CHAPTER I

INTRODUCTION AND SCOPE

General characteristics of transition elements with special reference to the chemistry of cobalt(II), nickel(II), copper(II) and zinc(II) are described. Introduction to solid state reaction thermal analysis methods, kinetics and mechanism of thermal decomposition reactions from TG data are given. An outline of present investigation and applications along with a concise review on thermal decomposition studies of complexes of hydrazine and its derivatives are also presented. The scope of present investigation is also given.
1.1 Introduction

In recent years, inorganic chemistry has experienced an impressive renaissance. Theoretical and experimental research in inorganic chemistry is flourishing and the output of research papers and reviews is growing exponentially\(^1\). It is interesting to note that 70% of the research in inorganic chemistry deals with various aspects of coordination compounds, which play important role in applied science and industrial technology. The development of coordination chemistry dates back to French revolution. Recent research activities are concerned with complexes of almost all the metals in the periodic table in their different oxidation states and with all possible coordination numbers ranging from two to twelve\(^2, 3\). Reason for this advancement may be attributed to the formulation of excellent theories of electronic structure of metal ions in coordination compounds and the availability of modern sophisticated instruments.

1.2 General characteristics of the transition elements

The d block and f block elements are generally called the transition elements, since their properties represent transition between the highly reactive metallic elements of the s block and the elements of the p block. The transition elements may be strictly defined as those elements, which have partly filled d or f orbitals. Transition metals are widely distributed throughout the earth’s crust and oceans.

The transition elements have certain general characteristics in common\(^1\). These are listed below.
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1. They are typical metals, most of which play important roles in industry.
2. They are practically hard, strong, high melting, high boiling metals, which conduct heat and electricity well.
3. They form alloys with one another and with other metallic elements.
4. Many of them are sufficiently electropositive to be dissolved in mineral acids, although a few are 'noble', i.e., they have such low electrode potentials that they are unaffected by mineral acids.
5. With very few exceptions they exhibit variable valence, and their ions and compounds are coloured at least in one, if not all the oxidation states.
6. Because of partially filled orbitals they form at least some paramagnetic compounds.
7. They form numerous complexes as a result of participation of incompletely filled d or f orbitals of appropriate energy in bonding with suitable ligands.

The ability to form complex species is at the maximum among the transition metal ions, because of favorable factors such as small cation size, comparatively large nuclear or ionic charge and appropriate electronic arrangements. These transition elements are further classified into three groups: (a) the main transition elements or d block elements, (b) the lanthanide elements and (c) the actinide elements. Generally, the most stable complexes are those, in which the metal ion is one of the transition elements - a consequence of the fact that it is only among these that the necessary orbitals are available without excessive demands on energy requirements. Among the three series of transition metals, the 3d metals dominate the field of coordination chemistry. As the present investigation is
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concerned with the thermal decomposition studies of complexes with metal ions such as Co(II), Ni(II), Cu(II) and Zn(II), it would be worthwhile to have a brief account of the chemistry of these metal ions.

1.2.1 Chemistry of cobalt(II)

Cobalt forms many complexes in both divalent and trivalent states. Divalent cobalt forms numerous complexes of varied stereo-chemical types. Octahedral and tetrahedral geometries are the most common, but there are a considerable number of square complexes as well as five coordinate complexes. The most common donor atom in Co(II) complexes is ‘N’, having ammonia and amines as ligands forming numerous complexes. Cobalt(II) forms tetrahedral complexes more rapidly than any other transition metal ions. Also, because of small energy difference between the tetrahedral and octahedral complexes, often the same ligand forms both the types of Co(II) complexes in equilibrium solution.

1.2.2 Chemistry of nickel(II)

Nickel(II) forms a large number of complexes encompassing coordination numbers 3 to 6 with varied structural types such as octahedral, trigonal bipyramidal, square pyramidal, tetrahedral and square planar geometries. The maximum coordination number of nickel(II) is six. Four coordinate Ni(II) complexes have both tetrahedral and square planar geometries. Square planar geometry that forms more stable complexes is preferred because the d8 configuration of Ni(II) with 8 electrons can occupy the four planar bonding orbitals more rapidly than the higher energy antibonding orbital in tetrahedral coordination.
1.2.3 Chemistry of copper(II)

The dipositive state is the most important for copper. The $d^9$ configuration makes Cu(II) subject to Jahn-Tellar distortion, if placed in an environment of cubic i.e., regular octahedral or tetrahedral symmetry, and this has a profound effect on all its stereochemistry. When six coordinate the octahedron is severely distorted. There are other stereochemical possibilities, of which the most important is distorted tetrahedral. Orange colour is characteristic of the distorted tetrahedral \( \text{CuCl}_4^{2-} \) ion. Numerous planar complexes of Cu(II) are also known.

1.2.4 Chemistry of zinc(II)

Complex anions with halides are formed by zinc. The \([\text{ZnX}_4]^{2-}\) complexes can be isolated as salts of large cations. Complex cations with ammonia and amine as ligands are well defined, and can be obtained as crystalline salts. Zinc(II) usually, has coordination numbers 4 – 6.

1.3 Nitrogen and oxygen donor atoms in ligands

Generally, ligands are either amines or dipolar molecules. The donor atom in the ligand, i.e., the coordination site possesses one or more lone pairs, which may be donated to a suitable cation to form a chemical bond. Ligands are classified on the basis of donor atoms. Electronegativity values of ‘N’ and ‘O’ are 3.0 and 3.5, respectively in Pauling’s scale. Although oxygen has two lone pairs and nitrogen has only one, the two lone pairs on oxygen get dissipated due to lone pair-lone pair repulsion. This means that the lone pair on nitrogen is more concentrated, and hence, more effective than the lone pairs on oxygen. This factor along with the lower
electronegativity of nitrogen compared to oxygen makes the nitrogen ligands generally stronger than the oxygen ligands. In the present investigation, hydrazine and substituted hydrazines have been used as ligands.

1.4 Solid state reactions

Of the states of matter, solid state is the most organized and, from a universal point of view, the least natural. In many ways it is also the most complex state of matter. It is, therefore, not surprising that attempts to study reactions in solid state meet with unusually difficult problems. Solid state reactions remain to this day the least understood of the chemical reactions from dynamic and mechanistic points of view.

The properties of the solid depend on the properties of the atoms that form the solid, on the arrangement of atoms in the solid, and on the condition such as temperature or pressure, under which the solid is examined. The ability of solids to withstand a shearing force, and to regain their original shape after a small deformation, is the property which most readily distinguishes them from substances in the other important states of matter, liquids and gases\(^\text{12}\).

A study of solid state reaction has three aspects, viz., phenomenological, thermodynamic and kinetic aspects\(^\text{13}\). The phenomenological study is concerned with the qualitative and semiquantitative observations of the phenomena occurring during the reactions. The thermodynamic approach is static in its outlook, and it relates to the initial, final and equilibrium states of the system and to the driving force behind the transformation. The kinetic study deals with the rate of
transformation of reactants into products and the mechanism of transformation. The theme of present investigation consists of a detailed investigation of kinetic aspect of some selected solid state reactions.

1.5 Thermal analysis methods

Even though various thermal analysis techniques were developed at the end of the 19th century, thermal analysis has been treated largely as a chemical analysis tool till the middle of the 20th century. Thermal analysis (TA) is a general term, which covers a group of related techniques, in which the temperature dependence of the parameters of any physical property of a substance and/or its reaction products is measured as a function of temperature, while the substance is subjected to a controlled temperature programme in a specified atmosphere. Based on the physical property measured the thermal analysis techniques are broadly classified as given in Table 1.1. Wendlandt, Liptay and Dunnb have published surveys of various thermal analysis techniques and their applications to numerous areas of research. Thermal analysis techniques are most extensively used to inorganic materials followed by polymers, metals, alloys and organic substances. Thermal analysis has wide range applications in minerals, ceramics, electronic materials, pharmaceuticals and food stuff and biological organisms. Several reviews and articles were reported on the thermal studies. In many cases, the use of a single thermal technique may not provide sufficient information. Under such circumstances more than one method may be used either independently or in conjunction. Among the various thermal analysis methods the most widely used method is
thermogravimetry (TG), followed by differential thermal analysis (DTA) and differential scanning calorimetry (DSC).

1.6 Basis of thermal analysis

Every substance is characterized by its free energy or free energy changes (ΔG), given by the expression

\[ \Delta G = \Delta H - T \Delta S \]

where, T is the temperature in Kelvin, ΔH is the change in enthalpy and ΔS is the entropy change for the reaction. At a given temperature every system has a tendency to attain a state, in which the free energy change is the minimum. Formation of more stable crystalline structure or another state with lower free energy may take place on gradually heating the sample via intermediate steps.30,31

1.7 Thermogravimetry

Thermogravimetry (TG) is defined as a technique, in which the mass of a sample is continuously recorded as it is heated or cooled at a constant rate in suitable environment. By using an automatic recording thermobalance a curve of mass change of the sample versus temperature can be obtained directly. Thus, the TG curve obtained gives information about the thermal stabilities and composition of the original sample, intermediate products and ultimate decomposition residue, if any. The main features of a thermogravimetric or TG curve are the following.
(a) The horizontal portions called plateaus indicate the regions of temperature, where there are no mass changes.

(b) The curved portions indicate mass loss.

(c) Thermogravimetric curve is quantitative, and hence, calculations on the stoichiometry of the compound can be made at a given temperature.

Some of the earliest applications of TG have been in analytical chemistry, particularly in standardizing the drying temperatures and ignition temperatures for precipitates which can be employed in gravimetry. Duval’s classic work on more than thousand gravimetrically useful precipitates testifies to this application\textsuperscript{14}. The applications of thermogravimetry and the factors affecting TG were discussed by Wendlandt\textsuperscript{13}. At present, the most widely used thermal technique to study the kinetics of solid state thermal decomposition reactions is thermogravimetry. The data obtained from TG are more quantitative than those obtained from DTA or DSC, because mass measurement has an order of magnitude higher accuracy and precision compared to the measurement of $\Delta T$ in DTA or $dH/dT$ in DSC.

A statistical analysis to demonstrate the variance of kinetic parameters obtained from TG, DTA and DSC has shown that the results obtained from TG have better precision than those obtained from the other two methods\textsuperscript{32}. However, TG is a more limited technique compared to DTA or DSC in the sense that the TG study is limited to reactions which involve mass changes.
1.8 Derivative thermogravimetry

The relationship between the rate of mass change and temperature or time is expressed by the derivative thermogravimetric (DTG) curve. A series of peaks are obtained instead of the stepwise curve, in which the areas under the peaks are proportional to the total mass of the sample. A horizontal portion in the TG curve gives a corresponding horizontal portion in DTG curve, because \( \frac{dm}{dt} = 0 \). A maximum in the DTG curve is obtained when the TG curve has an inflection point, where mass is being lost rapidly\(^{33}\). The height of DTG peak at any temperature gives the rate of mass changes at that temperature. The DTG is useful for many complicated determinations, and any change in the rate of mass loss may be readily identified as a thorough indication of consecutive reactions, and hence, mass changes occurring at close temperatures can be ascertained.

1.9 Differential thermal analysis

Differential thermal analysis (DTA) is the technique of recording the difference in temperature between a substance and reference material against either time or temperature as the two substances are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate. Usually, \( \alpha \) - alumina is used as the reference material, because it undergoes no processes involving enthalpy change over a wide range of temperature. The temperature of the reference material will go on increasing uniformly, but that of the sample under study will sometimes lag behind or rush past the temperature of the reference material, depending on whether an endothermic or exothermic process is taking place. Thus, a DTA curve gives an idea of the enthalpy changes occurring in the sample as it is continuously heated or cooled. In DTA, a plot can be between \( \Delta T \)
against temperature. If the heating or cooling is linear, the plot can be between $\Delta T$ and time. The temperature difference ($\Delta T$) should be plotted on the ordinate with endothermic reactions downward and $t$ or $T$ on the abscissa increasing from left to right.

Very little progress in instrumentation was made until the 1950’s. Wittels used DTA for micro calorimeter measurements$^{34}$. Stone, who used it in controlled atmosphere of $H_2O$ and $CO_2$, brought about an important development in DTA instrumentation$^{35}$. In 1957, Borchardt and Daniels developed the necessary theory for the application of DTA to the study of reaction kinetics$^{36}$. Now a day, DTA is extensively used for the study of heterogeneous reaction kinetics. Lombardi$^{37}$ has compiled a bibliography of all the books written on DTA/DSC and other TA techniques since 1937.

1.10 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a technique of recording the energy necessary to establish zero temperature between a substance and a reference material against time or temperature as the two substances are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate. The record is the DSC curve, which represents the amount of heat applied for unit time as ordinate against either time or temperature as the abscissa$^{38}$. Ever since the introduction of the first commercial equipment for the quantitative measurement of heat flows into and out of the sample during a transition, there has been considerable confusion about the naming of the instrument. A wide variety of labels were applied, *viz.*, quantitative differential thermal analysis (QDTA), dynamic enthalpy analysis (DEA), dynamic differential calorimetry (DDC) and differential scanning calorimetry (DSC). The term now generally accepted and approved by ICTAC is differential scanning calorimetry.
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There have been a number of different theories concerning the theoretical interpretation of the DTA and DSC curves. All the theories relate in some manner, the area of the differential curve peak to the various parameters of the sample and the instrument. The equations representing these parameters were developed through the use of conventional heat transfer relationship and the geometries of the sample and the sample holder.

The general theory for describing DTA and DSC was developed by Grey\textsuperscript{39}. This equation can be represented as

For DTA

\[
R \left[ \frac{dH}{dt} \right] = \left( T_s - T_r \right) + R \left( C_s - C_r \right) \left[ \frac{dT}{dt} \right] + R C_s \left[ \frac{d(T_s - T_r)}{dt} \right] \rightarrow (1)
\]

For DSC

\[
\frac{dH}{dt} = \left[ \frac{-dq}{dt} \right] + \left( C_s - C_r \right) \left[ \frac{dT_p}{dt} \right] - R C_s \left[ \frac{d^2q}{dt^2} \right] \rightarrow (2)
\]

where \( \frac{dH}{dt} \) is the heat generated by the sample per unit time, \( R \) is the controlling thermal resistance, \( C_s \) and \( C_r \) are the heat capacities of the sample and the reference material, \( T_s \) and \( T_r \) are the sample and reference temperatures, \( T_p \) is the temperature of the heat energy source and \( q \) is the quantity of heat.
1.11 Simultaneous TG/DTA measurements

The coupled thermal techniques such as TG/DTA can be employed on any given sample with a single run. This is also referred to as 'hyphenated techniques'. The pioneering TG/DTA system involves the use of a derivatograph to allow for the simultaneous collection of TG/DTA data\textsuperscript{40, 41}. The operation of coupled techniques provides an analyst with more comprehensive picture of the sample, which is being investigated.

1.12 Thermal decomposition kinetics from thermal analysis data

The kinetics of a solid state decomposition reaction differs fundamentally from that occurring in a homogeneous system, and the conventional concepts of concentration, order or molecularity have little applicability here. Indeed, these parameters are often considered not meaningful in explaining the observed systematic variations of rate that are measured during the progressive formation of the product. In the decomposition of solids, the concept of the reaction interface and lattice imperfections have been found to be of greater value.

The general approach in kinetics is to obtain an equation for the rate of the reaction. In the case of a solid state decomposition reaction

\[
A_{\text{(solid)}} \rightarrow B_{\text{(solid)}} + C_{\text{(gas)}}
\]

or

\[
A_{\text{(solid)}} \rightarrow B_{\text{(gas)}} + C_{\text{(gas)}}
\]

The derivation of kinetic equation is based on the following assumptions.
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(i) The rate of reaction is expressed as a unique function of temperature, $K(T)$, and conversion factor $f(\alpha)$, i.e.,

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad \Rightarrow \quad (3)$$

The term, $\alpha$ is called the degree of transformation or fractional decomposition and is defined at time 't'.

(ii) The conversion factor, $f(\alpha)$ is assumed to be of the form

$$f(\alpha) = \alpha^m (1 - \alpha)^n \quad \Rightarrow \quad (4)$$

Equations of this type have been derived for isothermal conditions from the theoretical models as well as from the experimental data. The exponents, 'm' and 'n' are called the homogeneity factors.

(iii) The simplifying assumption is that $m = 0$. This leads to a formal analogy with homogeneous kinetics. In such a case, the homogeneity factor 'n' can be identified with the reaction order 'n'.

(iv) For most of the reactions, the temperature dependence is found to be Arrhenius type, so that the term, $k(T)$ can be identified as the rate constant, $k$, which is related to temperature as

$$k = Ae^{-E/RT} \quad \Rightarrow \quad (5)$$

where 'A' is the pre-exponential factor, 'E' is the energy of activation; 'R' is the gas constant and 'T' the temperature in Kelvin.
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If a reaction is proved to be isokinetic over the range of temperature studied, the Arrhenius equation can be inserted into equation (3) to give

\[
\frac{d\alpha}{dt} = Ae^{\frac{-E}{RT}} f(\alpha) \rightarrow (6)
\]

There are two basic approaches in solving this equation: Mechanism non-invoking method and mechanism invoking method.

1.13 Mechanism non-invoking method

The mechanism non-invoking method is a simple extension of homogenous kinetics, where in it is assumed that

\[
\alpha = (1 - \alpha)^n \rightarrow (7)
\]

where 'n' is the order of the reaction in homogeneous kinetics. For solid state reactions, it is unjustifiable to use the term 'order of the reaction' in the same sense as used in homogeneous kinetics that is concerned with the effective collisions between molecules. Therefore, in this work 'n' has been described as order parameter, implying to have only empirical significance. Its physical significance is questionable and yet undefined.

Substituting for \(f(\alpha)\) in equation (6), we get

\[
\frac{d\alpha}{dt} = A \exp \left[ -\frac{E}{RT} \right] (1 - \alpha)^n \rightarrow (8)
\]
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The kineticist is interested in finding out three basic parameters, viz., ‘n’, ‘E’ and ‘A’ for a given reaction. Two normally used approaches for this are isothermal and non-isothermal methods.

1.13.1 Isothermal kinetics

Isothermal kinetics is the conventional method for the evaluation of kinetic parameters. It is based on the observation of the reaction at constant temperature, the determination of the rate equation for the reaction course, and the determination of the dependence of rate constants on temperature under static conditions. In isothermal kinetics the kinetic parameters are evaluated based on the rate equation

$$\frac{d\alpha}{dt} = k (1 - \alpha)^n$$

For the correct value of ‘n’, a plot of $\frac{d\alpha}{dt}$ versus $(1 - \alpha)^n$ will give a straight line with slope $= k$. However, the accuracy of determination of the tangent, $\frac{d\alpha}{dt}$ is basically poor, and hence, the integral approach is normally preferred.

Rearranging equation (9) and integrating, we get

$$\frac{1-(1-\alpha)^{1-n}}{(1-n)} = kt$$

which applies for all values of n, except n = 1, for which the equation is

$$- \ln (1 - \alpha) = kt$$
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The LHS of the integrated equations (10) and (11) can be put as \( g(\alpha) \), for convenience. Then a plot of \( g(\alpha) \) versus \( t \) gives a straight line with slope \( = k \). The plots can be made for various values of \( n \), and the order parameter is chosen as the one, which gives the best straight line as ascertained by the maximum correlation coefficient.

A prior knowledge of the correct form of \( g(\alpha) \) or the correct value of \( n \) is required for the evaluation of kinetic parameters by this method, unless one resorts to the iteration method of trying various values of \( n \) or \( g(\alpha) \). It has been attempted to circumvent this problem by a “\( g(\alpha) \) - free” approach.

From equations (5) and (10), we obtain

\[
g(\alpha) = kt = A \exp \left[ - \frac{E}{RT} \right] t \quad \rightarrow (12)
\]

or

\[
\ln t = \ln g(\alpha) - \ln A + \frac{E}{RT} \quad \rightarrow (13)
\]

Since \( \ln g(\alpha) \) is very small in comparison with \( \ln A \), \( E \) and \( A \) can be obtained from a plot of \( \ln t \) versus \( 1/T \), and usually \( t_{\frac{1}{2}} \), i.e., the time taken for \( \alpha = 0.5 \) is taken for this purpose. The dependence of kinetic parameters on the specific value chosen has been evaluated, which shows a pronounced dependence of \( E \) and \( A \) on the value chosen\(^{42} \). Therefore, it is necessary to exercise caution in calculating \( E \) and \( A \) by this method. One has to see the dependence of kinetic parameters on the \( \alpha \) value in such cases.
1.13.2 Non-isothermal kinetics

The greatest advantage of non-isothermal kinetics is that the results are obtained from a single measurement, while several measurements are required for isothermal kinetics. For a linear heating rate ($\Phi = \frac{dT}{dt}$), the rate equation (8) becomes

$$\frac{d\alpha}{dT} = \left(\frac{A}{\phi}\right) e^{(-E/RT)(1-\alpha)^n}$$

Equation (14) is the fundamental equation used in non-isothermal kinetics, when a linear heating rate is employed.

Several attempts have been made by various kineticists to derive convenient workable equations from equations (14), which could form the basis for the evaluation of kinetic parameters $A$ and $E^{13, 43 - 49}$. All the methods for obtaining the kinetic parameters from the above equation fall into three distinct categories, viz., differential, approximation and integral methods.

Before we proceed to review briefly these methods, some terms common to them may be defined. Consider the reaction,

$$A\text{ (solid)} \rightarrow B\text{ (solid)} + C\text{ (gas)}$$

Let the initial mass (at time $t_0$) of the reacting system be $m_0$ and let the mass of the solid residue at the end of the reaction (at the time $t_f$) be $m_f$. The total mass loss, $w_\infty$ at any intermediate stage may be denoted by ‘$w$’ (‘$w$’ would be equal to $m_0 - m$ and $w_\infty$ would be equal to $m_0 - m_f$).
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The amount of A decomposed at any instant would be proportional to the observed mass loss (w) at that instant. Therefore, the fractional decomposition is given by the equation,

\[ \alpha = \frac{m_0 - m}{m_0 - m_f} = \frac{w}{w_a} \]

Another term, \( w_r \) may be defined as \( w_r = w_{\infty} - w \). This term \( (w_r) \) would represent the mass loss that has yet to occur between the time \( t \) and \( t_f \). It can be seen that

\[ \alpha = \frac{w_a - w_r}{w_a} \]

Another term, \( c \) may be defined by \( c = 1 - \infty \). It follows that

\[ C = \frac{w_a - w}{w_a} = \frac{w_r}{w_a} \]

1.13.3 Differential methods

The most widely used differential method to obtain kinetic parameters from TG curves is the method developed by Freeman and Carroll\(^50\). The logarithmic form of equation (14) is

\[ \ln \left[ \frac{d\alpha}{dT} \right] = \ln \left[ \frac{A}{\phi} \right] - \left[ \frac{E}{RT} \right] + n \ln(1 - \alpha) \quad \rightarrow (15) \]
Differentiating with respect to \( \frac{d\alpha}{dt} \), (1-\( \alpha \)) and \( T \), and then integrating give the differential difference equation (16),

\[
\Delta \ln \left[ \frac{d\alpha}{dT} \right] = \left[ \left( \frac{-E}{R} \right) \Delta \left( \frac{1}{T} \right) \right] + n\Delta \ln(1-\alpha)
\]

which on transformation becomes

\[
\frac{\Delta \ln \left( \frac{d\alpha}{dT} \right)}{\Delta \ln(1-\alpha)} = \frac{-E}{R} \left[ \frac{\Delta \left( \frac{1}{T} \right)}{\Delta \ln(1-\alpha)} \right] + n
\]

Thus, a plot of \( \frac{\Delta \ln \left( \frac{d\alpha}{dT} \right)}{\Delta \ln(1-\alpha)} \) versus \( \frac{\Delta \left( \frac{1}{T} \right)}{\Delta \ln(1-\alpha)} \) gives a straight line with slope = (-E/R) and intercept = n

The Freeman–Carroll equation (17) has been widely used to study several dehydration reactions. The major disadvantages of this method are the following.

(a) The method is applicable only to a small region of the TG curve (where reliable slope values can be obtained).

(b) There is often difficulty in obtaining a reliable value for the reaction order.

(c) There is difficulty involved in the determination of the slope.
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1.13.4 Approximation methods

On rearranging and integrating the rate equation (14) between the limits \( \alpha = 0 \) at \( T_i \) and \( \alpha = \infty \) at \( T \), we get

\[
\int_0^\infty \frac{d\alpha}{(1-\alpha)^n} = \left[ \frac{A}{\phi} \right]^T \exp \left[ \frac{-E}{RT} \right] \int dT
\]

(18)

where \( T_i \) is the temperature of inception of the reaction and \( T \) is the final temperature as obtained from the TG curve. For convenience of integration, the lower limit, \( T_i \) of equation (18) is usually taken as zero\(^{51}\). This is justified because there is no perceivable reaction that occurs between the temperature zero and \( T_i \).

In the approximation method, the RHS of equation (18) is solved by approximation using the temperature, \( T_s \) corresponding to the maximum rate of decomposition. Horowitz and Metzger made a reasonable approximation for the term, \( \exp \frac{-E}{RT} \) in order to integrate it in the closed form\(^{52}\). The equation defines the term, \( \theta \), which is related to the inflection temperature, \( T_s \) and the temperature under consideration, \( T \) as

\[
T - T_s = \theta \quad \text{-----------------------------} (19)
\]

Since for all practical purposes \( \theta /T_s \ll 1 \), it can be shown that

\[
\frac{1}{T} = \frac{1}{(T_s + \theta)} = \frac{1}{T_s \left[1 + \frac{\theta}{T_s}\right]} \approx \frac{1 - \left(\frac{\theta}{T_s}\right)}{T_s} \quad \text{-----------------------------} (20)
\]

Substituting equation (20) in the exponential integral, we have
Substituting this in equation (18), we get

\[ g(\alpha) = \left[ \frac{ARTs^2}{\phi E} \right] \exp \left[ \frac{-E}{RTs} \right] \exp \left[ \frac{E\theta}{RTs^2} \right] \] \quad (22)

Taking logarithms, we obtain

\[ \ln g(\alpha) = \ln \left[ \frac{ARTs^2}{\phi E} \right] - \left[ \frac{E}{RTs} \right] + \left[ \frac{E\theta}{RTs^2} \right] \] \quad (23)

A plot of \( \ln g(\alpha) \) versus \( \theta \) will yield a straight line with slope \( \frac{E}{RTs^2} \).

Knowing the value of \( E \), the pre-exponential factor, \( A \) can be calculated from the above equation. The major disadvantage of this method is its dependence of \( Ts \), which is influenced by procedural factors such as sample mass and heating rate.

1.13.5 Integral methods

The integral methods are generally accepted as the most accurate among the methods available for the determination of kinetic parameters from the TG data\(^5\). This is justified because there is no perceivable reaction that occurs between the temperature zero and \( T_i \). The LHS of equation (18) can be readily integrated to get the expression, \( 1-(1-\alpha)^{1-n} / (1-n) \), and for convenience, this expression is denoted by \( g(\infty) \). The temperature integral
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on the RHS of the equation cannot be integrated in a closed form. Coats and Redfern evaluated the temperature integral with the aid of the Rainville functions \(^{53, 54}\). By substituting \(x = \frac{E}{RT}\) in the temperature integral in the RHS of equation (18), we get

\[
g(\alpha) = \frac{AE}{\phi R} \left[ \frac{e^{-x}}{x^2} \right] dx \quad \text{-----------------------------} (24)
\]

Using the Rainville functions, we get

\[
e^{-x} \cdot n = x^{1-b} e^{-x} \left[ \frac{(-1)^n (b)^n}{x^{n+1}} \right] \quad \text{-----------------------------} (25)
\]

The above equation can be transformed into

\[
g(\alpha) = \frac{AE}{\phi E} \left[ \frac{1 - 2RT}{E} \right] T^2 \exp \left[ \frac{-E}{RT} \right] \quad \text{-----------------------------} (26)
\]

OR

\[
\ln \left[ \frac{g(\alpha)}{T^2} \right] = \ln \left[ \left( \frac{AR}{\phi E} \right) \left( \frac{1 - 2RT}{E} \right) \right] - \left[ \frac{E}{RT} \right] \quad \text{-----------------------------} (27)
\]

This is known as the Coats-Redfern equation. Coats and Redfern have shown that for the usual nature of \(E\) and temperature range over which the reaction generally occurs, the term, \(\ln \left( \left( \frac{AR}{\phi E} \right) \left( \frac{1 - 2RT}{E} \right) \right)\) is sensibly constant, since \(\left( \frac{2RT}{E} \right) \ll 1\).
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A plot of $\ln \left( \frac{g\alpha}{T^2} \right)$ versus $1/T$ would, therefore, be linear, and $E$ and $A$ can be calculated respectively, form the slope and the intercept of the linear plot. These authors also have recommended a trial and error method for determining the form of $g(\infty)$, that is the value of ‘$n$’ is determined by trial and error. This drawback has overcome by the use of iteration method to get the best fit value of ‘$n$’ with the help of a computer.

1.14 Mechanism invoking methods

One of the main concerns of chemical kinetics is the elucidation of the mechanism of reaction under study. A mechanism can be defined as a mental model devised to explain facts. The elucidation of reaction mechanism for solid state thermal decomposition reactions is more complicated than is the case for homogeneous reactions. The heterogeneous process can be broadly divided into the following three basic steps.

1. Nucleation and growth of nuclei
2. Diffusion (transport of matter)
3. Phase boundary reactions

One of these steps will be rate determining, and several kinetic equations have been derived corresponding to these steps assuming different physico-geometric models. The kinetic equations that govern the reaction mechanism are based on the assumption that the form of $g(\infty)$ depends on the reaction mechanism.

For the mechanistic studies also both the isothermal and non-isothermal approaches are used. The exact reaction mechanism is obtained from the one that gives the best linear plot with the experimental date.
The kinetic parameters, A and E are then calculated respectively, from the slope and intercept as usual. Various equations have been derived for all these three processes assuming different physico-geometric models, and nine of them are listed in Table 1.2 as proposed by Satava\textsuperscript{56}. A detailed account of various reaction mechanisms encountered in solid state thermal decomposition is given below.

1.14.1 Nuclei formation and growth

The general expression for the rate of a solid state decomposition reaction, in which nucleation rate obeys a power law has been shown to be equal to

\[ k_1 t^{(\beta+\alpha)} = k_1 t^n \quad \text{-----------------------------} \]  

(28)

where \( n = (\beta+\alpha) \). When this equation is used, there may be uncertainty concerning the moment at which \( t = 0 \) due to thermal disturbances following the introduction of reactant to the heated zone. Another drawback of equation (28) is that as nuclei grow, the overall rate of reaction may be reduced through the cessation of reaction at those areas of contact formed by coalescence of the reaction interface and removal of potential nucleus forming sites on the surfaces through incorporation of such region into the growth of existing nuclei. Avrami\textsuperscript{57} has considered all these parameters and arrived at the general equation (29).

\[ -\ln (1-\alpha) = k t^n \quad \text{-----------------------------} \]  

(29)

Erofeev\textsuperscript{58} has derived a similar expression independently as
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\[-\ln (1-\alpha) = (k t)^n \quad \text{(30)}\]

and now the equation is often termed as Avrami–Erofeev equation. The Avrami–Erofeev equation for two dimensional growths of nuclei is

\[-\ln (1-\alpha) = k t^2 \quad \text{(31)}\]

and for the three dimensional growth is

\[-\ln (1-\alpha) = k t^3 \quad \text{(32)}\]

Mampel made an alternate approach to the problem of ingestion and overlap of nuclei\textsuperscript{59}. He considered that each particle in the solid might be nucleated with equal probability. The formation of nuclei (those nuclei which undergo two dimensional surface growth) can be thought of as random throwing of discs on to a plane surface. The fraction of the reactant undecomposed at any time corresponds to the uncovered portion of the plain surface. The disc falling within other discs are considered as full growth nuclei or 'phantom' nuclei, and the discs that cover one another partially are considered as overlapping nuclei for particles of small radius. Mampel obtained the relation

\[-\ln (1-\alpha) = k t \quad \text{(33)}\]

For highly dispersed system, where random nucleation results in only a single nucleus per particle, the kinetics is described by the above unimolecular law. The equation is akin to the one derived by Hume and Colvin for random nucleation\textsuperscript{60}.
1.14.2 Diffusion controlled reactions

When there are variations in composition within a solid, a relative mass transport can occur of the different types of atoms present, which tend to level out these variations, and it is this process known as diffusion. Diffusion in solids mainly occurs through the mobility of point defects. For a large group of heterogeneous reactions, the rate controlling process is diffusion. The important factors that govern the overall rate of reaction are the rate of particle transfer across the product layer and the rate of phase boundary reaction. Some of the important models proposed for diffusion controlled reactions are as follows.

(a) One dimensional transport process with constant diffusion coefficient assumes a parabolic law. The rate equation for this process is

\[ \alpha^2 = k t \] \quad (34)

(b) For two dimensional diffusion, where the reactant has cylindrical symmetry, the equation is

\[ \alpha + (1 - \alpha) \ln (1 - \alpha) = k t \] \quad (35)

(c) For three dimensional diffusion of spherical symmetry, Jander applied the parabolic law

\[ \left[ \frac{1 - (1 - \alpha)^{1/3}}{1 - \alpha} \right]^2 = k t \] \quad (36)

(d) For a reaction starting from the surface of spherical particles, Ginstling and Brounshtein derived the equation as
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\[ (1 - 2 \alpha /3) - (1 - \alpha)^{2/3} = k t \quad \text{(37)} \]

1.14.3 Phase boundary reactions

Here the reactant is assumed to have a definite geometrical form. The surface nucleation of the reactant takes place instantaneously and thus, interface will be established. Then if this interface moves with a constant velocity towards the centre of the particle, the reaction is deceleratory throughout because the reaction interface decreases continuously. According to Sharp et al., phase boundary reaction with cylindrical symmetry corresponding to two dimensional movement of the interface follows the equation

\[ 1 - (1 - \alpha)^{2/3} = k t \quad \text{(38)} \]

And for a sphere or a cube having three dimensional movement of the interface the equation becomes

\[ 1 - (1 - \alpha)^{1/3} = k t \quad \text{(39)} \]

This equation is also known as contracting cube equation\textsuperscript{12}.

1.15 Hydrazines and their complexes

The present investigation is concerned with the thermal decomposition studies of some transition metal complexes of hydrazine and its derivatives. Hydrazine, like other polybasic ligands offers the possibility of several different types of coordination behaviour towards metal ions. It can function as a monodentate ligand and as either a bridging or chelating
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bidentate ligand\(^{54}\). The methyl, ethyl, phenyl and dimethyl substituted hydrazines also act as ligands. Most of the alkyl and aryl substituted hydrazines act only as monodentate ligands. However, because of more steric hindrance from phenyl and the substituents on it, the coordination numbers are generally lower than that with alkyl hydrazine.

Hydrazine has nitrogen in -2 valence state. Nitrogen's natural tendency, however, is towards zero valence (N \(\equiv\)N), which gives off nearly six times as much energy as the N–N bond. This tremendous amount of energy is released not only during the decomposition of N\(_2\)H\(_4\) to N\(_2\), but also at the time of mixing with the oxidizer. Hence, they are used as fuels in rockets and spacecraft powered engines. As a strong reducing agent, hydrazine is used for corrosion control in boilers and hot water heating systems. It is the starting material for many derivatives, among which foaming agents for plastics, antioxidants, polymers, polymer cross linking and chain extending agents, as well as the biologically active pesticides, herbicides, plant growth regulators and pharmaceuticals are important\(^{68 - 70}\). Recently, more applications arise in nanochemistry\(^{71}\).

1.16 Thermal decomposition studies of transition metal hydrazine complexes – a concise review

Thermal decomposition studies of inorganic complexes have developed tremendously during the last three decades. It is almost impossible to review all the complexes of transition metals prepared so far in a simple review like this. Considering the scope of the present investigation, it would be proper and meaningful to have a comprehensive review on the thermal decomposition studies of metal complexes of hydrazine and substituted hydrazines.
Spectral, thermal and X-ray studies on some bis hydrazine metal glyoxylates and bis hydrazine mixed metal glyoxylates have been reported by Vikram and Sivasankar\textsuperscript{72}. The analytical, spectral and thermal studies of Co(II), Ni(II) and Zn(II) dicarboxylate complexes with hydrazine as bridged ligand have been reported by Sivasankar\textsuperscript{73}. Synthesis, thermodynamic stability constants and relaxation properties of neutral Gd(II) complex with \textit{p}-hydroxybenzoylhydrazine have been reported by Zhang \textit{et al}\textsuperscript{74}. Thermal and spectral studies of bis hydrazine metal glycolates and chloroacetates have been reported by Sivasankar \textit{et al}\textsuperscript{75}.

Synthesis, thermal, magnetic and spectroscopic characterizations of new copper(II) complexes containing 2–furoic hydrazide and 5–nitro-2-furoic hydrazide ligands have been reported by Fontes \textit{et al}\textsuperscript{76}. Chhabra \textit{et al} have reported synthesis, characterization and thermal studies of Ni/Co metal salts of hydrazines\textsuperscript{77}. The chemistry of metal hydrazine complexes of 4, 5-imidazolesuccarboxylic acid including their thermal behaviour and characterization has been reported by Premkumar and Govindarajan\textsuperscript{78}.

Preparation, characterization and thermal studies of hexavalent uranium dicarboxylates with hydrazine have been reported by Yasodhai and Govindarajan\textsuperscript{79}. Thermal behaviour of metal complexes with 2–(thiazolin–2-yl) hydrazine has been studies by Bernalte, \textit{et al}\textsuperscript{80}. Yasodhai \textit{et al}\textsuperscript{81} reported the preparation, characterization and thermal reactivity of transition metal complexes of hydrazine with citric acid. Thermal study of mixed ligand bis hydrazine complexes of cobalt, nickel and copper saccharinates were reported by Jebudak \textit{et al}\textsuperscript{82}. Sivasankar and Govindarajan have reported thermal, spectral and magnetic studies on glycine complexes of Co(II), Ni(II) and Zn(II) with hydrazine\textsuperscript{83}. Jordanovska and Trojko have reported the synthesis, characterization and
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mode of thermal decomposition of oxalate complexes of Cd(II) and Zn(II) with hydrazine\textsuperscript{84}.

Thermal decomposition kinetics of Co(II), Ni(II), and Cu(II) and Zn(II) complexes of dihydrazinium ethylenediaminetetraacetate has been reported by Saravanan \textit{et al}\textsuperscript{85}. Gad \textit{et al} reported the thermal stability of poly(methacryloylhydrazine) derivatives and their complexes with some transition metal chlorides\textsuperscript{86}. Thermal behaviour of the products isolated in uranium compound–hydrazine systems was studies by Macek \textit{et al}\textsuperscript{87}. Vandenbrook and House\textsuperscript{88, 89} reported the synthesis and thermal characteristics of dichlorobis(hydrazine)cadmium(II) and cadmium sulphate hydrazine complexes. Thermal reactivity of metal acetate hydrazinates has been reported by Mahesh and Patil\textsuperscript{90}. Preparation, characterization and thermal analysis of metal hydrazinocarboxylate derivatives have been reported by Ravindranathan and Patil\textsuperscript{91}.

Thermochemical analysis of solid isonicotinic hydrazide transition metal complexes has been reported by Sekkina \textit{et al}\textsuperscript{92}. Thermal studies of Co(II) complexes of hydrazine in the solid phase have been reported by Banerjee \textit{et al}\textsuperscript{93}. Costanzo \textit{et al} have reported photochemical and thermal behaviours of isocyanide complexes of hydrazines and iron\textsuperscript{94}. Thermal reactivity of metal formate hydrazinates has been reported by Ravindranathan and Patil\textsuperscript{95}. Thermal studies of solid state hydrazine complexes of Zn(II), Cd(II) and Mn(II) have been reported by Banerjee \textit{et al}\textsuperscript{96-99}. Preparation, characterization and thermal properties of di(N–isothiocynato)dihydrizinemetal(II) have been reported by Patel \textit{et al}\textsuperscript{100}. Mechanism of thermal composition of Ti, V and Cr oxalates and their complexes with hydrazine has been studies by Sharov \textit{et al}\textsuperscript{101}. Athavale and Padmanabha Iyer have reported the studies on some metal hydrazine
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complexes\textsuperscript{102}. Thermal decomposition of N\textsuperscript{15}-labelled hydrazine has been reported by Kant and Mc Mahon\textsuperscript{103}.

1.17 Scope of the present investigation

Hydrazine is the simplest diamine in its class of compounds, and may be thought of as derived from ammonia by the replacement of a hydrogen atom by the –NH\textsubscript{2} group. During the Second World War, Germany discovered the interesting property of hydrazine as a rocket fuel. Now, it is one of the most powerful liquid fuels among the current rocket propellants. However, the chemical uses of hydrazine now far surpass its use as a fuel. The bibliographic works on hydrazine by Audrieth and Ogg\textsuperscript{104}, Clark\textsuperscript{105}, Bottomley\textsuperscript{106} and Schmidt\textsuperscript{107} are indispensable bibles for chemists. The field of hydrazine chemistry and its applications are over widening. As it is a good complexing ligand numerous complexes have been synthesized and studied. The many advantageous properties of hydrazines are exploited in the field of photographic chemicals and dyes.

A search through the literature has revealed that no systematic work has been done on the thermal decomposition studies of hydrazine complexes. In view of the biological and industrial importance of hydrazine and its complexes, some complexes of Co(II), Ni(II), Cu(II) and Zn(II) with hydrazine, phenylhydrazine, benzoylhydrazine and isonicotinoylhydrazine in presence of sulphate and thiocyanate as counter anions have been studied presently. Thus, thermal decomposition studies of 32 complexes have been done using simultaneous TG-DTA techniques in two distinct atmospheres, \textit{viz.}, dynamic air and nitrogen with a view to compare their thermal behaviour. Thermal behaviour of these complexes including thermal stability, mode of decomposition and decomposition products has been discussed and correlated with the reaction conditions.
Apart from the phenomenological studies of the thermal decomposition of these complexes, the TG data obtained have been studied in detail for the evaluation of kinetic parameters such as order parameter, energy of activation, pre-exponential factor and entropy of activation for each of the major decomposition stages of these complexes. The Coats-Redfern equation has been used for the kinetic studies of the thermal decomposition of these complexes. Moreover, the mechanisms of the thermal decomposition reactions of these complexes have also been proposed, for which the mechanistic equations suggested by Satava have been used. These kinetic and mechanistic studied of the thermal decomposition reactions of these complexes have given a better understanding of the thermal behaviour of the complexes in a quantitative manner.

It is hoped that the present investigation is a definite contribution to the chemistry of hydrazine complexes, which have many industrial and technological applications.
### Table 1.1 Important thermal analysis techniques

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Derived techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>Thermogravimetry, TG</td>
</tr>
<tr>
<td></td>
<td>Evolved gas detection, EGD</td>
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<tr>
<td></td>
<td>Evolved gas analysis, EGA</td>
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<td>Emanation thermal analysis, ETA</td>
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<tr>
<td></td>
<td>Thermo particulate analysis, TPA</td>
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<tr>
<td>Temperature</td>
<td>Differential thermal analysis, DTA</td>
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<tr>
<td></td>
<td>Therodialatometry</td>
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<tr>
<td>Mechanical characteristics</td>
<td>Thermomechanical analysis, TMA</td>
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<td></td>
<td>Dynamic load thermo mechanical analysis, DLTMA</td>
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<td>Acoustic characteristics</td>
<td>Thermosonimetry, TS</td>
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<tr>
<td></td>
<td>Thermoacoustimetry</td>
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<td>Optical Characteristics</td>
<td>Thermooptometry</td>
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<td></td>
<td>Dynamic reflectance spectroscopy, DRS</td>
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<tr>
<td>Magnetic Characteristics</td>
<td>Thermomagnetometry, TM</td>
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<td>Electrical characteristics</td>
<td>Thermoelectrometry</td>
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<td></td>
<td>Dielectric thermal analysis, DETA</td>
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</table>


## Table 1.2 Important mechanistic equations

<table>
<thead>
<tr>
<th>Model code</th>
<th>Name of model equations</th>
<th>Equations in their integral form g(α)</th>
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<tbody>
<tr>
<td><strong>Diffusion controlled models</strong></td>
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</tr>
<tr>
<td>D₁</td>
<td>1) One dimensional</td>
<td>α²</td>
</tr>
<tr>
<td>D₂</td>
<td>2) Two dimensional</td>
<td>(1- α)ln(1- α)+ α</td>
</tr>
<tr>
<td>D₃</td>
<td>3) Three dimensional (Jander equation)</td>
<td>[1-(1- α)₁/³]²</td>
</tr>
<tr>
<td>D₄</td>
<td>4) Three dimensional (Ginshtling and Braunshtein equation)</td>
<td>1-2/3 α-(1- α)²/³</td>
</tr>
<tr>
<td>AJ</td>
<td>5) Anti Jander (Komastu) equation</td>
<td>[(1+ α)₁/²-1]²</td>
</tr>
<tr>
<td>ZLT</td>
<td>6) Zuravlev, Lesokhin and Tempelman equation</td>
<td>[(1-(α)₁/²-1]²</td>
</tr>
<tr>
<td><strong>Nucleation and growth controlled models</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Am</td>
<td>1) Avrami-Erofeev’s equation</td>
<td>[-ln(1-(α)¹/m], m =1.5,2,3 and 4</td>
</tr>
<tr>
<td>F₁</td>
<td>2) First order reaction (Random nucleation) (Mampel Equation)</td>
<td>-ln(1- α)</td>
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<td>Rₙ</td>
<td>3) Contracting phase boundary</td>
<td>1-(1- α)¹/m</td>
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<tr>
<td></td>
<td>(a) Spherical geometry n=3</td>
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</tr>
<tr>
<td></td>
<td>(b) Cylindrical geometry n= 2</td>
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