ABSTRACT

Energy security is one of the most important topics today. Every possible effort is being made to harness energy from different sources and improve the efficiency of energy production. Much of the research in energy sector is directed towards obtaining better understanding of the materials pertinent to energy production systems, especially their behaviour at high temperatures. Reliable thermodynamic data are required to predict such behaviour. Vapor pressure data offer a very good means of obtaining many thermodynamic parameters. The Knudsen Effusion Mass Spectrometric (KEMS) method in particular has several advantages over other conventional methods of vapor pressure measurement. The work presented in this thesis essentially pertains to KEMS.

The first part of the work presented here is about the vaporization studies conducted on the Fe-Al and Ni-Al binary systems, which find extensive applications in heat exchange systems turbines etc. These alloys, often termed as technical alloys, have many desirable properties like corrosion and oxidation resistance, low density, higher melting point, very good thermal conductivity and better forging quality. Reliable thermodynamic activity data on these alloy systems, particularly those concerning the B2 phase, are required to understand chemical and self diffusion in them.

The second part is about the construction of a new KEMS facility for the specific purpose of conducting vaporization studies on radioactive and air-sensitive substances and about the gas analysis studied conducted using this facility. The vaporization studies on nuclear fuel materials will help to understand the fuel behaviour, fuel-clad, coolant-clad and fuel-coolant interactions. Some exploratory vaporisation experiments were conducted with this home-built KEMS facility. Some gas analysis studies were also performed using this facility on the fission gas released from the irradiated fuel pins of the Fast Breeder Test Reactor (FBTR).

The Fe-Al and Ni-Al systems have been studied by various workers, using different techniques such as the isopiestic method, calorimetric method, EMF method and the KEMS method. Apart from inconsistencies among the data obtained by these methods, the activities of the individual components of these alloys are not available in wide temperature and composition ranges especially for the B2 phase, which is
particular importance. In the first chapter, a historical introduction to the previous work done by various workers using different methods is given. The need to conduct careful vaporization studies at wide temperature ranges covering the entire B2 phase composition in order to get reliable activity data for both the components is also emphasized.

Since vapor pressure measurement was chosen in this study, a brief account of the various vapor pressure measurement techniques is given in the second chapter. Methods such as the static method, isopiestic method, transpiration method and the various methods based on the Knudsen effusion technique are explained. Since the effusion method forms the basis of this study, it is discussed in greater detail than are the other methods. The KEMS method finds an even more detailed discussion. The primary purpose of this study was to obtain reliable vapor pressure and activity data, from which various thermodynamic parameters could be deduced. Therefore, details about using the Second and Third law methods and also the Gibbs-Duhem integration method to obtain such information from the measured quantities are also given. Finally, a very brief account of the EMF and Calorimetric methods is also included because many earlier studies on the Fe-Al and Ni-Al alloys were conducted using these two techniques.

The measurements on the Fe-Al and Ni-Al alloy systems were conducted at the Institute for Materials and Processes in Energy Systems (IWV-2), Forschungszentrum, Juelich, Germany. The Chapters III and IV are devoted for the description of the KEMS studies on these alloy systems. A brief description of the mass spectrometer employed and the preparation methods of the alloy samples used are given. The exact composition and its uniformity throughout the alloy sample are very important. This is especially so in the case of Ni-Al, since this alloy showed a very strong dependence of activity with composition (nearly a four fold change within a composition change of ~15 at%) around stoichiometric composition. Special preparation and characterization techniques were used. 11 alloy samples for Fe-Al and 13 alloy samples of Ni-Al with different compositions corresponding to the B2 phase were used in the present study.

Precision and sensitivity are unique features of a mass spectrometric measurement. When it comes to KEMS, accuracy of the measured temperature and the pressure calibration methods also assume great importance. During the course of the regular measurements, some important observations were made. An error between the different
ranges of the range selection switch of the mass spectrometer and an error at the extremes of the different measurement ranges of the optical pyrometer were identified. The high hydrocarbon backgrounds that existed also had an effect on the measured data. Corrective measures taken to account for or minimize these problems helped to obtain highly reliable data for these alloy systems.

Measurements were made in wide temperature ranges whenever possible. In the case of Fe-Al samples, measurements in temperature ranges as large as 400 K were made for many samples. The Ni-Al system had a different challenge. Since composition had a very strong influence on activity, in order to minimize the composition change during vaporization, the measurements on these alloy samples had to be performed at much lower upper pressure limit with minimum measurement time.

The standard evaluation procedure of calculating the partial pressure from ion intensity was followed, both for the Fe-Al and Ni-Al systems. The relationship used was

\[ p_i = \frac{kT}{\sigma_i} \sum_j I_{ij} \]  ......................................................... 1

where \( p_i \) and \( \sigma_i \) are the partial pressure and the ionization cross section of the vapor species 'i'. \( I_{ij} \) is the ion intensity of the ion 'j' representing species 'i'.

Considering Fe-Al system for example, the constant \( k_{Fe} = \frac{k}{\sigma_{Fe}} \) was determined by means of experiments on pure Fe before and after measurements with the alloy samples and the mean value of the constant obtained was used for the calculation of pressure. Therefore

\[ p_{Fe} = k_{Fe} \cdot I_{Fe}^+ \cdot T \]  ......................................................... 2
\[ p_{Al} = k_{Al} \cdot I_{Al}^+ \cdot T \]  ......................................................... 3

The constant \( k_{Al} \) was obtained from the relationship

\[ \frac{k_{Al}}{k_{Fe}} = \frac{\sigma_{Fe}}{\sigma_{Al}} \]  or  \[ k_{Al} = k_{Fe} \cdot \frac{\sigma_{Fe}}{\sigma_{Al}} \]  ......................................................... 4
The ionization cross section ratio, $\frac{\sigma_{Fe}}{\sigma_{Al}}$, required for this purpose was calculated before carrying out any experiment with an alloy sample, by conducting a series of measurements with the pure elements, to obtain a ratio (varying by not more than $\sim 5\%$).

The usual sequence of measurements (after establishing $\frac{\sigma_{Fe}}{\sigma_{Al}}$ ratio) was as follows:

1. Pre-calibration experiment with pure Fe to obtain $k_{Fe}$.
2. Cleaning the system by heating the empty Knudsen cell to $\sim 1700$ K (to drive out all traces of Fe, Al and other contaminants).
3. Duplicate runs (or more number of runs if required) with the alloy sample to ascertain consistency of pressure values between the different runs.
4. Post-calibration experiment with pure Fe.

Usually, an agreement within $5 - 10\%$ is obtained for pressure values between the different specimens of the same alloy sample.

From the measured pressure, the activity of a component $a_i$ was calculated as

$$a_i = \frac{p_i}{p_i^0} \quad \text{.................................. 5}$$

and the chemical potential change of mixing $\Delta_{\text{mix}}\mu_i$ using the relation

$$\Delta_{\text{mix}}\mu_i = RT \ln a_i \quad \text{.................................. 6}$$

where $p_i$ and $p_i^0$ denote the partial pressure of species ‘i’ over the alloy and the pure substance respectively.

The enthalpy of sublimation was calculated using either of the following relations

$$\frac{d \ln (I_i T)}{d (1/T)} = - \frac{\Delta_{\text{sub}} H_i}{R} \quad \text{.................................. 7}$$

$$\frac{d \ln p}{d (1/T)} = - \frac{\Delta_{\text{sub}} H_i}{R} \quad \text{.................................. 8}$$
The partial enthalpies and entropies of mixing were calculated using the following equation

\[ \ln a_i = \frac{\Delta_{\text{mix}} H}{R} \frac{1}{T} - \frac{\Delta_{\text{mix}} S_i}{R} \]

Component activities were also calculated using the normal Gibbs-Duhem (GD) integration method and/or by the Gibbs-Duhem Ion Intensity Ratio (GDIIR) method, by treating one alloy composition as the reference. GDIIR method was used wherever the ion intensity ratios were available. In some Al-rich compositions, the ion intensity ratio could not be obtained. In such cases, the normal GD method was used to obtain activity data.

In the case of the Ni-Al system also, a similar procedure was adopted for the experiments and for the evaluation of data. The Ni-Al system is known for its high vacancy concentrations, especially for compositions having more than 52 at % Al. It is reported that the effect of these vacancies on calculated thermodynamic parameters may not be significant when their concentration is less than 0.01%. At higher values, they can have an effect on the calculated values. For the first time, an attempt is made here to consider the effect of these vacancies on thermodynamic parameters.

The construction of a new HTMS facility mentioned before is described in great detail in Chapter V. Each important component in this facility like the glove box (with the recirculation, pressure control, purification, regeneration and purity monitoring systems), the mass spectrometer, the vacuum system (with high vacuum isolation), the high temperature furnace, temperature measurement device, sample change device, maintenance equipment and other auxiliary devices are considered separately. The significance of each component and the parameters to be considered in each of them to meet the experimental needs are given in a detailed manner.

Some tests were performed initially to ascertain that the targeted specifications are met. The results of these tests are given in Chapter VI. Some exploratory experiments were then conducted to commission the system as a high temperature mass spectrometer. The sensitivity of the experimental system was measured with pure silver and found to be reasonably good (\(10^{-3} - 10^{-4}\) Pa). The sensitivity factor may further improve by an order with the help of the ion counting system installed in the facility. The sublimation
enthalpies obtained on pure elements Fe, Ni and Ag showed good agreement with the recommended values in the literature, which clearly indicates that reliable thermodynamic measurements can be made with this system. These data also provided a rough correction factor for the measured temperature, which was further confirmed by direct measurement. As a further proof, a Fe-Al alloy sample (40 at% Al) was analysed in this equipment. The ion intensity ratio and the partial pressures measured for the individual elements also showed very good agreement with reported values. Results of these exploratory vaporization experiments are also given in this chapter.

In the last part of Chapter VI, the gas analysis experiments conducted using this experimental facility are discussed. Determination of the actual fission gas release from the irradiated fuel pellets into the plenum area is essential, particularly at high burn up levels, to decide about raising the power to successively higher levels. Fission gas release in fuel pins irradiated at the Fast Breeder Test Reactor at Kalpakkam, at various burn up levels (25,000 MWd/T, 50,000 MWd/T and 1,00,000 MWd/T) were analysed. Extensive calibration experiments were conducted initially with pure He, Kr and Xe (the gases of interest) and synthetic mixtures of various compositions made from these gases. Some difficulties encountered while making triple gas mixtures brought out the need to improve upon the design and sampling of the gas mixing system. Accordingly, a new system was designed and fabricated. A brief description of this facility is also included in this chapter.

In the concluding chapter, salient features of the KEMS investigations reported in Chapters III to VI are summarized.