

1.1 Introduction

Conventional lead-tin solder alloys have low cost and excellent properties required for soldering of electronic components. These alloys are very popular in electronic industries till last decades. The lead in lead-tin solder is very toxic. Now, everybody is aware of the adverse effect of lead on the health and environment. So, the scientific community is under high pressure to develop some alternatives to the conventional lead-tin solder alloys. There are three major sources of generation of lead: i) lead waste from manufacturing processes ii) occupational exposure iii) disposal of electronic equipment.

Nowadays in the automotive industry, large numbers of circuits are kept in the engine chamber. It reduces the quantity of wires, the vehicle weight and makes it cost effective. The thermal stresses in engine compartment are generated if the temperatures are more than 150°C. The hybrid circuit works up to an operating temperature of 170°C. Thermal fatigue is an important parameter for the measurement of its performance up to a temperature of 170°C. As the temperature increases, the strength of the solder joint decreases during thermal cycling. It occurs due to plastic deformation, recrystallization and grain growth in the materials/alloys. At high temperature, the performances of the conventional solder alloys are very poor due to degradation of the mechanical properties. The maximum working temperature of the solder alloy is 97% of its melting point temperature of the solder. There is a major concern for the mechanical properties, microstructure stability and the reliability of the solder joint. This bad effect of solder joint could be minimized by substituting other materials in place of lead. There were two options: one is to go for the high temperature soldering for which PCB should withstand at such a high temperature, the other option is to reduce the melting point of the new alloy by alloying with other elements.

1.1.1 Health hazards from inhaling and exposure to soldering fumes

The use of lead alloys causes several health related problems i.e. in U.S.A soil pollution is caused by the wood varnished that contains lead. The blood analysis could provide the information regarding lead poisoning. This limit is decided by the govt. That limit is 130 microgram/liter blood at the maximum for an untainted human being. In Germany, the people who are exposed to lead in the work place, this limit is 300 microgram/liter blood for women and 700 microgram/liter for man. This limit is 250 to 100 microgram/liter in USA. In the manufacturing sectors, lead causes only amino direct danger. The precautions like following of safety rules can prevent the breathing in floating and dried powder dust. Many attempts are made to reduce or ban the use of lead alloys in electronics. U.S.A. Congress has also brought in the tax proposal for discouraging the use of lead. In Europe, the lead is banned (excluding battery) in the vehicles as of 1st Jan 2002. But the maximum use of lead is for the battery and ammunition.

The amount of lead consumed by electronic industry is approximately 0.5-0.7%. Before we decide any alternative materials for soldering application, we must critically discuss their health hazards. In Europe and USA, this matter has been thoroughly deliberated among scientific community and has drawn the following inference about toxicity and lead-free solders.

- I) Cd is completely banned (high risk)
- II) Sb cannot be a major element in the solder alloy.
- III) Ag and Cu based lead-free solder alloys are classified as low risk materials in Europe.
- IV) Sn and Zn are present in the human diet and helpful for the human health, provided they are present within permissible limit.

- V) Bi can be used in lead free solders as it is classified as metal with medicinal uses (low risk)

1.1.2 Resistance to Lead-Free Soldering

Replacement of lead must be analyzed very critically in two contexts: Low cost and highly reliable materials. Lead is one of the cheapest elements among all common non-ferrous metals. The cost of the alloy will definitely increase if we replace lead with any other metal. Incidental cost will also increase as we go for a new alloy. We also have to invest for the use of new alloy. Reliability of lead-tin alloy is very good among the engineers. They have developed a very good comfort factor with the conventional soldering alloys. It will not be so easy for the new alloy to surpass it. It has been worldwide accepted that the lead free solder should be tin based.

The major drawback of this alloy is its high melting point as compared to its conventional counterpart. This is not accepted by industries. During the past few decades, evaluation of thermodynamic properties and equilibrium phase diagram of multicomponent alloys have been a challenging job for the materials scientists. Recently, the needs of physical and chemical data of the multicomponent solution have been growing enormously for the development of new materials. It is time consuming and expensive to perform a large number of experiments to obtain statistical relevance of the data. For extreme conditions (high temperature, high pressure and strong reactivity etc.), the thermodynamics is very useful tool that helps in understanding the properties of alloys and Ceramics. Low temperature data can be used to predict the behavior of materials at high temperature which is the main objectives of the researchers. As it is very difficult to perform the thermodynamic measurement at high temperature, the most commonly used thermodynamic equations are more reliable and accurate to predict than that measured at extreme conditions. But often high

temperature measurements are unavoidable in material science. It is very complex and costly to work in such situations. Therefore, the essential point is to choose the proper experimental technique and decisive measurements.

Several objectives are achieved by the thermodynamic assessment of the multicomponent solutions. In the first place, Multicomponent solutions [Witusiewicz et al. (2007)] are encountered during extraction and refining of metals in extractive metallurgy and alloy design and development in Physical and mechanical metallurgy. For the thermodynamic analysis of these processes it is essential to know the thermodynamic behavior of the multicomponent solution with high accuracy.

Hence, the correct experimental technique is required to choose for the particular multicomponent solution along with the theoretical models. Second, the phase diagrams are very important for the materials engineers as far as the choice of materials for the particular application is concerned. It is mandatory to determine the exact position of solidus and liquidus curve in the phase diagram with very good accuracy which is be done by the careful thermodynamic analysis of the relevant system. The thermodynamic analysis of the phase diagram requires reliable data with high degree of accuracy. Third, only electrical properties or magnetic properties or X – ray investigation cannot provide all the information about the constitution of the metallic system. Thus authentic thermodynamic data along with above investigations are essential to obtain the deeper insight into the constitution of the multicomponent metallic systems.

Several thermodynamic investigations have been conducted on multicomponent metallic solution including semi conducting compound which are very important scientifically. An accurate knowledge of thermodynamic data and phase diagram of this system is necessary. Thermodynamic data for most of the binary systems are available,

but the thermodynamic data for the ternary and/or multicomponent alloys are scarce [Moelans et al. (2003)]. Lead – tin alloy systems are the most popular among many available solder alloys in electronic circuit and packaging, because of its very attractive physico-chemical, mechanical and many other properties. The use of lead is restricted in many places because of its toxicity. Researches and scientist are working very hard to develop lead free solder alloys. They have predicted that the feasible lead free solder alloys must be tin based multicomponent alloys. The design of such alloys needs the accurate evaluation of several properties of those alloy systems. The information like stable and metastable equilibrium between various phases, position of solidus and liquidus in a phase diagram and composition of each phase in a multicomponent solution could be obtained from the phase diagram and thermodynamic data. The information of interfacial reaction between solder and substrate materials could also be obtained from the thermodynamic data. The design and development of lead free solder alloys needs careful understanding and critical analysis of thermodynamic properties and phase equilibria of the multicomponent alloys.

The Bi-In-Sn is one of the ternary alloys formed from the metals having low melting point. These alloys are always recognized by their small positive enthalpy of formation without the presence of any intermetallic compound. The accurate thermodynamic properties of this system are very essential to understand the various metallurgical processes in which multicomponent solutions take part. Though the related binaries of this ternary system are very extensively studied, but the systematic thermodynamic investigation of this ternary system is not available in the literature. Therefore, the thermodynamic study of Bi-In-Sn system was undertaken. Bi-In-Sn system is considered to be one of the potential lead-free solder alloys among the available lead-free solder alloys. Measurements of thermodynamic properties and determination of

phase diagram and of this system are the first step for the design of the new solder alloys. Since, no thermodynamic properties is available in the literature, the thermodynamic investigations of the Bi-In-Sn was undertaken.

In this chapter, the significance of the thermodynamic parameters, thermodynamic properties of solutions and different thermodynamic techniques for activity measurement have been discussed with reference to the liquid metallic solutions.

1.2 Significance of thermodynamic parameters

Thermodynamic data of alloys will give an idea of the nature of the system. Activity of components in solutions gives a measure of escaping tendency of atoms / molecules from the solution.

The enthalpy of solution is the heat evolved or absorbed on formation of one g. mol. of the solution from its constituents at a constant pressure. If the solution process is endothermic at a particular temperature, the heat is absorbed and the molar heat of formation is a positive quantity. In case of exothermic reaction, the heat is evolved and the molar heat of formation is negative quantity. The enthalpy of solution gives an idea about the nature of bonding. The enthalpy values are small in case of covalent compounds relative to those of ionic compounds, because a lesser energy change takes place due to the sharing of electron between the atoms.

The Gibbs energy of formation of a solution or a compound is an absolute measure of its stability in a given environment. In case the free energy of mixing of the alloy is less than that of the constituent phases, then that particular alloy is said to be stable one. From the nature of variation of free energy of formation as a function of temperature, one can easily assess the feasibility of formation of alloys. If the free energy of mixing decreases as a function of temperature, thermodynamic stability increases as a function of temperature.

The total entropy change in a solution is sum of the entropy changes due to vibrational, configurational, magnetic and electronic and other contributions. The magnetic and electronic contributions are important in case of alloys which involve one or more transition elements. Vibrational and configurational entropies dominate in total entropy. In a crystal, each atom vibrates about a given position and hence there is a randomness associated with the position of an atom at a given time. If each atom is moving in a cell, the vibrational randomness of the system is directly related to the volume of the cell. Larger the volume of the cell, the larger will be the randomness and hence the larger will be the entropy. The other important term, configuration entropy change gives an idea about the degree of order. This entropy becomes zero when the compound is perfectly ordered.

1.3 Thermodynamic properties of solutions

In a multicomponent system, the alloy under the specified conditions of pressure temperature and composition can be classified as homogeneous (single phase) or heterogeneous (multiphase). The single phase can be produced by adding a second component continuously to a pure metal without a phase change then an alloy is called a single phase mixture. The extent of formation of alloy is basically dependent on physical properties such as, crystal structure, size, electro negativity etc. of the constituent elements. Liquid metallic solutions in many respects are more amenable to study than are the corresponding solid solutions. The thermodynamic measurements are only possible if the conditions of the thermodynamic reversibility are satisfied. It is easy to achieve reversibility in liquid than solid system and departure from reversibility are in general more readily recognized in liquid solutions. The absence of strain energy reduces one of the significant variables in the liquid solutions. For these and other

reasons, the liquid solutions are more extensively investigated than solids especially with regard to thermodynamic properties free energy, enthalpy and entropy.

The most basic law concerning the thermodynamic behavior of solutions is Raoult's law, which states that the vapour pressure exerted by a component i (p_i^0) in the solution is directly proportional to its mole fraction (x_i) at the same temperature.

$$p_i \propto x_i;$$

$$p_i = p_i^0 x_i \dots\dots\dots(1.1)$$

Ideal solutions must obey the Raoult's law. Moreover, majority of the solutions deviate from Raoult's law because in general the interaction(s) between the atoms are not equal. So the vapour pressure of the component is given by

$$p_i = p_i^0 a_i \dots\dots\dots(1.2)$$

a_i is the activity, as that fraction of the molar concentration available for reaction. For ideal solution it will be seen that $a_i = x_i$, but if the solution deviates from Raoult's law $a_i = \gamma_i x_i$. γ_i is called the Raoultian activity coefficient. To know the behaviour of the individual components in solution, the activity of particular component in solution must be known.

1.4 Activity measurement techniques

Different techniques available for the activity measurement of components in solution can be broadly classified into three main groups viz. chemical equilibria, vapor pressure and electrochemical measurement.

1.4.1 Chemical Equilibria

The relationship between standard free energy of formation, ΔG^0 and equilibrium constant, K is as follows:

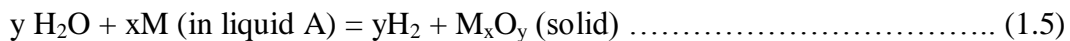
$$\Delta G^0 = -RT \ln K \dots\dots\dots(1.3)$$

For the reaction $A + B = C$, K is given by the relation:

$$K = \frac{a_C}{a_A \cdot a_B} \dots\dots\dots (1.4)$$

Measurements of equilibrium constant at different temperature would give ΔG^0 vs T relationship. From the slope and intercept of the plot we can estimate entropy and enthalpy, respectively (Gibbs – Helmholtz equation). This technique has been successfully applied to study different types of heterogeneous equilibria viz. solid-gas, molten metal-gas, molten metal-salt-gas, solid-liquid, liquid –liquid (slag-metal) etc. This technique is most convenient for the equilibria involving gases and vapours.

When one of the components of the solution participates in a chemical equilibrium involving other phases its activity appears in the equilibrium constant. As an example, consider the process in which the component M reacts with water vapour to form solid oxide and hydrogen:



The equilibrium constant K is defined as

$$K = \left(\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}} \right)^y \cdot \left(\frac{1}{a_M} \right)^x \text{ (Assuming activity of solid oxide to be unity)} \dots\dots (1.6)$$

At a constant temperature, the activity of the metal is obtained from K and $(p_{\text{H}_2\text{O}} / p_{\text{H}_2})$ ratio. Studies of this kind have been carried out with certain alloying elements in liquid iron. [Chen and Chipman (1947)] have calculated the activity of chromium in the liquid iron at 1595 °C by using $\text{H}_2 / \text{H}_2\text{O}$ mixtures. In a similar case, activity of vanadium in liquid iron has been determined by [Dastur (1948)] by equilibrating liquid iron with $\text{H}_2 / \text{H}_2\text{O}$ mixtures. By using various gas mixtures such as $\text{H}_2 / \text{H}_2\text{O}$, $\text{H}_2 / \text{H}_2\text{S}$, $\text{H}_2 / \text{C H}_4$ and H_2 / NH_3 , the activity of nonmetallic inclusions viz. O, S, C and N, respectively in liquid iron can also be obtained. The activity of S in liquid iron has been measured by

several researchers [Kitchener et al. (1949), Morris and Williams (1949), Sherman et al. (1950), White and Skelly (1947)] by different methods using H_2 / H_2S gas mixtures. Other systems in which thermodynamic properties of non metallic inclusions in liquid metal have been determined from gas-metal equilibria include: oxygen in iron [Chipman (1933), Fontana and Chipman (1936)] and copper [Girardi (1941)], hydrogen and nitrogen in a variety of metals [Chipman and Murphy (1935), Liang et al (1946), Sieverts (1912)], carbon in iron [Marshall and Chipman (1942)]. The experimental techniques adopted to obtain the various gas mixtures are described in [Rapp (1970)]. The main difficulties in this technique are the choice of a suitable crucible material for the reaction crucible, the slow attainment of chemical equilibrium in many systems especially those involving all solid phases, and analysis of the sample immediately after experiments.

1.4.2 Vapour Pressure Measurement

Vapour pressure measurement provides a simple method for determining the activity of any component in multicomponent system which is directly related with partial pressure:

$$a_A = \frac{p_A}{p_A^0} \dots\dots\dots (1.7)$$

Where p_A is the vapour pressure of the component, A over the multicomponent system and p_A^0 is the vapour pressure of pure A under similar conditions. The activities are related to the equilibrium constant and can be used to calculate the partial molar properties of mixing. Other thermodynamic properties can be obtained from the variation of equilibrium constant as a function of temperature. The experimental methods available for vapour pressure measurement can broadly classified into three main groups: static, dynamic and effusion. In the static methods, the vapours remain in

equilibrium with the sample in an enclosed vessel at a particular temperature whereas in the dynamic methods a constant rate of vaporization is maintained by continuous flow of an inert gas. In the last one, the vapour pressure is determined by the rate of evaporation of the sample under reduced pressure of the vapour species. The details of the technique and instrumentation have been discussed in several books and reviews [Rapp (1970), Kubaschewski and Alcock (1979), Kubaschewski (1972), Bockris et al. (1959), Abraham et al. conference (1981)].

1.4.3 Static Methods

In static method pressures greater than 10^{-3} atm., in equilibrium with the sample in an enclosed vessel at a particular temperature, are measured using appropriate pressure sensing devices. These methods are further classified into direct and indirect methods. The measurement of total pressure over the sample at a particular temperature in an enclosed vessel falls in the first category. Indirect methods are based on the measurement of the density of vapours in equilibrium with sample, or on the determination of temperature of phase change. The isopiestic method using the gas equilibrium technique for pressure measurement falls into a separate class.

1.4.3.1 Direct Methods

In direct static techniques the measurement of total pressure over the sample can be achieved by different pressure sensing devices viz. monometers, McLeod gauge, Bourdon gauge and isoteniscope. Direct static methods have been employed for the study of Bi_2Te_3 [Brebrik and Smith 1971], Zn_3As_2 [Gavrichev et al. (2002)] and $\text{Sb} - \text{As}$ [Ugai et al (1986)]. The vapour pressure measurement by monometer has been used extensively by Hilderbrand and Co-workers [Hilderbrand (1912), Hilderbrand and Eastman (1915), Hilderbrand (1920)] and Miller [Miller (1927)] in their work on amalgams (Zn-Hg , Tl-Hg , Cd-Hg , Pb-Hg , Sn-Hg , K-Hg). The isoteniscope method has

been used by Smoronova et al. [Smoronova et al. (1974), Smoronova and Nigmatova (1974)] for the measurement of vapour pressure of mercury over the ternary In -Tl- Hg and In -Bi- Hg alloys. The method has not been used extensively in high temperature measurements due to the problems associated with the materials of construction.

1.4.3.2 Indirect Methods

In the indirect methods, technique like vapour weight, thermal conductivity, vapour ionization, optical density and tracer have been employed for vapour density measurement. Optical absorption and tracer technique have been more widely used for vapour pressure measurement over various metallic systems at higher temperatures. The method of measurement of optical density of vapour is based on the fact that absorption of light by the vapours follows Beer's law.

This method is widely used to measure the thermodynamic properties of many metallic systems viz. Ag - In [Masson and Pradhan (1973)], Ge-Cd, Ge-Zn [Su et al.(1984)], Zn-Al, Zn-Ag, Zn-Cu, Zn-Au, Cd-Ag, Cd-Cu, Cd-Au [Schneider and Schmidt (1942)], Mg-Al, Zn-Al [Schneider and Stoll (1941)], Ag - Zn -Cd [Scatchard and Lin (1962)] and Cd-Hg-Na [Frauenshill and Halla (1949)]. Hirst and Olson [Hirst and Olson (1929)] measured the vapour pressure of mercury over thallium amalgams at room temperature by optical density method. Vapour ionization method was used by Poindexter [Poindexter (1926)] to measure the vapour pressure of mercury over sodium and potassium amalgams from -56 to 90°C. [Herbner et al.(1950)] used an absorption spectrum method for measuring the zinc vapour pressure of the six brasses over the temperature range 650-970°C.

1.4.4 Dynamic Methods

In dynamic methods a constant rate of vapourization of the condensed sample is attained. The most commonly dynamic method is the determination of the boiling point

of a substance. The more general dynamic method of determining vapour pressure of metals is the transpiration method. In this method a steady and controlled stream of inert gas is allowed to pass over the substance under investigation, at constant temperature. The vapour coming out of the reaction chamber is measured at different rate of gas flow. The value of vapour pressure is determined by extrapolation of the rate of weight loss to the zero flow rates. The vapour pressure (p_A) is calculated from the volume of transported substance (V_A) and volume of transported gas (V_g) at STP by assuming the validity of Boyle's law as follows:

$$p_A = \frac{V_A}{V_g + V_A} \dots\dots\dots (1. 8)$$

Volume of the transported substance V_A obtained from the measured weight loss. Information regarding the vapour density is however essential. This technique can be used for the measurement of vapour pressure from 10^{-6} atm to few atmospheres. The lower range may sometimes be exceeded when radio tracers are used for quantifying vapour species. This method has been employed to determine the thermodynamic properties of Fe-Mn [Steiler et al. (1972), Schultz et al. (1966)], Ag-Si [Tashy et al. (1968)], Pb-Sb [Richards (1961)], Cd-Hg, Zn-Hg, K-Hg [Pedder and Barratt (1933)], Mg-Bi, Pb-Bi [Prasad et al. (1977)], Cu-Zn, Cu-Cd Azakami and Yazawa (1968)] . The carrier gas technique has been used very extensively by Jellinek and co-workers [Burmeister and Jellinek (1933), Jellinek, and Rosner (1929), Jellinek and Rosner (1931) and Jellinek and Wannow (1935)] in studying various systems containing cadmium and zinc. The vapour pressure of Bi and Sb were measured by Azakami and Yazawa [Azakami and Yazawa (1967) for liquid, Bi, Sb, Cu-Bi, Cu-Sb alloys at 900-1200 °C by transpiration method. Kozuka et al. [Kozuka et al. (1961)] measured equilibrium vapour pressure of Zn in Zn-Al-Sn ternary system at 720°C. by carrier gas

method. Using Argon as carrier gas, equilibrium vapour pressure of each component of the fused Zn-Cd at 550°C and Zn-Sn alloy system at 670, 720 and 770°C were measured by Kozuka et al. [Kozuka et al. (1960)]. Thermodynamic investigations of liquid Zn-Al-Mg alloys were carried out by Kozuka et al. [Kozuka et al. (1960)] from the equilibrium vapour pressure measurement of zinc at 720°C by carrier gas technique.

1.4.5 Effusion Methods

The effusion methods include two principle techniques, known by the name of their inventors Knudsen [Knudsen (1909)] and Langmuir [Langmuir (1914)]. These methods are based on the kinetic theory of gases and are used to measure low pressure (less than 10^{-3} atm.) by measuring the rate of evaporation in vacuum. The Langmuir method involves the escape of molecules from the surface and vapour pressure is determined from the weight loss:

$$-\frac{dn_A}{dt} = \left(\frac{2\pi RT}{M}\right)^{1/2} p_A \dots\dots\dots (1.9)$$

Where n_A is the number of moles of A evaporated in time t , and M is the molecular weight of A.

In the Knudsen method the vapourising molecules escape through a small orifice having diameter less than the one-tenth of the mean free path of the vapourising species. The vapour pressure p_A of the volatile component A is given by:

$$p_A = \frac{m}{tu} \left(\frac{2\pi RT}{M}\right)^{1/2} \dots\dots\dots (1.10)$$

Where, m is the mass of component A of molecular weight M vapourising through an orifice of area u (in cm^2) in time t (in seconds). A correction factor due to channeling effect of the hole during evaporation and non-ideality of the orifice is needed in the

above equation. In the effusion methods the weight loss is measured either directly or collecting vapourising mass followed by analysis.

This technique has been employed for the estimation of thermodynamic properties of binary metallic systems: Al-Mg [Mose et al.(1998)], Cu-Pb [Zajaczkowski et al. (1997)], Sn-Sb, Al-Sb [Zajaczkowski and Botor(1995)], Ga-Sb [Zajaczkowski and Botor (1994)], Fe-Si [Botor et al. (1991)], Ag-Tb [Ivanov (1985)], Ag-Cu [Teberko and Vaisburd (1983)], Ag-Nd [Ivanov and Lukashenko (1983)].

The theoretical background and experimental details of Knudsen cell assemblies are available in the literatures [Abrahamin et al. conference (1981), Alcock (1979), Bardi et al. (1973), Piacente et al. (1985)]. The major problem faced by the experimentalists in the use of this technique is the identification of the vapour species. The method can only be employed when the vapour species are simple, chemically well defined and the molecular weight of the species are known. The interpretation of the data is difficult when complex and more vapour species are produced simultaneously in the vapourisation process. This limitation can be overcome by the use of mass spectrometer. The mass spectrometer – Knudsen cell combination technique has been employed for the measurement of thermodynamic properties of numerous binary and ternary systems:

La-Ga [Shoji et al. (1997)], Co-Al [Levin and Geld (1979)], Fe-Al [Jacobson and Mehrotra (1993)]. The problem of identification of vapourised species associated with the Knudsen technique can also be overcome by the application of the recoil momentum which is imparted to the Knudsen cell as a result of the effusion process. This method, known as torsion effusion, was developed by Volmer who modified Knudsen technique by two orifices of different diameters. Both the orifices point in opposite directions on both sides of suspension fiber of known torsion constant. A

torque is exerted by the effusion of molecules through the orifices. The vapour pressure is determined by the measuring the angle of torsion.

$$p = \frac{2\tau\theta}{(A_1d_1 + A_2d_2)} \dots\dots\dots (1. 11)$$

Where p is the total pressure in the cell, τ is torsion constant of the suspension wire, θ is the angular deflection and A_1 and A_2 are the orifice areas displaced, respectively, distances d_1 and d_2 from the axis of suspension. If the angle of rotation θ is measured, the pressure can be measured directly, independent of any knowledge of the molecular weights of the effusing molecules. Various binary and ternary metallic systems studied by Torsion – effusion technique are: In-Pb [Scardal et al. (1990)], In-Mg [Chirulli et al. (1983)], Tl-Zn [Ferro et al. (1980)], Ni-Zn [Cunat et al. (1978)], Pd-Pt [Darby and Myles (1972)].

1.4.6 Electrochemical Methods

The use of electrochemical technique in connection with thermodynamic and kinetic measurements is well established. In these techniques the thermodynamic properties are obtained from the open circuit emf of a suitable electrochemical cell. A large number of investigations were carried out at the end of the nineteenth century on the aqueous electrolytes and till the middle of the current century by molten salt electrolyte. In the last five decades a large numbers of system have been investigated by using solid electrolytes after [Kiukkola and Wagner (1957)] introduced calcia stabilized zirconia solid electrolytes for thermodynamic measurements.

1.4.6.1 General Principles

Consider a simple galvanic cell consisting of a metal A, a fused electrolyte (AM) and alloys of the system A-B-C: A / AM / A-B-C

The half cell reaction at different electrode may be written as:

$$A = A^{n+} + ne^{-} \dots\dots\dots(1.12)$$

$$A^{n+} + ne^{-} = A(\text{in } A-B-C) \dots\dots\dots(1.13)$$

The virtual cell reaction for the passage of coulombs of charge is:

$$A = A(\text{in } A-B-C) \dots\dots\dots(1.14)$$

The activity of component A in the multicomponent system A-B-C at temperature T, given by the relation:

$$\ln a_A = -\frac{nF}{RT} \dots\dots\dots (1.15)$$

Where n is the number electron transferred 'F' is the Faraday constant and E is the open circuit emf of the cell (1.14). Activities are calculated at various temperatures and subsequently, from the calculated activities, integral and partial molar thermodynamic properties are calculated employing suitable equations.

1.4.6.2 Theoretical Considerations

Though the above cell (1.14) seems to be fairly simple, a number of theoretical considerations [Oriani (1956), Taylor (1927) and Wagner and Werner (1963)] and careful planning is required to arrive at the correct reversible emf to obtain accurate thermodynamic data. The criteria for the reversibility are (i) measured emf should be independent of time at a given temperature (ii) measured emf should be reproducible irrespective of heating and cooling cycles (iii) emf should be recovered to a stable value if a small current is passed from cathode to anode or vice versa and a much larger impedance of the measuring instrument to that of the cell. In order to achieve reversibility of the cell following general considerations should be kept in mind.

The electrolyte should show exclusively ionic conduction. In case any electronic conduction occurs in the cell, Eqn. (1.15) has to be modified by more elaborate

relations derived by [Kiukkola and Wagner (1957)]. This correction requires the specified knowledge of the participating ion in the cell.

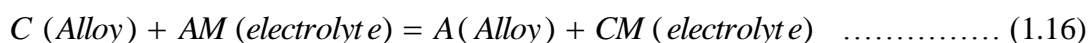
The participating ion should be only in one valence state which means that the presence of any oxidizing or reducing agent in the cell must be avoided.

The temperature range of operation must be high enough to enable diffusion to equalize activity gradient between the interior and at the surface of the alloy or compound electrode. According to [Oriani (1956)] an operating temperature level more than 0.3 to 0.4 of the melting point of the electrode is suitable.

In the molten salt electrolyte galvanic cell, the salts used should have low melting and high boiling point. The vapour pressure of the salts should be low in the temperature range of operation. The presence of concentration gradient or liquid junction in the electrolyte can alter the cell emf because of the irreversible nature of diffusion occurring in the electrolyte.

Transfer of materials from one part of the cell to another caused by flow of current, diffusion or physical mixing can cause the cell to have a mixed potential, resulting from the local shifts in electrolyte composition.

An exchange reaction may take place between the alloy and adjacent electrolyte:



In order to avoid this exchange reaction, metal A should be less noble than the alloy component C in the Alloy A-B-C due to exchange reaction the emf may change from the normal value.

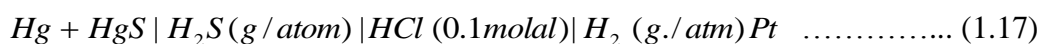
It is important that no thermal gradient should exist in the region of the cell containing electrode and electrolyte in order to avoid irreproducible thermo-emf. The electrode contact wires, as far as possible, must be identical. In case of different lead wires, a correction factor for thermo-emf should be employed. The correction factor must be

determined in a separate experiment without electrolyte in the temperature range of operation. The lead wire must be insoluble in electrode material to avoid altering the composition. A liquid metal with a high surface tension may not have good contact with the lead wires and hence an error of several millivolts in the cell emf may result.

1.4.6.3 Choice of Electrolyte

The proper selection of an electrolyte is an important aspect of the electrochemical technique. The available electrolytes can be classified into three main groups.

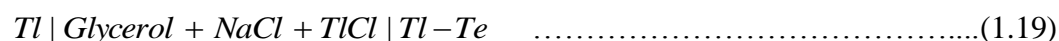
Aqueous and organic liquid electrolyte: The aqueous electrolyte is not popular because of the liquid junction potential and slow attainment of equilibrium. However, [Goates et al. (1951)] have studied HgS at 298 K by employing the following cell:



And



Moreover, complications arise due to liquid junction potential and a slow attainment of equilibrium makes it difficult to obtain reliable values, besides the limitations of temperature range of investigations. Hence the use of organic solvent has been encouraged to increase the temperature range of operation to a limited extent. [Terpilowski et al. (1965)] have employed the following electrochemical cell to measure the thermodynamic properties of Tl-Te system in the temperature range of 398-468 K.



Similar organic electrolyte cells are used further to investigate the thermodynamic properties of HgSe [Ratajczak and Terpilowski (1968)], HgTe [Ratajczak and Terpilowski (1969)], Tl-Se [Terpilowski et al. (1968)] and ZnSe [Terpilowski and

Ratajczak (1967)] by Terpilowski and co-workers. Chalcogenide systems viz. Bi_2Se_3 [Terpilowski and Ratajczak (1967)], Tl-S [Vasilev et al. (1971)], Tl-Se [Vasilev et al. (1967), Vasilev et al. (1969) and Vasilev et al. (1971)] and Tl-Te [Vasilev et al. (1968)] have investigated by Vasilev and co-workers using solution of salts in glycerol as an electrolyte. The application of (glycerol + KCl + LiCl) in the ternary system Tl-Ge-Se has been extended by Babanly and Kulieva [Babanly and Kulieva (1986)]. Partial and integral thermodynamic properties of formation of ternary compound TlBiSe_2 and Tl_9BiSe_6 and of solid solutions have been determined through physicochemical methods in Tl-Bi-Se system by Babanly et al. [Babanly et al. (1990)].

(a) Molten or Fused Salt Electrolytes

The choice of these electrolytes depends entirely on the system to be studied. A large number of thermodynamic data on alloys, salts and intermetallic compounds have been generated using molten salt electrolytes. In these studies the electrolyte used should be stable, ionic and chemically neutral with the system under investigation and should have low melting and high boiling points. Formation of complex anions among different salts in the melt should be avoided. In order to reduce the chances of solubility of electrode materials in electrolyte mixture, 3-7 wt.% of the salt or chloride of the conducting ion (common in the system under investigation) is dissolved in auxiliary solvent mixture. The chlorides of many metals, especially monovalent metals, satisfy these criteria. Mixtures of LiCl-KCl, LiCl-KCl-NaCl, KCl-NaCl and KCl-NaCl-ZnCl₂ have been often employed to investigate the thermodynamic properties of many chalcogenides. Many of the metal chlorides exhibit appreciable electronic conduction, especially when they are in contact with an element of its cation, but when dissolved in the mixtures of monovalent chlorides this electronic conduction is suppressed to a great extent. The main drawback of the use of chloride electrolytes, particularly at high

temperatures, is that due to slightest contamination with water vapour they form volatile complexes. Moreover, reaction with the container becomes a serious problem at elevated temperatures. Silica has been extensively employed for this purpose because it can be used at a high temperature of 1370 K (approximately), provided the water vapour is completely removed from the electrolyte.

The molten mixture of LiCl and KCl together with a small quantity of CdCl_2 was used for the first time in 1935, by Seltz and Dehaven [Seltz and Dehaven (1935)] to measure the thermodynamic properties of CdSb in the temperature range of 663 – 713 K. Since then the molten mixture of LiCl and KCl has been used to investigate a large number of alloys, chalcogenides and other similar systems. The binary metallic systems investigated using eutectic mixture of LiCl and KCl as electrolyte is: Bi-Te [Liu and Angus (1969)], Sn-Te [Bouteiller et al. (1977)].

The eutectic melt of KCl-NaCl also has been used for the thermodynamic investigations of the various binary and ternary metallic solutions. The activities of copper in Cu-Bi [Nikolskya et al.(1959)] liquid alloys were measured by Nikolskya et al. in the temperature range of 1150-1225 K. Alabyseev et al. have studied the thermodynamic properties of liquid Sb-Zn-Cd [Alabyshv and Lantratov (1963)] alloys in the temperature range of 823-1023 K. Thermodynamic properties of the liquid Al-Au [Lee and Yazawa (1969)] alloys were studied by Lee et al. in the temperature range of 973-1153 K. Suleimanov et al. have studied the thermodynamic properties of Pb-As [Suleimanova et al.(1974)] using the ternary eutectic melt of KCl, NaCl and ZnCl_2 as electrolytes. The eutectic melts of LiBr and KBr have been used as electrolyte for the thermodynamic investigations of the Bi-In [Terpilowski (1958)], In-Sb [Terpilowski (1959)] and In-Pb [Terpilowski and Gregorczy (1961)] in the temperature ranges of 671-773 K, 637-873 K and 773-873 K, respectively.

(b) Solid Electrolytes: The use of solid electrolytes has some distinct advantages over a molten salt electrolyte. One of which is that they can be used at much higher temperatures. In the last couple of decades, a lot of development has been made in the field of their applications. The construction and operation of an electrochemical cell with solid electrolytes is relatively less complicated and sometimes the electrolyte itself acts as a container, especially if the metals and alloys are in molten state. A solid electrolyte is a solid in which the mode of conduction is predominantly (> 99%) ionic. There are however, certain limitations which restrict the use of solid electrolytes, particularly at low temperatures. The main limitation is the occurrence of the electronic conduction and subsequent polarization due to the slow diffusion under highly reducing conditions. For accurate and reliable measurements, the electrolyte must have a minimum conductivity of $10^{-6} \Omega^{-1} \text{ cm}^{-1}$ which is only achieved at elevated temperatures. So far, only few solid halides and oxides (most commonly used: alkaline earth fluorides, calcia stabilized zirconia, yttria stabilized zirconia, yttria stabilized thoria and β - alumina) are known to be solid electrolytes and no sulphides and nitrides and carbide have yet been found suitable as solid electrolytes. This restricts the use of solid electrolytes to investigate the systems involving oxygen, fluorine or alkaline earth metals and hence the systems containing specific ions can only be investigated. After the discovery of the β - alumina as the solid electrolyte by Kummer [Kummer et al. (1972)] , this technique has been applied to the systems containing the ions viz. K^+ , Na^+ , Rb^+ , Cs^+ , Ag^+ , Li^+ etc. The details of theory, applications and the systems investigated by the solid electrolyte methods are described in several reviews [Srinivasa and Edwards (1984), Estell and Flengas (1970 and Roth (1972))]. The exhaustive lists of known solid electrolytes indicating the conducting ions have given by [Pratt (1990), Rapp and Shores (1970)]. Jacob and Waseda [Jacob and Waseda (1990)] have used

CaF_2 as solid electrolyte and equimolar mixture of $\text{Gd} + \text{GdF}_9$ as the reference electrode for the study of Pt-Gd system at the temperature between 925 and 1125K. [Reddy et al. (2001)] have designed an electrochemical cell based on CaF_2 solid electrolyte and Al-CaAlF_7 as reference electrode for the determination of thermodynamic properties of Ti-Al system in the temperature range 820-900 K. Nanko et al. measured the activity of aluminium in Pt-Al [Nanko et al. (1998)] solid solution by employing CaF_2 as an electrolyte in the temperature range 820 -900 K by a galvanic cell: $\text{AlF}_3/\text{CaF}_2/\text{Co}$, CoF_2 . Emf measurements of the cells with a CaF_2 solid electrolyte were used to determine the activity of Al in solid Co-Al [Schaller and Bretschneider (1985)] alloys (0 to 48.7 at. % Al) between 900 and 1050 K. Emf of cells based on CaF_2 solid electrolyte were employed to estimate the activities of Gd, Y, and Ce in Pd-rich alloys at 973-1073 K by Paasch et al. [Paasch et al. (1983)]. The thermodynamic properties of mixing of liquid Na-Sn [Alqasmi and Egan (1983)] alloys were determined by Alqasmi and Egan at 1023 -1123 K by an emf method using a CaF_2 solid electrolyte. Katayama et al. have measured the activity of Mn in Mn-In [Katayama et al. (1991)] and Mn-Bi [Katayama et al.(1990)] alloys in the temperature range 800-1100 K using CaF_2 as the solid electrolyte.

As we know that EMF technique is indirect heat measurement while calorimeter is direct heat measurement. So we go for calorimetric measurement for above system.

1.5 Calorimetric technique

To find the enthalpy change per mole of a substance A in a reaction between two substances A and B, the substances are added to a calorimeter and the initial and final temperatures (before the reaction started and after it has finished) are noted. Multiplying the temperature change by the mass and specific heat capacities of the substances gives a value for the energy given off or absorbed during the reaction.

Dividing the energy change by how many moles of A were present gives its enthalpy change of reaction. This method is used primarily in academic teaching as it describes the theory of calorimetry. It does not account for the heat loss through the container or the heat capacity of the thermometer and container itself. A great varieties of calorimeters serve to measure heats and heat capacities in various fields of application. In the following, a classification system for calorimeters and a couple of examples of different types of calorimeters will be presented. The aim is to give a structured survey of the whole field of calorimeter which may help to better recognize and evaluate the advantages and limitations to the DSC which results from their mode of operation.

1.5.1 Principle of calorimeter

Calorimetry is the technique of measurement of energy changes in the form of heat; the apparatus used to measure these changes is known as a calorimeter. The heat or enthalpy of formation of a compound can be directly measured by calorimetry. The enthalpy effect associated with any physical or chemical process or reaction is the most direct and sensible compared to any other effect and need to be precisely determined. Calorimetric techniques measure the enthalpy of a reaction, changes in enthalpy or heat content of a substance associated with changes in temperatures, changes in physical state such as melting and boiling, changes in chemical combination such as reaction or alloying, dissolution or changes of physical structure, annealing, recovery and grain growth etc. The successful and versatile use of the calorimetric technique in thermodynamic measurements has encouraged the development of various types of calorimeters.

Since the enthalpy effects are directly measured by the calorimetric technique the corresponding result can be reported with an estimated error which can be relied upon.

The quantities obtained directly from other techniques viz. chemical equilibria, vapour

pressure, and electrochemical methods are free energies from which corresponding enthalpies can be calculated only when the temperature coefficients of the free energy are known. A small error in the temperature coefficient may result in a large error in the enthalpy effect.

1.5.2 Classification of calorimeters

Variety of calorimeters employed for the determination of different parameters have been classified into five main groups viz. adiabatic, isothermal, isoperibol, constant temperature gradient and variable temperature gradient on the basis of the simplified heat flux equation:

$$Q = k (T_s - T_c) \dots \dots \dots (1.20)$$

Where, q , T_s and T_c are the heat flux, the temperature of the surrounding and the calorimeter, respectively, and k is the overall heat transfer coefficient. A number of reviews [Kubaschewski and Alcock (1979), Rapp, Bunshah (1970)] have appeared in the last two decades on calorimeter highlighting its importance, classifications, experimentation, and instrumentation.

1.5.2.1 Adiabatic calorimeters

When T_s and T_c are equal but not constant, the calorimeter is designated as an adiabatic calorimeter. The temperature of the surrounding, T_s , is equalized to that of the calorimeter. The heat effect is obtained from the temperature change and its water equivalent. Such calorimeter is generally, used for the measurement of heat capacities as well as the enthalpy of reactions but because of the requirement, $T_s = T_c$, its application is limited to slow reactions. The heat capacities of CdS [Beyer et al. (1983)], GaTe and InTe [Kerimov et al. (1971)] have been measured below room temperature by this calorimeter.

1.5.2.2 Isothermal calorimeter

The calorimeter in which $T_s = T_c = \text{constant}$ and q varies is known as an isothermal calorimeter. The heat effect produces of phase change of a substance at the transformation temperature. The heat effect is calculated from the latent heat of transformation and the quantity of the phase transformed. The use of isothermal calorimeter is limited to slow reaction, hence unsuitable for a study on chalcogenides.

It is generally used to study the binding of molecules from small molecules (eg. medicinal compounds) to larger macromolecules (DNA, Proteins etc.). It consists of two cells which are enclosed in a jacket. This jacket is adiabatic, which neither transfer mass nor heat.

1.5.2.3 Isoperibol calorimeter

A calorimeter where T_s remains constant and T_c changes during the course of a reaction is known as isoperibol type. The heat effect produces a temperature change in the calorimeter which gradually attains thermal equilibrium with its surroundings by exchange of heat. Such calorimeters can be employed for measurement of a number of thermodynamic parameters such as enthalpy of formation, solution or mixing, enthalpy of fusion, enthalpy of precipitation etc; hence they have received much attention with regard to the advancement of components. Isoperibol calorimeters are available in different design viz. solution, Bomb and Drop calorimeter types to suit different investigations. The microcalorimeter developed by Tian and Cavet falls in this category.

1.5.2.4 Solution calorimeter

Since the kinetics of most of the solid state reactions or processes are slow, involving a small quantity of net heat changes and very high activation barriers, these heats of reactions cannot be measured with precision by direct reaction calorimeter. In such

cases, the heat effect can be measured by following an indirect route e.g. rapid dissolution of the substance under investigation in a suitable solvent. The solvent is so chosen that both the compound and the mechanical mixture of the constituent elements dissolve in it fairly rapidly with a small heat effect. Various types of solvents such as aqueous solutions, liquid metals, liquid oxides, molten salts etc. have been used in solution calorimeters [Kubaschewski and Alcock (1979), Rapp (1970)]

The process of dissolution of metals, alloys and intermetallic compounds in a liquid metal or alloy is rapid so that the end state of the reaction is not only well defined and reproducible but is also attained quickly. By alternately dissolving a material from the standard state (A°) and from any other state (A) in a suitable solvent, and then applying Hess's law of constant heat summation the difference in the enthalpy between the two states, $H_A - H_{A^\circ} = \Delta H(T)$, is calculated for the dissolution processes.

Ticknor and Bever [Ticknor and Bever (1951)] for the first time realized the advantages of liquid metal solution calorimetry and fabricated the first calorimeter in 1951 with molten tin as a solvent. Since then a number of design and modifications have been introduced to increase the degree of accuracy. A liquid metal solution calorimeter of any design has the following essential components, namely, the dissolution chamber with the devices for the temperature measurement and control. Solution calorimeters can be employed for the determination of a number of thermodynamic quantity viz. enthalpy of formation, solution for mixing; the energy of order-disorder transformation, enthalpy interaction coefficient, enthalpy of precipitation, the heat capacity of metallic melts, and excess energy of metastable state and stored energy of deformation [Kleppa (1960) has pioneered the design of solution calorimeter. He has developed Calvet type

micro calorimeters for thermodynamic studies of refractory borides, silicides, salts and intermetallic etc.

1.5.2.5 Bomb calorimeter

In bomb calorimeter, the material, under study, is burnt in excess of oxygen (usually 25 atm.). The conventional oxygen-bomb calorimeter has not been successful for studies on chalcogenides. The results are unreliable because the combustion products cannot be precisely identified. This problem has been overcome by the use of fluorine as the oxidant for combustion. At the Argonne National laboratory, fluorine bomb calorimetry has been advanced for the measurement of molar enthalpies of a number of chalcogenides [Murray and Ohare(1984), Johnson (1980), Ohare (1986)] have studied the combustion of GeS_2 in fluorine, represented by:



From the standard values of enthalpy of formation of SF_6 and FeF_4 , the enthalpy of formation of GeS_2 has been calculated. A similar procedure has been adopted for the study of a number of chalcogenides viz. As_2S_3 [Johnson (1980)], GeS_2 [Ohare (1986)].

Calorimetric temperature is measured with a quartz crystal thermometer and is stored and processed by a minicomputer. The calorimeter has been calibrated by studying the combustion of benzoic acid in oxygen.

1.5.2.6 Constant temperature gradient calorimeter

The constant calorimeter in which both T_s and T_c varied in such a way that the term $(T_s - T_c)$ remained constant. In this technique, the time required for heating of the known and unknown samples is compared by heating the both through same temperature interval under the same temperature gradient. A method for determination

of heat capacity during heating and cooling has been described by Bullock [Bullock (1959)]. Bever and coworkers have advanced the constant temperature gradient calorimeter for determination of enthalpy of fusion and other thermodynamic properties near the melting point of materials.

However, in actual practice the maintenance of a zero temperature gradient is an ideal situation which cannot be realized.

1.5.2.7 Variable temperature gradient calorimeter

The principle of variable temperature gradient calorimeter is based on the differential thermal analysis. Transformations in metals and alloys during heating and cooling gives rise to arrests in their plots between differential temperature ($T_s - T_c$) and time. The duration of arrests accompanying a transformation can be translated to the heat effect on the basis of heat transfer considerations. Since this technique employs the differential temperature vs time plot. The apparatus employed in recent years a number of such DTA calorimeters have been developed on this principle.

The main advantages of DTA calorimetry are the simple construction and operation and direct sensing of heat effects. The technique is capable of measuring the enthalpy of formation of a compound, enthalpies of transformation and heat capacity etc. The degree of accuracy depends on the resolution of the peak, hence this technique is not very useful where the evolution of absorption of heat is small or reaction is slow. Its application for heat capacity measurement is also difficult. In recent years a number of such calorimeters have been designed and operated successfully for thermodynamic studies on metals, alloys, intermetallic compounds, salts, and ceramics.

In recent years there is a popular trend in using DSC which is commercially available under the trade names of Perkin Elmer, Du Point, Sitaram, Linseis etc. In differential scanning calorimetry, it is essential to maintain the same temperature over the sample

and the reference. This is possible if the energy supplied to both the sample and the reference is monitored accurately and the same energies are recorded for the heat effect calculation. In the calorimeter, the energies are independently supplied to sample and reference and their difference is plotted against time or temperature.

1.5.2.8 Drop Calorimeter

Drop calorimetry is a new method of calorimetry. This technique has been proven to be the best method for the accurate measurement of heat capacity at high temperature according to the literatures. This is very simple technique in which the sample is dropped from outside into the vessel inside the calorimeter at a given temperature. We can determine the enthalpy change associated with the chemical reaction or heating of a substance from one temperature to any other temperature. This method is widely used to measure the enthalpy of mixing, heat capacity and heat of transitions. The technique is also used to determine the specific heat of substances. It is a technique used for calorimetry, or the method of measuring the enthalpy of chemical reactions or phase transition as well as heat capacity. In order to measure the enthalpy, change of a chemical reaction having two reactants A and B, both the substances are dropped inside the calorimeter and initial and final temperature are measured (before and after the reaction). Heat absorbed and given off during the reaction is obtained from the temperature change and heat capacity of the substances dropped. Subsequently, it is converted to energy change per mole of a reactant by dividing of its number of moles. This method is explained to the students for the academic purposes or teaching. It does not consider the heat loss due to various means like thermometer and reaction vessel etc.

Principle and operation modes: In the drop calorimetry technique, a small quantity of substance is dropped from room temperature outside the calorimeter into the

experimental reaction chamber located inside the calorimeter surrounded by a furnace for heating, maintained at a known temperature.

Two types of Drop calorimeter operation are available:

1.5.2.9 Direct drop Calorimeter

In the direct drop Calorimeter (Figure 1.1) the sample is at temperature T_1 outside the calorimeter and the same is dropped into the calorimetric chamber maintained at T_2 . The total heat change associated with the elevating of the temperate of the substance from T_1 to T_2 is measured.

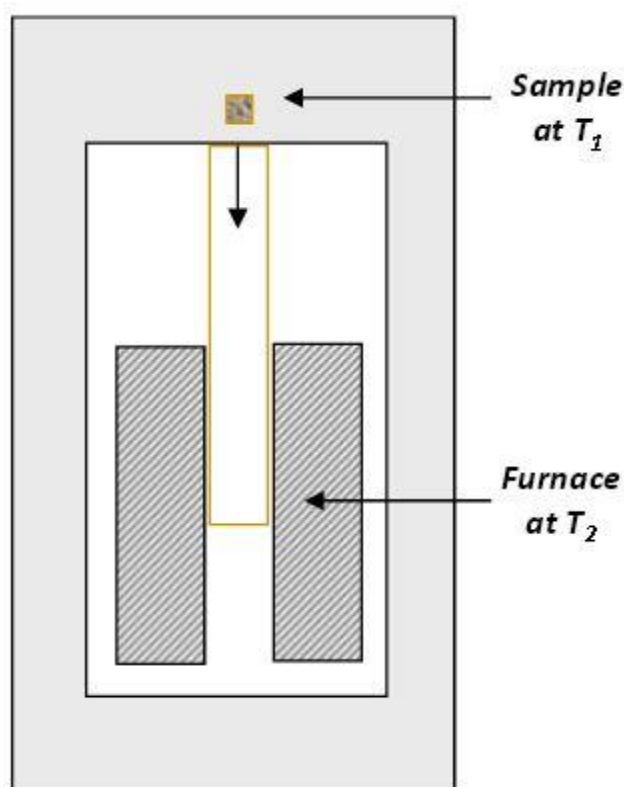


Figure1.1 Direct drop calorimeter

Applications of Direct Drop Calorimeter:

(a) *Determination of heat capacity*

For the measurement of heat capacity, the sample is dropped from the fixed initial temperature to the fixed calorimeter temperature. The amount of heat change between

these temperature ranges is measured by the calorimeter. The same experiment is repeated at different sample temperatures. Then the heat change is plotted as a function of sample temperature. Heat capacity is obtained from the plot using the following equation. In this method we measure the mean heat capacity of the material within the temperature range of measurements. It is essential to note that no phase transition takes place during heating of the sample from T_1 to T_2 .

$$\frac{\partial \Delta H}{\partial T} = C_p \dots \dots \dots (1.21)$$

(b) Determination of enthalpy of transition

To determine the enthalpy of transition, the sample is dropped into the calorimeter from starting temperature and heating is continued beyond the transition temperature of the substance up to a fixed temperature. Then the heat of transition is obtained by measuring the total heat absorbed (i. e due to transition and sensible heat of the substance) using the following equation. We need to know the heat capacity of the substance before transition and after transition to calculate the sensible heat.

$$\Delta H_{Total} = \int_{T_1}^{T_2} C_p \cdot dT + \Delta H_{Transition} \dots \dots \dots (1.22)$$

(c) Determination of reaction by ignition (direct synthesis)

In the case of some alloy synthesis, it is required to carry out at high temperature which requires very high rate of heating to attain high temperature. The good example is the Thermit reaction. In this case the pellets of both aluminium and ferrites are dropped into the calorimetric vessel and heated rapidly to the reaction temperature. Total heat requirement can be measured by the following equation:

$$\Delta H_{Total} = \int_{T_1}^{T_2} (x C_{pA} + y C_{pB}) \cdot dT + (\Delta H_A) + \Delta H(A_x B_y)_{formation} \dots \dots \dots (1.23)$$

it is essential to drop the pure A and B components for the calculation of heat of formation.

The term ΔH_A is the latent heat of melting of A that is needed to produce the reaction.

1.5.2.10 The solution drop calorimeter

In this technique (Figure 1.2), the sample is called solute at T_1 is dropped into the solvent (metal or metal oxide) in the calorimeter vessel at T_2 . The amount of heat measured by the calorimeter is on account of sensible heat of solute due to change of temperature and heat of dissolution of solute in the solvent.

Different Applications of solution drop calorimeter are:

(a) *Determination of heat of dissolution*

In this technique, mostly we measure the heat of dissolution of a metal in multicomponent alloys or oxides. To achieve this, a metal is dropped into a bath of alloy(s) (or oxides(s)) that acts as solvent.

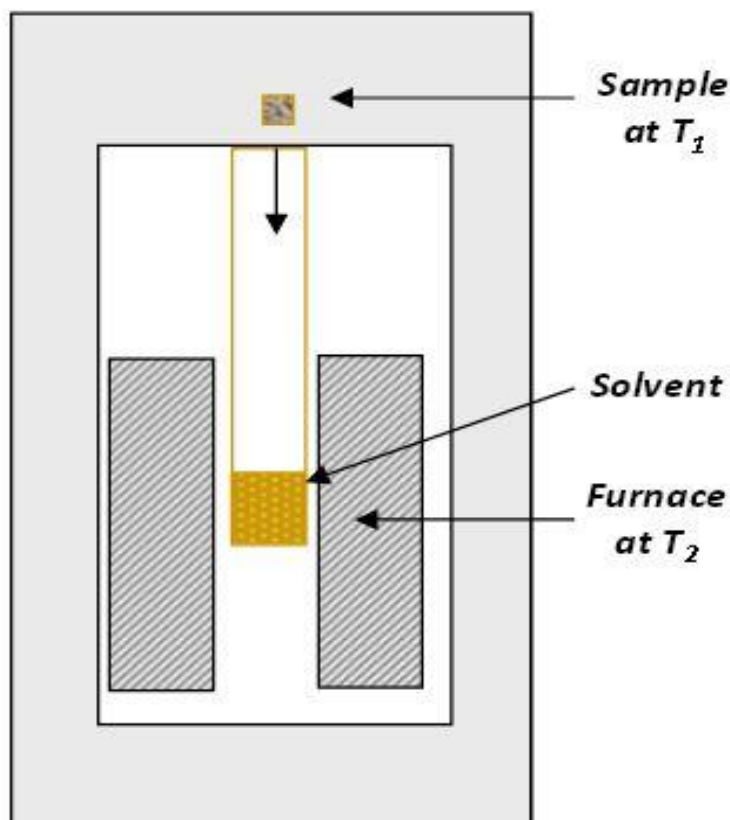


Figure 1.2 Solution drop calorimeter

The following heat relation will be used to calculate the heat of dissolution.

$$\Delta H_{Total} = \int_{T_1}^{T_2} C_p \cdot dT + (\Delta H_{Transition}) + \Delta H_{Solution} \dots\dots\dots(1.24)$$

The first term of the equation is the sensible heat of the dropped metal from T_1 to T_2 .

The last term is the heat of dissolution of the sample in the solvent. The second term may or may not be there depending on the transformation of sample takes place or not in the temperature range of T_1 to T_2 . Samples are dropped into the solvent successively to get the heat of dissolutions of the samples for the entire range of compositions.

(b) Determination of heat of formation

The enthalpy of formation of an alloy (or oxide) can be measured by the indirectly measuring the heat of dissolutions. For measuring the enthalpy of formation of an alloy of A_xB_y type, the following dissolutions are carried out in a suitable solvent:

- First dissolve pure A in the solvent
- Secondly, dissolve pure B in the same solvent
- At last dissolve pure A_xB_y alloy in the same solvent

The heat of formation of A_xB_y alloy is calculated from the following equation

$$\Delta H(A_xB_y)_{Formation} = x\Delta H(A)_{Solution} + y\Delta H(B)_{Solution} - \Delta H(A_xB_y)_{Solution} \dots\dots\dots(1.25)$$

1.5.2.11 MHTC 96 high temperature drop calorimeter from Seta ram, France

It is a type of drop calorimeter consisting of a thermopile which is a cluster of 20 thermocouples. Graphite tube resistance furnace of this calorimeter operates up to working temperature of 1593K. An automatic dropping device (Multi-sample Introducer) is used for the dropping of the sample from the top of the calorimeter. There is a provision of fixing the time interval in the multi sample introducer for the dropping of 23 samples (maximum). There is an alumina tube that connects the furnace

to the dropping device to guide the sample. Sample is dropped from automatic sample introducer to the crucible (placed in the furnace) by this tube. Furnace and crucible chambers are degassed by a vacuum pump connected to the instrument. The experiment is conducted in a flowing argon atmosphere to avoid oxidation of the samples. Control of process parameters and data acquisition and data evaluation is performed by the software supplied by the manufacturer.

MHTC96 high temperature drop calorimeter consists of the following parts:

(a) Motorized lifting device

This part lifts up the thermo gravimetric transducer so as to reach the experimenting crucibles.

(b) Multi-Sample Introducer

This is an automatic dropping device (Multi-sample introducer) used for dropping multiple samples one after another in a fixed interval of time. This device makes possible the consecutive introduction of 23 samples into the crucible into controlled atmosphere. It is necessary that each sample can fit inside a 1mm-to-5mm diameter sphere. The samples are loaded in a fluid-tight barrel linked to the crucible via the drop tube. The operator is then free to drop the samples automatically by fixing time interval between each drop. Multi-Sample Introducer comprises of:

- i.** A 23-sample introducer
- ii.** An electronic unit with a tactile screen, motor, belt transmission system and a protective cover.
- iii.** A template for adjusting the transmission belt tension.
- iv.** A 24V power supply module mounted in the rack.
- v.** A 24V power cable for the electronic unit.

(c) High temperature furnace

This is a cylindrical furnace hung from the cabinet's top plate. The heating element (1), fitted in the centre-line, is a graphite tube with its tapered end embedded in the cylindrical, copper, current intakes (2) (3) the lower current intake is fitted to the furnace by insulated bolts (4) and elastic washers (5). This arrangement makes possible expansion in the resistor. A graphite-felt sleeve (6) limits the resistor's heat loss. A sealed alumina tube (7) crosses the furnace through the centre of the heating element. It forms the experimenting chamber and enables insulation between the furnace's atmosphere and that of the experimenting chamber. This tube (7) is held at the top by the furnace's nose (8) and at the bottom by the lower mounting plate (9), which has O-rings (10) for sealing. The furnace bottom is blanked off by the lower flange (11) supporting the Temperature-control thermocouple (17) and the screening facility (18). Connected to this flange are the lower union for the sweeping gas inlet (14), the union for the vacuum pump (15) on the experimenting chamber and connector for the Temperature-control thermocouple (16).



Figure 1.3 Multi-Sample Introducer

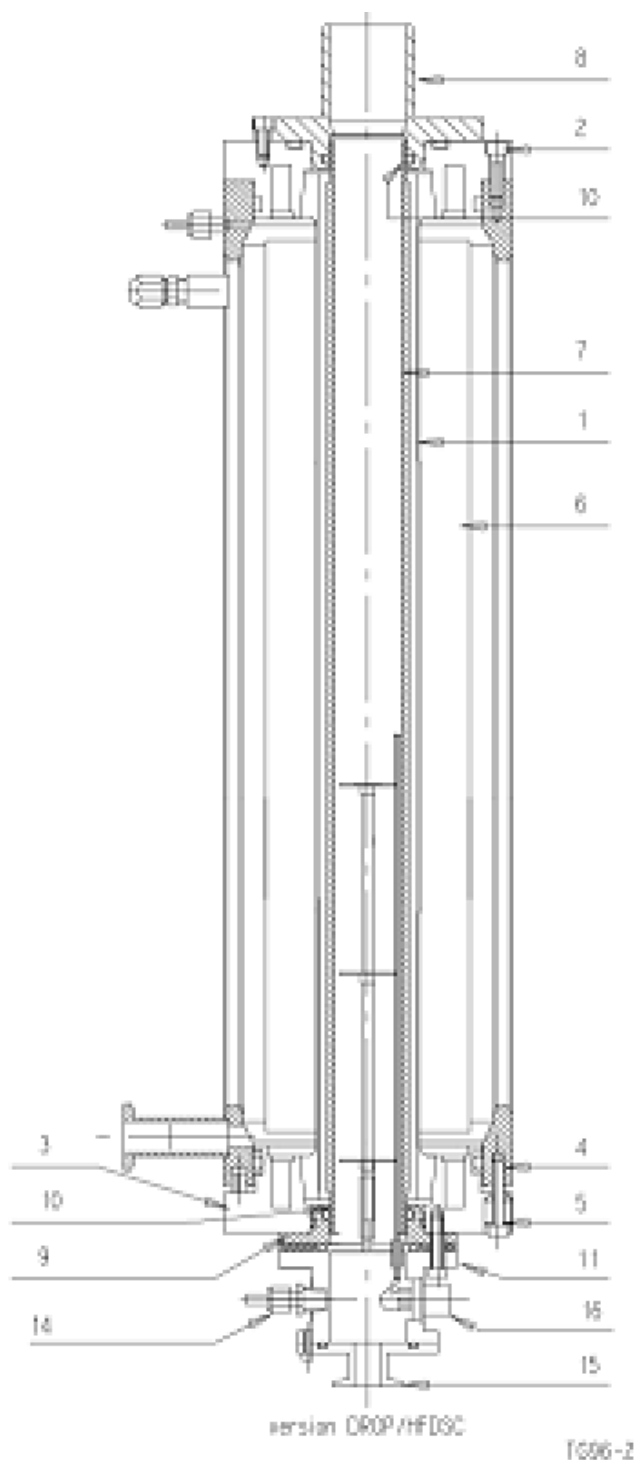


Figure 1.4 High Temperature Furnaces

(d) Degassing unit

Put argon sweeping in the furnace working area at 3.5 bar for 12 hours. Then run at least 5 heating cycles of 20°C–500°C at 10°C/min with an application of argon sweeping. Accumulate at the maximum cycles with application of argon sweeping. The furnace is then ready for operation.

(e) Drop tube

The basic version is equipped with an alumina drop tube having two functions:

- i. Guiding the sample during the drop or mixing experiment.
- ii. Exhausting corrosive vapours potentially given off by the sample.

(f) Crucibles

Alumina drop tube guides the samples from fluid tight barrel to the crucible. The drop calorimeter is equipped with cylindrical alumina crucibles having the following inner dimensions:

- i. Diameter = 13 mm
- ii. Height = 40 mm
- iii. Volume = 5.3 cm³ (working volume)

Do not exceed a filling height of 30 mm, so as to avoid any overflowing of the samples mixture. According to the samples, the choice is done between:

- Either an alumina crucible
- Or an alumina crucible with its platinum-lining.

(g) Software evolution controller

This central unit is integrated in the structure of the L96 Evo device, is composed of several electronic modules:

CPU module: This module runs the programming and temperature control for the thermal analyzer through the power module, according to the sequences set by the user. The acquisition and digitizing of the various signals (temperature, DTA/DSC, TMA signal) takes place. The transfer of the digitalized signals to a computer via an Ethernet interface.

Temperature acquisition modules: These modules execute the conditioning and the acquisition of two temperature signals (furnace temperature and sample temperature) via two thermocouples.

Gas panel module: It runs the opening or closing of the electro-valves on the gas panel, namely those of the Carrier Gases 1, 2 and 3, the Auxiliary Gas, the Protective Gas, purging and mixing of Auxiliary Gas with one of the Carrier Gases. The two mass flow rate regulators on the carrier gas and auxiliary gas circuits. It measures the pressure inside the analysis chamber and the flow rates of the Carrier and Auxiliary Gases.

Controller modules part: This unit is composed of:

- (a) The command module which controls the furnace and the electro-valves 230.
- (b) The box of the temperature control thermocouple.
- (c) The sample temperature measurement coming from the sensor head.
- (d) The low level amplifier module of DTA or DSC signals.
- (e) The gravimetric analysis function.

(h) Rear Power rack part

It contains:

- (a) The controller supply.

- (b) The CPU board with an Ethernet connection and the CAN connection which is sent inside the instrument through a cable.
- (c) The general power supply inlet controlled by the circuit breaker.
- (d) The mains supply redistribution for the peripheral functions (electro-valves, vacuum gauge, TMA box, gas control board, and controller).
- (e) The power control and its security function, ensured by means of the card.



Figure 1.5 MHTC96 High Temperature Drop Calorimeter

This technique has been successfully used for the measurement of the enthalpy of formation of binary, ternary and higher order alloys.