REACTIONS IN THE SOLID STATE

by

Michael Ewart Brown

A thesis submitted to meet the requirements of the degree
of Doctor of Science
of
Rhodes University
Grahamstown

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DEDICATION

This thesis is dedicated to my wife, Cindy,
and my family, Richard and Ruth,
Linda and André and Brandon,
for all their love and support.

ACKNOWLEDGEMENTS

CURRICULUM VITAE

MICHAEL EWART BROWN
Chemistry Department, Rhodes University, Grahamstown 6140, South Africa
Emeritus Professor of Physical Chemistry

PERSONAL DETAILS
Born: 12th July, l938   Nationality: South African
Married with two adult children.

ACADEMIC QUALIFICATIONS
B.Sc(Hons)(Witwatersrand, First Class, 1960), Ph.D (Rhodes, 1966)

PROFESSIONAL QUALIFICATIONS
FRSSAf (Fellow of the Royal Society of S.A.), MSA Chemical Institute
MRSC

CAREER OUTLINE
Rhodes University: 1962 - 1965 Junior Lecturer, 1967 - 1970 Lecturer,
                   1971 - 1977 Senior Lecturer, 1978 - 1985 Associate Professor,
                   1986 - 2003 Professor of Physical Chemistry.
1966 Research Officer, S.A. Chamber of Mines Research Laboratories.
1971 Leverhulme Visiting Research Fellow at Queen's University of Belfast.
1980 Visiting Research Fellow, Cavendish Laboratory, University of Cambridge.
1989 Visiting Research Fellow, ICI Explosives, Scotland.
1989 Allied Irish Banks Visiting Professor, Queen's University of Belfast.
1986 - 1991 Dean of Science, Rhodes University.
1994 Acting Dean of Research, Rhodes University.

RESEARCH FUNDING
A - rated by the National Research Foundation (NRF).
Significant funding from AECI Explosives Ltd.

AWARDS
1996 Mettler/NATAS international award for distinguished contributions to Thermal Analysis
1998 Vice-Chancellor's Distinguished Senior Research Award, Rhodes University.
2000 SA Chemical Institute Gold Medal
2003 Elected Fellow of the North American Thermal Analysis Society (NATAS).

INVITED LECTURES
1996 Mettler/NATAS Award Lecture at the 11th International Congress on Thermal Analysis and Calorimetry, Philadelphia.
1998 Invited Lecturer at the 11th National Symposium of the Indian Thermal Analysis Society, Jammu, India.
1998 Invited Lecturer at the 26th Symposium of the North American Thermal Analysis Society, Cleveland, Ohio.
2000 Plenary Lecturer 8th Conference on Calorimetry and Thermal Analysis, Zakopane, Poland.
2000 Plenary Lecturer 28th North American Thermal Analysis Society Conference, Orlando, Florida, USA
2001 SA Chemical Institute Gold Medal Lecture, Rhodes University

2002 Plenary Lecturer at the National Convention of the SA Chemical Institute, Port Elizabeth.

2003 Invited Lecturer at the 30th Symposium of the North American Thermal Analysis Society, Albuquerque, New Mexico.

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ORGANIZATIONS

Secretary of International Confederation of Thermal Analysis and Calorimetry 1996-

Editorial board of "Thermochimica Acta".

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BIOGRAPHICAL NOTES

After graduating with a BSc (Hons) in Chemistry from the University of Witwatersrand, a variety of circumstances resulted in my appointment as a Junior Lecturer at Rhodes University in Grahamstown. I registered for a PhD in solid-state chemistry under the direction of Professor Ernest Prout (of the Prout-Tompkins equation fame).   This research introduced me to the general area of "Reactivity of Solids", which was to remain my major research interest throughout my career.

After completing my PhD, I joined the Chamber of Mines Research Laboratories in Johannesburg as a Research Officer.   The research area assigned to me was related to the silver-refining processes in use at the Rand Refinery. After only a year away, I was offered a Lectureship back at Rhodes University.

Many changes had taken place in the Chemistry Department and I was fortunate to have a mentor in the person of Professor Leslie Glasser. With his guidance and experience we were able to obtain funding for equipment that was then becoming commercially available in the field of thermal analysis. These techniques added greatly to the information obtainable on the decomposition of solids and continue to be a major area of interest.

My first period of sabbatical leave was a year spent in 1971 at the Queen's University of Belfast. This was the start of a long, fruitful and extremely satisfying collaboration with Dr Andrew Galwey, which continues at present. Some of my recollections and appreciation of this friendship and collaboration are recorded in the Special Issue of the Journal of Thermal Analysis (Vol. 41 (1994) 252) prepared to celebrate Dr Galwey's 60th birthday. In 2002 a Special Issue of Thermochimica Acta (Volume 388, p1-460) was published in honour of our collaboration. It is entitled "Kinetics of Thermally Stimulated Reactions" and was edited by Sergey Vyazovkin and Takeo Ozawa.

My background in solid-state chemistry and thermal analysis led to generous support from AECI Explosives Ltd, including assistance with the purchase of equipment, for studies of the chemistry of the pyrotechnic delay fuses used in the gold mining industry.   A PhD student, Michael Beck, with very generous help from Dr Peter Laye of the University of Leeds, adopted a technique involving the measurement of temperature-time profiles in packed columns of burning pyrotechnics. This, together with the theory developed at Leeds, enabled very useful comparisons to be made between different preparations. Use was also made of finite-element computer codes, supplied by ICI Explosives, to compare the predicted behaviour with that measured. As part of this research, I was able to spend periods of leave at the Cavendish Laboratory, Cambridge, and at ICI Explosives in Scotland.

Through my interest in thermal analysis, I became involved in the founding of the Southern African Thermal Analysis Society. This later led to me becoming the SA representative on the Council of the International Confederation for Thermal Analysis and Calorimetry and to my current position as Secretary to that Council.

With the political and economic changes in the 1990s, the research priorities of companies changed and support for pyrotechnic research dwindled. Fortunately I was able to move in a new direction and collaborate with Prof B.D. Glass (now at James Cook University in Australia) on the thermal and photostability of drugs. This work continues.

Highlights of my career have been receiving the 1996 Mettler/NATAS international award for distinguished contributions to Thermal Analysis and giving the Award Lecture at the 11th International Congress on Thermal Analysis and Calorimetry, Philadelphia, the 1998 Vice-Chancellor's Distinguished Senior Research Award, Rhodes University, and the 2000 SA Chemical Institute Gold Medal. My associations with and membership of the North American Thermal Analysis Society (NATAS) have been very valuable to me and I have presented several invited lectures at NATAS Conferences. In 2003 I was elected a NATAS Fellow. Of the other invited lectures that I have given, those to the 11th National Symposium of the Indian Thermal Analysis Society, Jammu, India, and the 8th Conference on Calorimetry and Thermal Analysis, Zakopane, Poland, were very memorable.

PUBLICATIONS

BOOKS

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(1984) 105806.

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Chapman & Hall Ltd., London, 1988.

B2/2. "Introduction to Thermal Analysis: Techniques and Applications", M E Brown,
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2001, 264 pp.

B3. "Handbook of Thermal Analysis and Calorimetry, Vol.1, Principles and Practice"
Elsevier Scientific, Amsterdam, 1998, 691 pp. M.E. Brown, Editor and contributor of
two chapters: A.K. Galwey and M.E. Brown, "Kinetic background to Thermal Analysis
and Calorimetry" (77 pp) and V. Balek and M.E. Brown, "Less-common Techniques"
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B4. "Thermal Decomposition of Ionic Solids", A.K. Galwey and M.E. Brown,
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B5. "Handbook of Thermal Analysis and Calorimetry, Vol.2, Applications to Inorganic and
Miscellaneous Materials", Elsevier Scientific, Amsterdam, 2003, 905 pp.
M.E. Brown, Co-Editor and contributor of chapter: E.L. Charsley, P.G. Laye and
M.E. Brown, "Pyrotechnics" (30 pp).

RESEARCH PAPERS

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E G Prout and M E Brown, **Nature**, 203 (1964) 398-399.

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R4. The thermal decomposition of ammonium metavandate, 1: The stoichiometry of the decomposition, M E Brown and B V Stewart, **J. Thermal Analysis**, 2 (1970) 287-299.

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monohydrate. Part 2. Thermogravimetry and differential scanning calorimetry,
M E Brown, A K Galwey and A Li Wan Po, **Thermochim. Acta**, 220 (1993) 131-150.

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M E Brown, M J Tribelhorn and M G Blenkinsop, **J. Thermal Analysis,**
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R51. Kinetics of thermal decomposition of some mixed metal oxalates, A Coetzee,
M E Brown, D J Eve and C A Strydom, **J. Thermal Analysis,** 41 (1994) 357-385.

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Sb_2O_3 and KNO_3 as oxidants, R A Rugunanan and M E Brown, **Combustion Science and
Technology,** 95 (1994) 85-99.

R54. Combustion of binary and ternary silicon/oxidant pyrotechnic systems. Part III
Ternary systems, R A Rugunanan and M E Brown, **Combustion Science and
Technology,** 95 (1994) 101-115.

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Kinetic aspects, R A Rugunanan and M E Brown, **Combustion Science and Technology,**
95 (1994) 117-138.

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on nucleation and growth, M E Brown, A K Galwey, M A Mohamed and H Tanaka,
Thermochim. Acta, 235 (1994) 255-270.

R57. Temperature calibration in thermogravimetry using energetic materials, M E Brown, T T Bhengu and D K Sanyal, **Thermochim. Acta**, 242 (1994) 141-152.

R58. Thermal decomposition of barium and strontium peroxides, M J Tribelhorn and M E Brown, **Thermochim. Acta**, 255 (1995) 143-154.

R59. Combustion of some iron-fuelled binary pyrotechnic systems, M J Tribelhorn and M E Brown, **Thermochim. Acta**, 256 (1995) 291-307.

R60. Combustion of some zinc-fuelled binary pyrotechnic systems, M J Tribelhorn and M E Brown, **Thermochim. Acta**, 256 (1995) 309-324.

R61. A theoretical justification for the application of the Arrhenius equation to kinetics of solid-state reactions (mainly ionic crystals) A K Galwey and M E Brown, **Proc. Roy. Soc. (London),** A 450 (1995) 501-512.

R62. Benzodiazepine analogues. Part 9. Kinetics and mechanism of the azidotrimethylsilane-mediated Schmidt reaction on flavanones. P.T. Kaye, M.J. Mphahlele and M.E. Brown, **J. Chem. Soc. Perkin Trans. 2,** (1995) 835-838.

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R66. Reduction of tungsten oxides with carbon monoxide, D.S. Venables and M.E. Brown, **Thermochim. Acta**, 291 (1997) 131-140.

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R75. Thermal and structural studies of amide complexes of transition metal(II) chlorides. II: Kinetics, A N Nelwamondo, D J Eve and M E Brown, **Thermochim. Acta**, 318 (1998) 177-186.

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   J. Thermal Analysis and Calorimetry, 56 (1999) 1317-1322.

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   Thermochim. Acta, 357-358 (2000) 133-140.

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   A K Galwey and M E Brown, **J. Thermal Analysis and Calorimetry,**
   60 (2000) 863-877.

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C6. Thermal decompositon of nickel(II) squarate, M E Brown, A K Galwey and M Le Patourel, **Thermal Analysis (Proceedings of the Sixth International Conference on Thermal Analysis, Bayreuth, Germany, July l980)** Vol. 2, (Birkhauser Verlag, Basel, l980) 153-158.

C7. Thermal decomposition of nickel squarate, A K Galwey and M E Brown, **Reactivity of Solids (Proceedings of the Ninth International Symposium on the Reactivity of Solids, Krakow, Poland, September l980)** 665-669.

C8. Form and function of nuclei in decompositions of solids, M E Brown, G G T Guarini, R Reed and A K Galwey, **Reactivity of Solids (Proceedings of the Ninth International Symposium on the Reactivity of Solids, Krakow, Poland, September l980),** 625-629.

C9. Kinetics of solid-state reactions from isothermal rate-time curves, M E Brown and A K Galwey, **Thermal Analysis (Proceedings of the Seventh International Conference on Thermal Analysis, Kingston, Ontario, Canada, August 1982**), (Wiley-Heyden, Chichester, 1982) Vol. 1, 58-64.

C10. Isothermal DSC study of the thermal decomposition of potassium permanganate, M E Brown, K C Sole and M W Beck, Proceedings of the 8th ICTA, Bratislava 1985, **Thermochim. Acta,** 92 (1985) 149-152.

C11. Thermochemistry and reaction kinetics of the antimony/potassium permanganate pyrotechnic systems, M W Beck and M E Brown, **Pyrotechnics, Proceedings of the 10th International Pyrotechnic Seminar,** Fraunhofer-Institut Fur Treib- und Explosivstoffe, 1985, paper 14.

C12. A thermo-analytical study of the pyrotechnic reactions of black powder and its constituents, M E Brown and R A Rugunanan, Proceedings of the 9th ICTA, Jerusalem, **Thermochim. Acta,** 134 (1988) 413-418.

C13. A thermal study of the manganese/barium peroxide pyrotechnic system, M E Brown and R. L Drennan, **Proceedings of the 14th International Pyrotechnic Seminar,** Jersey, (1989) 423-432.

C14. Report on the workshop: Thermal Analysis Education, ICTA 1988, E A Turi, B Wunderlich, M E Brown and T Ozawa, **Thermochim. Acta,** 148 (1989) 13-35.

C15. Report on the workshop on kinetics held at ICTA-9, J H Flynn, M E Brown, E Segal and J Sestak, **Thermochim. Acta,** 148 (1989) 45-47.

C16.   Use of thermomagnetometry in the study of iron-containing pyrotechnic systems, M E Brown, M J Tribelhorn and M G Blenkinsop, Proceedings of the 10th ICTA, Hatfield, UK, 1992, **J. Thermal Analysis,** 40 (1993) 1123-1130. (see R50).

C17. Fuel/oxidant relationships in some binary pyrotechnic systems, M E Brown, M W Beck, R L Drennan, R A Rugunanan, M J Tribelhorn and M G Blenkinsop, **Proceedings of the 4th International Symposium on Explosives Technology and Ballistics,** National Institute of Explosives Technology, Pretoria Technikon, (1992) 391-405.

C18. Comparison of iron and zinc as pyrotechnic fuels, M J Tribelhorn, D S Venables, M G Blenkinsop and M E Brown, **Proceedings of the 5th International Symposium on Explosives Technology and Ballistics,** National Institute of Explosives Technology, Pretoria Technikon, (1994) 180-190.

C19. Computer modelling of pyrotechnic combustion, S J Taylor and M E Brown, **Proceedings of the 5th International Symposium on Explosives Technology and Ballistics,** National Institute of Explosives Technology, Pretoria Technikon (1994) 167-179.

C20. A thermoanalytical study of some zinc-fuelled binary pyrotechnic systems, M J Tribelhorn and M E Brown, Proceedings of the 6th European Symposium on Thermal Analysis, Italy 1994, **Thermochim. Acta,** 269/270 (1995) 649-663.

C21.   Isothermal kinetic analysis of solid-state reactions using plots of rate against derivative function of the rate equation, A K Galwey and M E Brown, Proceedings of the 6th European Symposium on Thermal Analysis,, Italy 1994, **Thermochim. Acta,** 269/270 (1995) 1-25.

C22. Report on the ICTAC Kinetics Committee (August 1992 to September 1994), M.E. Brown, R.M. Flynn and J.H.Flynn, **Thermochim. Acta,** 256 (1995) 477-483.

C23. Kinetics of solid state reactions by thermal methods, M E Brown, **Proceedings of the 11th National Symposium of the Indian Thermal Analysis Society,** Jammu, India, 1998, 1-8.

RESEARCH PAPERS PUBLISHED IN PROCEEDINGS OF LOCAL CONFERENCES

LC1.   Electron microscopic evidence for solid decomposition mechanisms, M E Brown, R H M Cross, A K Galwey and R Reed, **Proc. Electron Microsc. Soc. South Afr.,** 11 (1981) 37-38.

LC2.   Electron microscopic study of intersolid pyrotechnic reactions, M W Beck, M E Brown and R H M Cross, **Proc. Electron Microsc. Soc. South Afr.,** 12 (1982) 95-96.

LC3. Correlation between surface changes of potassium permanganate crystals and theoretical speculation on their decomposition mechanism, M E Brown, R H M Cross, K C Sole and M W Beck, **Proc. Electron Microsc. Soc. South Afr.,** 14 (1984) 153-154.

LC4. Thermal analysis of pyrotechnic oxidants: barium and strontium peroxides, R L Drennan and M E Brown, **Proceedings of the 2nd National Symposium on Explosives and Ballistics,** Pretoria (1990) 101-105.

PAPERS ON EDUCATIONAL TOPICS

E1. Xtal-line. A board game in crystallography, A Allsobrook, M E Brown and L Glasser, **J. Chem. Educ.,** 50 (1973) 688-9.

E2. Non-isothermal kinetics, M E Brown and C A R Phillpotts, **J. Chem. Educ.,** 55 (1978) 556-560.

E3. Determination of purity by differential scanning calorimetry, M E Brown, **J. Chem. Educ.,** 56 (1979) 310-313.

E4. Diagrams to illustrate the meaning of the activation energy of reaction, M E Brown and A Goosen, **Spectrum**, 20 (2) (1982) 10-13.

E5. Thermodynamically and kinetically controlled products, M E Brown, K J Buchanan and A Goosen, **J. Chem. Educ.,** 62 (1985) 575-578.

ARTICLES OF A GENERAL NATURE

G1. The role of defects in the decomposition of solids, M E Brown, **CHEMSA**, 5 (1979) 74-5.

G2. Thermal Analysis - a group of often-neglected techniques, M E Brown, **CHEMSA**, 7 (1981) 192-195.

G3. 80 years of Chemistry at Rhodes, M E Brown, D J Eve and T M Letcher, **CHEMSA**, 9 (1983) 136-139.

G4. Pyrotechnic Delay Compositions, M W Beck, M E Brown and D Cawthorne, **CHEMSA**, 10 June (1984) 398-401.

G5. 100 Years of Chemistry at Rhodes University, M E Brown, D J Eve, P T Kaye, D E A Rivett and G M Watkins, **S. A. J. Science,** 100 (2004) 530 - 538.

INTRODUCTION TO MY RESEARCH

I have chosen the title for this thesis, "Reactions in the Solid State", for two reasons:

Firstly, it is broad enough to cover all of my areas of research, which have been:

- Effects of irradiation on solids (PhD topic)
- Silver refining (while at the Chamber of Mines)
- Kinetics of decomposition of solids (with Dr A.K. Galwey and various others)
- Techniques of thermal analysis
- Pyrotechnic delay systems (with support from AECI Explosives)
- Thermal and photostability of drugs (with Prof B.D. Glass)

and, secondly, it was the title of the very successful book co-authored by Drs Andrew Galwey, David Dollimore and me.

A large part of my research has been involved in the writing and editing of books, so these are covered in a separate commentary, while commentary on the more than 100 papers to which I have contributed forms the main part of this compilation. It is hoped that the electronic format will enable ready access of to all aspects of my research, including electronic versions of the original papers. The reader will need a copy of Adobe Acrobat Reader to access these.

COMMENTARY - BOOKS

I have always enjoyed scientific writing and editing. My first experience in book publishing was the preparation of a chapter, in collaboration with Andrew Galwey and the late David Dollimore, for Volume 22 of a series on Comprehensive Chemical Kinetics for Elsevier. The chapter grew into a whole volume and became a highly-cited reference work, in spite of administrative blunders by Elsevier.

B1. "Reactions in the Solid State", M E Brown, D Dollimore and A K Galwey, Comprehensive Chemical Kinetics, Vol. 22, Ed. C H Bamford and C F H Tipper, Elsevier, Amsterdam, 1980, 340 pp. ISBN 0-444-41807-5

This was translated into Russian by a leading solid-state chemist, V. Boldyrev, see Chem. Abstr., 100 (1984) 105806, and is still regularly cited.

Inspired by this experience and the critical success of the above book, I wrote an introductory textbook on Thermal Analysis based on courses given for the SA Chemical Institute and various technikons.

B2. "Introduction to Thermal Analysis: Techniques and Applications", M E Brown, Chapman & Hall Ltd., London, 1988. ISBN 0-412-30230-6

The second edition of this well-received textbook, which has been recommended internationally for short courses on the topic, was published by Kluwer, Netherlands, in 2001.

B2/2. "Introduction to Thermal Analysis: Techniques and Applications", M E Brown, Second Edition, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2001, 264pp. ISBN 1-4020-0211-4

In 1994 an ambitious plan for a four-volume Handbook of Thermal Analysis and Calorimetry was proposed by Elsevier Scientific Publishers, with Prof P.K. Gallagher as the series Editor. I was invited to edit Volume 1, Principles and Practice. This appeared in 1998.

B3. "Handbook of Thermal Analysis and Calorimetry, Volume 1, Principles and Practice", Elsevier Scientific, Amsterdam, 1998, 691pp. M E Brown, Editor and contributor of two chapters: A K Galwey and M E Brown, "Kinetic background to Thermal Analysis and Calorimetry" (77pp) and V Balek and M E Brown, "Less-common Techniques" (26pp).)
ISBN 0-444-82085-X

At the same time Dr Galwey and I were busy rewriting material for a totally new version of B1 above, entitled:

B4. "Thermal Decomposition of Ionic Solids", A K Galwey and M E Brown, Elsevier Scientific, Amsterdam, 1999, 597pp. ISBN 0-444-82437-5

This book has received extensive citation.

I was later requested by Elsevier and Professor Gallagher to assist in the editing of Volume 2 of the Handbook of Thermal Analysis and Calorimetry. This volume, which contains close

to 1000 pages, covers applications of thermal analysis and calorimetry in a variety of areas of (mainly) inorganic chemistry. I contributed a chapter on pyrotechnics. The volume was published in November 2003.

B5. "Handbook of Thermal Analysis and Calorimetry, Volume 2, Applications to Inorganic and Miscellaneous Materials", Elsevier Scientific, Amsterdam, 2003, 905pp. M.E. Brown and P.K. Gallagher (Eds), and contributor of chapter: E.L. Charsley, P.G. Laye and M.E. Brown, "Pyrotechnics" (30pp). ISBN 0-444-82086-8.

I have been approached very recently (September 2005) to edit an additional Volume 5 to update the series.

REVIEWS OF BOOKS

JCS FARADAY II Oct 1981, p1967.

Comprehensive Chemical Kinetics, Volume 22. Reactions in the Solid State. Ed. by C. H. BAMFORD and C. F. H. TIPPER. (Elsevier, Amsterdam, 1980). Pp. 340. Price $170.25, Dfl 220.

This valuable and certainly comprehensive bibliographical survey has been prepared by Drs. M. E. Brown, D. Dollimore and A. K. Galwey. Reference is made to work published as recently as 1978.

When considering the value of volumes of this kind it is difficult to assess the relative importance in the authors' minds of the need to mention everything *vis-a-vis* the provision of a critical guide to what in their considered opinion is really worth reading. Certainly a more enlightened guide to the literature than that provided by *Chemical Abstracts* is required by the student approaching this field for the first time, but it seems to me that the present volume does not really meet this need in a useful way for, among unassuming references to seminal works, there appear not dissimilar comments on papers which in truth are absolute rubbish. To serious students concerned with reliable kinetics many of the papers referred to in this volume are best left unremarked. Sometimes ignorance really is bliss.

Having issued that warning, though, the book does make interesting, even amusing, reading for an old pro. The work begins with an attempt at categorisation, which in passing indicates well those areas of other subjects required by the solid-state kineticist. This is followed by a rather superficial account of the experimental methods available. Here we are given brief accounts of who did what, but rarely why the technique was thought to be appropriate. Thus there are particularly weak accounts of electrical measurements and the effects of pre-irradiation, both of which when seriously applied can raise e.g.a. (evolved gas analysis) from a routine plod to an art.

The third chapter on the theory of the kinetics is much better. While the authors have little to record in the way of theoretical advances in topochemical analysis during the last fifteen years, they do provide sound accounts principally of Erofe'ev's contributions and also tackle the awkward questions of particle size distribution effects and diffusion control, which some earlier accounts neglected. For my part I would have liked to have seen more on non-random nucleation, but perhaps the authors thought that this was encompassed by shape factors.

Chap. 4 deals with the decomposition of solids. It pays due regard to the pioneering work of Garner on dehydration and there is an attractive section on the Smith-Topley Effect,

though perhaps the contributions of Frost are undervalued. Curiously, though, the azides are not well discussed. In part this stems from a recent decline of interest in the excitonic mechanism, but I suspect the difficulties really arise because of the variability of kinetic form shown by barium azide. Since similar difficulties with silver oxalate and mercury fulminate have been resolved, might one suggest a complete re-examination of barium azide using modern techniques? For the rest this chapter provides brief descriptions of the behaviour of practically every crystalline inorganic compound which on heating evolves a gas. Some organic salts, though not the styphnates, are included. The authors' value judgements are represented by the relative brevity of their descriptions.

In chap. 5 the authors face real difficulties of presentation. They are concerned to describe reaction between inorganic solids. This means essentially interdiffusion between phases in contact. Once such reactions have been illustrated there is little more to add, though a short section on the catalysis of solid decompositions is included.

All-in-all this is a book which contains nearly everything a newcomer to this field would need to know and rather more besides. Without doubt, the best parts of the book are the chapter on the theory and the introductory bits of the chapter on decomposition. There are nearly 1300 references.

D A YOUNG *Received 4th July,* 1980

Comprehensive Chemical Kinetics. **edited by C.H. Bamford and C.F.H. Tipper, Vol. 22.** *Reactions in the Solid State.* **by M.E. Brown, D. Dollimore and A.K. Galwey, Elsevier, Amsterdam, 1980,340 pp., Dfl. 240.00.**

The book is divided into 5 chapters with 1294 references and 22 figures. The chapters deal with (I) the characterization and classification of materials and processes, (2) methods of experimental study, such as EGA, microscopy, magnetic and electric measurements, etc., (3) the theory of solid state reaction kinetics, including the laws of nucleation and crystal growth, advancement of reaction interface controlled by diffusion or phase boundary reaction as well as the kinetic investigations using rising temperature techniques, (4) decomposition reactions of solids covering the actual reactions of hydrates, hydroxides, oxides, azides, carbonates, phosphates, sulphates and, last but not least, ammonium salts, and (5) reaction between inorganic solids.

Although there exist several books covering the subject of solid state reactions, the authors have selected topics which are of current interest, e.g. the practical means of studying solid state reactions, the applicability of the non-isothermal regime, the obedience of resulting kinetic data to theoretical kinetic equations, etc. The book is recommended not only to those specialized workers in heterogeneous kinetics, but also to the more general reader, including students in material science. This clearly written text will surely become the essential textbook for all thermoanalysts interested in reaction dynamics.

JAROSLAV SESTAK *(Prague, Czechoslovakia)*

Thermal Decomposition of Ionic Solids
Elsevier, Amsterdam, ISBN 0-444-82437-5, NLG 680.00

J. G. Dunn

This thoughtful book provides a timely summary of the more theoretical aspects of the decomposition of ionic solids, together with an extensive review of published information on the decomposition of specific compounds. Chapter 1 gives an introduction to the properties of solids. Chapters 2 – 6 deal with topics such as stoichiometry and extent of reaction, kinetic models for solid-state reactions, the influence of temperature on reaction rate, analysis and interpretation of experimental kinetic measurements, and methods for the characterisation of reactants, intermediates and products. Chapters 7-17 is a thorough survey of the published literature on the decomposition of compounds, collected together under headings such as hydrated salts, oxides, carbonates, etc. These chapters alone make the purchase of the book worthwhile, as an examination of the content will enable ready identification of areas for research. There is a final rounding off chapter in which the authors discuss the current status of the subject, and then speculate on prospects for future studies.

The authors are to be congratulated on bringing together information spread over a wide time period and from a range of journals and texts. The material is well presented and organised, and written in a lucid style. Above all, the topics are written with an authoritative ring, indicative of the experience and expertise of the two authors. Their comments are critical as well as informative, and would be of value to the novice as well as the more experienced person.

One of the very appealing features of the text is the emphasis on the totality of any such decomposition study. The complete investigation of the decomposition of a solid should involve thorough characterisation of the starting material, followed by determination of properties such as thermal stability and decomposition temperature, a kinetic analysis if an appropriate single stage reaction has been identified, and the assignment of a solid state reaction mechanism. The mechanism should be confirmed if possible by the application of appropriate techniques to investigate surfaces and internal structures of individual particles. This, of course, is a very time consuming process, but on the other hand it is likely to be the only way in which some common threads can be distinguished between the various processes and the factors that control them.

Although the main methods used to carry out decomposition reactions are thermal analysis techniques, there is no emphasis on the reproduction of TG or DTA curves. More emphasis is given to the diagrammatic representation of reaction schemes, and photomicrographs of reacted solids.

This is a very useful and valuable book which I recommend to anyone interested in the thermal decomposition of ionic solids.

COMMENTARY - RESEARCH PAPERS

My interest in solid-state chemistry began with my PhD studies with Professor Prout. In the 1960s, irradiation effects were of major interest and little was known of the response of inorganic materials to exposure to penetrating radiation such as gamma rays. The techniques of crystal-structure determination using X-ray diffraction were just becoming available at that time, in a very labour-intensive form, and I attempted to detect the structural damage done to single crystals of potassium permanganate by high-energy gamma-irradiation. The kinetics of thermal decomposition of potassium permanganate had been shown by Prout to be very sensitive to pre-irradiation of the sample. Although the effects of irradiation were evident in the X-ray diffraction photographs, the Fourier syntheses used to produce electron-density maps averaged behaviour over numerous unit cells and could not reveal individual defects. With only crude analogue computers available, a two-dimensional projection of a structure was all that was feasible and this still took many weeks of numerical calculation using devices such as Beever-Lipson strips. Some kinetic studies of the thermal decompositions of other pre-irradiated solids in comparison to the original samples were done by time-consuming, manual recording of the pressure of gas evolved in a vacuum system during decomposition at various set isothermal temperatures. Three papers resulted from my PhD studies:

R1. Thermal decomposition of irradiated nickel oxalate, E G Prout and M E Brown, AMERICAN SOCIETY FOR TESTING MATERIALS, Special Technical Publication, 359 (1964) 38-49.

R2. X-ray scattering by irradiated single crystals of potassium permanganate, E G Prout and M E Brown, NATURE, 203 (1964) 398-399.

R3. Thermal decomposition of irradiated calcium azide, E G Prout and M E Brown, NATURE, 205 (1965) 1314-1315.

On my return to Rhodes University as a Lecturer in 1967, I looked around for a different area of solid-state chemistry, to avoid overlap with the irradiation studies of Professor Prout, then at the University of Cape Town. I was fortunate to obtain support from the Council for Mineral Technology for a study of the thermal decomposition of ammonium metavandate, which formed an important stage in the processing of vanadium ores. My first PhD student, B.V. Stewart, tackled this project with rather limited equipment, but this was more than compensated for by having the extremely creative advice of Professor Glasser available. The decomposition turned out to be complex, involving several stages. One of the most interesting findings was the dramatic reversibility of the reaction between the decomposition products, solid vanadium pentoxide and gaseous ammonia and water vapour. A mechanism for the decomposition based on the crystal structures of the reactants, intermediates and solid products was proposed. Several papers resulted from this project.

R4. The thermal decomposition of ammonium metavandate, 1: The stoichiometry of the decomposition, M E Brown and B V Stewart, J. THERMAL ANALYSIS, 2 (1970) 287-299.

R9. The thermal decomposition of ammonium metavandate, II: The kinetics and mechanism of the decomposition, M E Brown, L Glasser and B V Stewart, J. THERMAL ANALYSIS, 6 (1974) 529-41.

R10. The thermal decomposition of ammonium metavandate, III : A structural view of the mechanism of the decomposition, M E Brown, L Glasser and B V Stewart, J. THERMAL ANALYSIS, 7 (1975) 125-137.

Papers on some aspects of this study were presented at my first international conferences:

C1. The thermal decomposition of ammonium metavandate-differential enthalpic analysis, M E Brown and B V Stewart, Thermal Analysis (Proceedings of the Third International Conference on Thermal Analysis, Davos, Switzerland, August l971) Ed. H G Wiedemann (Birkhauser Verlag, Basel, l972), Vol. 2, 313-320.

C3. The reversible nature of the thermal decomposition of ammonium metavandate, M E Brown, L Glasser and B V Stewart, PROGRESS IN VACUUM MICROBALANCE TECHNIQUES, VOL. 2, (Heyden & Son, l973) 125-137.

Being able to attend the series of conferences (ICTA and later ICTAC), together with the parallel series on Reactivity of Solids (see more below), was very important to the development of my research.

Another colleague, Dr N.H. Agnew, and I carried out a study of the solid-state polymerisation of vinylpyridine coordination compounds. Hot-stage microscopy with polarised light was used very successfully to follow the process and we managed to take a ciné film of the movement of the polymerisation front through the reactant crystals. Results are reported in:

R5. Solid-state polymerisation of vinylpyridine coordination compounds, N H Agnew and M E Brown, J. POLYM. SCI., A1, 9 (1971) 2561-2574.

R6. Solid-state reactions of vinylpyridine coordination complexes II, N H Agnew and M E Brown, J. POLYM. SCI., CHEMISTRY EDN., 12 (1974) 1493-1503.

My collaboration with Dr A.K. Galwey of the Queen's University began during my first sabbatical leave in 1971. I was developing an interest in the techniques of thermal analysis that were becoming commercially available at that time and was also able to learn some variations of the more traditional techniques (evolved gas pressure measurements) in use at Queen's. Most importantly I was able to learn about the techniques for replication of the surfaces of crystals, developed so successfully by Dr Galwey and his colleagues in the Electron Microscopy Unit at Queen's. These techniques, together with later developments in scanning electron microscopy, have enabled many mechanisms determined from kinetics results to be supported by visual observation.

The thermal decompositions of metal carboxylates had been of interest to Dr Galwey as a result of his earlier work on heterogeneous catalysis by metals. The mechanism of decomposition of a metal carboxylate was thought to resemble closely the mechanism of decomposition of the carboxylic acid on that particular metal. I had done some similar work in examining the effects of irradiation on the decomposition of nickel oxalate (see above). The metal formates, being the apparently simplest examples in the series of possible carboxylates, were of particular interest to both of us. Nickel formate was an obvious choice, because of the importance of nickel metal as a catalyst and the work already done on nickel oxalate. This study continued over quite a time span. Some our initial findings were presented in the paper:

C2. Nucleation and growth of particles of nickel during the thermal decomposition of nickel formate, A K Galwey, M J McGinn and M E Brown, REACTIVITY OF SOLIDS (Proceedings of the Seventh International Symposium on the Reactivity of Solids, Bristol, July l972) Ed. J S Anderson, M W Roberts and F S Stone (Chapman and Hall, l972), 431-445.

Discussion that arose from this paper, led to collaboration with Prof B. Delmon from Belgium and resulted in a further paper being presented at the next conference in the series, and two further papers:

C4. The nucleation process in the thermal decomposition of nickel formate, M E Brown, B Delmon, A K Galwey and M J McGinn, REACTIVITY OF SOLIDS, (Proceedings of the 8th International Symposium, Gothenburg, Sweden,) Ed. J Wood, O Linquist, C Helgesson and N-G Vennerberg, Plenum, New York, l977, 221-226.

R14. A differential scanning calorimetric study of the thermal decomposition of nickel formate dihydrate, A K Galwey and M E Brown, PROC. ROYAL IRISH ACAD, (DUBLIN), 77B (1977) 456-471.

R15. Nucleus formation and the kinetics of thermal decomposition of nickel formate, M E Brown, B Delmon, A K Galwey and M J McGinn, J. CHIM. PHYS., 75 (1978) 147-158.

An obvious extension of the work on nickel formate was to compare its with the behaviour of copper(II) formate. Our study showed that the metal formates were unexpectedly complex, existing in different crystalline modifications that behaved differently during decomposition. A feature of many of the decompositions of copper(II) carboxylates was found to be the formation of a volatile copper(I) intermediate.

R11. Thermal decomposition of three crystalline modifications of anhydrous copper(II) formate, A K Galwey, D M Jamieson and M E Brown, J. PHYS. CHEM., 78 (1974) 2664-2670.

An interesting study that started as a student's project was on the thermal decomposition of lead citrate. It was difficult to prepare reactant samples that behaved reproducibly, but the solid residue of the decomposition in vacuum turned out, as shown by electron microscopy, to be fine droplets of pyrophoric lead metal imbedded in a carbon matrix. Exposure of this product to air resulted in immediate combustion. Since publication of the paper below, I have received several enquiries suggesting some potential uses of this pyrophoric product:

 R7. Thermal decomposition of lead citrate, M E Brown, J. CHEM. SOC. FARADAY I, 69 (1973) 1202-1212.

Manganese(II) oxalate dihydrate was another metal carboxylate selected for study. Not only was the solid product of decomposition predicted to be an oxide rather than a metal, but the influence of the conditions applied during the preliminary dehydration stage on the subsequent decomposition were also of interest. The collaboration was widened to include Dr D. Dollimore, then at the University of Salford, who had published some work on this compound. During the course of the study, some thermal analysis equipment had been

acquired at Rhodes and thermochemical aspects of the decomposition could be studied using differential scanning calorimetry (DSC). The resulting publications were:

R8. Thermal decomposition of manganese(II) oxalate dihydrate in vacuum and in oxygen, M E Brown, D Dollimore and A K Galwey, J. CHEM. SOC. FARADAY I, 70 (1974) 1316-1324.

R13. The thermochemistry of the decomposition of manganese(II) oxalate dihydrate, M E Brown, D Dollimore and A K Galwey, THERMOCHIM. ACTA, 21 (1977) 103-110.

C5. A thermochemical investigation of the decomposition of manganese(II) oxalate dihydrate, M E Brown, D Dollimore and A K Galwey, PROC. FIRST EUR. SYMP. ON THERMAL ANALYSIS, Ed. D Dollimore (Heyden, London, l976) 248-251.

Some of this work was collated and compared in:

R12. The mechanisms of the solid-phase thermal decomposition reactions of some transition-metal carboxylates, A K Galwey, D M Jamieson, M E Brown and M J McGinn, REACTION KINETICS IN HETEROGENEOUS CHEMICAL SYSTEMS, ed. P Barrett, Elsevier, Amsterdam, l975, 520-537.

This theme of attempting to discern patterns of behaviour in the thermal decompositions of metal carboxylates has continued over the years. Obvious extensions from formates were to acetates and malonates.

R34. A kinetic and mechanistic study of the thermal decomposition of nickel acetate, A K Galwey, S G McKee, T R B Mitchell, M E Brown and A F Bean, REACTIVITY OF SOLIDS, 6 (1988) 173-186.

R35. A kinetic and mechanistic study of the thermal decomposition of nickel malonate, A K Galwey, S G McKee, T R B Mitchell, M A Mohamed, M E Brown and A F Bean, REACTIVITY OF SOLIDS, 6 (1988) 187-203.

Although not a conventional carboxylate, the thermal decompositions of several metal squarates were also studied. The squarate anion, $C_4O_4^{2-}$, like the oxalate anion, contains no hydrogen, thus decreasing the complexity of product gas mixtures. The nickel salt decomposed by a nucleation and growth process yielding very small (< 50 nm diameter) particles and the possibility exists that nickel carbonyl is an unstable intermediate. The copper(II) salt followed the pattern of other copper(II) carboxylates in decomposing via a copper(I) intermediate.

R21. Thermal decomposition of copper(II) squarate, M E Brown, A K Galwey and M W Beck, ISRAEL J. CHEM., 22 (1982) 215-218.

R22. Thermal decomposition of nickel squarate dihydrate, A K Galwey and M E Brown, J. CHEM. SOC. FARADAY I, 78 (1982) 411-424.

R31. A thermoanalytical study of the thermal decomposition of silver squarate, M E Brown, H Kelly, A K Galwey and M A Mohamed, THERMOCHIM. ACTA, 127 (1988) 139-158.

R32. Thermal decomposition of silver squarate, A K Galwey, M A Mohammed and M E Brown, J CHEM. SOC. FARADAY I, 84 (1988) 57-64.

R33. Thermal decomposition of copper(II) squarate, A K Galwey, M A Mohammed, S Rajam and M E Brown, J CHEM. SOC. FARADAY I, 84 (1988) 1349-1356.

C6. The thermal decompositon of nickel squarate (thermochemical aspects), M E Brown, A K Galwey and M Le Patourel, THERMAL ANALYSIS (Proceedings of the Sixth International Conference on Thermal Analysis, Bayreuth, Germany, July l980) Vol. 2, (Birkhauser Verlag, Basel, l980) 153-158.

C7. The thermal decomposition of nickel squarate (kinetics and electron microscopy), A K Galwey and M E Brown, REACTIVITY OF SOLIDS (Proceedings of the Ninth International Symposium on the Reactivity of Solids, Krakow, Poland, September l980) 665-669.

Some of the conclusions drawn regarding the thermal behaviour of metal carboxylates have been incorporated in the book B4.   Steps that have been proposed as determining the rates of decompositions of metal carboxylates include rupture of one of the three different types of bond (the C - C bond, the C - O bond or the M- O bond) in the carboxylate group, or electron transfer at a M - O bond. Once some solid product has been formed, catalytic processes can occur on its surface. In spite of intensive study, there has not yet appeared any generally accepted pattern explaining the observed differences of thermal reactivity, which seem to be very dependent upon the metal cation. Reactions are also complicated by complete or partial dehydration steps prior to decomposition of the anion.

MISCELLANEOUS DECOMPOSITIONS

R17. High temperature thermal properties of KH_2PO_4 : phase transitions and decompositions, M E Brown, L Glasser and J Larson, THERMOCHIM. ACTA, 30 (1979) 233-246.

The major finding of the work described in R17 was that the evolution of gaseous acids from this system is extremely destructive to thermal analysis equipment, particularly the alumina insulation of the Perkin-Elmer DSC sample cell!

With the state-of-the-art thermal analysis equipment available to us, we were able to examine the thermal behaviour of compounds of interest to other research groups and to assist with the interpretation of the results (R19 and R26).

R19. The thermal decomposition of bis(trispyrrolidino phosphine oxide) tetranitrato uranium(IV), M E Brown, C P J van Vuuren and A Litthauer, THERMOCHIM. ACTA, 49 (1981) 333-349.

R26. A study of the complexes of $[(eta^5-C_5H_5Fe(CO)_2]_2\{mu-(CH_2)_n\}$ (where n=3-12) by mass spectroscopy and differential scanning calorimetry, J R Moss, L G Scott, M E Brown and K J Hindson, J. ORGANOMETALLIC CHEM., 282 (1985) 255-266.

During sabbatical leave in the Cavendish Laboratory of Cambridge University, I studied the thermal behaviour of the silver(I) and mercury(II) salts of 5- nitrotetrazole and of mercury(II) fulminate. These compounds had been suggested as alternative primary explosives to replace lead azide in detonators. The decompositions of all three compounds are strongly exothermic and the nitrotetrazole salts evolve up to 25% more heat per unit mass than mercury fulminate or lead azide. Although the quantities involved are small, the silver salt produces less environmentally hazardous products. We also did some unpublished studies of the detonation of these compounds using the high-speed photographic techniques available (including cameras originally built to photograph explosions of nuclear bombs!). The changes on detonation were, however, so rapid that the techniques could not provide adequate resolution.

R20. The thermal decomposition of the silver(I) and mercury(II) salts of 5- nitrotetrazole and of mercury(II) fulminate, M E Brown and G M Swallowe, THERMOCHIM. ACTA, 49 (1981) 247-258.

Some of the reactants that have been used in decomposition studies have received so much attention that they have achieved almost "model" status. Examples are calcium carbonate, calcium oxalate dihydrate, copper sulfate pentahydrate, ammonium perchlorate (an important propellant) and potassium permanganate (possibly because of its role as a portable source of gaseous oxygen in many school laboratories?). My PhD studies (see above) involved some studies of the effects of gamma-irradiation on the thermal stability of potassium permanganate and when new techniques, such as differential scanning calorimetry (DSC) and scanning electron microscopy (SEM), became available, it was of interest to see what additional information these techniques could provide.

R25. Isothermal DSC study of the thermal decomposition of potassium permanganate, M E Brown, K C Sole and M W Beck, THERMOCHIM. ACTA, 89 (1985) 27-37.

C10. Isothermal DSC study of the thermal decomposition of potassium permanganate, M E Brown, K C Sole and M W Beck, Proceedings of the 8th ICTA, Bratislava 1985, THERMOCHIM. ACTA, 92 (1985) 149-152.

R56. A mechanism for the thermal decomposition of potassium permanganate crystals based on nucleation and growth, M E Brown, A K Galwey, M A Mohamed and H Tanaka, THERMOCHIM. ACTA, 235 (1994) 255-270.

In spite of its "model" status, the decomposition of potassium permanganate remains an example of considerable complexity, coupled with high sensitivity to pre-treatment of the sample. Microscopic studies gave no evidence that decomposition results in extensive breakup of the crystals. The breakdown of the permanganate ion does not appear to be influenced by the nature of the cation, or by the crystal structure, but to occur in a disorganized layer by an electron transfer mechanism.

Under the auspices of the International Confederation for Thermal Analysis and Calorimetry (ICTAC), a cooperative project was organized in an attempt to identify a reaction that could be used as a *kinetics* standard. The reaction suggested was the thermal dehydration of lithium sulphate monohydrate. We did both isothermal and programmed temperature measurements of the rate of dehydration. Participants in the project demonstrated conclusively that the dehydration was NOT suitable as a kinetic standard because of the ready reversibility of the process under small changes of conditions.

R42. Reliability of kinetic measurements for the thermal dehydration of lithium sulphate monohydrate I. Isothermal measurements of pressure of evolved water vapour, M E Brown, A K Galwey and A Li Wan Po, THERMOCHIM. ACTA, 203 (1992) 221-240.

R48. Reliability of kinetic measurements for the thermal dehydration of lithium sulphate monohydrate. Part 2. Thermogravimetry and differential scanning calorimetry, M E Brown, A K Galwey and A Li Wan Po, THERMOCHIM. ACTA, 220 (1993) 131-150.

Professor D.J. Eve of the Rhodes Chemistry Department had considerable previous experience of the preparation and characterization of complex metal oxalates and we carried out several studies of such compounds for comparison with the information available on the simpler metal oxalates. Decompositions of the mixed oxalates, $MCu(ox)_2.xH_2O$, were all complex reactions and that of M = Fe was the most complex. The order of decreasing stability, as indicated by the temperature ranges giving comparable decomposition rates, was $NiCu(ox)_2 > CoCu(ox)_2 > FeCu(ox)_2$, which also corresponded to the order of increasing covalency as shown by X-ray photoelectron spectroscopy.

R49. Thermal analysis of some mixed metal oxalates, A Coetzee, D J Eve and M E Brown, J. THERMAL ANALYSIS, 39 (1993) 947-973.

R51. Kinetics of thermal decomposition of some mixed metal oxalates, A Coetzee, M E Brown, D J Eve and C A Strydom, J. THERMAL ANALYSIS, 41 (1994) 357-385.

R69. The thermal dehydration and decomposition of $Ba[Cu(C_2O_4)_2(H_2O)].5H_2O$, J Bacsa, D J Eve and M E Brown, J. THERMAL ANALYSIS, 50 (1997) 33-50.

A detailed study of the thermal behaviour of amide complexes of transition metal(II) chlorides was carried out by Mr Nelwamondo, Lecturer at the University of Fort Hare, under the supervision of Professor Eve and myself. Attempts were made to correlate structural, kinetic and thermochemical parameters. The activation energy for ligand decomposition appeared to increase with the basicity of the amide ligand.

R74. Thermal and structural studies of amide complexes of transition metal(II) chlorides. I: Stoichiometry, A N Nelwamondo, D J Eve, G M Watkins and M E Brown, THERMOCHIMICA ACTA, 318 (1998) 165-175 .

R75. Thermal and structural studies of amide complexes of transition metal(II) chlorides. II: Kinetics, A N Nelwamondo, D J Eve and M E Brown, THERMOCHIMICA ACTA, 318 (1998) 177-186.

SOLID-GAS REACTIONS

My first venture into solid-gas reactions was sponsored by the Council of Mineral Technology. The oxidation of chromium(III) chloride is an important stage in the preparation of chrome pigments. A feature of this study was the microscopic evidence obtained in support of the contracting-geometry kinetic model proposed.

R39. Oxidation kinetics of chromium(III) chloride, K C Sole, M B Mooiman and M E Brown, J. CHEM. SOC. FARADAY TRANS., 86 (1990) 525-530.

During the industrial manufacture of tungsten carbide, tungsten powder is carburised with either methane or carbon in the presence of hydrogen gas. Growth of tungsten particles occurs during reduction in hydrogen, by a mechanism involving the water vapour formed, and this decreases the value of the resulting product. Funding was received to examine the various ways of reducing tungsten oxides. The tungsten oxides were heated in a tube furnace under carefully controlled atmospheres and the evolved gases were analysed using dedicated infrared gas detectors. Under the conditions investigated, the reactions were controlled by mass transfer. The final product of the reductions with hydrogen and with hydrogen plus carbon was tungsten. The addition of carbon increased the rate of reduction but did not affect the phases formed. CO_2 was evolved at the start and CO mainly at the end of the process. The following papers resulted:

R63. Reduction of tungsten oxides with carbon Part 1: Thermal analyses, D S Venables and M E Brown, THERMOCHIM. ACTA, 282/283 (1996) 251-264.

R64. Reduction of tungsten oxides with carbon Part 2: Tube furnace experiments, D S Venables and M E Brown, THERMOCHIM. ACTA, 282/283 (1996) 265-276.

R65. Reduction of tungsten oxides with hydrogen and with hydrogen and carbon, D S Venables and M E Brown, THERMOCHIM. ACTA, 285 (1996) 361-382.

R66. Reduction of tungsten oxides with carbon monoxide, D S Venables and M E Brown, THERMOCHIM. ACTA, 291 (1997) 131-140.

MODELLING

A very interesting suggestion was made by a colleague, the late Dr R.B. English, that a possible mechanism for the decompositions of some solids could involve the change of structure from crystalline reactant to an eventually crystalline solid product along a pathway determined by the symmetry groups of the reactant and product. This pathway was assumed to involve the minimum possible changes in symmetry, while allowing for removal of any gaseous product at an appropriate stage. The energetics of the process were estimated from the consequent changes in lattice energy. This approach gave encouraging agreement with reported activation energies. These studies would not have been possible without the expertise that Prof L. Glasser had built up in the calculation of lattice energies.

R76. Modelling the thermal decomposition of solids on the basis of lattice energy changes. Part I: Alkaline-earth carbonates, A de La Croix, R B English, M E Brown and L Glasser, J. SOLID STATE CHEM., 137 (1998) 332-345.

R77. Modelling the thermal decomposition of solids on the basis of lattice energy changes. Part II: Alkaline-earth peroxides, A de La Croix, R B English, M E Brown and L Glasser, J. SOLID STATE CHEM., 137 (1998) 346-352.

KINETICS AND MECHANISMS

This has been an area of major interest. Several contributions have been made to the methods of numerical data-fitting:

R16. The distinguishability of selected kinetic models for isothermal solid-state reactions, M E Brown and A K Galwey, THERMOCHIM. ACTA, 29 (1979) 129-146.

C 9. Kinetics of solid-state reactions from isothermal rate-time curves, M E Brown and A K Galwey, THERMAL ANALYSIS (Proceedings of the Seventh International Conference on Thermal Analysis, Kingston, Ontario, Canada, August 1982) Vol. 1 (Wiley-Heyden, Chichester, 1982) Vol. 1, 58-64.

R36. Arrhenius parameters for solid-state reactions from isothermal rate-time curves, M E Brown and A K Galwey, ANALYTICAL CHEMISTRY, 61 (1989) 1136-1139.

C21.   Isothermal kinetic analysis of solid-state reactions using plots of rate against derivative function of the rate equation, A K Galwey and M E Brown, Proceedings of the 6th European Symposium on Thermal Analysis, Italy 1994, THERMOCHIM. ACTA, 269/270 (1995) 1-25.

C23. Kinetics of solid state reactions by thermal methods, M E Brown, Proceedings of the 11th National Symposium of the Indian Thermal Analysis Society, Jammu, India, 1998, 1-8.

In deriving reaction mechanisms it is essential to attempt to support kinetic results by complementary techniques, such as optical and electron microscopy:

LC1. Electron microscopic evidence for solid decomposition mechanisms, M E Brown, R H M Cross, A K Galwey and R Reed, PROC. ELECTRON MICROSC. SOC. SOUTH AFR., 11 (1981) 37-38.

C 8. Form and function of nuclei in decompositions of solids, M E Brown, G G T Guarini, R Reed and A K Galwey, REACTIVITY OF SOLIDS (Proceedings of the Ninth International Symposium on the Reactivity of Solids, Krakow, Poland, September l980) 625-629.

LC3. Correlation between surface changes of potassium permanganate crystals and theoretical speculation on their decomposition mechanism, M E Brown, R H M Cross, K C Sole and M W Beck, PROC. ELECTRON MICROSC. SOC. SOUTH AFR., 14 (1984) 153-154.

R68. Structures and functions of reaction interfaces developed during solid state dehydrations, M E Brown, A K Galwey and G G T Guarini, J. THERMAL ANALYSIS, 49 (1997) 1135-1146.

An additional "hardy perennial" is the question of the applicability of the Arrhenius equation and its accompanying Transition-State Theory to solid-state reactions. Some critics have gone as far as to label it the "erroneous equation". From the point-of-view of numerical methods, it has been shown that no alternative relationship suggested so far has any distinct advantage. In the two papers below, Dr Galwey and I developed a model based on the Band

Theory of solids that could explain the observed temperature dependence of the reaction rate. Although the Maxwell-Boltzmann energy distribution function that provides the starting point for a theoretical explanation of Arrhenius behaviour in homogeneous reactions is inapplicable to the immobilized constituents of a solid, the energy distribution functions for both electronic energy (Fermi-Dirac statistics) and phonon energy (Bose-Einstein statistics) approximate (for values significantly above the Fermi level) to the same form as that in the Maxwell-Boltzmann distribution and hence are capable of explaining the fit of k - T data to an Arrhenius-type equation. Interface levels, capable of accommodating electrons, (analogous to impurity levels in semiconductors, imperfection levels in crystals, etc.) are proposed to be present within the interfacial zone wherein chemical changes occur. These energy levels can be located within the forbidden range between the energy bands of the crystal. The actual energies of these levels will be sensitive to the particular species involved and energies distributed within a limited range are more likely than uniform energies. Such levels could be involved in the crucial bond redistribution steps and account for the increased reactivity at the reactant/product interface relative to more perfect crystalline regions. The occupancy of these levels is governed by distribution functions similar in form to that of the Maxwell-Boltzmann equation. The band model of solids may thus be extended to accommodate the bond redistributions during conversion of reactant to product.

R61. A theoretical justification for the application of the Arrhenius equation to the kinetics of solid state reactions (mainly ionic crystals),   A K Galwey and M E Brown, PROC. ROY. SOC. (LONDON), A 450 (1995) 501-512.

R87. Application of the Arrhenius equation to solid state kinetics: can this be justified?
A K Galwey and M E Brown, THERMOCHIM. ACTA, 386 (2002) 91-98.

Because of Professor Prout's association with Rhodes and Professor Tompkins's South African connections, as well as the importance of this mechanism of solid-state reactions, I carried out a literature survey of the way in which the Prout-Tompkins rate equation had been applied in solid-state kinetics. One of the unexpected findings was that the equation had been particularly popular in describing the kinetics of decomposition of drugs. This aspect was covered in a further paper. The curves of fractional decomposition against time predicted by the Prout-Tompkins model are very similar to those that can be predicted from a totally different model of decomposition accompanied by melting of the reactant (the Bawn model). This aspect was discussed in a further paper.

R71. The Prout-Tompkins rate equation in solid-state kinetics, M E Brown,
THERMOCHIMICA ACTA, 300 (1997) 93-106.

R78. Pharmaceutical applications of the Prout-Tompkins rate equation,
M E Brown and B D Glass, INT. J. PHARM., 190 (1999) 129-137.

R85. Decomposition of solids accompanied by melting - Bawn Kinetics,
M E Brown and B D Glass, INT. J. PHARM., 254 (2003) 255-261.

The whole field of kinetic analysis of programmed-temperature experiments continues to be controversial. I attempted to review some of the major aspects in a plenary lecture given in Philadelphia on the occasion of receiving the Mettler/NATAS Award: This paper has been frequently cited.

R67. Steps in a minefield - some kinetic aspects of thermal analysis, M E Brown,
J. THERMAL ANALYSIS, 49 (1997) 17-32.

At each ICTAC Congress there have been Workshops on Kinetics and I have been actively involved in these:

R29. Report on the workshop: Current problems of kinetic data reliability evaluated by thermal analysis, J H Flynn, M E Brown and J Sestak, THERMOCHIM. ACTA,
110 (1987) 101-112.

R30. Quantitative thermoanalytical studies of the kinetics and mechanisms of the thermal decompositions of inorganic solids, M E Brown, THERMOCHIM. ACTA,
110 (1987) 153-158.

C15. Report on the workshop on kinetics held at ICTA-9, J H Flynn, M E Brown,
E Segal and J Sestak, THERMOCHIM. ACTA, 148 (1989) 45-47.

C22. Report on the ICTAC Kinetics Committee (August 1992 to September 1994).
M E Brown, R M Flynn and J H Flynn, THERMOCHIM. ACTA, 256 (1995) 477-483.

C24. The theory and practice of thermoanalytical kinetics of solid-state reactions, H Tanaka and M E Brown, J. THERMAL ANALYSIS AND CALORIMETRY, 80 (2005) 795-797.

Arising from the Workshop held in Philadelphia in 1996, I initiated a project in which several common sets of numerical data (both isothermal and programmed temperature) were supplied to participants, who were invited to apply methods of kinetic analysis of their choice to extracting kinetic parameters. Two of the sets were simulated data from equally-weighted concurrent first-order reactions with known Arrhenius parameters, so that the reported parameters could be compared with the known values. Response to the Project was enthusiastic and the results were published:

R83. Computational aspects of kinetic analysis Part A: The ICTAC kinetics project - data, methods and results, M E Brown, M Maciejewski, S Vyazovkin, R Nomen and J Sempere, A Burnham, J Opfermann, R Strey, H L Anderson and A Kemmler, R Keuleers, J Janssens and H O Desseyn, Chao-Rui Li and Tong B Tang, B Roduit, J Malek and T Mitsuhashi, THERMOCHIM. ACTA, 355 (2000) 125-143.

This paper included several recommendations for tackling kinetic analyses. The major recommendations were that attempts should NOT be made to "guess" a set of unique parameters (kinetic triplet) from a single programmed-temperature experiment, and that isoconversional methods should be applied. The paper was followed by several other papers giving fuller discussions of various important aspects of kinetic analysis by some of the participants.

In an attempt to emphasize the importance of the complete kinetic triplet and to decrease the quoting of values of the activation energy in isolation, as well as to counter some poor choices of nomenclature, we published a paper:

R89. "Model-free" kinetic analysis? J D Sewry and M E Brown, THERMOCHIM. ACTA,
390 (2002) 217-225.

Two rather pessimistic views of progress in the field of solid-state reactions are given in:

R81. Kinetic aspects of the thermal stability of ionic solids, M E Brown and R E Brown, THERMOCHIM. ACTA, 357-358 (2000) 133-140.

R82. Solid-state decompositions : stagnation or progress?, A K Galwey and M E Brown, J. THERMAL ANALYSIS AND CALORIMETRY, 60 (2000) 863-877.

R81 is of special significance to me as the ideas and mathematical aspects were developed by my son, Richard Brown, as an aeronautical engineer. The paper uses mapping theory to discuss the difficulties of predicting the thermal stability of an untested ionic solid from the information accumulated on similar compounds. The conclusion was that such predictions are likely to be inaccurate and hence of little value.

R82 laments the lack of appearance of any theoretical basis, or identification of useful principles, for classifying the decompositions of solids. A major shortcoming is the lack of recent development or application of new experimental techniques which can give more direct chemical information about the processes occurring within the relatively inaccessible reaction zone, possibly of molecular dimensions. The most promising, but not generally available, technique has been diffraction studies using synchrotron radiation. Such studies have been able to show that reaction and recrystallization of any solid product are not necessarily completed within the same advancing zones and may not always occur concurrently. Changes which may occur behind the reaction front include secondary reactions between primary products and retexturing of the residual solid. Even apparently straightforward processes such as dehydrations are still incompletely understood.

In an invited lecture at the NATAS meeting in Albuquerque in 2003, I attempted to identify some recommendations for the publication of kinetics papers. These were that: (1) No papers with kinetic analyses based on experiments done at a single heating-rate should be accepted for publication; (2) The same restriction on publication should apply to kinetic studies on fundamentally irreproducible materials such as sewage sludge; (3) Values of E should not be reported and interpreted in isolation from the other members of the kinetic triplet and realistic uncertainties in the calculated values should be reported.; (4) Each reaction step in a complex process must be clearly defined so that alpha is also properly defined; (5) "Mechanism" should be reserved for physico-chemical steps and be clearly distinguished from "kinetic models", "rate equations" or "conversion functions"; (6) The final test of every kinetic analysis should be to use the parameters determined to construct calculated curves for comparison with the experimental results over a wide and representative range.

R98. Stocktaking in the Kinetics Cupboard, M E Brown, J. THERMAL ANALYSIS AND CALORIMETRY, 2005 in press.

Another very controversial aspect of solid-state kinetics is the so-called "compensation effect". I have been involved in some aspects of this debate that revolves around whether such effects are meaningful or are mathematical artefacts. I tend to support the latter view.

R18. Compensation parameters in heterogeneous catalysis, A K Galwey and M E Brown, J. CATAL., 60 (1979) 335-338.

R70. Arrhenius parameters and compensation behaviour in solid state decompositions, A K Galwey and M E Brown, THERMOCHIM. ACTA, 300 (1997) 107-115.

R88. The significance of "compensation effects" appearing in data published in "computational aspects of kinetic analysis": ICTAC project, 2000, M E Brown and A K Galwey, THERMOCHIM. ACTA, 387 (2002) 171-183.

Most of my work on kinetics has been restricted to solid-state reactions. An exception was a collaboration with Professor P.T. Kaye's organic chemistry group in examining a complex homogeneous reaction system:

R62. Benzodiazepine analogues. Part 9. Kinetics and mechanism of the azidotrimethylsilane-mediated Schmidt reaction on flavanones. P T Kaye, M J Mphahlele and M E Brown, J. CHEM.SOC.PERKIN TRANS.2, (1995) 835-838.

PYROTECHNICS

As a result of substantial funding for equipment and support of students from AECI Explosives Ltd, a large part of my research has been concerned with industrial applications of pyrotechnic reactions, particularly those used as delays in the detonators used to initiate rock-breaking in the gold mining industry. These combustion-type reactions involve mixtures of initially solid fuels and solid oxidants (together with several additives to improve their physical properties). Once initiated, however, the rate of the exothermic reaction can be extremely rapid and molten and gaseous intermediates are formed. Conventional thermoanalytical techniques, such as differential scanning calorimetry and thermogravimetry, are only marginally useful in the study of these rapid, violently exothermic processes and we received much help and guidance, from the group at the University of Leeds under the direction of Dr P.G. Laye, in setting up appropriate techniques and methods of analysis of the data produced. The main technique involved measurement of temperature-time profiles as the combustion front passed a thermocouple imbedded in a column of the pyrotechnic composition. We began our studies with a detailed examination of the antimony/potassium permanganate pyrotechnic compositions that were commonly used in the longer-period delay fuses. (Silicon/red lead compositions were the most common short-period delay compositions.) Our first papers in this new field of research were:

R23. Thermal analysis of antimony/potassium permanganate pyrotechnic compositions, M W Beck and M E Brown, THERMOCHIM. ACTA, 65 (1983) 197-212.

R27. Burning of antimony/potassium permanganate pyrotechnic compositions in closed systems, M W Beck and M E Brown, COMBUSTION AND FLAME, 65 (1986) 263-271.

R28. Modification of the burning rates of antimony/potassium permanganate pyrotechnic compositions, M W Beck and M E Brown, COMBUSTION AND FLAME, 66 (1986) 67-75.

C11. Thermochemistry and reaction kinetics of the antimony/potassium permanganate pyrotechnic systems, M W Beck and M E Brown, PYROTECHNICS, Proceedings of the 10th International Pyrotechnic Seminar, Fraunhofer-Institut Fur Treib- und Explosivstoffe, 1985, paper 14.

The rates of pyrotechnic reactions should probably be classified as being totally "sample controlled". Unlike other thermal analysis studies, the rate cannot be controlled by the temperature programme. The temperature profiles thus contain all the kinetic information available and use was made of the rigorous methods of extraction of kinetic parameters developed by Drs Boddington and Laye of Leeds University. For a complete analysis it was necessary to have a means of measuring the thermal conductivity (or thermal diffusivity) of the pyrotechnic compositions. We modified a probe method that had been used for measuring the thermal conductivity of soil samples and, at the same time, were able to improve the numerical analysis of the results obtained, with the help of a colleague in the Department of Mathematics, Prof N.J. Heideman:

R24. Application of a probe technique for measuring the thermal conductivity of pyrotechnic compositions, M W Beck, M E Brown and N J H Heideman,
J. PHYS. E, SCIENTIFIC INSTRUMENTS, 17 (1984) 793-799.

It was also of interest to see what visual information could be obtained through microscopic examination of the reactants and combustion residue:

LC2. Electron microscopic study of intersolid pyrotechnic reactions, M W Beck,
M E Brown and R H M Cross, PROC. ELECTRON MICROSC. SOC. SOUTH AFR., 12 (1982) 95-96.

Although we generally restricted our compositions to binary mixtures of a single fuel and a single oxidant, without any of the practical small-scale additives such as binders, the choice of systems to consider was still huge. One of the questions that we were trying to answer was whether the fuel and the oxidant interacted in the solid state, or whether the oxidant decomposed and the fuel was involved in a solid-gas reaction with the gaseous product of oxidant decomposition. We thus sought an "ideal" binary pyrotechnic system, which we specified as one in which both the decomposition of the oxidant and oxidation of the fuel should occur with simple stoichiometries. On these criteria, the antimony/potassium permanganate system was particularly *unsuitable*, in spite of its industrial importance.

Our survey suggested that the alkaline-earth metal peroxides might be suitable and we did a preliminary study of their thermal behaviour:

LC4. Thermal analysis of pyrotechnic oxidants: barium and strontium peroxides,
R L Drennan and M E Brown, PROC. 2nd NATIONAL SYMPOSIUM ON EXPLOSIVES AND BALLISTICS, Pretoria (1990) 101-105.

R58. Thermal decomposition of barium and strontium peroxides, M J Tribelhorn and
M E Brown, THERMOCHIM. ACTA, 255 (1995) 143-154.

Having selected an oxidant, one is faced with finding suitable fuels to make up binary compositions that would actually sustain combustion and which would give maximum combustion temperatures below the melting points of the thermocouples available. Of many such combinations tested unsuccessfully, we opted for a comparison of the behaviour of manganese and molybdenum as fuels, initially in binary combinations with the peroxides, above, as oxidants, and later as ternary systems with either mixed fuels or mixed oxidants:

C13. A thermal study of the manganese/barium peroxide pyrotechnic system,
M E Brown and R L Drennan, PROC. 14th INTERNATIONAL PYROTECHNIC
SEMINAR, Jersey, (1989) 423-432.

R45. Binary and ternary pyrotechnic systems of Mn and/or Mo and BaO_2 and/or SrO_2.
Part I: Thermal analysis, R L Drennan and M E Brown, THERMOCHIM. ACTA,
208 (1992) 201-221.

R46. Binary and ternary pyrotechnic systems of Mn and/or Mo and BaO_2 and/or SrO_2.
Part II: Combustion studies, R L Drennan and M E Brown, THERMOCHIM. ACTA,
208 (1992) 223-246.

R47. Binary and ternary pyrotechnic systems of Mn and/or Mo and BaO_2 and/or SrO_2.
Part III: Kinetic aspects, R L Drennan and M E Brown, THERMOCHIM. ACTA,
208 (1992) 247-259.

The choice of fuel has also to be modified by practical considerations such as cost and toxicity. To meet both of these requirements and the criterion of simple stoichiometry of the oxide, we chose zinc metal as a potential fuel:

C20.   A thermoanalytical study of some zinc-fuelled binary pyrotechnic systems,
M J Tribelhorn and M E Brown, PROC. 6TH EUROPEAN SYMPOSIUM ON
THERMAL ANALYSIS, Italy 1994, THERMOCHIM. ACTA,
269/270 (1995) 649-663.

R60. Combustion of some zinc-fuelled binary pyrotechnic systems, M J Tribelhorn
and M E Brown, THERMOCHIM. ACTA, 256 (1995) 309-324.

Results were not particularly encouraging and we abandoned the stoichiometry criterion in favour of using a cheap, readily available fuel, namely iron powder:

C18. Comparison of iron and zinc as pyrotechnic fuels, M J Tribelhorn, D S Venables,
M G Blenkinsop and M E Brown, PROC. 5th INTERNATIONAL SYMPOSIUM ON
EXPLOSIVES TECHNOLOGY AND BALLISTICS, National Institute of Explosives
Technology, Pretoria Technikon, (1994) 180-190.

R59. Combustion of some iron-fuelled binary pyrotechnic systems, M J Tribelhorn
and M E Brown, THERMOCHIM. ACTA, 256 (1995) 291-307.

In an attempt to increase the information obtained, we used thermomagnetometry (TM) as an additional technique.   TG curves for all three Fe/oxidant systems, iron/potassium permanganate, iron/barium peroxide, and iron/strontium peroxide, heated in powder form in nitrogen at 20 K min^{-1} showed superimposition of the oxidation of Fe on the decompositions of the oxidants. DTA traces showed strongly exothermic processes corresponding to ignition. The TM traces showed the same features as that of Fe in air, suggesting that reaction under these conditions is solid-gas with little or no interaction between Fe and the solid oxidants. In some mixtures the presence of unreacted Fe was apparent from the Curie transition at 780°C. Fe/oxidant pellets behaved differently from loose powders, but there was no conclusive evidence for solid-solid reaction mechanisms. Most of the observations could be explained by trapping of the gaseous products of oxidant decomposition within the pellets.

C16. Use of thermomagnetometry in the study of iron-containing pyrotechnic systems,
M E Brown, M J Tribelhorn and M G Blenkinsop, PROC. 10th ICTA, Hatfield, UK, 1992,
J. THERMAL ANALYSIS, 40 (1993) 1123-1130.

Another student began a parallel study using silicon powder as the (non-metallic) fuel in binary combinations with a variety of oxidants (excluding the well studied and very rapid burning silicon/red lead system). The main question in the field of pyrotechnic combustion, for which an answer is still being sought, is what factor is mainly responsible for determining the linear burning rate of an initially solid fuel/oxidant mixture? The major objective of this study was to obtain information on the role of different oxidants in reaction with a single, common fuel, silicon, which meets the criterion of a relatively simple oxidation stoichiometry. The maximum burning rate for the Si/oxidant sysyems studied followed the trend $KNO_3 > SnO_2 > Sb_2O_3 > Fe_2O_3$. The same trend was observed for the maximum temperatures recorded during combustion. The activation energies for combustion were in the reverse order with no value available for Si/KNO_3. The maximum temperatures approach, but still remain below the melting points of Si and the oxidants, which suggests that burning in both systems must occur either through solid-solid reactions, or that the products may form some lower melting eutectics. The Si/O_2 (g) reaction is known to be hindered by the formation of a protective layer of SiO_2 product. At one extreme, the oxidant could influence the reaction by its role, through thermal decomposition, in supplying oxygen (gas) for oxidation of the fuel. At the other extreme, simultaneous diffusion of two or more species through a developing layer of solid product may occur and the sizes and charges of the diffusing species may be important, as well as the maintenance of contact at the origins of the diffusion paths. Melting and/or vaporization of the oxidant will be important in the maintenance of such contact. In contrast to the thermal stability of Fe_2O_3 and SnO_2, KNO_3 melts at relatively low temperatures and also decomposes. Contact between fuel and molten oxidant will be good and Si/KNO_3 mixtures burn over a wide range of compositions. Mobility of Sb_2O_3 is expected to be relatively high through sublimation, but the range of burning rates in the Si/Sb_2O_3 system lies between that for the Si/Fe_2O_3 system and that for the Si/SnO_2 system, which could indicate that adsorption of unchanged Sb_2O_3 on Si surfaces precedes oxidation of Si. From the above discussion, it may be concluded that fuel/oxidant interactions may fit into one of several patterns lying between the extremes of solid-solid reactions involving diffusion of species derived from the fuel into the structure of the oxidant, and oxidation of the fuel by gaseous products of oxidant decomposition. Detailed knowledge is needed of the thermal behaviour of the fuel in oxygen and of the structural and thermal characteristics of possible oxidation products, as well as of the thermal stability of the oxidant and any likely decomposition products. The participation of liquid and/or gaseous phases may be difficult to detect, but is of great practical importance.

R43. Reactions of powdered silicon with some pyrotechnic oxidants, R A Rugunanan and
M E Brown, J. THERMAL ANALYSIS, 37 (1991) 1193-1211.

R52. Combustion of binary and ternary silicon/oxidant pyrotechnic systems.
Part I Fe_2O_3 and SnO_2 as oxidants, R A Rugunanan and M E Brown, COMBUSTION
SCIENCE AND TECHNOLOGY, 95 (1994) 61-83.

R53. Combustion of binary and ternary silicon/oxidant pyrotechnic systems.
Part II Sb_2O_3 and KNO_3 as oxidants, R A Rugunanan and M E Brown, COMBUSTION
SCIENCE AND TECHNOLOGY, 95 (1994) 85-99.

R54. Combustion of binary and ternary silicon/oxidant pyrotechnic systems.
Part III Ternary systems, R A Rugunanan and M E Brown, COMBUSTION SCIENCE AND TECHNOLOGY, 95 (1994) 101-115.

R55. Combustion of binary and ternary silicon/oxidant pyrotechnic systems.
Part IV Kinetic aspects, R A Rugunanan and M E Brown, COMBUSTION SCIENCE AND TECHNOLOGY, 95 (1994) 117-138.

Some review papers covering the findings of these and related studies are:

R38. Thermal analysis of energetic materials, M E Brown, THERMOCHIM. ACTA, 148 (1989) 521-531.

C17. Fuel/oxidant relationships in some binary pyrotechnic systems, M E Brown, M W Beck, R L Drennan, R A Rugunanan, M J Tribelhorn and M G Blenkinsop, PROC. 4th INTERNATIONAL SYMPOSIUM ON EXPLOSIVES TECHNOLOGY AND BALLISTICS, National Institute of Explosives Technology, Pretoria Technikon, (1992) 391-405.

Many of the pyrotechnic compositions tested resulted in high combustion temperatures that destroyed the measuring thermocouple. To cope with higher temperatures, a survey was done of the possible use of optical/infrared pyrometry. The conclusion was that the response times and spatial resolutions of available pyrometers were not adequate, even if one could devise a technique for viewing the combustion front rather than the exterior surface.

R44. The use of pyrometry in the study of fast thermal processes involving initially solid samples, R A Rugunanan and M E Brown, J. THERMAL ANALYSIS, 37 (1991) 2125-2141.

At the request of AECI Explosives, we undertook a study of the oldest pyrotechnic composition known to man - "gun powder", or more technically correct "black powder" - produced by the company in large quantities by a wet process that was safer than the more conventional dry mixing. Simultaneous TG-DTA studies of these black powder compositions after drying, as well as of binary mixtures of the constituents, in nitrogen, showed no reaction between sulfur and charcoal. The charcoal/KNO_3 combination undergoes a strongly exothermic reaction between 380 and 550 ^{o}C. During normal thermal analysis of sulfur-containing mixtures, sulfur vaporizes above its liquid-liquid transition (171 ^{o}C) and below the melting point of KNO_3 (315 ^{o}C) so there is no significant reaction between sulfur vapour and solid KNO_3. If the escape of sulfur vapour is decreased, through use of high heating rates, or a preheated furnace, some of the sulfur can be induced to react with molten KNO_3. The reaction between sulfur vapour and molten KNO_3 in ternary systems is regarded as the pre-ignition reaction, and the higher temperature oxidation of solid charcoal by molten KNO_3 propagates the combustion of black powder. In air, sulfur oxidizes at temperatures below the melting-point of KNO_3.

C12. A thermo-analytical study of the pyrotechnic reactions of black powder and its constituents, M E Brown and R A Rugunanan, PROC. 9th ICTA, Jerusalem, THERMOCHIM. ACTA, 134 (1988) 413-418.

The behaviour of black powder under the less-controlled conditions of ignition and combustion was examined by simultaneous measurement of temperature profiles and burning rates. Curves of burning-rate against composition for sulfurless mixtures of charcoal/KNO_3 and for mixtures with various proportions of sulfur were concave-down-type curves. The compositions of mixtures with maximum burning rates did not correspond with the compositions of mixtures with maximum enthalpy-of-reaction. Maximum temperatures of about l400 ^{o}C were recorded. Burning rates were found to decrease with increasing particle-size of the constituents; with increasing compaction of the mixtures, or when inert diluents or subsidiary fuels were added to these mixtures. Burning rates were also affected by moisture contents above 2%, and failure of burning occurred at > 15% moisture.

R37. A temperature-profile study of the combustion of black powder and its constituent mixtures, M E Brown and R A Rugunanan, PROPELLANTS, EXPLOSIVES AND PYROTECHNICS, 14 (1989) 69-75.

In addition to the practical testing of pyrotechnic compositions, it was of considerable interest to try to predict their combustion properties from the physical properties and thermochemical data available for the fuel and the oxidant. Some computer codes in use at ICI Explosives in the UK were made available to us and several simulations were done.

The two-dimensional simulation of DTA scans on a strongly exothermic sample, enables the progress of the reaction and the temperature distributions in the sample, sample container and instrument sensors to be examined. Of the several possible variables whose influence could be studied, we chose the thermal conductivity of the sample and did simulations of a sample with (a) high thermal conductivity (2000 W m^{-1} K^{-1}) and (b) a low thermal conductivity (0.30 W m^{-1} K^{-1}) typical of powder samples. The high value in (a) was chosen to attempt to approximate conditions of more uniform temperature distribution than expected for (b). If an assumption of uniform temperature and extent of reaction did apply to case (a), thermal runaway would still be expected, largely due to the poor thermal coupling between the sample containers and the furnace. The simulated DTA trace did show that thermal runaway occurs, although the variations of temperature and extent of reaction through the sample are relatively small compared to case (b). In case (b), the variation in temperature through the sample becomes more apparent and the thermal runaway is dramatic with the high temperatures and high values of extent of reaction developing most rapidly at the top centre of the sample. The difficulty of extracting kinetic information from such DTA traces was discussed.

R40. Kinetic analysis of simulated DTA responses, M W Beck and M E Brown, THERMOCHIM. ACTA, 164 (1990) 379-393.

R41. Finite element simulation of the differential thermal analysis response to ignition of a pyrotechnic composition, M W Beck and M E Brown, J. CHEM. SOC. FARADAY TRANS., 87 (1991) 711-715.

The finite-difference and the finite-element models were both useful for exploring the potential effects of variation of adjustable parameters on the combustion of pyrotechnic systems. With care, reasonable agreement between experimental and simulated results could be obtained. The kinetic parameters have the greatest influence on the simulations and reliable values of these parameters are required. The use of an autocatalytic-type of rate-equation, rather than the assumption of a simple order-of-reaction kinetic equation gave improved agreement between experiment and simulation.

C19.   Computer modelling of pyrotechnic combustion, S J Taylor and M E Brown,
PROC. 5th INTERNATIONAL SYMPOSIUM ON EXPLOSIVES TECHNOLOGY
AND BALLISTICS, National Institute of Explosives Technology,
Pretoria Technikon, (1994) 167-179.

We also modelled the packing of particles of fuel and oxidant and attempted to couple changes in burning properties to the degree of fuel/oxidant contact. On the assumption that the fuel and oxidant powders consisted of uniform spherical particles of different sizes, the calculated numbers of contact points were compared with the experimental burning rates of these mixtures. In spite of the severe approximations made, there was a qualitative connection between the calculated numbers of contact points and the measured burning rates of those pyrotechnic compositions which are presumed to burn mainly via solid-solid reactions.

R73. Fuel-oxidant particle contact in binary pyrotechnic reactions, M E Brown, S J Taylor and M J Tribelhorn, PROPELLANTS, EXPLOSIVES AND PYROTECHNICS,
23 (1998) 320-327.

In an invited lecture at the National Conference of the Polish Thermal Analysis Society, I reviewed the results of our pyrotechnic studies.

R85. Some thermal studies on pyrotechnic compositions, M E Brown,
J. THERMAL ANALYSIS AND CALORIMETRY, 65 (2001) 323-334.

Fuels have ranged from metals, such as iron, manganese and molybdenum, to non-metals such as silicon, carbon and sulfur, and oxidants have been oxides, peroxides and oxysalts. Some of the constituents are presumed to have remained in the solid state, while others have definitely melted, vaporized, or decomposed to yield some gaseous products. Mechanisms encountered thus cover the wide field of solid-solid, solid-liquid, solid-gas, and possibly even liquid-gas and liquid-liquid reactions. The main experimental techniques used have been thermal analysis, measurement and analysis of temperature profiles, and simultaneous burning rate determinations. The thermal conductivities of the constituents and the mixtures have also been measured and the reactants and combustion residues have been examined using scanning electron microscopy, infrared spectroscopy and X-ray diffraction. Most of the oxidants studied, except Fe_2O_3, Sb_2O_3 and SnO_2, decompose with some release of $O_2(g)$ at temperatures often well below the recorded values of the maximum combustion temperature. Sb_2O_3 melts and vaporizes and KNO_3 melts and decomposes. The melting points of the fuels are high (excluding Sb and the complex thermal behaviour of charcoal that puts it in a separate class of fuels). Substitution of SrO_2 for the apparently chemically similar oxidant, BaO_2, does not affect the burning rate of Mn/peroxide compositions as much as it affects the Mo/peroxide compositions. Variation of the constituents of the binary mixtures studied resulted in burning rates of from 2 to 115 mm s^{-1}.   A similar range could, however, be achieved by varying the composition from 20 to 70% fuel of the fixed binary combination, Fe/$KMnO_4$. Variation of the particle-size of the fuel in the Sb/$KMnO_4$ system from a radius of 14 to 2.0 μm changed the burning rate from 2 to 8 mm s^{-1}, compared to the range of 2 to 28 mm s^{-1} with change in composition.   Decreasing the particle-radius of Mo from 17.2 to 6.9 μm produced faster burning Mo/peroxide mixtures than were possible by varying the composition of the mixtures with the larger Mo particles.

Combustion studies of pyrotechnic systems are severely hampered by limitations of the techniques available. Both thermal analysis and temperature profile measurement using thermocouples are limited to temperatures below 1700 °C by the materials of construction. Materials available for use at higher temperatures usually require inert atmospheres and are thus incompatible with the presence of oxidants. Materials should also not alloy with the fuels which are often metals, usually with relatively low melting points. Thermal analysis is also limited by the response of the sensor system. The constraints above mean that the systems studied lie in a relatively limited region of the multi-dimensional matrix of variables and broader trends may be inaccessible until new techniques and/or sensors suitable for rapid measurement of high temperatures become available.

As happens in many areas of science, changes and advances in technology can have a dramatic effect on a research field. The development of an electronically timed delay fuse for detonators, although initially vastly more expensive than chemical delays, has provided such increased accuracy and reproducibility that the expense is warranted in special applications, such as the precision implosion of buildings. Like all such electronic devices, prices have gone down as demands have increased, and companies, such as AECI Explosives, have cut back on research on new chemical fuses while concentrating on improving the performance of existing chemical fuses.

As an offshoot of studies on some highly unstable compounds prepared by colleagues at the University of Fort Hare, we suggested the use of very small quantities of such strongly exothermic materials for the temperature calibration of thermobalances. The decompositions can give very sharp mass changes which can be related to the strong, sharp exotherms observed in a calibrated differential scanning calorimeter.

R57. Temperature calibration in thermogravimetry using energetic materials, M E Brown, T T Bhengu and D K Sanyal, THERMOCHIM. ACTA, 242 (1994) 141-152.

THERMAL AND PHOTOSTABILITY OF DRUGS

With the changes in the explosives industry described above, I was fortunate to be able to collaborate with Professor Beverley Glass of the School of Pharmaceutical Sciences. With her knowledge of pharmaceutical chemistry and expertise in photostability studies and my experience in thermal analysis techniques and solid-state kinetics, we chose as our main theme the comparison of the photostabilities of pharmaceuticals with their thermal behaviour and their general pharmaceutical activity. Of particular interest have been the effects of various cyclodextrins used as excipients in drugs on their thermal and photostabilities, possibly through formation of drug/cyclodextrin inclusion complexes. In spite of the move of Professor Glass to James Cook University in Australia, our collaboration continues.

In an earlier review (see above), I had examined the influence that the Prout-Tompkins rate equation had had in solid state kinetics, and had found that it had been extensively used in describing drug stability. We examined some of these applications in more detail.

R78. Pharmaceutical applications of the Prout-Tompkins rate equation,
M E Brown and B D Glass, INT. J. PHARM., 190 (1999) 129-137.

Many of the studies that we have published have been done in response to requests from the pharmaceutical industry for examination of their products. For example, propyl-piperazine-substituted phenothiazines are an important subclass of the phenothiazines due to their increased potency over the prototype chlorpromazine, with fluphenazine displaying the greatest neuroleptic potency due to increased affinity of the 13-hydroxyethyl side chain for the trifluoromethyl group that enhances interaction with the dopamine receptor. Consideration of the effects of these structural differences on their activity and photostability are important, as is the determination of the nature of the degradants which could have adverse effects, for example, the 2-hydroxy derivatives have been implicated in photosensitivity effects. Stability studies in solution showed perphenazine to be the least stable of all the derivatives. Although dechlorination and sulphoxidation occurred under all light conditions studied, dechlorination with subsequent photoreduction and substitution proved to be a major degradation pathway. For the trifluoromethyl derivatives, the sulphoxide and sulphone were identified as intermediates. In the solid-state studies, sulphoxidation appeared to be the major degradation pathway with the dechloro derivative isolated from perphenazine. Thus the design of these derivatives to include the trifluoromethyl group to improve activity over the chloro derivatives has merit, especially taking into account the instability of chloroaromatic compounds and the involvement of the photosubstituted product in photosensitivity reactions, while other pathways e.g. N-demethylation, sulphoxidation and aromatic hydroxylation are in common with those reported in in vivo metabolic pathways. The inclusion of the 3-hydroxyethyl group, as opposed to the methyl group, in the side chain to improve activity is questionable in terms of its effect on stability.

R79. Photoreactivity versus activity of a selected class of phenothiazines: A comparative study, B D Glass, M E Brown and P M Drummond, Drugs: Photochemistry and Photostability, (Ed. A Albini and E Fasani), Royal Society of Chemistry, Cambridge, UK, 1998, p.134-149.

Differential scanning calorimetry (DSC) is particularly useful in examining interactions between drugs and excipients for possible incompatibilities. This method can detect, but not indicate the extent of, destabilizing effects of excipients. Interpretation of the DSC results is not straightforward because many types of drug-excipient interaction are possible. These include eutectic formation, solid-solid reactions (possibly complicated by solid-phase transitions), solid-liquid reactions and solid-gas reactions (particularly hydrolysis by evolved water vapour). Mixtures of prochlorperazine maleate with beta- or gamma-cyclodextrin indicated partial inclusion of the drug in the cyclodextrin cavities.

R80. DSC screening of potential prochlorperazine-excipient interactions in preformulation studies, M E Brown, E M Antunes, B D Glass, M Lebete and R B Walker, J. THERMAL ANALYSIS AND CALORIMETRY, 56 (1999) 1317-1322.

Nifedipine is a highly photolabile, practically water-insoluble drug used therapeutically as a calcium channel antagonist for the treatment of various cardiovascular disorders. Bioavailability is poor and erratic following oral administration of crystalline nifedipine, due to its low aqueous solubility and slow dissolution rate within the gastrointestinal tract. Attempts were made to prepare solid-state nifedipine - cyclodextrin inclusion complexes using beta-cyclodextrin (BCD), gamma-cyclodextrin (GCD), 2-hydroxypropyl-beta-cyclodextrin (2HPBCD), randomly methylated-beta-cyclodextrin (RMBCD) and heptakis (2,6-O-dimethyl)- beta-cyclodextrin (DMBCD) and processes, such as kneading and heating methods, that could be easily and cost-effectively implemented in an industrial environment.

The behaviour of these mixtures was studied using differential scanning calorimetry (DSC), diffuse reflectance mid-infrared spectroscopy (FTIR) and X-ray diffractometry (XRD). DSC revealed the nifedipine melting endotherm with onset at approximately 171°C for the kneaded mixtures with BCD, GCD and 2HPBCD, thus confirming the presence of nifedipine in the crystalline state, while some decrease in crystallinity was observed in the DMBCD kneaded mixture. With RMBCD, however, broadening and shifting of the nifedipine endotherm and reduction in its intensity suggested that the kneading could have produced an amorphous inclusion complex. These differing extents of interaction of nifedipine with the cyclodextrins were confirmed by FTIR and XRD studies.

R90. Binary systems of nifedipine and various cyclodextrins in the solid state, thermal, FTIR, XRD studies, M E Brown, B D Glass and M S Worthington, J. THERMAL ANALYSIS AND CALORIMETRY, 68 (2002) 631-646.

Triprolidine hydrochloride (TPH) is a well-known antihistamine drug which is reported as being photosensitive. The thermal stabilities of TPH and of 1:1 molar and 1:1 mass ratio physical mixtures of TPH with beta-cyclodextrin (BCD) and with glucose were examined using DSC, TG and TG-FTIR, complemented by X-ray powder diffraction (XRD) and infrared spectroscopy. Thermal studies of the solid TPH/BCD mixtures indicated that interaction between the components occurs and it is possible that the TPH molecule may be least partially accommodated in the cavity of the BCD host molecule. XRD results supported this indication of inclusion. The results of molecular modelling suggested that TPH is most likely to be accommodated in the BCD cavity as a neutral triprolidine molecule with the toluene portion of the molecule preferentially included in the cavity. The study also showed TPH to be compatible with both glucose and BCD, which are potential excipients both in solid and liquid dosage forms. The presence of these excipients in dosage forms will thus not adversely affect the stability and the therapeutic efficacy of TPH.

R94. The thermal stability of triprolidine hydrochloride and its mixtures with c yclodextrin and glucose, V J Ndlebe, M E Brown and B D Glass, J. THERMAL ANALYSIS AND CALORIMETRY, 77 (2004) 445-457.

TPH and its binary mixtures with beta-cyclodextrin (BCD) and glucose, were irradiated using an Atlas Suntest irradiation chamber and conditions according to the guidelines of the International Committee on Harmonization (ICH). HPLC analysis was used to determine the extent of photodegradation. XRD results showed that changes in the TPH crystal structure had occurred during irradiation and that these changes increased with the time of irradiation. Although the potential for isomerization to the pharmaceutically inactive Z-isomer under the influence of UV-light exists, results have proved that this transformation for solid-state TPH would require more extreme light conditions. The results of this study thus illustrate the general light stability of TPH in the solid-state.

R95. Photostability of triprolidine hydrochloride and its mixtures with cyclodextrin and glucose, V J Ndlebe, M E Brown and B D Glass, J. THERMAL ANALYSIS AND CALORIMETRY, 77 (2004) 459-470.

Because of the molecular complexity of many drugs, we chose, in addition to this sponsored research, to do a more fundamental study, in as much detail as possible, of the interactions between some fairly simple organic molecules (benzoic and salicylic acids) and cyclodextrins,

to act as a reference point for extending these studies to examination of the aminosalicylic acids and their sodium salts, which are of greater pharmaceutical interest.

R84. Thermal studies on some substituted aminobenzoic acids, M K Rotich, B D Glass and M E Brown, J. THERMAL ANALYSIS AND CALORIMETRY, 64 (2001) 681-688.

The thermal behaviours of the substituted aminobenzoic acids (3-aminobenzoic acid (3-ABA), 4-aminobenzoic acid (4-ABA), 3-aminosalicylic acid (3-ASA), 4-aminosalicylic acid (4-ASA), and 5-aminosalicylic acid (5-ASA), as well as of the parent benzoic acid (BA) and salicylic acid (SA) as reference substances, and possible decomposition products: 2-aminophenol, 3-aminophenol and 4-aminophenol were examined. Most of the compounds began to sublime well before melting, generally with an increasing rate of mass loss beyond the melting points, which are considerably different for the different isomers. The differences in behaviour of 4-ASA and 5-ASA were the most remarkable, with 5-ASA being far more stable and apparently not decarboxylating readily. 4-ASA appears to sublime at temperatures below the melting point, becoming less stable and decarboxylating in the liquid form.

R91. Thermal studies on mixtures of benzoic and salicylic acids with cyclodextrins, M K Rotich, M E Brown and B D Glass, J. THERMAL ANALYSIS AND CALORIMETRY, 73 (2003) 671-686.

The thermal behaviours of benzoic and salicylic acids were compared with the behaviours of 1:1 molar ratio physical and kneaded mixtures of these acids with each of three different cyclodextrins (beta-, hydroxypropyl-beta-, and gamma-cyclodextrin). There were significant interactions in both physical and kneaded mixtures of benzoic acid and the cyclodextrins with interactions in the kneaded benzoic acid/gamma-cyclodextrin mixtures being the most extensive as might be expected for the cyclodextrin with the largest molecular cavity. The results for the mixtures of salicylic acid with the cyclodextrins were similar to those for benzoic acid mixture, with the kneaded salicylic acid/gamma-cyclodextrin mixture again showing the most interaction.

R92. Thermal studies on mixtures of aminosalicylic acids with cyclodextrins, M K Rotich, M E Brown and B D Glass, J. THERMAL ANALYSIS AND CALORIMETRY, 73 (2003) 687-706.

Comparison of the effects of the different cyclodextrins on the behaviour of the individual aminosalicylic acid isomers showed that hydroxypropyl-beta-cyclodextrin has the greatest interaction with 3-aminosalicylic acid and 5-aminosalicylic acid, followed by gamma-cyclodextrin, while beta-cyclodextrin generally shows the least interaction. For 4-aminosalicylic acid, the effect of GCD seems to be more marked than for 3-aminosalicylic acid and 5-aminosalicylic acid.

R93. Thermal studies on the sodium salts of aminosalicylic acids, M K Rotich, M E Brown and B D Glass, J. THERMAL ANALYSIS AND CALORIMETRY, 73 (2003) 499-508.

The DSC curves for the sodium salts of all of the isomers showed complex dehydration/decomposition endotherms. TG-FTIR results for the sodium salt of 3-aminosalicylic acid showed the evolution of carbon dioxide in three stages: below 150 °C, between 200 and 300°C and continuous formation up to 500 °C. This behaviour differs from

that of 3-aminosalicylic acid itself, which forms CO_2 between 225 and 290 °C. For the sodium salt of 4-aminosalicylic acid, the formation of carbon dioxide starts from 250 ºC and is still being formed at about 650 ºC. 4-aminosalicylic acid decarboxylates above 150 ºC. 5-aminosalicylic acid and its sodium salt showed no evolution of carbon dioxide below 600 ºC.

A recent area of interest has been the application of artificial neural networks to pharmaceutical problems, making use of the expertise of Dr S. Agotonovic-Kustrin.

R96. Modelling the thermal behaviour of carboxylic acid derivatives with cyclodextrin in the solid state, S Agotonovic-Kustrin, B D Glass, M E Brown and M K Rotich, J. THERMAL ANALYSIS AND CALORIMETRY, 77 (2004) 391-402.

The application of classical QSAR and molecular modelling to the inclusion complexation of natural and modified cyclodextrins (CDs) with carboxylic acid derivatives as guest molecules was examined. The information described above on the thermal behaviour in the solid-state of benzoic acid (BA), salicylic acid (SA), and various substituted aminosalicylic acids (3-aminosalicylic acid, 3-ASA, 4-aminosalicylic acid, 4-ASA and 5-aminosalicylic acid, 5-ASA), as well as on the thermal behaviour of 1:1 molar ratio physical and kneaded mixtures of these acids with each of three different cyclodextrins, beta-, (BCD) 2-hydroxypropyl-beta-, (HPBCD) and gamma-cyclodextrin (GCD), was modelled using stepwise multiple regression (SMR). Two models for the prediction of the percentage mass loss and enthalpy of dehydration of the physical mixtures were established with correlation coefficients (*r*) of 0.79 and 0.92, respectively. Decreased correlation in the thermal behaviour of kneaded mixtures indicated significant interaction and possible formation of inclusion complexes.

Recently we published a comprehensive review covering the attempts to relate thermal and photostabilities.

R97. The thermal and photostability of solid pharmaceuticals - A review, B D Glass, Cs Novak and M E Brown, J. THERMAL ANALYSIS AND CALORIMETRY, 77 (2004) 1013-1036.

The stability of drugs towards heat, moisture, oxidation and exposure to light is a topic of great practical interest and any degradation will usually adversely affect the therapeutic activity of the drug. Unless very special precautions are taken, most drugs will receive some exposure to light and will generally be expected to be able to tolerate room temperature. One of the interesting questions that arises in considering drug stability, and which is discussed in this review, is the possible correlation between thermal degradation and photodegradation. This general topic could be further subdivided into examining correlations between photodegradation in solution (including the influences of the solvent) and in the solid state. Far more studies of photodegradation of drugs in aqueous solution have been carried out than of solid drugs or drug formulations in the solid state, because of the experimental difficulties. Thermal degradation of drugs in solution (again including use of different solvents) does not appear to have been as extensively studied as has the thermal behaviour of solid drugs and drug formulations. These latter thermal studies have been of particular value in revealing actual and potential drug-excipient interactions and are essential for obtaining information on the conditions for existence of drug polymorphs. In the solid state, the temperatures required for thermal degradation at a measurable rate are generally far higher than the temperatures existing, even locally, during photolysis, so the mechanisms of thermal and photochemical degradation can be expected to differ. The thermal and photostability of different

polymorphic forms of drug substances is especially important. Various crystal forms of drug substances exhibit differences in thermal behaviour and also in photostability.

ARTICLES OF A GENERAL NATURE

Although the writing of monographs and textbooks has been by main contribution to the broader communication of my research area, I have published some more general reviews and popular articles.

G1. The role of defects in the decomposition of solids, M E Brown, CHEMSA, 5 (1979) 74-5.

G2. Thermal Analysis - a group of often-neglected techniques, M E Brown, CHEMSA, 7 (1981) 192-195.

G3. 80 years of Chemistry at Rhodes, M E Brown, D J Eve and T M Letcher, CHEMSA, 9 (1983) 136-139.

G4. Pyrotechnic Delay Compositions, M W Beck, M E Brown and D Cawthorne, CHEMSA, 10 June (1984) 398-401.

G5. 100 Years of Chemistry at Rhodes University, M E Brown, D J Eve, P T Kaye, D E A Rivett and G M Watkins, SA J. SCIENCE, 100 (2004) 530 - 538.

A very-talented Honours level student, Miss L.A. Collett, wrote a review under my supervision, which was publishable:

R72. Biochemical and biological applications of thermal analysis, L A Collett and M E Brown, J. THERMAL ANALYSIS, 51 (1998) 693-726.

Several topics have proved suitable for publication in educational journals:

E1. Xtal-Line, A board game in crystallography, A Allsobrook, M E Brown and L Glasser, J. CHEM. EDUC., 50 (1973) 688-9.

This described a three-dimensional version of "tic-tac-toe" or "noughts and crosses" with analogies to crystal structures.

E2. Non-isothermal kinetics, M E Brown and C A R Phillpotts, J. CHEM. EDUC., 55 (1978) 556-560.

This paper was one of the first more general attempts to describe the methods of kinetic analysis, at a level accessible by a non-specialist, that had been developed for extracting kinetic parameters from the results of programmed-temperature experiments in thermal analysis. Mr Phillpotts added his expertise in the developing area of computer graphics. The paper has been well-cited.

E3. Determination of purity by differential scanning calorimetry, M E Brown, J. CHEM EDUC., 56 (1979) 310-313.

The detailed analysis of the melting of substances containing small amounts of impurities is an interesting application of an important part of the theory of phase equilibria. This paper has also received many citations.

E4. Diagrams to illustrate the meaning of the activation energy of reaction, M E Brown and A Goosen, SPECTRUM, 20 (2) (1982) 10-13.

E5. Thermodynamically and Kinetically Controlled Products, M E Brown, K J Buchanan and A Goosen, J. CHEM EDUC., 62 (1985) 575-578.

These last two papers were attempts to clarify some important but confusing concepts.

CONCLUSIONS

In summary, my areas of research have been :
- Effects of irradiation on solids (PhD topic)
- Silver refining (while at the Chamber of Mines)
- Kinetics of decomposition of solids (with Dr A.K. Galwey and various others)
- Techniques of thermal analysis
- Pyrotechnic delay systems (with support from AECI Explosives)
- Thermal and photostability of drugs (with Prof B.D. Glass)

I have been extremely fortunate in my collaborations. The value of constructive discussion and criticism of one's own work by conscientious, reliable people cannot be overestimated. The result is always greater than the sum of the individual contributions, so it is difficult to give them relative weighting. Sometimes work has been divided on the basis of expertise and equipment available and the results have again been combined, while, on other occasions, one small suggestion has untangled masses of laborious data collection.

J.A. Hedvall, in his book, "Solid State Chemistry: Whence, Where and Wither", Elsevier, Amsterdam, 1966, described how a pronouncement by Aristotle was mistranslated into Latin (*corpora non agunt nisi liquida*) from the Greek (*ta hygra meikta malista ton somaton*). The Latin version was translated as: "no reactions could take place without the participation of liquid or gaseous phases" and was a great discouragement to early researchers. The correct Greek form was that: "it is mainly fluid substances that react". Hedvall recalls how these statements challenged him to study reactions in the solid state. The work of Hedvall and others, particularly that described in "Chemistry of the Solid State", edited by W.E. Garner (Butterworths Scientific Publications, London, 1955), challenged many others, including me, to do likewise. Even Aristotle could not have imagined how extremely complex reactions in the solid state would turn out to be. Neither would he have dreamed how important solid-state reactions would become in industry. Achievements have thus been mainly incremental and very dependent upon the development of experimental techniques. With the support of AECI Explosives Ltd., Rhodes University and the National Research Foundation and its predecessors, I have been able to use much of the best equipment. Techniques that offer considerable promise for unravelling more of the complexity in the future include: modulated temperature differential scanning calorimetry, micro-thermal analysis based on atomic force microscopy, improved evolved gas analysis systems, and real-time X-ray diffraction studies if synchrotron radiation should become more accessible.

REACTIONS IN THE SOLID STATE

by

Michael Ewart Brown

A thesis submitted to meet the requirements of the
degree of Doctor of Science
of
Rhodes University
Grahamstown

2005

(i)

CONTENTS

NAVIGATION

The enclosed CD contains all the material, including electronic copies of the original papers as .pdf files. When the CD is inserted in a CD-drive, there should be an automatic start with the appearance of the title page. Adobe Acrobat Reader 5.0 or later is required and can be downloaded from adobe.com

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Within sections, links to the original papers or chapters are indicated by small black rectangles.

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DEDICATION

This thesis is dedicated to my wife, Cindy,
and my family, Richard and Ruth,
Linda and André and Brandon,
for all their love and support.

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ACKNOWLEDGEMENTS

CURRICULUM VITAE

MICHAEL EWART BROWN
Chemistry Department, Rhodes University, Grahamstown 6140, South Africa
Emeritus Professor of Physical Chemistry

PERSONAL DETAILS
Born: 12th July, l938   Nationality: South African
Married with two adult children.

ACADEMIC QUALIFICATIONS
B.Sc(Hons)(Witwatersrand, First Class, 1960), Ph.D (Rhodes, 1966)

PROFESSIONAL QUALIFICATIONS
FRSSAf (Fellow of the Royal Society of S.A.), MSA Chemical Institute
MRSC

CAREER OUTLINE
Rhodes University: 1962 - 1965 Junior Lecturer, 1967 - 1970 Lecturer,
                   1971 - 1977 Senior Lecturer, 1978 - 1985 Associate Professor,
                   1986 - 2003 Professor of Physical Chemistry.
1966 Research Officer, S.A. Chamber of Mines Research Laboratories.
1971 Leverhulme Visiting Research Fellow at Queen's University of Belfast.
1980 Visiting Research Fellow, Cavendish Laboratory, University of Cambridge.
1989 Visiting Research Fellow, ICI Explosives, Scotland.
1989 Allied Irish Banks Visiting Professor, Queen's University of Belfast.
1986 - 1991 Dean of Science, Rhodes University.
1994 Acting Dean of Research, Rhodes University.

RESEARCH FUNDING
A - rated by the National Research Foundation (NRF).
Significant funding from AECI Explosives Ltd.

AWARDS
1996 Mettler/NATAS international award for distinguished contributions to Thermal Analysis
1998 Vice-Chancellor's Distinguished Senior Research Award, Rhodes University.
2000 SA Chemical Institute Gold Medal
2003 Elected Fellow of the North American Thermal Analysis Society (NATAS).

INVITED LECTURES
1996 Mettler/NATAS Award Lecture at the 11th International Congress on Thermal Analysis and Calorimetry, Philadelphia.
1998 Invited Lecturer at the 11th National Symposium of the Indian Thermal Analysis Society, Jammu, India.
1998 Invited Lecturer at the 26th Symposium of the North American Thermal Analysis Society, Cleveland, Ohio.
2000 Plenary Lecturer 8th Conference on Calorimetry and Thermal Analysis, Zakopane, Poland.
2000 Plenary Lecturer 28th North American Thermal Analysis Society Conference, Orlando, Florida, USA
2001 SA Chemical Institute Gold Medal Lecture, Rhodes University

2002 Plenary Lecturer at the National Convention of the SA Chemical Institute, Port Elizabeth.
2003 Invited Lecturer at the 30th Symposium of the North American Thermal Analysis Society, Albuquerque, New Mexico.

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ORGANIZATIONS
Secretary of International Confederation of Thermal Analysis and Calorimetry 1996-
Editorial board of "Thermochimica Acta".

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BIOGRAPHICAL NOTES

After graduating with a BSc (Hons) in Chemistry from the University of Witwatersrand, a variety of circumstances resulted in my appointment as a Junior Lecturer at Rhodes University in Grahamstown. I registered for a PhD in solid-state chemistry under the direction of Professor Ernest Prout (of the Prout-Tompkins equation fame). This research introduced me to the general area of "Reactivity of Solids", which was to remain my major research interest throughout my career.

After completing my PhD, I joined the Chamber of Mines Research Laboratories in Johannesburg as a Research Officer. The research area assigned to me was related to the silver-refining processes in use at the Rand Refinery. After only a year away, I was offered a Lectureship back at Rhodes University.

Many changes had taken place in the Chemistry Department and I was fortunate to have a mentor in the person of Professor Leslie Glasser. With his guidance and experience we were able to obtain funding for equipment that was then becoming commercially available in the field of thermal analysis. These techniques added greatly to the information obtainable on the decomposition of solids and continue to be a major area of interest.

My first period of sabbatical leave was a year spent in 1971 at the Queen's University of Belfast. This was the start of a long, fruitful and extremely satisfying collaboration with Dr Andrew Galwey, which continues at present. Some of my recollections and appreciation of this friendship and collaboration are recorded in the Special Issue of the Journal of Thermal Analysis (Vol. 41 (1994) 252) prepared to celebrate Dr Galwey's 60th birthday. In 2002 a Special Issue of Thermochimica Acta (Volume 388, p1-460) was published in honour of our collaboration. It is entitled "Kinetics of Thermally Stimulated Reactions" and was edited by Sergey Vyazovkin and Takeo Ozawa.

My background in solid-state chemistry and thermal analysis led to generous support from AECI Explosives Ltd, including assistance with the purchase of equipment, for studies of the chemistry of the pyrotechnic delay fuses used in the gold mining industry. A PhD student, Michael Beck, with very generous help from Dr Peter Laye of the University of Leeds, adopted a technique involving the measurement of temperature-time profiles in packed columns of burning pyrotechnics. This, together with the theory developed at Leeds, enabled very useful comparisons to be made between different preparations. Use was also made of finite-element computer codes, supplied by ICI Explosives, to compare the predicted behaviour with that measured. As part of this research, I was able to spend periods of leave at the Cavendish Laboratory, Cambridge, and at ICI Explosives in Scotland.

Through my interest in thermal analysis, I became involved in the founding of the Southern African Thermal Analysis Society. This later led to me becoming the SA representative on the Council of the International Confederation for Thermal Analysis and Calorimetry and to my current position as Secretary to that Council.

With the political and economic changes in the 1990s, the research priorities of companies changed and support for pyrotechnic research dwindled. Fortunately I was able to move in a new direction and collaborate with Prof B.D. Glass (now at James Cook University in Australia) on the thermal and photostability of drugs. This work continues.

Highlights of my career have been receiving the 1996 Mettler/NATAS international award for distinguished contributions to Thermal Analysis and giving the Award Lecture at the 11th International Congress on Thermal Analysis and Calorimetry, Philadelphia, the 1998 Vice-Chancellor's Distinguished Senior Research Award, Rhodes University, and the 2000 SA Chemical Institute Gold Medal. My associations with and membership of the North American Thermal Analysis Society (NATAS) have been very valuable to me and I have presented several invited lectures at NATAS Conferences. In 2003 I was elected a NATAS Fellow. Of the other invited lectures that I have given, those to the 11th National Symposium of the Indian Thermal Analysis Society, Jammu, India, and the 8th Conference on Calorimetry and Thermal Analysis, Zakopane, Poland, were very memorable.

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C1. The thermal decomposition of ammonium metavandate-differential enthalpic analysis, M E Brown and B V Stewart, **Thermal Analysis (Proceedings of the Third International Conference on Thermal Analysis**, Davos, Switzerland, August l971) Ed. H G Wiedemann (Birkhauser Verlag, Basel, l972), Vol. 2, 313-320.

C2. Nucleation and growth of particles of nickel during the thermal decomposition of nickel formate, A K Galwey, M J McGinn and M E Brown, **Reactivity of Solids (Proceedings of the Seventh International Symposium on the Reactivity of Solids, Bristol, July l972)** Ed. J S Anderson, M W Roberts and F S Stone (Chapman and Hall, l972), 431-445.

C3. The reversible nature of the thermal decomposition of ammonium metavandate, M E Brown, L Glasser and B V Stewart, **Progress in Vacuum Microbalance Techniques,** Vol. 2, (Heyden & Son, l973) 125-137.

C4. The nucleation process in the thermal decomposition of nickel formate, M E Brown, B Delmon, A K Galwey and M J McGinn, **Reactivity of Solids, (Proceedings of the 8th International Symposium, Gothenburg, Sweden,)** Ed. J Wood, O Linquist, C Helgesson and N-G Vennerberg, Plenum, New York, l977, 221-226.

C5. A thermochemical investigation of the decomposition of manganese(II) oxalate dihydrate, M E Brown, D Dollimore and A K Galwey, **Proc. First Eur. Symp. On Thermal Analysis**, Ed. D Dollimore (Heyden, London, l976) 248-251.

C6. Thermal decompositon of nickel(II) squarate, M E Brown, A K Galwey and M Le Patourel, **Thermal Analysis (Proceedings of the Sixth International Conference on Thermal Analysis, Bayreuth, Germany, July l980)** Vol. 2, (Birkhauser Verlag, Basel, l980) 153-158.

C7. Thermal decomposition of nickel squarate, A K Galwey and M E Brown, **Reactivity of Solids (Proceedings of the Ninth International Symposium on the Reactivity of Solids, Krakow, Poland, September l980)** 665-669.

C8. Form and function of nuclei in decompositions of solids, M E Brown, G G T Guarini, R Reed and A K Galwey, **Reactivity of Solids (Proceedings of the Ninth International Symposium on the Reactivity of Solids, Krakow, Poland, September l980),** 625-629.

C9. Kinetics of solid-state reactions from isothermal rate-time curves, M E Brown and A K Galwey, **Thermal Analysis (Proceedings of the Seventh International Conference on Thermal Analysis, Kingston, Ontario, Canada, August 1982**), (Wiley-Heyden, Chichester, 1982) Vol. 1, 58-64.

C10. Isothermal DSC study of the thermal decomposition of potassium permanganate, M E Brown, K C Sole and M W Beck, Proceedings of the 8th ICTA, Bratislava 1985, **Thermochim. Acta,** 92 (1985) 149-152.

C11. Thermochemistry and reaction kinetics of the antimony/potassium permanganate pyrotechnic systems, M W Beck and M E Brown, **Pyrotechnics, Proceedings of the 10th International Pyrotechnic Seminar,** Fraunhofer-Institut Fur Treib- und Explosivstoffe, 1985, paper 14.

C12. A thermo-analytical study of the pyrotechnic reactions of black powder and its constituents, M E Brown and R A Rugunanan, Proceedings of the 9th ICTA, Jerusalem, **Thermochim. Acta,** 134 (1988) 413-418.

C13. A thermal study of the manganese/barium peroxide pyrotechnic system, M E Brown and R. L Drennan, **Proceedings of the 14th International Pyrotechnic Seminar,** Jersey, (1989) 423-432.

C14. Report on the workshop: Thermal Analysis Education, ICTA 1988, E A Turi, B Wunderlich, M E Brown and T Ozawa, **Thermochim. Acta,** 148 (1989) 13-35.

C15. Report on the workshop on kinetics held at ICTA-9, J H Flynn, M E Brown, E Segal and J Sestak, **Thermochim. Acta,** 148 (1989) 45-47.

C16.   Use of thermomagnetometry in the study of iron-containing pyrotechnic systems, M E Brown, M J Tribelhorn and M G Blenkinsop, Proceedings of the 10th ICTA, Hatfield, UK, 1992, **J. Thermal Analysis,** 40 (1993) 1123-1130. (see R50).

C17. Fuel/oxidant relationships in some binary pyrotechnic systems, M E Brown, M W Beck, R L Drennan, R A Rugunanan, M J Tribelhorn and M G Blenkinsop, **Proceedings of the 4th International Symposium on Explosives Technology and Ballistics,** National Institute of Explosives Technology, Pretoria Technikon, (1992) 391-405.

C18. Comparison of iron and zinc as pyrotechnic fuels, M J Tribelhorn, D S Venables, M G Blenkinsop and M E Brown, **Proceedings of the 5th International Symposium on Explosives Technology and Ballistics,** National Institute of Explosives Technology, Pretoria Technikon, (1994) 180-190.

C19. Computer modelling of pyrotechnic combustion, S J Taylor and M E Brown, **Proceedings of the 5th International Symposium on Explosives Technology and Ballistics,** National Institute of Explosives Technology, Pretoria Technikon (1994) 167-179.

C20. A thermoanalytical study of some zinc-fuelled binary pyrotechnic systems, M J Tribelhorn and M E Brown, Proceedings of the 6th European Symposium on Thermal Analysis, Italy 1994, **Thermochim. Acta,** 269/270 (1995) 649-663.

C21.   Isothermal kinetic analysis of solid-state reactions using plots of rate against derivative function of the rate equation, A K Galwey and M E Brown, Proceedings of the 6th European Symposium on Thermal Analysis,, Italy 1994, **Thermochim. Acta,** 269/270 (1995) 1-25.

C22. Report on the ICTAC Kinetics Committee (August 1992 to September 1994), M.E. Brown, R.M. Flynn and J.H.Flynn, **Thermochim. Acta,** 256 (1995) 477-483.

C23. Kinetics of solid state reactions by thermal methods, M E Brown, **Proceedings of the 11th National Symposium of the Indian Thermal Analysis Society,** Jammu, India, 1998, 1-8.

RESEARCH PAPERS PUBLISHED IN PROCEEDINGS OF LOCAL CONFERENCES

LC1. Electron microscopic evidence for solid decomposition mechanisms, M E Brown, R H M Cross, A K Galwey and R Reed, **Proc. Electron Microsc. Soc. South Afr.,** 11 (1981) 37-38.

LC2. Electron microscopic study of intersolid pyrotechnic reactions, M W Beck, M E Brown and R H M Cross, **Proc. Electron Microsc. Soc. South Afr.,** 12 (1982) 95-96.

LC3. Correlation between surface changes of potassium permanganate crystals and theoretical speculation on their decomposition mechanism, M E Brown, R H M Cross, K C Sole and M W Beck, **Proc. Electron Microsc. Soc. South Afr.,** 14 (1984) 153-154.

LC4. Thermal analysis of pyrotechnic oxidants: barium and strontium peroxides, R L Drennan and M E Brown, **Proceedings of the 2nd National Symposium on Explosives and Ballistics,** Pretoria (1990) 101-105.

PAPERS ON EDUCATIONAL TOPICS

E1. Xtal-line. A board game in crystallography, A Allsobrook, M E Brown and L Glasser, **J. Chem. Educ.,** 50 (1973) 688-9.

E2. Non-isothermal kinetics, M E Brown and C A R Phillpotts, **J. Chem. Educ.,** 55 (1978) 556-560.

E3. Determination of purity by differential scanning calorimetry, M E Brown, **J. Chem. Educ.,** 56 (1979) 310-313.

E4. Diagrams to illustrate the meaning of the activation energy of reaction, M E Brown and A Goosen, **Spectrum**, 20 (2) (1982) 10-13.

E5. Thermodynamically and kinetically controlled products, M E Brown, K J Buchanan and A Goosen, **J. Chem. Educ.,** 62 (1985) 575-578.

ARTICLES OF A GENERAL NATURE

G1. The role of defects in the decomposition of solids, M E Brown, **CHEMSA**, 5 (1979) 74-5.

G2. Thermal Analysis - a group of often-neglected techniques, M E Brown, **CHEMSA**, 7 (1981) 192-195.

G3. 80 years of Chemistry at Rhodes, M E Brown, D J Eve and T M Letcher, **CHEMSA**, 9 (1983) 136-139.

G4. Pyrotechnic Delay Compositions, M W Beck, M E Brown and D Cawthorne, **CHEMSA**, 10 June (1984) 398-401.

G5. 100 Years of Chemistry at Rhodes University, M E Brown, D J Eve, P T Kaye, D E A Rivett and G M Watkins, **S. A. J. Science,** 100 (2004) 530 - 538.

INTRODUCTION TO MY RESEARCH

I have chosen the title for this thesis, "Reactions in the Solid State", for two reasons:

Firstly, it is broad enough to cover all of my areas of research, which have been:

- Effects of irradiation on solids (PhD topic)
- Silver refining (while at the Chamber of Mines)
- Kinetics of decomposition of solids (with Dr A.K. Galwey and various others)
- Techniques of thermal analysis
- Pyrotechnic delay systems (with support from AECI Explosives)
- Thermal and photostability of drugs (with Prof B.D. Glass)

and, secondly, it was the title of the very successful book co-authored by Drs Andrew Galwey, David Dollimore and me.

A large part of my research has been involved in the writing and editing of books, so these are covered in a separate commentary, while commentary on the more than 100 papers to which I have contributed forms the main part of this compilation. It is hoped that the electronic format will enable ready access of to all aspects of my research, including electronic versions of the original papers. The reader will need a copy of Adobe Acrobat Reader to access these.

COMMENTARY - BOOKS

I have always enjoyed scientific writing and editing. My first experience in book publishing was the preparation of a chapter, in collaboration with Andrew Galwey and the late David Dollimore, for Volume 22 of a series on Comprehensive Chemical Kinetics for Elsevier. The chapter grew into a whole volume and became a highly-cited reference work, in spite of administrative blunders by Elsevier.

B1. "Reactions in the Solid State", M E Brown, D Dollimore and A K Galwey, Comprehensive Chemical Kinetics, Vol. 22, Ed. C H Bamford and C F H Tipper, Elsevier, Amsterdam, 1980, 340 pp. ISBN 0-444-41807-5

This was translated into Russian by a leading solid-state chemist, V. Boldyrev, see Chem. Abstr., 100 (1984) 105806, and is still regularly cited.

Inspired by this experience and the critical success of the above book, I wrote an introductory textbook on Thermal Analysis based on courses given for the SA Chemical Institute and various technikons.

B2. "Introduction to Thermal Analysis: Techniques and Applications", M E Brown, Chapman & Hall Ltd., London, 1988. ISBN 0-412-30230-6

The second edition of this well-received textbook, which has been recommended internationally for short courses on the topic, was published by Kluwer, Netherlands, in 2001.

B2/2. "Introduction to Thermal Analysis: Techniques and Applications", M E Brown, Second Edition, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2001, 264pp. ISBN 1-4020-0211-4

In 1994 an ambitious plan for a four-volume Handbook of Thermal Analysis and Calorimetry was proposed by Elsevier Scientific Publishers, with Prof P.K. Gallagher as the series Editor. I was invited to edit Volume 1, Principles and Practice. This appeared in 1998.

B3. "Handbook of Thermal Analysis and Calorimetry, Volume 1, Principles and Practice", Elsevier Scientific, Amsterdam, 1998, 691pp. M E Brown, Editor and contributor of two chapters: A K Galwey and M E Brown, "Kinetic background to Thermal Analysis and Calorimetry" (77pp) and V Balek and M E Brown, "Less-common Techniques" (26pp).) ISBN 0-444-82085-X

At the same time Dr Galwey and I were busy rewriting material for a totally new version of B1 above, entitled:

B4. "Thermal Decomposition of Ionic Solids", A K Galwey and M E Brown, Elsevier Scientific, Amsterdam, 1999, 597pp. ISBN 0-444-82437-5

This book has received extensive citation.

I was later requested by Elsevier and Professor Gallagher to assist in the editing of Volume 2 of the Handbook of Thermal Analysis and Calorimetry. This volume, which contains close

to 1000 pages, covers applications of thermal analysis and calorimetry in a variety of areas of (mainly) inorganic chemistry. I contributed a chapter on pyrotechnics. The volume was published in November 2003.

B5. "Handbook of Thermal Analysis and Calorimetry, Volume 2, Applications to Inorganic and Miscellaneous Materials", Elsevier Scientific, Amsterdam, 2003, 905pp. M.E. Brown and P.K. Gallagher (Eds), and contributor of chapter: E.L. Charsley, P.G. Laye and M.E. Brown, "Pyrotechnics" (30pp). ISBN 0-444-82086-8.

I have been approached very recently (September 2005) to edit an additional Volume 5 to update the series.

REVIEWS OF BOOKS

JCS FARADAY II Oct 1981, p1967.

Comprehensive Chemical Kinetics, Volume 22. Reactions in the Solid State. Ed. by C. H. BAMFORD and C. F. H. TIPPER. (Elsevier, Amsterdam, 1980). Pp. 340. Price $170.25, Dfl 220.

This valuable and certainly comprehensive bibliographical survey has been prepared by Drs. M. E. Brown, D. Dollimore and A. K. Galwey. Reference is made to work published as recently as 1978.

When considering the value of volumes of this kind it is difficult to assess the relative importance in the authors' minds of the need to mention everything *vis-a-vis* the provision of a critical guide to what in their considered opinion is really worth reading. Certainly a more enlightened guide to the literature than that provided by *Chemical Abstracts* is required by the student approaching this field for the first time, but it seems to me that the present volume does not really meet this need in a useful way for, among unassuming references to seminal works, there appear not dissimilar comments on papers which in truth are absolute rubbish. To serious students concerned with reliable kinetics many of the papers referred to in this volume are best left unremarked. Sometimes ignorance really is bliss.

Having issued that warning, though, the book does make interesting, even amusing, reading for an old pro. The work begins with an attempt at categorisation, which in passing indicates well those areas of other subjects required by the solid-state kineticist. This is followed by a rather superficial account of the experimental methods available. Here we are given brief accounts of who did what, but rarely why the technique was thought to be appropriate. Thus there are particularly weak accounts of electrical measurements and the effects of pre-irradiation, both of which when seriously applied can raise e.g.a. (evolved gas analysis) from a routine plod to an art.

The third chapter on the theory of the kinetics is much better. While the authors have little to record in the way of theoretical advances in topochemical analysis during the last fifteen years, they do provide sound accounts principally of Erofe'ev's contributions and also tackle the awkward questions of particle size distribution effects and diffusion control, which some earlier accounts neglected. For my part I would have liked to have seen more on non-random nucleation, but perhaps the authors thought that this was encompassed by shape factors.

Chap. 4 deals with the decomposition of solids. It pays due regard to the pioneering work of Garner on dehydration and there is an attractive section on the Smith-Topley Effect,

though perhaps the contributions of Frost are undervalued. Curiously, though, the azides are not well discussed. In part this stems from a recent decline of interest in the excitonic mechanism, but I suspect the difficulties really arise because of the variability of kinetic form shown by barium azide. Since similar difficulties with silver oxalate and mercury fulminate have been resolved, might one suggest a complete re-examination of barium azide using modern techniques? For the rest this chapter provides brief descriptions of the behaviour of practically every crystalline inorganic compound which on heating evolves a gas. Some organic salts, though not the styphnates, are included. The authors' value judgements are represented by the relative brevity of their descriptions.

In chap. 5 the authors face real difficulties of presentation. They are concerned to describe reaction between inorganic solids. This means essentially interdiffusion between phases in contact. Once such reactions have been illustrated there is little more to add, though a short section on the catalysis of solid decompositions is included.

All-in-all this is a book which contains nearly everything a newcomer to this field would need to know and rather more besides. Without doubt, the best parts of the book are the chapter on the theory and the introductory bits of the chapter on decomposition. There are nearly 1300 references.

D A YOUNG *Received 4th July,* 1980

Comprehensive Chemical Kinetics. **edited by C.H. Bamford and C.F.H. Tipper, Vol. 22.** *Reactions in the Solid State.* **by M.E. Brown, D. Dollimore and A.K. Galwey, Elsevier, Amsterdam, 1980,340 pp., Dfl. 240.00.**

The book is divided into 5 chapters with 1294 references and 22 figures. The chapters deal with (I) the characterization and classification of materials and processes, (2) methods of experimental study, such as EGA, microscopy, magnetic and electric measurements, etc., (3) the theory of solid state reaction kinetics, including the laws of nucleation and crystal growth, advancement of reaction interface controlled by diffusion or phase boundary reaction as well as the kinetic investigations using rising temperature techniques, (4) decomposition reactions of solids covering the actual reactions of hydrates, hydroxides, oxides, azides, carbonates, phosphates, sulphates and, last but not least, ammonium salts, and (5) reaction between inorganic solids.

Although there exist several books covering the subject of solid state reactions, the authors have selected topics which are of current interest, e.g. the practical means of studying solid state reactions, the applicability of the non-isothermal regime, the obedience of resulting kinetic data to theoretical kinetic equations, etc. The book is recommended not only to those specialized workers in heterogeneous kinetics, but also to the more general reader, including students in material science. This clearly written text will surely become the essential textbook for all thermoanalysts interested in reaction dynamics.

JAROSLAV SESTAK *(Prague, Czechoslovakia)*

Thermal Decomposition of Ionic Solids
Elsevier, Amsterdam, ISBN 0-444-82437-5, NLG 680.00

J. G. Dunn

This thoughtful book provides a timely summary of the more theoretical aspects of the decomposition of ionic solids, together with an extensive review of published information on the decomposition of specific compounds. Chapter 1 gives an introduction to the properties of solids. Chapters 2 – 6 deal with topics such as stoichiometry and extent of reaction, kinetic models for solid-state reactions, the influence of temperature on reaction rate, analysis and interpretation of experimental kinetic measurements, and methods for the characterisation of reactants, intermediates and products. Chapters 7-17 is a thorough survey of the published literature on the decomposition of compounds, collected together under headings such as hydrated salts, oxides, carbonates, etc. These chapters alone make the purchase of the book worthwhile, as an examination of the content will enable ready identification of areas for research. There is a final rounding off chapter in which the authors discuss the current status of the subject, and then speculate on prospects for future studies.

The authors are to be congratulated on bringing together information spread over a wide time period and from a range of journals and texts. The material is well presented and organised, and written in a lucid style. Above all, the topics are written with an authoritative ring, indicative of the experience and expertise of the two authors. Their comments are critical as well as informative, and would be of value to the novice as well as the more experienced person.

One of the very appealing features of the text is the emphasis on the totality of any such decomposition study. The complete investigation of the decomposition of a solid should involve thorough characterisation of the starting material, followed by determination of properties such as thermal stability and decomposition temperature, a kinetic analysis if an appropriate single stage reaction has been identified, and the assignment of a solid state reaction mechanism. The mechanism should be confirmed if possible by the application of appropriate techniques to investigate surfaces and internal structures of individual particles. This, of course, is a very time consuming process, but on the other hand it is likely to be the only way in which some common threads can be distinguished between the various processes and the factors that control them.

Although the main methods used to carry out decomposition reactions are thermal analysis techniques, there is no emphasis on the reproduction of TG or DTA curves. More emphasis is given to the diagrammatic representation of reaction schemes, and photomicrographs of reacted solids.

This is a very useful and valuable book which I recommend to anyone interested in the thermal decomposition of ionic solids.

COMMENTARY - RESEARCH PAPERS

My interest in solid-state chemistry began with my PhD studies with Professor Prout. In the 1960s, irradiation effects were of major interest and little was known of the response of inorganic materials to exposure to penetrating radiation such as gamma rays. The techniques of crystal-structure determination using X-ray diffraction were just becoming available at that time, in a very labour-intensive form, and I attempted to detect the structural damage done to single crystals of potassium permanganate by high-energy gamma-irradiation. The kinetics of thermal decomposition of potassium permanganate had been shown by Prout to be very sensitive to pre-irradiation of the sample. Although the effects of irradiation were evident in the X-ray diffraction photographs, the Fourier syntheses used to produce electron-density maps averaged behaviour over numerous unit cells and could not reveal individual defects. With only crude analogue computers available, a two-dimensional projection of a structure was all that was feasible and this still took many weeks of numerical calculation using devices such as Beever-Lipson strips. Some kinetic studies of the thermal decompositions of other pre-irradiated solids in comparison to the original samples were done by time-consuming, manual recording of the pressure of gas evolved in a vacuum system during decomposition at various set isothermal temperatures. Three papers resulted from my PhD studies:

R1. Thermal decomposition of irradiated nickel oxalate, E G Prout and M E Brown, AMERICAN SOCIETY FOR TESTING MATERIALS, Special Technical Publication, 359 (1964) 38-49.

R2. X-ray scattering by irradiated single crystals of potassium permanganate, E G Prout and M E Brown, NATURE, 203 (1964) 398-399.

R3. Thermal decomposition of irradiated calcium azide, E G Prout and M E Brown, NATURE, 205 (1965) 1314-1315.

On my return to Rhodes University as a Lecturer in 1967, I looked around for a different area of solid-state chemistry, to avoid overlap with the irradiation studies of Professor Prout, then at the University of Cape Town. I was fortunate to obtain support from the Council for Mineral Technology for a study of the thermal decomposition of ammonium metavandate, which formed an important stage in the processing of vanadium ores. My first PhD student, B.V. Stewart, tackled this project with rather limited equipment, but this was more than compensated for by having the extremely creative advice of Professor Glasser available. The decomposition turned out to be complex, involving several stages. One of the most interesting findings was the dramatic reversibility of the reaction between the decomposition products, solid vanadium pentoxide and gaseous ammonia and water vapour. A mechanism for the decomposition based on the crystal structures of the reactants, intermediates and solid products was proposed. Several papers resulted from this project.

R4. The thermal decomposition of ammonium metavandate, 1: The stoichiometry of the decomposition, M E Brown and B V Stewart, J. THERMAL ANALYSIS, 2 (1970) 287-299.

R9. The thermal decomposition of ammonium metavandate, II: The kinetics and mechanism of the decomposition, M E Brown, L Glasser and B V Stewart, J. THERMAL ANALYSIS, 6 (1974) 529-41.

R10. The thermal decomposition of ammonium metavandate, III : A structural view of the mechanism of the decomposition, M E Brown, L Glasser and B V Stewart, J. THERMAL ANALYSIS, 7 (1975) 125-137.

Papers on some aspects of this study were presented at my first international conferences:

C1. The thermal decomposition of ammonium metavandate-differential enthalpic analysis, M E Brown and B V Stewart, Thermal Analysis (Proceedings of the Third International Conference on Thermal Analysis, Davos, Switzerland, August l971) Ed. H G Wiedemann (Birkhauser Verlag, Basel, l972), Vol. 2, 313-320.

C3. The reversible nature of the thermal decomposition of ammonium metavandate, M E Brown, L Glasser and B V Stewart, PROGRESS IN VACUUM MICROBALANCE TECHNIQUES, Vol. 2, (Heyden & Son, l973) 125-137.

Being able to attend the series of conferences (ICTA and later ICTAC), together with the parallel series on Reactivity of Solids (see more below), was very important to the development of my research.

Another colleague, Dr N.H. Agnew, and I carried out a study of the solid-state polymerisation of vinylpyridine coordination compounds. Hot-stage microscopy with polarised light was used very successfully to follow the process and we managed to take a ciné film of the movement of the polymerisation front through the reactant crystals. Results are reported in:

R5. Solid-state polymerisation of vinylpyridine coordination compounds, N H Agnew and M E Brown, J. POLYM. SCI., A1, 9 (1971) 2561-2574.

R6. Solid-state reactions of vinylpyridine coordination complexes II, N H Agnew and M E Brown, J. POLYM. SCI., CHEMISTRY EDN., 12 (1974) 1493-1503.

My collaboration with Dr A.K. Galwey of the Queen's University began during my first sabbatical leave in 1971. I was developing an interest in the techniques of thermal analysis that were becoming commercially available at that time and was also able to learn some variations of the more traditional techniques (evolved gas pressure measurements) in use at Queen's. Most importantly I was able to learn about the techniques for replication of the surfaces of crystals, developed so successfully by Dr Galwey and his colleagues in the Electron Microscopy Unit at Queen's. These techniques, together with later developments in scanning electron microscopy, have enabled many mechanisms determined from kinetics results to be supported by visual observation.

The thermal decompositions of metal carboxylates had been of interest to Dr Galwey as a result of his earlier work on heterogeneous catalysis by metals. The mechanism of decomposition of a metal carboxylate was thought to resemble closely the mechanism of decomposition of the carboxylic acid on that particular metal. I had done some similar work in examining the effects of irradiation on the decomposition of nickel oxalate (see above). The metal formates, being the apparently simplest examples in the series of possible carboxylates, were of particular interest to both of us. Nickel formate was an obvious choice, because of the importance of nickel metal as a catalyst and the work already done on nickel oxalate. This study continued over quite a time span. Some our initial findings were presented in the paper:

C2. Nucleation and growth of particles of nickel during the thermal decomposition of nickel formate, A K Galwey, M J McGinn and M E Brown, REACTIVITY OF SOLIDS (Proceedings of the Seventh International Symposium on the Reactivity of Solids, Bristol, July l972) Ed. J S Anderson, M W Roberts and F S Stone (Chapman and Hall, l972), 431-445.

Discussion that arose from this paper, led to collaboration with Prof B. Delmon from Belgium and resulted in a further paper being presented at the next conference in the series, and two further papers:

C4. The nucleation process in the thermal decomposition of nickel formate, M E Brown, B Delmon, A K Galwey and M J McGinn, REACTIVITY OF SOLIDS, (Proceedings of the 8th International Symposium, Gothenburg, Sweden,) Ed. J Wood, O Linquist, C Helgesson and N-G Vennerberg, Plenum, New York, l977, 221-226.

R14. A differential scanning calorimetric study of the thermal decomposition of nickel formate dihydrate, A K Galwey and M E Brown, PROC. ROYAL IRISH ACAD, (DUBLIN), 77B (1977) 456-471.

R15. Nucleus formation and the kinetics of thermal decomposition of nickel formate, M E Brown, B Delmon, A K Galwey and M J McGinn, J. CHIM. PHYS., 75 (1978) 147-158.

An obvious extension of the work on nickel formate was to compare its with the behaviour of copper(II) formate. Our study showed that the metal formates were unexpectedly complex, existing in different crystalline modifications that behaved differently during decomposition. A feature of many of the decompositions of copper(II) carboxylates was found to be the formation of a volatile copper(I) intermediate.

R11. Thermal decomposition of three crystalline modifications of anhydrous copper(II) formate, A K Galwey, D M Jamieson and M E Brown, J. PHYS. CHEM., 78 (1974) 2664-2670.

An interesting study that started as a student's project was on the thermal decomposition of lead citrate. It was difficult to prepare reactant samples that behaved reproducibly, but the solid residue of the decomposition in vacuum turned out, as shown by electron microscopy, to be fine droplets of pyrophoric lead metal imbedded in a carbon matrix. Exposure of this product to air resulted in immediate combustion. Since publication of the paper below, I have received several enquiries suggesting some potential uses of this pyrophoric product:

R7. Thermal decomposition of lead citrate, M E Brown, J. CHEM. SOC. FARADAY I, 69 (1973) 1202-1212.

Manganese(II) oxalate dihydrate was another metal carboxylate selected for study. Not only was the solid product of decomposition predicted to be an oxide rather than a metal, but the influence of the conditions applied during the preliminary dehydration stage on the subsequent decomposition were also of interest. The collaboration was widened to include Dr D. Dollimore, then at the University of Salford, who had published some work on this compound. During the course of the study, some thermal analysis equipment had been

acquired at Rhodes and thermochemical aspects of the decomposition could be studied using differential scanning calorimetry (DSC). The resulting publications were:

R8. Thermal decomposition of manganese(II) oxalate dihydrate in vacuum and in oxygen, M E Brown, D Dollimore and A K Galwey, J. CHEM. SOC. FARADAY I, 70 (1974) 1316-1324.

R13. The thermochemistry of the decomposition of manganese(II) oxalate dihydrate, M E Brown, D Dollimore and A K Galwey, THERMOCHIM. ACTA, 21 (1977) 103-110.

C5. A thermochemical investigation of the decomposition of manganese(II) oxalate dihydrate, M E Brown, D Dollimore and A K Galwey, PROC. FIRST EUR. SYMP. ON THERMAL ANALYSIS, Ed. D Dollimore (Heyden, London, l976) 248-251.

Some of this work was collated and compared in:

R12. The mechanisms of the solid-phase thermal decomposition reactions of some transition-metal carboxylates, A K Galwey, D M Jamieson, M E Brown and M J McGinn, REACTION KINETICS IN HETEROGENEOUS CHEMICAL SYSTEMS, ed. P Barrett, Elsevier, Amsterdam, l975, 520-537.

This theme of attempting to discern patterns of behaviour in the thermal decompositions of metal carboxylates has continued over the years. Obvious extensions from formates were to acetates and malonates.

R34. A kinetic and mechanistic study of the thermal decomposition of nickel acetate, A K Galwey, S G McKee, T R B Mitchell, M E Brown and A F Bean, REACTIVITY OF SOLIDS, 6 (1988) 173-186.

R35. A kinetic and mechanistic study of the thermal decomposition of nickel malonate, A K Galwey, S G McKee, T R B Mitchell, M A Mohamed, M E Brown and A F Bean, REACTIVITY OF SOLIDS, 6 (1988) 187-203.

Although not a conventional carboxylate, the thermal decompositions of several metal squarates were also studied. The squarate anion, $C_4O_4^{2-}$, like the oxalate anion, contains no hydrogen, thus decreasing the complexity of product gas mixtures. The nickel salt decomposed by a nucleation and growth process yielding very small (< 50 nm diameter) particles and the possibility exists that nickel carbonyl is an unstable intermediate. The copper(II) salt followed the pattern of other copper(II) carboxylates in decomposing via a copper(I) intermediate.

R21. Thermal decomposition of copper(II) squarate, M E Brown, A K Galwey and M W Beck, ISRAEL J. CHEM., 22 (1982) 215-218.

R22. Thermal decomposition of nickel squarate dihydrate, A K Galwey and M E Brown, J. CHEM. SOC. FARADAY I, 78 (1982) 411-424.

R31. A thermoanalytical study of the thermal decomposition of silver squarate, M E Brown, H Kelly, A K Galwey and M A Mohamed, THERMOCHIM. ACTA, 127 (1988) 139-158.

R32. Thermal decomposition of silver squarate, A K Galwey, M A Mohammed and M E Brown, J CHEM. SOC. FARADAY I, 84 (1988) 57-64.

R33. Thermal decomposition of copper(II) squarate, A K Galwey, M A Mohammed, S Rajam and M E Brown, J CHEM. SOC. FARADAY I, 84 (1988) 1349-1356.

C6. The thermal decompositon of nickel squarate (thermochemical aspects), M E Brown, A K Galwey and M Le Patourel, THERMAL ANALYSIS (Proceedings of the Sixth International Conference on Thermal Analysis, Bayreuth, Germany, July l980) Vol. 2, (Birkhauser Verlag, Basel, l980) 153-158.

C7. The thermal decomposition of nickel squarate (kinetics and electron microscopy), A K Galwey and M E Brown, REACTIVITY OF SOLIDS (Proceedings of the Ninth International Symposium on the Reactivity of Solids, Krakow, Poland, September l980) 665-669.

Some of the conclusions drawn regarding the thermal behaviour of metal carboxylates have been incorporated in the book B4.   Steps that have been proposed as determining the rates of decompositions of metal carboxylates include rupture of one of the three different types of bond (the C - C bond, the C - O bond or the M- O bond) in the carboxylate group, or electron transfer at a M - O bond. Once some solid product has been formed, catalytic processes can occur on its surface. In spite of intensive study, there has not yet appeared any generally accepted pattern explaining the observed differences of thermal reactivity, which seem to be very dependent upon the metal cation. Reactions are also complicated by complete or partial dehydration steps prior to decomposition of the anion.

MISCELLANEOUS DECOMPOSITIONS

R17. High temperature thermal properties of KH_2PO_4 : phase transitions and decompositions, M E Brown, L Glasser and J Larson, THERMOCHIM. ACTA, 30 (1979) 233-246.

The major finding of the work described in R17 was that the evolution of gaseous acids from this system is extremely destructive to thermal analysis equipment, particularly the alumina insulation of the Perkin-Elmer DSC sample cell!

With the state-of-the-art thermal analysis equipment available to us, we were able to examine the thermal behaviour of compounds of interest to other research groups and to assist with the interpretation of the results (R19 and R26).

R19. The thermal decomposition of bis(trispyrrolidino phosphine oxide) tetranitrato uranium(IV), M E Brown, C P J van Vuuren and A Litthauer, THERMOCHIM. ACTA, 49 (1981) 333-349.

R26. A study of the complexes of $[(eta^5-C_5H_5Fe(CO)_2]_2\{mu-(CH_2)_n\}$ (where n=3-12) by mass spectroscopy and differential scanning calorimetry, J R Moss, L G Scott, M E Brown and K J Hindson, J. ORGANOMETALLIC CHEM., 282 (1985) 255-266.

During sabbatical leave in the Cavendish Laboratory of Cambridge University, I studied the thermal behaviour of the silver(I) and mercury(II) salts of 5- nitrotetrazole and of mercury(II) fulminate. These compounds had been suggested as alternative primary explosives to replace lead azide in detonators. The decompositions of all three compounds are strongly exothermic and the nitrotetrazole salts evolve up to 25% more heat per unit mass than mercury fulminate or lead azide. Although the quantities involved are small, the silver salt produces less environmentally hazardous products. We also did some unpublished studies of the detonation of these compounds using the high-speed photographic techniques available (including cameras originally built to photograph explosions of nuclear bombs!). The changes on detonation were, however, so rapid that the techniques could not provide adequate resolution.

R20. The thermal decomposition of the silver(I) and mercury(II) salts of 5- nitrotetrazole and of mercury(II) fulminate, M E Brown and G M Swallowe, THERMOCHIM. ACTA, 49 (1981) 247-258.

Some of the reactants that have been used in decomposition studies have received so much attention that they have achieved almost "model" status. Examples are calcium carbonate, calcium oxalate dihydrate, copper sulfate pentahydrate, ammonium perchlorate (an important propellant) and potassium permanganate (possibly because of its role as a portable source of gaseous oxygen in many school laboratories?). My PhD studies (see above) involved some studies of the effects of gamma-irradiation on the thermal stability of potassium permanganate and when new techniques, such as differential scanning calorimetry (DSC) and scanning electron microscopy (SEM), became available, it was of interest to see what additional information these techniques could provide.

R25. Isothermal DSC study of the thermal decomposition of potassium permanganate, M E Brown, K C Sole and M W Beck, THERMOCHIM. ACTA, 89 (1985) 27-37.

C10. Isothermal DSC study of the thermal decomposition of potassium permanganate, M E Brown, K C Sole and M W Beck, Proceedings of the 8th ICTA, Bratislava 1985, THERMOCHIM. ACTA, 92 (1985) 149-152.

R56. A mechanism for the thermal decomposition of potassium permanganate crystals based on nucleation and growth, M E Brown, A K Galwey, M A Mohamed and H Tanaka, THERMOCHIM. ACTA, 235 (1994) 255-270.

In spite of its "model" status, the decomposition of potassium permanganate remains an example of considerable complexity, coupled with high sensitivity to pre-treatment of the sample. Microscopic studies gave no evidence that decomposition results in extensive breakup of the crystals. The breakdown of the permanganate ion does not appear to be influenced by the nature of the cation, or by the crystal structure, but to occur in a disorganized layer by an electron transfer mechanism.

Under the auspices of the International Confederation for Thermal Analysis and Calorimetry (ICTAC), a cooperative project was organized in an attempt to identify a reaction that could be used as a *kinetics* standard. The reaction suggested was the thermal dehydration of lithium sulphate monohydrate. We did both isothermal and programmed temperature measurements of the rate of dehydration. Participants in the project demonstrated conclusively that the dehydration was NOT suitable as a kinetic standard because of the ready reversibility of the process under small changes of conditions.

R42. Reliability of kinetic measurements for the thermal dehydration of lithium sulphate monohydrate I. Isothermal measurements of pressure of evolved water vapour, M E Brown, A K Galwey and A Li Wan Po, THERMOCHIM. ACTA, 203 (1992) 221-240.

R48. Reliability of kinetic measurements for the thermal dehydration of lithium sulphate monohydrate. Part 2. Thermogravimetry and differential scanning calorimetry, M E Brown, A K Galwey and A Li Wan Po, THERMOCHIM. ACTA, 220 (1993) 131-150.

Professor D.J. Eve of the Rhodes Chemistry Department had considerable previous experience of the preparation and characterization of complex metal oxalates and we carried out several studies of such compounds for comparison with the information available on the simpler metal oxalates. Decompositions of the mixed oxalates, $MCu(ox)_2.xH_2O$, were all complex reactions and that of M = Fe was the most complex. The order of decreasing stability, as indicated by the temperature ranges giving comparable decomposition rates, was $NiCu(ox)_2 > CoCu(ox)_2 > FeCu(ox)_2$, which also corresponded to the order of increasing covalency as shown by X-ray photoelectron spectroscopy.

R49. Thermal analysis of some mixed metal oxalates, A Coetzee, D J Eve and M E Brown, J. THERMAL ANALYSIS, 39 (1993) 947-973.

R51. Kinetics of thermal decomposition of some mixed metal oxalates, A Coetzee, M E Brown, D J Eve and C A Strydom, J. THERMAL ANALYSIS, 41 (1994) 357-385.

R69. The thermal dehydration and decomposition of $Ba[Cu(C_2O_4)_2(H_2O)].5H_2O$, J Bacsa , D J Eve and M E Brown, J. THERMAL ANALYSIS, 50 (1997) 33-50.

A detailed study of the thermal behaviour of amide complexes of transition metal(II) chlorides was carried out by Mr Nelwamondo, Lecturer at the University of Fort Hare, under the supervision of Professor Eve and myself.   Attempts were made to correlate structural, kinetic and thermochemical parameters. The activation energy for ligand decomposition appeared to increase with the basicity of the amide ligand.

R74. Thermal and structural studies of amide complexes of transition metal(II) chlorides. I: Stoichiometry, A N Nelwamondo, D J Eve, G M Watkins and M E Brown, THERMOCHIMICA ACTA, 318 (1998) 165-175 .

R75. Thermal and structural studies of amide complexes of transition metal(II) chlorides. II: Kinetics, A N Nelwamondo, D J Eve and M E Brown, THERMOCHIMICA ACTA, 318 (1998) 177-186.

SOLID-GAS REACTIONS

My first venture into solid-gas reactions was sponsored by the Council of Mineral Technology. The oxidation of chromium(III) chloride is an important stage in the preparation of chrome pigments. A feature of this study was the microscopic evidence obtained in support of the contracting-geometry kinetic model proposed.

R39. Oxidation kinetics of chromium(III) chloride, K C Sole, M B Mooiman and M E Brown, J. CHEM. SOC. FARADAY TRANS., 86 (1990) 525-530.

During the industrial manufacture of tungsten carbide, tungsten powder is carburised with either methane or carbon in the presence of hydrogen gas. Growth of tungsten particles occurs during reduction in hydrogen, by a mechanism involving the water vapour formed, and this decreases the value of the resulting product. Funding was received to examine the various ways of reducing tungsten oxides. The tungsten oxides were heated in a tube furnace under carefully controlled atmospheres and the evolved gases were analysed using dedicated infrared gas detectors. Under the conditions investigated, the reactions were controlled by mass transfer. The final product of the reductions with hydrogen and with hydrogen plus carbon was tungsten. The addition of carbon increased the rate of reduction but did not affect the phases formed. CO_2 was evolved at the start and CO mainly at the end of the process. The following papers resulted:

R63. Reduction of tungsten oxides with carbon Part 1: Thermal analyses, D S Venables and M E Brown, THERMOCHIM. ACTA, 282/283 (1996) 251-264.

R64. Reduction of tungsten oxides with carbon Part 2: Tube furnace experiments, D S Venables and M E Brown, THERMOCHIM. ACTA, 282/283 (1996) 265-276.

R65. Reduction of tungsten oxides with hydrogen and with hydrogen and carbon, D S Venables and M E Brown, THERMOCHIM. ACTA, 285 (1996) 361-382.

R66. Reduction of tungsten oxides with carbon monoxide, D S Venables and M E Brown, THERMOCHIM. ACTA, 291 (1997) 131-140.

MODELLING

A very interesting suggestion was made by a colleague, the late Dr R.B. English, that a possible mechanism for the decompositions of some solids could involve the change of structure from crystalline reactant to an eventually crystalline solid product along a pathway determined by the symmetry groups of the reactant and product. This pathway was assumed to involve the minimum possible changes in symmetry, while allowing for removal of any gaseous product at an appropriate stage. The energetics of the process were estimated from the consequent changes in lattice energy. This approach gave encouraging agreement with reported activation energies. These studies would not have been possible without the expertise that Prof L. Glasser had built up in the calculation of lattice energies.

R76. Modelling the thermal decomposition of solids on the basis of lattice energy changes. Part I: Alkaline-earth carbonates, A de La Croix, R B English, M E Brown and L Glasser, J. SOLID STATE CHEM., 137 (1998) 332-345.

R77. Modelling the thermal decomposition of solids on the basis of lattice energy changes. Part II: Alkaline-earth peroxides, A de La Croix, R B English, M E Brown and L Glasser, J. SOLID STATE CHEM., 137 (1998) 346-352.

KINETICS AND MECHANISMS

This has been an area of major interest. Several contributions have been made to the methods of numerical data-fitting:

R16. The distinguishability of selected kinetic models for isothermal solid-state reactions, M E Brown and A K Galwey, THERMOCHIM. ACTA, 29 (1979) 129-146.

C 9. Kinetics of solid-state reactions from isothermal rate-time curves, M E Brown and A K Galwey, THERMAL ANALYSIS (Proceedings of the Seventh International Conference on Thermal Analysis, Kingston, Ontario, Canada, August 1982) Vol. 1 (Wiley-Heyden, Chichester, 1982) Vol. 1, 58-64.

R36. Arrhenius parameters for solid-state reactions from isothermal rate-time curves, M E Brown and A K Galwey, ANALYTICAL CHEMISTRY, 61 (1989) 1136-1139.

C21.   Isothermal kinetic analysis of solid-state reactions using plots of rate against derivative function of the rate equation, A K Galwey and M E Brown, Proceedings of the 6th European Symposium on Thermal Analysis, Italy 1994, THERMOCHIM. ACTA, 269/270 (1995) 1-25.

C23. Kinetics of solid state reactions by thermal methods, M E Brown, Proceedings of the 11th National Symposium of the Indian Thermal Analysis Society, Jammu, India, 1998, 1-8.

In deriving reaction mechanisms it is essential to attempt to support kinetic results by complementary techniques, such as optical and electron microscopy:

LC1. Electron microscopic evidence for solid decomposition mechanisms, M E Brown, R H M Cross, A K Galwey and R Reed, PROC. ELECTRON MICROSC. SOC. SOUTH AFR., 11 (1981) 37-38.

C 8. Form and function of nuclei in decompositions of solids, M E Brown, G G T Guarini, R Reed and A K Galwey, REACTIVITY OF SOLIDS (Proceedings of the Ninth International Symposium on the Reactivity of Solids, Krakow, Poland, September l980) 625-629.

LC3. Correlation between surface changes of potassium permanganate crystals and theoretical speculation on their decomposition mechanism, M E Brown, R H M Cross, K C Sole and M W Beck, PROC. ELECTRON MICROSC. SOC. SOUTH AFR., 14 (1984) 153-154.

R68. Structures and functions of reaction interfaces developed during solid state dehydrations, M E Brown, A K Galwey and G G T Guarini, J. THERMAL ANALYSIS, 49 (1997) 1135-1146.

An additional "hardy perennial" is the question of the applicability of the Arrhenius equation and its accompanying Transition-State Theory to solid-state reactions. Some critics have gone as far as to label it the "erroneous equation".   From the point-of-view of numerical methods, it has been shown that no alternative relationship suggested so far has any distinct advantage. In the two papers below, Dr Galwey and I developed a model based on the Band

Theory of solids that could explain the observed temperature dependence of the reaction rate. Although the Maxwell-Boltzmann energy distribution function that provides the starting point for a theoretical explanation of Arrhenius behaviour in homogeneous reactions is inapplicable to the immobilized constituents of a solid, the energy distribution functions for both electronic energy (Fermi-Dirac statistics) and phonon energy (Bose-Einstein statistics) approximate (for values significantly above the Fermi level) to the same form as that in the Maxwell-Boltzmann distribution and hence are capable of explaining the fit of k - T data to an Arrhenius-type equation. Interface levels, capable of accommodating electrons, (analogous to impurity levels in semiconductors, imperfection levels in crystals, etc.) are proposed to be present within the interfacial zone wherein chemical changes occur. These energy levels can be located within the forbidden range between the energy bands of the crystal. The actual energies of these levels will be sensitive to the particular species involved and energies distributed within a limited range are more likely than uniform energies. Such levels could be involved in the crucial bond redistribution steps and account for the increased reactivity at the reactant/product interface relative to more perfect crystalline regions. The occupancy of these levels is governed by distribution functions similar in form to that of the Maxwell-Boltzmann equation. The band model of solids may thus be extended to accommodate the bond redistributions during conversion of reactant to product.

R61. A theoretical justification for the application of the Arrhenius equation to the kinetics of solid state reactions (mainly ionic crystals), A K Galwey and M E Brown, PROC. ROY. SOC. (LONDON), A 450 (1995) 501-512.

R87. Application of the Arrhenius equation to solid state kinetics: can this be justified?
A K Galwey and M E Brown, THERMOCHIM. ACTA, 386 (2002) 91-98.

Because of Professor Prout's association with Rhodes and Professor Tompkins's South African connections, as well as the importance of this mechanism of solid-state reactions, I carried out a literature survey of the way in which the Prout-Tompkins rate equation had been applied in solid-state kinetics. One of the unexpected findings was that the equation had been particularly popular in describing the kinetics of decomposition of drugs. This aspect was covered in a further paper. The curves of fractional decomposition against time predicted by the Prout-Tompkins model are very similar to those that can be predicted from a totally different model of decomposition accompanied by melting of the reactant (the Bawn model). This aspect was discussed in a further paper.

R71. The Prout-Tompkins rate equation in solid-state kinetics, M E Brown,
THERMOCHIMICA ACTA, 300 (1997) 93-106.

R78. Pharmaceutical applications of the Prout-Tompkins rate equation,
M E Brown and B D Glass, INT. J. PHARM., 190 (1999) 129-137.

R85. Decomposition of solids accompanied by melting - Bawn Kinetics,
M E Brown and B D Glass, INT. J. PHARM., 254 (2003) 255-261.

The whole field of kinetic analysis of programmed-temperature experiments continues to be controversial. I attempted to review some of the major aspects in a plenary lecture given in Philadelphia on the occasion of receiving the Mettler/NATAS Award: This paper has been frequently cited.

R67. Steps in a minefield - some kinetic aspects of thermal analysis, M E Brown,
J. THERMAL ANALYSIS, 49 (1997) 17-32.

At each ICTAC Congress there have been Workshops on Kinetics and I have been actively involved in these:

R29. Report on the workshop: Current problems of kinetic data reliability evaluated by thermal analysis, J H Flynn, M E Brown and J Sestak, THERMOCHIM. ACTA,
110 (1987) 101-112.

R30. Quantitative thermoanalytical studies of the kinetics and mechanisms of the thermal decompositions of inorganic solids, M E Brown, THERMOCHIM. ACTA,
110 (1987) 153-158.

C15. Report on the workshop on kinetics held at ICTA-9, J H Flynn, M E Brown,
E Segal and J Sestak, THERMOCHIM. ACTA, 148 (1989) 45-47.

C22. Report on the ICTAC Kinetics Committee (August 1992 to September 1994).
M E Brown, R M Flynn and J H Flynn, THERMOCHIM. ACTA, 256 (1995) 477-483.

C24. The theory and practice of thermoanalytical kinetics of solid-state reactions, H Tanaka and M E Brown, J. THERMAL ANALYSIS AND CALORIMETRY, 80 (2005) 795-797.

Arising from the Workshop held in Philadelphia in 1996, I initiated a project in which several common sets of numerical data (both isothermal and programmed temperature) were supplied to participants, who were invited to apply methods of kinetic analysis of their choice to extracting kinetic parameters. Two of the sets were simulated data from equally-weighted concurrent first-order reactions with known Arrhenius parameters, so that the reported parameters could be compared with the known values. Response to the Project was enthusiastic and the results were published:

R83. Computational aspects of kinetic analysis Part A: The ICTAC kinetics project - data, methods and results, M E Brown, M Maciejewski, S Vyazovkin, R Nomen and J Sempere, A Burnham, J Opfermann, R Strey, H L Anderson and A Kemmler, R Keuleers, J Janssens and H O Desseyn, Chao-Rui Li and Tong B Tang, B Roduit, J Malek and T Mitsuhashi, THERMOCHIM. ACTA, 355 (2000) 125-143.

This paper included several recommendations for tackling kinetic analyses. The major recommendations were that attempts should NOT be made to "guess" a set of unique parameters (kinetic triplet) from a single programmed-temperature experiment, and that isoconversional methods should be applied. The paper was followed by several other papers giving fuller discussions of various important aspects of kinetic analysis by some of the participants.

In an attempt to emphasize the importance of the complete kinetic triplet and to decrease the quoting of values of the activation energy in isolation, as well as to counter some poor choices of nomenclature, we published a paper:

R89. "Model-free" kinetic analysis? J D Sewry and M E Brown, THERMOCHIM. ACTA,
390 (2002) 217-225.

Two rather pessimistic views of progress in the field of solid-state reactions are given in:

R81. Kinetic aspects of the thermal stability of ionic solids, M E Brown and R E Brown, THERMOCHIM. ACTA, 357-358 (2000) 133-140.

R82. Solid-state decompositions : stagnation or progress?, A K Galwey and M E Brown, J. THERMAL ANALYSIS AND CALORIMETRY, 60 (2000) 863-877.

R81 is of special significance to me as the ideas and mathematical aspects were developed by my son, Richard Brown, as an aeronautical engineer. The paper uses mapping theory to discuss the difficulties of predicting the thermal stability of an untested ionic solid from the information accumulated on similar compounds. The conclusion was that such predictions are likely to be inaccurate and hence of little value.

R82 laments the lack of appearance of any theoretical basis, or identification of useful principles, for classifying the decompositions of solids. A major shortcoming is the lack of recent development or application of new experimental techniques which can give more direct chemical information about the processes occurring within the relatively inaccessible reaction zone, possibly of molecular dimensions. The most promising, but not generally available, technique has been diffraction studies using synchrotron radiation. Such studies have been able to show that reaction and recrystallization of any solid product are not necessarily completed within the same advancing zones and may not always occur concurrently. Changes which may occur behind the reaction front include secondary reactions between primary products and retexturing of the residual solid. Even apparently straightforward processes such as dehydrations are still incompletely understood.

In an invited lecture at the NATAS meeting in Albuquerque in 2003, I attempted to identify some recommendations for the publication of kinetics papers. These were that: (1) No papers with kinetic analyses based on experiments done at a single heating-rate should be accepted for publication; (2) The same restriction on publication should apply to kinetic studies on fundamentally irreproducible materials such as sewage sludge; (3) Values of E should not be reported and interpreted in isolation from the other members of the kinetic triplet and realistic uncertainties in the calculated values should be reported.; (4) Each reaction step in a complex process must be clearly defined so that alpha is also properly defined; (5) "Mechanism" should be reserved for physico-chemical steps and be clearly distinguished from "kinetic models", "rate equations" or "conversion functions"; (6) The final test of every kinetic analysis should be to use the parameters determined to construct calculated curves for comparison with the experimental results over a wide and representative range.

R98. Stocktaking in the Kinetics Cupboard, M E Brown, J. THERMAL ANALYSIS AND CALORIMETRY, 2005 in press.

Another very controversial aspect of solid-state kinetics is the so-called "compensation effect". I have been involved in some aspects of this debate that revolves around whether such effects are meaningful or are mathematical artefacts. I tend to support the latter view.

R18. Compensation parameters in heterogeneous catalysis, A K Galwey and M E Brown, J. CATAL., 60 (1979) 335-338.

R70. Arrhenius parameters and compensation behaviour in solid state decompositions, A K Galwey and M E Brown, THERMOCHIM. ACTA, 300 (1997) 107-115.

R88. The significance of "compensation effects" appearing in data published in "computational aspects of kinetic analysis": ICTAC project, 2000, M E Brown and A K Galwey, THERMOCHIM. ACTA, 387 (2002) 171-183.

Most of my work on kinetics has been restricted to solid-state reactions. An exception was a collaboration with Professor P.T. Kaye's organic chemistry group in examining a complex homogeneous reaction system:

R62. Benzodiazepine analogues. Part 9. Kinetics and mechanism of the azidotrimethylsilane-mediated Schmidt reaction on flavanones. P T Kaye, M J Mphahlele and M E Brown, J. CHEM.SOC.PERKIN TRANS.2, (1995) 835-838.

PYROTECHNICS

As a result of substantial funding for equipment and support of students from AECI Explosives Ltd, a large part of my research has been concerned with industrial applications of pyrotechnic reactions, particularly those used as delays in the detonators used to initiate rock-breaking in the gold mining industry. These combustion-type reactions involve mixtures of initially solid fuels and solid oxidants (together with several additives to improve their physical properties). Once initiated, however, the rate of the exothermic reaction can be extremely rapid and molten and gaseous intermediates are formed. Conventional thermoanalytical techniques, such as differential scanning calorimetry and thermogravimetry, are only marginally useful in the study of these rapid, violently exothermic processes and we received much help and guidance, from the group at the University of Leeds under the direction of Dr P.G. Laye, in setting up appropriate techniques and methods of analysis of the data produced. The main technique involved measurement of temperature-time profiles as the combustion front passed a thermocouple imbedded in a column of the pyrotechnic composition. We began our studies with a detailed examination of the antimony/potassium permanganate pyrotechnic compositions that were commonly used in the longer-period delay fuses.   (Silicon/red lead compositions were the most common short-period delay compositions.) Our first papers in this new field of research were:

R23. Thermal analysis of antimony/potassium permanganate pyrotechnic compositions, M W Beck and M E Brown, THERMOCHIM. ACTA, 65 (1983) 197-212.

R27. Burning of antimony/potassium permanganate pyrotechnic compositions in closed systems, M W Beck and M E Brown, COMBUSTION AND FLAME, 65 (1986) 263-271.

R28. Modification of the burning rates of antimony/potassium permanganate pyrotechnic compositions, M W Beck and M E Brown, COMBUSTION AND FLAME, 66 (1986) 67-75.

C11. Thermochemistry and reaction kinetics of the antimony/potassium permanganate pyrotechnic systems, M W Beck and M E Brown, PYROTECHNICS, Proceedings of the 10th International Pyrotechnic Seminar, Fraunhofer-Institut Fur Treib- und Explosivstoffe, 1985, paper 14.

The rates of pyrotechnic reactions should probably be classified as being totally "sample controlled". Unlike other thermal analysis studies, the rate cannot be controlled by the temperature programme. The temperature profiles thus contain all the kinetic information available and use was made of the rigorous methods of extraction of kinetic parameters developed by Drs Boddington and Laye of Leeds University. For a complete analysis it was necessary to have a means of measuring the thermal conductivity (or thermal diffusivity) of the pyrotechnic compositions. We modified a probe method that had been used for measuring the thermal conductivity of soil samples and, at the same time, were able to improve the numerical analysis of the results obtained, with the help of a colleague in the Department of Mathematics, Prof N.J. Heideman:

R24. Application of a probe technique for measuring the thermal conductivity of pyrotechnic compositions, M W Beck, M E Brown and N J H Heideman,
J. PHYS. E, SCIENTIFIC INSTRUMENTS, 17 (1984) 793-799.

It was also of interest to see what visual information could be obtained through microscopic examination of the reactants and combustion residue:

LC2. Electron microscopic study of intersolid pyrotechnic reactions, M W Beck,
M E Brown and R H M Cross, PROC. ELECTRON MICROSC. SOC. SOUTH AFR., 12 (1982) 95-96.

Although we generally restricted our compositions to binary mixtures of a single fuel and a single oxidant, without any of the practical small-scale additives such as binders, the choice of systems to consider was still huge. One of the questions that we were trying to answer was whether the fuel and the oxidant interacted in the solid state, or whether the oxidant decomposed and the fuel was involved in a solid-gas reaction with the gaseous product of oxidant decomposition. We thus sought an "ideal" binary pyrotechnic system, which we specified as one in which both the decomposition of the oxidant and oxidation of the fuel should occur with simple stoichiometries. On these criteria, the antimony/potassium permanganate system was particularly *unsuitable*, in spite of its industrial importance.

Our survey suggested that the alkaline-earth metal peroxides might be suitable and we did a preliminary study of their thermal behaviour:

LC4. Thermal analysis of pyrotechnic oxidants: barium and strontium peroxides,
R L Drennan and M E Brown, PROC. 2nd NATIONAL SYMPOSIUM ON EXPLOSIVES AND BALLISTICS, Pretoria (1990) 101-105.

R58. Thermal decomposition of barium and strontium peroxides, M J Tribelhorn and
M E Brown, THERMOCHIM. ACTA, 255 (1995) 143-154.

Having selected an oxidant, one is faced with finding suitable fuels to make up binary compositions that would actually sustain combustion and which would give maximum combustion temperatures below the melting points of the thermocouples available. Of many such combinations tested unsuccessfully, we opted for a comparison of the behaviour of manganese and molybdenum as fuels, initially in binary combinations with the peroxides, above, as oxidants, and later as ternary systems with either mixed fuels or mixed oxidants:

C13. A thermal study of the manganese/barium peroxide pyrotechnic system,
M E Brown and R L Drennan, PROC. 14th INTERNATIONAL PYROTECHNIC
SEMINAR, Jersey, (1989) 423-432.

R45. Binary and ternary pyrotechnic systems of Mn and/or Mo and BaO_2 and/or SrO_2.
Part I: Thermal analysis, R L Drennan and M E Brown, THERMOCHIM. ACTA,
208 (1992) 201-221.

R46. Binary and ternary pyrotechnic systems of Mn and/or Mo and BaO_2 and/or SrO_2.
Part II: Combustion studies, R L Drennan and M E Brown, THERMOCHIM. ACTA,
208 (1992) 223-246.

R47. Binary and ternary pyrotechnic systems of Mn and/or Mo and BaO_2 and/or SrO_2.
Part III: Kinetic aspects, R L Drennan and M E Brown, THERMOCHIM. ACTA,
208 (1992) 247-259.

The choice of fuel has also to be modified by practical considerations such as cost and
toxicity. To meet both of these requirements and the criterion of simple stoichiometry of the
oxide, we chose zinc metal as a potential fuel:

C20.   A thermoanalytical study of some zinc-fuelled binary pyrotechnic systems,
M J Tribelhorn and M E Brown, PROC. 6TH EUROPEAN SYMPOSIUM ON
THERMAL ANALYSIS, Italy 1994, THERMOCHIM. ACTA,
269/270 (1995) 649-663.

R60. Combustion of some zinc-fuelled binary pyrotechnic systems, M J Tribelhorn
and M E Brown, THERMOCHIM. ACTA, 256 (1995) 309-324.

Results were not particularly encouraging and we abandoned the stoichiometry criterion in
favour of using a cheap, readily available fuel, namely iron powder:

C18. Comparison of iron and zinc as pyrotechnic fuels, M J Tribelhorn, D S Venables,
M G Blenkinsop and M E Brown, PROC. 5th INTERNATIONAL SYMPOSIUM ON
EXPLOSIVES TECHNOLOGY AND BALLISTICS, National Institute of Explosives
Technology, Pretoria Technikon, (1994) 180-190.

R59. Combustion of some iron-fuelled binary pyrotechnic systems, M J Tribelhorn
and M E Brown, THERMOCHIM. ACTA, 256 (1995) 291-307.

In an attempt to increase the information obtained, we used thermomagnetometry (TM) as an
additional technique.   TG curves for all three Fe/oxidant systems, iron/potassium
permanganate, iron/barium peroxide, and iron/strontium peroxide, heated in powder form in
nitrogen at 20 K min^{-1} showed superimposition of the oxidation of Fe on the decompositions
of the oxidants. DTA traces showed strongly exothermic processes corresponding to ignition.
The TM traces showed the same features as that of Fe in air, suggesting that reaction under
these conditions is solid-gas with little or no interaction between Fe and the solid oxidants. In
some mixtures the presence of unreacted Fe was apparent from the Curie transition at 780°C.
Fe/oxidant pellets behaved differently from loose powders, but there was no conclusive
evidence for solid-solid reaction mechanisms. Most of the observations could be explained by
trapping of the gaseous products of oxidant decomposition within the pellets.

C16. Use of thermomagnetometry in the study of iron-containing pyrotechnic systems,
M E Brown, M J Tribelhorn and M G Blenkinsop, PROC. 10th ICTA, Hatfield, UK, 1992,
J. THERMAL ANALYSIS, 40 (1993) 1123-1130.

Another student began a parallel study using silicon powder as the (non-metallic) fuel in binary combinations with a variety of oxidants (excluding the well studied and very rapid burning silicon/red lead system). The main question in the field of pyrotechnic combustion, for which an answer is still being sought, is what factor is mainly responsible for determining the linear burning rate of an initially solid fuel/oxidant mixture? The major objective of this study was to obtain information on the role of different oxidants in reaction with a single, common fuel, silicon, which meets the criterion of a relatively simple oxidation stoichiometry. The maximum burning rate for the Si/oxidant sysyems studied followed the trend $KNO_3 > SnO_2 > Sb_2O_3 > Fe_2O_3$. The same trend was observed for the maximum temperatures recorded during combustion. The activation energies for combustion were in the reverse order with no value available for Si/KNO_3. The maximum temperatures approach, but still remain below the melting points of Si and the oxidants, which suggests that burning in both systems must occur either through solid-solid reactions, or that the products may form some lower melting eutectics. The Si/O_2 (g) reaction is known to be hindered by the formation of a protective layer of SiO_2 product. At one extreme, the oxidant could influence the reaction by its role, through thermal decomposition, in supplying oxygen (gas) for oxidation of the fuel. At the other extreme, simultaneous diffusion of two or more species through a developing layer of solid product may occur and the sizes and charges of the diffusing species may be important, as well as the maintenance of contact at the origins of the diffusion paths. Melting and/or vaporization of the oxidant will be important in the maintenance of such contact. In contrast to the thermal stability of Fe_2O_3 and SnO_2, KNO_3 melts at relatively low temperatures and also decomposes. Contact between fuel and molten oxidant will be good and Si/KNO_3 mixtures burn over a wide range of compositions. Mobility of Sb_2O_3 is expected to be relatively high through sublimation, but the range of burning rates in the Si/Sb_2O_3 system lies between that for the Si/Fe_2O_3 system and that for the Si/SnO_2 system, which could indicate that adsorption of unchanged Sb_2O_3 on Si surfaces precedes oxidation of Si. From the above discussion, it may be concluded that fuel/oxidant interactions may fit into one of several patterns lying between the extremes of solid-solid reactions involving diffusion of species derived from the fuel into the structure of the oxidant, and oxidation of the fuel by gaseous products of oxidant decomposition. Detailed knowledge is needed of the thermal behaviour of the fuel in oxygen and of the structural and thermal characteristics of possible oxidation products, as well as of the thermal stability of the oxidant and any likely decomposition products. The participation of liquid and/or gaseous phases may be difficult to detect, but is of great practical importance.

R43. Reactions of powdered silicon with some pyrotechnic oxidants, R A Rugunanan and
M E Brown, J. THERMAL ANALYSIS, 37 (1991) 1193-1211.

R52. Combustion of binary and ternary silicon/oxidant pyrotechnic systems.
Part I Fe_2O_3 and SnO_2 as oxidants, R A Rugunanan and M E Brown, COMBUSTION
SCIENCE AND TECHNOLOGY, 95 (1994) 61-83.

R53. Combustion of binary and ternary silicon/oxidant pyrotechnic systems.
Part II Sb_2O_3 and KNO_3 as oxidants, R A Rugunanan and M E Brown, COMBUSTION
SCIENCE AND TECHNOLOGY, 95 (1994) 85-99.

R54. Combustion of binary and ternary silicon/oxidant pyrotechnic systems.
Part III Ternary systems, R A Rugunanan and M E Brown, COMBUSTION SCIENCE AND TECHNOLOGY, 95 (1994) 101-115.

R55. Combustion of binary and ternary silicon/oxidant pyrotechnic systems.
Part IV Kinetic aspects, R A Rugunanan and M E Brown, COMBUSTION SCIENCE AND TECHNOLOGY, 95 (1994) 117-138.

Some review papers covering the findings of these and related studies are:

R38. Thermal analysis of energetic materials, M E Brown, THERMOCHIM. ACTA, 148 (1989) 521-531.

C17. Fuel/oxidant relationships in some binary pyrotechnic systems, M E Brown, M W Beck, R L Drennan, R A Rugunanan, M J Tribelhorn and M G Blenkinsop, PROC. 4th INTERNATIONAL SYMPOSIUM ON EXPLOSIVES TECHNOLOGY AND BALLISTICS, National Institute of Explosives Technology, Pretoria Technikon, (1992) 391-405.

Many of the pyrotechnic compositions tested resulted in high combustion temperatures that destroyed the measuring thermocouple. To cope with higher temperatures, a survey was done of the possible use of optical/infrared pyrometry. The conclusion was that the response times and spatial resolutions of available pyrometers were not adequate, even if one could devise a technique for viewing the combustion front rather than the exterior surface.

R44. The use of pyrometry in the study of fast thermal processes involving initially solid samples, R A Rugunanan and M E Brown, J. THERMAL ANALYSIS, 37 (1991) 2125-2141.

At the request of AECI Explosives, we undertook a study of the oldest pyrotechnic composition known to man - "gun powder", or more technically correct "black powder" - produced by the company in large quantities by a wet process that was safer than the more conventional dry mixing. Simultaneous TG-DTA studies of these black powder compositions after drying, as well as of binary mixtures of the constituents, in nitrogen, showed no reaction between sulfur and charcoal. The charcoal/KNO_3 combination undergoes a strongly exothermic reaction between 380 and 550 ^{o}C. During normal thermal analysis of sulfur-containing mixtures, sulfur vaporizes above its liquid-liquid transition (171 ^{o}C) and below the melting point of KNO_3 (315 ^{o}C) so there is no significant reaction between sulfur vapour and solid KNO_3. If the escape of sulfur vapour is decreased, through use of high heating rates, or a preheated furnace, some of the sulfur can be induced to react with molten KNO_3. The reaction between sulfur vapour and molten KNO_3 in ternary systems is regarded as the pre-ignition reaction, and the higher temperature oxidation of solid charcoal by molten KNO_3 propagates the combustion of black powder. In air, sulfur oxidizes at temperatures below the melting-point of KNO_3.

C12. A thermo-analytical study of the pyrotechnic reactions of black powder and its constituents, M E Brown and R A Rugunanan, PROC. 9th ICTA, Jerusalem, THERMOCHIM. ACTA, 134 (1988) 413-418.

The behaviour of black powder under the less-controlled conditions of ignition and combustion was examined by simultaneous measurement of temperature profiles and burning rates. Curves of burning-rate against composition for sulfurless mixtures of charcoal/KNO_3 and for mixtures with various proportions of sulfur were concave-down-type curves. The compositions of mixtures with maximum burning rates did not correspond with the compositions of mixtures with maximum enthalpy-of-reaction. Maximum temperatures of about l400 ^{o}C were recorded. Burning rates were found to decrease with increasing particle-size of the constituents; with increasing compaction of the mixtures, or when inert diluents or subsidiary fuels were added to these mixtures. Burning rates were also affected by moisture contents above 2%, and failure of burning occurred at > 15% moisture.

R37. A temperature-profile study of the combustion of black powder and its constituent mixtures, M E Brown and R A Rugunanan, PROPELLANTS, EXPLOSIVES AND PYROTECHNICS, 14 (1989) 69-75.

In addition to the practical testing of pyrotechnic compositions, it was of considerable interest to try to predict their combustion properties from the physical properties and thermochemical data available for the fuel and the oxidant. Some computer codes in use at ICI Explosives in the UK were made available to us and several simulations were done.

The two-dimensional simulation of DTA scans on a strongly exothermic sample, enables the progress of the reaction and the temperature distributions in the sample, sample container and instrument sensors to be examined. Of the several possible variables whose influence could be studied, we chose the thermal conductivity of the sample and did simulations of a sample with (a) high thermal conductivity (2000 W m^{-1} K^{-1}) and (b) a low thermal conductivity (0.30 W m^{-1} K^{-1}) typical of powder samples. The high value in (a) was chosen to attempt to approximate conditions of more uniform temperature distribution than expected for (b). If an assumption of uniform temperature and extent of reaction did apply to case (a), thermal runaway would still be expected, largely due to the poor thermal coupling between the sample containers and the furnace. The simulated DTA trace did show that thermal runaway occurs, although the variations of temperature and extent of reaction through the sample are relatively small compared to case (b). In case (b), the variation in temperature through the sample becomes more apparent and the thermal runaway is dramatic with the high temperatures and high values of extent of reaction developing most rapidly at the top centre of the sample. The difficulty of extracting kinetic information from such DTA traces was discussed.

R40. Kinetic analysis of simulated DTA responses, M W Beck and M E Brown, THERMOCHIM. ACTA, 164 (1990) 379-393.

R41. Finite element simulation of the differential thermal analysis response to ignition of a pyrotechnic composition, M W Beck and M E Brown, J. CHEM. SOC. FARADAY TRANS., 87 (1991) 711-715.

The finite-difference and the finite-element models were both useful for exploring the potential effects of variation of adjustable parameters on the combustion of pyrotechnic systems. With care, reasonable agreement between experimental and simulated results could be obtained. The kinetic parameters have the greatest influence on the simulations and reliable values of these parameters are required. The use of an autocatalytic-type of rate-equation, rather than the assumption of a simple order-of-reaction kinetic equation gave improved agreement between experiment and simulation.

C19.   Computer modelling of pyrotechnic combustion, S J Taylor and M E Brown,
PROC. 5th INTERNATIONAL SYMPOSIUM ON EXPLOSIVES TECHNOLOGY
AND BALLISTICS, National Institute of Explosives Technology,
Pretoria Technikon, (1994) 167-179.

We also modelled the packing of particles of fuel and oxidant and attempted to couple
changes in burning properties to the degree of fuel/oxidant contact. On the assumption that
the fuel and oxidant powders consisted of uniform spherical particles of different sizes, the
calculated numbers of contact points were compared with the experimental burning rates of
these mixtures. In spite of the severe approximations made, there was a qualitative connection
between the calculated numbers of contact points and the measured burning rates of those
pyrotechnic compositions which are presumed to burn mainly via solid-solid reactions.

R73. Fuel-oxidant particle contact in binary pyrotechnic reactions, M E Brown, S J Taylor
and M J Tribelhorn, PROPELLANTS, EXPLOSIVES AND PYROTECHNICS,
23 (1998) 320-327.

In an invited lecture at the National Conference of the Polish Thermal Analysis Society, I
reviewed the results of our pyrotechnic studies.

R85. Some thermal studies on pyrotechnic compositions, M E Brown,
J. THERMAL ANALYSIS AND CALORIMETRY, 65 (2001) 323-334.

Fuels have ranged from metals, such as iron, manganese and molybdenum, to non-metals
such as silicon, carbon and sulfur, and oxidants have been oxides, peroxides and oxysalts.
Some of the constituents are presumed to have remained in the solid state, while others have
definitely melted, vaporized, or decomposed to yield some gaseous products. Mechanisms
encountered thus cover the wide field of solid-solid, solid-liquid, solid-gas, and possibly even
liquid-gas and liquid-liquid reactions. The main experimental techniques used have been
thermal analysis, measurement and analysis of temperature profiles, and simultaneous burning
rate determinations. The thermal conductivities of the constituents and the mixtures have also
been measured and the reactants and combustion residues have been examined using scanning
electron microscopy, infrared spectroscopy and X-ray diffraction. Most of the oxidants
studied, except Fe_2O_3, Sb_2O_3 and SnO_2, decompose with some release of $O_2(g)$ at
temperatures often well below the recorded values of the maximum combustion temperature.
Sb_2O_3 melts and vaporizes and KNO_3 melts and decomposes. The melting points of the fuels
are high (excluding Sb and the complex thermal behaviour of charcoal that puts it in a
separate class of fuels). Substitution of SrO_2 for the apparently chemically similar oxidant,
BaO_2, does not affect the burning rate of Mn/peroxide compositions as much as it affects the
Mo/peroxide compositions. Variation of the constituents of the binary mixtures studied
resulted in burning rates of from 2 to 115 mm s^{-1}.   A similar range could, however, be
achieved by varying the composition from 20 to 70% fuel of the fixed binary combination,
Fe/$KMnO_4$. Variation of the particle-size of the fuel in the Sb/$KMnO_4$ system from a radius
of 14 to 2.0 μm changed the burning rate from 2 to 8 mm s^{-1}, compared to the range of 2 to 28
mm s^{-1} with change in composition.   Decreasing the particle-radius of Mo from 17.2 to 6.9
μm produced faster burning Mo/peroxide mixtures than were possible by varying the
composition of the mixtures with the larger Mo particles.

Combustion studies of pyrotechnic systems are severely hampered by limitations of the techniques available. Both thermal analysis and temperature profile measurement using thermocouples are limited to temperatures below 1700 °C by the materials of construction. Materials available for use at higher temperatures usually require inert atmospheres and are thus incompatible with the presence of oxidants. Materials should also not alloy with the fuels which are often metals, usually with relatively low melting points. Thermal analysis is also limited by the response of the sensor system. The constraints above mean that the systems studied lie in a relatively limited region of the multi-dimensional matrix of variables and broader trends may be inaccessible until new techniques and/or sensors suitable for rapid measurement of high temperatures become available.

As happens in many areas of science, changes and advances in technology can have a dramatic effect on a research field. The development of an electronically timed delay fuse for detonators, although initially vastly more expensive than chemical delays, has provided such increased accuracy and reproducibility that the expense is warranted in special applications, such as the precision implosion of buildings. Like all such electronic devices, prices have gone down as demands have increased, and companies, such as AECI Explosives, have cut back on research on new chemical fuses while concentrating on improving the performance of existing chemical fuses.

As an offshoot of studies on some highly unstable compounds prepared by colleagues at the University of Fort Hare, we suggested the use of very small quantities of such strongly exothermic materials for the temperature calibration of thermobalances. The decompositions can give very sharp mass changes which can be related to the strong, sharp exotherms observed in a calibrated differential scanning calorimeter.

R57. Temperature calibration in thermogravimetry using energetic materials, M E Brown, T T Bhengu and D K Sanyal, THERMOCHIM. ACTA, 242 (1994) 141-152.

THERMAL AND PHOTOSTABILITY OF DRUGS

With the changes in the explosives industry described above, I was fortunate to be able to collaborate with Professor Beverley Glass of the School of Pharmaceutical Sciences. With her knowledge of pharmaceutical chemistry and expertise in photostability studies and my experience in thermal analysis techniques and solid-state kinetics, we chose as our main theme the comparison of the photostabilities of pharmaceuticals with their thermal behaviour and their general pharmaceutical activity. Of particular interest have been the effects of various cyclodextrins used as excipients in drugs on their thermal and photostabilities, possibly through formation of drug/cyclodextrin inclusion complexes. In spite of the move of Professor Glass to James Cook University in Australia, our collaboration continues.

In an earlier review (see above), I had examined the influence that the Prout-Tompkins rate equation had had in solid state kinetics, and had found that it had been extensively used in describing drug stability. We examined some of these applications in more detail.

R78. Pharmaceutical applications of the Prout-Tompkins rate equation,
M E Brown and B D Glass, INT. J. PHARM., 190 (1999) 129-137.

Many of the studies that we have published have been done in response to requests from the pharmaceutical industry for examination of their products. For example, propyl-piperazine-substituted phenothiazines are an important subclass of the phenothiazines due to their increased potency over the prototype chlorpromazine, with fluphenazine displaying the greatest neuroleptic potency due to increased affinity of the 13-hydroxyethyl side chain for the trifluoromethyl group that enhances interaction with the dopamine receptor. Consideration of the effects of these structural differences on their activity and photostability are important, as is the determination of the nature of the degradants which could have adverse effects, for example, the 2-hydroxy derivatives have been implicated in photosensitivity effects. Stability studies in solution showed perphenazine to be the least stable of all the derivatives. Although dechlorination and sulphoxidation occurred under all light conditions studied, dechlorination with subsequent photoreduction and substitution proved to be a major degradation pathway. For the trifluoromethyl derivatives, the sulphoxide and sulphone were identified as intermediates. In the solid-state studies, sulphoxidation appeared to be the major degradation pathway with the dechloro derivative isolated from perphenazine. Thus the design of these derivatives to include the trifluoromethyl group to improve activity over the chloro derivatives has merit, especially taking into account the instability of chloroaromatic compounds and the involvement of the photosubstituted product in photosensitivity reactions, while other pathways e.g. N-demethylation, sulphoxidation and aromatic hydroxylation are in common with those reported in in vivo metabolic pathways. The inclusion of the 3-hydroxyethyl group, as opposed to the methyl group, in the side chain to improve activity is questionable in terms of its effect on stability.

R79. Photoreactivity versus activity of a selected class of phenothiazines: A comparative study, B D Glass, M E Brown and P M Drummond, Drugs: Photochemistry and Photostability, (Ed. A Albini and E Fasani), Royal Society of Chemistry, Cambridge, UK, 1998, p.134-149.

Differential scanning calorimetry (DSC) is particularly useful in examining interactions between drugs and excipients for possible incompatibilities. This method can detect, but not indicate the extent of, destabilizing effects of excipients. Interpretation of the DSC results is not straightforward because many types of drug-excipient interaction are possible. These include eutectic formation, solid-solid reactions (possibly complicated by solid-phase transitions), solid-liquid reactions and solid-gas reactions (particularly hydrolysis by evolved water vapour). Mixtures of prochlorperazine maleate with beta- or gamma-cyclodextrin indicated partial inclusion of the drug in the cyclodextrin cavities.

R80. DSC screening of potential prochlorperazine-excipient interactions in preformulation studies, M E Brown, E M Antunes, B D Glass, M Lebete and R B Walker, J. THERMAL ANALYSIS AND CALORIMETRY, 56 (1999) 1317-1322.

Nifedipine is a highly photolabile, practically water-insoluble drug used therapeutically as a calcium channel antagonist for the treatment of various cardiovascular disorders. Bioavailability is poor and erratic following oral administration of crystalline nifedipine, due to its low aqueous solubility and slow dissolution rate within the gastrointestinal tract. Attempts were made to prepare solid-state nifedipine - cyclodextrin inclusion complexes using beta-cyclodextrin (BCD), gamma-cyclodextrin (GCD), 2-hydroxypropyl-beta-cyclodextrin (2HPBCD), randomly methylated-beta-cyclodextrin (RMBCD) and heptakis (2,6-O-dimethyl)- beta-cyclodextrin (DMBCD) and processes, such as kneading and heating methods, that could be easily and cost-effectively implemented in an industrial environment.

The behaviour of these mixtures was studied using differential scanning calorimetry (DSC), diffuse reflectance mid-infrared spectroscopy (FTIR) and X-ray diffractometry (XRD). DSC revealed the nifedipine melting endotherm with onset at approximately 171°C for the kneaded mixtures with BCD, GCD and 2HPBCD, thus confirming the presence of nifedipine in the crystalline state, while some decrease in crystallinity was observed in the DMBCD kneaded mixture. With RMBCD, however, broadening and shifting of the nifedipine endotherm and reduction in its intensity suggested that the kneading could have produced an amorphous inclusion complex. These differing extents of interaction of nifedipine with the cyclodextrins were confirmed by FTIR and XRD studies.

R90. Binary systems of nifedipine and various cyclodextrins in the solid state, thermal, FTIR, XRD studies, M E Brown, B D Glass and M S Worthington, J. THERMAL ANALYSIS AND CALORIMETRY, 68 (2002) 631-646.

Triprolidine hydrochloride (TPH) is a well-known antihistamine drug which is reported as being photosensitive. The thermal stabilities of TPH and of 1:1 molar and 1:1 mass ratio physical mixtures of TPH with beta-cyclodextrin (BCD) and with glucose were examined using DSC, TG and TG-FTIR, complemented by X-ray powder diffraction (XRD) and infrared spectroscopy. Thermal studies of the solid TPH/BCD mixtures indicated that interaction between the components occurs and it is possible that the TPH molecule may be least partially accommodated in the cavity of the BCD host molecule. XRD results supported this indication of inclusion. The results of molecular modelling suggested that TPH is most likely to be accommodated in the BCD cavity as a neutral triprolidine molecule with the toluene portion of the molecule preferentially included in the cavity. The study also showed TPH to be compatible with both glucose and BCD, which are potential excipients both in solid and liquid dosage forms. The presence of these excipients in dosage forms will thus not adversely affect the stability and the therapeutic efficacy of TPH.

R94. The thermal stability of triprolidine hydrochloride and its mixtures with cyclodextrin and glucose, V J Ndlebe, M E Brown and B D Glass, J. THERMAL ANALYSIS AND CALORIMETRY, 77 (2004) 445-457.

TPH and its binary mixtures with beta-cyclodextrin (BCD) and glucose, were irradiated using an Atlas Suntest irradiation chamber and conditions according to the guidelines of the International Committee on Harmonization (ICH). HPLC analysis was used to determine the extent of photodegradation. XRD results showed that changes in the TPH crystal structure had occurred during irradiation and that these changes increased with the time of irradiation. Although the potential for isomerization to the pharmaceutically inactive Z-isomer under the influence of UV-light exists, results have proved that this transformation for solid-state TPH would require more extreme light conditions. The results of this study thus illustrate the general light stability of TPH in the solid-state.

R95. Photostability of triprolidine hydrochloride and its mixtures with cyclodextrin and glucose, V J Ndlebe, M E Brown and B D Glass, J. THERMAL ANALYSIS AND CALORIMETRY, 77 (2004) 459-470.

Because of the molecular complexity of many drugs, we chose, in addition to this sponsored research, to do a more fundamental study, in as much detail as possible, of the interactions between some fairly simple organic molecules (benzoic and salicylic acids) and cyclodextrins,

to act as a reference point for extending these studies to examination of the aminosalicylic acids and their sodium salts, which are of greater pharmaceutical interest.

R84. Thermal studies on some substituted aminobenzoic acids, M K Rotich, B D Glass and M E Brown, J. THERMAL ANALYSIS AND CALORIMETRY, 64 (2001) 681-688.

The thermal behaviours of the substituted aminobenzoic acids (3-aminobenzoic acid (3-ABA), 4-aminobenzoic acid (4-ABA), 3-aminosalicylic acid (3-ASA), 4-aminosalicylic acid (4-ASA), and 5-aminosalicylic acid (5-ASA), as well as of the parent benzoic acid (BA) and salicylic acid (SA) as reference substances, and possible decomposition products: 2-aminophenol, 3-aminophenol and 4-aminophenol were examined. Most of the compounds began to sublime well before melting, generally with an increasing rate of mass loss beyond the melting points, which are considerably different for the different isomers. The differences in behaviour of 4-ASA and 5-ASA were the most remarkable, with 5-ASA being far more stable and apparently not decarboxylating readily. 4-ASA appears to sublime at temperatures below the melting point, becoming less stable and decarboxylating in the liquid form.

R91. Thermal studies on mixtures of benzoic and salicylic acids with cyclodextrins, M K Rotich, M E Brown and B D Glass, J. THERMAL ANALYSIS AND CALORIMETRY, 73 (2003) 671-686.

The thermal behaviours of benzoic and salicylic acids were compared with the behaviours of 1:1 molar ratio physical and kneaded mixtures of these acids with each of three different cyclodextrins (beta-, hydroxypropyl-beta-, and gamma-cyclodextrin). There were significant interactions in both physical and kneaded mixtures of benzoic acid and the cyclodextrins with interactions in the kneaded benzoic acid/gamma-cyclodextrin mixtures being the most extensive as might be expected for the cyclodextrin with the largest molecular cavity. The results for the mixtures of salicylic acid with the cyclodextrins were similar to those for benzoic acid mixture, with the kneaded salicylic acid/gamma-cyclodextrin mixture again showing the most interaction.

R92. Thermal studies on mixtures of aminosalicylic acids with cyclodextrins, M K Rotich, M E Brown and B D Glass, J. THERMAL ANALYSIS AND CALORIMETRY, 73 (2003) 687-706.

Comparison of the effects of the different cyclodextrins on the behaviour of the individual aminosalicylic acid isomers showed that hydroxypropyl-beta-cyclodextrin has the greatest interaction with 3-aminosalicylic acid and 5-aminosalicylic acid, followed by gamma-cyclodextrin, while beta-cyclodextrin generally shows the least interaction. For 4-aminosalicylic acid, the effect of GCD seems to be more marked than for 3-aminosalicylic acid and 5-aminosalicylic acid.

R93. Thermal studies on the sodium salts of aminosalicylic acids, M K Rotich, M E Brown and B D Glass, J. THERMAL ANALYSIS AND CALORIMETRY, 73 (2003) 499-508.

The DSC curves for the sodium salts of all of the isomers showed complex dehydration/decomposition endotherms. TG-FTIR results for the sodium salt of 3-aminosalicylic acid showed the evolution of carbon dioxide in three stages: below 150 °C, between 200 and 300°C and continuous formation up to 500 °C. This behaviour differs from

that of 3-aminosalicylic acid itself, which forms CO_2 between 225 and 290 °C. For the sodium salt of 4-aminosalicylic acid, the formation of carbon dioxide starts from 250 ºC and is still being formed at about 650 ºC. 4-aminosalicylic acid decarboxylates above 150 ºC. 5-aminosalicylic acid and its sodium salt showed no evolution of carbon dioxide below 600 ºC.

A recent area of interest has been the application of artificial neural networks to pharmaceutical problems, making use of the expertise of Dr S. Agotonovic-Kustrin.

R96. Modelling the thermal behaviour of carboxylic acid derivatives with cyclodextrin in the solid state, S Agotonovic-Kustrin, B D Glass, M E Brown and M K Rotich, J. THERMAL ANALYSIS AND CALORIMETRY, 77 (2004) 391-402.

The application of classical QSAR and molecular modelling to the inclusion complexation of natural and modified cyclodextrins (CDs) with carboxylic acid derivatives as guest molecules was examined. The information described above on the thermal behaviour in the solid-state of benzoic acid (BA), salicylic acid (SA), and various substituted aminosalicylic acids (3-aminosalicylic acid, 3-ASA, 4-aminosalicylic acid, 4-ASA and 5-aminosalicylic acid, 5-ASA), as well as on the thermal behaviour of 1:1 molar ratio physical and kneaded mixtures of these acids with each of three different cyclodextrins, beta-, (BCD) 2-hydroxypropyl-beta-, (HPBCD) and gamma-cyclodextrin (GCD), was modelled using stepwise multiple regression (SMR). Two models for the prediction of the percentage mass loss and enthalpy of dehydration of the physical mixtures were established with correlation coefficients (*r*) of 0.79 and 0.92, respectively. Decreased correlation in the thermal behaviour of kneaded mixtures indicated significant interaction and possible formation of inclusion complexes.

Recently we published a comprehensive review covering the attempts to relate thermal and photostabilities.

R97. The thermal and photostability of solid pharmaceuticals - A review, B D Glass, Cs Novak and M E Brown, J. THERMAL ANALYSIS AND CALORIMETRY, 77 (2004) 1013-1036.

The stability of drugs towards heat, moisture, oxidation and exposure to light is a topic of great practical interest and any degradation will usually adversely affect the therapeutic activity of the drug. Unless very special precautions are taken, most drugs will receive some exposure to light and will generally be expected to be able to tolerate room temperature. One of the interesting questions that arises in considering drug stability, and which is discussed in this review, is the possible correlation between thermal degradation and photodegradation. This general topic could be further subdivided into examining correlations between photodegradation in solution (including the influences of the solvent) and in the solid state. Far more studies of photodegradation of drugs in aqueous solution have been carried out than of solid drugs or drug formulations in the solid state, because of the experimental difficulties. Thermal degradation of drugs in solution (again including use of different solvents) does not appear to have been as extensively studied as has the thermal behaviour of solid drugs and drug formulations. These latter thermal studies have been of particular value in revealing actual and potential drug-excipient interactions and are essential for obtaining information on the conditions for existence of drug polymorphs. In the solid state, the temperatures required for thermal degradation at a measurable rate are generally far higher than the temperatures existing, even locally, during photolysis, so the mechanisms of thermal and photochemical degradation can be expected to differ.   The thermal and photostability of different

polymorphic forms of drug substances is especially important. Various crystal forms of drug substances exhibit differences in thermal behaviour and also in photostability.

ARTICLES OF A GENERAL NATURE

Although the writing of monographs and textbooks has been by main contribution to the broader communication of my research area, I have published some more general reviews and popular articles.

G1. The role of defects in the decomposition of solids, M E Brown, CHEMSA, 5 (1979) 74-5.

G2. Thermal Analysis - a group of often-neglected techniques, M E Brown, CHEMSA, 7 (1981) 192-195.

G3. 80 years of Chemistry at Rhodes, M E Brown, D J Eve and T M Letcher, CHEMSA, 9 (1983) 136-139.

G4. Pyrotechnic Delay Compositions, M W Beck, M E Brown and D Cawthorne, CHEMSA, 10 June (1984) 398-401.

G5. 100 Years of Chemistry at Rhodes University, M E Brown, D J Eve, P T Kaye, D E A Rivett and G M Watkins, SA J. SCIENCE, 100 (2004) 530 - 538.

A very-talented Honours level student, Miss L.A. Collett, wrote a review under my supervision, which was publishable:

R72. Biochemical and biological applications of thermal analysis, L A Collett and M E Brown, J. THERMAL ANALYSIS, 51 (1998) 693-726.

Several topics have proved suitable for publication in educational journals:

E1. Xtal-Line, A board game in crystallography, A Allsobrook, M E Brown and L Glasser, J. CHEM. EDUC., 50 (1973) 688-9.

This described a three-dimensional version of "tic-tac-toe" or "noughts and crosses" with analogies to crystal structures.

E2. Non-isothermal kinetics, M E Brown and C A R Phillpotts, J. CHEM. EDUC., 55 (1978) 556-560.

This paper was one of the first more general attempts to describe the methods of kinetic analysis, at a level accessible by a non-specialist, that had been developed for extracting kinetic parameters from the results of programmed-temperature experiments in thermal analysis. Mr Phillpotts added his expertise in the developing area of computer graphics. The paper has been well-cited.

E3. Determination of purity by differential scanning calorimetry, M E Brown, J. CHEM EDUC., 56 (1979) 310-313.

The detailed analysis of the melting of substances containing small amounts of impurities is an interesting application of an important part of the theory of phase equilibria. This paper has also received many citations.

E4. Diagrams to illustrate the meaning of the activation energy of reaction, M E Brown and A Goosen, SPECTRUM, 20 (2) (1982) 10-13.

E5. Thermodynamically and Kinetically Controlled Products, M E Brown, K J Buchanan and A Goosen, J. CHEM EDUC., 62 (1985) 575-578.

These last two papers were attempts to clarify some important but confusing concepts.

CONCLUSIONS

In summary, my areas of research have been :
- Effects of irradiation on solids (PhD topic)
- Silver refining (while at the Chamber of Mines)
- Kinetics of decomposition of solids (with Dr A.K. Galwey and various others)
- Techniques of thermal analysis
- Pyrotechnic delay systems (with support from AECI Explosives)
- Thermal and photostability of drugs (with Prof B.D. Glass)

I have been extremely fortunate in my collaborations. The value of constructive discussion and criticism of one's own work by conscientious, reliable people cannot be overestimated. The result is always greater than the sum of the individual contributions, so it is difficult to give them relative weighting. Sometimes work has been divided on the basis of expertise and equipment available and the results have again been combined, while, on other occasions, one small suggestion has untangled masses of laborious data collection.

J.A. Hedvall, in his book, "Solid State Chemistry: Whence, Where and Wither", Elsevier, Amsterdam, 1966, described how a pronouncement by Aristotle was mistranslated into Latin (*corpora non agunt nisi liquida*) from the Greek (*ta hygra meikta malista ton somaton*). The Latin version was translated as: "no reactions could take place without the participation of liquid or gaseous phases" and was a great discouragement to early researchers. The correct Greek form was that: "it is mainly fluid substances that react". Hedvall recalls how these statements challenged him to study reactions in the solid state. The work of Hedvall and others, particularly that described in "Chemistry of the Solid State", edited by W.E. Garner (Butterworths Scientific Publications, London, 1955), challenged many others, including me, to do likewise. Even Aristotle could not have imagined how extremely complex reactions in the solid state would turn out to be. Neither would he have dreamed how important solid-state reactions would become in industry. Achievements have thus been mainly incremental and very dependent upon the development of experimental techniques. With the support of AECI Explosives Ltd., Rhodes University and the National Research Foundation and its predecessors, I have been able to use much of the best equipment. Techniques that offer considerable promise for unravelling more of the complexity in the future include: modulated temperature differential scanning calorimetry, micro-thermal analysis based on atomic force microscopy, improved evolved gas analysis systems, and real-time X-ray diffraction studies if synchrotron radiation should become more accessible.