2.1 Thermodynamic Study

Chemical thermodynamics play an important role in predicting the feasibility of chemical reactions from the thermal data. This is possible only if the necessary information is available over a desired temperature range for every species involved in the reaction. Therefore, the evaluation and correlation of thermodynamic data are important aspects of chemical thermodynamics. A knowledge of thermodynamic properties like heat of formation, enthalpy, entropy and free energy functions at different temperatures is finding ever increasing use in science and technology for the determination of the stability of chemical substances, the position of equilibrium in chemical reactions and in the study of detailed structure and energetics of atoms, gaseous molecules, crystals, liquids etc. Thermodynamic methods are thus useful in understanding many diverse phenomena.

The application of thermodynamic methods to systems at high temperature requires,

a) Identification of all species and phases present,
b) Determination of crystal structure, molecular geometry and vibrational, rotational and electronic levels,
c) Determination of heats of formation,
d) Measurement of equilibrium constant, and the heat capacities over a wide range of temperature.
The study of thermodynamics at high temperatures is based on the measurement of equilibrium pressures of the constituents of the reaction. The study of vaporization process on the equilibrium of the chemical reaction helps to establish the nature and energetics of chemical binding in gaseous state. Gilles has emphasised the importance of the following points in the study of high temperature chemical reactions:

i) The net reaction is to be established.

ii) The gaseous species are to be identified.

iii) Vapour pressure is to be measured.

iv) The kinetics may be studied.

v) Finally the detailed mechanism of the reaction is to be established.

2.2 Generalizations useful in High Temperature Reactions

The following generalizations are very useful in predicting the gaseous products of an equilibrium reaction at high temperature. The first two are given by Brewer and the third by Searcy. In view of their importance in the present work they are quoted below. A detailed discussion has been given in literature.

1) The higher the temperature of a gas-solid or gas-liquid equilibrium, more nearly equal will be the partial pressures of various species.

2) A gas will react only endothermically with a solid to produce a significant yield of reaction product if the reaction produces at least as many moles of gas as are consumed in the reaction.
3) All equilibrium reactions that yield products when the temperature is increased must be endothermic and must occur with an increase in entropy. This is known as the principle of successive entropies.

2.3 Methods for the study of equilibrium of a reaction

In the study of equilibrium reactions, one desires to know the partial pressures of each vapour constituent and the total vapour pressure at each temperature. Various experimental methods have been described to measure the equilibrium vapour pressure by Margrave, Nesmeyanov and Cooper and Stranks.

2.3.1 Vapour pressures

The vapour pressure of substance is defined as "the pressure of vapour in equilibrium with its condensed phase at a given temperature". The heats of vaporization and sublimation can be evaluated by the knowledge of variation of vapour pressure with temperature. These are necessary in calculating heats of formation, reaction and bond dissociation.

Equilibrium pressures by direct measurements

In the static method, the vapour pressures at fixed temperatures are determined with the help of various instruments viz. simple U tube manometers containing mercury or some other fairly non-volatile liquids for relatively high pressure determinations. Vapour density methods, sickle gauges, dew point method, boiling point method are a few of the techniques for measuring vapour pressures directly.
Indirect measurement of vapour pressures

Transpiration technique

A simple, very useful and accurate method is the flow or transpiration method for the determination of vapour pressure greater than $10^{-3}$ atmospheres. For measuring the pressures less than $10^{-3}$ atmospheres several techniques viz. Langmuir, Knudsen effusion, Torsion effusion, molecular flow effusion, optical spectroscopy and mass spectrometry are available.

Methods in which vapour pressures less than $10^{-3}$ atm. are measured.

2.3.2 Langmuir Free Evaporation\textsuperscript{55-57}

The method is based on the determination of the rate of evaporation of a sample from an open surface in a vacuum. The vapour and the condensed phase are in dynamic equilibrium. The amount of material evaporated per unit time from unit area of a specimen in vacuum is determined by the Langmuir relation.

Bradley and co-workers\textsuperscript{58-60} have developed this technique to a high degree of accuracy and have thoroughly investigated its theory. Although the method has the advantage in the determination of lower pressures, yet the pressure measured is not necessarily the equilibrium vapour pressure and the vapour species must be identified independently.
2.3.3 The Knudsen Effusion Method

The Knudsen method of measuring small vapour pressures is important for the determination of thermodynamic properties of vapours and condensed phases in equilibrium. A great amount of thermodynamic data at high temperatures has been obtained with the help of this method. The method is based on kinetic theory of gases by which the molecular flux at a boundary can be calculated for a gas at equilibrium. In this technique the vapour of a single species in equilibrium with its condensed phase is allowed to flow from an isothermal container through a small thin edged orifice into an evacuated space. The technique is described in detail in Chapter VI of the present work.

2.3.4 Torsion Effusion Method

In this method the sample is placed in an effusion cell suspended by a fibre. The cell contains two holes in the opposite sides displaced in opposite directions from the centre. The effusion of vapour through the holes causes a torque on the cell and rotational displacement of the cell is measured by a mirror attached to the suspension. This method has received a good deal of attention because of the speed with which the vapour pressure can be obtained and its use for the direct determination of the molecular weight of the effusing species. Searcy and Freeman\textsuperscript{61,62} have obtained low values for tin and germanium when compared to the mass spectrometric results. The scope and limitations of this method are discussed in detail by Gilles.\textsuperscript{47}
2.3.5 Molecular Flow Effusion Method

The molecular flow effusion method has been developed and worked during recent years by DeMarcus, Whitman, Balson, Farber. This method involves an impinging gas at the temperature of the reaction striking the reacting material at pressures allowing molecular flow. The concentration of the molecular constituents is determined by the equilibrium constant, employing the Knudsen equation.

\[
n = P \left( \frac{2 m k T}{\pi} \right)^{1/2}
\]

\( n \) - number of moles striking the surface

2.3.6 Optical Spectroscopy

None of the experimental methods described above enables one to determine the structure and thermodynamic properties of gases produced in the vaporization reactions. Optical spectroscopy can be used for the determination of molecular configuration and electronic, vibrational and rotational energy levels. Thus thermodynamic properties can be found out by statistical mechanical methods. However, this method has a limited scope in finding out correct dissociation energies of some compound although the data is sufficient in making a satisfactory estimate of entropy.

2.3.7 Mass Spectrometer

Mass spectrometer is one of the most important tools employed in high temperature chemistry. The method consists of ionization of the high temperature vapour by electrons and identification of resulting ions. The composition of vapours involving the following species: viz. Al, Si, Ge,
compounds such as HfO$_2$, TiB$_2$, GeTe, SnS, PbS and many others have been studied. Inghram and Drowart have given an excellent review on mass spectrometry and its application to high temperature chemistry.

2.3.8 Isotopic Exchange Method

The technique devised by Nesmeyanov and co-workers utilized molecular exchange between two specimens of chemically identical but of different isotopic composition. The rate of exchange between two specimens, one radio active and the other inactive is a function of the rate of evaporation from the active specimen and the rate of diffusion of molecules into the bulk of the inactive specimen.

2.4 The Transpiration Method

The transpiration method is one of the oldest and versatile techniques of studying heterogeneous equilibria involving gases and solids. Regnault and von Warternberg were the first to use this method. It is employed primarily for measuring vapour and dissociation pressures. It may also be applied to gas-solid or gas-liquid equilibria. It is one of the few methods that can be used to measure the vapour pressures of species in the presence of large concentrations of other gases. Excellent reviews by Kubaschewski and Evans, Margrave, Richardson and Alcock and Schäfer are available in the literature giving applications of the method and the descriptions of many experimental techniques employed in this field. The method deals with the measurement of transport of the material under study. The transport of a substance may be due to appreciable vaporization of the sample at that temperature or may be due to gas (inert or reactive) being passed over a condensed sample at a rate sufficiently low for
equilibrium conditions to be established. The gas is collected at some point downstream from the sample and is analysed to determine the vapour and dissociation pressures of the components in the sample.

In the vapour-condensed phase equilibria, the solid and liquid which will have no appreciable vapour pressures at that temperature can be transported by the formation of gaseous products of the reaction. In the following case the transport medium is the vapour B.

$$\text{aA (S / l) + bB (g) = cC (g)}$$  \hspace{1cm} (5)

Thus the transport of the solid substances presupposes the motion of a gas. In the above reaction if the transport medium has sufficient saturation pressure only at elevated temperatures, then it is added to an inert carrier gas in a heated saturator or is vaporized at the beginning of the system. 'B (g)' when passed over solid 'A', transports the solid 'A' and at the end of the reaction the system is condensed by cooling. If the reaction proceeds rather extensively and rapidly with the deposition of solid substance one makes use of very simple flow techniques. In this technique all the gaseous components migrate with the same speed and hence their ratios are easily known.

The gases are assumed to be ideal and the carrier gas must be saturated with the vapour of the material under study or the gaseous products of the reaction. The total pressure $P_t$ is proportional to the total number of gas molecules present $n_t$. 
For each component in the gas, the partial pressure $P_i$ is proportional to $N_i$ and by Dalton's law,

$$P_t = \sum P_i \quad \text{and} \quad n_t = \sum n_i$$

(16)

Thus for an inert flow gas 'f' and vapour species 'V'

$$\frac{P_v}{P_t} = \frac{P_v}{P_v + P_f} = \frac{n_v}{n_v + n_f}$$

(17)

where $n_v$ can be determined from the weight loss of the sample or from the weight gain of a cold finger or a trap in the flow system. If the molecular weight of the vapour species is known or assumed, $n_f$ results from flow rate calibration experiments and $P_t$ will be the atmospheric pressure if the system is in equilibrium with the atmospheres as is usually the case.

Though the method, in principle, is simple and capable of wide applications to the high temperature systems, yet in practice, the following difficulties are encountered.

a) the number of molecules vaporizing cannot be known unless the molecular weight of the vaporizing species is known.

b) the sample container may show weight loss at high temperature through diffusion, even when the flow rate is zero.

c) reactions of the sample with the walls of the container or flow gas are often difficult to prevent.
2.4.1 Importance of equilibrium in transport study

The success of the transpiration method depends on the attainment of equilibrium as given by the following:

1) All the reagents participating in the reaction must be at the equilibrium temperature. This will be facilitated by preheating the gases before they enter reaction zone.

2) The pressures of the equilibrium zone must be the same as that of the entire flow system. Temperature and pressure gradients cause the reverse reaction to occur, i.e. the reformation of solid reactants. The apparatus should be so chosen as to avoid these difficulties.

3) The reaction zone must attain equilibrium and remain undisturbed during the transport period.

4) Some unwanted reactions due to imperfect flow may decrease the surface area of the solid, gas or liquid under study so that the reaction rate will deviate far from equilibrium. For example, in the present system under study, Cd-CdCl₂, if the carrier gas contains appreciable amounts of O₂, air, water vapour, they will react with Cd or CdCl₂ hindering the reaction and giving much lower transport of CdCl₂. The carrier gas therefore has to be perfectly pure and dry.

5) The activity of solid or liquid phase must remain constant throughout the reaction.

6) Flow rate should be measured accurately.

7) Reactions between sample and the container material or flow gas and also with the walls of the tube should be avoided.
Very few refractory materials are useful for molten metals.
For equilibrium measurements, it is therefore necessary to test the materials for which the free energy change for a simple reduction by the liquid metal has a large positive value. Brewer has illustrated the use of thermodynamics in the search for a suitable container for melting titanium. If an extensive contamination or reaction occurs the material should be brought to equilibrium with liquid metal or reactive species so that it is saturated with respect to the solution, either of the metal or refractory material. This will minimise the attack or the container will be passivated. Attack by the melt normally involves the penetration through solid container by an intergranular solution process and the rate of this attack depends primarily on Kinetic factors e.g. diffusion and viscosity.

2.4.2 Saturation of carrier gas
The establishment of the saturation flow is the most important factor in achieving equilibrium. The flow or carrier gas should be saturated with vapour. The equilibrium flow rate range will vary according to the experimental set up and systems studied. The flow gas has to ensure equilibrium with solid or liquid. In the simplest case the solid substance is placed in a small vessel which in turn is placed inside a tube of 10 mm. diameter for example. It is better to have the substance in a granular form, packed loosely in the tube over a distance of a few centimeters. The gas passes over the solid and in an ideal case equilibrates with it completely.
For the above mentioned tube diameter and for the temperature of the solid above 500°c, satisfactory flow rates are usually in the range 30-160 ml. per minute (S.T.P.). When the reaction between gas phase or solid substance proceeds very slowly or when one is forced to use slow gas flow rates, large amounts of solid and long reaction zones are recommended.

The high flow rates can be used if the chemical reaction attains equilibrium quite rapidly. In the high temperature system in which equilibrium is not rapidly attained, diffusion rather than chemical reaction is usually the rate determining step. Such diffusion processes require longer temperature zones, larger surface areas of the sample and slow flow rates. If the flow rate is too high the carrier gas will not be saturated and the apparent pressures will be low. In some cases the heterogenous reaction proceeds so rapidly that equilibrium will be established at the solid material and the gas motion becomes the slowest step. The majority of the substances have velocity coefficients which are close to 1 i.e. the surfaces behave as if they are covered with saturated vapour. The quantity of vapour is a function of the saturation pressure and gas kinetics. Consequently a low velocity coefficient will be observed in the transportation from solid to gaseous state. If the carrier gas velocity is too low, the sample may be transported due to self diffusion and thermal diffusion. It is therefore essential to establish the saturation flow rates where the vapour pressure is independent of flow rate.
If an unsaturated gas flow is suspected, a series of experiments at various flow rates should be carried out until a range of flow rates is found for which the mass of sample transported per unit volume of flow gas remains constant. Thus a plot of \( n_v/n_o \) versus \( n_f \) (equation 17) should approach a plateau region for \( n_f \) values where saturation is complete. For unsaturated flow this plot will not level off. This has been discussed by Lapore and van Wazer. It has also been customary to make measurements at several flow rates and to extrapolate to zero flow rate to eliminate effect of lack of saturation. If an equilibrium between gaseous phase and a condensed phase is established with negligible diffusion effects the amount of vapour transported per unit time varies with flow rate of gas mixture. The effect of sample geometry, carrier gas flow rate and absolute magnitude of the vapour pressure on the apparent vapour pressure have been studied by Alcock and Hooper.

It can be shown that at sufficiently high flow rates, diffusion effects become negligible. Diffusion occurs when the rate of flow is too slow and the apparent pressures will be too high. Merten has derived the equation.

\[
P = \frac{m}{t_v} \cdot \frac{RT}{M} \left[ 1 - \exp \left( - \frac{Vl}{DA} \right) \right]
\]

where 
- \( P \) - pressure
- \( R \) - gas constant
- \( T \) - temperature \(^\circ\)K
- \( M \) - molecular weight of the species
- \( m/t_v \) - mass transported per unit time
- \( l \) - length of the capillary
- \( D \) - diffusion coefficient of the vapour
- \( A \) - cross sectional area of capillary
For a large value of $V$ (volume of flow gas) diffusion effects are important and the pressure assumes the normal value.

$$P = \left( \frac{m}{t_v} \right) \frac{RT}{M}$$ (19)

He has also pointed out that equation may be used to obtain not only the pressures but also diffusion coefficient in favourable cases. Ackerman et al have confirmed the validity of this equation. According to Merten reliable pressures can be calculated if experimental determinations are available at two significantly different flow rates for which saturation has been reached.

2.4.3 Advantages of Transpiration Method

The importance of this experimental technique can be realised in the case of the transport of silicon in chloride system. Schäfer by using the flow method, transported considerable amounts of SiCl$_2$ to a cold zone without disproportionation. At lower temperatures SiCl$_2$ combined with SiCl$_4$ to form SiCl$_6$, Si$_3$Cl$_8$ etc. Another important feature of this method is the ease with which corrosive unstable vapour species can be handled successfully and in a useful way.

2.4.4 Disadvantages of the Transpiration Method

a) The number of molecules vaporizing cannot be known unless the molecular weight of the vapour is known.

b) The difficult situation in this technique is to follow individual species in a heterogeneous system, where the
Products of the reaction are more than one gaseous species. Thus the study of the reaction involved in the overall process becomes difficult. But the arrangements leading to quantitative collection of the products, condensing on the cold finger, quenching methods and improved analytical techniques may help to solve this problem.

2.5. Thermodynamics as applied to Equilibrium Reactions

Determination of vapour pressures of the various components in a solid gas reaction

The amount of a solid substance transported by a gas stream in a definite time can be known by knowing the loss in weight of the sample or gain in weight due to the disproportionated solid in the cold trap. The amount of transporting agent passed and the volume of carrier gas passed can also be known. Then by assuming that the ideal gas law holds good in the equilibrium zone, the pressures can be estimated using the equation

\[
P V = nRT \quad (20)
\]

Since P, V and T are related to the atmospheric pressure, initial flow of gas at room temperature T, the equation becomes

\[
P = \frac{nRT}{V_r} \quad (21)
\]

The pressures of various components in a general reaction (eqn. 5) can thus be calculated as follows:
\[ P_c = \frac{C}{a} \cdot nA \cdot \frac{RT}{V_r} \]
\[ = \frac{C}{a} \cdot \frac{\Delta w}{M} \cdot \frac{RT}{V_r} \]

and \( P_B \) unreacted = \( (n_A - \frac{b}{a} \cdot nA) \cdot \frac{RT}{V_r} \)

\[ = (n_B - \frac{b}{a} \cdot \frac{\Delta w}{M}) \cdot \frac{RT}{V_r} \]

where \( \Delta w \) is the loss in weight of the substance, \( M \) is the molecular weight.

Then the equilibrium constant is given by

\[ K = \frac{P_c}{P_b} \]

2.5.1 The equilibrium constant

Thermodynamically the state of equilibrium of any process at constant temperature and pressure can be defined by the equation

\[ F = 0 \]

i.e. the free energy remains unchanged in any infinitesimal process occurring at constant temperature and pressure.

Therefore in a case of chemical equilibrium, it is important to acquire the information regarding the free energy change in the reaction. Thus for an equilibrium reaction of the type (5), the free energy change can be written,

\[ \Delta F^0 = -RT \ln k \]
2.6 **Treatment of the equilibrium data**

In high temperature thermodynamics one seeks a method which will conveniently yield value for the equilibrium constant \( K \) at any desired temperature for the reaction under study. Experimentally determined equilibrium data have been utilized to obtain standard enthalpy of the reaction. Two methods have been used, one called the 'Second Law Method' and the other 'Third Law Method'.

2.6.1 **Second Law Method**

This involves the utilization of the well known vant Hoff's equation with the usual log \( K \) vs \( 1/T \) plot. From the slope of the graph and the intercept one can calculate the heat and entropy of the process respectively. The fundamental basis for this plot lies in the change of standard free energy with temperature.

\[
\frac{d}{dT} \left( \frac{\Delta F^\circ}{T} \right) = \frac{\Delta H^\circ}{T^2} \frac{dT}{dT} = \Delta S^\circ \frac{d(1/T)}{d(1/T)}
\]  

(27)

Substituting equation 26 for \( F^\circ \) in equation 27, one obtains the vant Hoff's equation:

\[
\frac{d\ln K}{dT} = -\frac{\Delta H^\circ}{RT^2}
\]

(28)

or

\[
\frac{d(K\ln k)}{d(1/T)} = \frac{4.5758 \, d \log k}{d(1/T)} = -\Delta H^\circ
\]

(29)

Thus the slope of log \( K \) vs \( 1/T \) is \(-\Delta H^\circ/R\). If \( \Delta H \) is constant, the slope is constant and the plot is straight line. Since \( \Delta H \) usually varies slowly with temperature,
it is customary to assume a straight line relationship. This method of obtaining heats of reaction from equilibrium measurements is known as 'Second Law calculation'. It is especially useful in numerous cases where the only information available regarding the heat of reaction is derived from the equilibrium measurements.

In the above, it is assumed that $\Delta C_p^0$ for the process is constant over the temperature range investigated. From Kirchoff's equation,

$$\left[ \frac{\lambda (\Delta H^0)}{\gamma T} \right]_P = \Delta C_p^0$$

(30)

Therefore, if the heat capacity equation are available for the reactants and products an improved procedure is possible. The treatment includes the use of the following equation.

$$\frac{\Delta F}{T} = -R \ln K = \frac{\Delta H^0}{T} - \Delta a \ln T - \frac{1}{2} \Delta b T - 1/2 \Delta C T^{-2} + I$$

(31)

where I is constant.

$$\frac{\Delta H^0}{T} + I = \sum -R \ln K + \Delta a \ln T + 1/2 \Delta b T + 1/2 \Delta C T^{-2}$$

(32)

For each temperature at which a value of K is known the right hand side of the above equation can be obtained. As the left hand side of the equation is a linear function of $1/T$, a plot $\Sigma$ against $1/T$ gives a straight line with a slope $\Delta H_i^0$. From the value of $H_i^0$ one can obtain $\Delta H_i^0$ at any temperature range for which the heat capacity equations are applicable.
If the contribution of $\Delta c_p^o$ for the reaction is not constant over the temperature range, the resultant log $K$ vs $1/T$ plot will show a curvature or wide scattering of points. In such cases a plot which is more satisfactory than log $K$ vs $1/T$ is to be recommended, because it is easier to get the slope of a straight line than that of a curved line.

2.6.2 Third Law Treatment

This method as its name implies, is fundamentally related to the third law of thermodynamics through its use of absolute entropies and heat capacities. In practice, the free energy function $\left[ \frac{F_T^o - H_T^o}{T} \right]$ also referred as 'fef' is used whenever it is found in a tabulated form or can be calculated. The simplicity and usefulness of these free energy and heat content functions, especially in calculating the heat of reaction were demonstrated by Margrave.\textsuperscript{94}

The free energy function is related to the usual thermodynamic quantities in the following manner. By rearranging the fundamental free energy equation:

$$\Delta F_T^o = \Delta H_T^o - T \Delta S_T^o$$  \hspace{1cm} (33)

one obtains,

$$\frac{F_T^o - H_T^o}{T} = -S_T^o$$  \hspace{1cm} (34)

by adding the quantity $\left[ \frac{H_T^o - H_{T_{\text{ref}}}^o}{T} \right]$ to both sides of the equation one gets
where the superscript zero indicates the standard states, $T$ is the kelvin temperature and the reference temperature $T_{ref}$ is usually taken as $0^\circ K$ or $298^\circ K$. The conversion between the two reference temperatures is made by the use of the function $\Delta H_{298} - \Delta H_0$ as follows:

$$\frac{\Delta H_{298}}{T} + \frac{\Delta H_0}{T} = \frac{\Delta H_{298} - \Delta H_0}{T}$$

(36)

Since heat content difference and the entropy are related to the $C_p$ values, the free energy function can be evaluated from experimental heat capacity measurements

$$S^0_T = \int_{T_0}^{T_1} C_p \, d \ln T + \frac{\Delta H_{Tr}}{T_1} + \int_{T_1}^{T_2} C_p \, d \ln T + \int_{T_2}^{T} C_p \, d \ln T$$

(37)

and

$$\frac{H^0_T - H^0_{T_{ref}}}{T} = \int_{T_{ref}}^{T_1} C_p dT + \frac{\Delta H_{Tr}}{T_1} + \int_{T_1}^{T_2} C_p \, dt + \int_{T_2}^{T} C_p \, d \ln T$$

(38)

In the case of gaseous molecules it is possible to determine the value of "$f_{ef}$" directly through the use of statistical thermodynamics and spectroscopic data.
For a chemical reaction "fef" at a given temperature may be defined as:

\[ \Delta \text{fef} = \sum (\text{fef}) \text{ products} - \sum (\text{fef}) \text{ reactants} \]  

(39)

since \[ \Delta \text{fef} = \frac{\Delta F^0_T}{T} - \frac{\Delta H^0_{\text{Tref}}}{T} \]  

(from eqn.35)

and \[ \Delta F^0_T = -RT \ln K \]  

(from eqn.26)

\[ \Delta H^0_{\text{Tref}} = T \left[ \frac{\Delta F^0_T}{T} - \frac{F^0_T - H^0_{\text{Tref}}}{T} \right] \]  

(40)

or \[ \Delta H^0_{\text{Tref}} = T (-RT \ln K - \Delta \text{fef}) \]  

(41)

The advantage of the third law method is that each experimentally determined value of the equilibrium constant permits an independent evaluation of the heat of reaction.

The free energy functions vary quite slowly with temperature and hence may be obtained easily and accurately by simple interpolation and extrapolation procedures from values given at wide intervals. Furthermore temperature dependent errors are often hard to eliminate from equilibrium measurements. The temperature coefficient and the corresponding heat of reaction from the second law may be greatly in error whereas the third law heat does not change significantly.