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Chemistry in New Zealand

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Articles and features

Other columns

Comment from the President

Welcome to the April issue of *Chemistry in New Zealand*. As I mentioned in the last issue, 2018 is a year of change for the Institute because we have a new administrator following Richard Rendle's retirement. I am very pleased to announce that Dr Joanna M. Dowle has been appointed as the new NZIC administrator. Joanna is an experienced chemist with a PhD from Victoria University of Wellington and postdoctoral posts at the University of Chicago and the University of Auckland. Joanna also has considerable experience in administration and has attended her first NZIC Council meeting. I hope you will all make Joanna welcome as she settles into her new role within the NZIC.

2019 is the 150th anniversary of Dmitri Mendeleev's first report of the periodic table and over Christmas it was announced by IUPAC and the United Nations that 2019 will be the International Year of the Periodic Table of Chemical Elements (IYPT 2019; *https://iupac.org/united-nations-proclaims-international-year-periodic-table-chemical-elements*). This represents a huge opportunity to get chemistry out into the public eye. So I hope everyone within the NZIC will start thinking about events we could hold during 2019 to publicise our discipline and the periodic table.

Hopefully most of you will have seen the email with information from Mark Waterland about Pacifichem 2020 (*https://pacifichem.org*). As well as being an excellent conference in a very nice location, Pacifichem provides NZIC with a financial boost. The conference is run by the pacific rim chemical societies and NZIC receives a share of the conference profits. Mark and others recently negotiated an improved profit sharing arrangement for NZIC and some of the other smaller societies. As Mark's information email outlined you can be involved with Pacifichem as an attendee only, where you attend an organised symposia in your sub-discipline, or you also have the opportunity to be a symposium organiser (each symposium needs an organiser from each of the contributing societies). There are also a number of large poster sessions and a student poster competition so there are good opportunities for students too. I hope many of you will consider going to Hawaii in 2020.

Another opportunity that has come up recently is a special issue of *Chemistry – An Asian Journal* that will focus on chemistry in New Zealand. *Chemistry – An Asian Journal* is an international high-impact general chemistry journal published on behalf of the Asian Chemical Editorial Society, an association of 13 major chemical societies from Asia and the Pacific region, including NZIC. Because of our part ownership of the journal, NZIC receives a dividend for each paper that a New Zealand author publishes. My colleague at the University of Otago, Professor Sally Brooker, has just been appointed to the Editorial Board and is the first New Zealander to do so. Sally is keen to increase the profile of the journal in NZ, not least because NZIC gains financially for every paper published with a NZ corresponding author, so she has organised the New Zealand focused special issue which will be published in 2019. The submission deadline is Friday 30 November 2018, so I hope many of you will consider submitting some work – you will find more details in this issue.

On a related note, I received a copy of *Scientific Sleuthing* as a Christmas present and read it over the holiday period. It is an extremely nice book with lots of interesting New Zealand-based chemistry stories that show how important chemistry is to New Zealand. I recommend that you all have a look at the book as the next time someone asks why chemistry is important you could use a NZ-based story to convince them of our discipline's value.

Finally, for now, Paul Plieger has continued to do great work with the web designers and the new NZIC webpage is expected to become live soon with the hope that members will be able to renew memberships online this year.

James Crowley
NZIC President

New Zealand Institute of Chemistry

supporting chemical sciences

April News

Farewell, Richard…….

As most readers will be aware, Richard Rendle stepped down from his role as Honorary General Secretary of NZIC at the beginning of this year. Richard has been a stalwart of our organisation and was recently made HonFNZIC in recognition of the administrative duties he has tirelessly and cheerfully carried out over the past 10 years. We extend our sincere thanks to Richard and we wish him all the very best for the future.

Richard receiving his Honorary Fellowship certificate from Penny Brothers

…….and welcome, Joanna!

Stepping into the role as our new NZIC administrator is Joanna Dowle. Joanna obtained her PhD from Victoria University of Wellington in the area of natural products chemistry. Joanna will be working on a part-time basis from home while also looking after her two young children.

Joanna Dowle

AUCKLAND

University of Auckland

Welcome

Welcome to *Selina* ***Yang*** who is working as a technical assistant in the undergraduate teaching labs alongside *Katrina* ***Graaf***, *Sandra* ***Otty*** and *Jeff* ***Boyle***.

Farewell

On 11 December 2017 we held a School Colloquium, with Professor *Conrad* ***Perera*** talking on *The science behind juice processing*, followed by a reception. This was an opportunity for us to acknowledge Conrad's contributions to the Food Science programme and the School before his retirement.

Events

24th Symposium on Pure and Applied Coordination Chemistry

On 22-24 November 2017, The University of Auckland hosted SPACC24, focussing on aspects of coordination chemistry. There were two invited keynote speakers from the University of Auckland: Dr *Erin* ***Leitao*** with a talk entitled *Creating main-group molecules and polymers using catalysis* and Professor *Penny* ***Brothers*** who discussed *Lighting up sugars: linking BODIPY to sugars through boron*.

Green Chemistry Conference

New Zealand's first Green Chemistry conference, *Green Chemistry New Zealand 2017* (GCNZ17), was successfully held at the Science Centre from 8-9 December 2017. GCNZ17 was organised by the Centre for Green Chemical Science with support from the Vice Chancellor's Strategic Development Fund. The conference was attended by over 130 delegates from 13 different countries. We had 26 talks and 4 keynote lectures (presented by Professor Philip Jessop, Professor Amy Prieto, Professor Ning Yan and Dr Lauren Heine) covering all aspects of green chemistry, ranging from clean chemical synthesis and pollution prevention to next generation batteries and new biorefinery concepts. In addition to the lectures, we also had 35 poster presentations.

The poster prizes were sponsored by the Royal Society of Chemistry journals *Sustainable Energy & Fuels* and *Green Chemistry*. They were judged by Professor Amy Prieto (Colorado State University), who is a member of the advisory board of Sustainable Energy & Fuels, and Professor Philip Jessop (Queen's University, Canada), who is the chair of the editorial board of Green Chemistry.

Congratulations to the winners of our poster prizes! RSC Sustainable

The Role of Medicinal Chemistry in the Search for New Therapeutic Agents: Natural Products vs Peptide

Energy & Fuels Poster Prize: Stephen Lo (The University of Auckland) with Associate Professor *David* ***Barker*** and Dr *Bruno* ***Fedrizzi***: *Derivatisation of flavonoids extracted from food waste*.

Stephen Lo (right), winner of the RSC Sustainable Energy & Fuels Poster Prize with Prof Amy Prieto

RSC Green Chemistry Poster Prize: Ram Bhusal (The University of Auckland) with Associate Professor *Jonathan* ***Sperry***: *A sustainable approach for the synthesis of valued added nitrogen-heterocycles.*

Ram Bhusal (left), winner of the RSC Green Chemistry Poster Prize with Professor Philip Jessop

Nanocamp and Discovery Camp

During the week of 15-19 Jan 2018, investigators from the MacDiarmid Institute at the University of Auckland hosted NanoCamp and Discovery Camp on campus with the help of many PhD students and support staff. Approximately 25 students attended inspiring lectures related to nanoscience and had the chance to do some hands-on science, such as creating solar cells. A big thanks to *Michel* ***Nieuwoudt*** for organising the camp and everyone who contributed to making a memorable experience for our future scientists!

2nd Annual Teaching Symposium

On 16 February 2018 the School held their second annual teaching symposium. The symposium provided some interesting insights into student and staff responses to changes to the way we teach or conduct laboratories. Experiences from our own CHEM 310 and from the University of Sydney show that student engagement and appropriate group assessment activities can have positive effects beyond just those activities. Thank you very much to Kaitlin Beare and Sue Western for organising the symposium. Thanks also to Associate Professor *Geoff* ***Waterhouse***, Dr *Bruno* ***Fedrizzi***, Dr *Malini* ***Arewgoda*** and *Miriana* ***Horacek-Glading***, and our visitor Dr Alice Williamson, for their presentations.

Visitors

On 11 December 2017, Dr Anna McConnell from Kiel University, Germany, gave a seminar on *Metal-organic cages: expanding the toolbox of stimuli-responsive behaviour.*

On 14 December 2017, Associate Professor James Osborne, an extension enology specialist at the Oregon Wine Research Institute, Oregon State University, Corvallis, OR, USA, presented on *The state of the Oregon wine industry and wine microbiology research at the Oregon Wine Research Institute*.

On 15 December 2017, Dr Vedran Jovic based at the Lawrence Berkeley National Laboratory in California gave a seminar on *The electronic band structure of III-N semiconductors and metal oxides; materials for the electronic and renewable energy sectors.*

On 30 January, Professor Barry Sharpless, recipient of the 2001 Nobel prize in Chemistry, visited the University of Auckland and gave an inspiring lecture on *Click chemistry.*

On 16 February, *James* ***Crowley*** gave an exciting seminar entitled, *Functional metallosupramolecular architectures: molecular recognition and biological activity.*

On 20 February, the 2017 RACI Physical Chemistry Division Lecturer, Dr Lars Goerigk, presented an NZIC-sponsored lecture entitled, *An excursion to the density functional theory zoo: insights for electronic ground and excited states.*

Congratulations

Anoma ***Ratnayake*** won a Sustained Contribution Excellence Award, one of the Science Professional Staff Excellence awards. The award was in recognition of the key roles Anoma has played in support of the School of Chemical Sciences and the Head, and was very well deserved.

Dr *Wan-Ting* ***Chen*** won second prize in the postdoc/student poster competition at the MacDiarmid Institute Annual Meeting in Wellington (Nov 30-Dec 1).

PhD student *Aubrey* ***Dosado*** placed second in the student/postdoc poster competition at the ANSTO User Meeting 2017, held in Melbourne 22-24 November. This was a joint meeting incorporating the Australian Neutron Beam Users Group and the Australian Synchrotron with over 200 participants. Aubrey's poster was entitled *Upconversion phosphors for efficient solar energy capture*, with the prize being a certificate and an iPad (5th generation).

Kyriakos Varnava, won the Biomedical Imaging Research Unit (BIRU) electron microscopy image competition. Kyriakos is a PhD student supervised by Dr *Viji* ***Sarojini*** and Dr *Johannes* ***Reynisson***.

Mairi ***Robertson*** won the Baldwin's Prize for the top student in CHEM 392.

Congratulations to the ***Brimble*** group as Neuren Pharmaceuticals has been awarded a new patent for their drug NNZ-2591 (cyclic glycyl-2-allyl proline) concerning a method for treating an autism spectrum disorder or neurodevelopmental disorder. NNZ-2591 is a synthetic analogue of the naturally-occurring neurotrophic peptide cyclic glycine proline (cGP), and was synthesised in the Brimble

Kyriakos Varnava, winner of the electron microscopy image competition

Mairi Robertson (middle) with the Baldwins staff – solicitor, Nadia Ormiston (left) and Associate, Katherine Hebditch (right)

group. It is currently in pre-clinical development, where models have shown efficacy in treatment of a range of brain injuries, diseases and disorders.

Congratulations also to SapVax, the company in the US set up in conjunction with BioMotiv to develop cancer vaccines based on the ***Brimble*** group syntheses, for successfully raising $7.5 M. They have also reported their vaccines can activate human T cells *in vitro* and are about to move to *in vivo* testing. It is exciting to see that what started as a scientific collaboration between the Brimble and Dunbar groups is headed towards commercial success.

The following graduate teaching assistants (GTAs) have received certificates in recognition of completing advanced GTA training and acting as excellent demonstrators in the laboratory: *Daniel* ***Ayine-Tora*** (CHEM110), *Paul* ***Baek*** (CHEM240), *Alan* ***Cameron*** (CHEM120, CHEM390), *Courtney* ***Davy*** (CHEM91F, CHEM92F, CHEM150, CHEM120, senior inorganic), *Shama* ***Dissanayake*** (CHEM91F, CHEM92F, CHEM150), *Jessica* ***Fleming*** (CHEM110, CHEM230), *Megan* ***Jamieson*** (CHEM110, CHEM330), *Freda* ***Li*** (CHEM110), *Benjamin* ***Lu*** (CHEM110), *Mansa* ***Nair*** (CHEM240), *Cherie* ***Tollemache*** (CHEM210, CHEM320), *Reuben* ***White*** (CHEM110, CHEM230), *James* ***Wood*** (CHEM110, CHEM330) and *Ayesha* ***Zafar*** (CHEM120, CHEM150).

The school would especially like to thank *Alan* ***Cameron*** for his assistance in coordinating CHEM 120 and *Courtney* ***Davy*** for leading the Tuakana programme in David Salter's absence as well as *Ben* ***Lu*** and *Reuben* ***White*** who helped in CHEM 110 to cover for Kaitlin Beare's leave. These four really did put in a phenomenal effort to keep things running smoothly while a large fraction of the first year academic staff team were on leave.

The following members of staff at the University of Auckland were recently promoted:

- *Brent* ***Copp*** - promoted to Professor
- *Viji* ***Sarojini*** - promoted to Senior Lecturer above the bar (SL6)
- *Erin* ***Leitao*** - promoted to Senior Lecturer
- *Fan* ***Zhu*** - promoted to Senior Lecturer
- *Neill* ***Culley*** - promoted to Professional Teaching Fellow 3

Cather ***Simpson*** won third prize in the 2018 SPIE Startup Challenge in San Francisco in February with her presentation on Orbis Diagnostics. Orbis Diagnostics was started by Cather and *David* ***Williams*** for "point of cow" analysis of milk. For more information on the competition, other winners, and Orbis Diagnostics see http://optics.org/news/9/2/11.

Ben ***Zhang*** was the top scholar in chemistry in the NCEA scholarships. Ben was a high school student working with David Ware in the 10th-floor research laboratories last year and is heading to Harvard to study later this year.

Jonathan ***Chan*** was awarded the 2017 Prime Minister's Future Scientist Prize, along with $50,000. Jonathan was a high school student working with Associate Professor *Duncan* ***McGillivray*** and PhD student, Shinji Kihara, on a fog collection system.

Congratulations to the PhD candidates who successfully presented and defended their theses:

Aaron ***Tay***, thesis title: *Synthesis of boron porphyrinoids* (supervisors: Professor *Penny* ***Brothers*** and Dr *David* ***Ware***).

Hannah ***Holtcamp***, thesis title: *New tools and methods for CE-MS: applications in anticancer metallodrug research* (supervisors: Professor *Christian* ***Hartinger*** and Dr *Bruno* ***Fedrizzi***).

Auckland University of Technology

New Faces

We welcomed two new PhD students: Pablo Muñana and Dominique Rwizinkindi. Pablo will be working with Dr *Jack* ***Chen*** and Dominique will with Professor *Nicola* ***Brasch****.*

Emma Matthewman, Keegan Chessum, Paul Jun and Yue Shen joined us as summer students in the chemistry research lab. Emma and Paul are working with Dr *Cameron* ***Weber***, Keegan with Dr *Jack* ***Chen*** and Yue with Professor *Nicola* ***Brasch***.

Clement Roizard is visiting AUT for 6 months from ENS de Lyon to work with Professor *Allan* ***Blackman***.

Iana Gritcan joined Chemistry as a Senior Technician to help run the chemistry research lab. Iana is in the final stages of her PhD at AUT and has taught undergraduate chemistry labs across all year levels. We are very happy that she has now joined us on a more permanent basis.

Events and Invited Talks

AUT hosted a presentation from Associate Professor Jason Harper from the University of New South Wales entitled, *Adventures with azolium salts: from solvents to carbon acids*.

Dr *Cameron* ***Weber*** delivered invited talks at the School of Science Graduate Research Showcase entitled, *Using the nanostructure of ionic liquids to control chemical reactions* and at Scion entitled, *Ionic liquids and their mixtures: from structure to function.*

Professor *Nicola* ***Brasch*** and Professor *Allan* ***Blackman*** both delivered keynote lectures at the 24th International Symposium on Pure and Applied Coordination Chemistry. Nicola's talk was entitled, *Probing the mechanism of nitroxyl release from photoactive piloty's acid derivatives* and Allan's, *Photocatalytic* H_2 *evolution from a series of* Co^{III} *complexes.*

Dr *Jack* ***Chen*** travelled to the University of Siena, Italy, in January to deliver an invited 6 hour lecture series entitled, *Strategies for planning a synthesis – retrosynthetic analysis* for PhD students.

Congratulations

Dr *Jack* ***Chen*** received an $80,000 Catalyst: Seeding grant with Professor Leonard Prins from the University of Padua, Italy, entitled *Particle-based surfactants: a green solution for the chemical industry*.

Ruth ***Cink*** received a poster prize for her poster *Improvement for photoactive HNO donors: effect of a simple modification to the (hydroxynaphthalenyl)methyl phototrigger* at the 24th International Symposium on Pure and Applied Coordination Chemistry. She also received a Dodds-Walls Centre travel award of $1500 to allow her to travel to Hong Kong to perform experiments in the lab of Professor David Lee Phillips.

Dr *Cameron* ***Weber***, Emma Matthewman and Dr Tamar Greaves (RMIT) were successful in their application for beamtime in the Australian Synchrotron with experiments to be performed in April.

CANTERBURY

Fellow of the Royal Society of Chemistry

Congratulations to Associate Professor *Sarah* ***Masters*** (current chair of the NZIC Canterbury branch) who has been admitted as a Fellow of the Royal Society of Chemistry. Membership of the RSC denotes professional standing in chemistry and is a formal recognition of professionalism and experience.

Easterfield Prize

Many congratulations to Associate Professor *Sally* ***Gaw*** who was awarded the Easterfield Medal by the NZIC. The medal was donated by the Royal Institute of Chemistry (now the Royal Society of Chemistry) in honour of the late Sir Thomas *Hill* ***Easterfield*** KBE (Cantab), PhD (Wutzburg), FRSNZ, FRIC, HonFNZIC. He was well known for his contribution in the field of chemistry and will be remembered particularly for the inspiration and encouragement he gave his students during the many years he was Professor of chemistry at Victoria University College and for his infectious enthusiasm for chemical research. Sir Thomas was the first chairman of the New Zealand section of the Royal Institute of Chemistry and also one of the early Presidents of the NZIC. It is therefore fitting and in accordance with the wishes of the Council of the Royal Society of Chemistry that the two should act in association. Recipients of the medal must have less than twelve years of professional experience since completing their most recent relevant qualification and the major portion of the candidate's research work submitted must have been carried out in New Zealand as judged by the research work published during the twelve years immediately preceding the award.

Chemical Education Prize

Many congratulations to *Graham* ***Townsend*** who was awarded the Denis Hogan Chemical Education Award by the New Zealand Institute of Chemistry. This award is made to a person who, in the opinion of the NZIC Council, has made an important contribution to chemical education in New Zealand.

University of Canterbury

Congratulations

Marsden grant success

Designer catalysts for a sustainable future: Professor *Alison* ***Downard*** and Dr *Chris* ***Fitchett*** from the School of Physical and Chemical Sciences, and Dr *Aaron* ***Marshall*** from the Department of Chemical and Process Engineering at the University of Canterbury received a Marsden Fund grant to design more effective and stable electocatalysts. They will study how to tailor the molecular environment of well-known electrocatalysts (such as iron porphyrin) to achieve high reaction rates. For more details see: https://royalsociety.org.nz/what-we-do/funds-and-opportunities/marsden/awarded-grants/marsden-fundhighlights/2017-marsden-highlights/catalysts-for-sustainable-future/

Tech Jumpstart Awards Astrolab Prizes

Laser detection of nitrates in waterways and soils: Congratulations to Dr *Deborah* ***Crittenden*** and Associate Professor *Sally* ***Gaw*** for their development of an innovative laser detection tool with the ability to measure nitrates in the field using both soil and water samples. It promises to be portable and cost-effective with a low environmental impact and the capability of selecting only nitrates from the sample, avoiding other deposits or substances with similar structures. With the introduction of new legislative caps on nitrogen discharge, a portable nitrate measuring tool would enable farmers to conveniently measure nitrate levels on the farm, helping them to keep discharges within the new limits.

Miniature electrochemical sensing elements for detection of nitrate: Dr *Vladimir* ***Golovko*** and Dr *Aaron* ***Marshall*** have developed a novel electrochemical sensing system for nitrates. Along the lines of a digital thermometer, the electrode has the advantages of long life and durability, plus the ability to send information via a networked monitoring system. This would provide regional councils with a real-time view of nitrates in waterways across their catchment areas, enabling them to enforce the new legislative caps on nitrogen discharge.

Ralph H. Earle Jr. Seminar Prize

The chemistry postgraduate research showcase took take place on 15 November 2017. Each student was allocated 15 minutes to speak, with a further 5 minutes for questions/transition. At the event the Ralph H. Earle Jr. Seminar Prize was awarded to *Chris* ***Stinson***. The event coincided with the final Honours presentations, and Dr *Nigel* ***Lucas*** from University of Otago was present and assisted with the judging.

MANAWATU

The MBIE-funded collaborative project on metal-organic frameworks between NZ chemists and their counterparts at CSIRO had its initial workshop in Melbourne in early December. The NZ participants included *Shane* ***Telfer*** (Massey), *Geoff* ***Waterhouse*** (Auckland), *Paul* ***Kruger*** (Canterbury), *Carla* ***Meledandri*** and *Lyall* ***Hanton*** (both Otago).

Shane ***Telfer*** delivered a keynote talk at Crystal-31, the semi-annual meeting of the Society of Crystallographers of Australia and New Zealand (SCANZ) in Bunker Bay, south of Perth.

Shikeale Harris joined the ***Telfer*** group for a summer project exploring various aspects of the self-assembly of molecules based on truxene.

Liam McGarry joined the ***Rowlands*** group for a summer project working on C-H activation chemistry.

Suraj Patel joined the ***Rowlands*** group as part of a summer research paper and worked on paracyclophane foldamers.

Brodie Matheson received the IFS summer scholarship and joined the ***Plieger*** group to work on pyrazine mediated metal – metal communication.

Participants in the MBIE-funded collaborative project on metal-organic frameworks at CSIRO in Melbourne

OTAGO

The branch held its annual dinner in late November at the University of Otago Staff Club Gallery Restaurant. Emeritus Professor *Jim* ***Simpson*** spoke during the dinner, answering the question: *Frauds in small molecule crystallography: are they a thing of the past?* and provoking many follow-up questions from an attentive audience.

Chemistry Nobel Laureate, Professor K. Barry Sharpless (Scripps Research Institute) and Professor John Moses (La Trobe University) were visitors to the University of Otago on 29 January. Professor Sharpless presented an entertaining research seminar describing his many contributions to "click" chemistry, then later met with postgraduate students in an informal question and answer session. The branch was one of the sponsors that made the special visit possible.

The AGM of the Otago Branch was held on 31 January. Chair *Nigel* ***Lucas*** reported on activities and successes of the past year, and the committee for 2018 was elected.

University of Otago, Department of Chemistry

Big news from the Department of Chemistry this issue is the recent award of the 2017 Prime Minister's Emerging Scientist prize to *Carla* ***Meledandri***. This award is fantastic recognition of Carla's achievements in both fundamental and applied research and we look forward to more exciting research to come out of her lab and company in the future!

University of Otago researchers have helped uncover how New Zealand glowworms produce their glow. A multi-year study of the bioluminescence produced by the glowworms has been published in the online science journal, *Scientific Reports*. The study titled, *New Zealand glowworm bioluminescence is produced by a firefly-like luciferase but an entirely new luciferin,* was a collaborative effort between Otago's chemistry and biochemistry departments. Lead authors Drs *Oliver* ***Watkins*** (his PhD project) and *Miriam* ***Sharpe***, working with Professors *Nigel* ***Perry*** (chemis-

Carla Meledandri and the Prime Minister, Jacinda Ardern, at the 2017 Prime Minister's Science Prizes

Left to right: Santi Rodriguez-Jimenez, Sally Brooker and Ross Hogue at the December graduation ceremony

Left: Stuart Malthus adding his thesis to Sally's collection. Right: New Brooker's Bunch PhD student, Luca Bondi, hard at work in the lab

try) and Kurt Krause (biochemistry), have discovered that the New Zealand glowworms produce their light using a chemical reaction that is different to all other glowing creatures like fireflies. This was a University of Otago funded project, but was greatly assisted by the Plant & Food Research Bioactives team. A video put together during the research phase by United States based science and technology online publication *Science Friday* can be found at https://www.youtube.com/watch?time_continue=1&v=nsd9HmzIwRQ

Brooker's Bunch (Professor *Sally* ***Brooker***) celebrated the December graduation of (now) Dr *Ross* ***Hogue*** and Dr *Santiago* ***Rodriguez-Jimenez***, and the successful PhD oral examination of *Stuart* ***Malthus***. We also congratulate Ross on securing a postdoctoral fellowship with Dr Kathryn Toghill at the newly renovated Chemistry Department, Lancaster University, UK, on the research project *Synthetic chemistry for redox flow batteries* and Stuart on securing a postdoctoral fellowship with Dr John Brazier at Reading University and the Diamond Light Source in the UK, on the research project *Targeting the weakest links in DNA for selective structural recognition*. A new PhD student, *Luca* ***Bondi*** (MSc from Florence, Italy) has started in Brookers Bunch, and we have also welcomed two Honours students, *William* ***Pelet*** and *Alice* ***Endersbee***.

Keith ***Gordon*** gave an invited talk at the 24th International SPACC (Society of Pure and Applied Coordination Chemistry) Symposium in Auckland (November 2017) where he talked about modelling and measuring excited states. In December he attended the 15th Pacific Polymer Congress in Xiamen, China, where he gave an invited talk about the use of spectroscopy and computational chemistry in understanding solar cell material properties. In February 2018 he gave an invited talk at Pittcon, Florida, about low frequency Raman spectroscopy. Keith also celebrated his first year as Editor-in-Chief of Vibrational Spectroscopy (Elsevier) in January 2018 and became Head of Department in February.

Jonathan ***Barnsley*** is in the final stages of his PhD and is currently writing his thesis. *Spectroscopy of some donor-acceptor dyes* will discuss a number of organic donor-acceptor materials systems which have been systematically modified. *Joshua* ***Sutton*** presented a talk at the Pacific Climate Change conference (PCC2018) in Wellington at the end of February and had his first author paper published in *Molecules*. *Jeremy* ***Rooney*** presented his work to NZ Steel and their paint suppliers in October 2017. He is currently writing up his PhD thesis. Joseph Mapley has completed his BSc with Honours where he examined a series of substituted porphyrins and has undertaken a summer internship where he developed his skills with photon counting on a range of donor acceptor systems. He has begun his PhD with the KCG group where he will be using a range of spectroscopic techniques to analyse a series of photoactive compounds. *Georgina* ***Shillito*** presented a talk titled, *Photophysical properties of Re(I) and Ru(II) polypyridyl complexes with PAH donor groups* at the 11th Australasian Organometallics Conference (OZOM11) in Perth in January 2018. She was delighted to receive some NZIC funding for this conference.

Sam ***McIntyre***, *Kia* ***Paasi*** and *Elliot* ***Tay*** have completed summer internships with the Keith Gordon group. Sam carried out IR and Raman measurements of carrot and plum bioactives and applied statistical analysis methods to the data sets. This work was carried out in conjunction with the Food Science and Botany departments at Otago. Kia used Raman and IR microscopy to investigate a number of consolidants used to preserve harakeke fibres. This work was carried out in conjunction with the Centre for Materials Science and Technology at Otago. Elliot collected spectra for a number of projects which encompassed inorganic dyes, polymers and dog biscuits.

WAIKATO

University of Waikato

A number of students are either commencing or concluding their studies. *Raymond* ***Onyekachi*** **(**chief supervisor *Bill* ***Henderson*)** recently successfully defended his PhD thesis and has started working at The Drug Detection Agency (TDDA) in Auckland. Atiga Simeon (from Nigeria) and Aphiwat Kaewthoing (from Thailand) have started PhD research on mass spectrometry-directed synthesis in metal thiolate chemistry (both with *Bill* ***Henderson***).

Also with *Bill*, Ben O'Shea has submitted his Masters thesis on forensic applications of hydroxyquinoline compounds. Moh'd Beqain from Jordan has begun a PhD with *Michael* ***Mucalo*** on new types of hydroxyapatites, Nicholas Kuan (*Michèle* ***Prinsep***) has submitted his Masters thesis on biomarkers in honey and Sam Murray (*Michèle* ***Prinsep*** and Merilyn-Manley-Harris) has submitted his Honours dissertation on analysis of toxins in fish and algae.

WELLINGTON

Wellington Branch's final meeting of 2017 consisted of the Branch AGM and a tour de force of chemistry in *Penny* ***Brothers***' Presidential Address. At the time of writing, Branch activities have not yet kicked off but we're looking forward to engaging and diverse events this year.

VUW

Congratulations to the following students who have successfully defended their PhD theses in the past few months: *Sophie* ***Geyrhofer*** (now at MedSafe, supervisor: *Joanne* ***Harvey***), *Alex* ***Hunt-Painter*** (supervisors: *Mattie* ***Timmer****, Bridget* ***Stocker***) and *Putri* ***Fraser*** (supervisor: *Robin* ***Fulton***).

Long-time NZIC member *Kate* ***McGrath*** has announced her departure to take up the position of Deputy Vice-Chancellor and Vice-President (Research) at the University of Technology Sydney. We are very grateful for all her contributions to the NZIC and Victoria University, and wish her the very best in her new endeavours!

A number of excellent speakers have entertained and enlightened students and staff at Victoria in the past few months: Dan Nocera (Harvard University) on *Fuels to food from sunlight, air and water*, Lars Goerigk (University of Melbourne) as part of his 2017 RACI Physical Chemistry Division lectureship tour who spoke very lucidly about the complexities of density functional theory, Wolfgang Jaeger (Christian-Albrechts-University, Kiel) on electron microscopy of advanced materials, Lennart Bergström (Stockholm University) on nanocellulose-based materials and Philip G. Jessop (Queen's University, Canada) on switchable solvents.

ESR

Dr Helen ***Poulsen*** in collaboration with Dr Hilary Hamnett (ex ESR currently at Imperial College, UK) published a paper on the effect of lowering the legal drink drive limit in both New Zealand and Scotland in the Journal of Forensic Sciences. This information was picked up by the Scottish media - most notably by *Scotland on Sunday* on February 10, 2018 in an article entitled, *Deaths from drug driving rise after alcohol limit cut*.

Dr Sarah ***Russell***, Rui Shen Ong and Thalita van Awsegen attended the joint SOFT/TIAFT meeting in Boca Raton, Florida in early January. This was the 55th TIAFT (The International Association of Forensic Toxicologists) annual meeting, combined with SOFT (Society of Forensic Toxicologists), and had been rescheduled from September 2017 due to Hurricane Irma. It was the biggest gathering of forensic toxicologists ever. Sarah and Rui both had presentations which were well received.

Realising the hydrogen economy: economically viable catalysts for hydrogen production

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Introduction

Reducing the anthropogenic release of CO_2 over the next 50 years is seen as critical to preventing long-term climate warming.[1] Currently, our CO_2 emissions are largely driven by fossil fuel combustion, and thus there is significant interest in developing alternative carbon-neutral fuels. Molecular hydrogen is a highly promising fuel which has received a great deal of attention since the proposition of a hydrogen economy by John Bockris in 1970.[2] The key advantage of burning H_2 for energy is that its combustion produces water as the sole product (Eq. 1), thus avoiding the release of CO_2 and other harmful compounds.[3-5] In this way, H_2 could be burned in fuel cells to power cars, factories and homes without releasing greenhouse gases.

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \qquad \text{Eqn. 1}$$

With a low ignition temperature and light weight H_2 is also the primary contender for renewable aircraft or rocket fuel.[6,7] Outside of fuels, H_2 is used as a reactant in large-scale industrial processes such as the Haber-Bosch process to generate ammonia-based fertilisers.[8] However, as there are no naturally existing reservoirs of H_2 on Earth, the use of H_2 first relies on its production.

Presently, the majority of the H_2 supply on Earth originates from the steam reformation of natural gases.[9] The production of H_2 steam reformation not only depletes dwindling fossil fuel reserves, but also results in CO_2 emission, thus undermining the primary logic for H_2 fuels. Instead, H_2 can be produced by the electrochemical decomposition of H_2O in the water splitting reaction (Eq. 2).[4]

$$2H_2O \xrightarrow{\text{Catalyst}} 2H_2 + O_2 \qquad \text{Eqn. 2}$$

The electricity required to produce H_2 *via* electrolysis can be readily sourced from solar, hydro or wind power, thus tying H_2 fuel production to a renewable energy source.[5,9,10]

Electrochemical hydrogen evolution

The overall splitting of water can be divided into two electrochemical half equations:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad \text{Eqn. 3}$$

$$4H^+ + 4e^- \rightarrow 2H_2 \qquad \text{Eqn. 4}$$

Eq. 3 represents the oxidation of water (i.e. oxygen evolution), while Eq. 4 describes the reduction of the resulting protons in the hydrogen evolution reaction (HER).[11] In an electrolytic cell that produces H_2 from water, both of these half-cell reactions occur simultaneously, and both must be optimised in order to improve the overall water splitting process.[12] The present essay will focus on the HER, a deceptively simple reaction that also requires much attention and research. Primarily of interest is the requirement of an appropriate HER catalyst in order for the reaction to proceed with any appreciable rate.

The ideal electrocatalyst for hydrogen evolution would be both effective and cheap. Currently, pure Pt is the most effective catalyst for the reaction, but the monetary cost of this precious metal is commercially undesirable and has prohibited its widespread use to date.

Some research has sought to overcome the problem of cost by reducing the amount of Pt used in the catalyst.

One idea is to incorporate Pt nanoparticles into a cathode made of a cheap conducting material such as polyaniline.[13] As nanoparticles have a high surface-area-to-volume ratio, this reduces the amount of Pt used per unit of exposed surface. Similarly, by alloying Pt with a more abundant metal, the catalyst cost may be reduced while preserving the reactivity. Greeley *et al.*[14] used computational chemistry to screen across 256 alloy combinations formed by 16 different pure metals, shown in Fig. 1, left. The most promising alloy discovered after the authors' extensive screening was a Pt-Bi surface alloy that was both cheaper to synthesise and yielded a slightly higher experimental rate of H_2 production than pure Pt.[14] Although this option does somewhat reduce the amount of Pt required in the catalyst, the alloy's reliance on the rare metal has continued to make it commercially unfavourable at this stage. Indeed, many proponents of the hydrogen economy still argue that economically successful hydrogen production relies on the existence of an effective and cheap catalyst for the process that is constructed out of only Earth-abundant materials.[5,10]

Earth-abundant electrocatalysts

Several Earth abundant electrocatalysts such as the transition metal sulfides have been receiving recent attention.[15-17] One particularly interesting transition metal sulfide that has demonstrated highly promising catalytic activity towards H_2 evolution is molybdenum disulfide (MoS_2).[18-19] The MoS_2 catalyst was inspired by the presence of Mo in nitrogenase and hydrogenase enzymes,[18] which catalyse the reversible production of H_2 in biological systems using metal-sulfur assemblies.[20] MoS_2 in its solid form is naturally present as layered sheets, akin to graphite (Fig. 2a). These are individually stable, and can be cleaved to from 2D nanomaterials (Fig. 2b), or cut further to form nanoparticles as small platelets (Fig. 2c).[21-24]

In comparison with traditional pure metal HER catalysts, MoS_2 has a higher rate of H_2 production than non-precious metals (e.g. Cu, Ni, Co), yet the rate still falls short of Pt by around 102 - 105 times.[25-26] Thus there is considerable interest in seeking methods to optimise the cheap MoS_2 catalysts for hydrogen evolution, increasing their effectiveness and thus offering an affordable alternative to Pt in producing hydrogen.

Optimising catalysts using computational chemistry

Computational power has been a cornerstone of technological development in the 21st century, not only because of its many applications, but also because of the exponential increase in computer performance that has occurred over recent years. This in turn has caused marked advances in computer simulations that show ever increasing capability to describe the behaviour of a range of complex chemical systems with accuracy. For this reason, computational chemistry has grown to be a remarkable tool in catalytic investigations of chemical systems.

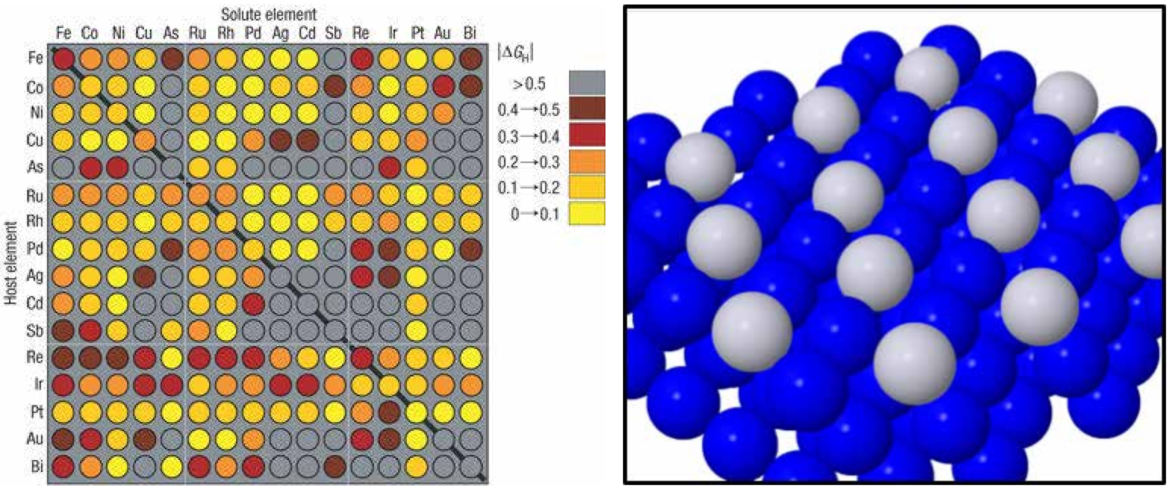

Fig. 1. Left: The hydrogen evolution activity of 256 alloys of pure metals tested by Greeley *et al.*[14] The catalytic activity increases with decreasing $|\Delta G_{H_{ads}}|$; Right: A representation of the Pt-Bi surface alloy: the most catalytically active alloy discovered by Greeley *et al.*[14] Key: Bi - blue, Pt - grey. Reprinted with permission, copyright 2006 Springer Nature.

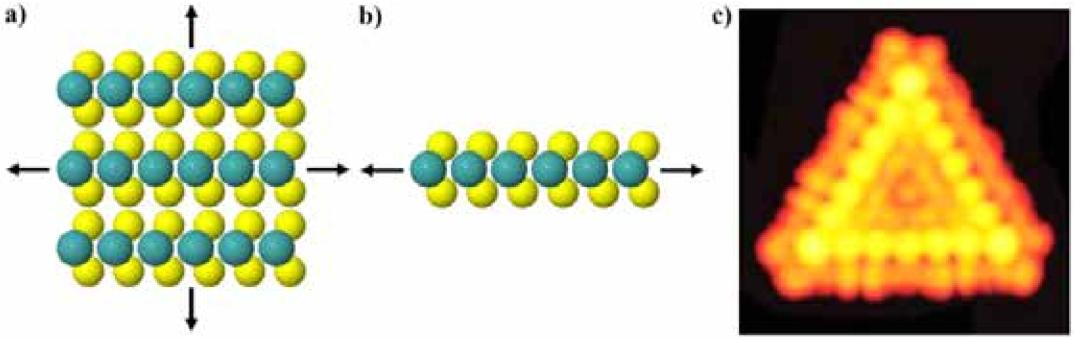

Fig. 2. (a) Bulk MoS_2 composed of layered sheets, (b) a single-layer MoS_2 sheet and (c) a transmission electron microscope image of a MoS_2 nanoparticle in the form of a hexagonal platelet, from Bruix *et al.*[24] with Mo in green, S in yellow (reprinted with permission, copyright 2015 American Chemical Society).

In the context of our research, computational techniques also give unparalleled mechanistic insight at the atomic level for the HER on MoS_2, and can be used to rapidly screen across different reaction conditions.

Past computational and experimental work on the HER has revealed that the reaction occurs through two mechanistic steps: first, a proton from solution (H^+) is adsorbed onto the catalyst surface. Second, the adsorbed hydrogen H_{ads} combines with either another surface-adsorbed hydrogen or a proton from solution, thus forming H_2.

The stability of the H-adsorbed intermediate state is crucial to catalyst performance as the energy of this intermediate completely determines the thermodynamic cost of the reaction (shown in Fig. 3). The free energy of H adsorption (ΔG_{Hads}) thus fully describes the thermodynamic favorability of the HER. If H is adsorbed too weakly to the catalyst surface (i.e. $\Delta G_{ads} > 0$), an energy cost must be paid to get H onto the surface (see Figure 3, bottom right). If H is bound too strongly to the surface (i.e. $\Delta G_{ads} < 0$), an energy cost must be paid to remove the H from the surface in the second combination step (see Fig. 3, bottom left). Ideally, H would adsorb to our catalyst not to weakly, or strongly, at $\Delta G_{Hads} = 0$, such that no thermodynamic cost is paid in the overall reaction (see Fig. 3, bottom centre). A "volcano" plot can be constructed by plotting the ΔG_{Hads} against the experimental performance of the catalyst (Fig. 3, top). Catalysts that have a hydrogen adsorption free energy close to zero (including both MoS_2 and pure Pt), tend to perform better experimentally. As a result, research aiming to optimise HER catalysts often seeks to tune this ΔG_{Hads} value to be as close to zero as possible.

Optimising MoS_2 using a catalyst support

One method of optimising MoS_2 *via* tuning ΔG_{Hads} and other properties is to place the catalyst on a supporting metal. The nature of the support affects the properties of the catalyst, and thus it can be used to tune catalytic properties to ideal values (e.g. $\Delta G_{Hads} \approx 0$) without altering the catalyst itself.

Tsai *et al.*[27] revealed that tuning ΔG_{Hads} *via* a support was indeed possible, and very powerful, in the case of MoS_2. Using a gold support for MoS_2 caused H to have a more positive free energy of H adsorption (ΔG_{Hads} = 0.39 eV) meaning H was more weakly bound to MoS_2 than for its unsupported counterpart (where ΔG_{Hads} = 0.06 eV). In contrast, a single-layer of graphene as a support caused MoS_2 to bind H more strongly (ΔG_{Hads} = - 0.25 eV). While neither of these supports produced a value of ΔG_{Hads} close to the ideal of zero, they do highlight the exciting behaviour of supports conferring tuning effects.

The role of reaction kinetics

It is imperative at this point to identify that, while Tsai's[27] findings are promising, they are not a complete description of the HER. The ΔG_{Hads} descriptor used quantifies the thermodynamics of H adsorption, but does not contain any information about the kinetic barriers (or activation energy) to the HER, which are integral to describing the *rate* of hydrogen evolution. The difference between the thermodynamic (red) and kinetic (blue) description of the HER is shown in Fig. 4. Note the additional energy barriers present when kinetics are considered.

The thermodynamic tendency for the reaction to occur (obtained as ΔG_{Hads}) is only a first approximation to the rate at which the reaction takes place. Typically, a reac-

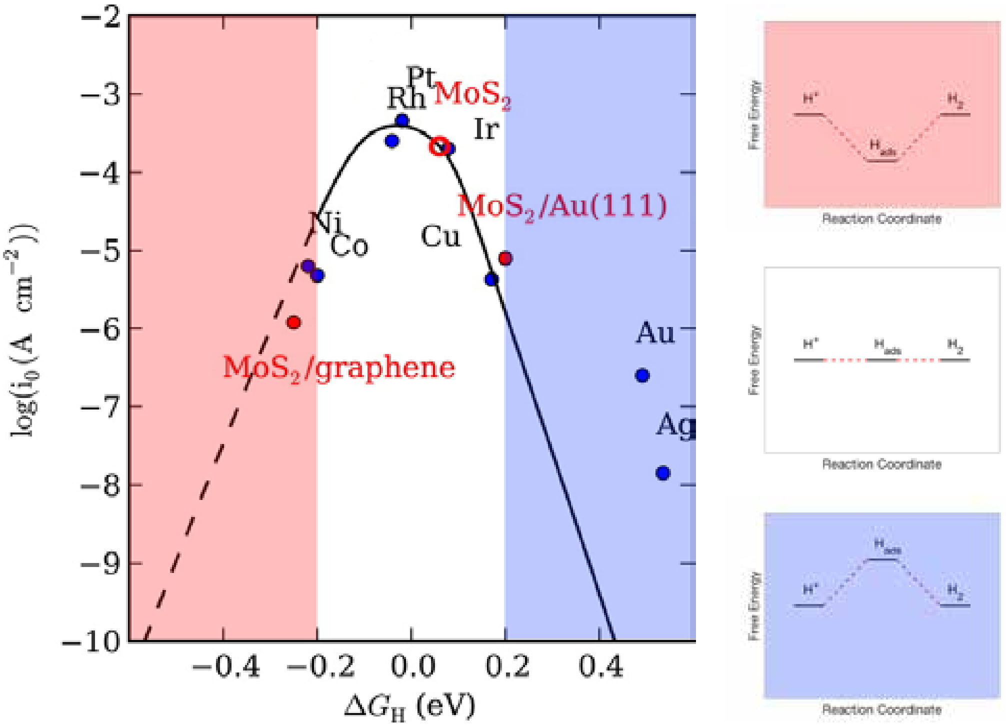

Fig. 3. Top: A volcano plot depicting the free energy for H adsorption (ΔG_{Hads}) of several pure metals and MoS_2: the vertical axis depicts the experimental rate of H_2 production in terms of the log of the current density[27] (adapted with permission, copyright 2014 American Chemical Society). Free energy diagrams are also depicted for the HER on catalyst surfaces which adsorb H too strongly ($\Delta G_{Hads} < 0$, bottom left), ideally ($\Delta G_{Hads} > 0$, bottom centre), and too weakly ($\Delta G_{Hads} \approx 0$, bottom right).

tion that is thermodynamically favourable will occur faster, but full description of the reaction kinetics can only be gained by mapping out the individual steps in the reaction mechanism and calculating the activation energy barriers to each of these steps – a task that is made possible with computational chemistry.

Huang *et al.*[28] have modelled both kinetics and thermodynamics when considering hydrogen evolution on unsupported MoS_2. However, they did not investigate supported MoS_2, which is a key focus of our current research. Thus, we chose to explore the kinetics of the HER with MoS_2 both on and off a gold support as a starting point.

Calculating kinetic barriers with computational chemistry

We calculate the kinetic barriers (activation energy) as the energy of the highest point on the reaction path converting reactants to products (the transition state) minus the energy of the initial reactants. In order to do this, the transition state must be located. In our research, this is done using the nudged elastic band (NEB) method.[29] NEB works by mapping out the entire reaction path. The initial and final states of the pathway are connected by a series of “images” representing structural geometries along the path. These images are connected by mathematical elastic bands, and their structural geometries are optimised in concordance with each other. This ensures that the image geometries lie along the minimum energy path connecting reactants to products – which is the pathway that would most likely be taken in the real reaction. Climbing image NEB[30] can be used to find the exact transition state by pushing the highest energy image to the apex of the reaction pathway.

At this stage, we have only studied the barriers to hydrogen desorption in the combination step from adsorbed hydrogen (H_{ads}) to H_2. We have found that when MoS_2 is supported on gold, formation of H_2 occurs with a notably lower barrier (0.61 eV) than on the unsupported surface (0.76 eV). The reaction paths mapped out along the minimum energy pathways are shown in Fig. 5. This finding is in line with the idea that the H adsorbed intermediate is less stable (higher energy) in the presence of a gold support, and more readily loses H_{ads} off the MoS_2 surface – forming H_2. It is possible that the lower barrier to desorption when on a gold support is also associated with a higher barrier to adsorption, where the unstable H_{ads} state has to be formed. This adsorption pathway is a focus of ongoing research in our group.

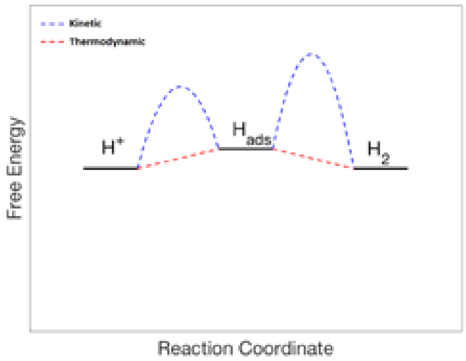

Fig. 4. A comparison of thermodynamic and kinetic costs to hydrogen evolution on a generalised weak-binding catalyst

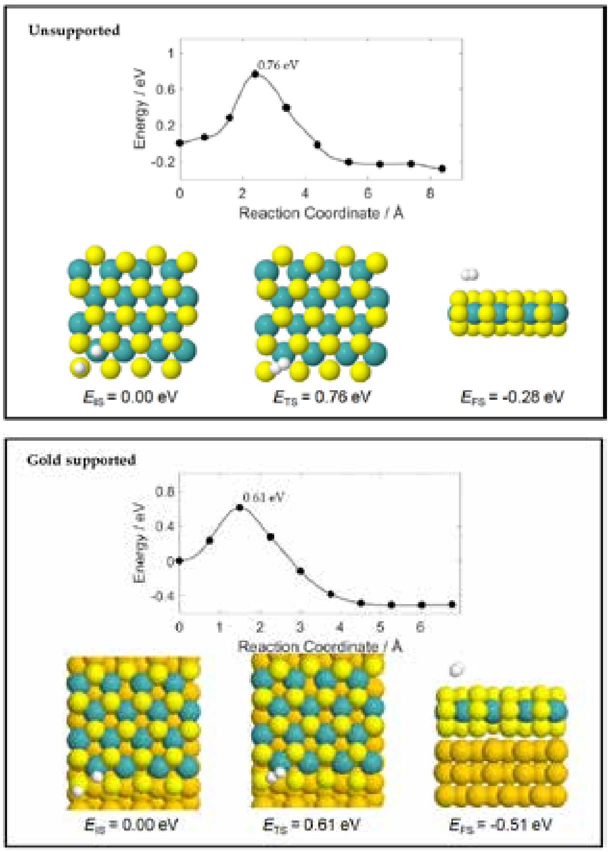

Fig. 5. The minimum energy reaction paths for the combination and desorption of H_{ads} on unsupported (top) and gold supported MoS_2 (bottom). The activation energy is shown on the path.

Summary

MoS_2 as a catalyst for the hydrogen evolution reaction has proven to be an interesting point of research due to both its efficiency and broad range of tunability when interchanging supports. Our research focuses on the importance of both thermodynamic and kinetic descriptions when optimising MoS_2 for hydrogen evolution, stressing that both these factors must be considered to produce an efficient catalyst. Moving forward a comprehensive description of tunable conditions and the effect these have on both the reaction thermodynamics and kinetics will be explored. Promising directions include testing new catalyst supports such as graphene and graphene oxide, as well as manipulating other factors such as applied potential.

References

1. Allen, M. R.; Frame, D. J.; Huntingford, C.; Jones, C. D.; Lowe, J. A.; Meinshausen, M.; Meinshausen, N. *Nature* **2009**, *458*, 1163–1166.
2. Bockris, J. O. In *Environmental Chemistry*; Bockris, J. O., Ed.; Springer US: Boston, MA, 1977; pp 549–582.
3. Veziro, T.; Barbir, F. *Int. J. Hydrogen Energy* **1992**, *17*, 391–404.
4. Zuttel, A.; Remhof, A.; Borgschulte, A.; Friedrichs, O. *Philos. Trans. A Math. Phys. Eng. Sci.* **2010**, *368*, 3329–3342.
5. Zuttel, A.; Borgschulte, A.; Schlapbach, L. *Hydrogen as a Future Energy Carrier*; John Wiley & Sons, 2011.
6. White, C.; Steeper, R.; Lutz, A. *Int. J. Hydrogen Energy* **2006**, *31*, 1292–1305.
7. Koroneos, C.; Dompros, A.; Roumbas, G.; Moussiopoulos, N. *Resour. Conserv. Recy.* **2005**, *44*, 99–113.

8. Gerhartz, W. *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley, 1988.
9. Crabtree, G. W.; Dresselhaus, M. S.; Buchanan, M. V. *Phys. Today* **2004**, *57*, 39–44.
10. Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15729– 15735.
11. Lasia, A. *Handbook of Fuel Cells*; John Wiley & Sons, 2010.
12. McCrory, C. C.; Jung, S.; Ferrer, I. M.; Chatman, S. M.; Peters, J. C.; Jaramillo, T. F. *J. Am. Chem. Soc.* **2015**, *137*, 4347–4357.
13. Grzeszczuk, M.; Poks, P. *Electrochim. Acta* **2000**, *45*, 4171–4177.
14. Greeley, J.; Jaramillo, T. F.; Bonde, J.; Chorkendorff, I.; Nørskov, J. K. *Nat. Mater.* **2006**, *5*, 909–913.
15. Li, Y.; Wang, H.; Xie, L.; Liang, Y.; Hong, G.; Dai, H. *J. Am. Chem. Soc.* **2011**, *133*, 7296–7299.
16. Voiry, D.; Salehi, M.; Silva, R.; Fujita, T.; Chen, M.; Asefa, T.; Shenoy, V. B.; Eda, G.; Chhowalla, M. *Nano Lett.* **2013**, *13*, 6222–6227.
17. Fujita, T.; Ito, Y.; Tan, Y.; Yamaguchi, H.; Hojo, D.; Hirata, A.; Voiry, D.; Chhowalla, M.; Chen, M. *Nanoscale* **2014**, *6*, 12458–12462.
18. Hinnemann, B.; Moses, P. G.; Bonde, J.; Jørgensen, K. P.; Nielsen, J. H.; Horch, S.; Chorkendorff, I.; Nørskov, J. K. *J. Am. Chem. Soc.* **2005**, *127*, 5308–5309.
19. Jaramillo, T. F.; Jørgensen, K. P.; Bonde, J.; Nielsen, J. H.; Horch, S.; Chorkendorff, I. *Science* **2007**, *317*, 100– 102.
20. Evans, D. J.; Pickett, C. J. *Chem. Soc. Rev.* **2003**, *32*, 268–275.
21. Helveg, S.; Lauritsen, J. V.; Lægsgaard, E.; Stensgaard, I.; Nørskov, J. K.; Clausen, B.; Topsøe, H.; Besenbacher, F. *Phys. Rev. Lett.* **2000**, *84*, 951–955.
22. Lauritsen, J. V.; Kibsgaard, J.; Helveg, S.; Topsøe, H.; Clausen, B. S.; Lægsgaard, E.; Besenbacher, F. *Nat. Nanotechnol.* **2007**, *2*, 53–58.
23. Li, T.; Galli, G. J. Phys. Chem. C **2007**, 111, 16192–16196.
24. Bruix, A; Füchtbauer, H. G.; Tuxen, A. K.; Walton, A. S.; Andersen, M; Porsgaard, S.; Besenbacher, F.; Hammer, B.; Lauritsen, J. V. ACS Nano **2015**, 9, 9322-9300.
25. Nørskov, J. K.; Bligaard, T.; Logadottir, A.; Kitchin, J.; Chen, J. G.; Pandelov, S.; Stimming, U. *J. Electrochem. Soc.* **2005**, *152*, 23–26.
26. Benck, J. D.; Hellstern, T. R.; Kibsgaard, J.; Chakthranont, P.; Jaramillo, T. F. *ACS Catal.* **2014**, *4*, 3957–3971.
27. Tsai, C.; Abild-Pedersen, F.; Nørskov, J. K. *Nano Lett.* **2014**, *14*, 1381–1387.
28. Huang, Y.; Nielsen, R. J.; Goddard III, W. A.; Soriaga, M. P. *J. Am. Chem. Soc.* **2015**, *137*, 6692– 6698.
29. Jónsson, H.; Mills, G.; Jacobsen, K. W. In *Classical and Quantum Dynamics in Condensed Phase Simulations*; Berne, B. J., Ciccotti, G., Coker, D. F., Eds.; World Scientific, 1998; pp 385– 404.
30. Henkelman, G.; Uberuaga, B. P.; Jónsson, H. *J. Chem. Phys.* **2000**, *113*, 9901–9904.

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Professor Sally Brooker has recently agreed to be the first New Zealander to be on the Editorial Board of *Chemistry – An Asian Journal* (or any of the ACES journals, in fact). She is keen to increase the profile of this journal, not least because the NZIC gains financially for every paper published with a NZ corresponding author, something she was not aware of herself until recently.

A special issue to celebrate NZ chemistry is being organised for 2019, so consider this your invitation to contribute to this issue. Doing so is a win-win, with a paper in a high impact international journal and the added bonus of financially supporting the NZIC. Just for this special issue, any corresponding author not based in NZ but who feels a connection to NZ (for example a graduate of a NZ University based overseas) can also be counted financially, so please add an acknowledgment to highlight that fact if this is you! **The submission deadline is Friday 30 November 2018**, so start planning your paper now.

From South America to Willy Wonka – a brief outline of the production and composition of chocolate

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Keywords: *chocolate*, *food chemistry*

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New Zealanders, and indeed the entire world, love chocolate. From the golden wrappings of the Whittakers range to the iconic triangles of Toblerone, chocolate is undoubtedly a cornerstone of confectionary in the modern world. The global chocolate industry was valued in 2015 at a huge ~NZ$140b and New Zealanders were reported to consume 4.8 kg/year of chocolate per person in 2014, rivalled only by Australia.[1,2] Despite this, few know where this marvellous confection arises, and indeed how much chemistry plays a role in turning the inedible cocoa fruit into a delicious indulgence. This essay hopes to outline the production of chocolate and cocoa, highlighting the chemistry that plays a role in the taste, colour and texture of this food staple, followed by a discussion of a select few compounds in chocolate that offer interesting physiological responses. It is hoped that by the end the reader will begin to understand why Augustus Gloop spoiled the chocolate when he fell into the chocolate river and why dogs shouldn't have chocolate.

Chocolate production

The chocolate tree's official name, *Theobroma cacao*, which translates to "food of the gods", aptly describes how the world views chocolate.[3] *T. cacao* grows in humid tropical forests, native to the eastern slopes of the Andes in South America (now the border of Brazil, Ecuador and Peru), and is a delicate plant that grows under the shelter of larger trees such as banana and palm trees.[3,4] The fruit of *T. cacao* holds pale violet seeds (or cocoa beans) that in turn consists of two nibs (cotyledons).[4] These nibs are composed of two key cell types: parenchymal cells, which contain fats, proteins and starch granules, and pigmented cells containing the key chemical compounds such as polyphenols which give chocolate its remarkable taste, colour and smell.[4]

The cocoa beans are initially fermented and dried for transport, with the fermentation a key step in cocoa production. Natural yeasts convert the sugars to alcohol, and the aerobic bacteria subsequently convert that to acetic acid.[4,5] The drop in internal pH causes the polyphenol and lipid membranes of the cell's vacuoles to trigger a range of enzymatic reactions, such as the oxidation of polyphenol which reduces the eventual bitterness of the product.[4,5] The reduced pH also contributes to the activation of peptidases such as carboxypeptidase that results in oligopeptide formation, which are able to act as precursors for the development of the cocoa aroma in the subsequent roasting of the beans (Fig. 1).[4,5]

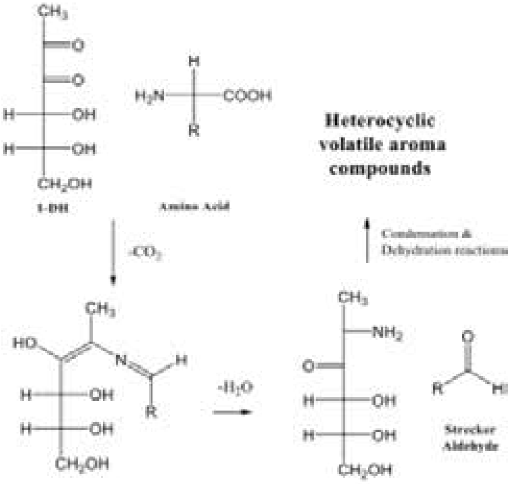

Fig. 1. Outline of key steps in Mailliard reactions pertinent to chocolate

The beans are roasted at 130 – 150°C for 30-45 minutes to promote Maillard reactions, where reducing sugars and amino groups at pH > 3 in the presence of water can form a range of products that result in characteristic flavours and colours.[5,6] The formation of addition compounds such as glucosylamines can further react to 1,2-enaminol, where further reaction is influenced by pH.[5] The formation of 3-deoxyhexoses (3-DH) is favoured under acidic conditions and dehyrdroreductones (1-DH) under basic conditions, which can subsequently play a role in Strecker degradation of amino acids into aldehydes (Fig. 1).[5] These aldehydes are not only active flavour compounds, but further reaction through aldol condensation yields heterocyclic aroma volatiles such as methylpyrazine. Leucine when reacted with glucose yields aroma notes of "sweet chocolate", whilst valine and glucose yield "penetrating chocolate".[5] Tetramethylpyrazine is the most abundant pyrazine at 6 ppm, and is reported to cause the "mocha milk coffee" notes.[5,6]

Following roasting, the cocoa nibs are extracted through light crushing of the bean in which it is encased (winnowing and grinding) and is subsequently milled to expose the cocoa butter and the homogeneous paste referred to as the cocoa liquor, composed of approximately 55% fats with dispersed nibs.[4] Cocoa liquor (mainly liquor destined for cocoa powder) often undergoes an alkalisation process known as Dutching.[4-5,7-8] This process uses the addition of sodium or potassium carbonate solution to increase the pH from 5.2-5.6 to 6.8-7.5, reducing bitterness and improving the dispersibility of cocoa powder in liquids.[4] The starch swelling and the cocoa mass forming a porous cell structure as a result of this alkalisation is what prevents the sedimentation in cocoa drinks.[4] The cocoa liquor can then be subjected to a defatting process to convert the liquor to cocoa powder by pressing the liquor in a hydraulic press at 90-100°C to 400-500 bar, isolating a portion of the fat from the cocoa (cocoa butter) to yield a cocoa cake at 10-24% fat.[4,5] Grinding of this cocoa cake results in cocoa powder, whilst the cocoa butter can be used in the production of chocolate.[4]

Cocoa liquor is also used to make chocolate, with a preference for the non-alkalinised form of liquor.[3,4] The combination of the liquor with sucrose, vanilla and milk is ground further to reduce nib particle size to ~25 µm using refining rollers.[4] The resultant chocolate paste is powdery with a sour flavour. Conching is the next step in the process to form chocolate, where residual volatile acids and moisture are removed, the viscosity is changed, and tannins are oxidised.[4,5] Initially the flaky paste is converted to a thicker paste by grinding and kneading at 65-75°C, which upon addition of cocoa butter and lecithin yields a free-flowing liquid.[3,5] The conching distributes the cocoa particles more evenly, surrounding them with a thin film of lipids.[5]

Tempering the chocolate is a key step in the determination of the final texture and whether or not "blooming" (the white spots that appear on old chocolate due to fat and sugar recrystallisation) occurs.[4-5,9-10] The cocoa mass from conching is cooled under stirring from 40-50°C to 18-28°C, allowing the cocoa butter within the chocolate to crystallise, with six polymorphs possible.[5,10] Form I is produced by rapid cooling in a freezer and is crumbly, has significant blooming and a melting point of 17.3°C.[10] In contrast, the more desirable form V is cooled slowly at room temperature and yields shiny, smooth chocolate and melts in the mouth due to the melting point of 33.8°C.[10] Whilst cooling at room temperature yields forms I-V, various techniques are used to convert forms I-IV to V.[10]

Interesting molecules in chocolate

Cocoa contains >500 different compounds, hence this essay will focus on a few key compounds found in chocolate, specifically those with a bioactive effect.[3]

Methylxanthines (Fig. 2) are found in reasonable quantities in cocoa, and are linked to a large range of diverse physiological responses.[3,10-12] Theobromine (3,7-dimethylxanthine) despite what the name suggests, does not contain bromine and is occurs at ~2% by weight and has 1 less methyl group than caffeine (1,3,7-trimethylxanthine) which occurs at ~0.2% by weight.[3] These methylxanthines are metabolised in the liver, and can modify the contractibility of the heart and blood vessels and increase heart rate.[3] Furthermore, they can act on the nervous system through non-selective antagonist activity of adenosine receptors to further modify the cardiovascular physiology.[3] Theobromine has also been shown to suppress capsaicin-induced cough in humans through suppression of the vagus nerve, and is shown to be potentially more effective than codeine in its cough suppression.[11] Higher doses of theobromine (>0.8 g of theobromine, ~50 g cocoa) is reported to cause headaches and tremors.[12] The LD_{50} (lethal dose for 50% of population) for theobromine is 1000 mg/kg hence would require a huge amount of chocolate, whilst for dogs it is 300 mg/kg. Milk chocolate will often not be harmful to dogs in small quantities, but dark chocolate with considerably more cocoa is incredibly toxic to canines.[12]

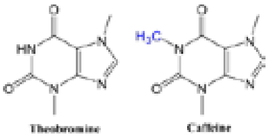

Fig. 2. Methylxanthines in cocoa: theobromine (3,7-dimethylxanthine) is found at ~2% by weight, compared to the more active caffeine (1,3,7-trimethylxanthine) at ~0.2% by weight

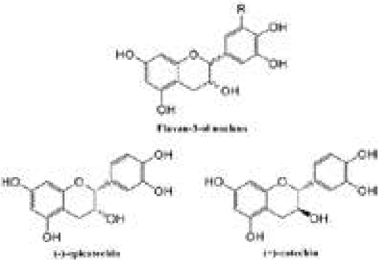

Fig. 3. Flavan-3-ol nucleus with the two most abundant flavanols in chocolate: (-)-epicatechin and (+)-catechin.

Catechin and epicatechin (Fig. 3), which belong to the group of compounds called the flavan-3-ols, are a widely researched component of chocolate.[3,7,8] These compounds are derived from 1,3-diphenylpropane and consist of a flavan-3-ol nucleus. (-)-epicatechin represents the majority of polyphenol content, with (+)-catechin as the second largest.[7,8] Cocoa powder, on a per-gram basis, has a significantly greater antioxidant capacity than other common sources such as cranberry and blueberry powders.[8] The antioxidant properties control the reactive oxygen species that damage DNA and cell membranes, offering a protective effect against diseases such as heart disease, cancer and neurodegenerative diseases.[8] Curiously, these molecules are unlikely to act directly as an antioxidant, rather induce production of endogenous antioxidant enzymes.[8] Cocoa flavanols are also reported to slow the rate of dementia in some diseases, due to the inhibition of enzymes responsible for triggering apoptosis.[13] Whilst the content of these flavanols in cocoa is high, the absorption and bioavailability of these compounds are somewhat unclear.[7,8,13] Furthermore, the roasting and alkalising processes drastically reduce the amount of flavanol present and hence the antioxidant capacity of cocoa is lowered as a result.[4-8]

Another class of compounds found in chocolate is the hydrophilic biogenic amines such as phenylethylamine and tryptamine.[3,5] Phenylethylamine is the human body's endogenous amphetamine and is found in high concentrations in chocolate. Phenylethylamine has been shown to significantly influence neurotransmitter activity, in particular, serotonin and dopamine. However, it is hypothesised that the activity of the monoamine oxidase B enzyme results in the breakdown of the phenylethylamine and other biogenic amines which are able to alter the neurotransmitter activities.

Concluding remarks

Upon examination, the processes for chocolate production and the chemistry associated with such an indulgence is not trivial. The processes required to take the seemingly inedible fruit and transform it into the magnificent food that is chocolate and cocoa is truly a feat of human experimentation and understanding of food science. Overall, no single molecule is responsible for our love for chocolate, yet a combination of compounds coupled with the delicious and complicated tastes results in that desire for just one more piece that leads to the inevitable consumption of the whole block.

References

1. International Cocoa Organization: https://www.icco.org/ (accessed 08/01/2018).
2. https://www.bloomberg.com/news/articles/2014-05-28/cocoa-shortage-looms-as-growers-opt-to-farm-rubber-commodities (accessed 08/01/2018).
3. Wilson, P. K.; Hurst, W. J.; (2015). *Chocolate and health: chemistry, nutrition and therapy* (1st ed.). Royal Society of Chemistry.
4. Caligiani, A.; Marseglia, A.; Palla, G. (2016). *Cocoa: Production, Chemistry, and Use.* In *Encyclopedia of Food and Health* (pp. 185-190). London, United Kingdom: Academic Press.
5. Afoakwa, E. O. (2010) *The Chemistry of Flavour Development during Cocoa Processing and Chocolate Manufacture*, in *Chocolate Science and Technology*, John Wiley & Sons, Ltd, Chichester, UK.
6. Andres-Lacueva, C.; Monagas, M.; Khan, N.; Izquierdo-Pulido, M.; Urpi-Sarda, M.; Permanyer, J.; Lamuela-Raventós, R. M, *J. Agric. Food Chem.* **2008**, *56*, 3111-3117.
7. Miller, K. B.; Hurst, W. J.; Payne, M. J.; Stuart, D. A.; Apgar, J.; Sweigart, D. S.; Ou, B., *J. Agric. Food Chem.* **2008**, *56*, 8527-8533.
8. Miller, K. B.; Stuart, D. A.; Smith, N. L.; Lee, C. Y.; Mchale, N. L.; Flanagan, J. A.; Hurst, W. J., *J. Agric. Food Chem.* **2006**, *54*, 4062-4068.
9. http://www.amanochocolate.com/sugar-and-fat-bloom-part-1/ (accessed 08/01/2018).
10. http://www.compoundchem.com/2014/04/19/the-polymorphs-of-chocolate/ (accessed 06/01/2018).
11. Usmani, O. S.; Belvisi, M. G.; Patel, H. J.; Crispino, N.; Birrell. M. A.; Korbonits, M.; Korbonits, D.; Barnes, P. J.; *FASEB J.* **2004**, *19*, 231-233.
12. http://toxnet.nlm.nih.gov/cgi-bin/sis/search2/r?dbs+hsdb:@term+@DOCNO+7332 (accessed 08/01/2018).
13. Valko, M.; Rhodes, C.; Moncol, J.; Izakovic, M.; Mazur, M.; *Chem. Biol. Interact.* **2006**, *160*, 1-40.

A day in the life of an outreach student

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Keywords: *outreach, education, science communication, chemistry in the community*

Geoffrey Weal is originally from Porirua, Wellington. He obtained BSc (Hons) degrees in both chemistry and physics from the University of Otago and is currently in the second year of his PhD in computational chemistry. During his studies, Geoffrey has volunteered for the Chemistry Outreach programme, in which he has promoted science to students of all ages, both in New Zealand and abroad. Geoffrey also leads the "Science for Supper" programme, which takes chemistry outreach to schools around Otago and Southland after working hours so that parents and the community can see what their children are learning in school.

Brianna is an undergraduate student at the University of Otago in the last year of a BSc in chemistry with a minor in physics. She is currently enjoying a summer studentship in the computational chemistry group. She has been involved in the Otago University Chemistry Outreach group for over two years and loves introducing kids to the weird and wonderful world of science.

Whiz. Bang! Whirl and BOOM! From the outside, this is what outreach is all about. But from the inside, underneath the "magic", there is simply a rough plan, no script, a great group of people and a bunch of experiments in the back of the ute. With tricks of sound and colour we can easily entertain and teach, but equally so with measuring cylinders and balances for conveying proper scientific practise.

Our goal is simply this: to demystify science and bring it down from the scary pedestal that it is put on and present it in a way that's obtainable for everyone. Science is not just for the talented students, and it's more far reaching than high-tech labs and whiteboards covered in complex workings. It's knowing to ask questions of the world we live in order to better understand it. If we pass on that message, then we are doing what we set out to do.

Let me describe a typical outreach day. It starts off like any other; get out of bed, have some toast and have a shower. Then the fun begins as I put on my black outreach T-shirt with cartoon scientists and a hydrogen peroxide stain on the back. Walking into the chemistry department, I see a bunch of fish boxes packed to the brim with gear and chemicals. There stands Dr Dave Warren, the outreach coordinator, getting the last boxes of beakers and conical flasks together. We fill up the liquid nitrogen dewar, grab a tub full of dry ice, pack up the truck and hit the road. As many as six chemistry (and non-chemistry) undergraduate and postgraduate students will attend today's outreach trip, all excited to hear what interesting yarns Dave has got for us today. What will this day bring I wonder?!

We arrive at the school, sometimes with children greeting us at the gate. Typically we visit primary and intermediate schools, as many students start to become discouraged from science between years five and seven (10 to 12 years old). However, outreach will visit high schools when invited. We drive up to the classroom and unload the gear. Ten minutes until the first class - time to set up the first experiment. The team sets up, talking to each other about what to get and how to lay out the experiment, while the senior students talk through an experiment they have mastered with the new outreach students. Teamwork is an important skill for every outreach student to learn. It takes a team to run a class of up to 30 children. Everybody in the team knows to be constantly on the lookout for any tasks that need to be done and to provide support for the person leading the experiment. Everybody working so well together is what makes outreach so enjoyable, and it is impressive to see new students pick this up so quickly.

The class of year fives pour into the classroom. They see large measuring cylinders bubbling away, and look, point, giggle and chat in awe about what is bubbling. The teacher quietens the class as one of the team takes the session. It is common for Dave to pick one of the students in the team to run a session. This is one way that students learn leadership and feel confident about being in charge of running a classroom. "Does anyone know what this might be?", we ask as we point to a pellet of dry ice. A few enthusiastic voices reply, "Liquid nitrogen?" "A really cold rock?" The children are thinking. "Is it ice?", one child asks. "Maybe. What does ice feel like on your skin?", we ask. "It's wet", another child responds. "Touch this. Does this feel wet?", we reply as we pass out little bits of dry ice. "No", the children observe inquisitively. "So it is ice?" "No!", the children answer as they play with the dry ice. A few more suggestion pop up, until one kid who remembers our last trip to the school or has seen it on Youtube yells out, "Dry ice!" "Very good!", we celebrate as we see science has stuck in this child's mind. We talk about what dry ice is and why it isn't wet - that it sublimes not melts. The teacher writes 'melt' and 'sublime' on the board, adding it to the literacy list for the school term. We add dry ice into the large measuring cylinder with a pH indicator, making the water bubble and change colour. It takes a bit of time, then all of a sudden the solution changes from green through to yellow and orange (Fig. 1). "WHOOOAAA!", the children exclaim in excitement. Just like that we have them hooked.

Fig. 1. A primary school student mesmerised by a bubbling dry ice experiment

Now to drive an important message home to the audience. A simple science experiment like this contains big scientific ideas. Dry ice increases the acidity of the water, which changes the colour of the solution. This has real life consequences. Carbon dioxide (CO_2) contributes to the greenhouse effect by reflecting outgoing infrared radiation back to earth. The amount of CO_2 in our atmosphere (and thus the greenhouse effect) has increased over the past decade due to the increased consumption of fossil fuels. What is not as well publicised is the affect that CO_2 has on our oceans. Just like in this simple experiment, increased global CO_2 causes the acidity of the oceans and seas to rise beyond what life has evolved to endure. For example, the shells of shellfish dissolve under acidic conditions, which prevents them from growing to their natural size. This can be devastating for the food chains they are a part of. These ideas are critical for young minds to hear and allows them to make their own decisions and opinions about the future they want to live in. We ask, "Do you want to make all these colours?" "YES!", the children enthusiastically yell.

Next thing, we are boiling up a red cabbage, which acts as a natural universal indicator (as it changes different colours at many pHs). Many of the experiments that the team perform do not require chemicals only a university can obtain. In fact, most ingredients we use come from a supermarket, which allows the children to perform these experiments at home. This sends the message that anyone can do science, no matter whether at home or in a big scientific facility.

The team leaps into action. The university students pass out equipment, fill beakers of solutions, crouch to the children's eye level and talk the children through the experiment in a kind and playful manner, inspiring the children into a science they themselves have been inspired into. Outreach is not just for the children but for university students as well. Outreach invites all university students, whatever their degree, to attend. Over many outreach sessions, students become more confident as they learn their way around the experiments and the children, as well as the rewarding process of contributing to the community. Students also become more aware of how to communicate very complex ideas in a simple way to someone without knowledge of that field. Many students lack this skill after graduating from university, even though it is vital for any student to develop for the career they pursue. Outreach provides the environment for students to learn this critically important skill. This is happening while the children squirt solutions together, make a big mess and a plethora of different colours (Fig. 2). Most importantly, all students attend to have fun.

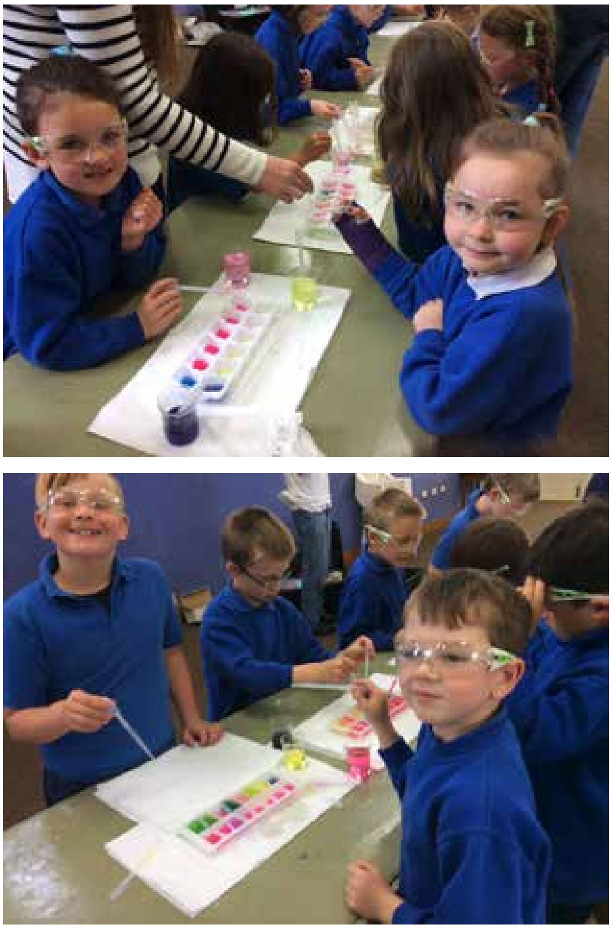

Fig. 2. Balclutha Primary School students make a big mess and a plethora of different colours using an acid, base and cabbage water

After a hard but enjoyable day of outreach, we clean all the glassware, wipe down the tables and pack the fish bins. We fill the ute and fall into the car seats as Dave drives us back to Dunedin. Halfway through the trip back to Dunedin, we always stop in at the dairy and get an ice cream, a longstanding outreach tradition.

If we are lucky, the children and teachers will invite us to attend or participate in out-of-school activities. In the past this has included helping in the school Olympics competition, playing at the end of year cricket game, zooming around on drift-trikes, and attending the end of year assembly. At the Waitahuna Primary School assembly, the children presented their long-term science experiments to their parents and community. One of the memorable experiments involved measuring the thickness of cow patties by finger depth, aiming to understand how fertile the land was from a cow pat.

Outreach allows students to travel around Otago, Southland and other parts of New Zealand - to schools, libraries and maraes and to interact with students of all ages. However, we would have never thought it would take us all over the world.

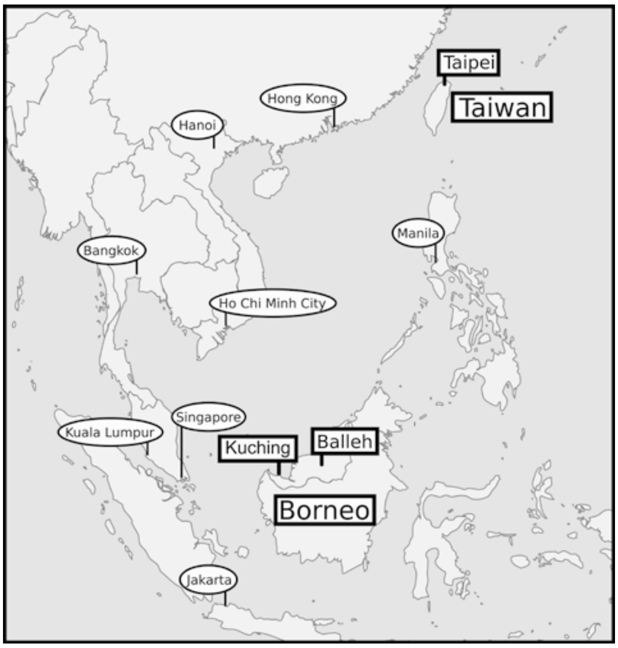

Fig. 3. Map of destinations travelled to by the outreach team (in boxes). Some well known cities are given in ovals.

So far, the outreach team has had the privilege to visit two countries (Fig. 3). The first was to Borneo, Malaysia. The Malaysian teachers' colleges, IPG Batu Lintang and Sarawak, invited us to travel to Kuching and to villages around the region of Sarawak, in Borneo.[1] This was a special experience as we got to travel to villages that we would have never known about or travelled to in our lifetimes.

A very special portion of this trip was our visit to the village of Balleh. This village consists of a few longhouses stretched along either side of the Batang Baleh river, a five hour boat trip on this river highway from the closest city. The outreach team stayed at SMK Balleh high school for a week. We arrived at the school from the jet boat, greeted by students and staff on the docks. Guided to the outdoor staff kitchen for a meal we met Speedy, the Principal of the school. He told us of the cultural significance of the land, the history of the people, and the distances the pupils travelled to this boarding school each weekend. All their students live on the river. They eat fish from the river, their parents work on the river and they travel to school via the river. This river is their lifeblood. Speedy also told us of the dedication of their teachers, whose husbands, wives, children and extended families do not live in Balleh. In fact, these teachers travel a total of 15 to 20 hours to be with their families at the weekends.

The team ran multiple classes each day with all the students of the school. One of the issues we faced was a language barrier, as English was not a first language of these students. However, fascinatingly, this did not cause a serious issue. The joy of science became a universal language that could be communicated to all the students (Fig. 4). The students became less shy once they had experienced us in the classroom. This allowed the students to approach us on our final day while we were testing toys for that night's science show (Fig. 5).

Fig. 4. SMK Balleh students play with PVA borax slime

Fig. 5. The students were curious about the toys we were playing with at SMK Balleh

"Would you like to have a go?" we asked them, holding out our new toys. This sparked a personal connection between us and the students. We continued to talk to each other about our lives in New Zealand and in Balleh. At the end of the science show, crowds of students came up to us, wanting photos and autographs, giving us their thanks and asking what we were doing next. Most importantly, the students wanted to keep in touch with us. We were lucky enough to catch up with one of these students the following year.

The second country that the team has visited is Taiwan. Annually, about 144 high school students from around Taiwan are selected to attend the Madame Curie High School Chemistry Camp. These students learn about a range of sciences and technologies, some developed in Taiwan. The outreach team of between six and eight people run a four hour project. This requires six months of precise choreography from Jacqui Kao, Prof. Chi-Young Lee and Dr. Dave Warren; from the vast amounts of equipment and chemicals required to the practicality of all 144 students preforming the experiments.

Otago student Sam Sutherland designed the first experiment for this science camp, based on his Masters research in polymer chemistry.[2] During Sam's research, he stumbled upon a literature report of a hydrogel created from nanoclay crosslinked with a diamine polymer. Sam created the hydrogels for the science camp. The students calculated the Young's modulus of the hydrogel by measuring the hydrogel's length of extension as 1 g aliquots of water were added to a bag, attached to one end of the hanging hydrogel (Fig. 6). The water acted as an applied force upon the hydrogel. The hydrogel's Young's modulus could be calculated from the gradient of the plot of the length of extension against water weight.

Fig. 6. Two students measuring the Young's modulus of their hydrogel

The students added water, measured the length of extension, and repeated. After half an hour, the students were shocked to see the hydrogel had stretched over 60 cm, was holding over 150 g of water and had not snapped. "When will it snap? Will it not break!" the students uttered in bewilderment.

This is an example of active research used to create outstanding outreach activities to inspire our future scientists and world leaders. This event is one of the toughest challenges for the outreach team each year. All the qualities of outreach - teamwork, leadership, confidence, teaching, seeing the bigger picture, inspiring - are applied with an excitement and energy to run this large class of students. The team thrills the students into the bright future and sheer joy that science has to offer (Fig. 7).

Fig. 7. The team hard at work to make the experiment a success

From overseas and back in New Zealand, behind the Whiz, Bang! Whirl and BOOM! that outreach displays on the outside, there is a deeper intention; to inspire the next generation of scientists, world leaders, artists, civil servants and engineers to think about the big problems facing our future and how we will deal with them. This is hugely important not just from a global perspective but also from a national perspective; to increase New Zealand's presence on the global scientific, technological and economic stage.

However, outreach only facilitates the teaching environment. Without the continuing effort of teachers and parents, children cannot continue to learn and appreciate science in their lives. Getting parents involved in their child's education is especially important as their parents' opinions and values reverberate in the home. However, it is rare that parents have the opportunity to experience what their children learn in the classroom. A new programme called 'Science for Supper' tries to address this by holding an after-work, interactive science session where both parents and children can learn about various scientific ideas with a range of exciting and messy experiments.

Our outreach programme continues to attract international attention. Besides our invitations to Taiwan and Malaysia, outreach has received interest from several international academics, some of whom have visited New Zealand. This includes Prof. Garon Smith, from the University of Montana, who often travels from the United States of America to New Zealand. He performs as 'G Wiz', the chemistry wizard, who shows that magic and science are simply one and the same (Fig. 8).

Fig. 8. Prof. Garon Smith as 'G Wiz', showing an experiment to the students

The success of outreach is due to the dedication of the extraordinary team of university students who repeatedly contribute their time. Outreach students have been involved in helping with or running outreach outings and events, designing experiments and programmes, videos, and even performing an outreach play. All this is done while studying for their university exams.

Fig. 9. Dr Dave Warren having fun riding a drift trike

A special mention must be made to Dr Dave Warren (Fig. 9). Dave began the outreach programme in 2008 and ever since has allowed it to grow, providing an opportunity for all students to contribute. His personality and leadership are aspects that help bring more students into the outreach programme and allow it to survive for everybody to enjoy.

If you would like to know more about chemistry outreach at the University of Otago, you can follow us on our Facebook page (https://www.facebook.com/chemotago/), website (http://www.otago.ac.nz/chemistry/outreach/index.html), YouTube (search Otagochemistry or NeverStop Recording) and twitter hashtag (#chemoutago) (Fig.10).

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References

1. Dougherty, I.*; University of Otago Magazine* **2016**, *43, 26-27.*
2. Warren, D. S.; Sutherland, S. P. H.; Kao, J. K.; Weal, G. R.; Mackay, S. M., J. *Chem. Educ.* **2017**, *94*, 1772-1779.

Fig. 10. The University of Otago chemistry outreach Facebook banner, including photos of the team, experiments, people and places

Ngaio Marsh's murderous chemistry

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Keywords: *Ngaio Marsh, crime novels, chemical murder*

Ngaio Marsh is probably still New Zealand's most well-known crime novelist.[1] Living alternately in New Zealand and Britain, she wrote more than thirty murder-mysteries, four of which are set in New Zealand, and six of which involve chemistry as the agent of death (Table 1).

Each of these chemical murders is described below – without giving away too much of the rest of the plot!

Book 3: *The Nursing Home Murder*, 1935

The story centres on the death of a patient following an emergency operation for appendicitis, leading to suggestions of poisoning by one of three injections given: hyoscine (for which the dose was prepared and injected by the surgeon; 'camphor', prepared and injected by the attending nurse, and a post-operative 'anti-gas', prepared by the attending nurse and injected by another doctor present.

An initial hypothesis suggested the patient was an unidentified drug addict, a nurse commenting that before the operation the patient "looked rather like a patient who had been given a drug – morphia for instance. It's a kind of frowning stare. I have often noticed it appear when the drug is starting to take effect". Eventually the focus of the investigation into the death turned to finding the 'extra' anesthetic to account for the amount found in the victim – much more than had been given by the surgeon. Eventually a syringe of the same anesthetic as that administered by the surgeon – hyoscine – was found concealed in part of trolley that carried gas cylinders (presumably nitrous oxide) for anesthesia – the property of an anesthetist who claimed he used gas rather than injections because of an earlier death by overdose for which he had been responsible. In fact, he had committed a number of similar murders-by-injection, of which he had kept a tally by marking his stethoscope.

Hyoscine injection is used as a pre-operative medication to produce sedation and amnesia. It is also used preoperatively to inhibit salivation and excessive secretions of the respiratory tract. In this particular case, it was probably used to stimulate a "decrease in gastrointestinal tone and gastric secretion". One of its effects is to dilate the pupils of the eyes – so the attending nurse was perhaps closer to the cause of death than she realised. As injected, 'Hyoscine' is a clear, colourless to straw coloured, sterile solution of hyoscine hydrobromide, the formula for which is $C_{17}H_{21}NO_4.HBr.3H_2O$; its molecular weight is 438.3.[2] Severe over-dosage may cause coma, respiratory depression, cardiac arrhythmia, and may result in death, as it did in Marsh's story.

Derived from the *Hyoscyamus niger*, henbane or stinking nightshade (Fig. 1), hyoscine was also suspected as the causative agent in the death of Cora Crippen, wife of Dr. Hawley Harvey Crippen, and was accepted at the time as the cause of her death, since her husband was known to have bought some at the start of the year.[3] It is a known recreational hallucinogen, and one might speculate that Marsh's knowledge about it was more from that perspective than a pharmacological one, given that its medical use didn't start until 1947[4] – well after she'd written about it.

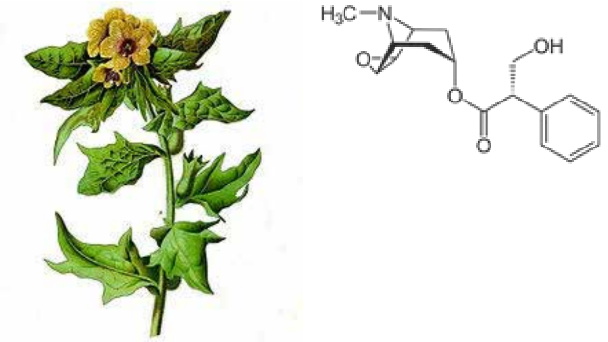

Fig. 1. *Left:* Henbane: *Hysocyamus niger*; image from https://en.wikipedia.org/wiki/Hyoscyamus_niger (accessed 08/02/2018). Above: Structure of hyoscine; image from https://en.wikipedia.org/wiki/Hyoscine (accessed 21/09/2017)

Table 1. Ngaio Marsh's New Zealand and chemical murders

Novel no.	Year of publication	Title	Chemical means of murder	Set in New Zealand
3	1935	The Nursing Home Murder	• Overdose of hyoscine (medical)	
4	1936	*Death in Ecstasy*	• Poisoning – prussic acid in wine	
5	1937	*Vintage murder*	Not applicable	• Yes
9	1940	*Death at the Bar*	• Cyanide poisoning with dart	
12	1943	*Colour Scheme*	• Drowning in geothermal water (NZ)	• Yes
13	1945	*Died in the Wool*	Not applicable	• Yes
14	1947	*Final Curtain*	• A 'lethal dinner of champagne & crayfish' was later thought to be arsenic poisoning	
21	1960	*False Scent*	• Poisoning with organophosphate	
31	1980	*Photo Finish*	Not applicable	• Yes

Book 4: *Death in Ecstasy*, 1936

This story revolves around the poisoning of a member of a religious sect using cyanide dissolved in wine. The method of making the cyanide is attributed to Abberley's *Curiosities of Chemistry*, published in 1865 by Gassock and Hauptmann of New York, but this book appears to be fictional.[5] Marsh writes that Abberley's book alleges that it is: "a simple but little known method of making sodium cyanide from wool, washing soda and iron filings". Actually hardly simple, it is subsequently described (p. 166):

"You take equal weights of wool and dried washing soda and iron filings. Cook at red heat for three or four hours. Allow to cool. Add water and boil for several hours. Pour off clear solution and evaporate same to small volume. When cool, yellow crystals separate out. And are these [crystals] sodium cyanide? They are not. To the crystals add a third of their weight of dried washing soda. Heat as before for an hour or two. While still hot, pour off molten substance from black residue. It will solidify on cooling to a white cake. *Alley houp!* Sodium cyanide as ordered."

While it has proved difficult to locate this 'recipe', hydrogen cyanide is released into the smoke associated with the combustion of materials such as grass clippings, green wood, tobacco, cotton, paper, wool, silk, weeds, and animal carcasses (although the release of cyanide from the combustion of plastics is recognized as much more significant).[6] Recognising that "Some of the chemical bonds in a protein like the lanolin in wool are peptide linkages (carbon-nitrogen bonds, essentially) and if wool is burned without a lot of excess oxygen, some cyanide might well be released",[7] this could be part of the basis of Abberley's method. Wool also contains keratin, which is soluble in alkaline solution.[8] This could explain the inclusion of washing soda in the first stage of the recipe, since in solution sodium carbonate has a pH of about 11.

Although considerable heat is said to be required for the reaction, that of a domestic fire is considered to be sufficient. The iron filings apparently needed for the reaction (probably to ensure a reducing environment) were found by the investigators to have been obtained from a poker in the suspect's flat.

Cyanide occurs naturally in plants such as white clover and cassava and in the seeds of fruits, including apples and apricots. Acid hydrolysis or enzyme action can release the cyanide from amygdalin, the glucoside to which it is bound.[9] Cyanide toxicity is associated with the ability to bond to Fe (III). Detoxification can be achieved with thiosulfate, which in the presence of the enzyme rhodonase, found in the liver and kidneys, converts the toxic cyanide to the less toxic thiocyanate:

$$CN^- + S_2O_3^{2-} \rightarrow SCN^- + SO_3^{2-}$$

In this case, death occurred rapidly, and the post mortem confirmed cyanide in the stomach of the victim by Liebig's method,[10] the eventual formation of white precipitate when silver nitrate was added being attributed to the reaction:

$Ag^+ + 2CN^- \rightarrow [Ag(CN)_2]^-$ followed by: $Ag^+ + [Ag(CN)_2]^- \rightarrow Ag[Ag(CN)_2]_{(s)}$

As an aside, during the investigation of the poisoning it was revealed that during their association with the sect, several members had become heroin addicts. One member is advised to seek help at a nursing home known to the investigating police inspector Alleyn. Perhaps Ironically, in an earlier 'murderous chemistry' tale by Marsh such a place is the venue of a medical poisoning (see Book 3).

Cyanide poisoning also features in one of Marsh's short stories – *Death on the Air*, first published in 1936 – in which the murder victim is electrocuted when he touches the knobs on his radio. The murderer connected the mains power directly to the metal knobs with which he has replaced the proper ones. The murderer confesses his crime, and before he can be apprehended and arrested, he writes to the Police: "I'm enclosing a note for Isabel [the victim's wife], who won't forgive me, and an official one for you. You'll find me in my bedroom upstairs. I'm using cyanide. It's quick…."

Book 9 *Death at the Bar*, 1940

The passage below sets the scene for this murder. "'Abel's rat-poisoning in the garage', said Parish. 'They've all gone out to see he doesn't give himself a lethal dose of prussic acid'. 'Good lord!' Watchman exclaimed. 'Is the old fool playing around with cyanide?'" It is revealed that: 'The chemist hadn't any of the stock rat-banes, but he poked around and found this stuff. I think he called it Scheele's acid…. And then he said the fumes of Scheele's acid mightn't be strong enough, so he gingered it up a bit.' 'What with?' 'Well – with prussic acid, I imagine.'"

Carl Wilhelm Scheele (1742-1786) – who gives his name to the 'Scheele's acid' referred to above – was an Enlightenment 'loner' who discovered several organic acids (including: citric acid, from lemons; lactic acid, from milk; malic acid, from apples; oxalic acid, from sorrel). Although he discovered oxygen before Joseph Priestley, his publication of this discovery was too late to give him priority.[11] A prolonged study of the coloured dye "Prussian blue" led to Scheele's isolation of prussic acid (or hydrogen cyanide), and this interest in dyes also resulted in his devising of "Prussian green" – copper arsenate, a poisonous compound initially used to colour confectionary![12]

In Marsh's story a man dies in a pub apparently after pricking his finger on a dart. The post-mortem revealed cyanide in his blood, but not in his stomach, the coroner commenting during the post mortem that 'since hydrogen cyanide is excessively volatile, the fact that none is found in the stomach did not preclude the possibility that the deceased had taken it by mouth". Later in the inquest, the physician initially called to the scene, observed, "The room did not smell of cyanide, but 'stank' of brandy. Brandy, by the way, is one of the antidotes given for cyanide poisoning, along with artificial respiration, potassium permanganate, glucose and half a dozen other remedies, none of which is much use if the cyanide has got into the bloodstream."

The cause of death was eventually attributed to the ingestion of cyanide vapour from the rat-poison. A demonstration with silver nitrate solution on another sample was described picturesquely: "On the surface of the prussic acid, a little spiral had risen. It became denser, it flocculated and the watch glass [covering the sample] was no longer transparent, but covered with an opaque whiteness." The 'whiteness' is Ag $[Ag(CN)_2]_{(s)}$, as earlier described for *Death in Ecstasy*.

Book 12 *Colour Scheme*, 1943

The publisher of this novel was fulsome in its praise:

"This splendid new novel by the famous Ngaio Marsh promises a rare feast of enjoyment. To begin with it has a refreshingly original setting in the beautiful North Island of New Zealand, Miss Marsh's own country, which she describes with fidelity and affection. There is, too, an unusually interesting set of characters. At the hot springs near Harpoon Inlet the retired Anglo Indian Colonel Claire and his wife have opened a thermal spa which attracts a good many visitors desirous of undergoing treatment…. Of the crime that so dramatically broke the tranquil atmosphere of the spa and the subsequent hunt for its perpetrator Miss Ngaio Marsh gives a lively and exciting account."[13]

The novel is set at a rather rustic thermal resort called Wai-ata-tapu. Not only is the name evocative of Wai-O-tapu, but the geothermal features described seem more like those at the Wai-O-tapu thermal area (Fig. 2) than those at Rotorua. It is also possible that Marsh was thinking of Waimangu before the 1886 eruption of Mount Tarawera which had similar geothermal features, but also had an accommodation house (Fig. 3) and an adjacent Māori settlement, whose residents could have mingled with the spa's clients and entertained them.[14]

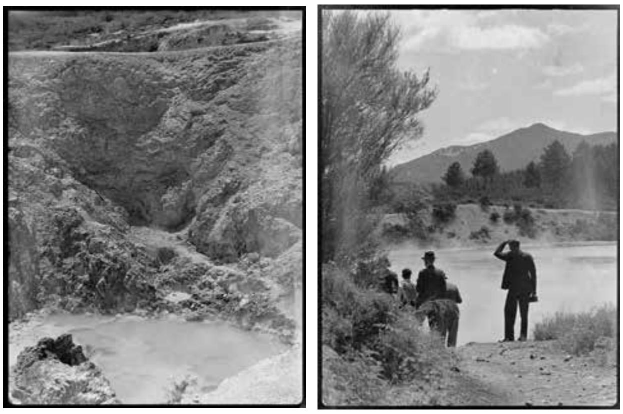

Fig. 2. The reality of Marsh's fictional Wai-ata-tapu? *Left:* View of a large crater at the base of volcanic terraces, Wai-O-tapu, about 1940. [Image: Alexander Turnbull Library, 1/4-091462-F] *Right:* Unidentified group of tourists beside the shore of the Champagne Pool at Wai-O-tapu, about 1940 [Image: Alexander Turnbull Library, 1/4-091465-F]

However, Marsh's writing about the chemistry of the water and the 'cures' for which the water and mud are used resemble those at Rotorua:

"On the alleged therapeutic properties of the baths you have evidently formed your own opinion. They consist, as you are aware of thermal springs, whose waters contain alkalis, free sulphuric acid, and free carbonic acid gas. There are also siliceous mud baths in connection with which my brother-in-law talks loosely and freely of radio-activity.[15] This later statement I regard as so much pious mumbo-jumbo, but again I am alone in my opinion. The mud may be miraculous. My leg is no worse since I took to using it."

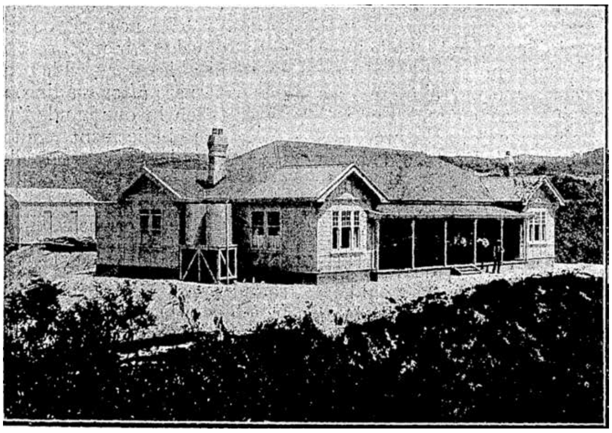

Fig. 3. Government Accommodation House, Waimangu. (*New Zealand Illustrated Magazine*, 01 April 1904). [image: Alexander Turnbull Library, Wellington, New Zealand. records/2774666]

And a little further on: "Tonks of Harpoon [Inlet] is the visiting medical man. I need say no more. Possibly it is an oblique recommendation of the waters that all of Tonk's patients who have taken them have at least survived." A night stroll in the geothermal area is suggested – "the path leading past the springs and round the shoulder of the hill that separated them from the native settlement. Their departure was hindered by Mrs. Claire who hurried from the house, full of warnings about boiling mud. 'But you can't miss your way, really', she added. 'There are little flags, white for safe and red for boiling mud… The sentence died away as a doubt arose in Mrs. Claire's mind about the propriety of saying that death by boiling mud would be a poor sequel to an evening of social solecisms."

As the party progresses they "… walked on and presently through the soles of their feet, received a strange experience. The ground beneath them was unsteady, quivering a little, telling them that, after all, there was no stability in the earth by which we symbolized stability. They moved across a skin and the organism beneath it was restless…." Of the spring area itself they observed: "It was perhaps fifteen feet across, dun-coloured and glistening, a working ulcer in the body of the earth. Great bubbles of mud formed themselves deliberately, swelled and broke with the sounds they had noticed a few minutes before and which were now loud and insistent. With each eruption unctuous rings momentarily creased the surface of the brew."

All this before the evening of a concert provided by local Māori during which one of their number disappeared, and was inferred to have fallen in or to have been deliberately pushed in to the mud pool . As others of the visitors passed the spring on their way back to the lodgings after the concert, "so still was the air that in the interval between snatches of Māori singers' voices "Taupo-tapu [the main mud-pool] and the lesser mudpots could be heard, placidly working in the dark, out on the native reserve: plop, plop-plop, a monstrously domestic noise."

Clothes are found in the spring and speculation abounds as to whether the victim feigned his death or was murdered. A statement by Dr. Ackringtron "If [he] is found before he gets clean away, he will be wearing hobnail boots" is prescient, for the next sentence records, "The group of men outside the window parted. Webley [a policeman] had taken something from the sack, He held it up. It was a heavy boot and it dripped mud." Human remains were ultimately recovered, the text saying:

"There, in the distance, the geyser's jet was, for a flash of time, erected like a plume in the air. …There, too, on the crest of the mound above Taupo-tapu, were Mr. Webley's men, black figures against a sombre background, figures that stooped, thrust downwards, and then laboriousy lifted…. It would have been much worse, of course, if they hadn't covered it, but though the sack was wet, it followed the shape beneath it in a hard eloquent curve…. Even when they were beyond the fence he could still hear the sound of Taupo-tapu, the grotesquely enlarged domestic sound of a boiling pot."

Of this novel, one of Marsh's biographers commented:

"*Colour Scheme* has aroused more interest than any other of her novels. The use of death by boiling in a mud pool could be seen as an attempt to locate the novel in the country, but equally as a sensational appeal to the exotic for international readers. It is only the rather startling setting which makes the plot differ from the conventional style."[16]

Drowning was often referred to in colonial times as the 'New Zealand death'.[17] Of course drowning in a geothermal mudpool may be complicated by the prospects of poisoning from hydrogen sulfide, which has been described as "due to a direct toxic effect on the brain, while others are almost certainly a result of hypoxia secondary to H_2S-induced respiratory insufficiency"; noting also that "pulmonary edema is a common consequence of poisoning and there is suggestive evidence of hyperactive airway responses in some individuals following brief H_2S-induced unconsciousness (knockdown).[18] The hazard to health of hydrogen sulfide is well recognised in towns such as Rotorua,[19] and, specifically, in geothermal pools.[20]

Book 14: *Final Curtain*, 1947

A gentleman who dies in his bed after consuming a large dinner is initially thought to have died from "a severe attack of gastroenteritis", perhaps triggered by eating too much New Zealand crayfish. The man is embalmed and buried before the possibility of murder is considered. Again rat-bane is implicated: this time the household has misplaced a tin of arsenic-based poison. However, because arsenic compounds might have been used in embalming, it was assumed that detection of the murderer could be difficult. Widely used for embalming war dead during the American Civil War,[21] arsenic compounds have been less commonly used in embalming fluids in the 20th century. Modern practice uses a mixture of compounds including formaldehyde (typically 5-35%), glutaraldehyde and methanol, as well as humectants and wetting agents. As it turns out, the chemist working on the case reported of the exhumed body, "First analysis completed. No arsenic anywhere".

Attention then turned to another possibility: the bottle of thallium acetate used to treat the household's children for ringworm might have been inadvertently or deliberately misused as the gentleman's post-prandial sleeping draught. Exhumation of the body showed that much of its full head of hair had fallen out. This proved to be significant because it was later found that the gentleman's cat which had been put down in the belief it had ringworm had actually consumed the gentleman's spilt medicine and its fur had fallen out – like its master's hair – because of thallium acetate poisoning.

Children seem to be no more sensitive to the acute toxic or lethal effects of thallium than adults.[22] However, the effects might be long-lasting: a case being noted of " intellectual impairment, residual ataxia and spastic paraparesis in a 42 year old man who was given oral thallium acetate for scalp ringworm at the age of 7".[23]

Ingestion of thallium as a colourless solution of its salts (e.g., $Tl^{(1)}(CH_3COO)$) gives rise to gastric and neurological disorders and rapid organ degradation. However, at low doses, symptoms are slow to appear and can easily be attributed to other ailments, which makes thallium rather discreet and why it is dubbed by Lennartson as the "poisoner's poison".[24] Incidentally, Ngaio Marsh is not the only murder-mystery author who 'used' thallium salts as a poison. Lennartson takes up the story:

"Agatha Christie made use of thallium in her 1961 novel *The Pale Horse* [25]— and in doing so actually saved a life. In 1977, a 19-month-old girl from Qatar was admitted to Hammersmith Hospital, London, suffering from a serious, unknown sickness. Without a diagnosis, the doctors could not do much. One of the nurses, however, was reading *The Pale Horse* and realised the similarities between the symptoms of her patient and Agatha Christie's fictitious victim. A urine sample revealed high levels of thallium and an antidote could be administrated — Prussian blue, which binds to the metal and helps expel it from the body. The subsequent publication[26] describing the case includes the following acknowledgement: "We are indebted to the late Agatha Christie for her excellent and perceptive clinical descriptions and to Nurse Maitland for keeping us up to date on the literature."

Book 21: *False Scent*, 1960

In this case, the victim is sprayed in the face with a pesticide – 'Slaypest' – diluted with a pungent perfume to mask the smell. The combination was still sufficiently potent to kill. The active ingredient in 'Slaypest' was initially named as "hexaethyltetraphosphate" and described as "a contact poison and very persistent' (although named as "tetraethylpyrophosphate" later on). Although no longer registered as a commercial pesticide product, hexaethyltetraphosphate would probably have been available for this purpose when Marsh wrote *False Scent*. As an organophosphate it is toxic, although the effects seem rather less than those described for tetraethylpyrophosphate,[27] an organic phosphate pesticide which acts as an inhibitor of cholinesterase. Tetraethylpyrophosphate is highly toxic by all routes of exposure.[28] While administration of oxygen followed by atropine sulfate either intravenously or intramuscularly might have prevented the fatality, the delay in raising the alarm and the time taken for a doctor with the antidote to arrive may well have been too long for this to be effective. The structures of both compounds are given in Fig.4.

Fig. 4. Structure of organophosphate insecticides, the differences of which were unlikely to have been of interest to Ngaio Marsh. *Left:* Hexaethyltetraphosphate. *Right:* Tetraethylpyrophosphate.

Ngaio Marsh's chemistry

Modern-day detective fiction writer P.D. James opines, "Writers of the Golden Age [of which Ngaio Marsh was one], and indeed for some decades after, were little concerned with forensic or scientific research."[29] The poisonous substances used by Marsh in her writing – cyanide, arsenic, thallium acetate, and organophosphates – were readily available at the time either for pest control or therapeutic applications. It is unlikely that she received any formal education in chemistry, but the fact that the first edition of *The Nursing Home Murder* acknowledges the contribution of a medical doctor – Dr. Henry Jellet,[30] who had cared for her during surgery, to the extent of his being identified as a co-author could suggest she may have sought advice on specialist medical and chemical matters, at least early in her writing career. However none of her subsequent novels are co-authored in this way, perhaps because "with more novels under her belt, Marsh realised that her real skill, vital as technical details and plot twist are, is her fine handling of character and place, neither of which could have been supplied by a medically-knowledgeable [or scientifically-knowledgeable] collaborator, and both of which are key in her work".[31]

Perhaps we can do no better than ask – as did P.D. James, "Stands the church clock at ten to three? And is there arsenic still for tea?"[32]

Author's note

Readers of crime novels who prefer Agatha Christie to Ngaio Marsh might enjoy Kathryn Harkup's book *A is for Arsenic - The Poisons of Agatha Christie (*Sigma Bloomsbury: London, 2015). In her book, Dr Harkup draws attention to Agatha Christie's training as an apothecary's assistant or dispenser providing her with the chemical knowledge that enabled her to use the 14 poisons across 14 novels that are discussed in Harkup's book.

Notes and references

1. Ngaio Marsh (1895-1982). For a biography, see: Lewis, M. *Ngaio Marsh: A Life*. Chatto & Windus: London, 1991.
2. Hyoscine injection: http://www.medsafe.govt.nz/profs/Datasheet/d/DBLHyoscineinj.pdf (accessed 19/09/2017).
3. Young, F. (ed.) *The Trial of Hawley Harvey Crippen*. Notable Trials Series. Edinburgh: William Hodge & Company: Edinburgh, 1920, p. xxvii; see also evidence, pp. 68–77.
4. Fischer, J.; Ganellin, C.R. *Analogue-based Drug Discovery*. John Wiley & Sons, 2006, p. 551.
5. 'My invisible library': http://52books.blogspot.co.nz/p/the-invisible-library.html (accessed 21/08/2017).
6. Hydrogen cyanide: New concerns for fire-fighting and medical tactics: http://www.fireengineering.com/articles/2009/06/hydrogen-cyanide-new-concerns-for-firefighting-and-medical-tactics.html (accessed 22/08/2017).
7. Weiner, R. Does burning wool release cyanide gas? http://www.madsci.org/posts/archives/1999-03/921131883.Ch.r.html (accessed 22/08/2017).
8. Goddard, D.R.; Michaelis, L. A study on keratin. *Journal of Biological Chemistry* **1934**, *106*, 605-614.
9. Fergusson, P.E., *Inorganic Chemistry and the Earth*. Pergamon: Oxford,1982, p. 350.
10. Liebig, J. Titration of cyanide with silver nitrate. *Justus Liebigs Anal. Chem*. **1851**, *77*, 102-105; also*: Journal of the Chemical Society* **1852**, *4,* 219. [Referred to in Vogel, A.I. *A Textbook of Quantitative Inorganic Analysis*, 3rd edition. Longmans: London, 1961, p. 74.]
11. Scheele, C.W. *Chemical Treatise on Air and Fire* (1777). Reprinted as: *Chemical Treatise on Air and Fire: A Selection* (Illustrated Edition). Dodo Press: England, 2009.
12. Burns, W.E. *Science in the Enlightenment – An Encyclopedia*. ABC-CLIO: Santa Barbara, 2003, pp. 259-260.
13. From the 1944 edition, "set up, printed and bound for the publishers by Coulls Somerville Wilkie Ltd., Dunedin"; published by Collins, London.
14. *Tarawera Eruption Centennial*. Rotorua District Council: Rotorua, undated but inferred as 1986, p. 25 (photograph of Wairoa township on the shore of Lake Rotomahana); p. 42 (photograph of the Rotomahana Hotel).
15. Priestley, R. The Rotorua Bathhouse radium activator: From therapeutic device to quack curiosity. In Cooper, A.; Paterson, L.; Wanhalla, A. (Eds.). *The Lives of Colonial Objects*. Otago University Press: Dunedin, 2015, pp. 247-251.
16. Robinson, R., Wattie, N. (Eds.). *Oxford Companion to English Literature*. Oxford University Press: Oxford, 1998.
17. The "New Zealand Death": Drowning in New Zealand History from a Socio-Historical Perspective. *Ricky1871's blog*. https://ricky1871.wordpress.com/2013/06/14/376/ (accessed 21/09/2017).
18. Milby, T.H.; Baselt, R.C. Hydrogen sulfide poisoning: Clarification of some controversial issues. *American Journal of Industrial Medicine* **1999**, *32*, 192-195.
19. Horwell, C.J.; Patterson, J.E.; Gamble, J.A.; Allen, A.G. Monitoring and mapping of hydrogen sulphide emissions across an active geothermal field: Rotorua, New Zealand. *Journal of Volcanology and Geothermal Research* **2005**, *139* (3-4), 259-269. The abstract notes, "Rotorua city can be divided into three regions—an area of low H_2S concentration in the west, a 'corridor' of high concentrations running north–south through the city centre where H_2S is being emitted, and an area of medium concentration to the east which is influenced by the prevailing wind direction, creating a plume from the central corridor." The health effects of H_2S in Rotorua are specifically referred to in: Bates, M.N.; Garrett, N.; Shoemack, P. Investigation of health effects of hydrogen sulfide from a geothermal source. *Archives of Environmental Health: An International Journal* **2001**, *57* (5), 405-411.
20. Bassindale, T.; Hosking, M. Deaths in Rotorua's geothermal hot pools: Hydrogen sulphide poisoning. *Forensic Science International* **2011**, *207* (1-3), e28-e29.
21. Bloudoff-Indelicato, M. Arsenic and Old Graves: Civil War-Era Cemeteries May Be Leaking Toxins (October 2015). http://www.smithsonianmag.com/science-nature/arsenic-and-old-graves-civil-

war-era-cemeteries-may-be-leaking-toxins-180957115/ (accessed 21/09/2017).

22. Munch. J.C. *Human* thallotoxicosis *J. Am. Med. Assoc.* **1934**, *102*, 129.
23. Barnes, M.P.; Murray, K.; Tilley, P.J.B. Neurological deficit more than thirty years after chronic thallium intoxication. *The Lancet* **1984**, *323* (8376), 562.
24. Lennartson, A. 'Toxic thallium'. *Nature Chemistry* **2015**, *7*, 610.
25. Christie, A. *The Pale Horse*. Collins Crime Club: London, 1961. For a synopsis, see: http://www.agathachristie.com/stories/the-pale-horse (accessed 22/09/2017).
26. Matthews, T.G., Dubowitz, V. Diagnostic mousetrap. *British Journal of Hospital Medicine* **1977**, 17, 607-608.
27. Hexaethyl tetraphosphate: https://pubchem.ncbi.nlm.nih.gov/compound/Hexaethyl_tetraphosphate#section=Top (accessed 22/08/2017)
28. TEPP: https://pubchem.ncbi.nlm.nih.gov/compound/tetraethyl_pyrophosphate#section=2D-Structure (accessed 22/08/2017)
29. James, P.D. *Talking About Detective Fiction*. Faber & Faber: London, 2009, p. 149.
30. Henry Jellett (1872-1948) was a specialist in midwifery and gynaecology, educated at Dublin University, and a long-time master of Rotunda Hospital. His obituary (*British Medical Journal* **1948**, *1* (4564), 1262-1263) noted, "When he finished his term as Master at the Rotunda he emigrated to New Zealand, where he was appointed consulting obstetrician to the Health Department... His very dominant character did not appear to suit the New Zealanders, and during his last years he devoted himself to growing apples and to his favourite sport of fishing. Jellett could not be called a popular man, but he was a very sincere worker in the fields of gynaecology and obstetrics and his work will be remembered for a long time." https://www.ncbi.nlm.nih.gov/pmc/articles/PMC2090153/pdf/brmedj03735-0048.pdf (accessed 22/09/2017).
31. Duffy, S. Introduction. In Marsh, N.; Jellett, H. *The Nursing Home Murder*. HarperCollins, Detective Story Club edition: London, 2017, p. vi.
32. James, P.D., *op. cit*, p. 66.

Some Unremembered Chemists

A series of articles that explores the lives and work of selected chemists who have made a significant contribution to the advancement of the discipline, the profession and well-being of mankind, yet who are little remembered.

Sir William Crookes (1832-1919)

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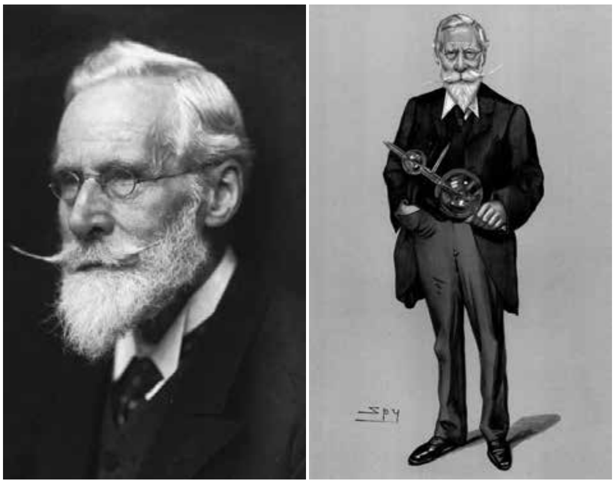

Sir William Crookes in 1906 (left) and caricature by Leslie Ward (1902-1903)

William Crookes was born at 5.30 pm on the evening of June 17, 1832 at 143 Regent Street in London, next door to his maternal uncle's bookshop.[1] He was the eldest of the sixteen children born to Joseph Crookes (1792–1884), a tailor from Masbro', near Rotherham in Yorkshire, and his second wife, Mary Scott of Aynhoe, a South Northamptonshire village near Banbury.[1] His home was also that to the five children of his father's first marriage whose wife June had died during childbirth in 1829.[2] In his teens, Joseph Crookes took an apprentice tailor position in Sheffield but did not serve the full time. Rather, in his late teens (at 18 or 19 years of age), perhaps as a result of differences with his seemingly authoritarian father,[2] he moved from Yorkshire to gain training in the West End (London) master tailor's shop of Mr Atkinson on Regents Street. Subsequently, Atkinson moved to 143 Regent Street taking Joseph with him as a partner and accepting him as a son-in-law when he married his daughter June. When June died, Joseph Crookes had five children to raise and he remarried fairly soon after her death and then, following Atkinson's death in the 1830s, he became sole proprietor of the business and began living over the shop with his family.[2] He was astute with his finances and became quite wealthy investing in property and living until he was 86 years old. In about 1840, the Crookes's moved to a new home that they named as Bute Cottage where William subsequently grew up (until he was 14 years of age). It was one of the Italianate chalets in the Park Village garden estate to the east of Regents Park. However, the boy had little formal school education as the employment of tutors was less expensive than sending all the children to school. He did go to a college in Weybridge called Prospect House some twenty seven kilometres from London, where he is recorded as attending from 1841-1846.[1] There his French art teacher noted his attention to detail and ability to draw, something he imparted to his subsequent scientific career. This began when, in 1848 at the age of fifteen, he entered the Royal College of Chemistry (RCC) in Hanover Square, London. It was a mere three years after its opening with August Wilhelm von Hofmann, the young inaugural director appointed from Bonn when he was a *privatdozent*. This 1845 appointment fitted to the industrialisation of England and the need for appropriate training in science and the subsequent moves.

The young William travelled daily by the omnibus from his then home of two years, Brook Green Farm near Hammersmith, the house of which his father extended and re-named Masborough House after his own birthplace; it was demolished after Joseph's death in 1884. The attraction that William Crookes found in science was atypical of his siblings and earlier family. His time at the RCC was noted by his extreme care and painstaking accuracy especially of his easily legible laboratory notes; within his first year he was awarded the Ashburton Scholarship. When that ended a year later he became junior assistant to Hofmann and then, in 1851, senior assistant until he left in 1854. During this period he undertook his own work including research in spectroscopy. His first published paper was on the subject of selenocyanides and read before the Chemical Society on June 20, 1851 after just two years at the RCC and when Crookes was merely 19 years of age. It appeared in the *Quarterly Journal of the Chemical Society* in 1852 and described new compounds of selenium.[3] In this paper Crookes described the preparation, analysis and properties of the selenocyanides from K, Ag, Pb, Hg, NH_3, Ba, Sr, Ca, Mg, Zn, Fe, and Cu - the majority of which were previously unknown.[3] Although his first paper, it was his last in pure chemistry.

Hofmann's connections with the Royal Institution, however, brought Crookes to the notice of Michael Faraday, who, with his friends Charles Wheatstone and George Stokes, led him into the world of chemical physics. He attended Faraday's lectures at the Royal Institution and became attracted to the work of Sir Charles Wheatstone. Like Crookes, Wheatstone had interests in the impact of light on matter and both were students of photography. Crookes' success in photographing the rings of certain crystals in polarised light only happened after Wheatstone provided the crystals and tourmaline plates for the experiments.[1,4] He had made a number of spectroscopic examinations before he left the RCC but, according to d'Albe,[1] these were unpublished though recorded in his laboratory notebook giving him claim to the law that adsorption and emission take place at the same wavelength. Of these, his examination of the spectrum of sodium from the coloured flame of sodium carbonate is reproduced from Crookes' original notebook by d'Albe.[5] It needs to be remembered that these experiments were performed during the infancy of spectroscopy and serve to illustrate Crookes' ability to design and construct his own equipment.

Crookes left the RCC in 1854 without a degree and no academic post to go to. Instead, he took an appointment as superintendent at the meteorological department of the Astronomical Observatory in Oxford and, once there, made significant improvements to the methods and procedures for the recordings. However, he only stayed for one year. Following Oxford, Crookes moved to Chester where he taught chemistry at the Chester Diocesan Training College (then College of Science and now the University of Chester) as the first science teacher but again, stayed for only one year. It was during this period that he courted Ellen Humphrey of Darlington, a town some 250 km distant but whose acquaintance he had made some years earlier through school friends of his sister. They were married at St. Pancreas Church in London on April 10, 1856, and had ten children of whom only three sons and a daughter survived into adulthood. The Crookes's celebrated their golden wedding in 1906 and Ellen died in 1916.

The original Chester Diocesan Training College (now Old College) in 1843, a year after it opened

Before his marriage William was back in London, though he had no job and little prospect of one. Despite the fact that his parents were well-off, the large number of siblings meant that William had to support himself and his wife. And so it was that for the most part, his subsequent enterprises were dictated by the possibility of commercial rewards. He chose to move into photography, an area in which he had experience. In 1854, with John Spiller, he had devised the first dry collodion process and for some ten years he worked enthusiastically at photography, editing journals on the subject, investigating the spectral sensitivity of the wet collodion process, and attempting to apply photography to the scientific recording of polarisation, astronomical objects, and spectra. He was also actively involved in independent research, journalism and consultancy.[6] In fact, William Crookes became a commercial scientist, an entrepreneur and scientific journalist with research achievements in chemistry, physics, and photography.[7]

During his year in Chester he had taken remarkably sharp images of the moon at 3 cm diameter using a telescope built by Mr Hartnup, a Liverpudlian, and with the help of Wheatstone he obtained a £20 grant from the Royal Society to enlarge them. This resulted in images enhanced some 20 times that were displayed at the Crystal Palace. Then there was another grant from the London Science and Art Department for experiments to provide a portable light source to allow photographs to be taken of objects in a dark room. The results of this study led to an improved *limelight* (calcium light) that was created by blowing an oxygen stream through a jet close to another blowing hydrogen with the mixed gas impacting on a ball of magnesia (MgO) held on a platinum wire. This produces an intense illumination which Crookes suggested was free from danger.[1] Then, in May and shortly after his marriage, Crookes accurately determined the specific gravity of eleven samples of iron rails for Indian railroads because of a perceived connection between durability and specific gravity. He further added to his income from his booklet *Handbook to the Waxed-Paper Process in Photography*, published by Chapman and Hall in 1857. The same year saw William become secretary and journal editor for the London Photographic Society (Vol. 4, July 1857–July 1858), but again the appointment lasted only the one year because he accepted a two year contract with Petter and Galpin to supply articles exclusively for the *Photographic News*. That same year of 1858 saw Crookes purchase the house at 20 Mornington Road near Regent's Park and he moved there with his daughter (his first child) and his mother-in-law. The house was fitted with a chemical laboratory which Crookes used for analytical work, consultancies and research.[1,6] His analysis of the optical sensitivity of photographic processes caused him to speculate privately on the origin of spectra and this was when the solution was published by Bunsen and Kirchhoff in 1860 announcing the discovery of caesium and rubidium from spectroscopic detection. Subsequently, everything in his home laboratory was examined through the spectroscope.

Shortage of money continued to influence Crookes's interests, as in his era science and business were integrated activities; the world of commerce frequently saw him drive many a hard bargain. Eventually, he made a comfortable living from his ventures, which included the sodium amalgamation method of gold extraction (worked in North Wales; see below) and the chemical exploitation of sewage as a fertiliser (exploited at the Crossness sewerage pumping station in Bexley, south east of London city), as well as electric lighting, but achieving financial success was hard. By the early 1880s he was comfortably off, and could afford to entertain on an impressive scale. The analytical consultancy flourished at his home.

During 1859, after consulting other members of the family, William Crookes purchased the copyright of the *Chemical Gazette* and on December 10 that year he published the first issue of his *Chemical News*, a weekly which he edited until 1906; it incorporated the Gazette. His plan was for the weekly to cover the breadth of chemistry and promote industrial activity and, if successful, would give him status and reputation. There was no journal devoted to chemistry, pharmacy or industry at that time and Crookes' efforts provided one. Initially the *News* was published by Spottiswoode and Co., but from January 1861 was published by Griffin, Bohn & Co. and printed by Reid & Pardon. Ownership was equally and jointly between the publisher, the printer and Crookes, and Crookes was paid 3½ guineas (£3-13-6) per week as editor (now close to $NZ850 per week for this part-time role) for which he had full control of the scientific content. Crookes included a report on Michael Faraday's 1859 Christmas lectures to young people and he gained permission to do the same for 1860. The reports were a major attraction of the 1861 volume, and the *Chemical News*, at four pence per issue (in 1861), became highly successful and a major influence on scientific progress. It numbered almost every noted chemist of its era among its contributors, though its ownership and production was entirely Crookes's by the end of the year.[1]

On February 22, 1861, William gave a lecture on platinum to the Royal Institution. This was subsequently included with Michael Faraday's lectures on the chemical history of a candle given to a juvenile audience at the Royal Institution as the 1862 book *The Chemical History of a Candle*, edited by Crookes. The following month saw what many regard as the most significant of William Crookes scientific discoveries. His former mentor, Hofmann, had in 1850 provided a sample of a by-product from a sulfuric acid factory in Tilkerode, in the Harz Mountains of northern Germany.[7,8] It was a sludge that contained the easily extracted selenium that Hofmann wanted. However, a considerable residue remained and this was set aside for subsequent examination as it appeared to contain tellurium, an element that gained Crookes's attention in 1861. Examinations indicated there was little tellurium, but when a flame test of the residue was run there was an unexpected bright green flash. This bright green line had never previously been seen and further investigation proved it to belong to a new element. It was subsequently extracted and isolated by Crookes. This information was presented at the Royal Institution on March 23,[9] and announced in the *Chemical News* of March 30, 1861 and *The Philosophical Magazine* for the following month. It took some seven weeks before the name of the new element was given as *thallium* after the Greek word *thallos*, meaning budding twig, a word then frequently used to describe the beautiful green tint of new vegetation. Samples of the metal, its sulfide and oxide were shown at the Great Exhibition of 1862 and recognition for the work came by the election of Crookes to Fellowship of the Royal Society in 1863. However, there was dissention as he received a rude shock with Professor Claude-Auguste Lamy of Lille University providing his own exhibit of thallium as an ingot at the Exhibition. Lamy was fortunate in that his father-in-law, Charles Kuhlmann, was a chemical industrialist whose improved sulfuric acid factory in Lille proved a rich source of thallium. With such an abundant supply of the raw material, Lamy was able to prepare sizable amounts of metallic thallium. On seeing Crookes exhibit of a few grains of metallic thallium, thallium oxide and thallium sulfide,[10] Lamy declared the metal sample a sulfide and received a prize for his exhibit. Crookes challenged the award with the prize jury as his claim for the discovery of thallium predated that of Lamy. The matter was settled when both gained medals and Crookes was given the rightful recognition for discovering the element. However, Crookes' study of the element continued and it was only in 1873 that he published his final determination of its atomic weight. He obtained his elemental thallium from the sulfate, then synthesised thallium nitrate from weighed quantities of absolutely pure thallium taking every precaution necessary to ensure the purity of his materials. Moreover, the balances were built especially for the research, the weights accurately tested, and the uncertainties determined. His weighing was carried out partly in air and partly in vacuum, all were reduced to absolute standards, and remarkably large quantities of thallium were employed in each experiment. The mean of ten closely agreeing determinations gave a value of 203.642 (ranging from 203.628 to 203.666).[11] The value accepted today is 204.38. This study confirmed Crookes's reputation for meticulous analytical precision and his experimental prowess was clear in delivering the fractional value; this was some time before the existence of isotopes was established.

In 1862 William Crookes applied for the chair in chemistry at the Royal Veterinary College in London but was unsuccessful, after all he had no academic qualification. Yet his desire to teach is illustrated by him giving an experimentally illustrated 20 lecture course at the Peckham Schools in South London that same year. He gave lectures also in various places on a number of subjects but the period in the 1860s from 1862 was one of limited income for Crookes. He took on a new editorial role with *The Quarterly Journal of Science* that first appeared on January 1, 1864. Later that same year he took on an apprentice for three years who got his chemical education from William, worked in the laboratory and lived with the Crookes family, all for £500 for the entire period. He contemplated moving to Manchester but nothing came of it.

During 1864 Crookes was attracted to industrial activity. There had been chemical reports on the action of sodium amalgam on metals in solution and he decided that he should investigate the impact of the amalgam on the native ores. This he did and by February 1865 he had lodged his first patent on the use of sodium amalgam in extracting gold and silver from ores; the specification did not appear until January of the following year. Crookes gathered a group of people interested in commercialising the process and obtained permission from the owners of the Gwynfynydd Mine in Snowdonia, North Wales to test several tons of ore. An application for a US patent was made but it was rejected because, unbeknown to Crookes, Professor Henry Wurtz had gained a patent in 1864. The tests in Wales had elicited some variations by Crookes in the procedures to the extent that Crookes was able to apply for and gain a new patent that included the use of three different amalgams. The manufacture of the sodium amalgam was by Johnson Matthey in London and Crookes had various collaborators gain patents for the process in South American and several other countries. There was some anonymity between Wurtz and Crooks on the claim of originality, but William's correspondence with the American quietened matters to a satisfactory resolution by 1867—the second patent was original to Crooks, the first to Wurtz. William's interest in gold abated over the next few years as the use of potassium cyanide increased.

Crookes was instrumental in settling the germicide to be used in the cattle plague of 1865-1867 in England and then he was employed to test various cattle with carbolic acid (phenol). His report *On the Application of Disinfectants in Arresting the Spread of Cattle Plague* formed a part of the third report of the Cattle Plague Commission. His conclusions ultimately were that the disease was due to germs carried by animals and humans, and that disinfecting with tar acids and sulfur fumigation should not be terminated. They were, and recurrence was evident in the early summer of 1867. In September of that year William's 21-year old younger brother, Philip, died of yellow fever. He was at sea on the CS *Narva* laying some of the first transatlantic cable lines. This had a significant influence on William as he had spent much time with Philip and he turned to spiritualism of which much has been written[12] and is not discussed further here. He returned to scientific chemistry but was sufficiently ill over 1868 and 1869 as to do little but nurture the *Chemical News*.

The work of Crookes continued to extend over both chemistry and physics and was characterised by its originality of conception, and the skill of the experimental execution; he was always more effective at experiment than in interpretation. Crookes's life was one of unbroken scientific and business activity. He worked regularly in his laboratory in the mornings and after dinner into the early hours. His scientific interests resulted in him becoming a well-known personality within the late Victorian scientific community.[2,13] From 1870 Crooks had sufficient income to employ research assistants, the adept Charles H. Gimingham (1870—1882) and James H. Gardiner (1882—1919). To the latter must be attributed the impressive bulk of Crookes's researches in his later years, including work on scandium and on *Crookes lenses* published when he was over eighty[1] (Crookes's lenses provided a blueish-grey shade of lens able to filter infrared rays, but they never became very popular because the shade created ashen shadows beneath the wearer's eyes; they evolved from his work on cataracts). However, it was two lines of research that occupied Crookes for many years during these periods. These were the properties of highly rarefied gases stimulated from use of a vacuum balance during the course of the thallium researches, and the investigation of the elements of the *rare earths* from shortly after 1880.

By 1873 Crookes had begun his experiments on radiant forces that came from his use of a vacuum balance in his thallium studies. He showed that the action of radiation on black and white surfaces were the same whereas light sources impacted more on the black surface.[14] From these observations Crookes designed and built his radiometer. It consists of a glass bulb from which much of the air has been removed to form a partial vacuum. Inside the bulb, on a low friction spindle, is a rotor with four vertical lightweight metal vanes spaced equally around the axis. The vanes are polished or white on one side and black on the other. When exposed to sunlight, artificial light, or infrared radiation (even the heat of a hand can be enough), the vanes turn with no apparent motive power, the dark sides retreating from the radiation source and the light sides advancing. Cooling the radiometer causes rotation in the opposite direction. The effect begins to be seen at partial vacuum pressures of a few torr, reaches a peak at around 10^{-2} torr and has disappeared by the time the vacuum reaches 10^{-6} torr.

Fig. 1. The Crookes radiometer

The radiometer (or light mill) was a cause of much debate in the years immediately following its invention, but in 1876 the phenomenon was accounted for from residual gas in the evacuated bulb impacting on the white and blackened surfaces—the white simply reflects whereas on the black surface some heat is absorbed and re-emits the radiation with greater force. However, it was not until 1879 that the correct explanation appeared.[15,16] Radiant energy from a light source warms the black side by black-body absorption faster than the silver or white side and the gas molecules can move from the cooler to the warmer side of the vane. Today the device is used mainly in physics education as a demonstration of a heat engine –

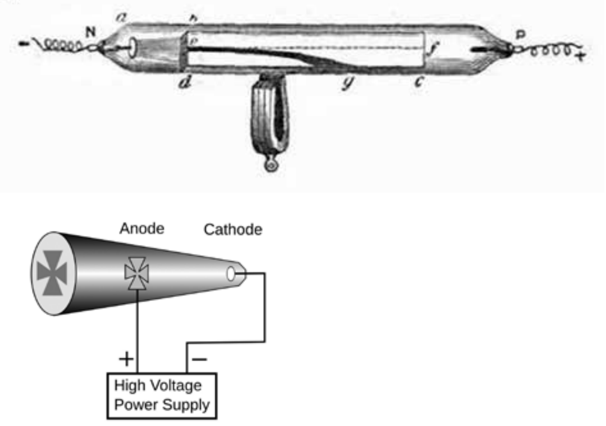

Fig. 2. Top: The original Crookes tube (from Wikimedia) -- see ref.17; bottom: schematic of the tube

run by light energy and since Mr John Brownrig gained instructions for manufacture of the radiometer (paying royalties) the instrument has been available from instrument makers.

The work that led to the radiometer drove Crookes to seek a mechanism for the rotation. In doing this, he passed electrical discharges through rarefied gases devising his evacuated tube from that developed by Heinrich Geissler in 1857. Geissler's tube was used to demonstrate the principles of electrical glow discharge, similar to modern neon lighting. The Crookes tube consists of a partially evacuated glass bulb of various shapes with a cathode and anode at opposite ends but evacuated to a much lower pressure (ca. 0.1-0.005 pascal) than that in the Geisler tube, though still holding a small amount of air.

It was his coworker Charles Gimingham who had improved the 1865 Sprengel mercury vacuum pump to allow this advance. When Crookes applied a high voltage to the electrodes in the tube he saw that the negative electrode (cathode) appeared to emit rays. What William Crookes found was that as he pumped more air out of his tubes, a dark area in the glowing gas formed next to the cathode. As the pressure got lower, the dark area, now called the *Crookes dark space*, spread down the tube, until the inside of the tube was totally dark. However, the glass envelope of the tube began to glow at the anode end. Crookes then conducted a series of ingenious experiments in which he showed that the rays travelled in straight lines, cast shadows and caused phosphorescence in objects upon which they impinged, produced heat by their impact, and were deflected by a magnetic field.[17] He thought that the rays were streams of particles of ordinary molecular magnitude not the electrons we now know. What was happening was that as more air was pumped out of the tube, there were fewer gas molecules to obstruct the motion of the rays (now recognised as electrons) from the cathode, so that, on average, they could travel a longer distance before they struck a gas molecule. By the time the inside of the tube became dark, the electrons were able to travel in straight lines from the cathode to the anode, without a collision. They were accelerated to a high velocity by the electric field between the electrodes, because they did not lose energy to collisions, and also because Crookes tubes were operated at a higher voltage. By the time they reached the anode end of the tube, they were going so fast that many flew past the anode and hit the glass wall. When the invisible electrons hit the glass walls of the tube they excited the atoms in the glass, making them fluoresce, usually a yellow-green. Later experimenters painted the back wall of Crookes tubes with fluorescent paint so that the beams were more visible. Following an earlier hint of Michael Faraday's, Crookes believed that he had discovered a fourth attenuated state of matter, which he called *radiant matter*.

It remained for J. J. Thomson in 1897 to demonstrate that the rays were not streams of particles of ordinary molecular magnitude, but subatomic electrons whose mass was $^{1}/_{1800}$ that of an atom of hydrogen. However, it was Crookes's success in producing a vacuum of the order of 0.1 pascal that made possible the discovery of X-rays as well as of the electron; his experimental work in this field was the foundation of nuclear physics and electronic theory. *Crookes's dark space* and the *Crookes tube* are part of the vocabulary of modern physics. It was characteristic of Crookes that, though already in his sixties, he readily and enthusiastically accepted the new interpretation of his work.

For many years Crookes conducted experiments with his assistant, James H. Gardiner on the rare earth elements (lanthanides) that are elements so similar to one another in chemical properties that special methods for their separation had to be devised. This exacting work was carried out by using spectroscopic methods to follow the course, and testing the completeness, of the separation and resulted in one of the most obscure regions in inorganic chemistry gradually becoming clearer. The work led Crookes to speculate on the existence of *meta-elements*, clusters of elements resembling one another so closely that in most ways they behaved like a single element.

Crookes's meta-elements are superficially similar to isotopes, the concept of which was put forward by Soddy, but only in 1913 from radioactivity studies. This was another field of Crookes activity. In 1900 he separated the active transformation product, uranium-X, from the decay of uranium (^{238}U). Uranium X_1 (simply uranium X before the discovery of uranium X_2) was an isotope of thorium, namely ^{234}Th (half-life = 24 d) [uranium X_2, sometimes known as brevium, is metastable protactinium (^{234}Pa; half-life: 1.159 min)]. Crooks observed the gradual decay of the separated transformation product, and the simultaneous reproduction of a fresh supply in the original ura-

Fig 3. The Crookes cathode ray tube. Left: power off; centre: with power - rays travel straight; right: with power and magnet - rays deflected down

nium. He also noted that when α-particles, ejected from radioactive substances, impinged upon zinc sulfide, each impact was accompanied by a minute scintillation. The flashes of light are created by individual α-particle collisions with the screen and this observation formed the basis of his spinthariscope that played an invaluable role in early work on radioactivity until the invention of the Geiger counter in 1908. The detection instrument was a device specifically intended to view these scintillations. It consisted of a small screen coated with zinc sulfide affixed to the end of a tube, with a tiny amount of a radium salt suspended a short distance from the screen and a lens on the other end of the tube for viewing the screen. Crookes named his device from Greek *spinthēr* or spark.

Scottish chemist Sir William Ramsay isolated helium in March 1895, having noticed a bright yellow line that matched the D_3 line observed in the spectrum of the sun. His samples were identified as helium by British scientist and astronomer Lockyer and William Crookes. Crookes' last work began from the occurrence of cataracts among furnace workers and his efforts to provide a glass that could be used in spectacles to minimise the effects.[2,18] Cataract disease was only added to the British government list of compensable diseases in December 1908 but some eight months earlier it sought the advice of the Royal Society on how glare and heat from glass furnaces and molten glass affected the physical and physiological conditions of the eye sufficiently to cause cataract formation. Crookes was a member and frequent stand-in chairman of the committee. He had previously shown that all of the transition metals were stable to 900°C after he found that platinum began to sublime at 1300°C. Moreover, in conducting the series of experiments, he found that the glare from the furnace would give a worker a massive dose of infrared radiation after three hours. He strove to find a coloured glass that could minimise this and be used in spectacles. Thus, he was more than competent to serve on the committee. By 1909, French and German studies had showed that pathological changes to the eye lens were caused by ultraviolet radiation. Together with his assistant Gardner, the conclusion they reached was that the type of glass used in Europe would be improved if the absorption spectra of different types of glass were known. The pair then provided the Royal Society with successful formulations after comparing some 160 different combinations of metallic glass with white glass. The tests had shown him that it was worth experimenting with glass mixtures containing small quantities of the oxides or salts of cerium, chromium, cobalt, copper, iron, lead, manganese, neodymium, nickel, praesodymium and uranium. However, he needed a further two years to conclude the work. The Royal Society committee concluded that it should be possible to make a glass opaque to infrared and ultraviolet radiation but Crookes had not been able to obtain the glass.[2] An interim report was sent to government some months earlier and Crookes was pressed to write-up his work to further impress government. Further funding was made available and Crookes's private report was subsequently formally presented to the Royal Society in 1913, one month into his presidency. The paper announced a formulation that cut off 90% of heat radiation, was opaque to ultraviolet light, and was relatively free of colour so that objects remained clear to the eye. Crookes noted that, besides glassworkers, there would be an advantage in preparing such coloured or tinted glasses to prevent glare for people exposed to sunlight reflected off cliffs, snow, or even electric light. Crookes was not the first to prepare tinted lenses for leisure use, but here was the origin of scientifically formulated Crookes lenses and the era of modern sunglasses.

Crookes wrote various technical books and translations, including his standard treatise, *Select Methods in Chemical Analysis* (1871), and the smaller *Diamonds* (1909), a subject to which he had devoted some study during his visits to South Africa in 1896 and 1905. He frequently served the government in an advisory capacity, and his work on the production of safety spectacles was, as noted previously, the basis of sunglasses and one of many contributions to public welfare. He was a man of science in the broadest sense, an influential personality, and a doyen of his profession, standing primarily for the widening and dissemination of chemical knowledge and its application to the problems of human life.

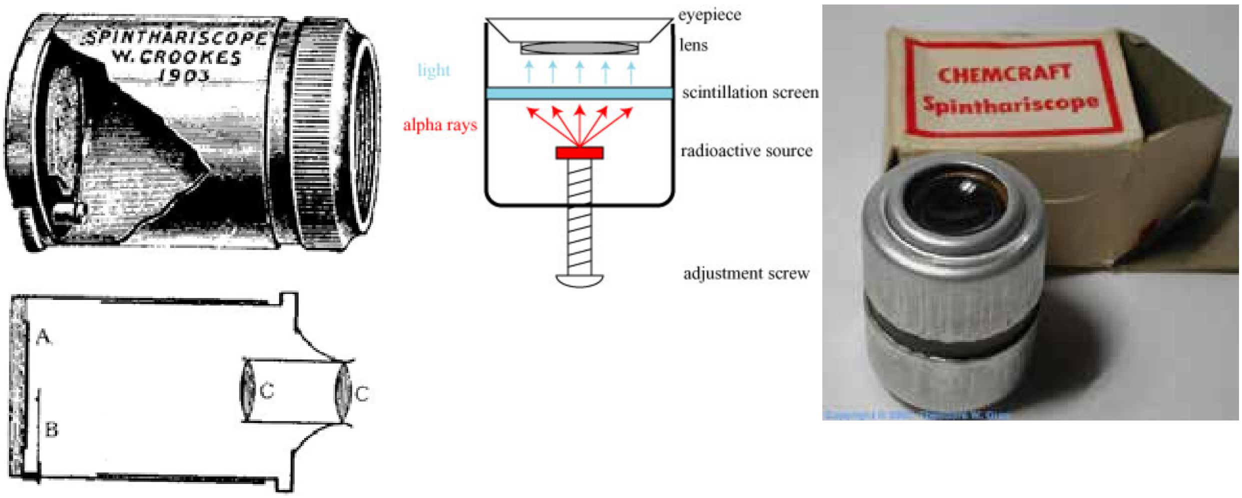

Fig 4. The Crookes spinthariscope, **a**: original; **b**: Crookes schematic (from *Practical Physics*, Institute of Physics); **c**: full schematic. The modern spinthariscopes does not use $Ra(NO_3)_2$ or $RaBr_2$; it is more likely to contain a small speck of thorium ore that cannot be removed

He was awarded the Royal, Davy and Copley medals (1875, 1888 and 1904), was Vice-President of the Royal Society three times (1895–96, 1907–08 and 1915–16), its Society's Foreign Secretary (1908–12) and its President (1913-1915). As the octogenarian president he was the oldest elected in its history. His life was one of unbroken scientific and business activity. He interests were broad, ranging over pure and applied science, economic and practical problems, and psychic research. All of these interests collectively made him a well-known personality and one of England's most celebrated and decorated scientists. He was knighted in 1897 (while president of the Society for Psychical Research) and received the Order of Merit in 1910. He also served as president of the Chemical Society, the Institution of Electrical Engineers, and the British Association.

References and Notes

1. Fournier d'Albe, E.E. *The Life of Sir William Crookes,* Fisher Unwin Ltd. London 1923; available from: https://archive.org/details/in.ernet.dli.2015.176056 (accessed 31/08/2017).
2. Brock, W.H. *William Crookes (1832–1919) and the Commercialization of Science*, Routledge, London 2008, pp. 586; see: https://books.google.co.nz/books?id=J-64DQAAQBAJ&pg=PT43&lpg=PT43&dq=Joseph+Crookes&source=bl&ots=6JcKyZbkv-&sig=HGw4XPD_52WgDq5JPVNkkgXKrx4&hl=en&sa=X&ved=0ahUKEwj667uZl4DWAhUFupQKHUtxA5wQ6AEIQDAJ#v=onepage&q=Joseph%20Crookes&f=falseCrookes, W (accessed 31/08/2017).
3. Crookes, W. *On the Selenocyanides*, *Quart. J. Chem. Soc. Lond.* ***1852**, 4*, 12-20; see: http://pubs.rsc.org/en/content/articlelanding/qj/1852/qj8520400012#!divAbstract.
4. Crookes, W. *On the Application of Photography to the Observation of certain Phenomena of Polarisation*, *J. Photographic Soc.* **1853**. *1*, 70-75.
5. See ref. 1, p. 26-27.
6. Chaston, J.C. *Sir William Crookes*, Platinum Metals Rev. **1969**, *13*, 68-72, available from Johnson- Matthey: http://www.technology.matthey.com/article/13/2/68-72/ (accessed 15/06/2017).
7. Marshall, J.L. and Marshall, V.R. *Rediscovery of the Elements: Thallium, Crookes, and Lamy*, *The Hexagon*, **2011**, *102*, 62-67; see: https://digital.library.unt.edu/ark:/67531/metadc111267/m1/6/?q=2011 (accessed 20/06/2017).
8. Marshall, J.L. and Marshall, V.R. *Rediscovery of the Elements: The Harz Mountains and Gottingen, The Hexagon,* **2012***, 103,* 4-9*;* see: https://digital.library.unt.edu/ark:/67531/metadc111273/m1/4/ (accessed 20/06/2017).
9. Crookes, W. *On the Discovery of the Metal Thallium*, *J. Soc. Arts* **1862**, *11,* 460-463, available at: http://www.jstor.org/stable/41323729?seq=2#page_scan_tab_contents (accessed 16/06/2017).
10. See ref. 1, p 76-79.
11. *Crookes, W. Proc. Royal Soc. Lond. (***1871-1872**) **1872**, *20*, 475-483; see: http://www.jstor.org/stable/113177.
12. See, e.g.: Doyle, Sir A.C. *The Researches of Sir William Crookes (1870-1874)*, *The History of Spiritualism*, **1926**, *1*, 236-257 available from https://archive.org/details/historyofspiritu015638mbp (accessed 22/06/2017).
13. Brock, W.H. *Crookes, Sir William (1832–1919).* In Oxford Dictionary of National Biography; see: http://www.oxforddnb.com/view/article/32639?docPos=&backToResults=%2Fsearch%2Fresults%2Fcontributors.jsp%3FcontributorId%3D753 (accessed 23/06/2017).
14. Crookes, W. *On Attraction and Repulsion Resulting from Radiation*, *Phil. Trans. Royal Soc. Lond.* **1874**, *23*, 501-527; see: http://rstl.royalsocietypublishing.org/content/164/501.full.pdf+html; Part II. Crookes, W. *Proc. R. Soc. Lond.* **1874**, *23*(156-163), 373-378; see: http://rspl.royalsocietypublishing.org/content/23/156-163/373.full.pdf+html.
15. *Reynolds, O. Phil. Trans. Royal Soc. Lond.* ***1879**, 170, 727–845 (doi:10.1098/rstl.1879.0078).*
16. *Gibbs, P. How does a light-mill work?* ***1996**; see:* http://math.ucr.edu/home/baez/physics/index.html.
17. Crookes, W. Popular Science Monthly, London, November 1879, Fig. 14 in *On Radiant Matter*, p.158-167; see: http://www.electrotherapymuseum.com/Library/SirWilliamCrookes/pages/1880Crookes0013.htm) (accessed 14/07/2017).
18. Brock, W.H. *The Royal Society's Glass Workers' Cataract Committee*, *Notes Rec. Royal Soc.* **2007**, *61*, 301-312.

Too big to pay: employee-inventor remuneration

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Should an employee involved in research be remunerated by their employer for making an invention when the employer obtains a benefit from the success of a patented invention?

The issue can be a contentious one. Employees may feel that they should be rewarded for their achievement and for any benefit the employer receives from that work. Conversely, an employer may consider that what the employee has done is part of the job that the employee is already employed and paid to do.

New Zealand and Australia have no provisions in their Patents Acts to provide remuneration to an employee for any commercial benefit that an employer receives from the success of an invention.[1] Instead, contract and common law rules apply. Some more fortunate employees may have IP clauses in their employment contracts that state they will receive some form of remuneration from their employer for successful inventions. If not, there is no obligation for an employer to remunerate an employee in New Zealand or Australia with respect to the success of a patented invention.

Even in countries where there is a statutory provision, such as in the UK,[2] China,[3] or Japan,[4] it does not necessarily mean that an employee will be duly remunerated. For example, the UK Patents Act 1977 provides that if an employer derives an *"outstanding benefit*", an employee is entitled to a fair share of that benefit (very nice if you can get it!). However, this turned out *not* to be the case for Professor Shanks who invented a biosensor for monitoring diabetes while working for Unilever. He took his dispute all the way to the UK Court of Appeal in 2017.[5]

Professor Shanks was employed by Unilever UK Central Resources Ltd. His expertise was in the field of liquid crystals and liquid crystal displays. While employed by Unilever, he worked on process engineering and process control sensors focussing on biosensors (rather than for medical diagnostics). He developed an interest in re-usable or disposable devices with biosensors for use in diagnostic applications and identified a number of possible opportunities: one of which was sensors for monitoring glucose, insulin or immunoglobulin levels in diabetics.

Professor Shanks had filled a 10 micron gap between glass plates of an LCD with liquid crystal many times in his work. He placed a liquid droplet on the edge of the cell and relied on capillary attraction to draw the liquid into the gap. He realised that this technique could be used with other liquids such as blood or urine. He also saw how this technique could be used with etched or printed planar electrodes and enzyme electrochemical methods to measure glucose concentrations in blood, serum or urine in what was called an Electrochemical Capillary Fill Device (ECFD). In October 1982, Professor Shanks investigated and built the first prototype ECFD at home, in his own time, using some slides from his daughter's toy microscope kit and some Mylar film as spacers, all held together with bulldog clips. Alongside the ECFD, Prof Shanks also developed a Fluorescent Capillary Fill Device (FCFD). Patent applications were filed, and granted, for both inventions.

Unilever had no interest in pursuing the patented technology itself and instead licensed the technology out to third parties. Consequently, the ECFD technology came to be used in most personal glucose testing products. The gross benefit Unilever received from the technology was calculated to be £24.5 million (approx. NZD $45 million at today's exchange rate), which is not too bad a return for a technology it had no real interest in. While Unilever received millions of pounds, Professor Shanks received only his contracted remuneration and £1.00 on assignment of his rights to Unilever. Professor Shanks believed that he was entitled to a reasonable portion of the benefit Unilever received for his contribution as an inventor under UK law.

Shanks took his case to Court: first the High Court, and then the Court of Appeal. In considering the case, the Courts considered the meaning of *"outstanding benefit"* and whether the benefit that Unilever really received was "outstanding."

While this invention was clearly a commercial success and the everyday person would most probably consider this sum of money to be an "outstanding" amount, the Courts disagreed. In the High Court, Unilever's main argument was that while the £24.5 million generated was a considerable amount, the sum was not very significant compared to the amount generated by the whole of the Unilever group over the same timeframe. Unilever argued that it regularly made large profits and the £24.5m represented only a small portion of their profits, and the patents did not provide an income every year. Consequently, the High Court decided that the amount of money made from the patents was not an "outstanding benefit" to Unilever as required by the wording of the UK Patents Act.

On reconsideration of the issue in the Court of Appeal, *"outstanding"* was noted to be a relative concept, which was to be measured against relevant factors (i.e. the economic and business realities of the employer organisation). Interestingly in the Court of Appeal, Briggs J. noted that it would be going too far to say that Unilever was "too big to pay", but Professor Shanks *might have been successful if his employer had a smaller undertaking than what Unilever had*. Ultimately it seems, that Unilever was "too big to pay."

It is clear that even in countries where a Patents Act provides provisions to remunerate an inventor, it is not a simple straightforward process. Employee inventor remuneration in the absence of a specific contractual agreement may still involve lengthy and expensive battles through the court system – and still result in a loss for the employee. It seems that provision of fair and reasonable remuneration to employee inventors for their contribution to the employer's success could avoid expensive litigation, particularly when there is a statutory provision, in a Patents Act.

If you have any queries regarding intellectual property related matters (including patents, trade marks, copyright or licensing), please contact:

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References and Notes

1. New Zealand Patents Act: http://www.legislation.govt.nz/act/public/2013/0068/latest/DLM1419043.html?src=qs; Australian Patents Act: http://www.austlii.edu.au/au/legis/cth/consol_act/pa1990109/. (accessed 17/4/2018)
2. UK Patents Act: http://www.legislation.gov.uk/ukpga/1977/37. (accessed 17/4/2018)
3. See Article 16 of the Chinese patents act: http://english.sipo.gov.cn/laws/lawsregulations/201101/t20110119_566244.html. (accessed 17/4/2018)
4. See Article 35 of Japanese Patents Act. Translation of the Japanese patents act: http://www.japaneselawtranslation.go.jp/law/detail/?co=1&yo=Patent&gn=&sy=&ht=&no=&bu=&ta=&x=0&y=0&re=02&ky=patent&page=1. (accessed 17/4/2018)
5. *Shanks v Unilever* [2014] EWHC 1647 (Pat), [2014] WLR(D) 242, [2014] RPC 29: (http://www.bailii.org/ew/cases/EWHC/Patents/2014/1647.html) and *Shanks* v *Unilever* [2017] WLR(D) 32, [2017] EWCA Civ 2, [2017] Bus LR 883: (http://www.bailii.org/ew/cases/EWCA/Civ/2017/2.html). (accessed 17/4/2018)

Stephanie Grant

Stephanie joined Baldwins in 2011 and works in the Wellington Office specialising in chemistry and biotechnology patents. Stephanie has also spent time working in the chemical industry in the UK and New Zealand and obtained her PhD in chemistry from the University of York, UK, in 2006.

Dates of Note

APRIL

21 ***Choh Hao Li***, born in 1912, was the Chinese-American biochemist and experimental endocrinologist who, with his co-workers, isolated in pure form six of the eight hormones known to be secreted by the anterior pituitary gland.

23 ***Max (Karl Ernst Ludwig) Planck***, the noted German theoretical physicist, was born in 1858.

Auguste Laurent, the French chemist who developed organic chemistry as a distinct science, died in 1853.

24 The day marks the 130th anniversary of the founding of the Eastman Kodak company by inventor George Eastman.

25 ***Charles Mauguin***, the French mineralogist and crystallographer who was one of the first to make a systematic study of the silicate minerals, died in 1958.

It is 65 years since *Nature* published the structure of DNA in a one-page article by ***Watson*** and ***Crick***.

27 ***Philip Hauge Abelson***, the American physical chemist who proposed the gas diffusion process for separating uranium-235 from uranium-238, was born in 1913.

28 This same date marks the birth in 1753 of ***Franz Karl Achard***, the German chemist who invented a process for the large-scale extraction of table sugar (sucrose) from beets. In 1801, Achard opened the first sugar-beet factory, in Silesia (now Poland).

Josiah Willard Gibbs, the American mathematical physicist and chemist known for his contributions to vector analysis and as one of the founders of physical chemistry, died in 1903.

29 ***Harold C. Urey***, the American awarded the Nobel Prize for Chemistry in 1934 for his discovery of deuterium, was born in 1893.

Georg Brandt, the Swedish chemist who was the first to discover a metal unknown in ancient times (isolated and named cobalt in 1730), died in 1768.

Albert Hofmann, the Swiss pharmacologist who discovered LSD (lysergic acid diethylamide) died on this day 10 years ago.

MAY

1 In 1683, a patent was awarded in England for the extraction of salt from sea water.

6 ***Henry Edward Armstrong***, the English organic chemist whose major research in substitution reactions of naphthalene was important to the synthetic dye industry, was born in 1848.

8 ***William Alexander (Alec) Waters***, the Welsh physical organic chemist wrote the first text-book on the subject (*Physical Aspects of Organic Chemistry*; 1935), was born in 1903.

Nevil Vincent Sidgwick, the English chemist who contributed to the understanding of chemical bonding, especially in coordination compounds, was born in 1873.

Victor Mordechai Goldschmidt, the German mineralogist who made important studies of crystallography, died in 1933.

10 ***Rudolf Schoenheimer***, the German-American biochemist whose technique of "tagging" molecules with radioactive isotopes made it possible to trace the paths of organic substances through animals and plants and revolutionised metabolic studies, was born on May 10, 1898.

12 ***Justus von Liebig*** was born in 1803.

In 1903, ***Carl Linde*** received two US patents for his Linde oxygen process and associated equipment.

13 ***George N. Papanicolaou***, the Greek-American cytologist and pathologist who devised the test now known as the 'Pap smear', was born in 1883.

In 1958, the Velcro trademark was registered for a fabric hook and loop fastener.

14 ***John Chipman***, the American physical chemist and metallurgist who studied the role of oxygen in iron and steelmaking, died in 1983.

The name *Vaseline* was registered as a trademark for the petroleum jelly developed by English-born chemist ***Robert Augustus Chesebrough*** in 1878.

15 ***Robert Hare***, the American chemist who devised the first oxy-hydrogen blowpipe, died in 1858.

In 1953, ***Stanley L. Miller***'s paper on the synthesis of amino acids under conditions that simulated primitive earth's atmosphere was published in *Science*.

16 ***Nicolas-Louis Vauquelin***, the French chemist who discovered the elements chromium (in 1797) and beryllium (in 1798), was born in 1763, 250 years ago.

21 ***Hans Berger***, the psychiatrist who recorded the first human electroencephalogram (EEG), was born in 1873.

Lyon Playfair, Professor of Chemistry at the Royal Manchester Institution who became FRS, Chief Advisor to Prince Albert for the 1851 Exhibition and subsequent politician, was born 200 years ago today; he died on May 29, 1898.

Hans Goldschmidt, the German chemist who invented the thermite (alumino-thermic) process adopted worldwide for welding railroad and streetcar rails, and is still in use for on-site welding, died in 1923.

25 In 1948, ***Andrew J. Moyer*** was granted a US patent for a Method for Production of Penicillin. He specified that his invention comprising large-scale fermentation, incubation of penicillin-producing mould in an aqueous nutrient medium of corn-steeping liquor, glucose and sodium nitrate could be used by or for the US Government for its purposes without royalty payments to him. Enough doses of his antibiotic were made in time to save the lives of a great many of the war-wounded not only for the climax of WW II, but also in the Korean War. This process is still in use today for the commercial fermentation production of penicillin and various other antibiotics.

26 ***Ascanio Sobrero***, the Italian chemist who discovered nitroglycerin by slowly adding glycerine to a mixture of nitric and sulfuric acids in 1847, died in 1888. When Sobrero discovered the explosive power of a single drop in a test tube, he named the new compound pyroglycerin and became horrified by the destructive potential of his discovery. He made no effort to develop that power himself, though it became known as nitroglycerin, or blasting oil. Two decades later, Nobel combined nitroglycerine with diatomaceous earth, making it safer to handle, but just as useful for blasting rock for construction and mining.

27 ***Wolfgang Ostwald***, the German chemist who devoted his life as a teacher, researcher, editor, and one of the founders of colloid chemistry, was born in 1883.

Ernst Ruska, the German electrical engineer who invented the electron microscope died this same day in 1988.

28 ***Ilya Prigogine***, the Russian-born Belgian physical chemist who received the Nobel Prize for Chemistry in 1977 for contributions to non-equilibrium thermodynamics, died in 2003.

30 ***Morris William Travers***, while working with Sir William Ramsay, discovered the element krypton in London in 1898.

JUNE

1 ***Antoine Lavoisier*** sat for the first time at the Royal Academy of Sciences 250 years ago today in 1768.

6 ***Edwin Gerhard Krebs***, the American biochemist and winner (with Fischer) of the 1992 Nobel Prize for Physiology or Medicine for discovering reversible protein phosphorylation, was born this day 100 years ago.

In 1878, liquid air was exhibited by James Dewar at the Royal Institution, London.

8 ***Ronald G.W. Norrish*** was the British chemist who shared the 1967 Nobel Prize for Chemistry (with Porter and Eigen) for their studies of very fast chemical reactions. Between 1949 and 1965 he collaborated with his former pupil Porter in the development of flash photolysis and kinetic spectroscopy for the investigation of very fast reactions. Norrish also made a significant contribution to chemistry when he corrected Draper's law that stated the amount of photochemical change is proportional to the intensity of the light multiplied by the time for which it acts. Norrish showed that the rate was, in fact, proportional to the square root of the light intensity. Norrish died in 1978.

11 In 1998, scientists deciphered the last of the genetic material of the bacterium that causes tuberculosis.

12 Evidence that bacteria are necessary to process nitrogen into a form useable by living creatures was presented by ***Sergey Winogradsky*** to the French Academy of Sciences in 1893.

14 Chlorophyll was patented as a therapeutic agent for use in the treatment of infection of the blood stream, infected parts, and for open cuts and wounds in 1938.

18 ***Jerome Karle***, the American physical chemist who shared the 1985 Nobel Prize in chemistry (with Hauptman) for development of direct methods for the determination of crystal structures which made possible the determination of 3D crystal structures such as hormone, vitamin and antibiotic molecules, was born 100 year ago today.

19 ***Friedrich Sertürner***, the German chemist who discovered morphine (1806) while trying to isolate the portion of opium that caused sleep, was born in 1783.

20 ***Kurt Alder***, the German organic chemist who was the co-recipient (with Diels) of the 1950 Nobel Prize for Chemistry for the development of the Diels-Alder reaction (1928), died in 1958.

Eugene W. Caldwell, the medical X-ray expert, died of X-ray burns 100 years ago.

21 ***Albert Sauveur***, the Belgian-born American metallurgist and one of the founders of physical metallurgy, was born in 1863.

The stereoscopic viewer was described in a paper by ***Charles Wheatstone*** in 1838.

In 1808, the isolation of the element boron was announced by ***Gay-Lusac***, nine days ahead of Davy who independently separated it and made his announcement on June 30 that year.

25 ***James Douglas***, the Canadian-American metallurgist, mining engineer and philanthropist who developed the copper mining industry in the US, died 100 years ago today.

Marie Curie went before the examination committee to successfully complete her PhD in 1903.

In 1783 ***Antonie Lavoisier*** announced to the French Academy of Sciences that water was the product formed by the combination of hydrogen and oxygen, a discovery made earlier by the Henry Cavendish in 1766.

29 ***Peter Waage***, the Norwegian chemist who published the law of mass action (with his brother-in-law ***Cato Guldberg***) in 1864, was born in 1833.

30 ***Lawrence Joseph Henderson***, American physiologist and biochemist who discovered the chemical means by which acid-base equilibria are maintained in nature, was born in 1878.

In 1808, ***Humphry Davy*** announced in a paper read to the Royal Society that he had separated the element boron, nine days after ***Gay-Lusac***.

JULY

1 ***Buckminster Fuller***, the architect who developed the geodesic dome and after whom the carbon isotrope C_{60} is named, died in 1983.

Harry Nicholls Holmes, the American chemist who first crystallised vitamin A, died in 1958.

Samuel Hahnemann, the founder of homeopathy, died in 1843.

6 ***Axel Hugo Teodor Theorell***, the Swedish biochemist who won the 1955 Nobel Prize for Physiology for his discoveries concerning the nature and mode of action of oxidation enzymes, was born in 1903.

7 ***Isaac Newton*** received his MA from Trinity College, Cambridge on this day in 1668, 350 years ago.

10 In 1908, ***Kamerlingh Onnes*** liquified helium for the first time.

12 ***Elias James Corey***, the American organic chemist who won the 1990 Nobel Prize for Chemistry for his development of the theory and methodology of organic synthesis, has his 90th birthday today.

Saul Dushman, the Russian-American physical chemist who was a world leader in vacuum science and technology, and author of several standard scientific textbooks on the subject, was born on this day in 1883.

18 ***Hartmut Michel***, the German biochemist who (with Deisenhofer and Huber) was awarded the Nobel Prize for Chemistry in 1988 for the determination of the three-dimensional structure of the proteins essential for photosynthesis, is 70 years old today.

Pierre-Louis Dulong, the chemist and physicist who helped formulate the Dulong-Petit law of specific heats in 1819, died in 1838.

It is 50 years since the inventor of the microchip, Intel Corporation, was incorporated.

19 ***Curtis Marbut***, the US geologist who is regarded as a cofounder of modern soil science, was born in 1863.

21 ***Rudolph A. Marcus***, the Canadian-born American chemist and 1992 recipient of the Nobel Prize for Chemistry for his work on the theory of electron-transfer reactions (the Marcus theory) is 95 today.

26 ***Paul Walden***, the Latvian chemist who, while teaching at Riga discovered the Walden inversion, was born in 1863.

Letter to the Editor

Re: Dates of Notes - Wilder Bancroft

In the previous issue of this journal (Volume 82, No. 1), Brian Halton's entry in his Dates of Note under February 7 mentioned the demise of Wilder Bancroft, sometime Professor of Physical Chemistry at Cornell University. This unleashed a flood of recollections for me. After a brief exchange with Brian and the Editor, I was persuaded to submit the following note.

I was not interested in Wilder Bancroft in his own right, but because he figured largely in the reminiscences[1] of the late Walter Kauzmann. Kauzmann was the prestigious biophysical scientist and polymath who, as a young man, was a student of Bancroft's at Cornell, and who was very nearly diverted from his future career by Bancroft's adherence to an outworn vision of physical chemistry. I had the privilege of knowing Walter Kauzmann slightly, and admiring him hugely, during my graduate school period at Princeton in the 1960s. For most of my time there, Kauzmann was Chairman of the Chemistry Department. After my thoroughly enjoyable MSc experience in Auckland, I went to Princeton with enormous expectations, which were largely unrealised. The tense, competitive environment did not suit my temperament, and by the time I left I was a very wrung-out young man. Kauzmann, however, transcended that atmosphere, and became for me a role model of how science academics should behave. For instance, by today's standards, he had (by number) quite a modest publication record, in part because he had a policy of encouraging his graduate students to publish their work under their names alone to help them launch their own careers, but also to ensure that they were prepared to take full responsibility for their work. That latter issue is inherent in his remarks about Bancroft.

Apart from his reminiscences, Kauzmann's contributions to science are summarised in a Festschrift issue of *Biophysical Chemistry*,[2] a *National Academy of Sciences* memoir,[3] and various accolades and tributes[4] after his death at the age of 92. He authored a number of books, in various areas of physical chemistry; one, with David Eisenberg (later a Distinguished Professor of Biological Chemistry at UCLA) became the "bible" on water.

In his reminiscences he recounts amusingly the famous meeting of the New York Academy of Sciences in 1951 at which Lars Onsager presented his theory for the concentration-dependent phase separation in solutions or suspensions of anisometric particles. Onsager was notorious for being a hopeless lecturer; so when he finished Debye took the floor and lucidly explained the significance of Onsager's work. Kauzmann remarked that it was always handy to have Debye around at such times. It was my experience that in Debye's absence Kauzmann was a pretty good substitute.

Among my fellow graduate students Kauzmann was seen as a rigorous taskmaster, best skirted around if possible. It fell to my lot to have him as internal thesis examiner and Chairman of my final oral examination panel. In those roles he was kind and supportive, on one occasion seriously taking my part against adverse assessments.

To anybody interested in the human side of science, and the motivations of great scientists, I thoroughly recommend Kauzmann's reminiscences and the other remembrances quoted.

Finally, my thanks to Brian Halton for his hard work in compiling the Journal pages that give rise to such recollections.

1. Kauzmann, W.J. *Protein Sci.* **1993,** *2*, 671-691.
2. *Biophys. Chem.* **2003,** *105*, 153-755.
3. McClure, D.S. *Nat. Acad. Sci. Biographical Memoirs* (http://www.nasonline.org/publications/biographical-memoirs/memoir-pdfs/kauzmann-walter.pdf).
4. Schellman, J.A. *Protein Sci.* **2010,** *19*, 363-371.

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