Thermochimica Acta, 200 (1992) 187–194
Elsevier Science Publishers B.V., Amsterdam

Twenty-five years of thermochemistry research — a personal review

J.O. Hill

Department of Chemistry, The National University of Singapore, Kent Ridge, Singapore 0511 (Singapore)

(Received 10 February 1992)

Abstract

The research in thermochemistry, conducted by the author over the period 1966–1991 is summarised and concisely reviewed. Significant advances have been made in the solution calorimetric determination of the standard formation enthalpies of coordination compounds, particularly metal dithiocarbamates, the application of thermometric titrimetry as an analytical technique, particularly for the determination of metals in aqueous systems of environmental significance and the rationalisation of speciation phenomena in aqueous metal–ligand systems, and the application of thermal analysis (TG, DTA, DSC, EGA and TMA) to study a wide variety of systems, particularly metal complexes. These thermal analysis studies also include the DSC determination of the sublimation enthalpies of metal complexes, the DTA study of phenols and phenol derivatives and a comprehensive TA study of Australian brown coal. This review reveals the diversity of application of calorimetric and thermal analysis techniques and the primary significance of thermodynamic data in the fundamental rationalisation of chemical phenomena.

Over the last 25 years, my research has focused primarily on the application of calorimetric and thermal analysis 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 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.

Reference 1 reports definitive thermochemical data for TRIS as a test substance in solution calorimetry. The reported neutralisation enthalpy value for the TRIS/0.1 M HCl reaction at 298 K is widely accepted as the "best available" reference for "performance testing" of solution calorimeters.

Correspondence to: J.O. Hill, Department of Chemistry, The National University of Singapore, Kent Ridge, Singapore 0511, Singapore.

Reference 2 reports the solution calorimetric determination of the ionisation enthalpy of 2,4-pentanedione in water and in 50% water–dioxan. The overall thermodynamics of this process are discussed.

References 3–6 report the standard formation enthalpies of four metal 2,4-pentanedionate complexes, as derived by solution calorimetry. 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.

References 7–11 relate to the solution thermochemistry of metal dithiocarbamate and xanthate complexes. Reference 7 reports the solution calorimetric determination of the standard formation enthalpy of diethylammonium diethyldithiocarbamate, a precursor in the formation of metal dithiocarbamate complexes. Reference 8 reports some solution thermochemistry of tris(diethyldithiocarbamato)Fe(III), from which the standard formation enthalpy of this complex can be derived once the standard formation enthalpy of sodium diethyldithiocarbamate is known. References 9 and 10 report the standard formation enthalpies of bis(diethyldithiocarbamato)Ni(II) and bis(diethyldithiocarbamato)Cu(II), as derived by solution calorimetry, using the definitive procedure developed in refs. 3–6. These are the first reported standard formation enthalpies of metal dithiocarbamate complexes derived by solution calorimetry. Reference 11 reports the solution thermochemistry of some nickel alkyl xanthates. The data are interpreted in terms of inductive and steric effects of the terminal alkyl group on the thermodynamic complex stability.

References 12–15 relate to the solution thermochemistry of organic compounds. Reference 12 reports the standard formation enthalpy of *N,N,N*-triacetylammonia, as derived by solution calorimetry. Reference 13 reports the standard solution enthalpy of pyridinium bromide in chloroform, as determined by solution calorimetry and the DSC determination of the fusion enthalpy of this salt. Hence the mixing enthalpy of pyridinium bromide and chloroform is derived. Reference 14 reports the standard formation enthalpy of 1,3-dimethylurea nitrate and the standard protonation enthalpy of aqueous 1,3-dimethylurea, as determined by solution calorimetry. Reference 15 discusses models for the linear correlation of thermochemical data for ureas with the degree of N substitution.

Reference 16 reports a novel calorimetric method for the determination of a distribution coefficient — that of bromine in water–carbon tetrachloride.

Reference 17 is a concise review of the thermochemistry and redox chemistry of vanadium, niobium and tantalum and is one of a compendium of reviews of the thermochemistry and electrochemistry of transition metal triads, compiled by Hepler. The thermochemical and electrochemical data cited in these reviews are generally accepted as selected definitive data.

Reference 18 reports a BASIC computer program for data analysis in thermometric titrimetry. This program is recognised as the most comprehensive of its type.

References 19–24 report the analytical determination of a variety of metal ions in aqueous solution by thermometric titrimetry. The methods developed are assessed for potential application to environmental systems.

Reference 25 investigates the thermometric titration of sulphide with permanganate in alkaline solution as a potential analytical method for the determination of sulphide in natural waters.

Reference 26 reports the analytical determination of phenols by thermometric titrimetry, using thallium ethoxide as titrant and benzene as solvent.

Reference 27 is a review of the application of TG, DTA, DSC and thermometric titrimetry in pharmaceutical science. These techniques have major significance in the context of purity determination and drug assay procedures.

Reference 28 is a review of the application of thermometric titrimetry to the determination of various species in environmental systems. It appears that thermometric titrimetry is of additional significance for the determination of speciation phenomena associated with such systems.

Reference 29 is a comprehensive and definitive review of 51 papers dealing with the thermodynamics of metal ion binding by synthetic macrocyclic compounds. The metal ion binding constants were determined by thermometric titrimetry and the initial data for alkali and alkaline earth metal cyclic polyether complexes were of key significance in rationalising the selectivity of macrocyclic compounds in metal ion complexation. Such selectivity has paramount biological significance. This review was published during the infancy of what is now a major area of inorganic chemistry.

References 30 and 31 report a thermometric titrimetry study of the complexation of alkaline earth metals by linear and macrocyclic polyaminocarboxylic acids. Factors influencing the thermodynamic stability of these complexes are discussed.

Reference 32 reports a thermometric titrimetry determination of the dilution enthalpy of aqueous iodic acid, thereby yielding the standard ionisation enthalpy of this acid. The corresponding standard free energy and entropy of iodic acid are calculated.

Reference 33 describes two well-tested experiments, suitable for the advanced level undergraduate laboratory. The first experiment involves a thermal analysis (TG, DTA) study of bis(thiocyanato)tetrapyridinenickel(II) and the thermal analysis of an oxalate mixture. The second experiment involves a thermometric titrimetry study of various simple systems using a "home-made" thermometric titrimetry system.

Reference 34 is a comprehensive review of 137 papers on the thermochemistry of the metal dithiocarbamate, dithiophosphate and xanthate complexes. The solution thermochemistry of these complexes is also included.

References 35–45 report detailed thermal analysis studies on metal dithiocarbamates using the techniques TG, DTA, EGA and pyrolysis/GC–MS.

References 37–45 represent the most comprehensive thermal analysis study available of tin dithiocarbamate complexes.

References 46 and 47 report a thermal analysis study of nickel and palladium alkyl xanthate complexes. Reference 47 was the first such study of these complexes to use MS to identify the volatile decomposition products.

Reference 48 reports the sublimation enthalpy of Ni(II) and Cu(II) diethyldithiocarbamate and diethylammonium diethyldithiocarbamate, determined by the sublimation bulb technique. This was the first report of a volatile diethyldithiocarbamate salt.

Reference 49 proposes benzoic acid as a calibrant in the DSC determination of sublimation enthalpy. Reference 50 reports the sublimation enthalpies of Ni(II), Cu(II) and Co(III) diethyldithiocarbamate complexes as determined by vacuum DSC. These are the definitive data for these complexes.

Reference 51 assesses sublimation enthalpy data available for metal 2,4-pentanedionate complexes.

References 52–55 report the sublimation enthalpies of 2,4-pentanedionate complexes of Be(II), Al(III), Cr(III), Fe(III), Co(III), Ni(II), Cu(II), VO(II) and Zr(IV).

Reference 56 is a concise review of 40 papers summarising the available thermal analysis data for metal 2,4-pentanedionate complexes.

Reference 57 is a thermal analysis study of some Ni(II) thiourea chloride complexes. Thermal degradation mass spectrometry (TDMS) is used to identify and characterise the volatile decomposition products.

Reference 58 is a combined DTA and XPS study of cis-platin. The data are consistent with cis–trans isomerism of the complex prior to decomposition.

References 59 and 60 represent thermal analysis studies of organometallic compounds. Reference 59 proposes thermal decomposition mechanisms, based on TG and DTA data, for dicyclopentadienyl zirconium diborohydride and bis(triphenylphosphine)borohydridocopper(I). Reference 60 describes the investigation by TG, of the thermal decarboxylation of some mercury(II) carboxylate complexes. Such mercury complexes are of considerable current interest in the context of providing precursors for organomercury systems.

References 61–63 present thermal analysis (TG, DTA) studies on molten salt systems. Reference 61 is a DTA study of the chromium(III) oxide/oxygen reaction in molten sodium carbonate. Reference 62 is a TG–DTA study of the thermal stability of some molten sulphur–oxyanionic salts and the corresponding eutectics.

Reference 63 is a TG study of the thermal decomposition of mercury(I) and mercury(II) sulphates.

Reference 64 is a thermal decomposition study of some cyclophane bis(sulphoxides). This study has some industrial significance in the context of large-scale synthesis of cyclophane dienes.

References 65–68 comprise a comprehensive DTA study of phenols and some corresponding derivatives. The "data bank" so obtained is invaluable for the rapid characterisation of phenols in the solid state.

References 69–77 represent a systematic and comprehensive thermal analysis study of Australian brown coal. Reference 69 is a review of the topic, which indicates the sparsity of such data available. Reference 70 gives some proximate analysis data for brown coal, as derived from TG. Reference 71 discusses relationships between specific energy and proximate and ultimate analyses, as related to brown coal. References 72 and 73 report TG studies of the pyrolysis characteristics of brown coal. Reference 74 is a thermal analysis investigation of the influence of exchangeable metal cations on the pyrolysis characteristics of brown coal. Reference 75 is a description of a computer program for the systematic kinetic analysis of TG data and is particularly applicable to the kinetics of coal pyrolysis. Reference 76 is a TG–DTA study of the oxidation of brown coal chars and ref. 77 is a DSC determination of coal specific energy.

Reference 78 recommends that a series of pure metals be used as temperature calibrants for TMA and that the DTA Certified Reference Materials (NIST) be used as secondary standards in this context. This paper represents the first proposals for temperature calibration in TMA.

Reference 79 reports a TMA study of selected compounds, to illustrate the diversity in application of this technique.

Reference 80 is a comprehensive set of published notes on each of the major thermal analysis techniques, with each of the eight parts subdivided into three major sections: a description of the basic principles of the technique; a description of the associated instrumentation; a discussion of a wide range of applications. This set of notes essentially formed the proceedings of a symposium on "Modern Thermal Analysis Techniques", conducted by the author and presented at several venues in S.E. Asia over the period October 1989 to February 1990.

Refinements in thermal analysis instrumentation and concomitant developments in electronics technology in recent years have resulted in a significant extension of the operational temperature range for thermal analysis techniques. Reference 81 is a review of some recent applications of extended temperature range TG, DTA, (STA), DSC, TMA (TDA), DMA and DETA techniques with particular emphasis on the study of materials of technological importance. This review indicates that "thermal analysis" is making a significant contribution to the "high-tech" age.

Reference 82 is a booklet entitled "For Better Thermal Analysis and

Calorimetry" published by the International Confederation for Thermal Analysis (ICTA). It 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, committees, publications and membership application procedures of ICTA.

REFERENCES

1 J.O. Hill, G. Öjelund and I. Wadsö, J. Chem. Thermodyn., 1 (1969) 111.
2 J.O. Hill and R.J. Irving, J. Chem. Soc. A, (1969) 2759.
3 J.O. Hill and R.J. Irving, J. Chem. Soc. A, (1966) 971.
4 J.O. Hill and R.J. Irving, J. Chem. Soc. A, (1967) 1413.
5 J.O. Hill and R.J. Irving, J. Chem. Soc. A, (1968) 1052.
6 J.O. Hill and R.J. Irving, J. Chem. Soc. A, (1968) 3116.
7 K.J. Cavell, J.O. Hill and R.J. Magee, Thermochim. Acta, 33 (1979) 377.
8 B. Annuar, J.O. Hill, D.J. Mclvor and R.J. Magee, Thermochim. Acta, 9 (1974) 143.
9 K.J. Cavell, J.O. Hill and R.J. Magee, J. Chem. Soc., Dalton Trans., (1980) 763.
10 K.J. Cavell, J.O. Hill and R.J. Magee, J. Chem. Soc., Dalton Trans., (1980) 1638.
11 K.J. Cavell. J.O. Hill and R.J. Magee, Thermochim. Acta, 8 (1974) 447.
12 J.O. Hill and I. Wadsö, Acta Chem. Scand., 22 (1968) 1590.
13 J.O. Hill, Thermochim. Acta, 35 (1980) 129.
14 R.H. Davies, A. Finch and J.O. Hill, Thermochim. Acta, 184 (1991) 243.
15 R.H. Davies, J.O. Hill and A. Finch, Thermochim. Acta, 188 (1991) 321.
16 J.O. Hill, I.G. Worsley and L.G Hepler, J. Phys. Chem., 72 (1968) 3695.
17 J.O. Hill, I.G. Worsley and L.G. Hepler, Chem. Rev., 71 (1971) 127.
18 R. bin Ahmad, J.O. Hill and R.J. Magee, Thermochim. Acta, 71 (1983) 25.
19 R. bin Othman, J.O. Hill and R.J. Magee, Mikrochim. Acta, 111 (1987) 337.
20 R. bin Othman, J.O. Hill and R.J. Magee, Thermochim. Acta, 122 (1987) 163.
21 R. bin Othman, N.G. Buckman, J.O. Hill and R.J. Magee, Thermochim. Acta, 157 (1990) 335.
22 J.O. Hill and S. Korce, Thermochim. Acta, 154 (1989) 49.
23 J.O. Hill and S. Lim, Thermochim. Acta, 188 (1991) 249.
24 J.O. Hill and S. Lim, Thermochim. Acta, 188 (1991) 255.
25 R. bin Ahmad, R.J. Magee and J.O. Hill, Thermochim. Acta, 98 (1986) 127.
26 J.O. Hill and S. Korce, Thermochim. Acta, 148 (1989) 341.
27 J.O. Hill, Thermochemical Methods in Pharmaceutical Manufacturing, Symposium Proceedings, The Institute of Drug Technology Ltd., Royal Pde., Parkville, Victoria 3052, Australia, 1981, pp. 5-27.
28 J.O. Hill, Bull. Singapore Natl. Inst. Chem., 18 (1990) 5.
29 R.M. Izatt, J.O. Hill and J.J. Christensen, Science, 174 (1971) 459.
30 G. Ewin and J.O. Hill, J. Chem. Soc., Dalton Trans., (1983) 865.
31 G. Ewin and J.O. Hill, J. Chem. Res., (S) (1985) 334; (M) (1985) 3501.
32 E.M. Woolley, J.O. Hill, W.K. Hannan and L.D. Hepler, J. Solution Chem., 7 (1978) 385.
33 J.O. Hill and R.J. Magee, J. Chem. Educ., 65 (1988) 1024.
34 J.O. Hill and R.J. Magee, Rev. Inorg. Chem., 3 (1981) 141.
35 C.G. Sceney, J.O. Hill and R.J. Magee, Thermochim. Acta, 11 (1975) 301.

36 C.G. Sceney, J.F. Smith, J.O. Hill and R.J. Magee, J. Therm. Anal., 9 (1976) 415.
37 G.K. Bratspies, J.F. Smith, J.O. Hill and R.J. Magee, Thermochim. Acta, 27 (1978) 307.
38 G.K. Bratspies, J.F. Smith, J.O. Hill and R.J. Magee, Thermochim. Acta, 19 (1977) 335.
39 G.K. Bratspies, J.F. Smith, J.O. Hill and R.J. Magee, Thermochim. Acta, 19 (1977) 349.
40 G.K. Bratspies, J.F. Smith, J.O. Hill and R.J. Magee, Thermochim. Acta, 19 (1977) 361.
41 G.K. Bratspies, J.F. Smith and J.O. Hill, Thermochim. Acta, 19 (1977) 373.
42 G.K. Bratspies, J.F. Smith and J.O. Hill, Thermal Analysis, in W. Hemminger (Ed.), Proc. Sixth Int. Conf. on Thermal Analysis, Birkhauser, Basle, 2 (1980) 147.
43 G.K. Bratspies, J.F. Smith and J.O. Hill, J. Anal. Appl. Pyrolysis, 2 (1980) 35.
44 G.K. Bratspies, J.F. Smith, J.O. Hill and P.J Derrick, J. Therm. Anal., 16 (1979) 369.
45 G.K. Bratspies, J.O. Hill and J.F. Smith, Thermochim. Acta, 133 (1988) 383.
46 K.J. Cavell, C.G. Sceney, J.O. Hill and R.J. Magee, Thermochim. Acta, 5 (1973) 319.
47 C.G. Sceney, J.O. Hill and R.J. Magee, Thermochim. Acta, 6 (1973) 111.
48 K.J. Cavell, J.O. Hill and R.J. Magee, Thermochim. Acta, 34 (1979) 155.
49 J.P. Murray, K.J. Cavell and J.O. Hill, Thermochim. Acta, 36 (1980) 97.
50 K.J. Cavell, J.O. Hill and R.J. Magee, Thermochim. Acta, 33 (1979) 383.
51 J. Sachinidis and J.O. Hill, Thermochim. Acta, 36 (1980) 59.
52 J.P. Murray and J.O. Hill, Thermochim. Acta, 63 (1983) 211.
53 J.P. Murray and J.O. Hill, Thermochim. Acta, 72 (1984) 341.
54 J.P. Murray and J.O. Hill, Thermochim. Acta, 109 (1987) 383.
55 J.P. Murray and J.O. Hill, Thermochim. Acta, 109 (1987) 391.
56 J.O. Hill, Therm. Anal. Rev. Abstr., 20 (1991) 1.
57 M.P.B. Attard, J.O. Hill, R.J. Magee, S. Prakash and M.N. Sastri, J. Therm. Anal., 31 (1986) 407.
58 S.P. Roe, J.O. Hill and R.J. Magee, Inorg. Chim. Acta, Lett., 115 (1986) L15.
59 B.D. James, B. Annuar, J.O. Hill and R.J. Magee, in R.S. Porter and J.F. Johnson (Eds.), Analytical Calorimetry, Plenum, New York, 3 (1974) 777.
60 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.
61 M.N. Sastri and J.O. Hill, J. Therm. Anal., 11 (1977) 323.
62 B.J. Meehan, S.A. Tariq and J.O. Hill, J. Therm. Anal., 12 (1977) 235.
63 S.A. Tariq and J.O. Hill, J. Therm. Anal., 21 (1981) 277.
64 J.O. Hill, P.J. Jessup and J.A. Reiss, J. Therm. Anal., 21 (1981) 271.
65 N.G. Buckman, J.O. Hill and R.J. Magee, J. Therm. Anal., 36 (1990) 289.
66 N.G. Buckman, J.O. Hill and R.J. Magee, J. Therm. Anal., 36 (1990) 2555.
67 N.G. Buckman, J.O. Hill and R.J. Magee, J. Therm. Anal., 37 (1991) 79.
68 N.G. Buckman, J.O. Hill and R.J. Magee, J. Therm. Anal., 37 (1991) 95.
69 J.O. Hill, S. Ma and S. Heng, J. Therm. Anal., 35 (1989) 2009.
70 J.O. Hill, E.L. Charsley and M.R. Ottaway, Thermochim. Acta, 93 (1985) 741.
71 S. Ma and J.O. Hill, Thermochim. Acta, 149 (1989) 269.
72 S. Ma, J.O. Hill and S. Heng, J. Therm. Anal., 35 (1989) 977.
73 S. Ma, J.O. Hill and S. Heng, J. Therm. Anal., 35 (1989) 1985.
74 S. Ma, J.O. Hill and S. Heng, 4th Australian Coal Science Conference Proceedings, Australian Institute of Energy, Brisbane, Australia, 1990, pp. 192–199.
75 S. Ma, G. Huang and J.O. Hill, Thermochim. Acta, 184 (1991) 233.
76 S. Ma, J.O. Hill and S. Heng, J. Therm. Anal., 35 (1989) 1611.
77 S. Ma, J.O. Hill and S. Heng, Thermochim. Acta, 190 (1991) 291.
78 E.L. Charsley, J.O. Hill, P. Nicholas and S.B. Warrington, Thermochim. Acta, 195 (1992) 65.
79 E.L. Charsley, N.G. Buckman and J.O. Hill, J. Therm. Anal., 36 (1990) 309.

80 J.O. Hill, S.E. Asian Thermal Analysis Symposium Proceedings: Modern Thermal Analysis Techniques, Parts 1–8, PL (Thermal Sciences) Ltd., Epsom, Surrey, 1990.
81 J.O. Hill and J.P. Redfern, 8th Indian Thermal Analysis Society Symposium — Workshop Proceedings, Bhubaneswar, Indian Thermal Analysis Society, Bombay, India, 1991, pp. 46–66.
82 J.O. Hill (Ed.), For Better Thermal Analysis and Calorimetry, 3rd edn., International Confederation for Thermal Analysis (ICTA), London, 1991.