Chemistry in New Zealand

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Articles and Features

Other Columns

Comment from the President

In June, I attended the opening function and some of the proceedings of a meeting of the Organising Committee of Pacifichem 2015 in Queenstown. This was the first meeting of the Pacifichem Organising Committee ever to be held in New Zealand and the New Zealand Institute of Chemistry was nominally the host. I very much enjoyed meeting the members of the committee who represent many of the countries of the Pacific basin. The task for the committee to achieve at this meeting was to review and select proposals for the technical program of Pacifichem 2015. My brief encounter with this process gave me a real insight into what a huge task this is and it is clear that a quality program will result from this process. Mark Waterland, the New Zealand representative on this committee, and representatives of the American Chemical Society are to be congratulated on arranging a very successful meeting which also showcased a beautiful part of our country to the international committee.

The NZIC prizes for 2014 were awarded as follows:

Prize for Chemical Science: Dr Peter Tyler, Ferrier Research Institute

Shimadzu Prize for Industrial and Applied Chemistry: Dr Bradley Williams, Ferrier Research Institute

ABA Books Denis Hogan Chemical Education Prize: Dr Suzanne Boniface, Victoria University of Wellington

Members elected to Fellows of NZIC:

Dr Paul Benjes, Callaghan Innovation Research Ltd (Glycosyn)

Dr Gavin Painter, Ferrier Research Institute

Dr James Crowley, University of Otago

Ms Jennifer Mason, Ferrier Research Institute

Dr Phillip Rendle, Ferrier Research Institute

Congratulations to all prize winners and new Fellows of the Institute.

Here at Waikato, we recently held the annual Analytical Chemistry competition for Year 13 students. It is a real pleasure to see the excellent practical results that some of these young analysts can achieve and the beautifully laid out and accurate calculations that the very best teams manage. All teams enjoyed the day and it is a wonderful chance for students and their teachers alike to meet University staff and in some cases, actually get some quality "hands-on" time with equipment that is not always readily available in their school. Our local branch sponsors this event and it events such as these that serve to highlight one of the functions of NZIC - encouraging and supporting future chemists!

On that note, this year, NZIC Chemical Education Trust Grants were made to the following schools: Garin College, Sacred Heart College (New Plymouth), Freyberg High School, St Joseph's Maori Girls' College, Waitaki Girls' High School, Hastings Girls' High School, East Otago High School, Kings High School, John Paul II College (Greymouth), St Mary's Diocesan School, Dunstan High School and Te Awamutu College. These grants were for the purchase of additional resources such as glassware, instruments and molecular models to enhance the teaching of chemistry and were up to $400 in value. I would like to encourage members to consider making a contribution to the Trust. Most of the Trust's funds arise from members adding a small donation (often between $10 and $50) to their annual subscription. All donations to the Trust are tax deductible.

Finally, at the time of writing I have completed a very enjoyable visit to the Auckland Branch and have arranged my visits to the rest of the branches in the near future, so look forward to meeting many of you then.

From the Editor

Thanks again to those of you who responded to the reader survey. The results are summarised on page 179. With such a diverse readership ranging from students to retirees, academics to industrial chemists and with the subject interests of members crossing every chemical field, there will always be conflicting views on what constitutes a relevant and interesting publication. Given the response rate of a little over 10%, the results can hardly be considered to be comprehensive. However, there were a number of points which came through quite clearly.

First and foremost, *Chemistry in New Zealand* is valued primarily as a way for members to keep in touch with what is happening throughout the country. The majority of respondents consider the journal to be relevant to them and feel that it helps them engage with NZIC. So, not surprisingly, the survey also showed that the Branch news section is considered to be very important to the majority of readers. The scientific articles got more of a mixed reception, with quite a number of comments relating to the issue of articles being too academic or technical.

Several respondents raised the question of whether we should move from a printed to an online publication. The addition of more photos, more colour and a more up to date look and feel to freshen up the journal were also requested. Contributions from sources other than the regular columnists, personal profiles and coverage of global chemistry issues were additional suggestions.

For a publication such as ours which has a limited budget and relies almost exclusively on voluntary contributions, there will always be constraints on what we can do. For example, colour printing is more expensive, special issues or topics require enthusiastic authors who are prepared to write articles and moving to an online publication would exclude some members and require additional resources. Nevertheless, I think we have gathered some useful feedback and suggestions that can be discussed with Council. Watch this space.

New Zealand Institute of Chemistry

Membership update

New Members 2013-2014 (MNZIC)

Auckland Branch*:* *Amir* ***Ali***, Al-Madinah School; *Daniel* ***Carleton***, Grayson Laboratories; *Alex* ***George***, *Kapish* ***Gobindlal***, AUT; *Chhaya* ***Narayan***, Elim Christian College; Mr *Peter* ***Skrine***, Kaitaia College; Dr *Christian* ***Miller***, Prof *Kevin* ***Smith***, University of Auckland; *Dwayne* ***Walsh***, Taipa Area School; *ZhengXi* ***Zhang***, Ballance Agri-nutrients

Waikato Branch: *Jasmine* ***Ahmu***, Huntly College; *Sandhya* ***Coll***, Westmount School; Dr *Laura G* ***Raymond***, Scion; *Michael* **Blackstock**, Whangamata Area School

Manawatu Branch: *Jon* ***Hawkins***, New Plymouth Boys' High School; Dr *Kevin* ***Kannan***, Nga Tawa Diocesan School; Dr *Ajay* ***Pannu***, Massey University; *Denise* ***Pester***, Tararua College; *Christopher* ***Rowse***, Zelam Agricultural Chemicals

Wellington Branch: *Bruce* ***Anderson***, Otaki College; Dr *John* ***Beal***, *Andrew* ***Durant***, Callaghan Innovation Research Ltd.; Dr *J. Robin* ***Fulton***, Dr *Martyn and* Dr *David* ***Herman*** all Victoria University; *Paul* ***Falloon***, Hutt International Boys' School; Dr *Hilary* ***Hamnett***, ESR; *David* ***Koedyk***, Baldwin Shelston Waters; Dr *Ashna* ***Khan***, Dr *Karl* ***Shaffer*** and Dr *Olga* ***Zubkova*** all Ferrier Research Institute; Dr *Ying (Sherry)* ***Xu***, CRL Energy Ltd.

Canterbury Branch: Prof *Alison* ***Downard***, University of Canterbury; *Leigh-Anne* ***Mansell***, Aoraki Polytech; Dr *Antonia* ***Miller***, Dr *Michael* ***Steward***, *Dion* ***Thompson*** and *Campbell* ***McNicoll*** all Callaghan Innovation Research Ltd.

Otago Branch: Dr *Humphrey* ***Feltham***, Prof *Russell* ***Frew***, Dr *Allan* ***Gamble***, Dr *Robert* ***van Hale***, Dr *John* ***van Klink***, Dr *Andrea* ***Vernall***, Dr *Shaliesh* **Goswami** and Dr *Jaydee* ***Cabral*** all University of Otago; *Jean* ***Wilson***, Northern Southland College; *Rui* ***Li***, South Otago High School

Overseas: Dr *Seino* ***Jongkees***, Japan

Student members

Auckland Branch: *Omer J* ***Chaudhary***, *Gaya H* ***De Zoysa***, *Andrew S* ***Eastabrook***, *Hugo Ka Ho* ***Fong***, *Mario* ***Kurbanik***, *Nelson* ***Lam***, *Katie* ***Lim***, *Ashley C* ***Lindsay***, *Bowen* ***Liu*** *Stefanie* ***Maslek***, *Rachelle* ***Quach***, *Matthew* ***Sullivan***, *Aaron* ***Tay***, *Alex* ***Anthony Samy***, *Homayon* ***Arabshahi,*** *Sandhya* ***Badrinarayanan***, *Alan* ***Cameron***, *Ravind* ***Chandra***, *Daniel* ***Chorley***, *Shama* ***Dissanayake***, *Morgan* ***Jay-Smith***, *Sarah* ***Ngen*** and *Xindi (Andy)* ***Wang*** all University of Auckland

Waikato Branch: *Kethsiri* ***Alwis***, *Dylan* ***McQuiston***, *Daniel* ***Rohrlach***, *Nicholas* ***Kuan*** and *Onyekachi* ***Raymond*** all University of Waikato

Manawatu Branch: *D Nirosha T* ***de Silva***, *Lujia (Luke)* ***Liu***, *Kelsey* ***Mortensen***, *David* ***Nixon***, *Christopher* ***Lepper*** and *Edwin* ***Lowe*** all Massey University

Wellington Branch: *Lucy Olivia* ***Gloag***, *Leah* ***Graham***, *Nina* ***Leeb***, *Andrew* ***McGrath***, *Kristiana* ***Santoso***, *Kalpani* ***Somarathne***, *Rosie* ***Somerville***, *Thomas* ***Bevan***, *Valentine* ***Chan***, *Christoph* ***Hasenoehri***, *Alex* ***Hunt-Painter***, *Stefan* ***Munneke*** and *Lia* ***van den Kerkhof*** all Victoria University

Canterbury Branch: *Carline* ***Bakker***, *Jennifer* ***Crowther***, *Chaminda* ***Jayasinghe***, *Siji* ***Rajan***, *Robert* ***Staniland***, *David* ***Young***, *Anna K* ***Farquhar***, *Nathaniel* ***Gunby***, *William* ***Kerr***, *David* ***Lim***, *Vivek* ***Poonthiyl*** and *Shane* ***Verma*** all University of Canterbury; *Tony* ***Bird*** and *Cameron* ***Wells*** both CPIT

Otago Branch: *Daniel* ***Killeen***, *Tae* ***Kim***, *Reece* ***Miller***, *Casey* ***Davies***, *Daniel* ***Preston*** and *Oliver* ***Watkins*** all University of Otago

Overseas: *Siobhan* ***Bradley***, University of South Australia

Resigned

Auckland Branch: Dr *James (Jim)* ***Mitchell***, *Lynne* ***Forster***, *Andrew* ***Dalebrook***, *Orla* ***Finch***, *Norman* ***Lodge***, *Marsilea* ***Booth*** and *Tim* ***Muller***

Canterbury Branch: *Sarah* ***Wilson-Coutts***, *Francine* ***Smith***, *Matthew* ***Ashworth***, *Paula* ***Rippon***, Mr *Martin* ***Downing***

Manawatu Branch: Dr *Alan Wayne* ***Limmer***, Prof *Geoffrey* ***Malcolm***, Dr *Alan* ***Metson***, *Nessha* ***Wise*** and *Heather* ***Velvin***

Otago Branch: Assoc. Prof. *John Franklin* ***Cutfield*** and *Carolyn* ***McLellan***

Waikato Branch: Dr *Shelley* ***Wilson***, Dr *Graham* ***Saunders***, Dr *Robert* ***Wilcock***, *Jane* ***Spenceley*** and *Hayden* ***Bosgra***

Wellington Branch: *Anna* ***Greaney***, Dr *Neil* ***Whitehead***, *Serena* ***Smalley***, *Alec* ***La Grow,*** *Claire* ***Turner***, *Vidhya,* ***Damodaran***, Dr *Anna* ***De Raadt***, Dr *Alan Geoffrey* ***Clark*** and *Noel Campbell* ***Dowrick***

Overseas: *Russell* ***McQueen***

Deceased

Auckland Branch: Dr *Thomas* ***Sprott***

Wellington Branch: Prof *Robin* ***Ferrier***, *Arthur* ***Wilson***, *John (Peter)* ***Hogg*** and Dr *David* ***Madle***

Canterbury Branch: *Robert* ***Cawley*** and Prof *Bruce* ***Penfold***

Otago Branch: Dr *David* ***Forss***

Oveseas: *Peter* ***Lever-Naylor***

New Zealand Institute of Chemistry

supporting chemical sciences

October News

Auckland

The University of Auckland

The School of Chemical Sciences converged on the Engineering Neon Foyer on July 11 to celebrate the Chemical Sciences Research showcase.

The day began with a welcome address by the Head of School, Professor *Kevin* **Smith** followed by two-minute presentations from first-year PhD students ranging in topics from MRNA-based methods for body fluid and cell type identification, to the role of C_6 compounds and SO_2 in sauvignon blanc wine aroma. Research into antimicrobial peptides (by Gayan) that could become a new tool in the fight against the kiwifruit disease PSA and work aimed at helping to create a "hydrogen economy" (by Zakiya) were amongst the 20 minute presentations by selected senior PhD students on the day. More than 100 projects were showcased by the students at this School's annual event.

Another highlight of the day included the keynote speech by Professor *Simon* **Hall**, an alumnus of the school and a successful businessman. In his talk entitled *Seizing opportunities, having fun and getting paid for it*, Professor Hall spoke about learning how to learn and the realities of academia and his subsequent successful career.

The day culminated with a prizegiving ceremony where guests from Fonterra, Shimadzu, and Fisher and Paykel presented students with awards for their presentations and poster designs. The prizegiving ceremony was followed by a networking 'mixer' organised by the School's Wine Science Programme.

Congratulations to PhD student Daniel Chorley, who was awarded the best poster prize at the 20th International Conference on Organic Synthesis (ICOS-20) in Budapest, Hungary. The prize was sponsored by the Royal Society of Chemistry, UK.

Professor *Margaret* **Brimble** shared career tips with more than 130 secondary school girls when she chaired the inaugural For Girls in Science forum (*www.nzherald.co.nz/nz/news/article.cfm?c_id=1&objectid=11309101*).

Dr *Ivanhoe* **Leung** joined the School of Chemical Sciences on 1 September. Ivan has been at the Department of Chemistry at Oxford, where he obtained both his MChem and DPhil degrees, and where he was subsequently a postdoctoral research as-

Gayan De Zoysa, left, and Zakiya Al-Azri (from *www.nzherald.co.nz/business/news/article.cfm?c_id=3&objectid=11291365* with permission)

Winners of (top) invited PhD student oral presentations Paul Hume, Zakiya Al-Azri, Christina Fullerton and Lisa Strover, and (bottom) two-minute first-year PhD student talks Ravishka Marishi Arthur, Matias Ivan Kinzurik and Xindi Wang with the Head of School Prof Kevin Smith sociate. His research interest lies in the application of NMR spectroscopy to study enzymes. These include mechanistic enzymology, the study of protein-ligand interactions and drug discovery. He is also interested in developing novel methods for ligand screening and quantification, and to apply such methods to screen fragment libraries and combinatorial libraries to aid the design of novel enzyme inhibitors. His goal at Auckland is to create a research group that targets enzyme systems of important biological interest, in particular those that may lead to new therapeutic treatments of diseases.

The New Zealand Institute of Advanced Study (NZIAS), Massey University, Auckland

Al ***Nielson*** attended the 41st International Conference on Coordination Chemistry (ICCC-41) in Singapore at the end of July where he gave an oral presentation on the outcome of deconstructing titanium oxo polymers. He also presented a poster on the synthesis of coordination compounds on computers which is an ongoing research theme at the Albany campus chemistry section where, along with colleagues *Peter* ***Schwerdtfeger*** and *John* ***Harrison*****,** computational chemistry is a major focus. The poster was given 'flash poster' status which required a short oral presentation to be given. Al also chaired one of the conference sessions. On arriving at the hotel adjacent to the Suntec Singapore convention centre there seemed to be all sorts of celebrations going on in the Marina Bay area. It turned out that this was not the way they welcome chemistry conference attendees but merely that it was Singapore National Day.

The Albany campus chemistry section this year ran the first intake of second year students through the BSc programme in chemistry that was introduced in 2013. The point of difference for the Albany BSc degree compared to other chemistry departments in NZ is that in the second and third years, a large teaching component consists of self-directed learning which involves an Oxford style tutorial system. In the advanced organic and inorganic laboratories, students are encouraged to spend as much time as they can to complete a fairly vigorous programme of experiments rather than be confined to a set period such as 3 hours. The computational research focus at the Albany campus is showing up in the degree with computational aspects, including the synthesis of inorganic and organic compounds on computers, being introduced. Students undertaking the Albany BSc degree must include physical chemistry at second and third year level and courses have been developed that facilitate the understanding of physical chemistry aspects where maths may be a problem for some students.

Peter Schwerdtfeger gave a plenary lecture in June at the CMMSE conference in Cadiz (Spain) on the topology of fullerenes and another lecture in July on the problem of simulating liquid mercury at the Chemical Bonding Conference in Kauai (Hawaii). Together with a team of researchers from Berkeley, including a former member of our group, *Andreas* ***Hauser***, he also landed a paper with a cover page on chiral separation in Angewandte Chemie, which made it into the news in Nature Chemistry.

Auckland Cancer Society Research Centre (ACSRC)

The ACSRC was successful in receiving more than $7 million in research grants in the latest Health Research Council (HRC) funding round. The largest grant was for nearly $5 million for a research programme led by radiation biologist and ACSRC Co-Director *Bill* ***Wilson***, looking into developing new prodrugs to combat hypoxia in cancer tumour cells and for investigation into biomarker-guided drug targeting of the tumour microenvironment in radiotherapy. Associate investigators on this grant include chemists *Michael* ***Hay*** and *Moana* ***Tercel.*** In addition, biologist *Adam* ***Patterson***, in collaboration with chemist *Jeff* ***Smaill***, was awarded two project grants for research into tumour necrosis and the silencing of oncogenic signalling in hypoxic tumour cells with the prodrug PR610.

Patrick ***O'Connor*** has been selected as the 2014 recipient of the Cancer Society Auckland "Keith & Meida Hepburn Young Scientist of the Year Award", which is awarded for excellence in cancer research over the preceding five years. Patrick, who joined the ACSRC in 2009, is the first chemist to receive this award, with the previous recipients comprising two biologists and one pharmacologist.

Fourteen members of the ACSRC, including six chemists, gave presentations at the Cancer and Drug Discovery Satellite meeting held in Queenstown on 24 and 25 August, as part of Queenstown Research Week which ran from 23-29 August. The meeting included a special evening session looking at an overview of drug discovery platforms in academic environments, with ACSRC Co-Director *Bill* ***Denny*** being one of the principal discussants.

Canterbury

On 21 August a reprise of *The chemistry of fireworks* was presented by *Anthony* ***Lealand*** of Fireworks Professionals Ltd., in conjunction with the New Zealand Institute of Chemistry (Canterbury Branch) at the University of Canterbury. The event was sold out and the audience oscillated between gasps of delight and asphyxiation courtesy of fumes that pushed the ventilation system to its limits!

The Canterbury-Westland Schools Science and Technology Fair was held on 24-25 August at the Addington Events Centre. The winners of the three NZIC Canterbury prizes (one senior and two junior) were:

Year 11-13

Dacre Herlihy, Lincoln High School

From Juice to Juice ($70)

Year 9-10

Amy Burney, Lincoln High School

The Natural Solution ($70)

Year 7

Cameron Hudson, Cobham Intermediate School

Energetic Energy Cookies ($60)

University of Canterbury

Events

CHEM-pare/COMM-trast exhibition opening

On 3 June the 2014 science communication exhibition was opened in the Edgar Stead Atrium of the Biology Research Building. This collaborative project between students in the Faculties of Science and Art focuses on communications between several different disciplines and the challenges and benefits this represents. The exhibition opening was supported by the local branch of the New Zealand Institute of Chemistry.

Over several weeks in June, Dr *Sarah* ***Masters*** and a merry band of post-graduate students engaged in science outreach (*www.outreach.canterbury.ac.nz*) visiting Burnside Primary School on four occasions to give lectures/demonstrations and an interactive workshop to all their year groups. Sarah and the team also visited Years 1 and 2 of St Margaret's College before Sarah made a brief appearance at Clyde Road Kindercare's preschool room.

On 16 June Professor *Ian* ***Shaw*** talked to all Burnside Year 12 and 13 chemistry students about molecular mimicry. This lecture has become an annual event and was well received.

Visitors

Lydia ***Carson*** and *Rachael* ***Lane*** were welcomed to the Department in July. Lydia will be working in the Department until 21 November. Rachel will be working with *Sally* ***Gaw*** for two months. Lydia completed her Honours year in the Department of Anthropology at Canterbury in 2012. Since then, Lydia has worked as a research assistant in the Department of Anthropology. In one of her projects she helped curate a photographic exhibition of images captured by the people of Canterbury after the 2010/2011 earthquakes (for more information see: http://www.canterbury.ac.nz/platform/2012/exhibitions/index.shtml). Rachael, a visiting EAPSI (East Asia and Pacific Summer Institutes) Fellow funded by the Royal Society of New Zealand and the US National Science Foundation, is working under the advisement of Dr Sally Gaw to determine emerging organic contaminants in storm water. Rachael is a PhD student from the University of Kansas whose primary research goal is to further understanding of organic contaminants in the environment.

Awards

The following students successfully defended their PhD thesis:

David Anderson (Golovko Group)
Rosanna Archer (Kruger Group)
Tammie Cookson (Parker Group)
Sedigheh Ghadamgahi (Marzi) (Golovko Group)
Dmitri Joseph (Parker Group)
Jan-Yves Ruzicka (Golovko Group)

On 16 May *Alison* ***Downard*** received an Honorary Doctorate (Doctor Honoris Causa) from the Universite de Rennes.

Tom ***Cotton*** has been awarded a Herchel Smith Research Scholarship and an Honorary Prince of Wales & C T Taylor Cambridge International Scholarship to pursue a PhD at Cambridge.

Nathaniel ***Gunby*** has been awarded a Todd Foundation Award for Excellence (Universities). Nathaniel used the award to attend the 10th Triennial Congress of the World Association of Theoretical and Computational Chemists (WATOC 2014), Santiago, Chile in October and presented a poster on his research into molecular dynamics simulations of CVD processes. Nathaniel has also been awarded a Lord Rutherford Memorial Research Fellowship for two years. This fellowship was founded by Arthur Sims and Agnes Marion Sims who, in 1941, made provisions for a fund of £10,000 to establish a scholarship to commemorate the late Baron Rutherford of Nelson, a former graduate of the University of Canterbury.

MANAWATU

The Manawatu Branch recently held a tour of the Massey University microbrewery. Along with touring the facilities, attendees were provided with samples of food prepared using the by-products of the brewing process and were able to taste some of the beer made at the facility. At the end of the tour, *Leonie* ***McKenzie*** was presented with the NZIC top 300-level chemistry student prize from last year.

Massey University, Institute of Fundamental Sciences

Nirosha ***De Silva*** and *Paul* ***Plieger*** recently attended the ICCC41 in Singapore. It was the largest ICCC held to date with almost 1100 delegates from 40+ countries presenting in ten parallel lecture streams. Nirosha is now tidying up the last bits of her research and has begun the process of writing her thesis. *Ajay* ***Pannu*** has now completed his two year post-doctoral position and is actively pursuing further employment in New Zealand.

Many staff and students from IFS attended the second Annual FUSSTA (Fundamental Sciences Student Association) Ball at the Palmerston North Convention Centre. The evening was enjoyed by all.

Haidee ***Dykstra*** attended the 2014 International Conference on Raman

Leonie McKenzie receiving her award from Paul Plieger

Spectroscopy in Jena, Germany. The conference was one of the largest in the history of ICORS, with over 900 attendees.

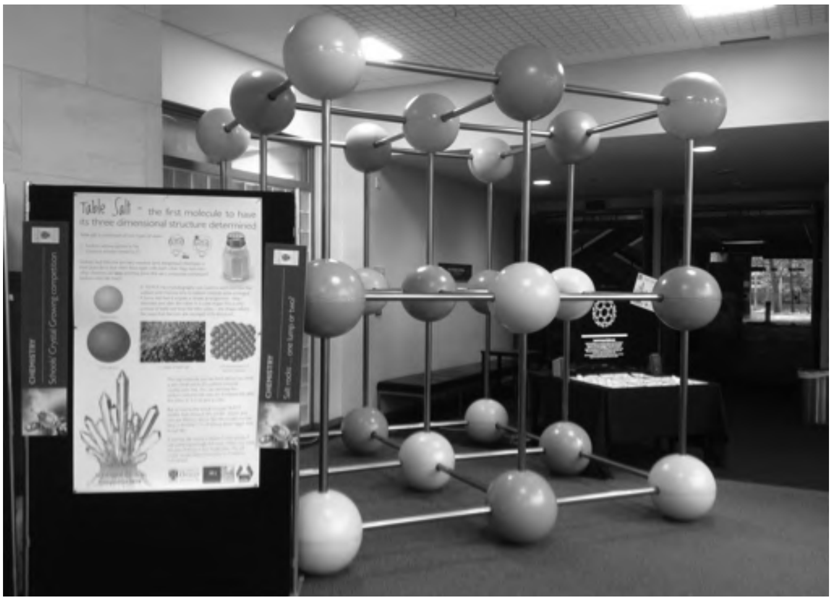
Hui ***Yang*** has joined the Telfer research group as a post-doctoral research fellow. At the start of his time at Massey, he gave a talk on his previous work on metal-organic frameworks. Another recent talk at Massey University was *Jiří* ***Kozelka*** who talked about antitumor platinum complexes and DNA.

OTAGO

To celebrate 2014 being the International Year of Crystallography, the Specialist Education Group of the New Zealand Institute of Chemistry and the Division of Sciences at Otago University organised a National School's Crystal Growing Competition, coordinated by *Dave* ***McMorran***. The competition involved school groups growing crystals of alum (potassium aluminium sulphate) over a set five-week period and then sending their best ones in for judging. School groups could enter in three sections – Junior (Years 7-8), Intermediate (Years 9-10) and Senior (Years 11-13).

After initial responses from more than 140 schools, almost 600 bags of alum were sent out to 83 schools from throughout the country. In many cases students found that growing the crystals was not as easy as they first thought. In the end, 23 schools from around New Zealand sent in a total of 83 crystals for judging. Judging criteria were based on those developed by the Chemical Institute of Canada; crystals were judged on the basis of size, shape and clarity.

The winning crystals in each of the three sections came from Wanganui Collegiate School (Senior), Napier Girls High School (Intermediate) and Peachgrove Intermediate School (Junior). The top crystals from each section were displayed at Dunedin's International Science Festival in early July, along with a series of posters about crystallography and a giant NaCl model (see photo).



A website (*http://neon.otago.ac.nz/outreach/crystals/index.html*) containing information about crystals and crystallography, as well as guidelines for growing crystals of alum, was developed. Full results of the competition can also be found there.

The Aurora Otago Science and Technology Fair was held at the Otago museum at the beginning of August. The Otago Branch of the NZIC has sponsored prizes for many years and this year was no exception. The Branch president *Guy* ***Jameson*** judged and he was very impressed by the quality of the projects covering a very wide area of science. Looking at those projects with a chemical theme, prizes were awarded to the following pupils:

Year 7

Ben Hackfath, "pH of Pines and Paddocks"

Jessie Penhey, "Bubble me Greasy"

Emily Cochrane, "Fluoride an Egg-cellent Protection"

Year 8

Sam Turner, "Natural Hand Cremes"

Amelia Scully, "Don't get in a Lather over Soap"

Christopher Hawkins, "Acid vs Acid"

Year 9

Jake Willmson, "What's the Water"

Year 13

Amy Carruthers and Nanako Shitura, "Analyse ye samples, while ye may"

Associate Professor John Moses from the University of Nottingham gave an excellent seminar on *The application of click chemistry in anticancer drug discovery*" to the local Otago branch of the NZIC on 13 August. A group of members went out for dinner with him that evening where the discussion continued. John has been visiting the University of Otago during August as a William Evans Fellow.

University of Otago, Department of Chemistry

Rob ***Middag*** presented on *The relationships of cadmium and zinc with major nutrients in the Atlantic Ocean* at the 2014 Ocean Sciences Meeting (February 23-28) in Honolulu, Hawaii. He also presented dissolved aluminium data during the GEOTRACES Intermediate Data Product release. During this event the website from which GEOTRACES data and 3D section plots can be downloaded was launched.

Sebastien ***Dhers*** of the Brooker group, along with *Stasi* ***Elliott*** and *Sara* ***Fraser*** of the Gordon group, all successfully defended their PhD theses during June-July. Completing MSc studies with distinction were *Bryce* ***Hoggard*** (Lucas group) and *Tae* ***Kim*** (Lucas & Crowley groups), both graduating at the August ceremony.

Matthias ***Fellner*** of the Jameson group won the student speaker award amongst tough competition at the Oxygen Theme meeting at Christchurch School of Medicine in early

July with a talk titled *A chromogenic assay of substrate depletion by thiol dioxygenases*.

Representing the department in July at the 26th International Conference on Organometallic Chemistry (ICOMC26) in Sapporo, Japan, followed by the 8th Australasian Organometallics Symposium (OZOM8) on Magnetic Island, Australia, were PhD students *Synøve* ***Scottwell*** and *James* ***Wright***. Supported by a NZIC travel grant, Synøve reported on the trip describing the ICOMC conference as "hugely interesting" with "over 1000 attendees, the event was a melting pot of fascinating people and fascinating chemistry", and noted her success in receiving one of the student poster prizes. A highlight of the conference for Synøve and James was being able to meet Nobel laureate Professor Ei-ichi Negishi and celebrate his birthday with him.

James Wright and Synøve Scottwell at ICOMC26 with Prof. Negishi

Two of Nigel Perry's current PhD students presented at overseas conferences recently. *Oliver* ***Watkins*** (co-supervised by Kurt Krause, Biochemistry) gave a talk on his breakthrough: *The unique bioluminescent chemistry of the New Zealand glowworm (Titiwai, Arachnocampa luminosa)* at the 18th International Symposium on Bioluminescence and Chemiluminescence in Uppsala, Sweden. *Daniel* ***Killeen*** (co-supervised by Keith Gordon) presented a poster on his mānuka manipulations: *Herbicidal β-triketones are compartmentalized in mānuka oil glands: localization by Raman microscopy* at the 24th International Conference on Raman Spectroscopy, Jena, Germany.

WAIKATO

NZIC Waikato Branch Analytical Chemistry Competition 2014

This annual event was held on 18 June. 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 24 teams competed in the event.

The task was to analyse a sample of $ZnSO_4.nH_2O$ using a gravimetric procedure for SO_4^{2-} and a volumetric method for Zn^{2+}. 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:

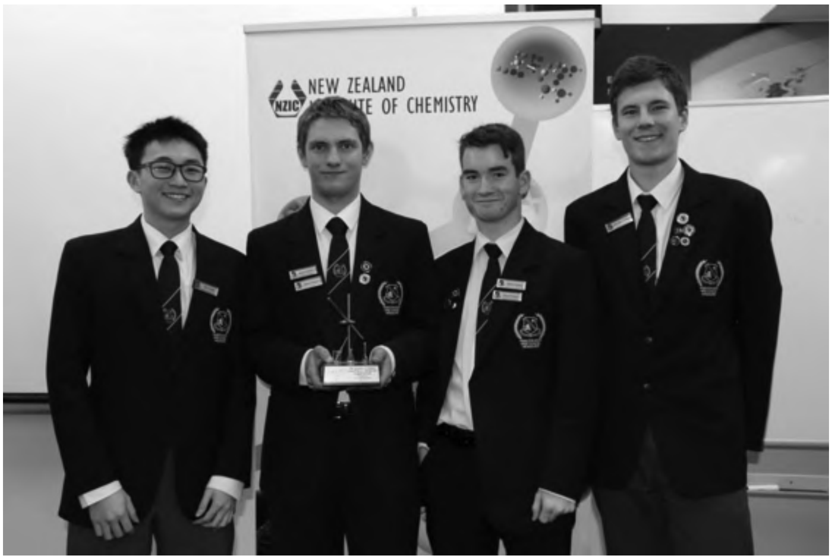
1st Prize: Hamilton Boys' High School 2 (Adam Cameron, Daniel Carson, Nic Portegys, Ben Yeung)

2nd Prize: Hamilton Boys' High School 1 (Alex Hartopeaunu, Ross McDougal, Codi Merito, Andrew Sledger)

3rd Prize: Tauranga Boys' College (Ryan Biggar, Luke Bradshaw, Keith Burnet, Jamie Taylor)

4th Prize: Lynfield College (Boaz Competente, Danielle Lim-Kwan, David Wu, Jessica Yao)

5th Prize: Tauranga Girls' College



The winning team from Hamilton Boys' High School. From left: Ben Yeung, Adam Cameron, Daniel Carson and Nic Portegys.

The Hamilton Boys' High School winning team at work in the laboratory.

(Melanie Duff, Emily McCarthy, Ada Ng, Christine Sutton)

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.

SCION

It is with great sadness that we report the death of Roger Newman who collapsed and died unexpectedly on 26 July 2014. Roger originally worked for the DSIR and later IRL, both based in Lower Hutt, and finally for Scion in Rotorua. A tribute article will appear in a later issue of the journal detailing Roger's considerable contribution to science both within New Zealand and on the global stage.

Hill Laboratories

Hill Laboratories celebrated its 30 year milestone in July. In July 1984 a young Waikato scientist by the name of Roger Hill left a small soil testing laboratory in Cambridge to launch his own business in Hamilton. Roger and his wife Anne's initial business intention, he says, was simply to "have a go" on their own. Yet three decades later the company, well-known nationally and internationally as Hill Laboratories, is the largest privately owned testing laboratory in the whole of New Zealand and has gone from being a solely agriculture-focussed laboratory with two full time staff in Hamilton to an internationally recognised laboratory with three major testing divisions and about 330 staff nationwide. For the first two years following its inception, Hill Laboratories remained solely focussed on agricultural testing. In 1986 it branched into environmental testing, and in 2000 into food and bioanalytical testing. Today, these remain Hill Laboratories' three key testing areas. To accommodate these areas, the company has grown to include four sites in Hamilton and two sites in the South Island; one in Christchurch and one in Blenheim. It also has an office in Japan for overseas samples. The company primarily engages in routine testing for both domestic and international markets. However, emergency testing is also occasionally required, with the Psa kiwifruit crisis and the grounding of the Rena being two cases in point.

Over the years, the success of Hill Laboratories has attracted ownership interest from international parties but Roger intends to keep the business 'home grown'. "We enjoy being an independent privately owned business. We first involved employees in ownership in 1990, and to this day we are 100 per cent owned by people working here. We anticipate remaining this way," he said. "The second person we ever employed, Ron Lindsay, has remained with us for the last 30 years and only resigned this month. This is a very poignant time for Anne and I, and we will miss having him around," he said.

Hill Laboratories founder and managing director Dr Roger Hill with a photo of him testing near inception of the company three decades ago.

In 2010 Hill Laboratories won the Deloitte Fast 50 award for the fastest growing mature business in the Central North Island, and the Westpac Waikato Business of the Year Supreme Award. Roger says that ultimately the company's steady growth and success can be primarily attributed to three things. "Firstly, we are fortunate to have committed and enthusiastic staff; secondly, we maintain a willingness to invest in the latest technology; and thirdly, we have been in the right place at the right time."

To celebrate the 30 year milestone, Roger and Anne will fly to each of the company's national branches, bringing food and festivities with them. "Looking back, we never imagined in our wildest dreams that Hill Laboratories would be as successful as it has been. Reaching 30 years makes Anne and I feel very proud, and we're looking forward to celebrating with the people who have journeyed with us along the way," he said.

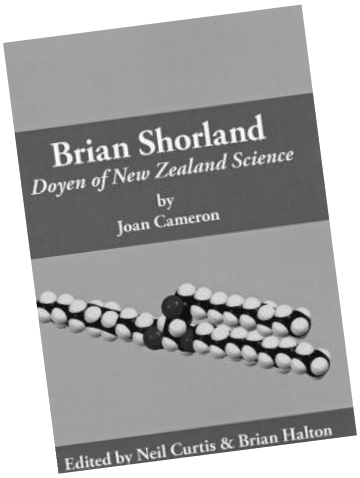
University of Waikato

Kyle **Devey** successfully defended his PhD thesis on *Productivity of analytical testing* recently. Kyle works for Hill Laboratories in Hamilton and was supervised by Brian Nicholson, *Michael* **Mucalo**, Gordon Rajendram and Roger Hill.

WELLINGTON

The Branch congratulates former Branch hairperson and long-standing supportive member Dr ***Dora Suuring*** who celebrated her 100th birthday in early July. She is still in residence in the family home. An article on Dora and her exploits appeared previously in this Journal (**2011**, *75*, 198-199).

Former *Chemistry in New Zealand* editor and long standing member of the Branch, Dr *Joan* ***(Mattingley) Cameron*** has had her book ***Brian Shorland – Doyen of New Zealand Science*** published by the New Zealand Association of Scientists. Edited by Professors Neil Curtis and Brian Halton, the book gives a fascinating history of not simply the life and times of eminent New Zealand biochemist and former director of the fats lab Dr Shorland, but also the evo-



lution of the science from the early 1920s in this country through to his death in 1999.

Copies of the work are available from Neil Curtis (*neil.curtis@vuw.ac.nz*) at a cost of $25 (p&p inclusive). An e-book version available from the NZAS for about $10 by the time this issue of CiNZ appears.

For its June meeting the Branch had a visit from New Zealand manufacturers of Trilogy skincare products. It was a hands on session in which each attendee made their own product using one of Trilogy's most popular moisturisers. It was an opportunity to find out more about the ingredients used in the products, and the success story behind the brand. The meeting was well attended and thoroughly enjoyed by all.

The 2014 NZIC High School Chemistry Quiz was held during the evening of 18 June and attracted some 34 teams from around the Wellington region, each with a cleverly crafted name. It followed the traditional afternoon titration competition. The quiz consisted of eight rounds that covered the student's knowledge of NCEA chemistry and general science. This year a *famous beards in science* round was included as well as a competition to *create your own molecule* using toothpicks and lollies, and then to name the creation and list its important properties.

The winning team came from Paraparaumu College with Hutt International Boys second and St Patrick's College (Kilbirnie) third. An event for teachers and parents was run alongside the quiz in which Kate McGrath outlined the capabilities and science of 3D printing.

Elephant's Toothpaste

MC Alan Dopson

The quiz was another successful event, enjoyed by all who attended. MCs Alan Dopson and Alex Hunt-Painter got the programme underway. Sarah Hoyte and Kathryn Allan provided the students with an excellent demonstration of *Elephant's Toothpaste* - the decomposition of hydrogen peroxide catalysed by potassium iodide - which generates columns of foam that were shot into the air.

The July meeting was held on the 29th of the month and comprised a materials-focused evening tour of Callaghan Innovation in Lower Hutt. It consisted of short talks and a tour of the respective laboratory facilities. The talks were: *An introduction to photonic chemistry* by *Bob* **Breukers** followed by his demonstration of the laser lab and its spectrometers; *Cement chemistry in New Zealand geothermal wells* by *Andy* **Durant** who then showed batching and casting, thermal analysis, micro-calorimetry, high temperature and pressure autoclaves and the mechanical testing facilities. *Processing routes for advanced ceramics* was described by *Pauline* **Calloch** who then showed the freeze casting, presses, furnace and processing labs, non-oxide ceramics, foamed metal structures and X-ray powder diffraction facilities. *Ian* **Brown** spoke on the *Industrial ceramics and 3D printing of titanium components* between the various talks and before the laboratories were available for touring.

August's speaker was *Colin* **Gooch**, the Technical Director of Resene, who eloquently educated the audience on *Technical issues in the paint industry - recent past successes; current issues and future concerns and opportunities*. He included aspects of formulation and the physical properties of paints and provided fascinating insight into the challenges associated with developing water-based paints both globally and from a personal perspective.

Victoria University – SCPS

Recent PhD students to complete their programmes and successfully defend their thesis (titles and supervisor in parenthesis) are: *Mario* **Alayon** (*Manipulating Sodium Caseinate Behaviour at the Interface: Applications for Concentrated Emulsion Formulation*; McGrath), *Kathryn* **Allen** (*Hybrid P,E Ligands: Synthesis, Coordination Chemistry and Catalysis*; Spencer), *Angelique* **Faramus** (*Semiconductor Nanocrystals Based on Group IV Materials*; Tilley) and *Andrea* **Kolb** (*Merino Becomes Noble: a study of nanogold, wool and nanogold-wool composites*; Johnston).

PhD student *Omar* **Alsager** who works with Dr *Justin* **Hodgkiss** in collaboration with VUW biologists (Professor Ken McNatty and PhD student Shalen Kumar) has designed a novel test to detect the female hormone oestrogen, a known contaminant in our waterways. Until now, the only tests available to detect it in drinking water need samples to be sent away for laboratory testing that can take days to come back. However, by combining the latest advances in design-your-own DNA and nanotechnology a *quick, easy and dirty* test has been developed.

The biologists designed a special piece of DNA that latches on to the oestrogen. Strands of these synthetically evolved receptors, called DNA aptamers, are mixed in with particles of nanogold and the DNA wraps itself around these forming a pink-coloured liquid. However, DNA prefers sticking to oestrogen more than gold, so when the hormone is present in the water, the DNA grabs it and changes shape which, in turn, causes the liquid to change to a purple-blue colour. As Alsager says: *In 10 minutes, you'll have your answer as to whether the water is contaminated or not.* The test is a world-first for its sensitivity, picking up levels of oestrogen equivalent to a pinch of salt in an Olympic-sized swimming pool.

Two of Professor *Jim **Johnson***'s PhD students, *Matthias **Herzog*** and *Michelle **Cook*** spent part of the European summer working at Institute of Technology at University of Karlsruhe with Professor Matthias Franzreb, using instruments unavailable in NZ. Matthias, a former German but long-time resident of NZ, is completing his PhD and spent almost six weeks there, whilst Michelle, having gained a first class MSc degree has started her PhD and was there for an essential introduction over a two week period. *Thomas **Bevan*** and *Jingjing **Wang***, PhD students with *Joanne **Harvey*** attended the ICOS20 conference in Budapest, Hungary, in early July. Both were privileged to give oral presentations and conducted themselves very creditably. *Rosy **Somerville***, an MSc student with John Spencer, attended a pre-conference in Kyoto and then the XXI conference on organometallic chemistry in Sapporo, Japan where she had poster presentations on her NZ work. *Joanne **Rogers***, a PhD student from Professor *Ken **MacKenzie***'s research group, attended the 11th Conference on Solid State Chemistry (SSC 2014) in Trencianske Teplice, Slovakia, in July; she presented as paper entitled *Novel luminescent materials based on gallium-aluminium silicate inorganic polymers*. Another PhD student from the group, *Mahroo Falah Poorsichani*, was one of two students from Victoria University selected to attend the Asia Nanotechnology camp in Tehran, Iran in October.

Dr *Joanne **Harvey*** has returned from a profitable leave spent at ETH Zurich and York University while Professors *Jim **Johnston*** and *John **Spencer*** are both on sabbatical leave. John is at York University working with Professor Duncan Bruce until mid-November and Jim is away until mid-February next year spending the first few months carrying out pilot scale development with Wools of NZ (UK) Ltd. in Ilkley, Yorkshire to scale-up some of his high value nano-impregnated wool products from laboratory to pilot and commercial scale operation. He also expects to visit collaborator Professor Joachim Kinkel at the Technische Hochschule in Nürnberg.

As the current NZ representative and elected member on the IUPAC Committee for Chemical Education, *Suzanne **Boniface*** attended the international committee meetings in Toronto and was then able to stay on for the IUPAC International Conference on Chemistry Education held on the campus of the University of Toronto in July. The conference, mostly attended by tertiary chemistry educators, had some days designed to interface with high school teaching. The opening keynote address was a delightful presentation by the 1986 Nobel Laureate, John Polanyi, who wove interesting aspects of his chemistry discoveries into a discourse about *How discoveries are made and why it matters*. Other keynote speakers focussed on research supporting student learning of representations in chemistry, green chemistry and taking advantage of technology for teaching.

Recent visitors have included Dr *Prem **Chapagain*** (Florida International University) who visited some of the chemists and physicists of the School and delivered his lecture: *Computational investigations of protein folding and dynamics*. Here he outlined why protein molecules fold into highly specific shapes in order to perform their function. The folding of proteins is a self-organising process in which a long-chain heteropolymer in a disorganised configuration spontaneously changes its shape to a highly organised structure and his discourse covered computer simulations of some model protein systems that has shed light on the protein folding dynamics, including alpha helix to beta barrel structural transformations in the C-terminal domain of the Transcription Factor RfaH.

The SCPS held its second *Dangling Bonds* event on 28 August. Staff and students showcased their current research to its partners, stakeholders and other potentially interested parties from outside VUW, in addition to colleagues from other university departments.

Thermodynamic modelling of reactions in materials chemistry

Ian Brown

Callaghan Innovation & the MacDiarmid Institute, Lower Hutt, New Zealand
(email: *ian.brown@callaghaninnovation.govt.nz*)

Keywords: *thermodynamics, ceramics, metallurgy, carbothermal reduction*

Thermodynamics and solid state reaction studies

In planning and undertaking any study involving reaction chemistry across the broad field of solid state materials, there are two simple questions to address: will this reaction proceed and can it proceed to completion under the planned conditions? To address these questions we must examine the effect of two major factors that control all chemical reactions – including those that determine outcomes in solid state chemistry – thermodynamics and kinetics. For many researchers, the study of thermodynamics is something undertaken in student years in physical chemistry course work. The principles and indeed many of the key equations that define the four laws of thermodynamics are tucked away in our heads and textbooks and these have been laid out and examined in legions of publications for over 100 years. This is not the forum to reproduce or review these underlying principles. The goal of this brief monograph is to demonstrate how thermodynamic analysis, using these simple principles and commonly available software, is a powerful analytical tool to complement observational studies we may undertake using the more usual experimental markers of the progress of a reaction, such as X-ray diffraction, thermal analysis and evolved gas analysis.

In 1875 Josiah Gibbs proposed that enthalpy, temperature and entropy could be expressed as a single quantity, now known as the Gibbs Free Energy of reaction ($\Delta G = \Delta H - \mathrm{T}\Delta S$). The Gibbs Free Energy remains our principal guide to the state of equilibrium or completion of any given reaction. The value of ΔG can also predict the direction of the chemical reaction under conditions of constant temperature and constant pressure. If ΔG is positive, the reaction requires external energy to occur and if it is negative, then it occurs without external energy input (it is spontaneous).

In this study the commercially available software HSC Chemistry[1] is used to examine how the Gibbs Free Energy can support our understanding and prediction of the outcome of solid state reactions in simple inorganic systems and in more complex ceramic and metallurgical processes.

Inorganic systems – the decomposition of calcite

The lime-limestone equilibrium is one of mankind's earliest industrially significant chemical reactions, with lime use in agriculture, cementing and glass making well documented for millennia. Recent work at Callaghan Innovation[2,3] has shown viable chemical engineering routes for using this process (known somewhat inaccurately as 'calcium looping') as the basis for a sustainable CO_2 capture mechanism for flue gases from thermal power plants, cement works and the like. The equilibrium reaction $CaCO_3 \rightleftharpoons CaO + CO_2$ provides a good test of thermodynamic modelling and enables examination of responses to changes in the mole ratios of reactants, temperature and pressure.

Fig. 1 shows the equilibrium data for one mole of $CaCO_3$ decomposing in an atmosphere of one mole of argon gas at a fixed pressure of 1 bar. The graph shows the reaction commencing above 450 °C and concluding above 1200 °C. The equilibrium temperature where moles of $CaCO_3$ and CaO are equal is 817 °C.

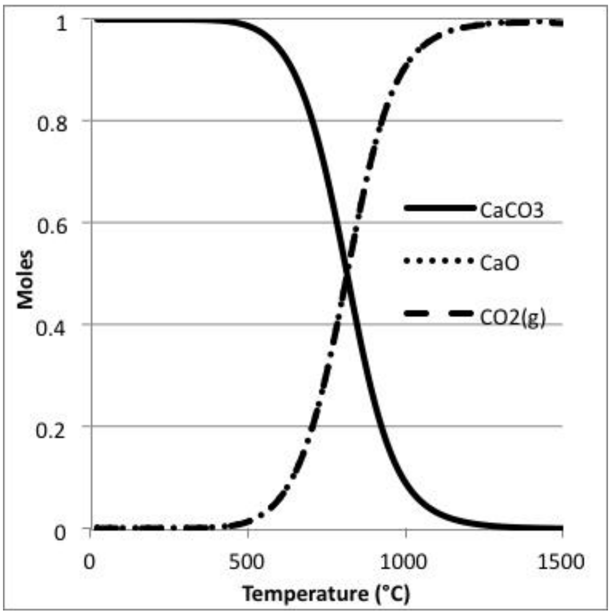


Fig. 1. Reaction equilibrium for $CaCO_3 \rightleftharpoons CaO + CO_2$. 1 mole calcite, 1 mole argon.

Fig. 2 shows the effect on the equilibrium of changing the gas environment by undertaking the experiment in 100 moles of argon, but still at 1 bar pressure. The crossover point for the equilibrium shifts significantly down in temperature to 617 °C. To undertake this calculation the model assumes that all reactants and products are confined in a single reaction vessel. What we learn is that by substantially reducing the partial pressure of CO_2 in this hypothetical reaction vessel the free energy for the reaction is significantly lowered. Effectively, we are simulating a flow reactor by progressively diluting the evolved CO_2 product gas and forcing the chemical equilibrium strongly from reactants towards products. An alternative way to model the equilibrium is to maintain a constant mole ratio of reactants but change the pressure that the model reaction vessel is subject to.

Fig. 3 shows the effect of reducing pressure on the de-

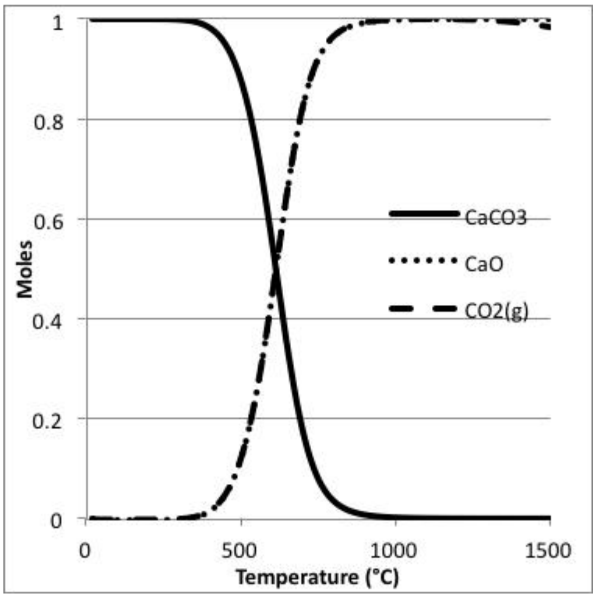


Fig. 2. Reaction equilibrium for $CaCO_3 \rightleftharpoons CaO + CO_2$. 1 mole calcite, 100 moles argon.

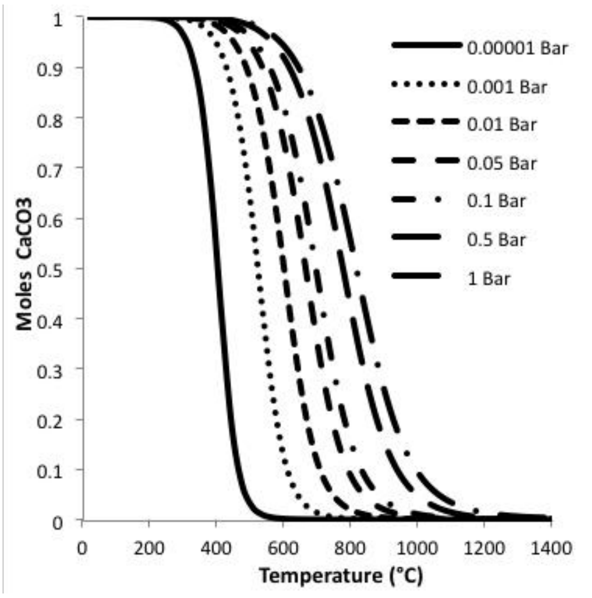


Fig. 3. Mass change for $CaCO_3$ decomposition under vacuum.

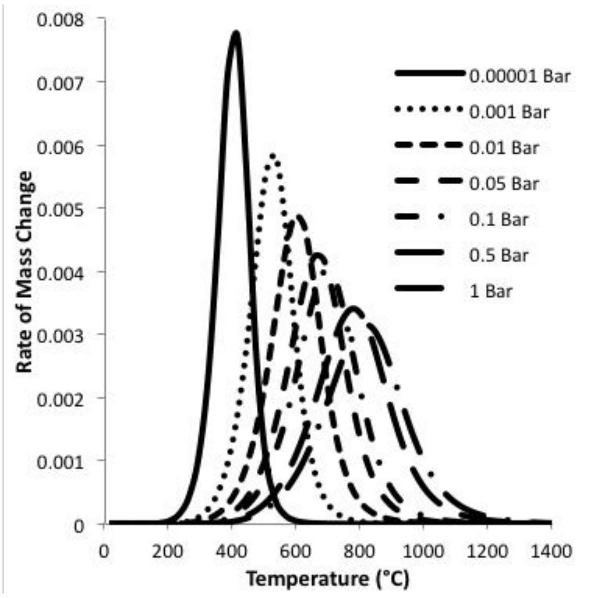


Fig. 4. Rate of mass change for $CaCO_3$ decomposition under vacuum.

composition profiles for calcite for the fixed molar ratio used in Fig. 1, namely 1 mole $CaCO_3$ and 1 mole argon. Effectively this is modelling a thermogravimetric analysis experiment of calcite decomposition. Taking this further, by applying a differential model (in this case a simple moving average) to the calcite deposition data curves we can generate the equivalent of a differential thermal analysis curve for each mole ratio/pressure condition. This is shown in Fig. 4.

The final thermodynamic analysis to examine for this equilibrium reaction is to quantify the effect of increasing the CO_2 partial pressure on the equilibrium. Thermodynamic laws would predict that increasing the CO_2 partial pressure will inhibit the reaction, delaying the onset of reaction and shifting the maximum rate of reaction to higher temperatures. Although this is borne out by examination of Fig. 5, the extent of inhibition of the reaction is at most some 30 °C and this effect saturates rapidly beyond 10 moles of additional CO_2 in the reaction environment. The effect of reduced pressure (Figs. 3 and 4) on the decomposition chemistry is much more substantial than the effect of increased pressure.

Having completed a comprehensive study of the thermodynamic behaviour of calcite decomposition under a diverse range of atmosphere conditions it is very informative to compare this data with real experimental data. In this case a well crystallised and well characterised calcite powder has been analysed by differential scanning calorimetry (DSC) under air, argon, nitrogen and CO_2 atmospheres over the temperature range from ambient to 1000 °C at 10 °C/min.

Fig. 6 shows the normalised calcite weight loss curves. It can be seen that both static and flowing environments of *non-participating* gases (air, N_2, Ar) result in a very tight data cluster with less than 20 °C separating the points of maximum rate of weight loss (Static Air: 754 °C; Flowing Air: 762 °C; Flowing N_2: 758 °C; Flowing Ar: 743 °C). Cross-referencing to Figs. 3 and 4 indicates that the equivalent atmosphere seen by the calcite material is 0.25-0.35 bar pressure. The CO_2 result is very different indeed, being a *participating* gas in the reaction chemistry. Even at the relatively low gas flow rates used in these experiments the reaction is greatly inhibited, with the temperature at the point of maximum rate loss being 933 °C. Given that Fig. 5 shows that the maximum rate of weight loss at 1000 bar CO_2 pressure is 885 °C, this gives us some idea of the extent to which diffusion barriers in the surface regions of the calcite grains are repressing this reaction. This is a good example of the extent to which kinetic factors can dominate over thermodynamic factors in determining product outcomes in some chemical equilibria.

Ceramic systems – silicon nitride synthesis by carbothermal reduction of silica

Silicon nitride (Si_3N_4) is a non-oxide ceramic, with a three dimensional covalent structure built up by corner-sharing SiN_4 tetrahedra. This material is an important high performance technical ceramic with high hot hardness, thermal shock resistance and fracture toughness. Silicon nitride-

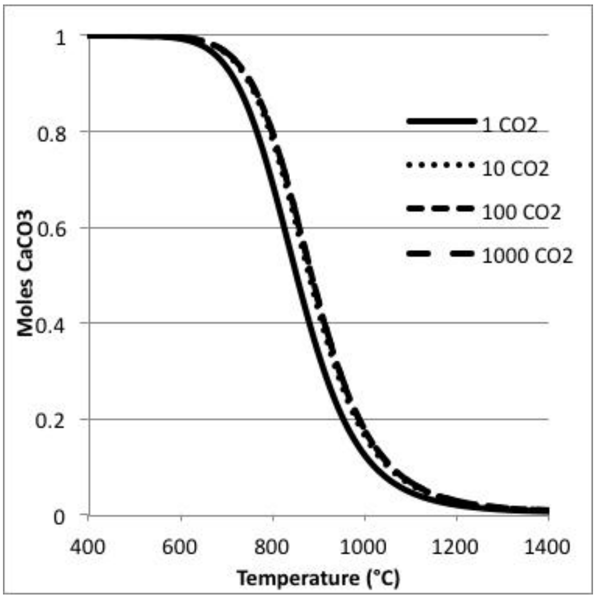


Fig. 5. Mass Change for $CaCO_3$ decomposition under CO_2 pressure.

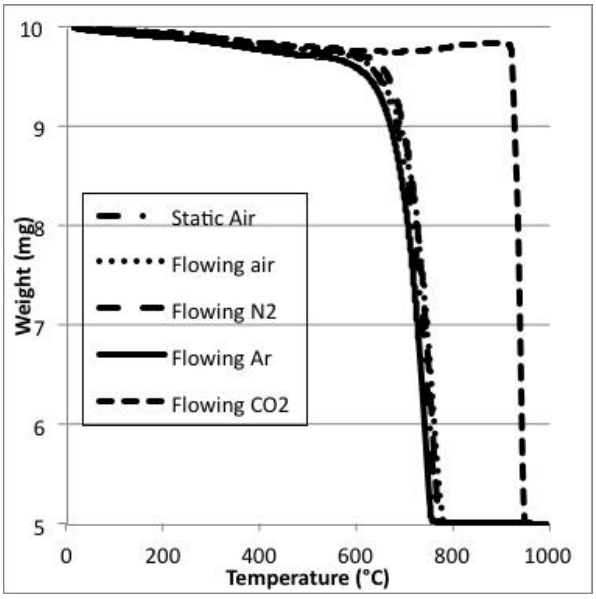


Fig. 6. Experimental DSC data for $CaCO_3$ decomposition under different atmospheres.

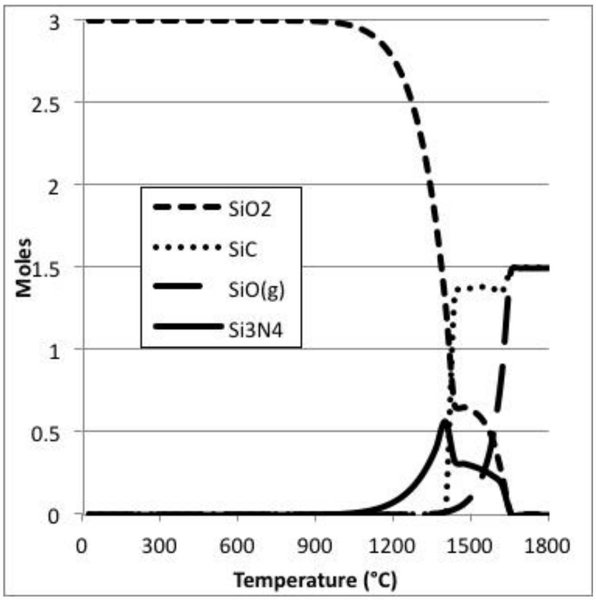


Fig. 7. Carbothermal reduction of SiO_2 to form Si_3N_4 under 10 moles N_2.

based cutting tools can cut cast iron, hard steel and nickel-based alloys with surface speeds up to 25 times faster than those obtained with tungsten carbide tools and are now used in considerable numbers to machine cast iron in the automotive industry and nickel superalloys in the aerospace industry.

One way to synthesis Si_3N_4 is to directly react the elements at elevated temperature:

$$3Si + 2N_2 \rightarrow Si_3N_4 \qquad (1)$$

Thermodynamic analysis shows that this reaction is highly exothermic with a strongly negative Gibbs free energy of reaction. While this sounds an ideal driver for completing the ceramic reaction, the reality is that this exothermic reaction is capable of generating sufficient heat to cause thermal runaway during the reaction. This can raise the reaction temperature above the silicon metal melting temperature of 1417 °C and create serious phase segregation through formation of agglomerates of molten Si droplets before the nitridation reaction has had time to achieve completion.

A different approach to silicon nitride formation is to reduce silicon dioxide (‘silica’) with carbon under a nitrogen atmosphere. This process is known as carbothermal reduction:

$$3SiO_2 + 6C + 2N_2 \rightarrow Si_3N_4 + 6CO \qquad (2)$$

In this case, analysis reveals that the Gibbs free energy does not become negative until above 1550 °C, at which point the enthalpy of the reaction is +1170 kJ. Having gas-solid reactants with gas-solid products allows plenty of variables to help manage and control this strongly endothermic process chemistry. Our first model fixes the silica and carbon levels at their molar levels in reaction 2 while varying the nitrogen content. What we find is that the molar volume of CO product gas (6 moles CO vs the 2 moles of reactant N_2) will effectively repress this reaction until such time as a substantial molar excess of nitrogen is achieved. Figs. 7 and 8 show the equilibrium for 10 and 15 moles of nitrogen respectively. The data show that even this large nitrogen excess is still insufficient to allow synthesis of the theoretical level (1 mole) of Si_3N_4. This level is not achieved until over 20 moles of nitrogen are used, an excess of 10 times the stoichiometric requirement. Figs. 9 and 10 show the equilibria calculated for 30 and 100 moles of nitrogen, respectively. It can be seen that at least 30 moles of nitrogen are required to generate a sufficiently wide synthesis temperature window for Si_3N_4 stability that would enable the practical and successful synthesis of phase pure silicon nitride.

A closer examination of these equilibrium data curves reveals an unexpected challenge. At the upper end of its stability window the Si_3N_4 product is thermodynamically unstable with respect to silicon carbide (SiC) and silicon monoxide (SiO). In Figs. 8-10 these two phases overlay one another. The latter phase is a particular problem due to its volatility. In a real reaction experiment under flowing nitrogen, the very same drivers that indicate that we should increase the nitrogen flow rate to reduce the partial

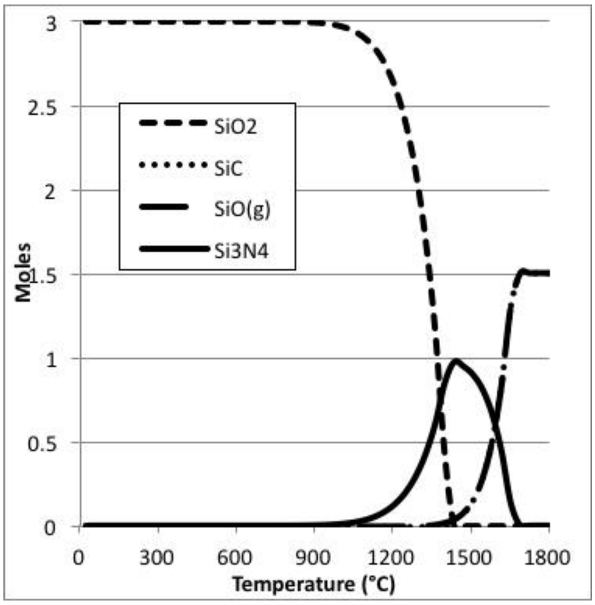


Fig. 8. Carbothermal reduction of SiO_2 to form Si_3N_4 under 15 moles N_2

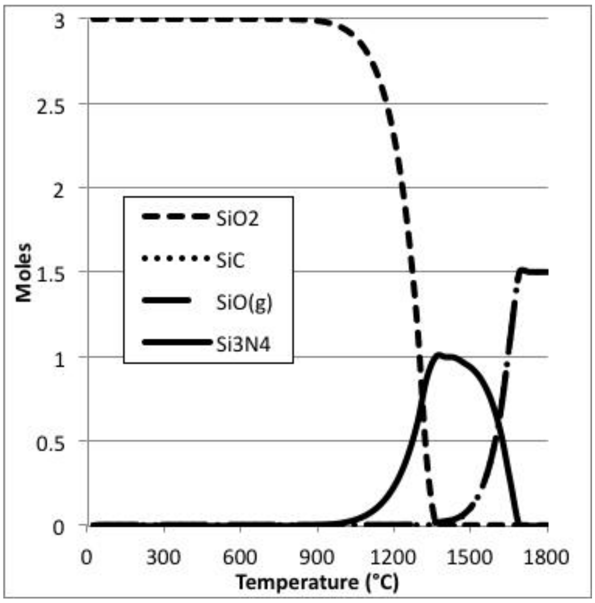


Fig. 9. Carbothermal reduction of SiO_2 to form Si_3N_4 under 30 moles N_2.

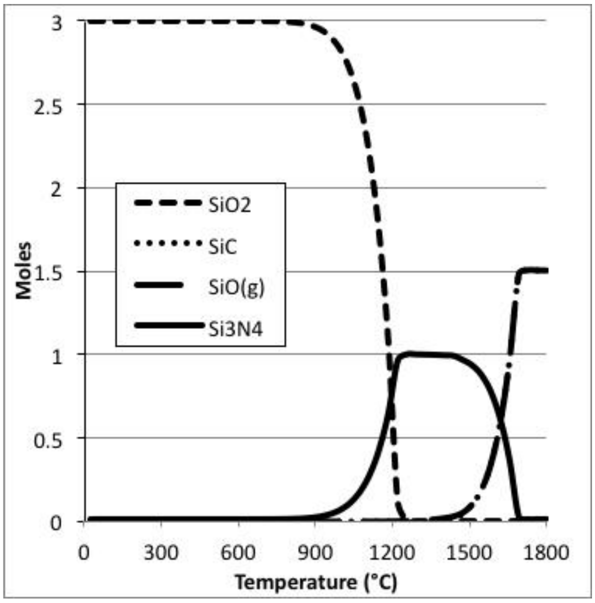


Fig. 10. Carbothermal reduction of SiO_2 to form Si_3N_4 under 100 moles N_2.

pressure of CO will also cause this volatile SiO phase to be removed, forcing the Si_3N_4 to decompose to SiC and SiO more quickly. This is a reaction system where compromise and careful optimisation is required to obtain phase pure Si_3N_4 product.

Metallurgical systems – reduction of titanium dioxide to titanium metal

Titanium has the highest strength to weight ratio of any metal. Methods for the manufacture of this high durability, high value metal are complex multistage processes often proceeding from the titanium ore rutile (TiO_2) via a $TiCl_4$ intermediate followed by reduction with reactive metals such as magnesium or sodium. The long-established Kroll process (1940)[4] and the more recent Armstrong process (1998)[5] use Mg and liquid Na respectively. Can thermodynamic analysis show us an alternative process route? Fig. 11 shows the Gibbs free energy for the reduction of titanium dioxide (titania) to form titanium metal using a range of reductants known to break metal–oxygen bonds.

It is clear from the data that well known reducing agents such as hydrogen and carbon are unable to reduce the strong Ti-O bonds to Ti metal under conventional temperature/pressure/time conditions. There is no temperature regime where the free energy for the reaction is negative, so the reaction cannot proceed spontaneously under any defined T-P-t conditions. Also shown are data for three metal reductants, aluminium, magnesium and calcium where the ΔG curves are strongly negative at all temperatures below 2000 °C. That is, there is a strong thermodynamic driver for the reduction to proceed. Some years ago researchers at the University of Waikato developed a titanium synthesis route based on Al metal reduction of titania.[6,7] A study of the drivers for this reaction provides a good exemplar for the role of thermodynamics in guiding reaction paths in process metallurgy. Consider the reaction:

$$3TiO_2 + 4Al \rightarrow 3Ti + 2Al_2O_3 \qquad (3)$$

This reaction is usually undertaken in an argon atmosphere to eliminate all risk of oxidation of either the reactants or products. The ΔG vs temperature data for this reaction is shown in Fig. 11, indicating a ΔG value of less than -100 kJ at all temperatures of interest. So our immediate expectation is that this reaction should proceed. Reality is different. The product formed when using the above stoichiometry is consistently a TiAl intermetallic phase. So what is wrong – has our modelling failed? The simple answer is the model works and we have leapt ahead without undertaking due diligence on the essentials of the analysis. Fig. 12 shows the mole fractions of reactants and products formed when 3 moles TiO_2 and 4 moles Al achieve equilibrium under argon.

The thermodynamic stability of the intermetallic phases AlTi and Al_3Ti is greater than that of pure Ti (the Gibbs Free Energy is more negative), so much of the reactant Al metal has associated with the intermetallic phases and has not been made available to reduce the TiO_2 beyond TiO. Fig. 13 shows the result of re-calculating the equilibrium

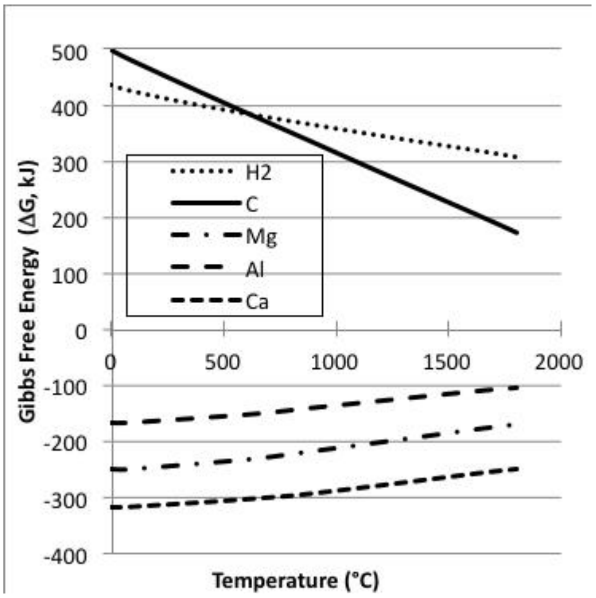


Fig. 11. Gibbs Free Energy as a function of temperature for TiO_2 reduction.

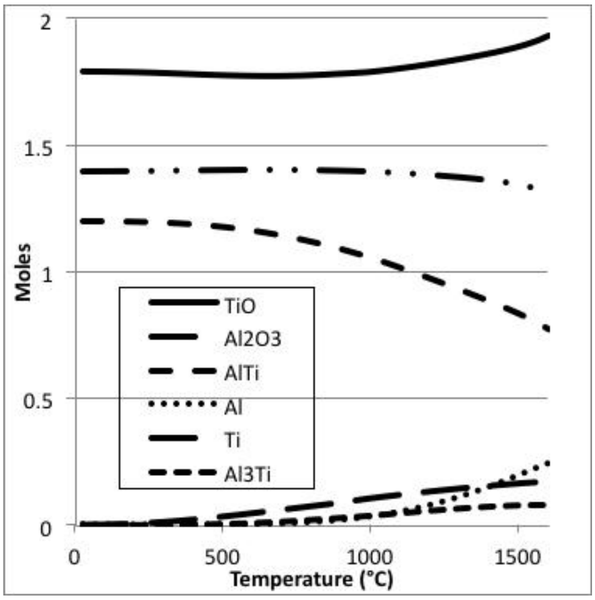


Fig. 12. Equilibrium mole fractions for the reaction $3TiO_2 + 4Al$ in argon.

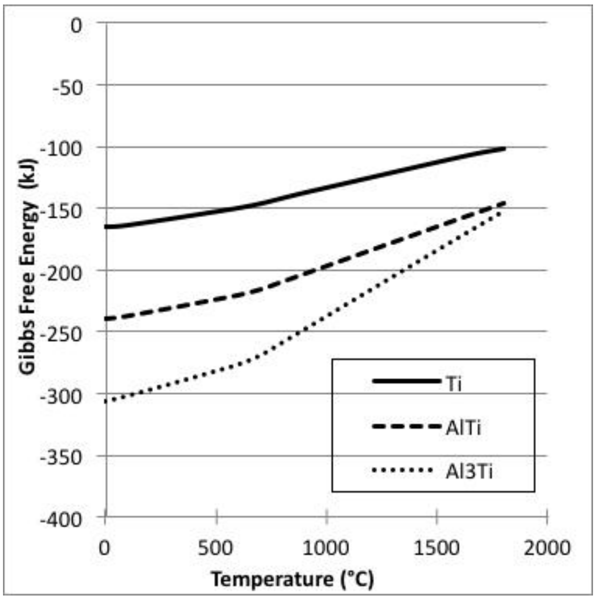


Fig. 13. Gibbs Free Energy as a function of temperature for Al reduction of TiO_2

using an excess of Al metal. The extent of the excess determines the ratio of AlTi to Al_3Ti in the products. The Δ*G* data can be recalculated based on stoichiometric formation of AlTi or Al_3Ti, using the equations:

$$3TiO_2 + 7Al \rightarrow 3AlTi + 2Al_2O_3 \qquad (4)$$

$$3TiO_2 + 13Al \rightarrow 3Al_3Ti + 2Al_2O_3 \qquad (5)$$

Fig. 13 shows Δ*G* data for reactions 4 and 5 shown alongside that for reaction 3. At lower temperatures Al_3Ti formation is strongly favoured but the free energy gap to AlTi closes at elevated temperatures. This Al reduction path for the synthesis of pure Ti metal is not favoured thermodynamically. Instead we have a novel path to synthesise Al-Ti intermetallic phases by controlling TiO_2/Al mole ratio and temperature to selectively form AlTi or Al_3Ti phases. Using this reaction path design in a practical process requires removal of the contaminant oxide phase, in this case Al_2O_3, from the product mixture. The removal of contaminant oxide phases will also be a feature of reduction reactions using other reactive metals, including Mg, Ca and Na. This goes some way to help explain why many of the current commercial synthesis routes proceed via $TiCl_4$ intermediates, as the removal of contaminant chloride salts may have more appeal than removal of oxide phases in a production process. Nevertheless, the TiO_2/Al reduction methodology developed at Waikato remains a valid path to synthesise high value intermetallic phases for the metallurgical industry.

Summary

Thermodynamic analysis can be applied across a wide range of reaction systems in solid state and materials chemistry. Researchers draw immense value from being able to predict whether a reaction can proceed, which reaction path and product set is preferred and which reaction intermediates may be encountered. However, as in every field of research, there are traps for the unwary and thermodynamic analysis has plenty, sufficient to warrant a brief examination:

The data: The quality of the modelling is only as good as the quality of the data used to compile the databases. The thermodynamic properties of many materials have been exhaustively measured and have been collated in a number of databases, e.g. Barin,[8] Janaf,[9,10] that have subsequently been drawn into software packages such as HSC Chemistry[1] and Thermocalc.[11] The database managers attempt to grade the quality of these data sets on the basis of the perceived experimental rigour of the measurement. Most commonly the data are derived by fitting heat capacity (C_p) vs temperature data to an established, albeit empirically derived, equation of state algorithm (known as the Kelley equation).[12] In some cases C_p data for chemical compounds which are absent from the databases can be found in current literature and most modern thermodynamic analysis software has options to enable users to readily integrate this new data into a working database.

The closed vessel model: The process for calculating the species present at chemical equilibrium places all reactants and products in the same closed space. In modelling a reaction where gas species form part of the chemistry, such as in the calcite decomposition or carbothermal reduction of silica examples given previously, the model conditions (moles of reactant, moles of carrier gas, system pressure) can be varied to simulate the conditions that would be encountered in a real flow reactor. In the real experiment the gas species may be removed from the reaction environment prior to equilibrium being established.

Kinetics: While thermodynamics provides the first filter for assessment of likely reaction paths and outcomes, the kinetics of any given reaction provide a second filter that may dramatically delay or temperature shift the progress of a reaction that might otherwise be expected to proceed readily. It must be understood that even drivers such as a strongly negative Gibbs free energy may not be sufficient to enable a reaction to go to completion in the temperature window that the thermodynamic model may indicate. The time frame to achieve equilibrium cannot be drawn from these models. The nitridation of silicon metal [reaction (1)] is a good case in point. The model shows highly negative ΔG and ΔH data at all temperatures above ambient and yet this highly exothermic reaction does not commence until well over 1000 °C because a very thin native oxide skin on the Si metal surface acts as a kinetic barrier, imposing diffusion control where perhaps none might have been expected.

Thermodynamic modelling can complement classic analytical techniques to assess the state and path of many solid state reactions. It cannot assess the rate of such reactions, so an ‘eyes wide open’ approach is vital in our interpretation of the modelling outcomes. A good dose of chemical common sense in combination with the knowledge of how to draw best value from thermodynamic modelling and software packages offers researchers a highly effective and little used chemical research tool.

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NZIC Annual General Meeting

The Annual General Meeting of the New Zealand Institute of Chemistry will be held on Monday 17th November at 4pm in the School of Science tearoom (F1.09), University of Waikato, Gate 8, Hillcrest Road, Hamilton.

Agenda:

1. Apologies
2. Minutes of 2013 AGM held at NZIC Conference Wellington Monday 2 December 2013
3. Matters arising
4. Financial Report including audited accounts
5. Election of Officers. Nominations:
    President: Ian Brown (Wellington)
    1st Vice-President: Paul Plieger (Manawatu)
    2nd Vice-President: (TBA Auckalnd)
    Treasurer: Colin Freeman
    Honorary General Secretary: Richard Rendle
6. Appointment of auditor:
    Move that Greta Vink be appointed auditor
7. Other Business

What makes a metal?

Nicola Gaston

School of Chemical and Physical Sciences, Victoria University of Wellington, PO Box 600, Wellington
(email: *nicola.gaston@vuw.ac.nz*)

Keywords: *metals, elements, quantum chemistry, periodic trends, nanotechnology*

In the age of the internet, the periodic table has taken on a life of its own. Periodic tables of everything from meat[1] to the characters of the Lord of the Rings[2] have been constructed, though they rarely serve to demonstrate anything more than their creators' lack of understanding of the concept of periodicity. The powerful connections between elements provided by their electronic shell structure is rarely better demonstrated than by the periodic table in its usual form; some exceptions exist, including the recent construction of a map of the elements modelled on the London Underground.[3] This manages to include the links between properties such as nuclear stability and phase under standard conditions, albeit it with the loss of the left-right ordering of the periodic groups.

So what exactly makes the periodic table in its usual form so powerful?

A good place to start is with the ability to make predictions about the behaviour of elements based on the chemical behaviour of their congeners. John Newlands and Lothar Meyer had contributed to the description of periodicity before Dmitri Mendeleev assembled the modern version; the attribution of the discovery to Mendeleev is in large part supported because he had the audacity to make predictions based on his table. No known element could be made to fit in the space after zinc, or between aluminium and indium in group 3: this observation was enough for Mendeleev to suggest the existence of gallium, though it was only given that name later by its experimental discoverer, Paul Emile Lecoq de Boisbaudran.[4]

Fig. 1 presents the elements of the periodic table coloured according to their date of discovery. It is clear that most activity in this respect occurred in the 19th century, which should be no surprise. Less obvious to many chemists, perhaps, is the extent of development that occurred in the 20th and into the 21st century. But with respect to the periodicity of the elements, there is little to remark; the probability of an element having been known before the introduction of modern chemical science relates primarily to the abundance of the element on earth, and its ability to occur in a solid elemental form under standard conditions of temperature and pressure. The coinage metals present an exception, as demonstrated by their ability to appear in native metallic form, such as the familiar nuggets of gold. This is clearly related to their chemical properties; in particular, their relative resistance to oxidation. But the chemistry is certainly not the whole story.

More commonly, we colour in elements according to their group in the periodic table, as shown in Fig. 2. The chemical groups are defined by a particular number and type of valence electrons – one *s*-electron in group one, five *p*-electrons in group 17. However, for convenience, we group the elements not only vertically but also horizontally – the transition metals, the lanthanides and the actinides all have more in common with each other than with the left or right hand sides of the periodic table, which it makes sense to acknowledge. However, in general, their chemical behavior still varies from one column to the next.

There are a few regions of the periodic table where the group that an element belongs to is not the primary predictor of its behaviour; in particular, the left half of the *p*-block, where the elements change from metallic to non-metallic both as a function of electron configuration and mass. An excellent example is gallium, which has the same crystal structure as the solid halogens, composed of pairs of atoms, but retains a metallic electronic structure.[5] Referred to as a 'molecular metal', the relationship between the curious structure of gallium and its low melting temperature is an area of current research interest.[6,7] A few other examples are notable: despite common usage, zinc and cadmium do not meet the criterion for belonging to the transition metals, which are defined as those elements which use their *d*-electrons in chemical reactions and bonds. Or in the IUPAC definition "an element whose atom has a partially filled *d* sub-shell, or which can give rise to cations with an incomplete *d* sub-shell".[8]

However, mercury has been shown to exist in oxidation state +4, and therefore may be referred to as a transition metal.[9] The reason for this deviation from periodicity is the influence of relativity on the inner electrons of a heavy atom such as mercury: this increases the binding of *s*-electrons which have a high probability of being near the nucleus, and deshields the *d*-electrons which consequently become more able to participate in chemical reactions.

The presence of the actinides and lanthanides at the bottom of the periodic table seems to imply that we treat them differently. This is not quite true: it is a matter of simple convenience to leave them outside of the main block of the table, to avoid the elongated form of the table shown in Fig. 3.

On the other hand, the chemistry of the lanthanides and actinides is more consistent within each row than if considered by column: this is not a bad reason to treat these *f*-elements outside of the block of 18 groups.

In a very real sense, the periodic table represents simply the ordering of the elements imposed by the Pauli exclusion principle: that each element with an additional electron must occupy the next rung on the ladder – or box in the periodic table.

Fig. 4 presents a slightly different version of the periodic table, focused on a single property: the lattice structure.

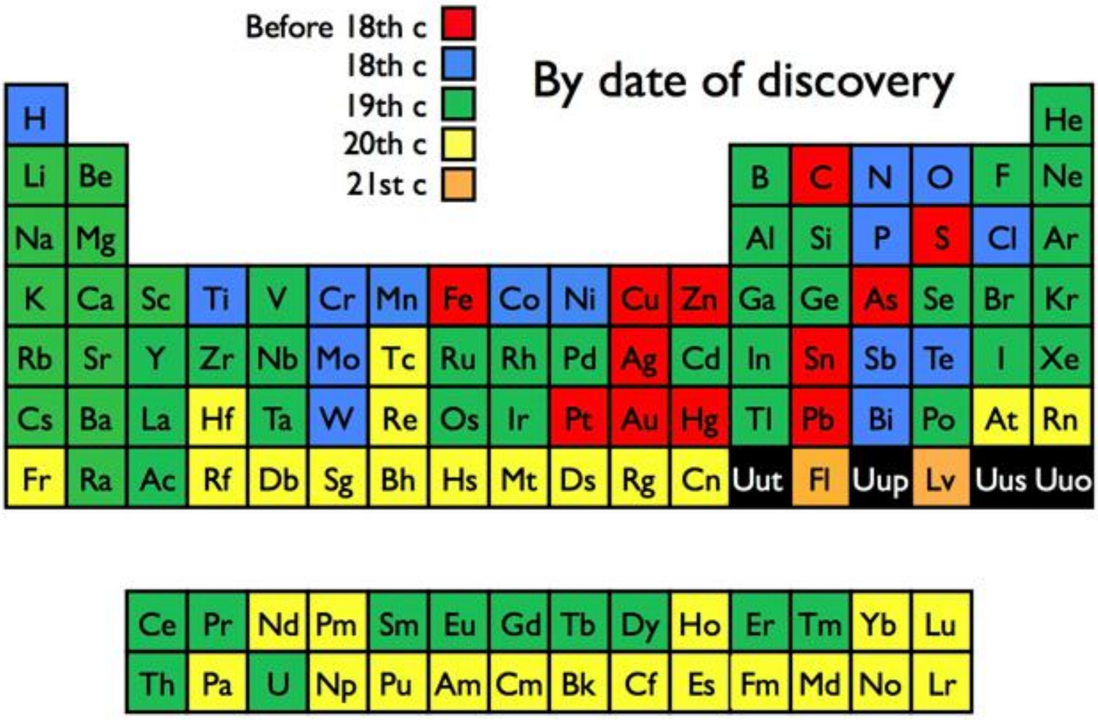

Fig. 1. The date of discovery of the elements

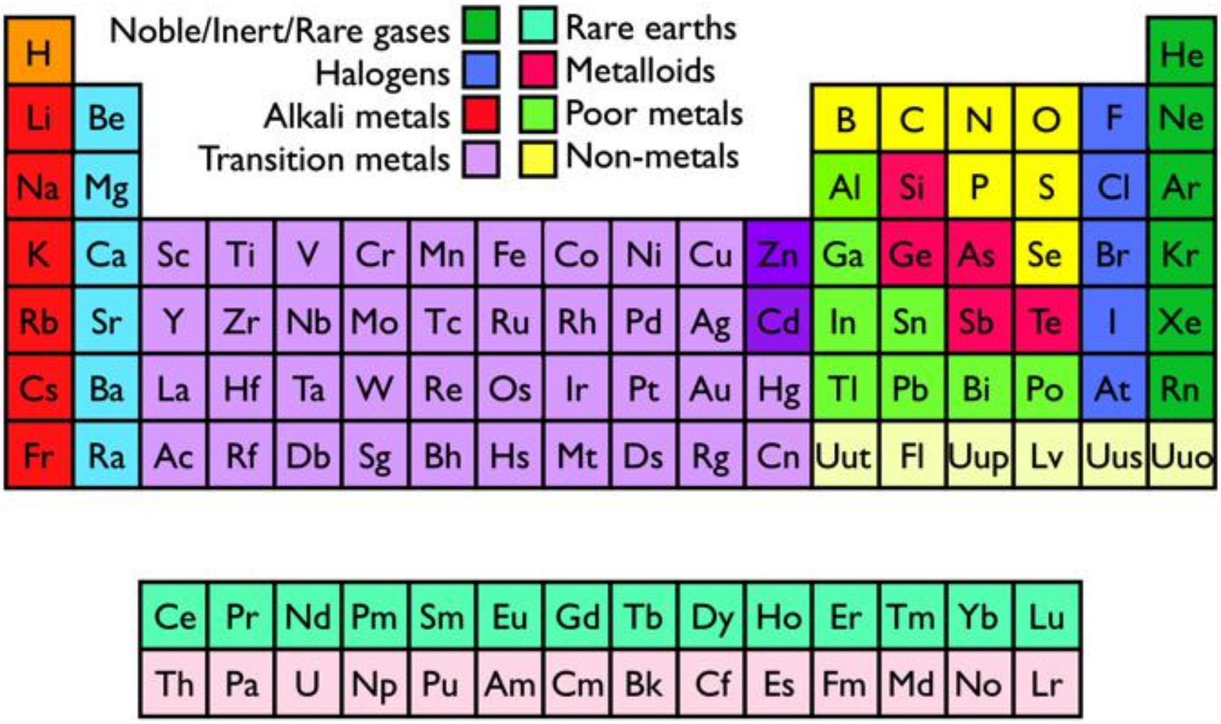

Fig. 2. The groups of the elements

Restricted to the metallic elements, due to the significantly more complex structures adopted by the non-metals, there is nonetheless significant variation in structure.

There is certainly some periodicity in the structures of the metallic elements. The alkali metals are robustly body-centred cubic (bcc); the overwhelming majority of metals (80%) fall into either bcc, or one of the two close-packed structures, face-centred cubic (fcc), or hexagonal close-packed (hcp). If we include the lanthanides, which crystallize in a hybrid fcc/hcp lattice, where the packing alternates between ABA… (hcp) and ABC… (fcc) , this proportion goes up to 88%. The alternating preference along the series of transition metals for bcc and fcc structures has been successfully explained in terms of a Jahn-Teller distortion[10] which changes the structural preference of the transition metals based on the filling of the *d*-orbitals; no such model to date can account for the preference for the hcp structure, which in any case should be close in energy to the fcc structure, which has the same density. The magnetic 3d transition metals, manganese, iron, and copper, are understood to deviate from the periodic trend due to their magnetic ordering. It is however in the *p*-block - the region of the periodic table known as the 'poor metals', that a complete absence of periodicity in structure is observed.

The rhombohedral structure of mercury has been shown to be due to relativity.[11] The mercury-mercury bond in the dimer is very weak, due to the inert nature of the closed $6s^2$ valence shell, which means binding is due entirely to dispersion interaction.[12] The closing of the band gap between the occupied s-shell and the valence p-orbitals happens as a function of size, at around 400 atoms. The metallic nature of bonding changes the mercury-mercury interaction significantly, reducing the bond length from 3.7 Å in the dimer to 3 Å in the bulk. The inertness of the s-shell is a relativistic effect due to the proximity of these electrons to the heavy nucleus, and results in a destabilisation of the underlying d-orbitals due to deshielding. Thus, at the short distances between mercury atoms in the bulk metal, the *d*-orbitals are able to interact strongly enough to cause modification of the lattice structure away from close-packing. It is also straightforward to show that the inclusion of relativity reduces the cohesive energy of bulk mercury, going some way to explaining its low melting temperature.[11] Recent simulations have demonstrated that the influence of relativity lowers the melting temperature by 105 K.[13]

A more extreme version of this relativistic effect on both structure and properties has been shown in calculations of the lattice and band structure of copernicium, the element formerly known as eka-mercury. The stabilisation of the valence *s*-electrons and corresponding destabilisation of the *d*-electrons is so significant that they change order of occupation, meaning that the valence band of the solid is primarily of *d*-character. The unoccupied p-shell remains high enough in energy that a small band gap opens up, transforming this element into a semi-conductor: the first one to be known in the *d*-block.[14]

But is the metallicity of an element as fundamental a property as we like to think? It is certainly one of the most basic categorisations of the elements that we are used to making – but it deserves some further thought. Just as we think of the phases of the elements – such as the essential liquidity of mercury – as the phases that they exist in under standard conditions of temperature and pressure, so are the structural phases of the elements – their preferred allotropes – simply the ones which are most stable under standard conditions. Under high pressure, the properties of the elements have been shown to change in remarkable fashion: hydrogen has been predicted to become metallic[15] though the experimental evidence remains controversial.[16-21] In no less surprising a manner, simple metals such as sodium and lithium, which define the metallic paradigm in most solid-state texts, have been shown to adopt dimeric structures which become insulat-

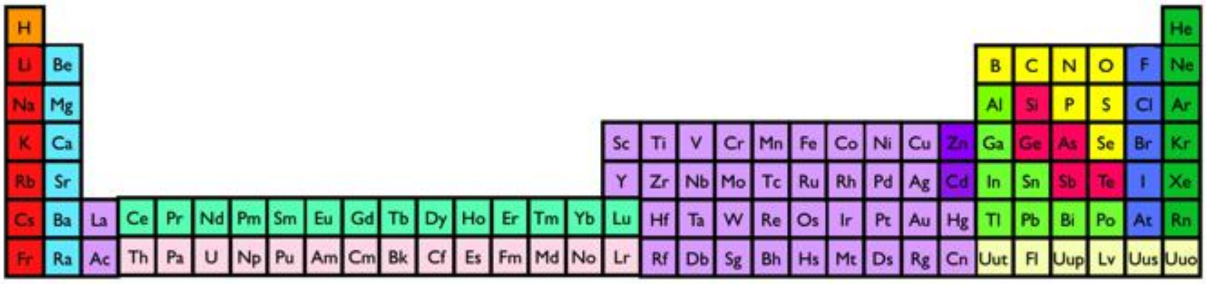

Fig. 3. An alternative way to include the lanthanides and actinides in the periodic table

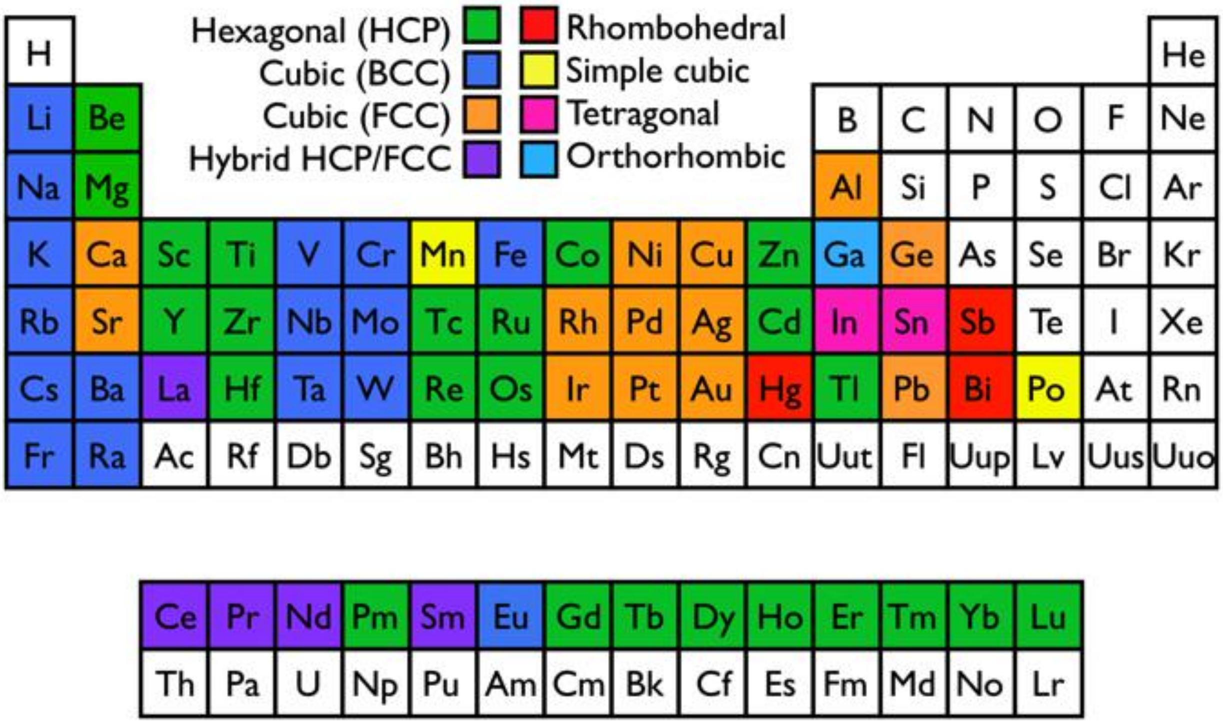

Fig. 4. Periodicity in the structures of the metallic elements

ing.[21,22] Thus, even the position of the boundary between non-metals and metals in the periodic table needs to be understood as contingent on conditions such as pressure and temperature.

Another variable, that is of equal importance, though which perhaps offers more promise for practical application, is that of size. As mentioned previously in the case of mercury, the overlap of bands necessary for the existence of the metallic state relies on bonding between a sufficient number of atoms. Additionally, the structures preferred at small sizes are often quite different to those familiar to us in the bulk: when the surface area to volume ratio is large, the preferred structures will be those that achieve close-packed surfaces, based on icosahedral symmetry, rather than the familiar close-packed cubic and hexagonal structures. Structure-property relationships – in particular, the interactions between structure and the electronic structure that determines metallicity – are highly sensitive, and thus contribute to the broad range of anomalous phenomena that may be observed at the nanoscale.

An excellent example of such anomalous behavior is the greater than bulk melting temperatures found for small gallium clusters, at sizes below a hundred atoms.[23-25] At these sizes, we know that the structures are very different from the paired structure of the bulk; it is however necessary that the cohesive energy per atom of these small clusters must be considerably lower than that of the bulk, due to the large number of atoms at the surface of the cluster, where they are under-coordinated. The normal paradigm of melting in small particles is that of melting point depression: as the surface area increases relative to the particle volume, the melting temperature should decrease – and so it does, for the vast majority of substances. Gallium is the only substance in which the melting temperature is systematically elevated across a range of particle sizes, from 17 to around 80 atoms, according to experiment.

In thermodynamic terms, we can think of size at the nanoscale having an effect similar but opposite to that of pressure in the bulk: smaller particles have a lower effective pressure, due to the dominance of the surface. The lowering of pressure should increase the relative stability of the less dense phase: and gallium is indeed one substance which, like water, has a greater density in the liquid phase than in the solid. Whether this argument is sufficient to explain the higher melting temperatures is, however, questionable without detailed simulation of the melting transition. Simulations to date have shown that there is certainly more to the argument: for example, it is not easy at these sizes to quantify a difference in density.[6,7]

All of these examples demonstrate just how many degrees of freedom affect the behavior of the elements, and their most basic properties. Whether an element is metallic or not can change, and it can change greatly. One of the first lessons of science is that even the question that you are asking is up for questioning. Outside the paradigm of standard conditions of temperature and pressure; far from the thermodynamic limit; the difference between liquid and solid, metal and non-metal, is open to question: and the answers both threaten and promise to be full of surprises.

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Wohlmann's waters and the Colonial Laboratory

Peter Hodder

Victoria Business School, Victoria University of Wellington *and* HodderBalog Social and Scientific Research, Wellington, New Zealand (email: *peterh@hodderbalog.co.nz*)

Keywords: *Wohlmann, Colonial Laboratory, water, thermal springs*

Chemical investigations in colonial New Zealand have been summarised as follows:[1]

"Chemistry in New Zealand in the nineteenth century falls conveniently into government, academic and industrial endeavours. It was largely analytical, initially geared to the Geological Survey and the Colonial Survey and the Colonial Laboratory, later to the needs of mining – gold, coal and ironsand – and later still in manufacturing and agricultural applications and settlement problems."

The first Colonial Laboratory was established in 1866 as a part of the Colonial Museum (itself opened in 1865), and thereby became one of James Hector's many responsibilities to science.[2] In its early years there was an increasing demand for the Laboratory's services, not only for the analysis of natural materials, coals and ores, in particular; but also analysis of samples provided by other Government departments (Table 1). Most of the analytical work during this period was undertaken by William Skey (Fig. 1A).

Table 1 suggests that analytical work on geothermal waters became a significant part of the Laboratory's activities from the 1880s. Certainly, the number of publications related to thermal springs increased significantly in the latter decades of the nineteenth century (Fig. 2).[3] Not all of these were specifically related to chemistry; they also included consideration of the scenic value and tourist potential.[4]

Fig. 1. A – Left: The inaugural analyst at the Colonial Laboratory, William Skey. He and James Hector had worked in Dunedin, and one of the conditions Hector made when appointed to the role of Director of the Colonial Museum was that Skey should be appointed as analyst. B – Centre: A.S. Wohlmann, the first Government balneologist, appointed in 1902. C – Right: J.S. Maclaurin, the second analyst of the Colonial Laboratory, appointed in 1901.

Table 1. Analytical work undertaken by the laboratory associated with the Colonial Museum, for selected years from 1866 to 1888, from Reports of the Colonial Laboratory in the Appendices to the Journal of the House of Representatives

Year	Coals	Ores*	Rocks and minerals	Soils	Mineral and potable waters	Building materials	Miscel-laneous and 'other'	Total samples analysed
1866	19	22				10		51
1868	105	106	130	34	16	71	65	527
1872								285
1873	39	76	47		14		69†	245
1874	35	66	77				166	356
1875	33	62	75				304‡	476
1876	18	41	49				25	133
1879	12	140	35		15		33	235
1880	18	195	57		15		38	323
1881	14	247	50		11		35	357
1882	13	129	58		21		40	265
1883	26	102	64		37¶		64	293

*Includes gold assays
† Includes 41 "appeals from the Secretary of Customs"
‡ Includes 128 "examinations of adulterants"
¶ Includes "work on analyzing the Taupo mineral waters – a work which has long been urgently required"

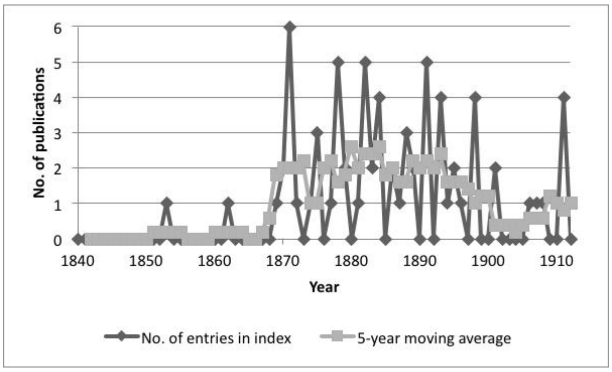

Fig. 2. Number of publications related to thermal springs for New Zealand's colonial period for each year from 1840 to 1912, compiled from a bibliography of New Zealand geology.

The recognition of the tourist potential of the thermal springs and their alleged health benefits led to the appointment of A.S. Wohlmann as Government Balneologist (Fig. 1B) in 1902.[5] On appointment, Wohlmann indicated that he would undertake a comprehensive survey of hot springs throughout New Zealand, and some of his wanderings were reported in the newspapers.[6] This, of course, had to be fitted in around his primary responsibilities for redeveloping the by-then decrepit bath-houses in Rotorua into a spa that would rival the established spas in Europe, some of which he had visited and made comment on prior to coming to New Zealand.

In 1907, the New Zealand Official Yearbook included a substantial compilation by Wohlmann of chemical analyses from over a hundred thermal waters around New Zealand (Table 2).[7] Many of these analyses were undertaken by Maclaurin (Fig. 1C) in the early years of Wohlmann's appointment. Wohlmann used a relatively straightforward chemical classification system for the waters analysed, based on the amount of chlorides, bicarbonate, sulfur-species and 'total solids'. Nearly a fifth of the analyses were of 'chalybeate' waters (type G in Table 2; typified in Europe by "bicarbonate of iron and free carbonic-acid gas", but in New Zealand also containing "large and sometimes enormous quantities of the sulphate"), which were therapeutically important in the European spas. About the same number of analyses were of 'alkaline sulphur' waters (type H1 in Table 2), which had a high content of silicates.

This information was subsequently published in a book,[8] for which the archival file relating to its preparation makes it quite clear that Wohlmann was a compiler of information provided by others rather than a field investiga-

Table 2. Analyses of thermal waters, by type and date, compiled from Wohlmann (1907)*

Analyst†	**Type of geothermal water**‡														**Total**
	A	***B1***	***B2***	***B3***	***C***	***D***	***E***	***F***	***G***	***H1***	***H2***	***H3***	***I***	***J***	
Pond	1								1		1				3
Skey	1	3	1	12		1			5	5	1				29
Hector									2	5			1		8
Unsp.	1				1			2	2	2	4	2			14
Year¶															
1878		1	1	1											3
1882									1		1				2
1883	1	1		1											3
1885	1		1	1											3
1886		1													1
1888		3													3
1889		1		1											2
1901	3														3
1902		1		2					1						4
1903	1	1	3	5		1									11
1904	2	2	3			3	1		7	3				1	22
1905		1	2	2		1			6	5	2				19
1906			1	1					1		4	1			8
Total	11	15	12	25	1	6	1	2	26	20	13	3	1	1	138

*Analyses of waters that fit more than one 'type' in the classification used by Wohlmann are included more than once in the compilation.

† 'Pond' indicates analyses undertaken by J.A. Pond; 'Skey', analyses undertaken by William Skey (see Fig. 1A); 'Hector', analyses reported by James Hector (but undertaken by others, probably William Skey).

‡Classification used by Wohlmann: ***A***, Simple (weakly mineralized); ***B1***, Muriated waters, Class I – Sodic muriated waters (very hot; dominated by NaCl); ***B2***, Muriated waters, Class II – Calcic-sodic muriated waters (dominated by NaCl, $MgCl_2$, $CaCl_2$); ***B3***, Muriated waters, Class III – Iodide muriated waters (NaI, MgI_2, and 'free iodine'); ***C***, Simple alkaline waters (dominantly $NaHCO_3$, small amount of NaCl, considerable 'carbonic acid gas'); ***D***, Muriated alkaline waters (considerable NaCl with $NaHCO_3$); ***E***, Muriated sulphated waters ('overwhelming proportion of chlorides' but also moderate $MgSO_4$); ***F***, Calcareous; ***G***, Chalybeate ($Fe(HCO_3)_2$ and 'free carbonic acid gas'); ***H1***, Sulphur waters, Class I – Alkaline sulphur waters (NaCl, with high amounts of silicates); ***H2***, Sulphur waters, Class II – Acid sulphate waters (strongly acid, high sulphate and sulphuric acid); ***H3***, Sulphur waters, Class III – Muddy Waters; ***I***, Arsenical Waters; ***J***, Mercurial waters (muriated water containing mercury derived from soil).

¶ Only years for which analyses are given are included; from 1901 these analyses were mainly undertaken by J.S. Maclaurin (see Fig. 1C)

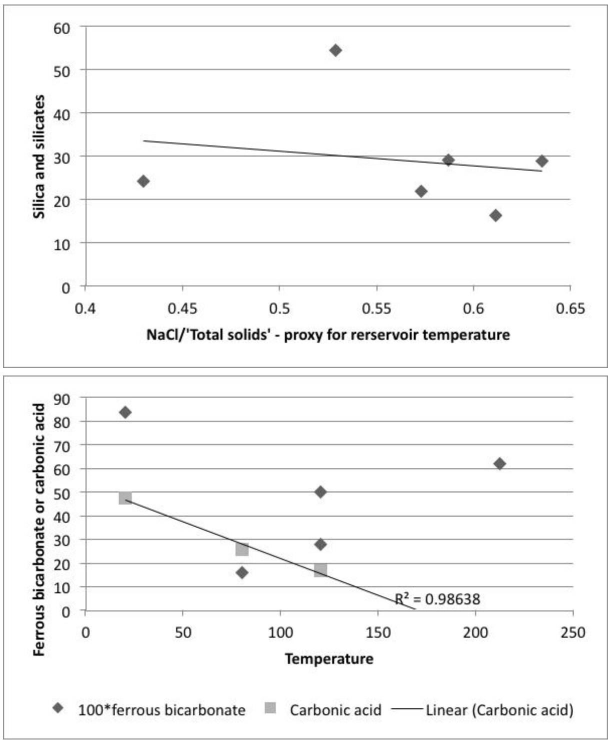

Fig. 3. Some correlations from Wohlmann's 1907 data. *Upper:* Ratio of NaCl to 'total solids' (a proxy for temperature) versus silica content in the 'alkaline sulphur' waters at Rotorua. *Lower:* Variation of $Fe(HCO_3)_2$ and carbonic acid with temperature in chalybeate waters; there is a strong relationship between carbonic acid content and temperature. (Concentrations in grains per gallon; temperatures in °F.)

tor or a chemical analyst.[9] For all that, Wohlmann was not prevented from reporting on the prospects of commercial development of other springs, e.g., Pipiriki, as described in a previous article in this journal.[10]

Given Wohlmann's primary interest in the therapeutic properties of the thermal waters – he was a medical man by training after all – it is not unexpected that he appears to have been particularly interested in the springs that contained iodine (25 analyses of type B3 in Table 2). He noted,

"The therapeutic value of such minute quantities of iodide has been much questioned… There remains the possibility, however, that the essentially active factor in these waters is not the iodide but the *free nascent iodine* [italics as in original document], which is almost always present. The pungent smell of this mineral may generally be detected for some distance round the source of an iodide spring, and where the thermal water is broken up by a fall into a spray or douche, under which circumstances free iodine seems to be liberated, the odour is particularly strong. It is conceivable that, quite apart from the iodine that is taken into the system when the water is drunk, quite an appreciable amount, and that in a highly active condition, may be inhaled with the water vapour and spray by the bather."

Apart from the known links of iodine with treatment of goitre, there is no clear evidence that subtle differences in chemical composition of thermal water contributed to the effectiveness of any cure alleged by 'taking the waters' – whether by drinking or bathing.[11] However, the warmth of the water in combination with its chemistry was perceived as generally beneficial. Wohlmann was perhaps at his most generous in this regard when he wrote that silicates in the 'alkaline sulphur waters' at Rotorua were responsible for these waters having a "peculiarly bland and satiny feel, and which makes them so valuable for bath purposes".

The chemical analyses reported vary widely in the number of constituents analysed, making comparisons between waters difficult. Within particular types of water, however, some interpretation of the compositional data is possible. For the 'alkaline sulphur waters', for example, there is a weak inverse relationship between the relative amount of NaCl and the amount of silica and silicates (Fig. 3A). This may be attributed to the relative amount of NaCl being considered a crude measure of temperature in the geothermal reservoir and the amount of silica is related to the near surface temperature of the thermal water. Similarly within the limitations of the small data set, there is an association between the temperature of chalybeate waters and the amounts of ferrous carbonate and carbonic acid they contain (Fig. 3B).

Although not a geologist, Wohlmann recognised that there was a variation in the chemistry of the waters with location. As examples he noted, "…in the central pumice plateau, from the south of Taupo to Rotorua, and thence on to the Bay of Plenty, the vast majority of the springs are very hot, and suphuretted, siliceous, and weakly mineralised; while along the east coast, from East Cape to Cape Palliser, muriated waters of high specific gravity, and containing iodides, predominate." (Table 3).

Modern interpretations of geothermal chemistry attribute the Bay of Plenty thermal waters with active volcanism, those in Northland with recent volcanism, and those in eastern North Island and the South Island with the compressional boundary between the Pacific and Indo-Australian tectonic plates.

Wohlmann never resiled from his view that the provision of a single major spa centred on Rotorua, with subsidiary spas in Te Aroha and Hanmer, was sufficient to meet the balneological needs of New Zealand and its tourists (Fig. 4). This was probably as well, since the popularity of 'taking the waters' in private baths (with its medical overtones), compared with public bathing (which was more obviously recreational) declined even during the colonial period. An example of this trend is shown for Te Aroha in Fig. 5. Moreover, overall patronage of nearly 44,000 bathers in 1909 at Te Aroha had declined to a mere 24,000 by 1926. By this time Wohlmann had returned to England.

As mentioned earlier, the analysis of these thermal waters was undertaken at the Colonial Laboratory, adjacent to the Colonial Museum, in Museum Street in Wellington. The local paper described a tour through the first laboratory building in 1866,[13] while it was still under construction:

"Entering the laboratory, the visitor will be in a hall or passage 10 ft long and 4 ft wide. Out of this, on the right will open the office, a room 10 ft by 10 ft and on the left

Table 3. Analyses of thermal waters, by type and location, that were compiled from Wohlmann (1907)

Location		Type of geothermal water*														Total
		A	*B1*	*B2*	*B3*	*C*	*D*	*E*	*F*	*G*	*H1*	*H2*	*H3*	*I*	*J*	
Northland							1		1	2					1	5
Auckland			6	1	2		2			1						12
Waikato	Te Aroha						3									3
	Other	4	1	1	1	1				1						9
Bay of Plenty	Rotorua				1					5	10	6	3			25
	Taupo				8					6	9	4		1		28
	Other	1	1							2		2				6
Eastern North Is.	Morere			2	2											4
	Other		2	3	9					3						17
Other North Island		1	3	3	2					1						10
South Island	Hanmer										1					1
	Other	5	2	2	1			1		4		1				16
Locality not now known									1	1						2
Total		11	15	12	26	1	6	1	2	26	20	13	3	1	1	138

*Types of water as in Table 2.

Fig. 4. Only one photograph of A.S. Wohlmann is known, that shown in Fig. 1B. However, this cartoon shows him (at left), being interviewed by a *Herald* reporter about the efficacy of Rotorua's thermal waters for a health resort.[12]

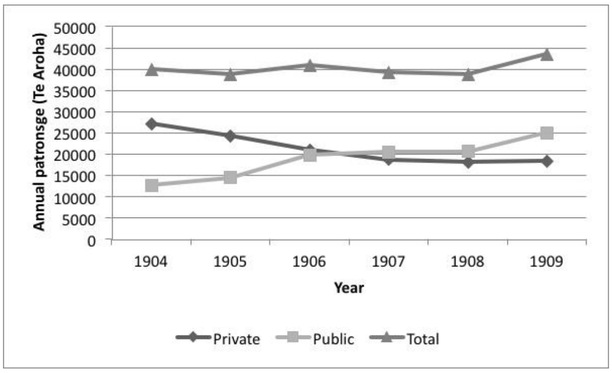

Fig. 5. Annual attendance at Te Aroha spa, 1904-1909. Data from *Appendices to the Journal of the House of Representatives*.

the weighing room, also 10 ft square. Through the weighing room, the visitor will pass into the furnace rom, 11 ft square, built with a brick floor and supplied with three improved furnaces. From this room, a door to the right will lead him to the room for chemicals, 11 ft by 10 ft, and through it to the store room, 10 ft square. Admission will also be obtained out of the furnace room to the analysis room, 10 ft square, and to the coal store, 10 ft by 4 ft. The whole building will be neat and compact. The furnace room will be furnished with a brick chimney, and also with a brick drain running northwards towards Sydney Street."

When Skey's successor, J.S. Maclaurin was appointed in 1901, James Hector noted in a memorandum to the Under Secretary of Mines, "The present laboratory has now been in use for over thirty years and is now in a very dilapidated state. Much of the lining is rotten, the floor and roof is out of order, the lighting is quite unsuitable for advanced laboratory work… As the laboratory is a constant menace to the safety of the Museum which contains Government property to the value of over 35,000 pounds I would suggest that the present laboratory be dismantled and that a new one be erected."[14] Hector's plea appears to have fallen on sympathetic Government ears, because a new building was reportedly erected in 1902, although by 1905 the Colonial Laboratory had moved into a more impressive brick edifice on an adjacent site in Sydney Street West (Fig. 6).[15]

The first laboratory building lingered on for another thirty years as one of a number of ancillary buildings to the nearby Colonial Museum. Its origins were largely forgotten until the whole complex was demolished in 1939 (Fig. 7), when a cellar inferred to have been part of the laboratory was discovered:[16]

"An interesting discovery during the removal [of the Colonial Museum] was a cellar hitherto unsuspected by many. It was described by a Press reporter at the time as a 'real damp, dark, and very medieval-looking dungeon.' The shifting of some cases had disclosed a ladder leading

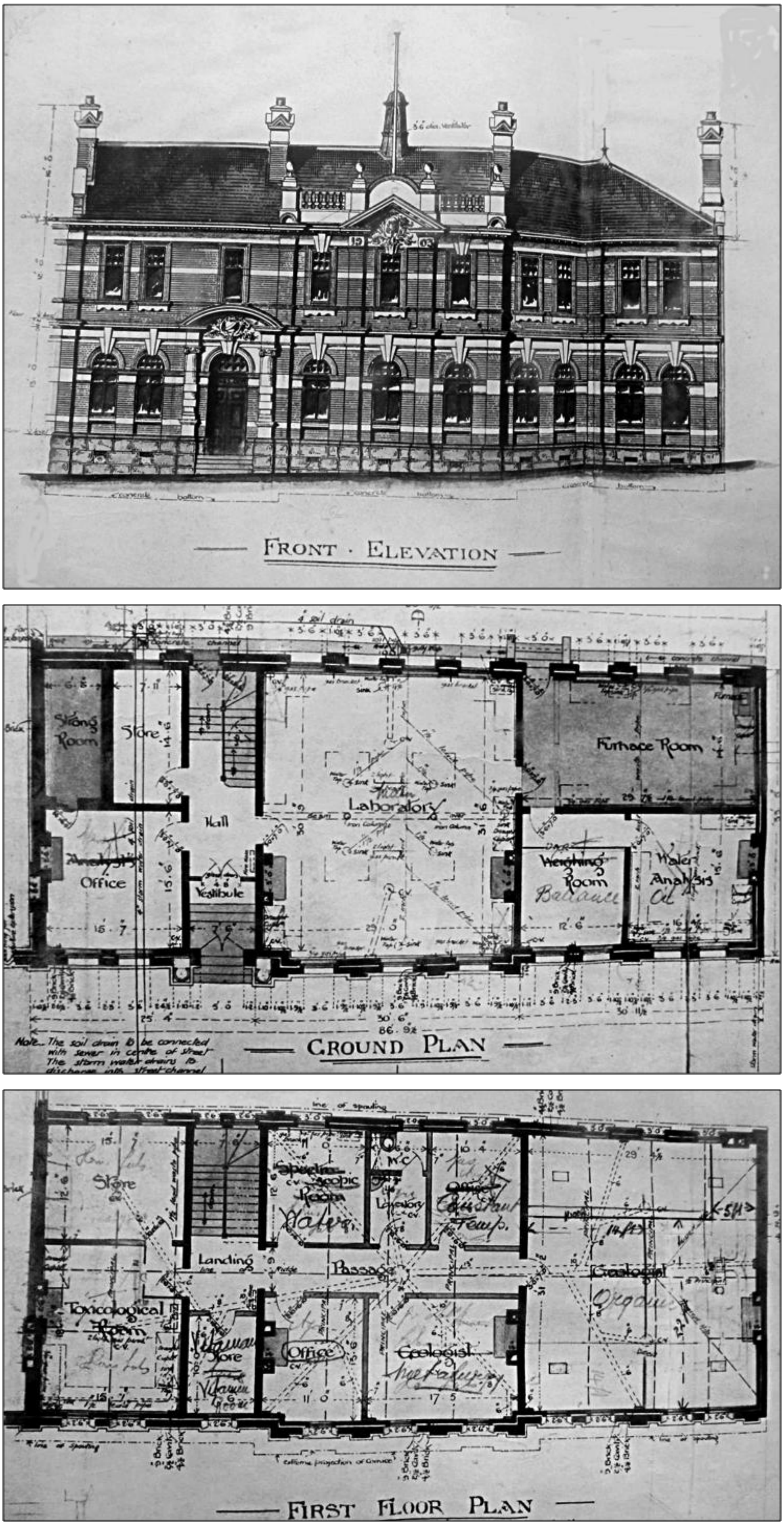

Fig. 6. The 1905 Colonial Laboratory Building. *Upper:* Front elevation; *Middle:* Ground floor plan; *Lower:* First floor plan; the dotted lines show ducts for ventilating the laboratories.

down below the floor level to a depth of about ten feet. Conjecture had it that in days long past the Government analysts and assayers used the fires there for the oven in the room above, which they used in the investigation of quartz [that allegedly contained gold] sent to them for assay. The existence of the cellar was, of course, known to the older men."

Wohlmann might have remembered this first Colonial Laboratory; he would certainly have approved of its demolition, consistent with his continuing requests for improved facilities during his term of office as the Government Balneologist. He died on 3 March 1944.

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Nanocomposites: From ancient masterpieces to value-adding nanotechnology

Andrea N. D. Kolb

School of Chemical & Physical Sciences, Victoria University of Wellington, PO Box 600, Wellington
(email: *andrea.n.d.kolb@gmail.com*)

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Introduction

Composites comprising metal nanoparticles (NPs) and glass, porcelain, gum arabic or gelatine have been known and investigated for hundreds of years.[1] For example, the Lycurgus Cup from the 4th century AD (Fig. 1), exhibited in the British Museum in London, is considered a masterpiece of the early glass industry. This work became famous for its dichroic effect that depends on the angle of the light shining on it; the cup appears red in transmitted light and green in reflected light.[2] As we know today, the effect arises from nanoparticulate gold–silver–copper alloys that are dispersed in the glass matrix of the cup.[3] Another famous use of nanoparticulate gold is the colourant "Purple of Cassius". Since the late 1600s, it has been used on a large scale as a decoration for factory-made ceramics,[4] and although pure gold, the colourant is available in shades of pink to maroon.

Fig. 1. The Lycurgus Cup (from Wikimedia Commons)

Optical properties of nanoparticles

The unusual colours of metal NPs arise from localised surface plasmon resonance (LSPR), which depends on the size, shape and dielectric function of the particle, and the refractive index of the surrounding medium.[5] This phenomenon is a result of the interaction of the electric field of light with the NP, which is accompanied by the absorption of a photon of energy by the particles. The gain in energy induces a dipole on the particle by collectively separating free conduction electrons (dense electron cloud) from the positively charged metal core. The separation of the electrons is confined to the boundaries of the metal particle due to the attractive forces of the positive core. The separating and restoring of the electron cloud results in an oscillation that is also called a "plasmon" of a NP. The oscillation resonates with frequencies in the visible and the near infrared region of the electromagnetic spectrum and creates a characteristic LSPR band (Fig. 2).[6] In simple terms, the dense electron cloud can be regarded as animated fans in a stadium who constantly perform a Mexican Wave. The steady performance creates a wave that travels continuously through the spectators. In the case of electrons, the collective oscillation is permanent and results in non-fading, distinctive colours. This makes gold NPs, for example, a highly effective colourant with a molar extinction coefficient that is approximately 2–5 orders of magnitude greater than that of conventional dyestuffs.[7,8]

In the case of 20 nm AuNPs, the LSPR band occurs at approximately 520–525 nm, which translates to a ruby red.[9] Smaller particles (10 nm) have a blue-shifted LSPR band and larger particles (30–100 nm) have a red-shifted band. Therefore, spherical AuNPs of 10–100 nm exhibit colours that range from red to pink, purple and lilac. Anisotropic particles, such as rods, 'dog-bones', plates, triangles, cubes and branched structures, possess both a transverse and a longitudinal axis which interact with the electric field of the incident light. Both interactions resonate with optical frequencies and occur as two separated LSPR bands. As a result, AuNPs of precise shape, dimension and length-to-width ratio can offer a powerful approach to engineering AuNPs with a wide colour gamut (Fig. 3).

Use of nanoparticles for the production of nanocomposites

Since the early 1900s, nanogold has been applied knowingly to produce nanocomposites. In the 1940s, for instance, nanogold–skin composites were produced by staining keratinous skin cells with AuNPs.[10] This staining technique uses an Au^{3+} precursor to impregnate the cells where it is reduced to Au^0 (AuNPs). The nanogold–skin composite is pink, deep red, reddish purple or purplish black, where the different colours represent different structural components of the skin. The reddish purple originated from very fine AuNPs and the deep purplish black was associated with rather coarse AuNPs.[10] In the 1950s, nanogold–wool composites were produced using a gold staining technique.[11] Like human hair, wool is a keratinous fibre with a complex and variable chemical and physical structure. The distribution, colour and colour intensity of the AuNPs showed that the gold deposition in the fibre was asymmetric, which helped to elucidate the bilateral inner structure of wool fibres.[11] In the 1970s, this staining technique was used commonly to produce a variety of metal–wool composites which were studied by electron microscopy.[12] The gold staining technique was a simple tool to learn about the histology of the substrate to which the AuNPs were attached. In more recent years, the focus in studying nanocomposites has turned from the concentration of the substrate component to the nanoparticle component of the composite and its unusual physicochemical properties. It has been realised that nanocomposites possess new or enhanced properties that exploit the natural synergy between the components. In the last decade, nanocomposites have been developed for application in the paper, textile and energy industries.

Nanocomposites can be produced using a chemical reaction to synthesise NPs in the presence of a substrate, which can include a variety of materials.[1,13] For example, both vegetable and bacterial cellulose were used as substrates in the production of nanocomposites comprising NPs of Au and Ag.[14,15] Such violet and grey nanogold–cellulose composites may find application in security paper production, while nanosilver–cellulose composites with antibacterial activity may be used for biomedical applications.[14,15]

In 2011, nanogold–wool composites for high value textiles and fashion apparels were reported.[16] The nanocomposite exhibited different colours, including deep purple (Fig. 4), which are associated with the LSPR properties of the AuNPs. The porous nature of wool and the affinity of gold for sulfur contained in the cystine amino acids were used to control the size of the AuNPs and to chemically bind them to the surface and within the wool fibre matrix. Because the AuNPs are chemically bound to the cystine, they do not wash or rub out and are also stable to UV light.[16]

Additionally in 2011, silver NPs (AgNPs) were used to colour merino wool fibres and fabrics (Fig. 5).[17] The AgNPs were produced by the reduction of Ag^+ to Ag^0 with trisodium citrate (TSC) directly on the wool fibre surface. The TSC simultaneously acts as a capping agent for the NPs and as a AgNP–wool linker. The nanosilver–wool composites exploit the LSPR properties of the AgNPs and are coloured in hues of yellow/orange, red/brown and brown/black depending on particle size. The coloured fibres and fabrics are anti-microbial, anti-static and durable, which makes them attractive candidates for applications in upholstery and carpets.[17]

The term "nanocomposite" is also commonly used to describe a material that consists of a substrate and pre-

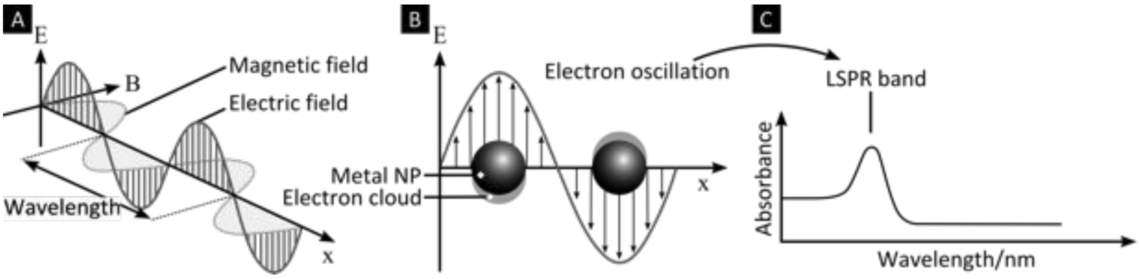

Fig. 2. Schematic illustration of LSPR of a metal NP. A: Electromagnetic field of light. B: LSPR occurs when the free conduction electrons of the NP interact with the electric field of the incident light of a suitable frequency. This induces a dipole by collectively separating the electrons from the positively charged metal core. This steady process of separating and restoring within the boundaries of the metal NP causes an oscillation of the separated, localised electrons (electron cloud). C: The oscillation of the surface electrons resonates with optical frequencies of light in the visible region and creates colours different from those of the respective bulk material.

Fig. 3. The many colours of nanoparticulate gold include shades of red, lilac, blue, turquoise and brown; from A.N.D. Kolb, PhD Thesis, Victoria University of Wellington, 2014.

Fig. 4. Purple nanogold–wool composites produced with AuNPs. Reproduced with permission from ref. 16. © 2011 Johnston and Lucas.

Fig. 5. Nanosilver–wool fibre composites produced with yellow AgNPs. Reproduced with permission from ref. 17. © 2011 American Chemical Society.

synthesised NPs which have been deposited onto the substrate in a separate work step. For over 15 years now, synthetic polymers, such as polyethylene (PE) and polyvinylalcohol (PVA), have been functionalised with metal NPs. The nanoparticle–polymer composites are produced by solvent-evaporation,[1] extrusion,[1] electrospinning,[18] or emulsion polymerisation.[19] Flexible nanosilver–PE composites appear yellow or red depending on the polarisation direction of the incident light. This makes them a potential colour filter to enhance the brightness and energy efficiency of light-emitting diodes (LEDs).[20] Composites comprising PVA and gold nanorods (AuNRs) with tuneable dimensions are also envisaged for the fabrication of thin film optical filters.[21]

In early 2011, the colouration of wool fabrics with anisotropic AgNPs of different colours was reported.[22] Colloidal AgNPs of different sizes and shapes were synthesised by the reduction of Ag^+ to Ag^0 with TSC in the presence of poly(vinylpyrrolidone) and H_2O_2. The AgNPs were blue (nanoprisms), red (thin nanodiscs) and yellow (thick nanodiscs), and the LSPR properties of the AgNPs deposited on the wool were essentially identical to those of the colloidal AgNPs (Fig. 6). [22] However, AgNPs are not stable to UV light and exposure is accompanied by an unattractive colour change over time.

In 2013, the colouration of cotton and silk fabrics with pre-synthesised AuNRs of different colours was reported.[23] The optical properties of AuNRs originate from two LSPR bands and can be precisely engineered by tailoring the longitudinal band. This approach resulted in AuNR–cotton and AuNR–silk composites that were brownish red, green and purplish red. The believed electrostatic AuNR–fabric interaction provided the AuNR–cotton composites with commercially acceptable wash fastness whereas the AuNR–silk composites failed the requirements. Furthermore, the AuNRs provided the composites with very good UV protection and anti-bacterial properties.[24]

The two examples of nanocomposites described above[22,23] were produced by binding pre-synthesised plasmonic NPs to a substrate where the binding was associated with electrostatic interactions. This type of bond is relatively weak and offers opportunity for improving the overall fastness.

Strong covalent bonds are achieved through specific wet-chemical approaches, such as the direct attachment of pre-synthesised carboxyl-functionalised microparticles (MPs) to amine-containing wool by an amide bond.[25] The reaction was assisted by the use of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide and *N*-hydroxysuccinimide as this combination supports amide bond formation under mild reaction conditions. The MP–wool composite showed moderate durability to solvent washing and poor laundering performance. Additionally, the covalent attachment of a reactive chemical entity to the wool surface after surface-bound lipid removal was investigated. This method provided a proof-of-principle for durable nanocomposites with wool as the substrate.[25] Both methods appear to be elegant and potential approaches for the production of more wash fast nanocomposites via a covalent NP–substrate bond.

Outlook

Nanocomposites consisting of precious metal NPs and materials have come a long way from Roman times to

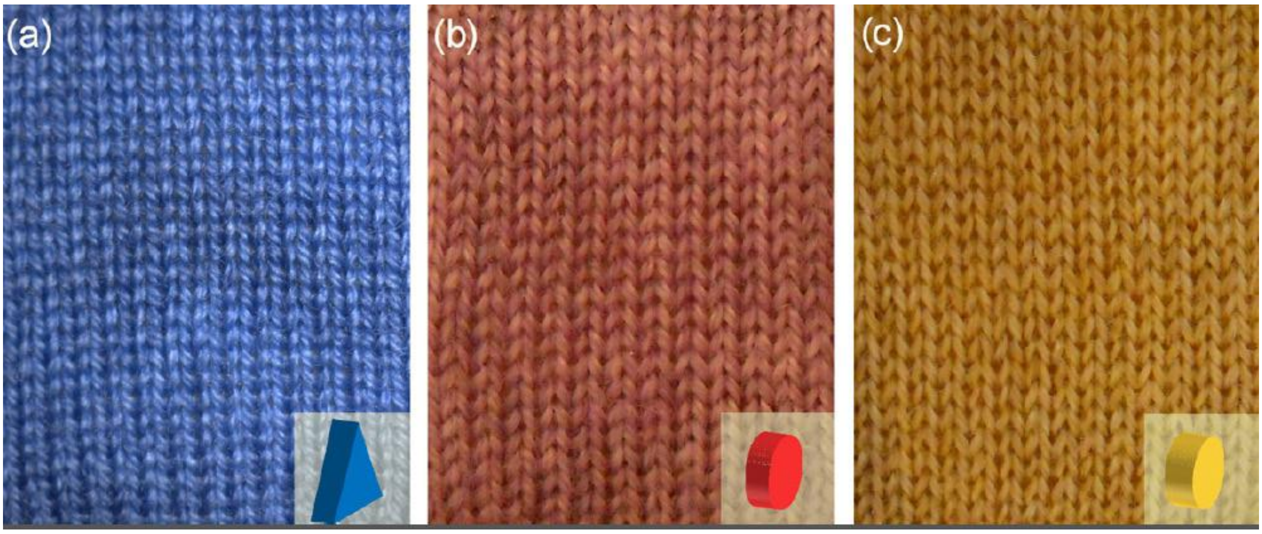

Fig. 6. Nanosilver–wool fabric composites produced with (a) blue, (b) red and (c) yellow AgNPs. Reproduced with permission from ref. 22. © 2011 Elsevier.

the present research in nanotechnology. Using plasmonic NPs as colourants for textile fibres presents an interesting approach to manufacturing finished, value-added products. This approach could be useful in the long-term success of the wool industry.

The latest research shows that even nature produces nanocomposites with AuNPs. The discovery that Eucalyptus trees mine gold from a depth of 30–50 m and deposit it through their leaves may be a new technique for gold site exploration.[26]

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Obituary: Dr Ian Walker

Unsung scientist introduced radar to New Zealand

Mike Crean

This article appeared in The Press, 16 August 2014. Reprinted with permission, Fairfax NZ.

Ian Walker was so dedicated to science and family he had no time for honours or awards.

Airline passengers fly around New Zealand in relative safety, thanks in great part to Dr Ian Walker.

Described by friend and colleague Professor Graeme Wake of Massey University as "an unsung hero", Walker worked in Britain on the development of radar and was instrumental in introducing it to New Zealand for use in aviation. He received little recognition and deserved much more, Wake says.

Walker was brought up in a devoutly Christian home. His father was a Methodist minister and World War I padre. His mother was the daughter of a Methodist missionary. Walker remained a humble Christian and never pushed his own case for recognition. He died peacefully in Christchurch last week, aged 97.

His early childhood was spent in Dunedin where he attended Arthur Street School. The family then moved to Auckland. As a pupil at Beresford Street School, he was awarded a scholarship in 1929 which gave him entry to Auckland Grammar School. He left school at 16 in the Depression for a job as trainee chemist in the laboratory of Westfield Freezing Co.

His work there including testing food for quality and safety and analysing ideas for new products and processes. He did part-time studies to gain a Senior National Scholarship and begin working towards a science degree.

Economic conditions deteriorated and he was made redundant in 1935. He then attended Auckland University fulltime and completed his BSc. He won a position as chemist with the Dominion Laboratory in Wellington and moved there in 1937. Studying part-time at Victoria University he gained an MSc in 1939.

World War II brought a shift in his focus from food chemistry to electronic physics. He worked in designing radar, first in New Zealand, then at the Radar Research and Development Establishment in England. Wake says Walker was a "generalist", able to move from food to radar and adept at combining theory with practice. He was influenced by radar pioneer Professor Ernest Marsden and worked with him to bring radar to New Zealand.

After the war Walker spent a year at Canada's Chalk River Atomic Research Laboratory. He then returned to England in a team of top physical scientists contributed by New Zealand to nuclear research as Britain was racing Russia to build an atom bomb. Based at the Atomic Energy Research Establishment at Harwell, he met his wife-to-be, Terry Earley. The Irish nurse worked in the medical section, caring for scientists exposed to radiation.

Walker wrote: "I wasn't very interested in girls. My sole interest was in science. And here we were, right at the very edge of the breaking wave of knowledge. Then Christmas came, 1946. I came into the canteen at lunch on Christmas Day. Everyone was disgruntled at having to work on Christmas Day. I looked across the table, and there was the most beautiful girl I had ever seen. Her beauty wasn't just physical, she radiated a vivacity and enjoyment of life I had never seen before. We chatted after lunch and I went back to work telling myself, you must stay away from that girl. She will disrupt your work. How true it was. Terry and I became inseparable and when I had completed my task at Harwell we married and she came back to New Zealand with me".

As Wake says: "Theirs was a true love story."

Walker re-joined the Dominion Laboratory in Wellington in 1949 and retired from it in 1977. By then it had become the Department of Scientific and Industrial Research (DSIR). He worked in the chemistry division and became its director in 1960. He became Assistant Director-General of the DSIR in 1972. He was made a Doctor of Science in 1962 and was appointed a Fellow of the NZ Institute of Chemistry on retirement.

He then worked under contract to DSIR to complete calculations and reports on his unpublished experimental work. He next accepted a post as senior research fellow at the University of Leeds, in England.

Wake then provided research facilities for Walker at Victoria University, Wellington. Wake says Walker did "world-class and groundbreaking" research there on spontaneous combustion of substances. He retired (again) in 1982.

He and Terry later moved to Governors Bay to be near family. Terry went blind in later years and he took great care of her until she died in 2009.

Granddaughter Rose says family and science were his obsessions. He loved his family and, with an "extraordinarily creative mind", entertained them with amazing stories. His fascination with science never waned, leaving him no time to consider suggestions of awards.

Wake says: "He was very energetic, vibrant and enthusiastic. He used to tire me out he was so impatient to get on with the research we were doing."

Walker kept fit by swimming almost every day, up to his late 80s.

Ian Kenneth Walker, born Auckland, February 19, 1917; died Christchurch, August 6, 2014. Pre- deceased by wife Terry (Therese) and son Patrick; survived by daughter Siobhan, sons Sean and Philip, five grandchildren and four great-grandchildren.

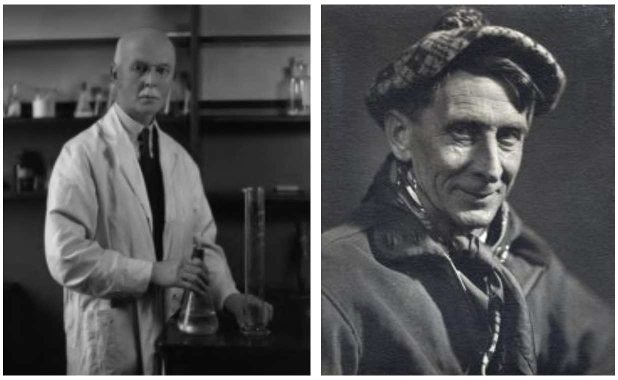
Some unremembered chemists

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

Sir Arthur Harden, FRS (1865-1940) & William John Young (1878-1942)

Brian Halton

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



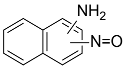
Left: Sir Arthur Harden FRS by Bassano Ltd. (© National Portrait Gallery London, with permission). *Right*: William John Young (courtesy University of Melbourne Archives)

Arthur Harden was born on Oct 12, 1865 at Moss Side in Manchester and William John Young some twelve years later on Jan 26, 1878, also in Manchester but in the suburb of Withington. They are connected not simply by their place of birth and education, but by their study of sugar fermentation and enzyme chemistry that took place at what became the Lister Institute in London. Harden was awarded the 1929 Nobel Prize in Chemistry jointly with German-born Swedish biochemist Hans von Euler of Stockholm University. Harden remained at the Lister Institute even beyond his 65th year after retirement in 1930. In contrast, Young left the Lister in 1913 migrating to Queensland, Australia, where he was the Biochemist at the Australian Institute of Tropical Medicine in Townsville for 7 years. In 1920, he moved to a lectureship at the University of Melbourne and rose to become the Foundation Professor of Biochemistry in 1938.

Sir Arthur Harden

Arthur Harden was the only son of Albert Tyas Harden, a Manchester business man who had married Miss Eliza MacAlister of Paisley, Scotland.[1] The family consisted of Arthur and his sisters who were brought up in a somewhat austere nonconformist atmosphere akin to the Scottish Presbyterians, renouncing the theatre and regarding Christmas almost as a pagan festival. At the age of 7 years Arthur attended a private school run by Dr Ernest Adam in the Manchester suburb of Victoria Park (the Victoria Park School). In 1877, at 11 years of age, he moved to Tettenhall College in Wolverhampton where he remained until he was 16, having stayed on for an additional term in order to qualify for the London matriculation. Then, in January 1882, he entered Owens College (Victoria University) Manchester, and studied chemistry under Professor (Sir) Henry Enfield Roscoe, then at the height of his fame as a teacher. He graduated with first class honours in 1885 and a year later was awarded the Dalton scholarship of the College.

Harden's first research was on *the action of silicon tetrachloride on aromatic amide compounds* and was published in the January 1887 issue of the Transactions of the Chemical Society.[2] From Manchester he proceeded to Erlangen and, under the direction of Otto Fischer, prepared a nitrosonaphthylamine (**1**) and investigated its properties that gave him his PhD degree. He returned to Manchester as junior and later senior lecturer and demonstrator under Professor H.B. Dixon who had succeeded Roscoe as Professor of Chemistry. Harden stayed there until 1897 when he was appointed chemist to the newly founded British Institute of Preventive Medicine, which later became the Lister Institute in London.



1

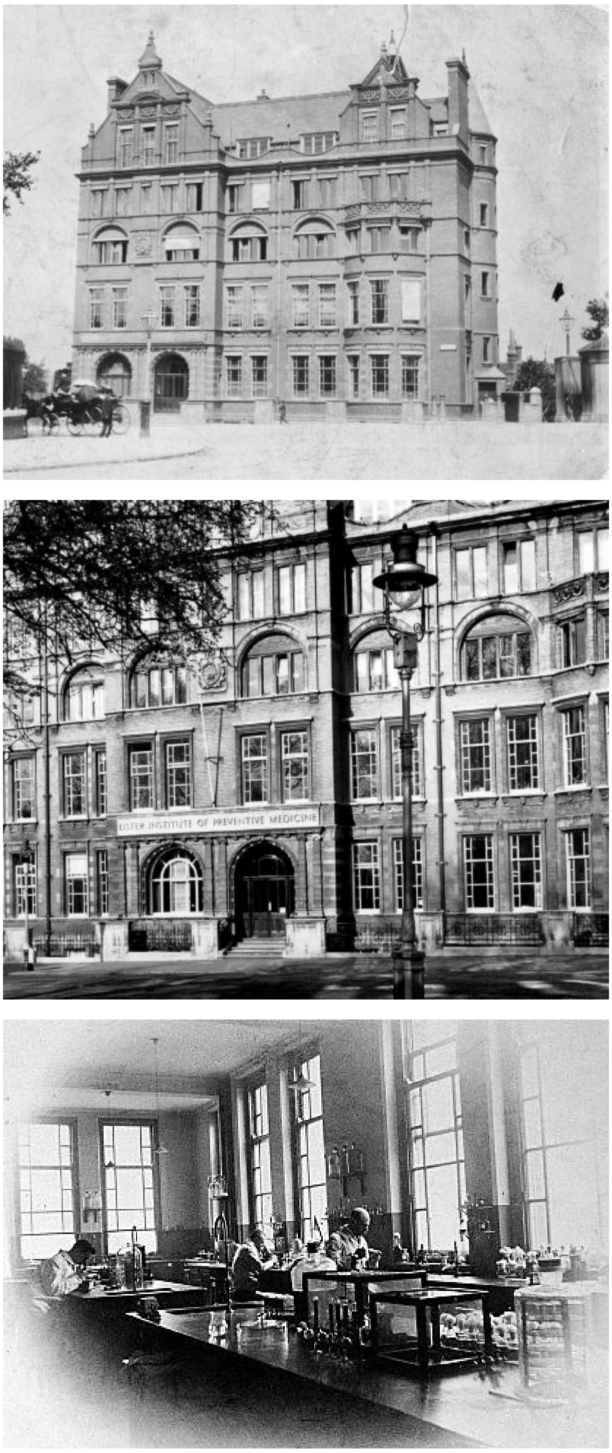
During his time at Owens College, Harden lectured to the honours students on the history of chemistry, a subject interest he shared with Roscoe. His interests were primarily in teaching and literary work, and he published only two papers based on laboratory study. With Roscoe he studied the notebooks of Manchester teacher and noted chemist John Dalton and concluded that it was his studies of gas diffusion that led him to formulate his atomic principles. They published their views in the Philosophical Magazine and in the Zeitschrift für Physikalische Chemie in 1897, and afterwards in a book entitled: *A new view of the genesis of Dalton's atomic theory*.[3] Moreover, Roscoe and Harden collaborated in writing a textbook to fulfil the needs of students for the higher South Kensington examination.

A short time after Harden joined the Preventive Medicine Institute in 1897 it was renamed the Jenner Institute (after the pioneer of smallpox vaccine) and then, in 1903, as the Lister Institute in honour of the great surgeon and medical pioneer, Dr Joseph Lister. Later it became a School of the University of London. At the time Harden joined the Institute, instruction in bacteriology and chemistry was provided for medical practitioners wishing to become Medical Officers of Health. Harden took responsibility for the chemical course, which was concerned mainly with the analysis of water and foods. However, after a few years, the medical schools in London introduced special teaching for a diploma in public health and this led to the Jenner Institute classes being discontinued. Harden then became a full-time researcher. Initially, there were two chemical departments at the Lister Institute (as it had become). One was 'Chemical' under Harden, the other 'Biochemical' presided over by S.G. Hedin who left in 1905. The two departments were merged in 1907 to become the Biochemical Department and Harden was placed in charge, a position that he held until his retirement in 1930. In 1912, in recognition of his outstanding work on bacterial chemistry and alcoholic fermentation, he was made Professor of Biochemistry at the University of London.

The Harden-Young collaborative years

Soon after the Institute of Preventive Medicine became the Jenner Institute, Harden showed interest in biology. His senior colleague there was Alan Macfadyen and he suggested that Harden could be interested in an investigation of the fermentation of sugars by bacteria. The initial objective was to find diagnostic means for the differentiation of varieties of *Bacillus coli*, but Harden adopted a wider scope. By keeping a carbon balance sheet based on the amounts of the various products isolated, he discovered several substances not previously known to be formed by such bacterial decomposition. Although several products of the fermentation of *B. coli* had been identified, Harden was the first to construct a picture of the breakdown process as a whole. His first paper on the action of *B. coli communis* and allied organisms on sugars appeared in 1899 in the Transactions of the Jenner Institute and a more extensive account in 1901.[4] In this, he compared the results of the fermentation of glucose with that of other hexoses and pentoses and on mannitol and glycerol. He showed that acetic acid and ethanol were formed in equimolecular proportions and that the two terminal alcohol groups were the source of them. In 1906 he published similar observations on the action of *B. lactis aerogenes*.[5] This organism gave a different amount of acetic acid and alcohol and one-third of the fermented glucose could not at first be accounted for; the deficit was found partly in the form of 3-hydroxybutanone (MeCOCHOHMe) and partly as the reduced butane-1,3-diol. The butanone proved to be the substance responsible for the colour reaction of the Voges-Proskauer test used as a diagnostic criterion by bacteriologists. Although further papers appeared in 1912, Harden's work on bacterial chemistry did not attract the attention at the time that it should – bacteriologists did not appreciate what it was about, and chemists found it too removed to be of general interest.

Eduard Buchner's 1897 discovery[6] that the cell-free juice expressed from yeast would ferment sugar impressed Macfadyen and Harden. However, the initial crude preparations of zymase (the enzyme complex that catalyzes the fermentation of sugar into ethanol and CO_2) had two drawbacks, i) the yeast juice produced a considerable amount of C_2H_5OH and CO_2 without the addition of sugar, and ii) it rapidly lost its power to ferment. Harden found that auto-fermentation was caused by enzymatic action on the glycogen expressed from the yeast cells and that it stopped when the supply was exhausted. He concluded that the deterioration in fermentation was from the destruction of the zymase by the protease also present in the expressed juice. While these investigations had no direct impact on understanding the chemistry of sugar fermentation, they led to two fundamental discoveries. The first was that the zymase would not convert sugar into alcohol unless another substance, a co-ferment that we now know as NAD (nicotinamide adenine dinucleotide), was present. The second was that phosphate was also necessary. In these studies Harden was powerfully supported by a number of able co-workers that he attracted to his laboratory.



The Lister Institute: *upper*, early 1900s; *centre*, 1930s, and *lower*, Harden in a laboratory (images courtesy of the Wellcome Library, London; see: http://archives.wellcomelibrary.org)

Notable amongst these were W. J. Young, R. Robison (who succeeded him), F.R. (Lord) Henley and Miss M.G. Macfarlane. Harden attracted these young collaborators because of his wide knowledge of chemistry and capacity to analyse data dispassionately and accurately define the justifiable interpretations. He was labelled a superb critic unduly suspicious of adventures into the realm of imagination!

Thus, the attention of Macfayden and Harden had focused towards yeast from the late 1890s and other experiments were started at the Jenner Institute aimed at obtaining a yeast antibody. In 1901, a paper appeared in collaboration with Roland[7] on the auto-fermentation and liquefaction of yeast. It is especially interesting as it cites the assistance of Mr William John Young, who joined the institute from Manchester after appointment as assistant to Harden in 1901; he arrived there in early 1902 designated as Assistant Biochemist. It can be but assumed that this acknowledgement is to experiments that Young conducted in Manchester. Nevertheless, it was from this time that Harden and Young began a fruitful collaboration on the biochemistry of carbohydrates that lasted some 10 years. With Young, Harden examined the preparation of yeast glycogen, and made a careful comparison of its properties with those of the glycogens obtained from the oyster and the rabbit.[8] Soon they found that boiled yeast juice, itself incapable of producing fermentation, greatly increased the amount of CO_2 evolved when added to a fermenting mixture of glucose and yeast juice. They attributed this stimulating effect to an increased activity of the alcoholic ferment and not to the diminution of proteolysis (the breakdown of proteins into smaller polypeptides or amino acids). By replacing the traditional gravimetric analysis for CO_2 by a simple volumetric one they were able to make frequent determinations of the CO_2 evolved and study the progress of the reaction at ten-minute intervals for as long as necessary.

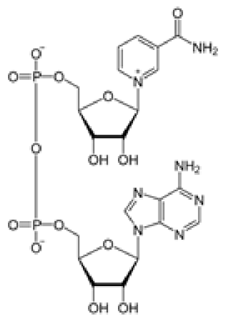
In 1903, the Jenner Institute again changed its name and became the Lister Institute with Dr C. J. Martin coming from his position of Professor of Physiology at the University of Melbourne to be its Director. In working on the antitoxin of snake venom, Martin had devised a gelatine filter that worked under high pressure and which he had applied to the separation of high-molecular colloids from crystalloids.[9] He suggested to Harden that perhaps it could be used for separating their yeast juice into its constituents. By using this filter, Harden and Young effected the separation of their juice into a clear solution and an oily residue. Separately, both of these solutions were inactive but together their activity was almost equal to that of the original juice.[10] A further paper dealt with the differences between the results obtained by Macfadyen, Rowland and Morris, and by Buchner in their respective investigations on yeast press juice. Their explanation was found to lie in the differences between the bottom and top yeasts that had been used in the two investigations. In this paper,[11] both prior studies had noted a considerable proportion of the sugar was converted into non-reducing substances and this was stressed and then accounted for by the conversion of sugar into polysaccharides.[12] The Institute of Brewing to which these researches were described showed much interest. Between the years 1906 and 1911, Harden and Young contributed six papers in all to the Proceedings of the Royal Society in which they described their classical researches on alcoholic fermentation and Young was awarded the DSc degree by the University of London in 1910 as a result of them.

The pair found that the phosphate entering into the fermentation reaction was changed into a form no longer capable of precipitation by the magnesia mixture employed, yet a solution of soluble phosphate could not replace the boiled juice. Another factor, for which Harden adopted the term co-ferment, was also present. Both phosphate and co-ferment co-operated together with the zymase of the unboiled juice to produced fermentation. Disappearance of either the ferment or the co-ferment brought the fermentation to an end. Usually it was the co-ferment that was expended first but it disappeared less rapidly in the presence of glucose than in its absence. Addition of phosphate led to the decomposition of an equivalent amount of glucose and a greater total amount of fermentation. The change of the phosphate to a form no longer precipitated by the magnesia mixture was explained when Young isolated the barium salt of a hexose diphosphoric acid. His demonstration of the slow conversion of the hexose diphosphate into hexose and phosphate by yeast juice was another important step.[13] The equations representing the reactions were given by him as:

$$2C_6H_{12}O_6 + 2Na_2HPO_4 = 2CO_2 + 2CH_3CH_2OH + C_6H_{10}O_4(PO_4Na_2)_2 + 2H_2O \quad \text{(Equation 1)}$$

$$C_6H_{10}O_4(PO_4Na_2)_2 + 2H_2O = C_6H_{12}O_6 + 2Na_2HPO_4 \quad \text{(Equation 2)}$$

The co-ferment was regarded as a substance containing a phosphoric group combined with a group of unknown composition by means of which the phosphate was passed to the sugar and a new phosphate group taken up. There followed a period of controversy and for about 25 years the nature of the coenzyme provoked much discussion and research. Harden and Young had correctly described it as a body in which phosphate was combined with some other group that took up and passed on the phosphate group, but it was only in 1937 that the independent work of Warburg[14] and of Euler[15] successfully established its structure as that of adenine pyridine diphosphonucleotide, named by Warburg and Christian as diphosphopyridine nucleotide, which by 1953 had become recognised as DPN and then, from 1961, it was changed to the now accepted nicotinamide adenine nucleotide (NAD, **2**) by the International Union of Biochemistry.[16] The partnership of Harden and Young gave the part played by phosphorylation in carbohydrate breakdown and the necessity for the intervention of both phosphate and coenzyme. It ended only with Young's appointment to the Australian Institute of Tropical Medicine at Townsville in 1912 when Robert Robison was appointed his successor. Harden went on to become (with Hans von Euler-Chelpin) the 1929 joint winner of the Nobel Prize in Chemistry for investigations on the fermentation of sugar and fermentative enzymes.



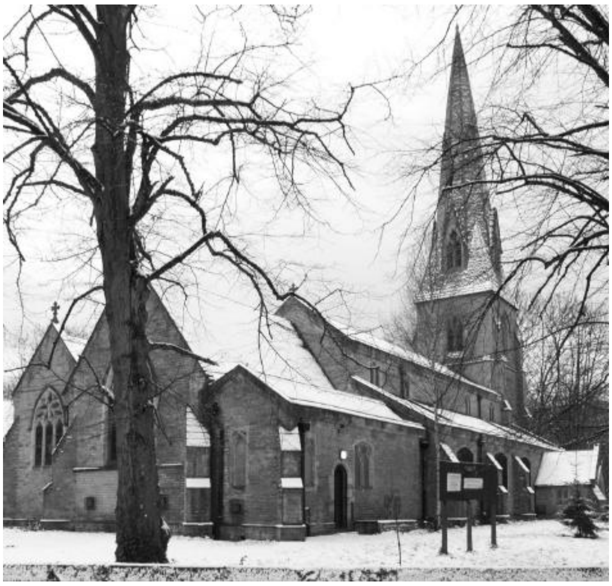
2, NAD

Whilst Harden formally retired on his 65th birthday he continued to go daily to his laboratory carrying on experimental work and correcting proofs until a year or two before his death. He was a founder-member of the Biochemical Society in 1911 and for 25 years from 1912 the editor of *The Biochemical Journal*. Arthur Harden was elected to the Fellowship of the Royal Society in 1909, awarded its Davy Medal in 1935 and was knighted in 1936. He served on the Council of the Chemical Society and became Vice-President. In 1900, he married Georgina Sydney Bridge of Christchurch, New Zealand. They had no children and she predeceased him in 1928. Arthur Harden died at his home Sunnyholme in Bourne End, Buckinghamshire, on June 14, 1940.

The great achievement of Harden and Young was the discovery that the process of phosphorylation and dephosphorylation forms the basis of carbohydrate metabolism. They elucidated the manner in which this process was brought about, since they discovered that a definite substance, the coenzyme, existed and suggested that its function was to take up and pass on the phosphate radical. Their evidence of phosphorylation was indisputable since they isolated two intermediates in which phosphate was bound to the hexose molecule, the 1:6-hexosediphosphate and the 6-hexosemonophosphate. Evidence of the process of dephosphorylation was given when they described the effects of a specific enzyme, a hexose diphosphatase, breaking down the hexose diphosphate with liberation of free phosphoric acid. The foundations of carbohydrate biochemistry were well and truly laid by these workers.

Professor William John Young

As recorded at the outset, W.J. Young was born in Manchester in 1878. He was the son of William John Bristow Young, a clerk, and his wife Hannah (née Bury). Educated locally at Hulme Grammar School, he showed interest in science and after leaving school he enrolled in Owens College. He graduated with his BSc in 1898 beginning research early in his career; he was granted the Levinstein and Dalton research exhibitions for 1899-1900 and 1900-1901, respectively, and graduated with his MSc in 1902. On July 30, 1903 he married Janet Taylor at St Margaret's parish church in Whalley Range, Manchester. After his fruitful collaboration on carbohydrate metabolism with Harden in London, Young applied for and was offered the position of Biochemist at the Australian Institute of Tropical Medicine in Townsville by a selection committee chaired in London by Dr. C.J. Martin (then Director of the Lister Institute). With his wife and young daughter Sylvia, Martin left London in late 1912 for Queensland.[17-19]



St. Margarets, Whalley Range, Manchester

Proposals for the Tropical Medicine Institute in Townsville were adopted in 1908 and Austrian Dr. Anton Breinl appointed its inaugural Director from his post at the Institute of Tropical Medicine in Liverpool. He arrived in Queensland on January 1, 1910, holding the reputation as one of the most promising medical scientists working in Britain;[20] he had discovered an organic arsenical cure for sleeping sickness in 1904. This discovery subsequently was exploited by Ehrlich to produce salvarsan (arsphenamine) for the treatment of syphilis. From 1910 till 1912, Breinl and his laboratory assistant (Fielding) were housed in a three-roomed building that had been the wardsmen's quarters in the grounds of Townsville hospital. It was only in 1912 when John Nicol, Henry Priestley and William Young were appointed to the staff that laboratory science was initiated in Northern Queensland allowing Townsville to become the birthplace of Australian biochemistry.[20]

William John Young arrived with his wife and daughter in early 1913 and it is said they had a happy time in Townsville.[17,18] William's work there, both alone and with Breinl[21] was mainly concerned with the metabolism of Whites living in the tropics and these studies led to four papers with Breinl, most notably that[22] in the Annals of Tropical Medicine and Parasitology in 1920. Young had a further four publications on the subject alone and another five on diverse topics. The success of the Institute[20] was such that, by 1920, it had adequately demonstrated that the tropical regions were habitable by a "working white race", as specific conditions such as leptospirosis (or Weil's disease) had been understood. It had served its purpose and was disbanded in 1921 to be subsumed into the newly founded Commonwealth Department of Health.

By then William John Young had moved to Melbourne as, in 1920, W.A**.** Osborne, Professor of Physiology at the University there had secured his appointment as lecturer in biochemistry to take charge of the subject. Soon after arriving in Melbourne, William developed an interest in the applied biochemistry of food preservation and transport, and subsequently became the leading Australian expert and innovator in this field. He solved problems associated with the conveyance of chilled meat, the preservation of citrus fruits and the ripening of bananas. Most likely he was the first academic in Australia to take a continuing interest in what is now recognised as food science and technology.[23] Young was promoted to Associate Professor of Biochemistry in 1924.

The year 1926 saw (Sir) Albert Rivett persuade the university to release Young to help the Council for Scientific and Industrial Research (CSIR) (with which he had worked closely) to establish laboratory and field studies into the biochemical problems of the cold storage of food. Despite Rivett's hopes of recruiting Young to the CSIR, William returned to his teaching duties in 1928, which included lecturing to agricultural, dental, medical and science students. However, Young remained a consultant to the CSIR and his recommendations led to the formation of the section of food preservation and transport in 1931. It was only in 1938 that William Young was appointed the inaugural Professor of Biochemistry at the University of Melbourne

By then he was the leading Australian expert and innovator in the field of food preservation and transport. He had solved problems associated with the conveyance of chilled meat and the preservation of citrus fruits and some of the methods that came from Young's studies are still used in the marketing of ripening bananas.[24] The Brisbane abattoir laboratory to study meat chilling had opened in 1932.[25] With the co-operation of Professors Bagster and Goddard of the University of Queensland, Young guided and planned in detail investigations on meat, fish, bananas and citrus, and provided room for the laboratory work to be performed in his own department. He was the first to train food technologists, though then they were not known as such, and he assisted C.P. Callister in his researches to become probably the first Australian DSc in food technology in 1931.[26] It was Callister who had developed Vegemite from brewer's yeast and marketed it in Australia in 1923.

Young was an active member of the Society of Chemical Industry of Victoria giving lectures and publishing various aspects of his work. Examples include *The Science of Fruit Preservation, Refrigeration of Beef, Preparation and Transport of Australian Chilled Meat; The ripening and transport of bananas in Australia*, and *An Experimental Shipment of Navel Oranges to Canada*. He had collaborated with W.A. Osborne whilst at the Townsville Institute[27] and he co-authored the text *Elementary Practical Biochemistry* with him through the first five of its six editions; it was published in Melbourne by W. Ramsay.

Young was an enthusiastic bushwalker and member of the Melbourne Wallaby Club holding the presidency during 1925-26. His contemporaries spoke of him as an indefatigable worker and a charming companion. He was gentle and modest with an uncommon sense of social involvement. He supported his profession holding the presidency of the Victorian Branch of the Australian Chemical Institute over 1938-39. William John Young died on 14 May 1942 in East Melbourne from a perforated gastric ulcer.

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Dates of Note

Richard Laurence Millington Synge, the British biochemist and 1952 Nobel Laureate (with Martin) for the development of partition chromatography, was born on October 28, 100 years ago, the same day as ***Jonas Edward Salk***, who developed the polio vaccine. ***Éleuthère Irénée du Pont***, the French-American industrialist who had worked for Antoine Lavoisier, migrated to the US in 1800 following the French Revolution. By 1803 he had established a small mill at Wilmington, Delaware, the foundation of the now internationally recognised company. Greenwich Mean Time (GMT) was adopted universally on November 1, 1884. ***Thomas Midgley*** Jr., the American engineer and chemist who discovered the effectiveness of tetraethyl lead $(C_2H_5)_4Pb$ in 1921, died on November 2, 1944, as did ***Thomas Anderson*** the Scottish organic chemist who discovered pyridine in 1874. ***Daniel Rutherford*,** the Scottish chemist who discovered the portion of air that does not support combustion, now known to be nitrogen, was born on November 3, 1749 and died on November 15, 1819. ***Ralph Wyckoff***, the American pioneer in the application of X-ray methods to determine crystal structures, died on this same date in 1994. November 4, 1869 saw the first issue of ***Nature*** appear in print. ***Paul Sabatier***, the French chemist who shared the 1912 Nobel Prize for Chemistry (with Grignard) for his metal-catalysed hydrogenation studies, was born on November 5, 1854. ***Hans von Euler-Chelpin***, the German-Swedish biochemist who shared the 1929 Nobel Prize for Chemistry with Sir Arthur Harden for work on the role of enzymes in the alcoholic fermentation of sugar (sse earlier in this issue), died on November 7, 50 years ago. ***Johannes Robert Rydberg***, the Swedish physicist, known for the Rydberg constant in his empirical formula that related the wave numbers of the spectral lines of an element, was born on November 8, 1854. ***Dmitry Iosifovich Ivanovsky***, the Russian microbiologist who from his study of mosaic disease in tobacco first reported the characteristics of a virus, was born on November 9, 150 years ago. It was the day in 1994 that saw the element 110, darmstadtium, (Ds) detected for the first time at the Gesellschaft für Schwerionenforschung (GSI) in Darmstadt, Germany.

Alfred Werner, the French-born Swiss chemist who was awarded the 1913 Nobel Prize for Chemistry for his founding research into the structure of coordination compounds, died on November 15, 1919. ***August Kundt***, the German physicist who developed a method (1866) to determine the velocity of sound in gases and solids in a tube named after him, was born on November 18, 175 years ago. ***John Robert Vane***, the English biochemist, who shared the 1982 Nobel Prize for Physiology or Medicine (with Bergström and Samuelsson) for the isolation, identification, and analysis of prostaglandins, died on November 20, ten years ago. ***Ancel Keys***, the American nutritionist and epidemiologist who identified the role of saturated fats in causing heart disease, died the same day. ***Henri Marie Laborit***, the French neurologist who discovered some of the earliest tranquilisers was born on November 21, 100 years ago. November 23 marks 50 years since the first successful coronary artery bypass graft was performed. ***Benjamin Silliman***, the American geologist, chemist and founder of the *American Journal of Science*, died on November 24, 150 years ago. ***Hermann Kolbe***, the well-known German chemist who accomplished the first generally accepted synthesis of an organic compound from inorganic materials, died on November 25, 1884. ***Chaim Weizmann***, the Russian-British-Israeli chemist who used bacteria for the synthesis of organic chemicals and who became active in politics leading to the establishment of Israel (1948), and then became its first president, was born on November 27, 1874. This is the same day as ***Bernard Jacques Flürscheim*** who made his fortune from the discovery of the high explosive tetranitroaniline. ***Enrico Fermi***, the Italian-born American physics Nobel Laureate, died on November 28, 60 years ago. ***Lewis Hastings Sarett*** the American organic chemist who prepared a synthetic version of the hormone cortisone from a 36-step process, died on November 29, 15 years ago. ***Andrew Jackson Moyer***, the American microbiologist who invented a method for mass-producing the antibiotic penicillin, was born on November 30, 1899. ***Robert A. Swanson*** who cofounded Genentech, Inc. - the research-based company that pioneered the biotechnology industry - died on November 30, 1999.

Philippe Lebon, the French engineer and chemist who invented illuminating gas, died on December 2, 1804. December 3 marks 30 years since the methyl isocyanate leak from the Union Carbide pesticide factory in Bhopal, India. ***Joseph Black***, the Scottish chemist and physicist who experimented with "fixed air" (CO_2), discovered bicarbonates and identified latent heat, died on December 6, 1799. December 7 marks 125 years since ***John Dunlop*** was issued his patent for the pneumatic tyre and is the day in 1884 that ***Louis Pasteur*** made his much-quoted remark, *In the fields of observation chance favours only the prepared mind*. Element 111, now roentgenium (Rg), was announced by the team at the GSI facility at Darmstadt on December 8, 1994. ***William Nunn Lipscomb*** Jr., the American physical chemist who won the Nobel Prize for Chemistry in 1976 for his studies of the boranes, was born on December 9, 1919. ***John W. Macklin***, the African-American analytical chemist known for refining the technique of Raman spectrometry, has his 75th birthday on December 11. ***Ludwig Mond***, the German-born British chemist and industrialist who perfected a method of soda manufacture, died on December 11, 1909.

Frank Harold Spedding, the American chemist who developed an economical process for reducing individual rare-earth elements to the metallic state, died on December 15, 1984. On December 15, 75 years ago, nylon was sold to hosiery mills to make women's stockings; marking the first commercial use of yarn for apparel. ***Bruce Nathan Ames***, the American biochemist and molecular biologist who developed the Ames test indicator for carcinogens, has his 85th birthday on December 16. It is the day in 1809 that French chemical contemporary and collaborator of Antoine Lavoisier ***Comte de Antoine Francois Fourcroy***, died. On December 18, 1839, ***John William Draper*** took his famous daguerreotype photo of the moon. ***Herbert C. Brown***, the English-born American chemist who developed organoboranes, died on December 19, ten years *ago.* ***Cyril Ponnamperuma***, the Ceylonese-American chemist, exobiologist and leading authority on the chemical origins of life, died on December 20, 1994. ***Edwin G. Krebs***, the American biochemist who shared (with Fischer) the 1992 Nobel Prize for Physiology or Medicine for discovering reversible protein phosphorylation (and not the Krebs of Krebs cycle fame), died on December 21, 2009. On December 22, 1879, ***Raoul Pierre Pictet*** announced his liquefaction of oxygen, while on December 25, 100 years ago, thyroxine was first crystallized by biochemist ***Edward C. Kendall***. ***Gerhard Herzberg,*** the German-Canadian awarded the 1971 Nobel Prize for Chemistry for his contributions to the knowledge of electronic structure and geometry of molecules, particularly free radicals, was born on December 25, 1904. ***Charles Martin Hall***, the American chemist who devised an inexpensive electrolytic method of extracting aluminium from its ore that enabled its worldwide use, died on December 27, 100 years ago. ***Kary B. Mullis***, the American biochemist, who devised the polymerase chain reaction (PCR) and shared the 1993 Nobel Prize for Chemistry (with Smith), has his 70th birthday on December 28. That day also marks the (accidental) discovery of dry cleaning 65 years ago. ***William Merriam Burton***, the American chemist who provided the first thermal cracking process that more than doubled the proportion of gasoline yield from crude oil, died on December 29, 1954. ***Jan Baptista van Helmont***, the Belgian chemist who recognized the existence of discrete gases and identified carbon dioxide, died on December 30, 1644.

Eugene Paul Wigner, the Hungarian-American physicist who shared the 1963 Nobel Prize for Physics (with Mayer and Jensen) for his contributions to the theory of the atomic nucleus and the elementary particles, died on January 1, 1995. This day 100 years ago in 1915 aspirin was made available in tablet form for the first time and, in 1935, Wirephoto™ was invented by AP News® enabling the transmission of photographs to member newspapers. ***Anselme Payen***, the French chemist who made important contributions to industrial chemistry and discovered cellulose, was born on January 6, 1795. On January 7, 1930, the element Fr (francium) was discovered while on 14 January 1970, L-dopa (levo-dihydroxyphenylalanine) was reported to benefit about 5% of the patients in reversing the progress of Parkinson's disease. ***Peter Waage***, the Norwegian chemist who, with his brother-in-law published the mass action law in 1864, died on January 13, 1900. ***Rolla N. Harger***, the American toxicologist and biochemist who invented the first blood alcohol testing machine called the Drunkometer, was born on January 14, 125 years ago. ***Artturi Ilmari Virtanen***, the Finnish biochemist who improved the production and storage of protein-rich green fodder, and won the 1945 Nobel Prize for Chemistry, was born on January 15, 1895. *Nicolas* ***Leblanc***, the French surgeon and chemist who developed a process for making soda ash (Na_2CO_3) from common salt (NaCl) in 1790 died on January 16, 1806. The process that bears his name was one of the most important industrial chemical processes of the 19th century. Sir ***Edward Frankland***, the father of valency and inventor of the chemical bond, was born on January 18, 1825. ***Adolf Friedrich Johann Butenandt***, the German biochemist who was the co-winner (with Ruzicka) of the 1939 Nobel Prize for Chemistry for pioneering work on sex hormones and primarily the isolation of estrone, died this same day 20 years ago. On January 19, 1915, a US patent was issued to ***George Claude*** of Paris that led to the neon sign. ***Horace Wells***, a pioneer in the use of surgical anesthesia using nitrous oxide in dentistry, was born on January 21, 200 years ago.

The Nagoya Protocol – what you should know

Tim Stirrup

Baldwins Intellectual Property, PO Box 5999, Wellesley St, Auckland
(email: *tim.stirrup@baldwins.com*)

In the chemical industries, a large number of our research materials are derived directly or indirectly from natural products or genetic resources. If you use either, you should know about the Nagoya Protocol. The Protocol is an extension agreement to the Convention on Biological Diversity (CBD) and its main aims are to facilitate access to genetic resources from each sovereign state, and to ensure the fair sharing of benefits arising from the research, development and commercialisation of those resources. The Protocol was initially adopted on 29 October 2010 in Nagoya, Japan and aims to provide a legal framework to regulate and legitimise the use of genetic resources and traditional knowledge,[1] particularly by third party countries or corporations. On 14 July 2014 Uruguay became the 50th state to ratify the Nagoya Protocol thus triggering the coming into force of the treaty itself some 90 days later. At present neither New Zealand nor Australia have ratified the Protocol.

Bioprospecting

The term bioprospecting is defined by the CBD Secretariat as "the exploration of biodiversity for commercially valuable genetic and biochemical resources".[2] Such resources are generally accepted to include chemical compounds, genes, micro-organisms, macro-organisms, and other valuable products from nature.

Bioprospecting (sometimes referred to as biodiscovery or biopiracy depending on your stance) is an age-old activity used to obtain new and improved products in industries including medicine, agriculture, cosmetics and materials science. It has the potential to increase economic prosperity and can encourage the conservation of habitats and biodiversity. Bioprospecting has led to many important medical innovations and the future use of genetic resources has potential to bring previously unknown or undeveloped medical treatments to the global population. One recent success story is the discovery of a new antibiotic – anthracimycin – said to be effective against anthrax and MRSA.[3] The compound is isolated from a marine actinomycete from the Pacific Ocean seabed off the coast of California.

The problem

When carried out in an unregulated fashion, bioprospecting can cause social resentment, especially where a community or country feels there has been an affront to their culture, rights or dignity. This often occurs where the bioprospector has not gained prior consent to access the resource from relevant stakeholders such as land-owners and indigenous/local communities. Environmental problems such as destruction of habitats and overexploitation of the genetic resource can also occur if bioprospecting is mismanaged or not effectively regulated.

The solution?

The Nagoya Protocol aims to establish accepted practices around bioprospecting and therefore reduce its negative consequences, especially by dominant states or corporations. To do this, states that have signed up to the Protocol will enact a set of legal principles that govern:

a) access to genetic resources;
b) sharing of benefits from the use of those resources; and
c) compliance with the principles agreed under the Protocol.

In practical terms, this means that if a researcher or collector wishes to remove genetic resources from the country of origin, or to make use of traditional knowledge they must (if the country requires) agree on the terms of access and how any benefits arising from the development of the resource are shared.

Access to genetic resources

A key tenet to the access principle is that the *user* of the genetic resource must obtain *prior informed consent* (PIC)[4] to access the resource from the *provider*. Informed consent means the *provider* is aware of who is accessing the resource, their general purpose, and the expected use of the resource. PIC may be granted via the state itself or, if the resource originates from an indigenous/local community, the *provider* state must first agree with the *provider* community terms under which access can be granted to *users*.

Benefit sharing

The second strand of the Nagoya Protocol is the establishment of measures to allow a share of the benefits arising from the *use* of genetic resources to be shared with the *provider*(s) of the genetic resources. Benefits may be monetary or non-monetary[5] and could include up-front payments, royalties or capacity building (e.g. innovation capacity, institutional development, education and training).

Compliance

Provider countries that have signed up to the Protocol will be expected to ensure that the genetic resources from within their jurisdiction have been accessed in accordance with prior informed consent and under mutually agreed terms. They should also have mechanisms to deal with disputes over access or ownership of the genetic resources and provide access to justice for relevant parties.

A bureaucratic burden?

The three principles of the Nagoya Protocol - access, benefit sharing and compliance - will be addressed in each signatory country by new or amended legislation, and/

or the formation of state administrative bodies. In some states, there is concern that the enactment of the Nagoya Protocol will lead to an excessive bureaucratic burden and restrict potential users of the genetic resources, possibly ultimately inhibiting rather than encouraging natural products research. A particular point of contention is that the definition of *use* of genetic resources includes not only research and development on the genetic or biochemical composition of genetic resources, but also their *subsequent applications and commercialisation*.

So what does this mean in practice? Well, the European Union (EU) has drafted legislation that requires any downstream users of a genetic resource to exercise *due diligence* to ascertain that genetic resources and associated traditional knowledge were accessed in accordance with legal requirements around access and benefit sharing from the provider state. This means that users would need to keep (for 20 years after their work has ended), and transfer to subsequent users, all information concerning when, where and how a resource was obtained, and details of the benefit sharing arrangements. It is likely that other states will follow the EU's general lead on this.

However, some researchers may view this as a serious bureaucratic burden that will be difficult to monitor. In addition, there is the issue of when such *due diligence* obligations are exhausted. As a case in point, Squibb's development of the drug captopril in the 1970s to treat hypertension and congestive heart failure ultimately resulted from research on snake venom isolated from the Brazilian arrowhead viper (*Bothrops jararaca*). However, the discovery process required many steps over a number of years. In summary, it involved fractionation and screening of the venom, identification of an angiotensin-converting enzyme (ACE) inhibitor candidate peptide, synthesis and trials to find an orally active analogue, compound efficacy optimisation by a number of chemical modifications, then animal and clinical trials.[6] There was no payment of royalties to the Brazilians who believed they were due.[7] Such a process is not unusual and begs the question of when a benefit sharing obligation should be present and when it is exhausted (especially if the provider knew nothing of the beneficial effect).

The lack of a signature on the dotted line from the USA will no doubt be a source of consternation for researchers from states bound by the Protocol as the strict obligations around access and benefit sharing will simply not apply to US-based institutions or corporates.

How do intellectual property (IP) and patents come into this?

There is a widely held misconception that patents can grant a monopoly covering genetic resources as they are found in nature (e.g. patenting genes in the human body, patenting native plants). This is incorrect; patent laws throughout the world exclude from patentability products as found in nature. Although there are some minor differences between countries exactly where the line is drawn, the general rule is that to constitute an invention, the resource must have been modified *by the hand of man*.

Despite this, there are some examples of patents inadvertently being granted covering products which already existed. For example in 1997 the United States Patent and Trademark Office (USPTO) granted a patent covering certain basmati rice lines and grains to a US company called RiceTec. The Indian government claimed that the patent covered existing lines of basmati that had been grown in India for centuries. They were outraged that a US corporation could engage in biopiracy and attempt to monopolise an age-old genetic resource. A USPTO review of the decision to grant led to RiceTec losing most of the coverage of the patent and restricted their monopoly to three rice strains developed by the company. In this case, it was initially difficult for the USPTO examiner to reject the application because prior knowledge regarding other types of rice that could have led to a finding of lack of novelty was not available in usual publications or was not published at all. Another issue was that at the time, the USPTO assessed novelty of inventions under the *relative novelty* threshold. This means that *prior use* is only regarded as novelty-destroying if that use occurred in the USA; use in India didn't compromise novelty. Such allegations of biopiracy have fuelled the fire against corporations and bioprospectors irrespective of whether they obtain prior informed consent and engage in access and benefit sharing partnerships or not.

Clearly the way to address concerns is to establish consistent and transparent guidelines and practices and that is exactly what Nagoya aims to do. However, it remains to be seen whether parties to the Protocol will meet their obligations under Nagoya.

Matauranga Māori (Māori Knowledge)

In New Zealand, the status of rights to genetic resources and traditional knowledge was the subject of a major Treaty of Waitangi claim – the Wai 262 *flora, fauna and cultural intellectual property* claim. The Ministry of Foreign Affairs and Trade (MFAT) has stated that New Zealand should not become Party to the Nagoya Protocol until domestic policy issues relating to the Wai 262 claim, and ambiguity regarding the application of the Protocol to certain sectors (e.g. agriculture), are resolved or clarified.[8]

The Wai 262 report by the Waitangi Tribunal was released in July 2011 and it recommended reforms to laws and policies affecting Māori genetic resources and traditional knowledge. In that report it was established that the Treaty of Waitangi allows the Crown to put in place laws and policies relating to research into and commercialisation of the genetic and biological resources in New Zealand. This includes IP laws, and laws controlling aspects of the research process such as bioprospecting and genetic modification. However, in return the Crown must protect the authority of the Māori people in relation to their taonga (treasure) species. The Tribunal also recommended that decisions about bioprospecting in areas under NZ Department of Conservation control be made jointly by the department and the affected communities.

Although the official government response to the Wai 262 claim has not yet been forthcoming, the new Patents Act 2013 does make some attempt to address Māori concerns regarding patents. These concerns are centred on the prospect that patents are granted for inventions that rely on Māori traditional knowledge or involve indigenous flora/fauna. The 2013 Act requires that a Māori Advisory Committee is established to advise the Commissioner on whether a claimed invention is derived from Māori traditional knowledge or from indigenous plants or animals; and if so, whether the commercial exploitation of that invention is likely to be contrary to Māori values. The new Act does not go so far as to provide the Committee with the right to make a determinative decision on patentability, and the Committee is only involved if invited to be so by the Commissioner.

The recognition of Māori interests in the legislative process for patents is an important one. Although the Committee will not have any say on whether an invention is novel, inventive or patentable in other respects, it will certainly provide a means for Māori concerns to be addressed. For example if it is contended that a component of a Māori traditional medicine is the subject of a patent application, the Committee will be able to raise such concerns. This could lead to the examiner making investigations to determine whether the invention is novel over the use of the traditional medicine or not.

The proposals of Wai 262 appear to fit well with the principles set out in the Nagoya Protocol and if the government is to adopt more of the proposals, the legal framework and principles regarding engagement with indigenous/local communities set out in the Nagoya Protocol would make a good starting point.

To date there appears to have been few policy developments around biodiscovery/bioprospecting activities in New Zealand and there is no comprehensive policy framework. Despite this, there is no indication that New Zealand has an acute biopiracy problem that needs addressing. As with many political hot-potatoes, perhaps impetus for change will only come if a high profile bioprospecting matter goes before the court of public opinion.

Some tips for compliance with the Nagoya Protocol

Despite the lack of a domestic framework for access and benefit sharing, general property law and environmental legislation (Wildlife Act, Fisheries Act, Conservation Act, Resource Management Act etc.) must still be respected when considering access to resource sites and use of material from those sites. If a researcher intends to access genetic resources, to reduce the risk of a claim under such laws, we recommend obtaining written prior informed consent from the land owner and any other party who may have a claim such as local iwi or conservation authorities. In addition, if the resource is likely to be shared with overseas partners, it would be prudent to put systems in place to ensure your collection complies with Nagoya Protocol requirements.

Neither New Zealand nor Australia has ratified the Nagoya Protocol and therefore the governments have no obligation to put its principles into effect. In turn, New Zealand-based researchers collecting or using genetic resources or traditional knowledge have no obligation to determine, document or declare where they originate. However, the legal framework currently being built in Europe and other countries may affect New Zealand researchers if they receive or transfer material overseas, or develop products from genetic resources for overseas markets. In such cases, they may be required to provide assurances to other countries as to the source of any material, irrespective of whether New Zealand signs up to the Protocol.

If you have any queries regarding intellectual property related matters (including patents, trademarks, copyright or licensing), please contact: tim.stirrup@baldwins.com or katherine.hebditch@baldwins.com, Patent Proze, Baldwins Intellectual Property, PO Box 5999, Wellesley Street, Auckland

References and notes

1. See *http://www.wipo.int/tk/en/tk/* accessed 30 September 2014
2. Bioprospecting is defined by the Convention on Biological Diversity (CBD) Secretariat (UNEP/CBD/COP/5/INF/7) as "the exploration of biodiversity for commercially valuable genetic and biochemical resources". Such resources are generally accepted to include chemical compounds, genes, micro-organisms, macro-organisms, and other valuable products from nature.
3. Jang, K. H. *et al.*, *Angew. Chem. Int. Ed.*, **2013**, *52*: 7822–7824
4. See Article 6 of the Protocol (http://www.cbd.int/abs/doc/protocol/nagoya-protocol-en.pdf). Accessed 30 September 2014
5. See Annex of the Protocol (http://www.cbd.int/abs/doc/protocol/nagoya-protocol-en.pdf) for more details. Accessed 30 September 2014.
6. Sneader W., *Drug Discovery. A History.* John Wiley & Sons Ltd. 2005 p280
7. See http://www.nytimes.com/2007/08/28/science/28biophtml?pagewanted=print&_r=0 Accessed 30 September 2014.
8. See http://www.mfat.govt.nz/Foreign-Relations/1-Global-Issues/Environment/7-Species-Conservation/geneticres.php Accessed 30 September 2014.

Tim Stirrup of Baldwins Intellectual Property in Auckland specialises in chemistry and biotechnology patents. Tim obtained his PhD in molecular biology from the University of Southhampton in the UK in 2007. He qualified as a registered New Zealand and Australian patent attorney in 2011.

Results of reader survey

NZIC members were invited to take part in a reader survey which was published in the April issue of *Chemistry in New Zealand* and made available for completion until 30 June. Approximately 700 members received the survey. There were a total of 89 responses, 88 of which were completed online and 1 returned by post. A summary of the results is shown below, including a selection of comments made by respondents, some of which have been edited for clarity and/or length. Suggestions for changes and improvements are being considered by the editor and will be discussed with Council.

1. Which regular content, if any, do you usually read?

Branch & NZIC news	82%	Dates of note	31%
Scientific articles	74%	Patent proze	26%
General interest articles	77%	I don't usually read any regular content	6%

Comments:

Scientific articles can be very academic.

Prefer articles that are more topical and aimed at a more general audience.

2. What is your opinion of the quality of the following aspects of *CiNZ*?

	Excellent	Good	Average	Poor	Very poor	No opinion
Content	13%	67%	20%	2%	0%	1%
Layout/design	14%	60%	23%	2%	0%	1%
Ease of reading	20%	49%	26%	2%	0%	2%
Photographs/images	15%	48%	31%	6%	0%	1%
Cover	14%	54%	30%	1%	0%	3%

Comments:

Too much detail in articles and not reader friendly.

Would like to see more colour.

3. How would you rate your overall interest in *CiNZ*?

I look forward to reading each issue	10%
I usually browse through the latest issue and read items that interest me	78%
I only occasionally read or browse through an issue	10%
I do not have any interest in it	1%

4. As an NZIC member, do you feel that *CiNZ* is relevant to you?

Yes	85%
No	15%

Comments:

As an overseas member it is my main contact with NZ chemistry.

As a chemist always, but as a professional, not really.

5. Do you feel that *CiNZ* helps you to engage with NZIC?

Yes, it definitely makes me feel connected to the wider chemistry community in NZ	22%
Yes, to some extent	57%
No, not particularly	17%
Not at all	3%
No opinion	1%

Comments:

I particularly like articles by/involving new graduates, as it helps keep enthusiasm up.

There isn't much about what chemists end up doing.

Branch news keeps me in touch.

I mainly use it to keep in touch with all my friends around NZ.

It is really the only thing that keeps me connected.

6. Please indicate your interest in the following potential new content.

Articles with an educational or secondary school slant which may have previously been aimed at *ChemEd NZ*	49%
Student essays	24%
Letters to the editor	65%
Science cartoons / "lighter" science content	66%
Book reviews	48%

Comments:

More content related to professional chemists would be interesting, for example salary surveys and reviews of new equipment.

More about chemistry in industry.

How chemistry is taught in high schools.

Highlights from the wider chemical / biochemical literature.

Quirky science.

Issues of national interest.

I think *CiNZ* could do a better job of collecting and representing the opinions of the scientific community.

7. What do you most like about *CiNZ*?

The overwhelming response to this question related to keeping up to date with news from around the country and what people were doing, summed up neatly by one respondent as “news and sense of community”.

8. What do you least like about *CiNZ*?

Very academic / highly technical articles (frequent comment from respondents).

Layout is cramped and hard to read.

Dated format.

Lack of colour.

Too university focussed.

Lack of freshness: material repeatedly sourced from the same places.

9. Do you have any suggestions for changes or improvements to *CiNZ*?

Move production online – provide links and photos, personal profiles, online discussion.

Commentary articles on trends/funding/significant global advancements in chemistry.

More engagement of chemists with other disciplines, for example invite molecular or cell biologists to write a viewpoint to stimulate discussion.

More engagement with industrial chemists.

More photos.

More colour.

Update layout.

Focus more on what people are doing in NZ rather than scientific articles.

10. Do you have any other comments?

I believe it is a worthwhile way to keep the community together.

Being retired, *CiNZ* is my main contact with chemistry and valued as such.

Science teachers are a large group of potential readers - an electronic format would allow access at school level with minimal cost.

Do more with the web.

Information on up-coming meetings around the country.

Maybe fewer issues per year, with occasional special issues focused on one topic, for example education.

Conference Calendar

Pacific Rim Symposium on Surfaces, Coatings and Interfaces (PacSurf 2014)

7-11 December 2014, Hapuna Beach Prince Hotel, Kohala Coast, Hawaii

This new conference is being organised by the American Vacuum Society (AVS) with a ssteering committee composed of representatives from Australia, Canada, Chile, China, Japan, Korea, Mexico, New Zealand, Singapore and Taiwan. Symposium attendees will interact during morning and evening sessions that will include plenary, invited and contributed presentations. The main topics for PacSurf 2014 will be focused on the latest advances in biomaterial interfaces, energy harvesting and storage, nanomaterials and thin films. There will be morning and evening technical sessions with the afternoons free for other activities and discussions.

See: *www2.avs.org/conferences/PACSURF/index.html*

International Conference on Materials Science and Engineering (ICMSE 2015)

23-24 January 2015, Paris, France

ICMSE 2015 aims to bring together leading academic scientists, researchers and research scholars to exchange and share experience and research results about all aspects of materials science and engineering. It also provides the premier interdisciplinary forum for researchers, practitioners and educators to present and discuss the most recent innovations, trends, concerns and practical challenges encountered, and the solutions adopted.

See: *www.waset.org/conference/2015/01/paris/ICMSE*

Advanced materials and nanotechnology (AMN 7)

8-12 February 2015, Nelson, New Zealand

AMN-7 is the seventh in our biennial series of meetings that focus on the latest research on advanced materials and nanotechnology. This event will continue the best traditions of previous events, which include a range of high-impact plenary presentations, cutting-edge invited and contributed talks, interactive poster presentations and convivial social events. The intimate scale of AMN conferences and the broad interests of fellow delegates offer many opportunities for networking and interdisciplinary discussions.

Parallel session presentations will be clustered around the following central themes: Biological Interface, Engineered Nanosystems, Molecular Materials, Nanoscale Structures and Physical Phenomena

In addition, the programme will feature sessions which will focus on the following topics: Organic Electronics, Graphene, Metal-organic Frameworks and Spintronics.

See: *www.amn-7.com/page.php?7*

Supramolecular Photochemistry: Faraday Discussion

15-17 September 2015, Downing College, Cambridge, UK

Natural and artificial photosynthesis
New information derived from the study of natural systems will be discussed and used to aid design of artificial photosynthetic systems. Attention will be given to both synthetic light-harvesting antennae and molecular devices capable of efficacious charge-separation.

Light-activated molecular machines and logic gates
The study of multi-component systems where illumination induces controlled mechanical movements (machines) and/or where light can be exploited as input/output information. The relevance to protein folding should not be missed.

Self-organization of photo-active nanostructures
Identifying new and improved ways to assemble supramolecular entities with a photo-active unit, such as liquid crystals, organo-gels, dendrimers, etc. Although synthesis plays a crucial role in the development of such species, the discussion will deal with the synergistic features of the actual assembly.

Luminescence sensing and imaging
The in-situ detection of changes in the local topology and in the concentration of selected substrates, including biologically relevant species.

Oral abstracts deadline: 8 December 2014

See: *www.rsc.org/ConferencesAndEvents/RSCConferences/FD/Photochemistry-FD2015/index.asp*

Pacifichem 2015

14-16 December 2015, Honolulu, USA, North America

The theme of Pacifichem 2015 is Chemical Networking: Building Bridges Across the Pacific, emphasisng the collaborative nature of chemistry as a multidisciplinary science and the opportunities to network with Pan-Pacific research groups at the Pacifichem meetings. Topic areas:

i. The core areas of chemistry
    1. Analytical
    2. Inorganic
    3. Macromolecular
    4. Organic
    5. Physical, theoretical and computational

ii. Multidisciplinary or cross-disciplinary areas of chemistry
    6. Agrochemistry, environmental and geochemistry
    7. Biological
    8. Materials and nanoscience

iii. Chemistry solutions to global challenges
    9. Chemistry of clean energy conversion, storage and production
    10. Bench to bedside: chemistry of health care
    11. Connecting chemistry to society

See: *www.pacifichem.org*

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