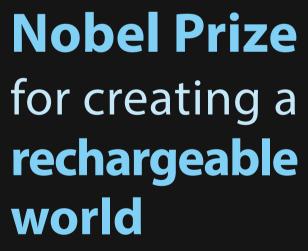
Chemistry November/December 2019 In Australia

November/December 2019



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- Discovering the periodic law of the elements
- Stepping up in the career stakes
- Chemistry reading on a budget







































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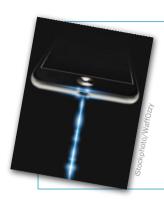


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cover story

Creating a rechargeable world

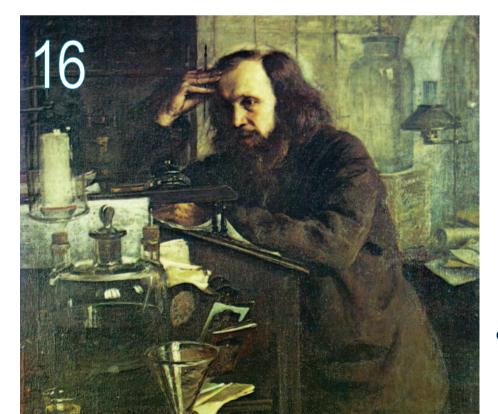
The 2019 Nobel Prize in Chemistry was awarded to John Goodenough, M. Stanley Whittingham and Akira Yoshino 'for the development of lithiumion batteries' such as those used in electric cars and mobile phones. Read more about the science Nobel prizes in this issue.

16 How I discovered the periodic law of the elements. By Dmitri Mendeleev

Dmitri Mendeleev speaks to us, through narrator Alf Larcher, about his life and work as he sought to determine how the properties of chemical elements are related.

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Message from the CEO

Hello RACI members. This is the last *Chemistry in Australia* of 2019 – can you believe it? Where has the year gone?

I think it is safe to say the year has flown by because it has been a very busy year and, I believe, a successful one.

On the financial side, the RACI made a surplus of \$100 000, only the third surplus in the last 15 years. We achieved this through the Divisions putting on some good conferences and also running four of these in house, saving on the professional conference organiser fees. I think we have proved we have the capabilities to manage our own conferences and this is something we must continue doing in future.

On the membership side, member numbers stayed virtually constant year on year after a steady decline over the last 20 years. I don't think we have completely turned the corner yet because our membership age demographic is getting older and there are many members moving into retirement. We are attracting lots of young, new members; the goal has to be to keep them and that means the RACI's offerings being far more relevant to their needs.

So what have we done during the year?

The main goals have been to modernise and standardise the way we do things and to create a method of retaining the corporate knowledge of the organisation. This has been addressed by creating a set of model rules for Branches and their Groups and the Divisions. The idea is to have a standard suite of governance rules for the business units that are based on the constitutional rules for the RACI as a whole, allowing for easy transference of knowledge between the various entities as people move around.

Aligned to this, we are putting together an operational manual template for the Branches and Divisions to document how the various business units operate so there can be no confusion when a new leadership team takes over and corporate knowledge is maintained.

The code of ethics has been modernised to reflect the new social paradigm, and the disciplinary rules are being reviewed to complement this.

In between this, Vicki Gardiner and myself have been involved in the Royal Society of Chemistry's initiative to create a Federation of Commonwealth Chemical Societies (Comm Chem), bringing together more than 50 nations with the goal of networking, sharing knowledge, developing the lesser developed chemical societies and starting new chemical societies in countries that don't have them. The first conference of Comm Chem is being held in the Caribbean in May next year and you have probably seen the call to find three early career chemists to represent the RACI there.

With the closing of the year, it's also the ending of the International Year of the Periodic Table. The RACI has been involved in many events to celebrate this – from running an expo in Melbourne to the stories of the periodic table competition, Periodic Table on Show and our updated 2011 artists' table with the four new elements.

In closing, the Board and national office staff would like to wish all members a safe and enjoyable festive season.

Roger Stapleford (roger.stapleford@raci.org.au) is RACI CEO.



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Chemistry in Australia

Lights out: putting the ambient air oxidation of monolayer WS, to bed

To protect monolayer semiconductor transition metal dichalcogenides (S-TMDs) from oxidation, they must be entirely shielded from light. Even short exposure causes oxidation severe enough to damage electrical contacts and completely destroy optical characteristics.

New research has shown that the oxidation of monolayers of tungsten disulfide (WS₂) in ambient conditions is due to the absorption of visible wavelengths of light.

The new work (doi: 10.1021/acs.nanolett.9b01599) is a collaboration between Monash University, the US Naval Research Laboratory and the University of Autonomous University of Madrid, and informs researchers working in the field to the heretofore unappreciated photo-sensitive nature of these materials, and more importantly, acts as a guide for completely avoiding oxidation in samples exposed to ambient conditions.

While oxidation of monolayer S-TMDs in ambient conditions is already known to occur, the mechanism behind it has not been clear.

The study shows for the first time that the oxidation of the S-TMD WS₂ in ambient conditions requires light of suitable wavelength: oxidation is caused by light energetic enough to cause electronic transitions in the WS₂, i.e. the observed oxidation in ambient conditions is photoinduced. The researchers postulate that this happens by two plausible mechanisms – Förster resonance energy transfer and photocatalysis. Due to the similar chemistry of S-TMDs, it is thought that this same effect should be observable in MoS₂ and other S-TMDs in the same materials family.

Atomically thin transition metal dichalcogenides such as WS₂ have garnered much interest over the past decade due to their extraordinary optical and electrical properties and, thus, possible use in future electronic and optoelectronic devices.

While past studies have found that monolayer S-TMDs may take weeks to visibly oxidise, this work shows that this may happen in as little as 7 days even in ultra-low light conditions.

The researchers studied monolayers of the S-TMD WS₂ grown by chemical vapour deposition. The samples were exposed to controlled amounts of light, and then characterised by optical microscopy, laser scanning confocal microscopy, photoluminescence spectroscopy, and atomic force microscopy.

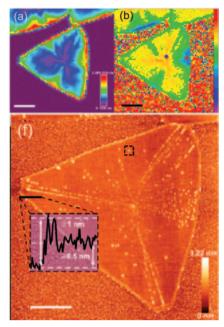
The researchers found that monolayer WS₂ exposed to ambient conditions in the presence of ambient light exhibited damage due to oxidation, which could be detected with laser scanning confocal microscopy and atomic force microscopy, though was not evident in conventional optical microscopy due to poorer contrast and resolution.

The study observed that this oxidation was not random and was correlated with 'high-symmetry', high-intensity edges and red-shifted areas in the photoluminescence spectroscopy map – areas thought to contain a higher concentration of sulfur vacancies.

In contrast, samples kept in darkness showed no signs of oxidation for up to 10 months.

The researchers then performed controlled exposures to very low-irradiance light at different wavelengths for long periods. The low intensity insured that any damage was not due to heating from the light. They found that samples exposed to light with enough photon energy to excite WS₂ showed oxidation, while photon energies below this threshold did not oxidise WS₂. This strong wavelength dependence and apparent lack of irradiance dependence suggests that ambient oxidation of WS₂ is initiated by photon-mediated electronic band transitions, i.e. photo-oxidation.

Monash University School of Physics and Astronomy



Photoluminescence spectroscopy has been a crucial technique for S-TMD characterisation, but, even with standard laser powers, can lead to oxidation. The researchers have been able to correlate regions in the photoluminescence map with oxidised regions in the S-TMD sample. Top: three-fold symmetric, red-shifted, bright crystal edges in monolayer tungsten disulfide (WS $_2$): (a) photoluminescent intensity map and (b) photoluminescent peak position (scale bars = 5 μ m). Bottom: The same crystal after oxidation, showing the oxide following these symmetric patterns (scale bar = 4 μ m).

Clarification

In the September/October issue (pp. 20-23), Dave Sammut explained that the Royal Australian College of General Practitioners (RACGP) has 'come out in favour of pill testing'. Although RACGP President Dr Harry Nespolon has added 'his voice to a growing chorus of calls to implement further pill testing trials at music festivals' (bit.ly/2RpQtWA), RACGP has not published an official position. The Royal Australian College of Physicians (RACP) (bit.ly/2ogNiD6) in an open letter to state premiers and chief ministers in January 2019 said that they 'believe the evidence currently available justifies the introduction of carefully designed pill testing trials in Australia'.

2019 science Nobel prizes

Physics: new perspectives on our place in the universe

The 2019 Nobel Prize in Physics was awarded 'for contributions to our understanding of the evolution of the universe and Earth's place in the cosmos', with one half to James Peebles 'for theoretical discoveries in physical cosmology' and the other half jointly to Michel Mayor and Didier Queloz 'for the discovery of an exoplanet orbiting a solar-type star'.

This year's Nobel Prize in Physics rewards new understanding of the universe's structure and history, and the first discovery of a planet orbiting a solar-type star outside our solar system.

Peebles' insights into physical cosmology have enriched the entire field of research and laid a foundation for the transformation of cosmology over the last 50 years, from speculation to science. His theoretical framework, developed since the mid-1960s, is the basis of our contemporary ideas about the universe.

The Big Bang model describes the universe from its very first moments, almost 14 billion years ago, when it was extremely hot and dense. Since then, the universe has been expanding, becoming larger and colder. Barely 400 000 years after the Big Bang, the universe became transparent and light rays were able to travel through space. Even today, this ancient radiation is all around us and, coded into it, many of the universe's secrets are hiding. Using his theoretical tools and calculations, Peebles was able to interpret these traces from the infancy of the universe and discover new physical processes.

The results showed us a universe in which just 5% of its

Radial Velocity Method

The star and planet orbit their common center of mass.

Spectral lines move towards the red as the star travels away from us.

As the star moves away from us, light waves leaving the star are stretched and move towards the red end of the spectrum.

Planet

Center of Mass

Star

The principle of measuring radial velocity using the Doppler effect. The star and the orbiting planet move around their common centre of mass, causing Doppler shifts due to stellar wobble. Stellar absorption lines that arise when radiation from the interior passes the stellar atmosphere will be red- and blue-shifted depending on whether the star is moving away from or towards Earth. These Doppler shifts give information about the planet's orbital period around the star and also set a lower mass limit. Las Cumbres Observatory

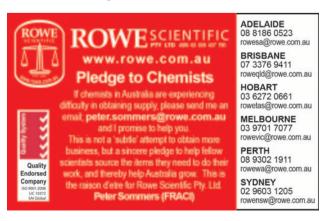
content is known, the matter that constitutes stars, planets, trees – and us. The rest, 95%, is unknown dark matter and dark energy. This is a mystery and a challenge to modern physics.

In October 1995, Mayor and Queloz announced the first discovery of a planet outside our solar system, an exoplanet, orbiting a solar-type star in our home galaxy, the Milky Way. At the Haute-Provence Observatory in southern France, using custom-made instruments, they were able to see planet 51 Pegasi b, a gaseous ball comparable with the solar system's biggest gas giant, Jupiter.

This discovery started a revolution in astronomy and more than 4000 exoplanets have since been found in the Milky Way. Strange new worlds are still being discovered, with an incredible wealth of sizes, forms and orbits. They challenge our preconceived ideas about planetary systems and are forcing scientists to revise their theories of the physical processes behind the origins of planets. With numerous projects planned to start searching for exoplanets, we may eventually find an answer to the eternal question of whether other life is out there.

This year's laureates have transformed our ideas about the cosmos. While Peebles' theoretical discoveries contributed to our understanding of how the universe evolved after the Big Bang, Mayor and Queloz explored our cosmic neighbourhoods on the hunt for unknown planets. Their discoveries have forever changed our conceptions of the world.

This year's Nobel Prize in Physics rewards new understanding of the universe's structure and history, and the first discovery of a planet orbiting a solar-type star outside our solar system.



Physiology or Medicine: sensing oxygen levels

The 2019 Nobel Prize in Physiology or Medicine was awarded jointly to William G. Kaelin Jr, Sir Peter J. Ratcliffe and Gregg L. Semenza 'for their discoveries of how cells sense and adapt to oxygen availability'. They identified molecular machinery that regulates the activity of genes in response to varying levels of oxygen.

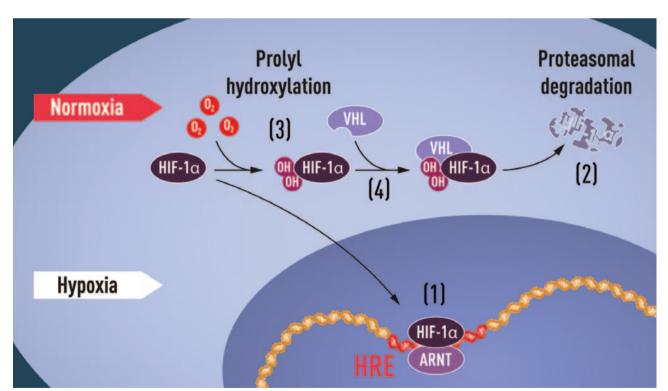
The seminal discoveries by this year's Nobel laureates revealed the mechanism for one of life's most essential adaptive processes. They established the basis for our understanding of how oxygen levels affect cellular metabolism and physiological function. Their discoveries have also paved the way for promising new strategies to fight anaemia, cancer and many other diseases.

During evolution, mechanisms developed to ensure a sufficient supply of oxygen to tissues and cells. The carotid body, adjacent to large blood vessels on both sides of the neck, contains specialised cells that sense the blood's oxygen levels. In addition to the carotid body-controlled rapid adaptation to low oxygen levels (hypoxia), there are other fundamental physiological adaptations. A key physiological response to hypoxia is the rise in levels of the hormone erythropoietin (EPO), which leads to increased production of red blood cells (erythropoiesis). The importance of hormonal control of erythropoiesis was already known at the beginning of the 20th

century, but how this process was itself controlled by $\boldsymbol{0}_2$ remained a mystery.

Semenza studied the EPO gene and how it is regulated by varying oxygen levels. By using gene-modified mice, specific DNA segments located next to the EPO gene were shown to mediate the response to hypoxia. Ratcliffe also studied $\rm O_2$ -dependent regulation of the EPO gene, and both research groups found that the oxygen-sensing mechanism was present in virtually all tissues, not only in the kidney cells where EPO is normally produced. These were important findings showing that the mechanism was general and functional in many different cell types.

Semenza wished to identify the cellular components mediating this response. In cultured liver cells he discovered a protein complex that binds to the identified DNA segment in an oxygen-dependent manner. He called this complex the hypoxia-inducible factor (HIF). In 1995, Semenza was able to publish some of his key findings, including identification of the genes encoding HIF. HIF was found to consist of two different DNA-binding proteins, so called transcription factors, now named HIF-1 α and ARNT. Now the researchers could begin to determine which additional components were involved and how the machinery works.



When oxygen levels are low (hypoxia), HIF- 1α is protected from degradation and accumulates in the nucleus, where it associates with ARNT and binds to specific DNA sequences (HRE) in hypoxia-regulated genes (1). At normal oxygen levels, HIF- 1α is rapidly degraded by the proteasome (2). Oxygen regulates the degradation process by the addition of hydroxyl groups (OH) to HIF- 1α (3). The VHL protein can then recognise and form a complex with HIF- 1α leading to its degradation in an oxygen-dependent manner (4).

Mattias Karlén/Nobel Committee for Physiology or Medicine

When oxygen levels are high, cells contain very little HIF- 1α . However, when oxygen levels are low, the amount of HIF- 1α increases so that it can bind to and thus regulate the EPO gene as well as other genes with HIF-binding DNA segments (see image). Several research groups showed that HIF- 1α , which is normally rapidly degraded, is protected from degradation in hypoxia. At normal oxygen levels, a cellular machine called the proteasome, degrades HIF- 1α . Under such conditions a small peptide, ubiquitin, is added to the HIF- 1α protein. Ubiquitin functions as a tag for proteins destined for degradation in the proteasome. How ubiquitin binds to HIF- 1α in an oxygen-dependent manner remained a central question.

At about the same time as Semenza and Ratcliffe were exploring the regulation of the EPO gene, cancer researcher Kaelin was researching an inherited syndrome, von Hippel-Lindau's disease (VHL disease). This genetic disease leads to dramatically increased risk of certain cancers in families with inherited VHL mutations. Kaelin showed that the VHL gene encodes a protein that prevents the onset of cancer. Kaelin also showed that cancer cells lacking a functional VHL gene express abnormally high levels of hypoxia-regulated genes; but that when the VHL gene was reintroduced into cancer cells, normal levels were restored. This showed that VHL was somehow involved in controlling responses to hypoxia. Additional clues came from several research groups showing that VHL is part of a complex that labels proteins with ubiquitin, marking them for degradation in the proteasome. Ratcliffe and his research group then demonstrated that VHL can physically interact with ${\sf HIF-1}\alpha$ and is required for its degradation at normal oxygen levels. This conclusively linked VHL to HIF-1 α .

Both Kaelin and Ratcliffe suspected that the key to 0,sensing resided somewhere on a specific portion of the HIF-1 α protein known to be important for VHL-dependent degradation. In 2001, in two simultaneously published articles they showed that under normal oxygen levels, hydroxyl groups are added at two specific positions in HIF- 1α (see image). This protein modification, called prolyl hydroxylation, allows VHL to recognise and bind to HIF-1 α and thus explained how normal oxygen levels control rapid HIF-1 α degradation with the help of oxygen-sensitive enzymes (so-called prolyl hydroxylases). Further research by Ratcliffe and others identified the responsible prolyl hydroxylases. It was also shown that the gene-activating function of HIF- 1α was regulated by oxygendependent hydroxylation. The Nobel laureates had now elucidated the oxygen sensing mechanism and had shown how it works.

Chemistry: creating a rechargeable world

The 2019 Nobel Prize in Chemistry was awarded to John Goodenough, M. Stanley Whittingham and Akira Yoshino 'for the development of lithium-ion batteries'. These laureates and their work will be featured in *Chemistry in Australia* in early 2020.

About the Nobel laureates

James Peebles was born in 1935 in Winnipeg, Canada. He obtained his PhD in 1962 from Princeton University, USA. He is Albert Einstein Professor of Science at Princeton University,

Michel Mayor was born in 1942 in Lausanne, Switzerland. He obtained his PhD 1971 from University of Geneva, Switzerland. He is a professor at University of Geneva, Switzerland.

Didier Queloz was born in Switzerland in 1966. He obtained his PhD 1995 from University of Geneva, Switzerland. He is a professor at University of Geneva, Switzerland, and University of Cambridge, UK.

William G. Kaelin, Jr was born in 1957 in New York. He obtained an MD from Duke University, USA. He did his specialist training in internal medicine and oncology at Johns Hopkins University, Baltimore, and at the Dana-Farber Cancer Institute, Boston. He established his own research lab at the Dana-Farber Cancer Institute and became a full professor at Harvard Medical School in 2002. He has been an investigator at the Howard Hughes Medical Institute since 1998. Sir Peter J. Ratcliffe was born in 1954 in Lancashire, UK. He studied medicine at Gonville and Caius College at Cambridge University and did his specialist training in nephrology at Oxford. He established an independent research group at Oxford University and became a full professor in 1996. He is the Director of Clinical Research at the Francis Crick Institute. London, Director of the Target Discovery Institute in Oxford and a member of the Ludwig Institute for Cancer Research.

Gregg L. Semenza was born in 1956 in New York. He obtained his BA in Biology from Harvard University, Boston. He received an MD/PhD from the University of Pennsylvania, School of Medicine, Philadelphia in 1984 and trained as a specialist in paediatrics at Duke University, USA. He did postdoctoral training at Johns Hopkins University, Baltimore, where he also established an independent research group. He became a full professor at the Johns Hopkins University in 1999 and since 2003 has been the Director of the Vascular Research Program at the Johns Hopkins Institute for Cell Engineering.

Nobelprize.org





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news on the market

Just add water: chemists suggest a fix for insoluble drugs

Stable metal-organic frameworks (MOFs) are prized for their ability to capture carbon dioxide or harvest atmospheric water, but researchers at the University of Michigan, USA, have developed a use for unstable metal organic frameworks: as a system for drug delivery (http://dx.doi.org/10.1002/ange.201907652).

Ninety per cent of drugs in development don't dissolve well or at all in the body, according to a 2012 study. MOFs are rigid, porous structures composed of metal linked by organic ligands. While researching unstable MOFs, chemist Adam Matzger realised they may work as a delivery system for these kinds of drugs.

'It struck us that while everyone was shooting for stable MOFs, we could use what we had learned about instability of MOFs to get a degradable substance that would rapidly release drugs. It was a really unexpected finding,' said Matzger.

The MOF delivery system takes advantage of one strategy of delivering insoluble drugs. The strategy is to deliver them in an amorphous form, meaning that the drugs are kept from crystallising. Once the drug compounds crystallise, they become less soluble – and therefore less bioavailable, which means less of the drug crosses into the bloodstream.

MOFs are able to keep these drugs in an amorphous state because of their porous structure. MOF-5 in particular looks like a set of cubes stacked on top of each other: picture an endlessly repeating 3D grid. When the researchers load a drug into this grid, the pores in the MOF compartmentalise the drug molecules, holding the compound in the desired amorphous state.

Researchers have previously used polymers to hold drug compounds in an amorphous state, but drug molecules could still migrate and crystallise in the polymer, which affects solubility and therefore how much of a drug is bioavailable. Because MOF rigidly holds drug molecules apart but quickly decomposes, drug dosage is easily controlled. The compound itself crosses into the bloodstream, while the MOF decomposes in the body.

The researchers decided to use MOF-5 for a few reasons. First, its metal component is zinc, a metal with low toxicity used in many supplements, and the organic component is terephthalic acid. Second, MOF-5 is relatively unstable, which the researchers demonstrated in separate work that examined the stability of different MOFs.

'What we do here is we increase the solubility while guaranteeing dosage stability,' Matzger said. 'This approach is relatively universal. We show it for three drugs, but the fact that the pores are too small to allow a crystal to form is going to be true for all drugs.'

University of Michigan



Avery introduces industrial label range to improve worker safety

Avery Products has introduced a range of heavy-duty signs and labels so businesses can provide safety messages in construction sites, warehouses, laboratories, offices and other facilities.

According to Safe Work Australia, work-related injury and disease costs \$61.8 billion to the Australian economy. So identifying risks in the workplace and providing adequate signage to mitigate those risks is the responsibility of every employer.

Businesses can now design and print safety labels and signs immediately from a laser printer, instead of having to wait long periods for professionally printed materials to arrive at sites where they are needed. When a dangerous situation occurs safety managers can take immediate steps to ensure their colleagues and workers are warned of any risks to their health and safety.

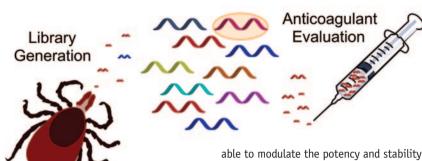
The Avery Industrial Label range combines durability, toughness and instant useability to warn workers of physical harm from dangerous construction zones, machinery, harsh environments, chemicals and other harmful scenarios. They are water resistant, tear proof, tamper proof and extremely durable, so they can handle the harshest environments for as long as they are required.

The Avery Industrial Range offer labels in a wide range of sizes and substrates to cover every situation and eventuality. They can be printed in minutes for free using Avery Design & Print software, available on the Avery website, so managers can have a sign or label ready to use almost instantly.

For more information on the Avery Industrial Range, visit www.averyproducts.com.au/industrial-solutions.

Rapid route to protein drug library

The last decade has seen a resurgence in the use of peptides and proteins as therapeutics, highlighted by an FDA approval rate that is now double that for small molecules. Despite the attractiveness of peptides and proteins, unlike the case for small molecules, it is not common to generate large numbers of candidate analogues for lead selection due to inherent difficulties associated with making these complex biomolecules. In a study led by researchers at the University of Sydney, rapid and efficient chemicalligation chemistry was used to access a library of 34 tick-derived anticoagulant proteins with site-specific tyrosine sulfation modifications (Watson E.E.,



Lead Selection

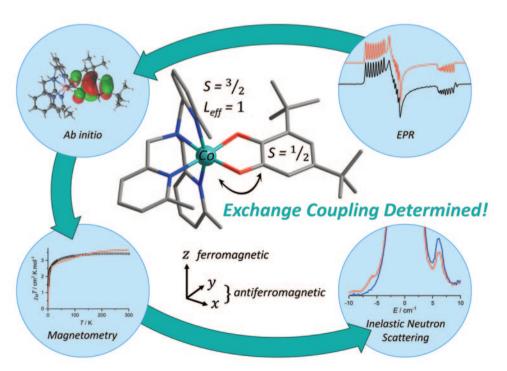
Ripoll-Rozada J., Lee A.C., Wu M.C.L., Franck C., Pasch T., Premdjee B., Sayers J., Pinto M.F., Martins P.M., Jackson S.P., Pereira P.J.B., Payne R.J. *Proc. Natl Acad. Sci. USA* 2019, **116**, 13 873–8). By combining total chemical synthesis with protein engineering, the researchers were able to modulate the potency and stability of the anticoagulant molecules and identify key structure—activity relationships, as is commonly done in traditional small-molecule medicinal chemistry. The synthetic platform developed provides a foundation from which to expedite the generation and identification of polypeptide and protein libraries to identify therapeutic leads for a range of diseases.

Radical new look into magnetic molecules

Magnetic molecules have a range of potential applications, including as molecular-based memories or switches and for nanoscale electronics and spintronics. Orbitally degenerate metal ions, such as high-spin octahedral cobalt(II), are promising for magnetic molecules because of their large magnetic moment. Binding these metal ions to

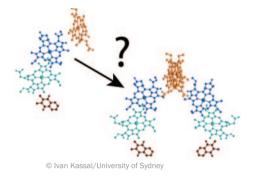
radical ligands allows the magnetic properties to be tuned. The metal-radical interaction can also be important for mediating electronic communication at interfaces within molecular devices. However, elucidating exchange interactions involving orbitally degenerate metal ions is an ongoing and considerable challenge, due to the single-

ion anisotropy and anisotropic exchange. A team led by Colette Boskovic and Alessandro Soncini at the University of Melbourne, in collaboration with researchers from Monash University, ANSTO and the University of Florence, has recently reported a significant breakthrough in this area (Gransbury G.K., Boulon M.-E., Mole R.A., Gable R.W., Moubaraki B., Murray K.S., Sorace L., Soncini A., Boskovic C. Chem. Sci. 2019, 10, 8855-71). This multitechnique experimental and theoretical study has clarified the exchange coupling between high-spin cobalt(II) and a coordinated semiguinonate ligand. Specifically, it found dominant ferromagnetic exchange that is similar in magnitude to the anisotropy parameters of the cobalt(II) ion and contains a significant contribution from spin-orbit coupling. Beyond providing a solution for this specific case, the methodology developed will be generally applicable for elucidating exchange coupling between orbitally degenerate metal ions and radical ligands. This will facilitate the development of bistable molecules and their integration into devices for quantum computing and molecular spintronics.



Better together: explaining dimeric photosynthetic reaction centres

Reaction centres are the workhorses of photosynthesis, converting sunlight into chemical energy. The original reaction centres are widely thought to have been single pigment-protein units, which, somewhere along the evolutionary line,

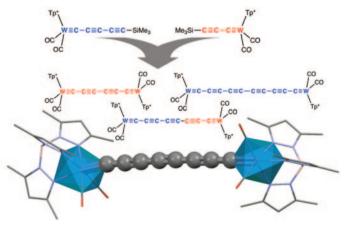


paired up into dimers. Today, all reaction centres are dimeric. Natasha Taylor and Ivan Kassal of the Universities of Queensland and Sydney have now provided a convincing explanation for why dimers have prevailed (Taylor N., Kassal I. Chem Sci. 2019, https://doi.org/10.1039/C9SC03712H). The most striking aspect of reactioncentre dimerism is the special pair, two chlorophylls so strongly coupled that they are best thought of as a single molecule. The unusually close contact results in delocalisation, a quantum effect in which energy or charge is on both molecules at the same time. This unusual feature seems too unlikely to

have arisen if it conferred no evolutionary advantage. Taylor and Kassal list several possible explanations for the dimerism. Although none of the possibilities can be definitively ruled out - given the billions of years of evolutionary distance - the most likely explanation is that the strong coupling and delocalisation in the special pair helped the reaction centre to collect excitation energy from nearby antenna pigments. Calculations show that this benefit likely outweighed the simultaneous decrease in charge-transfer efficiency. Overall, dimerisation could have increased the reaction centre's total efficiency by as much as 50%.

New carbon wires terminated by metal-carbon triple bonds

Chains of carbon atoms between two metal centres have been exciting chemists for over two decades due to their fascinating electronic and electro-optical properties. The vast majority of these compounds, however, have exploited single bonds, i.e. metal acetylides, as the key metal-to-carbon linkage. Compounds with metal-carbon triple bonds (carbynes) at both ends might be expected to increase the degree of interaction between the metal and carbon chain, and in turn lead to an enhancement of these useful properties. Previously, these bis(carbynes) were limited to two-, four- or six-carbon chains. Now, Richard Manzano and Tony Hill at the Australian National University have prepared a series of ditungsten carbon wires of the type $L_nW \equiv C - (C \equiv C)_m - C \equiv WL_n$ (m = 0-4), with up to 10 carbon atoms linked to metals by short W≡C triple bonds (Hill A.F., Manzano R.A. Angew. Chem. Int. Ed. 2019, 58, 15354-7). The observed optical and electronic properties of these wires are highly promising and are likely to inspire future studies into these rare linkages with a view to their application in nanodevices.

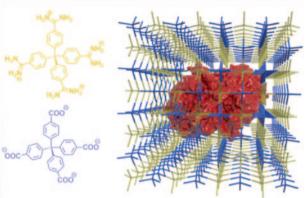


Promising new anticancer drugs

The Molecular Engineering Group at RMIT, co-led by Suresh Bhargava and Neda Mirzadeh, has a mission to develop goldbased anticancer drugs with minimal side effects compared with the widely used anticancer drug cisplatin. A recent preclinical study by the group, featured on the cover of Chemistry - A European Journal, has identified gold-based drugs that are 24 times more effective at killing cancer cells and better at inhibiting tumour growth than cisplatin (Reddy T.S., Pooja D., Privér S.H., Luwor R.B., Mirzadeh N., Ramakrishna S., Karri S., Kuncha M., Bhargava S. Chem. Eur. J. 2019, https://doi.org/10.1002/chem.201903388). The molecules were evaluated in preclinical tests and found to be highly cytotoxic against prostate, breast, cervical, melanoma and colon cancer cells. In animal trials, treatment with the molecules significantly inhibited tumour growth (up to 46.9% compared with 29% for cisplatin). The gold-based compounds inhibit the action of an enzyme found in cancer cells, thioredoxin reductase, that is linked to cancer progression and the development of drug resistance. In addition, the molecules have strong anti-inflammatory properties, giving them a dual therapeutic effect and potential application in the treatment of chronic inflammatory conditions such as arthritis.

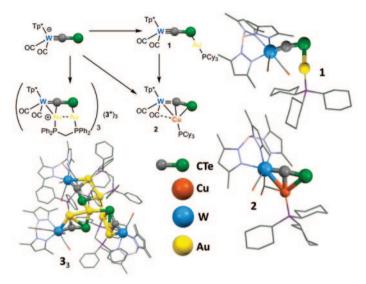


No-hassle enzyme encapsulation with HOFs



The harsh conditions used in certain biotechnological processes are deleterious to the activity of biomacromolecules. Encapsulation within porous materials can protect them from these exacting conditions, such as heat, acids or other denaturing agents. Recent work by researchers at the University of Adelaide, Australian National University and Graz University of Technology (Austria) has shown that porous hydrogenbonded organic frameworks (HOFs) can be used to encapsulate and preserve enzymes, while still retaining their bioactivity (Liang W., Carraro F., Solomon M.B., Bell S.G., Amenitsch H., Sumby C.J., White N.G., Falcaro P., Doonan C.J. J. Am. Chem. Soc. 2019, **141**, 14298–305). HOFs are crystalline, porous materials held together by hydrogen bonds between organic components. The team prepared HOF-based biocomposites composed of tetraamidinium and tetracarboxylate building blocks and fluorescein-tagged enzymes catalase or alcohol oxidase. The biocomposites were prepared simply by combining aqueous solutions of the two building blocks and the enzyme. The research team found that the HOF can protect the enzymes from conditions that would typically lead to activity loss, particularly offering stability where certain metal-organic framework (MOF) materials fail. In all, protective HOF biomolecule coatings could provide valid alternative materials to MOFs: they are metal free, have larger pore apertures, and are stable over a wider, more biologically relevant pH range.

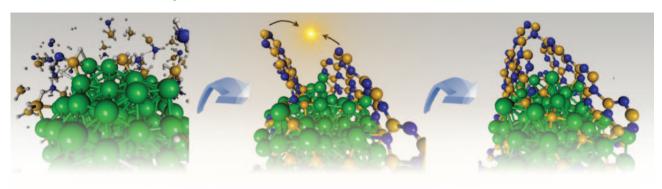
First multimetallic carbon tellurides



The interplay of carbon monoxide and metals has been a feature of industrial chemistry that dates back 110 years to Mond's process for nickel refining. Our understanding of the way in which metals activate CO underpins numerous catalytic processes that incorporate cheap CO into high value-added commodity chemicals. In contrast, we know far less about how the heavier congeners CSe and especially CTe bind to one or more metals. Compounds in which CSe binds to two metals are exceedingly rare and those involving CTe were previously unknown. Now, the group of Anthony Hill at the Australian National University has succeeded in preparing the first multimetallic CTe, C₂Te and C₂Te₂ complexes, involving tungsten and gold or copper with two different bridging modes and a nonametallic W₂Au₆(μ-CTe)₃ derivative that adopts a mixture of different bonding modes (Frogley B.J., Hill A.F., Onn C.S., Watson L.J. Angew. Chem. Int. Ed. 2019, 58, 15349-53). The gold(I) and copper(I) fragments were found to be reasonably labile and may serve as convenient 'CTe delivery agents' for the future preparation of new examples of this rare class of compounds.



New mechanism explains formation of boron nitride nanotubes



Ammonia Borane CVD

CVD = chemical vapour deposition

Boron nitride nanotubes (BNNTs) were discovered only a few years after carbon nanotubes (CNTs) in the 1990s. However, whereas the nucleation and growth of CNTs is now well understood, there is almost no understanding of how BNNTs

CNTs is now well understood, there is almost no understanding of how BNNTs nucleate and grow, and it is commonly assumed that the nucleation and growth of these two different nanomaterials are fundamentally similar. Alister Page's group at the University of Newcastle has recently reported a novel mechanism to

BN Network Fusion

explain how BNNTs nucleate on molten nickel catalyst nanoparticles, based on reactive non-equilibrium molecular dynamics simulations (McLean B., Webber G.B., Page A.J. J. Am. Chem. Soc. 2019, 141, 13 385–93). Strikingly, the simulations showed that BNNT tips nucleate via the fusion of independent planar BN networks that first extrude away from the catalyst surface. This fusion mechanism results in BNNT tip structures with sharp tips and flat edges,

BNNT Nucleation

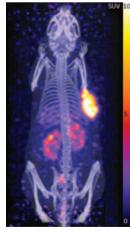
consistent with experimental observations. These simulations provide an alternative explanation for BNNT nucleation that does not require energetically unfavourable topological defects, such as pentagon or heptagon rings, in the BNNT tip structure. They also provide the first evidence to challenge the long-held presumption that BNNTs and CNTs nucleate in similar ways.

Copper-based radionuclides for cancer theranostics

The principle of using the same molecule for both diagnosis and therapy is called theranostics. Copper-64 is a radionuclide that can be used for diagnostic imaging, while copper-67 is a radionuclide that can be used for targeted radiotherapy. Both imaging and therapy require the copper radionuclide to be efficiently and selectively delivered to tumour tissue. The prostate membrane antigen (PSMA) is a membrane-bound carboxypeptidase that is over-expressed in metastatic prostate cancer, making it an excellent theranostic target. To develop a new copper-based

theranostic for prostate cancer, a collaborative team from the University of Melbourne and the Peter MacCallum Cancer Centre synthesised macrobicyclic cage amine sarcophagine copper complexes tethered to either one or two lysine-ureido-glutamate functional groups that bind to PSMA (Zia N.A., Cullinane C., Van Zuylekom J.K., Waldeck K., McInnes L.E., Buncic G., Haskali M.B., Roselt P.D., Hicks R.J., Donnelly P.S. Angew. Chem. Int. Ed. 2019, 58, 14991–4). The bivalent agent, in which two targeting groups are tethered to a

single copper complex, dramatically outperforms the monomeric agent with respect to tumour uptake and retention. The high tumour uptake and retention of the bivalent agent suggest that it is a promising diagnostic for prostate cancer and could be used to guide therapy with a copper-67 variant.



Electrophilic methylating agent activated by electrochemistry

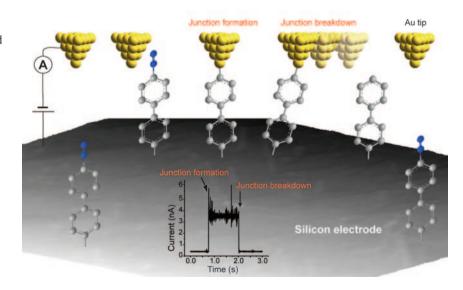
Alkoxyamines are important compounds in polymer synthesis due to their ability to form a persistent nitroxide and a carbon-centred radical at elevated temperatures, thus facilitating controlled radical polymerisation. However, using a combination of experimental and computational chemistry, researchers at the Australian National University recently showed that, by electrochemically oxidising these molecules, they can instead generate carbocations. Building on this work, and in collaboration with researchers from the University of Tasmania, they have now demonstrated that the simplest of these alkoxyamines, TEMPO–Me, becomes a powerful electrophilic methylating agent when oxidised by electrochemistry

(Norcott P.L., Hammill C.L., Noble B.B., Robertson J.C., Olding A., Bissember A.C., Coote M.L. J. Am. Chem. Soc. 2019, **141**, 15 450–5). Rather than generating a carbocation, the methylation proceeds via an S_N^2 mechanism when combined with an appropriate nucleophile. Conventional methylating agents such as iodomethane, dimethyl sulfate or diazomethane suffer from acute toxicity, and often can be volatile and/or explosive. Using this new electrochemical methylation process, the reactive species is generated and consumed in situ, completely eliminating the need to handle hazardous reagents. This chemistry can be conducted at room temperature, open to the air, in a simple undivided electrochemical cell set-up.

Stable contacts for molecular electronics

Single molecules are predicted to play a key role in the future of miniaturised electronics. One of the biggest challenges facing molecular electronics today is the lack of mechanically stable singlemolecule contacts to metal or semiconducting electrodes. In a study led by Nadim Darwish at Curtin University, single molecules, terminated by diazonium salts at both ends, were used to form covalent bonds to both gold and silicon electrodes, mimicking standard metal-insulator-semiconductor diodes (Peiris C.R., Vogel Y.B., Le Brun A.P., Aragonès A.C., Coote M.L., Díez-Pérez I., Ciampi S., Darwish N. J. Am. Chem. Soc. 2019, 141, 14788-97). The singlemolecule circuits survive for more than a second at room temperature, a duration that had previously been unreachable. The ability to form mechanically stable

single-molecule circuits on the time scale of seconds allows the electronic properties of single molecules to be probed with a level of detail that was previously inaccessible and brings us a step closer towards the realisation of single-molecule electronics.



Compiled by **David Huang** MRACI CChem (david.huang@adelaide.edu.au). This section showcases the very best research carried out primarily in Australia. RACI members whose recent work has been published in high impact journals (e.g. *Nature*, *J. Am. Chem. Soc.*, *Angew. Chem. Int. Ed.*) are encouraged to contribute general summaries, of no more than 200 words, and an image to David.

How I discovered the periodic law of the elements By Dmitri Mendeleev

Dmitri Mendeleev speaks to us, through narrator **Alf Larcher**, about his life and work as he sought to determine how the properties of chemical elements are related.

t is February 1869 and I, Dmitri Mendeleev, have just completed an important figure for my textbook, Osnovy khimii [Principles of chemistry], which orders the 63 known elements to demonstrate their periodicity of chemical and physical properties.

I would like to tell you how I came to make this discovery. So, let us begin.I am 35 years old and have recently been appointed Professor of General Chemistry at St Petersburg University, St Petersburg, Russia. My story starts where I was born - in a small village just outside Tobolsk in Siberia, many kilometres east of where I am now. My beloved mother noticed that I was doing well in Science subjects at secondary school and, after I graduated, she endured the long and arduous journey to bring me to a teachers' college in St Petersburg (see July/August issue, p. 14, for Maria Mendeleeva's story). The college trained teachers and conducted basic scientific research in return for newly graduated teachers completing placements in a regional area for two years. The college was in the grounds of the University of St Petersburg, with university students and the public having limited access.

I was 16 when I arrived and I found it

difficult at first - the other students were from local areas and could visit nearby family, but my mother had died shortly after bringing me there and most of my family were in far-off Siberia. But the college looked after me well as I studied and lived there. A professor from the university, Alexandr A. Voskresenskii, looked out for me and encouraged my scientific interests. For my master's research project, under the mentorship of Professor Voskresenskii, I studied organic isomorphism, where two different organic molecules have the same crystalline structure. In this project, I developed important skills of classification and looking at the physical properties of compounds and linking them with structure. For this research I was given the Gold Medal, and in 1856 I successfully completed all my studies and graduated from the college.

Dmitri was thus a trained teacher, and clarity of presentation in an ordered manner would have been of utmost importance to him. Professor Voskresenskii continued to be a significant influence throughout the rest of Dmitri's life. Apart from being a dedicated teacher, he was an acclaimed organic chemist, making several important contributions to the field, including the isolation and identification of theobromine in cacao (coffee) beans.

y posting after graduation was a regional school in the Crimea, but with war breaking out in the area it was a difficult place to teach, and I had to move around to avoid the conflict. I was glad when my posting was over and in 1859 I left for Heidelberg, Germany, where I had successfully applied for a governmentfunded visit to the laboratories of Robert Bunsen, I found the laboratories there very uncomfortable, being noisy and full of fumes - so much so that I set up my own laboratory in my apartment. There I became totally engrossed in chemical research, studying the capillary effect and the critical point of alcohol-water solutions.

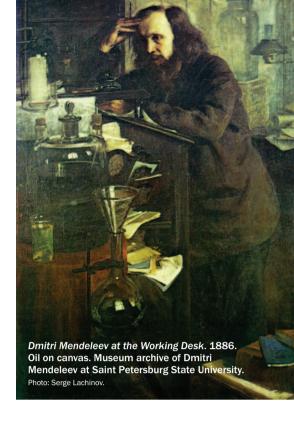
While at Heidelberg I was able to attend the first Chemical Congress, held at Karlsruhe in Germany in 1860. where I heard the Italian chemist Stanislao Cannizzaro speak and represent his countryman Amadeo Avogadro's hypothesis, making the distinction between atoms and molecules and defining valence more accurately. I heard how this new understanding was used to recalculate and reassign many elemental atomic weights. This started me thinking could the elements now be ordered on these corrected values? I was so excited about what had occurred at Karlsruhe that I wrote about it to Professor Voskresenskii, who published my letter in the St Petersburg local newspaper. Shortly after the Congress, it was time to leave Heidelberg and my many friends, and I was deeply moved when my German patron Emil Erlenmeyer organised a party for me before I left.

Dmitri seems to have forged his powerful personality at Heidelberg. He was away from Russia and thus his Siberian origins may have emancipated him from being an outsider – he was just another visiting academic from Russia. At any gathering, it appears that Dmitri was at the centre of the conversation.

returned to St Petersburg in 1861, having to restart my career in Russia. I was in debt after borrowing money to set up the laboratory in Heidelberg and had to find an apartment to live in. It was the middle of the academic year and teaching positions were scarce, so I decided to approach a publisher about translating J.R. Wagner's German text on chemical technology, and publishing my own organic chemistry textbook. I was keen to bring the new chemistry I had learnt in Germany to Russia. Luckily for me, the publisher agreed, and I began busily writing. I completed my book Organicheskaia khimiia [Organic chemistry] a few months after and it was well received by students. I was also awarded the Demidov prize of the Imperial Saint Petersburg Academy of Sciences for outstanding scholarly work - the judges were impressed that the book was the first Russian-language chemistry textbook written. I used the prize money to clear my debts, after which I approached my mentor Professor Voskresenskii, who was able to give me some teaching work at the University of St Petersburg. This was not enough to support me and my wife Feozva Leshcheva, whom I married in 1862, but I was able to pick up more teaching at the Technological Institute in St Petersburg.

I continued teaching at both institutions, also defending my Doctor of Science dissertation entitled 'On the Combinations of Water with Alcohol'.

In 1867, I was appointed Professor of Chemistry at the University of St Petersburg, the chair becoming available on the retirement of Professor Voskresenskii. I was now responsible for the teaching of General Chemistry, with all students in the Science faculty required to attend my lectures. I set about my work, using a new broom to sweep away the dated textbooks, including my own, which we based on translations of German texts. Karlsruhe had changed the chemical landscape and many more elements had been



discovered in recent years. I was determined not to present my students with an undefined array of the chemical elements – I would find order in the system!

I began writing *Osnovy khimii* in early 1868, completing the first volume in January of this year (1869). This details the practices of chemistry and how chemical knowledge is acquired, which was important to my students as their course contained a major practical component. It also allowed me to review how the critical properties of chemical compounds and elements are determined and how they could be prone to error. My mind was ticking.

It was time to address the issue of the organisation of the elements. I wrote each of the 63 known elements on a separate card with their newly assigned atomic weights and their physical and chemical properties, e.g. density, valency, oxide composition. How should I order them? I began by using their atomic weight, concentrating firstly on the lighter elements.

The process by which Dmitri ordered the elements has been the subject of constant conjecture over the decades. The idea that it came to him in a dream was favoured for some time, but has been

discounted by recent sources who favour a process using cards, concentrating initially on the light elements. Dmitri's discovery process described in this article is imagined and not based on fact. While Dmitri's original manuscript corrections of his first ordering exist, the workings that led to his original discovery do not.

began by placing my first card, that of the element with the lowest atomic weight (hydrogen – atomic weight 1), on the left side of the bench that I was working on. I then placed the next card of the element of the next lowest atomic weight (lithium - atomic weight 7) below it and so on to sodium (atomic weight 23) in a single column. I had begun volume 2 of my chemistry textbook discussing the composition and properties of common salt and knew the alkali metals and halogens well. I noticed that lithium and sodium were in my single column, one near the top, the other at the bottom. Why were these similar alkali elements so far apart? Perhaps my list should be ordered in two columns instead of one. I moved my hydrogen card further to the left, to head another column, then moved lithium underneath hydrogen, not immediately below but next to its chemical cousin sodium in the second (original) column. I continued this trend by placing the other alkali earths next to sodium and lithium in a row across the columns in order of increasing atomic weight. Similarly, I added the halogens next to fluorine in

another row across the table. The arrangement so far looked very neat (see below).

I continued with the next highest atomic weight element after sodium, being magnesium (atomic weight 24). Once again, instead of extending the second column. I started a third column, placing it next to beryllium, which had similar chemical properties, e.g. both had a valency of +2, forming oxides of composition RO, R being a generic symbol for an element. The next elements in increasing atomic weight in this third column were aluminium, silicon, phosphorus and sulphur. To my amazement, after these elements, the third column was completed by the halogen and alkali earth elements (Cl and K), which I had placed as rows previously. Order in the elements was emerging!

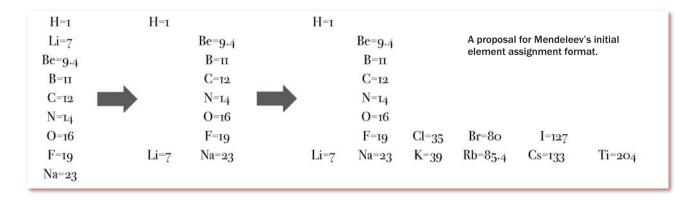
The next elements after potassium were calcium of valency 2 and titanium of valency 4. I thus reasoned that a new yet undiscovered element must exist after calcium, having valency 3. By averaging the atomic weights of its neighbours, I estimated its atomic weight to be 45. I thus placed a card with a question mark below calcium in the third column.

Dmitri named the proposed element ekaboron, the prefix from the Sanskrit word for 'one' and 'boron' for the lowest atomic weight member of the valency 3 elements (group 3). From the chemical and physical properties of its neighbouring elements and other members of its group, It was time to address the issue of the organisation of the elements.
I wrote each of the 63 known elements on a separate eard ...

Dmitri boldly predicted a long list of his new element's properties. He also cheekily predicted how this element would be discovered!

Note that below eka-boron, erbium and yttrium (Yt, symbol now Y) and indium are listed in the figure with question marks and are not classified in the system. This is understandable because the first is a lanthanoid whose position in the periodic table would not be determined for decades, while the atomic weights for the other two elements are incorrect. Dmitri correctly ignored these as he ordered the rest of the elements.

Let's continue with Dmitri's imagined sorting of his elemental pack of cards.



knew the valency of the element after eka-boron must be four and I still had titanium in my stack of cards, which was definitely of that valency. I thus began the fourth column with titanium, starting well above bromine, whose position I had determined previously. Progressing down the group, I listed the remaining elements with increasing atomic number, starting with vanadium, until I reached zinc and arsenic, the latter having similar chemical properties to phosphorus but which was two places after zinc. To effect this alignment. I had to leave two spaces after zinc to account for two more yet-to-be discovered elements. I temporarily named them ekaaluminium and eka-silicon, according to their adjacent elements, and whose atomic weights I averaged to calculate the atomic weights of the new elements to be 68 and 70 respectively. The elements that I placed after these eka-elements were the previously placed arsenic then selenium, with their chemical and physical properties fitting well with the elements in each of their rows. After bromine and rubidium, I placed strontium, which also fitted well with the calcium row. The next card after strontium was zirconium, which had the same valency (4) and similar properties to titanium, and I thus decided to place it next to this element on top of a fifth column.

Dmitri placed four lanthanoid/actinoid elements at the end of column 4 that were not classified by his system and whose atomic weights were once again later shown to be incorrect or, in the case of didymium, mis-assigned (it was eventually shown to consist of two elements – praseodymium and neodymium). The lanthanoid/actinoid elements were to perplex him and many other scientists until American chemist Glenn Seaborg found their correct place in 1945. Once again, Dmitri extensively listed the properties of his proposed new elements eka-aluminium and eka-silicon, including

ОПЫТЪ СИСТЕМЫ ЭЛЕМЕНТОВЪ,

ОСНОВАННОЙ НА ИХЪ АТОМНОМЪ ВЪСЪ И ХИМИЧЕСКОМЪ СХОДСТВЪ.

						Α
			Ti=50	Zr=90	?=180.	B
			V=51	Nb = 94	Ta=182.	
			Cr=52	Mo = 96	W=186.	С
			Mn=55	Rh=104,4	Pt=197,1.	D
			Fe=56	Ru=104,4	Ir=198.	E
		Ni=	-Co=59	Pd=106,6	Os=199.	F
H=1			Cu=63,4	Ag=108	Hg=200.	G
	Be= 9,4	Mg=24	Zn = 65,2	Cd=112	-	Н
	B=11	Al=27,3	?=68	Ur=116	Au=197?	
	C=12	Si=28	?=70	Sn=118		J
	N=14	P=31	As=75	Sb=122	Bi=210?	K
	O=16	S=32	Se=79,4	Te=128?		L
	F=19	C1=35,5	Br=80	I=127		M
Li=7	Na=23	K=39	Rb=85,4	Cs=133	Tl=204.	N
		Ca=40	Sr=87,6	Ba=137	Pb=207.	0
		?=45	Ce=92			
		?Er=56	La=94			
		?Yt=60	Di=95			
		?In=75.6	Th=118?			

Д. Мендельевъ

Dmitri Mendeleev's first published ordering of the elements, entitled 'An Attempt at a System of Elements, Based on Their Atomic Masses and Chemical Affinity'. Row labels (in red) have been added by author. Wikimedia/NikNaks

in German publications, making his proposals available to an international audience. The publications did not make much of an impact, some people commenting that every gap in his proposed system did not require a new element. But Dmitri was not finished – as he progressed through the elements, he would make more controversial predictions.

continued to add elements below zirconium in increasing atomic weight: niobium, molybdenum, rhenium ... until I reached the place before the previously placed iodine (atomic weight 127). My next element was tellurium (atomic weight 128) which should rightly be placed after iodine to take the place of caesium. This was,

impossible, I thought – iodine and caesium are in their correct places among the alkalis and halogens respectively. I concluded the atomic weight of tellurium must be incorrect and placed it before iodine in the same row as oxygen, with which it had similar properties.

I continued down to barium with all the elements seeming to fall into place until I reached tantalum (atomic weight 182), which I knew was an analogue of niobium. I thus began the sixth row with tantalum, but one place down, so that tantalum lined up with niobium, calculating the atomic weight of the new yet-to-be discovered element to be 180. I completed column 6 from tantalum to lead – the elements did not align as well as in other columns. I

suspected that more atomic weights were incorrect, but for now this was all I could do.

So that is how I came to my first attempt at ordering the elements and the figure that I have completed for my textbook. My system has aligned the elements so that each column adds another member to the horizontal group of elements with which it has similar chemical properties; I have discovered the periodic law of the elements! It is not perfect, and I have much work to do, but I believe it will help my students enjoy and understand chemistry. I also think that my first effort is worthy enough to let my chemical colleagues know about, especially since after the Karlsruhe Congress I know many like me have been trying to order the elements. To let them know, this month I will print single-sheet drafts of my ordered elements (150 in Russian and 50 in French) and distribute them to various chemists. The title will be 'An Attempt at a System of Elements, Based on Their Atomic Weight and Chemical Affinity'. I will also prepare a paper on my discovery ('The correlation of the Properties and Atomic Weights of the Elements'), which I will read at the newly established Russian Chemical Society in March. Shortly after that, I will have also finished the second volume of my textbook, which will contain my ordering of the elements at its centre.

I am not sure where this work will take me; will my work be remembered in 50, 100, 150 years? I know not, but I hope I have contributed to chemistry is some small way at least!

Mendeleev

Apart from his brilliance and perseverance as a chemist, Mendeleev was a great writer, able to guickly put pen to paper and publish his results. This is a great example for any scientist of how to obtain primacy of any idea, which many of his contemporaries, who were working on similar ideas, did not do. In his writings, he never used the term 'periodic table' for his system, instead using the terminology 'periodicity of the elements' or the 'periodic law of the elements'. As his, and subsequent investigators', orderings were presented as 'tables of ordered elements' and the like, the term 'periodic table' came into use after Dmitri's time. Dmitri's original ordering would undergo many refinements, with him constantly publishing the new versions.

In 1875, the rather remarkable French chemist Lecoq de Boisbaudran published the properties of a new element that he found in rocks in a mine in the Pyrenees, calling it gallium. It was six years after Dmitri had published his original work and he had been scouring the newly published literature about new elements that would validate his predictions. He must have been very pleased when he found Lecoq's publication; gallium's properties matched his eka-aluminium very closely.

The predictions are based on the proposed valency of eka-aluminium and chemical/physical trends across the table (easy to say now, but you must remember Dmitri was working in 1869). And as he predicted, gallium was identified by spectroscopy, a technique developed by Bunsen and Kirchhoff in whose laboratory Dmitri had studied and perhaps gained

... Mendeleev was a great writer, able to quickly put pen to paper and publish his results.

insights on how important the technique would be. He would, however, continue to push his luck, not 'being happy' with Lecog's initial determination of gallium's density of 4.7 g/cm³, writing to him insisting that the density should be around 5.9 as determined from his desktop calculations. Lecog must have been surprised but rechecked his density - sure enough, he had been mistaken and revised his figure to 5.935. very close to the one Dmitri predicted (the currently accepted value is 5.904 q/cm³, which is even closer to Dmitri's prediction). The scientific world began casting its gaze to St Petersburg.

Dmitri had to wait another four years (1879) before Swedish chemist Lars Fredrik Nilson and his team discovered scandium and until 1886 for German chemist Clemens Winkler to discover germanium. Both these elements had properties close to those predicted by Dmitri for eka-boron and eka-silicon. Some of his predictions Dmitri would not bear witness to: hafnium, the analogue of titanium and zirconium of predicted atomic weight 180, was discovered in 1923 (atomic weight 178.5), 16 years after his death from influenza.

It was not until the work of English physicist Henry Moseley in 1913 that it

Properties of eka-aluminium (as predicted by Mendeleev) and gallium

Property	Eka-aluminium	Gallium
Atomic mass	68	69.723
Melting point (°C)	low	29.76
Density (g/cm³)	5.9	5.9
Oxide formula	Ea ₂ O ₃ (density 5.5 g/cm³) (will dissolve in acids and alkalis)	Ga ₂ O ₃ (density 5.88 g/cm ³) (dissolves in acids and alkalis)
Chloride formula	EaCl ₃ (volatile)	GaCl ₃ (volatile)

A scorecard for Mendeleev's element assignment in which the 1869 ordering is transposed to the present-day format. The last row of the periodic table (atomic numbers 87–118) and the lanthanoids/actinoids are not shown because they were largely unknown at the time.

was understood that the periodic table was ordered by atomic number (the number of atomic neutrons), which follows, in most instances, atomic weight. There are so-called inversions where (rarely) the order of the elements given by atomic number does not follow the order by atomic weight, due to an unusual distribution of isotopes in one of the pair of elements, boosting its (average) atomic weight. One such inversion is tellurium/iodine where iodine is of higher atomic number but lower atomic weight than its atomic number predecessor tellurium. Dmitri incorrectly questioned the atomic weight of tellurium, but impressively 'stuck to his guns' and was correct to swap the order between it and iodine to keep each in their correct 'chemical families'. Another inversion occurs with nickel and cobalt, with their mixture of isotopes also resulting in their atomic weights being very similar, but inverted. Both display variable valencies, with 2 being common, making them difficult to differentiate. It seems that Dmitri in this case wisely did not want to take a risk on differentiating the two, making them equivalent in his first table.

His original table is arranged differently from the present-day format,

where his rows are arranged in columns and his column as rows. The table shown transposes Dmitri's element assignment and notation to the current periodic table format, with Dmitri's original rows labelled alphabetically in both figures so they can be cross-referenced. The success of each of Dmitri's elemental orderings is colour-coded so he can be given an overall 'scorecard'.

From the number of red highlighted elements, it is evident that Dmitri's table was far from perfect. He seems to have had difficulty in correctly identifying the members of the Be group IIA and Zn group IIB elements, placing zinc and cadmium in group IIA and calcium and strontium in a separate group. It is for this reason that some sources claim that Dmitri's prediction of scandium is a lucky guess, but Dmitri's strategy of requiring a valency 3 element before the adjacent valency 4 element titanium was correct. The grouped elements nickel and cobalt are in the correct region of the periodic table, as is the following element Pl (the original symbol for palladium).

Many of the higher atomic weight elements are mis-assigned, perhaps because they display multiple valency states, which makes them difficult to categorise. In his 1871 table, Dmitri adopted a configuration similar to today's, where he backed away (mistakenly) from his hafnium prediction but made several other predictions about the existence of new elements. Some of these were correct, e.g. technetium not officially discovered until 1937, once again after Dmitri's death, by Italian scientists Emilio Segrè (physicist) and Carlo Perrier (mineralogist), while other predictions of the lanthanoid/actinoid family were, perhaps understandably, not correct.

His first 'attempt (opyt)' at ordering is, however, remarkable for 1869, as can be seen from the large areas of green in the periodic table scorecard shown. The helium group noble gases, some of which were discovered in Dmitri's lifetime, fitted perfectly into his system. The discovery of periodic properties of groups of elements across rows and down columns of his ordered elements, the four correctly predicted elements and the correct ordering of tellurium and iodine makes Dmitri's first ordering attempt a monumental piece of work.

Alf Larcher FRACI CChem is a petroleum, environmental and industrial chemist with an occasional urge to write science articles. The author has used mainstream references (full list available upon request) from recognised sources.



Telling your story using the powerful STAR formula is all it takes to boost success in job interviews.

nterviews are pretty much the worst way to select new candidates ... apart from all the other ways. That might be a blatant paraphrasing of the famous Churchill quote, but the whole interview process is truly fraught. Myriad studies show how interviews are flawed: from unconscious bias to inconsistency in questioning, 'halo' or 'horn' effects, stereotyping and many other problems. More than one study has shown that the outcome of interviews may be determined in the first seconds of meeting. Your fate might be decided before you even sit down.

Regardless, graduates today can expect to have many jobs over the course of their careers. Most will have many different careers over their lifetimes. And collectively that means plenty of interviews in your future. So developing good interview techniques and an understanding of how you will be evaluated are two very powerful ways to improve your chances of success in getting the jobs you want.

This is what the manager, recruiter or HR person is trying to achieve: they want to find a person who can do the job, will add something to the business, will 'fit' with the organisation quickly, and won't create new problems (such as personality difficulties) that will take up more of their time.

They only need one great candidate, but how can they winnow the field? Resumés and cover letters give very little truly useful guidance – not least because a percentage of those resumés are going to contain a range of big and little 'exaggerations'.

After a shortlist has been made, aptitude and psychometric testing might help to some extent, but that's time consuming and expensive.

For most organisations with limited time and resources that just leaves the interview. That interview has to be as 'standard', fair and perceptive as possible. It has to interrogate hard skills, but just as importantly it has to make judgements on a range of factors that can be only loosely defined. So

most interviewers will use a range of techniques to learn about the candidate, foremost among which is the practice of behavioural-based interviewing.

The basic theory is that the best predictor of a candidate's future behaviour is their past behaviour. It is seldom helpful to ask, 'In a given situation, what would you do?' Instead, the behavioural technique asks a more informative set of questions: 'When you were faced with this type of situation, what did you do? How did that work out? What did you achieve? What did you learn?' The box shows some examples of common behavioural questions.

Some behavioural-based interview questions

'Tell me about a time when you ...'

- had to go above and beyond to get a task done
- had to balance competing priorities to achieve an outcome
- had to achieve an impossible deadline
- had to resolve a conflict with a colleague
- had to work with a difficult colleague or someone you didn't like
- showed initiative in your work
- had to exhibit leadership
- had to be strategic to meet your priorities
- failed at a task.

The benefit to you as the candidate is that you get to talk about your experiences in the best possible light, and in your own words. This isn't just your experiences in career positions, but also at university, in your volunteer work, and in the jobs that you have taken along the way. With choice of which stories you tell, you have a measure of control over the interview.

A 'standard', and very powerful, formula helps to answer these questions. It's called 'STAR stories' structure: Situation, Task, Action, Result. **S**ituation: Describe a situation you were in or task you needed to accomplish.

Task: What goal were you working towards?

Action: Describe actions you took to address the situation. What specific steps did you take and what was your particular contribution?

Result: What was the outcome of your action, what did you accomplish?

The point is that you are going to tell a story about yourself that helps the interviewer understand you better. How do you think? How do you respond to challenges? Are you innovative, entrepreneurial? Are you engaged, committed? Do you take personal responsibility for outcomes, even if it's not in your job description? Do you work collaboratively? Do you learn from your mistakes?

When you look at that list, you can see that it is about how you walk through life, regardless of whether you've even ever worked in a professional/career environment. Taking responsibility, being entrepreneurial and getting along with others when under pressure can happen as well at a supermarket as it can in an R&D lab.

Moreover, you can plan ahead. Just as comedians don't think up their jokes on stage – even for the 'spontaneous' audience interactions – you can think about the stories that speak to your behaviours long before the interview. You can plan the basics of your stories under the STAR structure, and then just 'riff' off those ideas in the interview as you respond to the question variation that you actually get asked.

Start by thinking of some examples when you did something out of the ordinary. When did you earn praise? When did you stand out from your colleagues? When did you think to yourself, 'I did really well there'? What have you done that you are proud of?

Then step through the four letters of the acronym. Build a story, and write it

down. Use action verbs – I arranged, I accomplished, I achieved, I completed, and so on. Talk about your own contribution, even if that was as part of a team – use 'I', not 'we'.

Be specific in your answer. *This* is the task I needed to do. Don't use generalisations. Quantify your outcomes if you can. Be concise – don't wander off into extraneous detail.

Say I am interviewing a graduate candidate whose only work experience is as part of a summer project at university. I ask her to "Tell me about a time when you had to go above and beyond to get a task done." Using the STAR structure, she replies:

[Situation] Last summer, I was one of three assistants working for the Supremium project at the New Element Research Centre at uni. The team was working on a critical experiment that would run continuously for a week.

[Task] The three assistant researchers were tasked with monitoring the equipment in shifts, collecting samples and doing immediate assays. As I could be more flexible than the others, I offered to take the night shift. In my downtime between samples, I was comparing my data to the other assistants', and I found some anomalies that concerned me.

[Action] I decided to re-run both my own samples and those from the last two shifts. The data showed that my shift and the last both agreed, but that some of the assays differed from the morning shift. I then looked through his notes, and found what appeared to be a problem with his methodology. But since we were all still fairly new to this work, I still considered it possible that I could be wrong. So I waited after my shift, and spent a couple of hours working alongside the morning shift assistant so that we could figure the issue out together and make sure that we both had the answer right.

[Result] I was pretty pleased with the outcome. I felt a lot more confident on my next night shift, and I felt that I'd really played my part in some important work.

Consider the messages that this story sends to the interviewer. The

candidate showed willingness to take on the less convenient shift, and she took ownership of ensuring the outcomes for the work. She was diligent enough to check and double check her work, and when she found a potential problem, she wasn't dogmatic. She showed empathy for her colleague by not embarrassing him with his mistake, and she showed the dedication to take the extra time to get the outcome right. Every one of these are behaviours that would recommend her to any workplace.

By contrast, I once asked a student in a mock interview to describe a time when he had to work as part of a team to get a task done. He proudly told me about a time that his group of students had been asked to model three climate change scenarios. The team wanted to model zero change, a moderate and an extreme scenario. However, he insisted that it was pointless to do the zero model 'because everybody knows that climate change is already significant'. The team completed the task and received a good mark.

Listening to that story, the two messages I received were that he was sufficiently intellectually arrogant that he wasn't willing to even consider a position that differed from his view, and in a team scenario he would stubbornly refuse to cooperate until he gets his way. I don't want either of

those behaviours anywhere near my lab. So always stop and consider the subtext. Is your story conveying the message you intend?

Over the course of the interview, your aim is to be the best version of yourself – not misrepresenting, just offering an emphasis on your best qualities. Prior to your interview, consider the qualities that are required by the role, and what you have to offer. What makes you special? That's something that you should know about yourself as a general policy in life.

Ultimately, the key to success in interviews lies in great preparation, open communication and your willingness to articulate what you offer. Do your research, use your networks, and you'll be successful.

The RACI's Career Development Programme offers a range of advice and support to young chemists: webinars, networking events, mentoring, lectures and workshops. The 2020 national mentoring program is open for applications (bit.ly/2mmEVVg). We welcome and encourage participation from students in their final year of study: undergrad or postgrad.

Dave Sammut FRACI CChem and **Chantelle Craig** are the principals of DCS Technical, a boutique scientific consultancy providing services to the Australian and international minerals, waste recycling and general scientific industries.



Interviews 101

There are some simple things that you can get right or very, very wrong in an interview.

- Do your preparation before you go to the interview. Use your research skills and your network to learn as much as you can about the company, the job and the interviewer(s). Make notes.
- Dress appropriately, or just a little conservatively, for the workplace you are going to.
- Turn up on time. Don't be early (wait nearby until it is time to go in), and never, ever be late. Respect your interviewer's time.
- Practise active listening. Be attentive, and confirm by using clarification.
- Remember that an interview is a twoway street. You owe it to both yourself and your employer to make sure that you actually want this job, not just any job.
- Be prepared to ask questions of your own that show you are interested. For example: How is performance measured for this role? What are the attributes of your top performers? What are the one or two key factors that really drive results for the company?
- If you are interested in the role, say so.
 Don't leave the interviewer in any doubt about your enthusiasm. Then follow up with an email thanking the interviewer for their time the basic courtesies are so seldom used that they help distinguish you.

Dave's special tip

Your first inclination is probably to say no to the offer of a beverage at an interview you don't want to inconvenience your host. But consider saying 'Thank you. A water would be lovely.' Take every opportunity to be positive. Simple friendliness and openness will carry you a long way in an interview. Also, the giving and receiving of a small act of hospitality at the beginning of a relationship is a way of creating an initial bond. Most importantly, a glass of water is a really useful prop. You can pause, take a sip, and consider your response to a difficult question. In this way, you maintain your poise, rather than filling the void with a vacant 'ummmmmm'.

Periodic table chart collaboration for nationwide distribution

The RACI has partnered with Haines to develop a periodic table chart for distribution to schools nationally. The periodic table is a touchstone as a learning tool for chemistry. But with new elements added as recently as 2016, many of the posters hung in classrooms around Australia are out of date.

Haines is an Australian owned and operated business supplying school science equipment. Haines is committed to supplying educational resources that are relevant to the Australian science and maths curriculum and in principle are engaging for students.

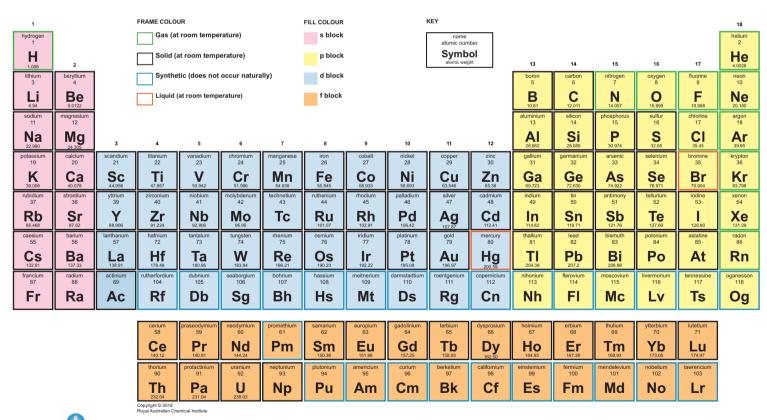
Haines surveyed professional chemistry educators on the resources they required to complement their craft and support state curriculum, while engaging their students. It was highly endorsed; educators required a large periodic table that was up to date and could be visible to all students in the classroom.

The chart features the elements up to oganesson. The usual information on names, symbols, atomic numbers, atomic masses and group numbers is available. For the discerning students, the chart is colour-coded by block, with an additional coloured box to designate the physical state of each element at room temperature. The periodic table chart has been produced to a size that it is visible from the back of the classroom to assist with student engagement and learning.

This is an exciting partnership for the RACI as we achieve our mission to improve the quality of life through leadership in the field of chemical sciences. We hope that this chart will spark the imaginations of students and ignite in them a lasting love for chemistry.

The periodic table chart is available to purchase through the Haines website, haines.com.au.

Periodic Table of the Elements











RACI puts the spotlight on chemistry

To celebrate the International Year of the Periodic Table (IYPT) with our community and to promote the chemical sciences to the general public, it was with great pleasure that the RACI held an IYPT Expo during National Science Week on Sunday 11 August in Melbourne.

The expo took shape by contributions of RACI member volunteers with the objective of visitors leaving the expo with the knowledge that chemistry plays a central role in our lives.

Gaining media attention in the lead-up to the expo with a feature article in *The Age*, the expo drew a crowd of more than 600 attendees. On the day, crowds gathered to experience the wonders of chemistry.

Catering to all ages, the expo delighted and engaged all with a range of activities. One activity included the elements of light, where visitors explored how chemistry can produce light and colour. For the young and young at heart, volunteers demonstrated a range of chemistry reactions, including how to make slime and transform everyday kitchen ingredients into a fizzy sherbet.

Professor Stuart R. Batten FRACI CChem, who has spent many months collecting element sets for schools around Australia, showcased his personal collection. The crowd was delighted to see and handle his pure element samples, a unique experience for all.

Visitors were put to the challenge with a chemical element scavenger hunt. The scavenger hunt required visitors to search for items containing the elements based on the provided clues. If successful, they were awarded a certificate and element hadge.

We ended the day with local five-year-old chemistry aficionado Maximus. Maximus wowed the crowd with his recital of all 118 elements on the periodic table.

More than 80% of responded attendees would attend the expo if it became an annual event. One attendee commented, 'The presentations were a good time length to move through the expo and allow others to move through at the same speed. The scavenger hunt was fun and the certificates and badges and posters are proudly pinned up at home. It was a great start for science week which both my boys are celebrating at school and kinder this week. Thank you to hosting this'.

This day would not be possible without RACI volunteers, who made the day such a success not only by volunteering their time but also by engaging visitors in the wonders of chemistry and getting visitors excited about chemistry.

As we approach 2020, we look forward to continuing to provide further outreach activities to further promote and engage all in the chemical sciences.

New Fellow

Edith Chow has more than 15 years' experience as an electroanalytical chemist developing chemical sensing systems for environmental, food and health-related applications. She received her BSc(Hons) in Chemistry (2002) and PhD in Chemistry (2006) from the University of New South Wales. Her PhD was supervised by Professors Justin Gooding and Brynn Hibbert and involved the development of peptide-modified biosensors for the electrochemical detection of heavy metal ions. She published 14 papers as a result of her PhD.

Following graduate studies, Chow held a postdoctoral fellowship at CSIRO, under the leadership of Dr Burkhard Raguse. As an electroanalytical chemist, Chow applied her expertise to the field of nanotechnology to co-invent a gold nanoparticle chemiresistor sensing system for trace analysis of organics. The success of this platform technology saw her promoted to research scientist in 2008 and senior research scientist in 2010. Chow has

led both strategic-based and industryfunded research projects to enable improvements to the technology and the realisation of a field monitoring device. She was a visiting scientist at Stanford University, working with Professor Zhenan Bao in organic electronics, where she developed carbon nanotube-based transistors for biosensing applications. Chow also has a strong interest in paperbased electrochemical and colorimetric devices as low-cost sensing platforms. She has collaborated with universities and supervised two honours students and one PhD student to completion.

Chow is a strong advocate for chemistry through her involvement in STEM Professionals in Schools and the National Youth Science Forum. In particular, she has been a strong role model for women and girls in her field. She has partnered with many schools to devise fun science activities and has encouraged girls to pursue careers in STEM. She is a sought-after speaker at career and panel events.



Chow's excellence in science and communication has been recognised through numerous awards, including a CSIRO Julius Career Award (2010–12), NSW Young Nanotechnology Ambassador (2010), NSW Young Tall Poppy (2015) and UNSW Alumni Award in Science & Technology (2019). She has been on the organising committee for several conferences, and has presented invited talks both nationally and internationally. Outside of work, Chow enjoys spending time with her family, hiking, photography and good food.

Liversidge Medal awarded to polymer chemist

Professor Martina Stenzel (University of NSW), an expert in polymer chemistry, is the first woman in almost 90 years to be awarded the Royal Society of NSW's Liversidge Medal. The science prize recognises Australian scientists who have made an outstanding contribution to chemistry research.

Stenzel is widely regarded as a global pioneer in the application of novel polymer architectures. By developing chemical techniques for new polymer architectures, Stenzel is creating 'smart' nanoparticles for drug delivery that are revolutionising the way disease is targeted and treated.

Her work focuses on the fundamental processes that underpin nanoparticle design to make them suitable for the delivery of proteins, DNA or metal-based drugs to treat cancer – specifically ovarian and pancreatic cancer.

Stenzel said she hopes her award will

encourage more women to enter the

fields of chemistry and physics.

As Co-Director at UNSW's Centre for Advanced Macromolecular Design, Stenzel leads a team of 20 researchers working to combine synthetic polymers with nature's building blocks such as carbohydrates, peptides and proteins. The team works at the intersection of polymer science, nanoparticle design and medicine.

The creation and adaptation of nanoparticles for various biomedical applications is the focus of Stenzel's current research. By designing nanoparticles of different shapes, sizes and surface functionalities the nanoparticles can then be 'loaded' with various drugs, mimicking a water-filled sponge.

'The beautiful thing about nanoparticles is that they can be modified in endless ways,' Stenzel said. 'We are trying to better understand the physical properties of these drug-loaded nanoparticles as it is directly linked to the biological activity. The aim is to create nanoparticles with the right



properties that can invade cancer cells but not attack healthy cells.

Stenzel said that while nanoparticles were most commonly used in cancer treatment, they could potentially be used to treat many other diseases, including Parkinson's disease, Alzheimer's, diabetes and infectious diseases.

The Liversidge Medal, awarded every two years, is given on the recommendation of the RACI. Stenzel will give the Liversidge Lecture in February 2020. The lectures are published in the Journal and Proceedings of the Royal Society of New South Wales.

UNSW

Top stories from the periodic table

Storytelling brings people closer together. Conceived by the RACI in recognition of the International Year of the Periodic Table, Stories from the Periodic Table collects, publishes and celebrates the personal connections we have to the periodic table and its elements.

Potassium BY JESSICA McCOURT

At the age of 23, I received a life-changing diagnosis of chronic kidney disease and was told that my kidney function had been reduced to about 20% within a five-year time frame. The level of potassium in my body was high. The kidneys maintain regulation of your body's ion concentration levels. As the disease progresses to an advanced stage, the kidneys lose the ability to do this, and you need to keep your eye on those ions. I can recall looking over results from blood tests and seeing all different names of elements and compounds, with measured numbers, wondering to myself 'what does all this mean?' Interested in gaining a better understanding, I embarked on researching the many functions of those two cherished 'beans' we call kidneys, and six months later found myself sitting outside of a classroom, about to plunge into an undergraduate chemistry bridging course.

Little did I know that the element potassium in its cationic form would be the source of fuel that was about to ignite like a combustion reaction, releasing a large amount of heat that could not be extinguished, kindling a passion for scientific curiosity that would be of great assistance to both my kidney and my academic journey. That consisted of a total of three years until I was blessed by the ultimate heroic act of human kindness someone can give – the gift of life!

I looked down at the periodic table of elements for the very first time, my eyes scanning the physical arrangement and all the different elements on it. A few captured my attention – phosphorus, sodium and calcium – before I observed one that stood out above the rest. There it was, in all its magnificence – potassium, with its elemental symbol K, located in group 1, the alkali metals, atomic number 19 and mass number 39.098 g/mol. I was in absolute astonishment; the connection between chemistry and the vital role it plays in the human body had been established. All my answers to the unanswered questions I had were sitting right in front of me, hidden under the surface waiting to be discovered. To examine all the mysterious secrets that lie within, deciphering the trends of periodicity and how they interrelate to the chemical concepts determining the structure of chemical compounds and their reactivity.

The monument that Dmitri Mendeleev has gifted us, and the scientific knowledge passed down from teacher to student, has





ed Duncal

led to the synthesis of modern medicines that allow me a quality of life that cannot be described with words. When you have a transplant, you must take medicines to 'trick' the immune system. Not all superheroes wear capes; mine wear lab coats.

Jessica McCourt was diagnosed with chronic kidney disease in 2015 and received a kidney transplant in 2018. By day, she majors in organic and medicinal chemistry at the University of Newcastle. By night, she raises awareness of organ donation. Inspired by her experience, Jessica hopes to pay it forward by one day developing drugs that make transplantation possible.

New Periodic Table on Show available

In celebration of the International Year of the Periodic Table in 2019, we are pleased to launch the latest Periodic Table on Show. With new artists' impression artwork completed for elements 112–118 by printmakers Linda Abblitt (113, 115, 117) and Tina Curtis (114, 116, 118), the Periodic Table on Show is now up to date.

RACI Periodic Table on Show posters are now available to purchase online for \$15 plus postage (racichemedcentral.com.au) or discover the science and artists' descriptions at raci.org.au/IYPT.

Manganese

BY IVO ROLF SEITENZAHL

On Earth, chemical reactions occur naturally. However, the conditions necessary to create new chemical elements through nuclear fusion are only found in stars, either during their lives or when they die. Virtually all elements on Earth heavier than boron were made in stars over 4.6 billion years ago, before the Sun and the planets formed.

I work in the field of explosive nucleosynthesis: I study how heavy elements are created in supernova explosions, when thermonuclear fusion turns carbon and oxygen into heavier elements. I think about the synthesis of elements such as silicon, iron or nickel on an almost daily basis. It's hard to make a choice, but when hard pressed about my favourite element, it would have to be the element with atomic number 25: manganese.

Manganese is monoisotopic – it has only one stable isotope, ⁵⁵Mn. In and of itself that is nothing special, as it shares this property with 25 other elements. However, this means that when we see the element manganese, we know for sure which isotope it is. We can then use this information to learn more about the kind of stars that explode as thermonuclear supernovae.

Manganese is synthesised almost exclusively when its 'radioactive grandparent' ⁵⁵Co decays. With a half-life of about 17.5 hours, ⁵⁵Co decays to ⁵⁵Fe, which in turn decays to ⁵⁵Mn with a half-life of about 1000 days. However, not all ⁵⁵Co will become manganese. The problem is that ⁵⁵Co likes to capture a proton to turn into ⁵⁶Ni. If this happens, then the ⁵⁵Co is destroyed and no manganese is produced, as ⁵⁶Ni eventually decays to stable ⁵⁶Fe. Therefore, if we want copious amounts of manganese to be synthesised, we don't want too many protons to be around after ⁵⁵Co has been produced.

It turns out that there is a dividing line between producing a lot and very little manganese at a density of about 200 million times the density of water. If carbon and oxygen undergo thermonuclear fusion at a density greater than this, there will be very few protons around, and most of the ⁵⁵Co produced is free to decay to produce manganese. Conversely, at lower densities than this, most of the ⁵⁵Co will capture protons, turning into ⁵⁶Ni, with little manganese produced.



The density of the exploding carbon and oxygen in a thermonuclear supernova is related to the mass of the star that is exploding. While most astronomers agree that the stars that explode as thermonuclear supernovae are so-called white dwarf stars, the masses of the stars that are exploding are very much debated.

To help solve this debate, my work has used the observed abundance of manganese relative to iron to conclude that approximately half of these supernovae arise from the incineration of very compact and dense white dwarf stars near the Chandrasekhar-limit, ~1.4 solar masses. So if you ever wondered where most of the approximately 12 milligrams of manganese in your body came from, now you know!

Ivo Seitenzahl is interested in how elements are created in nuclear fusion reactions when supernovae explode. He grew up in Germany, spent 10 years studying astrophysics in the USA, and eventually emigrated to Australia as a postdoctoral researcher. He is now an ARC Future Fellow at UNSW Canberra. When he isn't studying stellar explosions, he raises plants, ducks and his three young children.

Recipients of PM's Prizes for Science 2019

The RACI warmly congratulates the following RACI members, who were announced as recipients of Prime Minister's Prizes for Science in October.

- Professor Elizabeth New FRACI CChem was awarded the Malcolm McIntosh Prize for Physical Scientist of the year 'for pioneering imaging tools that allow scientists to see deeper into cells than ever before'.
- Professor David Huang FRACI CChem, Professor Guillaume Lessene FRACI CChem, Associate Professor Peter Czabotar and Professor Andrew Roberts were awarded the Prime Minister's Prize for Innovation 'for their roles in inventing, developing and commercialising a breakthrough anti-cancer drug'.

Poems from the periodic table

To celebrate the International Year of the periodic table, Double Helix magazine ran a poetry competition for school-aged students with support from RACI. Here are the winners as judged by Michelle Neil FRACI CChem.

Winner: Primary school category

Calcium By Daisy Herr, age 10

Calcium is a metal with the atomic number twenty, you might think that it sounds boring, but you'll soon see it does plenty.

This element, sometimes referred to as 'the scaffolder', holds things up, from bones in our bodies to buildings much older.

Most of the calcium in my body is in my teeth and bones, I got it from eating dairy – milk, cheese and ice-cream in cones

My body uses it for other things, it helps my muscles grow,

it's also a clotting factor, so when I get cut my blood doesn't flow.

It's the fifth most abundant element in the Earth's crust, it's in limestone and marble.

that means calcium is in David, the Sphinx, the Taj Mahal and other marvels.

It's used in many things – wax crayons, plastics, toothpaste and cement,

fireworks, fertilisers, cosmetics and lights that are fluorescent.

2019 is the International Year of the Periodic Table, so I say thank you calcium for beautiful buildings and keeping us stable.

I loved this poem as it explained how the element of calcium (Ca) was relevant to the author's everyday life as well as being in many other of the world's marvels. I was also impressed with how the author mentioned the International Year of the Periodic Table in a poem! Well done!' says Michelle.

Winner: Secondary school category

A Periodic Poem By Sam Lang, age 15

The Periodic Table; sorting all known elements. In different groups and periods, so finding one makes sense,

They all have different isotopes and radioactivity ...

These building blocks – what are some uses that we can easily see?

Hydrogen (H), as rocket fuel, can fly us into space. Beryllium (Be) helps keep nuclear fission in its place. Helium (He) has many uses, from welding to balloons, and living things need carbon (C) — morning, night and noon.

Argon (Ar) gas is used in lights, which pushes back the dark.

while fluoride (F) in our toothpaste lets us fight off dental plaque.

Our devices with us daily, have lithium (Li) batteries, and potassium (K) found in most our soils, supports the plants and trees.

Whether natural or synthetic, solid, liquid, gas, all in the Periodic Table – ordered by atomic mass.

'This poem stood out for me as the author told us of how not one, but eight elements are used in everyday life. Did you know that potassium (K) is found in most soils and is used to grow healthy plants, which in turn we eat to keep us healthy? No? Now you do!' says Michelle.

To find out more about *Double Helix* – CSIRO's magazine for young readers – visit www.doublehelix.csiro.au.

William Ivo (Bill) Whitton Advocate for scientific and industrial research

Australia has lost an indefatigable advocate for scientific and industrial research. Bill Whitton was born in Sandringham, a bayside suburb of Melbourne, on 4 October 1924 and died in Melbourne on 25 August 2019. His father was Ivo Whitton, the only amateur golfer to have won the Australian Open five times (1912, 1913, 1926, 1929 and 1931).

Bill completed a BSc in Chemistry at the University of Melbourne in 1944 and enlisted in the Australian Imperial Force on 24 February 1945. After basic training, he was sent to the School of Military Engineering as a student attending the Potential Officer Course. He left the AIF on 19 November 1945 with the rank of Acting Lieutenant, and resumed his studies at the University of Melbourne.

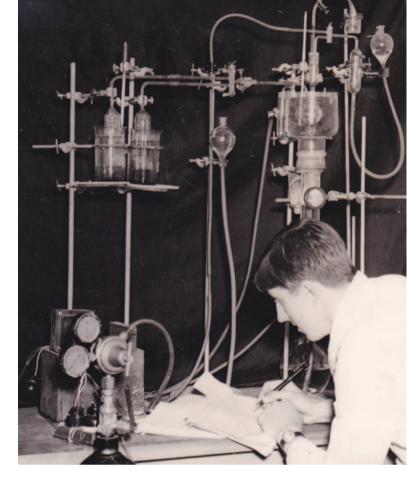
His choice of a topic for his Master's thesis exemplifies his lifelong commitment to applications-oriented research. The thesis commences with an explanation of why the work was started: 'On the 20th August, 1945, four of the crew of the S.S. Samarkand, berthed in Geelong, died after entering a deep tank on that vessel.' Mr G.A. Ampt, Bill's Master's supervisor, had done some preliminary experiments for the coroner and found that the corrosion of iron would absorb all the oxygen in the tank. Bill's thesis gave a sound scientific basis to this finding.

He chose the University of St Andrews, Scotland, for his PhD studies. He was a fine golfer and was attracted to its proximity to the famous golf links, although he studied at the University College in Dundee about 18 kilometres away. His PhD topic was the more academic 'The thermodynamics of adsorption and hysteresis'.

He married Elizabeth Hunter on 7 September 1951 at a ceremony at the Savoy Chapel in London.

He took up a position in the Research Department of ICIANZ in 1952 and worked there until 1959 when he was appointed Technical Manager and Director of ICI(NZ) Ltd. He returned to Australia in 1963 as Research Manager ICIANZ Ltd. During this period, the ICI ANZ Research Laboratories at Ascot Vale were responsible for a number of internationally significant research achievements, including inventing the flame ionisation detector for gas chromatography, a new route to manufacture vinyl chloride monomer via the oxychlorination of ethylene, and the first economic synthesis for an internationally important veterinary drug tetramisole. Bill was an executive director of ICI Australia Ltd from 1970 to 1982.

It was during this time that he became an active participant in discussions on developing a science policy in Australia. His 1972 paper in the ANZAAS journal *Search* is still worth reading today. He reminds his readers that the quest for a science policy commenced with Federation and that one of the early advocates, the Victorian Public Works Minister F.W. Hagelthorn,



'was especially interested in the development of primary and secondary products through science, and co-operation of academics and industrialists'. Bill then adds a characteristic comment 'I don't think this has been achieved either.'

He joined CSIRO as the Director of the Institute of Industrial Technology in 1983 and had the opportunity to 'work from the other side'. At that time in the organisation's history, the role of the institute director was still being developed and he did not achieve as much as he would have liked before ill health resulting from his climbing adventures in Nepal forced his early retirement.

He became an Associate of the RACI in 1948 and a Fellow in 1959. He was very active in the formation of the Australian Academy of Technological Science (now the Australian Academy of Technology and Engineering) and was a Foundation Fellow in 1977.

In 1964, a group of managers of Australian industrial research, including Bill, decided to meet on a regular basis to improve the quality of research management in Australia and stimulate and develop an understanding of research as a force in economic, industrial and social activities.

This was the start of the Australian Industrial Research Group of which Bill was the second president from 1968 to 1970.

Bill became a member of the Royal Melbourne Golf Club in 1946, was the Club Captain from 1991 to 1994 and was made a Life Member in 2005.

He is survived by four children and four grandchildren.

Tom Spurling FRACI CChem and Phil Weickhardt FRACI CChem

Chemistry for \$5 a read

Charing Cross Vinnies in Sydney has one of the largest and best selections of preloved books (outside Lifeline stores) I have encountered. (In this age of self-funded retirement, haunting such outlets becomes a rewarding pastime.) These books tend to have highly attractive titles that must lure the locals into buying them, only to find they are stocked with (shock, horror) chemistry. Thus, many are discarded in pristine condition.

Some of these have authors I had never heard of, I soon realised their potential for seducing unsuspecting students into giving chemistry, at least initially, a fair go.

A is for arsenic: the poisons of Agatha Christie Katherine Harkup, Bloomsbury, 2015, 320 pp.

Few novelists other than Christie can claim to have been read by pathologists as reference material for real poisoning cases. Her knowledge came from direct experience with poisons and a lifetime interest in the subject, though not as a practising murderer.

The author, Karthryn Harkup, an English chemist, did her PhD on the chemistry of phosphines but after postdocs she decided to take her hand out of the fume cupboard and put it to the keyboard to write this fabulous book.

Her chapter structure is as follows: A is for Arsenic, B is for Belladonna, C is for Cyanide, D is for Digitalis, E is for Eserine, H is for Hemlock, M is for Monkshood, P is for Phosphorus, R is for Ricin, S is for Strychnine, T is for Thallium and V is for Veronal.

In her introduction, Harkup discusses Christie's long career and how she became an expert in poisons. She analyses Christie's style, showing how she broke all the rules accepted by crime writers at that time.

Harkup also breaks her chapters into sections (as follows) rather than having a free-flowing prose. She discusses the poison, its history, its chemistry and then its medical properties. This is solid stuff.

She follows this with real-life criminal cases that may have influenced Christie's choice for particular books. Finally, she outlines the way Christie handles the relevant stories.

There are two appendices. The first is an 18-page table that lists 18 Agatha Christie novels and short stories in order of

publication, and the cause of death in each of them. The method of death is annotated as to whether it was suicide, medication withheld, 'attempted murder' or whether an invented drug was used. The second appendix provides a selection of the chemical structures used in the book so that they can be compared for similarities and differences. A complete set can be found at

https://harkup.co.uk/index.php/writing/a-is-for-arsenic.

Then follows a selected bibliography of forensic science and other more popular publications, including some revealing how Harkup obtained all this information.

There is a good index.

My impression is that Harkup's PhD may have been a lot easier than researching and certainly writing this book!

The disappearing spoon

Sam Kean, Black Bay Books, 2011, 390 pp.

The disappearing spoon, by American Sam Kean, also sounds like a detective novel and does dazzle you with 'true tales of madness, passion, adventure betrayal and obsession, as well as, en passant, the history of the periodic table'.

Unlike Harkup, Kean is an established science writer published in prestigious US magazines, so on commencing his book he had a database of the research from his day job at his

It has 30 pages of 'notes and errata' backed up with more updated information on a website. There is a Reading Group Guide that includes 'A conversation with Sam Kean', followed by 'Questions and topics for discussion'.

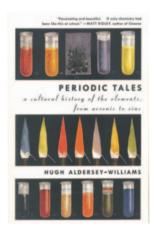
This makes it a soft sell for hesitant potential students and some more hesitant teachers. It is a very readable exposition.

Periodic tales: a cultural history of the elements, from arsenic to zinc

Hugh Aldersey-Williams, Harper Collins, 2011, 420 pp. Englishman Hugh Aldersey-Williams is the author of numerous books on architecture, design and a few, like this one, related to science.







I find his literary style an absolute delight. Reading this is unlikely to seduce you into exploring chemistry much further, but it makes a convincing case that chemistry has made a fascinating contribution to our history and culture.

The chemist's English

Robert Schoenfeld, Wiley-VCH, 1985, 173 pp.

Are you now inspired to start your own popular writing career? If so, have I got a book for you! By an Australian! And by a chemist!

The chemist's English was written by a national treasure, the much-loved late Robert (Bob) Schoenfeld, an erstwhile member of the RACI. Schoenfeld's book, now in its third edition, consists of a collection and revision of 30-plus articles, published in the Proceedings of the Royal Australian Chemical Institute (forerunner of Chemistry in Australia). Bob wanted to give his devoted readers an appetite for good English rather than teach it.

The style is such that each chapter with its heading could morph into an airport novel. I'll take one relevant to the final book I discuss: Chapter 6, 'Amazing revelations: English scientists secretly practice German vice!'

The vice is assembling a sausage-string of nouns and running them together to form a supernoun. In chemists' English this is a 'noun agglomerate assembly mania'. The German language, at least, admits only nouns, whereas we chemists throw in a few adjectives to lengthen the chain. But we at least leave spaces!

When chemists turn the spaced sausage into an acronym, only the inner cabal can understand to what we are referring. As Schoenfeld tells it, 'That Fellow Acronym He All Time Make Trouble'.

A nice finale to this summary is Chapter 20, 'An Investigative Examination of Driveliferous Jargonogenesis'. Citing the opening paragraph of a paper in a computer science journal, Schoenfeld says:

... the authors can do much better when they want to; they are, in fact, amongst the world's leading specialists in the art of compressing information ... why this lengthy, nebulous opening paragraph?

The answer is, surely, that there are occasions when we feel that jargon is demanded of us. The problem of jargon is a social one rather than one of syntax.

Schoenfeld's book will alert you to such pitfalls, help you write clearer scientific papers and perhaps referee those of your colleagues. If you want to switch to writing for the general public, it will make you even more aware of how much your style will need to change.

The 'German vice' leads me to my last book, which recalls my bilingual upbringing.

Schottenfreude: German words for the human condition

Ben Schott, Text Publishing, 2013, 96 pp.

I didn't find this book at Vinnies, but remaindered in our august National Library of Australia's bookshop, at a price quadruple that of my usual outgoings.

Schott makes a virtue of the 'German vice' because it can help us succinctly describe modern issues or (as it does in science) technologies. Even Schoenfeld admits this. So enjoy *Leertretung* (stepping onto a stair that's not there) or *Kraftfahrzeugsinnenausstattungsneugeruchsgenuss* (enjoying a new-car smell).

It is not clear which words are in use or which Schott has invented; I suspect most are the latter! However, each word has a fascinating literary accompaniment.

More about these books

There are many online reviews of the books I have discussed. The review to consider depends on whether the book is for your children, arts students, science students or the general public. A is for arsenic:

www.theguardian.com/books/2015/sep/05/agatha-christies-poisons-crime-fiction

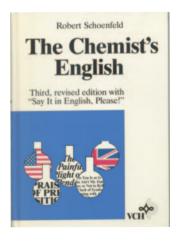
Periodic tales:

www.publishersweekly.com/978-0-06-182472-2 www.iecsi.org/buchnotes-12-2014.html

The chemist's English:

https://pubs.acs.org/doi/pdf/10.1021/ed064pA173.1

Ben Selinger FRACI CChem





Beyond chemistry: George Orwell and 1984

Just over 70 years ago George Orwell's book *Nineteen eighty-four* was published and is now recognised as a major classic of dystopian fiction. Those of you who have read the book will remember Orwell's then seemingly prescient visions:

The Party, the Ministries of Peace, Love, Plenty and Truth,
Newspeak and the Telescreen, which could never be turned off.
Already, there were signs of their advent. Today, in one form or other, we are surrounded by real manifestations of those visions, yet 1984 arrived and ended much like the Y2K problem, with much concern expressed but no significant impact.

Nevertheless, many people, myself included, recognise a growing movement that enables social control to be exercised through disinformation (or withholding of information) and surveillance, and that is of concern.

But what, you might ask, has George Orwell got to do with *Chemistry in Australia*?

In the January 1984 issue of *Chemistry in Australia*, I wrote an editorial entitled, 'Futurology, From Prophecy to Rational Prediction'. It began by noting that it was 34 years ago that month since George Orwell had died in London, just seven months after his satirical novel *Nineteen eighty-four* had been published and achieved immediate acclaim.



George Orwell c. 1940. Cassowary Colorizations/CC BY 2.0

Since that time I have learned much about George Orwell: to begin with his name was not George Orwell at all, that was his nom de plume. His real name was Eric Blair. In Australian vernacular Blair/Orwell might be described as a 'knock about bloke'. He was born in India and educated at Eton. For six years he served in the Indian Imperial Force in Burma. He then lived for two years in Paris, before returning to England as a schoolteacher. Later he worked in a bookshop (see below and opposite). In 1937, he went to Spain and fought with the Republicans in the Spanish Civil War. During World War 2, he was a member of the (UK) Home Guard and worked for the BBC. Subsequently, he wrote for several newspapers in England, and for a time was a special correspondent in France and Germany. George Orwell is also credited with coining the term 'Cold War' to describe the standoff between the Soviet Union and the USA, in a 1945 essay entitled 'You and the atomic bomb'.

When we visited family in Hampstead (London), we sometimes had coffee at a shop on the corner of Pond Street and South End Road NW3. One day I caught sight of a plaque on the wall of the building which states: 'George Orwell Writer 1903–1950, lived and worked in a bookshop on this site 1934–1935'.

In the cover story of *Review* in *The Weekend Australian*, 8–9 June 2019, corresponding with the 70th anniversary of publication of *Nineteen eighty-four*, Rosemary Neill examined aspects of Orwell's life and writing, and the reaction of others to it, in particular the claims that *Nineteen eighty-four* borrowed from an earlier dystopian novel, *We*, by the Russian author Yevgeny Zamyatin.

Neill discovered in her extensive research that as early as 1954, Isaac Deutscher suggested that Orwell had taken Zamyatin's plot, characters and some themes and used them without attribution. Surprisingly, it caused little reaction at the time. But, as always, there are two sides to an argument. In his

Neill discovered in her extensive research that as early as 1954, Isaac Deutscher suggested that Orwell had taken Zamyatin's plot, characters and some themes and used them without attribution. Surprisingly, it caused little reaction at the time.



This plaque in South End Road, London, marks the site of a former bookshop where George Orwell worked and lived in the 1930s. The plaque was defaced and has since been restored.

2019 book, *The Ministry of Truth – a biography of George Orwell's* 1984, Dorian Lynskey absolves Orwell of overt plagiarism, although conceding that Orwell was clearly influenced by Zamyatin. Other writers inspired by *We* have dutifully acknowledged the source of their inspiration.

But author and blogger Gabriel Valjan sees it the other way in his 2013 blog comparing the novels of Zamyatin and Orwell. He also told Neill that he strongly believed that an author should be obliged to make some kind of acknowledgement that certain aspects of a work have been 'borrowed'. He went on to say that to claim Orwell's borrowing was 'no big deal' is simply being disingenuous. It is probable that living modern-day authors, when copyright law is more widely understood and administered, would be sensitive to even the slightest hint of plagiarism.

Orwell's name has been perpetuated in the adjective 'Orwellian', especially in reference to totalitarian development of a state. Duncan Fine, a Sydney lawyer and columnist for *The Age* wrote recently about the introduction of security guards at AFL football matches in Melbourne, an act he described as 'at once menacing and also meaningless'; to which might be added, 'Orwellian'.

Orwell's name has been perpetuated in the adjective 'Orwellian', especially in reference to totalitarian development of a state.

On 21 August 2019, David Streitfeld wrote in the New York Times International Edition under the headline 'Orwell didn't write that (the typos give it away)' that a well-known American online retailer has been selling counterfeit Orwell books, possibly as many as 13 titles, including Nineteen eighty-four. These fake books can easily be recognised by their amateurish cover designs and poor-quality printing and often are full of typos. The publishers of these books are taking advantage of Orwell's continuing good reputation, seeking to seize a share of the market from his (genuine) books, which continue to sell well. Some fake authors claim to improve the original text (but Orwell was recognised as a master of the English language). Others are just blatant 'knock-offs', ignoring copyright, or are published in countries where the books are not copyright.

The large American publishers and their trade group are working to address this problem, but because of the way the book trade works, it is complex and difficult. The online retailer referred to above has removed the offending titles from their lists.

P.G. Lehman FRACI CChem

This column features the learning of chemical professionals about a subject outside their area of expertise. Readers interested to contribute are invited to contact the Editor (wools@westnet.com.au) for further information.



Peter's learning list

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Fine D. Op-ed, The Age, 19 June 2019.

Streitfeld D. The New York Times International Edition, 21 August 2019, p. 1.

Metals I have known

As we come to the close of the International Year of the Periodic Table, this column is a reflection on the metals in wine with which I have worked over the last 35 years or so. The column interfaces with 'Elements of wine' on page 37. The metals are discussed here in order of their atomic number.

In the early 1990s, there were claims that wine contained toxic levels of **aluminium**. A survey showed that white wine contained on average a higher Al concentration than red wine. Bentonite, used in white wine production to assist in achieving protein stability, was identified as a source of Al. The acidity of wine is such that the passive oxide layer on aluminium metal is removed, leading to its dissolution. The origin of the extremely high Al concentration in one wine was traced to the remains of an Al ladder that had been left in the tank after cleaning! Al in wine is tightly bound to anions of tartaric acid and citric acid, which raises the issue of its bioavailability. But interest in Al toxicity of wine faded, so we did not pursue the study any further.

The interest in **potassium** is linked to the precipitation of potassium hydrogen tartrate, which, when it occurs in bottle, can give the appearance to consumers of glass shards. While the precipitation process is fairly well understood, a simple routine analytical measurement of K was not readily available. So, we developed a procedure using a K ion selective electrode (ISE). However, the uptake by wineries was slow, with winemakers expressing concern that 'an electrochemical method is not appropriate in wine laboratories', undoubtedly without realising how pH is measured.

The precipitation of **calcium** L(+) tartrate is an insidious process, sometimes occurring after the wine is bottled and in the marketplace. Using a Ca ISE, we were able to show that molecular calcium tartrate exists in wine, adding to the complexity of establishing a simple precipitation model. Several wine components inhibit the precipitation process, the most efficient of which is the acidic polysaccharide rhamnogalacturonan I. Rhamnogalacturonan I is a component of pectin, but unfortunately it is broken down by pectolytic enzymes used in wine making. A range of other precipitation inhibitors are available commercially.

Iron contamination of wine is minimal, although traces are sufficient to cause oxidative processes, especially when light exposure occurs. Iron(III) tartrate is photoactive, which can lead to enhanced colouration in bottle, especially in clear or pale green bottles. Fe mediates the degradation of tartaric acid into glyoxylic acid that links catechin-type phenolic compounds, with consequent colour enhancement. Fe speciation, both chemical and oxidation state, remains a challenge to be resolved.

Copper is the one metal with which I have had a love—hate relationship over the last 35 years. I have written frequently about Cu in these columns and so will not repeat much here. Its chemistry is highly complex because it has the ability to mediate oxidative reactions and is associated with the removal and reformation of sulfidic off-odours. Use of stripping potentiometry has been a boon in aiding our understanding because the direct probe into wine allows a direct measure of labile and non-labile Cu and identifies the importance of sulfide in influencing the labile concentration. Nanoparticle tracking analysis led us to an understanding of the frustrations of removing copper sulfide by membrane filtration. The next step is to relate our existing knowledge to the control of copper-induced spoilage.

One of the more fascinating issues that I have encountered was concern regarding a proposal to construct a crematorium in a major wine tourism region. It was suggested that **mercury** from dental amalgams would be vented to the atmosphere and then taken up by grapes. Putting aside the fact that the amount of Hg that might reach the atmosphere would be negligible, we were able to show that Hg in grape juice was readily removed by yeast cells during fermentation, resulting in a concentration below the level of detection. This was sufficient to calm the concern.

Lead is another metal about which there is considerable emotion in terms of its potential toxicity. The concentration of Pb in wine nowadays is very low, considerably lower than when lead solder or lead lining was used in wineries and miniscule in comparison to Roman times when lead acetate was used as a sweetener. We utilised stripping potentiometry with medium exchange to examine both the total Pb concentration and its speciation. This technique showed that there was essentially no labile lead and the binder was identified as the acidic polysaccharide rhamnogalacturonan. Using classical complexation capacity plots, we determined the binding constant for the Pb/rhamnogalacturonan II reaction. Plots for actual wine samples resembled those for model systems, confirming the significance of this interaction and underscoring its significance in addressing the bioavailability of lead.

I have not given any references here, but would be happy to provide details of the issues that I have discussed. I also acknowledge the contribution of the many co-workers and postgraduate students with whom I have worked over the years.



Geoffrey R. Scollary FRACI CChem (scollary@unimelb.edu.au) has been associated with the wine industry in production, teaching and research for the last 40 years. He now continues his wine research and writing at the University of Melbourne and the National Wine and Grape Industry Centre at Charles Sturt University.

Elements of wine

The main components of wine are water and ethanol, and these typically represent about 98% of a wine's volume. It is the other 2% that contribute to the bewildering range of flavours and styles available to the consumer today. Within this 2%, nearly every known naturally occurring element has been found in at least some wines, at concentrations ranging from parts per trillion for some of the rarer elements, through to hundreds of grams per litre for oxygen. The outside back cover shows a periodic table highlighting the typical concentrations found in wine for each element. Ranges shown are averages across a wide selection of wines; any given wine may not contain all elements indicated.

Modern techniques such as inductively coupled plasma mass spectrometry (ICP-MS) can provide a picture of the elemental make-up of wine and shed light on some of the significant impacts of the 2%. By far the largest elemental contributors to wine are oxygen, hydrogen and carbon, mostly in the water and ethanol components. Unsurprisingly, these elements also make up the bulk of some of the most significant flavour. odour and mouth-feel compounds found in wine, such as the organic acids, sugars, tannins (in red wines) and glycerol. Many of these organic compounds are derived either directly from grapes or by transformation during fermentation of materials found in grapes. Less well known is the surprising impact in wine of the other elements of the periodic table, particularly the metals, which typically represent less than 0.1% of the elemental composition of a wine.

Some of the key impacts of metals in wine are:

- K and Ca influence wine buffering, pH and tartrate stability
- Cu, Fe, Al, Mn and Zn can contribute to the production of unpleasantsmelling volatile sulfur compounds (e.g. 'rotten egg', 'drain' characters) as well as the loss of positive varietal thiols (e.g. 'fruity', 'passionfruit')

... nearly every known naturally occurring element has been found in at least some wines ...

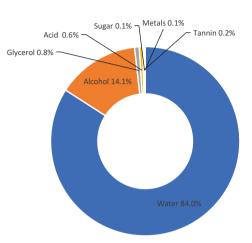
- Cu and Fe in particular are key to oxidation and reduction processes that govern how wine matures over time and the loss of the preservative SO₂ during storage. Mn and Zn can also play a role in wine development
- Cu, Fe, Pb, As, Mn, B and Na have all been involved in wine regulatory issues in certain export markets, an important consideration for Australia, which exports more than half the wine it produces.

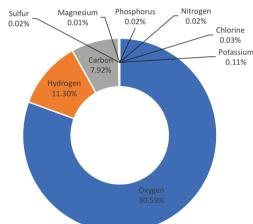
Some of the key sources of metals in wine are the:

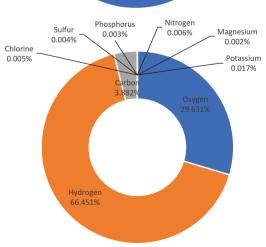
- vineyard: Most metals are found in the grapes, having originated from water and soils. However, some metals, such as Cu, are stripped during fermentation by yeast
- winery: Fe, Cr and Va can come from the stainless steel used in storage vessels, Cu and Zn from old brass fittings. Bentonite fining to remove haze-forming proteins can add Pb, Al, As, Mn, Ca and Na. Cu is often added directly in the form of CuSO₄ to remove unpleasant odours caused by hydrogen sulfide and methanethiol produced by yeast during fermentation
- package: Sn can be contributed by some forms of screw cap liners and Al levels are increased in wines packaged in cans. Glass, surprisingly, does not seem to contribute significantly to Si and B levels found in wine.

All trace metals found in Australian wines are present at levels orders of magnitudes below those considered to have any negative health impacts. They are generally at levels typical of or lower than those found in many other natural foods and beverages.

Eric Wilkes MRACI CChem and **Matthew Wheal** are at the Australian Wine Research Institute.



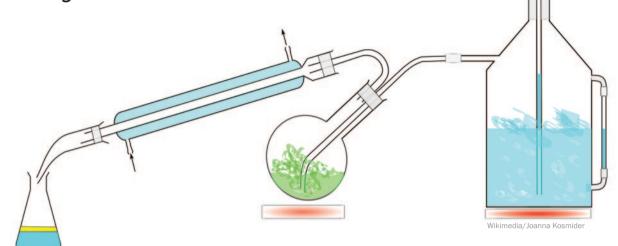




Composition of a typical red wine.
Top: Percentage composition. (White wine composition is similar but generally has a lower alcohol component and very little tannin.)
Centre: Elemental composition by weight.
Bottom: Relative numbers of different atoms of the nine most common elements.

The essence of distillation

Physical chemistry – how the physical properties of substances relate to their chemical make-up – is at work right in front of our noses.



Liquids in a mixture, even if they do not dissolve in each other very much, evaporate together more or less independently, forming vapours.

Eucalyptus and other lovely essential oils (their odour is their essence) would char if heated to boil off the vapour directly because that needs temperatures of 200–300°C. By using steam, the temperature never rises much above 100°C. This protects the oils. The same is true for throwing lavender oil onto a sauna's hot coals, so mix it with water first.

You probably know that most of your taste comes courtesy of your nose. It is less appreciated that evaporating water generally brings the aroma molecules to your nose. The aromas



You could find your local fish and chip shop with your eyes closed. iStockphoto/VadimZakirov

of frying food are released by steam, and freshly brewed hot coffee tastes a lot better than the forgotten, cooled version.

Nothing beats a wood fireplace on a cold winter's evening. Wood contains an awful lot of natural chemicals and they become more awful when heated and charred. Luckily, they have high boiling points and mostly burn close to the red-hot wood. However, if you use unseasoned green timber, the extra water provides perfect conditions for co-evaporation of the nasties that condense in your flue, build up and later catch fire.

One of the anomalies in studies of disease in Vietnam veterans attributed to a dioxin contaminant in Agent Orange is that navy personnel and their passengers have shown an overall higher rate of associated disease than their directly sprayed army and airforce counterparts. A 2002 Australian Government commissioned study (bit.ly/2ZWukQ3), much quoted in the USA, had provided a plausible mechanism for this observation. Distillation removes inorganic contaminants such as sodium, calcium and magnesium salts - but not necessarily organic ones. After all, distilling wine does not produce potable water but instead concentrated, aromatic, more alcoholic brandy, and peat 'contaminated' water is used to make the unique Scotch whisky. The navy's distillation of contaminated saline water increased rather than decreased some of these critical organic chemical contaminants in the resultant drinking water. Today, reverse osmosis is the preferred method of water purification.

Co-distillation can happen at ambient temperatures; it doesn't require boiling. This is pleasant in eucalypt forests here at home, but it can also be disastrous, causing pollutants to spread all over the globe.

You don't need to distil eucalypt leaves to enjoy the wonderful fragrance of a eucalypt forest. The mixture of oil and



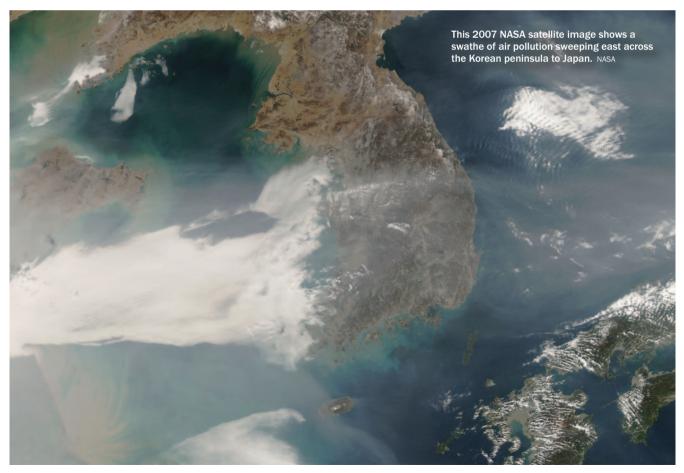
water in the leaves will still co-distil (slowly, continuously) at ambient temperature.

On a global scale, POPs (persistent organic pollutants), such as DDT, PCBs, HCB and many other industrial organic molecules (often chlorinated), were once widely used in agriculture and industry. They are not biodegraded (which is why they were chosen) and have very high boiling points.

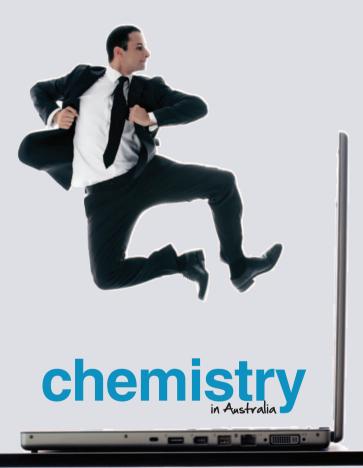
POPs have spread globally to contaminate once-pristine places such as Antarctica. What is true for eucalyptus oil is true

of the POPs, even if they are much less volatile. The process is very slow, but it's been happening for decades. Entering waterways, even if just suspended, gives them a large volume and extensive surface from which to evaporate, and then float off around the planet.

Ben Selinger FRACI CChem is Emeritus Professor of Chemistry at ANU and, along with ANU colleague Associate Professor Russell Barrow, released the sixth edition of *Chemistry in the marketplace* (CSIRO Publishing) in June 2017. For more information, visit www.publish.csiro.au/book/7366.



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Four simple steps and you're up to date. Do it today!





More meaty chemistry

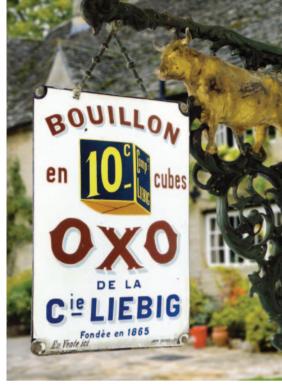
At about the time that I received the LEMCO cook book that I described in my last Letter (September/October p. 41), there were two other events that brought the extract of beef to my attention. The first was a move in 2017 to celebrate the sesquicentenary of meat canning by the Melbourne Meat Preserving Company on the banks of the Maribyrnong (then the Saltwater) River in the western suburbs of Melbourne. The proposed celebration came to nothing but by then, ever diligent, I had done the background research.

I thought the Melbourne company had manufactured the meat extract, but when I consulted an authoritative source – Keith Farrer's A settlement amply supplied (1980) – I saw that only sheep were processed there, and that the beef industry was further north. Meat extract was manufactured by a Mr Tooth at Yengarie, near Maryborough in Queensland in the late 1860s, and by Charles Tindal at Ramornie, near Grafton, New South Wales. Both emphasised the importance of chemical supervision in their industry ... and both were ticked off by LEMCO for illegally using Baron Liebig's name in the designation of their products.

The second event to come to my attention was the publication of a history of LEMCO, written by Professor Lucia Lewowicz, a historian and philosopher of science at the University of the Republic in Montevideo, Uruguay. When she visited the abandoned site of the meat works, where many of the old buildings remain, she was surprised that nobody had taken any interest in its history. Nor could they explain to her why there was a bust of the famous German chemist at the site. These oversights she set out to rectify.

The business, Société Fray Bentos, Giebert et Compagnie, was founded in Belgium in 1866 by German engineer George Christian Giebert and decided to establish their works on land owned by August W. Hoffmann in the newly formed Republic of Uruguay. This was Fray Bentos, on the Uruguay River about 300 kilometres north-west of Montevideo, close to the Argentine border and 160 kilometres north of Buenos Aires that lies on the other shore of the Rio de la Plata across from Montevideo.

Giebert was obviously well-connected to German chemists, since he was also personally known to Liebig. It was from Liebig that they got the process details and permission to use his name on the product, and the company name soon changed to Liebig's Extract of Meat Company Limited (LEMCO). Because so much company information was in German, Lewowicz (whose native language is Spanish) spent some time in Germany learning the language while



she dug into archives in Giessen and Altona (a suburb of Hamburg), following those visits with time in Antwerp and Port Sunlight in England, home of Unilever.

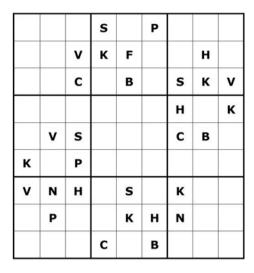
Her book is written in side-by-side columns of German and English, and contains some wonderful photographs. These include some of the colourful postcards in which the company advertised its products. In England, I had purchased the one shown here, and I offered it to Lucia for her archive. She declined gracefully, saying that she already had thousands, but she was pleased to receive that battered copy of the LEMCO cookbook to add to her treasures.

The LEMCO company also marketed another beef extract called Oxo, that was also available in solid form, as shown in the picture. In London, the company had owned a building on the south side of the Thames but when they ceased operating there it was repurposed for retail and commercial activities, including a restaurant entitled The Oxo, which occupied the top floor. I had a wonderful view of Thameside when I dined there some years ago.



Ian D. Rae FRACI CChem (idrae@unimelb.edu.au) is a veteran columnist, having begun his Letters in 1984. When he is not compiling columns, he writes on the history of chemistry and provides advice on chemical hazards and pollution.





Difficulty rating: hard

The symbols for the elements hydrogen, boron, carbon, fluorine, nitrogen, phosphorus, sulfur, potassium and vanadium are used. Complete the grid so that each 3 × 3 box, column and row contains all nine elements.

events

27th R&D Topics Conference

1-4 December 2019 Flinders University, Adelaide, SA www.rndtopics.com

RACI Chemical Education Division Symposium Contemporary Challenges in Chemistry Education: Innovation, Research & Practice

5-6 December 2019, Canberra Institute of Technology, Bruce Campus, Canberra, ACT www.ivvy.com.au/event/CED948

Inorganic19 (IC19)

15-19 December 2019 Wollongong, NSW

www.ivvy.com.au/event/IND895/home.html

Abstracts for Herbicide Discovery & Development 2020

In conjunction with the RACI Synthetic and Organic Group WA 15-17 January 2020, Crawley campus, University of Western Australia, Perth, WA HDD2020.org

20th Australasian Polymer Summer School

11-13 February 2020, Kioloa Campus (NSW South Coast), Australian National University, NSW polymersummerschool.wixsite.com/apss

International Coalition for Energy Storage and Innovation Conference

1-4 March 2020, Dockside Function Centre, Sydney, NSW icesi2020.com

RACI events are shown in blue.

11 13 12 14 15 19 18 20 23 25 30

Across

- 9 Displayed five elements. (5)
- Beryllium/neon micro-structure put 10 back together. (9)
- Dyes tin compound. How compact it 11
- 13 Concentrate of four elements. (7)
- 14 One of us cites tin's reaction. (9)
- 17 Presents man with a territory in a state. (5)
- 18 Countryman put shingle out. (7)
- 19 F/Ne clue broken: dosimetry unit. (7)
- 21 The rhenium place. (5)
- NEDDER process for cleaning filters. (9)
- Con profits in astatine. (7) 26
- 28 Directed to the side coming after 13. (7)
- Hypothesise charges for opinions. (9)
- 31 Dug up over cloth. (5)

- 1 Throwaway lines: arsenic team is included. (6)
- 2 Growing molybdenum unit disintegrated. Not good. (8)
- 3 A two-element con. (4)
- Achromatic 15 Down SI unit of absorbed ionising radiation. (4)
- 5 Cl₂F scent? Faulty objective. (10)
- Birds over gypsum earth environment (4)
- 7 Complex polymer used to make
- Four mean without a drink. (8)
- C₇H₅N₃O₆ can make a lot of 15 Down. (3)
- 15 Unwanted data hullabaloo. (5)
- 491538322 on check. (10)
- 17 Load with junk . . . (5)
- ... then play around with E + pV. (8) 18
- 20 Such a little one using nitrogen routine. (8)
- 22 Pass over pasty selenium. (6)
- 24 Pressure from two elements (3)
- 25 Place to conceal Spooner anion. (6)
- 27 Heed C or F perhaps. (4)
- Lean record. (4)
- 29 Spell period. (4)

Graham Mulroney FRACI CChem is Emeritus Professor of Industry Education at RMIT University. Solution available online at Other resources.



OZOM – a tradition of more than 25 years

12th Australasian Organometallics Meeting

The 12th Australasian Organometallics Meeting (OZOM12) was held at the School of Chemistry, University of Melbourne, 9–12 July 2019. The lecture venue was the historic Masson lecture theatre that was built in 1938. OZOM has been running for more than 25 years in locations across Australia and New Zealand. The 2019 meeting maintained the traditional emphasis on presentations from students and early career researchers, as well as 10 invited plenary, keynote and special topics speakers.

More than 100 delegates were treated to talks and posters on a range of topics on fundamental and applied organometallic chemistry (see below, abstracts available at https://ozom12.wordpress.com). Among the delegates were

Professors George Koutsantonis, Lou Rendina and Mark Humphrey, who have attended all OZOM meetings. In a slight departure from previous meetings, two special topics lectures were delivered by organic chemists Professor Ian Rae, who discussed the efforts of Sir Masson and his student Norman Wilsmore in trying to isolate diethylmagnesium, and Professor Mark Rizzacasa, who highlighted the role of organometallic and metal complexes in

modern organic synthesis. Another innovation was a lunchtime workshop for early career researchers on 'The ARC assessment process' led by a panel consisting of Professors Lou Rendina, Mark Humphrey and Paul Low. The best talk and poster presentations by early career researchers were recognised by seven different, hotly contested, awards.

The conference was generously supported by science and technology company sponsors Chem-Supply Pty Ltd, Ezzi Lab, John Morris Group, PerkinElmer and Scitek. Morning tea was sponsored by Brunetti. Wines for the poster session and conference dinner were sponsored by Lethbridge Wines, represented by winemaker Dr Marie Collision (a former University of Melbourne PhD chemistry graduate).

We would like to thank the RACI, previous OZOM organisers (for helpful advice), all the delegates, helpers, sponsors and the School of Chemistry, University of Melbourne, for a successful meeting.

OZOM12 organising committee: Richard OʻHair (Chair), Vicki Blair (Treasurer), Carol Hua, Paul Donnelly and Melissa Werrett.

Plenary, keynote and special topics speakers and student winners

Plenary 1: Penelope Brothers

The chemistry of boron with pyrrole ligands: tales from the world of porphyrins, corroles, phthalocyanines and BODIPY

Plenary 2: Frank Edelmann My 40-year organometallic journey through the periodic table with frequent stops at the

rare-earth elements

Plenary 3: Monica Perez-Temprano Synergistic cooperation between mechanistic Investigations and catalysis:

towardsrational design

Plenary 4: Heinrich Lang From small tailor-made molecules to new materials

Keynote 1: Melissa Werrett Bismuth nanocellulose composites and their efficacy towards multi-drug-resistant

bacteria

Keynote 2: Becky Fuller A tale of two cities: electrostatic potentials are a chemist's best friend and new

beginnings with trigonal lanthanoid magnets

Keynote 3: Nick Cox High-field pulse EPR: a new biophysical toolbox for the study of metalloenzymes

Keynote 4: Annie Colebatch Main group pyridyl ligands: from the molecular to the supramolecular

Special Topic 1: Ian Rae Nineteenth century organometallics in Melbourne

Special Topic 2: Mark Rizzacasa Married at first sight: total synthesis and metal complexes

Best ECR Talk: Harrison Barnett Detection and reactivity of a bridging C1 ligand

Best ECR Talk: Kirralee Burke Exploring properties of novel Ga(III) and Bi(III) flavonolate complexes

Best ECR Talk: Rebekah Duffin Anti-Leishmanial activity of organometallic antimony(V) and gallium(III) quinolinolato

complexes

Best ECR Talk: Jamie Hicks Nucleophilic aluminium: synthesis, structural and reaction chemistry of the aluminyl

anion

Best ECR Poster: Daniel Harrison Simple metallation of terminal acetylenes: synthesis of high-purity metal acetylide

half-sandwich complexes

Best ECR Poster: Rachel Steen Selective activation of alkynes through cumulene intermediates

Best ECR Poster: Kuppusamy Yuvaraj Reductive trimerisation of CO to the deltate dianion using activated magnesium(I) compounds



'Heat map' periodic table of elements in wine*

* Amounts are typical concentrations. See page 37 to find out more about the Australian Wine Research Institute's research into the elemental composition of wine.



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