Preface

Thermal analysis techniques have a crucial role in characterizing qualitatively and quantitatively a variety of materials over a considerable temperature range. Solid state reactions, phase transitions, determination of phase diagram and measurement of specific heat have widely been studied using thermoanalytical techniques. These studies have been of utmost importance in understanding several aspects of the physicochemical phenomena of solids influenced by thermal energy and have come to be regarded as an integral part of solid state chemistry.

The present investigation is chiefly concerned with a multi-pronged study of the thermal decomposition of some selected nickel amine complexes. An extensive study on the phenomenological, kinetic and mechanistic aspects of the thermal decomposition of these amine complexes have been carried out to have an insight into the complex solid state decomposition reactions. Nonisothermal TG/DTA coupled with mass spectroscopy (MS), temperature resolved X-ray diffraction (TR-XRD) and scanning electron microscopy (SEM) were mainly employed for the investigations. TG/DTA coupled MS studies and temperature resolved X-ray diffraction (TR-XRD) are of immense use in identifying the evolved gaseous products and to find the structural/phase changes involved during the thermal decomposition reactions. A search through the literature revealed very few attempts have been made so far in utilizing TG-MS and TR-XRD studies to probe the nature of the gaseous species evolved and to find the structural changes occurring during the thermal decomposition of the nickel amine complexes. In the present investigation, we have attempted to exploit these two *insitu* analytical techniques exhaustively to understand the nature of the various
transient intermediates and other species formed during the thermal decomposition.

It is a well-established fact that the procedural factors have a telling influence on the thermal decomposition pattern. Although knowledge of the dependence of kinetic parameters on procedural factors is not new, attempts have been made only comparatively recently to study the dependence quantitatively. In this doctoral work, an attempt is made to evolve mathematical correlations between the procedural factors (sample mass and heating rate) and the kinetic parameters (activation energy and pre-exponential factor) for dehydration and deamination reaction using thermogravimetry. The present work also aims at exploring the possible connection (if any) between the reaction type and correlation of kinetic parameters with procedural factors.

In this thesis, **Chapter 1** gives a general introduction of solid state reactions, factors affecting solid state reactivity and reactions of single solids. This introductory chapter also gives the principles and working details of different thermoanalytical techniques like TG, DTA and DSC and factors affecting these techniques. A brief account on solid state thermal decomposition kinetics and a comparison between isothermal and nonisothermal methods is also given in this chapter along with the scope of the present study.

**Chapter 2** presents a brief review on the recent advances in the solid state kinetics. The chapter describes certain mathematical methods used in the kinetic analysis using TG. Details of model free isoconversional methods for the kinetic analysis are also discussed in this chapter.
Chapter 3 gives the details of the instrumental techniques, preparation and characterisation of the complexes and the procedural details employed in the study.

Chapters 4-7 describe the thermoanalytical investigation of seven nickel amine complexes. Detailed phenomenological, kinetic and mechanistic aspects of the thermal decomposition of these complexes are discussed.

Chapter 8 focuses the results of our detailed study of the correlation of kinetic parameters and procedural factors in thermogravimetry.

Chapter 9 gives the conclusions of the major findings of this investigation along with the future outlook.

Note: The references in each chapter are listed at the end of the chapter itself for convenience. This sometimes implies listing of the same reference repeatedly in different chapters. However, such an arrangement helps immediate reference and facilitates information retrieval. Therefore this arrangement is effected in the thesis.