



## **30 YEARS OF RESEARCH IN THERMAL ANALYSIS AND CALORIMETRY**

**A personal review**

***J. O. Hill***

School of Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia

### **Abstract**

The research in thermal analysis and calorimetry, conducted by the author over the period 1964 to 1993, is summarised and concisely reviewed. The major investigations have focussed on thermal analysis studies of coordination compounds, particularly the metal dithiocarbamate complexes. A significant solution calorimetric study of some metal dithiocarbamate complexes has also been undertaken. DSC has been applied to determine the sublimation enthalpies of many metal dithiocarbamate and metal pentane-2,4-dionate complexes and solution calorimetry has been applied to study the thermochemistry of the latter group of complexes. Thermal analysis investigations of several inorganic molten salt systems have been initiated. Thermometric titrimetry has been applied to study metal-macrocyclic ligand systems in aqueous media and particularly those systems of environmental significance. Temperature calibration standards for TMA have been proposed and TMA has been applied to study the mechanical properties of several common inorganic compounds. DTA has been applied to study a wide variety of phenols and has subsequently been applied as an analytical technique to determine the components of solid state phenol mixtures. Thermometric titrimetry has been applied to determine the phenolic content of wines. A comprehensive thermal analysis study of Australian brown coal has been undertaken, involving the DSC determination of coal specific energy, a TG/DTA study of the coal pyrolysis and combustion processes and a TG/DTA and EGA study of the cation catalytic effect on the coal pyrolysis process. Thermal analysis and calorimetric techniques have been extensively publicised and promoted by the publication of specialist reviews, the presentation of symposia review papers and the oral presentation of short courses, particularly in the SE Asian region. This review essentially reveals the diversity of possible application of thermal analysis and calorimetric techniques and the primary significance of thermodynamic data in the fundamental rationalisation of chemical phenomena.

**Keywords:** calorimetry, personal research review, thermal analysis

Over the last 30 years, my research has focussed primarily on the application of thermal analysis and calorimetric techniques to study the thermal characteristics of a diverse range of chemical systems, with special emphasis on coordination compounds and systems of biological and environmental significance. This review of these studies is designed as a personal tribute to my many graduate students and collaborators, who, collectively over this period, have generated many of the research initiatives and the majority of the original data summarised here.

Major thermal analysis and calorimetric studies have focussed on a variety of inorganic systems and particularly on the metal complexes of dithiocarbamic and xanthic acids. The latter area has been comprehensively reviewed, initially in 1981 [1] and up-dated recently in 1994 [2]. The early thermal analysis studies of metal dithiocarbamate complexes [3–5] involved the application of TG, DTA, EGA and pyrolysis/GC–MS techniques to derive the relevant thermal decomposition mechanisms and to correlate the thermal stability of these complexes with intrinsic structural features. A most comprehensive thermal analysis study of tin dithiocarbamate complexes has been reported [6–14], which mainly involved the application of the Thermal Degradation Mass Spectrometry (TDMS) technique to elucidate the relevant thermal decomposition mechanisms. The thermal analysis literature on tin dithiocarbamate complexes has recently been reviewed [15]. The early solution calorimetric studies in this area involved the determination of the standard formation enthalpy of diethylammonium diethyldithiocarbamate [16], a precursor in the formation of metal dithiocarbamate complexes and an investigation of the solution thermochemistry of tris(diethyldithiocarbamato)Fe(111) [17]. Solution calorimetry has also been applied to determine the standard formation enthalpies of bis(diethyldithiocarbamato)Ni(11) [18], -Cu(11) [19] and, to complete the series, more recently, of tris(diethyldithiocarbamato)Co(111) [20]. The solution calorimetric data available for metal dithiocarbamate complexes has recently been comprehensively reviewed [21] and trends in the derived metal-sulphur bond dissociation enthalpies are interpreted in terms of intrinsic structural features of these complexes. The sublimation enthalpies of bis(diethyldithiocarbamato)Ni(11), -Cu(11) and of diethylammonium diethyldithiocarbamate have been determined by the sublimation bulb technique [22]. This study was the first to report a volatile diethyldithiocarbamate salt. Benzoic acid has been proposed as a calibrant in the DSC determination of sublimation enthalpy [23] and this technique has subsequently been applied to determine the sublimation enthalpies of bis(diethyldithiocarbamato)Ni(11) and -Cu(11) and of tris(diethyldithiocarbamato)-Co(111) [24]. A limited thermal analysis study of metal xanthate complexes has also been made, involving bis(ethylxanthato)Ni(11) [25] and -Pd(11) [26] complexes. The latter was the first study to apply ‘on-line’ MS to identify the vola-

tile decomposition products. The solution thermochemistry of a series of bis(alkylxanthato)Ni(II) complexes has also been studied [27] and the data are broadly interpreted in terms of the inductive and steric effects of the terminal alkyl group of the ligand on the thermodynamic complex stability.

The thermochemistry of metal pentane-2,4-dionate complexes has been extensively studied. The available thermal analysis data for these complexes has been comprehensively reviewed [28] and trends in such data have been evaluated. The sublimation enthalpies of a variety of metal pentane-2,4-dionates have been determined by a variety of methods: spoon gauge, sublimation bulb and vacuum DSC [29–33]. The sublimation enthalpy data available for metal complexes of pentane-2,4-dione and related ligands have been comprehensively reviewed [34]. The standard formation enthalpies of tris(pentane-2,4-dionato)Al(III), -Cr(III), -Mn(III) and -Fe(III) have been determined by classical solution calorimetry [35–38]. These data were the earliest of their type and the general experimental procedure developed has become widely accepted as the definitive method for the solution calorimetric determination of standard formation enthalpies of metal complexes generally. The solution calorimetry data available for metal pentane-2,4-dionate complexes, together with the derived metal-oxygen bond dissociation enthalpies, have been comprehensively reviewed [39]. Trends indicating correlations between these metal-oxygen bond dissociation enthalpies and the structures of the parent complexes are discussed.

Thermal analysis studies of several other types of metal complexes have been undertaken. Nickel(II) thiourea chloride complexes have been studied by TDMS and the relevant thermal decomposition mechanisms are proposed [40]. A combined XPS and DTA study of cis-platin has been undertaken [41]. The data are consistent with cis-trans isomerism of the complex, prior to decomposition. Several organometallic systems have also been studied by TG and DTA. Thermal decomposition mechanisms, based on TG and DTA data, are proposed for dicyclopentadienyl zirconium borohydride and bis(triphenylphosphine)-borohydridocopper(I) [42]. The thermal decarboxylation of some mercury(II) carboxylate complexes has been studied by TG [43]. Such complexes are precursors in the synthesis of a wide variety of organo-mercury complexes. The thermal decomposition mechanisms of a series of metal complexes of cacodylic acid have been derived, based on TG data, together with compositional analysis data for the final residues [44].

The early thermodynamic data for selective metal ion binding by synthetic macrocyclic ligands have been comprehensively reviewed and assessed [45]. The metal ion binding constants and the complexation enthalpies were determined by thermometric titrimetry and the initial data for alkali and alkaline earth metal cyclic polyether complexes were of key significance in the rationalisation of the metal selectivity property of macrocyclic ligands generally. The

thermodynamics of complexation of alkaline earth metals by linear and macrocyclic polyaminocarboxylic acids have been determined by thermometric titrimetry [46, 47]. The principal factors influencing the thermodynamic stability of these complexes are discussed in terms of the macrocyclic effect.

Thermometric titrimetry has been applied to study a variety of metal-ligand interactions in aqueous solution, for example, the complexation of metal ions by the colorimetric indicator, xylenol orange [48] and the complexation of cobalt(II) by metallochromic indicators [49]. The interaction of metal ions with EDTA [50], iron(III) with thiocyanate [51], cadmium(II) with ferricyanide [52] and silver(I) with thiosulphate [53], have all been studied by thermometric titrimetry, with the overall aim of rationalising the associated speciation phenomena. The application of thermometric titrimetry to the determination of a variety of inorganic species in environmental systems has been reviewed [54] and the major emphasis of each study is the determination and rationalisation of the speciation phenomena involved. The thermometric titration of sulphide with permanganate in alkaline aqueous solution is proposed as a potential analytical method for the selective determination of sulphide in natural waters [55].

Some thermal analysis studies of molten inorganic systems have been undertaken: a DTA study of the chromium(III) oxide/oxygen reaction in molten sodium carbonate [56]; a TG/DTA study of the thermal stability of some molten sulphur/oxyanionic salts and the corresponding eutectics [57] and the thermal decomposition of mercury(I) and mercury(II) sulphates [58].

Some miscellaneous thermochemical studies of inorganic systems have been made. A thermal analysis evaluation of the low temperature synthesis of  $\text{BaBiO}_3$  has been conducted [59]. The perovskite phase of  $\text{BaBiO}_3$  has important application as a heterogeneous catalyst. It has been recommended that a series of pure metals be used as temperature calibrants for TMA and that the (ICTAC) DTA Certified Reference Materials be used as secondary standards in this context [60]. These recommendations represent the first proposals for temperature calibration in TMA. A range of common inorganic compounds has subsequently been studied by TMA to illustrate the diversity in general application of this technique. Two well-tested thermochemical experiments, suitable for undergraduate study, have been reported [61]. The first of these involves a TG study of bis(thiocyanato)tetrapyridinenickel(II) and the TG analysis of a solid state alkaline earth metal oxalate mixture. The second experiment involves a thermometric titrimetry study of several inorganic reactions, using a simple 'home made' thermometric titrimetry system. A concise review of the thermochemistry and redox chemistry of the vanadium, niobium and tantalum triad has been compiled [62]. The thermochemical and electrochemical data cited in this review are generally accepted as selected definitive data.

Several organic systems have been studied by thermal methods. Definitive thermochemical data for tris(hydroxymethyl)aminomethane (THAM) as a 'test substance' in solution calorimetry has been reported [63]. The derived neutralisation enthalpy for the THAM/0.1M HCl reaction at 298 K is widely accepted as the definitive reference value for performance testing of solution calorimeters.

Solution calorimetry has been applied to determine the ionisation enthalpy of pentane-2,4-dione in water and water/dioxan [64]. The overall thermodynamics of this process is discussed. The standard formation enthalpy of N,N,N-triacetylammonia has been derived by solution calorimetry [65]. The standard solution enthalpy of pyridinium bromide in chloroform has also been derived by solution calorimetry and the fusion enthalpy of this salt has been derived by DSC [66]. Hence, the mixing enthalpy of pyridinium bromide and chloroform is deduced. The standard formation enthalpy of 1,3-dimethylurea nitrate and the standard protonation enthalpy of 1,3-dimethylurea have been determined by solution calorimetry [67]. Models have been proposed for the correlation of thermochemical data for ureas with the degree of nitrogen substitution [68].

The applications of TG, DTA, DSC and thermometric titrimetry in pharmaceutical science have been reviewed [69]. These techniques are of major significance in the context of purity determination and drug assay procedures. A DSC compositional analysis of 3 model binary systems of pharmaceutical significance has been conducted [70]. Mixtures of known selected composition for each of the systems 3,5-dinitrobenzoic acid/benzoic acid, paracetamol/4-aminobenzoic acid and acetylsalicylic/salicylic acid have been prepared and analysed by DSC. The respective compositions derived from applications of the van't Hoff equation were correlated with the corresponding theoretical values and the corresponding fusion temperatures and fusion enthalpies, as obtained from the relevant DSC profiles. Linear correlations were found to exist between the theoretical compositions, fusion temperatures and fusion enthalpies for each of these systems and it is apparent that with suitable calibration procedures, the DSC compositional analysis method can be applied to determine drug purity at the 90–95 mole% level. This level is of considerable interest in drug stability studies and has real significance in purity assays of commercial pharmaceutical preparations.

Thermal methods have also been applied to the analytical determination of organic species. The analytical determination of phenols by thermometric titrimetry has been reported [71]. The analytical procedure involves the use of thallium ethoxide as titrant and benzene as solvent. A comprehensive DTA study of phenols has been undertaken [72–75]. The study involved halo-, methyl-, methyl,halo-, nitro-, amino-, polyhydroxy-phenols and naphthol and of the corresponding *p*-nitrobenzoylchloride, *p*-phenylazobenzoylchloride and

3,5-dinitrobenzoylchloride derivatives, prepared 'in-situ' by heating the solid state mixtures of phenol and acid chloride in a DTA system. These data collectively provide a reference data base for the identification and characterisation of a wide variety of phenols by conventional thermal analysis techniques. The general analytical procedure was subsequently applied to study binary phenol mixtures [76]. The general method involves adding the chosen acid chloride to the solid state binary phenol mixture and obtaining the corresponding DTA profile, which is subsequently compared with those in a bank for phenols, binary phenol mixtures and binary phenol derivative mixtures. The method offers rapid identification of phenols in the solid state. The 'titratable acid' and 'total phenolics' content of selected Australian wines have been determined by thermometric titrimetry, via thermometric titration with hydroxide ion [77]. The 'titratable acid' and 'total phenolics' content have also been determined by the well-established routine potentiometric and spectrophotometric methods, respectively and the sensitivity of the thermometric titrimetry method is at least comparable to that of the routine methods. A separate thermometric titrimetry study of tartaric and gallic acids has provided further insight into the complex interactions prevalent in the wine matrix.

A miscellaneous thermal analysis study of some cyclophanes has been undertaken [78]. A TG study of a series of cyclophane bis(sulphoxides) has shown that thermal decomposition of these compounds occurs in two stages with the stepwise loss of sulphoxide groups. Such stepwise thermal cleavage is rationalised in terms of the stereochemistry of the sulphoxide groups and the strain associated with the resultant products. This study has some industrial significance in the context of the commercial synthesis of cyclophane dienes.

Thermal analysis techniques have been applied to study organic 'energy storage' materials. The relative resistance to thermal degradation of pinus-radiata and its radiation-induced wood polymer composites has been studied by TG [79]. The TG investigations of these systems were supplemented by flammability tests to investigate the relative efficiencies of different polymer systems as flame-retardant impregnates. The increase in mass of the ash residue from the composites compared to that obtained from the untreated wood samples indicated the relative efficiency of the polymer coating system used. The derived flame retarding efficiency index for the polymers decreased in the order 3 : 2 polyacrylonitrile-vinylidene-chloride, polymethylmethacrylate-acrylonitrile, polymethylmethacrylate-vinylidene chloride, polymethylmethacrylate. Extensive thermal analysis studies of Australian brown coal have been undertaken. The proximate analysis of the 5 major lithotypes of Australian brown coal has been determined by the classical TG method [80]. Possible linear empirical relationships between specific energy and proximate analysis data for brown coal have been investigated [81]. Linear equations relating specific energy and ultimate analysis

data for brown coal have also been derived. These various relationships are useful for the preliminary estimate of the specific energy of a brown coal sample, since the experimental determination of proximate and ultimate analysis data is considerably less tedious than the traditional bomb calorimetric determination of specific energy. DSC has also been applied to the direct determination of brown coal specific energy [82]. A 'standard coal sample' was used for DSC calibration. The specific energy of the coal sample is derived directly via measurement of the total combustion peak area. However, by suitable geometrical subdivision of the combustion peak, it is possible to simultaneously derive the individual combustion enthalpies of the constituent volatile matter and residual tar. The DSC determination of coal specific energy agrees with that determined by conventional combustion bomb calorimetry to within 3%, but the DSC method is more rapid and less tedious than the conventional calorimetric method. TG has been applied to study the pyrolysis of brown coal [83]. Pyrolysis is shown to be a three-stage process, involving the loss of absorbed water, the spontaneous evolution of volatile matter and carbonisation. The kinetics of the brown coal pyrolysis process have also been investigated by TG. A preliminary aspect of this study was the development of a computer programme, 'KNIS' for the systematic kinetic analysis of non-isothermal TG data [84]. This programme is particularly suitable for the derivation of the pyrolysis kinetics of brown coal, since it enables an automatic regional kinetic analysis of the overall TG data and incorporates 12 solid state decomposition models. Subsequently, an extensive kinetic analysis of the pyrolysis of brown coal was undertaken – based on the derived non-isothermal TG data [85]. Fundamentally, brown coal exhibits two identifiable pyrolysis stages and two regions of linearity with respect to Arrhenius kinetic analysis. The three-dimensional diffusion integral kinetics model  $D_3$  is valid for the overall pyrolysis process and the activation energy for the primary pyrolysis stage of brown coal is dominated by chemical decomposition processes, whereas the secondary stage is essentially a combination of intrinsic mass and heat transfer processes. Simultaneous TG/DTG–DTA and EGA techniques have been applied to study the catalytic effect of a series of cations on the pyrolysis of brown coal [86, 87]. It appears that copper(II) has the most significant catalytic effect. The supplementary EGA studies further characterised and quantified the cation catalytic effect by providing gas release profiles for the overall process. The cation catalytic effect is related directly to the extent to which the initial temperature of gas release is lowered, as compared to that for an 'acid-washed' reference coal. Simultaneous TG/DTG–DTA has been applied to study the combustion of brown coal [88]. The combustion process is characterised by moisture release, volatilisation, ignition and burn-off. The DTA combustion peak area is linearly related to the specific energy of the sample. Simultaneous TG/DTG–DTA has been applied to

study the combustion of brown coal chars [89]. It is apparent that the volatile matter content and reactivity of these chars decrease as char formation temperature increases. Char oxidation is essentially consistent with first order kinetics. The overall conclusion of this study is that only chars formed at relatively low pyrolysis temperatures are of commercial significance. Finally, the thermal analysis studies of Australian coals have been reviewed [90] and the recent thermal analysis studies of Australian brown coal have also been reviewed [91].

A few traditional physical chemistry systems have been studied by thermal methods. A novel solution calorimetric method has been devised for the determination of a distribution coefficient – that of bromine in water/carbon tetrachloride [92]. Thermometric titrimetry has been applied to study the thermodynamics of ionisation of aqueous iodic acid [93]. The ionisation enthalpy of iodic acid was derived directly from dilution enthalpy determinations. A computer programme in 'BASIC' has been compiled for data analysis in thermometric titrimetry [94]. This programme is the most comprehensive of its type.

Much sustained effort has been concentrated on the promotion of thermal analysis and calorimetry, especially in India, SE Asia and Australia, by compiling general reviews, by presenting review papers at international conferences and by presenting comprehensive short courses at tertiary institutions. Thermal analysis applications in Materials Science have been reviewed [95]. An attempt has been made to revive interest in the traditional calorimetric techniques, by reviewing selected inorganic applications of solution calorimetry, thermometric titrimetry, flow microcalorimetry and bomb calorimetry [96]. An attempt has been made to revive interest in thermochemistry at the High School level, by compiling a short review, focussing on the relevance of thermochemistry in the modern world [97]. Several contributions have been made to the bi-annual Indian Thermal Analysis Society Symposia [98–101] and the educational and research perspectives of thermal analysis in SE Asia [102] and Australia [103] have been addressed. Short courses on 'Thermal Analysis' have been presented in Melbourne, Australia [104], in Bangkok, Thailand [105] and at several other venues throughout SE Asia [106]. Finally, a booklet entitled 'For Better Thermal Analysis and Calorimetry' (Edition 111), has been compiled [107]. This booklet is published by ICTAC and is an invaluable handbook for those working in the fields of thermal analysis and calorimetry and consists of two parts. Part 1 lists references to the history of thermal analysis and calorimetry, details the nomenclature, standardisation procedures, data presentation recommendations and gives an extensive guide to the thermal analysis and calorimetry literature. Part 2 details the history, structure, administration, committee structures, publications and membership application procedures of ICTAC. The booklet has been circulated to thermal analysts and calorimetrists around the world.



This 30 years record of research in thermal analysis and calorimetry was climaxed in 1992 by the award of a Doctor of Science (DSc) degree by the University of London, UK [108].

## Conclusions

With respect to the four major research areas covered in this review, it is perhaps appropriate to survey possible future initiatives. It is clear that the thermochemistry of the metal dithiocarbamate family of complexes has advanced very substantially over the last decade, whereas that of the metal xanthates has only marginally progressed. With respect to the thermal analysis studies of these complexes, the major aim of future research will certainly be focussed on an assessment of thermal stability and derivation of the relevant decomposition mechanisms. If the derived TG data are of sufficient accuracy, then it is possible to derive kinetic parameters for the thermal decomposition process. Thermal decomposition data generally should be rationalised in terms of the structures of the parent complexes and variations in thermal stability should be correlated with systematic metal complex structural variations, particularly with respect to variation of the metal centre and variation of terminal alkyl and aryl substituents of the dithiocarbamate and xanthato moieties. If such research is to achieve an acceptable level of credibility, then it is essential that certain fundamental criteria be adopted. The atmosphere for thermal decomposition should be inert, since an air atmosphere inevitably leads to secondary oxidation reactions. If the derived thermal decomposition mechanisms are to have credibility, the volatile decomposition products, the solid state intermediates and the final residues must be identified and characterised. The volatile decomposition products can be characterised by 'on-line' EGA techniques, such as MS and FTIR and the solid state intermediates and final residues can be characterised by chemical and X-ray diffraction analysis. Derived kinetic data for the thermal decomposition processes only have credibility if corresponding decomposition reactions are defined and the reaction sequence specified. It is most evident from recent published research in this area, that the fundamental criteria discussed here have not been adopted and hence it is apparent that little real progress has been made with respect to the thermal analysis investigations of metal dithiocarbamate and xanthate complexes.

The general experimental procedure for the solution calorimetric determination of the standard formation enthalpies of metal complexes has been well established and the method for the derivation of the corresponding metal-ligand bond dissociation enthalpies has been systematically defined. As a consequence, the solution thermochemistry of the metal dithiocarbamate and metal pentane-2,4-dionate complexes has been systematically developed over the last

two decades, such that the derived metal-ligand bond dissociation enthalpies for these complexes are associated with an acceptable level of confidence and, in consequence, trends in such data have structural significance. Future studies in this area should concentrate on variation of the metal centre and structure of the ligand, but such research will continue to be impeded by the lack of reliable methods for the determination of sublimation enthalpies of metal complexes. In this context, the High Temperature Drop Calorimetric method appears to have considerable promise.

Thermometric titrimetry is clearly an ideal technique for the rationalisation of speciation phenomena associated with coordination compounds. Further studies in this area will inevitably focus on extending the range of metal-ligand systems already investigated to include those of biological and environmental significance. Thermometric titrimetry will continue to be the principal technique for the determination of the thermodynamic parameters associated with metal/macrocylic ligand interactions. The potential of thermometric titrimetry as an analytical technique has no obvious limitations.

The scope for further thermal analysis studies of brown coal is limitless. TG has been shown to be a very valuable technique for the investigation of brown coal pyrolysis and combustion processes. The definition of these processes in terms of the complex chemical and physical phenomena involved can be markedly enhanced by the application of coupled techniques, such as TG-FTIR and TG-MS, such that the components of the volatile matter can be identified and the principal low molecular weight effluent gases (CO, CO<sub>2</sub> and H<sub>2</sub>S) can be quantified and an accurate temperature profile for their evolution derived. Apart from the commercial significance of such characterisations, these data have major significance in quantifying the degree of pollution associated with conventional coal-fired electricity generators. An obvious extension of the application of TG to the study of brown coal pyrolysis is the derivation of the relevant kinetic parameters for this fundamental process. It is well known that the derivation of kinetic parameters from thermal analysis data is associated with many hazards and particularly when complex systems such as coal are involved. However, our preliminary studies have at least set the scene for further, more refined and detailed approaches. We have confirmed that the pyrolysis process is associated with two well-defined stages, the first of which is chemical in nature and the second is a combination of several physical processes. The activation energies of these two stages are quite different – the activation energy for the first stage is some four times greater than that for the second stage. Whereas little real significance can be attached to individual kinetic parameters, in view of the large uncertainties involved, relativities in such data have meaningful significance and these provide much impetus for further study in this area. There is obvious scope for further DTA and DSC studies of brown coal pyrolysis and

combustion processes, particularly when these are combined simultaneously with TG studies. DTA is particularly useful for the characterisation of the individual and sequential thermal events inherent in these processes and we have shown that the total area of the DTA or DSC combustion peak is directly proportional to the specific energy of the coal sample. Further, with appropriate sub-division of this peak area, the individual enthalpies of the volatile matter and residual char may be derived – thereby rapidly quantifying the ‘energy content’ of the coal sample. The DSC method provides a rapid and reproducible procedure for the determination of coal specific energy but the credibility of the method depends upon a reliable procedure for the enthalpy calibration of DSC. We have suggested that a ‘standard coal’ be used in this context. This issue could well be investigated by the ICTAC Standardisation Committee. The study of brown coal by the thermomechanical methods is wide open. Brown coal is a complex, flexible, ‘sponge-like’ matrix and the mechanical properties of this system are of considerable commercial significance. The ability of brown coal to act as a ‘host’ for a variety of ‘guest’ systems, provides many challenging thermomechanical projects. TMA in particular can be applied to determine the ‘swelling index’ of the coal and this parameter is known to exhibit subtle variation with the source of the coal and the lithotype involved. This parameter alone is of major significance in the rationalisation of the many selectivity properties shown by brown coals for metal ions and a variety of other ‘guest’ species. Swelling index is also of importance in the correlation of moisture content of the coal with the lithotype involved, since the magnitude of this parameter is critically dependent on the bulk moisture content. Much useful information can be obtained from the application of other thermomechanical techniques to brown coal. In this context, the study of brown coal briquettes and brown coal chars by DMA and DETA at ambient temperatures can yield valuable mechanical data for these systems, which may in turn provide insights into future commercial applications of these important by-products. Finally, it should not be overlooked that the development of the TG method for the determination of the proximate analysis of coal was a major revolution in coal technology and it now appears that all the major thermal analysis techniques are of prime significance in the determination and rationalisation of coal intrinsic properties.

This review of my research in thermal analysis and calorimetry over the last 30 years has shown that these techniques have a diversity of application unmatched by other conventional analytical techniques and that thermodynamic data, in their many forms, are of prime significance in the rationalisation of physical and chemical phenomena.

\* \* \*

It is most appropriate that I sincerely acknowledge colleagues in the Department of Chemistry, La Trobe University, Melbourne, Australia, who have consistently provided encouragement and support for my research effort throughout my entire academic career: Professor James Morrison, Associate Professors Bob Brownlee, Trevor Broxton, Terry Cardwell, Bob Cattrall, Maureen Mackay and Drs. Neville Arthur, Jeffrey Rowe and Shabbir Tariq. I would also like to acknowledge colleagues in the Department of Chemistry, National University of Singapore and especially Professor Sim, Keng Yeow, Head of the Department, for their support and encouragement during the tenure of a Senior Teaching Fellowship (1990–1994). Finally, I sincerely acknowledge La Trobe University for providing financial support for my entire research programme over more than two decades.

## References

- 1 J. O. Hill and R. J. Magee, *Rev. Inorg. Chem.*, 3 (1981) 141.
- 2 J. O. Hill, J. P. Murray and K. C. Patil, *Rev. Inorg. Chem.*, (1994).
- 3 B. Annuar, J. O. Hill and R. J. Magee, *Thermochim. Acta*, 8 (1974) 439.
- 4 C. G. Sceney, J. O. Hill and R. J. Magee, *Thermochim. Acta*, 11 (1975) 301.
- 5 C. G. Sceney, J. F. Smith, J. O. Hill and R. J. Magee, *J. Thermal Anal.*, 9 (1976) 415.
- 6 G. K. Bratspies, J. F. Smith, J. O. Hill and R. J. Magee, *Thermochim. Acta*, 27 (1978) 307.
- 7 G. K. Bratspies, J. F. Smith, J. O. Hill and R. J. Magee, *Thermochim. Acta*, 19 (1977) 335.
- 8 G. K. Bratspies, J. F. Smith, J. O. Hill and R. J. Magee, *Thermochim. Acta*, 19 (1977) 349.
- 9 G. K. Bratspies, J. F. Smith, J. O. Hill and R. J. Magee, *Thermochim. Acta*, 19 (1977) 361.
- 10 G. K. Bratspies, J. F. Smith and J. O. Hill, *Thermochim. Acta*, 19 (1977) 373.
- 11 G. K. Bratspies, J. F. Smith and J. O. Hill, 'Thermal Analysis' W. Hemminger, Ed., Proc. 6th ICTA, Birkhauser, Basel, Vol. 2 1980, p. 147.
- 12 G. K. Bratspies, J. F. Smith and J. O. Hill, *J. Anal. Appl. Pyrolysis*, 2 (1980) 35.
- 13 G. K. Bratspies, J. F. Smith, J. O. Hill and P. J. Derrick, *J. Thermal Anal.*, 16 (1979) 369.
- 14 G. K. Bratspies, J. O. Hill and J. F. Smith, *Thermochim. Acta*, 133 (1988) 383.
- 15 J. O. Hill and S. Chirawongaram, *J. Thermal Anal.*, 41 (1994) 511.
- 16 K. J. Cavell, J. O. Hill and R. J. Magee, *Thermochim. Acta*, 33 (1979) 377.
- 17 B. Annuar, J. O. Hill, D. J. Melvor and R. J. Magee, *Thermochim. Acta*, 9 (1974) 143.
- 18 K. J. Cavell, J. O. Hill and R. J. Magee, *J. Chem. Soc., Dalton Trans.*, (1980) 763.
- 19 K. J. Cavell, J. O. Hill and R. J. Magee, *J. Chem. Soc., Dalton Trans.*, (1980) 1638.
- 20 J. O. Hill and K. J. Cavell, *Thermochim. Acta*, 223 (1993) 187.
- 21 J. O. Hill and J. P. Murray, *Rev. Inorg. Chem.*, 13 (1993) 183.
- 22 K. J. Cavell, J. O. Hill and R. J. Magee, *Thermochim. Acta*, 34 (1979) 155.
- 23 J. P. Murray, K. J. Cavell and J. O. Hill, *Thermochim. Acta*, 36 (1980) 97.
- 24 K. J. Cavell, J. O. Hill and R. J. Magee, *Thermochim. Acta*, 33 (1979) 383.
- 25 K. J. Cavell, C. G. Sceney, J. O. Hill and R. J. Magee, *Thermochim. Acta*, 5 (1973) 319.
- 26 C. G. Sceney, J. O. Hill and R. J. Magee, *Thermochim. Acta*, 6 (1973) 111.
- 27 K. J. Cavell, J. O. Hill and R. J. Magee, *Thermochim. Acta*, 8 (1974) 447.
- 28 J. O. Hill, *Therm. Anal. Rev. Abstr.*, 20 (1991) 1.
- 29 J. Sachinidis and J. O. Hill, *Thermochim. Acta* 36 (1980) 59.
- 30 J. P. Murray and J. O. Hill, *Thermochim. Acta*, 63 (1983) 211.
- 31 J. P. Murray and J. O. Hill, *Thermochim. Acta*, 72 (1984) 341.
- 32 J. P. Murray and J. O. Hill, *Thermochim. Acta*, 109 (1987) 383.
- 33 J. P. Murray and J. O. Hill, *Thermochim. Acta*, 109 (1987) 391.
- 34 J. P. Murray and J. O. Hill, *Rev. Inorg. Chem.*, 13 (1993) 125.

- 35 J. O. Hill and R. J. Irving, *J. Chem. Soc., A*, (1966) 971.
- 36 J. O. Hill and R. J. Irving, *J. Chem. Soc., A*, (1967) 1413.
- 37 J. O. Hill and R. J. Irving, *J. Chem. Soc., A*, (1968) 1052.
- 38 J. O. Hill and R. J. Irving, *J. Chem. Soc., A*, (1968) 3116.
- 39 J. O. Hill and J. P. Murray, *Rev. Inorg. Chem.*, 13 (1993) 157.
- 40 M. P. B. Attard, J. O. Hill, R. J. Magee, S. Prakash and M. N. Sastri, *J. Thermal Anal.*, 31 (1986) 407.
- 41 S. P. Roe, J. O. Hill and R. J. Magee, *Inorg. Chim. Acta, Lett.*, 115 (1986) L15.
- 42 B. D. James, B. Annuar, J. O. Hill and R. J. Magee, 'Analytical Calorimetry', Vol. 3 R. S. Porter and J. F. Johnson, Eds., Plenum Press, New York 1974, p. 777.
- 43 T. S. A. Hor, Y. Quah and J. O. Hill, 8th Indian Thermal Analysis Society Symposium Proceedings, Bhubaneswar, Indian Thermal Analysis Society, Bombay, India 1991, pp. 141-145.
- 44 L. W. Lup and J. O. Hill, *Proceed.*, Science Research Congress, National University of Singapore, 1991, p. 101.
- 45 R. M. Izatt, J. O. Hill and J. J. Christensen, *Science*, 174 (1971) 459.
- 46 G. Ewin and J. O. Hill, *J. Chem. Soc., Dalton Trans.*, (1983) 865.
- 47 G. Ewin and J. O. Hill, *J. Chem. Res.*, (S) (1985) 334; (M) (1985) 3501.
- 48 R. bin Othman, J. O. Hill and R. J. Magee, *Microchim. Acta*, 111 (1987) 337.
- 49 R. bin Othman, J. O. Hill and R. J. Magee, *Thermochim. Acta*, 122 (1987) 163.
- 50 R. bin Othman, N. G. Buckman, J. O. Hill and R. J. Magee, *Thermochim. Acta*, 157 (1990) 335.
- 51 J. O. Hill and S. Korce, *Thermochim. Acta*, 154 (1989) 49.
- 52 J. O. Hill and S. Lim, *Thermochim. Acta*, 188 (1991) 249.
- 53 J. O. Hill and S. Lim, *Thermochim. Acta*, 188 (1991) 255.
- 54 J. O. Hill, *Bull. Singapore Natl. Institute Chem.*, 18 (1990) 5.
- 55 R. Bin Ahmad, R. J. Magee and J. O. Hill, *Thermochim. Acta*, 98 (1986) 127.
- 56 M. N. Sastri and J. O. Hill, *J. Thermal Anal.*, 11 (1977) 323.
- 57 B. J. Meehan, S. A. Tariq and J. O. Hill, *J. Thermal Anal.*, 12 (1977) 235.
- 58 S. A. Tariq and J. O. Hill, *J. Thermal Anal.*, 21 (1981) 277.
- 59 G. K. Chuah, S. Jaenicke, K. S. Chan, S. T. Khor and J. O. Hill, *J. Thermal Anal.*, 40 (1993) 1157.
- 60 E. L. Charsley, J. O. Hill, P. Nicholas and S. B. Warrington, *Thermochim. Acta*, 195 (1992) 65.
- 61 E. L. Charsley, N. G. Buckman and J. O. Hill, *J. Thermal Anal.*, 36 (1990) 309.
- 62 J. O. Hill, I. G. Worsley and L. G. Hepler, *Chem. Rev.*, 71 (1971) 127.
- 63 J. O. Hill, G. Ojelund and I. Wadso, *J. Chem. Thermodyn.*, 1 (1969) 111.
- 64 J. O. Hill and R. J. Irving, *J. Chem. Soc., A*, (1969) 2759.
- 65 J. O. Hill and I. Wadso, *Acta Chem. Scand.*, 22 (1968) 1590.
- 66 J. O. Hill, *Thermochim. Acta*, 35 (1980) 129.
- 67 R. H. Davies, A. Finch and J. O. Hill, *Thermochim. Acta*, 184 (1991) 243.
- 68 R. H. Davies, A. Finch and J. O. Hill, *Thermochim. Acta*, 188 (1991) 321.
- 69 J. O. Hill, 'Thermochemical Methods in Pharmaceutical Manufacturing', Symposium Proceedings, The Institute of Drug Technology Ltd., Parkville, Victoria 3052, Australia, 1981, pp. 5-27.
- 70 G. Becket, S. B. Quah and J. O. Hill, *J. Thermal Anal.*, 40 (1993) 537.
- 71 J. O. Hill and S. Korce, *Thermochim. Acta*, 148 (1989) 341.
- 72 N. G. Buckman, J. O. Hill and R. J. Magee, *J. Thermal Anal.*, 36 (1990) 289.
- 73 N. G. Buckman, J. O. Hill and R. J. Magee, *J. Thermal Anal.*, 36 (1990) 2555.
- 74 N. G. Buckman, J. O. Hill and R. J. Magee, *J. Thermal Anal.*, 37 (1991) 79.

- 75 N. G. Buckman, J. O. Hill and R. J. Magee, *J. Thermal Anal.*, 37 (1991) 95.
- 76 J. O. Hill, N. G. Buckman and R. J. Magee, *J. Thermal Anal.*, 39 (1993) 795.
- 77 J. O. Hill, S. Korce, S. Lim and G. R. Scollary, *Thermochim. Acta*, 209 (1992) 301.
- 78 J. O. Hill, P. J. Jessup and J. A. Reiss, *J. Thermal Anal.*, 21 (1981) 271.
- 79 S. N. Wong, N. Binti Abdul Rahim, L. Chia and J. O. Hill, *Proceed.*, Science Research Congress, National University of Singapore, 1992. p. 68.
- 80 J. O. Hill, E. L. Charsley and M. R. Ottaway, *Thermochim. Acta*, 93 (1985) 741.
- 81 S. Ma and J. O. Hill, *Thermochim. Acta*, 149 (1989) 269.
- 82 S. Ma, J. O. Hill and S. Heng, *Thermochim. Acta*, 190 (1991) 291.
- 83 S. Ma, J. O. Hill and S. Heng, *J. Thermal Anal.*, 35 (1989) 977.
- 84 S. Ma, G. Huang and J. O. Hill, *Thermochim. Acta*, 184 (1991) 233.
- 85 S. Ma, J. O. Hill and S. Heng, *J. Thermal Anal.*, 37 (1991) 1161.
- 86 S. Ma, J. O. Hill and S. Heng, *Proceed.*, 4th Australian Coal Science Conference, Australian Institute of Energy, Brisbane, Australia, 1990, pp. 192–199.
- 87 S. Ma, J. O. Hill and S. Heng, *Thermochim. Acta*, 197 (1992) 79.
- 88 S. Ma, J. O. Hill and S. Heng, *J. Thermal Anal.*, 35 (1989) 1985.
- 89 S. Ma, J. O. Hill and S. Heng, *J. Thermal Anal.*, 35 (1989) 1611.
- 90 J. O. Hill, S. Ma and S. Heng, *J. Thermal Anal.*, 5 (1989) 2009.
- 91 J. O. Hill, *ICTAC NEWS*, 26 (1993) 27.
- 92 J. O. Hill, I. G. Worsley and L. G. Hepler, *J. Phys. Chem.*, 72 (1968) 3695.
- 93 E. M. Woolley, J. O. Hill, W. K. Hannan and L. G. Hepler, *J. Solution Chem.*, 7 (1978) 385.
- 94 R. Bin Ahmad, J. O. Hill and R. J. Magee, *Thermochim. Acta*, 71 (1983) 25.
- 95 H. S. O. Chan and J. O. Hill, *Bull. Singapore Natl. Inst. Chem.*, 20 (1992) 55.
- 96 J. O. Hill, *Bull. Singapore Natl. Inst. Chem.*, 20 (1992) 75.
- 97 J. O. Hill, *Australian Chemistry Resource Book*, C. L. Fogliani, Ed., Mitchell Printery, Charles Sturt University, Bathurst, NSW 2795, Australia, 12 (1993) 48.
- 98 E. L. Charsley and J. O. Hill, 6th Indian Thermal Analysis Society Symposium – Workshop Proceedings, New Delhi, Indian Thermal Analysis Society, Bombay, India, 1987, pp. 6–14.
- 99 J. O. Hill, 7th Indian Thermal Analysis Society Symposium – Workshop Proceed., Srinagar, Indian Thermal Analysis Society, Bombay, India, 1989, pp. 73–82.
- 100 J. O. Hill and J. P. Redfern, 8th Indian Thermal Analysis Society Symposium – Workshop Proc., Bhubaneswar, Indian Thermal Analysis Society, Bombay, India, 1991, pp. 46–66.
- 101 J. O. Hill, 9th Indian Thermal Analysis Society Symposium – Workshop Proceed., Goa, Indian Thermal Analysis Society, Bombay, India, 1993, pp. 49–66.
- 102 J. O. Hill and S. Chirawongaram, *Proceed.*, Malaysian Silver Jubilee Chemical Congress, Kuala Lumpur, Malaysia, 1992, p. 13.
- 103 J. G. Dunn and J. O. Hill, *Proc.*, RACI - 12th Australian Symposium on Analytical Chemistry (12AC), Perth, Western Australia, 1993, pp. 7.
- 104 J. O. Hill in 'Thermal Analysis Short Course', R. A. Shanks, Ed., Technisearch Ltd., Royal Melbourne Institute of Technology, Melbourne, Australia, 1989, pp. 1–12.
- 105 J. O. Hill, 'A Short Course in Thermal Analysis', Parts 1–8, Chulalongkorn University Press, Bangkok, Thailand, 1989, pp. 95.
- 106 J. O. Hill, SE Asian Thermal Analysis Society Symposium Proceed., 'Modern Thermal Analysis Techniques', Parts 1–8, Polymer Laboratories Ltd., Epsom, Surrey, UK, 1990.
- 107 J. O. Hill, Ed., 'For Better Thermal Analysis and Calorimetry', 3rd Edn., International Confederation for Thermal Analysis and Calorimetry (ICTAC), London, 1991, pp. 93.
- 108 J. O. Hill, DSc Thesis, Vols 1–4, University of London, UK, 1992.

**Zusammenfassung** — Die vom Autor im Zeitraum 1964 bis 1993 geführte Forschungsarbeit im Bereich Thermoanalyse und Kalorimetrie wird zusammengefaßt und kurz rezensiert. Die wichtigsten Forschungsarbeiten konzentrierten sich auf die Untersuchung von Koordinationsverbindungen, im speziellen auf Metalldithiocarbamat-Komplexe. Unter anderem wurde eine bedeutende Lösungskalorimetrie-Untersuchung von einigen Metalldithiocarbamat-Komplexen durchgeführt. DSC wurde zur Bestimmung der Sublimationsenthalpien vieler Metalldithiocarbamate und Metallpentan-2,4-dionatkomplexe und Lösungskalorimetrie zur Untersuchung der Thermochemie der letzteren Komplexgruppe eingesetzt. Thermoanalytische Untersuchungen einiger anorganischer geschmolzener Salzsysteme wurden initiiert. Thermometrische Titrimetrie wurde zur Untersuchung metallmakrocyclischer Ligandensysteme in wäßrigem Milieu angewendet, insbesondere an Systemen mit Bedeutung für die Umwelt. Es wurden Temperaturkalibrierungsstandards für TMA vorgeschlagen und TMA zur Untersuchung mechanischer Eigenschaften einiger gewöhnlicher anorganischer Verbindungen eingesetzt. DTA wurde zur Untersuchung eines breiten Kreises von Phenolen und anschließend als eine Analysetechnik zur Bestimmung der Komponenten von Phenolgemischen im festen Zustand eingesetzt. Thermometrische Titrimetrie wurde zur Bestimmung des Phenolgehaltes von Weinsorten angewendet. Es wurde eine umfassende thermoanalytische Untersuchung australischer Braunkohle unternommen, einschließlich der DSC-Bestimmung der spezifischen Energie der Kohle, einer TG/DTA-Untersuchung der Kohlepyrolyse- und Verbrennungsprozesse sowie einer TG/DTA- und EGA-Untersuchung des kationischen Katalyseeffektes auf Kohlepyrolyseprozesse. Durch die Veröffentlichung von Spezialisten-Rezensionen, die Präsentation von Symposien-Rezensionen und die mündliche Präsentation von Kursen, insbesondere in der Südostasienregion wurden thermoanalytische und kalorimetrische Techniken ausführlich publiziert und gefördert. Vorliegende Arbeit bringt insbesondere die Verschiedenartigkeit von möglichen Anwendungen der Thermoanalyse und der kalorimetrischen Techniken und die erstrangige Bedeutung thermodynamischer Daten für eine grundlegenden Rationalisierung chemischer Erscheinungen zum Ausdruck.