Chemistry in New Zealand

Volume 80, No.4, October 2016

Articles and Features

Other Columns

Editor's comment

As I write this I have just returned from attending the NZIC-16 conference in Queenstown. Congratulations to all of the organisers and student helpers for delivering such a well-run, enjoyable event. The quality of the oral presentations and posters was very high, covering a broad range of topics, and the plenary sessions were informative and interesting. The student talks and posters were also of a very high standard, with the eventual winners of the student prizes certainly well deserved. You will find more news and photos from the conference in this issue.

Also in this issue is a summary of the salary survey results. I found it really interesting to compile the data and compare the findings with those from ten years ago when the last survey was carried out. While there is plenty that could be better about the science system in New Zealand in general and the funding system in particular, those who have worked overseas will know that the grass is not always greener elsewhere. As always I welcome comments or feedback you may have on the results of the survey, or indeed any other items published in our journal.

Finally, as this is the last issue for 2016, I would like to thank everyone who contributed material to *Chemistry in New Zealand* over the past year as well as those who assisted with the production of each issue. Best wishes for a successful end to the year and I look forward to receiving your articles and news in 2017.

Cath Nicholson

Comment from the President

At the time of writing this I am reflecting on the recently held successful NZIC conference in Queenstown. Big congratulations should go to the Manawatu branch for their brave (some might say risky) gamble to hold the NZIC national conference mid-year and at a (more) exotic location. The organisation of these conferences is fraught with dilemmas, balancing such factors as cost vs. appealing location, talk length vs. number of talks, choice of plenaries, etc. I think the organisational team has done a very good job at balancing these factors in an increasingly crowded conference calendar.

In this issue the results of the salary survey are now presented. It is rather encouraging (and a little surprising) to see that the median salaries for chemists across the board are well ahead of the CPI. It appears that government salaries are increasing at a rate faster than the others, however, which is probably not surprising to most! Postgraduate students should be encouraged to see what their qualification can potentially earn them later in life.

It is in this issue that the NZIC prize winners for the year are usually announced. Unfortunately due to the timing of the conference the Council meeting has been pushed back in the year which means that the announcements for the prizes will now appear in the January issue. All is not lost though for those that crave these announcements. I can proclaim that the winner of the NZIC student talk competition was Lewis Dean from the Waikato Branch. He gave a very entertaining presentation on the sequestration of natural products by nudibranchs from bryozoan prey species.

Also published in this issue is my presidential report of 2016 as presented at the recent AGM. Please take the time to read this. It outlines what the Council is attempting to do to modernise the NZIC this year and next as well as describing some of the activities of the NZIC this year. Of note is our relationship with Wiley-VCH which provides funding to the NZIC when we publish in *Chemistry – An Asian Journal*, *Asian Journal of Organic Chemistry* and *ChemNanoMat*. We, of course, also still have a relationship with RSC so publishing in PCCP also provides a small income source to the NZIC.

I would like to remind members that Richard Rendle, our honorary general secretary, has signalled his intention to retire from all things NZIC at the end of next year (2017). If you are interested in taking on this position please inform either Richard directly or myself.

Finally, as this is the final issue of CiNZ for 2016, this is also my last Presidential comment but it is not the end of me! I hope to see you all soon as I complete my presidential tour of the branches. All the best for the remainder of the year!

Paul Plieger

NZIC President 2016

NZAS Awards 2016

On 8 September the NZ Association of Scientists announced their awards for 2016. Two chemists were the recipients of their prestigious medals.

The **Marsden Medal** (for a lifetime of outstanding service to the cause or profession of science, in recognition of service rendered to the cause or profession of science in the widest connotation of the phrase) was awarded to Distinguished Professor Margaret Brimble CNZM FRSNZ FNZIC, School of Chemical Sciences, University of Auckland. Professor Brimble is internationally recognised for her world-leading contributions to the synthesis of bioactive natural products and novel peptides with wide ranging applications across the life sciences industry.

The inugural **Beatrice Hill Tinsley Medal** (for outstanding fundamental or applied research in the physical, natural or social sciences published by a scientist or scientists within 15 years of their PhD, and formerly the Research Medal) was awarded to Associate Professor Guy Jameson, Department of Chemistry, University of Otago. Dr Jameson is a gifted biophysical chemist who has made outstanding contributions to the fields of biophysical chemistry and materials science. He is interested in the chemistry of metalloproteins - proteins that contain metal atoms or clusters – and his research involves spectroscopic and kinetic investigations of iron-containing enzymes and compounds.

Our congratulations to Margaret and Guy.

New Zealand Institute of Chemistry

supporting chemical sciences

October News

AUCKLAND

School of Chemical Sciences Research Showcase 2016

The 8th Annual SCS Research Showcase was successfully held on 8 June at the University Business School. More than 280 participants attended the meeting, which included a poster session, 41 two-minute talks by 1st year PhD students and eight 15-minute talks by invited PhD students. The day concluded with a keynote lecture by Professor Ray Norton from Monash University.

We would like to offer our congratulations to all the prize winners on their well-deserved prizes.

Second Year Poster Competition

First: Matheus Vargas

Second: Ruben White

Third place: Ayesha Zafar

General Poster Competition

First: Katie Parish

Second: Lakshika Perera

Third: Mona Alzahrani

MacDiarmid Prize for Best Materials Science Poster

Mona Alzahrani

Two-Minute First-Year PhD Student Talks

First Prize: Jared Freeman

Second Prize: Matheu Broom

Third Prize: Chloe Cho

Audience Choice

Andrew Chan and Ankita Gangotra

15-Minute Talks by Invited PhD Students

First: Ben Frogley

Second-equal: Alissa Hackett and Charles Kong

Attendees of the 8th Annual SCS Research Showcase

Winners of the Second Year Poster Competition: Ayesha Zafar, Matheus Vargas (right) and Ruben White (2nd from right) with the Dean of Science, Professor John Hosking (left) and Head of School, Prof Kevin Smith (centre).

Winner of the MacDiarmid Institute Prize in Materials Science: Mona Alzahrani with Prof David Williams.

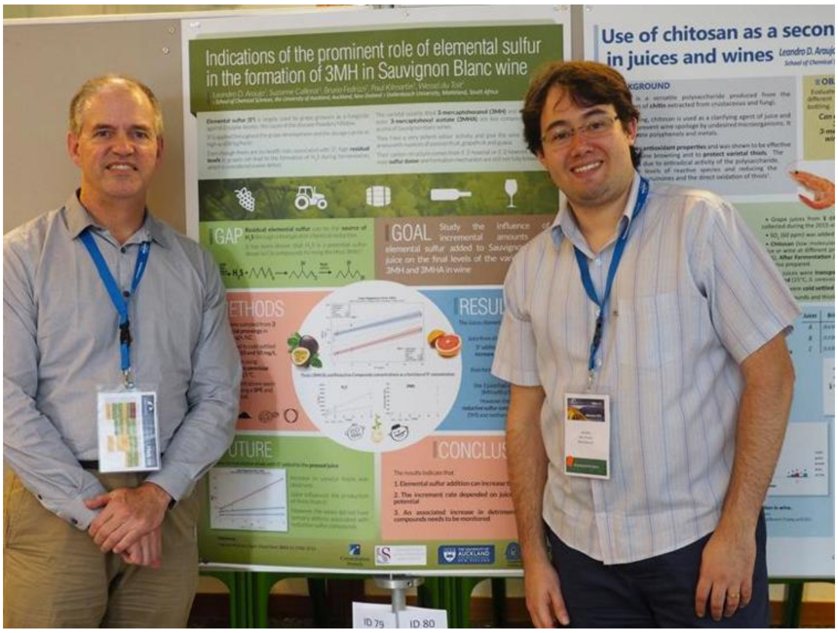
Winner of the General Poster Competition: Katie Parish with Prof John Hosking (left) and Prof Kevin Smith (right).

Winner of the Two-Minute First Year PhD Student Talks: Jared Freeman with Deputy Vice-Chancellor for Research, Prof James Metson (left) and Prof Kevin Smith (right).

Audience Choice Winners of the Two-Minute First Year PhD Student Talks: Andrew Chan and Ankita Gangotra with Prof James Metson (left) and Prof Kevin Smith (right).

Winners of the 15-Minute Invited PhD Student Talks: Charles Kong (2nd from left), Alissa Hackett and Ben Frogley with Prof James Metson (left) and Prof Kevin Smith (right).

Speakers of the 15-Minute Invited PhD Student Talks: (from left to right) Alissa Hackett, Ben Frogley, Charles Kong, James Wood, Samuel Davidson, Hyung Kang, Jessica Suda Yoko and Daniel Ayine-Tora with Prof James Metson (left) and Prof Kevin Smith (right).



Leandro Dias Araujo with his supervisor Professor Paul Kilmartin.

Congratulations

Professor *Christian* ***Hartinger*** was awarded a prestigious Outgoing Hood Fellowship for 2016-2017, providing outstanding opportunities for research initiatives to be developed with collaborators at the University of Cambridge. For more details see: *www.science.auckland.ac.nz/en/about/news/news-2016/2016/07/hood-fellowships.html*

Associate Professor *Cather* ***Simpson*** won both her category award and the supreme award at the Kiwinet Research Commercialisation Awards. Cather also won a prize at the Silicon Valley Forum World Cup Tech Challenge for her start-up company. Well done Cather! For more see: *www.nzherald.co.nz/nz/news/article.cfm?c_id=1&objectid=11666782*

Dr *Johannes* ***Reynisson*** was named a Fellow of the Royal Society of Chemistry. Well done Johannes!

Distinguished Professor *Margaret* ***Brimble***, Associate Professor *Brent* ***Copp*** and Dr *Jonathan* ***Sperry*** were recently successful in securing research funding from the HRC, Auckland Medical Research Foundation and the MBIE Catalyst Fund respectively.

Recent PhD completions

Yang Zhi – PhD in food science, jointly supervised by Associate Professor Yacine Hemar, Professor Sahraoui Chaib (King Abdullah University of Science and Technology, Saudi Arabia) and Dr Qinfen Gu (Australian Synchrotron).

Anis Arzami – PhD in food science, jointly supervised by Associate Professor Yacine Hemar and Professor Sylvie Marchesseau (Montpellier University, France).

Horace Yeung – PhD in chemistry, jointly supervised by *Margaret* ***Brimble****, Chris* ***Squire****, Paul* ***Harris*** and *Ted* ***Baker***. His PhD research was published on the front cover of Angewandte Chemie and as a VIP paper.

Seong Nam – PhD in chemistry, supervised by *Penny* ***Brothers*** with co-supervisor *David* ***Ware*** and advisor *Geoff* ***Waterhouse***.

Congratulations to Leandro Dias Araujo, who received the best student poster award at the Macrowine 2016 conference in Geneva where around 200 posters appeared. Leandro presented on the topic: *Impact of elemental sulfur residues in sauvignon blanc juice on the formation of varietal thiols.*

Congratulations to PhD student Andrew Chan whose poster titled *Now you see me...now you don't! Right?* won 1st prize in the poster competition at the joint MacDiarmid Institute-Dodd Walls Centre Symposium held in Queenstown in August. Andrew is supervised by Dr Geoff Waterhouse and Dr Dongxiao Sun-Waterhouse.

Velocity Innovation Challenge

Congratulations to both Paul Baek and Dr Nihan Aydemir (supervised by Professor *Jadranka* ***Travas-Sejdic***) as the winners of this year's Velocity Innovation Challenge! Their entrepreneurial ideas and an accompanying business proposal derived from their research projects were selected out of the 370 entries from staff and students across all eight faculties at the University of Auckland. The entries were: Patch & Go - Paul Baek, Professor Jadranka Travas-Sejdic and MagnoPCR - Nihan Aydemir, Professor Jadranka Travas-Sejdic, Professor David Williams

Auckland Cancer Society Research Centre (ACSRC)

The Division of Medicinal Chemistry of the American Chemical Society has inducted ACSRC Director *Bill* ***Denny*** into its Hall of Fame. This is a significant recognition of Bill's contribution to medicinal chemistry and follows on from Bill being the recipient of the Division's Medicinal Chemistry Award in 2014.

Associate Professor *Michael* ***Hay*** was the recipient of a Health Research Council Project Grant in the 2016 funding round for a project entitled *Novel radiosensitisers for head and neck cancer*. The grant is for $1,198,115 over three years.

UNIVERSITY OF CANTERBURY

INSPIRE

Vladimir ***Golovko*** attended the INSPIRE event in Nelson, April 13-15, giving a series of workshops entitled, *The catalyst – license to create* to school students from Year 6 onwards. All participants appeared to enjoy themselves and actively participated in the discussions, although delivering material to the youngest students was a real challenge. Some historical aspects of how chemistry contributed to our civilisation in various ways was also highlighted.

INSPIRE is run by the education charity Ministry of Inspiration which aims to inspire youth in science, technology, engineering, arts, maths & society (STEAMS). It is an inspirational ideas sharing festival for students aged 8-18 that encourages participants to think dynamically and creatively about their future. The multiday programme includes challenging workshops, thought provoking discussions and hands on experiments. Presenters include researchers, scientists, innovators, artists, and business leaders who share their energy, knowledge and opportunities for their subject. 2016 was the fifth year of INSPIRE and was its biggest yet as it included several events for the community in addition to three student days (two upper primary and one for secondary). INSPIRE is made possible through the support of its partners and sponsors as well as the generosity of speakers and a large crew of volunteers who gift their time. INSPIRE occurs once a year but the Ministry of Innovation is active all year round delivering a range of events and programmes for students. For more information see: *www.ministryofinspiration.org*

TV3's *Story*

Professor *Ian* ***Shaw*** and his research team appeared in TV3's *Story* programme on 9 May at 7.00pm, discussing the health risks of plastics in the kitchen: *Plastic in our kitchens: risk-free or slowly poisoning us?* For more information see: *www.newshub.co.nz/searchresults?q=plastic+in+our+kitchen&submit*

Postgraduate Student Research Showcase

The Department of Chemistry held its 5th Postgraduate Student Research Showcase afternoon on 9 June. This was an event that celebrated the past and prospective research endeavors of our 2nd year PhD students. For the first time a poster session was also introduced to enable other members of the department to showcase their research as well. There were 7 excellent presentations during two sessions, given by *Amanda* ***Inglis****, Nneka* ***Ekekwe****, Yu* ***Bai****, Hui* (Hector) ***Ye****, Yifei* ***Fan****, Robert* ***Staniland*** and *Stewart* ***Alexander***. At the conclusion of the Showcase, the judges (*Sally* ***Gaw****, Paul* ***Kruger*** and *Matt* ***Polson****)* deliberated to decide the winner of the Ralph H. Earle Jr. Seminar Prize. This prize results from a generous bequest given to the department by the late Ralph H. Earle Jr. (Ralph was a postdoctoral fellow in the department in 1965), because of his strong belief that chemists should appreciate the importance of being able to verbally communicate their subject. The prize is awarded annually for the best review seminar presentation given in the Department of Chemistry by a second year postgraduate student. The prize was awarded to Stewart Alexander from the Fairbanks group for his presentation entitled *Aqueous synthesis of glyoconjugates*. The RSC prizes for the best talk and poster were awarded to Robert Staniland and *Samantha* ***Bodman***, respectively. Audience participation was excellent, with lots of insightful questions being forthcoming. Overall the presentations were superb and the quality of the delivery and research contained within them would allow them to sit comfortably within the programme of any international meeting. The students were a credit to themselves, their research groups and to the department. Following the presentations there was a drinks reception sponsored by the Canterbury Branch of NZIC and ChemSoc.

Awards and appointments

PhD completions:

Andrew ***Wallace*** under the supervision of *Deborah* ***Crittenden*** and co-supervision of *Bryce* ***Williamson***: *Molecular orbitals – their uses and their limitations.*

Janadari ***Kariyawasam*** under the supervision of Sally Gaw: *Synthesis of nitrogen mustards on Co(III), and related reaction chemistry.*

Gert-Jan ***Moggré*** under the supervision of Professor *Emily* ***Parker*** and co-supervision of Professor *Peter* ***Tyler***: *The reaction mechanism and inhibition of ATP-PRTase enzymes.*

Pravesh ***Tyagi*** has joined the department as a PhD student. He is doing his PhD in biochemistry under the supervision of Ian Shaw in the human toxicology research group. He completed his undergraduate degree in pharmaceutical sciences at Uttar Pradesh Technical University, India and an MSc in toxicology at Jamia Hamdard University, India. His MSc project focused on investigating the therapeutic role of the tree *Terminalia arjuna* in experimental arthritis in Wistar rats. After completing his postgraduate degree, he joined Evalueserve (a global scientific services provider) as a research associate in the chemical safety and regulatory affairs business unit. Pravesh then moved into a senior research associate position, where he conducted human and environmental safety assessment of chemicals. This included hazard assessment, safe value derivation, daily chemical exposure calculations, margin of safety calculations, preparation of product information files for cosmetic ingredients and summarising toxicity study reports. His interests include indoor games especially chess, jogging and exploring new places.

Leon ***Philips*** has been awarded the tile of Emeritus Professor by the University Council. Leon retired at the end of 2014, after over 54 years of distinguished service. Congratulations, Leon!

Visitors

Two Erskine visitors were welcomed to the department:

Professor *Stephen J.* ***Loeb***, the Canada Research Chair in Supramolecular Chemistry and Functional Materials in the Department of Chemistry and Biochemistry at the University of Windsor. He completed his PhD at the University of Western Ontario under the supervision of Chris Willis and was a postdoctoral fellow with Martin Cowie at the University of Alberta. He was elected a Fellow of the Chemical Institute of Canada in 1997, a Fellow of the Royal Society of Chemistry in 2007 and was the 2012 recipient of the Canadian Society for Chemistry's Rio Tinto Alcan Award for outstanding achievement in inorganic Cchemistry. He has made significant contributions to the design and synthesis of interlocked molecules (rotaxanes and molecular shuttles) and recently pioneered their incorporation into metal-organic framework materials.

Professor *Amanda* ***Ellis***, who graduated with a PhD in applied chemistry from the University of Technology Sydney in 2003. She then undertook two postdoctoral studies in the US+, including Rensselaer Polytechnic Institute and New Mexico State University. After these she returned to New Zealand as a Foundation for Research Science and Technology (FoRST) Postdoctoral Research Fellow at Industrial Research Ltd (now Callaghan Innovation). In 2006 Amanda commenced at Flinders University as a teaching/research academic. Since then she has secured over $20m in funding from ARC (Australian Research Council) and non-ARC sources and has published over 128 peer-reviewed journal articles (with over 2400 citations) on projects involving novel polymer coatings, functionalised carbon nanotubes and graphene, microfluidics, genotyping and DNA nanotechnology. She is currently an ARC Future Fellow (2014-2018), the Deputy Associate Dean of Research for the Faculty of Science and Engineering at Flinders University, a Board member of the Royal Australian Chemical Institute (RACI), a Board member of the Membrane Society of Australia, a previous Chair of the RACI, National Polymer Division (2013-2015) and a co-founder and executive member of the Australia & New Zealand Micro/Nanofluidics group.

MANAWATU

Dr *Catherine* ***Whitby*** gave a joint public lecture with Dr Geoff Willmott (University of Auckland) on *A materials history of the world* in Tauranga on August 15 which was attended by 120 people. The talk was part of a regional lecture series sponsored by the MacDiarmid Institute. She has also welcomed Ms Floriane Bahuon, a Masters student from the École Nationale Supérieure de Chimie et de Physique de Bordeaux, who is doing an internship in her lab.

Massey University also welcomed Maulik Mungalpara who started as a graduate research student under Associate Professor *Gareth* ***Rowlands***.

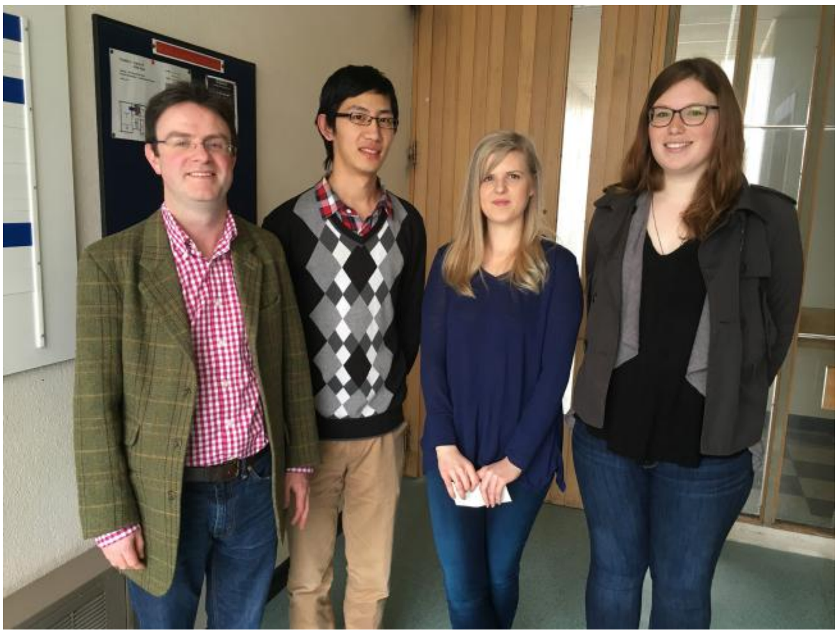
Several students from Fontys University of Applied Sciences in The Netherlands have begun internships in the Institute of Chemistry, including Vera Solberg under the supervision of Dr *Vyacheslav* ***Filichev*** and Ruth Verbroekken under the supervision of Professor *Shane* ***Telfer***.

In June, Massey hosted two guest speakers – Dr Pierre-Francois Loos, ARC Research Fellow at ANU and Visiting Erskine Fellow at Canterbury, as well as Dr Frederique Vanholsbeeck, Senior Lecturer in Biophysics at the University of Auckland.

OTAGO

An essay competition was held for students to write on a chemistry-related topic of their choice. First place was awarded to *Gemma* ***Cotton*** with her essay entitled, *Camouflaged chameleon skin, invisible butterfly wings and touch responsive leaves: how nature has provided the future of advanced materials*. Second place went to the essay co-written by *Caitlin* ***Casey-Stevens*** and *Mingrui* ***Yang*** about their research entitled, *From theories to real life: computational approaches to ammonia synthesis*. Both essays can be found in this issue.

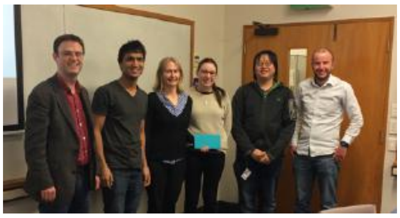
This year the Otago Branch held its inaugural NZIC Chemistry Quiz on 26 July in the Department of Pharmacy. Quiz master was *Dave* ***McMorran*** and nine teams took part with team members ranging from 1st years to academic staff from across the university. The overall winners were the *Periodic Table Dancers* with *Team Bonding* and *Reflux and Chill* close behind. *Andrea* ***Vernall*** is thanked for all her hard work organising such a successful event and we look forward to the return next year!



Left to right: Guy Jameson, Mingrui Yang, Gemma Cotton, Caitlin Casey-Stevens.

1st Prize: Periodic Table Dancers

2nd Prize: Team Bonding



3rd Prize: Reflux and Chill

The Aurora Otago Science and Technology Fair was held at the Otago museum at the beginning of August. The Otago branch of the NZIC once again sponsored prizes. The Branch chair *Guy* ***Jameson*** judged the prizes and, as every year, was very impressed by the quality of the projects covering a very wide area of science. Considering those projects with a chemical theme, prizes were awarded to the following pupils:

Year 7

Tagiilima Feleti, Kalevini Hotesi (Brockville Primary): *Apple sunscreen*

Robbie Abbott-Ramsay, Reagan Tobin (Brockville Primary): *Exploding mentos*

Isabella Bryson (Fairfield): *Salt assault*

Caleb Simpson, (Kavanagh College): *Can liquids conduct electricity?*

Year 8

Braydon Foote (Strath Taieri): *It's on fire*

Annabelle Ring (Kavanagh College): *Vitamin C you later*

Daisy Kilto-Thomas (Portobello School): *Can water float on water?*

Year 9/10

Gracie Woodhouse, Ella Sheat (East Otago High School): *Cheap milk: is it worth it?*

Year 11

Hayden McAlister (Otago Boys High School): *Friendly fire*

The recent NZIC conference was well-attended by Otago branch members with MSc student *Marina* ***Roxburgh*** and PhD student *Beth* ***Lippett*** picking up poster prizes. Both Marina and Beth work with *Lyall* ***Hanton*** and *Steve* ***Moratti***.

NZIC-16 poster prize winners Beth Lippett (left) and Marina Roxburgh (right)

University of Otago, Department of Chemistry

Jaydee ***Cabral*** was recently awarded $90,000 by the University of Otago Equipment Advisory Committee to go towards the purchase of a GeSUN Bioscaffolder, 3D-bioprinter. She also gave an oral presentation at the Queenstown Molecular Biology Meeting (QMB) Stem Cells and Regenerative Medicine Satellite in late August in Nelson.

In July, members from the University of Otago Chemistry Outreach spent three weeks in Taiwan and Malaysia, teaching over 700 students the fun of chemistry. *Dr Dave* ***Warren,*** a professional practice fellow at the University of Otago who runs the Outreach program, led his team consisting of *Marina* ***Roxburgh****, Jacqui* ***Kao****, Geoffrey* ***Weal****, Sage* ***Robinson****, Sam* ***Sutherland*** and *Sean* ***Mackay*** from the big cities of Taipei and Kuching, to the rural school SMK Balleh which is only accessed by river.

Twenty students and ten teachers learnt about mānuka bioactives during three days of visits to the Plant & Food Research unit in Dunedin. This was part of a residential science camp for Year 13 students by the University of Otago Advanced School Sciences Academy (OUASSA) to introduce them to the world of research science through a range of practical projects. *Elaine* ***Burgess*** guided the students through an experiment to show the herbicidal properties of mānuka extracts, designed to be run at schools as an Outreach experiment. *Catherine* ***Sansom*** explained GC-MS for analysis of the bioactive molecules in mānuka extracts. This would also be used in the Outreach experiment, to determine the local mānuka chemotype around each participating school, which would then be plotted on a map on a dedicated web page. *John* ***van Klink*** explained the use of HPLC for purifying bioactive molecules, and NMR spectroscopy for determining structures. Students and teachers were enthusiastic, so we will follow this up to find participants to run pilot experiments at their home schools. This will give us better background for another bid to the *Unlocking Curious Minds* fund.

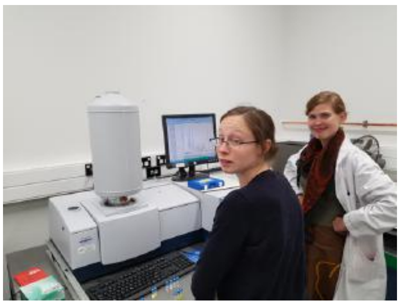
Elaine ***Burgess*** and students from the OUASSA studying the herbicidal properties of mānuka extracts

Once again, the group of *Keith* ***Gordon*** has been very busy. *Sara* ***Miller*** attended the Dodd-Walls Centre Symposium in late June, and in July worked with visiting researcher Tiina Lipiäinen from the Faculty of Pharmacy, University of Helsinki, looking at drug polymorphism and its detection with low frequency Raman spectroscopy.

Outreach team with students from SMK Muara Tuang

Students from SMK Balleh carrying out experiments

Students from SMK Balleh



Sara Miller and Tiina Lipiäinen using the FT-Raman system

Research fellow *Cushla* ***McGoverin*** (Department of Physics, University of Auckland) has been visiting *Keith* ***Gordon***'s laboratory to use the Raman spectrometers, particularly the new Witec system. Cushla will be collecting Raman mapping data from bovine cartilage samples to assess areas of cartilage degradation. In addition, Cushla will be collecting Raman data from porcine blood serum to optimise sample preparation for future studies involving human blood. Cushla's lab visit has been funded by the Dodd-Walls Centre for Photonic and Quantum Technologies.

Jonathan ***Barnsley*** recently engaged in a Claude McCarthy funded collaborative visit to Wollongong University. Work was carried out in conjunction with David Officer's research group and investigated bio-inspired dye protection methods for dye sensitised solar cells. Jonathan also gave oral presentations on benzothiodiazole spectroscopy and computational chemistry at the Dodd Waals/MacDiarmid/ARC symposium in Queenstown and at ICORS (International Conference on Raman Spectroscopy) XXV conference in Fortaleza, Brazil.

Jonathan ***Barnsley*** has published two papers this quarter, both with the group of *James* ***Crowley***. The first was published in *Inorganic Chemistry* on *Structural, electronic, and computational studies of heteroleptic Cu(I) complexes of 6,6'-dimesityl-2,2'-bipyridine with ferrocene-appended ethynyl-2,2'-bipyridine ligands* and describes the spectroscopy and computational studies on these systems, which can pivot about the ferrocence moiety to provide actuation. The second paper was published in JACS on *Controlled formation of heteroleptic* $[Pd_2(L_a)_2(L_b)_2]^{4+}$ *cages* in which *Dan* ***Preston***'s successful series of heteroleptic systems was reported. Jonothan's computational calculations suggested that the *cis*-isomer was more stable that the *trans*-isomer and that the heteroleptic palladium(II) cages are kinetically metastable intermediates rather than the thermodynamic product of the reaction.

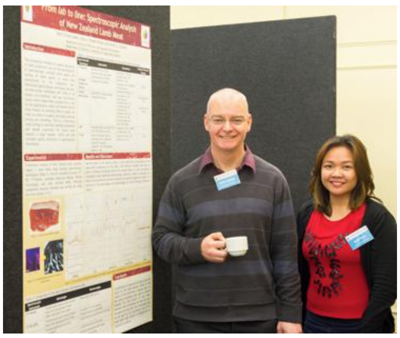
Keith ***Gordon*** attended the summer school organised by The Center for Exploitation of Solar Energy, Department of Chemistry, University of Copenhagen; he described work on solar cells and spectroscopy to probe such systems and materials.

Chris ***Larsen***, *Holly* ***van der Salm*** and *Georgina* ***Shillito*** recently published work with *Nigel* ***Lucas*** on the donor-acceptor systems in which it is possible to alter the emission signal across the entire visible spectrum. The work *Tuning the rainbow: systematic modulation of donor–acceptor systems through donor substituents and solvent* was published in *Inorganic Chemistry*.

In June *Georgina* ***Shillito*** presented a joint talk with *Sara* ***Miller*** at the Otago Science Festival regarding the range of applications of Raman spectroscopy and was recently awarded a Fanny Evans postgraduate scholarship for women for her PhD studies. She recently attended the ICORS XXV conference in Fortaleza, Brazil where she presented a poster of her work on Ru(II) dppz donor-acceptor complexes. In early September she attended a computational chemistry, Gaussian workshop in Japan at the Tokyo Institute of Technology.

Work by *Jeremy* ***Rooney*** and *Keith* ***Gordon*** entitled, *Sub-micron Raman mapping of ultramafic fault rock textures* is to be presented at the American Geological Union held in San Francisco, December 12-16. The work is in collaboration with Dr Steve Smith and Matt Tarling from Otago's Geology Department and was conducted on the new high resolution Witec microscope. Findings reveal undocumented sub-micron intergrowths of serpentine and dehydration of serpentine in slip surfaces. Jeremy was also in Fortaleza, Brazil, presenting his MSc work titled, *Vibrational spectroscopic methods to identify & quantify adulterants in weightloss herbal medicines*.

Ruth Eloisa ***Sales*** attended the Dodd-Walls Centre (DWC) Symposium at the end of June in Queenstown where she presented a poster entitled, *From Lab to line: spectroscopic analysis of New Zealand lamb meat*. She will be at the University of Auckland for a three-week collaborative visit as a speaker at the DWC sensing theme seminar and to conduct coherent anti-Stokes Raman spectroscopy (CARS) and optical coherence tomography (OCT) experiments for the meat samples.



Keith Gordon and Ruth Eloisa Sales

Congratulations to *Geoff* ***Smith*** who successfully defended his PhD on 20 August and graduated.

Anna ***Garden*** gave lectures on density functional theory at the summer school on *Modelling methods in computational chemistry* organised by the University of Iceland.

Carla ***Meledandri*** was joint winner (with Daniel Holland of the University of Canterbury) of the Norman F. Barry Trust Emerging Innovator Award in the 2016 KiwiNet awards. This is a very prestigious award recognising an up-and-coming entrepreneurial researcher. Well done Carla!

WAIKATO

Waikato NZIC Analytical Chemistry Competition 2016

This annual event was held on June 15. Invitations were sent to schools in the wider Waikato/Bay of Plenty region to send teams of four students to the university for the day to carry out an analysis. A total of 22 teams competed in the event. The task was to analyse a sample of $BaCl_2.nH_2O$ using a gravimetric procedure for Ba^{2+} and a volumetric method for Cl^-. This allowed the value of n to be calculated in the empirical formula by difference. This was a demanding task in the time available but some excellent results were achieved. The competition allowed enthusiastic Year 13 chemists to spend a day in the university laboratories working on an experiment that would be beyond the resources of their schools. Rivalry was fierce but the main emphasis was on enjoying the experience and meeting students from other schools.

Results were:

First: Hamilton Boys' High School 1 (Lachlan Cate, Ben Lambourne, Cameron Paul, Cameron Salisbury)

Second: Tauranga Girls' College (Bayley Coster, Emma Godden, Jada Mataroa, Grace Wright)

Third: Hamilton Boys' High School

Waikato NZIC Analytical Chemistry Competition prize winners: Hamilton Boys' High School's Lachlan Cate, Ben Lambourne, Cameron Paul and Cameron Salisbury with competition judge and chief organiser Associate Professor Michèle Prinsep.

NZIC-16 student talk competition winner Lewis Dean, Waikato (centre) and runner up Megan Jamieson, Auckland (right) with NZIC President Associate Professor Paul Plieger (left)

2 (Lucas Clarke, Matthew Handford, Tai Lohrer, Isaac Poole)

Fourth: Waikato Diocesan School for Girls (Sarah Adeane, Horim Choi, Su A Kim, Nikita Lyons)

Fifth: Putaruru College (Daniel Armstrong, Vijini Moratu-Waduge, Hannah Saies, Brad Wharehoka)

The day involved many of the chemistry department staff in setting up the competition and supervising the labs. Bryant Hall and Student Village provided excellent lunches (sponsored by the Waikato Branch of the NZIC) and Hill Laboratories generously donated the prizes.

University of Waikato

Michael ***Mucalo*** attended the ISE International Conference on Electrified Interfaces (ICEI 2016) in Singapore in July. He gave the first oral presentation in the conference entitled, *In situ IR, XAS and ESMS-based studies of electrically polarised nickel, copper and gold electrode systems with pseudohalide ions in neat DMF and DMSO electrolytes*. His presentation was co-authored by Kethsiri Alwis (University of Waikato), Bridget Ingham (Callaghan Innovation), Peter Kappen and Chris Glover (both of the Australian Synchrotron) and was the result of PhD research conducted by Dr Kethsiri Alwis in the School of Science at Waikato University.

Michèle ***Prinsep*** attended the workshop *Unlocking Australia's Deep Sea Biodiscovery Potential* at the University of Wollongong in July and gave a presentation entitled, *Marine biodiscovery in New Zealand: opportunities & challenges*.

Michèle's student *Lewis* ***Dean*** attended NZIC-16 in Queenstown in August and gave a talk on his Honours project entitled *Chemical theft: the sequestration of natural products by New Zealand nudibranchs* as the Waikato Branch representative in the student paper competition. Lewis was very pleased to win the competition and received a US$500 Amazon gift card and a signed copy of *The Disappearing Spoon* by Sam Kean, one of the plenary conference speakers. Another of Michèle's students, Ashleigh Browne, has recently submitted her Masters thesis on New Zealand marine bioactive natural products for the control of Psa, and has started a position as technical advisor at New Zealand Manuka Group based in Opotiki.

WELLINGTON

The NZIC/VUW Wellington Secondary Schools Chemistry Quiz was held on 15 June and was attended by over 100 school students from 15 schools around the Wellington region. The quiz was hosted by students from the NZIC Branch committee and VUW, with *Dylan* ***Webb*** as quizmaster. Questions probed the students' knowledge of various chemistry concepts and lateral thinking, including naming chemistry that killed the researchers working on it, general science, pop science, guessing countries' abbreviations based on the periodic table and questions tailored to the NCEA curriculum. First prize went to *Get Money, Spend Money, Antimony,* from Wellington College. *The Mol Men* from Paraparaumu College were second and *Fluorine Uranium Carbon Potassium Bismuth Technetium Helium Sulfur Germanium Thulium Oxygen Neon Yttrium* (a.k.a. *Missing Molybdenum*) from Wellington College came in third. Alongside the quiz there were chemical demonstrations, a best costume competition (the prize went to *Functional Group*, depicting Fe-catalysed transformation of aldehydes and ketones), table art (prize winner: *Total Borons*) and best team name (winner: *Reflux & Chill*). There were spot prizes for interpretative dance depicting delocalised electrons in metals and for their advanced knowledge of the periodic table! Support from the sponsors is gratefully acknowledged, in particular VUW Science Faculty, School of Chemical and Physical Sciences, MacDiarmid Institute, MetShop, Graphic & X.

NZIC/VUW Wellington Secondary Schools Chemistry Quiz

Professor *Lyall* ***Hanton*** of Otago University delivered the 2016 Mellor Lecture on 10 August at Victoria University. The Mellor Lecture is presented on a three year cycle at the Wellington Branch and it was highly appropriate that Professor Hanton (the Mellor Professor of Chemistry at Otago University) spoke to the Branch on *Mellor and new materials chemistry: polymer gel materials.* For the first segment of his talk, Lyall gave us a great summary of the life and contribution of Joseph Mellor, the Otago-trained chemist and ceramist whose extraordinary 16-volume *Comprehensive treatise on inorganic and theoretical chemistry* is one of the definitive works in chemistry that adorns the shelves of most chemistry libraries in the world (see: This journal **2014**, *78*, 85-89). Lyall then described his current research in polymer gels which are emerging as a new actuator technology. These gels swell and de-swell due to the coordination of metal ions to pyrimidine-hydrazone cross linkers which leads to the unfolding of helical strands into a linear geometry. A great Mellor Lecture, well delivered and well attended.

The NZIC-16 conference in Queenstown was attended by about 20 Wellington Branch members, many of whom presented talks and posters. It was an excellent conference and provided a great chance to appreciate some of the science being undertaken around NZ and overseas, as well as to catch up with colleagues and friends. At the conference, *Justin* ***Hodgkiss*** delivered his Easterfield Medal Lecture on ultrafast spectroscopy and its applications in development of photovoltaic materials. *Phil* ***Rendle*** presented the NZIC Industrial Chemistry Prize Lecture as the joint recipient with *Paul* ***Benjes***. The prize recognises the successes of the GlycoSyn-Ferrier Research Institute joint venture for cGMP chemistry (synthesis and analysis). He described the preparation of keratin sulfate and related compounds as standards for diagnosis and on-going monitoring of Morquito's syndrome.

Postgraduate student *Ryan* ***Schwamm*** was awarded an NZIC Wellington Branch Student Travel

Grant to attend the International Conference on Organometallic Chemistry 2016 (ICOMC2016), 16-23 July in Melbourne. The conference featured presentations on a broad range of chemistry, linking organometallic chemistry to subjects ranging from materials science to medicinal chemistry, by some of the most influential chemists in organometallic chemistry. Ryan presented a poster titled, *Synthesis, characterisation and reactivity of a bismuth radical*" focussing on work that was recently published in *Angew. Chem. Int. Ed.* Ryan enjoyed meeting like-minded individuals with whom he was able to discuss challenges and ideas.

Postgraduates *Justin* ***Butkus*** and *Shyamal* ***Prasad*** were also awarded NZIC Wellington Branch Student Travel Grants to attend and present posters at the Gordon Research Conference 2016 on Electronic Processes in Organic Materials, which was held in Lucca (Barga), Italy, 5-10 June. It was a specialist conference with leading researchers in the field held in a remote site in the beautiful Italian mountains, providing great opportunities for developing new ideas and relationships.

Victoria University (VUW)

Congratulations to *Joanne* ***Rogers*** (supervisor: *Ken* ***MacKenzie***) and *Joe* ***Gallaher*** (supervisor: *Justin* ***Hodgkiss***) for successful defence of their theses and completion of their PhD degrees.

Rob ***Keyzers*** is on research and study leave at the University of California San Diego where he is using mass spectrometry for metabolomics research, hosted by Pieter Dorrestein. *Mattie* ***Timmer*** is also on research and study leave based initially at the School of Chemical and Physical Sciences, VUW and then travelling to the Netherlands. *Peter* ***Northcote*** has recently completed research and study leave at the Ferrier Institute, VUW.

Gary ***Evans*** delivered his inaugural professorial lecture entitled, *A love of chemistry, drugs and other things* on 12 July. Gary discussed his earliest experiments as a child, through to the new therapeutic agents he has been involved in developing to the clinic and market.

The School of Chemical and Physical Sciences held a public event, *Dangling Bonds*, on July 25, at which *Bridget* ***Stocker*** (chemistry) and Melanie Johnston-Hollitt (physics) spoke about the very topical research areas of immunology and gravitational wave detection, respectively. The audience was enthralled and asked many questions. Afterwards, intriguing demonstrations of interferometry and herd immunity were held during the social time.

Joanne ***Harvey*** travelled to New Hampshire in late July to attend the Gordon Research Conference on *Natural Products and Bioactive Compounds*, held in early August at Proctor Academy in Andover. She presented a short talk and poster entitled, *Side-chain analogues of TAN-2483B as kinase inhibitors*. The conference provided stimulating opportunities to interact with scientists with similar interests from academia and industry.

VUW hosted an interdisciplinary seminar by David Wishart (Alberta, Canada) on 11 August entitled, *Why NMR matters in metabolomics.* He demonstrated the utility of NMR as a high-information analytical technique that can be used even for small samples such as those typically obtainable in metabolomics. The audience was drawn from a wide range of workplaces and disciplines, including Magritek Ltd, biology, chemistry, engineering and physics fields.

BRANZ

Trish ***Shaw*** attended the Surface Coatings Association of New Zealand conference in Wellington, 8-9 July. *Catherine* ***Nicholson*** attended the NZIC-16 conference in Queenstown, 21-24 August and presented a poster entitled *Development of a durability assessment methodology for polymeric construction materials using FTIR spectroscopy and chemometrics*. *Nick* ***Marston*** delivered a professional development training module on *Durability and materials performance* to the New Zealand Institute of Building Surveyors in Wellington on 24 August.

New Zealand Institute of Chemistry

President's Annual Report 2016

It was decided by council at the February meeting that a hard look at the NZIC organisation was overdue. As such a sub-committee was established to look at various parts of the organisation, its function, its operational structure and its visibility as an organisation. I note that recently the American Chemical Society has published its strategic plan for 2016 and beyond with the focus areas of chemical information provider, an enabler of careers for members, improving chemical education and communicating the value of chemistry. I would suggest the goals of the NZIC are not too dissimilar. The response to my magazine editorial call from the general membership with regards to areas that members feel need attention has been non-existent. I do worry that the apathy shown is a reflection that the NZIC is not considered relevant to its members. I hope this is not the case.

A review of the rules of the society have revealed a number of inconsistencies present that are not in keeping with current practice. In other cases (such as in the area of conference sponsorship) a robust policy is lacking and will be introduced in the coming months. In addition, the website has been identified as an area of urgent modernisation. I believe this is the ideal tool to provide additional benefit to the members and a plan has begun to replace the existing website.

Membership

Our current membership stands at 698. This is made up of members, fellows, students, retirees, people overseas and those that do not pay a subscription (honorary members, etc.). A constant frustration for the secretary is chasing those members who have not paid. The subscriptions are the Institute's primary income source and non-payers jeopardise the financial viability of the organisation. Consideration is being given to an online payment system (possibly linked to the website) with automated email reminders to help in this regard.

Election of Fellows

At the meeting in February the following members were elected to the Fellowship of the Institute:

Professor Nicola E. Brasch, Auckland University of Technology

Associate Professor Cather M. Simpson, University of Auckland

Associate Professor Michele R. Prinsep, University of Waikato

NZIC Prizes

Due to the timing of the NZIC conference this year these will be decided at the November meeting.

NZIC Representation

This year the following appointments have been made / continued:

Pacifichem Organising Committee: Associate Professor Mark Waterland FNZIC (Massey). Mark has been active in ensuring that a recent RACI proposal to negotiate a new profit sharing model for Pacifichem does not negatively impact on us.

ACES: Associate Professor's Paul Plieger and Guy Jameson attended the ACES meeting in Melbourne. Note: the NZIC is a co-owning society in the following journals, so publishing in these journals will provide a modest income source for NZIC. The journals are: Chemistry – An Asian Journal, Asian Journal of Organic Chemistry and ChemNanoMat.

Other Activities

Scientific Sleuthing: Chemical discoveries made in New Zealand is very near completion and is now on offer for sale to schools and members. This is the follow-up to the popular "New Zealand is Different, Chemical Milestones in New Zealand History" (published in 1999 and produced in two print runs)

Specialist Groups

The level of activity of the NZIC specialist groups continues to be very variable. Some groups are not active whereas others are very active such as the Chem Education group.

Visit of the President to Branches

I kick off my presidential tour in the Manawatu at the beginning of September, the delay in these tours has been compounded by a heavy teaching commitment in semester one and my involvement in the NZIC annual conference held in late August. I will visit Wellington in early November but at this stage other dates are yet to be confirmed.

Representation at Meetings

I represented/will represent the NZIC at four meetings this year:

1. Asian Chemical Editorial Society (ACES) with Associate Professor Guy Jameson (Otago)
2. RACI Inorganic Chemistry AGM
3. Constituent Organisation Forum of the Royal Society of New Zealand (end of November)
4. Skype meeting with Professor Tamotsu Takahashi (FACS) discussing closer collaboration between NZIC and the Japanese chemical society with regard to younger researchers.

Future NZIC Conferences

The next NZIC conference is to be organised by the Canterbury/Marlborough Branch.

NZIC Salary Survey Response

The NZIC salary survey has been conducted and the responses are published in this issue. A response rate of 31% (down from 38% in 2006) was recorded. The results make for interesting reading.

Concluding Remarks

It is clear our membership continues to decline slowly but surely. We have seen general declines in all forms of memberships, except for perhaps Fellows which remain steady at ~120. The overall decrease in membership is 13% (804 -> 694) over the last four years which is clearly unsustainable. With it we face declining revenues which will impact future activities. The Council is working hard to develop new ways to offer more benefits to the members but the local Branches are at the frontline in demonstrating the benefits the NZIC can offer. I encourage members to be innovative, positive and engaging when promoting and providing NZIC events.

I would like to thank Council for their work and support of the NZIC during this year. I think every year the demands on people increase and it takes true dedication to devote the time to this position. I would like to especially like to thank Richard Rendle (Hon. General Secretary) and Colin Freeman (Treasurer) who have given generously of their time. After many years as secretary, Richard has indicated he will step down at the end of 2017 and on behalf of the NZIC membership I thank him for his unwavering dedication, enthusiasm and service to the Institute. A big thank you to Catherine Nicholson for her work as Editor of CiNZ. The magazine operation is now a very slick and frugal enterprise.

Paul Plieger FNZIC
President
16 August 2016

Camouflaged chameleon skin, invisible butterfly wings and touch responsive leaves: how nature has provided the future of advanced materials

Gemma C. Cotton

Department of Chemistry, University of Otago, PO Box 56, Dunedin 9054 (email: *gcotton1@hotmail.com*)

Keywords: *biomimicry, nanotechnology, materials design*

Gemma completed her BSc (Hons) in forensic science at the University of Lincoln, UK, and was subsequently accepted for an MSc there working with Pfizer on the design of antibacterial silver nanoparticle (AgNP) materials including low cost water treatment systems for developing countries. She briefly spent time at the University of Cordoba, Spain, studying oenology. She then moved to Dunedin to undertake a PhD in advanced materials and nanotechnology in the Meledandri Group, Department of Chemistry, University of Otago. She is in the final stages of her PhD investigating the preparation of antibacterial AgNP materials for the treatment of oral infections.

Introduction

The future of materials research has, to some extent, already been paved by our past; millions of years of evolution presents sophisticated, integrated materials exhibiting multifunctional behaviours. Biomimicry is a sustained field in chemistry which focuses on the development of synthetic materials capable of responding to stimuli in a controllable and predictable fashion from examples observed within the natural world around us. The ability to encompass the complexity of biological or natural materials presents significant but fascinating challenges. Bioinspiration of metamaterials, which are materials where the observed behaviour results from the structure rather than composition, requires synthesis of structures on the nanoscale level to which external and internal stimuli will induce the sought after physiochemical response from minute but orchestrated changes at the molecular level. Biomimicry allows for the continual improvement and advancement in the performance of materials that could provide humanity with an expansion of smart technology. This article discusses a few recent advances in the bioinspired devices.

Colour changing chameleons

Until recently, it was believed that the colour change observed in chameleons was controlled by pigment-containing organelles. This belief was applied across many animal taxa that demonstrated skin brightness changes and the dispersion and aggregation of melanosomes within dermal chromatophores was examined. Chromatophores are small sacks of pigments that are manipulated by attached muscles resulting in colour changes. Chromatophore dependency can be seen in cuttlefish which quickly and accurately shift colour instantaneously to match the environment. However, the chameleon is somewhat different as it displays a unique system of finely tuned colour brightness and colour hue in response to physiological conditions. Teyssier *et al*. discovered a much more complex reason behind this phenomenon that is so crucial for camouflage, communication, courtship and thermoregulation in the structure of the chameleon's skin.[1] Photonic crystal layers are actually responsible for the remarkable colour regulation with specific iridophore cells containing guanine nanocrystals of different shape, size and orientation. These can be thought as a multilayer of nano-reflectors with alternating high and low refractive indices that interfere with emitted wavelengths. Photonic crystals are periodic dielectric nanostructures that affect the motion of photons, which gives rise to interesting optical phenomena such as the spontaneous emission, high reflecting omni-directional mirroring and low loss waveguiding.[2] Depending on the multi-dimensional structure (Fig. 1), the photons either can or cannot be transmitted through the crystal. To produce visible effects the periodicity of the photonic crystal has to be approximately half the wavelength to be diffracted, i.e. between 200 nm (blue) and 350 nm (red). The iridescent colours observed in opals and peacock feathers are derived from well organised photonic crystals.

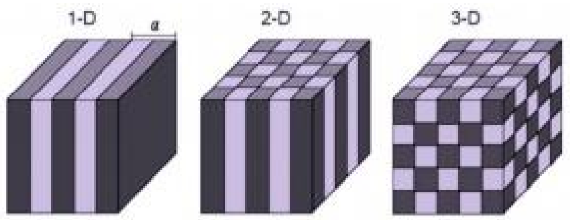


Fig. 1. Schematics of one, two and three-dimensional photonic crystals. The colours represent alternative refractive indices. The spatial period of the material is the lattice constant, α. From ref 2, reprinted with permission.

The chameleon's skin possesses an unseen evolutionary novelty in a complex layering system. The upper layer contains yellow and red pigmented chromatophores whereas the bottom layer contains dark melanin pigmented cells which appear as black or brown. The central layer is constructed of guanine nanocrystals that change in response to external stimuli. When the chameleon is in a relaxed state, the nanocrystals are organised into a dense network, reflecting short (blue) wavelengths. This is why we usually see green chameleons, as the blue light reflected through the middle layer is interfered with by yellow pigments in the upper layer which results in a green emission. However, in an excited state, the nanocrystals are reorganised into a looser lattice of nanocrystals, allowing the reflection of longer wavelengths (yellows and reds). More precisely, the distance of the nanocrystals when excited are on average 30% larger than when in a rested state.[1] Examples of the wide variety of crystal assemblies are shown between species in Fig. 2.

There is a shift in selectivity of wavelength reflectance dependant on the corresponding increase and decrease in distance among nanocrystals. The nanocrystals are structured in rows of parallel platelets that alter their inclinations simultaneously to change the distance between them and thus the nanocrystals. The structural colour is dynamic and responds directly to external stimuli. The bright red skin, however, behaves slightly differently; the iridophores containing the nanocystals are partially replaced by red pigmented chromatophores suggesting that the brightness increases although the skin hue does not change. Chameleons have evolved to possess two populations of iridophores; the colour altering nanocrystals and a deeper set of iridophores that reflect light closer to the infrared wavelengths (Fig. 3). The lower iridophores are responsible for internal temperature con-

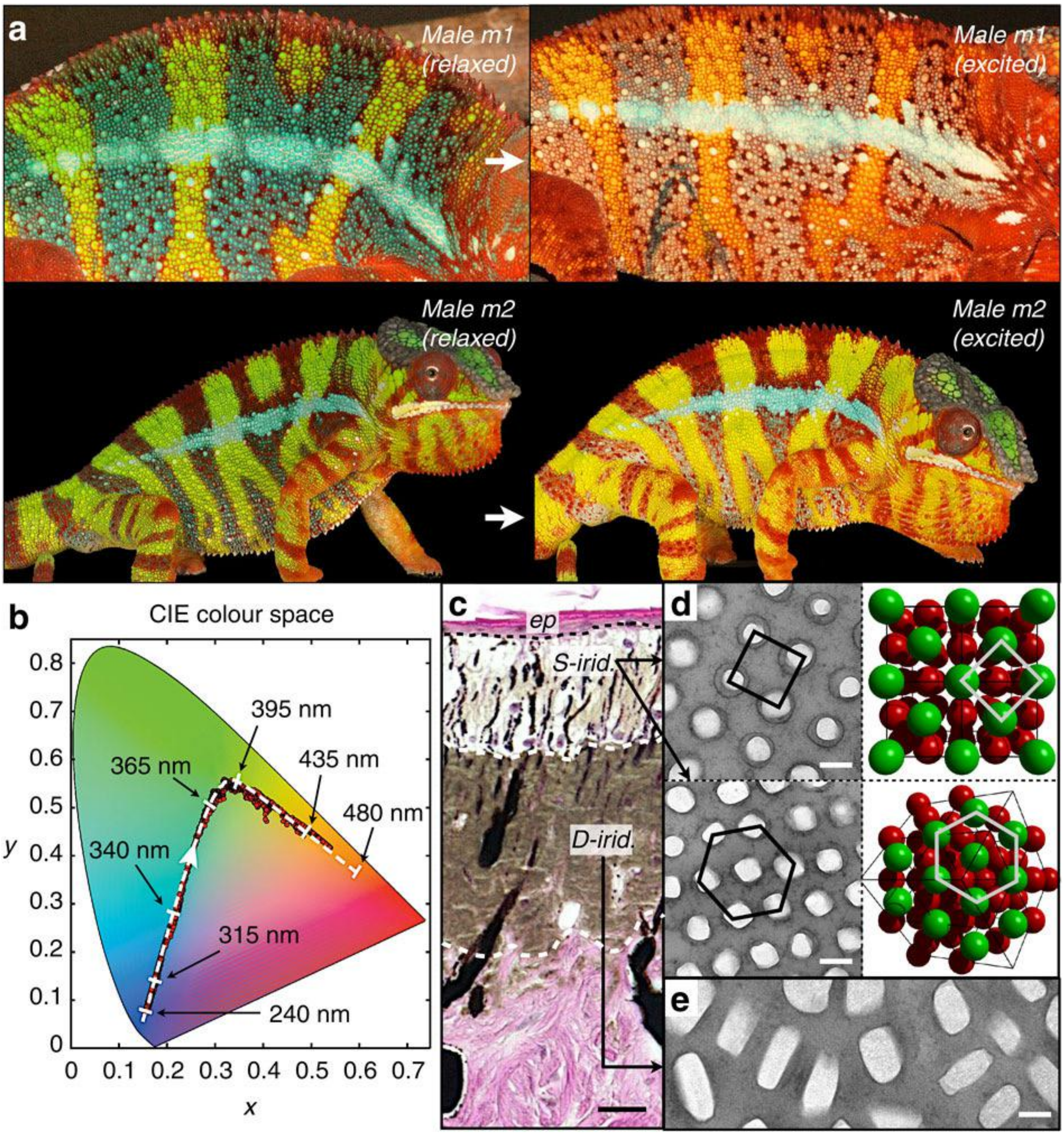


Fig. 2. Colour change and iridophore types in panther chameleons. (a) The reversible colour change presented for two males (m1 and m2) from a relaxed to excited state. (b) Red dots: time evolution in the CIE (International Commission on Illumination) chromaticity chart of a third male with green skin; dashed white line: optical response in numerical simulations using a face-centred cubic (FCC) lattice of guanine crystals with lattice parameter indicated with black arrows. (c) Haematoxylin and eosin staining of a cross-section of white skin showing the epidermis (ep) and the two thick layers of iridophores (d) TEM images of guanine nanocrystals in S-iridophores in the excited state and three-dimensional model of an FCC lattice (shown in two orientations). (e) TEM image of guanine nanocrystals in D-iridophores. Scale bars: (c) 20 mm; (d, e) 200 nm. From ref 1, reprinted with permission.

trol and explain why chameleons can endure the heat more so than other species of lizard. The combination of the two functionally different layers provides the chameleons with superior adaptation for efficient camouflage and moderation of solar radiation.

But what does this all mean for scientists? Well, it could provide us with something amazing, such as stimuli responsive camouflage and temperature controlled clothing and materials. Teyssier *et al*. were able to induce geometric shifts of the nanocrystals *in vitro* by subjecting the skin to hypertonic solutions which generated the osmotic pressure necessary to shrink the crystal lattice.[1] In doing so they were able to visualise the gradual shift of colour across the whole visible spectrum of individual cells. By controlling the crystal lattice in expansion and contraction, materials chemists could utilise the reversible shifts in colour to create smart fabrics. This evolutionary trait is already inspiring material design such as e-skin.[3] This e-skin is a layering system of pressure sensors based on pyramidal microstructured polydimethylsiloxane (PDMS) dielectric layers, spray-coated with single walled carbon nanotubes (SWNT). It is capable of correlating the applied pressure to the brightness of the devices as well as

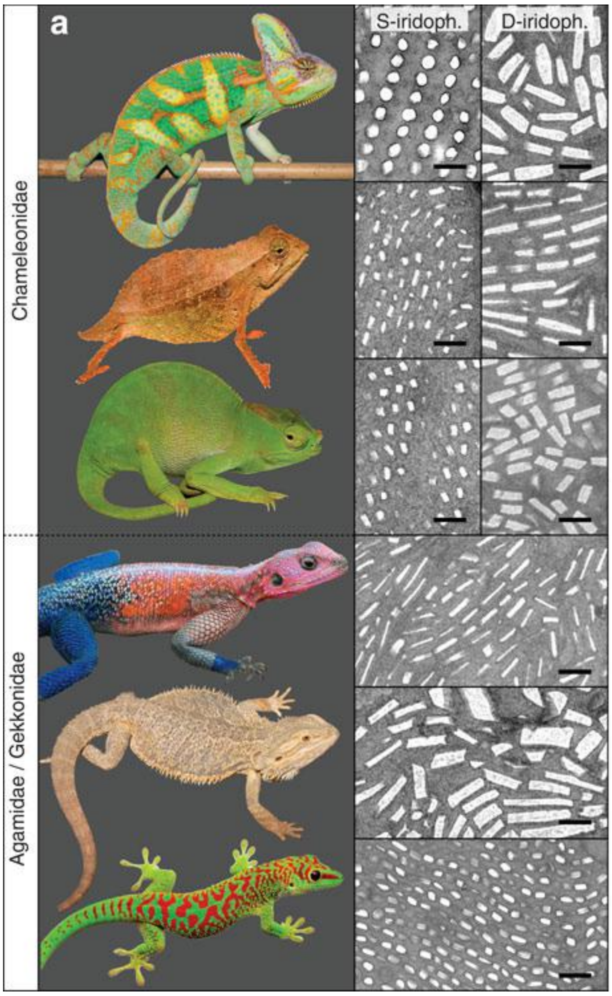


Fig. 3. In addition to *Furcifer pardalis* other chameleonidae (top to bottom: *Chamaeleo calyptratus*, *Rhampholeon spectrum* and *Kinyongia matschiei*) exhibit two superposed layers of (S- and D-) iridophores, whereas agamids (the sister group to chameleons) and gekkonids have a single-type iridophore layer (top to bottom: *Agama mwanzae*, *Pogona vitticeps* and *Phelsuma grandis*). Scale bar: 500 nm. From ref 1, reprinted with permission.

spatially mapping the applied pressure (Fig. 4). The technology could find use in interactive wearable devices, robots, military applications and prosthetic devices.

Yu *et al.* present an alternative stance creating a layered material of artificial actuators and photodectectors which provide operation across the full visible spectrum.[4] The responses of the photodetectors define the pattern of thermal actuation and, therefore, the resulting patterns of colouration; selective actuation of these photodefined chromatophores/leucophores yields programmable patterns of black and white.[4] To the same endeavour, choleric liquid crystals (CLCs) are used increasingly to achieve object radiation camouflage with the environmental background. Liquid crystals are matter with the flow of liquids and the self-orientation of crystals and are used in optical displays such as LCD televisions. When CLCs are combined with a colour detection device to determine the colour of the object's background and a subsequent thermocouple to apply a certain voltage magnitude and polarity, a resulting temperature change alters the colour of the liquid crystals to match the colour of an object's background providing adaptive concealment.[5] Current research is progressing slowly in respect to chameleon-inspired camouflage, with more focus on electronic implementations. However, it is the chemical and nanostructured architecture that must be highlighted. The Meledandri research group in the Department of Chemistry at the University of Otago has demonstrated the accurate control of nanocrystal fabrication for desired applications.[6] Efforts should be made towards combination of these crystalline synthetic control methods with incorporation into stimuli responsive polymeric networks in the attempt to recreate the instantaneous self-regulating colour change of the chameleon.

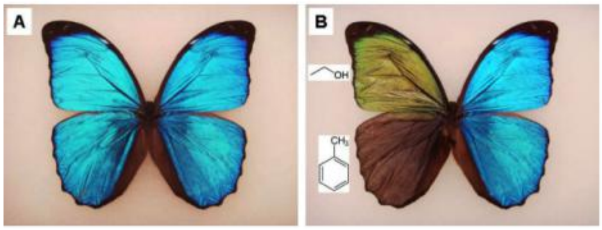
Exotic optical phenomena in butterfly wings

Whilst they are delicate and fragile, butterfly wings may hold the key for many potential advancements in materials science. Examples of numerous optical phenomena are to be found on the surface of the wings including multilayer interference, diffraction, Bragg scattering, Tyndall scattering, and Rayleigh scattering. Both intricate architectures of photonic crystals, as seen within chameleon skin, and Christmas tree like structures are responsible for the array of colours exhibited by many butterfly species. There are, however, a few butterflies that have won researchers hearts; the invisible glasswing, the iridescent Morpho and the perfectly black swallowtail.

Invisibility through metamaterials is a holy grail of material science – who wouldn't want Harry Potter's invisibility cloak? Well the good news is that research is getting ever closer to solving the riddle and examples of natural structures can aid us in this search. The glasswing butterfly (*Greta ora*) possesses a material that is much sought after as a means of invisibility. As its name suggests, the glasswing butterfly has wings that demonstrate both low absorption and reflection of light and as such, the wings are transparent. Such adaption is rarely seen within terrestrial organisms due to the large difference between the refractive indices of living tissues (n = 1.3–1.55) and air (n = 1) which results in significant surface reflections. Secondly, most terrestrial organisms require pigmentation to protect themselves against the comparably high levels of ultraviolet radiation on land. Thirdly, as buoyant forces are absent on land, supporting anatomical structures are needed and they are often opaque.[7] The glasswing butterfly achieves this scientific feat by possessing randomly sized nanopillars of high aspect ratio; the random height and width of these pillars is the origin of the omni-directional anti-reflection properties of this butterfly. Doctoral student Randwanul Hasan Siddique, who discovered the phenomenon, states that "In contrast to other natural phenomena, where regularity is of top priority, the glasswing butterfly uses an apparent chaos to reach effects that are also fascinating for us humans."[7] The structures have no regard for regularity and as such, when light reaches the surfaces only one or two rays are reflected, achieving the low absorption and reflection necessary to produce camouflage by transparency. In comparison with plain glass, which reflects about 8% of light under normal incidence, the glasswing reflection of 2% in the visible region is about four times lower while their refractive indices are quite close. Siddique *et al*. optimised the variance of the distribution and the shape of the pedestals, producing almost perfect antireflection surfaces which could be engineered for a broad range of wavelengths and viewing angles.[7] Such anti-reflective surfaces could be adapted to improve the light collection in solar cells or for an efficient light extraction of the substrate modes in light-emitting diodes or even enhancing the performance of optical, optoelectronic and electro-optical devices such as glasses, mirrors, lens, photodetectors, surface-emitting lasers, and displays and in optical sensing or imaging.

The Morpho butterfly (*Morpho peleides*) has already provided bioinspired commercially available devices for explosive material sensors.[8] Morpho butterflies are commonly recognised by their large iridescent blue wings, caused by the presence of highly arranged photonic crystal structures on the wing surface. However, they also possess another beautiful phenomena, the ability to sense chemicals within the environment. As discussed previously, the photonic structures cause optical interference, absorbing and bending light, but when a chemical is bound to the jagged photonic structures, the emitted colour is altered (Fig. 6). The sensor, due to its nanoscale architecture, is 300 times smaller and consumes 100 times less power than current desktop detectors and allows for the sensitive identification of hazardous materials such as chemical oxidisers and explosives. Classical techniques for the selective identification of chemical vapours requires the use of analytical instruments based on gas chromatography, mass spectrometry, or a combination of both; however, the cost and size of instrumentation is high. The Morpho butterfly's scales provide high selectivity of vapour sensing through photonic sensors which have been mimicked into small scale sensor arrays. Careful sensor design requires two synergistic design aspects; a resonant structure to enhance the vapour response and an open air structure that provides full interaction with all regions of the material. The design was already in existence on the wings of the Morpho butterfly and allowed for a superior synthetic sensing system offering high degrees of control over the nanostructure geometry and physical mechanism of light interference.

Fig. 6. Photographs of the colour changes of a Morpho butter-



fly upon exposure to liquids of different refractive index showing (A) before exposure to liquids and (B) after exposure of the left fore- and hindwing to ethanol (n = 1.362) and toluene (n = 1.497), respectively. From ref 8, reprinted with permission.

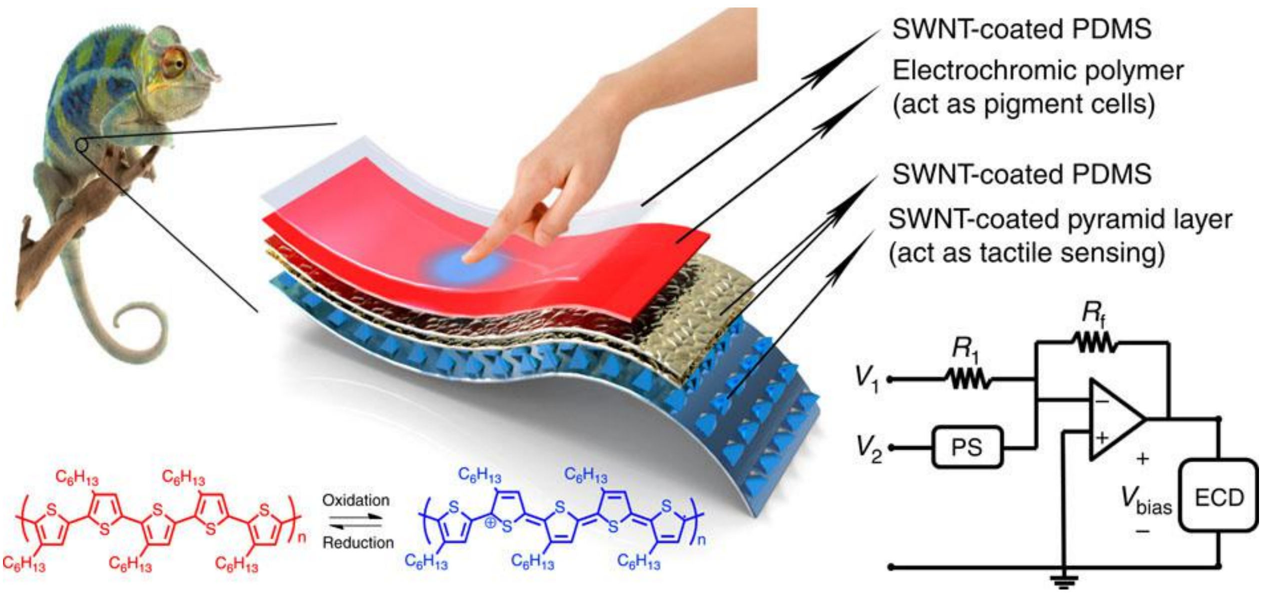


Fig. 4. Schematic of the pressure sensitive chameleon inspired e-skin device. Bottom left: neutral and oxidised states of the electrochromic polymer in poly (3-hexylthiophene-2-5-diyl). Bottom right: a schematic of the circuit layout (PS, pressure sensor; ECD, electrochromic device). From ref 3, reprinted with permission.

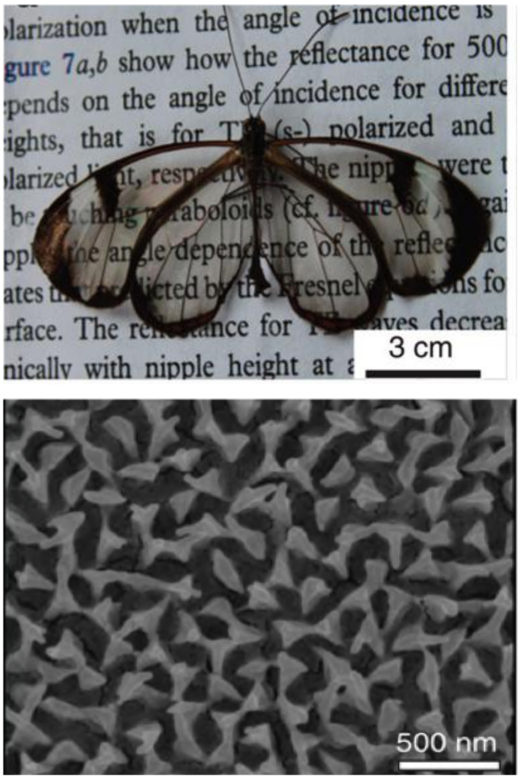


Fig. 5. (Top) Photo of a glasswing butterfly and (bottom) SEM image showing the quasi-random positioning of the pillars that is confirmed by the two-dimensional Fourier power spectrum of the position of the nanostructures. From ref 7, reprinted with permission.

The art of total blackness is a complex task, one that has been achieved by two species of swallowtail butterflies (*Troides aeacus* and *Papilio helenus*). This adaptive ability can be utilised in modern day technology in the production of solar collectors. Finding renewable sources of energy is a pressing problem for society and new technologies that produce efficient solar trapping is key for both electricity generation and catalysis. The answer could be on the tiny wings of a butterfly. Butterflies cannot generate enough heat through their own metabolism to remain active indefinitely and therefore must utilise their scaled wings as a means of absorbing heat through solar rays. As with the chameleon, scientists initially thought the deep black colour on the butterfly's wings was due to the presence of melanin. However, when observed with an electron microscope a unique nanoscale structure was found to exist.[9] The wings are actually arranged into overlapped elongated rectangular scales, similar to a roof on a house. The margins of the scales are lined with ridges that lead to small holes on either side of the scale which open up to an underlying layer. The ridges act as tunnelling pathways, reflecting shorter light into the holes that opened up to the lower wing membrane, whilst longer wavelengths are absorbed by the main scale body (Fig. 7). Fan *et al.* used the wing, paired with titanium dioxide and platinum nanoparticles, to perform as a catalyst in water splitting for hydrogen gas generation.[9] The wing produced H_2 gas from water at more than twice the rate of unstructured compound catalysts. The research suggests the promising use of mimicking the elaborate creations of nature and the implementation of nanoscaled winged structures for renewable energy devices.

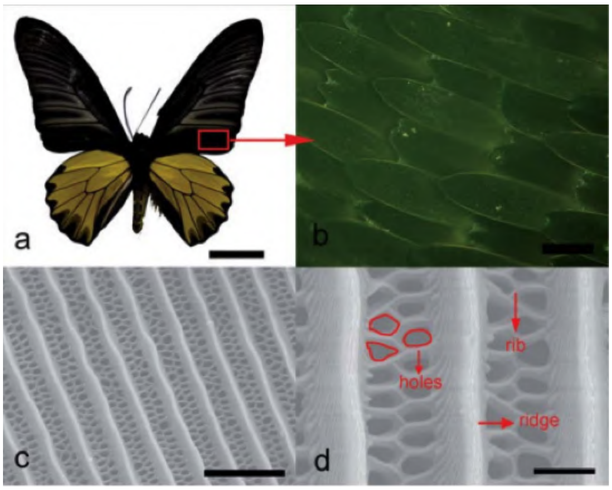


Fig. 7. (a) Photograph of the butterfly *Troides aeacus*, scale bar: 2 cm. (b) Optical microscopic image of the surface scales of the black winged area, scale bar: 50 μm. (c) FESEM image of the microstructures of the scales, seen in (b), scale bar: 5 μm. (d) Expanded view of (c) presenting the core nanoarchitecture responsible for light trapping effects; holes, ridges and ribs. From ref 9, reprinted with permission.

The Green Hairstreak butterfly (*Callophrys rubi*) has attracted attention for its gyroid structured wings (Fig. 8).[10] Gyroid structures are chiral periodic structures with cubic symmetry which consist of intertwining and curved surfaces. They often demonstrate amazing light interactions and create a mechanically strong structure. The strong chirality properties of the gyroid structure allow for the manipulation of optical circular dichroism. In order to replicate the 3D gryoid nanostructure an optical two beam super-resolution lithography fabrication method was developed to produce structures with superior resolution, uniformity and controllability.[10] In creating the new fabrication method, the material exceeded the properties of the structure observed in nature. The mechanical strength, resolution and uniformity was significantly increased through fabrication control producing materials that possessed increased optical phenomena and functionality. The synthetic gyroid structures could create compact, light-based electronics because, thanks to their smaller size, larger numbers of devices can be integrated onto a single chip.

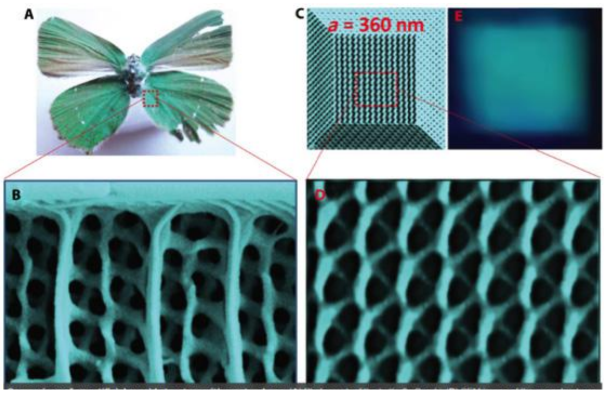


Fig. 8. Comparison of an artificial and natural gyroid structure. (A) Photograph of *Callophrys. rubi*. (B) SEM of the nanostructure found within the butterfly wings with a periodicity of 350 nm. (C) An artificial gyroid nanostructure. (D) Magnified image of the artificial gyroid nanostructure; the unit cell size is 350 nm. From ref 10, reprinted with permission.

Touch responsive leaves

With much delight many of us have played with the mimosa leaf at some point; when touched, the leaf rapidly recoils onto itself and the stem falls. The movement is generated by the movement of water into or out of motor cells, which is driven by the osmotic flux of ions such as K^+.[11] At the base of the leaf the pulvini contains the mechano- and photo-receptors that allow the dynamic response to external stimuli. The output reaction or movement is controlled by the tissue hierarchy and geometrical constraints at the micrometre and nanometre scale.[12] The biomimetic movement in relation to the mimosa leaf is interesting, inspiring the production of haptic (touch-responsive) fabrics; these fabrics typically contain actuators and sensors that collect information and replay movements depending on the input.[13] For instance, researchers at MIT have constructed a scarf that simulates human touch to the wearer.[14] In a similar fashion, distance touch objects are ever increasing, where fabrics or objects can imitate strength, length and temperature of touch from a paired object across the other side of the world. Comparable fabrics are increasingly used in motor rehabilitation treatments where the fabric corrects the input movement with a responsive output movement. The technology has much progressed from plant life to the world of virtual reality, where the input of movements into worn garments relates to movement within the virtual world.[15]

Fig. 9. Photograph of the touch responsive mimosa leaf.[16]

Conclusions

Millions of years of adaptation for survival has progressed the diverse world we now live in. On a daily basis, humanity is faced with challenges that have already been solved by the natural world offering superior functional properties of adhesion, hydrophobicity, self-cleaning optical responses, antibiofouling, mechanical strength and many more. A clever combination of chemistry, sensory systems and structure can inspire new ideas and mechanisms for implementation to the synthetic chemical world creating our own technological evolution.

References

1. Teyssier, J.; Saenko, S. V.; van der Marel, D.; Milinkovitch, M. C. *Nat. Commun.* **2015**, *6*, 6368(1-7).
2. Matin, T. R.; Leong, M. K.; Majlis, B. Y; Gebeshuber, I. C. *AIP Conf. Proc.* **2010**, *1284*, 5-14.
3. Chou, H.-H.; Nguyen, A.; Chortos, A.; To, J.W.F.; Lu, C.; Mei, J.; Kurosawa, T.; Bae, W.-G.; Tok, J. B.-H.; Bao, Z. *Nat. Commun.* **2015**. *6*, 8011(1-10).
4. Yu, C.; Li, Y.; Zhang, X.; Huang, X.; Malyarchuk, V.; Wang, S.; Shi, Y.; Gao, L.; Su, Y.; Zhang, Y.; Xu, H.; Hanlon, R. T.; Huang, Y; Rogers, J. A. *Proc. Nat. Acad. Sci.* USA **2014**, *111*, 12998-13003.
5. Reynolds, R.F.; Kinsella, M. J. *Thermal and visual camouflage system*, **2002**, see: https://www.google.com/patents/US6338292 (accessed 04/07/2016).
6. Rodpun, K.; Lucas, N. T.; Tan, E. W.; Meledandri, C. J. *Cryst. Growth Des.* **2016**, *16*, 3940–3946.
7. Siddique, R.H.; Gomard, G.; Holscher, H. *Nat. Commun.* **2015**, *6*, 6909(1-8).
8. Potyrailo, R.A.; Bonam, R. K.; Hartley, J. G.; Starkey, T. A.; Vukusic, P.; Vasudev, M.; Bunning, T.; Naik, R. R.; Tang, Z.; Palacios, M. A.; Larsen, M.; Le Tarte, L.A.; Grande, J. C.; Zhong, S.; Deng, T. *Nat. Commun.* **2015**, *6*, 7959(1-12).
9. Zhao, Q.; Guo, X.; Fan, T.; Ding, J.; Zhang, D.; Guo, Q. *Soft Matte*r, **2011**, *7*, 11433-11439.
10. Gan, Z.; Turner, M. D.; Gu, M. *Sci. Adv.* **2016**. *2*, e1600084(1-6).
11. Ueda, M.; Yamamura, S. *Tetrahedron* **1999**, *55*, 10937-10948.
12. Burgert, I.; Fratzl, P. *Phil. Trans. R. Soc. A* **2009**, *367*, 1541-1557.
13. Malshe, A.; Rajurkar, K.; Samant, A.; Hansen, H. N.; Bapat, S.; Jiang, W. *CIRP Ann. Manuf. Techn.* **2013,** *62*, 607-628.
14. Bonanni, L.; Vaucelle, C.; Lieberan, J.; Zuckerman, O. In: *CHI'06 extended abstracts on human factors in computing systems.* Association for Computing Machinery **2006,** 580-585.
15. Singh, A.V.; Rahman, A.; Kumar, N. V. G. S.; Aditi, A. S.; Galluzzi, M.; Bovio, S.; Barozzi, S.; Montani, E.; Parazzoli, D. *Mater. Design* **2012**, *36*, 829-839.
16. Image by John Tann from Sydney, Australia - Mimosa pudica leaves, CC BY 2.0, see: https://commons.wikimedia.org/w/index.php?curid=38233041 (accessed 04/07/16).

A comparison of empirical potentials for calculating the structural motifs of Au, Ag, Cu, Pt and Pd nanoclusters up to 10,000 atoms

Stephanie Lambie

Department of Chemistry, University of Otago, PO Box 56, Dunedin 9054
(email: *stephanielambie@hotmail.com*)

Keywords: *nanoclusters, computational chemistry, empirical potentials*

Steph grew up in Dunedin and was educated at Columba College. She then continued her education close to home, attending the University of Otago. Her Bachelor's degree was completed last year with a double major in chemistry and oceanography. Following graduation, Steph worked as a research assistant for Dr Anna Garden studying structural motif dominance shifts in varying sizes of nanoparticles. She began her Master's degree in chemistry at Uppsala University, Sweden, in August.

Introduction

Nanoclusters have a variety of roles across many fields, being a vital player in nanomaterials and nanotechnology and many industrial processes.[1] Two features define nanoclusters; firstly, large surface area to volume ratio, giving rise to a large area on which reaction can occur, and secondly, differing reactivities of under co-ordinated sites on the particle.[1,2]

Much work has been carried out characterising the structure and properties of nanoclusters <200 atoms.[3-12] However, knowledge of the structural preference of clusters >1000 atoms is scant. Density functional theory (DFT) calculations scale at a rate of N^4 or N^5, where N is the number of electrons in the cluster,[13] making DFT calculations of clusters >500 atoms impractical. To combat this, semi-empirical potentials have been designed to approximate the energetics of larger clusters without the need for such exhaustive resources. Preferences in geometry and structure are not common between metals, meaning calculations must be carried out explicitly for individual metals and each specific semi-empirical potential. Therefore, even for the less resource intensive semi-empirical potentials, computational constraints quickly become a defining factor. Further, each new potential comes with a unique set of limitations that need to be appreciated so that the best potential for each individual situation can be selected. A better understanding of each potential in modelling of clusters may be able to focus research efforts and streamline resource use.

Three underlying structural motifs are evident among nanoclusters; icosahedra, decahedra and octahedra (Fig. 1). Icosahedra are characterised as almost spherical and having a close packed surface with 20 distorted (111)-like facets.[14] The decahedral structure is characterised by twinned tetrahedra, with 10 (111) facets. Truncation of each tetrahedron to reveal (100) facets yields a more spherical and more stable cluster. An even more stable structure may be obtained by truncating the corners to obtain (111)-like re-entrant corners.[15] Octahedral clusters contain (111) and (100) facets and have an underlying face-centered cubic (FCC) crystal structure.

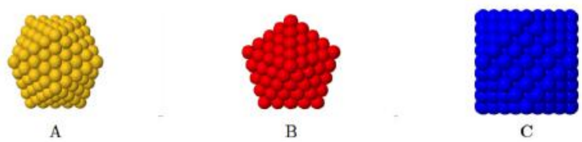


Fig. 1. The three different underlying structural motifs, shown fully close-shelled at the magic cluster N = 309: (A) icosahedral, (B) decahedral, (C) octahedral.

The aim of this study was to characterise the structural preference of five transition metals, Ag, Au, Cu, Pd and Pt, using four semi-empirical potentials: Effective Medium Theory (EMT) under standard parameterisation and Rasmussen parameterisation; Rosato, Guillope and Legrand (RGL) potential and the Sutton Chen potential. Finally DFT was used for quantitative comparison of semi-empirical potential results on selected nanoclusters < 309 atoms.

Models

EMT

EMT calculates the energy of an atom in an arbitrary environment by first calculating the energy of the atom in a properly chosen reference system; the effective medium.[16] The energy difference between the reference system, commonly FCC, and the real system is then calculated. However, EMT (standard parameterisation) is unable to describe the elastic properties of Cu, Au and Ag, due to an underestimation of an intrinisic stacking fault.[17] To resolve this issue, the Rasmussen parameters were developed to investigate cross-slip using atomistic theory. The EMT potential takes the form:

$$E_i = E_c(n_i) + E_{AS}(i) \quad \text{(Eq. 1)}$$

where $E_c(n_i)$ is the cohesive energy of an atom embedded in an electronic density, n_i from its neighbouring atoms and E_{AS} is the atomic sphere correction which describes the change in energy when an atom is moved from the real to the reference system.

RGL potential

The RGL potential is a simple semi-empirical model used to simulate thermodynamics of FCC transition metals based on the second moment approximation.[18] Atomic relaxation is assumed to take place on the top surface layer only.[19] The RGL potential can be represented as:

$$E_i = \left[\sum_{j,r_j<r_c} A\exp\left[-p\left(\frac{r_j}{r_0}-1\right)\right] - \left(\sum_{j,r_{ij}<r_c} \xi^2 \exp\left[-2q\left(\frac{r_j}{r_0}-1\right)\right]\right)^{\frac{1}{2}} \right]$$

(Eq. 2)

where r_{ij} is the distance between atoms *i* and *j*, r_0 is the equilibrium nearest neighbour distance in the bulk metal, p and q are the repulsive interaction range and attractive range, respectively, while A is a parameter fitted to experimental values of the cohesive energy and r_c is the cut off radius of the interactions (in our calculations, this was set to include the effects of the 2nd nearest neighbour and linked smoothly to zero at the 3rd nearest neighbour distance). In Equation 2, the first term describes the pairwise repulsion of the Born Mayer type, and the second defines the n-body attractive contribution.

Sutton Chen potential

The Sutton Chen potential was developed to account for van der Waals interactions between separated atomic clusters in the description of metallic bonding at a short range.[20] It incorporates an approximate many body representation of the delocalised metallic bonding.[4] The Sutton Chen potential is expressed mathematically as:

$$E = \varepsilon \sum_i \left[\frac{1}{2} \sum_{j\neq i} \left(\frac{\alpha}{r_{ij}}\right)^n - c\sqrt{\rho_i} \right] \quad \text{(Eq. 3)}$$

where: $$\rho_i = \sum_{j\neq i}\left(\frac{\alpha}{r_j}\right)^m \quad \text{(Eq. 4)}$$

In Equations 3 and 4, r_{ij} is the distance between atoms *i* and *j*, *α* is the bulk lattice constant, *c* is a dimensionless parameter, ε is a parameter with dimensions of energy, while the exponents n and m are integers.[20]

DFT

DFT uses electron density to approximate the Schrödinger equation, because for many-electron systems the wavefunction is unknown. Therefore, the wavefunction can be estimated with a variety of different functionals to generate an approximate solution to the Schrödinger equation. However, the exact form of the functional describing the electron density of many-electron systems is also unknown. Accordingly, the functional used to approximate the Schrödinger equation must be carefully selected. The DFT calculations in this study used the functional Perdew-Burke-Ernzerhof as modified for solids (PBEsol).

Results and discussion

Icosahedra exhibit a layered structure and are defined solely by the number of shells, n. Perfect icosahedra only exist at certain sizes where there is a closed shell. These are the so-called "magic numbers". The icosahedra geometry requires a distortion of tetrahedra, resulting in high internal strain. Therefore, this structure is predicted to be the most stable of the motifs at small nanocluster sizes. Octahedral clusters are defined by the length, *i*, of the edge and the corner truncation, *j*. Octahedra that fulfill the *i* = 2*j* + 1 are called cuboctahedra and exist at the same magic numbers as the icosahedra. The octahedra calculated in this study were those within the range *i* = 2 to *i* = 30 and *j* = 0 to *j* = [(*i* -1)/ 2] if *i* was even and *j* = [*i*/2 -1] if i was odd. Truncated octahedra expose more (100) surface, presenting a higher surface energy but counter-balancing this is low internal strain resulting in the expectation that octahedra will dominate at large sizes. Decahedral clusters are defined by three indices, p, q, and r, where p and q are the dimensions of the (100) facets perpendicular and parallel to the principal rotation axis, respectively. Marks decahedra are those in which atoms at the (100)-(100) edges are removed. The index, r, gives the depth of the Marks re-entrance at the corners.[15] "Magic" decahedral clusters have square (100) facets and no re-entrance corners; when p = q and r = 0. The decahedral clusters in this study were restricted to p = 30, q = 1 to q = p+3 and r = 0 t r = p+3. Decahedra have less internal strain than icosahedra, making them favourable at intermediate sizes. It should also be noted, that for all metals and structural motifs only clusters up to 10,000 atoms in size were considered.

For closer inspection of relative structural motif preference, the stability of the clusters was represented in terms of Δ, a representation of energy per atom corrected for the surface area to volume ratio, thus partly removing the influence of size effects. In Equation 5, E_{tot} is the total energy of the cluster, *N* is the number of atoms in the cluster and E_{coh} is the cohesive energy of the metal of interest:

$$\Delta = \frac{E_{tot} - NE_{coh}}{N^{2/3}} \quad \text{(Eq. 5)}$$

Following is an in depth analysis of the empirical calculations for Au. The other four metals, Ag, Cu, Pd and Pt, will then be discussed briefly. Finally, the results obtained using the empirical potentials will be compared to DFT calculations of selected magic clusters.

Gold

The relative stability of icosahedral, decahedral and octahedral Au clusters up to 10,000 atoms are shown in figure 2. All of the potentials predicted icosahedra to be favoured at sizes <200 atoms. At sizes >200 atoms, the icosahedra motif becomes unstable with icosahedra Δ values increasing rapidly. For the RGL, EMT (Rasmussen parameters) and Sutton Chen potentials, the most stable icosahedra structural motif occurred at N =147 (4th shell icosahedra), indicated by a minimum Δ value. However, the EMT potential (standard parameters) predicted the lowest Δ for the icosahedral motif to be at N =55 (3rd shell icosahedra).

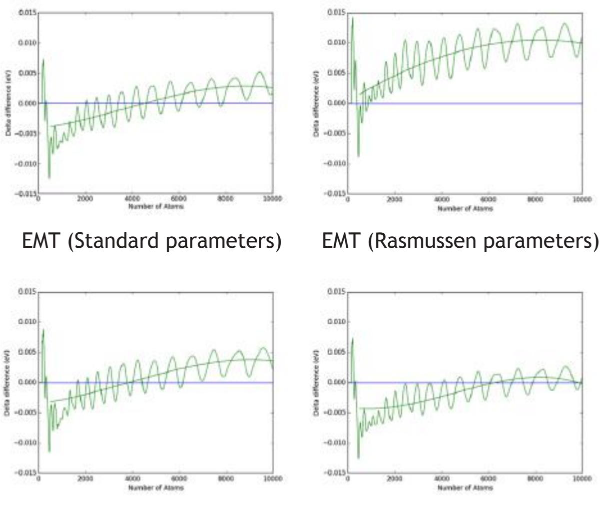


Fig. 2. Δ as a function of cluster size with reference to octahedral bulk for Au (Δ represents the energy per atom roughly divided by the surface area to volume ratio, see text – a lower value of Δ indicates a more stable cluster). Black represents the icosahedra structural motif, blue the octahedral motif and red the decahedral motif. Magic clusters are denoted with squares, while symmetric and asymmetric truncations are depicted plotted with dots. The colour bar at the bottom projects the associated colour of the most stable cluster at a given size in order to give a visual, binary depiction of preferred structure.

In contrast to the icosahedra structural motif which exists only at "magic" cluster sizes, many truncations for decahedra and octahedra are allowed as these structures do not have a closed shell requirement. Further, truncated octahedral and decahedral motifs often have a higher degree of stability as reflected by their lower Δ values (Fig. 2). All of the potentials show fluctuation between decahedral and octahedral motifs but the degree to which the fluctuation occurs differs between potentials. EMT (Rasmussen parameters) predicted octahedra to become more stable from smaller cluster sizes, seen by the blue dots being at a lower Δ (Fig. 2). The Sutton Chen potential calculated decahedral preference to a larger cluster size. Alternatively, the RGL and EMT (standard parameters) predicted very similar structural preference, between the Sutton Chen potential and EMT (Rasmussen) calculations. However, while the RGL and EMT (standard parameters) agree, this does not neccessarily imply that the calculations are quantitatively or even qualitatively correct. Further comparison to both DFT and experiment is required.

In the colour bar projection at the bottom of Fig. 2, the underlying geometrical structure of the most stable cluster at a given size can easily be identified. The colour bar shifting from predominantly red at smaller cluster sizes to predominantly blue at larger cluster sizes reflected the shift in motif dominance from decahedral at smaller sizes to octahedral at larger sizes. It is crucial to note that while the colour bar projection displays the most stable cluster at a given size, other clusters are also stable (Fig. 2). Therefore, co-existence of other structures is not only possible, it is highly likely. Bearing in mind the likely co-existence of a variety of structures, a new parameter was established to quantitatively describe the dominance shift from decahedral to octahedral. This parameter calculated the Δ difference between the decahedral minimum and the octahedral minimum, averaged over 1,000 clusters and plotted as a function of the average cluster size. A polynomial was fitted to the Δ difference plots and the point at which the fitted polynomial crossed at x = 0 (representing a shift from decahedral dominance to octahedral dominance) was defined as the "structural motif dominance shift" (Fig. 3).

The structural motif dominance plots shows a number of fluctuations in dominance where the structural preference shifts from decahedral to octahedral and then back to decahedral (Fig. 3). However, the dominance shift we have defined is the “best fit” of this data. In future, it would be interesting to also conduct this calculation to quantify the dominance shift from icosahedral to decahedral dominance under the different potentials.

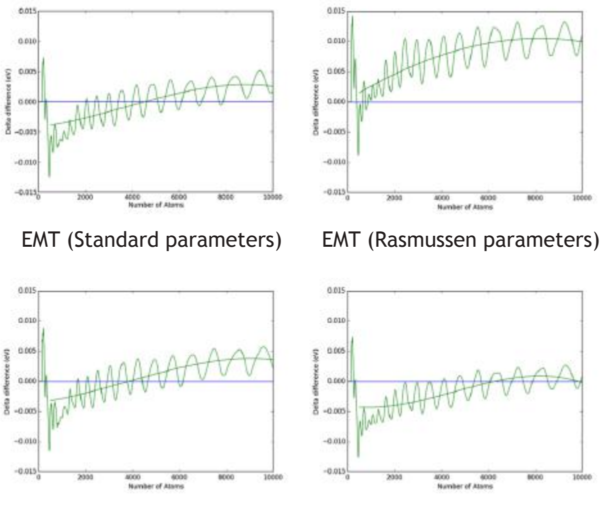


Fig. 3. Δ difference averaged over 1,000 clusters as a function of mean number of atoms across the 1,000 clusters for Au. The fitted polynomial was used to describe the dominance shift from decahedral to octahedral clusters. Negative values mean decahedral dominance while positive values are indicative of octahedral dominance.

Other metals

The shift in structural dominance has been calculated for Ag, Au, Pd and Pt and the results are summarised in Table 1.

Table 1. Structural motif dominance shift as calculated using a fitted polynomial to Δ difference between octahedral and decahedral motifs, averaged over 1,000 clusters.

	Potential			
Metal	**EMT (standard)**	**EMT (Rasmussen)**	**RGL**	**Sutton Chen**
Ag	<1000	2686	>10000	>10000
Au	4495	<500	3828	6261
Cu	6738	1584	>10000	>10000
Pd	6475	-	7274	>10000
Pt	4394	-	6794	7072

Silver

All four potentials agreed that the icosahedral motif was dominant to N ~ 250 atoms. At N >250 atoms, the potentials diverged in their predictions. The RGL and Sutton Chen potentials were in concordance, predicting the decahedral motif to be dominant to 10,000 atoms, beyond which we have not calculated. However, the EMT potential (standard parameters) showed a shift toward octahedral motif dominance from approximately 8,000 atoms onwards. Finally, EMT (Rasmussen parameters) predicted the octahedral motif as being the most stable from a much smaller size, ~3,000 atoms.

Copper

Icosahedra were predicted by all of the potentials to be the dominant motif at small sizes. EMT (standard and Rasmussen parameterisation) predicted icosahedra as the most stable motif to ~1,200 atoms, while the RGL potential did not predict icosahedra to be as stable, shifting to decahedral dominance at ~1,000 atoms and the Sutton Chen potential predicting this shift to come earlier still at ~500 atoms. The EMT calculations (standard parameters) then predicted fluctuation between decahedral and octahedral dominance, with the dominance shift from decahedral to octahedral being at 6,738 atoms. EMT (Rasmussen parameters) predicted octahedral dominance from much smaller cluster sizes; 1584 atoms, a point of difference to the other three potentials. Finally, the RGL and Sutton Chen potentials were in agreement, both predicting that after early icosahedral dominance, decahedra were the prevalent motif to 10,000 atoms.

Palladium

Icosahedra were predicted by all three potentials to ~200 atoms in size. From here, RGL and EMT (standard parameters) showed very similar predictions with fluctuations between decahedral and octahedral structural motifs being evident. Furthermore, both potentials predicted the dominance shift to octahedral structures at ~7,000 atom clusters. In contrast to the RGL and EMT potentials, the Sutton Chen potential predicted decahedral to be the dominant motif to 10,000 atoms with no prediction of octahedral clusters becoming more stable in this size range.

Platinum

Platinum was the metal for which the potentials agreed the best. All three potentials displayed icosahedral dominance to ~200 atoms. At cluster sizes >200 atoms, dominance fluctuated between decahedral and octahedral motifs fairly consistently up to 10,000 atoms. The only difference of note was that EMT (standard parameters) predicted a dominance shift to octahedral at a smaller size than the RGL and Sutton Chen potentials, but otherwise agreement between the three potentials was good.

Performance of the potentials

Shao *et al*.[5] found that the Sutton Chen potential had a tendency to calculate less strained and more ordered structural motifs at small sizes, reducing the likelihood for icosahedra at small sizes, while they also stated that the RGL potential at small sizes preferred highly strained, disordered motifs. For Ag, Au, Pd and Pt, this was a difficult conclusion to draw due to the small range in which icosahedra were favoured. However, for Cu, the extended preference for the icosahedra allowed for the selectivity of each of the potentials for the icosahedra motif to be examined. Using Cu as an example, our Sutton Chen calculations were in agreement with Shao *et al.*, with the existence of the icosahedral geometry being reduced under the Sutton Chen potential, compared to the other potentials. However, the RGL potential calculations for Cu did not show preference for strained, disordered motifs (which would manifest in a prolonged preference for icosahedra) when compared to EMT (standard and Rasmussen parameterisation). In our calculations, RGL and EMT (standard and Rasmussen parameterisation) showed similar predictions for icosahedra. However, discrepancy between our calculations and the findings of Shao *et al.* could be due to our use of Cu as an example, while their study focussed on Ag.

Comparison to DFT

For ordering of the structural preference, the semi-empirical potentials were in agreement with DFT (Table 2). When using DFT and all four potentials for Au, Ag and Cu clusters at magic cluster sizes up to 309 atoms, icosahedra were the most stable, decahedral the second most stable while the octahedral structure was the least stable (Table 2). However, when the magnitude of the difference between the Δ of the most stable motif and the Δ of the remaining two motifs is considered, there appeared to be little consistency in the predictions of the potentials compared to DFT. DFT commonly predicted a Δ difference of at least twice that of the potentials. It was also crucial to note that while at small sizes all of the potentials predict structural preference reliably, it was at larger cluster sizes, typically >1,000 atoms, that the potentials diverged in their calculations, thus where agreement in ordering between DFT and potentials could be more telling. However, due to the resource intensive nature of DFT, it was unfeasible to carry out calculations on larger clusters; a self-evident example of the limitations of computational techniques.

Therefore, it can be said that at small sizes, all of the potentials do well at reproducing trends in structural preference. This conclusion has been drawn by others, with Jacobsen *et al.*[16] stating that while the absolute accuracy of the EMT potential is limited, the trends in surface energies of nanoclusters were reasonably well described. Baletto *et al.*[14] concluded that the RGL potential quantitatively predicted the dominant diffusion mechanisms on noble and transition metal surfaces. While we observed qualitative agreement, no quantitative agreement was seen for any of the potentials with DFT calculations. Differences between the quantitative agreement of the RGL potential found by Baletto *et al.* and our findings may lie in the different properties being calculated; while their statement refers to diffusion mechanisms, our calculations focus on cluster energetics.

Conclusions

In general, compared to the other three potentials,

Table 2. The difference between the lowest Δ structural motif and the other two, higher Δ motifs was calculated at selected magic cluster sizes. Pt and Pd DFT calculations are still running at the time of publication, therefore are not presented here. EMT(Sta) corresponds to EMT (standard parameters), EMT(Ras) is EMT (Rasmussen parameterisation), RGL is the Rosato, Guillope and Legrand potential, while SC is the Sutton Chen potential.

			Δ difference / eV				
Metal	**Size**	**Geometry**	**DFT**	**RGL**	**EMT(Sta)**	**EMT(Ras)**	**SC**
Au	55	ico	0.000	0.000	0.000	0.000	0.000
		deca	0.065	0.026	0.042	0.061	0.028
		octa	0.124	0.033	0.052	0.074	0.037
	147	ico	0.000	0.000	0.000	0.000	0.000
		deca	0.117	0.012	0.028	0.053	0.017
		octa	0.144	0.019	0.037	0.060	0.026
Ag	55	ico	0.000	0.000	0.000	0.000	0.000
		deca	0.136	0.091	0.080	0.092	0.089
		octa	0.200	0.105	0.097	0.109	0.111
	147	ico	0.000	0.000	0.000	0.000	0.000
		deca	0.171	0.076	0.069	0.082	0.081
		octa	0.214	0.088	0.085	0.096	0.103
	309	ico	0.000	0.000	0.000	0.000	0.000
		deca	0.115	0.062	0.057	0.073	0.069
		octa	0.165	0.073	0.072	0.084	0.091
Cu	55	ico	0.000	0.000	0.000	0.000	0.000
		deca	0.208	0.097	0.112	0.118	0.075
		octa	0.282	0.117	0.138	0.138	0.092
	309	ico	0.000	0.000	0.000	0.000	0.000
		deca	0.189	0.084	0.100	0.101	0.059
		octa	0.245	0.105	0.116	0.112	0.074

EMT (Rasmussen parameters) overestimated octahedral dominance for Cu, Ag and Au, thus the dominance shift from decahedral to octahedral comes at smaller cluster sizes. Conversely, compared to the other potentials, the Sutton Chen potential overestimated decahedral dominance, therefore the dominance shift from decahedral to octahedral commonly occured at cluster sizes **>** 10,000 atoms. When verification was made with DFT, all of the potentials did well at predicting the structural motif preferences at small sizes. However, none of the potentials had a quantitative relationship to calculated DFT values. The prediction of energies and properties of large nanoclusters is clearly not a trivial task and caution must be exercised in the use of empirical potentials. However, we have demonstrated that they have utility in predicting trends and, moreover, are reasonably robust with respect to the specific choice of empirical potential.

References

1. Gavnholt J.; Schiøtz J. *Phys. Rev. B*, **2008**, 77, 035404(1-10).
2. Honkala K.; Hellman, A.; Remediakis I.; Logadottir A.; Carlsson A.; Dahl S.; Christensen C.; Nørskov. J. *Science*, **2005**, *307*, 555-558.
3 Arslan, H. *Int. J. Mod. Phys. C* **2007**, *8*, 1351-1359.
4. Doye J.; Wales D. *New J. Chem.* **1998**, *22*, 733-744.
5. Shao X.; Liu X.; Cai W. *J. Chem. Theory Comput.* **2005**, *1*, 762–768.
6. Alamanova D.; Grigoryan V.; Springborg M. *J. Phys. Chem.* **2007**, *111,* 12577-12587.
7. Wu X.; Chen S.; Sun Y.; Chen Y. *Comp. Theor. Chem.* **2012**, *1002*, 43-48.
8. Michaelian K.; Rendón N.; Garzón I. *Phys. Rev. B* **1999**, *60*, 2000-2010.
9. Grigoryan V.; Alamanova D.; Springborg M. *Eur. Phys. J. D* **2005**, *34*, 187-190.
10. Apra E.; Ferrando R.; Fortunelli A. *Phys. Rev. B* **2006**, *73*, 205414.
11. Hijazi I.; Park Y. *Eur. Phys. J. D* **2010**, *59*, 215-221.
12. Myshlyavtsecv A.; Stishenko P. *Adsorption* **2013**, *19*, 795-801.
13. Voter, A. F. *Embedded atom method potentials for fcc metals: Ni, Pd, Pt, Cu, Ag, Au, Al*. Los Alamos Unclassified Technical Report NO LA-UR 93-3901, **1993**.
14. Baletto F.; Ferrando R.; Fortunelli A.; Montalenti F.; Mottet C. *J. Chem. Phys.* **2002**, *116*, 3856-3832.
15. Marks, L. D. *J. Cryst. Growth* **1983**, *61*, 556-566.
16. Jacobsen K.; Stoltze P.; Nørskov, J. *Surf. Sci.* **1996**, *366*, 394-402.
17. Rasmussen, T.; Jacobsen, K. W.; Leers, T.; Pedersen, O.B. *Phys. Rev. B* **1997**, *56*, 2977-2990.
18. Rosato V.; Guillope, M.; Legrand, B. *Phil. Mag. A* **1989**, *59*, 321-336.
19. Gupta, R. P. *Phys. Rev. B* **1981**, *23*, 6265-6270.
20. Sutton A.; Chen J. *Phil. Mag. Lett*. **1990**, *61*, 139-146.

From theories to real life: computational approaches to ammonia synthesis

Caitlin Casey-Stevens, Mingrui Yang*

Department of Chemistry, University of Otago, PO Box 56, Dunedin 9054

(email: *yanmi578@student.otago.ac.nz*)

Keywords: *ammonia synthesis, computational chemistry, density functional theory*

Caitlin attended school in Mosgiel then moved into Dunedin for undergraduate study. During her undergraduate degree, she spent a semester abroad at the University of North Carolina at Chapel Hill, USA. She graduated in early 2016 with a BSc, with a major in chemistry and minor in mathematics. This year she is working toward an Honours degree, with the research component focussing on the Haber-Bosch reaction using computational chemistry.

Mingrui (Ray) is originally from Shandong Province, China. He spent one and a half years at Avondale College in Auckland then moved to Dunedin for undergraduate study at the University of Otago in 2013. He is currently doing his final year of a BSc with a double major in chemistry and mathematics and a minor in physics. He intends to pursue postgraduate study in chemistry after he completes his BSc.

Introduction

Since the invention of computers, computational power has been growing rapidly. This has correlated with the increasing use of computers in science, not only for uses such as data processing and storage, but also as an increasingly powerful tool for understanding and predicting scientific phenomena in fields as diverse as climate modelling and artificial intelligence. Computational chemistry was born from the discoveries and developments of quantum mechanics in the 20th century. From these discoveries, accurate methods of approximating electronic and atomic behaviour were developed and with the improvements in computer technology, chemical structures and properties can now be reliably predicted. As such, computational techniques are now a common tool at the chemist's disposal.

Computational studies can provide a unique, microscopic view of chemical reactions to help us understand the precise mechanisms taking place. Since the age of alchemy, a chemical reaction is no longer just an observable phenomenon but a detailed process with many complicated intermediary states which may not be able to be determined directly from experiments. However, chemical reactions can be simulated on a computer on a molecular or atomic level, and the behaviours and interactions of molecules can be described and understood.

Computational studies can also predict the properties of chemicals that are yet to be synthesised and aid in the design of new materials, whether they are new drugs to treat a given disease or new catalysts for a desired process. Today, there are 118 elements in the periodic table,[1] and an uncountable number of molecules in the world. Hence it is uneconomical, even impossible, to examine all possible structures and properties of these atoms and molecules experimentally. Computer simulations offer a pragmatic solution where large numbers of structures can be investigated, saving both time and money compared with an experimental approach. From these simulations, a guideline can be constructed to help direct experimentalists towards the most promising materials.

Both of these benefits of computational chemistry are exploited in our research group, where we use computational techniques to study catalysis of small molecule reactions on metal-based surfaces. We describe here recent applications of computational techniques for understanding and optimising the synthesis of ammonia (NH_3), which is a pre-eminent catalytic process in use today. The computational technique favoured for this research is density functional theory (DFT), which is a method that approximates solutions to the mathematical cornerstone of chemistry, the Schrödinger equation.

Industrial synthesis of ammonia

Ammonia is primarily synthesised by the Haber-Bosch process (Eq. 1), which was created by Fritz Haber in 1910 and adapted for industrial production by Carl Bosch by 1913, as a response to the increasing demands for nitrogenous fertiliser.

$$N_2(g) + 3H_2(g) \xrightarrow[\text{Fe or Ru}]{\text{400-600 °C, 200 atm}} 2NH_3(g) \qquad \text{(Eq. 1)}$$

At the time, these demands were barely being met by the supply of guano (seabird excrement) and the inefficient Birkeland-Eyde[2] and Frank-Caro industrial processes.[3] The Haber-Bosch process revolutionised the world, enabling the production of more nitrogenous fertiliser, therefore increasing food production, and ultimately, the ability to feed a larger population, and has deservedly been labelled "the most important invention of the 20th century".[4] Today, the Haber-Bosch process produces 140 million tonnes of NH_3 per year, 85% of which is used for fertiliser manufacture. This scale means NH_3 production is second only to sulfuric acid in tonnage produced per year.[5]

The Haber-Bosch process is undoubtedly important with its key role in feeding the world. However, it comes at a cost – energy. The high-energy nature of the process is due to the intense conditions required to make the reaction proceed. In order to break the N-N bond[6] (bond dissociation energy = 945 $kJmol^{-1}$) a metal catalyst, often iron or ruthenium, is used. However, the rate at ambient temperature is still low and so a high temperature (500 °C) is used to increase the rate to an appreciable value.[7] This however, pushes the equilibrium in the opposite direction to that required. This can be overcome, according to Le Châtelier's principle, with the application of a very high pressure[7] (200 atm) to return the equilibrium to a position favourable for NH_3 production. These intense conditions result in the Haber-Bosch process consuming around 2% of energy produced globally per year. Reducing the energy use of the Haber-Bosch reaction is clearly a desirable objective, and two approaches deserve attention: (1) improving the process, or (2) replacing the process, both of which can be aided using computational chemistry.

Op*timising the Haber-Bosch process*

Optimising of the Haber-Bosch process has now had more than 100 years of work. A major focus has been determining exactly how it works, i.e. the mechanism(s) the process proceeds by. There are two mechanisms by which the reaction could proceed, commonly termed the associative and dissociative mechanisms (Fig. 1). Both reactions proceed by first adsorbing dinitrogen (N_2) to the catalyst surface. From here onward they differ; the next step for the dissociative mechanism is the dissociation of the N_2 to give atomic nitrogen (2N) on the catalyst surface, followed by subsequent hydrogenation steps to give NH_3. In contrast, the associative mechanism proceeds by hydrogenation of the N_2 first, adding at least one H before the dissociation of the dinitrogen bond. The Haber-Bosch reaction could proceed solely v*ia* one mechanism, or could proceed with contributions from both mechanisms.

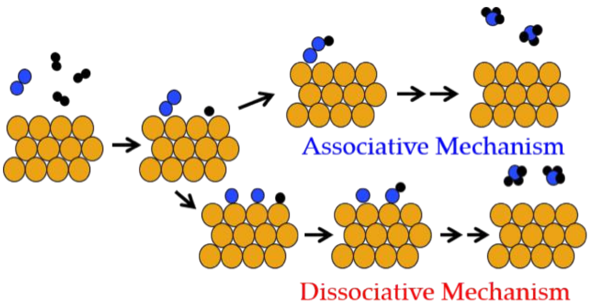


Fig. 1. Associative and dissociative mechanisms of ammonia formation (from ref 17, reprinted with permission, copyright 2015 ACS)

Determination of the mechanism is not a trivial problem, as the intense conditions required to form ammonia are also conditions that drastically prohibit the use of many analytical techniques. Efforts to solve the problem include kinetic studies, the use of $^{30}N_2$ as a tracer, exploration of the effects of co-adsorbates, and spectroscopic techniques.[8,9] A fifty year review of this work suggested that evidence pointed toward the dissociative mechanism dominating, although concluded the issue wasn't decisively resolved.[8]

Six decades after the process was designed, the seminal work in the field was published by Ertl.[10] In this, electronic spectroscopy techniques, such as Auger spectroscopy, allowed Ertl to directly observe the catalyst surface during the reaction. However, these techniques require ultra high vacuum (UHV) conditions, a far cry from the industrial pressures. The results of these studies have been extrapolated to atmospheric pressure using kinetic studies, and further extrapolated to 20 atm using reactivity trends, leading to a conclusion that there is no 'pressure gap' effect, a phenomenon where reaction pathways under UHV are drastically different to those under high pressure. From the work, it was concluded that the reaction goes *via* the dissociative pathway, with the dissociation of dinitrogen as the rate-determining step. Computational chemistry was subsequently used to model the reaction profiles of both mechanisms on a flat Ru (0001) surface and further confirmed that the dissociative mechanism had a much lower energy profile and was the dominant mechanism.[11]

Optimisation of the efficiency of the Haber-Bosch process was thus focussed on lowering the barrier to dinitrogen dissociation. So-called 'promoters' are one of the approaches to this end. These are other metals or compounds that are used to dope the bulk metal catalyst. Promoters are classified in two broad groups; structural or electronic. Structural promoters affect the stability and structure of the catalyst active site; in NH_3 formation structural promoters, such as aluminium oxide, increase the surface area available for N_2 adsorption by restructuring the surface.[12] Electronic promoters affect the electronic structure of the active site, promoting adsorption of reactants; in NH_3 formation, the addition of potassium increases electron density of the substrate, inducing an increase in N_2 adsorption energy and decrease in the energy of the rate determining step.[12] An alternative means of optimising the process, which is gaining in popularity for many catalytic reactions, is the use of nanoparticle catalysts. These are of interest compared to extended catalysts due to two major advantages: a high surface to volume ratio, and an abundance of unique active sites. Nanoparticles have a much higher surface to volume ratio than a bulk catalyst, offering essentially more "bang for one's buck". The second advantage is perhaps more subtle, the prevalence of under-coordinated active sites. Surface atoms in general are under-coordinated, i.e. they have fewer nearest neighbours than a bulk atom, resulting in these atoms having a higher energy than bulk atoms. The coordination of an adsorbate lowers the energy of the system. Some surface atoms, on sites such as steps or edges, termed 'active sites', are even more under-coordinated than others, and as such can be more preferential adsorption sites. These sites may also stabilise transition states, and thus improve the rate of reaction. From cursory inspection of a nanoparticle's shape in comparison to an extended catalyst surface (Fig. 2), it is obvious that nanoparticles have far more of these active sites, and hence are of great interest.

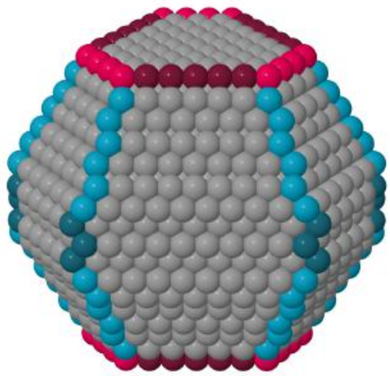


Fig. 2. An example Ru nanoparticle with some possible active sites highlighted.

Previous computational and experimental work on active sites and nanoparticle catalysis has shown not only that active sites are beneficial over planar sites, but also that some active sites are more beneficial than others. Dahl *et al.*[13] investigated N_2 dissociation at defect sites on an extended Ru (0001) surface, analogous to an active site on a nanoparticle, in a particularly elegant combined experimental and computational study. This study used a previous result that found Au preferentially absorbed at the defect site, effectively blocking it from participating in the reaction. Comparing the rate of reaction between the 'blocked' and 'non-blocked' surfaces, it was found that adsorption rate at the defect site was nine orders of magnitude higher than the planar surface, indicating the defect site entirely dominated the reactivity of the surface. A model of the active site yielded a dissociation barrier for N_2 dissociation in excellent agreement with experiment.

Computational work on the associative desorption of H_2 from Pt nanoparticles recently showed not only that active sites dominated over planar sites, but also that different active sites showed drastically different reactivity.[14] Two different edges were found to differ in reactivity by 0.3 eV, which corresponds to a difference in rate of approximately five orders of magnitude at room temperature. The formation of NH_3 on nanoparticles has the potential to be even more exciting, as the different active sites could give rise not only to differences in reactivity, but also differences in mechanisms. Hence, the associative mechanism that was found to be inactive on the flat catalyst could indeed contribute to NH_3 formation on nanoparticle catalysts.

Research has already begun to investigate the formation of NH_3 on nanoparticle catalysts using computational techniques. Initial work by Honkala *et al.* used DFT in combination with grand canonical Monte Carlo simulations in order to find a calculated rate for the dissociative mechanism on a Ru nanoparticle within a factor of 3 to 20 of the experimental rate.[15] This work is noteworthy as the only experimental parameter was particle size distribution and cemented the place of computational techniques in the field of catalysis, particularly the ability to search for new catalysts. However, this study had limitations in that only a single active site and one type of mechanism were assumed. Working toward nanoparticle catalyst design, Gavnholt and Schiøtz developed a method for achieving detailed information about the structure of Ru nanoparticles.[16] They used this method to assess the prevalence of various active sites at different size ranges. It was found that the number of the particular active sites used by Honkala *et al.* was perhaps overestimated and that other active sites may be active towards N_2 dissociation, with the combined effect that the excellent agreement obtained in the initial study was perhaps somewhat fortuitous. However, once again, only a dissociative mechanism has been considered.

Currently our group is working towards a more comprehensive understanding of NH_3 formation on Ru nanoparticles, inspired by and building on the results of Honkala and Gavnholt and Schiøtz. We are investigating both dissociative and associative mechanisms on a variety of active sites on Ru nanoparticles. Initial results have found that the associative mechanism may indeed play a role in other active sites[17] and that many sites may be active towards dinitrogen dissociation.[18] Future directions may include investigating the effect of co-adsorbates, in order to more accurately reflect a real life scenario, and the global optimisation of Ru nanoparticles at differing size ranges, in order to understand at which size range the surface features which dominate the reactivity are most common, hence which size nanoparticles may be most effective for NH_3 formation.

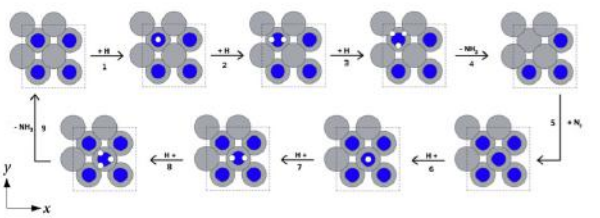
Electrochemical catalysis: an alternative to the Haber-Bosch process

In contrast to the Haber-Bosch process, ammonia is produced in bacteria in nature by the enzyme nitrogenase,

$$N_2 + 8H^+ + 8e^- \rightleftharpoons 2NH_3 + H_2 \qquad \text{(Eq. 2)}$$

which uses solvated protons, electrons and atmospheric nitrogen at ambient conditions as shown in Equation 2:

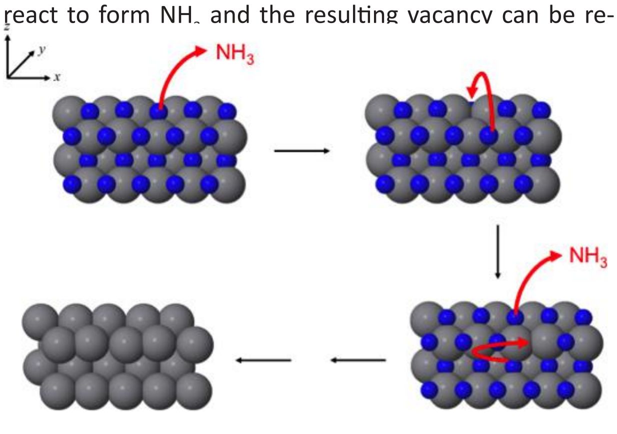
It is thus alluring to try and mimic the enzymatic processes in a man-made electrochemical set-up. In recent years, much research has been devoted to development of electrochemical processes of NH_3 formation. For example, in 2007 the electrocatalytic synthesis of NH_3 in an H^+ conducting cell with an Fe-based catalyst was studied by Ouzounidou *et al.*[19] In 2009, Pappenfus *et al.* developed an electrochemical process using ionic liquids driven by wind energy.[20] Amar *et al.* achieved electrochemical synthesis of ammonia in solid-state electrolytes in 2011.[21] Although these approaches have been shown to produce NH_3 at a reasonable rate with good yield, for widespread industrial application a simple catalyst is desired. Hence many pure transition metals surfaces have been investigated as an NH_3 synthesis electrocatalyst. However, for the vast majority of these, the surface simply gets saturated in hydrogen, as the protons bind more strongly to the surface than N_2, preventing the absorption of N_2 and thus preventing the reaction from proceeding to form NH_3.[22] Recently, the use of metal nitride catalysts to circumvent this problem has been investigated; rather than



adsorbing N_2 to the catalyst surface in the first step, one of the surface N atoms can be used. This is known as a Mars-van Krevelen mechanism, as shown in Fig. 3.

Fig. 3. Mars-van Krevelen mechanism of formation of NH_3 by absorbing N_2 on the (100) facet of the rocksalt structure of vanadium nitride. The crystal structure shown repeats in *x* and *y* directions periodically.

In the first part of the Mars-van Krevelen mechanism, one NH_3 molecule is formed by successive hydrogenation of a surface N atom (Steps 1-3). This NH_3 may then desorb from the surface, leaving an N vacancy (Step 4). For the mechanism to continue, the N vacancy is refilled with free N_2 from the gaseous phase (Step 5). Once the vacancy is refilled then another NH_3 molecule will form (Steps 6-8), completing the catalytic cycle. A crucial step is the filling of the N vacancy by N_2. On some metal nitrides, the vacancy is more likely to be refilled by oxygen atoms, which causes poisoning of the catalyst, hence the catalytic cycle cannot be completed.[23] Another possibility is that the vacancy could be refilled with an N atom from the bulk of catalyst. This surface N can then in principle react to form NH_3 and the resulting vacancy can be re-



filled with more N from the bulk. In this way N "leaks" from the catalyst and the catalyst decomposes as shown in Fig. 4.

Fig. 4. The leaking processes of bulk N atoms from VN rocksalt structure. The leaking leads to the decomposition of VN and destroys the catalyst eventually. The crystal structure shown repeats in *x* and *y* directions periodically.

A series of computational investigations of transition metal nitrides including ZnN, NbN, CrN,VN, MnN, MoN, OsN and RuN has been carried out for both the rocksalt (RS) and zincblende (ZB) crystal structures. Two facets were considered for each crystal structure, the (100) and (111) facets of the RS structure and the (100) and (110) facets of the ZB structure.[23,24] It has been predicted that the (100) facet of rocksalt VN is a particularly promising catalyst, which is unlikely to be poisoned by H or O, or decompose by leaking N atoms from the bulk, and forming NH_3 with a decent yield at low applied potentials.[24] This has been predicted on the perfect theoretical surface, but under experimental conditions catalysts are usually not perfectly planar but rather contain a number of defects, such as steps or edges. These defect sites often dominate the reactivity of catalyst. An example mentioned previously was the work on steps versus planar sites of a Ru (0001) surface which found step sites to be more reactive than the planar sites, to the tune of 9 orders of magnitude difference in the rates of N_2 dissociation.[13] Current work in the group investigates stepped surfaces of VN (100), which more accurately mimic the surface of a real catalyst, as these defects may influence the stability and reactivity. In particular, stability of the catalyst is investigated with respect to the propensity of these defect surfaces to leak nitrogen from the catalyst, which may render the real-life catalyst inactive.

The main objective of this research is to begin investigation of the electrochemical reduction from N_2 to NH_3 on defect VN (100) surfaces. The major outcome of the present study is the deduction of the preferred replenishment mechanism on the defect sites. If the mechanism of replenishment by gaseous N_2 is dominant, the catalytic cycle could, in principle, carry on continuously and hence will produce NH_3 efficiently. However, if it is preferred to refill the vacancy from the bulk N then this leaking will eventually render the catalyst inactive. These results will be valuable for experimentalists, as it will tell if the catalyst is applicable or not for real-life industrial production of ammonia.

Future directions of research depend on the preferred mechanism. If the catalyst is found to leak, then it may be possible to block the potential leaking sites on the catalyst with some inactive material e.g. Au atoms. Conversely, if it is found that the vacancy will be refilled by gaseous N_2, the full mechanism of electrochemical reduction from N_2 to NH_3 of these sites requires study, rather than just the vacancy replenishment.

Conclusions

Ammonia synthesis is a key aspect in supporting our population but the energy intensive nature of the current industrial process has motivated endeavours toward improving the process. In our group, research to this end has so far been directed towards investigation of ruthenium nanoparticles for catalysis and the identification of structural features favourable towards ammonia formation, as well as investigation of a potential vanadium nitride catalyst for an electrochemical method. The future of this work will be influenced not only by preliminary results, but also the ever-expanding power of computational techniques and the continually widening scope of the field of computational chemistry.

References

1. See: IUPAC 2016: http://iupac.org/what-we-do/periodic-table-of-elements/ (accessed 04/07/16).
2. Birkeland, K. *Trans. Faraday Soc.* **1906**, *2*, 98–116.
3. American Chemical Society National Historic Chemical Landmarks. *Discovery of the commercial processes for making calcium carbide and acetylene*, http://www.acs.org/content/acs/en/education/whatischemistry/ landmarks/calciumcarbideacetylene.html (accessed 04/07/16).
4. Smil, V. *Nature* **1999**, *400*, 415.
5. The Essential Chemical Industry online: *Ammonia*, http://www.essentialchemicalindustry.org/chemicals/ammonia.html (accessed 04/07/16).
6. Barrett, J.; Malat, M. A. *Fundamentals of Inorganic Chemistry: An Introductory Text for Degree Studies*, Horwood: Chichester, England, 1st ed. 1998.
7. Smil, V. *Sci. Am.* **1997**, *277*, 76–81.
8. Emmett, P. H. in *The Physical Basis for Heterogeneous Catalysis*, (Ed.: Drauglis, E., Jaffee, R. I.) Springer US, Boston, MA, 1975, 3–34.
9. Ertl, G., *Catal. Rev. Sci. Eng.* **1980**, *21*, 201–223.
10. Ertl, G.; Weiss, M.; Lee, S. *Chem. Phys. Lett.* **1979**, *60*, 391–394.
11. Rod, T. H.; Logadottir, A.; Nørskov, J. K., *J. Chem. Phys.* **2000**, *112*, 5343.
12. Bencic, S. *Ammonia Synthesis Promoted by Iron Catalysts: Literature Report*; Department of Chemistry, Michigan State University, 2001.
13. Dahl, S.; Logadottir, A.; Egeberg, R. C.; Larsen, J. H.; Chorkendorff, I.; Törnqvist, E.; Nørskov, J. K. *Phys. Rev. Lett.* **1999**, *83*, 1814–1817.
14. Skúlason, E.; Faraj, A. A.; Kristinsdóttir, L.; Hussain, J.; Garden, A. L.; Jónsson, H. *Top. Catal.* **2014**, *57*, 273–281.
15. Honkala, K.; Hellman, A.; Remediakis, I. N.; Logadottir, A.; Carlsson, A.; Dahl, S.; Christensen, C. H.; Nørskov, J. K. *Science* **2005**, *307*, 555–558.
16. Gavnholt, J.; Schiøtz, J. *Phys. Rev. B* **2008**, *77*, 035404.
17. Garden, A. L.; Skúlason, E., J. *Phys. Chem. C* **2015**, *119*, 26554–26559.
18. Casey-Stevens, C.; Lambie, S.; Skúlason, E.; Garden, A. L. **2016** (in preparation).
19. Ouzounidou, M.; Skodra, A.; Kokkofitis, C.; Stoukides, M. *Solid State Ionics,* **2007**, *178*, 153– 159.
20. Pappenfus, T. M.; Lee, K.-M.; Thoma, L. M.; Dukart, C. R. *ECS Trans.* **2009**, *16*, 89–93.
21. Amar, I. A.; Lan, R.; Petit, C. T. G.; Tao, S. J. *Solid State Electrochem.* **2011**, *15*, 1845 –1860.
22. Skúlason, E.; Bligaard, T.; Gudmundsdottir, S.; Studt, F.; Rossmeisl, J.; Abild-Pedersen, F.; Vegge, T.; Jonsson, H.; Norskov, J. K. *Phys. Chem. Chem. Phys.* **2012**, *14*, 1235–1245.
23. Abghoui, Y.; Garden, A. L.; Hlynsson, V. F.; Bjorgvinsdottir, S.; Olafsdottir, H.; Skúlason, E. *Phys. Chem. Chem. Phys.* **2015**, *17*, 4909–4918.
24. Abghoui, Y.; Garden, A. L.; Howalt, J. G.; Vegge, T.; Skúlason, E. *ACS Catal.* **2016**, *6*, 635–646.

Peter Kemnitz (PK) Grant, MSc(NZ), PhD(Cantab), FNZIC

Peter Kemnitz (PK) Grant passed away on 5 May 2016 aged 85 years. PK completed his BSc in 1951 and his MSc (1st Class Hons) in 1953 at the University of Otago and his PhD in 1957 at the University of Cambridge and was a member of Emmanuel College. PK was appointed as a lecturer in the Department of Chemistry at the University of Otago in 1962 after having spent time as a postdoctoral fellow at the University of Nottingham and as a research scientist at the Department of Scientific and Industrial Research (DSIR) in Wellington. As a student PK was awarded the 1949 NZIC prize for the top first year student in chemistry. A member of the NZIC from 1958, he was the organising secretary for the 1969 annual conference in Dunedin and the chairman of the Otago Brach in 1977 as well as the Otago delegate to the NZIC Council from 1979-1981. In 1977 he was elected as a Fellow of the NZIC. PK was appointed to a personal chair in chemistry at the University of Otago in 1980 and retired in 1991. During his time at Otago he supervised 27 4th-year students, 7 MSc students, 15 PhD students and 1 postdoctoral fellow as well as giving approximately 80 lectures per year in organic chemistry.

PK was known as the "bionic arm" as he could write so quickly on the blackboard with chalk – no white boards back then – although ironically he helped Stephens, the pen company, develop inks for marker pens used on white boards. The sweet smell of those pens is perhaps thanks to PK! He could draw the backbone of cholesterol without the chalk ever leaving the board. But perhaps his great skill was his ability to be able to dictate in such a way that just as you forgot the last bit of the sentence he picked up from just where you had forgotten and would repeat it so you could get the notes down correctly. He expected that students would be able to solve the laboratory problems he set them and many students well remember the challenge and pleasure of correctly identifying compounds in the third year organic labs. He is acknowledged by his PhD students as having huge influence on them and being a steadying and guiding hand. All of these things reflect PK's student-oriented focus.

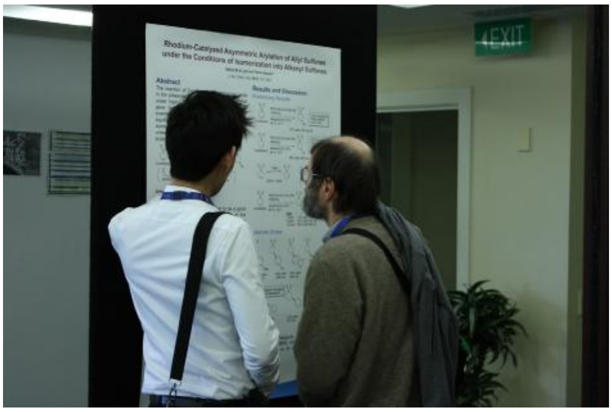
As a PhD student, PK played rugby for Cambridge at Twickenham and he had an abiding interest in sport. It was always a good topic to talk with him about. He was a killer squash player.

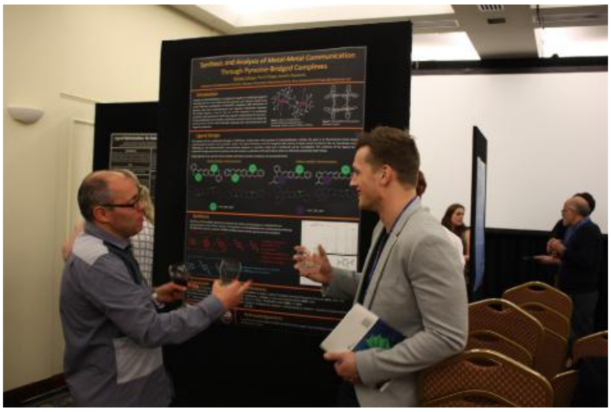
He is remembered in the Department of Chemistry at the University of Otago by the PK Grant prize awarded to the 4th-year honours student with the highest mark in their research project for experimental skill and research methodology. It sits alongside the Joseph and Emma Mellor prize for the overall best fourth year student in chemistry but the PK Grant prize has a focus on experimental excellence which was so typical of its namesake.

Lyall Hanton

Department of Chemistry, University of Otago

NZIC-16, Queenstown, 21-24 August 2016





An economic and sociological perspective on New Zealand's colonial chemistry

Peter Hodder

Victoria Business School, Victoria University of Wellington, Wellington, New Zealand *and* HodderBalog Social and Scientific Research, Paraparaumu Beach, Wellington, New Zealand

(email: *peterh@hodderbalog.co.nz*)

Keywords: *Colonial Laboratory, William Skey, economic history, 'long depression', Wellington Philosophical Society*

New Zealand's colonial period has been considered a 'post-Enlightenment society'[1] in which – akin to Britain a century earlier – "technological progress occurred in an environment where experimentation and innovation were becoming a way of life, embracing a wide variety of skills".[2] An environment in which so much was new and unfamiliar prompted investigations of the land's flora, fauna and geology, and recognition of the potential for the seemingly abundant natural resources to be of economic benefit to a frontier society.

As exploration for resources proceeded and commerce expanded in colonial New Zealand, James Hector – the country's leading scientific administrator of the time[3] – saw the necessity for an analytical chemistry laboratory. The first building for the Colonial laboratory was associated with the Colonial Museum in Wellington's Sydney Street. This "neat and compact building" which included weighing and analysis rooms and a furnace room "furnished with a brick chimney", and with "a brick drain running northwards towards Sydney Street",[4] built in 1866, soon proved to be inadequate, Hector noting in 1866 that the Laboratory was "extremely imperfect and not at all in keeping with the importance of the questions that have frequently to be decided by the experimental operations there carried on." [5]

And just what was 'carried on' there? There are extensive – although incomplete – records of samples received by the Colonial Laboratory for analysis,[6] and some of the annual reports of the Laboratory detail the number and types of materials analysed.[7] The variations in the number of samples received and analysed over time are shown in Fig. 1, with notable 'dips' in both samples and analyses in the mid-1880s. As described later, this broadly mirrors trends in the wider New Zealand economy.

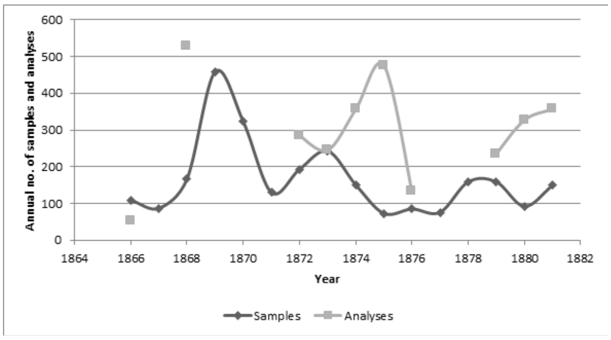


Fig. 1. Variation of number of samples received and analysed by the Colonial Laboratory from 1865 to 1881. Data are not available for every year, but, as expected, the number of analyses generally exceeds the number of samples, and increases in the number of samples are usually followed by peaks in the number of analyses. There is a pronounced slump in samples and analyses in the mid-1870s. Both plots increase rapidly towards the end of the colonial period. The peak in samples for 1869 is attributed to accession into the Colonial Laboratory of samples collected during geological investigations in Otago that had been stored in Dunedin.

In 1885, the Colonial Laboratory passed from being an adjunct of the Colonial Museum to being under the control of the Minister of Mines, coinciding with a short-lived 'gold rush' in Wellington,[8] and leading to a far-fetched suggestion of School of Mines there.[9] Subsequently, it became part of the Mines Department. As might be expected by such a 'takeover', the number of analyses of ores became an increasingly prominent component of the Laboratory's work – more than doubling between the mid-1860s and the turn of the century (Table 1).

The first Colonial Analyst was William Skey (see Appen-

Table 1. Analytical activities of New Zealand's Colonial Laboratory

Year	The Colonial Laboratory was responsible to …	Types of material analysed by Colonial Laboratory								
		Coals and oils		***Rocks and minerals***		***Metals and ores***		***Waters***		***Total§***
		Number and % of analyses								
		No.	%	No.	%	No.	%	No.	%	No.
1868*	Colonial Secretary	105	20%	130	25%	106	20%	16	3%	527
1883†	Minister of Mines	26	9%	64	22%	102	35%	37	13%	293
1900‡	Mines Department	43	6%	60	9%	309	46%	92	14%	674

*At this time, the Colonial Laboratory, the Colonial Museum and the New Zealand Institute were all managed by James Hector; 1868 was the first year for which the *Transactions of the New Zealand Institute* were published.

† The Colonial Laboratory passed to the control of the Minister of Mines in 1885; the high proportion of metals and ores analysed a couple of years earlier provides some justification for the transfer, but it also coincided with prospects for a gold-mining industry and school of mines in Wellington.

‡ The Colonial Laboratory came under the control of the Mines Department in 1893, and from that time was no longer directly associated with the New Zealand Institute; analysis data for 1900 from Hughson and Ellis, p. 16 (reference 17).

§ Includes analyses of building materials, adulterated products, manures, customs examinations, etc.

dix). Not only was he responsible for the work of the Colonial Laboratory, but he also published his ideas and results of his investigations,[10] often in the *Transactions of the New Zealand Institute* (Fig. 2). About thirty of his papers that were published in the *Transactions* were also published overseas, generally in London's *Chemical News* (see also Table 4)

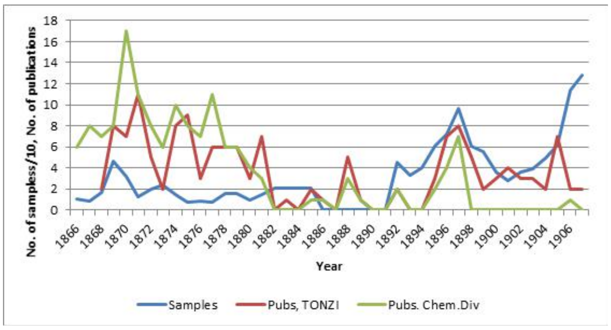


Fig. 2. Variation of samples received by the Colonial Laboratory, chemistry publications in the *Transactions of the New Zealand Institute* (here referred to as TONZI), and all publications (as compiled by Chemistry Division, DSIR, in 1965; see reference 10), from 1866 to 1907.

Publication in the *Transactions* was for most of the colonial period overseen by James Hector: he was effectively peer reviewer as well as editor. That Skey was appointed by Hector to his role at the Laboratory – and perhaps the location of the Colonial Laboratory in Wellington – may have contributed to Skey's being the author of more than 80 articles related to chemistry that were published in the *Transactions* in its first forty years. By comparison, James Pond, an analytical chemist, appointed as analyst for Auckland in 1882 under the 'Adulteration Prevention Act 1880,[11] published a mere 11 papers in the Transactions in the period 1874-1899. Interestingly, Skey's successor, J.S. Maclaurin – formerly assistant to James Alexander Pond, the Auckland analyst, published little in the Transactions (see Table 4).

Publication in the *Transactions* was invariably preceded by the research being "read before" the Wellington Philosophical Society or one of the other constituent societies of the New Zealand Institute, probably at a gathering similar to that portrayed in Fig. 3.[12]

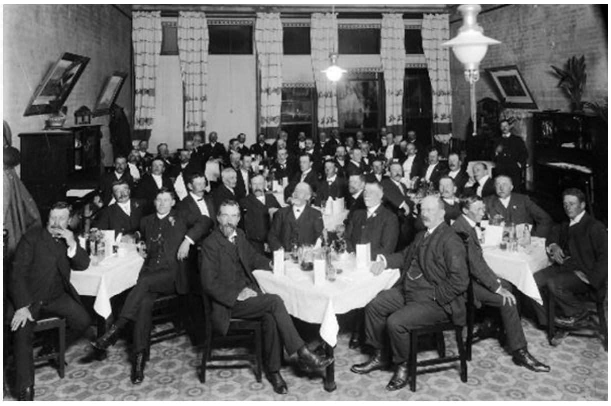


Fig. 3. A modern description of scenes such as that pictured above is: "Males dominated public places and public life. The public dinner, lubricated by considerable quantities of alcohol, was a common part of social life. Usually only men attended, although on occasion women would gather in the galleries and watch" (reference 8). Image: Alexander Turnbull Library, Ref. 1/1-004056-G

Such societies included Members of Parliament and the elite of the colonial towns among their members, who listened to presentations from amateur and professional scientists and others to the ensuing discussion at regular meetings during the year, probably believing as did Birmingham's 'Lunar Men' a century earlier, that a "technocratic fix … could bring paradise on earth: just as chemists could make pure air to cure diseases, so knowledge could light the fuse of democratic change".[13] The membership of the Wellington Philosophical Society, "reconstituted in 1867 from the defunct New Zealand Society",[14] peaked in the mid-1880s (Table 2); while the proportion of influential people in its membership list declined throughout the colonial period.[15]

Table 2. The Wellington Philosophical Society*

Year	Number of members	**Potentially influential public servants†**		**Members of Parliament‡**	
		No.	***%***	***No.***	***%***
1870	107	3	2.8%	8	7.5%
1875	181	5	2.8%	10	5.5%
1880	274	4	1.5%	11	4.0%
1885	256	4	1.6%	10	3.9%
1890	151	4	2.6%	8	5.3%
1895	144	3	2.1%	4	2.8%
1900	154	1	0.6%	3	1.9%

*Members of the constituent societies of the New Zealand Institute were listed annually in the *Proceedings of the New Zealand Institute.*

†Includes members of the judiciary and prominent scientist-managers such as Hector and Skey.

‡As identified by the title "the Hon", together with a New Zealand town as an address.

The annual number of articles related to chemistry – and geology – published in the *Transactions* from its inception in 1868 to when New Zealand became a Dominion in 1907, i.e., the first forty years of publication, is shown in Fig. 4.

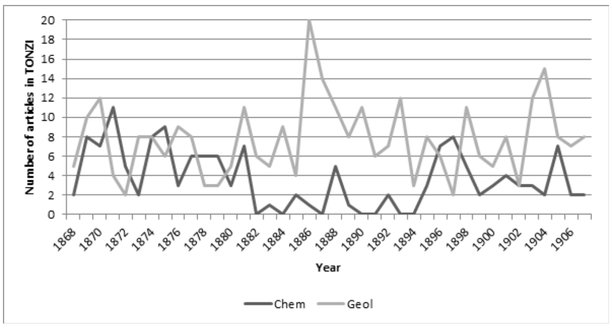


Fig. 4. Variation in the number of chemistry and geology articles published in the *Transactions of the New Zealand Institute*, 1868 – 1907. The Colonial Analyst, William Skey, wrote most of the chemistry papers published in the *Transactions* until 1900.

The lower numbers of publications in the 1880s and into the 1890s (red and green lines of Fig. 2 and black line of Fig. 4) can be attributed to the effect of the 'long depression', when resources were capped and economic activity suppressed. The trend in 'balance of payments', i.e., *E-I*, the difference between exports (*E*) and imports (*I*) for New Zealand's colonial period is shown in Fig. 5.[16]

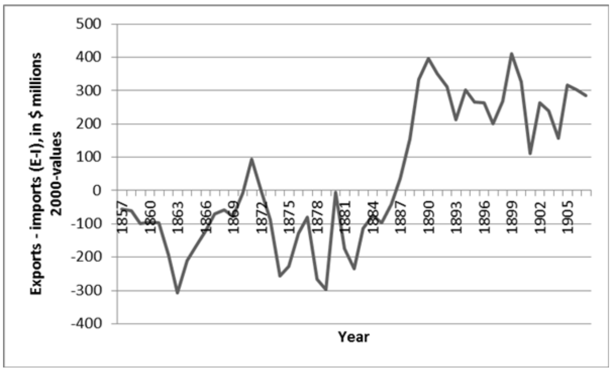


Fig. 5. Variation in the difference between exports and imports through New Zealand's colonial period. Early exports of gold and wool could not fund the development of a colonial infrastructure, so New Zealand borrowed heavily. This continual deficit was particularly the case from the mid-1870s to the mid-1880s, and was only arrested when New Zealand became 'Britain's farm'.

The Colonial Laboratory survived during the long depression, although the Geological Survey – the source of many of the Laboratory's samples[17] – received no finance from 1892 (when geologist Alexander McKay was transferred to the Mines Department[18]). Figure 4 suggests that during this period, the geologists continued to undertake field-work and write up their research, perhaps with little remuneration, while Skey, the Colonial Analyst, retained his employment position, dividing his time between his analysis of the fewer samples received and his research.

Both the Colonial Laboratory and the Geological Survey became part of the Mines Department in 1893[19] and 1897,[20] respectively. Canadian geologist J.M. Bell was appointed as Director of the Survey in 1904,6 by which time the economy had revived somewhat.[21]

In fact, the economic position in New Zealand was poor for much of the Colonial period. As historian Michael King described it, the 'long depression' between 1876 and 1891 "began with falling wool prices in 1877 and merged into a period of worldwide recession in which the New Zealand economy did not grow for around sixteen years."[22] The saviour for the New Zealand economy was the use of refrigeration for long-distance transport of mutton and lamb in 1882, of which King observed, "It is difficult to see how New Zealand could have survived as a viable country had it had to continue to rely solely on wool and grain and extractive commodities (in particular, kauri gum, timber and gold) for its national income… Rather than the country's being forced to wrestle with these considerations, however, the coincidence of refrigeration technology and a guaranteed market in Britain (see Fig. 6[23]) would soon deliver to New Zealand one of the highest standards of living in the world,"[24] by becoming 'Britain's farm'.[25]

The time-trend for the relative proportions of laboratory investigations, analytical results, and theory deduced for the chemistry papers in the *Transactions* is shown in Fig. 7. Curiously perhaps, the years of greater economic depression are characterised by more papers published on 'applied' than 'pure' chemistry topics. This is in broad agreement with that based on the distribution deduced from the narrative 'Skey the Chemist',[26] shown in Table 3.

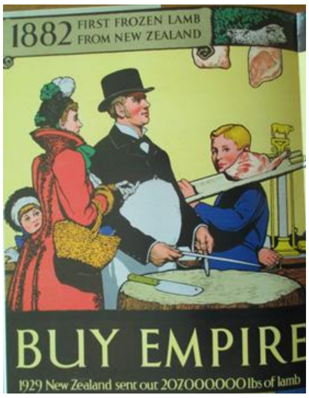


Fig. 6. Part of 'Buy Empire Every Day' advertisement in the 1930s, promoting the purchase of New Zealand frozen meat in Britain.

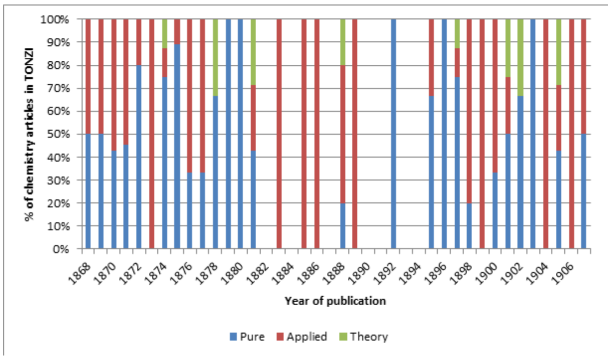


Fig. 7. Relative proportions of pure, applied and theoretical chemistry deduced from papers published in the *Transactions of the New Zealand Institute*, 1868-1907.

Skey can be considered the dominant chemist in colonial New Zealand, eclipsing his fellow analyst Pond and his successor Maclaurin (Fig. 8). Although a competent chemist, Maclaurin's enduring contribution to New Zealand chemistry was the ornate edifice in Sydney Street West which housed the Colonial Laboratory from 1902, and became the centerpiece of the Department of Scientific and Industrial Research for nearly fifty years from its inception in 1926.[27]

At least in terms of research productivity, Skey also eclipsed the first university-based chemists (see also Fig. 8), including Canterbury's controversial Professor A.W. Bickerton[28] and his successor W.P. Evans,[29] and Victoria's Professor T.H. Easterfield.[30] To this end, Table 4 compares Easterfield's, Skey's and Maclaurin's research outputs. The table also shows the change in distribution of Easterfield's publications across New Zealand and overseas journals during his professional life, being dominated by British and Australian journals while has was at Victoria University College, but by New Zealand journals once he moved to the Cawthron Institute in Nelson. This change is indicative of the quest for professional recognition through publication of research in international journals that came to dominate New Zealand academia in subsequent decades.

Appendix: William Skey – the undistinguished poet

Aside from his prowess as a chemist, William Skey was also a poet, of whom it has been said, "If contemporary reviews are to believed then he has the dubious honour

Table 3. Distribution of selected papers with William Skey as author, by topic as described in 'Skey the Chemist',* for 1865-1897, here inferred to be 'pure' chemistry ■, or 'applied' (including analytical) chemistry ■, or 'laboratory technique' ■.

Year	Topics† in "Skey the Chemist"							
	A	***B***	***C***	***D***	***E***	***F***	***G***	***H***
1865								
1866	#1‡					#4		
1867	#12 #14					#11		#12
1868		#131	#17					
1869			#24			#22	#27	#25
1870	#30		#34 #41			#31		
1871			#55				#54	
1872			#63			#62		#61
1873					#69		#71	#70
1874								
1875			#17§	#84				
1876		#95					#92	
1877					#99			
1878					#112	#110		
1879								
1880								
1881				#120 #122			#125	
1882								
1883								
1884				#127				
1885								
1886					#128			
1887								
1888					#130			
1889					#132			
1890								
1891								
1892		#133						
1893								
1894	#135	#135						
1895	#136	#136						
1896		#137 #140						
1897	#141	#141						

*Hughson and Ellis, pp. 25-270 (see reference 17)

†Broad topic areas: ***A***, Cyanide processes in relation to gold; ***B***, Amalgamation processes for gold recovery; ***C***, Formation of precious metals; ***D***, Petrology – leading to identification of new mineral; ***E***, Natural resources; ***F***, Surface chemistry; ***G***, Organic chemistry; ***H***, Abilities as a "versatile experimentalist"

‡ Numbers following the #-symbol identify papers cited in the Chemistry Division (1965) compilation (see reference 10)

§ Noted as the 'Second edition' of the paper

of being a contender for the title of New Zealand's worst nineteenth century poet."[31] Among his poems was one related to shaving (Fig. 9).[32]

References and notes

1 Olssen, E. *N.Z. J. History* **1997**, *31* (2), 187-218.

2 Burns, J.M. Fire and light: how the Enlightenment transformed our world. Thomas Dunne: New York, 2013, pp. 166-182.

3 Nathan, S. 'Running the show' in *The amazing world of James Hector*. Awa Science: Wellington, 2008, pp. 105-112; Nathan, S. *James Hector: explorer, scientist, leader.* Geoscience Society of NZ: Lower Hutt, 2015.

4 *Wellington Independent*, **1866**, 15 December, p. 5.

5 *Appendices to the Journal of the House of Representatives*, **1886**, D9.

6 Record of samples books (24994), 1886 – *c.*1949. Archives New Zealand.

7 Hodder P. *Chem NZ* **2014**, *78* (4), 158-163.

8 Brodie, J.W. *Terawhiti and the goldfields.* Karori Historical Society: Wellington, 1986, p. 129 *et seq.*

9 Minister of Mines. *Appendices to the Journal of the House of Representatives*, **1886**, C2, 10-11.

10 Chemistry Division Papers 1865-1965. *N.Z. DSIR. Information Series*

Table 4. Distribution of articles published in New Zealand and other journals by T.H. Easterfield, foundation professor of Chemistry at Victoria University College,* compared with that for William Skey and J.S. Maclaurin†

Activity	Date range of publications	Publications in journals published in …						Total
		New Zealand		Britain		Elsewhere		
		No.	%	No.	%	No.	%	
T.H. Easterfield								
Early professional life – in England	1883-1896	0		13	100%	0		13
At Victoria University College	1899-1917	9	39%	6	26%	8	35%	23
At Cawthron Institute, Nelson	1921-1940	4‡	80%	1	20%	0		5
Whole career	1883-1940	13	32%	20	48%	8	20%	41
WILLIAM SKEY								
1st Colonial Analyst, Wellington Whole career	1863-1897	86	60%	58§	40%	0		144
J.S. Maclaurin								
2nd Colonial Analyst, Wellington	1901-1907	1	100%		0	0		1
Dominion Analyst, Wellington	1907-1930	2¶	33%	4	67%	0		6
Whole career	1901-1930	3	43%	4	57%			7

*Compiled from Bibliography of papers by Thomas Hill Easterfield, that appends his obituary, in: *Trans. Proc. Roy. Soc. NZ* **1950**, *78*: 383-384.

† Compiled from: Chemistry Division Papers 1865-1965. *DSIR Information Series* **1965**, *48*. (reference 10)

‡ Three of these were published in the *New Zealand Journal of Science and Technology*, established in 1918, which provided chemists with a local alternative to publishing in the *Transactions*.

§ All but one of these papers was published in *Chemical News.*

¶ One of these was published in the *New Zealand Journal of Science and Technology*.

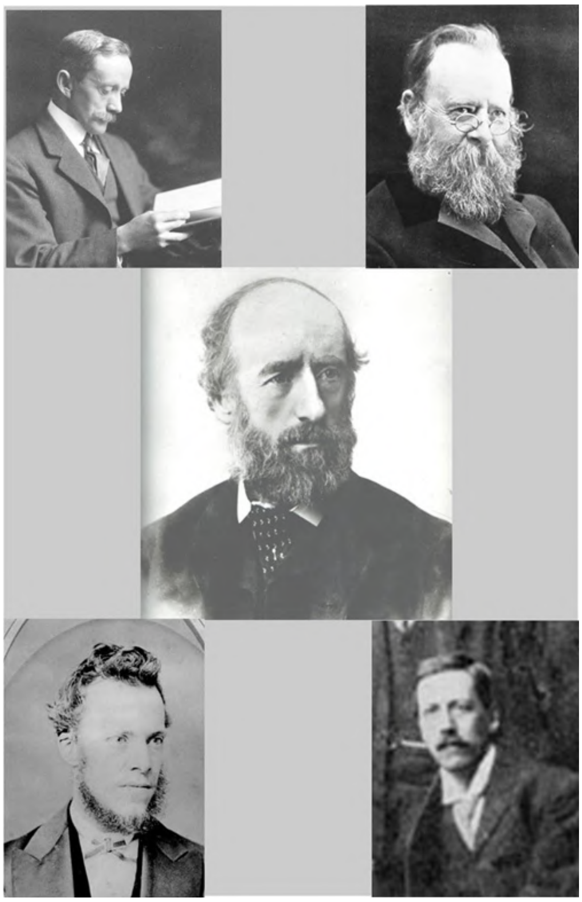
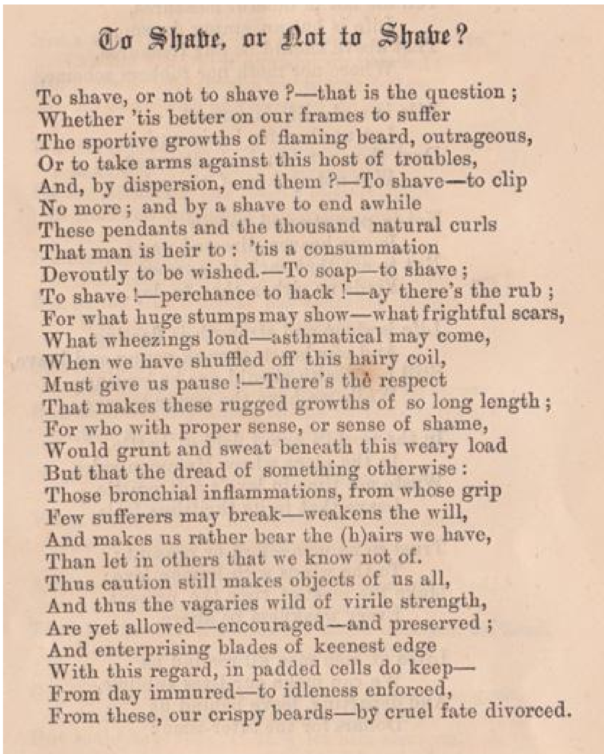


Fig. 8. Faces of New Zealand's colonial chemistry. *Centre:* William Skey, the first Colonial Analyst, (http://www.teara.govt.nz/en/biographies/2s29/skey-william); *Upper left:* James Scott Maclaurin, second Colonial Analyst (http://www.teara.govt.nz/en/photograph/687/james-scott-maclaurin); *Lower left*: James Alexander Pond, Auckland analyst (http://www.teara.govt.nz/en/biographies/2p24/pond-james-alexander) *Upper right:* Canterbury's first chemistry academic: A.W. Bickerton (http://www.teara.govt.nz/en/biographies/2b23/bickerton-alexander-william) *Lower right:* Victoria's first chemistry academic: Thomas Hill Easterfield in 1904 (http://www.teara.govt.nz/en/photograph/23/young-victoria-college-academics-1904-1).



To Shave, or Not to Shave?

To shave, or not to shave ?—that is the question ;
Whether 'tis better on our frames to suffer
The sportive growths of flaming beard, outrageous,
Or to take arms against this host of troubles,
And, by dispersion, end them ?—To shave—to clip
No more ; and by a shave to end awhile
These pendants and the thousand natural curls
That man is heir to : 'tis a consummation
Devoutly to be wished.—To soap—to shave ;
To shave !—perchance to hack !—ay there's the rub ;
For what huge stumps may show—what frightful scars,
What wheezings loud—asthmatical may come,
When we have shuffled off this hairy coil,
Must give us pause !—There's the respect
That makes these rugged growths of so long length ;
For who with proper sense, or sense of shame,
Would grunt and sweat beneath this weary load
But that the dread of something otherwise :
Those bronchial inflammations, from whose grip
Few sufferers may break—weakens the will,
And makes us rather bear the (h)airs we have,
Than let in others that we know not of.
Thus caution still makes objects of us all,
And thus the vagaries wild of virile strength,
Are yet allowed—encouraged—and preserved ;
And enterprising blades of keenest edge
With this regard, in padded cells do keep—
From day immured—to idleness enforced,
From these, our crispy beards—by cruel fate divorced.

Fig. 9. "To shave or not to shave", a poem by William Skey, of pertinence perhaps to the portraits in Fig. 8.

1965, *48*, 56 pp.

11 Pond, James Alexander: http://www.teara.govt.nz/en/biographies/2p24/pond-james-alexander, accessed 16 May 2016.

12 Binney, J.; Bassett, J.; Olssen, E. *The People and the land – Te tangata me te whenua – An illustrated history of New Zealand 1820-1920*. Allen & Unwin: Wellington, 1990, p. 237.

13 Uglow, J. *The lunar men: the friends who made the future.* Faber & Faber: London, 2002, p. xvii.

14 Wellington Philosophical Society, The Community Archive: http://thecommunityarchive.org.nz/node/65939 accessed 7 June 2016.

15 Ordinary members. Wellington Philosophical Society. *Proc. New Zealand Institute* **1870**, *3*, 358; **1875**, *8*, xliv; **1880**, *13*, xxiv; **1885**, *18*, 445; **1890**, *23*, 643; **1895**, *28*. 770; **1900**, *33*, 589.

16 Data downloaded from www.teara.govt.nz/files/g-24334-data.txt, accessed 6 June 2016.

17 Hughson, W.M.; Ellis, A.G., *A history of Chemistry Division*. NZ Department of Scientific and Industrial Research: Wellington, 1981, p. 28.

18 Geological exploration: http://www.teara.govt.nz/en/geological-exploration/page-3, accessed 10 May 2016.

19 Hughson and Ellis, *op. cit*., p. 16.

20 Mortimer, N. '150 years of the New Zealand Geological Survey' [Editorial]. *New Zealand J. Geol. Geophys.* **2015**, *58* (4), 317-318. A history of the Survey at its centenary is: Burton, P. 'The New Zealand Geological Survey, 1865-1965: New Zealand Geological Survey Handbook'. *DSIR Information Series* **1965**, *52*, 147 pp.

21 Lloyd Pritchard, M.F. *An Economic History of New Zealand to 1939*. Collins: Auckland, 1970.

22 King, M. *The Penguin History of New Zealand*. Penguin: Auckland, 2003, pp. 233-234.

23 Alsop, P.; Stewart G. *Promoting prosperity: The art of early New Zealand advertising*. Craig Potton: Nelson, 2013, pp. 184-185.

24 King, op. cit., pp. 237-238.

25 *The Reserve Bank and New Zealand's Economic History.* Reserve Bank of New Zealand: Wellington, 2007.

26 Hughson and Ellis, op. cit., pp. 25-27.

27 Hodder, A.P.W.; Hodder, C. 'Sydney Street West: a first place for science in Wellington'. *J. Roy. Soc. NZ* **2017**, in press.

28 Burdon, R.M. *Scholar errant: a biography of Professor A.W. Bickerton*. Pegasus Press: Christchurch, 1956.

29 Professor William Percival Evans [Obituary]: http://rsnz.natlib.govt.nz/volume/rsnz_88/rsnz_88_04_009830.pdf, accessed 16 May 2016.

30 Askew, H.O. *Trans. Proc. Roy. Soc. NZ* **1950**, *78*: 381-383; see also: Easterfield, Thomas Hill: http://www.teara.govt.nz/en/biographies/3e1/easterfield-thomas-hill, accessed 16 May 2016; Halton, B. *Chemistry at Victoria, the Wellington University. A personalized account of the hundred years from 1899.* School of Chemical and Physical Sciences, Victoria University of Wellington: Wellington, 2012, pp. 3-5, http://www.victoria.ac.nz/scps/about/history/history-of-chemistry

31 https://historygeek.co.nz/2012/11/17/to-shave-or-not-to-shave/, accessed 16 May 2016.

32 Skey, W. *The Pirate Chief, and the Mummy's Complaint, with various Zealandian Poems*, Haggett and Percy: Wellington, 1889.

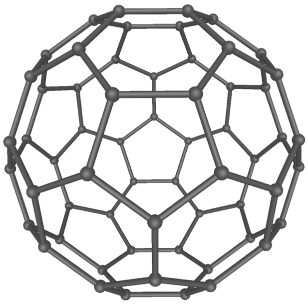
Sir Harold (Harry) Walter Kroto (1939-2016)

Taken from images at AMN-3, 2007 (courtesy of The MacDiarmid Institute, Wellington)

Of the Nobel Laureates in chemistry over the past 25 years the name of Harry Kroto is probably the most recognised. His 1996 award with Robert Curl and Richard Smalley for the 1985 discovery of C_{60}, the first of the fullerenes (*Nature* **1985**, *318*, 14 November, 162-163) represented the beginning of a new era in chemistry – the new carbon allotrope led the surge into previously uncharted nanotechnology.

Harry Kroto was born in Wisbech, Cambridgeshire, England on October 7, 1939, son of Edith and Heinz Krotoschiner, German refugees to the UK where his mother had been evacuated on the outbreak of war. Harry's family name stems from a town in Silesia, where his Jewish father's family originated. However, his parents were both born in Berlin and his father, as an *enemy alien*, was interned on the Isle of Man during the war. As a baby Harry and his mother were moved to Bolton in Lancashire in 1940. In Germany, Kroto's father had run a family business printing faces and other images on toy balloons and, after the war, he became a toolmaker at an engineering company in Bolton and then, in 1955, set up his own small factory, again making balloons as well as printing them. He then shortened the family name to Kroto. Harry spent much of his school holiday time working in the factory. His education was at the Bolton School Boys' Division, where he showed a particular talent for graphic design and art; he played the Duke of York to school mate Ian McKellen's Henry V in a school play. After gaining his Advanced School Certificate, Harry entered the University of Sheffield in 1958 where his interests moved from organic chemistry to quantum chemistry and spectroscopy gaining him his BSc and PhD (1964) (Thesis: *The Spectroscopy of Free Radicals produced by Flash Photolysis*). Kroto then spent two years as a postdoctoral researcher in electronic and microwave spectroscopy at the National Research Council in Ottawa, Canada and a year at Bell Laboratories in New Jersey prior to joining the University of Sussex, initially as a postdoctoral researcher and soon appointed to a lectureship there. He was elevated to a professorship in 1985.

Harry Kroto's interests focussed on giant stars and interstellar gas clouds where, surprisingly, he found evidence for long and abundant carbon chain molecules that he believed had been formed in stellar atmospheres and not in clouds. In order to simulate the reactions involved, he made contact with chemical physicist Richard Smalley and senior physical chemist, Robert Curl at Rice University in Houston, Texas. Smalley's research was in cluster chemistry, an important part of chemical physics and his self-designed and built laser-supersonic cluster beam apparatus was able to vaporise almost any known material into a plasma of atoms. Using this equipment over 11 days in 1985, Kroto in collaboration with these two and their students found that clusters of 60 carbon atoms were most abundant and stable. They proposed a truncated icosahedral structure for C_{60} that is a football-shaped polyhedron of sp^2 hybridised fused-ring aromatics containing 20 hexagons and 12 pentagons in which all the carbon atoms occupy identical positions. The diameter of the cage is about 70 pm, some 6-10 times as large as the H atom. It is a highly symmetrical and exceptionally stable, not breaking until about 1100 °C. It is the molecular version of the geodesic dome designed by the American architect R. Buckminster Fuller for the 1967 Montreal World Exhibition (MWE); the molecule is also known as a buckyball.



Top: The Buckminster Fuller geodesic dome at the US Pavilion, 1967 Montreal World Exhibition (from Historic Notlab). Bottom: the C_{60} icosahedral fullerene. Created by Michael Ströck on February 6, 2006, from https://commons.wikimedia.org/wiki/File:C60a.png).

The discovery of Buckminster-fullerene in 1985 was followed by much synthetic activity that led to larger carbon cages and nanotubes thus giving rise to the new area of nanotechnology. The fullerenes have now been found to exist in the interstellar dust as well as in geological formations on earth. They are formed when vaporised carbon condenses in an atmosphere of inert gas that give clusters containing from a few to hundreds of atoms. After cooling and condensing, the carbon clusters can be analysed. C_{60} has been isolated, initially in a purple benzene solution then as a mustard coloured solid. Sadly, Smalley and Kroto later disagreed on how to apportion the credit for the discovery between them and recalled the sequence of events differently, creating tensions. Eventually, Curl, the senior partner in the experiments, said that they agreed to disagree and *kind of got over it*.

Harry Kroto remained at Sussex University and, for the decade from 1991, was a Royal Society Research Professor. However, as time went by, he became increasingly concerned with the short-sighted approach of government and funding bodies to back pure scientific research, and was worried by the decline of scientific culture in Britain's schools and universities. Only hours before the announcement of his Nobel Prize his application for a £100,000 grant to the engineering and physical science research council for further research into fullerenes was declined. As administrative bureaucracy increased he elected to further his work at Florida State University in Tallahassee where he remained from 2004 until 2015, when he retired and moved back to England.

Harry Kroto had always been an enthusiastic promoter of chemistry and science in general, and his lectures and presentations were models of clarity, logic and humour. He took science to a wide range of audiences worldwide. In 1994 he established the *Vega Science Trust*, to provide an independent broadcast archive of noted scientists describing their work. Later, the *Global Educational Outreach for Science, Engineering and Technology* (Geoset) was set up to provide first-rate teaching material on the websites of participating universities for free download, dominantly for teachers. Recognising that the best educators are often the young he set up the *Innovative Use of Technology in Science Learning Prize* last year with his wife Margaret, to be awarded to the best five-minute science, technology, engineering or maths (Stem) video by school children aged 11-18 from anywhere in the world. He devoted much of his time and energy to visiting schools, giving public lectures and workshops, and engaging children of all ages in science.

Harry was elected a Fellow of the Royal Society in 1990, was knighted in 1996 and served as president of the Royal Society of Chemistry from 2002 to 2004. He received numerous awards including some 42 honorary degrees but, in protest, returned two of them to the British universities that closed their chemistry departments.

Harry joined the International Science Advisory Board of the MacDiarmid Institute in 2007 to aid its international positioning in terms of science focus and international benchmarking. He then visited New Zealand to deliver plenary lectures at successive Advanced Materials and Nanoscience (AMN) conferences in 2007 (Wellington) and 2009 (Dunedin) at which he also provided lectures for the public and visited schools. His Wellington lecture attracted a capacity audience of 1550 to the St. James Theatre.

He died on April 30 2016 from motor neurone disease (amyotrophic lateral sclerosis) at his home in Lewes, East Sussex. He is survived by Margaret, his wife of 53 years, and their sons Stephen and David.

Brian Halton

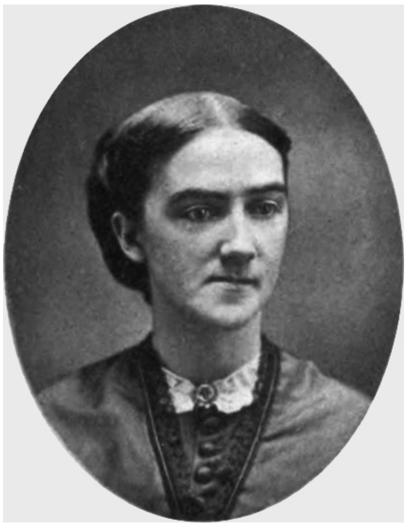
Some Unremembered Chemists

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.

Ellen Swallow Richards (1842-1911)

Brian Halton

School of Chemical & Physical Sciences, Victoria University, PO Box 600, Wellington 6140
(e-mail: brian.halton@vuw.ac.nz)

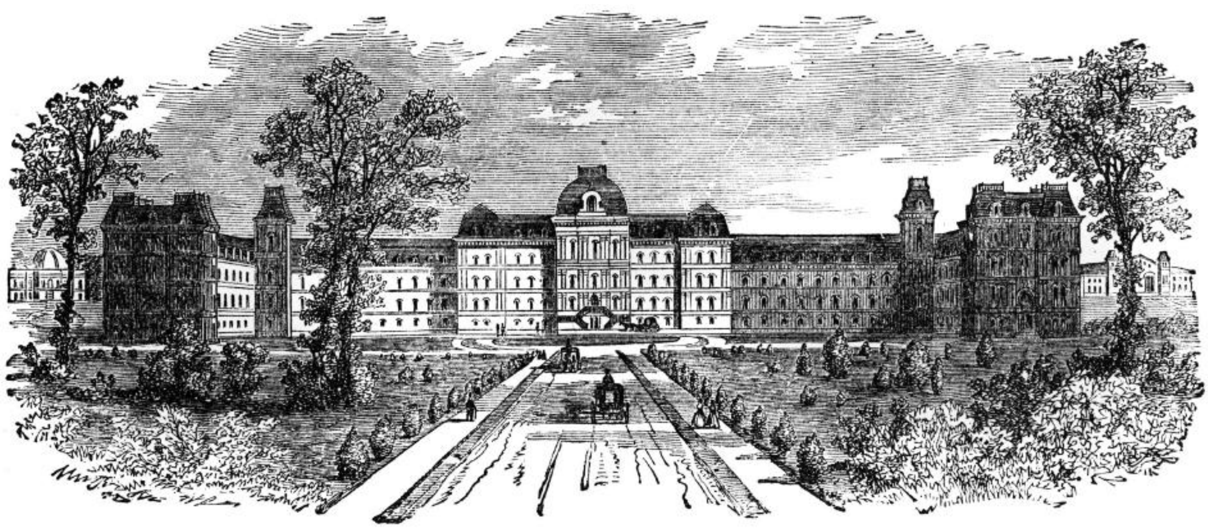




Ellen Henrietta (Swallow) Richards in about 1858 (courtesy of MIT Museum), 1870 and the 1890s

Ellen Henrietta Swallow was born on December 3, 1842 on a farm near the village of Dunstable, in rural northern Massachusetts. She was the only child of well-educated but relatively poor New England parents, Peter Swallow and Fanny Gould Taylor.[1,2] Her father divided his time between teaching and farming having inherited half of his father's farm. Ellen received most of her early education from them at home. Her life was directed to being helpful and assisting others as expected in that puritanical region of the US. However, she focussed on new ways of doing it with a passion for usefulness and a longing for pioneering. When she was 16 years old her father sold his farm and moved to a general store in nearby Westford so as to raise the money for his daughter's education. Ellen worked in the store to make her contribution to this. Her work serving behind the counter grew to include the bookkeeping and purchase of supplies.

Her father was her most ardent supporter in gaining a college education and a scientific training at a time when such things were almost unknown among women. She was enrolled at the then private Westford Academy, one of the oldest high schools in the US, graduating in 1862 having studied much Latin, some French and a little Maths.[1] She was to have started teaching after leaving the academy but a bad bout of measles and its aftermath prevented this and it was only in the following May that her teaching career began. In 1863, to enlarge his business, her father moved the family to nearby Littleton. Her mother had been and was frequently ill and so, by early 1865, Ellen was back at home looking after her, the house, and helping her father in the store. As Littleton was close enough to Worcester for Ellen to attend lectures she moved and lived there for the 1865-1866 winter. After returning home Ellen focused her energy on assisting in the store, and spent long periods looking after her ill mother, still determined to continue formal education despite a lack of money. She saved every penny despite the 1866-1868 years being ones of ill health and deep depression. Nonetheless, by the time she was almost 26 she had saved enough money, but as there were no colleges open to women in New England she went to the recently opened Vassar College in Poughkeepsie on the Hudson River (some 125 km north of New York City). It had taken in its first class of 353 students paying $350 for tuition and residence just three years earlier, offering young women a liberal arts education equal to that of the best men's colleges of the day.

She started on September 17, 1868 with some $300 and as a 25-year old was a special student. Although co-educational, then it was a pioneer college for women's education in the eastern US that became one of the Seven Sisters colleges, the women's equivalent of the Ivy League. Vassar's main building was fitted for teaching sciences by its Professors Maria Mitchell (Astronomy and the first academic appointee) and Charles Farrar (Chemistry and Physics). These subjects and their teachers attracted Ellen and she devoted much time to studying astronomy



Vassar College (*ClipArt ETC*, Florida Center for Instructional Technology, College of Education, University of South Florida)

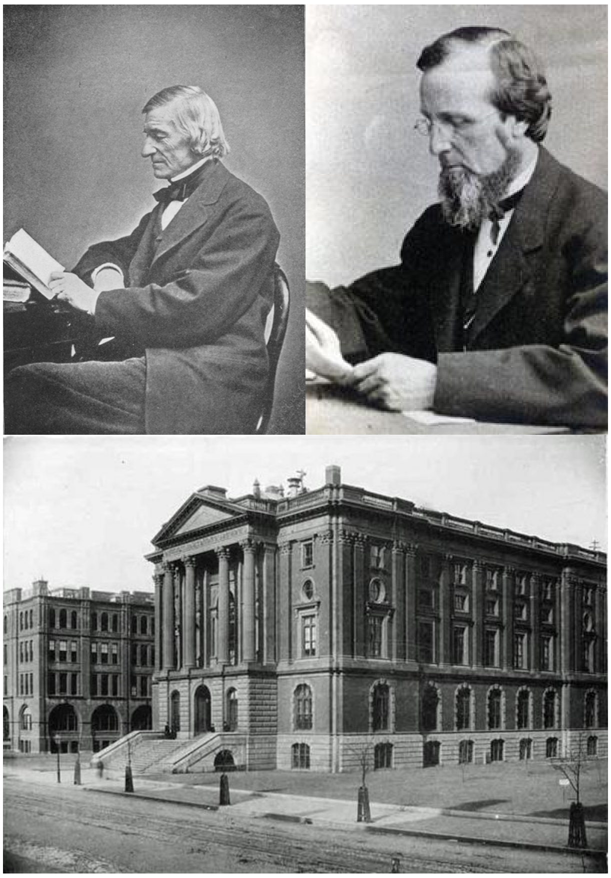
under Mitchell, the most important woman scientist in 19th century America and one of the first women science professors. However, Farrar's influence led Ellen into chemistry with the idea that science should help in the solution of practical, everyday problems. Her immediate need was to meet the fees and because she had taught, Farrar allowed Ellen to tutor in the evenings.

Farrar seems to have given Ellen, one of his more ardent students, a good basic chemical education. Early in her second year he advised the students to take special care with their analytical work and be accurate as *'the profession of an analytical chemist is very profitable and means very nice and delicate work fitted for ladies' hands'*.[1] He was of the view that his students should be aware of all aspects of chemistry and planned a visit to the West Point Iron and Cannon Foundry for industrial experience but the college principal refused to let it happen as women on the workshop floor could give the institution bad publicity. Farrar provided a range of daily life examples such as 'strong' (rancid) butter containing butyric acid and not to be eaten, and the need for appropriate house ventilation (he burnt candles at different heights below an open window in an otherwise closed room, recording the time it took before they went out). Farrar encouraged Ellen through her time at Vassar, even addressing her as Professor Swallow a little ahead of her graduation with a BS on 21 June 1870.

Ellen Swallow took little notice of the advice to seek employment as an analytical chemist, but wanted more. For her immediate future she had secured a teaching post in Argentina under a government scheme, but the existing Paraguayan War worsened and the Argentinian government had to break the contract. As a result, she took what was probably her first holiday in years, returning to the area of her childhood, spending three weeks there and deciding to seek a career in chemistry. She wrote to the Boston commercial chemists, analysts and assayers, Merrick and Gray, seeking an apprenticeship. Merrick, a professor at the Massachusetts College of Pharmacy and consultant in the company replied to Ellen saying that they were unable to take her. Surprisingly for 1870, he suggested that she try to gain entry to the Institute of Technology in Boston (MIT) even though it did not take women. She wrote to the Institute knowing full well that gaining entry would be difficult but gave her Vassar professors as referees. As she received no early response she wrote to Booth and Garrett of Philadelphia as Booth's laboratory in Pennsylvania had taught chemistry for some 35 years. With associate Thomas H. Garrett joining in 1848, the firm had gained a strong reputation and, according to the *Scientific American*, a course in the laboratory was a necessity for the chemist of the time which it regarded of more value than a college diploma. The mid-November reply said that they had no vacancy, offered alternatives, and insisted that they '*desired to see proper means of livelihood thrown open to females'*. Swallow responded to this and it led to the offer of a studentship at a cost of $500 p.a. but urged her to gain entry to a scientific school if she could not afford it.

On Ellen Swallow's 28th birthday, her case, having been in the hands of the MIT secretary, was formally put to the faculty for its December 10 meeting. They recommended to the MIT Corporation (the Trustees)[3] the admission of Miss Swallow as a special student in chemistry but resolved that the admission of women as special students was an experiment with each case to be treated on its merits.[1] As it happened, women students were in a small minority at MIT (numbered in dozens) prior to the completion of the first women's dormitory in 1964. On December 14, 1870, the MIT President J.D. Runkle wrote to congratulate Ellen on her admission, asked her to come to see him and advised that '*you shall have any and all advantages which the Institute has to offer without charge of any kind*', this because he could then say she was not a student should anyone wish to object. It was not, as Swallow thought, a result of her financial plight.

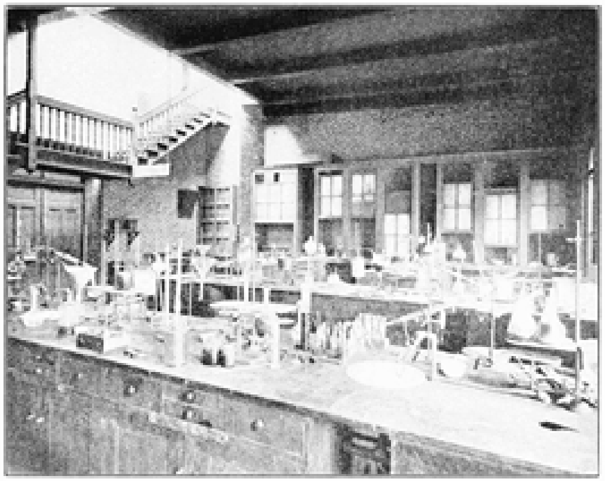
In early January 1871, Ellen Swallow, already holding a BS degree entered MIT as a third year student. She met with mathematician Dr. Runkle, President for 8 years from 1870 and strong supporter of her admission who was keen to see her succeed. The only woman working in the Roger's Building was the assistant in charge of the chemical store room, Mrs. E.A. Stinson and with whom Ellen formed a strong long lasting friendship. Stinson



Top left: William Barton Rogers. Founder and First (and Third) President of MIT; top right: John Daniel Runkle, the second MIT President. bottom: the 1865 Rogers Building in the foreground with the 1883 Walker Building in the background – from an 1889 photogravure.

thought Ellen too frail and delicate to succeed in what was regarded as a difficult course and said so to Runckle. His response was: *But did you notice her eyes? They are steadfast and they are courageous. She will not fail.*[1] In settling to her life at MIT, Ellen Swallow changed little in her habits, determined to become a part of the institution. She continued her attention to routine chores but extended them to the college, e.g. she and Stinson swept a lecture theatre when the Janitor was taken ill, tidied staff areas and even sewed clothes and the like for the professors, all in addition to her classes. In essence she made herself an indispensable part of chemistry at MIT. She boarded at the house of a friend from Westford Academy throughout her student days, but catered and cleaned for herself to save money until her finances improved. Her ability as a student, her dedication to study and the accuracy of her laboratory work led to Professor Ordway (metallurgy and industrial chemistry and a noted consultant on technical chemistry) letting her work for him, which previously had never happened with a student. It was during that first year that her father was struck by a train engine in the Worcester Union station and died shortly after. Ellen had been sick at the time and was at home. She remained there tending her mother for the remaining part of the 1871 teaching year. During the last months of the year she was supporting herself, settling her father's estate and making a daily return journey to MIT some 50 km distant to keep up with her study.

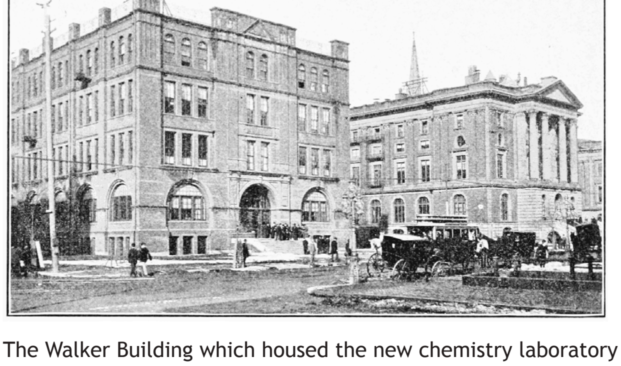
Returning to Boston in 1872 to continue her studies without the need for travel, she remained Ordway's assistant. However, in the summer of that year, Professor William R. Nichols, Head of Chemistry was engaged by the State to extend his earlier (1870) analysis of the waters of Mystic Pond and report on the quality from an industrial and sewerage pollution perspective. Although opposed to women's education, Nichols asked Ellen Swallow to be his assistant for this work accepting nothing short of absolute accuracy in her analytical results - the work was among the most advanced in *sanitation* (now environmental) chemistry in the world.[4,5] She did this as well as the work for Ordway, her classes and study, and her general assistance to anyone. So impressed by her results, Nichols acknowledged in his report that it was she who had performed most of the analyses. This led to her becoming involved in the later (1887) State wide water survey (see below). Then Ordway's work on oils led to contact with Edward Atkinson, the inventor of the Aladin oven (see below). In 1873 Ellen H. Swallow graduated BS in chemistry with a thesis on '*Some sulpharsenites and sulphantimonites from Colorado*'. She also gained an MA from Vassar College that year having simultaneously worked on a thesis on the amount of vanadium in iron ore. In that same year she acquired a 7 g black sample of the rare mineral samarskite that had reddish brown dark streaks and a vitreous lustre[6] [Samarskite is a radioactive rare earth mineral series that includes samarskite –Y: $(YFe^{3+}Fe^{2+}U,Th,Ca)_2(Nb,Ta)_2O_8$ and samarskite-Yb: $(YbFe^{3+})_2(Nb,Ta)_2O_8$) or $(Y,Fe^{3+},U)(Nb,Ta)O_4$)]. Her very careful analysis led to an insoluble residue that she said contained an element yet to be found and sometime later, samarium and gadolinium were isolated from the ore.[7]



An MIT chemistry laboratory 1870s

With her MA, two BS degrees and experience in analysis, Ellen Swallow was suitably qualified for entry into a doctoral programme but women did not take such courses then and, despite her astonishing record, no one was willing to support the needed application; MIT did not graduate a woman with a PhD until 1884. Undeterred by this she remained at MIT as a resident graduate continuing to conduct various analyses as earlier and devised a new method for determining the amount of nickel in various ores in 1877. She was essentially an unpaid chemistry lecturer at MIT from 1873 to 1878. During 1873 and the following year she was courted by the professor of mineralogy and assaying, and head of the department of mining engineering, Robert H. Richards, with whom she worked in the mineralogy laboratory. Richards proposed in the chemistry laboratory and they were married on June 4, 1875. They took their honeymoon in Nova Scotia - accompanied by the entire mining class that Robert was teaching! Robert Richards, who became professor of metallurgy in 1884, was a strong supporter of his wife's ambitions and she of his. They spent the summers of 1881 and 1882 in the copper regions of Northern Michigan where he was studying methods of concentrating and smelting copper and she his analyst. In 1879 she was recognised by the American Institute of Mining and Metallurgical Engineers as their first female member

One of the first matters Ellen Richards pressed MIT for was a Woman's Laboratory. This followed from the Lowell Free Lectures and the increased need for laboratory instruction in science. Most teachers were women and there was a clear need for instruction for them. In fact, Ellen had taught a course for sixteen women at Boston Girl's High School with one of its female staff in 1873. Most were over 20 years of age and half were school teachers. To press her cause, Ellen appeared before the Woman's Education Association in late 1875 with the result that the MIT authorities were approached with an offer to equip a laboratory for women and provide the necessary books (the institution was in a dire financial state at that time). The result was for MIT to admit special students in chemistry without regard to sex in early May of 1876 and set up the Woman's Laboratory which opened in November under the charge of Prof. Ordway with Mrs. Richards as assistant. It was housed in a portion of a one-story structure located between the sites of the Rogers and Walker Buildings. Over the following seven years, Ordway and Ellen worked in the lab without pay and Ellen, through her husband's support, donated an average of $US1,000 each year to it. 1879 saw Ellen recognized by MIT, becoming an assistant instructor without pay, teaching the curriculum in chemical analysis, industrial chemistry, mineralogy, and applied biology. The laboratory was very successful. In 1883, MIT began awarding undergraduate degrees to women on a regular basis without need for special admission – and Mrs. Richards was heavily involved in ensuring that appropriate facilities for women were provided and in place. Moreover, a new laboratory had been created with space to accommodate all students irrespective of gender and the Woman's Laboratory was closed and removed when the Walker Building was erected. Her dedication to experimental science for women led her to becoming a founding member of the Naples Table Association for promoting laboratory research by women in 1898 (an equivalent to that set up in Naples, Italy with a small fully equipped laboratory[8]).



The Walker Building which housed the new chemistry laboratory

In 1884 MIT opened a separate laboratory for sanitary (environmental) chemistry with Mrs. Richards as instructor, a position which she held until her death. Professor Nichols was head until his death in 1886 when Thomas M. Drown took over. For many years Ellen directed the entire instruction in the chemistry of air, water and foods for chemists, biologists and sanitary engineers, and only relinquished the chemistry of food supplies when the pressure of other affairs made this necessary. Then in 1886, the Massachusetts Legislature passed an Inland Waters Act to provide a comprehensive programme to protect the state's rivers, streams, and ponds. As part of the implementation of the Act, the Lawrence Experiment Station was founded in Lawrence in 1887, and headed by Professor Drown, whose principle mission was to develop practical methods for treating the growing volumes of wastewater that were seriously degrading surface waters in the state. The laboratory of sanitary chemistry was the world's first trial station for drinking water purification and sewage treatment. In 1887, the laboratory was asked to conduct a study of water quality statewide for the Massachusetts State Board of Health. Ellen Richards, who had been chemist to the Board of Health from 1872 to 1875 was asked to carry out the analyses and became Board of Health water analyst from 1887 to 1897. The study took two years and involved monthly sampling from the chosen sites with more than 20,000 samples in total analysed as soon as possible after arrival at the lab. It was the first such study in America, and Ellen's data were used to find causes of pollution and improper sewage disposal. In carrying out their analysis of the data Richards and Drown generated what became known as the *Normal Chlorine Map*. All places with natural unpolluted waters that had the same chlorine concentration were joined by lines on a map and termed *isochlors*. When completed, it was found that the isochlors roughly paralleled the coastline and that the difference in chlorine concentrations between the different lines was similar to the distance of the line to the sea shore. The conclusion was that all places the same distance from the shore should have the same chlorine level and if above this it was due to pollution (the Cape Cod peninsula with water on all sides was excluded). The concept of the map and the way it was derived found much use worldwide. As a result of the study, Massachusetts established the first water-quality standards in America and its first modern sewage treatment plant at Lowell. The Lawrence Experiment Station grew into an engineering laboratory that performed pioneering research on the treatment of water supply, sewage, and industrial waste. Moreover, the practical engineering principles developed there led to dramatic reductions in water-borne diseases such as typhoid. Among many other works in sanitation was an investigation of the sanitary condition of the public school buildings in Boston but little heed of it was taken.

Ellen Richards' dedication to her students was inspiring, and her personal and financial sacrifice for her pupils amazing.[9] The full effectiveness of her laboratory will probably never be adequately known as she also maintained an extensive private practice in sanitary chemistry for many years, and acted in an advisory capacity for a very large number of public and private institutions. Her publications relating to sanitation have been numerous and varied, and she maintained active membership in and participation at the meetings of local and national societies dealing with water supplies and public health problems. From her work in the new lab, Ellen Richards became one of the foremost sanitary chemists in the world.

Her time at the Women's Laboratory made Ellen Richards very meticulous in applying scientific principles to domestic situations. These included nutrition, pure foods, clothing, physical fitness, sanitation, and efficient home management that led to the creation of home economics - especially efficient practices that would allow women more time for pursuits other than cooking and cleaning. In essence it was a very early application of 'time-and-motion' with science to the home. When she had a gas oven installed in her home she also had a meter put in place so that she could record the amount of gas used to cook the meal, the recipe for it, and the length of time needed for preparation, thus giving an indication of the total cost of the meal. She also ensured that the house was appropriately ventilated and had a water back (wet-back) installed for winter heating by the living room fire and a small heater in the basement for summer use. In 1882, she published *The Chemistry of Cooking and Cleaning: A Manual for Housekeepers* (see below).

Her interest in the environment led her in 1892 to introduce the word "oekology' (ecology) in the US which had been coined in German to describe the '*household of nature*'. Together with Marion Talbot (an 1880 Boston University graduate) they became the founding mothers of the Association of Collegiate Alumni (ACA) in 1882, with the aim of opening the doors of higher education to other women and to finding wider opportunities for their training. She was elected an honorary life member in 1907. From the ACA came in 1883 the *Sanitary Science Club* comprised of some fifteen women graduates who met in the Richards' home to learn about home science, each studying their own home. It led to her 1898 booklet with Talbot on *Home Sanitation*. Furthermore, home study was promoted and Richards became one of its promoters, a forerunner of this century's correspondence school. The ACA was the forerunner of what is now the American Association of University Women (AAUW). It became a leading advocate for education and equity for all women and girls. Today, there are more than 100,000 members, 1,300 branches, and 500 college and university partners nationwide.

In 1889 Ellen Richards set up the New England Kitchen which gained financial support from industrial manufacturers and other sources. It had an Atkinson Aladin oven installed and tested. The aim was to provide an open kitchen that prepared and cooked nutritious lunches that could be sold at cost, each with its contents and nutritional value provided. In many ways it was the first takeaway outlet in the US. It opened on January 1, 1890 and led to other equivalent kitchens. By repeated chemical analysis the methods of preparing a dish were brought to perfection giving a food whose consistency varied only slightly from day to day. One, with a constitution akin to milk fat was welcomed by the medical practitioners of the city. The existence of the kitchen led some years later to hygiene requirements in restaurants. Success was daunted, however, by one lady gaining publicity for saying '*I don't want to eat what's good for me; I'd rather eat what I'd rather*'. Ellen campaigned tirelessly for the new discipline of home economics as it became known and pioneered an equivalent kitchen at the Chicago Exhibition of 1900 - the Rumford Kitchen.[10] It was part of the Massachusetts State exhibition and laid bare all the cooking processes to the public. Visitors could buy any one of four different lunches each for 30 cents, the food value of which was carefully computed and provided on the bill of fare (see a typical menu below). The kitchen provided the first simple explanation and

	Ounces	Grams	Food Value in Grams: Proteid	Fat	Carbo-hydrates	Calories
Voit's Standard. One-quarter of one day's ration			24.5	14.0	125.0	742.0
Atwater's Standard. One-quarter of one day's ration			31.2	31.2	114.0	882.0
Baked Beans	8.4	238.1				
Brown Bread	4.2	119.1				
One Roll	2.0	56.7	26.3	35.6	131.4	979.3
Butter	0.7	19.8				
Apple Sauce	5.3	150.2				

A Rumford Kitchen menu from 1900 (taken from ref. 1, p. 221)

demonstration of the terms protein, carbohydrate, calorie, and that scientific methods underline nutrition. She became a consultant to a wide range of publicly funded state institutions that were required to cater to large numbers (hospitals, asylums, schools, etc.). An outcome of this endeavour was a successful plan to serve school lunches in Boston, another area in which Ellen Richards became the authority. She established programmes of study and organised conferences on home economics. Then, growing from discussions at several summer conferences that began in 1899 held at Lake Placid in New York State, the American Home Economics Association was formed in Washington DC in 1908 with Richards as its first president. In 1909 it established a Graduate School of Home Economics. W.O. Atwater, known for his studies of human nutrition and metabolism, said of Ellen Richards: '*The science of household economics is what chemists call a state of supersaturated solution; it needs only the insertion of a needle to start a crystallisation*'. Her efforts led to home economics becoming a subject of serious study for all. During this time she introduced the word "euthenics" (eugenics by Francis Galton) to the language meaning the science of the environment controlled for right living, an area that has received increasing attention. Throughout her life and despite the numerous commitments she had, Ellen Richards continued to travel for her work and with her husband for his. Her last trips were to Mexico in 1901 and Alaska in 1903, each one with her portable water laboratory taking samples and outlining future study where needed. She was a model of efficiency.

At home, it was customary for the Richards to invite students who had little money to board in return for doing the housework. It was also customary for them to entertain their students giving dinner parties with occasional entertainment. Prof. Richards taught glassblowing at MIT and often gave demonstrations after dinner. One of his more noted skills was to blow a water hammer much to the enjoyment of the guests. Later in life when in her 50s Ellen eased her puritanical upbringing to the extent of developing an interest in theatre, which she and Richard took to attending on Friday evenings.

An 1850-1874 Water hammer (courtesy of Martijn Zegel, Teylers Museum, Haarlem, Netherlands)

Richards served on the board of trustees of Vassar College for many years and was awarded an honorary doctor of science degree there in 1910. She served as a consultant to the Manufacturers Mutual Fire Insurance Co. from very early in her career. She died on March 13, 1911 at her home in Jamaica Plain, Massachusetts, now a National Historic Landmark (the Ellen Swallow Richards House). In her honour, MIT designated a room in the main building for the use of women students, and in 1973, on the occasion of the hundredth anniversary of her graduation, established the Ellen Swallow Richards professorship for distinguished female faculty members. Prof. Robert Richards re-married in June 1912 (to Lillian Jameson) and remained married until her death in 1924. Surviving both wives, he lived to 101 years of age and died on March 27, 1945.

Ellen Swallow Richards was the foremost female industrial and environmental chemist in the United States in the 19th century, pioneering the field of home economics. She was a pragmatic feminist, as well as a founding ecofeminist who believed that women's work within the home was a vital aspect of the economy. There are few women, if any, alive today who would be able to devote themselves so totally and with as much energy as Ellen Richards displayed. Citation 11 lists the books, booklets and pamphlets she published, many of which are digitised for complimentary download.[11]

A few of her writings and quotations appear below:[12]

Ellen and Robert Richards in 1904

Girls may learn that rice is a carbohydrate and peas and beans are not only carbohydrates but also albuminoids, without learning the connection of these facts with everyday life.

Where are the fruits of chemical science? In the self-rising flour in bread powders, in washing powders, in glove cleaners, and in a hundred patent nostrums (medicines).

If you keep your feathers well-oiled the water of criticism will run off as from a duck's back.

Postscript

The first Home Science course to be taught in New Zealand was at Otago University College in 1911 with Anna Hedges of New York the original appointee to the inaugural chair. Unfortunately ill health prevented her taking up the post and Winifred Boys-Smith was then appointed professor of home science and domestic arts from London, arriving in January 1911 with Miss G.H. Rawson as lecturer. By then elderly, Professor of Chemistry James Gow Black was dubious of Boys-Smith and her abilities to teach chemistry and offered to provide notes on some of the chemical processes for her! From 1911 to 1919 the student roll in the discipline rose from 5 to 60. Over time Boys-Smith was supplemented by other academic women in posts where they taught chemistry, botany and the biological sciences. Elizabeth Gregory became lecturer in chemistry and nutrition in the 1932-1933 period.[13]

Acknowledgements

I am grateful to Drs. Joanne Harvey and Margaret Halton for helpful comments.

References and Notes

1. For a full biography see: Hunt, C.L. *The life of Ellen H. Richards*, Whitcomb & Barrows, 1912 available for download from Archive Library at https://archive.org/details/lifeofellenhrich00huntrich.

2. Talbot, H.P., *Technology Review*, 1911, *13*, 365-373; Ellen Swallow Richards, Vassar Encyclopedia, see: https://vcencyclopedia.vassar.edu/alumni/ellen-swallow-richards*; Ellen Swallow Richards, Civil War Women http://civilwarwomenblog.com/ellen-swallow-richards/;* Ellen Swallow Richards. Timeline at: *onlinelibrary.wiley.com/doi/10.1002/9781118923849.oth1;* MIT archives, Index to material about Ellen Swallow Richards at *https://libraries.mit.edu/archives/exhibits/esr/esr-bibliography.html.*

3. On incorporation in 1861 MIT as we know it was the Massachusetts Institute of Technology and Boston Society of Natural History,

but the original institute was known as the Boston Institute until it moved across the Charles River to Cambridge in 1916.

4. Haywood, J. K. (John Kerfoot), 1873-1928; Smith, Bernard Howard; United States. Bureau of Chemistry; United States. Department of AgricultureThe water analyses involved several species, e.g. Cl^-, Na^+, CO, H_2S and trace metals. The chloride analysis was much the same then as now, see: Mineral waters of the United States: I. Classification and methods of analysis: II. Commercial waters: III. Saratoga waters sampled at source available from Archive Library at: https://ia801806.us.archive.org/11/items/mineralwatersofu91hayw/mineralwatersofu91hayw.pdf.
5. Francis, E. *Practical Examples in Quantitative Analysis, Forming a Concise Guide to the Analysis of Water, Etc*. 1873, Kessinger Legacy Reprints, 2010.
6. Swallow, E.H., *Analysis of Samarskite from a New Locality, Proc. Boston Soc. Nat. Hist.* **1875**, *17*, 424-428; see: https://ia601409.us.archive.org/35/items/proceedingsofbos17bostuoft/proceedingsofbos17bostuoft.pdf.
7. Halton, B. *Chem in NZ*, **2016**, *80*, 45-50.
8. Sloan, J.B. *The Founding of the Naples Table Association for Promoting Scientific Research by Women, 1897, Signs*, **1978**, *4*(1), 208-216.
9. Ellen Richard's contribution to her students is best described in ref. 1.
10. The Rumford Kitchen and the World's Fair 1893, see: http://ellenswallowrichards.com/?page_id=28.
11. Books by E.H. Richards:

    The chemistry of cooking and cleaning; a manual for housekeepers, Estes & Lauriat, Boston 1882, pp. ix, 90.

    Food materials and their adulterations, Home Science Publishing Co. Boston, 1898, pp. iv, 183;

    Home sanitation: a manual for housekeepers (with Talbot, M), Home Science Publishing Co., Boston 1898, pp. 85.

    The cost of living as modified by sanitary science, J. Wiley & sons, New York 1899, pp. 1, 121.

    Plain words about food: the Rumford kitchen leaflets, 1899, pp. 176;

    Air, water and food from a sanitary standpoint (with Woodman, A.G.), J. Wiley & sons, New York 1900, pp. 226.

    The cost of food: a study in dietaries, J. Wiley & sons, New York 1901 pp. v, 161; pp. 1, 12

    The dietary computer. Explanatory pamphlet; the pamphlet containing tables of food composition, lists of prices, weights, and measures, selected recipes for the slips, directions for using the same, J. Wiley & Sons, New York, 1902, pp. 1, 54;

    First lessons in food and diet, (Boston, Whitcomb & Barrows, 1904) Whitcomb & Barrows, Boston, 1904. pp. iv, 52;

    The art of right living, Whitcomb & Barrows, Boston 1904, pp. 1, 50.

    The cost of shelter, J. Wiley & sons, New York 1905, pp. vi, 136.

    Good luncheons for rural schools without a kitchen, Whitcomb & Barrows, Boston, 1906, pp. 1, 12;.

    Sanitation in daily life, Whitcomb & Barrows, Boston 1907, pp. ix, 82.

    Laboratory Notes on Water Analysis. A Survey Course for Engineers, J. Wiley & sons, New York 1908, pp. iii 49;

    The cost of cleanness, by Ellen H. Richards, J. Wiley & sons, New York, 1908, pp. v, 109.

    Euthenics, the science of controllable environment; a plea for better living conditions as a first step toward higher human efficiency, Whitcomb & Barrows, Boston 1910, pp. xii, 162.

    Conservation by sanitation; air and water supply; disposal of waste (including a laboratory guide for sanitary engineers), Wiley, New York 1911, pp. xii, 305.
12. For more of Richard's quotations, see: http://www.brainyquote.com/quotes/authors/e/ellen_swallow_richards.html.
13. Thompson, G.E. *A History of the University of Otago, 1869–1919*, J. Wilkie & Co., Dunedin 1920.

Dates of Note

October

22 ***Charles Glen King***, the US biochemist who discovered vitamin C in 1932 was born this day in 1896. Its structure was quickly determined and it was synthesised by scientists such as Haworth and Reichstein in 1933.

23 ***Albert Szent-Gyorgyi***, the Hungarian biochemist awarded the 1937 Nobel Prize for Physiology or Medicine for his discoveries in connection with the biological combustion processes, with special reference to vitamin C and the catalysis of fumaric acid, died in 1986.

28 ***John Boyd Dunlop***, the Scottish inventor who pioneered the pneumatic tyre, died in 1921.

24 ***Nathaniel Wyeth***, the American chemist and inventor of the PET plastic beverage bottle while employed by DuPont, was born in 1911.

28 ***Johan August Arfwedson***, the Swedish chemist who discovered lithium in 1817 in a compound in petalite but was unable to isolate it, died 175 years ago in 1841.

29 ***Arne Tiselius***, the Swedish biochemist awarded the 1948 Nobel Prize for Chemistry for his work on electrophoresis and other methods of separating and detecting colloids and serum proteins, died in 1971.

31 ***Robert Sanderson Mulliken***, the American chemist and physicist, and 1966 recipient of the Nobel Prize for Chemistry for fundamental work concerning chemical bonds and the electronic structure of molecules, died this day 30 years ago.

November

2 ***Peter Debye***, the Dutch physical chemist whose studies of dipole moments, X rays, and light scattering in gases brought him the 1936 Nobel Prize for Chemistry and after whom the dipole moment unit of measurement is named, died in 1966.

3 ***Eugen Baumann***, the German chemist who found the thyroid gland to be rich in iodine and the first to recognise the element naturally occurring in animal tissue, died in 1986.

5 ***Neil Kensington Adam***, the English physical chemist who continued Langmuir's work of 1917 on surface films and was the inaugural Professor of Chemistry at Southampton University, was born in 1891.

This day in 1906 ***Marie Curie*** gave her inaugural lecture as the first woman lecturer at the Sorbonne.

7 This is the day in 1911 when the Swedish Royal Academy of Sciences decided to award the 1911 Nobel Prize for Chemistry to Madame Marie Sklodowska Curie, Professor at the Faculty of Sciences of Paris, in recognition of the part she has played in the development of chemistry: by the discovery of the chemical elements *radium* and *polonium*; by the determination of the properties of radium and by the isolation of radium in its pure metallic state; and finally, by her research into the compounds of this remarkable element.

The 1911 Nobel Chemistry Diploma

16 ***Joel H. Hildebrand***, the US educator and chemist famed for his1924 monograph *Solubility* (later editions: *Solubility of Non-Electrolytes*) that became the classic reference for almost a half century, was born in 1881; the Hildebrand solubility parameter carries his name.

18 ***George Wald***, the American biochemist who received (with Granit) the 1967 Nobel Prize for Physiology or Medicine for his work on the chemistry of vision disclosing the presence of Vitamin A in the retina of the eye, was born in 1906.

Walther Hermann Nernst, the German scientist and one of the founders of modern physical chemistry who in 1889 devised his theory of electric potential and conduction of electrolytic solutions (the Nernst Equation) and introduced the *solubility product* to explain precipitation reactions, died in 1941.

19 ***Yuan T. Lee***, the Taiwanese-American chemist who shared (with Herschbach and Polanyi) the 1986 Nobel Prize for Chemistry for his role in the development of chemical reaction dynamics, has his 80th birthday today.

21 ***Nicolas Clement-Desormes***, the French chemist who collaborated with his subsequent son-in-law Charles-Bernard Desormes in the exact determination of the composition of carbon monoxide and carbon disulfide died 175 years ago in 1841.

22 Sir ***Hans Adolf Krebs***, the German-born British biochemist who (with Lipmann) gained the 1953 Nobel Prize for Physiology or Medicine for the discovery in living organisms of the series of chemical reactions known as the tricarboxylic acid cycle (the Krebs cycle), died in 1981.

24 ***Robert L. Banks***, the American chemist who co-discovered crystalline polypropylene polymer with J. Paul Hogan working for Phillips Petroleum in 1946, was born in 1921.

26 ***David Shemin***, the American biochemist who pioneered the use of radioactive and stable isotopes to trace chemical pathways by which the body creates its own materials and discovered the metabolic pathway by which the cell synthesises heme, vitamin B-12 and related compounds, died 25 years ago today.

In 1801, ***Charles Hatchett*** announced to the Royal Society in London that he had discovered a new element he named columbium (Cb) from analysis of a piece of columbite, a black mineral from New England. Hachett discovered that it contained a "new earth" which implied the existence of a detectable but non-isolable new element. Rediscovered 40 years later by German chemist, Heinrich Rose, it is now called niobium.

27 ***Anders Celsius***, the Swedish astronomer famed for the temperature scale he developed (see December 25 below), was born in 1701.

28 ***Dieudonné Dolomieu***, the French geologist and mineralogist after whom the mineral dolomite was named, died in 1801.

30 ***Smithson Tennant***, the English chemist best known for his discovery of the elements iridium and osmium he found in the residues from the solution of platinum ores in 1803, was born in 1761.

John Mercer, the English chemist and industrialist who invented the mercerisation process for treating cotton, died this day 150 years ago in 1866 (see *this Journal* **2013**, *77*, 26-28 and 82-89).

December

2 ***Isabella Karle***, the American chemist who worked for the United States Naval Research Laboratory and whose *Symbolic Addition Procedure* has become the method of choice for structure determination from X-ray diffraction data on crystalline materials, even in computerised programs, was born in 1921 and has her 95th birthday today.

4 ***Benjamin Silliman*** Jr., the American chemist whose report on the potential uses of crude oil products gave impetus to plans for drilling the first producing oil well, near Titusville, PA., was born 100 years ago today.

5 ***Werner Heisenberg***, the German physicist and philosopher who discovered a way to formulate quantum mechanics in terms of matrices and after whom the principle is named, was born in 1901.

Carl Cori, the American biochemist who, with his wife Gerty, discovered a phosphate-containing form of the simple sugar glucose, and its universal importance to carbohydrate metabolism, was born in 1896.

8 *The* ***coaxial cable*** gained its first US patent this day in 1931.

Harrison Brown, the American geochemist known for his role in isolating plutonium for its use in the first atomic bombs, died in 1986.

9 In 1921, tetraethyl lead was given its first laboratory test as an anti-knock additive to gasoline fuel.

10 ***Alfred Bernhard Nobel***, whose fame needs no explanation, died this day in 1896, 120 years ago. The prizes in Chemistry, Literature, Peace, Physics, and Physiology or Medicine were first awarded in 1901.

In 1801, ***Robert Hare*** (1781-1858) presented to the Chemical Society of Philadelphia his paper, *Memoir of the Supply and Application of the Blow-Pipe* that presented the twenty-year-old scientist's discovery of the intense production of heat with his oxyhydrogen blow-pipe, progenitor of the welding torch.

Melvil Dewey, the American librarian who developed library science in the US with his Dewey decimal classification in 1876 for library cataloguing, was born in 1851.

11 This is the day in 1911 that Marie Curie received her second Nobel Prize and the first person to be awarded a second Nobel Prize (see November 7, above).

12 ***Alfred Werner***, the French-born Swiss chemist whose studies of the structure of coordination compounds brought him the 1913 Nobel Prize for Chemistry for showing that stereochemistry was not just the property of carbon compounds, but was general to the whole of chemistry, was born 150 years ago in 1866.

Eugen Baumann, the German chemist who discovered that the thyroid gland was rich in iodine, not previously known to occur naturally in animal tissue, making the thyroid gland unique in being the only tissue to contain iodine, was born in 1946 (see November 3 above).

13 ***Jean Servais Stas***, the Belgian chemist, notable for his accurate determinations of atomic weights, died this day 125 years ago in 1891.

15 ***Maurice Wilkins***, the New Zealand-born British biophysicist, whose X-ray diffraction studies of DNA with Watson and Crick gave them the 1962 Nobel Prize for Physiology or Medicine, was born 100 years ago today.

16 ***Frederick George Donnan***, the British chemist born in Ceylon whose research contributed to the development of colloid chemistry, died in 1956.

18 Sir ***Joseph John Thomson***, the English physicist who helped revolutionise the knowledge of atomic structure by his discovery of the electron (1897) that gave him the 1906 Nobel Prize for Physics, was born in 1856.

G.N. Lewis coined the word *photon* in a letter published in *Nature* in 1926, when he suggested that it would *seem inappropriate to speak of one of these hypothetical entities as a particle of light, a corpuscle of light, a light quantum, or a light quant, if we are to assume that it spends only a minute fraction of its existence as a carrier of radiant energy, while the rest of the time it remains as an important structural element within the atom*.

20 ***Robert Jemison Van de Graaff***, the American physicist and inventor of the Van de Graaff generator, was born in 1901.

Richard Julius Petri, the German physician and bacteriologist remembered for the Petri dish, died in 1921.

This day in 1951, the first electricity ever generated by atomic power began flowing from the Experimental Breeder Reactor-1 turbine generator when Walter Zinn and his Argonne National Laboratory staff brought it to criticality with a core about the size of a football. After start-up the power gradually increased over several hours. The next day, EBR-1 generated enough electricity to supply all the power for its own building.

23 Sir ***Joseph Henry Gilbert***, the English chemist who as co-director with John Bennet Lawes of the Rothamsted Experimental Station, Hertfordshire, for over 50 years established a premier reputation for research at the first organised agricultural experimental station in the world, died this day in 1901.

Wilhelm Hisinger, the Swedish mineralogist who from one of his iron mines at Bastnäs found a mineral of unusually high density and from which Martin Klaproth and Jöns Berzelius isolated the new element cerium in 1803, was born 250 years ago in 1766.

25 ***Ernst Ruska***, the German electrical engineer who invented the electron microscope, was born this day in 1906.

Adolf Windaus, the German organic chemist awarded the 1928 Nobel Prize for Chemistry for services rendered through his research into the constitution of the sterols and their connection with the vitamins (the first Nobel prize for work in human nutrition), was born on Christmas day in 1876.

Herman Frasch, the German-born American petroleum scientist who invented the Frasch Process for sulfur mining, was born in 1851.

William Gregor, the English clergyman, mineralogist and chemist who discovered the element titanium, contained in a magnetic black sand (now known as ilmenite, $FeTiO_3$), was born in 1761.

Christmas day in 1741 saw the Centigrade temperature scale devised by astronomer ***Anders Celsius*** and incorporated into a Delisle thermometer at Uppsala in Sweden.

26 ***Henry Eyring***, the Mexican-born American theoretical chemist whose primary contribution was in the study of chemical reaction rates and intermediates, died in 1981.

27 ***Percy Gilchrist***, the English metallurgist known for the Thomas-Gilchrist process (1876-77) he developed as assistant to his cousin whereby low-phosphorus steel (Thomas steel) was produced in Bessemer converters and adopted throughout Europe, was born in 1851.

28 In 1931, ***Irene Joliot-Curie*** reported her study of the unusually penetrating and energetic gamma rays released when beryllium was bombarded by alpha particles.

29 ***Charles Macintosh***, the Scottish chemist and inventor who manufactured rubberised cloth used for waterproof clothing, was born 250 years ago today.

30 ***Robert Boyle***, the Anglo-Irish chemist noted for his pioneering experiments on the properties of gases, died this day in 1691.

January

1 ***Edward Joseph Hoffman***, the American biomedical physicist who helped create the PET Scanner (Positron Emission Tomography), has his 75th birthday today.

Alexander Stanley Elmore, the British technologist who with his brother Francis Edward jointly developed the flotation processes to separate valuable ore from worthless rock, was born this day 150 years ago.

Martin Heinrich Klaproth, the German chemist, a founder of analytical chemistry who discovered uranium, zirconium and cerium, and contributed to the identification of others, died this day 200 years ago.

In 1872, the metric system was officially introduced in the German empire.

2 ***Rudolf Clausius***, one of the founders of thermodynamics, was born this day in 1822.

4 Baron ***Louis Bernard Guyton de Morveau***, the French chemist who with Lavoisier and others established a systematic chemical nomenclature to distinguish elements from compounds, and liquified ammonia, was born in 1737.

William Draper, the English-American chemistry pioneer in photochemistry, died this day in 1882 (see this Journal, **2013**, *77*, 136-141).

7 ***Stephen W. Hawking*** has his 75th birthday today.

8 ***Melvin Calvin***, the American biochemist who showed how carbon dioxide is incorporated into green plants gaining the 1961 Nobel Prize for Chemistry, died this day in 1997.

Galileo Galilei died this day 475 years ago in 1642.

9 ***Har Gobind Khorana***, the Indian-born American biochemist who (with Nirenberg and Holley) shared the 1968 Nobel Prize in Physiology or Medicine for their interpretation of the genetic code and its function in protein synthesis, was born this day in 1922.

Bernard le Bovier de Fontenelle, the French science writer whose *Conversations on the Plurality of Worlds* (1686), was one of the first works to present science for the lay reader, died in 1757.

10 Lord ***Alexander R. Todd***, the British biochemist whose studies on the structure and synthesis of nucleotides, nucleosides, and nucleotide coenzymes gave him the 1957 Nobel Prize for Chemistry, died in 1977.

It was this day in 1947 that Stanford University reported the isolation of the polio virus following three years of National Foundation for Infantile Paralysis-funded research.

12 ***Johan August Arfwedson***, the Swedish chemist who discovered lithium in the mineral petalite and died on October 28 (see above), was born this day in 1792.

13 This day in 1942 marks 75 years since Henry Ford's US patent for construction of an automobile using plastic was issued.

14 ***Cato Maximilian Guldberg***, the Norwegian chemist who, with his brother-in-law Peter Waage, formulated the law of mass action, died this day in 1902.

16 ***Anders Gustav Ekeberg***, the Swedish chemist who in 1802 discovered the element tantalum, was born this day 250 years ago in 1767.

American ***Robert Jemison Van de Graaff*** of generator fame was born on December 20 (above) and died this day 50 years ago.

19 ***Carl Graebe***, the German organic chemist who with Carl Liebermann synthesised the orange-red dye alizarin used in the textiles industry that quickly supplanted the natural source from the madder plant, died in 1927.

20 ***Dmitry Ivanovich Mendeleyev***, the noted Russian chemist who developed the periodic classification of the elements, died in 1907.

21 ***Konrad Bloch***, the German-born American biochemist who shared the 1964 Nobel Prize for Physiology or Medicine with Lynen for their discoveries concerning the natural synthesis of cholesterol and of fatty acids, was born in 1912.

It is the day in 1807 that the London Institution received a royal charter from King George III to *promote the diffusion of Science, Literature, and the Arts, by means of Lectures and Experiments, and by easy access to an extensive collection of books, both ancient and modern, in all languages.* The full name in the charter was the *London Institution for the Advancement of Literature and The Diffusion of Useful Knowledge*. Its incorporation came after the Royal Society (1663) and Royal Institution (1800).

Extensions of term for patents in New Zealand – what are they and how will they be affected by the Trans-Pacific Partnership Agreement?

Katherine Hebditch

Baldwins Intellectual Property, PO Box 5999, Wellesley St, Auckland, *katherine.hebditch@baldwins.com*

One of the most controversial aspects of the Trans-Pacific Partnership Agreement (TPPA) was the prospect that New Zealand would be forced into allowing extensions to the term of patents and that this could result in higher prices for medicines. In this article we talk about what patent term extensions are, how they are calculated and compare the present proposals for extensions in New Zealand to other jurisdictions.

What are patent term extensions?

The normal full term of a standard patent is 20 years, although the patent owner has to pay renewal fees to keep the patent alive, so it can lapse earlier.[1]

At the end of its term the patent expires and information in the patent is free to be used by anyone else. This is usually the point at which generic manufacturers will enter the market, unless there are any other patents blocking their way.

Some countries allow extensions to the 20 year term of a patent under certain circumstances. New Zealand is presently not one of them, but to meet the obligations of the TPPA will need to start doing so.

When are extensions allowed?

There are two general types of patent term extensions:

1. An extension allowed because the patent office was slow to examine and grant the patent.
2. An extension allowed for a patent related to a pharmaceutical-type product because regulatory approval must be obtained before the product can be sold.

The first type of extension is partly dependent on the backlog of patent applications waiting to be examined by a patent office and partly dependent on the actions of the patent office examiner and patent applicant during examination. There is usually some form of calculation which will lengthen or shorten the extension based on the actions of each party. In the United States, where there is a long backlog of patent applications waiting to be examined, this type of patent term extension is common and can extend the patent by months or even years.

The second type of extension is dependent on how long it takes for a pharmaceutical product to obtain marketing approval via a country's regulatory process. As a pharmaceutical product cannot be sold until it has the appropriate approvals, e.g. via Medsafe in NZ, patent term extensions are made available to compensate.

The law around how the Intellectual Property Office of New Zealand (IPONZ) will deal with patent term extensions is still being finalised and will only come into effect if the TPPA is ratified by enough countries. However, at the time of writing this article it appears that it will be very difficult to get the first type of extension in New Zealand. This is partly because IPONZ is presently very quick to examine patent applications. It is also partly because in the present proposals for how the extension would be calculated, any periods of time during examination that are outside the direction or control of IPONZ will be discounted from the extension calculation.[2]

The first type of extension would be available for all patents, no matter what the subject matter. The second type of extension is only available for pharmaceutical-type patents. So what is the reasoning behind this special treatment for pharmaceuticals?

Pharmaceutical-type patent extensions

Pharmaceutical-type patent term extensions are generally viewed as a form of compensation for the very prolonged development and regulatory time required to bring a new pharmaceutical to market.

A patent application is generally filed very early in the development process because it must be filed before the invention is made publically available or before anyone else patents the invention.[3] For a simple mechanical type invention, certain industry standards may have to be met, but often the product can be put on the market soon after the patent has been filed. For a pharmaceutical-type product, before it can be put on the market it must get regulatory approval which is usually obtained by showing safety and efficacy through a series of long and expensive trials. Thus a pharmaceutical often cannot be put on the market for several years after the patent is filed. The pharmaceutical-type patent extension is a means to compensate for the delay in being able to sell the product.

For convenience this type of extension is often referred to as pharmaceutical-type extension, but depending on the laws of the country in question, they can apply to other products that require regulatory approval. In the United States, human drug products, animal drug products, medical devices, food additives or colour additives can attract patent term extension. In Australia, a patent term extension is only available for a patent related to a product which is a pharmaceutical substance *per se* or a pharmaceutical substance produced by the use of recombinant DNA technology.

How are pharmaceutical-type patent term extensions calculated in other countries?

Pharmaceutical-type extensions are calculated in different ways in different countries. However, in the main they are calculated based on the difference between (i) the filing date of the patent or the grant date of the patent and (ii) the date of regulatory approval.

For example, in Australia the extension time is calculated as the amount of time between the filing date of the patent and the first regulatory approval, minus five years. In addition, the extension can never exceed five years. For example, if regulatory approval was granted 8 years after the patent was filed, the extension time allowed would be 3 years. The term of the patent would be 23 years but the patent term in which the product can be sold, sometimes called the *effective* patent term, is 15 years.

The extension is to provide additional time during which the patent can be exploited because for a pharmaceutical the *effective* patent term can be short.

How will the pharmaceutical-type extensions be dealt with in New Zealand?

As noted previously, the law around how IPONZ will deal with patent term extensions is still being finalised. However, the present proposals for the new law are that this type of extension will, like Australia, only be available for patents related to a product which is a pharmaceutical substance *per se* or a pharmaceutical substance produced by the use of recombinant DNA technology.

However, the proposals for calculation of the extension are very different to Australia and our larger trading partners. The calculation will be based on compensating for delays by the regulatory body, i.e. Medsafe, in processing the marketing approval rather than the overall length of time for a pharmaceutical to get to market.

The proposals are that an extension will only be available if marketing approval is allowed after the patent is granted and it takes more than 3 years between the date marketing approval is applied for and the date it is granted (or 5 years for the pharmaceutical substance produced by the use of recombinant DNA technology). Any time during the marketing approval process which is considered outside the direction or control of the regulator can also be disregarded for the purposes of calculating the extension. For example, if the applicant is asked by the regulator for more information the time it takes for that information to be supplied will likely not be included in the calculation.

The length of the extension will be the shortest of:

1. The length of time it takes to get marketing approval over the three or five years (minus time periods outside the control of the regulator)
2. The time between grant of the patent and obtaining marketing approval
3. Two years.

In effect, the extension could be a maximum of two years but will likely be much shorter, if allowed at all.

This method of calculating the extension is very different to the way the extensions are calculated in Australia. The proposed New Zealand approach is much closer to the present method used in Singapore, but allows for fewer extensions.[4] It seems likely that using this approach much fewer and shorter extensions will be granted than is the case in Australia, where they are still rare.

If the TPPA is ratified New Zealand will have to allow patent term extensions, but it seems that the proposed options will rarely provide any significant extensions. While the prospect of extensions was controversial, it appears in reality that they are unlikely to have a major effect in New Zealand. Whether the current proposals will meet New Zealand's actual obligations under the TPPA (if it is ratified) is a question that will probably be raised at some point.

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

katherine.hebditch@baldwins.com Patent Proze, Baldwins Intellectual Property, PO Box 5999, Wellesley Street, Auckland

References and notes

1. Renewal fees must be paid to keep a patent in force. If these are not paid the patent will lapse. A patent can also be revoked or surrendered.
2. See Trans-Pacific Partnership Agreement Amendment Bill (Part 8) at: http://www.legislation.govt.nz/bill/government/2016/0133/latest/whole.html and Consultation on Trans-Pacific Partnership Agreement Amendment Bill: Patent Term Extensions – Proposed Regulations: http://www.mbie.govt.nz/info-services/business/intellectual-property/tpp-intellectual-property-chapter/consultation-on-proposed-patent-term-extension-regulations.
3. The invention must be “new” and inventive to gain patent protection. In some countries there is a grace period of usually 6 months to 1 year for disclosure by the inventor.
4. Compare to Singapore Patents Act, Patents Rules 51A(7) and (8).

2016 NZIC salary survey summary

Catherine L. Nicholson

Editor, Chemistry in New Zealand (email: *stevecath.nicholson@xtra.co.nz*)

Introduction

The previous remuneration survey of NZIC members was carried out in 2006.[1] In late 2015 the NZIC Council decided it was timely to survey the membership again to review what had changed – or had not changed – over the past ten years.

The first change was the way in which the survey was conducted. In contrast to the 2006 survey, which was posted out to members, the 2016 survey questionnaire was set up online using SurveyMonkey and the link to it was emailed to 470 financial members of NZIC, excluding those known to be students, retired or otherwise unwaged. The survey was open to respondents from 1-31 March 2016. 145 responses were received, representing a response rate of 31%, down from 38% in 2006. Not all respondents answered every question.

The consumer price index (CPI) increase over the ten year period from the first quarter of 2006 to the first quarter of 2016 was just under 22%.[2] The CPI increase between the first quarters of 2015 and 2016 was 0.4%.[2]

93% of respondents were currently in chemistry-related employment, with 85% reporting that they worked full time (Fig. 1). Two individuals (1.4%) were unemployed with one respondent having been actively seeking work for six months and the other respondent for 18 months.

The industry sectors represented by survey respondents are shown in Fig. 2. As some people worked across more than one sector, the total was over 100%. In the "other" category respondents cited construction, forensics, environmental science, analytical science, defence, food, pharmaceuticals and IT. 44% of respondents worked in the education sector.

12% of respondents had been with their current employer for twelve months or less. Another 12% indicated that they intended to change employer in the next twelve months, with 65% of those citing that their reasons were related, or partly related, to wanting an increase in remuneration.

6% were currently studying for a qualification while 37% held degree-level qualifications in subjects other than chemistry.

The median base salary was $100,000, an increase of 30% from $77,000 in 2006 and well ahead of the consumer price index (CPI) increase of almost 22% from the first quarter of 2006 to the first quarter of 2016. As most respondents did not give a dollar value for any benefits they received in addition to their base salary, remuneration packages could not be quantitatively compared and all figures reported relate only to base salary.

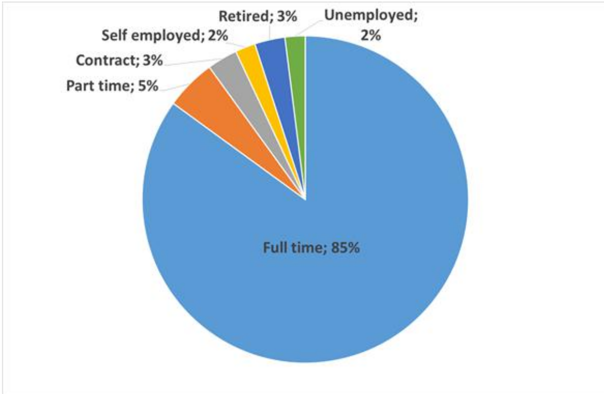


Fig. 1. Employment status of survey respondents

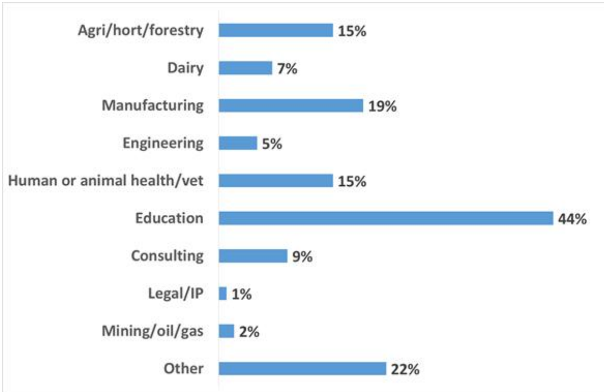


Fig. 2. Industry sectors employing survey respondents

Salary variation by gender

72% of respondents (104 individuals) were male, 28% (41 individuals) were female. The median base salary for men was $111,000, ranging from $30,000 to $250,000. The median base salary for women was $80,000, ranging from $40,000 to $160,000. Fig. 3 compares these gender-based salaries to the overall remuneration levels reported in the 2000, 2006 and 2016 NZIC salary surveys.

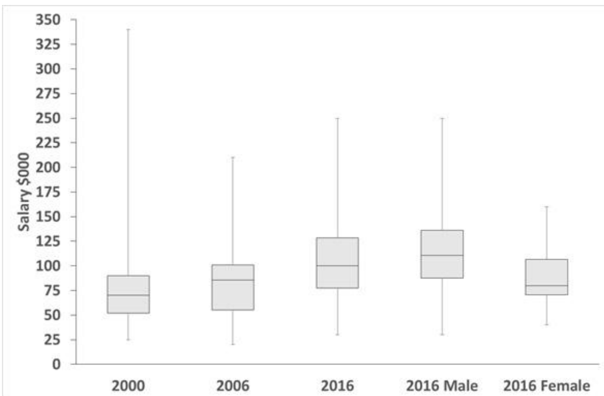


Fig. 3. Box and whisker plot of salaries for men and women in 2016 showing a comparison with overall results from the 2000, 2006 and 2016 NZIC salary surveys

The discrepancy in salary between genders this year had also been noted in the 2006 survey. While the numbers of women participating in both surveys were low, the last survey showed that 23% of women but only 9% of men worked part-time and this was contributing, at least in part, to the substantial gender difference in median salaries. This survey showed that these numbers had remained remarkably similar over the past ten years, with 22% of women and 9% of men being employed in a part-time capacity in 2016.

Of the men who were not employed full-time, just under half were over 60 years of age, semi-retired or fully retired while only one female respondent was retired. To investigate the skewed gender salaries further, the effect of the part-time workers was removed. The median base salary for women working full-time was $99,000, ranging from $49,500 to $160,000.

Although only two male respondents (1.9%) had indicated taking a break of one year from employment during the course of their careers, 16% of female respondents spanning the age range 30-59 reported having been on parental leave at some stage in their career. Interestingly, while these women were all employed full-time, the median base salary for this group was $85,000, 16% lower than the median salary for the full-time women overall. Perhaps this provides some evidence for anecdotal observations that women who take career breaks for family reasons are disadvantaged financially when they return to the workforce. However, a much larger dataset for this group would be required in order to examine this issue in more detail.

Salary variation by age

Fig. 4 shows the age distribution of survey respondents. Just over half of respondents were aged 40-59, with 26% aged 40-49 and 27% aged 50-59. Another 26% were under 40 and the remaining 21% were over 60.

Table 1 shows the median base salary for each age group with data from the 2006 survey included for comparison. Since only two individuals in the age group > 69 provided salary details, this age group is not shown in the table.

In 2006, respondents in their 50s had the highest median salaries. Ten years later this had shifted quite dramatically to the 60-69 age group who were now enjoying the highest earnings. This may at least in part be due to the highest earners in 2006 carrying their salaries into their 60s a decade later. The 60-69 age group was composed predominantly of men (96%) holding PhDs (87%). The increase in base salary over the past decade was well above the CPI increase of 22% across all age groups, including the youngest chemists.

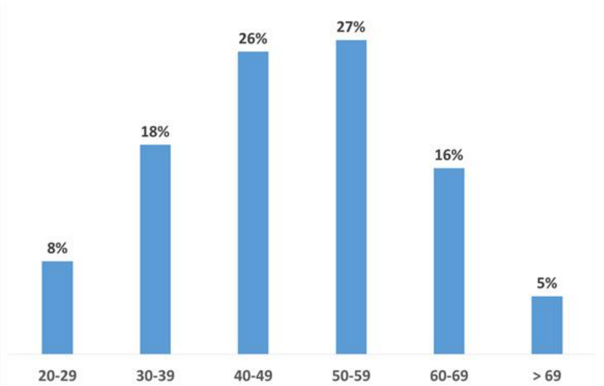


Fig. 4. Age distribution of survey respondents

Table 1. Salary variation by age

Age[3]	Median salary 2016	Median salary 2006	Increase from 2006
20-29	$65,000	$50,000	30%
30-39	$88,000	$60,000	47%
40-49	$110,000	$79,000	40%
50-59	$113,000	$84,000	35%
60-69	$142,000	$82,000	73%
All ages	$100,000	$77,000	30%

Salary variation by highest chemistry qualification

Fig. 5 shows the highest chemistry qualification held by survey respondents. 69% held a PhD, up from 57% in 2006. Table 2 shows the median base salary by qualification with data from the 2006 survey included for comparison. Since the NZCS data comprised only three individuals who worked both part and full-time, a median salary for this group was meaningless and is therefore not shown in the table.

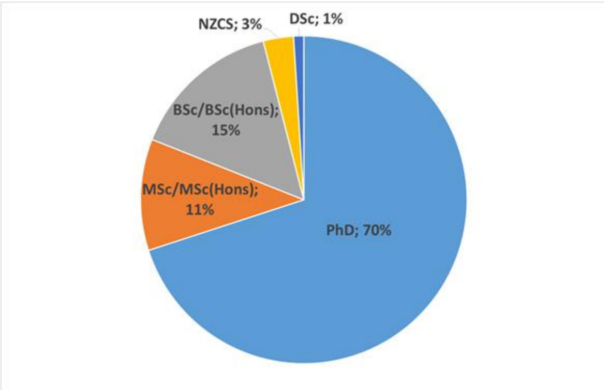


Fig. 5. Highest chemistry qualification held by survey respondents

Table 2. Salary variation by highest chemistry qualification

Qualification	Median salary 2016	Median salary 2006	Increase from 2006
BSc & BSc Hons	$75,000	$62,000	21%
MSc & MSc Hons	$78,000	$60,000	30%
PhD	$112,000	$84,000	33%

In this survey there was a minimal increase in base salary from BSc to MSc level but a 44% increase to PhD level. The 21% increase in salary from 2006 for those with a BSc was just below the CPI increase over the same period but postgraduates with an MSc or PhD did better with 30% and 33% salary increases respectively.

Salary variation by region

As shown in Fig. 6, 79% of respondents lived in the North Island, 20% in the South Island and two individuals were based overseas. In 2013 approximately 76% of the New Zealand population lived in the North Island and 24% in the South Island.[4] This represents a shift from ten years ago when the split of respondents between the islands was 70% North Island and 30% South Island, reflecting the demographics in 2006.

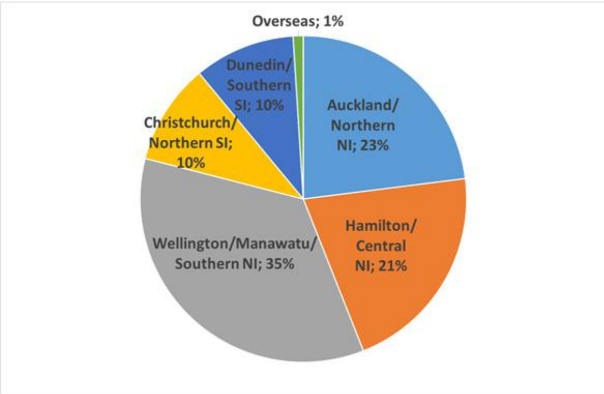


Fig. 6. Location of survey respondents

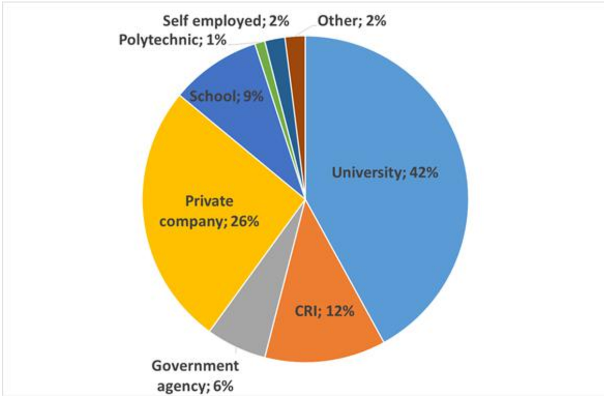


Fig. 7. Employment sectors of survey respondents

Table 3 shows median base salary by location of respondents. The regional split was different between surveys so a direct comparison between the two was not possible. In 2006, Christchurch had the lowest and Dunedin the highest salaries and this has remained the case a decade on. In the 2006 survey it was suggested that a possible reason for the low ranking of Christchurch was its relatively high proportion of part-time workers. This was not borne out in the current survey as 20% of respondents in Dunedin worked part-time compared to 14% in Christchurch.

Table 3. Salary variation by region

Region	Median salary
Auckland / Northern NI	$99,000
Hamilton / Central NI	$95,000
Wellington / Southern NI	$105,500
Christchurch / Northern SI	$88,000
Dunedin / Southern SI	$126,000

Salary variation by sector

The distribution of the chemistry workforce by sector is shown in Fig. 7. 42% of respondents worked in a university.

Table 4 shows that in 2016 the government sector overtook universities as having the highest paid employees. Private companies, CRIs and schools retained the same ranking as in the previous decade. CRIs and schools slightly lagged the CPI increase with 20% and 21% increases in salaries respectively while university salaries have increased by 29% and government salaries by 36% since 2006.

Table 4. Salary variation by sector

Sector	Median salary 2016	Median salary 2006	Increase since 2006
University	$116,000	$90,000	29%
Government	$120,000	$88,500	36%
Private	$95,000	$78,000	22%
CRI	$90,000	$75,000	20%
School	$73,500	$60,500	21%

Salary variation by job function

Fig. 8 shows the range of job functions reported by survey respondents. In the "other" category respondents were involved in customer/client services, intellectual property, technical assistance in schools, scientific literature activities and certification of hazardous substances. As many respondents had more than one main job function, the percentage over all categories is more than 100%. Almost one third of respondents were involved in the combined teaching and research category.

Table 5 shows salary variation by job function. To aid comparison with 2006 data, jobs that involved administration, management, sales or marketing were similarly broadly labelled as desk work. Those involving lab testing and R&D were broadly labelled as bench work. Separate categories were maintained for teaching only and for teaching & research. Data from respondents who indicated they had responsibility for several job functions spanning multiple categories were excluded from the analysis.

Table 6. Median base salaries of other professions in NZ

Profession	Reference source	Year	Median base salary
Chemist	NZIC salary survey	2016	$100,000
Engineer: Civil	IPENZ remuneration survey[5]	2015	$81,000
Engineer: Structural			$80,000
Lawyer:[6] large private practice	NZ Law Society & Hays legal salary guide[6]	2015	$144,000
medium private practice			$102,000
small private practice			$83,000
in-house corporate			$145,000
in-house government			$132,000
GP	RNZCGP workforce survey[7]	2015	$126,000 - $150,000
Accountant	NZICA remuneration survey[8]	2015	$144,119

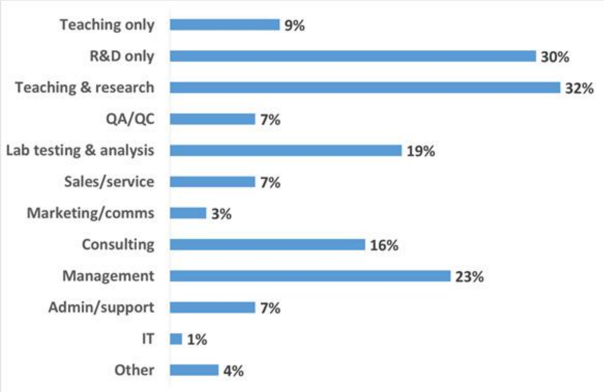


Fig. 8. Job functions of survey respondents

Table 5. Salary variation by job function

Job function	Median salary 2016	Median salary 2006	Increase since 2006
Teaching & research	$126,000	$93,000	35%
Desk	$130,000	$84,000	55%
Bench	$87,500	$71,000	23%
Teaching only	$74,500	$60,500	14%

In 2016 desk work had overtaken teaching & research as the highest paid category with a substantial 55% increase in pay since 2006. Bench work pay was slightly above the CPI increase at 23% while teaching & research increased by 35%. Those involved only in teaching received a substantially lower increase of 14%.

Promotions and changes in employer or position description

One quarter of all respondents received a promotion in the previous twelve months, up from less than a fifth reported in 2006. Of those promoted, 94% received an associated pay increase, the median increase being 4.1%. The CPI increase between the first quarters of 2015 and 2016 was just 0.4% in comparison. In 2006, 78% of respondents received a median salary increase of 5% with their promotion.

9% of had respondents changed employers in the previous year. 77% of these employees (44% in 2006) received a median increase of 4.2%.

19% of respondents had a change in position description without a change in employment. Almost three quarters of these employees received a median salary increase of 12% (compared to just under half of these employees receiving a median increase of 7% in 2006), almost three times the increase associated with a promotion in the same job or a change of employer.

Benefits

As noted in the introduction, respondents did not generally assign a dollar value to any benefits associated with their employment. Nevertheless, of those currently employed, 85% received at least one benefit, up from 57% a decade ago. Unsurprisingly, superannuation / kiwisaver topped the list of benefits with 92% of respondents receiving this, most likely related to the introduction of Kiwisaver on 1 July 2007. Other common benefits included health insurance, performance bonuses and a car or car allowance. Commission, overtime, income protection insurance and life insurance were among the less common benefits reported by several individuals.

Training and professional development

81% of respondents received training of some type in the previous year, up from 65% ten years ago, with 68% of these people having attended a conference. Of the latter, 71% had attended a second conference or had been given other training, up from 29% ten years ago.

Fair pay and unpaid public good work

In response to the question, *In your current employment, do you feel that the total remuneration for your job fairly reflects your qualifications, skills and experience?* 69% of respondents said yes and 31% said no. It was very interesting to note that the median base salaries for these two groups were almost identical, with those who said they were paid fairly receiving a median salary of $101,000 and those who did not feel that they were paid fairly receiving a median salary of $100,000.

In response to the question, *During the course of your career have you undertaken tasks you consider to be "science/public community good" work, additional to your formal job responsibilities, for which you have been unpaid?* 70% of respondents said yes and 30% said no.

Remuneration levels of other professions in New Zealand

It is very difficult to directly compare salaries across different professions since there are a wide range of variables which influence remuneration and hence very wide salary ranges are reported. Table 6 shows indicative remuneration levels for engineers, lawyers, doctors and accountants in comparison to chemists in New Zealand.

Optimism about chemistry-related employment in New Zealand

In response to the question, *Overall, do you feel optimistic/positive about chemistry-related job opportunities in New Zealand?* respondents were fairly evenly split, with 36% saying yes, 39% saying no and 25% saying they did not know. This question prompted a range of responses as reproduced below (some comments have been edited for length / clarity).

- Although my job is great and a good use of my skills and degree, I don't see a lot of good chemistry jobs in NZ outside of CRIs, universities or government. This may change (or be changing) but I have yet to see some of these small companies take off.
- The Government, as a primary employer of chemistry graduates, is passively allowing a sinking lid of chemistry (and physics) employment across all of its agencies. There is little scope for young chemistry graduates to take up a chemistry-aligned career while MBIE funding processes are so underfunded and so unstable.

- Science employment and funding seems to be shrinking in NZ. Many of my colleagues have lost their jobs and are struggling to find new jobs.
- The competitive government system within CRIs doesn't lead to any certainty in continuity of employment for young scientists. So no, I am not encouraging when asked about recommending science as a career option for young people.
- Research funding is too complex, involves too much admin and not enough actual research funding.
- I feel that for all the people who are undertaking science-based study there is a significant lack of jobs for recent graduates and there is also a decreasing number of science roles for people with advanced degrees. A PhD can seriously hamper job opportunities as you're seen as over qualified for a lot of jobs!
- Neutral at the moment. Could be worse could be a lot better.
- Severe age-related discrimination appears to exist, particularly with recruiters. Chemists over 50 seem to be unemployable.
- Very hard to get a chemistry academic position if you don't know the right people, politics play a major factor. Research funding is hard to obtain for 'unprecedented' work, with more funding going to (for want of a better word) derivative or safer option proposals. However, nothing exciting comes from walking the same path that has been walked many times before you.
- There does not appear to be many opportunities for development chemists in New Zealand. Most interesting development work seems to take place overseas, with the results provided to local companies.
- Only in certain fields. Dairy is always reliable but fields like renewable energy not so.
- A PhD more or less condemns students to go overseas. The best degree for employment in NZ is the 240 point MSc Hons. Most of our graduates get chemistry-related jobs.
- Not particularly optimistic - there seems to be sparingly few jobs for a much larger number of graduates.
- I have a son completing an MSc. Not many job opportunities available in NZ.
- It depends on the area and job type. Analytical chemistry jobs are common, especially in agriculture-related areas. Pharmaceutical chemistry appears to be doing reasonably well funding-wise. R & D chemistry jobs in other areas are rare in NZ, especially for postdoctoral-level positions. From what I can gather, one university in Australia might be offering more "contestable, bring your own project/ideas" type postdoctoral positions each year than the whole of NZ combined.
- As a profession we could benefit from more chemistry-related careers being available in NZ. However, there are a surprising number of chemistry-related jobs for those who are prepared to look for them.
- Too much pressure on performance and commercialisation.
- There are probably limited opportunities, and so the trend of moving from graduate-level science roles to careers in other professions and/or management is likely to continue.
- I do enjoy my job with all of its challenges. But I also know that if I wanted to leave that there are very few alternative chemistry job options available in NZ.
- These are very few and at relatively low levels. Students graduating with chemistry degrees have little prospect of finding such employment in NZ.
- Given the lack of a "chemical industry" in NZ, I believe many of our graduates (and myself) find it disappointing that they cannot find employment, other than for a rare and fortunate few, in their given discipline. Most end up in other areas.
- There is still the challenge of chemists being relatively poorly paid compared to other professions (not speaking of my personal circumstances).
- I think opportunities are declining overall, but my organisation is currently hiring. However, the quality of people applying is low and invariably those New Zealanders applying are overlooked in preference to overseas applicants.
- So long as NZ companies plough profits into dividends (and extravagant salaries for CEOs) and not into R&D and into growing the value of the company, prospects for increased employment of scientists in general and chemists in particular, at levels commensurate with qualifications remain incompatible with a first world technologically advanced country.
- Opportunities and funding are limited. There seem to be more opportunities overseas, at least for PhDs in chemistry. Analytical chemistry seems to be the only occupation which offers much in the way of jobs in NZ.
- Science needs promotion in NZ. Science job security in government needs more improvement for long-term movement of graduates into science in NZ. In general I believe permanent positions should be really permanent in the sense of not dependent on getting funding for projects within the work. Funding sources in NZ are relatively few. There should be less time spent on applying for funding and more on doing work with agreed and continually refreshed, appropriate aims.
- More personally optimistic for a continuing chemistry career now that I am permanent. Very, very worried for younger chemists making the transition from PhD/postdoctoral to relatively secure salaried positions.
- Research funding has been shrinking in real terms and the rearrangement of funding pools/non peer-reviewed applications via MBIE has made obtaining funding more difficult.

Concluding remarks

The final question in the survey was optional and asked respondents for any further comments that they wished to make. Once again there was a range of opinions expressed and it is perhaps fitting that the concluding remarks on the 2016 salary survey are left to the respondents themselves (some comments have been edited for length/clarity).

- I do have a worry that our postgraduate chemistry schools are dominated by offshore students who we (NZ) fund to do their degrees at the expense of sustaining or growing capability in CRIs. Such money is wasted as the majority of these students will leave NZ after completion because they cannot get jobs here or they wish to return home.
- I always advise people not to get involved in science/R&D because the pay is not good enough.
- There is a small but steady chemistry work community. I am very up-beat that there will be a growing groundswell in the biotech and high value manufacturing chemistry related industries. Furthermore, I hope that the increased environmental pressure on agri-chemicals and industrial commodities will see new chemical science being required to fill this gap. International legislation is making this increasingly prescriptive but hopefully the NZ science and regulatory environment will provide enough leeway to introduce new commodities and products into the market derived from new NZ-invented chemistry.
- Since the 1980s the salaries, career stability and employability of chemists in NZ have all declined. This needs urgent attention!
- NZ is a small country with finite funding sources and it is often the case that research proposals and job applications are judged by people who (for better or worse) already know you. Double blind processes would be very useful and would eliminate or help to mitigate the effect of prejudice in decision-making processes.
- In days gone by, many manufacturing companies employed technical specialists. However, it now seems that most chemical development work is outsourced to other places rather than having expertise in-house. This is good for the external parties but leaves the company in a weaker position as they become increasingly reliant on offered technology and ultimately risk losing control of their technical knowledge.
- There are very few opportunities for chemistry graduates in NZ, especially for those who have a terminal degree. I have been unemployed for more than three years since I arrived in NZ and many employers are reluctant to hire those who possess postgraduate qualifications. Further, many are underemployed and also many chemists change their career paths since graduating from college or arriving in NZ.
- It's rough in NZ, it's rough elsewhere. Looking forward to retirement that will not be as cosy as it might have been had I followed $$ instead of heart.
- My salary is exceptional and not standard in NZ.
- My employer provides zero transparency around its salary bands so staff have no way of knowing whether working harder would be worth it financially. A recent NBR article covers the issue well: http://www.nbr.co.nz/article/most-people-have-no-idea-whether-they%E2%80%99re-paid-fairly-h-p-185191
- I may have missed it but I think it would be good to pull out skills and experience more in this survey – I think there is a mismatch in what many employers are prepared to pay compared to chemistry skills and experience offered by employees. Equally, this could be applied to recent graduates.
- The bulk of my work is international consulting but based from NZ. I choose to live in NZ.
- Glad you are coordinating a refresh of science related jobs in NZ to assist science in NZ.
- Chemistry related jobs are now so diverse in nature that it is hard to categorise, eg food industry, biochemistry, wince, beer, recruitment, operations, process engineering, etc.
- There seems to be growing momentum in the (bio) technology/chemistry sector and the relevance of academia-industry partnerships. Despite this, there are no obvious mechanisms for turning this into building a sustainable technology/chemistry sector in NZ, including the creation of long-term jobs for skilled people. There seems to be a worrying subjugation of chemistry to a supporting facet of multidisciplinary efforts, instead of an equal partner.

Acknowledgements

Thanks go to Ian Brown, Michael Burgess, Paul Plieger and Richard Rendle for critiquing, refining and testing the salary questionnaire and to all of the respondents who took the time to participate in the survey.

References and notes

1. 2006 NZIC salary survey summary, *Chem NZ*, Oct 2006, 93-97.
2. Statistics New Zealand, CPI data updated 18 July 2016, www.stats.govt.nz.
3. Categories differ slightly between the 2016 and 2006 surveys.
4. Statistics New Zealand, 2013 census data, www.stats.govt.nz.
5. IPENZ remuneration survey snapshot 2015: https://ipenzproduction.blob.core.windows.net/cms-library/docs/default-source/news-publication/remuneration-survey/ipenzremsurvey-snapshot2015-lr.pdf?sfvrsn=4 (accessed 19/08/16).
6. NZ Law Society & Hays legal salary guide 2015. Data shown for lawyers with 10+ years of post-qualifying experience: http://www.lawsociety.org.nz/__data/assets/pdf_file/0005/90635/NZLS-Salary-Guide-2015-Final-Version.pdf (accessed 19/08/16).
7. Royal New Zealand College of General Practitioners workforce survey results 2015, summarised on nzDoctor.co.nz: http://www.nzdoctor.co.nz/in-print/2016/march-2016/16-march-2016/up-and-downs-in-earnings-for-gps-on-salary-or-contract-latest-figures-from-mas.aspx (accessed 19/08/16).
8. Chartered Accountants Australia and New Zealand, 2015 New Zealand remuneration survey: http://www.nzica.com/Resources-and-benefits/Remuneration-Survey/Results-2015.aspx (accessed 19/08/16).

Author Index for *Chemistry in New Zealand*, Vol. 80, 2016

Subject Index for *Chemistry in New Zealand*, Vol. 80, 2016