

chemistry

June–August 2021

in Australia

Climate change: a Grim perspective

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- COVID-19 masks: how layering and materials matter
- Targeting poaching with synthetic science
- Emergency risk communication: how to get it right
- Embracing alternative fuels: the questions we should be asking

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cover story

Climate change: atmospheric facts and figures

In day-to-day life, climate change can seem intangible. But long-term records of global temperatures and atmospheric composition and their correlations show that climate change is real.

Aerial view of Cape Grim Baseline Air Pollution Station, Cape Grim/Kennaook, Tasmania.

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Make Australia make again From steam engines to the essential soaps of synthetic biology

The original cutting-edge technical approach to the design of modern motor vehicles was to use an external combustion engine. A steam engine. Now before we smile too much at this idea, it is important to know too, that at this time, more than 100 years ago, there was also serious technical debate as to whether electric vehicles were in fact the best option for personal transportation. Early electric cars were quieter, could go faster and didn't explode, but they had limited range and were slow to 'refuel'. These limitations are still familiar to us today. Imagine our world now if we had continued to develop electric vehicles and built up the infrastructure to support them. Imagine if we had conducted *more than a century of research* into practical, technical developments and the chemistries that improved the efficiencies of electric vehicles. Certainly, the planet would have been better off for it.

Internal, not external, combustion engines are the predominant power source of our modern cars. Apparently, however, there are some technical advantages in using external over internal combustion. Perhaps reflecting this, in the early days, external combustion vehicles represented the clear majority of all vehicles registered. Probably our professional cousins, the mechanical engineers, are best placed to argue the advantages and efficiencies of one system over another. However, for us chemists, perhaps the most significant benefit relates to pollution. An external combustion engine can use a green fuel and a fuel burning process that delivers very low carbon monoxide, nitrogen oxides and unburned carbon in the exhaust emissions. Again, we can only speculate as to the impact on the world's air pollution levels had we persisted with external combustion, steam-powered cars.

Australia plays a significant role in this story because as recently as the late 1970s, Australians were developing the most efficient steam-engine-powered cars ever made. A steam-powered Ford Falcon was used to parade around important politicians and featured in many motor shows and displays of the time. RMIT and University of Melbourne graduate Ted Pritchard was the pioneer

In part, this submission indicated that we need a strong domestic chemical manufacturing industry to underpin the development of any new technologies. Without this capability, Australia will be forced to continue to rely on global supply chains.

of this field, but despite some government funding and vocal support from Queensland cane farmers who saw benefits in using biofuels in the engine, his vision of Australians manufacturing his technology did not eventuate. The demise of this dream proved rich fodder for sub-editors at the time: 'Pritchard engine runs out of steam', *The Australian* 1978; 'Full steam ahead! The Pritchard car', *The Independent Australian* 1979; 'Steam car dream goes up in smoke', *The Australian* 1980; 'Pollies all steamed up', *The Telegraph* 1980. Despite this, thankfully the inventive ideas didn't die and decades later morphed into the technology that now underpins the renewable-energy-based, electricity-generating, technology of the West Australian company Uniflow Ltd.

Surprisingly, it was electricity (and batteries) that enabled the dominance of internal combustion engines over the last 100 years. Broken arms were not uncommon injuries for drivers of the first internal-combustion-powered vehicles, as they had to start the engine with a hand crank. The invention of the electric starter motor and reliable battery chemistry to power the starting process, combined with the manufacturing might of Ford's Model T assembly lines, led to the dominance of internal combustion technology. It is ironic that it is again electricity and batteries that today could lead to the demise of the internal combustion engine as electric vehicles take over our streets.

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Much of the focus of new and improved battery technologies centres on redox chemistry using lithium. Australia is one of the world's leading producers of lithium and recent funding of a large cooperative research centre, the Future Battery Industries CRC, headquartered at Curtin University, is certainly welcome. Despite this, Australia's ability to viably produce lithium batteries remains frustratingly far off. Indeed, chemists are especially aware that, over the last few decades, Australia has lost much of its capability to manufacture the things that are essential for our modern society. Instead, we typically import, according to the Bureau of Statistics, about \$2.5 billion each month in chemicals and related goods. This increases to more than \$5 billion if you include fuels and lubricants. The COVID-19 pandemic has shown us the fragility of some of our supply lines and this is a concern to chemists, but it should be a worry to all Australians.

Recently, the Australian Academy of Science, with input from leading chemists from the RACI, made a submission to the federal government regarding the emerging technologies that may prove to be critical to Australia's future prosperity and stability. In part, this submission indicated that we need a strong domestic chemical manufacturing industry to underpin the development of any new technologies. Without this capability, Australia will be forced to continue to rely on global supply chains. As evidenced during the pandemic, these supply chains risk disruption from global events and border closures, leaving Australia unable to produce sufficient quantities of many of the key chemicals that are essential for our way of life. Nowhere is this more evident than in the health sector. Australia imports more than 90% of its drugs and during the initial months of the pandemic nearly ran out of key medications such as Ventolin; even paracetamol was in short supply. The inability to make these drugs in Australia is not only important for existing medications and active ingredients.



The manufacture of novel mRNA vaccines, the approach that will most rapidly be able to respond to virus mutations, is built on complex synthetic biology. However, vaccine manufacture also relies on the availability of special lipids. Lipid nanoparticles must be made to deliver the vaccine; otherwise, the mRNA breaks down and can trigger unwanted immune responses. Such sophisticated 'soaps' are necessary to wrap the negatively charged mRNA in positively charged cationic lipids that thereby allow the mRNA to survive long enough to reach our cells and evoke the necessary response.

Recent announcements by the federal government of funding for pilot-scale manufacture of mRNA vaccines in Queensland and Victoria are welcome. But we must also remind our political leaders that the jigsaw has many pieces.

Without critical chemicals and reagents, and the chemists to make and monitor them, Australia stands very alone.



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Industry in Australia?

The March–May issue was certainly a bumper edition! As well as the rich mix of articles about advances in chemistry, I found the articles about Ötzi the Iceman and Goethe, and Geoff Scollary's contribution on the chemical influences on terroir in wine, especially fascinating.

However, it was Ian Maxwell's incisive article discussing the feasibility of domestic solar panel manufacturing in Australia that I found to be profoundly important. It laid out with great clarity the reasons that making solar panels in Australia should not be part of the desired post-pandemic manufacturing revival, which is the subject of much political discussion at this time.

I wonder if an examination of proposals to re-establish a domestic vehicle industry by making electric passenger vehicles here would stand up to a similar forensic examination. Would we obtain the batteries from elsewhere or make them here, and if we did propose to manufacture them here, how reliant would we be on foreign suppliers for the necessary technology, including chemicals? Perhaps a more fundamental question should be, what sort of manufacturing industries should be established here? What industries best use our current scientific and technological capabilities? What industries best use locally available raw materials and semi-finished products and reduce our reliance on critical imports? What industries employ the best mix of highly skilled technical specialists and other skilled and semi-skilled workers? Aside from the biomedical industries, which are offering green shoots of promise for Australia, where else can we look?

I believe that governments should not be in the business of attempting to pick winners. Ian Maxwell points out that part of the Chinese success story has been that the Chinese government has allowed the entrepreneurial spirit (combined with a strong work ethic) of its people to flourish by making it easy to do business. Much the same point is made by Matt Ridley in his latest book *How innovation works and why it flourishes in freedom* (Harper Collins, 2020). By 'freedom', Ridley means freedom from excessive regulation and excessive control in its broadest sense. Instead of a government-mandated, taxpayer-funded approach to new industry, should we not be making it easier for entrepreneurs to seek out and/or create new niche industries by simply getting out of their way?

Tom K. Smith FRACI CChem

Adelaide obituaries

As usual, in my devouring perusal of my now seldom editions of *Chemistry in Australia*, I read Ian Rae's letter first, followed by the obituaries, when they appear. Although I do not know all whose lives are related, it is always interesting to see the familiar paths taken through my contemporaries' lives. In the December 2020 – February 2021 edition, I noted that both Bruce West and Robert Morton had connections to Adelaide.

Strangely, early in my working life, I learnt of the tragic death of another chemist named Robert Morton, also with an Adelaide connection.

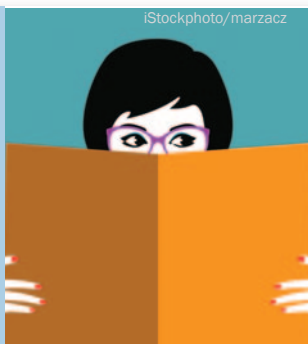
In 1963, I was working as a technical assistant in the Russell Grimwade School of Biochemistry at the University of Melbourne with Dr Richard Jago, an eminent biochemist involved with research into dairy flavours. Dr Jago became extremely upset in September 1963, when he learnt of the untimely and unfortunate death, at 43 years old, of Professor Robert Morton at the University of Adelaide. Dr Jago had apparently gained his PhD under the auspices of Bobby Morton during his Melbourne years.

Dr Morton's accidental death was caused by inhalation of the highly inflammable solvent acetone, used as part of the media in an experiment and which caught fire by being kept warm with electric radiators. Long before the formal and mandatory introduction of OH&S and the EPA. More details about Professor Morton can be seen at [https://en.wikipedia.org/wiki/Robert_Morton_\(biochemist\)](https://en.wikipedia.org/wiki/Robert_Morton_(biochemist)).

Dr Jago was overseeing a biochemistry PhD student, now Emeritus Professor Robin Anders at La Trobe University, who has had an interesting and, I believe, rewarding career, including a long period in New Guinea. From both Dr Jago and Robin, who I assisted with laboratory experiments, particularly using a Wahburg apparatus, I learnt many positive traits to be practised in a laboratory, which I tried to emulate throughout my years in laboratories in product development and application – humility, patience, good humour and the generous and proper treatment of a very raw, junior chemist, among other attributes. These were not taught as part of my education, even at the tertiary level. I will be forever grateful for the 15 months I spent in their presence.

Anthony F. Zipper FRACI CChem

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Flow chemistry trial for making drugs locally and fast

Can we guarantee supply of essential drugs in a global crisis? Australia may soon be able to produce essential drugs – including anaesthetics and treatments for antibiotic-resistant superbugs – rapidly and entirely onshore, ending the need to import them.

A collaboration between Melbourne chemical company Boron Molecular and DMTC Ltd (formerly the Defence Materials Technology Centre) is testing a new system capable of synthesising drugs at scale, quickly and continuously.

‘The system uses flow chemistry’, said Boron Molecular’s Director of Business Development, Dr Oliver Hutt. ‘It should give us the sovereign capability to produce life-saving drugs right here. We’ll be able to avoid supply chain delays from foreign manufacturers.’

The World Health Organization publishes a list of medicines considered essential for public health and disease treatment. These include antibiotics, antivirals, plasma substitutes and treatments for a wide range of conditions such as migraine, tuberculosis, cancers and heart disease.

The new system means that Australia will have the capacity to produce many, even most, of them onshore. They include:

- lidocaine, a local anaesthetic
- praziquantel, a critical treatment for parasitic worms
- rifampicin, for treating leprosy
- linezolid, an essential treatment for the superbug methicillin-resistant staphylococcus aureus (MRSA), and drug-resistant tuberculosis.

‘Australia doesn’t have the capacity to produce these domestically at short notice’, Hutt said.

‘That means we are subject to supply and cost issues on the other side of the world. This approach, if successful, means we can create the materials right here – making our medical system more flexible, more controllable and more resilient.’

Flow chemistry has been pioneered in Australia by CSIRO, and the CSIRO team is also supporting the DMTC project.

The method uses a precise balance of thermal and ingredient input controls that enable a chemical reaction to occur

continuously. The process is often safer, more precise and less expensive than traditional batch manufacturing.

DMTC Medical Countermeasures Program Leader Dr Felicia Pradera said the pilot program currently underway seeks to provide proof-of-concept that flow chemistry can be used to make large quantities of specific medications on demand.

‘A “platform” technology is one that validates a development pathway – once that process is proven with one therapeutic asset, the knowhow and expertise would be transferable to support Australia’s efforts to develop local manufacturing capability for other classes of pharmaceuticals’, Pradera said.

Pradera added that it was crucial to ensure that all medications produced by the system meet regulatory approvals.

‘This important project contributes to the ongoing development of Australian capability in therapeutic manufacturing and to building secure, stable local supply chains’, Pradera said.

Boron Molecular

Dr Josh Boyle from Boron Molecular working with a flow reactor. DMTC



Layering, material choice matter in COVID-19 masks

Wearing a face mask can protect you and others from COVID-19, but the type of material and how many fabric layers are used can significantly affect exposure risk, finds a study from the Georgia Institute of Technology (US).

The study measured the filtration efficiency of submicron particles passing through a variety of different materials. For comparison, a human hair is about 50 microns in diameter while 1 millimetre is 1000 microns in size.

‘A submicron particle can stay in the air for hours and days, depending on the ventilation, so if you have a room that is not ventilated or poorly ventilated then these small particles can stay there for a very long period of time’, said Nga Lee (Sally) Ng, associate professor and Tanner Faculty Fellow in the School of Chemical and Biomolecular Engineering and the School of Earth and Atmospheric Sciences.

The study was conducted during the US spring 2020, when the pandemic triggered a global shutdown of most institutions. Communities faced massive shortages of personal protective equipment, prompting many people to make their own masks. Georgia Tech quickly set up the study because it already had ‘a great system for testing filtration efficiency using existing instruments in the lab’, Ng recalled.

The study’s findings were used to shape homemade face mask recommendations in the US last April, and are published in *Aerosol Science and Technology* (doi.org/10.1080/02786826.2021.1905149).

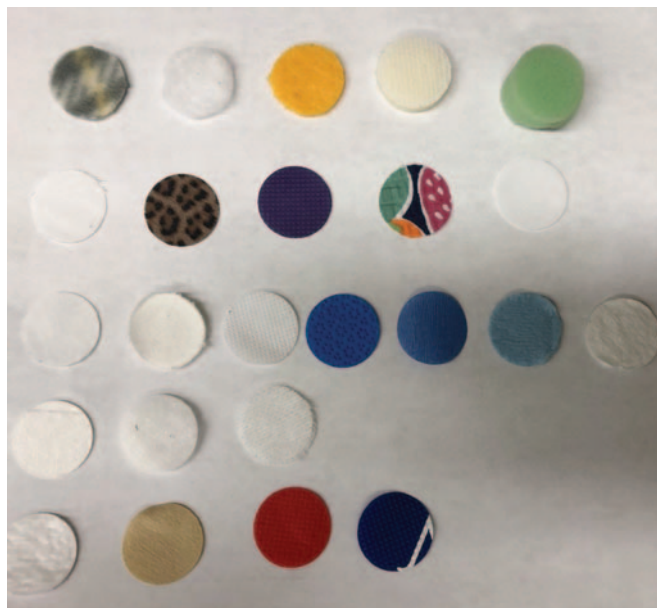
The researchers tested 33 different commercially accessible materials not limited to cloth fabrics, including single-layer woven fabrics such as cotton and woven polyester, blended fabrics, non-woven materials, cellulose-based materials, materials commonly found and used in hospitals, and various filter materials.

‘We learned there was a lot of variability in filtration performance even in the same type of material’, Ng said.

‘We found commercially available materials that provide acceptable levels of submicron particle rejection while still maintaining air flow resistance similar to a surgical mask’, said Ryan Lively, an associate professor and John H. Woody Faculty Fellow in the School of Chemical and Biomolecular Engineering. ‘These materials combine fabric fibre density, a maze-like structure, and fibre surface chemistry to effectively reject submicron particles.’

The best-performing materials for homemade masks were blackout drapery and sterilisation wrap widely used for packing surgical instruments. Both materials are commercially available.

The researchers said people should avoid using filters such as a HEPA/MERV or vacuum bags unless they are certified to be fibreglass free because often such filters on their own may release glass fibres that can be inhaled. Other materials to avoid for masks include loose-knitted material, batting fabric, felt, fleece, or shiny, reusable shopping bags.



Some of the mask fabric samples tested by Georgia Tech researchers. Taekyu Joo, Georgia Tech

Multilayered samples performed much better than single-layer samples, but people should pay attention to breathability. The two-layered and three-layered samples tested show an overall filtration efficiency of about 50% for submicron particles. Mask fit is also important because particles can easily escape through gaps at the nose or through the sides of the mask.

The analysis showed that properly fitted and multilayer masks reject 84% of particles expelled by a person when one person wears it. If two people are wearing these types of masks, then particle transmission reduces by 96%.

A final takeaway of the research was the importance of universal mask wearing.

‘The best way to protect ourselves and others is to reduce exhaled particles at the source, and the source is our face,’ Ng said, adding, ‘That really gets amplified when everyone starts wearing masks.’

She expressed optimism that the findings will motivate people to more widely embrace mask wearing if they are sick and need to be in public.

‘Not everyone understands the importance of airborne virus transmission, and the importance of wearing a mask’, she said. ‘I hope that the practice will continue to help reduce the release of these viral particles into the environment and help protect others.’

Georgia Institute of Technology



A detection dog in training.

Courtesy of Auburn University College of Veterinary Medicine

K9 chemistry: a safer way to train detection dogs

Trained dogs are incredible chemical sensors, far better at detecting explosives, narcotics and other substances than even the most advanced technological device. But one challenge is that dogs have to be trained, and training them with real hazardous substances can be inconvenient and dangerous.

Scientists at NIST (the US National Institute of Standards and Technology) have been working to solve this problem using polydimethylsiloxane (PDMS). PDMS absorbs odours and releases them slowly over time. Enclose PDMS in a container with an explosive or narcotic for a few weeks until it absorbs the odours, and you can then use it to safely train dogs to detect the real thing.

But a few weeks is a long time, and now NIST researchers have developed a faster way to infuse PDMS with vapours. In *Forensic Chemistry* (doi.org/10.1016/j.forc.2020.100290), they describe warming compounds found in explosives, causing them to release vapours more

quickly, then capturing those vapours with PDMS that is maintained at a lower temperature, which allows it to absorb vapours more readily. This two-temperature method cut the time it took to 'charge' PDMS training aids from a few weeks to a few days.

'That time savings can be critical', said NIST research chemist Bill MacCrehan. 'If terrorists are using a new type of explosive, you don't want to wait a month for the training aids to be ready.'

MacCrehan infused PDMS with vapours from dinitrotoluene (DNT), which is a low-level contaminant present in TNT explosives but the main odorant that dogs respond to when detecting TNT. He also infused PDMS with vapours from a small quantity of TNT. Co-authors at the Auburn University College of Veterinary Medicine then demonstrated that trained detection dogs responded to the DNT-infused PDMS training aids as if they were real TNT.

While this study focused on DNT as a proof of concept, MacCrehan said he

believes the two-temperature method will also work with other explosives and with narcotics such as fentanyl. Some forms of fentanyl are so potent that inhaling a small amount can be harmful or fatal to humans and dogs. But by controlling how much vapour the PDMS absorbs, it should be possible to create safe training aids for fentanyl.

Other safe training aids already exist. Some are prepared by dissolving explosives and applying the solution to glass beads, for example. 'But most have not been widely accepted in the canine detection community because their effectiveness has not been proven', said Paul Waggoner, a co-author and co-director of Auburn's Canine Performance Sciences Program. 'If you put an explosive in a solvent, the dogs might actually be detecting the solvent, not the explosive.'

MacCrehan devised a PDMS 'charging station' with a hot plate on one side and a cooling plate on the other. He prepared various samples by placing the DNT on

the hot side, where the chemical was warmed to 30–35°C – well below the temperature that would cause TNT to detonate. The PDMS was kept at 20°C on the other side of the charging station.

MacCrehan loaded the DNT-infused PDMS samples, which hold their charge for up to a few months, into perforated metal cans. He also loaded several cans with blanks – PDMS samples to which no vapours were added. He labelled the cans with codes and shipped them to Auburn University.

At Auburn, researchers had trained six labrador retrievers to detect TNT using real TNT explosives. They then conducted a study to determine if the dogs would alert to the PDMS in the NIST samples as if it were real TNT.

This study was ‘double blind’: neither the dog handlers nor the note-takers who scored the dogs’ responses knew which containers underwent which preparation. This is important because dogs are keenly attuned to the body language of their handlers. If the handlers knew which samples were prepared with DNT, they might inadvertently cue the dogs with the direction of their gaze, a subtle shift in body position or some other subconscious gesture. And if the note-takers knew which samples were which, they might over-interpret the dogs’ responses.

The dogs alerted to all the DNT-infused PDMS samples. They did not alert to the blanks, meaning that they were responding to the DNT, not to the PDMS itself.

The dogs did not respond as consistently to PDMS that was infused with limited quantities of TNT. However, MacCrehan explained that the very small amounts of TNT he used for this purpose may not have contained sufficient amounts of DNT to fully infuse the samples.

MacCrehan will experiment with ways to safely prepare PDMS training aids for the improvised explosives TATP and HMTD, which are extremely unstable and detonate easily, so having safe training aids for them will be especially useful.

Lightning reveals extreme radical behaviour

Lightning breaks apart nitrogen and oxygen molecules in the atmosphere and creates reactive chemicals that affect greenhouse gases. Now, a team of atmospheric chemists and lightning scientists have found that lightning bolts and, surprisingly, subvisible discharges that cannot be seen by cameras or the naked eye produce extreme amounts of the hydroxyl radical ($\bullet\text{OH}$) and hydroperoxyl radical ($\bullet\text{OOH}$).

The hydroxyl radical is important in the atmosphere because it initiates chemical reactions and breaks down molecules such as the greenhouse gas methane. $\bullet\text{OH}$ is the main driver of many compositional changes in the atmosphere.

‘Initially, we looked at these huge $\bullet\text{OH}$ and $\bullet\text{OOH}$ signals found in the clouds and asked, what is wrong with our instrument?’ said William H. Brune, distinguished professor of meteorology at Penn State. ‘We assumed there was noise in the instrument, so we removed the huge signals from the dataset and shelved them for later study.’

The data was from 2012 from an instrument on a plane flown above Colorado and Oklahoma, looking at the chemical changes that thunderstorms and lightning make to the atmosphere.

But a few years ago, Brune and co-workers looked at the data again and saw that the signals were really $\bullet\text{OH}$ and $\bullet\text{OOH}$. They looked to see if these signals could be produced by sparks and subvisible discharges in the laboratory. Then they reanalysed the 2012 dataset and were able to link the huge signals seen by the instrument flying through the thunderstorm clouds to the lightning measurements made from the ground.

The results are reported in *Science First Release* (doi.org/10.1126/science.abg0492) and the *Journal of Geophysical Research – Atmospheres* (doi.org/10.1029/2021JD034557).

Brune notes that aeroplanes avoid flying through the rapidly rising cores of thunderstorms because it is dangerous, but can sample the anvil, the top portion

of the cloud that spreads outwards in the direction of the wind. Visible lightning happens in the part of the anvil near the thunderstorm core.

‘Through history, people were only interested in lightning bolts because of what they could do on the ground’, said Brune. ‘Now there is increasing interest in the weaker electrical discharges in thunderstorms that lead to lightning bolts.’

Most lightning never strikes the ground, and the lightning that stays in the clouds is particularly important for affecting ozone, and important greenhouse gases, in the upper atmosphere. It was known that lightning can split water to form $\bullet\text{OH}$ and $\bullet\text{OOH}$, but this process had never been observed before in thunderstorms.

What confused Brune’s team initially was that their instrument recorded high levels of $\bullet\text{OH}$ and $\bullet\text{OOH}$ in areas of the cloud where there was no lightning visible from the aircraft or the ground. Experiments in the lab showed that weak electrical currents, much less energetic than visible lightning, could produce these same components.

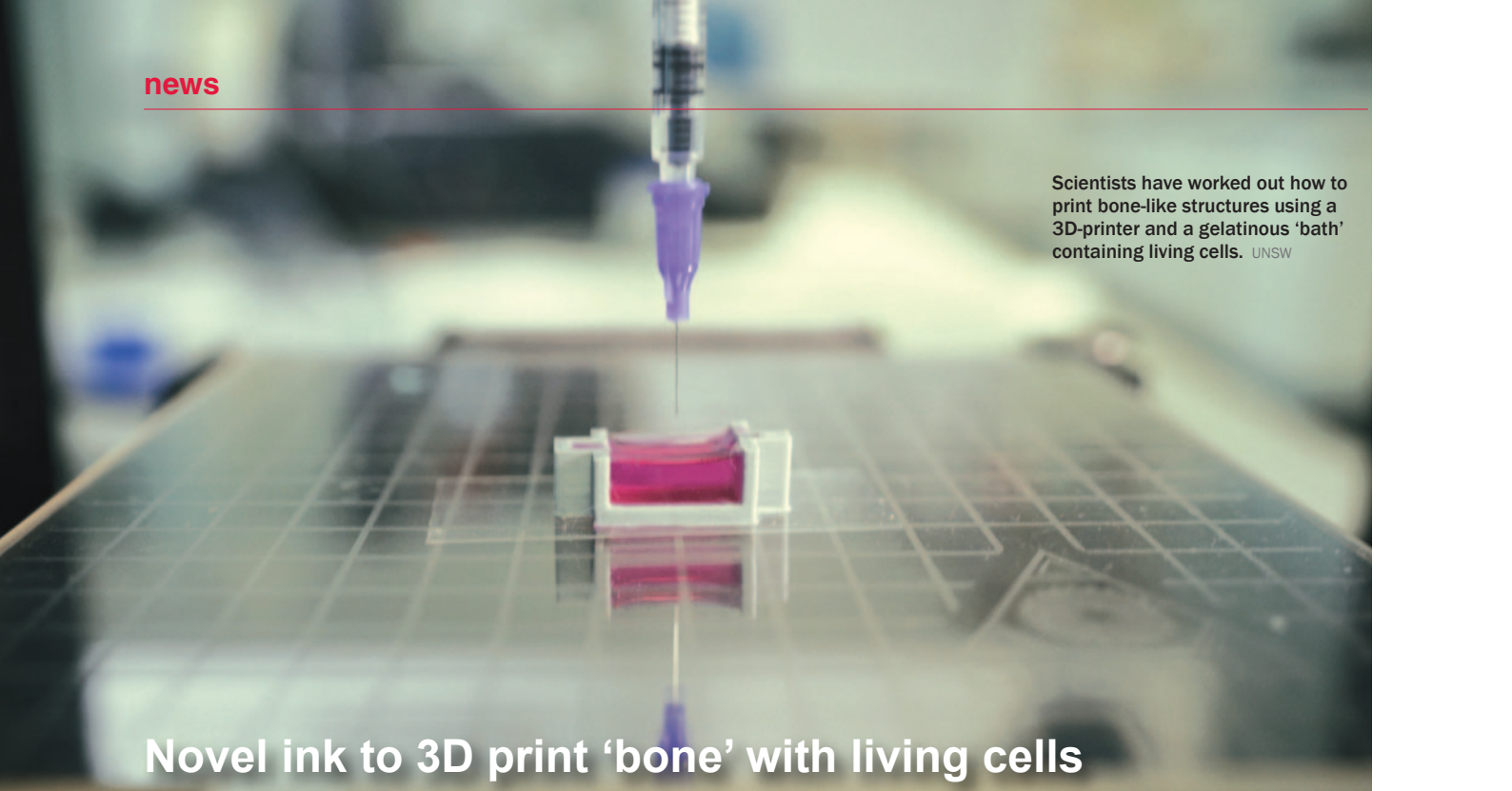
While the researchers found $\bullet\text{OH}$ and $\bullet\text{OOH}$ in areas with subvisible lightning, they found little evidence of ozone and no evidence of nitric oxide, which requires visible lightning to form. If subvisible lightning occurs routinely, then the $\bullet\text{OH}$ and $\bullet\text{OOH}$ these electrical events create need to be included in atmospheric models. Currently, they are not.

According to the researchers, ‘Lightning-generated $\bullet\text{OH}$ in all storms happening globally can be responsible for a highly uncertain but substantial 2–16% of global atmospheric $\bullet\text{OH}$ oxidation.’

Brune noted that the results are highly uncertain: it is not known how these measurements apply to the rest of the globe. Most thunderstorms occur in the tropics and have a different structure from thunderstorms over high plains.

Penn State University

NIST



Scientists have worked out how to print bone-like structures using a 3D-printer and a gelatinous 'bath' containing living cells. UNSW

Novel ink to 3D print 'bone' with living cells

Scientists from UNSW Sydney have developed a ceramic-based ink that may allow surgeons in the future to 3D-print bone parts complete with living cells that could be used to repair damaged bone tissue.

Using a 3D-printer that deploys a special ink made up of calcium phosphate, the scientists developed a new technique, known as ceramic omnidirectional bioprinting in cell-suspensions (COBICS), enabling them to print bone-like structures that harden in a matter of minutes when placed in water.

While the idea of 3D-printing bone-mimicking structures is not new, this is the first time such material can be created at room temperature – complete with living cells – and without harsh chemicals or radiation, said Dr Iman Roohani from UNSW's School of Chemistry.

Associate Professor Kristopher Kilian who co-developed the technology with Roohani says the fact that living cells can be part of the 3D-printed structure, together with its portability, makes it a big advance on current state-of-the-art technology.

Up until now, he says, making a piece of bone-like material to repair bone

tissue of a patient involves first going into a laboratory to fabricate the structures using high-temperature furnaces and toxic chemicals.

'This produces a dry material that is then brought into a clinical setting or in a laboratory, where they wash it profusely and then add living cells to it', Kilian said.

'The cool thing about our technique is you can just extrude it directly into a place where there are cells, like a cavity in a patient's bone. We can go directly into the bone where there are cells, blood vessels and fat, and print a bone-like structure that already contains living cells, right in that area.'

'There are currently no technologies that can do that directly.'

The researchers describe how they developed the special ink in a microgel matrix with living cells in *Advanced Functional Materials* (doi.org/10.1002/adfm.202008216).

'The ink takes advantage of a setting mechanism through the local nanocrystallisation of its components in aqueous environments, converting the inorganic ink to mechanically interlocked bone apatite nanocrystals', Roohani said.

'In other words, it forms a structure that is chemically similar to bone-

building blocks. The ink is formulated in such a way that the conversion is quick, non-toxic in a biological environment and it only initiates when ink is exposed to the body fluids, providing an ample working time for the end-user, for example, surgeons.'

He said when the ink is combined with a collagenous substance containing living cells, it enables in-situ fabrication of bone-like tissues that may be suitable for bone tissue engineering applications, disease modelling, drug screening, and in-situ reconstruction of bone and osteochondral defects.

'I imagine a day where a patient needing a bone graft can walk into a clinic where the anatomical structure of their bone is imaged, translated to a 3D printer, and directly printed into the cavity with their own cells', said Kilian.

'This has the potential to radically change current practice, reducing patient suffering and ultimately saving lives.'

The scientists will perform in vivo tests in animal models to see if the living cells in the bone-like constructs continue to grow after being implanted in existing bone tissue.

University of New South Wales

Anion impurities in commercial PbI_2 : impact on perovskite solar cells and remediation

Lead halide perovskites are among the most promising materials for next-generation photovoltaics, with efficiencies now approaching the best silicon devices.

A critical aspect of all high-efficiency devices is the use of PbI_2 as a precursor, both to enable the formation of the underlying perovskite structure and to provide passivation effects of the grain boundaries. The purity of this precursor material plays a vital role in determining the device performance. It is of paramount importance to use PbI_2 with high-grade purity levels in solar cell fabrication.

Batch-to-batch variability of PbI_2 precursors, even with metal purity levels of 99.99% and greater, is a major limitation to achieving intra- and inter-lab reproducibility of lead halide-based perovskite solar cells.

Limited reproducibility is a barrier to increasing the efficiency and commercial viability of these solar cells.

Monash University's Professor Jacek Jasieniak said his group has experienced recurring issues with the reliability of commercially available PbI_2 precursors, as have many other researchers around the world.

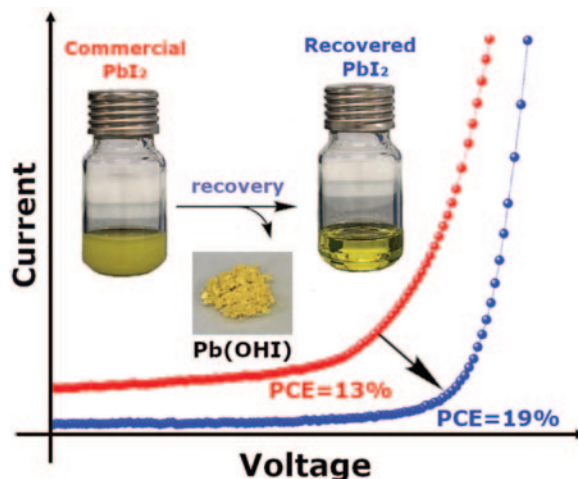
'When you get the precursors to make perovskites, despite the fact they're quoted at a given purity, they rarely behave the same,' he said.

'Most people would assume it was a bad batch and merely buy new precursors.'

'In our lab, we've had to throw out five or six perfectly good batches of lead halide precursors because they exhibit variable solubility and never gave us excellent solar cell efficiencies. The issue was that the quoted purity on the precursors was always very high. As such no-one knew what the problem was.'

Work by the ARC Centre of Excellence in Exciton Science, published in *ACS Materials Letters* (doi.org/10.1021/acsmaterialslett.1c00098), identifies that Pb(OH)I is the primary impurity that causes these adverse issues.

Through a systematic investigation into the role of synthesised Pb(OH)I within $\text{Cs}_{0.05}(\text{FA}_{0.85}\text{MA}_{0.15})_{0.95}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ perovskite films and solar cells, it is shown that this impurity



Perovskite solar cell photo conversion efficiency comparison.

induces segregated PbI_2 and $\delta\text{-FAPbI}_3$ phases and reduces the ensuing solar cell performance characteristics.

To avoid these issues, a facile, high-yield, remediation process amenable to any PbI_2 precursor batch is introduced. Through its use, reliably high-performing metal halide perovskite solar cells are achieved.

Jacek said: 'We did a bit of digging and unveiled that there's an impurity in the lead oxyiodide that emerges from flawed synthetic control by the manufacturers. We show that you can have 1% of this impurity and you will never know from your absorption or X-ray measurements.'

'However, you will get a lower efficiency in your solar cells, but you will never know that it's originated from the lead precursors. We outline exactly how that can happen. We also develop a remediation process for the entire lead iodide batch.'

'You can actually recover high purity lead iodide from your poor lead iodide formation. And if you do that, you can get really high efficiency.'

'This knowledge contribution is important because it highlights the fact that anion purity is as important as metal purity, which is what's usually quoted in precursors.'

The published work highlights the need for stricter synthetic protocols and better certification of precursors by manufacturers to achieve reproducibility and maximise efficiency in perovskite devices.

ARC Centre of Excellence in Exciton Science



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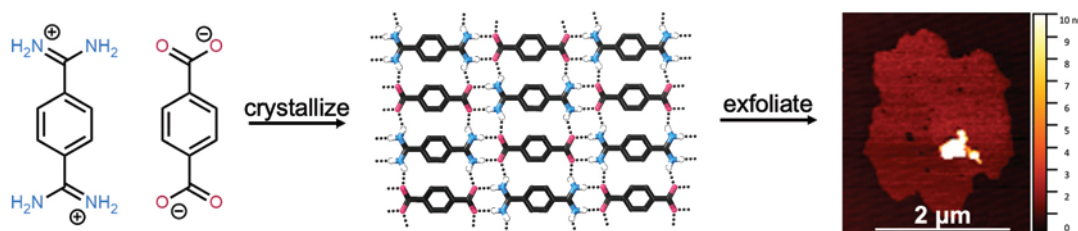
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Stable hydrogen-bonded nanosheets

2D materials such as graphene, boron nitride and metal chalcogenides have unique physical properties arising from their sub-nanometre thickness. While 2D materials based on reversible covalent bonds and coordination bonds have been reported, and display unusual materials properties, a general strategy to prepare 2D materials based on weaker interactions such as hydrogen bonding was until recently not known. Now, researchers at the Australian National

University and University of Sheffield (UK) have demonstrated that hydrogen-bonded frameworks can be exfoliated into free-standing 2D nanosheets (Nicks J., Boer S.A., White N.G., Foster J.A. *Chem. Sci.* 2021, **12**, 3322–7). They prepared layered crystals held together by strong charge-assisted amidinium carboxylate hydrogen bonds and used an ultrasound-assisted liquid exfoliation technique to produce atomically thin hydrogen-bonded organic

nanosheets with high aspect ratios. These nanosheets were remarkably stable and maintained their crystallinity and monolayer structures even after several days in water at 80°C. Preliminary experiments revealed that the nanosheets exhibit effective fluorescence quenching of organic dye molecules. The very large effective surface areas of these molecular 2D materials could be useful in applications such as catalysis, sensing and separations.

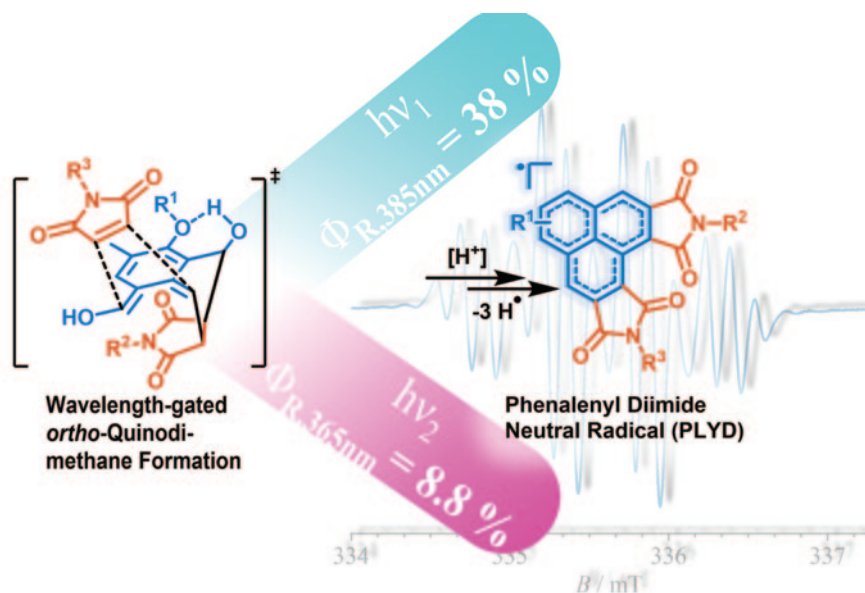


Light control of radical modular synthesis

Polycyclic aromatic (di)imides are a ubiquitous structural motif in organic dyes and find wide application in organic light-emitters and photovoltaic cells. On the other hand, the phenalene motif, in which three aryl rings share three C–C bonds, is important in organic spin chemistry, having an uneven number of

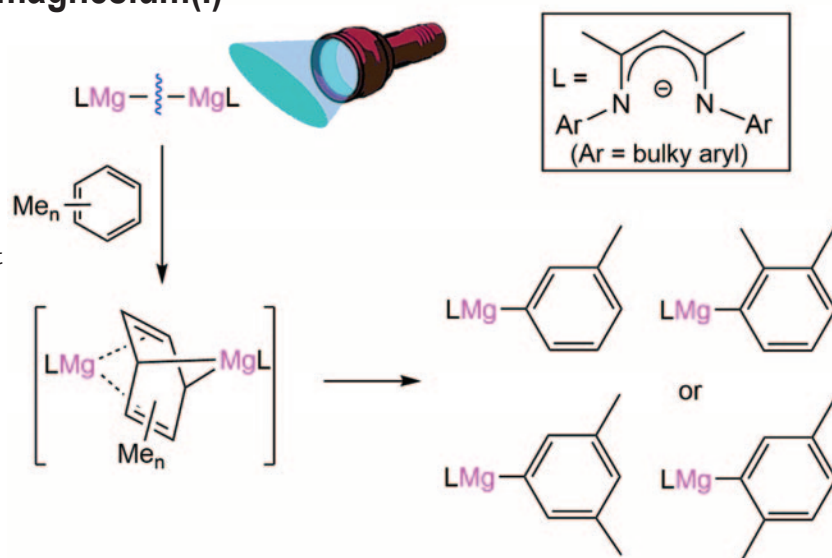
electrons in its neutral state, rendering it a neutral radical. Now, researchers in the Soft Matter Materials Laboratory at the Queensland University of Technology, in collaboration with the Max Planck Institute for Polymer Research and the Karlsruhe Institute of Technology (Germany), have pioneered a wavelength-

gated synthesis that combines these two structural motifs into one scaffold named a phenalene diimide (Feist F., Walden S.L., Alves J., Kunz S.V., Micallef A.S., Brock A.J., McMurtrie J.C., Weil T., Blinco J.P., Barner-Kowollik C. *Angew. Chem. Int. Ed.* 2021, **60**, 10 402–8). In this process, methylisophthalaldehydes and maleimides undergo two consecutive light-induced Diels–Alder reactions to afford hexahydrophenalene 1,6-diol diimides efficiently (82–99% yield) and with excellent diastereoselectivity (seven adjacent stereocentres, 62–98% d.r.). The wavelength-gated nature of the stepwise addition enables the modular assembly of heterobifunctional phenalene diimide scaffolds solely by choice of substrate and wavelength. Subsequent elimination and oxidation reactions afforded a new class of persistent phenalenyl diimide neutral radicals, which were characterised by EPR spectroscopy and cyclic voltammetry. The approach simplifies the generation of tailor-made spin-active molecules.



Activating inert C–H bonds with magnesium(I)

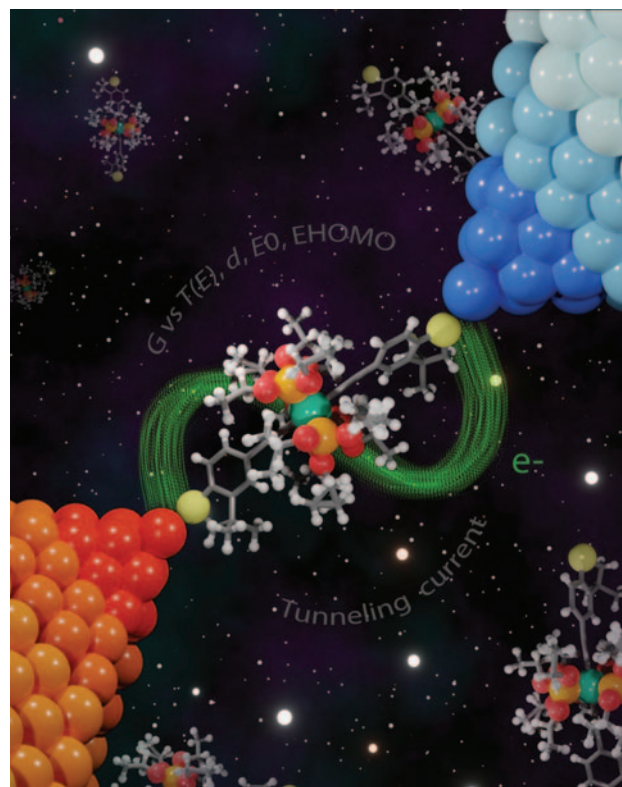
The selective activation and subsequent functionalisation of inert C–H bonds in simple hydrocarbons is central to the value-adding syntheses of more complex molecules such as pharmaceuticals. The use of d-block metal complexes to achieve such activations has dominated this field. Recently, several low-oxidation-state p-block complexes have been shown to similarly activate simple arene C–H bonds, but typically with poor selectivity. Now, the group of Cameron Jones at Monash University and his theoretician collaborator Laurent Maron at the University of Toulouse (France) have shown that the clean activation of C–H bonds in benzene, toluene and xylenes can be achieved with complete regioselectivity at room temperature by irradiating solutions of dimagnesium(I) compounds with blue or UV light (Jones D.D.L., Douair I., Maron L., Jones C. *Angew. Chem. Int. Ed.* 2021, **60**, 7087–92). The reactions proceed via doubly reduced ‘Birch-like’ intermediates, which can be isolated in some cases. Calculations suggest that irradiation of the dimagnesium(I) compounds leads to cleavage of their Mg–Mg bonds and generation of highly reactive transient magnesium(I) radicals,



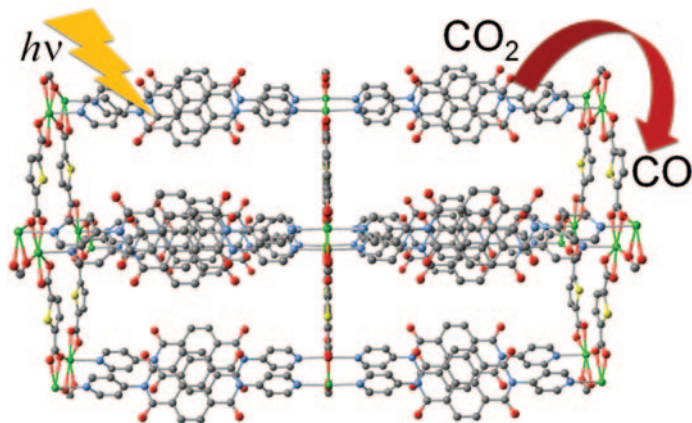
which effect the C–H bond-activation processes. There is considerable scope to fully develop the chemistry of photoactivated magnesium(I) compounds and their application to organic synthesis.

How molecular structure controls single-molecule conduction

With the advent of techniques to make an electrical contact to molecules on a (semi)conducting substrate, it has become possible to measure single-molecule conductance and related properties such as rectification and gated transistor-like response. Beyond molecules for electronics, molecules demonstrating high molecular conductivity with high Seebeck coefficients and low thermal conductivity are now leading to design concepts for molecular thermoelectric materials. All of these outcomes depend on understanding the nature of through-molecule conductance. Recent research by a team from the Universities of Western Australia, Liverpool (UK), Lancaster (UK) and Autonoma de Madrid (Spain) has expanded understanding of molecular-structure–electronic-property relationships in single-molecule junctions (Naher M., Milan D.C., Al-Owaedi O.A., Planje I.J., Bock S., Hurtado-Gallego J., Bastante P., Abd Dawood Z.M., Rincón-García L., Rubio-Bollinger G., Higgins S.J., Agraït N., Lambert C.J., Nichols R.J., Low P.J. *J. Am. Chem. Soc.* 2021, **143**, 3817–29). By comparing the conductance and thermopower of organic and organometallic ‘molecular wires’ with properties such as redox potentials, HOMO–LUMO energies and gaps, various ‘single-parameter’ models of molecular conductance could be tested. The trends in molecular conductance were best rationalised from consideration of the complete molecular junction, with conductance values well described by transport calculations carried out at the DFT level of theory based on the Landauer–Büttiker model.

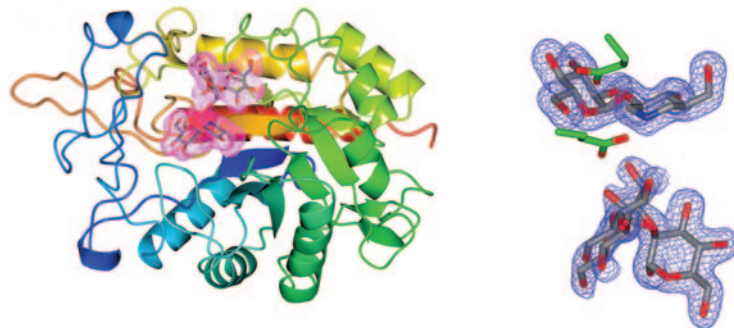


Light-harvesting metal–organic frameworks



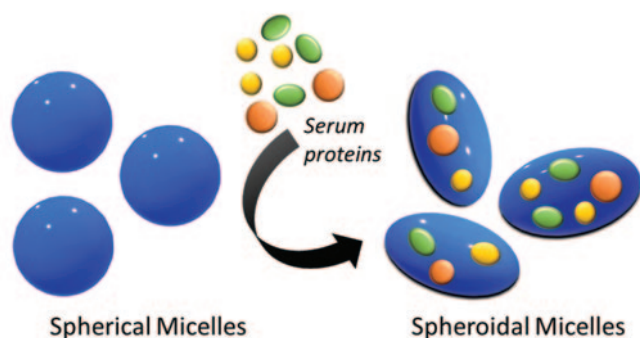
Metal–organic frameworks (MOFs) represent a highly tuneable structural platform upon which to design new types of light-harvesting materials. The D'Alessandro group at the University of Sydney have recently shown that MOFs containing 'cofacially aligned' light-activated ligands known as naphthalenediimides (NDIs) function as photocathodes that could be applied in solar energy harvesting devices (Ding B., Chan B., Proschogo N., Solomon M.B., Kepert C.J., D'Alessandro D.M. *Chem. Sci.* 2021, **12**, 3608–14). Structurally, the cofacial ligands are akin to double-glazed windows in a house. At a functional level, irradiation of the MOF with visible light generates a long-lived photoexcited radical that is stabilised by a through-space mixed-valence interaction between the NDI ligands. This radical was exploited to reduce CO_2 to CO at a mild reduction potential, demonstrating the potential of this mechanism in other applications for which the conversion of light to electrical energy is required.

Sugar-coated viral proteins an antiviral target



A significant proportion of human proteins are modified by carbohydrate structures attached to asparagine residues to give N-linked glycoproteins. Researchers at the University of Melbourne and the Universities of York, Oxford and Birmingham (UK) have determined the 3D structure of one of the enzymes involved in the correct processing of N-linked glycans, a glycosidase named endomannosidase, and have developed inhibitors that allow control of protein glycosylation (Sobala L.F., Fernandes P.Z., Hakki Z., Thompson A.J., Howe J.D., Hill M., Zitzmann N., Davies S., Stamatakis Z., Butters T.D., Alonzi D.S., Williams S.J., Davies G.J. *Proc. Natl Acad. Sci. USA* 2020, **117**, 29 595–601). These inhibitors were shown to disrupt host processing of N-linked glycans of two encapsulated viruses, reducing their infectivity in cellular models. This study highlights the potential for developing antiviral drugs by targeting host N-linked glycan processing pathways.

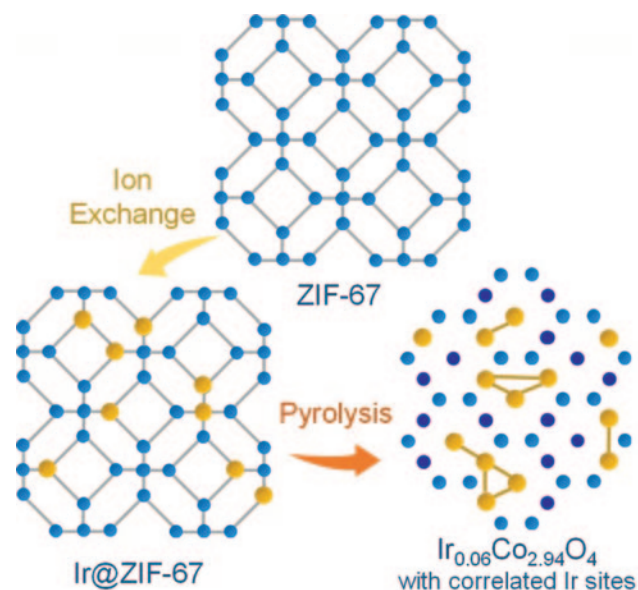
Serum proteins change shape of nanoparticle drug carriers



Nanoparticles are widely investigated as a tool to deliver therapeutic drugs. It was assumed that these nano-sized carriers could circulate around the bloodstream and stay unnoticed by the body's defence mechanisms. But it is now known that most particles are quickly covered with blood

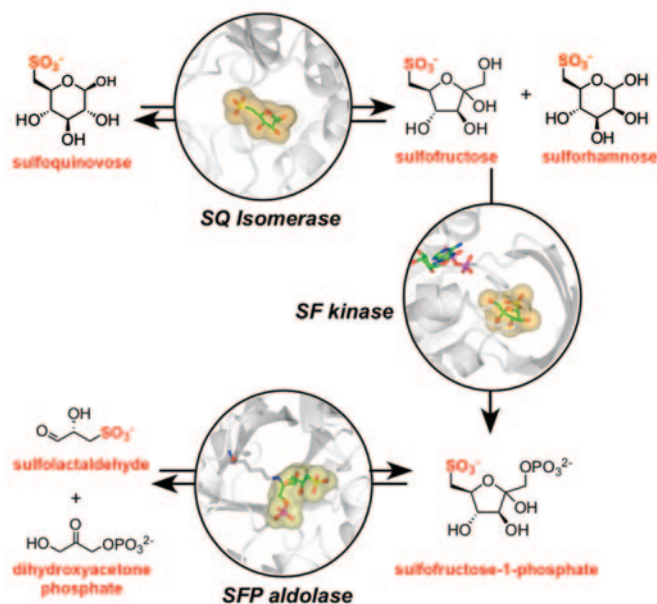
proteins, covering the often carefully designed nanoparticle surface. Researchers have so far focused on the thickness of the protein corona and the type of proteins absorbed, as these factors can influence whether the nanoparticle is detected by the immune system. Now a team led by Martina Stenzel at UNSW Sydney has shown that adsorbed proteins can deform nanoparticles (Cao C., Zhang L., Kent B., Wong S., Garvey C.J., Stenzel M.H. *Angew. Chem. Int. Ed.* 2021, **60**, 10 342–9). With the help of scattering analysis, it was revealed that spherical micelles based on sugar-based polymers were deformed into spheroidal micelles. This shape change could have wider implications as it is known that non-spherical nanoparticles interact differently with their biological environment. While this system might be unique, many soft nanoparticles could be expected to undergo shape changes when covered by blood proteins.

New type of single-atom catalyst with short-range order



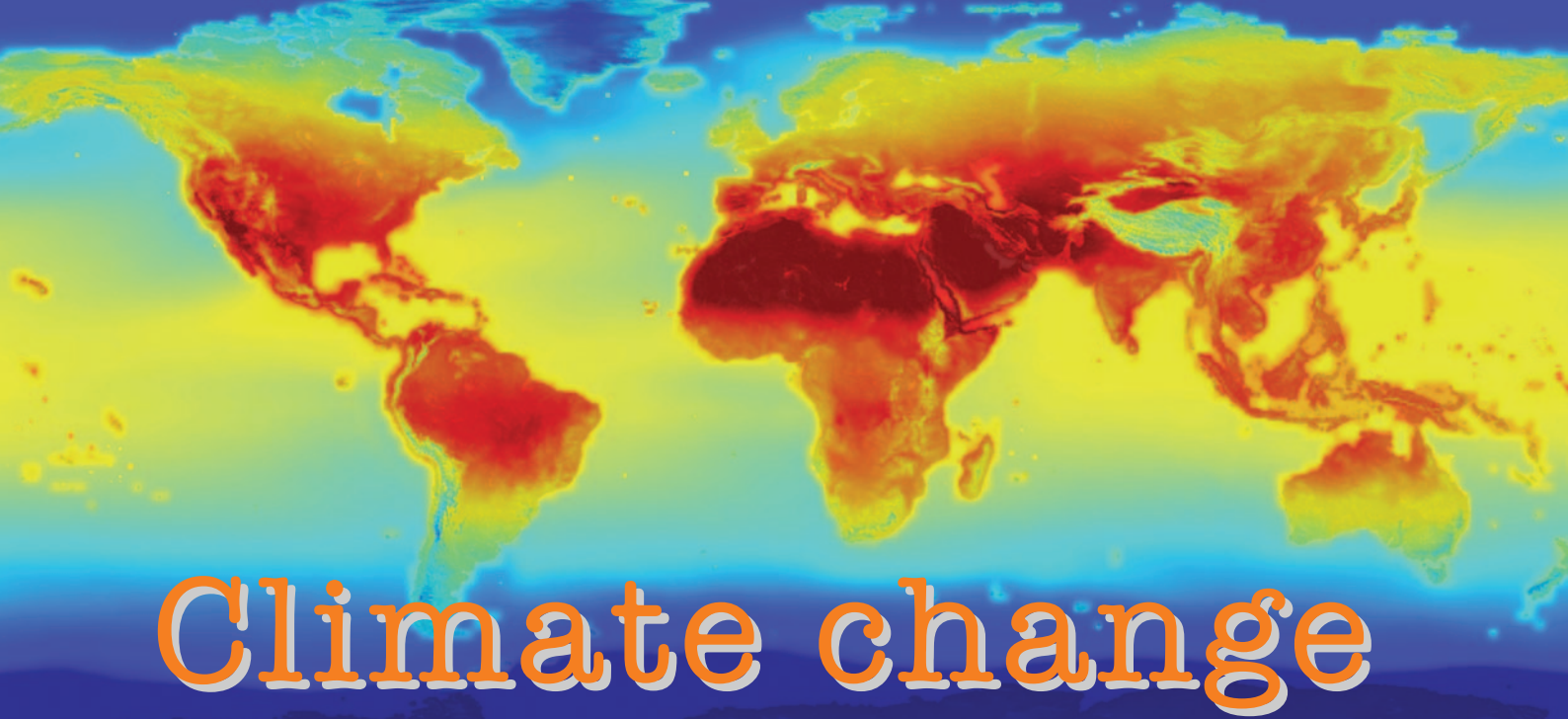
Researchers from the University of Adelaide have reported a new class of short-range ordered iridium single atoms integrated into the cobalt oxide spinel structure for highly efficient electrocatalytic water oxidation (Shan J., Ye C., Chen S., Sun T., Jiao Y., Liu L., Zhu C., Song L., Han Y., Jaroniec M., Zhu Y., Zheng Y., Qiao S.Z. *J. Am. Chem. Soc.* 2021, **143**, 13, 5201–11). Noble metals have exceptional electronic structures and unrivalled activity for a wide range of catalytic applications. But they are restricted by a limited choice of geometric structures spanning single atoms, clusters, nanoparticles and bulk crystals. To overcome this limitation, iridium single atoms were accommodated into cationic sites of the cobalt oxide spinel with short-range order and an identical spatial correlation as the host lattice. The resultant $\text{Ir}_{0.06}\text{Co}_{2.94}\text{O}_4$ catalyst exhibited two orders of magnitude higher electrocatalytic activity than the parent oxide as well as significantly improved corrosion resistance for the challenging oxygen evolution reaction under acidic conditions. This work eliminates the 'close-packing' limitation of noble metals and offers a promising opportunity to create analogues with desired topologies for various catalytic applications.

How nature recognises sulfo-sugars



The sulfosugar sulfoquinovose is produced by most photosynthetic tissues and is metabolised by a wide range of bacteria through the process of sulfoglycolysis. Yet little is known about how sulfoglycolytic enzymes recognise these enigmatic sugars. Researchers at the University of Melbourne, the Walter and Eliza Hall Institute, the University of York (UK), and Hosei, Kyoto and Meiji Universities (Japan) have delineated the mechanism and structural basis for sulfosugar metabolism for three consecutive enzymes in the sulfoglycolysis pathway in *E. coli* (Sharma M., Abayakoon P., Epa R., Jin Y., Lingford J.P., Shimada T., Nakano M., Mui J.W.-Y., Ishihama A., Goddard-Borger E.D., Davies G.J., Williams S.J. *ACS Cent. Sci.* 2021, **7**, 476–87). As part of this work, a new sugar, sulforhamnose, was discovered that is an intermediate in the pathway and functions as a transcription factor derepressor. Notably, all sulfoglycolytic enzymes can distinguish between related intermediates in glycolysis, demonstrating the functional compartmentalisation of sulfoglycolysis from glucose metabolism.

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.



Climate change

Atmospheric facts and figures

BY **DAVID W.T. GRIFFITH, PAUL J.B. FRASER**
AND **IAN E. GALBALLY**

In day-to-day life, climate change can seem intangible. But long-term records of global temperatures and atmospheric composition and their correlations show that climate change is real.

The NASA global data set from 2015 pictured above combines historical measurements with data from climate simulations using the best available computer models to provide forecasts of how global temperature (shown) and precipitation might change up to 2100 under different greenhouse gas emissions scenarios. NASA

The overwhelming majority (97%) of atmospheric and climate scientists agree that climate change is happening (doi.org/10.1088/1748-9326/11/4/048002). Yet for more than a decade in Australia, a small but influential minority in science, politics, industry, business and the media continue to promote climate-change scepticism, or even denial, so that Australia has fallen well behind other developed economies in addressing climate change and energy policy.

Despite the scientific consensus, as atmospheric scientists we are often asked by our friends and scientific colleagues 'Is it real?' The purpose of this article is to set out the basic observations and physical understanding that show that, yes, it is real, and to provide further resources for readers to access factual, peer-reviewed information.

Simple physics of the greenhouse effect

Try this thought experiment: imagine Earth with its moon in orbit 148 million kilometres from the sun, all three at absolute zero temperature. Now 'switch on' the sun with its surface temperature of 5800 K, radiating energy according to Planck's law with maximum emission intensity in the visible spectrum and providing a total solar energy flux of approximately 1360 W/m² at the distance of Earth's orbit. All of this energy reaches the surface of the moon but on Earth approximately one-quarter is scattered back to space by air particles and clouds. The surfaces of Earth and the moon absorb more than 90% of this energy (the rest is reflected), causing them to heat up. The heated surfaces in turn emit radiation back to space (again, Planck's law, but now with maximum emission in the infrared) until they reach thermal equilibrium where the outgoing infrared radiation

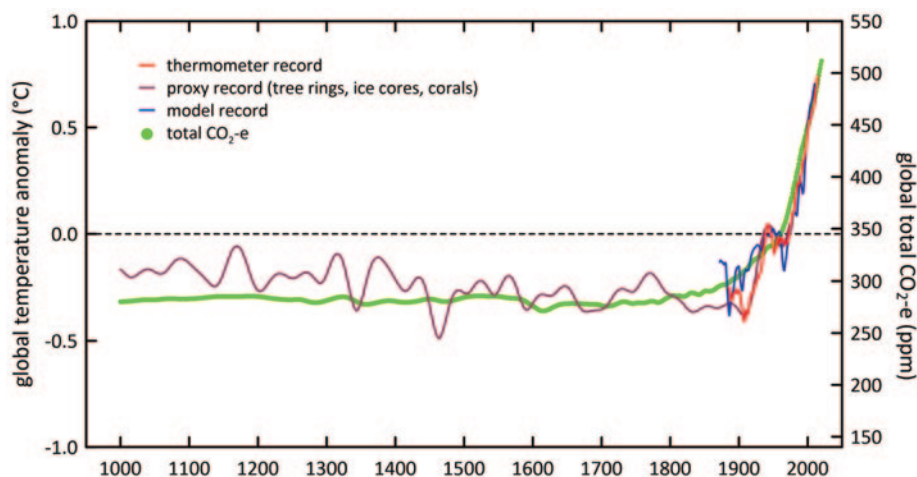
balances incoming solar radiation. The moon's mean surface temperature comes to equilibrium at -18°C , but on Earth the mean surface temperature is $+15^{\circ}\text{C}$. The difference, 33°C , is principally due to the greenhouse effect. How does this work?

With surface temperatures around 250–300 K, Earth's and the moon's emissions are centred in the infrared, maximising at a wavelength near $10\text{ }\mu\text{m}$. The moon does not have an atmosphere and this infrared radiation escapes unimpeded to space. However, Earth's atmosphere contains several trace gases that absorb infrared radiation near $10\text{ }\mu\text{m}$, most important among them being water vapour (H_2O), carbon dioxide (CO_2), methane (CH_4), ozone (O_3), nitrous oxide (N_2O), and several long-lived halogenated trace gases such as CFC-11 (CCl_3F) and sulfur hexafluoride (SF_6), collectively referred to as synthetic greenhouse gases. Aerosols also play a role by either absorbing incoming solar radiation or scattering it back to space. Greenhouse gases (GHGs) are transparent to the incoming visible solar radiation but absorb some of the outgoing infrared, thus heating the atmosphere. The net effect is to act as a 'blanket', re-emitting some of the absorbed outgoing infrared energy back to the surface and raising the surface temperature. The net greenhouse effect currently warms Earth's surface relative to the no-atmosphere case (e.g. the moon) by 33°C .

Measuring and modelling the greenhouse effect

Increasing concentrations of GHGs in the atmosphere increase its infrared opacity and further heat Earth's surface by enhancing the greenhouse effect. The science of GHGs and global warming involves three main components:

1. Measuring and understanding the concentrations of the GHGs in the atmosphere, and how they are



Global average direct and proxy temperature records, global average mole fraction of GHGs expressed as CO_2 equivalent ($\text{CO}_2\text{-e}$), and model simulations of global average temperatures forced by the observed increases in GHG $\text{CO}_2\text{-e}$ in the global atmosphere over the past 1000 years; global $\text{CO}_2\text{-e}$ data is derived from CSIRO's global observing network for CO_2 , CH_4 and N_2O , from CSIRO measurements on air extracted from Antarctic ice (<https://gaw.kishou.go.jp>) and from the AGAGE global network for synthetic GHGs (CFCs etc., <https://agage.mit.edu/data/agage-data>); global temperature data (direct, proxy and modelled) is found at www.cru.uea.ac.uk/cru/data/temperature/HadCRUT3-gl.dat; NASA GISS: <https://data.giss.nasa.gov/gistemp/>; NOAA NCDC: www.ncdc.noaa.gov/cag/global/time-series/globe/land_ocean/; Gaffney O., *Global Change Magazine*, IGBP, vol. 77, 2011, and the IPCC 5th Assessment Report. Nada Derek

changing. This is a complex interplay of natural and anthropogenic sources and sinks with atmospheric and oceanic chemistry and biology.

2. Calculating the radiative balance between the atmosphere and the surface using global climate models to quantitatively determine both the current temperatures and how temperatures will change under different scenarios of increasing GHG concentrations.
3. Understanding the variability of incoming solar radiation both from the sun and due to scattering and absorption of the incoming solar radiation by Earth's atmosphere.

There is no question that increasing GHG concentrations will lead to higher surface temperatures. The greenhouse effect is real – the scientific challenge is to make accurate calculations of its magnitude and changes into the future. The social and political challenges are much more difficult.

Earth's surface temperature and GHG levels are increasing together

In response to increasing radiative forcing due to increasing amounts of GHGs, Earth's surface temperature is increasing. The graph above illustrates the total atmospheric amount of GHGs (as CO_2 equivalent ($\text{CO}_2\text{-e}$)) and Earth's surface temperature observed and calculated from models incorporating the GHG increase, over the past 1000 years. While the clearly strong correlation does not of itself imply causality, global climate model calculations show that radiative impacts of the increasing GHG amounts are entirely consistent with the observed temperature increase. With current knowledge, no other mechanism can be or needs to be invoked to explain the temperature change.

GHGs and climate forcing

After water vapour, CO_2 is the most important GHG, contributing 57% of the climate forcing due to GHGs since pre-industrial times, followed by CH_4

(16%), the group of synthetic GHGs (12%) and N_2O (5%). These gases are described as long-lived GHGs with atmospheric lifetimes of two years or more, and consequently are relatively well mixed globally.

Tropospheric O_3 has an atmospheric lifetime of approximately three weeks and makes up about 10% of the total atmospheric O_3 column (~90% is in the stratosphere, 15–40 kilometres above the surface). Tropospheric O_3 is described as a short-lived or near-term GHG and its contribution to climate forcing is slightly less than that of CH_4 .

NOAA's Global Monitoring Laboratory in the US (www.esrl.noaa.gov/gmd) maintains the Annual Greenhouse Gas Index (AGGI), shown in the graph below. The AGGI illustrates both the continuing growth and relative importance of each long-lived GHG to the total. From this graph, we see that total additional radiative forcing in the early 2020s due to all GHGs will be 50% higher than in the reference year of 1990.

Australian contributions to GHG measurements and emissions

CSIRO commenced the first Australian background atmospheric CO_2 measurements in the middle-troposphere (5–10 kilometres) over south-east Australia in 1972 and at the surface at Kennaook/Cape Grim, north-west Tasmania (see box p. 21) in 1976. These measurements were accompanied at Kennaook/Cape Grim by O_3 in 1976, N_2O and CFCs in the late 1970s, CH_4 in the early-1980s and other synthetic CFCs from 1998; they have continued to the present day.

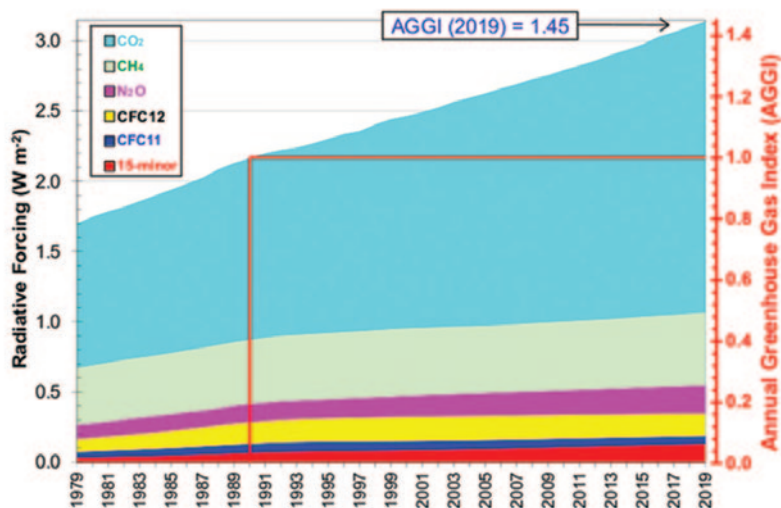
Observations of Southern Hemispheric GHGs have been extended back 2000 years by measurements on air trapped in Antarctic ice and firn.

In 2018, Australia reported to the United Nations Framework Convention on Climate Change GHG emissions of 537 million tonnes in CO_2 -e terms (after adjustment for negative emissions due to land use/land use change): 70% CO_2 , 23% CH_4 , 4–5% N_2O and 2–3% synthetic GHGs.

Carbon dioxide

CO_2 has very large two-way exchange fluxes between the atmosphere and Earth's surface dominated by biosphere uptake (photosynthesis leading to carbon storage in plants and soils) and emissions (respiration by plants and animals). Anthropogenic exchanges of CO_2 are tens of times smaller and are dominated by one-way emissions to the atmosphere from fossil fuel use and cement manufacture. Around half of these emissions are taken up by the biosphere and dissolve in the oceans, the remainder stay in the atmosphere. There are also secondary anthropogenic effects through impacts on the biospheric fluxes (e.g. land use change and deforestation). The Global Carbon Project (www.globalcarbonproject.org) provides detailed global accounting for CO_2 , CH_4 and N_2O .

CO_2 comprises currently (2018) 70% of Australia's anthropogenic GHG emissions in CO_2 -e terms, with 95% from the energy sector (stationary and mobile) and 5% from industrial processes. This is the simple consequence of fossil fuel combustion.



NOAA's Annual Greenhouse Gas Index vs time since 1979. Radiative forcing (left-hand axis) is the additional radiative heat load due to each long-lived GHG in $W\ m^{-2}$ at Earth's surface. The AGGI (right-hand axis) is an index of the warming relative to the reference year 1990.

NOAA Global Monitoring Laboratory, Boulder, Colorado, USA (<https://esrl.noaa.gov/gmd>)

Observations of Southern Hemispheric GHGs have been extended back 2000 years by measurements on air trapped in Antarctic ice and firn.

Methane

CH₄ is the second-most important long-lived GHG after CO₂ and is a major source of water vapour and HO_x radicals in the stratosphere. CH₄ is emitted to the atmosphere roughly equally from natural and anthropogenic sources. The natural sources are predominantly wetlands (30%), the oceans (10%) and lakes and rivers (5%). Wildfires contribute less than 1%. The anthropogenic sources are fossil fuel mining and combustion (15%), ruminants (cattle, sheep etc., 15%), landfills and waste (10%), rice agriculture (5%) and biomass burning (largely biofuels, 5%).

Currently (2018), CH₄ makes up 23% of Australia's GHG emissions in CO₂-e terms, with 53% from the agriculture sector, 36% from energy and 11% from waste.

Nitrous oxide

N₂O is the third-most important long-lived GHG after CO₂ and CH₄ and is the dominant source of reactive nitrogen in the stratosphere, contributing significantly to stratospheric O₃ chemistry. N₂O is emitted to the atmosphere from natural (60%) and anthropogenic (40%) sources. The natural sources are predominantly microbial activity in soils (35%) and the oceans (20%), while the major anthropogenic sources are nitrogenous fertilisers (25%), fossil fuel combustion (5%), biomass burning (5%) and microbial activity in rivers affected by agricultural run-off (3%).

Currently (2018), N₂O makes up 4–5% of Australia's GHG emissions in CO₂-e terms, with 72% from agriculture, 16% from the energy sector, 9% from industry and 3% from waste.

Synthetic greenhouse gases

The synthetic GHGs currently (2018) make up 2–3% of Australia's GHG emissions in CO₂-e terms, 100% from the industrial processes sector, 99% from the refrigeration/air conditioning

industries (hydrofluorocarbons – HFCs), 1% from aluminium production (perfluorocarbons – PFCs). Many other halogen-containing stratospheric ozone-depleting substances (such as the CFCs) are also effective GHGs.

Tropospheric ozone

Unlike the long-lived GHGs, tropospheric O₃ is not emitted into the atmosphere but is formed there primarily through the atmospheric photochemistry of nitrogen oxides and reduced carbon compounds, both of which are emitted into the atmosphere from natural sources and human activities. The main absorption band of O₃ is at 9.6 μm near the peak of outgoing radiation and its contribution

Unlike the long-lived GHGs, tropospheric O₃ is not emitted into the atmosphere but is formed there primarily through the atmospheric photochemistry of nitrogen oxides and reduced carbon compounds ...

to climate forcing is slightly less than that of CH₄. Tropospheric O₃ is the means by which part or all of the radiative forcing of CH₄, CO, volatile organic compounds and NO_x are realised. Since the start of background measurements in 1896 tropospheric O₃ has risen by 30–70% in the mid and high latitudes of the Northern Hemisphere.

Atmospheric aerosols

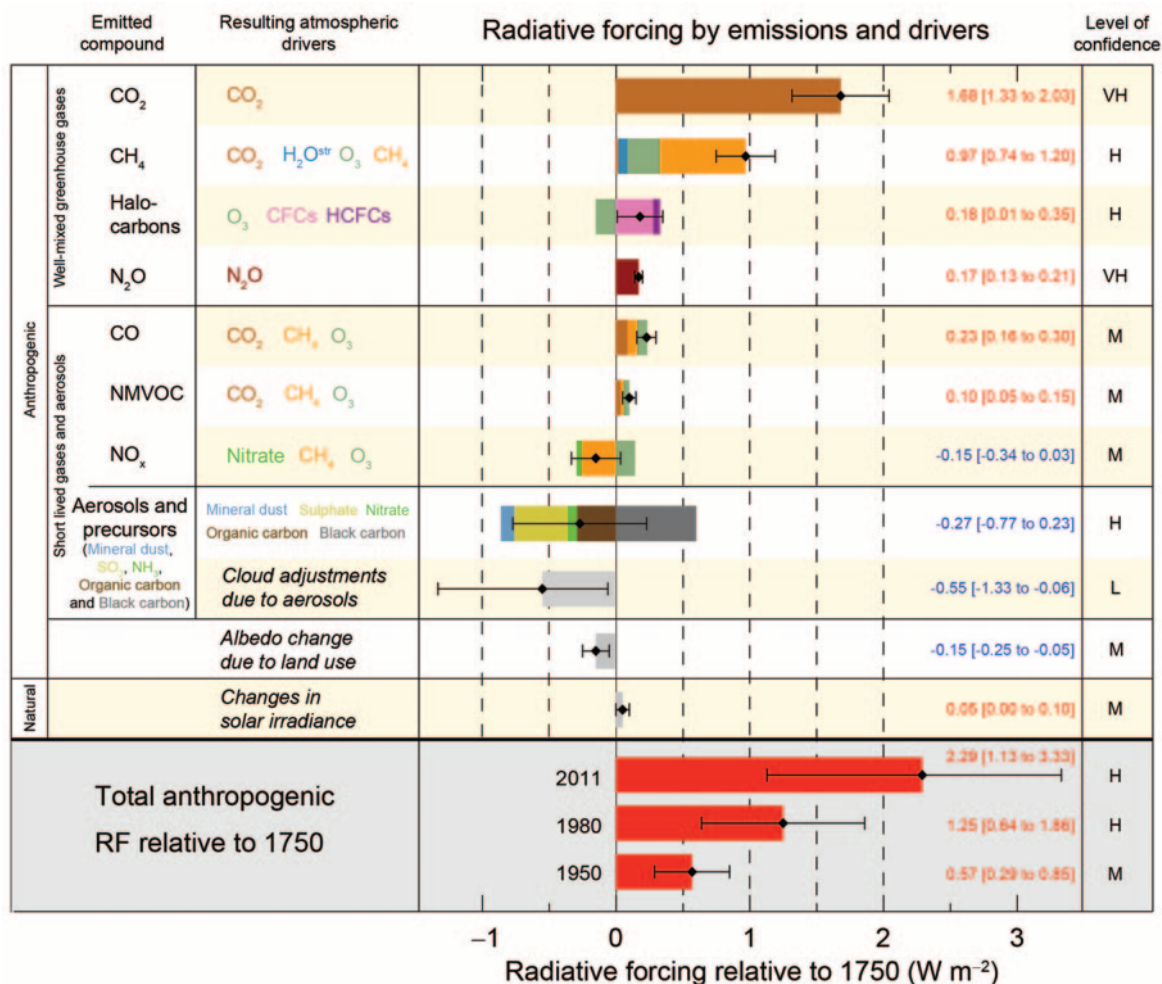
Atmospheric aerosols contribute to Earth's radiative balance in two main ways. In the stratosphere, aerosols are formed largely by condensation of water vapour on H₂SO₄ nuclei, with episodic but significant additions from large volcanic eruptions such as Mt Pinatubo in 1991. Aerosols scatter incoming solar radiation back to space and act to cool Earth's surface. In the troposphere, aerosols such as black carbon from biomass fires absorb radiation and contribute a positive warming effect. Overall, aerosol contributions to radiative forcing appear to be climate neutral or have a small cooling effect, but with considerable uncertainty.

Changes in ozone-depleting substances, tropospheric ozone and atmospheric aerosols are not accounted for in national GHG inventories but are very important components of global climate change models.

Water vapour

Water vapour is the single most effective GHG, absorbing virtually all radiation between 5.6 and 7.7 μm (1800–1300 cm⁻¹). Atmospheric levels of water vapour are controlled by evaporation, condensation and meteorology rather than any chemical process, and are dependent on feedback from atmospheric and ocean temperatures. Water vapour is not usually included in discussions of increasing GHG amounts due to human activities but the feedback loops between atmospheric and surface temperatures and atmospheric water vapour content are included in all climate change models, approximately doubling the direct temperature increase due to the other GHGs.

The graph on page 22 is from the most recent Intergovernmental Panel on Climate Change report, and presents the relative radiative forcing of the directly emitted GHGs and aerosols.



Comparative radiative forcing (RF) of various GHGs and aerosols.

Climate change 2013: The physical science basis, in contribution of Working Group I (WGI) to the Fifth Assessment Report (AR5) of the Intergovernmental Panel on Climate Change (IPCC)

Atmospheric impacts of the COVID pandemic

The 2020 COVID pandemic significantly reduced atmospheric emissions of GHGs through reduced industrial activity and particularly of CO₂ from reduced fossil fuel use in the transport sector. However, it is too early to see a clear impact on atmospheric amounts of CO₂ – the reduced 2020 emissions reduce CO₂ atmospheric amounts by much less than 1 part per million; this COVID signal is swamped by the natural variability of the many times larger biospheric fluxes.

Simple physics tells us that the greenhouse effect is real, and that increasing levels of GHGs will increase global temperatures. Current global climate models suggest temperature rises of 2–5°C this century, dependent on the scenario chosen for reducing GHG emissions. The human, social and environmental consequences will be immense; adaptation to these changes is another story. Three decades ago, humankind created then avoided a similarly catastrophic problem of global dimension – the threat of increased UV radiation exposure due to stratospheric O₃ loss. The problem was avoided with

political and industrial will by massively reducing global emissions of O₃-depleting halogenated compounds to the atmosphere. Dealing with GHG-induced climate change is a far larger economic, social and technical problem, but addressing the major source, fossil fuel emissions in energy production and transport, is paramount.

David W.T. Griffith FRACI CChem is Emeritus Professor, University of Wollongong. **Paul J.B. Fraser** FRACI CChem is Honorary Fellow, CSIRO Oceans and Atmospheres. **Ian E. Galbally** FRACI CChem is Post Retirement Fellow, CSIRO Oceans and Atmospheres and Honorary Professorial Fellow, University of Wollongong.

Kennaook/Cape Grim Baseline Air Pollution Station

Since 1976, the Kennaook/Cape Grim Baseline Air Pollution Station on the north-west tip of Tasmania has been a key station in a global network monitoring long-term changes in the clean atmosphere. Winds from the south-west sector bring Southern Ocean air from the cleanest part of the global atmosphere, air that last crossed land in South America. Kennaook/Cape Grim CO₂ and other GHG data can be downloaded for a range of gases from the Cape Grim and CSIRO websites (www.bom.gov.au/inside/cgbaps).

Kennaook/Cape Grim is operated by the Australian Bureau of Meteorology as a joint venture with CSIRO, and includes collaborations with ANSTO, universities and international partners.



Bureau of Meteorology; Paul Krummel, CSIRO

Further resources

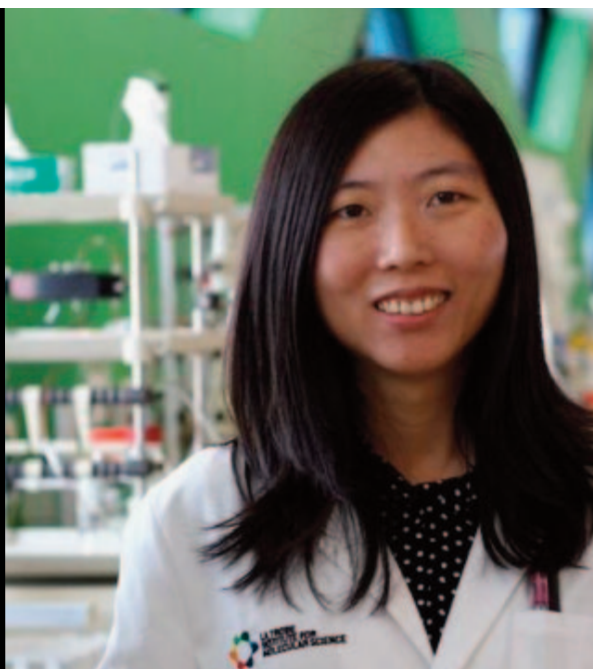
The following institutions, organisations and websites publish a wide variety of reliable, quality-controlled GHG data, tutorial material and analysis for further information.

• Advanced Global Atmospheric Gases Experiment (AGAGE)	agage.mit.edu
• Australia's National Greenhouse Gas Inventory	industry.gov.au/policies-and-initiatives/australias-climate-change-strategies/tracking-and-reporting-greenhouse-gas-emissions
• Cape Grim Baseline Air Pollution Station	www.bom.gov.au/inside/cgbaps
• Global Atmosphere Watch (GAW) GHGS	public.wmo.int/en/resources/library/wmo-Greenhouse-gas
• Global Carbon Project (GCP)	www.globalcarbonproject.org
• Intergovernmental Panel on Climate Change (IPCC)	www.ipcc.ch
• NOAA Global Monitoring Laboratory	www.esrl.noaa.gov/gmd
• Tropospheric Ozone Assessment Report	igacproject.org/activities/TOAR
• World Data Centre for Greenhouse Gases (WDCGG)	gaw.kishou.go.jp



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"I have built many
new connections
and they've
opened more
opportunities for
me to advance
my career."

Dr Yuning Hong, MRACI
RACI member since 2015



Hard reality

Rhino horn is still prized as a status symbol and for its perceived medicinal properties. Can the science of synthetics fortify the battle against poaching, ask **Dave Sammut** and **Chantelle Craig**.

I'll remember the moment for the rest of my life ... mostly in a cold sweat at 3 am. Me, standing unprotected, too far from the jeep for a run to safety, turning around to find a mother rhino just 25 metres away and facing my way.

That was back in late 2018, when I was fortunate to be on safari in Sabi Sands Game Reserve in South Africa, one of the best places on the continent to see wild rhino, whose numbers are dwindling. From more than half a million at the beginning of the 20th century, the World Wildlife Fund estimates that just 27 000 remain worldwide.

There are five surviving species of rhino: the black rhino and the white rhino in Africa; and the Javan, Sumatran and greater one-horned rhinos in Asia. All are threatened to some extent.

As for most threatened species, loss of habitat is a big factor in the decline of rhinos in the wild. But poaching also places enormous pressure on animals that are already too close to extinction. According to data from UK-based conservation charity Save the Rhino, numbers of African rhinos poached rose alarmingly from 60 in 2006 to 1346 in 2015, roughly where this story begins.

Desperate to stem the losses, wildlife NGOs and private enterprise began arguing about whether science can play a part in changing demand for exotic animal products – not just rhino horn, but lion bones, pangolin scales and elephant ivory.

Chemically speaking, there is nothing particularly special about rhino horn. It includes mainly calcium and melanin in a keratin matrix. In a manner similar to human hair and nails, it is produced by epidermal cells that undergo keratinisation and die.

Composition varies with the species and diet, but the northern white rhino horn contains 2% arginine, 5% lysine, 9% cholesterol, 3% taurine, 0.2–1% hexosamines (fructosamine and glucosamine) and 0.2% sphingosine in the keratin matrix, with

significant inorganic content: 66–70% sulfur, 15–19% potassium, 5–9% calcium, 0–3% iron, 0.2–0.4% titanium and 0–4% zinc. The organics can typically vary $\pm 20\%$, depending on diet.

... the horn contains two separate phases: one of hair-like filaments, built around a central core of circumferential layers; and the other surrounding and filling in the spaces between the filaments as a matrix.

A detailed 1993 study using scanning electron microscopy, X-ray diffraction and energy-dispersive X-ray spectroscopy found that the horn contains two separate phases: one of hair-like filaments, built around a central core of circumferential layers; and the other surrounding and filling in the spaces between the filaments as a matrix. Together, they form a 'biological composite, structurally similar to metal, ceramic or polymer based composites' (bit.ly/3uyXWS9).

The authors of that paper hypothesised that the production of synthetic rhino horn to flood the market 'could reduce, or possibly eliminate poaching pressure on these animals'. It's an interesting idea: if it were possible to produce a synthetic that is indistinguishable from the natural product, at a fraction of the cost of the illicit product, would this

undercut and destroy the market for poachers?

Let's start by looking at the markets for rhino horn. For the longest time, powdered rhino horn has been said to be linked to traditional Chinese medicine as an aphrodisiac. However, experts including Eric Dinerstein, WWF's chief scientist for 25 years, said in an article by Jeremy Hsu for *Scientific American* that this is largely Western misunderstanding, and the evidence of usage in traditional Chinese medicine for aphrodisiac properties is weak (bit.ly/3dTaFJ0). According to Hsu, this appears to be backed up by surveys of end-users of the illicit product.

Instead, the markets for rhino horn appear to centre on three uses, primarily in Vietnam, and to some extent China. Although the Convention on International Trade in Endangered Species of Fauna and Flora has made international trade in rhino horn illegal since 1977, WWF says the demand is still high, so rhino poaching in both Africa and Asia continues to grow.

First, Hsu and others report evidence of a wealthy class of epicures who add the powdered horn to alcoholic beverages as a mark of status and exclusivity. People use the horn because it is expensive and rare, and as a mark of power in the disregard for the law. Few report any belief in aphrodisiac properties, although some do say they believe in hangover curative properties.

Second is the purchase and use of rhino horn by some Vietnamese women for the treatment of fever in their families. This is reported to be associated with traditional Chinese medicine, which may also be claiming the use of rhino horn for the treatment of cancer.

Third (and somewhat surprisingly, given their lack of visual appeal) is a substantial demand for artefacts made of rhino horn – cups, jewellery and other *objets d'art*.

So, while conservationists and regulators alike seek to disrupt supply

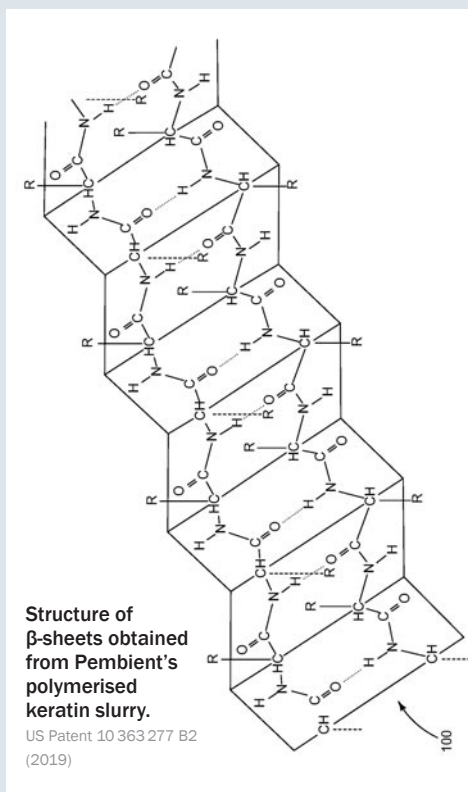
Synthesising rhino horn

US Patent 10 363 277 B2 (2019) describes Pembient's claims for the production of synthetic rhino horn. It sources the keratin base either from sheep's wool at pH 5–5.5, with a molecular weight of 3500–4500 daltons, or from genetically modified yeast. One part keratin is reacted with three parts of calcium hydroxide for 12–48 hours at 40–50°C under a nitrogen atmosphere.

The resultant slurry, containing polymerised keratin that is rich in β -sheets is dried at 70–90°C to <1% moisture. These β -sheets were selected because key proteins could be trapped between them to better match the composition of natural horn.

The dried powder is dissolved in a potassium phosphate buffer, and a range of organics are added: 2% arginine, 5% lysine, 9% cholesterol, 3% taurine, 0.2% hexamines (fructosamine and glucosamine) and 0.2% sphingosine. After mixing, a half part of 20–50% hydrogen peroxide is added to encourage disulfide/hydrogen bond formation in the β -sheets, trapping the additives. Again, the powder is dried at 70–90°C to <1% moisture.

Before that step, the β -sheets are of relative small size, with a limited number of disulfide bonds. The newly synthesised product is then analysed to check matches against known physical properties of rhino horn: a density of 1.122–2.222 g/cm³ and attenuated total reflection spectra with peaks at the appropriate locations for the primary organic components. Hardness is measured using a scale generally employed for rubber and some plastics: rhino horn has a Shore A hardness of 92–96 and a Shore D hardness of 68–72.



of poached rhino horn (which is beyond the scope of this story), several companies have been established that seek to disrupt the *markets* for the illicit product.

Most prominent among these companies is Pembient Inc in the US. Pembient hoped to produce a synthetic rhino keratin base from sheep's wool or from a recombinant protein secreted from genetically modified yeast (see box). To this can be added appropriate trace elements, amino acids, rhino DNA or rhino cells

to achieve a chemical profile reflecting the natural product (bit.ly/3s0ily2). This material would then be 3D-printed, possibly onto a structural mould.

However, a large and vocal group of wildlife NGOs argue that these products made by Pembient – and the other companies seeking to synthesise animal products – will make the poaching problem significantly worse. They have the same laudable goal, but say that the scientists are dabbling in matters that they don't properly understand.

'It's almost a knee jerk reaction, if you talk to most conservationists – they don't like synthetics, end of story', said economist Associate Professor Frederick Chen in a report published by *Mongabay* (bit.ly/3mx0bTw). Chen, based at Wake Forest University in North Carolina, focuses on the economics of conservation, and has modelled the introduction of synthetic products to the market: '... there is still a lot of detail and unknowns that need to be discussed and hammered out. The conversation in the community ... has not been able to get to that point so far'.

On World Rhino Day in 2015, an international coalition of 10 wildlife NGOs published a joint statement calling on the US to ban research by several US companies into synthetic rhino horn (bit.ly/3mxSD2D). They argued that introducing synthetic rhino horn into an unpredictable market could have unintended and unpredictable consequences. It could remove the stigma associated with purchasing and using such products, which is known to act as a brake on demand.

Synthetic rhino horn could hamper law enforcement if it is so similar to the natural product that perpetrators can use ignorance as an excuse and if testing to identify the real thing is expensive or difficult. But even if identifying differences was feasible, or if DNA profiling was used to distinguish between existing types of natural horn, buyers are likely to still attempt to obtain poached rhino horn, say many wildlife NGOs.

It is also feared that people with scientifically unproven beliefs about rhino horn may view production of synthetic product as a sign that their beliefs are correct. This is particularly the case because a lot of traditional Chinese medicine treatments use several natural products. Identifying and selecting particular ingredients perceived to be active in the rhino horn mix can be difficult, and so demand for the real product would likely remain strong.

That same demand issue also applies to the wealthy beverage market. Surveys show that demand is not based on the properties of the product itself, but on its status as a rarity and its high price. It has been predicted by detractors that there would remain a strong or even increased demand (based on reduced stigma), and some surveys suggest that there will always be a segment of the market preferring wild product as long as it is available (bit.ly/329nIAB), regardless of the status of the species.

The disagreement isn't helped by the fact that none of the companies proposing to develop synthetics is reported to be offering any funding for conservation efforts, and that this becomes tangled up with arguments about foreign companies profiting exclusively off the genetic diversity of poorer nations. Also, synthetic bear bile has existed for decades, and yet this has not decreased the market demand for this cruel product. Similarly, up to 90% of the material already illicitly traded as rhino horn is thought to be made from other horns, such as water buffalo, and this has not affected its price.

Faux leopard fur has been successfully taken up by the Shembe Church in southern Africa, considered to represent 'the principal culture-religious use of illegal leopard skins in the world' (doi.org/10.1111/csp2.289). However, it could be argued that as fur is not valued for its *properties* or how it is used, then it is a different market.

The economic modelling of the rhino horn market by Wake Forest University in 2017 concluded that the outcomes of synthetic horn production would be strongly dependent on market structure (doi.org/10.1016/j.econ.2017.06.003). For example, if synthetic producers were to argue



The greatest threat to African elephants, according to WWF, is illegal poaching for ivory, so this species also stands to benefit from the science of synthetics. Dave Sammut

... economic modelling ... concluded that the outcomes of synthetic horn production would be strongly dependent on market structure.

that their product was in some way superior to the natural version, they could place a premium on price and this could actually drive poaching up. But if competition in the market from multiple synthetic producers drove prices down, this might undercut poaching.

It was even argued that synthetic producers could deliberately produce inferior product to reduce market sentiment for the product as a whole – but it's hard to think of any product anywhere where a company has deliberately taken that approach.


Ultimately, the university concluded '... the results here show how important it is that we have a clear understanding of the economics of synthetic horns if we care about the

most effective way to save the rhinos'.

As a direct result of NGO pressures, Pembient walked back its plans after its launch in 2015. It gave up a planned collaboration in China to produce rhino horn beer, and it ceased marketing products such as rhino horn face cream. Other companies working on synthetic rhino horn in the US no longer exist.

This is an unusual situation. Every single party in the debate about synthetic rhino horn wants the same outcome. Everyone has their heart in the right place. They only differ in *how* to achieve protection of the species.

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



Emergency risk communication for chemical release incidents

iStockphoto/Christopher Freeman

Good communication of emergency risk is about more than robust procedures; an understanding of communication practice is also needed, writes **Madeleine Thomas**.

Many people in Melbourne will remember the August 2018 fire at a Tottenham warehouse. The warehouse was illegally storing unknown chemical and industrial waste in a large number of 44-gallon drums. The fire (often referred to as the West Footscray fire) produced a plume of black smoke that could be seen from across the city. Seven months later, another fire started at a chemical waste storage facility in Campbellfield. This warehouse

contained stockpiled and incorrectly stored chemicals. A black smoke plume was emitted and was seen across residential areas of Melbourne.

Challenges of emergency risk communication

The release of hazardous chemicals into the environment presents a significant threat to human health. These incidents, such as chemical spills and fires, are incredibly challenging for emergency response teams to manage. When chemical

release incidents occur, emergency responders face significant uncertainty and a need to urgently act to protect public health. Part of the public health response strategy includes emergency risk communication.

To ensure communications are timely and accurate, practitioners must quickly make sense of the hazardous situation and the communication options available. However, time and time again, we see emergency risk communication activities being met with criticism from the public and other stakeholders.

While chemical storage and handling in Australia is generally good when compared globally, we still have a long history of chemical release incidents. Notable incidents include the chemical leak at Kooragang Island in 2011 and several large-scale fires in Melbourne, including the West Footscray fire in 2018 and the Campbellfield fire in 2019. The 2011 chemical release incident on Kooragang Island in New South Wales involved the emission of chromium(VI) from an ammonia plant. While most released chemicals fell on site, some moved off site and fell on surrounding residential areas. It took several days for residents to be provided with information about the incident. Accordingly, the public inquiry highlighted delayed and inadequate communication to the public about the health risks the chemical leak presented.

Similarly, a public inquiry into fires at waste and recycling facilities across Victoria, including the West Footscray fire and the Campbellfield fire, highlighted a public view of poor communication by government agencies, including that the information provided to the community was inadequate.

Although there are emergency response procedures to guide practitioners, each incident is unique, which means there will be decisions that need to be made when new issues arise. Practitioners work in complex, time-critical environments that require both individual decision-making and the coordination of decisions within government emergency response teams. These practitioners are pivotal to what, how and when information is communicated to the public. Therefore, to be effective and efficient at communicating, government emergency response agencies need to look inwards to their practitioners and practices.

Building a deeper understanding of practice

Academic risk communication research tends to focus on the public, being those receiving communication. While an audience focus is understandable, there is also a need for research focusing on the communicators. To address this, my PhD research explores government emergency risk communication practice. It provides a deeper understanding of the practitioners, their practices, and the context in which this communication occurs. It shows how communication practices are not simply mechanical and objective; rather they are intuitive, collaborative and responsive. My research highlights the role of practitioners' lived experience and the history of past similar public health events, and the influence of the organisational context.

My research focuses on practitioners who are tasked with assessing the risk to human health and determining the best communication methods and messages. So far, it comprises two studies: a scoping literature review and interviews with practitioners. The scoping review synthesises existing evidence on government risk communication practice for chemical pollution and explores the influence of the organisational context. The interviews with practitioners gather insights into their lived experiences working during smoke events from major fires in Victoria.

Pressure to get it right

Practitioners' experiences of working during chemical release incidents can be stressful and exhausting. Practitioners often have to work long and late hours, and deal with competing demands, political and social pressures, and uncertainty about the information at hand. They feel pressure to 'get it right', with the public and other stakeholders expecting accuracy of their

assessments. The expectation of accuracy is understandable for public health threats, as the consequences of inaccuracy can be significant health impacts for affected communities. However, despite practitioners' best intentions, with hindsight their interpretation of a situation may not necessarily be seen to be accurate. Due to inherent uncertainties with available information and the time-critical nature of emergencies, decisions often have to be made with incomplete data.

My research highlights how past lived experiences are viewed by practitioners as a key facilitator of practice. These experiences assist practitioners in interpreting the situation, aiding in their pursuit of accuracy. It provides them with the knowledge to better assess the chemical hazard and understand how to operate within the emergency response structures. Shared lived experiences lead to shared understandings of the chemical hazard and of how to work collaboratively. Working together during an incident can lead to personal relationships and a sense of camaraderie that can help with more efficient future response efforts. The occurrence (or absence) of past similar public health events is key to providing practitioners with the lived experiences they currently hold.

A public inquiry into fires at waste and recycling facilities across Victoria ... highlighted a public view of poor communication by government agencies ...

Learning from the past

Current communication practices are a product of the history that sits before them. Practices evolve over time in response to changes in the social and political environments. These changes are often triggered by significant emergency incidents that are accompanied by communication practices that are perceived as poor by the public and other stakeholders. Emergency response agencies need to review and learn from these incidents. Where there has been a history of similar events, communication practices are likely more developed and refined. More evolved practices will likely include procedures outlining current best-practice for communication methods and messages, and the implementation of frameworks to support collaboration across government organisations.

It is also essential to recognise that communication activities originate within an organisation. Several organisational factors can influence risk communication practice. Organisational capacity factors include human resources, inter-organisational relationships, strategic prioritisation and program management. Organisational motivation factors include culture and the perceptions of practitioners. External environmental

factors include scientific knowledge and technology, the media, stakeholders' level of interest and the political, legal and economic environment. These organisational factors are linked and interact.

Understanding how these factors enhance or restrain practitioners' work is important for creating an environment that supports them. Capacity and motivation are factors that organisations can work to directly and proactively influence. Organisations can make it a strategic priority to fund and resource communication activities. For effective risk communication, there is a need for human resources to comprise both scientists (such as environmental scientists, human health risk assessors and toxicologists) and communication professionals (such as risk and science communicators and community engagement specialists). Having a strong organisational culture, sufficient capacities and capabilities, and meaningful relationships with stakeholders will move organisations towards strategic and proactive responses.

Moving beyond procedures

My research provides an intimate understanding of what communication practices for chemical release incidents entail. It emphasises the human aspect, highlighting that

emergency response teams are made up of people. It is important to understand that communication practices are intuitive and collaborative and recognise the pressure practitioners face. It is still essential to provide practitioners with procedures to guide them during these incidents, and train them on what to communicate. However, there is also a critical need to train practitioners on what the experience of working will be and how to perform their roles during these incidents.

If we want to improve emergency risk communication and best support practitioners, we need to appreciate the complexity of working during chemical release incidents. Understanding the relationship of practice with context and the critical role of lived experiences will hopefully help governments prepare for future incidents. The more we can support practitioners in their pursuit of accuracy and timeliness, the more likely it will be that emergency risk communication is effective. Improving risk communication practice will ultimately lead to greater protection of the public.

Lessons for managing hazardous chemicals

For those handling chemicals, it is good to be aware of the challenges

Assisting emergency response teams

In preparing for an incident, consider how you may assist emergency response teams. Ensure emergency response procedures are in place and that individuals working at your sites understand these procedures. Past lived experiences help people make sense of an incident. Running through potential emergency response drills can help people step through what they might need to do if an incident occurs. Exercises considering how or when chemical release incidents may occur will help prepare people for any potential incidents. They may also help prevent an incident occurring in the first place.

If an incident does occur, timely notification of the incident is a critical first step.

Emergency response teams need to urgently build a picture of the incident. They will need to rapidly answer these key questions:

- What chemicals are involved?
- How will these chemicals move through the environment?
- What are the adverse human health and ecological impacts from exposure to these chemicals?

Ensuring chemical manifests can be quickly shared with emergency response teams is a way to assist emergency response teams promptly understand the situation. Manifests should contain exact details and quantities of chemicals kept on site. Keeping these in electronic forms can aid with rapid information sharing.

If we want to improve emergency risk communication and best support practitioners, we need to appreciate the complexity of working during chemical release incidents.

involved in managing chemical release incidents. Ideally, chemicals will be managed in a way that prevents chemical releases. However, even with best-practice management procedures, an incident may still occur.

For all chemicals on a site, it is critical to understand the fate and transport of these chemicals in the environment and the human health and ecological toxicity. This information should be readily available and provided to emergency response teams during an incident. Moving towards green chemistry, such as chemical synthesis with an aim of new

compounds having no adverse human health or ecological effects, should help reduce future impacts from chemical release events.

Acknowledgements

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Madeleine Thomas (madeleine.thomas@monash.edu) is at BehaviourWorks Australia, Monash Sustainable Development Institute, Monash University.

More than 140 firefighters attended the warehouse fire in Tottenham in August 2018. The warehouse was not registered to store the many drums of chemicals found on site.

Ben Schubert www.benschubertphotography.com.au



STEM Ambassadors to foster parliament's links to science



Associate Professor Danielle Skropeta

Paul Jones, University of Wollongong

Science & Technology Australia (STA) has announced 17 new STEM Ambassadors. STA's STEM Ambassador program – which began in 2019 – pairs science and technology professionals with their local federal MPs and senators.

The new cohort of STA STEM Ambassadors will meet regularly with their local federal MPs and senators in 2021 to deepen connections between policymakers and the STEM sector.

Throughout the year, STEM Ambassadors meet with their local parliamentarian to bring their science

expertise and networks to assist evidence-based policymaking. The ambassadors are drawn from STA's member organisations and come from a diverse range of academic backgrounds and interests.

This year, one of the 17 new STEM Ambassadors to join the program is an RACI member. Associate Professor Danielle Skropeta FRACI CChem of the University of Wollongong is the STEM Ambassador to Federal Member for Cunningham Sharon Bird MP. Speaking to the RACI, Danielle said 'I am looking forward to this opportunity to help raise the profile of chemical sciences (and medicinal chemistry) nationally, as well as the broader STEM fields'. Danielle is the RACI's Margaret Sheil Leadership Awardee for 2021 and was presented with her award at the NSW Fellows Luncheon in May in Sydney.

This year, Danielle also joins a team of 100 women from across the world on the Homeward Bound STEM advocacy program.

The other new STEM Ambassadors are:

- Applied mathematician and apiarist Dr Shannon Algar, University of Western Australia
- Professor of fisheries and river management Lee Baumgartner, Charles Sturt University
- Marine biologist and shark researcher Charlotte Birkmanis, University of Western Australia

- Foetal physiologist Dr Emily Camm, Hudson Institute of Medical Research
- Rejane Langlois Research Fellow Dr Matthew Faria, University of Melbourne
- Motor neurone disease expert Dr Fleur Garton, University of Queensland
- Neuroscientist Professor Adam Guastella, Sydney University
- Cognitive scientist Dr Celia Harris, Western Sydney University
- Blowfly expert Associate Professor Michelle Harvey, Deakin University
- Technology consultant Maddie Holly
- Soil scientist Dr Chelsea Janke, University of Queensland
- Audiology expert Dr Dona Jayakody, University of Western Australia
- Engineer and creator of Her Bold Universe, Meg Pannozzo
- Mathematician Associate Professor Artem Pulemotov, University of Queensland
- Academic tutor Dr Priya Rani, RMIT University
- Rivers and water policy expert Dr Margaret Shanfield, Flinders University

STA Chief Executive Officer Misha Schubert welcomed the new STEM Ambassadors and congratulated them on their selection from a highly competitive field.

'Science has been Australia's salvation in tackling COVID-19. Australia needs to continue to build on that strong relationship between the STEM sector and parliamentarians to prepare Australia to meet future challenges', she said.

'The STEM Ambassador program empowers experts to become effective advocates for science and the sector, and to use their expertise to inform policy to shape Australia's future.'

'We're delighted to welcome the new STEM Ambassadors and look forward to seeing them develop a strong working relationship with their local MPs and senators to make sure science and technology are at the forefront of policy thinking.'

Further information about the partnerships is available at scienceandtechnologyaustralia.org.au/news.

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New Fellows



Dr **Mukund Chorghade** is Founder, President and Chief Scientific Officer, THINQ Pharma/MVRC Research and Ayurvedya Healthcare Innovations. He is the CSO, Chicago Discovery Solutions and APINOVO. He holds or has held adjunct research professor, visiting fellow and visiting scientist appointments at Caltech, Harvard, MIT, Northeastern, Northwestern, Princeton, Rutgers, and Chicago universities (US), British Columbia (Canada), Cambridge and Strathclyde (UK)

universities, College de France, Universite' Louis Pasteur (France), ICT, CSIR, KHRC (India), and others.

He provides synthetic chemistry and pharmaceutical development expertise to academic laboratories, and pharmaceutical and biopharmaceutical companies. His research interests are in drug discovery and development process chemistry derived medicinal chemistry, and traditional medicine derived new chemical entities. His discovery of sterically protected and electronically activated metalloporphyrin catalysts called 'chemosynthetic livers' finds utility in drug metabolism, valorisation of biomass and environmental remediation. He is also qualified as an expert in patent trials.

Chorghade earned his BSc and MSc degrees from the University of Poona (India) and a PhD in organic chemistry from Georgetown University (US). He completed postdoctoral appointments at the University of Virginia and Harvard University, and directed research groups at Dow Chemicals, Abbott Laboratories, CytoMed and Genzyme. He has been a recipient of three Scientist of the Year Awards and is on the scientific advisory boards of several corporations and foundations. He has been honoured by election as a Fellow of the Maharashtra, Andhra Pradesh, and Telangana Academies of Sciences. He has been a featured speaker in several national and international symposia. He is a certified CGLP/cGMP professional.

Chorghade was privileged to become an American Chemical Society member in 1982, was Section Chair of Brazoria (1990), Northeastern Section (2007) and Princeton (2019), and serves on the Board of Directors of Princeton. He is an active participant in ACS's Career Services, Professional Development, Entrepreneurship and the Small Chemicals Businesses Division. He was the Secretary of the Division on Chemistry and Human Health of IUPAC and served on the Commissions on Biotechnology, Medicinal Chemistry, and the US National Committee for PAC. He was the Chair of the RSC Committee on Process Chemistry and Technology (2018–20).

Professor **Youhong Tang** was an Australian Research Council-Discovery Early Career Researcher Award Fellow (2012–14) at Flinders University. Currently, he is the Deputy Director of International Laboratory for Health Technologies (2018–21) and the Project Manager of ACSRF-Joint Research Centre on Personal Health Technologies (2019–22), a research leader at the Institute for NanoScale Science and Technology (ERA rank 5 in Nanotechnology and Materials Engineering in 2018) and on the management committee for the Medical Device Research Institute at Flinders University. He is a Project Management Professional (PMP), Project Management Institute (PMI) (US) since 2008 and was elected as a Fellow of Royal Society of Chemistry (FRSC) in 2018.

Tang obtained his PhD from the Department of Chemical and Biological Engineering, Hong Kong University of Science and Technology in 2007 and moved to Flinders University in 2012 from the University of Sydney. He is a material researcher with research interests mainly focused on (1) the structure–processing–property relationship of polymeric (nano)materials and fibre reinforced composites and (2) biomaterials, chemo/biosensors and their devices with aggregation-induced emission features.

Tang has published more than 200 refereed journal articles and 14 book chapters and edited seven books in the last 10 years.

He is also on the editorial boards of various international journals, including *Applied Composite Materials* (2020–), *Aggregate* (2020–) and a community board member of *Materials Chemistry Frontiers* (2019–). He has been invited to serve as a lead editor of special issues in prestigious journals, including *Topics in Current Chemistry* on aggregation-induced emission (2020–21) and *Materials Chemistry Frontiers* on luminogenic bioprobes for personal health technologies (2020–21) and he chaired or co-chaired various prestigious conferences, including Symposium T: 3rd International Symposium on Aggregation Induced Emission In: 9th International Conference on Materials for Advanced Technologies. Singapore 2017; Theme Session Co-Chair & Scientific Committee Member, the 17th Congress of the Asian-Pacific Confederation of Chemical Engineering, Hong Kong 2017; Chair, 4th International Symposium on Aggregation Induced Emission, Adelaide, Australia 2019 and Co-Chair, Symposium of Building Advanced Materials by Self-assembly, Materials Research Society 2021 Spring meeting (US) 2021.



David Buckingham

An international force in molecular science

Professor A. David Buckingham CBE FRS FAA, who died in Cambridge (UK) on 4 February 2021, was one of the world's leading theoretical chemists. He provided distinctive fundamental insights into electric, magnetic and optical properties of molecules, including aspects of intermolecular forces and non-linear optics. Based in England for most of his career, David never forgot his Australian origins and maintained close ties with our local scientific community.

Born in 1930, David grew up in Sydney and excelled at both Barker College and Sydney University, where his BSc(Hons) and MSc research in the School of Chemistry was supervised by Professor R.J.W. Le Fèvre. David developed novel adaptations of dielectric theory to evaluate 'true' electric dipole moments of small molecules from measurements in dilute solution. He graduated with the University Medal in Chemistry and was also an accomplished sportsman, particularly in cricket. After captaining Barker's First XI in 1946 and 1947, he gained a cricket blue at Sydney University in 1953, played first-class cricket in England (1955–60), and was a long-serving (1990–2009) president of the Cambridge University Cricket Club.

In 1953, the prestigious Shell Postgraduate Scholarship enabled David to commence PhD studies at Cambridge in the Theoretical Chemistry Department headed by Professor J.E. Lennard-Jones, who was prominent in the field of intermolecular forces where David himself would gain comparable fame. Lennard-Jones was leaving Cambridge, so David was supervised by young Dr John Pople (who would later win a Nobel Prize). They combined admirably, generating many highly innovative publications.

In subsequent years (1955–65) at Oxford University, as lecturer in chemistry with college duties at Christ Church, David enhanced his international reputation as a highly productive physical scientist. Although primarily a theoretician, he also had experimental aspirations. He took advantage of excellent technical facilities at the National Physical Laboratory, Teddington. There, David and Dr Ray Disch (from Harvard) used polarised light to detect a tiny refractive index difference (i.e. birefringence) in gas-phase carbon dioxide by orienting the molecular electric quadrupole moments in an inhomogeneous high electric field. As a result, Peter Debye (after whom the pre-SI unit for electric dipole moments is named) suggested that 'Buckingham' cgs units should be used for electric quadrupole moments.

When David moved to Bristol in 1965 as the inaugural Professor of Theoretical Chemistry, he was joined by a lively international brigade (including myself – his first Australian PhD student), which outnumbered the English locals. Instruments transferred from Teddington to Bristol demonstrated that theory and experiment are sometimes inseparable. Significant progress was made in the emerging field

of non-linear optics, on NMR of oriented molecules, in computation of atomic and molecular properties, and on key aspects of intermolecular forces.

In 1969, David returned to Cambridge as Professor of Chemistry, Head of Theoretical

Chemistry, and Fellow of Pembroke College. He assembled an impressive team of researchers and new staff, investigating topics such as *ab initio* and semi-empirical molecular theory, intermolecular-force modelling of van der Waals molecules, measurements of Raman optical activity, and further studies of electro-optic, magneto-optic and nuclear effects. David's stimulating lectures posed intellectual challenges for even the most able students, and his post-seminar questions usually tested the speaker. His contributions to scientific publishing, as the editor of leading journals in chemical physics, were much appreciated by the scientific community.

David Buckingham's many honours and awards include his FRS (1975) and CBE (1997). In 2008, the Australian Academy of Sciences elected him as a Corresponding Member. He was a Fellow of the RACI and had won its Masson Memorial Scholarship in 1952 and its Rennie Memorial Medal in 1958.

Throughout his career, David maintained a keen interest in Australian science and politics (not to mention cricket!). During regular visits to Australia, his lectures and personal contact have influenced generations of young Australian scientists. Some have spent periods as PhD students, postdoctoral fellows or study-leave visitors with him in Bristol and Cambridge.

David retired in 1997, when a lively international symposium was organised at Pembroke College, but he remained active at Cambridge and on the conference circuit for many years after that. He and his devoted wife of 55 years, Jill, always maintained a warm, hospitable household and have three children and eight grandchildren.

David Buckingham always sought excellence. His intellectual and athletic agility served him well in science, sport and daily life. He was quick to speak up for his beliefs and inspired others to do likewise. David's legacy is a formidable body of scientific knowledge, together with the enduring example of his vigorous personality.

Brian J. Orr FRACI CChem



David Buckingham lecturing to the 50th anniversary meeting of the Sydney University Chemical Society in March 1979.

Maurice Mulcahy

Lifelong CSIRO scientist

Maurice Mulcahy (1920–2020) was born in St Arnaud, Victoria, and graduated BSc at the University of Melbourne in 1941 and MSc in 1942. He went on to Oxford to do a PhD (strictly, a DPhil) with C.N. Hinshelwood. On his return to Melbourne from England, he went to the CSIRO Lubricants and Bearings Section in Parkville, where he had worked between his MSc and his departure for Oxford. He remained there until 1959 when he transferred to the CSIRO Division of Coal Research and Mineral Chemistry (later known as the Fossil Fuels Division) in North Ryde, New South Wales, where he remained until retirement, ultimately becoming Assistant Chief. He was a cradle Catholic and, appropriately, lived at the then fairly new Newman College while he was studying at the University of Melbourne. He was also, as a result of his time at Oxford, very much an Anglophile. He was married to Jeanne and they had five children.

Honours came his way in abundance. The RACI Rennie Memorial Medal is an early career award, and Mulcahy received it in 1948. He was made FRACI in 1953. He received the Oxford DSc in 1971 and was elected Fellow of the Australian Academy of Technological Sciences and Engineering (FTSE) in 1980. A clue to his rise to eminence can be gained by noting the scientists with whom he collaborated and published. At CSIRO Lubricants and Bearings, he worked on liquid explosives with F.P. Bowden (FRS 1948) and A.D. Yoffe. Each of them was later to hold a permanent academic post at Cambridge. Mulcahy's DPhil work at Oxford was, as noted above, supervised by

Honours came his way in abundance. The RACI Rennie Memorial Medal is an early career award, and Mulcahy received it in 1948. He was made FRACI in 1953.

C.N. Hinshelwood (Nobel laureate 1956) and was on gas kinetics. Both at Oxford and much later when on sabbatical from CSIRO, he worked with C.F. Cullis, who became a professor at City University in London and himself had a sabbatical with Mulcahy at CSIRO.

Mulcahy did some lecturing at the University of Melbourne when he was with CSIRO Lubricants and Bearings and was a good instructor. His book *Gas kinetics* (Thomas Nelson, London 1973) became a widely used student text and it is to his credit that he wrote it concurrently with the heavy responsibilities of his CSIRO post.

After Maurice retired, he and Jeanne went to live in Hawks Nest in the Hunter region of New South Wales, but they also had pied-à-terre on Sydney's north shore. That enabled him to keep up a link with CSIRO Fossil Fuels and to attend scientific events in Sydney. The final time I was in his company was at a conference banquet in the idyllic setting of the restaurant at Taronga Park Zoo.

Clifford Jones FRACI CChem

members **raci news**

RACI Board statement on proposed cuts to Melbourne University chemistry funding

RACI President Professor Steven Bottle FRACI CChem, in a response for and on behalf of the RACI Board, has expressed the RACI's deep concerns about the proposed cuts to teaching positions and technical staff positions in chemistry at the University of Melbourne. These cuts come after the loss of staff in chemistry and other sciences due to funding issues at educational institutions, including the Australian National University and Murdoch University.

Professor Bottle's comments follow a report published in *The Age* on 3 April after the newspaper obtained internal documents showing that 11 units in chemistry, physics, biology and earth sciences have been flagged for suspension or 'discontinuation' as part of its 'pandemic reset program'. According to the report, staff were told that the chemistry school at the University of Melbourne 'is no longer financially viable'.

In his response, sent as a letter to *The Age* and a statement to RACI members, Professor Bottle said 'Chemistry is a central STEM field and is vital both to the future of the University of Melbourne and to Australia as a nation.'

'The RACI urges the federal government to redouble its support for STEM research and teaching in Australian universities. Further, we strongly encourage the University of Melbourne to ensure key STEM fields such as chemistry, which may be expensive to run in terms of space and technical support, are not unduly punished when the University is looking for short-term savings in these difficult times. Cutting resources for a core discipline such as chemistry is counter-productive for a university that is striving to be world-class and for a country seeking greater sovereign technical and manufacturing capability in post-pandemic times.'

Professor Andrew Holmes FRACI CChem, Melbourne Laureate Professor Emeritus at the School of Chemistry, Bio21 Institute, University of Melbourne, commented on Professor Bottle's statement: 'The Royal Australian Chemical Institute is the peak body representing the chemical sciences in Australia and it correctly identifies chemistry as a core STEM discipline that is a key component of national development and a major contributor to the overall strength of a great university.'

Specifically about heat

It is cold outside and suddenly you feel the urge to urinate. Why? Well, you expend a lot of metabolic energy in keeping a bladder full of waste water at body temperature. Better to dispose of the water ASAP. Divers feel the urge to purge even more pressing.

Why? Water has a surprisingly high specific heat. That is why a hot water bottle is great for cold beds. If you prefer a 'wheat' bag, fillings with good heat retention include corn and jasmine rice (which smells nice, too) (bit.ly/3tbD5mS).

Specific heat is a measure of the heat-holding capacity of a material – how much heat is needed to raise the material's temperature. Just heating or cooling a substance doesn't require much heat. More heat is involved when a material changes phase; from solid to liquid and particularly from liquid to vapour. Chemical reactions can produce much more heat. Some chemicals are used to store, use and generate heat.

Coming in from the cold, you heat a bowl of clear soup and a bowl of heavy French onion soup. If the two soups are served at the same high temperature, which one will burn your lips more? The specific heat of a soup that is mainly water is greater than the specific heat of a soup in which solid vegetables replace an equivalent volume of water.

Since antiquity, water has been used to store winter cold for cooling buildings in summer. Water is an example of a phase-change material – a substance that absorbs a great deal of heat by melting or undergoing other physical transformations.

For example, it takes 334 J/g to melt ice, but around 4 J/g to increase the temperature of water by a further one degree. And that's why you throw another ice block into the Esky.

By comparison, the heat of vaporisation of liquid water is huge, about 2260 J/g. This makes water the preferred substance for putting out most fires (unless the situation means it will do more harm than good). It's cheap and easy to spray onto bushfires. Phase-change materials are used in fire-protective clothing to absorb and thus reduce the rate of heat penetration. Research is focused on providing layers of different fabrics that themselves have an enhanced heat melting energy.



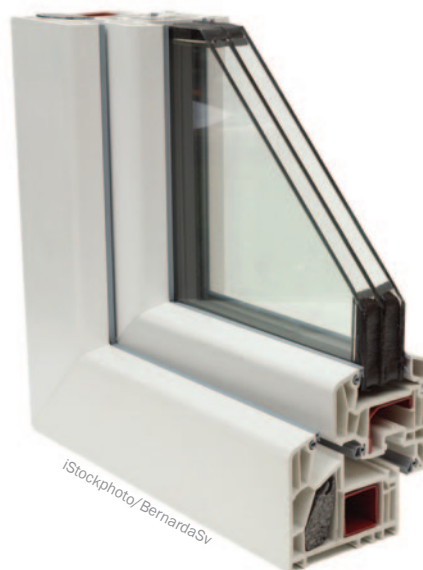
iStockphoto/Adrian Vidal

Eating your soup, you are grateful for those double-pane windows you had installed to reduce heat transmission. The vacuum between the panes removes convection and thus heat transfer (in both directions). Vacuums require stronger panes and better seals. Therefore, a gas is used, with argon preferred. Argon's specific heat is ten times lower than helium's. Hydrogen's is 14 times higher than nitrogen's. Anything special about those ratios?

Chemists love their moles but for everyday practical purposes we buy, sell and measure materials in grams. Changing from kilograms to atomic/molecular masses, we see that all the mono-atoms (argon and helium) have the same *molar* heat capacities, as do all diatomics. The polyatomics can be more complicated because they have more vibrational and rotational modes for storing energy.

So, a monatomic gas with a low specific heat will transmit less heat across the window space.

The equal volume panes comprise one filled with argon and one filled with helium at the same pressure and temperature. Thanks to Avogadro, we know there will be an equal number of atoms. Thermodynamics concludes that the thermal conductivity of gases is proportional to the specific heat and thus inversely proportional to the atomic/molecular mass. Look up a table of thermal conductivities (bit.ly/3vxxwLYr) and plot atomic/molecular mass versus thermal conductivity. What other gases look promising and what might be the reason that they are not used?



iStockphoto/BernardaSv

Solar houses often use large concrete slabs exposed through a northern window to warm up in the sun and then release that energy at night when it is cool (bit.ly/3tbDVjw). Thermal energy storage has become a sophisticated energy-saving option often employing phase-change materials.

Still feeling cold after the soup? These hand warmers contain iron powder, salt, water and activated carbon. Expose the pouch and air diffuses through the permeable cover, which incorporates iron and other components. Salt water provides the electrolyte; being adsorbed on activated carbon electrically connects separate pieces of iron in environments with different oxygen concentrations. Basically, you are getting heat from the rusting of iron.

A number of different materials can be used to retain the moisture needed for reaction: pulverised wood, polyacrylate polymer and vermiculite (aka kitty litter).

Users want quick warmth, but they also want it to last. The finer the iron, the larger the surface area exposed for reaction and the faster and the more intense the reaction. The size of the holes admitting oxygen affects the rate of reaction.

This type of warmer is single use. Reusable warmers harness the heat released when a supersaturated solution of sodium acetate is shocked into suddenly crystallising (by hitting it!). Boiling the packet after use dissolves the crystals and you can start again. This takes us back to phase change materials.

Ben Selinger FRACI CChem (benselinger39@gmail.com) is Emeritus Professor of Chemistry at ANU.

The finer the iron, the larger the surface area exposed for reaction and the faster and more intense the reaction.



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"In short, my RACI membership is about the people I have met, the contacts I have established and the friends I have made. It's all about networking, and being involved"

Dr Richard Thwaites
Honorary FRACI CChem
RACI member since 1971

New fuel for old

Today we are constantly assailed with statements about our being in a state of transition away from fossil fuels and that soon the transport fuels, which have delivered us prosperity for the past 100 years, will be replaced with alternatives. This, we are assured, will lead us to a bright, new and cleaner future. In particular, we are told that electric vehicles and possibly hydrogen vehicles will take over from fossil fuel-powered vehicles. Unlike revolutions of previous ages, this revolution is being driven by the ambitions of our leaders in government rather than from the consumer perspective.

Fossil-fuel-based transport took over from mainly horse-drawn vehicles in the late 19th century. Looking back, an alternative to horse-drawn vehicles was becoming a necessity if large cities such as London or Paris were to prosper. The geographic size of these two metropolises was reaching the limit of the transport system (horse) to deliver fuel (straw, oats etc.) from outside the city limits to the centre and remove waste (horse manure) back to rural areas. From this perspective, the internal combustion engine allowed for the growth and expansion of mega cities, which could not occur if horse-drawn vehicles were the only mode of transport.

We must remember that the replacement of horse-drawn vehicles with the internal combustion engine was not sudden.

Total replacement took decades and horse-drawn transport lingered on in many industries well into the second half of the

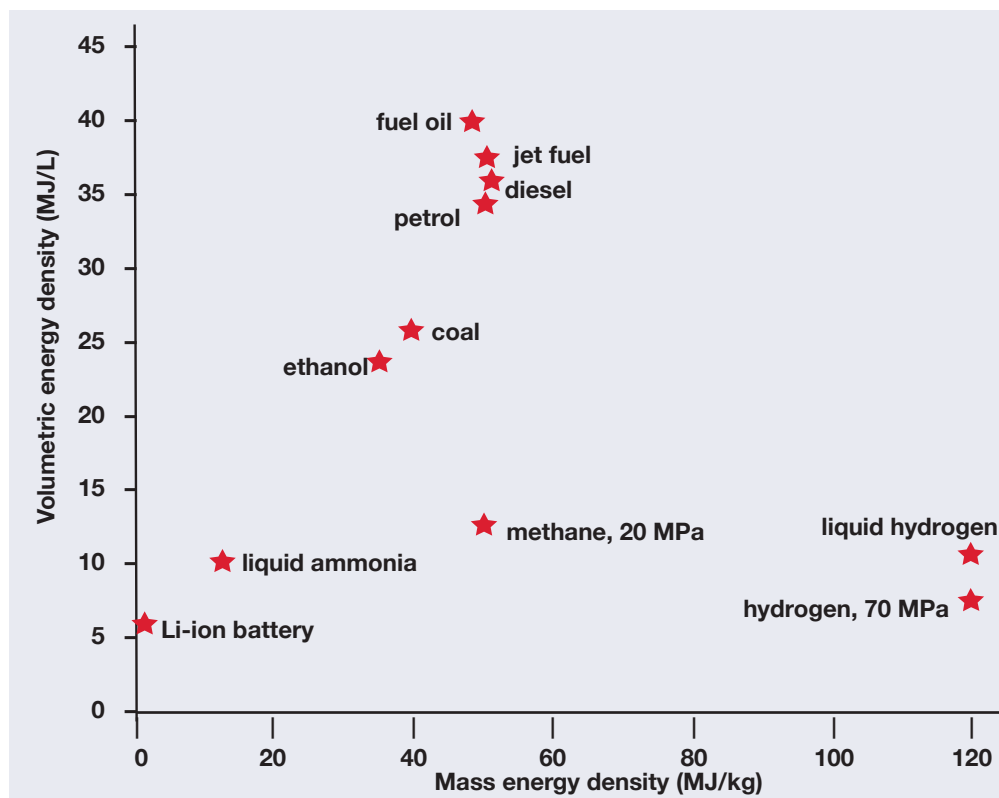
20th century. I can remember milk being delivered by horse-drawn cart – an early example of a fully autonomous driving vehicle. The horse (usually a Clydesdale called Dobbin) would learn the route and pull the cart at a sufficiently low speed to allow the milkman to make his deliveries and return with the empties without the cart stopping once. When Dobbin was replaced by electric milk floats, the milkman had to work harder because he had to keep stopping. Furthermore, ponies were often used in mines, particularly coal mines, to haul coal from the working coal face to coal hoists or to the surface.

In many cases, the ponies spent their entire lives underground. The use of ponies in collieries dates from the *UK Mines Act* of 1842 which banned the use of women and children in underground operations. Women and children could of course be used on surface operations.

We are told that within 30 years the use of internal combustion engines operating on fossil fuels will cease, with some jurisdictions moving to ban their sale. So what will be the impact of replacing fossil-fuel vehicles on a city from the perspective of goods movement and transport logistics? The graph is an attempt to answer this question.



Plot of volumetric energy density against mass energy density for selected fuels.



A key parameter is the volumetric energy density – how much energy you can get in the tank. The graph plots the volumetric energy density of fuels against their mass energy density. It is immediately evident that conventional fossil fuels have a high volumetric energy density. Ethanol (a renewable biofuel) is somewhat lower. The problem for the touted alternatives, batteries and hydrogen, is that they have much lower volumetric energy densities.

Liquid hydrogen and hydrogen compressed to 70 MPa (700 atmospheres) have very high mass energy densities but volumetric energy densities less than 10 MJ/L. Compressed methane is not much better, and liquid ammonia, which, despite the enormous safety

issues involved, has been proposed as a vehicle fuel, is still less than 10 MJ/L in volumetric energy density.

Lithium-ion batteries have a volumetric energy density even lower at less than 5 MJ/L. Note this is the idealised density and represents a limit for this technology, with the current commercial batteries being lower than this.

For a more realistic assessment of the relative efficacy of fuels, we need to consider other factors, such as the weight of the container vessel (tank). For cars, this varies from about 10 kg (60 L) for fossil fuels, to about 140 kg for a hydrogen tank at 70 MPa pressure, carrying about 5 kg of hydrogen, to 540 kg for a lithium-ion battery (Tesla Model S).

On the benefit side for alternative fuels is the higher efficiency of the motive power being delivered. Modern petrol engines are between 25% and 30% efficient; diesel engines are somewhat higher at about 35%. Hydrogen fuel cells have approximately 60% efficiency and battery technology could deliver 90% efficiency.

The data in the table gives some pertinent pointers. This data has been assembled from relatively available sources so is approximate. It is presented to give a broad outline of issues to be considered in determining the relative merits of the transport fuel options.

The horse is assumed to be a workhorse weighing 600 kg and requiring 100 MJ/day of energy. This is provided as oats in a bag. The power output (1 horsepower, 0.75 kW) is optimistic, as is the efficiency at which the oats can be turned into motive power.

Three examples of internal combustion engines are a small petrol car (e.g. Ford Fiesta), a large diesel (e.g. Toyota Land Cruiser) and a truck (e.g. Kenworth). Maximum power data is taken from various company sales brochures and websites. The data for the hydrogen fuel cell vehicle is taken from Toyota Mirai sales literature and the data for the lithium battery case is for a Tesla S, as reported by Wikipedia.

The following columns in the table give fuel volumetric energy data and a lower estimate taking into account the mass of the container. The efficiencies of the engines may be on the high side.

As can be seen, the power (rate of doing work) for the battery vehicle is very high. This underpins the enthusiasm of many for this type of vehicle – it's very fast. However, the data

indicates that as far as the energy carried in the vehicle, hydrogen fuel cells and lithium-ion batteries are broadly the same but are well below those of conventional fossil fuels. In fact, they are very similar to that of a horse. Full power cannot be applied for long (final column).

A further point of distinction is the time to bring the vehicles back to a fully charged state. We know that fuel refilling for liquid fossil fuels is less than five minutes and is not much more for LPG vehicles, which would imply that hydrogen refuelling would be similar (Toyota claims five minutes). However, battery recharging times are much longer – 10 hours for a Tesla S or one hour on a fast charger.

It is energy in any form that moves people and goods across an urban network. An immediate deduction from this is that for a non-fossil-fuel transport fleet, for the same amount of goods to be carried, there will have to be many more transport vehicles on the road. The data also emphasises the superior performance of fossil fuels for towing large loads (caravans etc.) over long distances. This duty seems well out of reach for the alternative fuel vehicles.

As more and more players adopt the target of zero carbon emissions by 2050, it is important to think about the implications of this objective and try to identify and mitigate any unintended consequences from the adoption of alternative fuels:

- Considering the geographic extent of Australian cities, would it be possible to efficiently distribute necessary goods (food etc.) from large warehouses, which are usually on the periphery of the city, to locations on the far side of the city?
- The use of biofuels (ethanol and biodiesel) is strongly supported by many in rural areas. If we prevent the sale of conventional vehicles after a certain time (e.g. 2030, in nine years time), are we not condemning to redundancy the various biofuel initiatives around the nation?

If we are to fully embrace alternative fuels and place barriers to the purchase and use of conventional vehicles, then these and other questions need to be addressed.



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

Relative performance parameters for various transport fuels

	Fuel		LHV fuel (MJ/L)	LHV fuel with tank	Power (kW)	Engine efficiency (%)	Recharge time (min)	Relative performance	Time at max power (h)
Horse	600 kg	Oats	6.00	6.00	0.75	15	120.00	3.84	0.10
Internal combustion engine	Small	Petrol	32.72	25.17	147.00	30	5.00	32.22	2.14
	Large	Diesel	35.92	30.61	284.11	35	5.00	45.72	4.13
	Truck	Diesel	35.92	30.61	380.31	35	10.00	45.72	20.32
Fuel cell	Fuel cell	Hydrogen	4.76	0.17	128.00	60	5.00	0.43	0.05
Li-ion battery	Battery	Electricity	2.49	0.26	615.00	90	60.00	1.00	0.14

Wine in a can, perhaps?

ABC Rural News posted an article in December 2020 that addressed the uptake of wine in 250 mL aluminium cans (<https://ab.co/33fbab8>). The uptake would appear to be driven by people in the 25–34 age bracket. This market group is well known for seeking new approaches that challenge many traditions, such as ‘wine is only OK if stored in glass’. The sleek can shape plus the images that may be printed on the can give the product attributes that are attractive to this age cohort (see Wine Australia’s market bulletin at bit.ly/2Rkxpdg). Using cans for wine has some environmental appeal, with high recycling rates and a lower carbon cost associated with transport.

When using an aluminium can to store wine, it is essential to isolate the wine from contact with the aluminium: we showed many years ago that wine is a highly effective ‘solvent’ for aluminium (*Am. J. Enol. Vitic.* 1992, vol. 43, pp. 166–70). A synthetic liner, preferably a thermoset polymer, is now widely used. This liner gives what Professor Gavin Sachs of Cornell University calls a ‘plastic bottle with a super thin wall’.

Cans, if filled and sealed properly, have essentially no oxygen ingress, even via the ring-pull closure. This means that wine oxidation is not a problem. Flavour scalping – removal of flavour compounds by the liner – is minor, if it occurs at all. Tainting, or flavour change resulting from interaction between wine compounds and the liner, is also essentially non-existent, with one major problem.

The problem is the production of hydrogen sulfide and some other organo-sulfur off-odour compounds in the wine during storage, and this is where the detailed chemistry comes to the forefront of research. Intriguingly, the sulfidic off-odours are perhaps more common in white and rosé wines and less common in red wine. White and rosé wines are generally at a lower pH than red wines, resulting in a higher proportion of the sulfur dioxide being present in the molecular (SO_2) form.

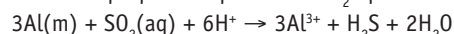
Dr Eric Wilkes MRACI CChem and Neil Scrimgeour of the Australian Wine Research Institute (AWRI) recently published the results of a benchmarking study on 16 canned wines (*Grapegrower and Winemaker*, March 2020, pp. 68–71). Over a five-month period, most of the wines exhibited a significant increase in the aluminium concentration, despite the presence of a protective liner. Examination of the inner surface of the cans by scanning electron microscopy demonstrated the presence of pitting on the inner surface, thus providing a pathway for leaching aluminium into the wine. Many wines showed an increase in the H_2S concentration, at times considerably higher than the aroma perception threshold of 1.1–1.6 $\mu\text{g/L}$, as confirmed by a bench tasting exercise.

Wine composition is inherently variable, as are the practices of filling the can and the headspace volume remaining after filling. This creates difficulty when trying to interpret the observations of the 16-can trial in terms of individual wine components. To examine the individual components, the AWRI

group established a trial using one wine with variations in pH and SO_2 concentration. In addition, chloride was varied as this can affect degradation of the inert oxide layer on the surface of the aluminium. Copper(II) was also used because it is now known that this can act as a store or reservoir for sulfide (doi.org/10.1111/ajgw.12450). The amount of oxygen in the sealed can, known as total packaged oxygen (TPO), was also examined.

The results to date are quite fascinating, demonstrating some rather complex chemistry at work. The combination of aluminium metal and copper(II) leads to a marked increase in the production of H_2S , especially at low TPO values.

The presence of copper(II) is not mandatory, as aluminium metal alone leads to some increase in H_2S production. However, aluminium(III) salts do not have any impact on H_2S production. This has led to the proposed equation for H_2S production:



Any Al^{3+} released would most probably bind immediately to tartrate and, based on our 1990 unpublished data, be essentially sequestered and not available for further reaction.

This equation does not consider the role of copper(II). Recent AWRI results show that if copper species are removed from the wine by using cross-linked polymers before adding aluminium metal, there is an obvious lowering in H_2S production with respect to the controls. Clearly, there is a lot more work required to understand the complex interactions that are occurring in the production of H_2S .

The AWRI research is part of an international effort with Cornell University and Enartis, a US-based company that provides support for the wine industry worldwide. Enartis recently hosted two webinars (bit.ly/3nK8vzA and bit.ly/3egCHPT) on canned wine. There is a lot of great information here. For example, Professor Gavin Sachs of Cornell University is working on film composition and its link to H_2S production. More will come out from this work in the future.



Geoffrey R. Scollary FRACI CChem (scollary45@gmail.com) 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. In writing this article, I acknowledge the considerable help given by Dr Eric Wilkes of the AWRI.

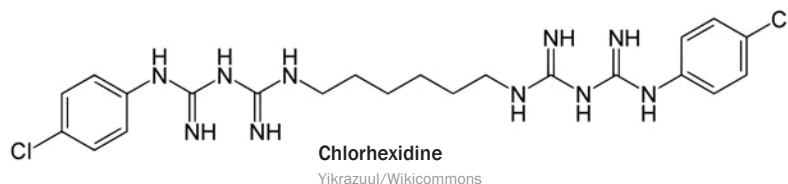
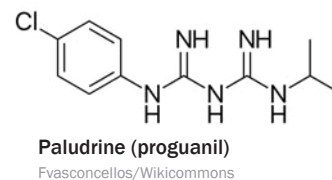
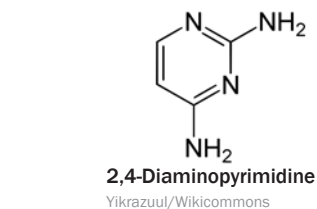


It's nitrogen all the way

When I use a product containing a named chemical, I like to check the molecular structure, and this sometimes leads me on a search for other chemical substances with similar structures or incorporating similar functional groups. The one that started this reverie is chlorhexidine, a topical antiseptic that is marketed under many names and can be a minor constituent of mouthwashes and toothpastes. The story of its discovery makes interesting reading because it involves one of the masters of the art of making organic chemicals with marketable properties, Frank (Francis Leslie) Rose (1909–1988), who worked in the dyestuffs division of Imperial Chemical Industries, near Manchester. Rose and his colleague Frank Curd (1909–1948) were among a group of dyestuffs chemists who were transferred in 1936 to the new Medicinal Chemicals Section, the precursor of the Pharmaceuticals Division that was formed in 1954.

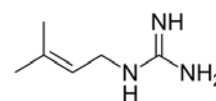
Finding drugs to treat malaria was one of the aims of the section, and Rose and Curd found some activity in derivatives of 2,4-diaminopyrimidine, of which they synthesised a great number. As the structures piled up, each one guided by hopeful signs of biological activity, they began to wonder if the really active part of their molecules was the guanidine residue embedded in their pyrimidines and whether they could dispense with the rest of the pyrimidine skeleton and still have an active drug. One of the best candidates had a second guanidine residue and, probably reasoning that two guanidines would be better than one, they synthesised a number of bisguanides, among which was the successful antimalarial drug Paludrine.

Some of the ICI team's bisguanides turned out to have bactericidal properties, and that led them to chlorhexidine, which, as you can see, is closely related in structure to Paludrine. As with many bio-active substances that have served us well over the years (at least six decades in this case), concerns about chlorhexidine's effectiveness and

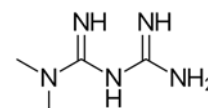


toxicity, especially carcinogenicity, have begun to restrict its use and it could soon go the way of once-common substances like phenacetin.

Quite independently, another bisguanide entered the pharmacy in the mid-20th century – metformin, which is used for the control of type 2 diabetes. Its story starts in medieval times, when it was known that the frequent urination we now identify as a consequence of the lack or malfunction of insulin could be relieved by extracts of the seeds of the European plant *Galega officinalis*, known as French lilac, goat's rue or Italian fitch (shown here). The active ingredient galegine was identified in 1914 and a decade later it was shown to be isoamylene guanidine. Guanidine itself and simple derivatives like galegine were unsuitable for therapeutic use, but they were good leads for further investigations that led, in mid-century, to several bisguanides. Metformin, has been widely used by people with diabetes, and taking it is also touted as a way to improve one's 'health span'. Research on this is difficult to conduct, but some enthusiasts are taking a gram each day. One writer noted, however, that 'hundreds of drugs that work in mice never make it into humans' and that he doesn't take metformin 'because I'm not a mouse'.



Galegine
Ed (Edgar181)/Wikicommons



Metformin
Fvasconcellos/Wikicommons



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 is an editor of *Historical Records of Australian Science*.



Galega officinalis

Epibase/CC BY 3.0

Chem2021

12–13 July 2021, virtual conference

RACI Chem2021 is the first Victorian Branch meeting focusing on the work of early–mid-career chemists. The online meeting will showcase the excellent chemical research done by emerging chemists in Victoria in all areas of the chemical sciences. It aims to create a platform for emerging chemists, strengthen professional networks and spark collaborations between early- and mid-career chemists.

Registration includes two half-day conference sessions and an evening poster session (12 July) and trivia night (13 July), all online.

raci.org.au/events

Chemeca 2021

27–28 September 2021, virtual conference

The 50th Chemeca will bring together chemical engineers and scientists from Australia, New Zealand and across the globe to share insights and innovations relevant across the wide range of industries. The theme for Chemeca 2021 is Advance, Disrupt and Sustain.

chemeca.org

RACI 2021 National Congress

3–8 July 2022, Brisbane

raci2022.com

International Conference of Microreaction Technology

27–30 November 2022, Melbourne

The International Conference of Microreaction Technology (IMRET), the largest and longest running international meeting in the field of microreactor devices and flow chemistry, will be held now for the first time in Australia. IMRET16 has new been rescheduled. More information will be released shortly.

flowchemistrysociety.com/events

17th Pacific Polymer Conference

10–14 December 2022, Brisbane

PPC17 has been rescheduled. For more information or to register your interest, visit ppc17.com.au.

20th International Conference on Biological Inorganic Chemistry

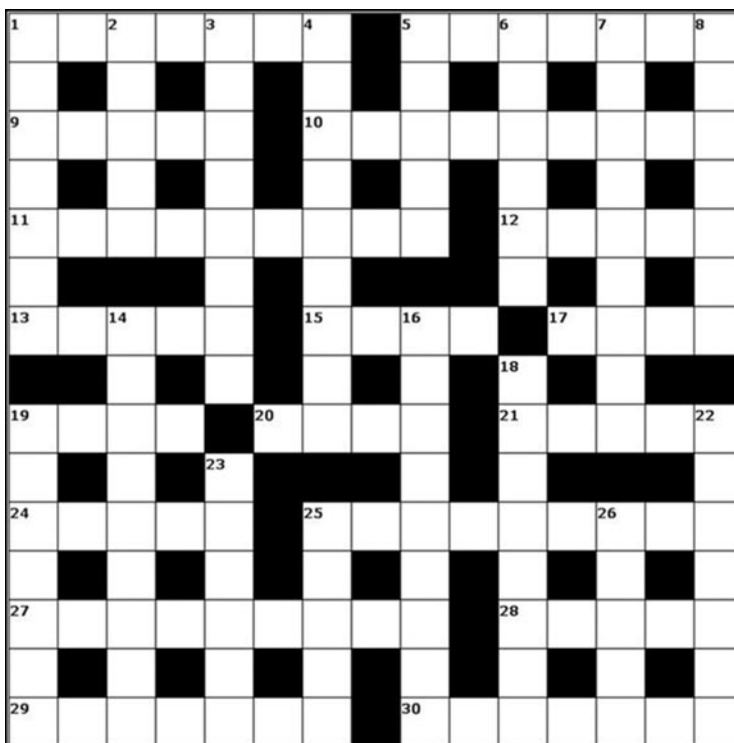
July 2023, Adelaide

Due to the ongoing COVID-19 pandemic, the local and international organising committees have decided to postpone the Adelaide ICBIC20 from July 2021. To maintain the scheduling of the ICBIC series and timing against cognate conferences, such as ICCO, ICBIC20 will now take place in Adelaide in July 2023.

The Society of Biological Inorganic Chemistry aims to deliver a virtual event in the middle of 2021 to ensure that our community can remain connected and active through this period. More details will be announced in the SBIC newsletter.

icbic2021.org

RACI events are shown in blue.



Across

- 1 Novel ceramic is optically inactive. (7)
- 5 Room for five elements. (7)
- 9 Ways to obtain money. (5)
- 10 Flags bases for comparison. (9)
- 11 Viral base model may assume different values. (9)
- 12 Six booming water particles in the air. (5)
- 13 Fatty Spooner's tablet cover. (5)
- 15 Seconds beta adrenergic agonists becoming an advantage. (4)
- 17 Fight four hanging on to 71. (4)
- 19 One element over another: move fast. (4)
- 20 Three elements remain. (4)
- 21 A bound pair of a particle and its antiparticle derived by addition of a hydron to the hydride of any element of the nitrogen, chalcogen or halogen families. (5)
- 24 Easy turnover in system migration. (5)
- 25 Isotope of one? Rue edit. Alter with hesitation. (9)
- 27 Interpose new measures of disorder of the systems. (9)
- 28 A N⁺ perhaps? Negative. (5)
- 29 Gap rule broken for protective equipment. (7)
- 30 Pub frauds Spooner sixes. (7)

Down

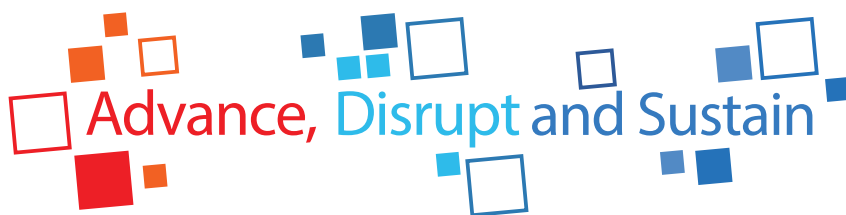
- 1 Old measure of radiation to ground discharge. (7)
- 2 Six mop seat. (5)
- 3 $\mu \times 110 =$ condiments. (8)
- 4 Once volts were applied to improve solubility. (9)
- 5 Kind group. (5)
- 6 Notice pipe formed by direct combination. (6)
- 7 A family of mathematicians blur line with oxygen distribution. (9)
- 8 Live over uranium debris. (7)
- 14 Criterion for reaction rate remap. (9)
- 16 A class guy got smashed and discovered the composition of water. (3-6)
- 18 Advance cut off heard to not participate in bonding. (4,4)
- 19 Wash your hands and say g'day to The Singing Cowboy. (7)
- 22 Start with 42 men, and take on 117 for a short time. (7)
- 23 Draw back from two elements and bring up another. (6)
- 25 Execution hit receives oxygen. (5)
- 26 Came up in non-imitation with both ($>C=NH$) and ($-C(=O)-OH$) functional groups. (5)

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

Chemeca 2021

27-28 September, Virtual+

Register Now



Registration is open

Chemeca is the annual conference for the Australian and New Zealand community of chemical and process engineers and industrial chemists. Together, participants will learn and share industry knowledge, experiences, ideas and insights that help the industry continue to grow. Registration is open for Chemeca 2021 and there are discounts for members of The Royal Australian Chemical Institute (RACI), Institution of Chemical Engineers (ICHEME), Engineers Australia and Engineering New Zealand.

To secure your place register at www.chemeca.org



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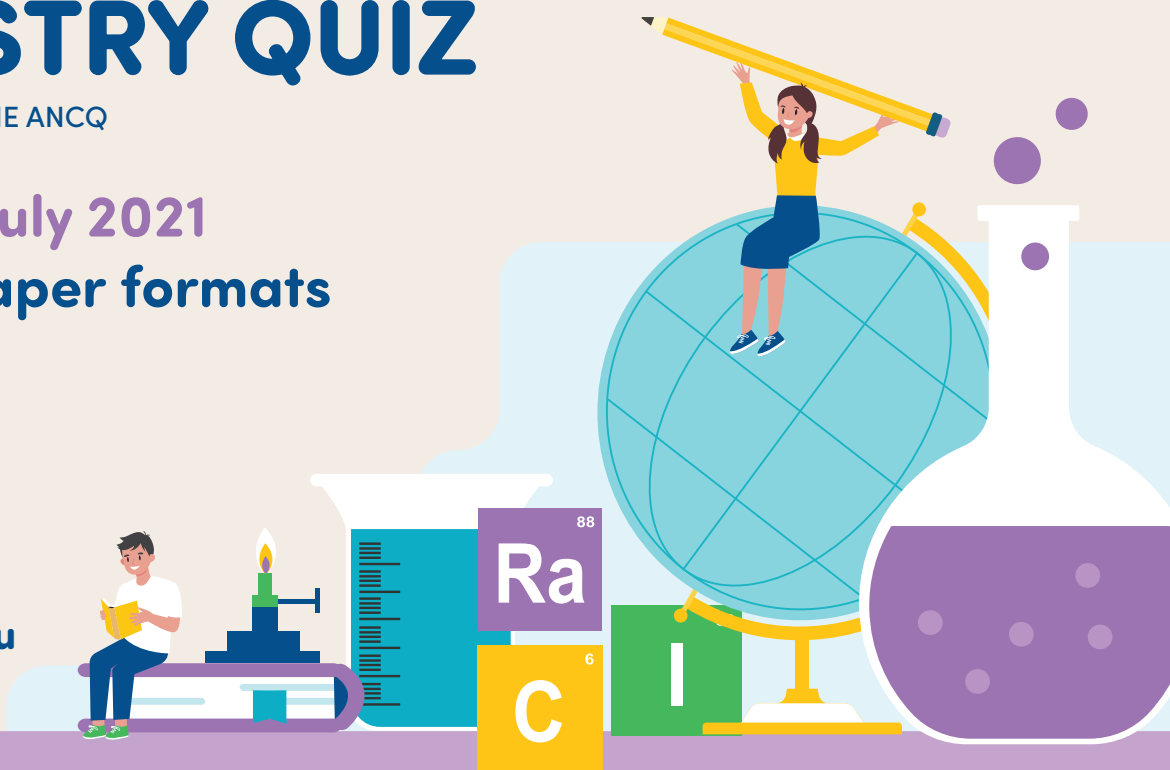
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8 March - 11 June

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Register by
11 June 2021



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