Chemistry in New Zealand

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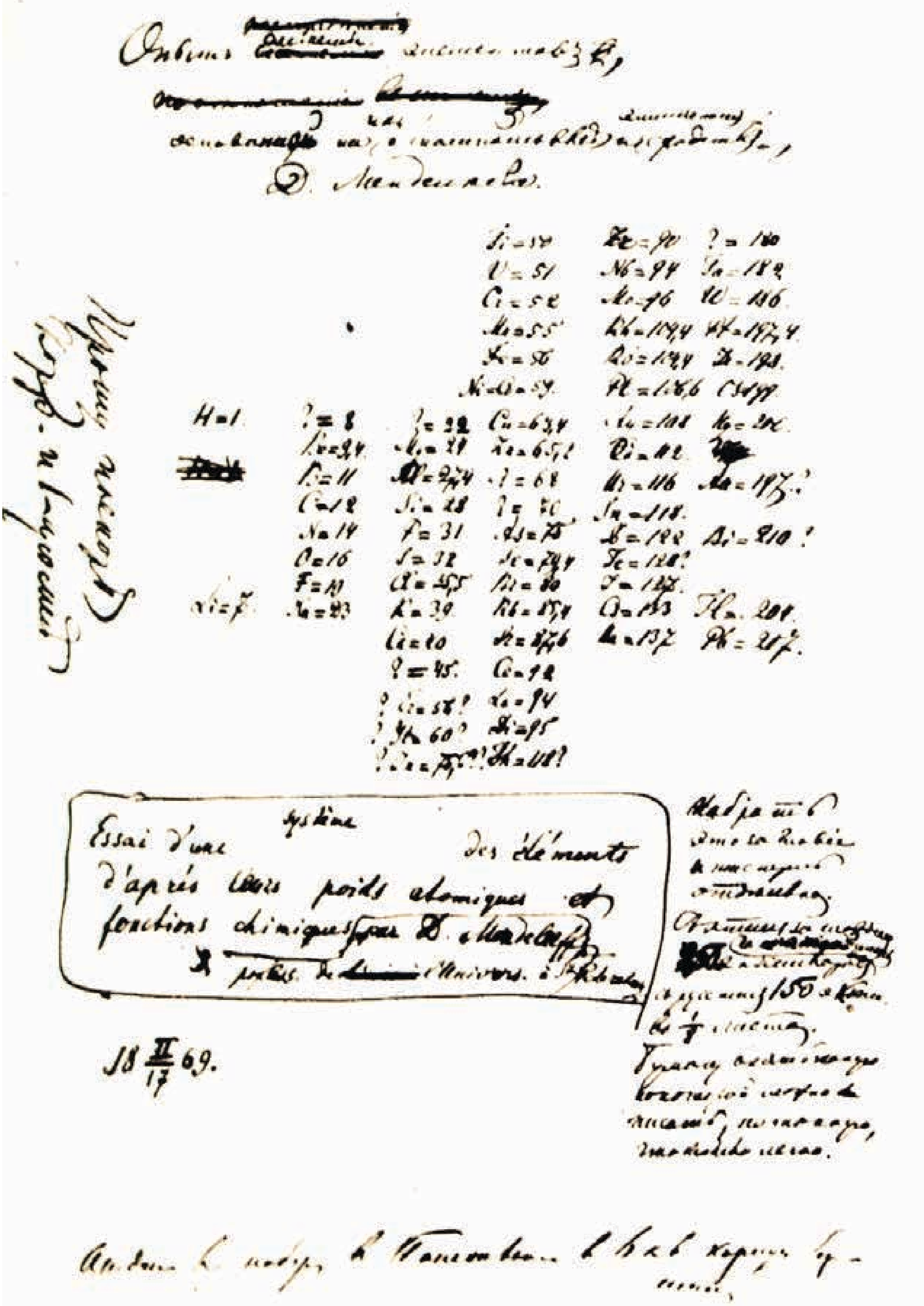

Essai d'une système des éléments
d'après leurs poids atomiques et
fonctions chimiques par D. Mendeleeff

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On the cover: Mendeleev’s handwritten version of the periodic law, based on atomic weight and chemical resemblance. The United Nations have designated 2019 the International Year of the Periodic Table of Chemical Elements. It marks 150 years since Mendeleev’s first table. See article by Brian Halton, page 12.

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Comment from the President

Welcome to the New Year and the first issue of *Chemistry in New Zealand* for 2019. It is an honour to serve as the President of the Institute for the next two years and I hope I am able to continue the excellent work of the past two Presidents, James Crowley (2018) and Penny Brothers (2017). As you will know from previous editions of *Chemistry in New Zealand* when Penny was President, she advocated for a change from a one year to a two year term for the President. This rule change was voted in at the 2017 AGM and therefore it is an honour to hold the first two year presidential role. The NZIC Council hope that the new two year term for the President will allow for better continuity of leadership within the NZIC and allow the President, along with Council, to be more productive for you, the members.

2018 saw Joanna Dowle join us as our new administrator and it has been a pleasure working with her on various projects. I look forward to more collaboration in 2019 and beyond. Joanna replaced Richard Rendle and we will see another big change on Council with the retirement of Colin Freeman as our Institute treasurer. Colin has worked tirelessly for many years keeping our books in order, auditing the branch accounts and generally ensuring that we have funds to continue operating. On behalf of the Institute I thank Colin for his years of hard work and service to NZIC and wish him well for whatever he takes on next. We expect a new treasurer to be announced soon.

I hope by now that you have all had a chance to explore the new website, development of which was driven by Paul Plieger. The new website has modernised our subscription model, moving from paper and mail to an online system for membership and membership renewals. If you have not had a chance to explore the website then I encourage you to do so, and, if you have suggestions regarding content then please let myself or Joanna know.

There will be plenty happening this year for members to get involved with. As part of the celebration of the centenary of IUPAC in 2019, you are invited to join in a Global Women's Breakfast. The event is titled "Empowering Women in Chemistry: A Global Networking Event". It will be held on a single day – 12 February. The aim of this event is to assist women chemists to expand their network of contacts, both locally and internationally. Women at different stages of their individual careers can inform each other about their career progress, and together explore opportunities, in professional development and in research or teaching horizons. Various branches are getting organised with a breakfast event, and I hope that you will be able to come along and support this, as we celebrate in New Zealand before handing over to Australia, initiating a handshake around the world! 2019 is also the 150th anniversary of Dmitri Mendeleev's first report of the periodic table. We have various events planned for the year including a schools competition, element of the week discussion on Radio New Zealand and collaboration with the Science-Technology Roadshow. The events will culminate at our NZIC national conference, NZIC XIX, to be held in Christchurch from 24-28 November 2019. As conference chair I look forward to welcoming all of you to Canterbury and Christchurch for a fantastic conference celebrating all aspects of Chemistry in New Zealand and beyond.

Sarah Masters
NZIC President

Biographical Note

Sarah Masters is an Associate Professor at the University of Canterbury. She obtained her BSc(Hons) and PhD from the University of Edinburgh under the guidance of Professor David Rankin (1997 – 2001). In 2005 she was awarded the prestigious Royal Society of Edinburgh/BP Fellowship (2005-2010), only one of which was awarded every two years, to carry out research on gas phase molecular structure. She started her independent academic career at the University of Canterbury, Department of Chemistry in 2011 and has since moved through the ranks to Associate Professor (2019). Her major research interests are in gas and fluid phase molecular structure determination, utilising the combined power of experimental and computational methods. Sarah has been on the NZIC Canterbury Branch Committee since 2013, served as Canterbury Branch Chairperson (2015 – 2018) and has sat on the National Council since 2016.

New Zealand Institute of Chemistry

supporting chemical sciences

January News

NZIC News

Royal Society Te Aparangi Fellows

Professors *Cather* ***Simpson*** and *Emily* ***Parker*** have been elected as new Fellows of the Royal Society Te Aparangi.

Cather is internationally renowned for her contributions to fundamental new knowledge about how light interacts with matter. A Professor of Physics and Chemistry at the University of Auckland, her research has achieved seminal insight into multidisciplinary areas ranging from ultrafast dynamics of heme proteins, laser-generated force on sperm, and laser beam-shaping to transform materials at the microscale. She also applies that research to address important practical challenges, and thereby generates transformative impact through both. Since 2012, she has delivered 11 plenary and keynote lectures and garnered $23.9m in external research funding as principal investigator. She is founding inventor in two science startup companies, including Silicon Valley award-winner Engender. In 2016, she was Kiwinet's Baldwins Researcher Entrepreneur and BNZ Supreme winner, and a Ministry of Primary Industries Champion. Stellar outreach and teaching, including a National Teaching Excellence award, complement her exceptional research strengths.

Emily has made a sustained contribution to the understanding of enzyme function at the molecular and organism level. This new knowledge has been applied to the design and synthesis of enzyme inhibitors as potential drugs, especially antibiotics. It has also led to the use of enzymes as tools in the manufacture of valuable bioactive compounds. Based in the Ferrier Research Institute at Victoria University of Wellington, her research has been published extensively in high quality scientific journals and she has been a regular invited speaker at international symposia. She has contributed to the next generation of scientists through her post-graduate teaching and has served with distinction in leadership roles in national and trans-Tasman scientific organisations.

Chemistry jobs on NZIC website

NZIC is launching a chemistry jobs page on our website (nzic.org.nz/chemistry-jobs/). This page aims to collate available chemistry jobs and openings in New Zealand. It is for any advertisements for open positions or jobs relating to the field of chemistry, including chemistry PhD scholarships and postdoc appointments. This service is **free for current NZIC members**, otherwise the cost is $50 per advertisement.

If you have a job opening, a PhD scholarship or a postdoc position available, please send your ad (including any images or external links) to nzic.office@gmail.com to be featured on the jobs page.

The University of Auckland

Welcome

Welcome to Lynette Carter as the new Chemistry Facilities Coordinator and John Lau as the Group Services Coordinator.

Farewell

We said goodbye to Sue Western in October 2018, who has been our Group Services Coordinator (GSC) for the year since Anoma was seconded to a team leader role. The GSC is a critical role in the School, ensuring staff and GTAs get hired and paid, organising travel, organising events, and generally being the point person for staff and graduate students. We thank Sue very much for her contributions and wish her well in her future roles.

Events

Courses and Careers Day

In August 2018, Courses and Careers Day was very well attended, with most of our lectures being full or almost full – indeed, parents were asked to leave *Margaret* ***Brimble***'s medicinal chemistry lecture so that more potential students could attend. *James* ***Wright*** introduced our new Green Chemical Science specialisation. He gave an excellent description of many of the environmental issues that we as scientists could address and examples of steps already being taken before describing the new major, stressing its interdisciplinary nature. The Food Science and Nutrition information talks and table organised by *Peter* ***Swedlund*** and *Clare* ***Wall*** were also very well attended, with the smoothie bike an extra drawcard. Thank you to *Malini* ***Arewgoda*** and *Sue* ***Western*** for organising the day, and to *Jon* ***Sperry***, *Malini* ***Arewgoda***, *David* ***Salter***, *Kaitlin* ***Beare***, *James* ***Wright***, *Matthew* ***Sullivan*** and *Shi-Wei* ***Kim*** for giving advice at the SCS stands. Thanks also to all the graduate students and staff who performed demonstrations, including Ayesha Zafar, Bikimi Bitrus, Dianna Truong, Mejo Remanan, Roy Lai, Sneh Patel, Sunandita Ghosh, Ravnit Singh, Faith Huang, Anna Worthington and Andy Wang.

Faculty Postgraduate Research Showcase 2018

Commencing on 10 September 2018, the exciting week-long event featured postgraduate posters displayed across the ground floors of the science buildings, opportunities to hear about research from students, people's choice voting and other competitions. This showcase provided an excellent opportunity for research students to present their research to their peers and the University of Auckland staff and student community.

Renaming the Faculty of Science on the 125th anniversary of Women's Suffrage in New Zealand

On 19 September 2018 the Faculty of Science honoured many women after whom the Faculty, together with its Schools and Departments, are named. We were the Joyce, Lady Waters School of Chemical Sciences within the Dame Charmian O'Connor Faculty of Science. Three of the honourees were present in person – Dame Charmian O'Connor, Joyce, Lady Waters, and Vivienne Cassie-Cooper – while the son of Dame Mira Szaszy also attended and read out part of his mother's biography. Both Charmian and Joyce spoke very well, with Charmian noting that the event marked the leadership, courage, and determination to achieve exhibited by the honourees. Charmian also commented that there is still work to be done to attain gender equity; that there should be no need to comment on Margaret Brimble's gender when describing her election as a Fellow of the Royal Society, and that Charmian was waiting on the selection of the first female(s) as Head of the School of Chemical Sciences, Dean of Science, and Vice Chancellor of the University of Auckland. Joyce was the second female PhD graduate from the Department of Chemistry (the first being June Sutor in 1953) and she says about her first job in England (at ICI): "Jobs for women were not favoured in industry but I was fortunate that someone had been appointed to a position as a crystallographer but he was unable to take it up immediately and I was appointed to temporarily fill the gap." Joyce was the first female President of the NZ Institute of Chemistry. She was appointed to the Physical Sciences committee for the Foundation for Research, Science and Technology, which was set up in 1990 to allocate science funding in NZ, and she was the only woman appointed to the first PBRF Physical Sciences panel in 2003.

Oktoberfest

A very big thank you to *Tilo* ***Sohnel*** and his group for putting on a very successful Oktoberfest and thank you also to *Viji* ***Sarojini*** for giving our third-year students an introduction to postgraduate study. Sue and Hayley are also acknowledged for their assistance with the event. We had over 30 students attend the postgraduate introduction, and many of them indicated they were very interested in studying with us next year.

BASF Kidslab

Thank you to all staff and students who were involved in the BASF Kidslab in November, especially *Katrina* ***Graaf*** for leading the event and *Peter* ***Swedlund*** who did presentations and demonstrations for all 6 sessions. The following people were part of the wonderful team that made BASF kidslab so successful in 2018 - **Technical staff:** Sandra Otty, Selina Yang (who helped with preparation and all three days of Kidslab followed by cleanup), also Stuart Morrow, Pooja Yadav and Albina Avzalova who helped with some sessions; **Postgraduate students:** Dianna Truong, Taniela Lolohea, Andrew Earl, Kyriakos Varnava, Rasangi Sabaragamuwa, Roy Lai, Megan Jamieson, Matthew Sullivan, Shi Min Tan, Luis Camacho, Joseph Vella, Xiaotong Lyu, Mohinder Naiya, Kirsty Anderson, Jessica Liyu, Reuben White, Courtney Davy, Jinal Patel, Bikimi Bitrus; **Office staff**: huge thanks to Anna-Marie Simcock who did all the background organising with the schools, doing the P-card orders and staff to make sure we had the children here in the first place (!) and John Lau for the contracts and being Anna-Marie's back up.

It takes a variety of people to make this event happen. At UoA we are very lucky to have such dedicated staff and GTAs that get behind the outreach activities and are so enthusiastic and passionate about educating the children that science is fun. The team were complimented many times by the teachers and BASF staff about how wonderful they are.

Visitors

On 3 September 2018, Dr David Lunn from OxSyBio in Oxford, UK gave a seminar entitled, *Biofabrication of artificial tissues for diagnostic and therapeutic applications*.

On 7 September 2018, Dr Marcus Jones from AUT presented a talk entitled, *The technological future of quantum dots: is it golden, or do they have a silver lining?*

On 24 September 2018, Professor Mary Garson, University of Queensland, presented a talk entitled, *Game of terpenes: structures, stereochemistry and chemical ecology of nudibranch metabolites*.

On 19 October 2018, Dr Tim Allison from the School of Physical and Chemical Sciences, University of Canterbury gave a NZIC sponsored seminar entitled, *Revealing the direct action of a chemical chaperone using native mass spectrometry*.

Congratulations

Congratulations to Dr Leandro Dias Araujo (Wine Science) and Jessica Suda (PhD, Food Science) on the birth of their son Enzo.

Congratulations to Dr *Jóhannes* ***Reynisson*** and his research group & collaborators (Dr *Lisa* ***Pilkington***, Associate Professor *Yacine* ***Hemar*** and Distinguished Professor *Margaret* ***Brimble***) for their paper, *A chemometric analysis of compounds from native New Zealand medicinal flora* that was published in *Chemistry – An Asian Journal*. It was featured in Stuff News.

Congratulations to Buzhe Wu, a PhD student in *Margaret* ***Brimble***'s group with *Paul* ***Harris***, whose paper in the RSC flagship journal *Chemical Science* has been selected as the paper for "Pick of the Week". The paper resulted from a collaboration with *Robert* ***Keyzers*** at Victoria University.

Congratulations to Mahsa Motshakeri for winning the best poster prize for the Symposium on *Nanomaterials for electroanalytical chemistry and electroanalytical tools for studying nanomaterials* at the 69th Annual Meeting of the International Society of Electrochemistry, held in Bologna, Italy, 2-7 September 2018. Mahsa's poster was chosen from 68 posters presented in this Symposium, and she received a prize of 300 Euros (M. Motshakeri, J. Travas-Sejdic, A.R.J. Phillips and P.A. Kilmartin, *Electrochemical and HPLC analysis of milk uric acid with minimum interference from ascorbic acid*).

Congratulations to the following staff for successes in the 2018 MBIE funding round:

Claude ***Aguergaray*** and *Cather* ***Simpson***: *Point-of-care device: instant prostate cancer diagnosis*

Margaret ***Brimble*** (with VUW/ Ferrier Institute): *Fungal factories: synthetic biology for the manufacture of high value products*

Margaret ***Brimble*** (with VUW/ Ferrier Institute): *Efficient drug development from transition state theory*

Margaret ***Brimble*** (with Cawthron Institute): *Rationally designing a 'smart' marine antifouling biocide based on novel synthetic peptides*

Congratulations to Distinguished Professor *Margaret* ***Brimble*** who was one of the Trailblazers featured in the NZ Herald to mark the 125th anniversary of Women's Suffrage in New Zealand.

Congratulations to the 105 spring graduates who received qualifications from the School of Chemical Sciences either in person or in absentia, including 9 PhD graduates, 21 Masters graduates and 13 BSc(Hons) graduates. We joined the graduates, their families and friends in celebrating this significant milestone in their lives.

Congratulations to Andrew Chan (supervisors *Cather* ***Simpson*** and *Ben* ***Mallett***) who was awarded first prize in the Faculty Poster competition.

Congratulations to Roshan Khadka (Supervisors *Jadranka* ***Travas-Sejdic*** and *Andrew* ***Kralicek***) who was awarded the People's Choice award for most engaging poster talk at the Faculty of Science Postgraduate Research Showcase in September 2018.

Congratulations to team *So Basic*, consisting of *Nina* ***Novikova***, *Stuart* ***Morrow***, *Hannah* ***Holtkamp***, *Andy* ***Wang***, *Ben* ***Mallett***, and *Thomas* ***Minniee***, who won the Faculty of Science Quiz Night.

Congratulations to *Helen* ***Morten*** who gave birth to her second daughter Lucie Ford on 24 September 2018. Isobel seems to be very proud to be a big sister.

Congratulations to *Kaitlin* ***Beare*** who has been awarded a CLeaR SEED Innovation in Teaching Grant for 2019. Her project is titled, *Auto-text analysis for just-in-time teaching*, and aims to develop tools for analysing student writing as part of formative assessment in large chemistry courses.

An interview of *Rebecca* ***Deed*** talking about teaching the art of wine science and about our Wine Science Programme at the University of Auckland was featured on Radio New Zealand in Oct 2018. Here's the abstract: "You could say Rebecca Deed's stellar career in the science of wine was more accidental than chosen. At secondary school her preferred subjects were English, History and French but her tertiary studies led her onto an entirely different path. At 33 she's not just a lecturer in Wine Science at Auckland University but also a national senior wine judge. She's just finished with the New World Wine Awards and will later in the year be judging at the New Zealand Aromatic Wine Competition in Christchurch. She talks about her unusual twists while studying and how it's led to her whole family holding their own tasting competitions. She also has some tips for novice wine drinkers."

Margaret ***Brimble*** is one of the two New Zealand scientists featured in the book *Profiles of women scientists in Asia: their inspirational stories*, produced by the Association of Academies and Societies of Sciences in Asia.

Juliet ***Gerrard*** was featured in the National Portrait section of stuff.co.nz, due to her new role as the Prime Minister's Chief Science Adviser.

Congratulations to Rakesh Arul, from the Photon Factory, who was awarded a Cambridge-Rutherford Memorial PhD Scholarship.

Congratulations to *Cather* ***Simpson***, for being made a Fellow of the Royal Society Te Aparangi. She was recognised for her contributions to fundamental studies of the interaction of light with matter as well as for her applied and commercial research.

Congratulations to all those staffwho received Marsden Grants:

Ivan ***Leung*** was successful with his Fast Start application, *Unravelling the structural and molecular basis of ethylene biosynthesis in plants* which was awarded $300,000.

John ***Sperry*** received a standard Marsden grant of $888,000 for, *Electrifying chemical synthesis*, with *Paul* ***Kilmartin*** as AI.

Margaret ***Brimble*** and *Paul* ***Harris*** were associated with two grants. *Margaret* ***Brimble*** was PI on the $935,000 grant, *Unleashing new generation lanthipeptides from nature to combat antimicrobial resistance* with AIs *Ghader* ***Bashiri***, *Paul* ***Harris***, and Deborah Williamson of the University of Melbourne. **Paul Harris** was the PI on a $939,000 Marsden grant from the Cellular, Molecular and Physiological Biology panel with the topic, *Sweetening biological therapeutics - chemical synthesis of glycoprotein mimics* with AIs *Margaret* ***Brimble***, *Sung Hyun* ***Yang***, and *Lyn* ***Wise*** (Otago).

Paul ***Hume*** (now at VUW) received a $300,000 Fast Start grant for his application, *Next-generation small molecule acceptors for use in organic solar cells* with *Geoff* ***Waterhouse*** as AI.

Congratulations to the *Hungry Hippos*, who won the Best Scientific Content and Best Display awards in the student product development competition at the International Union of Food Science and Technology conference in Mumbai in October 2018. The team members were Anna Worthington, Luodan Xu, Reeva-may Hollick, Xiaoying Zhang, Xiaoying Guan and Ziting Xie. Their project was a fortified dry mix for traditional New Zealand Maori sourdough-style bread.

Congratulations to Roshan Khadka, a PhD student supervised by Professor *Jadranka* ***Travas-Sejdic*** and Dr *Andrew* ***Kralicek*** (Plant and Food Research), whose paper has been recently published in the highly prestigious *Biosensors and Bioelectronics* journal. Part of his supplementary data have also been published in another journal - *Data in Brief*.

Engender Technologies, a spinout from the Photon Factory led by

Cather **Simpson**, has been acquired by CRV International, a co-operative of 27,000 dairy and beef farmers, for an undisclosed sum. Engender was co-founded by Cather, seed investment firm Pacific Channel and Auckland UniServices in 2011. It has developed a novel laser technology that investigates and can separate X- and Y-bearing bull sperm cells. It is intended that Engender's staff will remain in New Zealand retaining a strong research relationship with UoA.

Congratulations to PhD candidates Ben Daniels and Chloe Cho who successfully presented and defended their theses. Ben's thesis was entitled, *Total synthesis of lumazine-containing compounds* (supervised by Distinguished Professor *Margaret* **Brimble**). He worked with Comvita identifying biomarkers to authenticate NZ manuka honey. Chloe's thesis was entitled, *Structure-activity relationships of guanidinylated biodegradable antimicrobial polycarbonates* (supervised by Dr *Jianyong* **Jin** and Distinguished Professor *Margaret* **Brimble**) and was funded by the MBIE Biocide Tool Box Research programme.

Auckland University of Technology

New Faces

We welcome a new PhD student, Ravi Allam, who will be working with Dr *Jack* **Chen**.

Events and Invited Talks

AUT hosted an NZIC seminar by Dr *Yacine* **Hemar**, Riddett Institute and Jiangnan University entitled, *Material science approach to milk and dairy systems*.

Dr *Marcus* **Jones** gave invited talks at both the University of Auckland and the University of Otago entitled, *The technological future of quantum dots: is it golden or does it have a silver lining?*

Dr *Cameron* **Weber** gave an invited talk at the University of Otago entitled, *All for one or one for all? Ionic liquid mixtures and nanostructured ionic liquids as neoteric solvents.*

Professor *Nicola* **Brasch** gave a seminar sponsored by the Dodd-Walls Centre at Victoria University of Wellington entitled, *Probing the mechanisms of nitroxyl release from photoactive Piloty's acid derivatives.*

Dr *Jack* **Chen** and Dr *Cameron* **Weber** organised a Science Sizzler event at AUT in September for approximately 120 Year 10 students who are part of the Health Science Academies at James Cook, De La Salle, Onehunga, Auckland Girls Grammar and Waitakere High Schools. The event involved hands-on activities from the chemistry, food science and microbiology departments at AUT and was assisted by the fantastic help of many AUT technical, academic and teaching staff.

Professor *Allan* **Blackman** and Dr *Jack* **Chen** kicked off an AUT Careers Day at Auckland Grammar School with *Chemistry with a Bang!* highlighting chemistry as a fascinating area of study and its contributions to society.

Members of the School of Science at AUT assisted the University of Auckland with organising the FYSEC (First Year Science Educators) Colloquium held at both universities on 3-4 December 2018. FYSEC is a forum for tutors and lecturers from tertiary institutions and high schools to explore

Students at the Science Sizzler

AUT Careers Day at Auckland Grammar

the challenges of teaching first-year science.

Congratulations

Dr *Marcus* ***Jones*** has been appointed as an Associate Investigator of the Dodd-Walls Centre.

Dr *Cameron* ***Weber*** has successfully obtained a Marsden Fast Start grant for the project *Structure and reactivity in nanostructured ionic solvents* worth $300,000 as Principal Investigator. Cameron is also a Key Researcher on a $10M MBIE Research Programme Grant led by Scion entitled, *Bark biorefinery: unlocking new hydrophobic polymers and mountains of wealth*.

Dr *Jack* ***Chen*** published an article in *Angewandte Chemie* entitled, *Substrate-induced self-assembly of cooperative catalysts*, together with students Pablo Solis Munana and Chloe Zhijun Ren. This work was supported by a Catalyst: Seeding grant.

PhD students of Professor *Nicola* ***Brasch***, Dominique Rwizinkindi and Vinay Bharadwaj, have been awarded a Dodd-Walls PhD scholarship and a Dodd-Walls travel grant respectively to present at the IONS Conference on Optics, Atoms, and Laser Applications (IONS KOALA) in Sydney.

CANTERBURY

Trivia and Truffles

The Canterbury branch of the NZIC held its annual Trivia and Truffles quiz at the University of Canterbury Club on 19 November. Eleven teams competed for the various prizes on offer, with rounds on moles, music, food and drink, sport and The Chase to name a few. A great effort from all the teams, with lots of fun and some very witty answers. Peer marking also resulted in some colourful feedback for the teams. The winning team were *Three Brits and a Bryce* (*Bryce* ***Williamson****, Antony* ***Fairbanks****, Dan* ***Foley*** *and Alison* ***Foley***), second were *CHONK* (*Sarah* ***Lilley****, Ben* ***Howard****, Daniel* ***Smith*** *and Colm* ***Healy***), and third were *Hey everyone! Just here to beat CHONK* (*Nic* ***Bason****, Zach* ***Stueven****, Lily* ***Hermanspahn****, Nathan* ***Harvey-Reid***). Pity the third team didn't finish second! *Ohm sweet Ohm* won the best team name while *The International Team* came last and got a small prize for their efforts. Well done all and a great evening of fun was had.

Winners of the Trivia and Truffles quiz: Three Brits and a Bryce

The second-placed team: CHONK

The third-placed team: Hey everyone! Just here to beat CHONK

The well attended NZIC Winter Warmer was held on 23 August with mulled wine and mince pies.

University of Canterbury

***He Puna Pūtaiao UC Science programme*.**

A six week UC Science programme, He Puna Pūtaiao was held for Year 10 Māori students that engages them in the culture of science by involving them in scientific research. Using the context of water quality in Te Waihora (Lake Ellesmere), the students are mentored by University of Canterbury scientists in literature reviews and collecting and analysing data in the field, before presenting their findings both in e-book format and as a research poster displayed at a Pō Whakanui at the end of the programme.

Lectures

Royal Society of Chemistry and the New Zealand Institute of Chemistry lecture

On the 26 September the Royal Society of Chemistry and the New Zealand Institute of Chemistry Canterbury Branch presented a lecture by Professor Mary J Garson, School of Chemistry and Molecular Biosciences, University of Queensland, Australia, entitled, *Game of Terpenes: Structures, stereochemistry and chemical ecology of nudibranch metabolites*.

School of Physical and Chemical Sciences Te Kura Matū Seminar Series

On 10 October *Shane* ***Telfer***, MacDiarmid Institute of Advanced Materials and Nanotechnology, Institute of Fundamental Sciences, Massey University, Palmerston North, presented the lecture *Multicomponent metal-organic frameworks.*

MANAWATU

In September, Dr Han Yin (Ben) joined the ***Telfer*** group as a MacDiarmid funded post-doctoral fellow to work on multicomponent MOF membranes. *Matt* ***Cowan*** of the University of Canterbury and *Jianyong* ***Jin*** of the University of Auckland have been collaborating with *Shane* ***Telfer*** on gas sorption measurements. On 24 October, Matt gave a seminar on *The highest permeance* CO_2 *membrane ever made and other separation stories.* Jianyong gave a talk on *Synthesis of polymers of intrinsic microporosity* on 12 November.

The ***Rowlands*** group welcomed Shashank Tiwari as a new PhD student in December. *Gareth* ***Rowlands*** gave two talks recently - one at the New South Wales Southern Highlands Conference on Heterocyclic Chemistry in August and the second at Organic 18: RACI Organic Division National Conference in December, held at the University of Western Australia.

Marilyn Anderson of La Trobe University, Melbourne gave a seminar on *Production of peptide pharmaceuticals in plants* on 24 November. A seminar on *Direct electricity production from algae, bacteria and plants* was given by Chris Howe of the University of Cambridge.

Vyacheslav ***Filichev*** attended the 10th International Conference on Porphyrins and Phthalocyanines in Munich, Germany. He gave an invited talk on the session devoted to porphyrin assemblies on bioinspired templates. He visited Professor Guido Clever at TU Dortmund and gave a talk titled, *TINA-DNA assemblies in biomedical and fluorescence applications*.

In November, Harikrishnan Kurup, a PhD student jointly supervised by *Vyacheslav* ***Filichev***, *Geoffrey* ***Jameson*** and *Elena* ***Harjes*** successfully passed his 1st year PhD confirmation.

Sam ***Brooke***, *Joel* ***Cornelio***, *Hossein* ***Etemadi***, *Arka* ***Gupta***, *Harikrishnan* ***Kurup***, *Subo* ***Lee***, *Liam* ***McGarry***, *Yangdong* ***Su*** and *Omid* ***Taheri*** gave presentations on their research at the Massey-Victoria Chemistry Symposium held at Victoria University, Wellington on 9 November. Arka Gupta won the Best Presentation Award and Liam McGarry's presentation was highly commended.

Bernhard ***Auer***, *Nisansala* ***Bandara***, *Sam* ***Brooke***, *Joel* ***Cornelio***, *Omid* ***Taheri*** and *Jin* ***Wong*** attended the MacDiarmid Annual Symposium at the University of Auckland between 21 - 23 November. Omid Taheri presented his work on *Metal-organic frameworks for gas separation* and Sam Brooke spoke on *Investigation of edges of* MoS_2 *nanostructures using Raman and X-ray spectroscopies.*

OTAGO

The branch facilitated a tour of the Allpress coffee roastery in Dunedin on the afternoon of 2 November. 10 coffee-loving NZIC members toured the roasting facilities and tasted several different varieties of beans and brewing techniques. It was an informative and stimulating afternoon and the staff at Allpress are thanked for their enthusiastic tour guiding and *Christina* ***McGraw*** is thanked for organising the event.

University of Otago, School of Pharmacy

Sameek ***Singh*** and *Andrea* ***Vernall*** attended the Medicinal Chemistry and Chemical Biology Conference 18 - 21 November 2018, Brisbane, Queensland. Sameek presented a poster and Andrea gave a talk. Congratulations also to Sameek for graduating with his PhD.

University of Otago, Department of Chemistry

A huge congratulations to *Nigel* ***Lucas*** for his successful Marsden proposal, *Carbon nanocones by design: atomically-precise molecular containers*. In

MacDiarmid Institute investigators, students and postdoctoral fellows from the Department of Chemistry, University of Otago this project, Nigel and his team are working on the rational synthesis of conical carbon nanostructures as a new class of molecular container to be applied in supramolecularly-assembled materials and host-guest chemistry. Well done, Nigel!

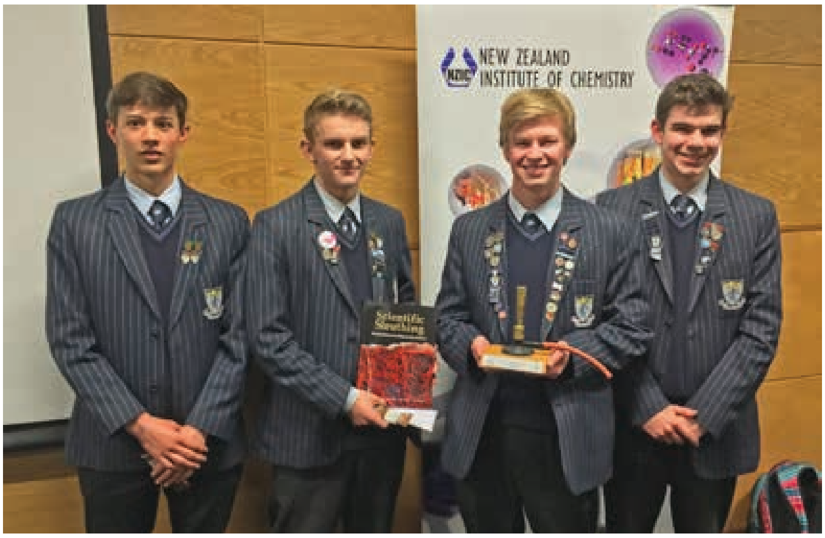
More congratulations to *Dave* ***Warren*** who won the Premier Lecturer in Summer School at the Otago University Students' Association (OUSA) Teaching Excellence Awards. Well done, Dave, we know there are many, many students who can attest to your teaching skill and boundless enthusiasm!

Congratulations to *Calum* ***Gordon*** who jointly won the prize for the best student talk at the Otago Energy Research Centre (OERC) annual symposium. Calum gave a great talk on his undergraduate research project in the group of *Anna* ***Garden*** on optimising the rate of hydrogen evolution reaction on MoS_2 catalysts by using graphene oxide supports and is currently working in the group of *Carla* ***Meledandri*** as a summer student.

Welcome to *Jonathan* ***Falconer*** who has joined the group of *Carla* ***Meledandri*** as a postdoctoral research fellow. Jonathan will be here for 12 months to research metal-organic frameworks and study the antimicrobial properties of silver. *Leon* ***Escomel*** and *Andreas* ***Durrmann*** are visiting the group of *Sally* ***Brooker*** as internship students from Lyon, France and Bayreuth, Germany, respectively.

Jaydee ***Cabral*** presented at the World Congress on Advanced Treatments & Technology in Wound Care, 15-16 October, London with a talk entitled, *Biomaterials for regenerative cell therapy*.

There was a big turnout by Otago Chemistry at the MacDiarmid Institute for Advanced Materials and Nanotechnology's annual symposium in late November. *Anna* ***Garden***, *James* ***Crowley*** and *Jono* ***Barnsley*** presented their research at the symposium and many other staff and students participated in the excellent and constructive discussions around the future directions and science of the Institute.



Prizewinners in the 2018 Otago-Southland High School Chemistry Quiz Night. Top to bottom: 1st place *Randal* (King's High School); 2nd place *Avocadoes Number* (Taieri College); 3rd place *Applied Physics* (Otago Boys' High School).

This year's Otago-Southland High School Chemistry Quiz (the 16th) saw 33 teams from schools around Dunedin and from further afield meet in the Otago Museum's Hutton Theatre to battle for the Bunsen Burner of Wisdom. After the usual feed of pizza from Poppas Pizzas, and an initial round of *Oxidants and reductants*, things got down to business with six rounds of questions of both a chemical nature as well as general knowledge, including a 'name that chemistry-related song' audio-visual round for the first time. Teams also contributed chemical haiku for extra prizes, with the winning haiku being:

Neon turns me on
Like a filament lightbulb
That sh*t ain't boron

(The Colonials, King's High School)

Chemistry is hard
NA is an element
Also is my grade

(Teresa's Angels, James Hargest High School)

If your teacher throws
Sodium chloride at you
Call cops, that's a salt

(Avocadoes Number, Taieri College)

The overall top-placed teams this year were: First: *Randal* (King's High School); Second: *Avocadoes Number* (Taieri College); Third: *Applied Physics* (Otago Boys' High School).

Quizmaster *Dave* ***McMorran*** is thanked for his excellent organisation of another successful and entertaining quiz, along with generous sponsors Poppas Pizzas, the Otago University Bookshop, the Otago branch of the NZIC and the University of Otago.

WAIKATO

University of Waikato

Nearly 150 students from the greater Waikato region and Bay of Plenty participated in the annual ChemQuest competition, held at the University. This was a fun-filled evening for students studying NCEA level 2 chemistry and a hard fought contest. Prizes were shared right across the Greater Waikato and Bay of Plenty region and were awarded as follows:

1st Place: Otumoetai College (John Austin, Alice Cerdeira, Daniel Lee)

2nd Place: Tauranga Boys' High School (Benjamin Adams, Ryan Hastie, Ronan Yip)

3rd Place: Western Heights High School (Maddison Hagger, Nikiah Pubben, Kesia Shoebridge)

4th Place: Hamilton Boys' High School (Jeffrey Luo, Harsheel Singh, Xinyuan Zhai)

5th Place: Hamilton Boys' High School (Liam Ballard, Sam Kim, Carl Stephens)

The quiz was generously sponsored by the Waikato Branch of NZIC (major sponsor), Hill Laboratories and the Faculty of Science and Engineering, University of Waikato. Question master was *Michèle* ***Prinsep***, ably assisted by numerous other staff and students from the Department.

The RSC Australasian Lecturer, Professsor Mary Garson, visited Hamilton in September and gave a fascinating and very well attended lecture entitled, *Game of terpenes: structures, stereochemistry and chemical ecology of nudibranch metabolites*.

The winners of ChemQuest 2018 from Otumoetai College, Tauranga. From left to right: John Austin, Alice Cerdeira, Daniel Lee.

NZIC President *James* ***Crowley*** visited Waikato in November and gave a fascinating and very topical talk on *Rise of the nano-machines: mechanically interlocked molecules and synthetic molecular machines*.

It is with great sadness that we announce the death of Associate Professor *Alan* ***Langdon***, who passed away after a long battle with illness on 1 September 2018. A full obituary for Alan is found elsewhere in this issue of the journal.

Scion

Scion has welcomed three new chemists to its fold. Dr Miruna Petcu comes to us from Ligar (Hamilton), a start-up company manufacturing molecularly imprinted polymers, where she held the position of Chief Science Officer. Miruna will be working on a range of projects from functional packaging to 3D printing. Dr Helena Quilter has travelled about as far as you can and relocated from the Centre for Sustainable Chemical Technologies at the University of Bath (UK) where she specialised in terpene derived polymers. Helena was using homogeneous catalysts to promote ring-opening polymerisation to form bio-based polyesters. Her background is a natural fit for Scion's projects around bio-based performance materials. Dr Angelique Greene from the US has joined us from Washington University in St. Louis where she researched smart polymers, hydrogels and elastomers. Angelique's background will complement several Scion teams developing functional and responsive polymers and composites for new applications such as 4D printing.

Dr Warren Grigsby and his Ligate™ team were presented with the Science Impact Award at the Science New Zealand Awards for their development of a new 100% bio-based resin. This chemical technology has been scaled to multi-tonne quantities and is now being assessed for uptake by a global company.

WELLINGTON

The 2018 Curtis Lecture was presented on 14 November by Professor Paul Bernhardt from the University of

Queensland. His lecture started with a description of Emeritus Professor *Neil* ***Curtis***' contributions to chemistry, especially in his seminal discovery and synthesis of macrocyclic ligands, before linking neatly from there into Professor Bernhardt's own research in electrochemical catalysis.

September's meeting was *Tailor Skincare: blending science with business* by Sara Quilter from Tailor Skincare. She spoke about the process of combining business and science in the context of starting Tailor Skincare in her dad's shed with a cake mixer and leading to the full scale-up of multiple different products. This included a moisturiser production demo and everyone got to take some moisturiser home!

NZIC Student Travel Grants were awarded to *Chriselle* ***Braganza***, *Jordan* ***McCone***, *Loc* ***Tran***, *Joe* ***Bracegirdle***, *Deanna* ***Ayupova*** and *Xu* ***Tao*** this year. Tao and Jordan attended the International Convention on Organic Synthesis (ICOS-22) in Florence, Italy, in September. Tao's oral communication was entitled, *Towards the synthesis of pateamine A analogues*; Jordan's flash presentation and poster were on *A structure-based approach to kinase inhibition based on the natural product (-)-TAN-2483B*. Loc attended an ACS Meeting in Boston during August, presenting on *A new method for nitrate remediation of water*. Deanna took part in a computational course on cancer biology in Paris in September. Joe attended a course on tropical seaweed biodiversity and clean processing technology. Chriselle travelled to Japan to perform research in a collaborator's laboratory.

NZIC member *Gary* ***Evans*** (Ferrier Institute, VUW) has recently become the Chief Scientist at MBIE. Congratulations also to *Emily* ***Parker*** (Ferrier Institute and SCPS, VUW) on election as a Fellow of the Royal Society Te Apārangi. *Tim* ***Kemmitt***, who has been at Callaghan Innovation (previously IRL) for 27 years, as well as recently on the Wellington Branch committee, has moved to Avertana Ltd - a mineral extraction company in Auckland.

Brian Halton with recent PhD graduate Amira Brackovic

VUW

21 September 2018 marked 50 years to the day since *Brian* ***Halton*** arrived at Victoria University of Wellington! The School of Chemical and Physical Sciences and the science community in Wellington celebrated this achievement with an afternoon party. There were speeches, where we heard about highlights of Brian's time at VUW, memories of past and current staff and students, and even a limerick composed for the event, as well as many photos, and a cartoon prepared by *Brendan* ***Burkett*** (ChemScrapes) to mark the occasion.

Congratulations to the following students who successfully defended their PhD theses in the past few months: *Jonathan* ***Tailby*** (supervisors *Ian* ***Brown*** and *John* ***Spencer***), *Amy* ***Foster*** (supervisors *Bridget* ***Stocker*** and *Mattie* ***Timmer***), *Amira* ***Brackovic*** (supervisors *Joanne* ***Harvey*** and *Peter* ***Tyler***) and *Parth* ***Vashishtha*** (supervisor *Jonathan* ***Halpert***).

Two new nanomaterials chemists have joined the physical chemistry team at the School of Chemical and Physical Sciences. *Renee* ***Goreham***, previously a research fellow in *Thomas* ***Nann***'s team, has been on the NZIC Wellington Branch committee this year, and has been the student liaison representative on the committee. Her research interests are in extra-cellular vesicles for diagnostic and drug delivery applications, and the interactions of metal nanoparticles with biomolecules. *Nathaniel (Nate)* ***Davis*** works on the synthesis of nanomaterials for optoelectronic applications such as photovoltaics, light emitting diodes and luminescence solar concentrators. Originally from Sydney, Australia, Nate obtained his PhD in physics from the University of Cambridge, UK before taking up an Oppenheimer Early Career Research Fellowship, also at Cambridge.

Chemistry at Victoria University has hosted a number of excellent speakers recently. Mary Garson (University of Queensland) gave the RSC Australasian Lecture on complex terpenes from marine nudibranchs; Douglas MacFarlane (Monash University) presented the Craig Medal Lecture on materials for energy export; Elizabeth Krenske (University of Queensland) spoke on quantum chemical calculations of synthetic chemical reactions; *Nicola* ***Brasch*** (Auckland University of Technology) presented on nitroxyl release mechanisms, with relevance to biochemistry and drug delivery; *Anna* ***Garden*** (University of Otago) presented a seminar on modelling heterogeneous catalysis; while *Mike* ***Price*** and *Mat* ***Anker***, postdoctoral researchers within the School, spoke about ultrafast spectroscopy and indium *N*-heterocyclic carbenes respectively.

Periodicity and approaches to periodic classification

Brian Halton

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The United Nations have designated 2019 the International Year of the Periodic Table of Chemical Elements. It marks 150 years since Mendeleev's first table.

Periodicity and the evolution of the periodic classification date back many centuries, but it is predominantly from some fifteen chemists in the early to mid-nineteenth century that its development and Mendeleev's classification became possible. The discovery of the periodic system arose from a number of scientific developments, and not a single discovery by Dmitri Ivanovich Mendeleev. That all substances were made of fundamental building blocks stems from the ancient Greek and Hellenistic Egyptian philosophers and their nature became an object of debate through the centuries. It was Lucretius who proposed that they existed in 400 BC and they were named atoms (from the Greek *atmos* for indivisible). Early atomic theory attempted to explain the properties of matter by assigning attributes to atoms that could match the attributes of matter that they combined to form, such as colour, slipperiness, and liquidity. Philosophers categorised what was around using property and function, and it was from this type of approach that the periodic table of elements came.

In the Middle Ages, alchemists sought to make gold and silver from lead. While their efforts failed, the investigations led (ultimately) to a systematic understanding of the chemical world. They also established the wherewithal that gave us the periodic table of elements. International trade, and especially that from the Silk Road between China and Europe, influenced the alchemists. Chemical knowledge breached cultures and borders so that some 17 elements were known by about 1750 and 33 by the mid-19th century. Their recognition was a prerequisite to the construction of the periodic table. Elements such as gold, silver, tin, copper, lead and mercury were recognised from antiquity, but the first scientific discovery of an element occurred only in 1649, the discovery of phosphorus by Hennig Brand. He allowed 50 buckets of urine to stand until they putrefied and bred worms. He then boiled the urine to a paste and heated it with sand, thereby distilling elemental phosphorus from the mixture. Brand reported his discovery in a letter to Gottfried Leibniz, and, thereafter, demonstrations of the element and its ability to glow in the dark, or phosphoresce, excited public interest. During the next 200 years, a vast body of knowledge concerning the properties of elements and their compounds was acquired. As the number of known elements grew, scientists began to recognise patterns in properties, and began to develop classification schemes from what they knew. They tried to organise the elements systematically into groups with similar properties. Although aspects of the early periodic table have been covered in publications of this Institute,[1] the designation of 2019 as the Year of the Periodic Table by the UN justifies a closer look at the time leading up to its release in 1869.

Hennig Brandt: The Alchemist Discovering Phosphorus from Joseph Wright, Derby, Oil on canvas 1771.

Dmitri Mendeleev is the name every chemist takes as the one who discovered the periodic table of the elements one hundred and fifty years ago. However, a significant number of chemists had been investigating patterns in the properties of the elements before him. The earliest attempt at elemental classification was by Antoine Lavoisier in 1789 when he published a list of the then known elements (and presuming that his prediction of silicon was included but only isolated by Berzelius in 1823). He grouped them into gases, metals, nonmetals, and earths. Chemists then spent the following century searching for a more precise classification scheme based on their properties.

The early 19th century saw the Law of Definite Proportions enunciated by Frenchman Joseph Proust in 1797 and demonstrated experimentally, and John Dalton proffered the atomic theory to explain the laws of conservation and definite proportions. Then, in 1815 and 1816,[2] Englishman William Prout anonymously published two papers in which he noted that the atomic weights measured for the elements known at that time were whole multiples of the atomic weight of hydrogen.[3] This implied the hydrogen atom to be the only truly fundamental particle, and he called it *protyle*. Moreover, he felt that the atoms of the other elements were made of groupings of various numbers of hydrogen atoms. Prout's hypothesis, while not borne out later by more accurate measurements of atomic weights, was sufficiently fundamental to the insight of the structure of the atom that, in 1920, Rutherford chose the name of the newly discovered proton to give credit to, among others, Prout. Prout also argued that the term *compound* applied only to materials with fixed proportions. Apparently, he did not realise the essential importance of his work lay in its verification of Avogadro's hypothesis, namely equal volumes of gases, under identical physical conditions, contain equal numbers of molecules. These works provided the fundamental evidence of matter existing as pure compounds rather than mixtures of any proportion. It was from these observations, and the atomic theory of John Dalton beginning in 1803, that the need for a systematic method of organising the elements was recognised.

Left: Joseph Proust; right: William Prout from a miniature by Henry Wyndham Phillips

Several more attempts appeared over the following century.[4-6] In 1817, Johann Döbereiner showed that the combining weight (atomic weight) of strontium lies midway between those of calcium and barium. Some years later, he concluded that many of the elements fell into groups of three based on their chemical properties. He termed these triads and it became known as *The Law of Triads*. Examples include chlorine, bromine and iodine, and lithium, sodium and potassium. Moreover, he showed that the atomic mass of the middle element was the average of the first and third. However, little attention was paid to the triads as judged by the number of publications during the 1829-1850 period. Leopold Gmelin worked with this system and, by 1843, he had identified ten triads, three groups of four, and one group of five. Jean-Baptiste Dumas classified non-metals into groups as early as 1828 and identified the triad sulfur, selenium and tellurium. Published work in 1857 described the relationships between various groups of metals.

Left: Johann Döbereiner, right: Leopold Gmelin

It was H.F.M. Kopp, who established a standard for experimental work involving specific volumes in 1839 and also sought a relationship between the elements. He found that the specific volumes of homologous elements are about the same or differ by ca. 2, e.g. Cl, Br, I; Mn, Ni, Co; Au, Ag; Na, K. Yet, despite all of this, no chemist was able to identify a relationship between all the known elements. Later in his career from 1850, Max von Pettenkofer published and spoke about the numerical relations between the atomic masses of analogous elements almost annually.[7] His theories rejected triads and he expanded the connections between the elements to larger groupings. He argued that the weights of different elements in a group implied multiples of a certain number that varied based upon the group. In his 1850 remarkable address to the Royal Academy of Sciences, entitled: *About the regular intervals in the equivalent numbers of the so-called simple radicals*,[8] Pettenkofer revealed his mastery of chemical principles in what was a lead up to the periodic law of the elements. His intent in addressing the Academy was to seek support to make the necessary precise determinations of various atomic weights in order to verify the mathematical relationships between certain of the elements. His classic report, published in an obscure journal, was reprinted in Liebig's *Annalen der Chemie und Pharmacie* (1858)[9] when his priority was threatened.

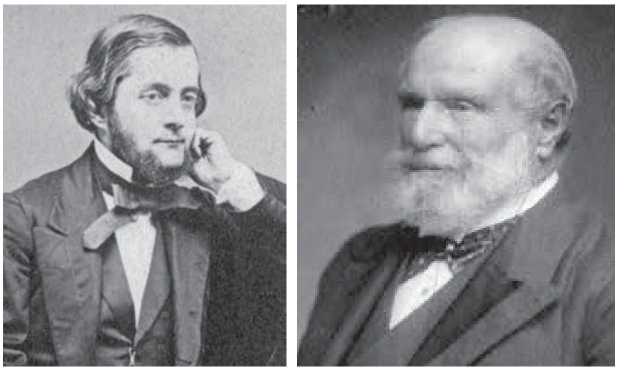
Left: Max von Pettenkofer; right: André Dumas

In 1899 the German Chemical Society awarded him a gold medal commemorating the fiftieth anniversary of the historic address. As early as 1828 the well-known French chemist André Dumas had classified non-metals into three groups. Then, in 1851, he gave a lecture to the British Association for the Advancement of Science[10] *On Atomic Volume and Atomic Weight* and was aware of triads but not of Pettenkofer's work. He felt that the middle element of recognised triads could be a compound of the two outer members, and that the component of the metallic triads could perhaps merge into one another - alchemy revisited. Another German chemist, Peter Kremers[11] was also looking for relationships between elements, but ones with little in common. He found that certain elements such as O, S, P, Se, and Ti differed in atomic weight by 8, and found additional triads. He also found that when the atomic weights of the metal is divided by 4 it gave a whole number with an odd numbered remainder, while those of the metalloids had an even number remainder. From this, he concluded that the number 4 had to be the atomic weight of a base element. Multiplying this base elemental weight by an odd number gave that of a metalloid and, consequentially, that the attraction of a metal for a non-metal was reduced to this relationship – even and odd atomic weights. This was published in 1852.

John Hall Gladstone followed with his 1853 publication: *On the relations between the atomic weights of analogous elements* in the Philosophical Magazine.[12] Here, his interest in triads was evident but, more importantly, in 1853 he arranged the known elements in order of increasing atomic weight using the values given in Liebig's Jahresberichte in 1851. He was the first chemist to do so. He saw nothing unusual in the numbers congregating around 28 and 52 and with only one between 80 and 99; then followed a group of four. Gladstone had a mathematician show that the probability of such an unusual occurrence was 250:1, and he went on to find the numerical relations to be of three kinds. The first had the atomic weights of analogous elements the same; the second in multiple proportions, and the third had them differ by certain regular increments. In the first class were Cr, Mn, Fe, Co, Ni with atomic weights approximating to 28 (O=8); Pd, Rh and Ru about 52, and Pt, Ir, and Os approximating to 99. In the second class, Pt and Au were double the Pd group. His third class was of elements whose intermediate one has properties between those of the other two, e.g. Li, Na, and K.


John Hall Gladstone

These last four exponents show that by the 1850s the attention of the European chemists on relationships between the elements was rapidly increasing, and, by 1854, activity was evident from the USA with J.P. Cooke, the inaugural professor of chemistry at Harvard (from 1850). He arranged the elements into six groups with six series of homologous substances akin to organic chemistry. His results related well to those of Pettenkofer[13] but he felt that his results followed those of Gladstone and he considered that elemental groups had to follow a mathematical series that gave atomic weight of 8 + *n* x 8 (or 4 + *n* x 8). Although he carried out a lot of work on atomic weights, Cooke was of the view that the series he created was an expression of divine law as opposed to chance. He used atomic weights to predict the properties of unknown elements and was of the view that there was a relationship with the laws of astronomy.


Left: Josiah Parsons Cooke; right William Odling (courtesy of John Odling-Smee)

In 1857, Ernst Lenssen published articles[14] saying that he had classified all the (known) elements except niobium into triads by using half of the accepted atomic weights, quite unusual at that time. He took his thoughts further and put the triads into groups of threes, which he termed *enneads*. In his second paper that year, he noted that the colours of most of the elements in each triad were complimentary and that this held for those of the flames from burning them in oxygen. Despite his factual observations, he offered few theoretical explanations. Thus, by 1858, the chemists of the era had expanded Döbereiner's suggestions and showed that similar relationships extended beyond the triads of elements; fluorine was added to the halogens and magnesium to the alkaline-earth metals. Then oxygen, sulfur, selenium, and tellurium were classed as one family of elements and nitrogen, phosphorus, arsenic, antimony, and bismuth as another. That same year of 1857 saw Dumas focus on mathematical equations that could account for the increase in atomic weight within groups of chemically similar elements as well as the organic chemistry homologous series. Also in 1857, William Odling of Guy's Hospital in London carried out a major review of all the periodicity data. He gained a better feel for the properties of elements and concluded that elements related to one another only when they had many properties in common.[15] He was convinced that the elements in a compound needed comparison. This conclusion came from the three series of acids, viz. HCl-$HClO$-$HClO_4$, H_2S-H_2SO_4, and H_3P-H_3PO_4. Here, each series represents five compounds of analogous combinations of Cl, S, and P. He was cautious in defining his 13 groups[16] and did not initially include F with the other halogens or O with S, Se, and Te because he found few relationships. He became the first chemist to see a relationship between four groups as F gives HF, N provides NH_3, O gives H_2O, and C provides CH_4; its origin came only after Kekulé's revelation of the quadrivalence of carbon earlier in that same year of 1857.

In the following year, Dumas noted the numerical relationships between the members of the fluorine and nitrogen groups, and the oxygen and magnesium groups of five and four, respectively, e.g. F (19), N (14) and Ca (20), S (16). After a revision of the atomic weights, Dumas found that the fluorine and nitrogen groups had a regular mathematical progression, namely *a, a+b. a +2b+b', a+2b+2b'+b''*, etc. This discovery was important because it led to a relationship between *all* the elements. In addition, 1858 also saw textile chemist John Mercer[17] review the similarities between the F, O, N, and Mg groups, and provide a simple mathematical relationship between the atomic weights of the elements as shown in Parnell's book (p. 324 and 325).[18] Mercer had a clear grasp of the octet and the periods (based on O = 8)

By 1860, Avagadro had re-determined atomic weights of many of the elements, and M.C. Lea in the USA did much mathematical maneuvering with the numbers to add some new relationships between the atomic weights of the elements.[19] He also concluded that vanadium was to be included in the nitrogen group. By the time of the Karlsruhe Congress in 1860, at which reprints of Cannizzaro's 1858 paper on atomic weights were circulated, atomic and molecular weights were still in dispute but the offprint did much to convince the delegates of the correct interpretation because of the more accurate list of the atomic mass of the elements.

Left: John Mercer; right: Alexandre Émile Béguyer de Chancourtois

It was the next 13 years that led to the formal discovery of the periodic system and table. The first real composed periodic table was made, not by a chemist, but by geologist Alexandre Émile Béguyer de Chancourtois. He was Inspector of Mines in Paris at a time when scientists specialised much less than they do today. A systematist by nature, he began classifying the chemical elements in 1862 and offered his views to the French Academy of Science, which were published in serial form in *Comptes Rendus* that year and subsequently summarised in the Bulletin of the French Geological Society.[20] He provided the first functioning system of elemental organisation of the elements based on Cannizzaro’s 1858 atomic weights. It was a spiral graph arranged on a cylinder, which he termed the *vis tellurique* (telluric helix) because tellurium (Latin *tellus* - earth) was centred in the middle of the graph. The diagram is plotted with the atomic weights on the outside of a cylinder such that one complete turn corresponded to an atomic weight increase of 16 units, the approximate atomic weight of oxygen as shown in Fig. 1. The elements followed their increasing atomic weight such that similar elements lined up vertically above or below one another. He was, therefore, the first scientist to see that the properties of the elements are the properties of numbers, viz. periodicity, when arranged in order of increasing atomic weights. Although presented to

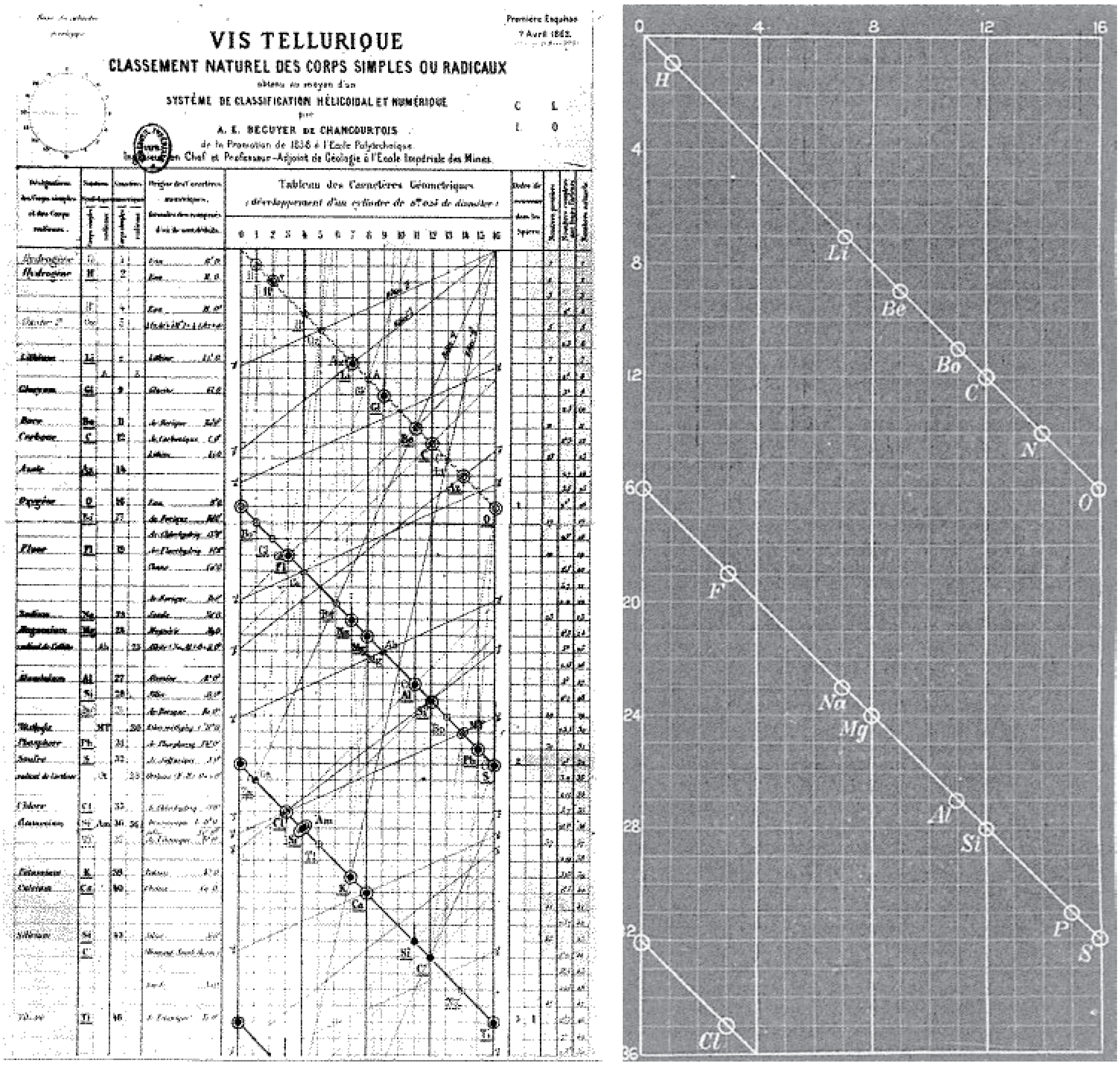


Fig. 1. Left: Béguyer de Chancourtois’s original spiral diagram; right: the first turn of the spiral from ref. 21 (with permission of Springer-Nature).

the French Academy of Sciences and published by it, the work received little attention from chemists, most likely because the diagram (Fig. 1) was omitted in the original publication and only appeared later in a less read geological pamphlet. A subsequent paper by Hartog[21] in *Nature* provides extracts of the original publications, more complete citations, and much useful comment. Much more recently, the spiral of Béguyer de Chancourtois has been brought to life by the elegant 3D artistic version created by Professor Scott McIndoe of the University of Victoria, British Columbia as illustrated in Fig. 2.

Fig. 2 The artistic de Chancourtois spiral that contains samples of each element (courtesy of Professor McIndoe)

A year after de Chancourtois' revelations, John Newlands[22,23] was classifying elements into seven groups as well as exploring numerical relationships among their atomic weights. For example, his first group consisted of lithium (at. wt. 7), sodium (23), potassium (39), rubidium (85), caesium (123), and thallium (204). The relations among the equivalents of this group is simply: 1Li + 1K = 2Na and 1Li + 2K = 1Rb, etc. However, he was mistaken about new element 163 and in placing thallium with the alkali metals. Nonetheless, he made predictions, contrary to many modern accounts that accord this to Mendeleev. In 1864, Newlands published a short table containing 12 elements and showed that in two series of six elements each one differed from its equivalent in the other set of six by 16 units or very close to it. Another table he published the same year included 33 of the then known elements.

John Newlands

In 1865, Newlands reported that when the chemical elements are arranged in order of increasing atomic weight, those with similar physical and chemical properties occur after each interval of seven elements – it became the *Law of Octaves*. Newlands was one of the first to detect a periodic pattern in the properties of the elements. However, it was in his 1866 lecture to the Chemical Society that he produced an even more comprehensive table that contained 62 elements. One of his comments was misconstrued and the table appeared only in *Chemical News*[24] in 1866; it is reproduced in Fig. 3.

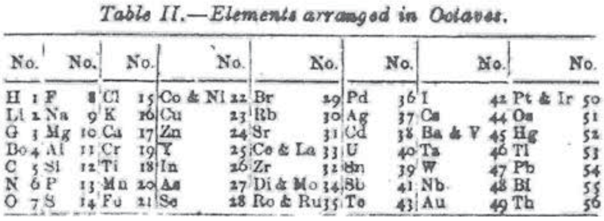
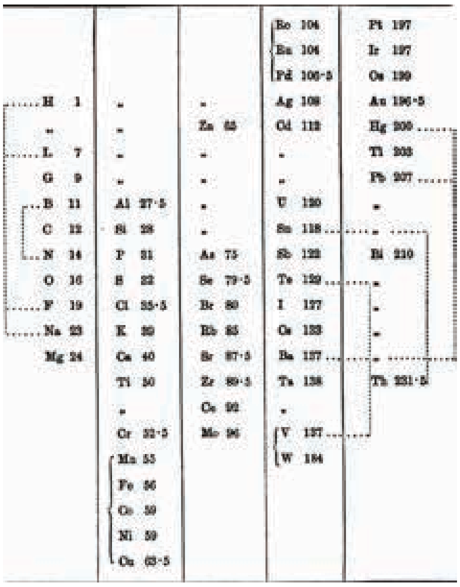


Table II.—Elements arranged in Octaves.

	No.		No.		No.		No.		No.		No.		No.		No.
H	1	F	8	Cl	15	Co & Ni	22	Br	29	Pd	36	I	42	Pt & Ir	50
Li	2	Na	9	K	16	Cu	23	Rb	30	Ag	37	Cs	44	Os	51
G	3	Mg	10	Ca	17	Zn	24	Sr	31	Cd	38	Ba & V	45	Hg	52
Bo	4	Al	11	Cr	19	Y	25	Ce & La	33	U	40	Ta	46	Tl	53
C	5	Si	12	Ti	18	In	26	Zr	32	Sn	39	W	47	Pb	54
N	6	P	13	Mn	20	As	27	Di & Mo	34	Sb	41	Nb	48	Bi	55
O	7	S	14	Fe	21	Se	28	Ro & Ru	35	Te	43	Au	49	Th	56

Fig.3. J.A.R. Newlands table of the elements 1866 (taken from ref. 24)

At the time Newlands published his 1864 table with 12 elements, William Odling published his containing 57 elements shown as Fig. 4.[25] This table overcame the tellurium-iodine problem and even managed to get thallium, lead, mercury and platinum into the right groups (something that Mendeleev failed to do at his first attempt). Odling had proposed that oxygen had an atomic weight of 16 in 1858, and identified ozone as O_3 in 1861 (from which he was nicknamed Ozone Odling[26]). Despite this, his work and table did not get the recognition they deserved. He had a significant interest in inorganic nomenclature and the periodic system of classification that he proposed in 1864 was independent of the work of Newlands. His classification (Fig. 4) shows a clear distinction between main and sub-group elements, the first to do so, which demonstrates that some analogous elements needed separating into two sub-groups in order to provide genuine periodicity of their properties.[25] He included 57 of the 60 elements then known and arranged them in order of increasing atomic weight, but he made exceptions. This resulted in him inverting iodine (127) and tellurium (129), again the first to do so, and in 1864, the only pair with very close atomic weights, Co/Ni. His paper stated that there were spaces in the order of atomic weights, but whether these were for then unknown elements is not clear. Odling's system came from known chemical phenomena and prediction. He was always comprehensive and attempted to systematise wherever possible. In 1868, he provided another table in which he omitted 11 elements but had several better placed.[27]



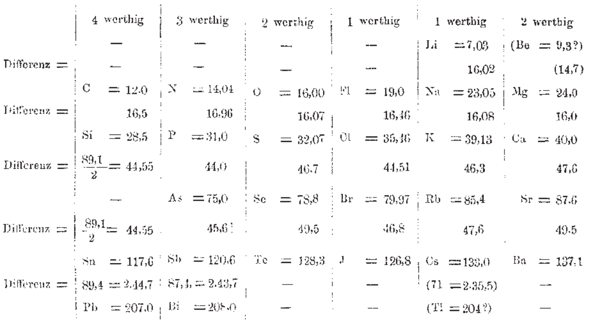
			Ro 104	Pt 197
			Ru 104	Ir 197
			Pd 106·5	Os 199
H 1	•	•	Ag 108	Au 196·5
•	•	Zn 65	Cd 112	Hg 200
L 7	•	•	•	Tl 203
G 9	•	•	•	Pb 207
B 11	Al 27·5	•	U 120	•
C 12	Si 28	•	Sn 118	•
N 14	P 31	As 75	Sb 122	Bi 210
O 16	S 32	Se 79·5	Te 129	•
F 19	Cl 35·5	Br 80	I 127	•
Na 23	K 39	Rb 85	Cs 133	•
Mg 24	Ca 40	Sr 87·5	Ba 137	•
	Ti 50	Zr 89·5	Ta 138	Th 231·5
	•	Ce 92	•	
	Cr 52·5	Mo 96	V 137	
	Mn 55		W 184	
	Fe 56			
	Co 59			
	Ni 59			
	Cu 63·5			

Fig. 4. The Odling Table of the Elements (taken from ref. 25)

There were other players in this era. Because of his political appointments, Dumas made only limited contributions and the Danish-American Gustavus Hinrichs[28] who was Professor of Chemistry at the University of Iowa published in 1866 a paper claiming that the properties of elements are functions of their atomic weights. He stated his ideas as early as 1855 and is one of the discoverers of the periodic laws. He proposed a *pantogen* theory with one primary form of matter, a *panatom*, from which all elements came. They arose by one of two possible combinations to give *trigonoides* composed of regular triangles – the non-metals – and the metallic *tetragonoides* with squares. He divided each of these into families and then sub-divided the families. He also provided algebraic formulae to account for his families and was aware of the similarities between the elements and organic homologues. His depiction of the elemental system was in the form of a spiral with the elements placed into the structure according to their atomic mass.

The last contribution prior to Mendeleev came from Lothar Meyer. He was a qualified medical doctor who had worked with Bunsen in Heidelberg and shown the effect of carbon monoxide on the blood, and that oxygen combines with the haemoglobin in blood. He noted, as J.A.R. Newlands did, that if the elements are arranged in the order of atomic weight, they fall into groups of similar chemicals with physical properties repeated at periodic intervals.

Gustavus Hinrichs



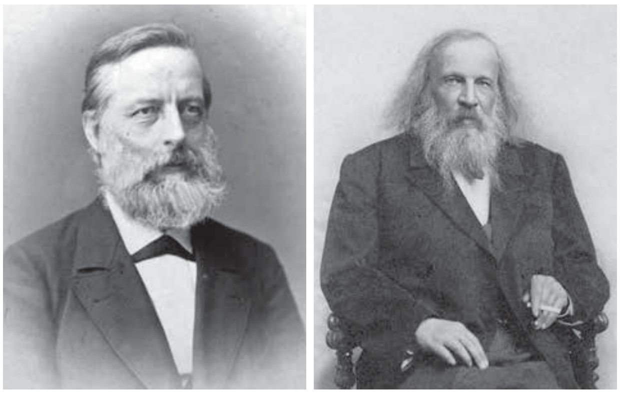
	4 werthig	3 werthig	2 werthig	1 werthig	1 werthig	2 werthig
	—	—	—	—	Li = 7,03	(Be = 9,3?)
Differenz =	—	—	—	—	16,02	(14,7)
	C = 12,0	N = 14,04	O = 16,00	Fl = 19,0	Na = 23,05	Mg = 24,0
Differenz =	16,5	16,96	16,07	16,46	16,08	16,0
	Si = 28,5	P = 31,0	S = 32,07	Cl = 35,46	K = 39,13	Ca = 40,0
Differenz =	$\frac{89,1}{2}$ = 44,55	44,0	46,7	44,51	46,3	47,6
	—	As = 75,0	Se = 78,8	Br = 79,97	Rb = 85,4	Sr = 87,6
Differenz =	$\frac{89,1}{2}$ = 44,55	45,6	49,5	46,8	47,6	49,5
	Sn = 117,6	Sb = 120,6	Te = 128,3	J = 126,8	Cs = 133,0	Ba = 137,1
Differenz =	89,4 = 2.44,7	87,4 = 2.43,7	—	—	(71 = 2.35,5)	—
	Pb = 207,0	Bi = 208,0	—	—	(Tl = 204?)	—

Fig. 5. The Meyer 1864 table of 28 elements taken from Ref. 29.

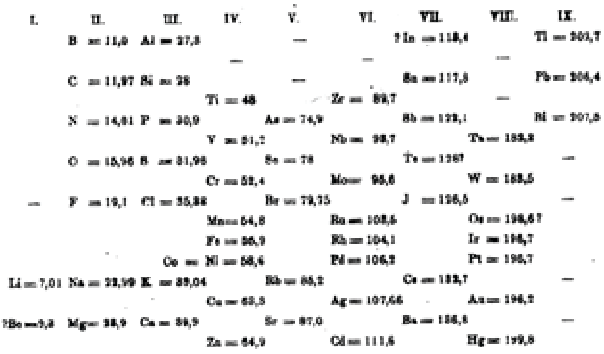
He began writing a textbook[29] in 1862 that appeared in 1864, convinced that it needed a classification of the elements. This book contains an early version of the periodic table containing 28 elements (56 were know at that time) classified into six families by their valence (Fig. 5), a term he introduced. Meyer saw the elements differed from each other in atomic weight by 16 or a multiple thereof, and that the values around 46 and in the 87-90 range were most important. He did not predict any new elements but left gaps and he did not correct any atomic weight. Because his classification covered only 28 of the then known elements it is not a periodic classification as such but close to one. In 1868, he provided another table comprising of 53 elements. It was intended for the second edition of his text that appeared in 1872.[29] However, much like Béguyer de Chancourtois, Meyer's new table did not appear in the edition and was reproduced only in 1895.[30,31]

Meyer provided a table of 50 elements that appeared in periodical form[32] only in the 1870 literature (Fig. 6). The 1870 table appeared a few months after Mendeleev's classic paper, which is why Mendeleev is the recognised founder of the periodic table. The Mendeleev 1869 table placed the then known 63 elements and left spaces for a further three; it appears below as Fig. 7.[33]

It is because Lothar Meyer had not published a table comparable to that of Mendeleev before Mendeleev that he is not credited as the discoverer of the periodic system, and this despite his 1870 table being virtually identical. Some historians of science consider both as co-creators of the periodic table, but Mendeleev's accurate prediction about undiscovered elements enables him to have the larger share of the credit, if not all of it. A long and bitter dispute between Meyer and Mendeleev even-

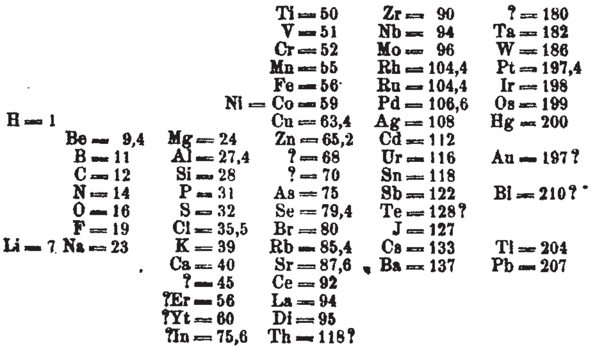


Left: Julius Lothar Meyer (1883); right: Dmitri Ivanovich Mendeleev (1890s)



I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
	B = 11,0	Al = 27,3		—		?In = 113,4		Tl = 202,7
			—		—		—	
	C = 11,97	Si = 28		—		Sn = 117,8		Pb = 206,4
			Ti = 48		Zr = 89,7		—	
	N = 14,01	P = 30,9		As = 74,9		Sb = 122,1		Bi = 207,5
			V = 51,2		Nb = 93,7		Ta = 182,2	
	O = 15,96	S = 31,98		Se = 78		Te = 128?		—
			Cr = 52,4		Mo = 95,6		W = 183,5	
—	F = 19,1	Cl = 35,38		Br = 79,75		J = 126,5		—
			Mn = 54,8		Ru = 103,5		Os = 198,6?	
			Fe = 55,9		Rh = 104,1		Ir = 196,7	
		Co =	Ni = 58,6		Pd = 106,2		Pt = 196,7	
Li = 7,01	Na = 22,99	K = 39,04		Rb = 85,2		Cs = 132,7		—
			Cu = 63,3		Ag = 107,66		Au = 196,2	
?Be = 9,3	Mg = 23,9	Ca = 39,9		Sr = 87,0		Ba = 136,8		—
			Zn = 64,9		Cd = 111,6		Hg = 199,8	

Fig. 6. The Lothar Meyer 1870 table modified from ref. 33



			Ti = 50	Zr = 90	? = 180
			V = 51	Nb = 94	Ta = 182
			Cr = 52	Mo = 96	W = 186
			Mn = 55	Rh = 104,4	Pt = 197,4
			Fe = 56	Ru = 104,4	Ir = 198
		Ni =	Co = 59	Pd = 106,6	Os = 199
H = 1			Cu = 63,4	Ag = 108	Hg = 200
	Be = 9,4	Mg = 24	Zn = 65,2	Cd = 112	
	B = 11	Al = 27,4	? = 68	Ur = 116	Au = 197?
	C = 12	Si = 28	? = 70	Sn = 118	
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210?
	O = 16	S = 32	Se = 79,4	Te = 128?	
	F = 19	Cl = 35,5	Br = 80	J = 127	
Li = 7	Na = 23	K = 39	Rb = 85,4	Cs = 133	Tl = 204
		Ca = 40	Sr = 87,6	Ba = 137	Pb = 207
		? = 45	Ce = 92		
		?Er = 56	La = 94		
		?Yt = 60	Di = 95		
		?In = 75,6	Th = 118?		

Fig. 7. The original Dmitri Mendeleev Periodic Table of 1869 abstracted and modified from ref. 34

tuated in which each laid claim to priority and others became involved.[34] Even the London correspondent of the *Deutsche Chemische Gesellschaft* claimed priority for the English discoverer of the periodic system, William Odling (see above) in 1871. Lothar Meyer's main contribution is, therefore, his recognition of periodicity as shown by his atomic mass vs atomic volume plot. This clearly shows a periodic pattern as the atomic volume rises to peaks and then falls again with the most electropositive elements at the peaks (Fig.8). It formed a part of his 1870 paper.[32]

Mendeleev's text for inorganic chemistry, *Principles of Chemistry* appeared in two volumes, over 1868 and 1870. It became the standard text for the field until the early 1900s. He knew that a critical reason for peoples' difficulty in understanding chemistry was the lack of any clear system for classifying the known elements. Therefore, he set out to organise and explain the elements beginning with the *typical* elements: hydrogen, oxygen, nitrogen, and carbon. Then he included the low atomic weight halogens, which were readily available in nature and reacted easily with other elements. He began the process using atomic weights as a principle of organisation, but these alone did not present a clear system. At this time, Mendeleev was unaware of much, if not most of the advances made elsewhere in the previous few years. To put some order into his study of chemical elements, he made up a set of cards, writing the name, atomic weight and the properties of the each of the 63 elements known by then on a card. He took the cards everywhere he went. On February 17 1869 he began to organise the elements with his cards, working continuously for 3 days and nights. One account has an exhausted Mendeleev falling asleep and having a dream where all the elements fell into place as required. He wrote the sequence down immediately, naming his discovery the *periodic table of the elements*. Despite who had priority, it is noteworthy that both Meyer and Mendeleev received the 1882 Davy medal from the Royal Society.

After Meyer's 1870 paper, Mendeleev published further comment in which he said the system itself was essentially complete but that the location of some elements needed to be improved.[35] However, he did not term his system *periodic.* In his original paper it was a *classifica-*

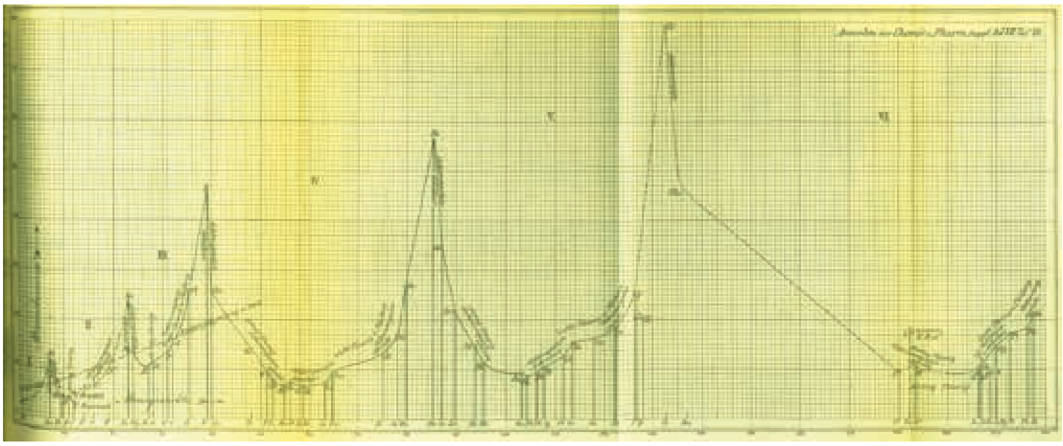


Fig. 8. The Meyer atomic weight vs atomic volume plot (courtesy of Carmen Giunta, Professor of Chemistry, Le Moyne College, Syracuse, NY)

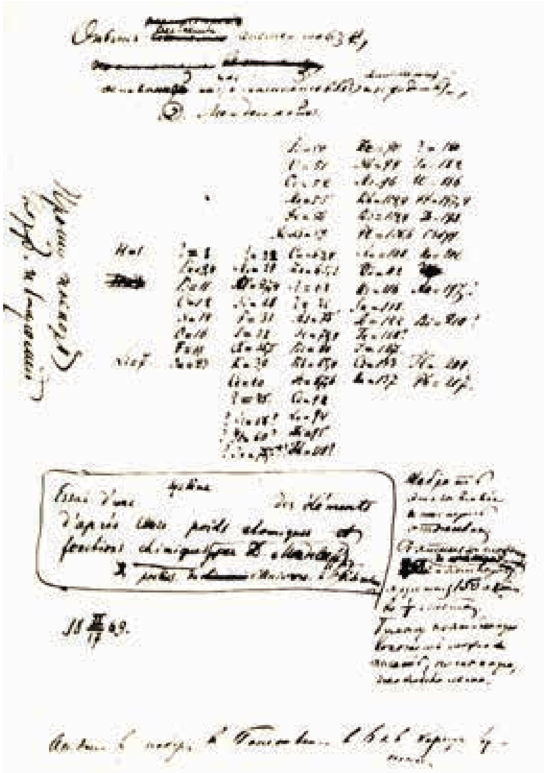


Fig. 9. Mendeleev’s handwritten version of the periodic law, based on atomic weight and chemical resemblance - D. I. Mendeleev, 17 February 1869

tion of elements and division of elements, then *natural system* but in 1871 in a precedence dispute with Odling[36] he referred to it as a *periodic system* and this has stayed. Meyer never used the term periodic. Since 1870, the periodic table has evolved has gone in both depiction and complexity. The circular spiral, screw, sphere, etc., have all given way to the two-dimensional form that we all know so well. It was Bohr’s system, created in 1922, that finally put all of the elements in their correct places with room only for those unknown.

Acknowledgements

I am grateful to John Odling-Spee for the images and information of William Odling, Prof. Carmen Giunta and Kari Zhe-Heimerman of Le Moyne College for locating and providing Figure 9 from their archive, and Professor Scott McIndoe for his de Chancourtois spiral images and his useful comments.

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Arranging the elements creatively: alternative forms of the periodic table

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Keywords: *ADOMAH periodic table, elements, spiral periodic table*

In the previous article, we discovered how the periodic table developed to the form we are now familiar with. Although this is the form which is the most popular, it does have certain limitations. For example. hydrogen constitutes 90% of the known universe but its place in the periodic table is very much open to debate. Hydrogen can lose an electron, making it right to position it above the alkali metals. However, it can also gain an electron, which is a characteristic of halide elements. Lanthanides and actinides are placed at the bottom of the table, making them appear as footnotes. This may be done deliberately, to fit the entire table into a single page but it still may be cause for confusion.[1] Additionally, the advent of new techniques for measuring the properties of heavy elements of above atomic number 100, have shed new light on their electronic configuration. For e.g. Sato *et. al.* conducted both theoretical and experimental studies on atoms of lutetium (Z = 71) and lawrencium (Z = 103) and made scientists question the position of these elements.[2] These drawbacks have inspired scientists to create other, improved versions of the periodic table to circumvent these ambiguities and is the topic of this article.

Benfey's spiral periodic table

One of the first spiral periodic tables was published by Hinrichs in 1867.[3] Subsequently, other scientists proffered their own design of spiral charts, amongst notably by Quam and Quam (1934),[4] Janet (1928),[5] and Benfey (1964).[6] A modern version of Benfey's table is shown in Fig. 1.

With hydrogen at its centre, the elemental families radiate out in a clockwise spiral manner, developing two periods of 8 followed by two of 18, then two of 32, etc. The main features are that each colour represents a group of elements, such as the alkali metals, metalloids etc., while each spiral encodes a period. Transition metals, lanthanides and actinides are placed together with the other elements as in the traditional periodic table. Unlike the traditional periodic table, however, there is no gap between transition metals and the f-block elements.

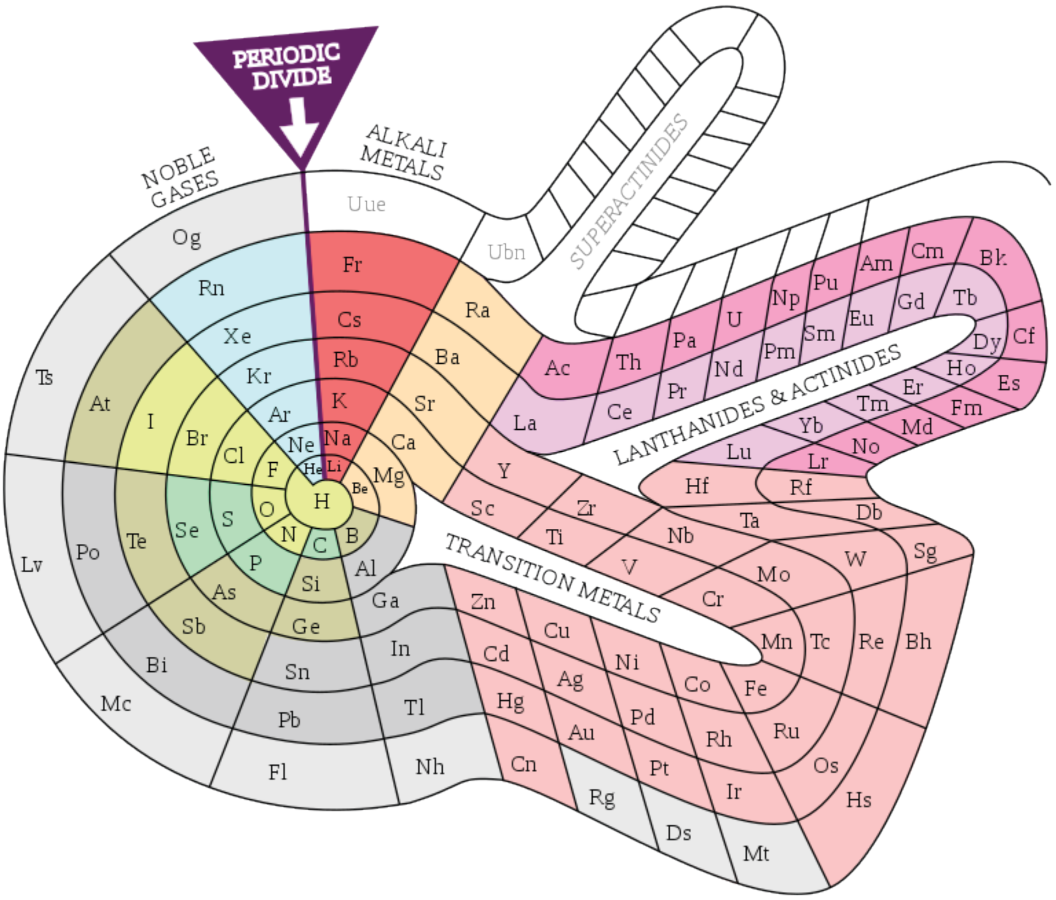

Fig. 1. Theodor Benfey's spiral periodic table. Image created by DePiep and obtained from Wikipedia under a Creative Commons license (https://commons.wikimedia.org/wiki/File:Elementspiral_(polyatomic).svg)

They are arranged continuously, with different colours indicating their classification. This form gives a better interpretation of the relationships between elements according to their properties and electronic configuration. Hydrogen, whose position is always ambiguous, is coloured the same as the other gases like oxygen or chlorine. This is a drawback, as it focuses on physical state rather than chemical behavior. Except for d- and f-block elements, it is hard to predict the electronic configuration of other elements.

Harrison's spiral periodic table

Robert W. Harrison presented a new form of the spiral periodic table as a chemical galaxy which displays both groups and periodicity in a spiral radial format (Fig. 2).[7] The arrangement follows the density wave theory of spiral galaxies where the density and rotation of matter increases towards the centre. Consequently, elements are arranged from the outer sphere to the centre according to their density. In contrast to Benfey's spiral form, hydrogen is placed on the outside and the heavier elements are positioned inwards. Colours indicate groups of elements; e.g. halides are shown in red, alkali metals in bright yellow, transition metals in grey, etc. A unique feature is the placement of elements with similar oxidation states in the same column. For example beryllium, magnesium, calcium, zinc, strontium, cadmium, barium and mercury which commonly exist in the +2 state are in the same column. Boron, aluminium, scandium, gallium, yttrium, indium and thallium exhibit the +3 state and are also in the same column. Some exceptions are metals like chromium and molybdenum that are placed the nonmetallic elements sulfur and oxygen. Hydrogen, which generally cannot be considered as part of any group, has been placed with the halides.

Unfortunately, the lanthanides and actinides are placed separately which is understandable for this model but nonetheless, undesirable. This periodic table spirals inwards, and hence the discovery of new elements may eventually close the spiral completely, a problem not seen in Benfey's model. Another disadvantage is the decreasing size of the columns with increasing atomic number, making it difficult to read.

The ADOMAH periodic table

The ADOMAH periodic table was developed by Valery Tsimmerman in 2006.[8] A feature of this design is the use of the quantum numbers this table uses quantum numbers to arrange the elements, an idea which is useful for predicting electronic configuration. The primary

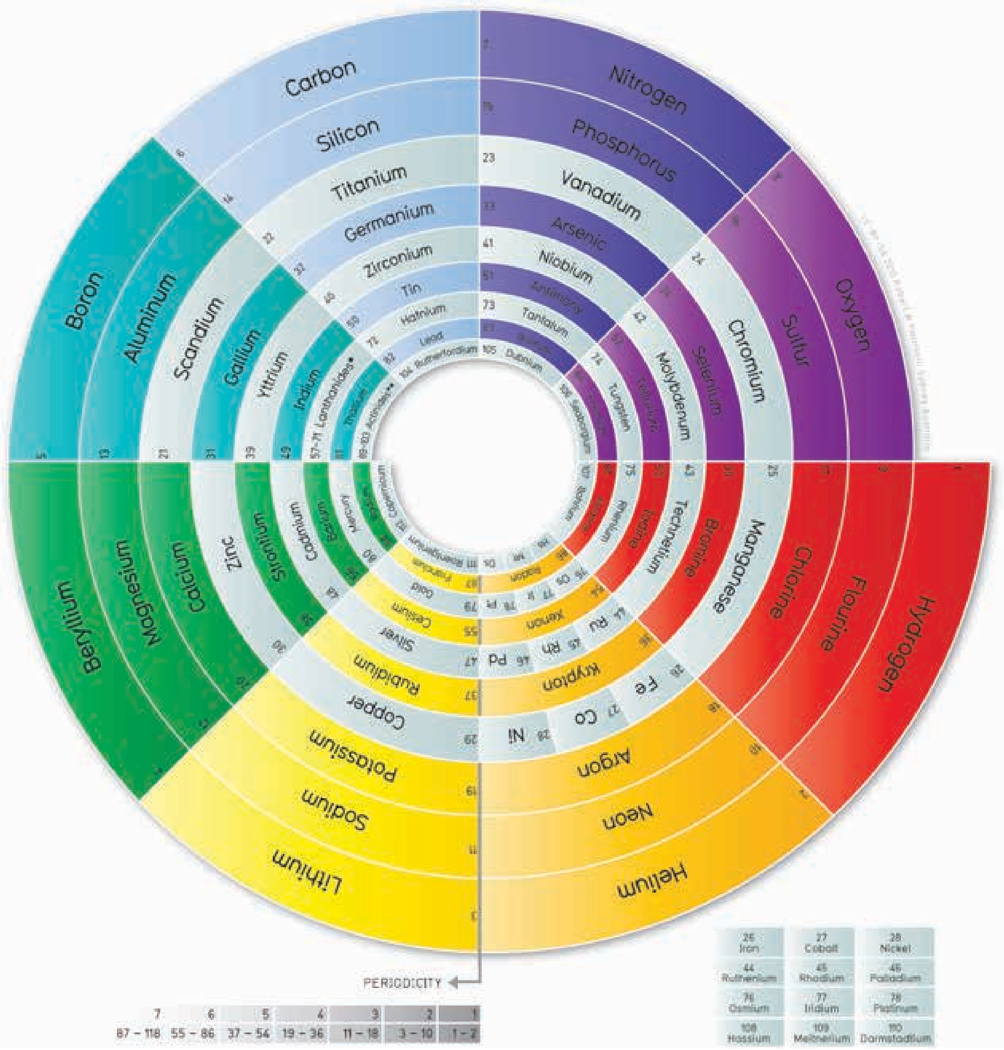

Fig. 2. Spiral periodic table developed by Robert Harrison. Image created by Robert Harrison and obtained from Wikipedia under a Creative Commons license (https://commons.wikimedia.org/wiki/File:Spiral_Periodic_Table.jpg).

quantum number (n) indicates the outermost shell of the element's atom. The azimuthal quantum number (l) corresponds to the orbitals, i.e. s = 0, p = 1, d = 2, and f = 3. The empirically derived Madelung Rule, which states that orbitals with lower (n+ l) values are filled before than those with higher (n+ l) values, is accounted for and the Aufbau principle is obeyed.

The ADOMAH table retains elements in groups; the s-block elements with l = 0 are at the bottom and the f-block elements with l = 3 are placed at the top (Fig. 3). Sandwiched between these are the p- and d-block elements. Colour coding is used mainly to highlight similar properties, e.g. the alkali metals are in red, noble gases are in light blue. Tsimmerman later realised that the four blocks of elements can be represented as slices of a tetrahedron, making the ADOMAH table a three-dimensional version of organising the elements.

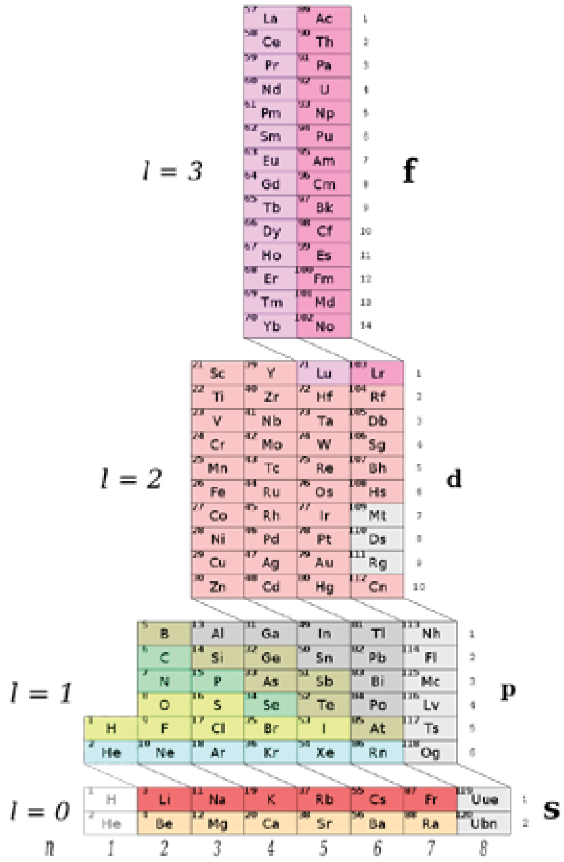

Fig. 3. The ADOMAH periodic table developed by Valery Zimmerman based on quantum numbers. Image from Wikipedia created by DePiep and obtained from Wikipedia under a Creative Commons license (CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=27764720).

Conclusions and outlook

Over 200 years, there have been hundreds of versions of the periodic table. The common idea behind developing these is to provide a better representation of the behaviour of elements. Each element has its own uniqueness and a broad spectrum of physical and chemical parameters, which makes the development of a periodic table that addresses all these parameters quite a challenge. With the advent of more sophisticated and sensitive techniques to probe atoms, there are possibilities of rethinking the positioning of some elements,[2] turning the periodic table not into a static icon but rather to a dynamic one, constantly evolving over time. Scientists have synthesised elements up to atomic number 118. If element 119 is to be discovered, one interesting concept that would open up is the possibility of a g-block, whose existence is only hypothetical.[9] Where should the g-block elements be added? Finally, at the end of the day, all periodic tables are only representations for our convenience. Nature, however, does not necessarily have any regard for human convenience.

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Mendeleev's music: notes on the periodic table

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Keywords: *periodic table, Mendeleev, music*

The 150th anniversary of the publication of the periodic table of the elements occurs in 2019.[1] Mendeleev's role in the development of the table has been the subject of prose[2] and song.[3] Indeed, it has been claimed that music played a part in the table's genesis:

"On February 17, 1869, exhausted by lack of sleep and lack of progress, Mendeleev listened distractedly to his family playing chamber music as he dozed off in the room next door. Falling into a deep sleep, Mendeleev suddenly saw the individual atomic elements drifting before him. They swayed to the sound of the chamber music, aligning themselves in unique and beautiful patterns that varied slightly in time with the songs being played. Slowly but surely, they began to flow together in the shape of a table in which each building block was placed according to its atomic weight, starting with the lightest and ending with the heaviest element sinking into their rightful positions. When the table was complete, Mendeleev awoke with a start, understanding that what he had just dreamt could be the answer he had so long been looking for.

> "He jotted down the table from his dreams and, as he later explained to a close friend, his vision was nearly flawless: 'I saw in a dream a table where all elements fell into place as required…Only in one place did a correction later seem necessary.' "[4]

A variant of this tale asserts that Mendeleev's arrangement of the elements came to him while he was listening to a performance of Schumann's Piano Quintet, Opus 44A.[5] Daniel Morris has played this particular quintet and also knows the periodic table well. To him:

> "the connection is fantastically clear. The second theme of the Quintet's first movement is presented first by the piano in a fragmentary seven-note melody. It breaks off and, then, is repeated in the same way. Next, piano and cello take up the same melody a third time but, this time, the viola continues with an inversion—a development—of the original melody. This pattern is repeated and, finally, there is an extensive development of the theme."[6]

Relationship between periodicity of elemental properties and music

At about the time Mendeleev's version of the periodic table appeared, an association between the regularity of the variation of properties of the chemical elements and the periodicity of musical notes was suggested by John Newlands: 'the law of octaves',[7] which Scerri describes as

"… the elements showed a repetition in their chemical properties after intervals of eight elements. Newlands went so far as to draw an analogy between a period of elements and a musical octave, in which the tones display a repetition involving an interval of eight notes (counting from one note of C, e.g., to the next note C inclusive."[8]

The essence of Newlands' idea is shown in Fig. 1.[9]

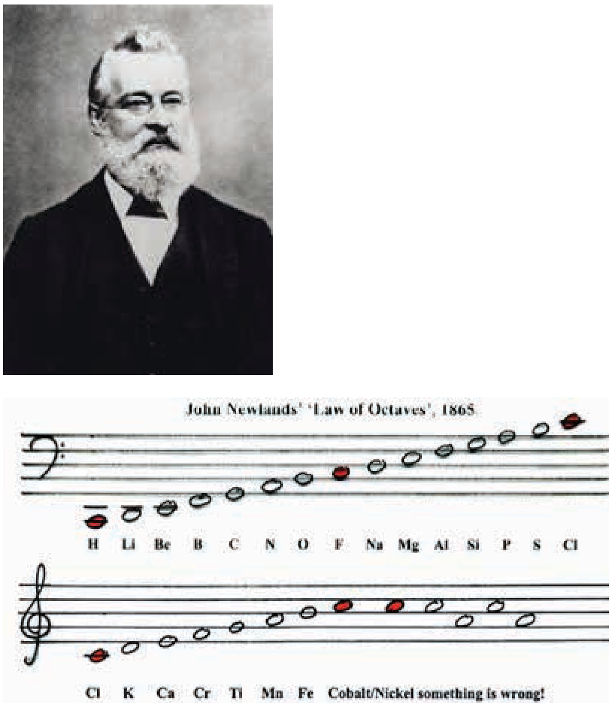


Fig. 1. Musical interpretation of John Newlands' Law of Octaves. Image of Newlands from: https://en.wikipedia.org/wiki/John_Newlands_(chemist)

Extending this idea to include chemical elements not known to Newlands, i.e., the Mendeleev table,[10] and more modern views of atomic structure yields the observation:

> "This law of octaves is derived from the fact that eight electrons can fit within the second and third orbital of an atom, just as eight musical notes fit within the diatonic scale of a sonic octave. In theory a person could map the 88 notes of the piano onto the first 88 elements of the periodic table and compose music through a study of actual chemistry."[11]

A limitation to this particular musical score is that it ignores the fact that two magnesium atoms combine with one molecule (two atoms) of oxygen.

More recently, an association between chemistry and music has been attributed to their common language – mathematics,[12] asserting:

> "Interesting music can be created as chemical reactions—mediated by instrumentation and mathematics (e.g., spectrometry and discrete Fourier transformation)[13]—yield data that can be combined with prin-

> ciples of music theory to produce sounds. Sound files resulting from converting data to musical notation are then playable and manipulable on the computer; the sound data can also be represented on musical staves and played on musical instruments."

The paper then observes that an earlier paper in the series presented:

> "…musical properties of atomic spectra of selected atoms of groups IA [the alkali metals, i.e., Li to Fr], VIIIA [the inert gases, i.e., He to Rn], and period 2 [Li-Ne]. The literature wavelength values are first converted to frequencies and are then transformed into musical notes using music theory. The music produced by each atom is not similar and appears to be quite distinctive."

Based on this statement Kumbar "explores musical properties of the periodic table based on atomic spectra. When atoms are clustered together like groups, periods, metals, and so forth, they tend to generate unique and distinct music", concluding that: "on a macro level, it is intuitive to conclude that the pitch of the musical notes increases from left to right in any period and decreases from top to bottom in any group similar to first ionisation energy" (Fig. 2).[14]

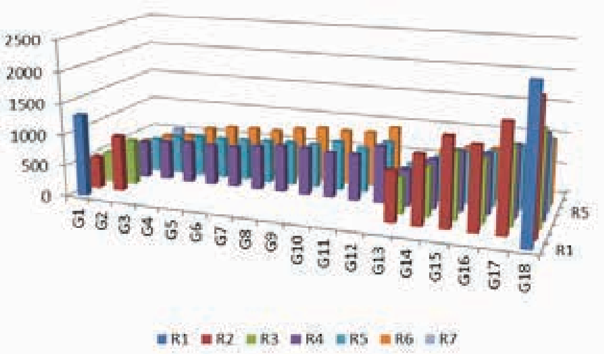


Fig. 2. Variation of first ionisation energy (in KJ mol^{-1}) by groups, from G1-G18, and rows, from R1 to R7, of the periodic table

The sequences across the upper rows of Kumbar's periodic table (Fig. 3) are simply scales. and the combinations down the columns are inter-octave chords. A more recent commentator on Kumbar's approach has observed:

> "To construct his table, Kumbar grabbed a few lines from each element's emission spectrum. He then mathematically transformed the energies of elemental electronic transitions into characteristic notes played by each atom. Kumbar also notes that "*atoms...clustered together...tend to generate unique and distinct music*." Perhaps each element could be considered a player in a nanoscale symphony: for instance, silver bromide (AgBr) plays a beautiful open third (C6-E6), while bleach (sodium hypochlorite, NaOCl) plays more of an inverted C#min chord, stretched across three octaves (E5-G6-C#7)."[15]

This approach of "grabbing a few lines from the spectra" may seem somewhat *ad hoc*, by comparison with which later efforts described in this paper appear more systematic and scientific.

The elements' own music

The emission and absorption spectra of atoms are associated with their vibrational frequencies, and the spectra for hydrogen were the starting point for Mark Stephen John's compositions.

> "Hydrogen, the most abundant element, the lightest known element, the element that is in every part of our body is the framework for this composition. As I work with the tones from the elements, I find a beautiful consonance between the colors [of the hydrogen absorption spectrum – Fig. 4]. It is quite mind bending to step out of my experience with tuning based upon 440 Hertz and the equal tempered tuning of the piano, and, into tones that are vibrating from, into, with, the world around us."[16]

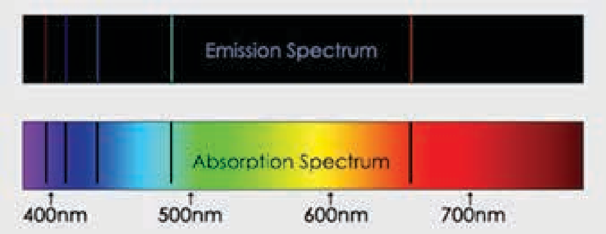


Fig. 4. Absorption and emission spectra of hydrogen - the inspiration for Mark Stephen John's compositions

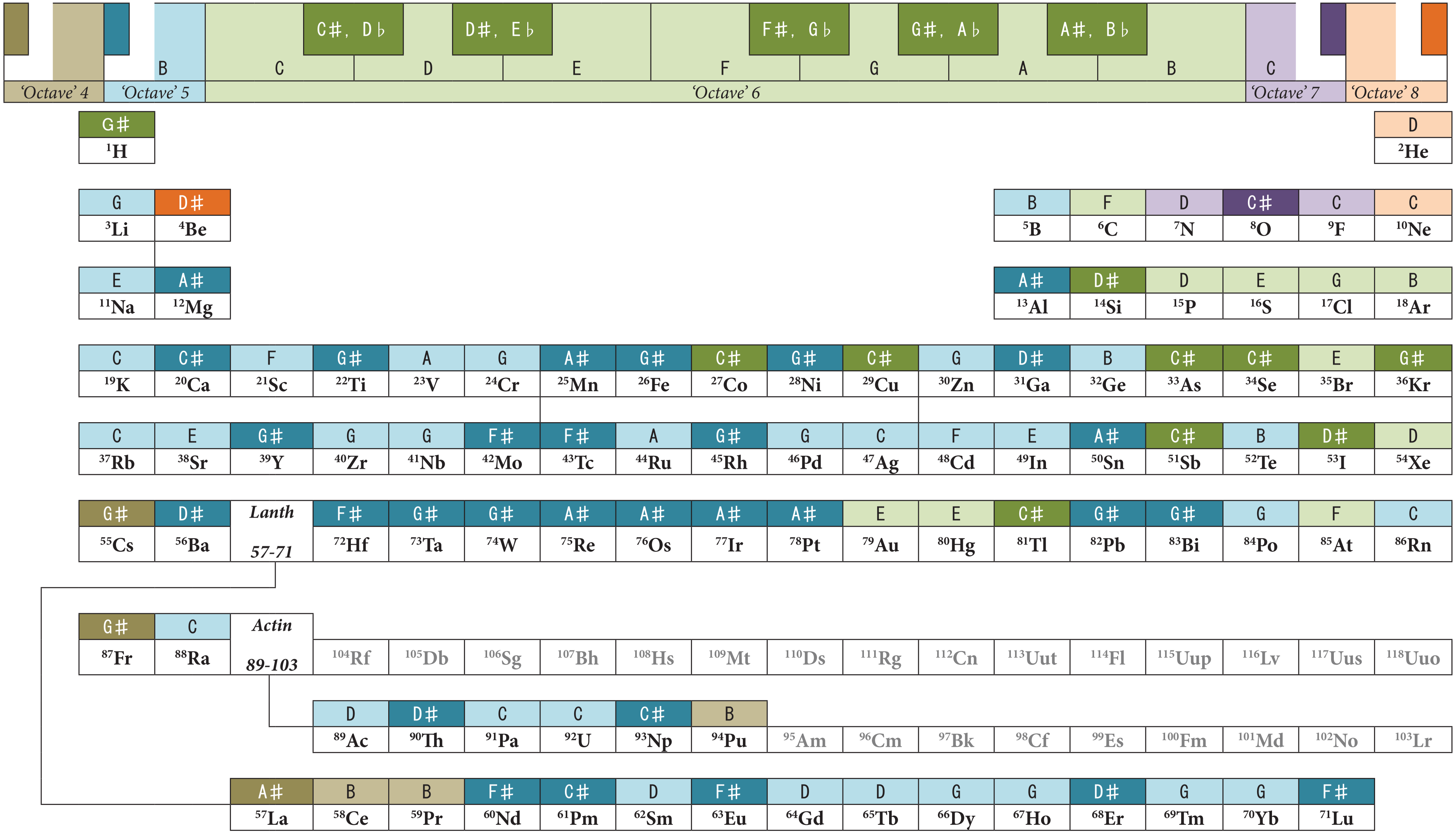
John's website provides musical 'scales' and 'soundscapes' for 17 elements which he identifies as contributing to human health (Fig. 5), with the implication that more are to follow. Similar – but rather longer – soundscapes were composed, arranged and performed live at The Bunker New York 10 Year Anniversary in January 2013,[17] while Tussey (2014) has composed a range of soundscapes for oxygen.[18]

The natural frequencies of vibration of the elements also provide the basis for Asegun Henry's intention to find "unique 'musical' signatures of every element on the period table" – of which the first 'signature' on his website is that for diamond-structured silicon:

> "We have to slow down the vibrations of the atoms so you can hear them, because they're too fast, and at too high frequencies, but you'll be able to hear the difference between something low on the periodic table and something like carbon that's very high. One will sound high-pitched, and one will sound low."[19]

A more technical explanation of Henry's approach is given below:

> "For many decades, phonon transport at interfaces has been interpreted in terms of phonons impinging on an interface and subsequently transmitting a certain fraction of their energy into the other material. It has also been largely assumed that when one joins two bulk materials, interfacial phonon transport can be described in terms of the modes that exist in each material separately. …. we examine the assumption of using the bulk materials' modes to describe the interfacial transport. The results indicate that when two materials are joined, a new set of vibrational modes



	B	C	C#, D♭	D	D#, E♭	E	F	F#, G♭	G	G#, A♭	A	A#, B♭	B	C	D
'Octave' 4	'Octave' 5	'Octave' 6												'Octave' 7	'Octave' 8

G#																	D
^{1}H																	^{2}He
G	D#											B	F	D	C#	C	C
^{3}Li	^{4}Be											^{5}B	^{6}C	^{7}N	^{8}O	^{9}F	^{10}Ne
E	A#											A#	D#	D	E	G	B
^{11}Na	^{12}Mg											^{13}Al	^{14}Si	^{15}P	^{16}S	^{17}Cl	^{18}Ar
C	C#	F	G#	A	G	A#	G#	C#	G#	C#	G	D#	B	C#	C#	E	G#
^{19}K	^{20}Ca	^{21}Sc	^{22}Ti	^{23}V	^{24}Cr	^{25}Mn	^{26}Fe	^{27}Co	^{28}Ni	^{29}Cu	^{30}Zn	^{31}Ga	^{32}Ge	^{33}As	^{34}Se	^{35}Br	^{36}Kr
C	E	G#	G	G	F#	F#	A	G#	G	C	F	E	A#	C#	B	D#	D
^{37}Rb	^{38}Sr	^{39}Y	^{40}Zr	^{41}Nb	^{42}Mo	^{43}Tc	^{44}Ru	^{45}Rh	^{46}Pd	^{47}Ag	^{48}Cd	^{49}In	^{50}Sn	^{51}Sb	^{52}Te	^{53}I	^{54}Xe
G#	D#	*Lanth*	F#	G#	G#	A#	A#	A#	A#	E	E	C#	G#	G#	G	F	C
^{55}Cs	^{56}Ba	*57-71*	^{72}Hf	^{73}Ta	^{74}W	^{75}Re	^{76}Os	^{77}Ir	^{78}Pt	^{79}Au	^{80}Hg	^{81}Tl	^{82}Pb	^{83}Bi	^{84}Po	^{85}At	^{86}Rn
G#	C	*Actin*															
^{87}Fr	^{88}Ra	*89-103*	^{104}Rf	^{105}Db	^{106}Sg	^{107}Bh	^{108}Hs	^{109}Mt	^{110}Ds	^{111}Rg	^{112}Cn	^{113}Uut	^{114}Fl	^{115}Uup	^{116}Lv	^{117}Uus	^{118}Uuo
			D	D#	C	C	C#	B									
			^{89}Ac	^{90}Th	^{91}Pa	^{92}U	^{93}Np	^{94}Pu	^{95}Am	^{96}Cm	^{97}Bk	^{98}Cf	^{99}Es	^{100}Fm	^{101}Md	^{102}No	^{103}Lr
		A#	B	B	F#	C#	D	F#	D	D	G	G	D#	G	G	F#	
		^{57}La	^{58}Ce	^{59}Pr	^{60}Nd	^{61}Pm	^{62}Sm	^{63}Eu	^{64}Gd	^{65}Tb	^{66}Dy	^{67}Ho	^{68}Er	^{69}Tm	^{70}Yb	^{71}Lu	

Fig. 3. Musical periodic table (modified from Kumbar 2007, Fig. 5[12])

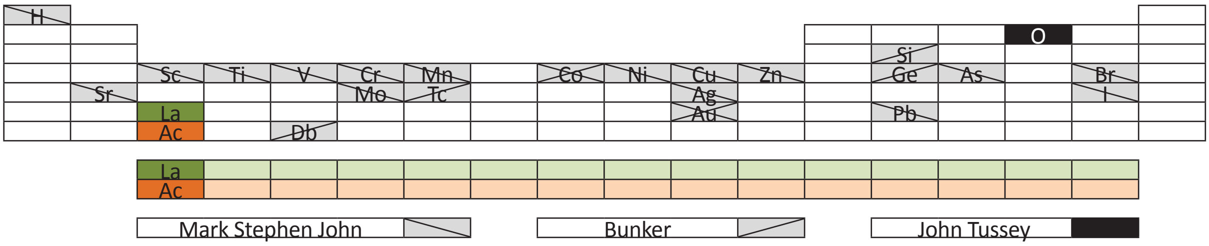


Fig. 5. Elements for which soundscapes have been developed

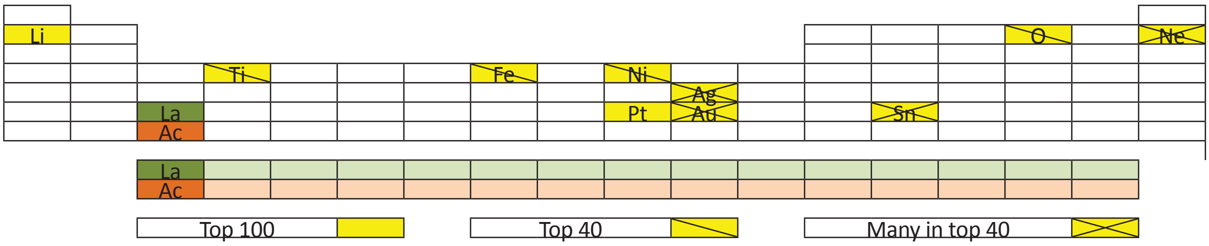


Fig. 6. Chemical elements as the subject of chart-topping pop music, 1960-2005

Fig. 7. The periodic table of musicians. *Left:* Elvis Presley. *Right:* Table under construction; 100 such plaques are currently available, compared with 118 elements in the 'real' periodic table[33]

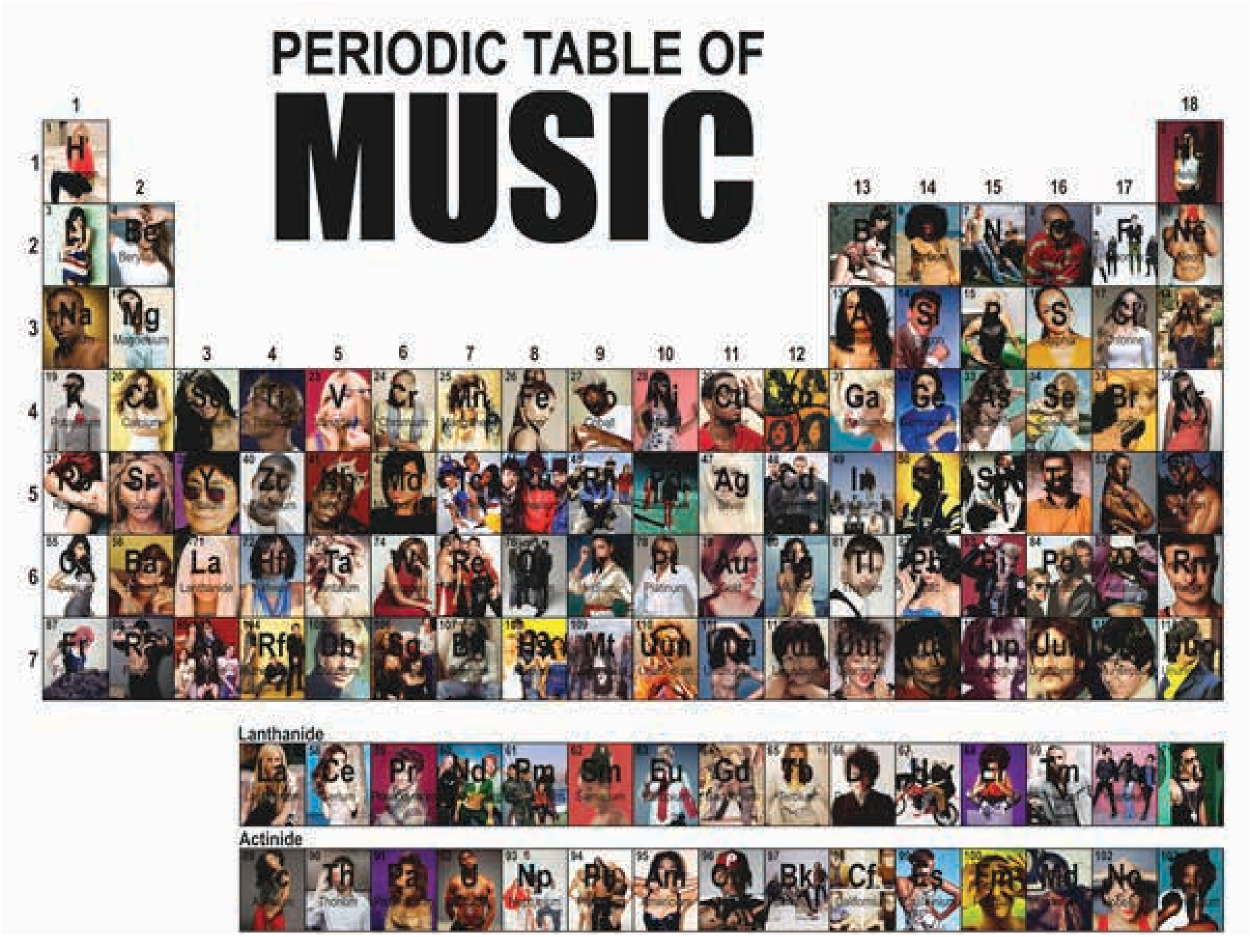


Fig. 8. Recent musicians taking the place of chemical elements in the periodic table[36]

Table 1. Top popular songs for neon, tin, silver and gold, 1960-2005*

Year	Neon (#4)	Tin (#3)	Silver (#2)	Gold (#1)
2005				*Gold Digger*, Kanye West featuring Jamie Foxx [10]
1993				*Fields of Gold*, Sting [11]
1985	*In Neon*, Elton John [1]			
1983				*Gold*, Spandau Ballet[12]
1979				*Gold,* John Stewart [13]
1978				*The Power of Gold*, Dan Fogelberg and Tim Weisberg [14]
1976			*Silver Star,* The Four Seasons [6]	
1975				*Sister Golden Hair*, America [15]
1974		*The Tin Man*, America[3]		*After the Gold Rush*, Prelude [16]
1972				*Heart of Gold*, Neil Young [17]
1971		*One Tin Soldier*, Coven [4]		*Golden Years*, David Bowie [18]
1970		*One Tin Soldier*, The Original Caste [5]	*Silver Bird*, Mark Lindsay [7]	*Band of Gold*, Freda Payne[19]
1967	*Neon Rainbow*, The Box Tops [2]			*Silence is Golden*, The Tremeloes[20]
1966				*Band of Gold*, Mel Carter [21]; *Pandora's Golden Hee-bie Jeebies*, The Association [22]
1965				*Goldfinger*, Shirley Bassey [23]
1963				*Little Band of Gold*, James Gilreath [24]
1962			*Silver Threads and Golden Needles*, The Springfields [8]	*Silver Threads and Golden Needles*, The Springfields [8]
1960			*White Silver Sands*, The Black Bill Combo [9]	*Dutchman's Gold*, Walter Brennan with Billy Vaughn and his Orchestra [25]

*Youtube Links (accessed 27 August 2018; number of views shown below are at that date)

Neon
[1] https://www.youtube.com/watch?v=Pe_4rZwegLc (24, 272 views)
[2] https://www.youtube.com/watch?v=Ga9fd8f0THo (177,103 views)

Tin
[3] https://www.youtube.com/watch?v=7uJL8er_tV0 (7,248,649 views)
[4] https://www.youtube.com/watch?v=7U9UQb80ZcI (345,881 views)
[5] https://www.youtube.com/watch?v=6itauSnrSZA (678,004 views)

Silver
[6] https://www.youtube.com/watch?v=PWoY91zeQ1Y (87,581 views)
[7] https://www.youtube.com/watch?v=xVv0EGiY7k4 (336,738 views)
[8] https://www.youtube.com/watch?v=uz6HB9HYQz4 (201, 884 views)
[9] https://www.youtube.com/watch?v=4VD5cLnDYGU (130,500 views)

Gold
[10] https://www.youtube.com/watch?v=6vwNcNOTVzY (198, 601,340 views)
[11] https://www.youtube.com/watch?v=KLVq0IAzh1A (34,568,326 views)
[12] https://www.youtube.com/watch?v=ntG50eXbBtc (11,464,343 views)
[13] https://www.youtube.com/watch?v=GPjhHcLpfr4 (733,371 views)
[14] https://www.youtube.com/watch?v=8bxiI47Q12s (308,670 views)
[15] https://www.youtube.com/watch?v=XIycEe59Auc (15,093,940 views)
[16] https://www.youtube.com/watch?v=W2Taxuott5s (528,023 views)
[17] https://www.youtube.com/watch?v=Eh44QPT1mPE (75,965,757 views)
[18] https://www.youtube.com/watch?v=JUuRGRcY9O0 (441,085 views)
[19] https://www.youtube.com/watch?v=DtauQj65_4w (779,034 views)
[20] https://www.youtube.com/watch?v=n03g8nsaBro (8,268,243)
[21] https://www.youtube.com/watch?v=CX4BFKPXrtQ (5,611 views)
[22] https://www.youtube.com/watch?v=SxZoneBoMo4 (650 views)
[23] https://www.youtube.com/watch?v=51Wg6k9cWhM (3,116,418 views)
[24] https://www.youtube.com/watch?v=JuGBZf2nir4 (93,884 views)
[25] https://www.youtube.com/watch?v=6Ej5SuiGnlo (2,195 views)

> are required to correctly describe the transport. As the modes are analyzed, certain classifications emerge and some of the most important modes are localized at the interface and can exhibit large conductance contributions that cannot be explained by the current physical picture based on transmission probability.” [20]

The elements in human music

Of course, the chemical elements themselves can be the subject of music and songs, some historical examples of which are given in Reverter (2007),[21] although mostly the ‘elements’ referred to are the four Greek ones: earth, air, fire and water;[22] or the five Chinese ones: earth, air, fire, wood and metal.[23] Of particular interest in Reverter’s compilation is the Nobel Symphony composed by American composer Steve Heitzeg, a work commissioned by Gustavaus Adolphus College to commemorate the centennial of the Nobel Prizes in 2001.[24] The fifth movement, dedicated to the chemistry prize, is titled “Chemistry: Anthem and Elements” and comprises a hymn and variations which feature Linus Pauling, the Curies, the element tungsten, and the isotope carbon-14.[25]

Many former chemistry students will be aware of the song of the Periodic Table developed by Tom Lehrer,[26] which recites the elements up to atomic number 102 in an order that fits the meter of the song of which it is a parody: the Major-General’s Song from Gilbert and Sullivan’s *The Pirates of Penzance*.[27] The song has been updated in 2018[28] in order to include the recent discovery of element 118 Oganesson (Og).[29] (Incidentally, Oganesson has a New Zealand connection in that Peter Schwerdtfeger from Massey University has been involved in computing its electronic structure.[30]) Other songs that explore the elements have also appeared from time to time,[31] and individual chemical elements have featured in popular music. As at 2013, and shown in Fig. 6:

> “… there have been ten elements that have had at least one song bearing its exact name place in the top 100 since the chart’s introduction in 1958; in alphabetical order – gold, iron, lithium, neon, nickel, oxygen, platinum, silver, tin and titanium. Of those ten, eight have made the top-40 (everything except for platinum and lithium), and four have had multiple top-40 hits.” [32]

These songs and their popularity (as Youtube views) are listed in Table 1; the most popular are the 2005 rap-composition *Gold Digger* by Kanye West (~200 million views) and the 1972 hit-song *Heart of Gold* by Neil Young (>75 million views).

Appropriation of the periodic table

Musicians – rather than their music – also feature in wall charts that mimic the periodic table. One example of this appropriation of science by art is the ‘Periodic Table of Musicians – a Wall of Music’, where the names of individual artists are used on plaques which can then be assembled into the form of a table (Fig. 7).[33]

A heavy rock pictorial version of this type of appropriation is also available, in which “Instead of hydrogen to helium, here you'll find Smashing Pumpkins to Spinal Tap – 118 artists that have defined this music genre arranged following the logical ordering of The Periodic Table of Elements”, observing that “many of these elements are as unstable as their chemical counterparts.”[34] Similarly, in a “periodic table of jazz” the chemical elements are replaced by instruments and composers;[35] and there is a table that simply overlays the symbols of the elements with images of those involved in pop music (Fig. 8).[36]

Conclusion

This paper has shown that music may have played a part in Mendeleev’s design of the periodic table. Its potential periodicity attracted the interest of Newlands and its actual periodicity attracted the interest of Kumbar, both seeking in their different ways to make an analogy with music. The variation of electronic structure along rows and down columns of the table has provided a link via spectroscopy to the natural vibrations and energy levels of atoms, which in turn has suggested that the atoms themselves ‘make music’. The table has inspired the composition of music, albeit that in one such song the lyrics are a somewhat banal recitation of element names; and it has been appropriated as an art form for the promotion of music and musicians. Moreover, the periodic table’s components – the chemical elements – have themselves been the inspiration of music and song. The periodic table is thereby more than multidisciplinary chemistry.[37] The linkage of the periodic table to and from the world of music serves as a demonstration that it is linked to human experience and culture more widely. In this way, this paper complements previous work that shows that the ecological development of the table proposed by Scerri[38] bears a strong similarity to the way in which aspects of human life and experience develop and which are well illustrated in fictional plots[39] and in quests specifically.[40]

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Luminescence in metal-organic frameworks: origin and applications

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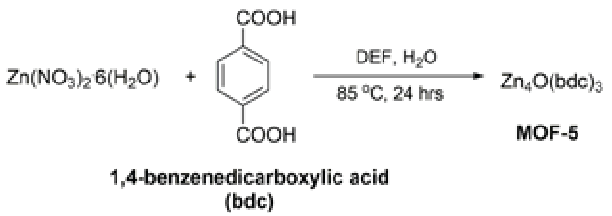
Metal-organic frameworks

The IUPAC defines Metal-Organic Frameworks (MOFs) as 'coordination networks with organic ligands containing potential voids'.[1] To put this in simple words, MOFs are a class of crystalline, porous materials made by using metal ions or clusters attached to organic ligands by multiple coordination bonds. The ligands are also called linkers and the metal clusters are called secondary building units, abbreviated as SBUs. A prototypical example is MOF-5, which is a zinc-based MOF with bdc linkers (Scheme 1). The vast array of linkers and SBUs has paved the way for the explosion of interest in research on MOFs. Applications of MOFs include areas like gas sorption and separation,[2] catalysis of various fundamental organic transformations,[3] studying reaction intermediates,[4] luminescence based sensors[5-8] and removal of heavy metal ions,[9-10] among many others. More focused discussions on MOFs have been published in this magazine over the years.[11-14] This article aims to explain the mechanisms of luminescence, the ways to induce this phenomenon in MOFs along with its various applications.



Scheme 1. The procedure to make the first reported metal-organic framework MOF-5, using zinc nitrate to form the Zn_4O secondary building unit (SBU), and bdc as the organic linker. The method uses DEF (*N*,*N*-diethylformamide) as a solvent.

Luminescence occurs when a substance emits light on the application of energy. This energy can be delivered in the form of photons (fluorescence and phosphorescence), chemical reactions, electricity, ionising radiation, sound, or in some cases even by mechanical stress. When the energy is supplied by incident photons, luminescence occurs due to transitions between a molecule's electronic energy states, as shown by the Jablonski diagram in Fig. 1. The molecule undergoes excitation from a singlet ground state (S_0) to a singlet excited state (S_1). In this S_1 state, the molecule loses energy as heat and relaxes to the lowest vibrational level of S_1 (internal conversion) and finally returns to the ground state (S_0) with the emission of a photon. This process, where all transitions are between singlet states, is called fluorescence. Due to the loss of energy by internal conversion, the emitted photon has a lower energy than the incident photon.

On the other hand, some molecules can change their spin in the excited singlet state (S_1) and undergo intersystem crossing to an excited triplet state (T_1). Further decay from the T_1 back to the singlet ground state (S_0) results in phosphorescence. However, the $T_1 \rightarrow S_0$ transition is 'forbidden' and hence the rate constants for phosphorescence are much lower than those for phosphorescence.[15-16]

Various molecules are known to show fluorescence. Some examples include aromatic molecules like perylene, fluorescein, rhodamine dyes, and complexes of lanthanide ions. Examples of phosphorescent substances include iodine,[15] complexes of noble metals,[17] and brominated BODIPY dyes[18] among others. All these lumines-

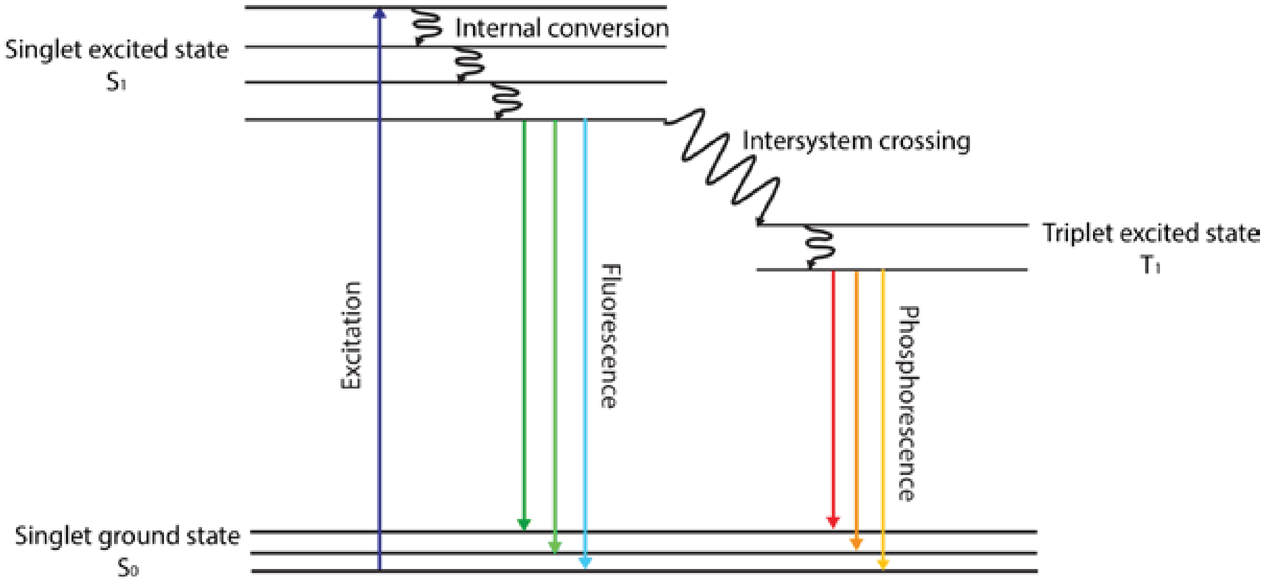


Fig. 1. Jablonski diagram for fluorescence and phosphorescence

cent molecules have been used in applications ranging from probes for detection of chemicals, phosphors in display screens, components of optical instruments, lasers, and cellular imaging.[16, 19]

These moieties can be used as building blocks for MOFs to make the resulting MOF luminescent. This offers distinct advantages: (1) the synthesis of MOFs is straightforward, requiring metal salts and appropriate linkers; (2) the crystalline nature of MOFs arranges luminophores in precise positions making it easier to explain luminescent behaviour; (3) the porosity of MOFs can be used to encapsulate mixtures of photoactive guests to perform photophysical studies - the constituents of the MOF interact with the guest and consequently modify the luminescence making them ideal candidates for chemical sensors[20-21] and (4) the stability of MOFs makes them highly reusable and also easily processable into coatings or membranes.

Mechanisms of MOF luminescence

Fig. 2 shows the approaches that have been explored to make MOFs luminescent. These can be sub-categorised as: (a) using luminescent organic linkers; (b) emission from the secondary building units (SBUs) such as lanthanide clusters; (c) energy and charge transfer processes and (d) encapsulated guest molecules. A description of these approaches follows.

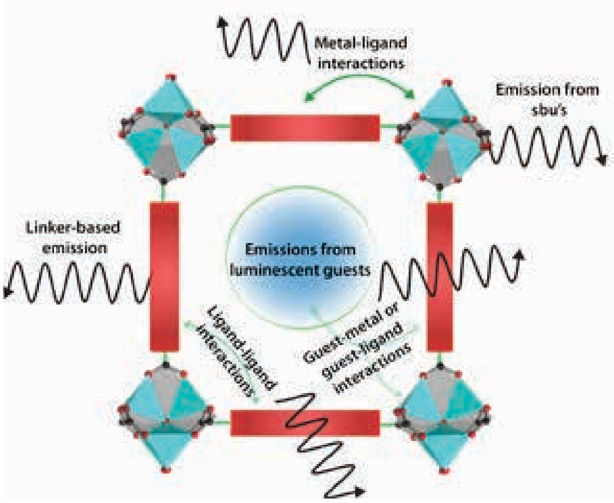


Fig. 2. Diagram showing the possible mechanisms for luminescence in metal-organic frameworks

Using luminescent organic linkers

Organic compounds with strongly conjugated backbones have strong emissions which are possible because of electronic transitions involving their π orbitals. The increased degree of conjugation causes a decrease in the π-π^* energy gap, and thus competing luminescence pathways involving the SBUs become less efficient. It also helps when the metal part of the MOF consists of metals with closed shell configurations e.g. magnesium(II), zinc(II) and cadmium(II). This reduces the probability of charge transfer interactions, making the luminescence completely ligand-centered.[22] However, to coordinate to the metal, the organic compounds need to be functionalised with appropriate coordinating groups such as carboxylic acid, pyrazole or nitrile. Such functionalised fluorophores containing anthracene, stilbene, pyrene and quinoxaline-based backbones have been used to make MOFs and their fluorescence properties have been studied.[23]

Luminescence from SBUs

Ions of lanthanide and actinide elements (f-block elements) are known for their sharp emission bands. These arise from f-f transitions from the inner 4f or 5f orbitals, which are less sensitive to the chemical environment. MOFs made using these ions have been well explored for their luminescence properties. Unfortunately, the luminescence is weak since these f-f transitions are Laporte forbidden. By complexing the lanthanide ion to an appropriate linker, more intense luminescence can be obtained by exploiting the antenna effect,[24] discussed further in the next section.

Energy and charge transfer interactions

The formation of MOFs can place photoactive moieties in close proximity and in favourable orientations. This enables electronic interactions like charge transfer and energy transfer to occur between them resulting in changes in the emission spectrum. Some of these changes are shifts in the emission maximum, reduced intensity, loss of vibronic features, band broadening, and improved emission lifetimes. In MOFs, charge transfer (CT) between ligands and metal is a possibility. Transitions due to CT interactions are both spin and Laporte allowed making them highly intense. Additionally, encapsulated photoluminescent guests can interact with the ligands or SBUs and cause further changes in the emission.[20]

One example is a MOF consisting of copper(I) SBUs with 4-hydroxypyridine-2,6-carboxylate linkers which shows strong blue luminescence bands (398 nm and 478 nm) even though the free ligand glows green (526 nm). This change is caused by metal to ligand charge transfer (MLCT). Another example for a MOF showing MLCT is manganese(II) complexed to benzimidazole-based linkers showing a broad band between 625-850 nm. On the other hand, ligand to metal charge transfer (LMCT) has been observed in zinc(II) and cadmium(II) MOFs. Since these metal ions have filled d orbitals, reducing them via LMCT requires high energy UV light ($\lambda < 350$ nm). A recent computational study has shown that LMCT is possible in cerium(IV) MOFs based on a UiO-66 (a MOF developed by the University of Oslo) topology. By careful functionalisation of the ligand, the LMCT parameters can be further tuned to achieve photoactivated water splitting.[25]

As mentioned previously, lanthanide f-f transitions are weak and are forbidden by the Laporte selection rule, which states that electronic transitions without a change in azimuthal quantum number (Δl) of ±1 are not allowed. For f-f transitions, $\Delta l = 0$, making them Laporte forbidden, resulting in low intensity. The antenna effect can be used to circumvent the low intensity. This effect involves the use of appropriate linkers, which absorb incident photons and directly transfer energy to the lanthanide energy levels, leading to intense luminescence.[26] Oxalic acid, 3-Nitrophthalic acid, 4-pyridinecarboxylic acid, thiophene-derivatised carboxylates are some of the few linkers used to explore the antenna effect.[23]

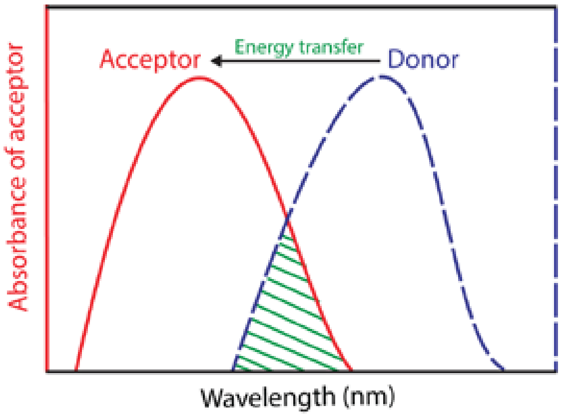


Fig. 3. For efficient energy transfer, the absorption of the acceptor and the emission of the donor must match, resulting in spectral overlap (shown by the shaded area)

The final category within energy transfer interactions are those that happen between the ligands, i.e., ligand to ligand energy transfer. This is possible for MOFs made with different ligands, each having their own unique photophysical properties. For efficient energy transfer, both donor and acceptor molecules should be separated by a distance within 1-10 nm. Their orientation also plays a role, as energy transfer occurs through dipole-dipole interactions. Finally, and most importantly, the emission of the donor must overlap with the absorption band of the acceptor (Figure 3). Determining both the distance and orientation can be quite a challenge when the donor-acceptor pair are in solution or part of a protein. However, in MOFs, both these parameters can be interpreted quite well as the crystal structure of the MOF can be used to study the distances and orientations of the linkers, aiding in precise design and optimisation of a MOF with desirable properties.[20]

Photoactive guests

The porous nature of MOFs can be used to encapsulate photoactive guests and may lead to interesting photophysical behaviour. Fluorescent dyes trapped in MOFs have been used for applications like temperature sensing and white-light emission (described in the following section). Under conditions of high temperature and low pressure, the classic sandwich complex ferrocene has been trapped in a MOF with terbium(III) based SBUs. Changes from the guest-free state include broadened emission indicating interactions between the terbium SBU and ferrocene.[27] Another interesting idea is the trapping of lanthanide ions in non-lanthanide MOFs, which is seen to increase the luminescence efficiency of the lanthanides.

Applications of MOF luminescence

The most common application of MOF luminescence is sensing, which monitors changes in luminescence based on the analyte of interest. The presence of explosives, volatile organic compounds, heavy metals, anions, gases, and vapours are some analytes which are detectable even at low concentrations using MOF luminescence. The analytes change the chemical environment within the MOF, reducing or intensifying the emission behaviour. Interactions between the analytes and the constituents of the MOF include hydrogen bonding, energy transfer, antenna effects, and π-π interactions. One highly sought-after goal with MOFs is white light emission (WLE), as this has tremendous potential for application, especially in display devices. Researchers have used a variety of strategies to achieve WLE, involving mixtures of lanthanides, dyes and in rarer cases by using organic linkers. Other less researched applications are pH measurement, biological sensing, thermometry and second harmonic generation but nonetheless MOFs have fared well in all these areas.

Anion and cation sensing

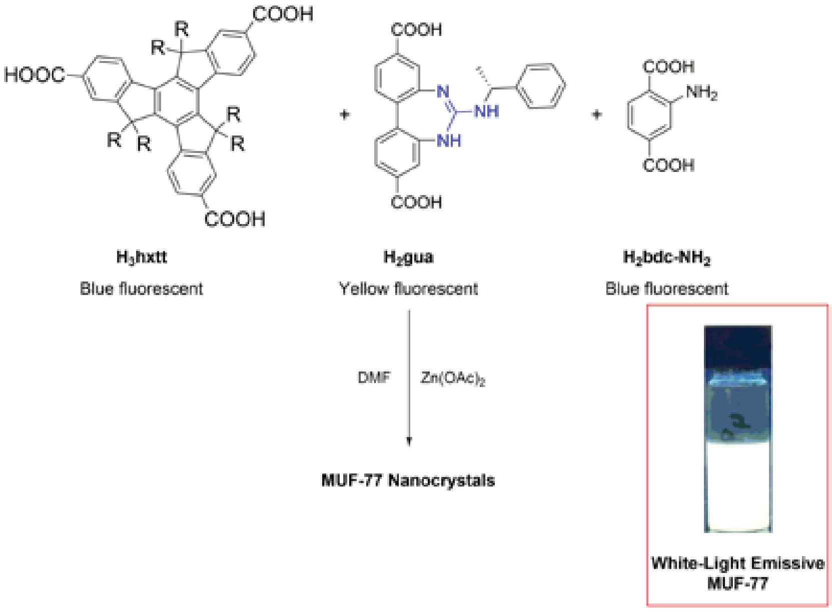
The predominant mechanism for anion and cation sensing is the perturbance of energy transfer. Using energy transfer becomes advantageous as this phenomenon is dependent on the interplay of a plethora of factors. Perturbing any of these factors can affect luminescence, which in turn can be used for sensing. An example is the copper MOF reported by Zhao *et. al.* comprising bipyridine based linkers and sensitive to iodide anions.[28] The I^- ions are oxidised by the MOF struts to I_3^- which in turn block the LMCT between the bipyridine and copper SBU, resulting in quenching of fluorescence *i.e.* in 'turn-off' behaviour. A europium MOF with benzophenone tetracarboxylate linkers was synthesised as a film, which was able to detect carbonate anions. The adsorption of carbonate is antagonistic to LMCT transitions, leading to luminescence quenching.[29]

Approaches for sensing cations are also based on similar ideas. The binding of copper(II) and cobalt(II) to pyridine-3,5-dicarboxylate linkers in a europium MOF showed quenching behaviour. This has been attributed to impedance of the antenna effect by the pyridine linkers. In another instance, a tenfold decrease in the fluorescence lifetime has proved useful for sensing copper(II) in simulated physiological systems using the MOF $Eu_2(FMA)_2(OX)(H_2O)_{4(}$where FMA = fumarate and OX = oxalate).[30] There are many other MOFs capable of sensing transition metal ions owing to the paramagnetic nature of the ions which in turn affect fluorescence.[31-32]

WLE

With its applications in display devices and lighting, WLE has been investigated in MOFs, either by using a dichromatic (mixing blue and yellow emissions) or trichromatic (mixing red, green and blue) approach. Gai *et. al.* were able to obtain WLE of a series of MOFs using varying ratios of erbium(III), terbium(III), and dysprosium(III) which have emissions in the red, green, and blue regions respectively.[33] Other trichromatic ideas have included the encapsulation of mixtures of emissive dyes[34] and noble metal complexes of iridium or platinum.[35-36]

Research in the Telfer group at Massey University has shown that WLE is possible with only emission from the organic ligands. Three fluorescent organic ligands emitting in the blue and yellow regions were used to make a zinc MOF belonging to the MUF-77 (Massey University Framework-77) system[37-38] which gave white light on UV excitation (Scheme 2). Further tunability was made possible by systematically attaching different R groups on



Scheme 2. The ligands used for the synthesis of white light emitting MUF-77 developed by the Telfer group at Massey. The guanidine group attached to the H$_2$gua (shown in blue) is capable of hydrogen bonding. A vial containing MUF-77 nanocrystals is also shown, which glows white under UV irradiation.

H$_3$hxtt and incorporating the resulting ligand into MUF-77. An interplay of energy transfer interactions between the ligands was observed which gave a handle to modulate the colour temperature of the WLE. H$_3$hxtt and H$_2$gua linkers were identified as the donors and acceptors respectively. The hydrogen bonding nature of the guanidine group was used for interaction with guest molecules such as benzaldehyde and nitrobenzene to modify the fluorescence.[39]

pH sensing

Even though MOFs are highly stable in organic solvents and sometimes in water, most of them are destroyed under acidic or basic conditions, due to breaking of the coordinate bonds between the ligands and the metal centres. However, examples of acid and base stable MOFs exist, which makes them potentially useful for pH sensing. One example is UiO-66-NH$_2$, a MOF with zirconium SBUs and 2-aminoterephthalate acid linkers. The luminescence intensifies between pH 1-9 because of the deprotonation of ammonium groups to amine. By further converting the amine to a diazo group, the pH sensitive range can be extended between 1-12. Incorporating fluorescein isothiocyanate (FITC) into the linkers of UiO-66 showed varying luminescence in the pH range 4-8. FITC being biocompatible made this MOF applicable for measuring pH changes in living cells.[40]

Conclusions and outlook

MOFs have shown tremendous potential for applications that can directly impact the way we live but their high cost of production make efficient commercialisation quite rare. The same goes for many luminescent MOFs which if mass produced profitably could be ubiquitous owing to their predictable structure-property relationships, stability, and reusability. Nonetheless, commercialisation is quite an active area of research with groups of scientists and engineers working collaboratively to make this a reality.

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Catalytic coordination cages

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Keywords: *cages*, *molecular flask*, *supramolecular catalysis*

Cages and catalysis

Reaction chemistry involving supramolecular cages has expanded significantly since the early examples in the late 20th century.[1-2] The field has rapidly moved from formation and characterisation to more application-based research. The applications of these cages are extensive, ranging from the storage of explosive compounds[3] to the elucidation of reaction mechanisms.[4] A functional application that has gained momentum in recent years is the use of coordination cages for catalysis.

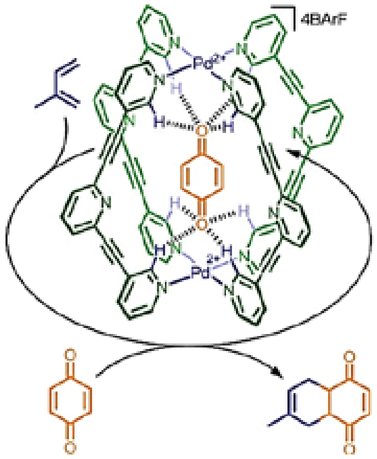

Fig. 1. M_2L_4 catalytic cage catalysis of a Diels-Alder reaction. Adapted with permission from ref 5. Copyright (2018) American Chemical Society.

The advantages of catalysis are clear and numerous, prompting focused research on the development of novel catalytic strategies, some of which draw inspiration from highly effective natural catalysts: enzymes. Supramolecular cages are cavity containing structures that allow for mimicry of enzymatic catalysis principles; amongst these are substrate specificities, the proximity effect and preorganisation. This mimicry raises several unique advantages over the use of traditional catalysts alone.[6]

Supramolecular cages consist of convergent building blocks known as synthons, which self-assemble into a variety of structures, each containing unique microenvironments. These microenvironments have properties that differ significantly to those of either the individual components, or the solvent phase alone. The designable, tunable synthon building blocks are one of the main determinants of cage structure and functionality, and they allow for the strategic adjustment of both internal and external cage properties.[7-8]

This review will focus primarily on self-assembled metallo-organic coordination cages, as opposed to organic capsules or other (continuous) supramolecular assembles such as metal organic frameworks (MOFs) and zeolites (both natural and synthesised).

Advantages of cage catalysis

There are many different structural, electronic and chemical properties of supramolecular cages, each of which have a role to play in their catalytic activities. These properties combine to create the unique advantages observed in cage catalysts. A key focus of these is the impressive selectivities afforded to both substrates catalysed and products formed, although the downside is a reduced substrate diversity. Increases in catalytic efficiency and efficacy also have clear advantages from both economical and environmental viewpoints, offering alternatives to more toxic and expensive catalytic materials, and reducing the consumption of some that cannot be replaced.

This article divides common cage properties into interior and barrier properties, and explores examples and consequences relating to these.

Interior properties

One principle common to all host-guest catalytic cages, is the increase in effective molarity (EM), where guest components experience a significantly elevated local concentration once encapsulated within the host cage, causing a proximity effect.[9] This can force interactions and reactions to occur that are otherwise statistically and/or thermodynamically unfavorable, and slow to occur in more dilute 'bulk' solutions.[10]

Cages used in this manner are termed 'molecular flasks' and account for the majority of catalytic cage publications. The steric, electronic, and polarity restrictions within these hosts can pre-organise and restrict encapsulated guests to particular orientations. This not only accelerates reactions, but also significantly alters the molecules' chemo-, regio- and stereo- selectivities. Reaction pathways are influenced and unusual products can be formed that are typically unfavourable and/or not observed in bulk solvent reactions or with traditional catalysts. An interesting recent example of this involved the "Artificial Diels-Alderase" illustrated in Fig. 1. With this simple M_2L_4 capsule, some of the (significantly accelerated) Diels-Alder reactions experienced nearly complete reversal of substrate chemoselectivity while others saw changing ratios of product regioisomers, favouring formation of typically less favoured structures.[5]

Cage microenvironments can also shift pathway favourability by stabilising otherwise unfavourably high energy transition states (TSs).[11-12] In a dramatic example published by Raymond, Bergman and co-workers,[12] this stabilisation contributed to the cage system that achieved acceleration of 1,4-pentadien-3-ol Nazarov cyclisation of more than two million fold. TS stabilisation is also a key factor in the aforementioned M_2L_4 Diels-Alder catalytic cage.[5]

Facilitation of multicatalyst reactions is a challenge yet to be fully overcome with the high specificity of cage interiors, where altering geometries and multiple components can make these difficult to catalyse. There is, however, an opportunity in this challenge: non-enzymatic chemistry that involves multi-catalyst reactions usually requires individual purifications and workups, so there is much scope for increasing the efficiency.[6]

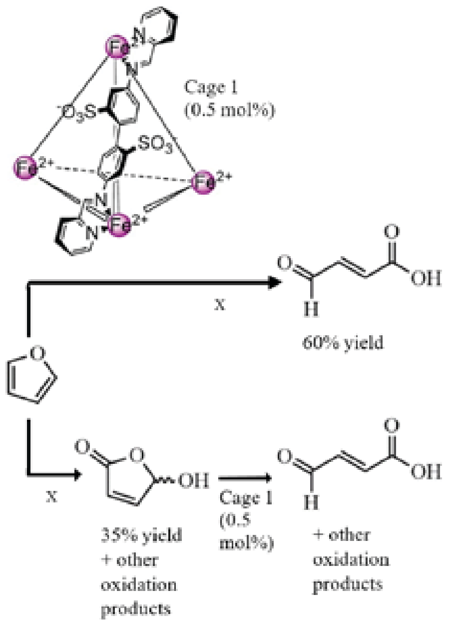

Fig. 2. Furan oxidation to fumaraldehyde in the presence and absence of Cage 1. X = X= O_2, methylene blue (3.5 mol%), D_2O, pD 4, hv, 25°C. Adapted with permission from ref 14. Copyright (2013) American Chemical Society.

The Nitschke group are among researchers that have explored this, effectively using a coordination cage in the multistep oxidation of small molecules.[6, 13] In the presence of their cage (Fig. 2) in a one pot reaction, furan was oxidised to fumaraldehyde with a significantly increased rate and yield, and a reduced number of side products. Time consuming purification of intermediates was also avoided.[14]

Cages can also act as co-catalysts by stabilising traditional catalysts that are prone to degradation, imparting structural stability to improve their catalytic lifetimes.[15] This host-guest effect comes with a second advantage – the sensitive components are isolated and protected from undesirable outside interactions.

Barrier and framework structural properties

The properties involved in cage catalysis are far from limited to the interior of the cages, with barrier and 'wall' effects significantly contributing to their catalytic activities.

In addition to microenvironment restrictions, cage hosts also impart reaction specificity (and reduce side product formation) through selective guest encapsulation, controlling which compounds gain passage into the interior, e.g. uptake of more hydrophobic molecules through to the similarly hydrophobic interior of water soluble cages.[16] Toste *et al.* used this barrier control in the second stage of a one-pot reaction, where catalytic turnover is typically inhibited by solution components, however increased conversion rates were achieved by separating the Au(I) catalyst within a M_4L_6 cage.[13]

In addition to using cage frameworks as barriers, recent research has begun to explore the incorporation of catalytically active sites into the frameworks themselves. Some of the latest examples of this include the series of mixed metal coordination cages designed by Cui *et al.*,[17] which contain metal-salen species capable of asymmetric catalysis. One of these cages, featuring both Cr and Mn salen active sites (Fig. 3), displayed impressive enantiomeric excesses of up to 99.9% with sequential epoxidation and ring opening reactions; this is increased, with reduced catalyst loading, over the use of individual cage components in solution.

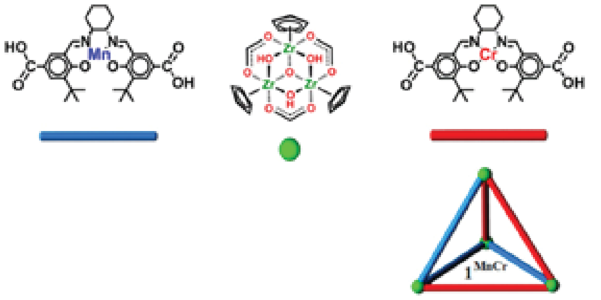

Fig. 3. Schematic representation of a catalytic Cr Mn Salen cage. Adapted with permission from ref 17. Copyright (2013) American Chemical Society.

A high turnover rate, vital to effective catalysts, is a major obstacle that arises with the enclosed nature of many cage designs, with product inhibition interfering with the cycle.[5,18] In most examples, catalytic turnover is driven by the altered molecular properties of the products, resulting in them having a poorer affinity for the restrictive cage interior and being expelled.[18] Many cages that effectively facilitate unusual product formation, such as the molecular flask shown in Fig. 4,[19] cannot be classed as true catalysts[18] as they require external stimuli to promote product release, such as changes in pH, solvent or compound ratios, which results in reversible disassembly.[20]

Other challenges arise in rationally designing cages for specific reactions, and in synthesising large cages. Coordination chemistry self-assembly processes provide ways

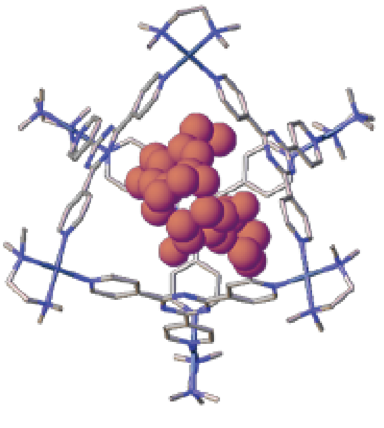

Fig. 4. Molecular flask facilitation, lacking turnover, of an unusual Diels-Alder cycloaddition.[19] Image produced from CCDC file deposition number 747422.

around these, with the lability and wealth of knowledge of metal-ligand interactions allowing for thermodynamic rearrangement and the construction of increasingly complex structures.[11]

Accompanying this approach are possible limitations in component scope, in that coordinating metal species must be sufficiently kinetically labile to allow for rearrangements to energy minima. Construction strategies to solve this have arisen in the form of fragment-based approaches, such as that presented by Metherall and Ward.[21] They used kinetically inert components (e.g. containing Ru) combined with more labile ions to create heterometallic cages. This approach provides an interesting avenue for increasing structural diversity.

The future of cages in catalysis

The use of self-assembled cages in catalytic processes has come a long way since its inception, with novel developments continuously increasing the range of useful applications. Mediated by properties included, but not limited to those described in this review, coordination cages hold their own as an emergent class of catalysts. Several obstacles have arisen in the process, however the proven and potential future advantages of these systems justify the research into strategies to overcome them.

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Defective dicubane review

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Introduction

The defective dicubane molecular topology was first reported in 1989 by Pierpont *et al.*[1] who, whilst exploring the coordination chemistry of *o*-semiquinones, synthesised a tetranuclear Fe(III) complex. A defective dicubane, or more commonly known as a 'butterfly complex', is composed of two face-sharing cubanes, each with an opposite vertex missing,[3] as illustrated in Fig. 1. A butterfly complex consists of two central metal ions known as the 'body' and two outer metal ions, known as the 'wings or wingtips'. This nomenclature allows for easy differentiation between mixed metal and mixed oxidation systems, as the literature has shown that for both systems the same metal and/or oxidation state occupy either both body positions or both wingtips, never one of each.[4] There is a vast range of applications for defective dicubane complexes including: single molecule magnets, photoluminescence, and catalysis. This review article will focus on the design and synthesis of this specific topology, with close examination of a few examples.

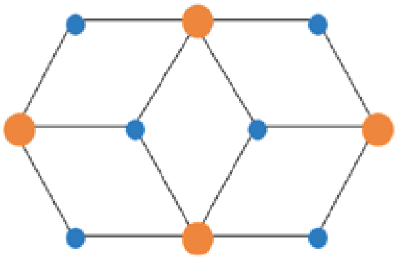

Fig. 1. Schematic diagram of the defective dicubane topology. Large circles represent metal ions, smaller circles represent bridging groups.

Design

When designing a ligand for use in a coordination cluster, the most important factor to consider is the choice of metal(s) being used. This is because different metals require different binding site compositions; transition metals (3*d*) require smaller binding sites with donor atoms of nitrogen and/or oxygen,[5] whereas lanthanides (4*f*) require larger binding sites with oxygen donor atoms.[6] When designing defective dicubanes not only are the ligand-metal interactions important, but additional co-ligands, metal anions, and the reaction solvent used also need to be considered as they can all end up in the final structure, most commonly as bridges between metal ions.

Key requirements for the ligand include multiple binding sites of varied size, donor atoms consisting primarily of oxygen and nitrogen, and elements of structural flexibility or rigidity. When designing a heterometallic complex, the ligand and binding site composition becomes very important in relation to the positioning of metal ions in either the body or wingtips.

There are many different approaches to ligand design found throughout the literature. Some researchers design small flexible ligands capable of coordinating one type of metal and include co-ligands that can coordinate the other set of metal ions. This method was adopted by Powell *et al.*[7] in the design and synthesis of a heterometallic 3*d*/4*f* complex. They used the ligand H_2bdea (*N,N*-Bis(2-hydroxyethyl)butylamine) to coordinate the 3*d* ions in the wingtips and pivalic acid to coordinate the 4*f* ions in the body (Fig. 2.). By using a flexible ligand such as H_2bdea, in addition to coordinating the 3*d* ions, the ligand could also provide bridges between metal ions. Another approach to ligand design is a ligand which has multiple binding sites that can coordinate metal ions in both the body and wingtips. This approach was used by Liu *et al.*[2] who designed a double-headed vanillin derivative (*N,N'*-bis(3-methoxysalicylidene)-1,3-diamino-2-propanol) (shown in Fig. 2.) to coordinate Ni(II) ions in the body and wingtips.

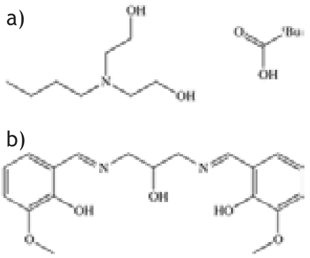

Fig. 2. The ligand and co-ligand utilised by Powell *et al.*[6] is shown in a) H_2bdea (left), pivalic acid (right); the ligand utilised by *Liu et al.*[7] is shown in b) (*N,N'*-bis(3-methoxysalicylidene)-1,3-diamino-2-propanol.

In addition to ligand and co-ligand consideration, the metal anions and solvent/s used in synthesis need to be carefully chosen, as they can form bridges or occupy coordination sites. Methanol is a common solvent chosen for synthesis as it is capable of forming $\mu_{1,2,3}$ methoxide bridges, with the most common being a μ_3 bridge between body metal ions. Popular anions used are chloride, acetate, and nitrate as they are capable of both filling vacant coordination sites and bridging metal ions. An example of anion bridging is shown by Hänninen *et.al.*[8] who formed a tetranuclear Co(II) complex with μ_3 chloride bridges, simply by using a $CoCl_2$ salt and non-coordinating solvent.

Synthesis

When synthesising any metal complex there is always an element of spontaneity and this is particularly true in defective dicubane syntheses. Commonly, synthetic methods entail one-pot syntheses, adding everything together and stirring for a period of time; however, some researchers such as Boskovic *et al.*[9] and Powell *et al.*[7] employ stepwise syntheses to produce defective dicubanes. One method involves taking an existing metal complex, generally with cubane or triangular topology, and adding an excess of co-ligand and base, followed by stirring either at room temperature or with heat.[9] Another method, generally employed for heterometallic structures where 4*f* ions are found in the body positions, is to initially react the ligand with one of the metals, then after a period of time add the second metal and generally a quantity of base and/or co-ligand and react further.[4b]

Magnetism

Magnetism is one of the most common properties of a defective dicubane that is explored by researchers. The origin of magnetism in a complex arises from the selected metal ion(s) and their associated anisotropy. It has been shown that the overall magnetism can be enhanced through exchange pathways present in a defective dicubane.[10]

Exchange interactions

An exchange interaction in a complex is an interaction between two metal centres, originating from the overlap of their two partially occupied atomic orbitals. Superexchange pathways on the other hand, are the result of the overlap of partially occupied atomic orbitals of a metal centre and molecular orbitals of an intermediate ligand.[11] Superexchange pathways are a key feature of the defective dicubane topology, as within a typical defective dicubane there are several exchange interactions. The most common exchange interactions as depicted in Fig. 3 are labelled: J_1, J_2 and J_3. Due to the large distance between the wingtips, the J_4 exchange interaction (the interaction between both metal ions labelled '2') is negligible and does not contribute to the overall coupling. This property is appealing to researchers as the different exchange pathways can be altered to varying degrees by simply changing the metal(s), co-ligand, or solvents used.[7, 12]

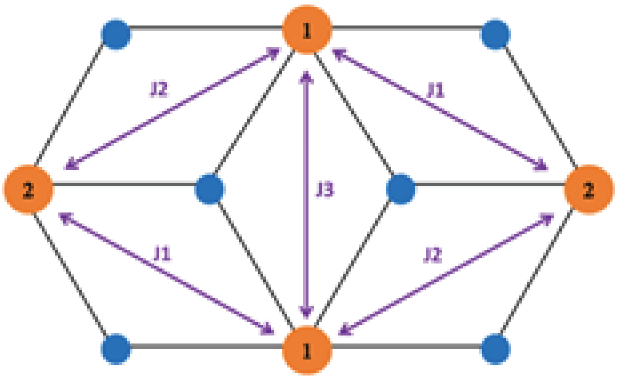

Fig. 3. Exchange interactions found within a typical defective dicubane. Large circles represent metal ions, with 1 and 2 representing different metals or different oxidation states; smaller circles represent bridging groups.

The effect of different bridging groups was explored by the research group of Liu *et al.*,[2] who produced two tetranuclear Ni(II) defective dicubanes differing only by the bridging groups between the two body ions as shown in Fig. 4. Structure one has azide groups, whereas structure two has methoxide ions bridging. The difference in the exchange couplings between the structures indicate that the bridging groups have an effect not only on the direct exchange pathway, but also other pathways found in the structure. Structure one has the greatest ferromagnetic coupling for the body/body coupling, however the body/wingtip coupling is weaker. The opposite is found for structure two, as the body/body coupling is weaker than found for the azide structure, but the body/wingtip coupling is greater indicating the methoxide bridging group enhances the coupling of adjacent Ni(II) ions, making that coupling the most effective exchange pathway.

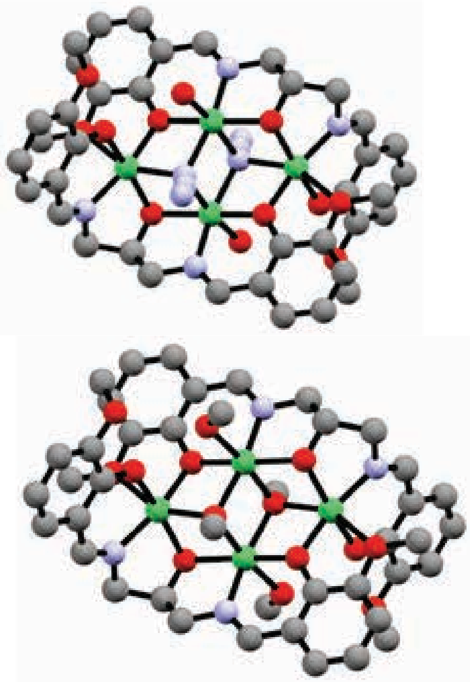

Fig. 4. Tetranuclear Ni(II) defective dicubanes produced by Liu *et al.*; Structure one containing azide bridges (top), Structure two containing methoxide bridges (bottom). Green: Nickel(II), red: Oxygen, blue: Nitrogen, grey: carbon; hydrogens omitted for clarity. Image produced from CCDC 1409533 & 1408299.[7]

Single molecule magnets (SMMs)

Magnetic properties are commonly observed in defective dicubanes, thus their potential application in the field of single molecule magnets (SMMs) is often explored. A SMM is a coordination complex that produces magnetism derived purely from molecular based hysteresis. This is the result of large ground spin states and magnetic anisotropy of the complex, which can result in the slow relaxation of magnetisation.[13] First reported by Novak *et al.*[14] in 1993, popularity in the field has increased rapidly due to their many potential applications, such as information storage and spintronic devices.[15] Many examples of SMMs can be found throughout the literature but until recently the main problem limiting their commercial use was the temperature above which they can no longer retain magnetisation for an unlimited period (blocking temperature). For a SMM to be commercially functionable, the blocking temperature needs to exceed 77 K (the temperature of liquid nitrogen); as of October 2018, this has been achieved with a new record blocking temperature of 80 K[16] surpassing the previous record of 60 K.[17] The cause for low blocking temperatures had been due to fast relaxation of magnetism, most commonly caused by quantum tunnelling of magnetisation (QTM).[18] As shown by the new record blocking temperature, researchers are beginning to discover methods to overcome this.

Throughout the literature SMMs have been reported that contain a defective dicubane topology; this topology rapidly became popular when it was discovered that by enhancing exchange interactions in a complex, QTM effects could be efficiently quenched.[10, 19] Some examples of these defective dicubane SMMs include heterometallic structures such as: Zn(II)/Dy(III)[4c] (Fig. 5) and Co(III)/Dy(III)[4d] complexes with anisotropy barriers of 202.04 cm^{-1} and 168.08 cm^{-1} respectively, and a homometallic Mn(II)/Mn(III) complex with an anisotropy barrier of 102.17 cm^{-1}.[4a]

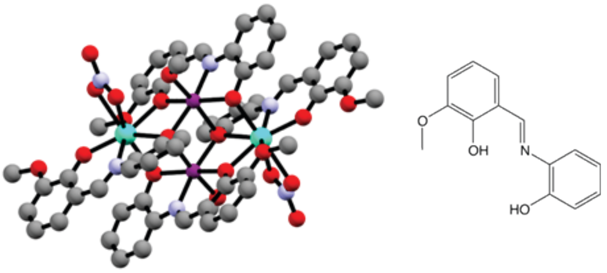

Fig. 5. Zn(II)/Dy(III) SMM with the highest anisotropy barrier (202.04 cm^{-1}) of the defective dicubanes. The ligand utilised was *N*-(2-Hydroxyphenyl)-3-methoxysalicylideneimine (right). Purple: Zinc(II), light green: Dysprosium(III), red: Oxygen, blue: Nitrogen, grey: Carbon. Hydrogen atoms omitted for clarity. Image produced from CCDC 1519272.[3c]

Other applications

In addition to their potential application as SMMs, defective dicubanes have a wide range of other properties that researchers have targeted for application such as DNA cleavage, LEDs, and catalysis. The research groups of Gungor *et al.* and Li *et al.* targeted the photoluminescent properties of their complexes for use in optoelectronics and telecommunication devices respectively.[20]

Catalysis is another area of chemistry that has been explored for the use of defective dicubane complexes; Kostakis *et al.* trialled a series of heterometallic Zn(II)/Ln(III) complexes as catalysts for Michael addition between nitrostyrene compounds and barbituic acid derivatives. Their research illustrated that heterometallic butterfly complexes are ideal candidates for catalysis as the two different metal centres provide two uniquely different active sites; the 3*d* centre coordinates the barbituic acid derivative, while the 4*f* centre coordinates the nitrostyrene substrate. With the two metal centres being in close proximity, it allows for the substrates to be brought close to each other and the transfer of an α-proton can occur, followed by nucleophilic attack. This results in the regeneration of the catalyst and production of the desired michael addition product. The results obtained by Kostakis *et al.* indicated Zn(II)/Y(III) and Zn(II)/Yb(III) complexes were the most effective at catalysing this specific Michael addition, reducing reaction time significantly.[21]

Conclusion

With the increasing popularity of the defective dicubane topology, it has been shown that the design and synthesis of these complexes is key in order to produce complexes capable of a number of vastly different applications.

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Chemistry revisited in Canterbury

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In 2017 the Chemistry Department of the University of Canterbury merged with the Physics Department and moved into its 4th home - the new Rutherford Regional Science and Innovation Centre (RRSIC) on the Ilam campus (Fig. 1), next to the old Rutherford Building which had housed chemistry and physics as separate departments since 1967 (Fig. 2). Prior to that it started life in the Old Tin Shed (Fig. 3) on the original Christchurch city site in 1873 and moved to its second home, a new chemistry building, in 1910 (Fig. 4).

Fig. 1. The new Rutherford Regional Science and Innovation Centre (RRSIC)

Fig. 2. The old Rutherford Building (chemistry far end, physics near end)

After 35 years in the Old Tin Shed, a tender for a new building was let in December 1908 for £8,168, the foundation stone was laid on 4 June 1909 and the building was opened on 23 February 1910. Blue Halswell basalt was the main stone used, with Oamaru limestone for the facings, Hoon Hay basalt for the columns, Timaru basalt for the steps, and patterned blue slate for the roof. Its ground area was 100 x 50 feet and it rose to 60 feet in a central tower. The two lower floors were concrete and the upper floor jarrah. The ground floor had the first year laboratory at the west end and the senior laboratory at the east end. Ground level windows allowed the basement to have natural light. The first floor had a lecture theatre seating 100, a physicochemical laboratory, a preparation room, a professor's room, a demonstrator's room, a collection room, a reading room and a balance room. A large attic was the glass store.

Professor W.P. Evans must have had great foresight and great persuasive powers to get the College Board of Governors in 1908 to invest in a building which would be

Fig. 3. The Old Tin Shed

The Chemistry Department, backing on to Hereford Street, which was the Department's home from 1910 until the move to Ilam in 1966.

Fig. 4. The second home of the Chemistry Department - Old Chemistry

almost adequate to serve the needs of chemistry for 50 years. At the end of the second World War, when student numbers increased enormously, two “temporary buildings” in the South Quadrangle were needed to house advanced teaching laboratories and were subsequently used as research laboratories, and further buildings on the campus were taken over by chemistry before the move to Ilam.

When the “new” building was completed in 1910 it had just two permanent academic staff, Professor Evans and demonstrator Samuel Page. Both Evans and Page retired at the end of 1922 and Henry George Denham was appointed to the Chair. His first act was to appoint John Packer in 1923 with the title lecturer. He succeeded Denham as head of department in 1944. The Chemistry Department became the first department in the College to have three academic staff members with the appointment of H.N. Parton as a lecturer in 1930 followed by R.J.McIlroy in 1941. From 1945 the number of students increased rapidly as did the number of staff, both academic and technical.

Once the move of the University from the city to Ilam was completed, the city campus became the Christchurch Arts Centre, with the chemistry building called Old Chemistry. The earthquakes of September 2010 and February 2011 did enormous damage from which the Arts Centre is slowly recovering. One of the buildings that suffered least damage was Old Chemistry and in 2017 the strengthened building was once again occupied by the University, housing the Department of Classics, the Teece Museum showcasing the Logie Collection of Antiquities and the performance activities of the School of Music. A retired chemist made the suggestion that as the Arts Centre was retaining the name “Old Chemistry” for the building, for heritage and historical reasons there should be a permanent reminder in the building of its chemistry past.

This idea was enthusiastically taken up by the Faculty of Arts and a committee was set up to plan the form this reminder should take. It was also decided to mount an exhibition at the Arts Centre’s Pumanawa Gallery highlighting the history of the building and showing some of the equipment used in it prior to the move to Ilam in 1967. These pieces of equipment once reflected up-to-date technologies. Displaying a selection of old instruments created the opportunity for four current chemistry students to research the history and uses of this old equipment, write labels for the exhibition and learn valuable skills in the important area of scientific communication. The three retired chemists on the committee had a wonderful lesson on the art of curating an exhibition from the other two authors of this paper.

Figs. 5–9 show some of the exhibition including photographs of the five Heads of Department up until 1966: A.W. Bickerton, W.P. Evans, H.G. Denham, J. Packer and J. Vaughan.

Fig. 5. Heads of Department

Fig. 7. John Blunt and Robin Mann at the exhibition opening

Fig. 6. Old polarimeter

Fig. 8. View of the exhibition

Fig. 9. Visitors at the exhibition

On the evening of the opening day of the exhibition, invited guests who had been staff in Old Chemistry, relatives of these staff, or members of COGs (Chemistry Old Guys and Gals - retired staff of the recent Chemistry Department) inspected the exhibition and then proceeded to Old Chemistry for a ceremony to unveil the permanent reminder of chemistry's role in the building. This is a beautiful old two-pan balance in its original case on the third floor (which was the glass store when the building originally opened) and a brass plaque. Professor Paul Miller, Deputy Pro-Chancellor Arts, explained the background of exhibition and John Packer, son of Professor J. Packer, likened this ceremony to a Chemistry Department family reunion. Then Sally Page, grand-daughter of Samuel Page who joined the department in 1879 and retired at the end of 1922, unveiled the balance. Figs. 10 – 13 are photographs taken at the ceremony.

Fig. 10. Paul Miller

Fig. 11. John Packer

Fig. 12. Sally Page with Robin Mann unveiling the Balance

Fig. 13 Guests viewing the unveiling ceremony

We wish to acknowledge the University of Canterbury Foundation's enthusiastic support and financial assistance for this project.

A tribute to Brian Halton

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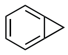
The name Brian Halton is familiar to many NZIC members. Brian has served the Institute in many roles over the years, including as President in 1986 and Editor of *Chemistry in New Zealand* from 2001 to 2011. Brian stepped down as Consulting Editor for *Chemistry in New Zealand* at the end of 2018, ending almost 45 years of continuous service to NZIC. His contributions have been sincerely appreciated and will be missed.

Brian Halton completed his PhD studies at the University of Southampton and carried out postdoctoral work at the University of Florida before moving to his first ongoing academic position at the Victoria University of Wellington in 1968. His choice of independent research program was influenced by prior experiences of the behaviors of strained organic compounds and photochemistry, as well as the resources and facilities available to him in his new home. As such, the chemistry of cyclopropanes, especially those variants wherein the three-membered ring "embraces" two adjacent carbons of an aromatic ring [the parent compound is known as benzocyclopropene (**1**)],[1] became a focal point of his life-long and extraordinarily fertile research programme in organic chemistry. Brian's passionate pursuit of the synthesis of such deceptively simple target compounds and the attendant study of their chemical properties burgeoned into a body of research that is captured in more than 160 journal articles, reviews, book chapters and books. His name is inextricably linked with the chemistry of benzocyclopropenes as well as with cyclopropene chemistry more broadly.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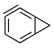
Brian's fastidious, persistent, rigorous and yet flexible pursuit of research rubbed off on all those postgraduate and postdoctoral students who had the good fortune to work with him. He reveled in the unexpected result and the opportunities for new research that they offered. As a consequence of Brian's ever-quick eye for new and fertile topics in chemistry, he developed a multitude of collaborations with people in and well beyond New Zealand. These included notable chemists in North America, Europe and Asia. Many remarkable molecular structures (e.g. **2**-**7**) and processes emerged from these highly productive alliances and were then exploited in various ingenious ways.

In later years, Brian channeled his penchant for incisive research and writing into the chronicling of chemical histories, most especially those of the Wellington region.[2] In a related vein, he was also a most energetic contributor to *Chemistry in New Zealand* and wrote many articles for it including delightful summaries of the research undertaken by recently announced Nobel Laureates in chemistry. Similarly, his autobiography *From Coronation Street to Consummate Chemist*[3] is a compelling read that traces a remarkable life devoted to family, friends and science. It is full of pithy observations about research as well as academic life more generally and is a must read for young organic chemists setting out to make a name for themselves in the inevitably challenging government-funded research environment.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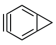
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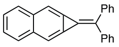

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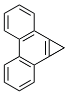
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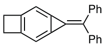

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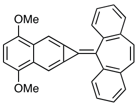

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Brian Halton's truly exceptional contributions to science and academia have been acknowledged in numerous ways including through election to the Fellowships of the New Zealand Institute of Chemistry and Royal Society of New Zealand (in 1977 and 1992 respectively), the award of the NZIC's ICI Prize for Excellence in Chemical Research (in 1980) and of the Shorland Medal of the New Zealand Association of Scientists (in 2002). These most fitting of honours punctuate an extraordinary career filled with scientific brilliance, academic discipline and a true compassion for his fellow travellers.

References

1. Halton, B. *Cycloproparenes*. In: *Strained Hydrocarbons* (H. Dodziuk, Ed), Wiley-VCH, Weinheim, **2009**, 179-193, 201-203.
2. See, for example, Halton, B., *Chemistry at Victoria, The Wellington University*, **2012** [ISBN 978-0-475-12396-1 (digital edition)].
3. Halton, B. *From Coronation Street to a Consummate Chemist*, **2011,** https://www.victoria.ac.nz/scps/about/attachments/from-coronation-street-to-a-consummate-chemist.pdf (accessed 20/12/18).

Keith Andrew Hunter PhD, FNZIC, FRSNZ, 1951-2018

New Zealand science has lost one of its true leaders with the passing of Keith Hunter on 24 October 2018. Keith was an outstanding scientist whose contributions to science and scientists were prestigious.

After completing his BSc and MSc degrees at Auckland, Keith won a Rutherford scholarship and chose to research the chemistry of marine colloids under the supervision of Professor Peter Liss (FRS) at the University of East Anglia. It was while he was there that the Climate Research Unit was established. The interaction with these scientists had a great impact on Keith and sparked his career in researching the ocean's role in our climate system and responses to climate change.

Keith returned to New Zealand to take up a lectureship at Otago University in 1979 where he established the first trace metal cleanroom for measuring ultra low levels of elements in environmental samples. He pioneered studies of the marine biogeochemistry of biologically active trace metals. This research focused on the role of iron in controlling phytoplankton growth in the Southern Ocean, and on the mechanisms used by phytoplankton to acquire iron under conditions of low availability.

More recently Keith's research focussed on the marine chemistry of carbon dioxide, in particular the air-sea exchange of CO_2 and its effect on ocean acidification. His work included the development of high-precision techniques for the measurement of CO_2 species and pH, particularly sea-going automated methods.

Keith's scientific output was formidable. He co-authored >140 papers including several in Science and Nature, one of which has received more than 1800 citations. Keith contributed to the research community through serving on the editorial teams of several journals including *Environmental Chemistry*, *Environment International*, *Marine Chemistry*, and as co-editor in chief of *Marine & Freshwater Research* for 2 years. Keith was a vital member of numerous national and international panels including co-chair, Scientific Committee on Oceanic Research (SCOR) Working Group *The Biogeochemistry of Iron in the Ocean,* Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP) Working Group 38, *The atmospheric input of chemicals into the ocean*, and the Marsden and PBRF panels, which he also chaired.

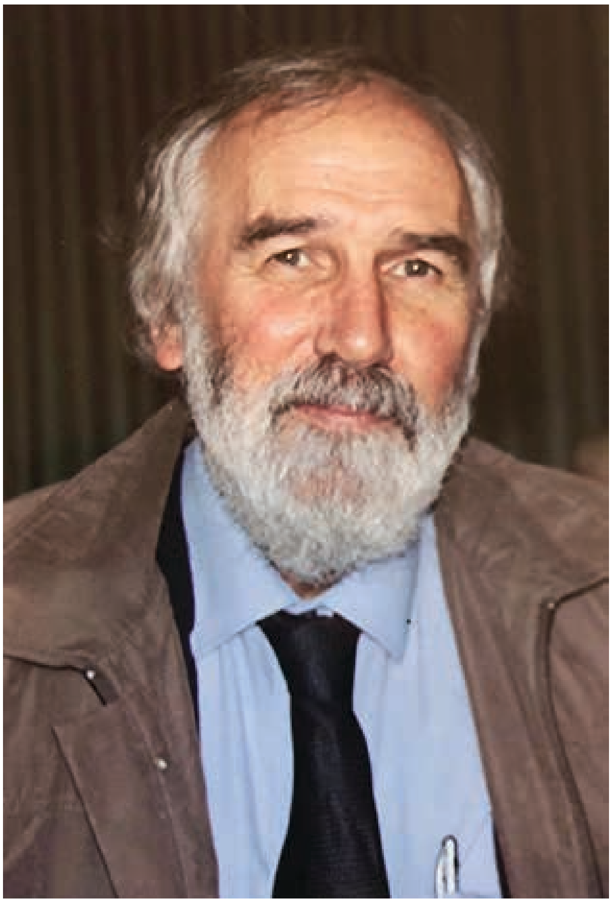
Keith's outstanding contributions were recognised through his numerous awards and prizes including the University of Otago Distinguished Research Medal (2007), the Prime Minister's Science Prize (2011, joint winner), the University of Otago Distinguished Research Group Award (2012) and the Marsden Medal (2014). He was elected Fellow of the NZIC in 2006 and served as President 1999-2000. He was elected a Fellow of the Royal Society of New Zealand in 1997.

It is no surprise that Keith was rapidly promoted through to full Professor and was HoD of Chemistry for five years until he took up the position of PVC Sciences (2009) where he served until his retirement. During much of that time, Keith was also a Director at NIWA, where he had a great influence in their strategic planning.

As formidable and phenomenal these metrics are, they only convey one aspect of Keith - his incredible intellect and ability. If you skim through his papers, you quickly realise how interdisciplinary and collaborative his work was. Keith was no doubt a leader, but also a team player. When considering Keith's contribution, it is not just the papers, grants and prizes but the people he helped, guided and mentored. Keith co-supervised 37 PhD and 30 MSc students over his career. In his roles as HoD and then PVC, Keith was renowned for the enthusiastic support he provided, especially for younger staff. Above all, Keith is remembered for his kindness and cheerfulness. It is that contribution to helping students and colleagues that is Keith's lasting legacy. If the worth of a life is measured by the people we influence then Keith Hunter had a life well lived.

Contributed by Russell Frew
Department of Chemistry
University of Otago

Alan George Langdon PhD, FNZIC, 1942 - 2018



Alan was an enthusiastic chemist and scientist who made many contributions to the University of Waikato, as well as to other research institutions and industries in the wider region. His career was marked by a wide range of interests which led to unusually broad achievements in teaching, research and administration. Alan passed away on 1 September 2018 at the age of 75.

A proud Taranaki farming scion, Alan's early chemistry training from Victoria University culminated in a PhD in 1968, supervised by Alex Wilson. This training developed his long-standing interests in surface chemistry and radiochemistry.

After a postdoctoral period at the University of North Carolina, Chapel Hill, Alan returned to New Zealand in 1971 to a lectureship in physical chemistry at the University of Waikato, initiating over forty years of dedicated service. His appointment was in the very early days of science teaching at Waikato so Alan's first task was to establish (in conjunction with Peter Morris) the physical chemistry teaching programme and facilities. Alan was an enthusiastic proponent of classical thermodynamics in his teaching although this was not always appreciated by students – in the era of teaching assessment questionnaires, Alan lamented that no one could expect rave reviews from students in statistical thermodynamic lectures.

Early research was in surface adsorption chemistry, with emphasis on practical applications. This developed into an interest in environmental contaminants in rivers and estuaries. A productive collaboration with other Chemistry Department staff, with the Forest Research Institute (now Scion) and NIWA provided a wealth of useful data in a series of papers reporting the presence of resin acid and chlorinated organic compounds in biologically treated pulp mill effluents discharged into the Waikato and Tarawera Rivers, the persistence of chlordane and other organochlorine compounds in Manukau and Tauranga harbour sediments and the persistence of polyaromatic hydrocarbons (PAHs) in intertidal sand flat sediments adjacent to a populated municipal area.

From there came imaginative developments in water purification processes, which led to novel filtration elements based on readily-available pumice and the production (with PhD student Hilary Nath) of a prototype low-cost, portable electrical water purification apparatus for harvested rainwater and bore water that would be especially applicable in developing territories. As a sideline, Alan's appreciation of fine wines stimulated an interest in the chemistry involved in oenology and some significant research in oak-aging processes and by-product isolation resulted. He was also interested in adsorption of proteins on surfaces, which gave rise to studies on cleansing routines in the dairy industry, and enzyme recovery methods.

In all of his research, Alan was conscious of practical applications which were reflected in many of his publications being technical reports, together with three patents. Through collaborations with industry and other research organisations Alan was very successful in gaining funding for projects that he used to support over 80 MSc and PhD students. These students benefitted from interesting, practical projects that were meticulously supervised by Alan.

Alan was always aware of the importance of linking academic chemistry to the wider world. He became a strong advocate for the University of Waikato's BSc(Tech) degree which involved supervised industry placements to go with the academic papers. This was a very innovative idea at the time, and needed much of Alan's well-known tenacity at times to maintain and develop the programme against some opposition from less imaginative colleagues. An MSc(Tech) was subsequently introduced and these beginnings morphed into a separate Centre for Technology. As its founding Director, Alan provided the academic leadership and a significant proportion of the course development and teaching that enabled the Centre to become a highly efficient teaching and research unit. From these technology developments ultimately came the establishment of the School of Engineering at Waikato, which can be regarded as a direct descendant of Alan's pioneering efforts. Towards the end of his career Alan had a joint appointment between the Chemistry Department and the School of Engineering, and as is often the case in such arrangements he contributed at least a 75% equivalent to each area!

Alan was heavily involved in other aspects of University organisation. He served for a very long time as Radiation Safety Officer (successfully managing several testing "crises" about which the less said the better…..), was sub-Dean of the School of Science, served on many ad hoc committees, was an active member of the Association of University Teachers, and continued as a local Science Fair judge long after his formal retirement in 2012. His contributions were formally recognised by his election as an Honorary Fellow of the University of Waikato following his retirement.

Alan's achievements are all the more remarkable because of the debilitating health issues that he experienced in the second half of his career, but which he never referred to as a handicap.

Alan was a keen supporter of NZIC activities, and was elected a Fellow in 1985.

On one of his sabbatical leaves in 1975, at Imperial College, he met Margaret who became his wife. They had three children Gareth, Owen and Claire, of whom Alan was enormously proud. Alan himself built (literally!) the family home on a small block of land outside Hamilton where he could relive his farming childhood by regularly chasing stock that had breached the fences, and by growing grapes that were converted to his much-feared Chateau Pukeko wines.

Alan will be much missed as a reliable and dedicated colleague, as a conscientious teacher and supervisor of research students, as a convivial host, an entertaining raconteur and good friend. He leaves a permanent scientific legacy through all of his research students now dispersed in the scientific and engineering community with successful careers of their own, and through the technology and engineering programmes at the University of Waikato.

Contributed by Brian Nicholson, Alistair Wilkins, Michael Mucalo & Janis Swan

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Book review: *A Guide to the Elements*

Stwertka, A. *A Guide to the Elements*. Oxford University Press: Oxford, 4th ed. 2018, 263 pp.

Recently I was reading an Australian novel about eucalypts, in which – unexpectedly – the chemist's periodic table was mentioned:

"The attempt to 'humanise' nature has a long and distinguished history. Once a given subject is broken down into parts, each one identified, named and broken into groups – the periodic table, strata of minerals, weight distribution of prizefighters – the whole is given limits and becomes acceptable, or, digestible, almost."[1]

In his introduction to the 4th edition of *A Guide to the Elements*,[2] author Albert Stwertka makes the same point:

"Open a chemistry textbook and the chances are that there will be a periodic table, often in bright colors, printed on the inside cover of the book. Its constant use by chemists emphasizes the central role the periodic table plays in making sense of what otherwise might be a chaotic jumble of facts about the elements and their many molecular combinations."

…. except that Stwertka sees no need for the Australian novelist's "almost". Stwertka's book exudes confidence in and acceptance of the decades – or, in some cases, centuries – of scientific observation and investigation into the chemical elements. His is a positive and positivist view of the development of knowledge about the chemical elements, and of Mendeleev's role in compiling the periodic table. The introductory chapter's ten pages comprise informative sections on Mendeleev's table, 'the nuclear atom', 'isotopes' and the 'modern periodic table', but at this stage of the book the author provides the reader with not even a hint of the uncertainties, the controversies, or the vanities that are the hallmarks of other recent books about the periodic table.[3]

Each element has its own chapter, which is headed by a graphic showing the element's position in the latest version of the periodic table. The element's group is also identified on the first page of the chapter but could have been complemented by identifying groups of elements with similar properties to the element under discussion on the graphic at the head of the page. This would have enabled horizontal relationships to be shown (e.g., transition elements, lanthanides and actinides), and could have included 'knight's move' (e.g. Ag-Au-Hg-Tl) and triads (e.g. Zn-Cd-Hg), even if not going so far as to include some of the more unexpected combinations.[4] This would have enhanced the 'connectedness' between elements, which is not always obvious in the text. In the chapter on potassium, for example, the comment is made that "Potassium was first isolated by Sir Humphry Davy in 1807. As in *many of his previous discoveries* [italics added], Davy used electrolysis as a means of separating elements from their compounds". My interest piqued, the comprehensive index shows that Davy's discoveries included: sodium in 1807 (p. 57); potassium in 1807 (p. 77); boron in 1808 (p. 33); magnesium, calcium and barium in 1808 (p. 60, p.79, p. 150); and chlorine in 1810 (p. 73). The discovery of eight new elements by one man in four years seems sufficiently impressive to warrant a specific mention or cross-references in the text; that this was not done misses potentially valuable opportunities to highlight more of the connections between the elements.

	Atomic number	89	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
	Primary reference – page number	204	224	226	227	229	230	231	232	233	234	235	237	239	241	243	245
		Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
Secondary reference	Ac																
	Rf			●	●												
	Db				●												
	Sg																
	Bh				●		○	●	●								
	Hs				●			●	●				●				
	Mt						○		●								
	Ds						○						●				
	Rg						○		●		●						
	Cn								●				●				
	Nh													●	●		
	Fl														●		
	Mc														●		
	Lv																
	Ts														●		
	Og														●		

Fig. 1. Distribution of cross references in text (●) and images (○) for transactinide elements. There was a greater variety of teams - both collaborative and competitive - in the discovery of these elements than for the transuranic elements (see Fig. 2).

	Atomic number	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
	Primary reference – page number	204	205	207	208	211	212	214	215	216	217	219	220	221	222	223
		Ac	**Th**	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
Secondary reference	Ac															
	Th															
	Pa															
	U	●	●				●									
	Np						●									
	Pu				●		□				●					
	Am							□								
	Cm								■						●	
	Bk									■						
	Cf										■					●
	Es											■	●	●		
	Fm												■			
	Md													■		
	No														■	
	Lr	●														■

Fig.2. Distribution of cross references in text (●) for transuranic elements. Glen T Seaborg, discoverer of elements Pu and Am (□), was also a member of a group of researchers that included Albert Ghiorso and discovered the elements Cm through Lr (■).

H **190**																	He **120**
Li **154**	Be **71**											B **101**	C **310**	N **250**	O **100**	F **111**	Ne **29**
Na **108**	Mg **77**											Al **73**	Si **134**	P **77**	S **111**	Cl **74**	Ar **71**
K **74**	Ca **126**	Sc **44**	Ti **52**	V **45**	Cr **64**	Mn **61**	Fe **94**	Co **45**	Ni **51**	Cu **67**	Zn **72**	Ga **73**	Ge **26**	As **54**	Se **42**	Br **47**	Kr **68**
Rb **24**	Sr **40**	Y **57**	Zr **49**	Nb **47**	Mo **26**	Tc **68**	Ru **21**	Rh **28**	Pd **30**	Ag **102**	Cd **58**	In **37**	Sn **55**	Sb **30**	Te **23**	I **72**	Xe **59**
Cs **68**	Ba **38**	*La **72**	Hf **49**	Ta **60**	W **41**	Re **30**	Os **29**	Ir **26**	Pt **96**	Au **97**	Hg **117**	Tl **51**	Pb **84**	Bi **31**	Po **63**	At **27**	Rn **58**
Fr **14**	Ra **62**	†Ac **28**	Rf **39**	Db **29**	Sg **70**	Bh **20**	Hs **11**	Mt **22**	Ds **31**	Rg **29**	Cn **31**	Nh **46**	Fl **53**	Mc **36**	Lv **38**	Ts **55**	Og **55**

*	Ce **30**	Pr **53**	Nd **53**	Pm **38**	Sm **30**	Eu **30**	Gd **53**	Tb **30**	Dy **26**	Ho **28**	Er **29**	Tm **27**	Yb **31**	Lu **31**
†	Th **47**	Pa **23**	U **85**	Np **25**	Pu **48**	Am **29**	Cm **29**	Bk **29**	Cf **46**	Es **29**	Fm **26**	Md **18**	No **25**	Lr **29**

Fig. 3. Comparison of lengths of entries (as number of lines of text) for elements in Stwertka's *A Guide to the Elements*. Shading indicates those elements for which the descriptions also include at least one image.

In contrast, the more recent discoveries of the transactinide elements are cross-referenced in the text of the chapters (as shown schematically in Fig. 1), and their 'connections' referred to in the introduction and celebrated in the epilogue. Collectively, these chapters provide an insight into the collaboration and competition – both scientific and political – that were involved in the discovery of these elements which, with the passage of time, historians of science will doubtless re-examine and re-interpret.[5] The transuranic elements present a similar

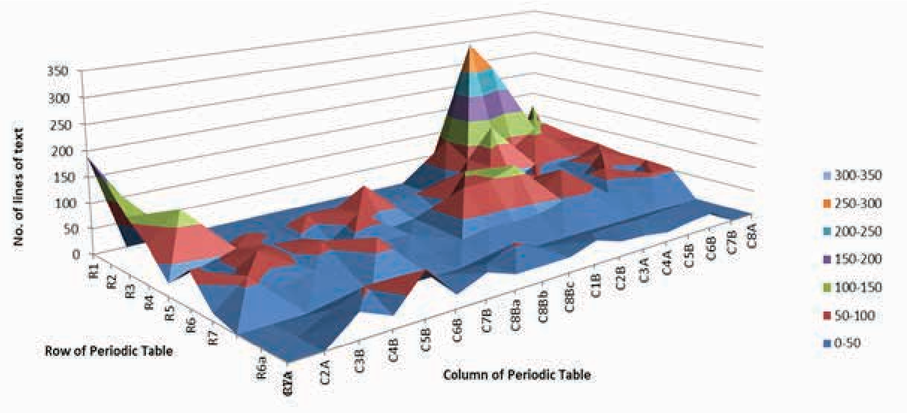
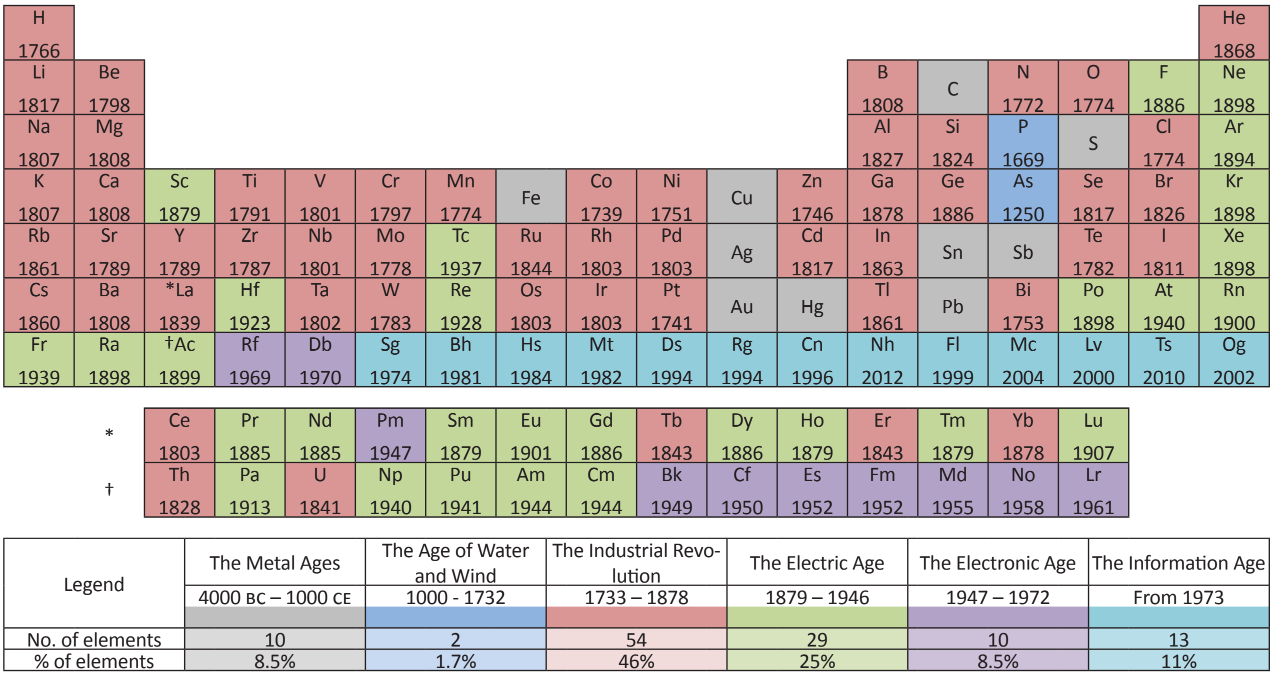


Fig. 4. Distribution of lengths of entries (as number of lines of text) for elements in Stwertka's *Guide*, by row and column of the periodic table.



H 1766																	He 1868
Li 1817	Be 1798											B 1808	C	N 1772	O 1774	F 1886	Ne 1898
Na 1807	Mg 1808											Al 1827	Si 1824	P 1669	S	Cl 1774	Ar 1894
K 1807	Ca 1808	Sc 1879	Ti 1791	V 1801	Cr 1797	Mn 1774	Fe	Co 1739	Ni 1751	Cu	Zn 1746	Ga 1878	Ge 1886	As 1250	Se 1817	Br 1826	Kr 1898
Rb 1861	Sr 1789	Y 1789	Zr 1787	Nb 1801	Mo 1778	Tc 1937	Ru 1844	Rh 1803	Pd 1803	Ag	Cd 1817	In 1863	Sn	Sb	Te 1782	I 1811	Xe 1898
Cs 1860	Ba 1808	*La 1839	Hf 1923	Ta 1802	W 1783	Re 1928	Os 1803	Ir 1803	Pt 1741	Au	Hg	Tl 1861	Pb	Bi 1753	Po 1898	At 1940	Rn 1900
Fr 1939	Ra 1898	†Ac 1899	Rf 1969	Db 1970	Sg 1974	Bh 1981	Hs 1984	Mt 1982	Ds 1994	Rg 1994	Cn 1996	Nh 2012	Fl 1999	Mc 2004	Lv 2000	Ts 2010	Og 2002
	*	Ce 1803	Pr 1885	Nd 1885	Pm 1947	Sm 1879	Eu 1901	Gd 1886	Tb 1843	Dy 1886	Ho 1879	Er 1843	Tm 1879	Yb 1878	Lu 1907		
	†	Th 1828	Pa 1913	U 1841	Np 1940	Pu 1941	Am 1944	Cm 1944	Bk 1949	Cf 1950	Es 1952	Fm 1952	Md 1955	No 1958	Lr 1961		

Legend	The Metal Ages	The Age of Water and Wind	The Industrial Revolution	The Electric Age	The Electronic Age	The Information Age
	4000 BC – 1000 CE	1000 - 1732	1733 – 1878	1879 – 1946	1947 – 1972	From 1973
No. of elements	10	2	54	29	10	13
% of elements	8.5%	1.7%	46%	25%	8.5%	11%

Fig. 5. Dates of discovery of chemical elements related to a chronology of technology.

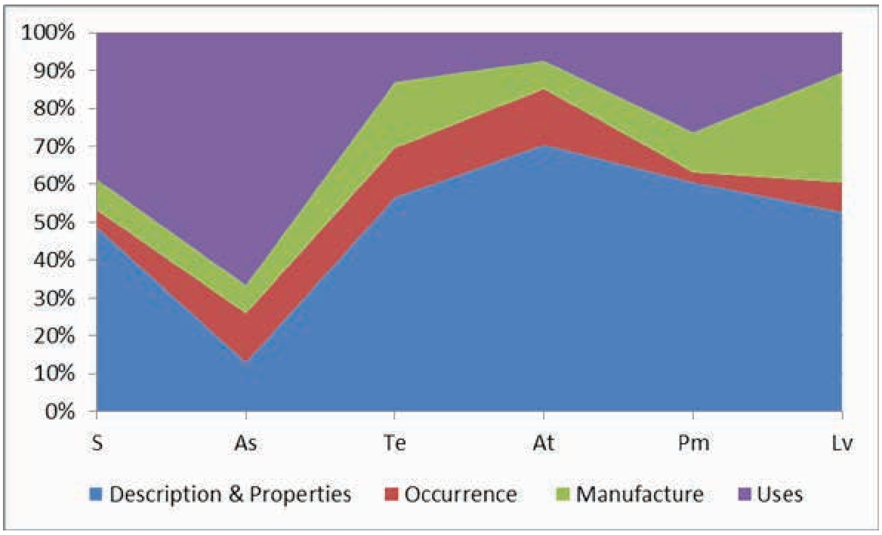


Fig. 6. Distribution of types of information about the element related to its age of discovery. S represents the 'metal ages'; As, 'the age of water and wind'; Te, 'the industrial revolution'; At, 'the electric age'; Pm, 'the electronic age'; Lv, 'the information age'.

Table 1. Comparative content analysis for selected elements

Atomic No.	Element	Scerri's *A Tale of Seven Elements*									Stwertka's *A Guide to the Elements*								
		No. of pages	**Rank**								Rank								No. of lines of text
43	Technetium	28	1	▨													▨	1	68
61	Promethium	20	4	▨	▨	▨	▨								▨	▨	▨	3	38
72	Hafnium	16	5=	▨	▨	▨	▨	▨								▨	▨	2	49
75	Rhenium	16	5=	▨	▨	▨	▨	▨						▨	▨	▨	▨	4	30
85	Astatine	10	6	▨	▨	▨	▨	▨	▨				▨	▨	▨	▨	▨	5	27
87	Francium	21	3	▨	▨	▨					▨	▨	▨	▨	▨	▨	▨	7	14
91	Proactinium	26	2	▨	▨							▨	▨	▨	▨	▨	▨	6	23

opportunity, although in this case the lesser amount of textual 'connection' is compensated by their having a common group of co-discoverers (Fig. 2). For many readers these later chapters of the book may be relatively new material and will be appreciated for their clarity of explanation, including the concept of the "island of stability", unhelpfully prematurely mentioned on p. 16.

The chapters are of variable length (Figs. 3 & 4), their contents reflecting the author's selection of information about the discovery of the element, its natural occurrence, properties, industrial uses, and what makes it interesting in the modern world. As expected, the elements of the first three rows of the periodic table have the longest chapters: the 'top ten' being: carbon (310 lines of text), nitrogen (250), hydrogen (190), lithium (154), silicon (134), helium (120), sulfur and fluorine (both 111), sodium (108) and oxygen (100). In general, the least information is provided for the lower transition series, while the recent discoveries of the later transactinide elements have clearly attracted Stwertka's attention, no doubt because of his research interest in atomic physics (referred to in the biographical note on p. 263).

The *Guid*e includes a chronology of the dates of discovery of the elements. I have used this information in Fig. 5 in a periodic table that shows the distribution of discoveries in terms of a chronology of major technological developments.[6] A selection of elements from these 'ages' suggests that the balance of text between various categories of information varies systematically: description and properties of the element dominating the text about more recently discovered elements, while uses of the elements dominate the text of 'older' elements (Fig. 6). This variety makes the format of the chapters different for each element, which certainly makes the book more readable as a whole. Moreover, most chapters include at least one fact likely to surprise the reader. Most chapters also include images to leaven the text; these are generally related to the element's discoverer(s), its occurrence in nature, or its industrial or commercial use (see Fig. 3).

Of course the ultimate selection of material is not only dependent on what information is available, but the author's own preferences for using it. The idiosyncratic choice of material to include is apparent from Table 1, where the amount of text devoted by Albert Stwertka and Eric Scerri[7] to selected elements in their books is compared. Of the seven elements, both authors provide relatively more information about technetium and rather less about astatine, while francium and protactinium are more interesting to Scerri than they are to Stwertka.

This highly readable *Guide to the Elements* is certainly a guide, and thereby of value to chemists and their students. However, the absence of chemical equations and the limited quantitative data in this book may widen its appeal. In particular, its wealth of historic and technological information may assist social scientists and historians of science in their interpretations and re-interpretations of the periodic table and the history of chemistry. This multiplicity of actual and potential uses will ensure that this book has a place on the shelf of books that inspires my interdisciplinary research; maybe it deserves a place on your bookshelf too.

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References and notes

1. Bail, M. *Eucalyptus.* Melbourne: Text Publishing Co., 1998, pp. 35-36.
2. Previous editions were in 1996, 2002, and 2012.
3. Examples include: Scerri, E. *The Periodic Table: Its Story and its Significance*. Oxford: Oxford University Press, 2007; Scerri, E.; Restrepo, G. (eds.). *Mendeleev to Oganesson: a Multidisciplinary Perspective on the Periodic Table*. Oxford University Press: Oxford, 2018. Stwertka does include a few such books in his list of 'Selected Readings' at the end of the *Guide* on pp. 256-257.
4. Rayner, Rayner-Canham, G. Organising the transition elements. In Scerri and Restrepo, *op. cit*., pp. 195-205.
5. The prospect for a more politically based history of chemistry is discussed in: Rocke, A.J. *Nationalizing Science: Adolphe Wurtz and the Battle for French Chemistry*. MIT Press: Cambridge (Massachusetts) and London (England), 2001, pp.373-419.
6. Bunch, B.; Hellemans, A. *The Timetables of Technology: A Chronology of the Most Important People and Events in the History of Technology*. Simon & Schuster: New York, 1993.
7. Scerri, E. *A Tale of Seven Elements*. Oxford University Press: Oxford, 2013.

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