Mo. This result is consistent with the values in the alloy 3. From these results, the alloy should contain least Cr (best for corrosion resistance) and small amounts of other alloying elements which can decrease the activity of Cr and having high corrosion resistance to molten salts. larger Mo is desired since the activity of Ni is decreasing with the addition of Mo.

Vaporization of two borosilicate glasses have been done in temperature range 950-1050K. The vaporizing behavior and partial pressures have been determined. It is found that Ca containing glass shows larger vapor pressure compare with Ba contained glass. In the case of Ca glass, a small amount of Ca+ observed which may be coming from CaO or other Ca compounds whereas, in Ba glass, there weren't any ions observed which are coming from Ba containing compounds. which means that Ba is quite stable in the borosilicate matrix. There wasn't any intensity coming from ions of other oxides like Al2O3 TiO2 SiO2. The glass containing Ba is comparatively suitable for vitrification because of low vapor pressure. Also, the vapor pressure of glass can be used for finding the volatile loss while processing in the vitrification also for designing the off-gas system.

#### **5.2. FUTURE SCOPE**

The materials that have been tested here have enormous applications in the nuclear industry. This work can give the thermodynamic stabilities of these materials which can be used to select suitable materials for the applications also thermodynamic functions that have been calculated by this project can be used for modeling of these materials properties. The activity behavior of Cr and Ni when some other alloying elements are added like Fe, W can give a better understanding of selecting the best Hastelloy for the molten salt reactor. In the future one can test the thermodynamic properties of FLiBe for comparison with FLiNaK, also the effect of the thermodynamic property when nuclear fuel added to the salt in the form of fluorides (for selecting primary molten salt where it contains  $UF_4$ -ThF<sub>2</sub> dissolved in it) and the vaporization behavior of nuclear materials. In case of glasses with more measurements with different compositions can give a better understanding of the volatile behaviors of these glasses also volatile behaviour of radioactive elements containing these glasses can give a better understanding of the high temperature stability of these vitrified products.

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