Chemistry March/April 2020 March/April 2020 March/April 2020

March/April 2020



Seeing flowers in a different light

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- Who are 'younger' chemists and what do they have in common?
- Lithium and the 2019 Nobel Prize in Chemistry
- Tapping into your passion to engage an audience







































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chemistry in Australia

March/April 2020

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cover story

Seeing flowers in a different light

Six years ago, David Oldfield started taking photos of Australian native flowers in UV light, with his wife's garden as the perfect source of specimens. Guided by websites and the results of a literature review, he produces striking images such as those featured in this issue.

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16 'Younger' chemists: who are they?

Age or career stage? 'Younger' chemists do not easily fit a single category, but they do have something in common: a need for support.

20 From Luigi to lithium: the 2019 Nobel Prize in Chemistry

Rarely is an element the focus of a Nobel Prize, but in 2019 the third element (lithium) took centre stage. The Nobel Prize in Chemistry 2019 was awarded for contributions to the development of the lithium-ion battery. This light and powerful rechargeable battery has revolutionised consumer electronics and laid the foundation of our wireless society.

24 BRIDGE: tapping into a passion for science

Engaging audiences is central to careers in science and research. How to do it? Get comfortable and tell your story.



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From the President

It has been an exceptional start to the new decade. Extreme weather events and major bushfires, to an extent that is unprecedented internationally, have ravaged our country, our communities, our families. The RACI and I send our condolences and best wishes to all of those who have been affected by these events.

In January, the RACI was represented by Science & Technology Australia at the Science Roundtable held by Minister for Industry, Science and Technology, Karen Andrews. It was good to see the Minister engaging with scientists, not only as part of the recovery and rebuilding to be done in the short term, but also in establishing new systems and policies to mitigate future events.

Australian and international scientists have been warning of the effects of climate change and we are now seeing evidence of those predictions. Is the loss of biodiversity – our unique flora and fauna – just the start of these impacts?

And so, in the same way that Minister Andrews reached out to scientists in relation to the bushfires, it is imperative for the Australian government to start serious conversations with scientists, including chemists, and develop policies and strategies to reduce our impact on the environment and climate.

Over the past few months I have seen first hand how highly regarded the Australian chemistry community is internationally. In December, I attended the General Assembly of the Federation of Asian Chemical Societies (FACS). Dave Winkler FRACI CChem has been the President of FACS for the past two years and, with the assistance of Roger Stapleford, he has modernised the organisation's statutes and governance. Dave's vision for the Asian Chemistry Congress to be the premier congress of the Asia–Pacific also led to the agreement of a rebranding to AsiaChem. The leadership required to achieve this change in just two years is to be congratulated.

Over the past four years, there have been discussions about the formation of a Federation of Commonwealth Chemical Societies. The RACI has been actively involved in the development of the Federation, its purpose and constitution, and its first Congress to be held in May 2020. Australia has been represented by Andrew Holmes FRACI CChem, Roger Stapleford RACI CEO and myself. The constitution is in draft form and the new Executive Board will finalise the governance of the Federation in preparation for the first General Assembly in Trinidad Tobago in May. The vision of the Federation is *One community, one voice, catalysing equality for all.*

The Federation will differentiate itself from other Federations the RACI contributes to by:

- developing policies to advance priority areas of work, including those covered by the United Nations Sustainable Development Goals
- establishing strong networks that enhance chemists' profiles throughout the Commonwealth
- having a strong focus on diversity and inclusion.
 I am very humbled to have been appointed as the President Elect of the Federation.

The first Commonwealth Chemistry Congress being held in Trinidad Tobago will be attended by three early career chemists from Australia. Isobelle Stone will present her research as an oral presentation in the Green Chemistry & Catalysis theme. Philip Norcott and Sinead Kaveney will present posters in the same theme.

The Federation's focus on connecting early career chemists from academia and industry with policy development will benefit Australian chemists by enhancing their international reputation as the thought leaders of today and tomorrow and will influence government policy.

Now is an opportune time for members to use the RACI's relationships with international and local organisations to help change minds and shape Australia's future as well as that of our neighbours.



Vicki Gardiner FRACI CChem (president@raci.org.au) is RACI President.



EDITOR

Sally Woollett Ph (03) 5623 3971 wools@westnet.com.au

PRODUCTION EDITOR

Catherine Greenwood catherine.greenwood@bigpond.com

ADVERTISING SALES

Mary Pappa Ph/fax (03) 9328 2033/2670 mary.pappa@raci.org.au

PRODUCTION

Control Publishing publishing@control.com.au www.control.com.au

BOOK REVIEWS

Damien Blackwell damo34@internode.on.net

RESEARCH HIGHLIGHTS

David Huang david.huang@adelaide.edu.au

EDUCATION RESEARCH HIGHLIGHTS

Reyne Pullen r.pullen@unsw.edu.au

GENERAL ENQUIRIES

Robyn Taylor Ph/fax (03) 9328 2033/2670 chemaust@raci.org.au

PRESIDENT

Vicki Gardiner FRACI CChem

MANAGEMENT COMMITTEE

Helmut Hügel, Colin Scholes, Madeleine Schultz, David Springer, Richard Thwaites

CONTRIBUTIONS

Contributors' views are not necessarily endorsed by the RACI, and no responsibility is accepted for accuracy of contributions. Visit the website's resource centre at chemaust.raci.org.au for information about submissions.

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Plastic roads: are they the answer?

The recycling or the reuse of 'plastic' in bitumen roads is being claimed as a major advance in recycling of plastic wastes and the avoidance of the plastic going to landfill (e.g. bit.ly/2RBEHpq, ab.co/38mCPrl).

Improved initial properties of the roads have been claimed but no long-term data has been presented. The inventors purport that by showing the absence of microplastics in the initial road formulations, they can assume long-term durability for the road surface and that microplastics will not be formed as a consequence of degradation. This may be based on a belief that these microplastics only form when the plastic degrades in water or in the oceans.

This has been shown to be incorrect in many studies and is highlighted in a recent article in *Chemistry in Australia* by Bolan and Bradney (July/August 2019, p. 19) where a range of polymers has been shown to form microplastics on land.

The concern that microplastics may form as a consequence of long-term degradation of the plastic used in roads has been raised by a number of authors and, if correct, this represents a serious environmental problem (e.g. bit.ly/2Rf350q, bit.ly/2sEMZ7k).

We therefore caution against further widespread field trials of plastic in roads in Australia until appropriate studies are conducted. Some studies have been alluded to in press releases by the proponents of plastic road technology, but no data has been released for scrutiny by the public or the scientific community.

It should be noted that the road surface is a harsh environment, being subject to extremes in temperatures, weather and mechanical stress.

The idea of plastic in roads sounds exciting, and this usage would reduce the amount of plastics sent to landfill, but it is imperative that this does not lead to widespread pollution of our waterways and other environmental problems. We suggest that serious studies on experimental roads are needed to demonstrate that microplastics or other breakdown products of road weathering are not being formed as the road ages.

Graeme Moad FRACI CChem and David Solomon AC, FRACI CChem

'Your say' guidelines

We will consider letters of up to 400 words in response to material published in *Chemistry in Australia* or about novel or topical issues relevant to chemistry. Letters accepted for publication will be edited (no proof supplied) for clarity, space or legal reasons and published in print and online. Full name and RACI membership type will be published. Please supply a daytime contact telephone number (not for publication).

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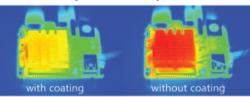
Coating helps electronics stay cool by sweating

Mammals sweat to regulate body temperature, and researchers from Shanghai Jiao Tong University (China) are exploring whether our phones could do the same. In a study published in Joule (https://doi.org/10.1016/ j.joule.2019.12.005), the authors present a coating for electronics that releases water vapour to dissipate heat from operating devices - a method that could prevent electronics from overheating and keep them cooler than existing strategies.

The development of microelectronics puts great demands on efficient thermal management techniques, because all the components are tightly packed and chips can get really hot,' said senior author Ruzhu Wang. 'For example, without an effective cooling system, our phones could have a system breakdown and burn our hands if we run them for a long time or load a big application.

Larger devices such as computers have fans to regulate temperature. However, fans are bulky, noisy and energy consuming and thus unsuitable for smaller devices such as mobile phones. Instead, phase change materials (PCMs), such as waxes and fatty acids, have been used for cooling in phones. These materials can absorb heat when they melt. However, the total amount of energy exchanged during the solid-liquid transition is relatively low.

In contrast, the liquid-vapour transition of water can exchange 10 times more energy than PCM solid-liquid transition. Inspired by mammals' sweating mechanism, Wang and his team studied a group of porous materials that could absorb moisture from the air and release water vapour when heated. Among them, metal organic frameworks



Infrared image comparison of the heat sinks with and without MIL-101(Cr) coating.

Chenxi Wang

(MOFs) were the most promising because they could store a large amount of water and thus take away more heat.

'Previously, researchers have tried to use MOFs to extract water from the desert air, Wang says. 'But MOFs are still really expensive, so large-scale application isn't really practical. Our study shows electronics cooling is a good real-life application of MOFs. We used less than 0.3 grams of material in our experiment, and the cooling effect it produced was significant.

The team selected a type of MOF called MIL-101(Cr) because of its good waterabsorbing capacity and high sensitivity to temperature changes. They coated three 16-square-centimetre aluminium sheets with MIL-101(Cr) of different thicknesses -198, 313, and 516 micrometres - and heated them on a hot plate.

The team found that MIL-101Cr coating delayed the temperature rise of the sheets, and the effect increased with coating thickness. While an uncoated sheet reached 60°C after 5.2 minutes, the thinnest coating doubled the time and didn't reach the same temperature until 11.7 minutes. The sheet with the thickest coating reached 60°C after 19.35 minutes of heating.

'In addition to effective cooling, MIL-101(Cr) can quickly recover by absorbing moisture again once the heat source is removed, just like how mammals rehydrate and ready to sweat again,' Wang says. 'So, this method is really suitable for devices that aren't running all the time, like phones, charging batteries and telecommunications base stations, which can get overloaded sometimes.

Wang and his team tested a coated heat sink on a microcomputing device. Compared to an uncoated heat sink, the coated one reduced the chip temperature by up to 7°C when the device was run at heavy workloads for 15 minutes.

The team plans to improve the material's thermal conductivity and bring the cost down.

Cell Press

Towards safer disposal of printed circuit boards

Printed circuit boards are vital components of modern electronics. However, once they have served their purpose, they are often burned or buried in landfills, polluting the air, soil and water. Most concerning are the brominated flame retardants added to printed circuit boards to keep them from catching fire. Now, Jujun Ruan and colleagues reporting in Sustainable Chemistry & Engineering (https://doi.org/ 10.1021/acssuschemeng.9b05071) have developed a ball-milling method to break down these potentially harmful compounds, enabling safer disposal.

Metallic components (30%) can be recovered from crushed circuit boards by magnetic and high-voltage electrostatic separations, leaving behind non-metallic particles (70%), including resins, reinforcing materials, brominated flame retardants and other additives. Scientists have linked compounds in brominated flame retardants to endocrine disorders and foetal tissue damage. Therefore, the researchers wanted to develop a method to remove the flame retardants from waste printed circuit boards so that they wouldn't contaminate the environment.

The researchers crushed printed circuit boards and removed the metallic components by magnetic and highvoltage electrostatic separations, as is typically done. Then, they put the nonmetallic particles into a ball mill - a rotating machine that uses small agate balls to grind up materials. They also added iron powder, which prior studies had shown was helpful for removing halogens, such as bromine, from organic compounds. After ball-milling, the bromine content on the surface of the particles had decreased by 50%, and phenolic resin compounds had decomposed. The researchers determined that during the ball-milling process, iron transferred electrons to flame retardant compounds, causing carbon-bromine bonds to stretch and break.

American Chemical Society

Reducing the carbon footprint of asthma inhalers

Researchers at Monash University are using X-ray scattering and computer modelling in order to find a low-global warming replacement propellant for asthma inhalers.

About 339 million people worldwide, including 2.7 million Australians, suffer from asthma. Most rely on inhalers.

In 2015, the estimated cost of asthma in Australia was \$28 billion. About 40 000 Australians are hospitalised with asthma each year.

By 2030, the propellant tetrafluoroethane (HFC-134a) will be banned from use in pressurised metered-dose inhalers, leaving asthma sufferers without a solution.

In 2019, the Kigali amendment to the Montreal Protocol mandated the beginning of a 10-year phase-out of HFC-134a – a potent greenhouse gas. Just 1 kg of HFC-134a is equivalent to 1430 kg of carbon emissions.

The pharmaceutical industry is now in a race to transition to more environmentally friendly solutions for asthma inhalers.

The problem is that most potential replacements are highly flammable and unsuitable for human consumption, and dry powder inhalers are not yet suitable for all drugs.

Daniel Duke (Monash University) is working with colleagues at the Woolcock Institute of Medical Research (Sydney) and Argonne National Laboratory (Illinois, USA), as well as a major drug company, to reduce the carbon footprint of inhalers by using synchrotron X-ray technology and advanced computer models.

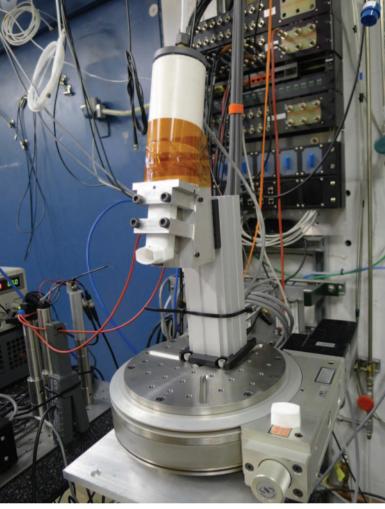
This technology allows researchers to see what happens to the spray particles inside the inhaler, and measure the density and quantity of the drug that various propellants can deliver.

'What we're trying to do is find out whether there are alternative propellants, which behave properly, from the options that are safe. HFC-134a was previously found in our air conditioners and fridges before it was banned due to its high emission of greenhouse gases,' Duke said.

'Pharmaceutical companies have stuck with HFC-134a because it works very well; and, most importantly, it's safe for human consumption. One problem is all the environmentally friendly options that have gone into your air conditioner and fridge are flammable or toxic, and we don't know if they're safe for the human body if ingested.

'Another issue is some chemicals have lower pressures and lesser densities, which means they carry less of the drug into the airway. That means we'll also need to look at redesigning pressurised metered-dose inhalers to maximise performance.

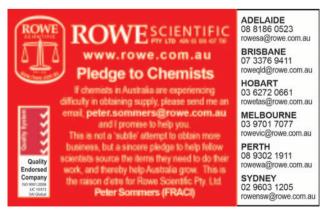
'Essentially, we're doing all the groundwork to give the drug companies the confidence to go to clinical trials knowing that all the engineering, chemistry and physics problems have been put to bed, and all they have to do is make sure that it's effective and safe for patients.'



An inhaler being tested at the Australian Synchrotron.

The research team comprises Duke and Professor Damon Honnery (Monash University); Brandon Sforzo and Alan Kastengren (Argonne National Laboratory); Professor Paul Young (University of Sydney) and Professor David Schmidt (University of Massachusetts-Amherst).

Monash University



ANSTO's Graduate Institute now open

ANSTO's Graduate Institute has opened for Australia's best and brightest emerging science and engineering minds, and the first five New South Wales government-funded Industry Foundations Scholarships have been awarded.

The Institute is a key part of ANSTO's Innovation Precinct. The first cohort of Industry Foundations Scholars will work within ANSTO to support industry and deliver innovation for Australia.

The Graduate Institute is benefiting from a NSW government grant of \$12.5 million committed in February 2019, for the development of ANSTO's Innovation Precinct.

NSW Minister for Better Regulation and Innovation, Hon. Kevin Anderson, and ANSTO's Graduate Institute Director, Professor Andrew Peele, were at the official launch.

'This world-class precinct for graduate students will become the training ground for the next generation of industry leading scientists and engineers – in NSW and beyond,' Anderson said.

Peele said it was the access to the collaborative

opportunities as much as the cutting-edge infrastructure that will give graduates the edge.

'The Institute will see Australia's emerging scientific minds working under guidance of some of Australia's leading scientists, while having access to ANSTO's national industry partners and leading infrastructure,' he said.

The six successful recipients of the Industry Foundations Scholarships will spend at least six months at an ANSTO facility in support of industry projects.

Amy MacIntosh (Macquarie University) is among the awardees. Her project centres on developing an ecological framework for closure of offshore petroleum structures, with BHP as the industry sponsor.

'I'm very excited to have the opportunity to learn new skills from ANSTO's very experienced staff and mentors, while building my overall knowledge and experience,' MacIntosh said.

ANSTO





Professor Claudine Stirling in the University of Otago's Clean Lab.

A world-class research facility producing filtered air 100 000 times cleaner than outside air is the newest addition to the University of Otago's Mellor Laboratory.

The completion of a metal-free Clean Lab is the most extensive of its kind in New Zealand.

Professor Claudine Stirling, Director of Otago's Centre for Trace Element Analysis, said the Clean Lab is designed to protect the metals under analysis from both people and the environment.

'Metals participate in all sorts of different processes and they exist everywhere including on us,' Stirling said.

'A lot of metals that provide useful information exist at very low levels, down to parts-per-trillion concentrations or even lower, so it's crucial to reduce background levels as much as possible.'

Even a speck of dust is loaded with metals so can potentially contaminate a sample being tested, Stirling explained.

The Clean Lab's high design specifications include the filtered air being renewed 100 times an hour, positively pressured rooms that ensure any residual air moves from the inside to the outside of the labs, and high-purity water on tap for processing samples.

The Clean Lab will support a growing diversity of applications from earth sciences to archaeology, and forensics to climate change.

Underlying the research undertaken in the Clean Lab is the recognition that different environments are defined by different metal isotope and metal concentration signatures.

Stirling said the facility will be able to support new areas such as biomedical cancer research and how nutrients are absorbed by the body.

Stirling's own research on environmental change during periods of global warming will also benefit from the new facility. Through the analysis of trace metals and their isotopes, one of her aims is to reconstruct how ocean deoxygenation progresses as climate warms.

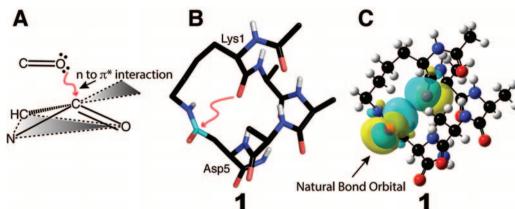
'The lab will allow us to achieve this by enabling minute amounts of the elements to be extracted, without contamination, from a wide variety of different sample types ranging from seawater to sediment to rocks.'

The Clean Lab consists of a series of rooms, including two equipped with individual workstations allowing three or four scientists to work in each room simultaneously, and also for the separation of incompatible sample types.

University of Otago

Novel long-range interaction for alpha helix stabilisation in peptides

Researchers from the University of Queensland have shown that a novel long-range n to π^* interaction between a main-chain amide oxygen and a uniquely positioned carbonyl group in the linker of a cyclic pentapeptide (1) is able to help optimally stabilise the smallest known alpha helix in water (Hoang H.N., Wu C., Hill T.A., Dantas de Araujo A., Berhardt P.V., Fairlie D.P. Angew. Chem. Int. Ed. 2019, 58, 18 873-7). An n to π^* interaction is the sharing of lone-pair electron density from a carbonyl oxygen into the empty π^* orbital of a nearby carbonyl group (A) and in protein backbone amide units has been demonstrated to help stabilise α -helices. This research highlights a novel interaction, with a

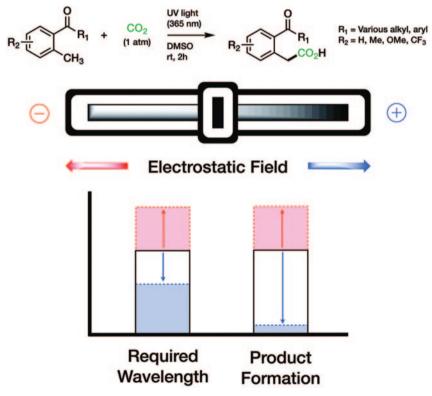


covalent amide bond outside of the helical backbone (B, C), and could lead to new approaches to synthetically stabilise peptide structures in water. The discovery of this novel n to π^*

interaction and its structure-inducing properties highlights that greater recognition of n to π^* interactions should be given in medicinal, computational and structural chemistry.

Electric fields cooperatively promote ground and excited state reactivity

The demonstration that electric fields can be used to catalyse and control the reactivity or selectivity of chemical reactions has recently sparked immense interest, with both theoreticians and experimentalists exploring a range of avenues for harnessing these effects. Now researchers from the Australian National University have shown that the electric fields from remote charged functional groups can selectively and cooperatively promote both ground- and excited-state chemical reactivity in the same system (Blyth M.T., Noble B.B., Russell I.C., Coote M.L. J. Am. Chem. Soc. 2020, 142, 606-13). As a demonstration of this principle, the team used electrostatics to both red shift and improve the efficiency of Murakami's photochemical CO₂ storage reaction (J. Am. Chem. Soc. 2015, 137, 14063-6). Strikingly, they showed that, contrary to the conventional understanding of electrostatic effects, catalysis can actually increase with solvent polarity. This counterintuitive result occurs when polarisation is significant, and provides a way forward for addressing the solvent



polarity versus solubility trade-off normally associated with using charged functional groups for electrostatic catalysis.

Highbred hydrocarbon hybrids

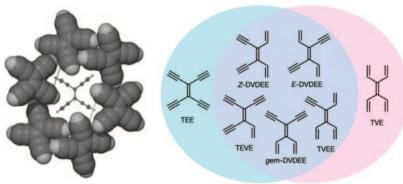
The beating heart of research in chemical science is the design and synthesis of new molecular structures. If fundamental new information is sought, then the simpler the structure, the better. Tetraethynylethylene (TEE) and tetravinylethylene (TVE) are two such simple structures: each molecule only has ten carbon atoms. Synthetic chemists at the Australian National University wondered if the five possible TEE–TVE 'hybrid' molecules carrying both ethynyl and vinyl groups about the central C=C bond could be made (Horvath K.L, Magann N.L., Sowden M.J., Gardiner M.G., Sherburn M.S. *J. Am. Chem. Soc.* 2019, **141**, 19 746–53). They devised a unified approach to synthesise these five new hydrocarbons, involving Ramirez dibromo-olefinations of cross-conjugated ketones followed by cross-coupling reactions.

Dynamical thinking uncovers new mechanistic paradigm for cytochrome P450s

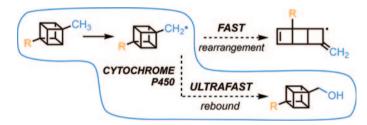
Cytochrome P450s – nature's C–H activation catalysts par excellence – are generally thought to hydroxylate their substrates by first abstracting a hydrogen atom to form an intermediate substrate radical. Recent collaborative work from the University of Queensland and University of Adelaide has uncovered an important new dimension to this mechanistic paradigm (Sarkar M.R., Houston S.D., Savage G.P., Williams C.M., Krenske E.H., Bell S.G., De Voss J.J. *J. Am. Chem. Soc.* 2019, **141**, 19 688–99). The work studied the oxidations of methylcubanes, which notionally proceed via cubylmethyl radical intermediates. Cubylmethyl radicals undergo some of the fastest rearrangement processes known to chemistry ($k > 10^{10} \text{ s}^{-1}$ at 25°C), yet their oxidations by a bacterial P450 gave only the

Rivalling DNA and RNA

The DNA and RNA triplet codon/anticodon system that underpins cellular protein synthesis has served as a template for the design of self-assembled donor (D)-acceptor (A) hydrogen-bonded duplex systems in water. Progress on generating a duplex as strong as double-stranded DNA has been slow despite more than two decades of work on related systems in organic solvent. Now, Hegui Gong and Jonathan Sessler at Shanghai University (China) and Pall Thordarson at UNSW report a novel strong AAAA-DDDD quadrupole bis(quanidinium):dicarboxylate heteroduplex (Sun Y., Gu J., Wang H., Sessler J.L., Thordarson P., Lin Y.-J., Gong H. J. Am. Chem. Soc. 2019, 141, 20146-54). The heteroduplex formation is driven by charge-assisted hydrogen bonding, which is a relatively unexplored motif in supramolecular chemistry. In-depth analysis of isothermal calorimetry titration data showed that the magnitude of the binding affinities of these heteroduplexes in water exceeds 7 kcal mol⁻¹ ($K_2 > 10^5 \text{ M}^{-1}$) – rivalling or exceeding those of DNA or RNA duplexes. The reported



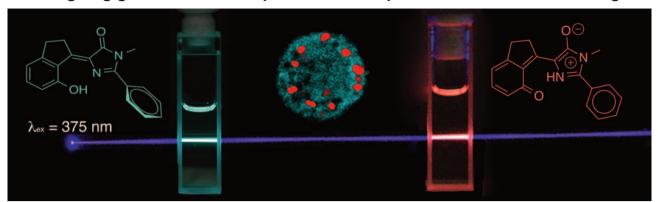
TEE and TVE were also prepared, and the first single-crystal X-ray analysis of TEE was performed. All five hybrid compounds were more stable towards acid than TVE, and more thermally/air stable than TEE, which undergoes explosive decomposition in solvent-free form. TEE and TVE have been used previously as building blocks in materials-based applications and in step economic synthesis, respectively. The new hybrids have potential uses in these and other fields.



direct hydroxylation products, with no evidence of any rearrangement. The lifetimes of the radical 'intermediates' in these P450-catalysed hydroxylations must therefore be ultrashort – a few picoseconds or less. The researchers proposed that the enzyme dynamically merges the C–H abstraction and C–O bond formation processes into a tightly coupled process, effectively bypassing a discrete radical intermediate. Related dynamical concepts likely underpin numerous other aspects of P450 catalysis, as well as other C–H activation processes.

heteroduplex building blocks are easily functionalised, making them attractive for the construction of complex functional structures akin to DNA origami.

Redesigning green fluorescent protein chromophore for ratiometric sensing



Green fluorescent protein (GFP) is widely used in biotechnology because it can be genetically encoded. In 2002, Remington observed GFP mutants that display dual blue/green emission (deGFP). The design and synthesis of small molecules that mimic the dual emission of deGFP could find a range of applications in chemistry and biology that require ratiometric sensing. Dual fluorescence probes that are sensitive to their environment are an unmet challenge in quantitative fluorescence in biological systems because there are few molecules that display dual fluorescence. This challenge has now been met by a team led by Peter Karuso at Macquarie University, who successfully redesigned the chromophore of deGFP to generate, for the first time, a small-

molecule analogue (o-LHBPI) that displays roughly equal levels of fluorescence at two wavelengths separated by well over 100 nm (Chatterjee S., Ahire K., Karuso P. J. Am. Chem. Soc. 2019, 142, 738–49). This rare dual emission results from normal Franck–Condon emission in the cyan and red emission from an excited-state intramolecular proton transfer. The team found that the new fluorophore fluoresces cyan in acetonitrile and red in water and demonstrated preliminary applications for the ratiometric sensing of biomolecules in solution and the two-colour staining of live human cells. Their results open the door to using GFP chromophore analogues in biotechnological applications that require quantitative ratiometric fluorescence.

Synthesis of membrane proteins via peptide ligation

Peptide ligation chemistry provides unique access to modified polypeptides and proteins. However, lipidated and integral membrane proteins are a crucially important section of the proteome that remain largely inaccessible by current synthetic methods. This is due to the poor aqueous solubility of these biomolecules and their propensity to aggregate and form colloidal structures. Recently, researchers at the University of Sydney have developed of a new method called reductive diselenide-selenoester ligation (rDSL) that overcomes these limitations and allows peptide fragments to be ligated down to nanomolar concentrations at the 21st amino acid selenocysteine (Chisholm T.S., Kulkarni S.S., Hossain K.R., Cornelius F., Clarke R.J., Payne R.J. J. Am. Chem. Soc. 2020, 142, 1090-100). The rDSL ligation technology can be coupled with an

in situ photodeselenisation reaction to afford native peptide and protein products. The power of the one-pot rDSL-photodeselenisation manifold was highlighted through the rapid and efficient synthesis of the FDA-approved lipidated therapeutic tesamorelin and two analogues of the integral membrane protein FXYD1.

Moving molecules to the right place to react by light

The discovery that the steep electromagnetic field gradient of a high-intensity monochromatic laser can be used to control the movement of atoms and molecules was recently recognised by the award of the 2018 Nobel Prize in Physics. Now researchers at the Queensland University of Technology have revealed that small-molecule locomotion can be achieved with low-intensity visible light by using plasmonic metal nanoparticles to effectively increase the electromagnetic field gradient; they then exploited this process to selectively draw molecules to a catalytic surface to react (Peiris E., Sarina S., Waclawik E.R., Ayoko G.A., Han P., Jia J., Zhu H.-Y. Angew. Chem. Int. Ed. 2019, 58, 12 032-6). The researchers showed that the product selectivity of alkyne hydroamination by aniline on catalytic Au Co alloy nanoparticles was photoswitchable, vielding imine (cross-coupling product of aniline and alkyne) under visiblelight irradiation and 1,4-diphenylbutadiyne in the dark. Light irradiation accelerated the catalytic cross-coupling by several orders of magnitude even at a very low (millimolar) overall aniline concentrations. The researchers proposed that the intense fringing electric field generated around the nanoparticles upon absorbing low-intensity light produces a sharp electric field gradient that selectively enhances

Light, nickel, catalysis!

Carbon-nitrogen (C-N) bond-forming reactions are ubiquitous in the synthesis of pharmaceuticals, organic materials and fine chemicals. In the push towards more sustainable synthetic methodologies, several groups have recently explored novel light-driven C-N cross-coupling reaction systems. To date, however, these systems have required the use of relatively expensive iridium complexes or UV light. More importantly, the mechanisms of these complex, usually dual-component, systems has not been resolved. Now, Max Kudisch, Chern-Hooi Lim and Garret Miyake, together with Pall Thordarson at UNSW, have demonstrated the key role of Förster-type energy transfer in a nickel-based dual-catalytic light-driven C-N cross-coupling system (Kudisch M., Lim C.-H., Thordarson P., Miyake G.M. J. Am. Chem. Soc., 2019, 141, 19479-86). They showed that a visible-light-excited organic phenoxazine is superior to conventional iridium complexes as the photocatalyst in this dual photocatalytic nickel system. Through detailed binding studies, they revealed the key role of a 1:3 nickel-amine complex in the catalytic cycle of these C-N cross-coupling reactions. Unexpectedly, they showed that the photocatalyst activates the nickel catalyst via Förster-type energy transfer,



adsorption of the polarisable aniline molecules on the catalyst, thereby altering the aniline/alkyne ratio at the catalyst surface and switching product selectivity. The phenomenon could open up new opportunities for light-induced switching in applications besides controlling reactivity in organic synthesis.

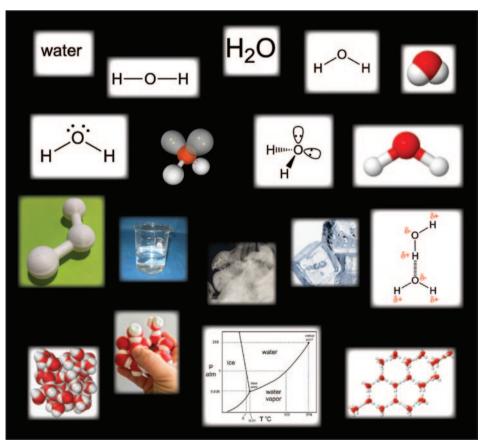
 $\label{eq:free_prop} \textit{FRET} = \textit{F\"{o}} \textit{rster} \textit{ resonance energy transfer } \textit{PC} = \textit{photocatalyst}$

and not by photo-inducted electron transfer as had been assumed, a discovery that will facilitate both the prediction and discovery of new reactivity in light-driven nickel catalysis.

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.

Symbolic representations prevalent in largeclass teaching

Chemistry teachers share a vast array of multimodal representations with their students, who must possess a degree of representational competence to be able to recognise, interpret, construct, transform and connect between these representations. Learning is made possible through noticing or discerning something in a representation and reasoning about it in a meaningful way. In this study, the distribution and combination of representations that were adopted in a lecture resource (PowerPoint slides), used in a single-semester first-year chemistry course, were analysed (Ferreira J.E.V., Lawrie G.A. Chem. Educ. Res. Prac. 2019, **20**(4), 902–23, https://doi.org/10.1039/c9rp00001a). Hierarchical cluster analysis was applied to identify patterns and connectivity between representations while also aiming to identify any critical combinations of specific representations that may exist. It was found that students had been presented with at least 3367 separate representations in lectures during a single semester. Symbolic representations were the most prevalent form adopted by lecturers and there was very limited use of macroscopic representations in lectures. Five topic clusters were identified through statistical analysis - the highest number of representations that had potential to combine to support construction of understanding were observed in the cluster addressing concepts including spontaneity and redox. The outcomes of this study inform instructional design that supports development of students' representational competencies.



Examples of multiple forms of representation of the structure and properties of water.

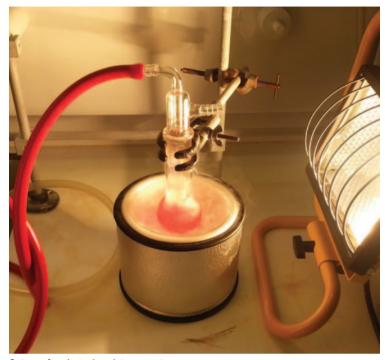
Employability skills underdeveloped in science subjects

Generic skills are the key skills and capabilities transferable to a wide range of tasks and contexts beyond the university setting (e.g. communication, critical thinking, team-working). As in many disciplines, the importance of generic skills for science graduates' employability is well reported in the literature, from perspectives of policymakers to those of employers and graduates. While a considerable body of research has been explored on students'. recent graduates' and employers' perspectives of generic skills, the perspectives of science academics - the catalysts for inculcating such skills appear to have been largely ignored. In order to address this gap in the scholarly literature, Mahbub Sarkar, Tina Overton, Christopher Thompson and Gerry Rayner studied the perspectives of science academics at an Australian and a UK university regarding the promotion of generic skills in the subjects they teach (High. Educ. Res. Dev. 2019, https://doi.org/10.1080/07294360. 2019.1664998). The study found that many generic skills (e.g. leadership, adaptability, commercial awareness, and ICT skills) were neither developed nor assessed in a large number of science subjects, with several large development-assessment gaps. Academics reinforced calls for a shift from traditional content-focused transmissive pedagogies to more problem-based open-inquiry approaches along with incorporating workintegrated learning and embedding reflection into pedagogy and assessment practices for promoting the generic skills employers increasingly demand from science graduates.

Undergrad science experiments: a cross-disciplinary approach

For nearly two decades, the Australian national project Advancing Science and Engineering through Laboratory Learning (ASELL) has been using an evidence-based approach to improve undergraduate experiments. Alexandra Yeung, Scott Cornish, Scott Kable and Manjula Sharma present the ASELL Students Laboratory Experience (ASLE) survey, administered to 2691 students in five disciplines: biochemistry, biology, chemistry, physics and pharmacology (*Int. J. Innov. Sci. Math. Educ.* 2019, **27**(3), 25–40). The 14-item survey probes students' perceptions of an experiment, a practical or fieldwork. An exploratory factor analysis extracted two factors, 'experiment-based motivators' and 'course-level resources', and both factors correlate well with 'overall' learning experiences.

This study found 'course-level resources' taper off after an optimum value is achieved, indicating that further investment in these aspects does not necessarily influence student perceptions of their learning experiences. However, 'experiment-based motivators' do not taper off, suggesting that further investment can influence experiences. These insights can help practitioners effectively design and modify laboratory activities.



Set-up of a photochemistry experiment.

Dr Alan Payne

Compiled by **Reyne Pullen** MRACI CChem (reyne.pullen@sydney.edu.au). This section showcases exciting chemistry education research carried out primarily in Australia. RACI members whose recent work has been published in prominent chemistry education journals (e.g. *Chem. Educ. Res. Pract., J. Chem. Educ., J. Res. Sci. Teach.*) are encouraged to contribute general summaries, of no more than 200 words, and an image to Reyne.





Age or career stage? 'Younger' chemists do not easily fit a single category, but they do have something in common: a need for support.

hen students decide on a chemistry undergraduate degree, they are told that this qualification can open doors to almost any industry. But younger chemists are finding that just getting that degree is no longer enough. Today's younger chemists face challenges they feel poorly equipped to deal with. However, they are more interconnected than ever and so support networks for younger chemists are cropping up in Australia and abroad.

The International Younger Chemists' Network (IYCN) is one such organisation. We attended the first General Assembly of the IYCN as delegates for Australia in July 2019. A total of 43 delegates attended from 33 countries, including Australia, Germany, the US, France, Italy and China. There were also delegates from Papua New Guinea, Nigeria, Egypt and Ecuador, and some virtual attendees.

The mission of the network seemed clear: 'to connect and empower

younger chemists globally'. But when the discussion came to defining the membership of the organisation – 'younger chemists' – the debate grew heated. Should this be defined as an age, a career marker, or both? This question has been bothering us ever since. Who is a 'younger' chemist?

The question has no straightforward answer. Based on the word 'younger', it is tempting to draw a line by a specific age. The European Younger Chemists' Network automatically accepts members of the European Chemical Society who are younger than 35. In our research, we have seen opportunities and awards offered to scientists no older than 30–45.

However, not everyone reaches the same career stage at the same age. Increasingly, awards and opportunities for younger chemists are defined by career markers, often years after their terminal degree. They may make allowances for career breaks. These definitions are more inclusive to chemists who follow a non-linear career pathway or experience interruptions.

BY ANNA Ahveninen and Joshua Marlow

This version is also widely accepted by the younger chemists themselves. When we spoke to the chairs of each of the RACI's five groups for younger chemists, all described their membership in career terms.

'It doesn't necessarily matter how old you are. It's about where you are in the career progression,' said Karin van der Pal, PhD student at Curtin University and Chair of the Western Australian Young Chemists' Society.

The IYCN has adopted a two-pronged definition that includes members based on an age (35 and under) and a career marker (five years following their terminal degree). 'It's an interesting question whether you go with "younger" or "early-career". For us, the two are effectively synonymous,' said Dr Lori Ferrins, Chair of the IYCN, Assistant Professor at Northeastern University (US) and Aussie expat. 'I think for us it was about making sure that the people who need the support have the support that they want.'

Dr Monika Szabo, postdoctoral researcher at CSIRO and Chair of the Victorian Young Chemists' Group, also finds the question more difficult to answer. Although she too gave a definition in years past a terminal degree, she added: 'In one way, I think there needs to be a defined age group, because you're still learning and you still haven't got the experience, say, a younger researcher in their 40s might have.'

Whether we adopt a definition according to age or to career stage, this lack of experience is the greatest challenge that younger chemists encounter. 'Everyone always wants to hire someone with experience, because they have the training,' said Karin.

Finding opportunities to get that crucial experience is also challenging. 'In this job environment, where it's tougher than ever, and the competition is harder ... you have to put in a lot more effort than before to secure that entry-level job,' said William Li, Chair of the New South Wales Young

Chemists' Group. William is a recent science and chemical engineering graduate from the University of New South Wales with a full-time job as a quality control chemist.

Renata Kucera, PhD student at Flinders University and Chair of the South Australian Young Chemists' Group, disagreed. 'I think that anyone at any stage of their career can have a hard time finding a job,' she said.

The breadth of an undergraduate chemistry degree as opposed to the specificity of many jobs was identified as a pitfall for younger chemists. 'I've only had the one role, but it seems to me that [the knowledge required by] every job is going to be intensely specific to that job,' said an early-career analytical chemist who asked not to be identified. 'I think having more industry exposure in university would be great.'

The pathway is no clearer for PhD graduates. Monika told us that she encounters many PhD graduates who wouldn't know where to start looking for opportunities outside academia. And staying in research is no cakewalk either, she said: 'It's super hard to get funding for fellowships. It's highly competitive.'

Many students think they need to spend years working internationally to establish their research careers at a time when many might wish to settle down. There is often too little support for early-career researchers to relocate. This is likely made worse for Aussie researchers because of our geographical inconvenience. 'When I moved to Boston, I moved straight out of my PhD,' said Lori. 'There was no money for relocation, and I was broke when I got here. And it sucked.'

Some of the younger chemists we

... not everyone reaches the same career stage at the same age.

interviewed described problems that go beyond career obstacles. 'My main concern is that I think younger chemists tend not to be taken very seriously,' said Lori.

The early-career analytical chemist agrees. 'Everyone loves fresh ideas ... but at the end of the day, people aren't actually that willing to change their protocols and procedures,' they said. 'Especially because of a suggestion made by someone who hasn't been at the company for a long time at all.'

Younger chemists may also feel as though their abilities are undervalued. Lori told us about having her skills underestimated by a senior colleague – only because she's a younger chemist. William, too, described a stint as a junior chemist during which he was made to do low-skilled work he felt overqualified for. 'Their justification was that I'm the least experienced in that section, and they've got no time to train me,' he said.

Here, physical age may matter. 'I was overlooked for a role purely based on the fact that one person ... said that I was immature,' said the early-career analytical chemist.

Not all of the younger chemists we spoke to had experienced similar situations, however. 'We were working on this project ... Just because I was less experienced, I didn't get less work, and I didn't get the easier work,' said Renata. 'I felt like I was always acknowledged and treated fairly.'

James Beckett, PhD student at the University of Queensland and Chair of the Queensland Young Chemists' Group, saw a lack of experience — whether perceived or real — as an advantage that younger chemists have over their senior counterparts. 'They don't have any preconceptions about what they should be doing or how things should be done,' he said. This could translate to younger chemists being easier to train in new roles or skills. '[Later in your career] you might have more knowledge, but I think your ability to adapt to new situations is not

quite as strong as someone who is fresh out of the gate.'

'I think being a little doe-eyed translates to being a more conscientious worker, because you care about things more,' added the early-career analytical chemist. 'I've always been too eager to do more.'

'I think that they [younger chemists] are motivated,' agreed Lori. 'They can see that there are issues that need to be dealt with, and I think that they have the driving force to be able to do it.'

Younger chemists might even have specific skills that established chemists lack. 'Young chemists have grown up with technology and a lot more of us are fluent in technology, and that's a big difference,' said Karin. 'Social media is very big as well now ... One benefit of having the Young Chemists' Society is that we communicate to each other over Facebook, which means that everyone can make sure that they're heard.'

The freedom to explore opportunities was also identified as an advantage younger chemists may have. 'You're still early enough [in your career] to maybe move from an academic environment to an industry environment,' said Monika.

'You can take those risks to explore new things,' Lori said. That could mean anything from moving around the world to choosing a start-up over an established multinational company – provided favourable personal circumstances and adequate support.

Providing support to all younger chemists is exactly why groups such as the RACI Young Chemists' Groups and the IYCN exist. They hope to connect younger chemists with the support, knowledge and opportunities they need to succeed. But most importantly, they exist to connect younger chemists with each other. 'The Young Chemists' Group is all about linking aspiring chemists, no matter where they come from or where they live or what sort of chemistry they are interested in,' said William.

'The IYCN is really aimed at bringing together younger chemists from all across the globe,' agreed Lori. 'One of the things that we're trying to do is make sure that we can capture opinions not just from America or Europe, but all over the world.'

Younger chemists represent a different demographic in more ways than just by age. In 2018, the Royal Society of Chemistry reported that 44% of all chemistry undergraduate students in the UK were women, as opposed to 9% of professors. When considering how we can best support younger chemists, chemists must also recognise how they differ from previous generations in terms of gender identity, race, background, disability or sexuality.

A younger chemist is someone who is establishing their career in the chemical sciences. Anxiety about employment opportunities was a common thread throughout each of these interviews. Universities generally don't illuminate many career pathways outside climbing the academic ladder. A younger chemist's own lack of knowledge of the job market is matched by employers who might not even know what a chemist is. Finding even that entry-level job can be a hurdle.

Young Chemist groups: who to contact

IYCN: iycnglobal.com
RACI:

• New South Wales: William Li, william.li1@outlook.com

Queensland: James Beckett, james.beckett1@uqconnect.edu.au
 South Australia: Renata Kucera, renata.kucera@flinders.edu.au
 Victoria: Monika Szabo, monika.szabo@csiro.au

• Western Australia: Karin van der Pal, karin.vanderpal@postgrad.curtin.edu.au

IYCN vision

Connect and empower younger chemists globally.



IYCN mission

The International Younger Chemists Network (IYCN) supports and advocates for younger scientists working across the chemical sciences towards a globally sustainable future.

Next IYCN meeting

IYCN General Assembly, to be held concurrently with the next IUPAC General Assembly in Montreal, Canada 2021.

The value of a recent graduate, a younger chemist, is not always clear – whether that is to employers, or to the younger chemists themselves.

However, graduate chemists will have recently spent years showcasing their ability to learn and to adapt. Few could make it through that gauntlet of lab work, report writing and exam cramming without a passion for the science.

A younger chemist is someone whose knowledge and network may contain gaps. A younger chemist needs additional support from their peers and from mentors to find a foothold in their field of choice. Help offered respectfully by experienced and established chemists will be welcomed with open arms by each of the groups we spoke to.

As we've discovered while writing this article, a younger chemist is also welcoming to anyone who feels as though they might not fit the mould. 'At the end of the day,' said James, 'There's nothing to gain by excluding people based on their age.'

Anna Ahveninen MRACI (@Lady_Beaker) is a younger chemist and science communicator. Having recently left the RACI, she now works in communications at the Australian Academy of Science. Josh Marlow (@PhD_in_Training) is about to submit his PhD thesis on the topic of nanoparticles in liquid crystals, and has been working under Dr Rico Tabor at Monash University.

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chemistry in Australia





BY PETER KARUSO

Rarely is an element the focus of a Nobel Prize, but in 2019 the third element (lithium) took centre stage. The Nobel Prize in Chemistry 2019 was awarded for contributions to the development of the lithium-ion battery. This light and powerful rechargeable battery has revolutionised consumer electronics and laid the foundation of our wireless society.

n the night of
10 December 2019 in
Stockholm, Sweden, the
Nobel Prize in Chemistry
was given 'for the development of
lithium-ion batteries' to M. Stanley
Whittingham, the first to invent a
lithium-ion battery, John B.
Goodenough, the first to use metal
oxides as the cathodes, and Akira
Yoshino, who invented carbon-based
anodes that made Li-ion batteries a
practical reality.

Batteries: a short history

In 1781, at the University of Bologna in Italy, Luigi Galvani noticed that frog legs occasionally twitched when they were hung from a brass hook and allowed to touch an iron trellis. So Galvani joined together a length of each metal to form a brass and iron arc that made the leg muscles contract when touched. Galvani had just unknowingly invented the first battery. Being an anatomist, he attributed the muscle contraction to 'animal electricity'. He believed the metals merely conducted the electricity from one part of the frog to another. One of

the earliest readers of his published findings in 1791, Italian chemist and physicist Alessandro Volta came to a very different conclusion. He thought the electricity came from the two metals used in the arc. This led to a bitter scientific feud but also to the invention of the Voltaic pile in 1799, ushering in our modern understanding of electricity.

Volta's 'pile' was a stake of 45 copper discs and 45 zinc discs separated by brine-soaked paper. Each cell is capable of 0.8-1.1 V so this pile would have been capable of generating about 40 V. News of this pile came to Britain in the form of a letter to the President of the Royal Society, Sir Joseph Banks, in March 1800. In his excitement, Banks leaked the letter to several close colleagues, including surgeon Anthony Carlisle and chemists William Nicholson and Humphry Davy, well before the letter was read to the Royal Society in September. This allowed Carlisle and Nicholson to publish the discovery of electrolysis in July 1800, using Volta's pile. Humphry Davy showed that the electricity came from a chemical

reaction, not by the voltage difference between the two metals as believed by Volta.

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Anode (oxidation): Zn \rightarrow Zn^{2+} + 2e^- Cathode (reduction): CuO + H_2O + 2e^- \rightarrow Cu + 2OH^- or 2H_2O + 2e^- \rightarrow H_2 + 2OH^-
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In a macabre twist, Galvani's nephew Giovanni Aldini, while a staunch partisan of 'animal electricity', did not ignore Volta's pile. Aldini used it to tour the capitals of Europe – his most famous exhibition took place in 1803 at the Newgate Prison in London, UK. He inserted metal rods into the mouth and ear of the corpse of recently executed murderer George Foster and used Volta's pile to animate Foster. According to the official description:

On the first application of the process to the face, the jaws of the deceased criminal began to quiver, and the adjoining muscles were horribly contorted, and one eye was actually opened. In the subsequent part of the process the right hand was raised and clenched, and the legs and thighs were set in motion.

Not surprisingly, some observers thought Aldini was bringing Foster back to life. Mary Shelley knew all about Galvani, Volta and Aldini from Humphry Davy and William Nicholson, who were friends of her father, and she attended many of Davy's public lectures. In 1816, during a cold and wet summer in Geneva with Lord Byron and her husband to be, Percy Shelley, she wrote the novel *Frankenstein*.

From the chemistry of Volta's pile came the lead–acid (sulfuric acid) battery in 1854 (Wilhelm J. Sinsteden), demonstrated by Gaston Planté in 1859:

Anode (oxidation):
Pb +
$$HSO_4^- \rightarrow PbSO_4 + H^+ + 2e^-$$

Cathode (reduction):

PbO₂ + HSO₄⁻ + 3H⁺ + 2e⁻ \rightarrow PbSO₄ + 2H₂O

This reaction can produce 2.0-2.1 V. Six cells are combined in series to produce the magic 12V required for a modern car battery. Their high peak currents compensate for their low weight-to-charge ratio so they are still the battery of choice to power vehicles. Lead-acid batteries were the first secondary battery (they can be recharged). Volta's pile, like normal disposable batteries, is described as primary. Applying a voltage to the lead-acid battery reversed the above reactions, converting PbSO, to PbO, at the anode and PbSO, to Pb at the cathode.

The next great development came when Swedish chemist Waldemar Jungner invented and patented the nickel-iron (Ni-Fe) and nickelcadmium (Ni-Cd) batteries in 1899. In 1901, Thomas Edison patented the Ni-Fe battery in the US, which resulted in a long and costly patent dispute between the two. Edison eventually won, only because he had far greater financial resources than Jungner. The Ni-Fe batteries eventually became known as Edison batteries and were touted as the preferred battery for electric cars in the early 1900s. Electric cars actually predate steam and petrol cars, being most popular between 1850 and 1910. Ni-Fe batteries are notable in their durability, able to survive continuous recycling for up to 20 years. These batteries led to the nickel-metal hydride batteries commercialised in 1989.

M. Stanley Whittingham

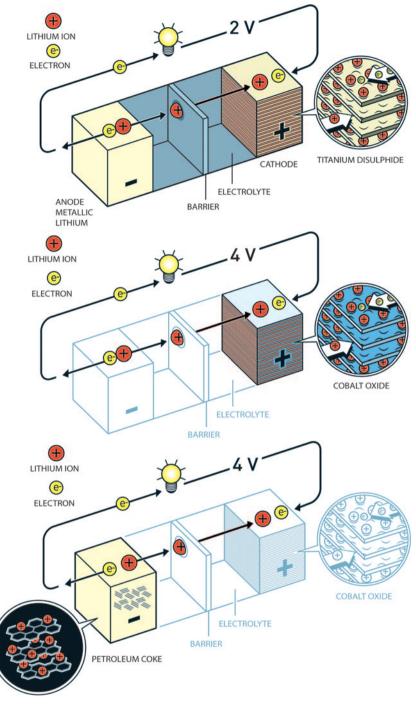
Whittingham was born on 22 December 1941 in Nottingham, UK. He was educated at Stamford School for boys in Lincolnshire 1951–60 and then read Chemistry at Oxford (BA 1964, MA 1967 and DPhil 1968). After completing his DPhil with P.G. Dickens (tungsten bronzes), Whittingham went to Stanford as a postdoc, working for Robert Huggins, who introduced him to solid state ionic phenomena. Specifically, he studied the transportation of sodium (Na+) and

silver (Ag^+) ions in solid electrolytes (intercalation) with a view to producing superconducting materials. This research would set the stage for his discovery of the Li-ion battery.

By 1969, US production of oil could not keep pace with demand and the US (like the rest of the world) became dependent on cheap oil from the Middle East. Large oil companies such as Exxon were keen to diversify, predicting the 1973 oil crisis, and set up research facilities such as the Exxon Research and Engineering Company in Clinton, New Jersey, to which Whittingham was recruited in 1972. His mandate was to work on anything as long as it had nothing to do with petroleum. His research on tantalum disulfide (TaS_o) superconductors did not go well but he did notice that the conductivity of TaS_a changed when potassium ions (K⁺) were intercalated. Upon further investigation, he found that the material was surprisingly energy rich and he could easily measure a 2 V potential - as good as a lead-acid battery. This called for a change of tack and he started investigating these materials for energy storage purposes.

He changed the cathode from TaS. to titanium disulfide (TiS_a) and replaced K+ with Li+ and produced the first rechargeable Li battery. The choice of Li was no accident - a quick look at the SI Chemical Data book reveals Li has the highest standard electrode potential (-3.04 V) of any metal and is the lightest $(\rho = 0.534 \text{ g/cm}^3)$. Whittingham's design was thus a Li metal anode that would give up an electron and migrate to the cathode as Li+, being intercalated into the TiS_a. Upon recharging, the Li+ would migrate back to the Li cathode.

Whittingham took his invention to Exxon Headquarters in New York city; after a 15-minute meeting, the top brass decided they could commercialise this new battery. But everything was to be done in total secrecy in case their competitors in



Comparison of the basic designs of Whittingham's, Goodenough's and Yoshino's Li-ion batteries. Johan Jarnestad/The Royal Swedish Academy of Sciences

the nearby Bell Laboratories should get wind of this invention. Production had its setbacks, all to do with Li's other unique properties. Li is highly reactive and can burn when it comes into contact with water or air. It can even burn in the absence of oxygen. This led to several Li fires at the Exxon labs. But worse was yet to come. Repeated charging and discharging cycles of the early Li⁺ ion batteries resulted in the Li⁺ ions returning to the cathode, not as a flat plate but as dendrites, whiskers of pure Li metal

that could pierce the barrier between anode and cathode and short out the battery with spectacular results. To make the battery safer, Li was replaced by a LiAl alloy but this reduced the number of cycles the battery could achieve from thousands to tens.

Nonetheless, the battery was announced to the world in 1976 and plans were underway to scale the battery to eventually power a car. Unfortunately, the price of oil dived in the early 1980s and Exxon discontinued Whittingham's battery research.

After 16 years at Exxon,
Whittingham became a manager at
Schlumberger-Doll Research, an
oilfield services company that had an
interest in electronics and
semiconductors. However, he stayed
there for only four years before
becoming an academic at the State
University of New York at Binghamton
in 1988, where he remains a
distinguished professor of chemistry
and materials science and
engineering.

John B. Goodenough

John Goodenough was born in Jena, Germany, to American parents. His parents' relationship was 'a disaster'. At 12, he was sent to a private boarding school at Groton and rarely heard from his parents again. He struggled with dyslexia and could not read, but he was good at maths and won a place, and an aid package, to attend Yale. He went on to graduate summa cum laude in mathematics in 1943 and was promptly conscripted to World War II.

After the war, Goodenough, then an army captain in the meteorological service posted in the Azores, received a telex ordering him to Washington, DC. Some unspent GI Bill budget money was to be used to put 21 returning army officers through PhDs in physics. Goodenough had taken almost no science as an undergrad but for reasons unknown a Yale maths

professor added his name to the list. He soon found himself at the University of Chicago where he studied under some of the leading physicists of the era, including Edward Teller and Enrico Fermi. He finished his PhD (under Clarence Zener) in 1952, and went to work at MIT's Lincoln Laboratory, joining a team that was working on a new system of computer memory.

In the mid-1950s, Goodenough and Junjiro Kanamori developed the empirical Goodenough-Kanamori rules, which rationalised the magnetic properties of metal oxides that would become important in the development of modern random access memory (RAM). By the mid-1970s, Goodenough became obsessed with finding a solution to the energy crisis that had spurred Whittingham to explore battery development, but this could not be done at the Lincoln Laboratories because they were funded by the air force and energy was the responsibility of the National Lahs

In 1976, Goodenough applied for a position as professor of the Inorganic Chemistry Lab at Oxford and was surprised to be selected, considering he had virtually no chemistry background. In that same year, Exxon unveiled the Li-ion battery, which was briefly commercialised by Exxon before the aforementioned tendency for these batteries to explode and catch fire became apparent. Goodenough thought he could create a more powerful battery than Whittingham's by replacing the TiS. with a metal oxide, with which he was very familiar from his days at MIT. Goodenough asked two postdocs to systematically work through all the metal oxides to see which ones could accommodate the most Li+ ions that could be pulled out by applying a potential of 4 V. The answer came back as cobalt oxide (CoO₂). The new battery was completed in 1980, using lithium tetrafluoroborate in propylene carbonate as the electrolyte and Li

metal or $\mathrm{Li}_{0.1}\mathrm{V}_2\mathrm{O}_5$ as the anode. The discovery of CoO_2 cathodes allowed the use of anodes of much higher potential than Li metal but these proved more difficult to find. Interestingly, Oxford declined to patent the new battery, which is too bad because it turned into a multibilliondollar-a-year business.

In 1986, Goodenough hit the English mandatory retirement age of 65 and left Oxford to join the University of Texas at Austin in the Cockrell School of Engineering departments of Mechanical Engineering and Electrical Engineering. There he has continued his research on ionic conducting solids and electrochemical devices and at the age of 97 still feels he has one more big breakthrough in him.

Akira Yoshino

The final breakthrough for the 2019 Nobel Prize came in 1985 from Japan. In the West, the low cost of petroleum products in the 1980s put an end to battery research. However, in Japan electronics companies were very motivated to find light and powerful batteries to power their new mobile devices (mostly radios, cordless telephones and cameras).

Akira Yoshino was born in Osaka, Japan, in 1948. He went to Kitano High School, a European-style school founded in 1873. He then earned his BSc (1970) and MSc (1972) in Chemistry from Kyoto University and went to work for Asahi Kasei Corporation. He started working on polyacetylenes - they had recently been reported as organic conductors by Hideki Shirakawa (Nobel Prize, 2000) and there was a lot of interest in using these molecules in microelectronics. In 1981, Yoshino began to investigate rechargeable batteries made from polyacetylene to avoid the dangers of solid Li metal anodes of Whittingham's battery but was unable to find a suitable cathode. In 1983, he read about Goodenough's CoO₂ anode and paired this with his polyacetylene anode to produce his

first working battery. Other carbonaceous materials were tried and eventually, and somewhat ironically, petroleum coke was found to make the best anode. A prototype was finished in 1986.

This marks a new concept in Li-ion batteries, based on the transfer of Li+ ions rather than the conversion of Li+ to Li metal. The Yoshino battery was the first Li+ ion battery that contained no metallic lithium. The battery was lightweight, developed more than 4 V and, most importantly, was safe and could be punctured without catching fire. Another safety feature was that if the battery overheats, as in the case of a short circuit, the barrier between anode and cathode melts, closing off the pores to prevent rapid discharge. The official launch of the new battery was in 1991 and championed by Sony; however, it did not really catch on until 1996 and the advent of laptop computers.

oday, an electric car can outrun a Bugatti Veyron (16cylinder quad turbo) in a standing quarter-mile and electric trucks and mining machinery are already in production, with companies such as Renault, Volvo and MAN leading the way. However, the real driving force behind an electric vehicle revolution will be AI and selfdriving technologies. This will change the car from a transportation method to a social space where all occupants can consume media, correspond, work and socialise. Na-ion batteries are under development and already display some unique advantages over Li-ion batteries such as a wider range of operating temperatures and lower costs. Energy storage is also essential for transforming energy production to a decentralised, carbon-free system, where energy can be produced from renewable sources and stored in high power density batteries, thereby lessening the impact of climate change.

Peter Karuso FRACI CChem, FRSN is the Professor of Chemistry at Macquarie University, Sydney.

BRIDGE Tapping into a passion for science

Engaging audiences is central to careers in science and research. How to do it? Get comfortable and tell your story.

BY SHANNON RYAN

ommunicating scientific research is vital to its viability, yet researchers rarely receive training in engaging with the general public. As if conducting research isn't difficult enough, scientists are expected to be expert communicators with a firm grasp of skills more commonly learnt in an English degree than a science one.

Not surprisingly, most scientists fall short of this expectation. The consequences of this skill gap are real, and they're having an impact on job security and career progression for researchers.

Securing grant funding is becoming more competitive and increasingly difficult. Most scientific grant applications clearly explain how something will be done, but they rarely touch on why it should be done. A lack of success in securing grants directly impacts on the ability to have a career in research, and unfortunately government funding for research is not a growth industry.

Overall, the inability to communicate science – whether to government, colleagues or the general public – can decrease the occurrence, impact and translational potential of research.

Government isn't the only game in town

There are other funding options beyond government: consumers represent a critical – and often overlooked – engine of research funding. Mater – a Catholic not-forprofit involved in health care, research and education – is trying to connect with this supporter base. The



BRIDGE provides scientists with comprehensive training on how to effectively engage with consumers and convey the importance of their research in an accessible way.

BRIDGE provides scientists with comprehensive training on how to effectively engage with consumers and convey the importance of their research in an accessible way. The focus is less on methodology and more on why the research is going to benefit the community.

Bringing together science communicators, philanthropic engagement experts and mentor researchers, the BRIDGE program idea, which is understandable, relevant and attractive to a target audience – and conveys the importance of their research.

It's simple – but that doesn't mean it's easy

There are a few basic premises that any good science communicator needs to know (this applies to everyone who wants to communicate anything):

- 1. What is it that you are trying to say? What's the most important point for your audience to walk away with?
- 2. Who are you communicating to?
 What do you know about your
 audience, their education level and
 familiarity with your topic?
- 3. What do you want the outcome of this communication to be? Are you trying to solicit a gift, inform your audience, or win a grant from peers? It's pretty simple. But it's important not to confuse 'simple' with 'easy'.

Be kind to your audience and to yourself

Only a very few, strange, strange, people actually enjoy public speaking. For the rest of us it's an

organisation's approach is founded upon the simple idea that scientists speaking about their own research make the best science communicators.

To upskill researchers at Mater and improve researcher interaction with consumers and attract interest from potential donors. Mater has launched the BRIDGE program. The acronym comes from 'BRInging researchers and Donors to GEther', but it also links into the benefits of the program: bridging the gap in understanding between researchers and the public, and bridging the gap between sources of funding for projects. The program is collaboratively developed and delivered in partnership by Mater Research and Mater Foundation.

provides researchers with tools that assist in creating a broader awareness of their research through academic channels, government and other funding bodies and philanthropic agencies.

The program is open to researchers at any stage of their career. Once they move through the two workshops, participants have shown a marked improvement in their ability to communicate with the public. They've taken the step from including exhaustive amounts of detail, to framing presentations around one key

uncomfortable experience that we only do when we have to. Standing in front of a large number of people who are fidgeting, playing with their phones or whispering among themselves is enough to make you nervous. When we get nervous, we typically fall back on what we know best. In the case of a scientist, that's science specific to their field; and when you're talking to someone who doesn't have a similar background to you, that's often the wrong approach to take. The tools used to put a presentation together can also help you in more informal communication.

The BRIDGE program provides researchers with tools that assist in creating a broader awareness of their research through academic channels, government and other funding bodies and philanthropic agencies.

Thinking about how you talk about your work can help improve communication with your colleagues, stop you from boring your cousins to death over Christmas dinner when they ask how work is going, and help you explain to your boss or director how your work aligns with the goals of your organisation.

Stripping out jargon is important. Spend a minute thinking about your audience. They may be (they will be) unfamiliar with the jargon used in your field. During your presentation, article or dinner conversation, you may be introducing people to brand new concepts, as well as new language. If you want them to walk away familiar with your research, be kind to them. Build their knowledge up to the point that they can comfortably walk away with the point you think is most important.

People only have a limited attention span, and there is no shortage of research showing how the human brain is incapable of storing much information in working memory. Once people become overwhelmed – and this can happen simply by having too much information on a slide – they go into shutdown mode and are liable to take advantage of the next distraction they can find. Presenters are effectively competing with devices for the attention of their audience.

Tell a story

There's no room for debate; science fiction is objectively cool (just saying).

Spaceships, geostationary satellites, mobile telecommunicators, world spanning communications networks, cloning – all the best ideas come from science fiction. Because that's what sci-fi is, the examination of an idea; and this is a particularly useful tool for scientists to consider when talking about their work.

Isaac Asimov, an author from the golden age of science fiction described sci-fi as 'that branch of literature which is concerned with the impact of a scientific advance upon human beings'. And when it comes to



those of us interested in, but not educated in, your field – the consumers, donors, fundraisers, marketing and communications teams, specialists from different fields – that's what we need to know.

It's not the charts, the publications or the references, it's the ideas you are exploring, the impact of your work on people, and even the characters making those breakthroughs. It can sound trite, but do not underestimate the power of a story pitched to the right audience.

One of the first projects I reported on as a young science communicator was mobile genetic elements, sequences of DNA that can move from one location in the genome to another. I had never heard of this, and after interviewing the researcher I spent an afternoon going down the rabbit warren of Wikipedia (seven pages deep before I even started to come back up!) trying to wrap my mind around an entirely new concept.

At a recent conference in Brisbane, I watched a postdoc researcher explain these transposable elements to an audience of Year 7 science students. She used Star Wars Stormtroopers and Clone Troopers to explain the difference between a gene such as BRACA-1, of which we only have one copy – the Stormtrooper – and these 'jumping genes', which effectively clone themselves – Clone Troopers – meaning we can have hundreds of copies of the gene throughout a single cell.

In a five-minute presentation, she introduced a new concept to an audience completely unfamiliar with her field, and informed them how she was investigating these jumping genes to better understand how cancer metastasises. She helped them create meaning by putting her work in to a context that was more familiar for the audience. It's not rocket science (another undeniably cool area of science, it has to be said)!

It's a toolbox, not a template

There is no one right way to communicate research, but there are a lot of wrong ways. At the end of the day, you have to be comfortable with the way you are talking about your work.

At Mater we've developed the BRIDGE program to help researchers tap into their own passion to help them communicate not just what they do, but why they do it, and why it matters to their audience.

The program provides a toolbox rather than a template. One of the most valuable components of the program is feedback from fellow researchers. Hearing constructive advice from peers and colleagues with expertise in different and diverse fields is of enormous benefit. And the realisation that even fellow scientists need to understand your work at a lay level is invaluable. Research has become so specialised that it is possible, even likely, that people in adjacent fields will have only minimal exposure to the work that you do.

Just think of a psychologist and geneticist talking about their work. They're both in the medical research space, both aiming to improve people's quality of life, yet they may barely share a language between them if they don't strip out their jargon. Even for these highly intelligent people, George Bernard Shaw (allegedly) summarised the challenge well: 'The single biggest problem in communication is the illusion that it has taken place'. I say 'allegedly', because there's debate whether he ever said that quote, or if it should be attributed to William H. Whyte. Unlike plenty of medical research challenges, that's a conundrum that may never be solved.

It's ok to leave people wanting more

It's all too easy to provide more information than is needed; but this can be counter-productive.

There are two simple reasons to consider paring back the amount of information you share:

- 1. In your allocated 10 minutes, as speaker number 7, in a three-day conference, your audience has already been bombarded with information. Their brains are already overwhelmed and tired. So what is the most important thing you want them to walk away with? If they only remember one thing about your presentation, what is it that you want that to be?
- 2. You can always provide more information. If you have engaged their attention enough that they want to know more, congratulations! If you write a book, and people want you to write another one so that they can learn more, that is the definition of success.

There is no one right way to communicate research, but there are a lot of wrong ways.

So next time you have to present, write an article, or explain to a family member what you do for a living, I hope you take a few moments to think about the best way you can communicate your work.

Take a moment to think about what is interesting and important about your work, and what it is that your audience actually needs to know.

With a bit of practice, you'll have your audience focused on you, and not on their phones.

Shannon Ryan (Shannon.Ryan@mater.org.au) is a Philanthropic Engagement Manager at Mater. He plays a key role liaising between Mater Research and the philanthropic ministry Mater Foundation.

Beyond chemistry: In a different light

Many flowers exhibit dark patterns visible under ultraviolet (UV) light, but invisible to the human eye. Honeybees have been studied extensively as pollinators and their eyes have been shown to be sensitive to UV, blue and green light. It is widely believed that the UV patterns of flowers assist pollinators to find nectar or pollen on the flowers. There have not been many studies of visual systems of Australian insects.

The sensors in modern consumer digital cameras are designed to produce images as we see them. They achieve this by having a so-called UV-IR cut filter installed in the light path in front of the digital sensor, which blocks all wavelengths outside the wavelength range of human eyes, from blue at around 400 nm to red at around 700 nm. The first step in taking UV images is to have the UV-IR cut filter removed and replaced, in clean-room conditions, with a clear non-absorbing filter, as can be done by Camera Clinic in Melbourne.





Hibbertia humifusa (rising star guinea flower), visible light (top) and UV light (bottom).

When I started attempting to take UV flower photographs about six years ago, I was guided by a wonderful website (www.ultravioletphotography.com) that answered all my questions. I was surprised to find that nobody else on that website was taking photos of Australian native flowers in UV light. That was too much of a challenge for a Yorkshireman to resist and you will now find some of my images on that site (Blum A.B. 2016). The method used to take UV images is covered in my Learning List (Rørslett B. 2013, Blum A.B. 2013). There is also a very useful link ('Cadmium' 2019) that shows the false UV colours obtained through narrow (10 nm) pass band filters, which range from green at 325 nm, through yellow at 350 nm to blue at 383 nm. The range of false UV colours in my UV photographs of some Australian native flowers range from pale cream to dark blue, which may give an approximate idea of the wavelength of the reflected UV light.

The colours seen in these UV images are false colours due to the interaction of UV light with the red, green and blue dyes used in the Bayer array on the digital sensor, which produce the colours we see with our eyes in visible light (Crowther J.M. 2019).

A picture is said to be worth a thousand words, so look at *Hibbertia humifusa*, the rising star guinea flower, photographed in the Grampians of Victoria in visible light and UV. The insect in the UV shot, which was not present for the previously taken visible image, gives some idea of the size of the flower. The stamens, which are yellow in visible light, become dark grey or black in UV light, which corresponds to the dark pattern visible in many flowers as mentioned. It seems likely that UV-absorbing pigments are expressed in the stamens and anthers of the flowers in order to protect the genetic material of the flowers from UV degradation. Pollinating insects, which can see in UV light, may then be able to orient themselves to visit those areas. The petals themselves show a pale cream false UV colour.

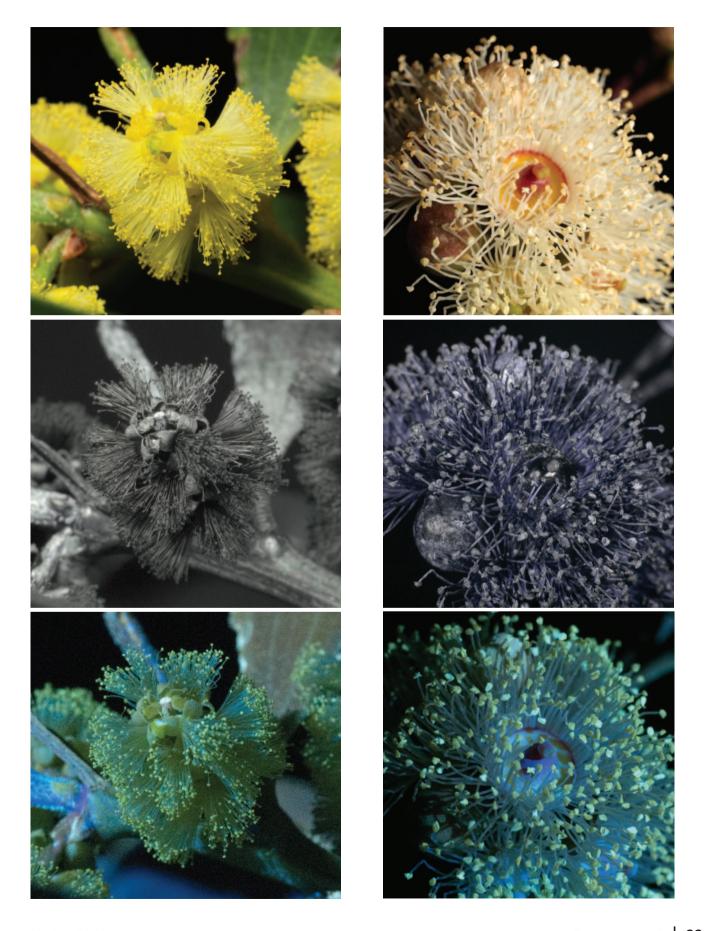
My wife, Sue, has been an enthusiastic grower of Australian native plants for many years. If I place a garden-grown flower in my studio and take visible and UV photographs using flash as I do in the field, then darken the room and illuminate the flower with a UV-LED (light-emitting diode), with peak emission at 365 nm, I can take a photograph of the UV-initiated visible fluorescence (UVIVFL) of the flower. I have found it impossible to take UVIVFL images 'in the bush' as it is next to impossible to set up a dark tent to exclude daylight. The visible, UV and UVIVFL images become a complementary set to describe and investigate the floral structure.

When I started in this field in 2013, I did a literature survey for pigments of Australian native flowers and found that in 1924 James Mathew Petrie at the University of Sydney had

Opposite page:

Left: Acacia longifolia (Sydney golden wattle), top to bottom: visible light, UV light and UVIVFL light.

Right: Eucalyptus camaldulensis (river red gum), top to bottom: visible light, UV light and UVIVFL light.





worked on the yellow pigment of *Acacia longifolia*, Sydney golden wattle. He identified the watersoluble pigment as a rhamnose glucoside of kaempferol, a flavonol found in a large range of plants.

Kaempferol has UV maximum absorption at 265 and 365 nm, the latter being in the centre of the UV-A region covered by these UV photographs, which are taken through a Baader U filter that passes radiation between 320 and 380 nm.

I photographed *Acacia longifolia* to get the visible, UV and UVIVFL images shown. Stamens are the most conspicuous part of the acacia flowers. In the UV image, the yellow stamens have become black, as would be expected from the UV properties of kaempferol. We can see, in the UVIVFL image, the pale yellow fluorescence of the pollen on the anthers, supported on green filaments, with insignificant small green petals at the base of the stamens. Kaempferol has a reported fluorescence maximum at around 550 nm in the green region of the visible spectrum.

Eucalyptus flowers resemble those of acacias by being effectively bundles of stamens. Eucalyptus camaldulensis (river red gum) displays, in visible light, cream flowers consisting of buff anthers on pale translucent filaments, with an orange stigma, which become in UV, dark grey anthers on dark blue filaments, with a dark grey stigma and in UVIVFL pale yellow

anthers on light blue/green filaments, with a blue/green stigma. The pigments in these flowers are probably different from those in acacias but they may perform the same UV-protective functions for the genetic material in the plants.

Native orchids are attractive plants to grow and photograph, as shown here with *Pterostylis obtusa*, the blunt-tongue greenhood. The flower, which is bright green in visible light, becomes light-blue to grey in UV and vivid red and blue in UVIVFL. The red colour seen in the UVIVFL image is probably due to chlorophyll fluorescence.

Thelymitra nuda, the plain sun orchid, is an attractive flower in visible light, with blue petals, a white column and tuft and a yellow crest, which in UV becomes light blue petals, column and tuft with a black crest, turning in UVIVFL to deep blue fluorescent petals with a light blue column and tuft and yellow crest.

It is a very privileged position to be able to see these features in UV and UVIVFL. One thing I quickly learnt, was to avoid trying to predict how the UV and UVIVFL images would look. I would love to hear from anyone who could guide me to papers that contain UV-vis spectra of Australian native flowers.

David Oldfield FRACI CChem (dsoldf@netconnect.com.au) took early retirement in 1999 after working for 32 years at what became Aeronautical and Maritime Research Laboratory, Maribyrnong in The Defence Scientific and Technology Organisation (DSTO). He was Hon. Treasurer of the RACI Polymer Division for 20 years from 1975. David has been an enthusiastic amateur photographer from his school days in the West Riding of Yorkshire and gained his Fellowship of the Royal Photographic Society in 1997.

Biliana Cvetanov

Opposite page:

Left: *Pterostylis obtusa* (blunt-tongue greenhood), top to bottom: visible light, UV light and UVIVFL light. Right: *Thelymitra nuda* (plain sun orchid), top to bottom: visible light, UV light and UVIVFL light.

David's learning list

Atlas of Living Australia, www.ala.org.au.

Blum A.B. 2013 'How to make a custom light profile', www.ultravioletphotography.com/content/index.php/topic/621-photo-ninja-how-to-make-a-custom-light-profile.

Blum A.B. 2016 'Australian wildflower index', www.ultravioletphotography.com/content/index.php/topic/1769-australian-wildflower-index.

'Cadmium' 2019 'UVP page with examples of "Sparticle" colours on post #55',

www.ultravioletphotography.com/content/index.php/topic/3567-clone-wars-newcomers-are-the-casualties/page__st__40.

Crowther J.M. 'Understanding colour reproduction in multispectral imaging: measuring camera sensor response in the ultraviolet, visible and infrared' *Imag. Sci. J.* 2019, vol. 67(5), pp. 268–76.

Dyer A.G. 'Reflection of near-ultraviolet radiation from flowers of Australian native plants' *Aust. J. Bot.* 1996, vol. 44, pp. 473–88. Dyer A.G., Garcia J.E., Shrestha M., Lunau K. 'Seeing in colour: a hundred years of studies on bee vision since the work of Nobel Laureate Karl von Frisch' *Roy. Soc. Vic.* 2015, vol. 127, pp. 66–72.

Elliot W.R., Jones L.J. Encyclopaedia of Australian plants suitable for cultivation, Lothian, Melbourne, 1980.

Hempel de Ibarra N., Langridge K.V., Vorobyev M. 'More than colour attraction: behavioural functions of flower patterns', *Curr. Opin. Insect Sci.* 2015, vol. 12, pp. 64–70.

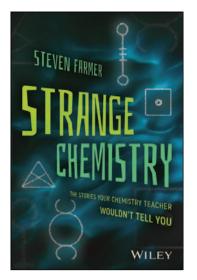
Horridge A. The discovery of a visual system. The honeybee, CABI, Boston, MA, 2019.

Koski M.H., Ashman T.-L., 'Dissecting pollinator responses to a ubiquitous ultraviolet floral pattern in the wild' *Funct. Ecol.* 2014, vol. 28, pp. 868–77.

Petrie J.M., 'CXXVIII. The yellow pigments of Australian acacias' Biochem. J. 1924, vol. 18(5), pp. 957-64.

Rørslett B. 2013 'How to make a UV photograph', www.ultravioletphotography.com/content/index.php/topic/80-how-to-make-a-uv-photograph.

Rørslett B. 2013 'How to make UV colours reproducible', www.ultravioletphotography.com/content/index.php?/topic/81-how-to-make-uv-colours-reproducible.



Strange chemistry: the stories your chemistry teacher wouldn't tell you

Farmer S., John Wiley and Sons, 2017, paperback, 346 pp.,

ISBN 9781119265269, approx. \$70

If you share my passion for knowing and seeking out all manner of weird and wonderful matters chemical, I guarantee you will love this book. Strange chemistry: the stories your chemistry teacher wouldn't tell you will also provide you with plenty of enriching and entertaining material

to enhance the teaching and learning of chemistry. Even if you are merely regaling your friends with tales of 'mad honey' or how to kill somebody with eye-drops, both covered in this book, you are bound to have their attention, utterly free of any thought bubbles flashing, 'Isn't Chemistry soooo ... boring!'

Rhododendrons, particularly *Rhododendron luteum* and *Rhododendron ponticum*, which grow around the Black Sea, contain neurotoxins called grayanotoxins, which are transferred via nectar to honey.

In small doses, this 'mad' honey is intoxicating and hallucinogenic, and still finds use as an aphrodisiac (a bedroom sweet?). Larger amounts lead to loss of coordination, muscle weakness, slowed heartbeat, low blood pressure and ultimately death. Xenophon wrote of this in 401 BCE. In 67 BCE, the King of Pontus, Mithradates IV's army retreated before Pompey the Great's troops, leaving behind mad honey-containing honeycombs in the path of the Romans. The Romans ate the honey, became incapacitated and were subsequently overcome. Defeat is normally associated with a bitter taste, but in this instance it was sweet! And, if you think chemical warfare started with Fritz Haber and World War 1, think again!

Australian authorities propose drug-testing drivers with renewed vigour, leading me to question my wisdom in enjoying my poppy-seeded toast topped with honey from bees, which, just possibly, may have supped on poppies.

If you are a coffee addict, rest assured you are on safe ground. A lethal dose of caffeine is of the order of five grams, which equates to about 30 cups of coffee, so you would have to try pretty hard if you were planning a caffeine-fuelled exit.

The author recounts questioning his classes on appropriate aphrodisiacs, eliciting answers such as alcohol, cocaine, chili peppers and oysters. His favourite response, however, was 'money', which led him to lament that generally chemists are not known for their great wealth. He claims testosterone is the only proven aphrodisiac, for both men and women. Viagra fails at the first hurdle: it increases performance but not desire.

Cellulose, probably the world's most abundant organic compound, is discussed in the book. Humans, unlike many

animals, are unable to digest cellulose, although we can happily digest starch with its different acetal linkages. This does not stop organisations slipping cellulose into all manner of processed foodstuffs: it is cheap and it will not hurt you. Next time you find yourself munching on 'fast food', just be aware that you may be chewing on a bit of wood (with the lignin stripped out) or a bit of paper (which is predominantly cellulose). That just might explain the taste! Quite possibly, your appetite for processed food may never be the same again.

These are just a few examples, picked more or less at random from this very interesting book. Equally, if you want to learn all sorts of interesting things about pesticides, how bullets work, how and why drugs of addiction work, explosives, radioactive fallout, how breathalysers work, why (finger) nail beauticians are at risk from toluene (dizziness and impaired kidney function), formaldehyde (a potent carcinogen) and dibutyl phthalate (a suspected teratogen) ingestion, why mercury compounds are used as preservatives in formulations such as eye-drops, and much, much more besides, all documented under arching themes in 11 chapters, then here is a book to be relished and avidly consumed (but not eaten; remember, you cannot digest cellulose, irrespective of the relish).

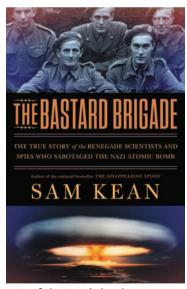
Author Steven Farmer from Sonoma State University, California, has produced a most interesting, engaging, inspiring and informative book. It is easy to read and I enjoyed it immensely. I highly commend it for your interest and attention.

R.J. Casey FRACI CChem

The Bastard Brigade: the true story of the renegade scientists and spies who sabotaged the Nazi atomic bomb

Kean S., Hodder and Stoughton, 2019, paperback 453 pp., ISBN 9781529374872, \$22.99 (Amazon.com.au)

New York Times' bestselling science writer Sam Kean's most recent book, The Bastard Brigade, is a story of intrigue and melodrama



built around the World War 2 developments of the atomic bomb. Some of the best-known names in the history of theoretical chemistry are involved, but Kean's writing style, which usually provides anecdotes about significant discoveries, is relatively submerged. In Kean's own words, this book is more unified, more a novel, telling a larger overall story dealing with 'renegade scientists and spies who sabotaged the efforts of the Nazis' to produce weapons of war.

The core players in the Bastard Brigade were Samuel Goudsmit (nuclear scientist), Moe Berg (famed baseball player), Colonel Boris Patch, Bill Donovan (Head, Office of Strategic Services (OSS), precursor of the CIA) and General Leslie Groves (Head, Manhattan Project).

The book has 59 chapters in Parts I–VI: Pre-War, 1940/41, 1942, 1943, 1944 and 1945. Kean's story tracks the early discoveries (Part I) of radioactivity, including α -particles, γ -rays (the Joliot-Curies) and neutrons (Chadwick and Fermi), and the significant discoveries of transmutation (the Joliot-Curies), nuclear fission (Otto Hahn and Lise Meitner) and neutron moderators of the fission process (Fermi's group).

In 1939, the Nazis established the Uranium Club, driven by Kurt Diebner (a military ordinance scientist, not held in high

regard by his peers). Eight physicists and chemists made up this group, initially excluding Werner Heisenberg. The scientists were assigned one of two projects: uranium enrichment, or building a 'uranium machine' (nuclear reactor). Heisenberg took on the latter with his friend and younger colleague Carl Friedrich von Weizsäcker.

Part II 1940/41 describes Weizsäcker's preference for uranium-238 as a nuclear fuel rather than pursuing ²³⁵U enrichment. ²³⁸U absorbs a neutron to become ²³⁹U before undergoing β-decay (the neutron transforming into

a proton, with an electron emitted) to give element 93, neptunium, easily isolated chemically. A further β -decay provides the highly dangerous plutonium (element 94).

The Uranium Club's Walther Bothe was responsible for building the 'moderator' for the uranium machine. He experimented with readily obtained and multiple sources of 'purified' carbon (graphite), only to find impurities absorb rather than moderate the neutron flux.

By the time the allies joined the 'reactor race' in 1942 (Manhattan Project), Heisenberg had built prototype reactors incorporating graphite and heavy water as moderators. Heisenberg pushed to acquire heavy water from the Norsk Hydro plant in German-occupied Norway. Kean describes the British–Norwegian espionage to destroy the electrolysis units at the Norsk Hydro plant and secure stocks of heavy water for the allies.* However, the plant was recommissioned in months, due to Heisenberg's pressure.

There is mention of a 1941 meeting between Heisenberg and his mentor Niels Bohr in Copenhagen. The meeting ended in the dissolution of a long-term friendship because Heisenberg pressured for disclosure of allied nuclear activities. I prefer Michael Frayn's play *Copenhagen* (1998) that explores the conflicting views about that meeting.

The need for secrecy was paramount, but Kean notes that the US had no effective spy or espionage agencies at that time. In addition, many of the world's best nuclear scientists were behind enemy lines. Kean's portrayal suggests a degree of bungling and failure before the 'spies' got their act together. This especially applies in attempts to cajole, kidnap or even assassinate some key scientists as the book evolves. The 'secrecy' carried into their own camp when Robert Oppenheimer (Manhattan Project) was later subjected to interrogation by the Bastard Brigade, suspected of collaboration with the Russians.

Kean's descriptions of Heisenberg create a dichotomy: on the one hand a vigorous Nazi sympathiser working for the dominance of the Reich, on the other a proponent of 'Jewish' science, and a dedicated (even arrogant) scientist aiming to

achieve major advances in science. After capture and interrogation by his old friend Goudsmit, Heisenberg boasted a 670% increase in neutrons ('a measly amount'). Goudsmit offered Heisenberg a job in the US, to be answered 'Germany needs me', the exact response from an offer made in 1939.

The scenario Kean provides on the Nazi developments of 'vengeance' (V-weapons) in Parts IV and V brings in Werner von Braun, the infamous Peenemunde bunkers, and the attempts by Joe Kennedy to fulfill his

ambitions to become a war hero. Kennedy died piloting a fault-ridden 'flying bomb' aimed at the V3-bunkers in Mimoyecques.

Part VI 1945 also shows that the Bastard Brigade (comprising the OSS, the Lightning-A, and the Manhattan Project's own intelligence 'Alsos' unit) had grown and commandeered equipment and resources to search out German scientists. This 'competition' was also against the Russians. Werner von Braun was hoisted off to continue his work on rocketry through to the Apollo space program in the US. Following capture, all the Uranium Club members were detained in England, where they were secretly 'spied-upon'. Most later returned to senior positions in Germany.

I found *Bastard Brigade* an easy and interesting read and especially recommend it to those of the younger generation with an interest in scientific history, not tainted by war. It stirs ethical thinking about nuclear weapons then and now. Reference sources are present but limited, and the descriptions of 'American' spies, agents and heroes often fail to acknowledge the other allied nations involved.

The Manhattan Project proved a relative success, though a horrifying experience for all mankind. Goodness knows what would have happened if the Uranium Club had created a nuclear bomb – but was this its goal?

Alan J. Jones FRACI CChem

March/April 2020 Chemistry in Australia 33

By the time the allies

(Manhattan Project),

Heisenberg had built

incorporating graphite

prototype reactors

and heavy water as

joined the 'reactor

race' in 1942

moderators.

^{*}See the overdramatised movie *The Heroes of Telemark* (1965). The 2016 Norwegian TV series *The Heavy Water War* is more realistic.



The basis of everything: Rutherford, Oliphant and the coming of the atomic bomb

Ramsey A., HarperCollins, 2019, hardback, 374 pp., ISBN 9781460755235, \$39.99; e-book ISBN 9781460709559 \$19.99; audio book ISBN 9781460780893

The basis of everything: Rutherford, Oliphant and the coming of the atomic bomb is a highly readable and

fascinating account of the lives of two great antipodean scientists: a New Zealander, Lord Ernest Rutherford of Nelson (Nobel laureate, Chemistry 1908), and an Australian, Sir Mark Oliphant, a foundation professor at the Australian National University and a sometime Governor of South Australia.

This is a story of great science, which ultimately led to the development of the atomic bombs (one made with uranium, 'Little Boy', and one with plutonium, 'Fat Boy') deployed on Hiroshima and Nagasaki in 1945, bringing World War 2 to an abrupt and terrible end and plunging our world into a future undermined forever with the latent threat of nuclear annihilation, as the current president of the US so frequently sees fit to remind us.

However, in many senses all this is peripheral. This is a story about two men, both humbly born (Rutherford the son of a New Zealand flax farmer, Oliphant the son of a public servant of limited means), both the beneficiaries of scholarships to enable their secondary education (Nelson in Rutherford's case, Adelaide in Oliphant's), both influenced by strong mothers, both with astonishing serendipity in their lives' paths, both tormented with the premature deaths of their children, both brilliant scientists and inveterate tinkerers with gadgets, devices and machinery from an early age, along with all the faults, uncertainties, foibles and idiosyncrasies of us lesser mortals. Let me give you some flavour of the book.

This is a story of great science, which ultimately led to the development of the atomic bombs ... deployed on Hiroshima and Nagasaki in 1945, bringing World War 2 to an abrupt and terrible end ...

For example, you will read of how Rutherford attended Canterbury College, Christchurch, where he was heavily influenced by the professor of chemistry (ironically, he won the Nobel Prize in Chemistry in 1908) but then turned to physics.

There was one 1851 scholarship for New Zealand when Rutherford applied. He missed out. Next year he applied again. Again he missed out. However, the scholarship provided but a slender income, the nominated recipient was married, and he decided it was financially infeasible and withdrew. Rutherford got the nod. There is a line in Shakespeare's Julius Caesar that goes, 'There is a tide in the affairs of men, which taken at the flood, leads on to fortune. Omitted, all the voyage of their life is bound in shallows and in miseries'. Rutherford was faced with two choices: he could marry his school teacher fiancée Mary and settle, probably as a teacher, in the back blocks of the South Island of New Zealand; or he could 'bite the bullet', prepare himself for a (presumably celibate) life of penury and head off, borrowing money from his family for the boat fare, to Cambridge and the Cavendish Laboratory to work with J.J. Thomson. He chose the latter path and, eventually, succeeded Thomson (in 1919) as Cavendish Professor.

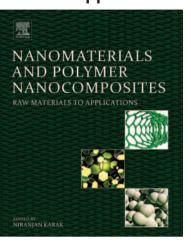
Similarly, you will read in this book of how, from a reasonably shaky start, great serendipity also characterised Oliphant's life's course, leading ultimately to his pivotal roles in the invention of radar and the initiation of the Manhattan Project. Oliphant was devastated and absolutely mortified by the deployment of the bombs: he had foreseen that a series of escalating demonstrations of the power available would very quickly lead to armistice.

After the war, he returned to Australia to help set up the ANU. That was a frustrating, annoying period of his life, which caused him great stress and anguish and made him rue the day he ever accepted the challenge. Along the way, he had rejected awards and honours, always arguing that it was not him but his team who deserved the award. Eventually, Prime Minister Robert Menzies convinced him that a knighthood would be good for Australian scientific prestige, so he reluctantly became Sir Mark and, indeed, Governor of South Australia.

Everybody should read this book. It is one of the great stories of science, but vastly more importantly, it is a story about people: about their triumphs and failures; happiness and despair; greatness and ordinariness; good fortune and bad. In short, a great story of life and, for me at least, a great tale featuring many of the heroes of my youth. I cannot recommend it too highly. There are a few very minor blips in the science, to no great effect. If I tell you that author Andrew Ramsey is not a scientist but a well-respected and widely known cricket journalist, you will surely forgive him. The book is easy to read and filled with fascinating insights. You *must*, *must*, *must* read it! To paraphrase Isaac Newton, 'If I (you) have seen further, it is because I (you) have stood on the shoulders of (these two) giants'. And yet, they were but mortal men!

R.J. Casey FRACI CChem

Nanomaterials and polymer nanocomposites: raw materials to applications



Karak N. (ed.), Elsevier Inc., 2019, paperback, 432 pp, ISBN 9780128146156, \$272.95; ebook, ISBN 9780128146163, \$461.93

Nanomaterials and polymer nanocomposites is an interesting, intriguing and informative book.

Although you will find reference in the Bible to Moses's early-post-natal expedition down the Nile in a fibre-reinforced boat (reed-reinforced pitch) and to various early works on incorporation of colloidal gold into glass (and colloids are but a tiny tad bigger than nanoparticles), composite

polymeric materials have largely emerged over the past 70 years from the quest to modify the physical properties of synthetic polymeric materials, thus extending and enhancing their application. And, this has been very successful too! All of which leads to the question of why one might wish to incorporate nanomaterials (they are, after all, not terribly easy to make) into polymeric matrices. There is the intrigue.

This book will inform and enhance your knowledge about nanomaterials, explaining exactly what they are, how you can make them, how and why you might incorporate them into polymeric matrices, and what properties the resulting materials might manifest. The coverage is comprehensive, ranging across synthesis techniques to characterisation and applications of nanoparticles and nanomaterials in polymers. The chapters mostly centre on particular nanomaterials; for example, metals and metal oxides, clay and POSS (polyhedral oligomeric silsesguixane), carbon dots, graphene and carbon nanotubes, silicon-based nanomaterials, cellulosic, and bio-based polymeric materials. They are comprehensive, superbly referenced and largely stand-alone, and will bring you smoothly from novice to researcher in a wellwritten and eminently readable manner. Nanomaterials in polymers bear some resemblance to colloidal systems: you could say they both seem to embody some elements of the recondite! That is what happens when you start playing with systems having very large interfacial areas: they can be hard to make (unless you are an analytical chemist where, to your chagrin, colloidal precipitates have been known to form with overwhelming facileness!). But they can have very interesting properties.

There are myriad uses of nanomaterials. For example, silver nanoparticles have been around in photographic emulsions for a very long time, as well as in pigments and paints, and conductive/antistatic composites. More latterly, the developments have utilised the antimicrobial and antibacterial properties of silver nanoparticles in the manufacture of specialised sterile clothing, medical instruments, water filters as

... silver nanoparticles have been around in photographic emulsions for a very long time ...

well as ethylene scavengers in packaging films designed to delay ripening of fruit such as bananas. And, yes, incorporation of silver nanoparticles into your nylon socks or the polymeric inner sole of your running shoes will alleviate the stink and make you much more popular about the place!

Other metallic nanoparticles find use in optical nano-coatings, in creating special materials with interesting magnetic and electronic effects, in micro-electronics, in antimicrobial and packaging materials. Nanocomposites containing metal oxides are used in bone repair, in the manufacture of LEDs and in gas separation membranes.

Carbon nanotubes and graphene are utilised in materials for advanced micro-electronics and sensors, in biosensors, drug delivery systems and tissue engineering. These materials are the very reason your computer's lithium-ion battery does its job.

I trust I have given you some sense of the wide range of useful materials resulting when polymers and nanomaterials are brought together. They, and many more besides, are all covered in this book.

Editor Niranjan Karak is located at the Advanced Polymer and Nanomaterial Laboratory at Tezpur University in India. He has assembled 19 co-contributors, mainly, but not exclusively, from India, to write the chapters of the book. Each chapter adheres to a consistent and logical progression and coverage. The standard of the chapters is, therefore, uniform and high. Karak has done a very good job.

So, who might want to read this book? Certainly chemists and materials scientists, particularly those with an interest in polymer composites and those interested in the preparation, utilisation and applications of nanomaterials. It would also be a good textbook for use in an appropriate materials science course, at both undergraduate and postgraduate levels. If you are thinking about tackling a PhD in materials science, then this book might be a good place to start. It nicely bridges a gap between adding macro-materials (about which a lot is known) and adding micro-materials (about which I suspect the knowledge is not so profound) to polymers.

R.J. Casey FRACI CChem

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From a cat's whisker

It is surprising how little students learn these days about how things actually work and how they hardly ever see the 'guts' of the devices they use. 'No serviceable parts inside' is a common label warning. People of my vintage, on the other hand, made things or pulled them apart.

I was shocked recently to see a reasonably sophisticated calculator for sale for only a couple of dollars - solar cell included! This led me to ponder whether the transistor could be designated as the most dramatic and pervasive invention of the 20th century.

Post-war (1945-48), Sydney was suffering from regular power blackouts (along with other shortages). No power for electronic valves (tubes) meant no radio. No radio meant missing crucial episodes of Biggles, Superman and The Argonauts Club. Unfortunately, hurricane lamps provided light for homework (neat handwriting please).

My dad, an electrical engineer, scrounged a pair of ex-army earphones. He attached them across a coil of thin wire wrapped around an empty cardboard toilet roll, continued it as a long aerial strung through the window to a tall tree with the other end attached to a metal stake in the ground. A variable condenser (capacitor) completed the tuned circuit that covered the range of the carrier frequencies of all the strong local radio stations.

However, the pièce de résistance was a 'cat's whisker', which made the music for my ears, literally. No moggie was depilated; this crucial element consisted of a fine-tipped copper wire just touching the surface of a pea-sized chip of galena (a black silvery lead sulfide ore).

The radio waves from the stations' transmitters covered frequencies roughly from 500 to 1500 kilocycles per second and these were amplitude modulated (AM) with sound waves

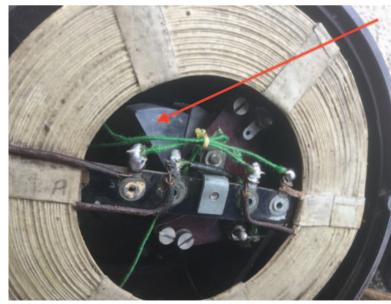


November 1925.

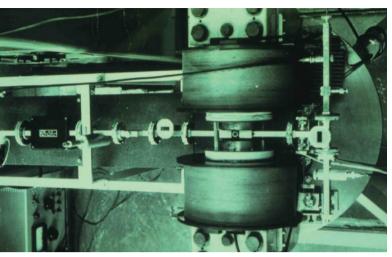
ranging roughly from 20 to 20 000 cycles per second. The cat's whisker/galena short circuited the higher frequency carrier wave to earth but demodulated (rectified; turned AC into DC), the information part of the radio signal (the sound), and this was fed to the earphones (bit.ly/36esBrt). You had to find a 'sweet spot' on the galena surface for this to work, so no one was allowed near you in case it was lost in vibration.

The variable condenser is like interlocking fingers opening and closing, thereby changing the overlap of the plates of the condenser and hence its capacitance, which in turn shifts the tuned circuit frequency to the next station.





A commercial-type crystal radio (c. 1920s). Left: the very fine cat's whisker wire hovering above a chip of galena mineral. Right: down below the coil, is the variable condenser (attached to the tuning dial).



A lab-built electron spin resonance spectrometer with permanent magnet, field modulating coils and 3 cm microwave plumbing supplied by an ex-army radar microwave generating klystron (that we rumoured could jam police radar).

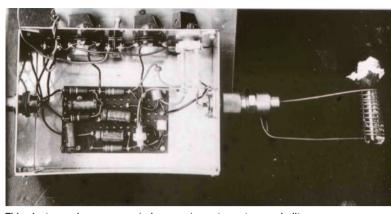
Thoughts of cat's whiskers triggered W.B. Shockley and colleagues' 1948 invention of the solid-state transistor (at Bell Telephones), for which they received the 1956 Nobel Prize. Unlike a diode, this could now amplify signals. W.H. Schottky (another worthy of the time), was a leader in metal-semiconductor junction theory, the basis of operation of most of the early crystal detectors. This was an early example of nascent ideas on quantum mechanics explaining real macroscopic effects.

1950s radios were richly endowed with 5–7 transistors powered by a dry cell battery. Some replaced the cat's whisker, others amplified the signal, while the last group rectified the sound wave. Aerials and earths were no longer necessary but were provided to improve reception. Radios had been liberated from a power point. But on Cronulla Beach they all tended to disconcertingly and synchronously change stations with the changing temperature! This was solved by replacing doped germanium with doped silicon, which has a larger electronic gap and is thus less heat sensitive. But it required a more challenging metallurgy.

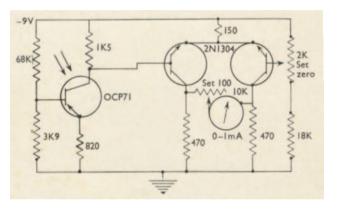
In both cases, chemical purity was the key to success. This was established by a process called zone refining, which we also used to bring organic materials (such as pyrene) to spectroscopic purity. Impurities were carried along in the molten zone doing a slow transit and concentrated in a slug at the end of the sample tube, to be dumped.

In 1960, chemical instrumentation had taken advantage of these developments and some valve units were being replaced with solid-state power-rectifying diodes and transistor circuits.

However, the pièce de résistance was a 'cat's whisker', which made the music for my ears, literally.



This electron spin resonance (microwave) spectrometer was built with the help of Gibb Bogle, CSIRO Radiophysics, next door). On the right is a mini-PMR instrument (water probe with manganese ions for paramagnetic relaxation) to measure the magnetic field strength, as part of my MSc studies, 1962.



Schematic diagram of the student IR colorimeter.

Education in Chemistry 1968, vol. 5(2)

A popular transistor, OC-71 (bit.ly/38xrJQ7) could be scratched to emulate the more expensive photosensitive OCP71, which became the basis of an interesting student lab experiment. The sensitivity of this transistor to near-infrared allowed the building of a simple student IR colorimeter to measure the spectral shift that occurred when copper ions were complexed with different ligands, such as ammonium and chloride.

The microchip was developed in 1959 and today a chip containing billions of transistors costs roughly the same as a single transistor did in 1954. Now there is a supercomputer that has more than a trillion transistors (econ.st/30IyaND).

Think what else electronic miniaturisation has done for (and to) our society – phones and drones; satellites (GPS) and space exploration; medical devices (from bionic ears, diabetes monitors and gut-exploring robots). Social media has drastically changed global society and politics. And the OCP71 was, in retrospect, the first primitive accidental silicon solar cell.

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.

Rare earth lanthanides: a difficult separation

In the past few years, there has been an increasing interest in the production of rare earths in Australia, where the US Geological Survey estimates reserves at 3.4 Mt. China is the world's primary source of rare earths, producing 120 kt/year out of a world total of 170 kt/year, and with 44 Mt reserves. Rare earths are now seen by the US as strategic materials.

Rare earths are not all that rare. They are more common than precious metals and as common as some of the commodity metals, such as lead. The problem is that separation into the individual elements is somewhat arduous.

The term 'rare earth' covers not only the lanthanides (f-block elements) but also scandium and yttrium, which are found along with the lanthanides. A major source of rare earths is monazite sand, which is found on many beaches in Brazil and India. Monazite is particularly rich in cerium. The typical composition of monazite sand is as follows and can be considered a rare earth, thorium phosphate:

 $\begin{array}{ccc} {\rm CeO_2} & 30\% \\ {\rm Di_2O_3} \ ({\rm mixed\ lanthanides}) & 32\% \\ {\rm ThO_2} & 6.50\% \\ {\rm P_2O_5} & 28\% \\ {\rm SiO_2} & 1.50\% \end{array}$

Another significant source is carbonatites such as bastnasite, which have a high lanthanum content. The rare earths are formed from fission of uranium and thorium so that the ores contain these parent elements and hence come under regulations designed for the nuclear industry. A typical bastnasite composition is:

CeO 50% La₂0₃ 32% Pr₆0₁₁ 4% Nd_2O_3 13% Sm₂O₂ 0.50% Eu₂0₃ 0.10% 0.20% $Gd_{3}O_{3}$ Other rare earths 0.20%

The bastnasite deposits are rich in the lighter rare earths (La to Gd). The heavier rare earths (Tb to Lu) are more common in ion-exchanged clay mineral deposits found widely in southern China. One form of ion-exchanged clay is red mud (waste from alumina extraction), which is being extensively researched as a source of rare earths.

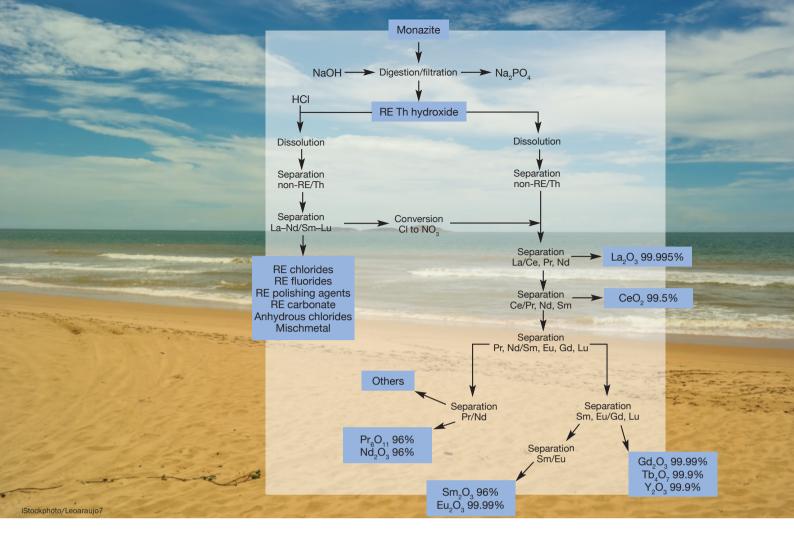
For the major uses of rare earths – catalysts (60%) and ceramics (15%) – it is often not necessary to separate the individual rare earths, and there

are several methods for separating the rare earth elements from unwanted minerals. Lanthanum and cerium are mostly the elements of interest. The fact that cerium has two stable oxidation states (III and IV) assists in its separation. One of the main uses is in cracking catalysts in which zeolite-Y (faujasite) is ion exchanged with rare earth elements (preferably with a high lanthanum or cerium content). The resulting catalyst rare earth-Y has higher Brønsted acidity than the normal hydrogen zeolite. Rare earth exchange into the zeolite also has the effect of increasing the stability of the zeolite in the presence of steam. This facilitates separating the hydrocarbon-cracked products from the zeolite, using steam. Most refineries use the fluid cat-cracking process for producing gasoline from heavier hydrocarbons, so the world demand for rare earths for this is large. Cerium is in high demand as a catalyst promoter for vehicle catalytic converters where the cerium increases the activity of the platinum group metals (Pt, Pd) for oxidation of unburnt hydrocarbons in the vehicle exhaust.

The problems come when individual elements in the lanthanide series are required. Europium was used as a phosphor for early (cathode ray) colour TVs. Fortunately, europium has two oxidation states (II and III), which can be used to extract europium from the mix. Today there is increased interest in other individual elements; for example, neodymium and samarium for powerful magnets and other rare earths for electronic components. The other elements have only one stable oxidation state (III) so separation of the individual elements is somewhat laborious.

Rare earths and radioactive isotopes and typical selling prices of the oxide

Rare earth	Atomic no.	Radioactive isotopes			2018 price
		Isotope	%	Decay mode	USGS \$/t as rare earth
Scandium (Sc)	21				
Yttrium (Y)	39				
Lanthanum (La)	57	128	0.038	beta	2000
Cerium (Ce)	58	142	11.1	alpha	2000
Praseodymium (Pr)	59	141	100	alpha	
Neodymium (Nd)	60	144 150	23.87 5.6	alpha beta	51 000
Promethium (Pm)	61				
Samarium (Sm)	62	147	14.94	alpha	
Europium (Eu)	63				56 000
Gadolinium (Gd)	64				
Terbium (Tb)	65	159	100	alpha	461 000
Dysprosium (Dy)	66	156	0.052	alpha	180 000
Holmium (Ho)	67	163	100	alpha	
Erbium (Er)	68				
Thulium (Tm)	69	169	100	alpha	
Ytterbium (Yb)	70				
Lutetium (Lu)	71	175 176	2.5 2.5	alpha beta	



The sand at Setiba Beach in Brazil is rich in monazite – a source of rare earth metals.

The Rhone-Poulenc process for separating monazite sand (RE = rare earth) (after I. McGill, 'Rare earth metals', in *Handbook of extractive metallurgy*, vol. 3, Wiley-VCH, 1997, pp. 1695–741 (1997)).

In the early days, the elements were separaed by exhaustive fractional crystallisation, which has been used to separate and characterise the elements. The main process for separation is by liquid–liquid extraction in which an aqueous solution of mixed rare earth elements (usually as nitrates) is contacted with a hydrocarbon stream containing a ligand, which selectively extracts the rare earths. Several different ligands can be used but dialkyl phosphinic acids are a common type. This results in an organic stream richer in one element over another. A cascade of separators can be used to separate individual elements.

Early work on the separation process was conducted at the Argonne National Laboratory in the US and the process was developed by workers at Rhone-Poulenc. The Rhone-Poulenc process for separating the more commercially important elements from monazite sand illustrates the complexity of the problem (see diagram above).

There have been several attempts to establish a rare earth separation industry in Australia. As may be judged from the diagram, the separation process is energy intensive. The prevailing high cost of energy in Australia (especially on the east coast) presents a major hurdle.

Unfortunately, the main problem centres on the radioactive nature of the starting materials and the products. Most of the rare earths have radioactive isotopes. Apart from promethium, the rare earths have very long half-lives (more than 10⁷ years). All the isotopes of promethium are unstable (less than 17 days) and this element is not found in nature. There is a significant issue with thorium and uranium found in the ores but as unwanted materials. Because of their use in the nuclear industry, production of uranium and thorium is highly controlled and regulated. The antipathy of Australia's politics to the nuclear industry has stymied many proposals.

The current development by Lynas Corporation relies on exporting relatively benign carbonatite concentrate to Malaysia and performing the upgrading (value adding) there. Another potential source is at the BHP Olympic Dam operation but as yet the separation of rare earths has not proved economically feasible.



Duncan Seddon FRACI CChem is a consultant to coal, oil, gas and chemicals industries specialising in adding value to natural resources.

Sparkling wine foam

The appearance of foam when a sparkling wine is poured into a glass is regarded as an important sensory perception feature, especially for marketing. Further, the formation and duration of a ring of bubbles around the glass/liquid surface interface, or the mousse, together with the size or diameter of the bubbles are also perceived quality factors from a consumer's point of view.

Over the years that I taught sparkling wine production to oenology students, I was constantly intriqued as to what

wine components drive the foam behaviour. It seemed that it had to be a yeast output resulting from the secondary fermentation. This idea was reinforced by the apparent relationship between ageing on lees post-secondary fermentation and foam behaviour; that is, the longer the time on lees, the better the foam quality seemed to be. These observations obviously exclude consideration of carbonated wines, that is those made by injecting carbon dioxide into a wine post primary fermentation.

I was fortunate to meet Professor Andrea Curioni of the University of Padova at a wine conference where he outlined the measurements that had been performed on Prosecco at his university. After developing a standard pouring technique, foam behaviour was recorded by video camera. The image, kindly provided by Andrea, shows one result. The foam decreases smoothly with a consequent small increase in liquid height. Six Prosecco wines were examined by pouring the sample into the glass up to a specified height (one can see the marker on the left side of the glass), with each pouring replicated six times. Five of the six wines had maximum foam height above the liquid surface between 6 and 8 centimetres while one only made it to 1.7 centimetres. Foam decay times for four wines ranged from 5 to 8 seconds, with one (the low foam height) taking only 1.7 seconds, while one with an initial good foam height was still decaying after about 20 seconds.

These original experiments have not been published. I was fortunate to get access to all the images for use in my teaching program and the students loved the challenge of making their own foam assessment. In follow-up work, the Padova group published in 2014 (Food Hydrocoll. vol. 34, pp. 202–7) the results of 'reconstitution' experiments where five macromolecular fractions were isolated from a Prosecco wine and added back to the wine before ageing on lees. One fraction containing yeast mannoproteins showed the best foam behaviour, while grape-derived proline-rich proteins had no impact. An apparent cooperative effect between the two fractions gave a better 'foamability' than the individual fractions.



Many studies have attempted to define the critical chemical compounds that influence sparkling wine foam. These have been recently reviewed in *Critical Reviews in Food Science and Nutrition* (2019, vol. 59, pp. 2072–94). Drawing conclusions is, as the review authors point out, difficult due to differences in foam assessment techniques and production methods (bottle fermentation, tank fermentation or carbonation) as well as the time of ageing on lees. Many of the studies are focused on the style of wine common to the region where the research was performed (e.g. Champagne, Prosecco, Cava) and this also makes drawing broad conclusions a challenge.

In an attempt to address some of the present limitation in our knowledge, Bruna Condé in her doctoral program at the University of Melbourne used synchronous fluorescence spectroscopy to examine the 'chemical interactions influencing foam characteristics' (Beverages 2019, vol. 5, paper 54). Using a rather fancy robotic pourer with computer vision (Food Control 2017, vol. 71, pp. 383-92) to measure foam behaviour, fluorescence spectra were recorded for several sparkling wines after a range of wine compounds were added. Interpretation of the spectra showed that mannoproteins were linked to foam stability whereas phenolic compounds had a tendency to increase the number of smaller bubbles. The possibility of a polyphenolic compound-protein interaction influencing foam behaviour was also proposed. The authors recognised that their results may reflect the response of the additions made to the wine.

While reconstitution experiments have their place, there is a clear need for metabolic profiling of actual unadjusted wines, coupled with an agreed procedure for assessing foam behaviour and then relating the fluorescence spectra to foam behaviour. Extensive data analysis using advanced chemometrics techniques should allow the identification of critical wine components.



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.

Reviews and reflections

In 1940 the Macmillan company published a *Textbook of physical chemistry* and a couple of years later a rather cryptic but decidedly unfavourable review of it by E.A. Guggenheim appeared in the *Transactions of the Faraday Society*. 'In a certain city', it began, 'a councillor with grandiose ideas conceived the curious desire of having a picture of the whole city painted on a single canvas'. After commenting on the fine buildings in the city, Guggenheim went on to say that no 'painter could be found to attempt the task' until 'a certain travelling artist' was found to do it. 'Every building, large or small, ancient or modern, beautiful or hideous, useful or useless was included on his canvas, but the product of his toil was not a picture because he had omitted to pay any regard to perspective. The name of the city was Physical Chemistry and the name of the painter Samuel Glasstone.' Ouch!

The editor must have had second thoughts about the wisdom of offending a well-known author, so he asked N.K. Adams to re-review Glasstone's book. 'In the city referred to in a recent review', Adams wrote, 'there were many young and somewhat inexperienced immigrants, needing urgently a comprehensive guide-book' to help them appreciate the important works of art in the city. 'A well-known art critic', he continued, 'resident in the city ... took exception to the illustrated guide-book', but Adams felt it was 'an informative, and in many respects very clear, panorama of the city', so with 'considerable respect for both the critic and the author', he 'rushed immediately to buy a copy'.

Guggenheim's analogy probably owes something to the introduction in an earlier book, *Thermodynamics* by G.N. Lewis and Merle Randall (1923), that was brought to my attention by John Casey. 'There are ancient cathedrals which, apart from their consecrated purpose, inspire solemnity and awe. Even the curious visitor speaks of serious things, with hushed voice, and as each whisper reverberates through the vaulted nave, the returning echo seems to bear a message of mystery. The labour of generations of architects and artisans has been forgotten, the scaffolding erected for their toil has long since been removed, their mistakes have been erased, or have become hidden by the dust of centuries. Seeing only the perfection of

Physical chemists as reviewers are less forgiving of their peers, and Guggenheim was well known for his acerbic reviews and what he called 'being mischievous'.

the completed whole, we are impressed as by some superhuman agency. But sometimes we enter such an edifice that is still partly under construction; then the sound of hammers, the reek of tobacco, the trivial jests bandied from workman to workman, enable us to realize that these great

TEXTBOOK OF
PHYSICAL CHEMISTRY

BY

SAMUEL GLASSTONE, D.Sc., Ph.D.
Formerly Research Associate of Princeton University
and Professor of Chemistry in the University of Oklahoma

SECOND EDITION

MACMILLAN AND CO. LIMITED
ST. MARTIN'S STREET, LONDON
1956

structures are but the result of giving ordinary human effort a direction and a purpose'. And then, 'Science has its cathedrals, built by the efforts of a few architects and of many workers'.

Reviews of books in other branches of chemistry attract more jocular comments such as 'this is a book to dip into from time to time but too heavy to read in bed' and 'one measure of readability is whether or not a book can be enjoyed in the bath'. Physical chemists as reviewers are less forgiving of their peers, and Guggenheim was well known for his acerbic reviews and what he called 'being mischievous'. He damned van Ness's book on non-electrolyte solutions as pompous, and wrote that 'this pomposity is paralleled by platitudinous padding in plenty'. Van Ness came back with 'perhaps my monograph suffers from the same "pride and prejudice" ascribed to Professor Guggenheim's well-known book Thermodynamics by "a distinguished American reviewer". He was referring to George Scatchard's review of Guggenheim's 1949 Thermodynamics. An advanced treatment for chemists and physicists for which he suggested that subtitle. In his review published in 1950 in the Journal of Chemical Education, Scatchard wrote that the present book was 'essentially a matured version' of Guggenheim's Modern thermodynamics by the methods of Willard Gibbs (1933) 'grown to about twice the size', and concluded that 'it is hard to name a group which will find this book useful'.

Many people found Glasstone's book useful. He shrugged off the criticism and went on to produce a second edition in 1956. I still have my copy: a masterpiece in 1320 pages.



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.

Conference of Metrology Society of Australasia

3-5 March 2020, Melbourne, Vic. metrology.asn.au/msaconnected/events-menu/msa2020melbourne

Fundamentals of Process Safety

30 March 2020, Perth, WA

icheme.org/career/training/courses/fundamentals-ofprocess-safety/30-march-3-april-2020-perth-australia

Physical Chemistry Student Conference

15-17 April 2020, Flinders University, Adelaide, SA physchemstudentconf.com

Queensland Analytical Group Water Symposium

17 April 2020, Translational Research Institute, Brisbane, Qld raci.org.au/events/event/QAGWater2020

Process Safety Leadership and Culture

24 June 2020, Melbourne, Vic. icheme.org/safety-leadership

Joint meeting of RACI Organic Chemistry and Medicinal **Chemistry and Chemical Biology divisions**

5-8 July 2020, University of Wollongong, NSW omc2020.org.au

International Symposium on Macrocyclic and Supramolecular Chemistry

12-16 July 2020, Sydney, NSW ismsc2020.org

International Conference of Microreaction Technology

8-11 December 2020, Melbourne, Vic. imret2020.com

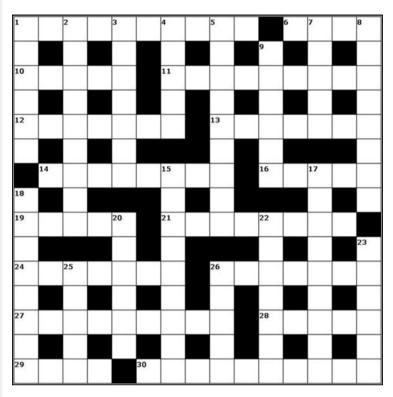
RACI events are shown in blue.



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cryptic chemistry



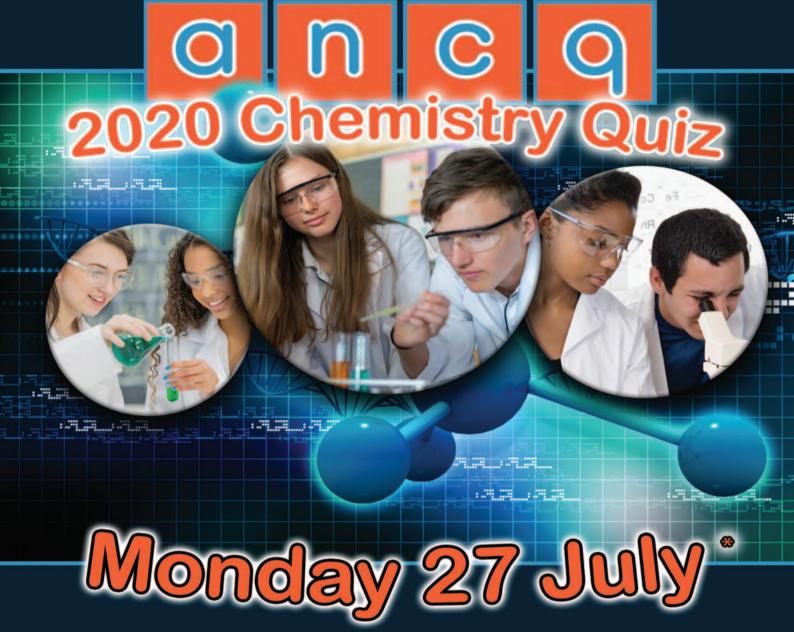
Across

- Charge holders devouring a crisp taco. (10)
- Black forest cake held back functions. (4)
- Four elements hit on the head. (5)
- 11 & 26 Across Precipitate curbed pollution's mess. (9,7)
- The first four elements. (7) 12
- Back orbital on SO radical. (7)
- Little one's urine not tested. (8)
- 16 Five elements demonstrated. (5)
- 19 See 1 Down
- 21 Separate manifest. (8)
- 24 Unpredictable car tire blew. (7)
- 26 See 11 Across.
- 27 Unusual calibrate of bugs. (9)
- 28 Be out of sulfur in it. (5)
- 29 Flexible child's play. (4)
- Below 20 Hz for niacin's transformation. (10)

Down

- 1 & 19 Across Restyle Cal radical to produce lactone. (6,5)
- Extended ton men rip off. (9)
- Make up carbon on sulfur: one way. (7)
- The honeymoon is over, love. Starting RSH. (5)
- Sense siblings are after 75 electrical components. (9)
- By itself. By itself again! Metal on metal sulfide! (5)
- Turning Spooner about con job. (8)
- Grants metal slumps. (6)
- Changes in current flow producing an EMF in channel charge. (9)
- 17 Manoeuvre so Council block. (9)
- 18 Look like the French after embers put out. (8)
- 20 Significantly sooner. (6)
- Miss ore mining for different 22 structures. (7)
- 23 Fixed interference. (6)
- 25 Shakes ore. (5)
- Opposite a molecule showing charge separation. (5)

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



The ANCQ is an international competition with papers translated into seven languages. In 2019, over 95,000 students from Australia and 20 other countries, including India, Germany & China, participated in the Quiz.

The Quiz is available in both hard copy and online formats.

racichemedcentral.com.au/ancq

REGISTRATIONS OPEN: 2 March - 12 June

ENQUIRIES: ancq@raci.org.au

* Some flexibility does exist if this date clashes with another school event.









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