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Chemistry and pathways to net zero for sustainability

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Chemistry needs to play a central role in achieving 'net zero' emissions of greenhouse gases (GHGs) into the atmosphere to prevent changes to the climate that will have catastrophic impacts for humanity and for many ecosystems on the planet. International action to limit global warming to 1.5 °C has framed as a key goal the reduction of global emissions to as close to zero as possible by 2050, with any remaining emissions re-absorbed from the atmosphere. Chemistry underpins innovative approaches to reducing emission of the key GHGs, comprising CO₂, CH₄, N₂O and fluorinated gases, and to the recapture of gases already in the atmosphere. Rapid progress is needed in the application of green and sustainable chemistry and material circularity principles in developing these approaches worldwide. Of critical importance will be the incorporation of systems thinking, recognition of planetary boundaries that define safe operating spaces for Earth systems, and an overall reorientation of chemistry towards its roles in stewardship of the Earth's material resources and in sustainability for people and the planet.

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Sustainability spotlight

International negotiations to address global warming have set the target of 'net zero' – reduction of global emissions of greenhouse gases (principally CO₂, CH₄, N₂O and fluorinated gases) to as close to zero as possible by 2050, with any remaining emissions being reabsorbed from the atmosphere. Essential chemistry contributions to achieving this target must go beyond today's compartmentalised approach to innovation in new materials and processes. Rather, they should be rooted in a reorientation of chemistry towards sustainability, embracing movements, frameworks, and tools embodied in prioritising chemistry's leading role in the material stewardship of planetary resources. This aligns chemistry with the UN Sustainable Development Goals including clean energy, responsible consumption and production, and climate action.

1. Introduction

Leaders in governments, industry, academia and wider society are increasingly expressing extreme concern at the polycrises^{1,2} that are significantly degrading multiple, entangled systems on Earth. Sufficient perturbations in these systems risk leading to tipping points being reached, resulting in long-term changes to the planetary environment and consequently threatening humanity's prospects for survival and wellbeing.³ There is clear evidence^{4–6} that human activities are causing planetary-scale changes on land, in the ocean, and in the atmosphere, with dramatic and long-lasting impacts, including on the climate

system. Four key climate change indicators – greenhouse gas (GHG) concentrations, sea level rise, ocean heat and ocean acidification – set new records⁷ in 2021 and there is increasing evidence that biogeochemical flows are transgressing planetary boundaries that define safe operating spaces for a number of Earth systems.^{8–10}

As long ago as 1896, Swedish physical chemist Svante Arrhenius predicted that changes in atmospheric CO₂ levels could substantially alter the planet's surface temperature through the greenhouse effect and, in 1938, Guy Callendar connected CO₂ emissions from industry with global warming.¹¹ With evidence accumulating of the impact of GHG emissions on climate, the establishment of the Intergovernmental Panel on Climate Change (IPCC) in 1988 signposted a new era of inter-connection between science and social and political movements aiming to prevent long-lasting changes to the Earth's climate.¹² In 1990, the First IPCC Assessment Report played a decisive role in the creation of the United Nations Framework Convention on Climate Change (UNFCCC), a key international treaty to reduce global warming and cope with the consequences of climate change. The Second Assessment Report in 1995 led to the 1997 Kyoto Protocol, which called for reducing the emissions of six

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greenhouse gases in 41 countries plus the European Union to 5.2% below 1990 levels. However, the impact of the Protocol was considerably weakened by the failure of many of the leading GHG emitters to join or ratify it. The annual meetings of the Conference of the Parties (COP) to the UNFCCC have provided an ongoing mechanism for review of country commitments and a channel for attempts to increase efforts. A major milestone, following the IPCC's Fifth Assessment Report, was the Paris Agreement, a legally binding international treaty on climate change adopted by 196 Parties at COP21 in Paris on 12 December 2015, which entered into force¹³ on 4 November 2016. This has served as the motive force for the 'net zero' approach,¹⁴ which is providing a target that helps align societal concern, scientific evidence and innovation and policy-making.

The net zero target is at the forefront of efforts to keep global warming within safe limits,^{14,15} agreed by countries to be a rise of not more than 1.5 °C above pre-industrial levels by 2050.^{16,17} Net zero means reducing global emissions of greenhouse gases (GHGs) to as close to zero as possible by 2050, with any remaining emissions re-absorbed from the atmosphere.

Many countries have already pledged national targets to contribute to achieving net zero, although target dates and details of national commitments vary widely.^{18–20} Moreover, these commitments must be backed by credible action and, to date, few countries have provided climate plans detailing the action they will take. According to the 2022 report²¹ of the United Nations Environment Program (UNEP), the national commitments so far do not add up to a credible pathway to limiting global warming to 1.5 °C and the problem has been highlighted that some actors engage in 'net-zero greenwashing' with empty pledges.²² There is considerable urgency to taking the necessary steps, since global warming has already reached 1.1 °C above pre-industrial levels. A decrease of 45% in GHG emissions compared with 2010 levels is now needed by 2030 to put the world on track to the 1.5 °C limit by 2050. On the present course, however, 2030 emissions will have increased by more than 10% from their 2010 level.²³ Many governments,²⁴ private sector companies^{25,26} and scientists²⁷ agree that pathways to reaching net zero by 2050 are now extremely challenging, requiring governments, businesses, investors and citizens to



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engage in a total transformation of the energy systems and production/consumption systems that underpin our economies.^{12,28–30}

Essential contributions are required from science and technology (S&T), including chemistry.^{31–33} Industry in general is responsible for around a quarter of global emissions. As the third-largest industrial emitter of CO₂, related both to energy production and material processing, the chemical industry (chemicals & petrochemicals, not including cement) is an important driver of the climate crisis.³⁴ CO₂ intensity over recent years has been fairly stable, producing around 1.3 t CO₂ per tonne of primary chemicals. The chemical industry therefore must contribute both to reducing its own direct emissions (involving approaches at conceptual and practical implementation levels) and to helping devise ways to assist other sectors to address theirs. Key inputs will include technological innovation, efficiency gains and higher recycling rates, with emphasis on carbon-neutral processing and the requirement that every material component should, as far as practical at the elemental, compound or composite level, have repeated use *via* recycling to maximise material circularity.

This Perspective considers the connection between net zero and chemistry – the pivotal roles that chemistry, as the science of transformation of matter, can play in achieving it, and the orientations, knowledge and skills that chemists need in order to ensure that the net zero objective translates into sustainability as the outcome. This will bring to the foreground (1) the importance of recognizing and understanding the intimate connections between chemistry processes and Earth systems, highlighting the value of systems thinking as a core competence needed by chemists; (2) the need for the nuanced translation of circular economy ideas into their specific physical adaptation as material circularity,³⁵ through chemistry and other disciplines,^{36,37} to provide the material/molecular basis of sustainability; (3) the value of adopting the planetary boundaries³⁸ framework to help ensure that anthropogenic activities are contained within the safe operating spaces of Earth systems;

and (4) the opportunity for chemistry to develop and display its role in the stewardship of the Earth's material resources, which are embodied in our elemental heritage.

2. Greenhouse gases, chemistry and net zero

Global emissions of GHGs, which in particular include CO₂, CH₄, N₂O and fluorinated gases,³⁹ have risen steeply since the mid-20th Century, doubling from 1970 to a total of about 60 gigatons of CO₂-equivalent by 2019 and comprising five main categories (Fig. 1).⁴⁰ Each of the GHGs has a different global warming potential (GWP) (a measure of how much energy the emissions of 1 ton of a gas will absorb over a given period of time, relative to the emissions of 1 ton of CO₂) which results in some relatively low-concentration GHGs having a substantial environmental impact.

Several complementary approaches can reduce GHG emissions in the atmosphere. Broadly speaking, these include modifications to existing processes to reduce production of and/or to capture or destroy GHGs prior to emission, substitution of existing processes by new ones that are carbon-neutral and intrinsically produce less GHGs; and sequestration to recapture GHGs that have already been emitted into the atmosphere. Five main categories of emissions (Fig. 1) are discussed below.

2.1 Shifting away from fossil fuel-derived CO₂

Carbon dioxide derived from fossil deposits accounted for almost two thirds of the total GHGs emitted in 2019, from applications that generate heat, light and power through combustion and that use carbon and hydrocarbon feedstocks to synthesise a multitude of other useful materials. Innovative options are urgently needed for a 'clean energy transition', replacing coal, gas and oil-derived power with primary energy produced from renewable sources such as wind or solar, to dramatically reduce carbon emissions while extending the availability of the non-renewable fossil hydrocarbons as raw materials for synthesis.

However, although the clean energy transition makes economic sense,⁴¹ solutions are not simple. The scale of the energy decarbonization issue was already highlighted two decades ago when chemistry Nobel laureate Richard Smalley coined the term 'The Terawatt Challenge'.⁴² He noted that in 2004 the vast majority of energy being consumed was from oil, gas, and coal, and that, beyond replacing this with a comparable level of power from sources that did not emit CO₂, power production would need to increase fourfold to about 60 terawatts by 2050. Annual global power production has indeed continued to grow rapidly,^{43,44} almost doubling between 2000 and 2022, and, while renewable energy forms have made an growing contribution, the use of fossil fuels has also risen (Fig. 2) and, with it, global fossil fuel CO₂ emissions have continued to increase.⁴⁵

It is notable (Fig. 2) that nuclear energy makes a substantial contribution to global electricity production, amounting to 9% in 2022. While the energy-generation step in nuclear fission reactors does not release GHGs, the precursor steps (from



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the German Chemical Society and is also a member of the Göttingen, North Rhine-Westphalian and Norwegian Academies of Sciences. His work has been concerned with cyclophanes, highly unsaturated hydrocarbons and aromatic compounds. He is currently an Emeritus Professor in the TU BS.



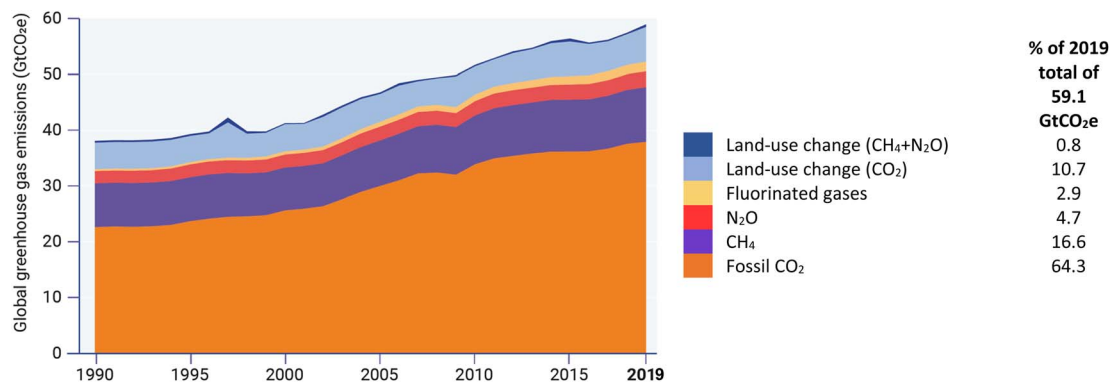


Fig. 1 Global greenhouse gas emissions 1970–2019 (freely reproduced from ref. 40, Fig. 2.1).

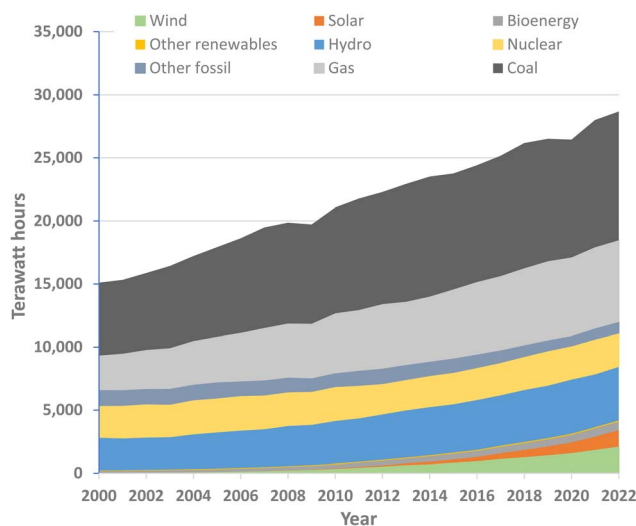


Fig. 2 World electricity generation by source (drawn from data published in ref. 44).

mining and refining the uranium ore to producing the concrete for power stations) and the post-reactor storage and further processing of spent fuel, coolant and other irradiated materials at the reactor site have significant environmental impacts. In many of the countries using nuclear power generation, governments have vacillated over policies on sustaining existing nuclear energy stations and investing in new ones. However, in view of the present poor level of global progress towards net zero, it is argued that nuclear energy needs to continue making a substantial contribution at least to mid-century.^{46–48} Molten salt thorium reactors provide an important alternative to ²³⁵U-based reactors.^{49–51} Their advantages include that Th is more abundant in nature than U and when irradiated with fissile material such as recycled plutonium (generated from fast-breeder reactors), Th fuels can breed fissile ²³³U *in situ*.⁵²

Shifts to alternative power sources display complex systemic challenges. Currently used wind and solar technologies have strong dependencies on some elements that have limited practical availability, lack supply-chain resilience and are 'energy-critical' elements⁵³ for which competition is increasing.

Rare-earth elements, including neodymium, praseodymium, dysprosium and terbium, are extensively used in the permanent magnets for wind turbines, as well as for electric vehicles. A 2022 report⁵⁴ from the International Energy Agency (IEA) flagged the steeply increasing demand for these elements, which is projected to accelerate. The IEA report emphasised the need for countries to ensure that their energy systems remain resilient and secure as they expand efforts towards the clean energy transition.

For solar power, conventional high-performance optoelectronic devices for capturing sunlight rely on single-crystalline inorganic semiconductors, such as silicon or gallium arsenide. With 173 000 terawatts of solar energy striking the Earth continuously – more than 10 000 times the human world's total energy use – there has been growing interest in the improved performance that can be obtained, for example, with compounds of indium⁵⁵ and also in applications of other materials such as halide perovskites and organic semiconductors,⁵⁶ including in single-junction organic solar cells.⁵⁷ The direct current generated can be stored in a variety of energy carriers, including by H₂ production from water splitting using photocatalytic, photoelectrochemical, photovoltaic-electrochemical, solar thermochemical, photothermal catalytic, and photobiological technologies.

Chemistry's contributions include improved efficiencies and cleaner processes in the extraction, refining and recovery of rare earths, as well as in the development of new processes and materials for these important energy production efforts, requiring collaboration with other disciplines.^{58,59} Recent advances across these technologies have been reviewed, with comparisons using criteria of efficiency, durability, cost and environmental impacts (from lifecycle assessment to completely identify and assess the global warming potential and acidification potential of each process).⁶⁰ The currently demonstrated approaches of solar H₂ production with high efficiency and durability generally show low production cost but high environmental impact, in a trade-off that currently impedes the large-scale implementation of solar H₂ production. Photoelectrochemical artificial leaves have potential to lower the costs of sustainable solar fuel production by integrating light harvesting and catalysis within one compact device, but



have been limited in their scalability. In one innovation, light-weight artificial leaves have now been fabricated, onto which perovskite-BiVO₄ layers have been deposited that show high efficiencies and improved scalability. Moreover, as floating systems they have the potential to be used in open-water applications, thus avoiding competition with land use.⁶¹ In another innovation, ultra-thin photovoltaics have been transferred onto light-weight and high-strength composite fabrics, providing portability of power source with the wearer.⁶²

Different approaches are required for mobile energy sources for different modes of transportation. In the case of land transport, options for alternatives to batteries which can be re-charged at intervals include green hydrogen and ammonia as fuels. In the case of shipping, which currently accounts for around 3% of GHG emissions,^{63–65} ammonia is also being explored as a fuel while the present emphasis for sustainable aviation fuel⁶⁶ is focused on biofuel production pathways. In each case, there are major challenges in achieving net zero goals. Production of both hydrogen and ammonia currently depends on fossil fuels and generates large amounts of CO₂ (see below, Section 4), while aviation biofuels generate CO₂ that needs to be offset.

Construction of the hardware and infrastructure required for renewable power sources using currently employed processes and scaled to the projected global levels will require massive additional transformation of materials⁶⁷ whose production also consumes substantial energy and releases significant amounts of GHGs. For example, about 30 billion tonnes of concrete is used each year, making this the most abundant manufactured material on the planet.⁶⁸ The cement sector is the third-largest industrial energy consumer and the second-largest industrial CO₂ emitter globally, making it essential that this sector moves towards net zero.⁶⁹ Concrete is an aggregate typically containing sand, crushed stone, and cement. The calcium oxide used as the binder in Portland cement is prepared by decomposition of limestone at c. 900 °C, liberating CO₂. More than 4 Gt of cement is produced annually and CO₂ emission by the cement industry accounts for 7% of annual GHG production. In recent decades, fly ash (a residue from coal-fired power stations, whose main constituents are oxides of silicon, aluminium, iron and calcium) and other waste materials such as slag from blast furnaces have been used as supplementary cementitious materials. Sustainable alternatives to traditional concrete are being explored,^{70,71} including options for materials described as 'C-negative', for binders (*e.g.* ferrock containing iron dust from steel production,⁷² graphenecrete in which graphene partly replaces the cement,⁷³ bio-polymer concrete based on a polyurethane binder⁷⁴), for aggregates (*e.g.* hempcrete containing the inner woody core of the hemp plant mixed with lime⁷⁵), or both (*e.g.* polymer concrete incorporating calcium silicate as binder and waste polymers as fillers⁷⁶). Emerging chemistry contributions include use of the reaction $\text{CaCO}_3 + 2\text{NaOH} \rightarrow \text{Ca(OH)}_2 + \text{Na}_2\text{CO}_3$ as an alternative that decarbonizes the limestone at ambient temperature and simultaneously captures the CO₂ in a product that can be stored or used for regeneration of CO₂ as required.⁷⁷ There has also been demonstration⁷⁸ of key steps in a carbon-negative process for manufacturing cement

from widely abundant seawater-derived Mg²⁺, involving conversion of Mg(OH)₂ into carbonates through reaction with CO₂. Recycling of used concrete is also being explored, both for reuse of bulk material and recovery of chemical components.^{79,80} It should also be noted that concrete absorbs CO₂ from the atmosphere, partly offsetting the amount liberated in its production.⁸¹

Steel is the most widely used metal in the world, traditionally produced from iron oxide ores by very energy-intensive reduction processes using coal or coke that liberate 1.8 tonnes CO₂ per tonne of steel, as a global average. In 2020, world production of 1.86 billion tons of steel contributed 7–9% of annual global anthropogenic carbon emissions.⁸² As a critical component of the energy transition, including use in wind turbines, grid infrastructure, electric vehicles and solar installations, as well as having many other applications in construction and engineering, global demand for steel is expected to rise by more than a third by 2050. Major reductions in GHG emissions in steel production are therefore essential in moving towards net zero.⁸³ Major contributions to achieving this goal can come from increased recycling of steel and cleaner processes for reducing oxide ores in primary production of iron (*e.g.*, using electrolysis⁸⁴ or hydrogen^{85,86}). Carbon capture technology has not yet been applied at scale in steelmaking, but is now being explored.⁸⁷

Copper is the 'metal of electrification', and its availability is regarded as essential to all energy transition plans. A market analysis report⁸⁸ in 2022 suggested that there will be a growing supply-demand gap, as global refined copper consumption is predicted to rise steeply. The report highlighted three main options for increasing supply: new mines or major expansion of existing mines; increasing output as a percentage of a mine's total capacity; and recycling through extracting copper from discarded batteries, old wiring, and other equipment. Alternative metals such as aluminium have conduction disadvantages but may be chemically tuneable,⁸⁹ while new materials such as carbon nanotube wires may offer metal-free options.⁹⁰

Commentaries on the material requirements for achieving net zero tend to focus mainly on ones discussed above as examples where supply, demand and production factors are critically important. However, there are many other materials that need to be considered in assessing the viability and sustainability of pathways to net zero. These include a range of 'critical minerals', such as those required for batteries. A typical electric vehicle requires six times the mineral inputs of a conventional car, with lithium, nickel, cobalt, manganese and graphite being crucial to battery performance, longevity and energy density, while rare earth elements are essential for permanent magnets required for electric vehicle motors.

A current area receiving strong attention is the search for alternatives to lithium. Lithium-ion batteries are presently regarded to be the most effective technology for vehicle electrification. The degree of interest in research on lithium-ion batteries is signalled by a machine-generated summary of research published in 2019, which identified more than 53 000 articles published in the previous three years.⁹¹ Current areas receiving strong attention include the search for alternatives to



lithium. Ion batteries based on the cheaper and more abundant sodium are being commercialised for some applications, but do not currently provide the same range or speed of charging afforded by lithium. For stationary grid storage, batteries based on iron/air/water systems are also being commercialised.⁹² The three most commonly used metals in cathode materials for Li-ion batteries (nickel, manganese, cobalt) are expensive and cobalt, in particular, is in limited supply, and alternatives are being examined, including lithium iron phosphate. Under exploration are alternatives to the traditional anode material, graphite, include silicon nanoparticles, which may help increase energy density and speed up charging.⁹³ While the chemistry and physics of batteries themselves are central to power performance, from a perspective of sustainability and net zero goals, it is clear that a host of other factors need to be considered as well, including the total energy and material inputs to manufacturing, the source of electricity for recharging, the fate of battery materials and potential for recovery and reuse, and the wider environmental impacts as assessed by life cycle assessment studies.⁹⁴ Clean energy transitions will have far-reaching consequences for metals and mining, especially for those metals which have high geographical concentration of production, including lithium, cobalt and rare earths. Security of supply is compounded by a range of factors, including geopolitics, long project development lead times, declining resource quality, growing scrutiny of environmental and social factors and the impact of mining in areas with high water stress levels.⁴³

2.2 Reducing release of fluorinated gases

These first became a cause for alarm in the 1970s to 1980s, with the discovery that chlorofluorocarbons (CFCs) widely used in refrigerants and aerosols were accumulating in the atmosphere and causing depletion of the stratospheric ozone layer. The 1985 Vienna Convention and subsequent 1987 Montreal Protocol banned the use of CFCs, in an example of rapid global action that demonstrated the potential for chemistry, science in diplomacy and international concern to combine on an environmental issue.⁹⁵ As a result, total column ozone is recovering and is expected to return to 1980 values around 2066 in the Antarctic, around 2045 in the Arctic, and around 2040 for the near-global average.⁹⁶ This example also demonstrates the potential for incomplete solutions and adverse consequences, however. Unfortunately, the hydrofluorocarbons (HFCs) chosen to replace CFCs turned out to be powerful GHGs, the five most commonly used HFCs being between 150 and 5000 times more potent than CO₂.⁹⁷ HFCs are now being phased out following the agreement of 197 countries to the 2016 Kigali Amendment to the Montreal Protocol.⁹⁸

What will replace HFCs as refrigerant gases? Apart from possessing suitable physical parameters (including low freezing point, low condensing pressure, high evaporator pressure, high critical pressure, and high vapour density) and chemical properties (including oil solubility, low water solubility, low reactivity) to work efficiently in refrigeration systems, the next-generation refrigerant must meet a host of additional requirements relating to the safety of people (*e.g.* low toxicity and

flammability) and planet (minimal short- and long-term impacts if released into the environment). At present, some hydrofluoroalkenes and hydrocarbons, as well as ammonia (already used in much industrial refrigeration) are being considered as HFC replacements for domestic use, but all have drawbacks.⁹⁹ This remains an area awaiting further chemical innovation.

Sulphur hexafluoride has been extensively used as a dielectric gas for electrical insulation in high-voltage settings and a considerable proportion tends to leak into the atmosphere, where it acts as an extremely powerful GHG with a GWP of about 23 900 and atmospheric residence of up to 3200 years.¹⁰⁰ As a result, its use is regulated and the ongoing search for alternative gases for use in power applications currently focuses on fluorocarbon compounds, including perfluoroketones and perfluoronitriles.^{101,102} However, in view of the persistence and environmental effects of fluorocarbon compounds,¹⁰³ other approaches are of increasing interest, include the use of clean air as the insulating medium.¹⁰⁴

2.3 Managing emissions of methane and nitrous oxide

Methane in the atmosphere arises from a range of processes,¹⁰⁵ with two thirds of the global emissions (estimated at around 590 Mt in 2020)¹⁰⁶ attributed to human activities including use of fossil fuels, burning biomass and biofuels, agriculture and landfills and waste (Fig. 3).¹⁰⁷

With a shorter lifetime in the atmosphere but a greater capacity to absorb heat, weight-for-weight CH₄ has 84–87 times the 20 year GWP of CO₂, but 28–36 times when considering its impact over a 100 year time-frame.⁹⁴ Globally, atmospheric methane concentrations¹⁰⁸ rose from 722 ppb in pre-industrial times to 1895 ppb by 2021, the highest value in at least 800 000 years¹⁰⁹ and constituting a ‘methane emergency’.¹¹⁰ In the use of fossil fuels, more than 7 MT per year of CH₄ escapes from the extraction, transmission and incomplete combustion of hydrocarbon fuels, more than 4 MT per year from coal and 9 MT per year from bioenergy.¹¹¹ It is estimated that these ‘fugitive emissions’¹¹² could be reduced by 26% using existing technology. Consequently, efficient and cost-effective new processes and technologies are needed,^{113,114} not only for the fossil fuel-related release¹¹⁵ but also to cut CH₄ emissions from the other sources. Attention is also being given to developing ways to remove CH₄ from the atmosphere. One method being explored is to release iron-fortified sea water aerosols into the atmosphere, resulting in CH₄ oxidation with hydroxyl radicals.¹¹⁶ The wider impacts (*e.g.* on animal health) of such an approach need to be assessed.

Nitrous oxide, N₂O, along with NO and NO₂, is generated in internal combustion engines, as well as by burning plant materials, and by the decomposition of nitrogenous fertilizers derived from ammonia. N₂O is of particular concern because it is 310 times more powerful than CO₂ as a GHG and, in addition, it damages the ozone layer. Human activity is now emitting N₂O faster than it is being destroyed in the upper atmosphere (primarily by solar radiation), so it is accumulating at 0.2–0.3% per year.¹¹⁷ Atmospheric concentrations of N₂O reached 331



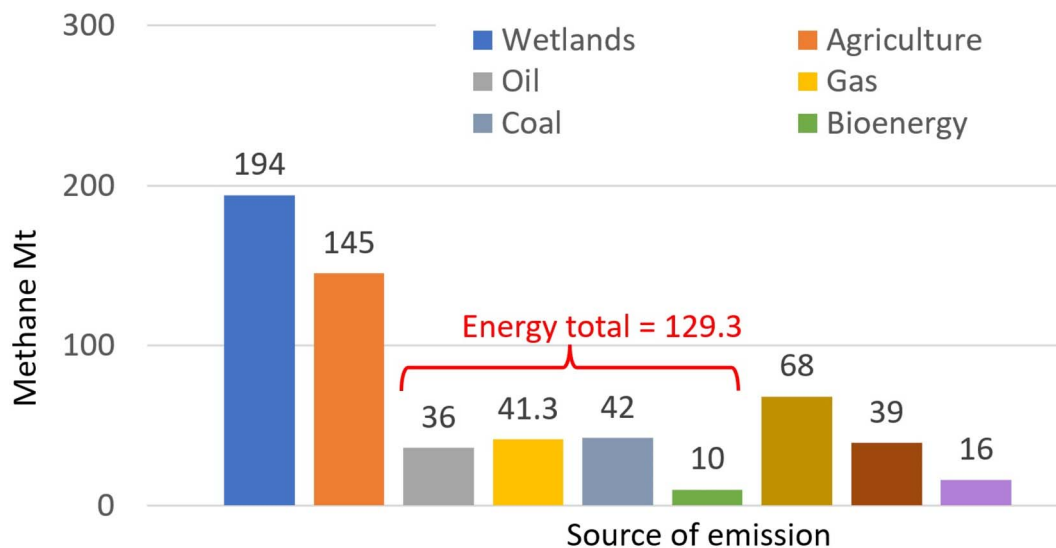


Fig. 3 Global emissions of methane: Mt in 2020 by source. (Drawn from data published in ref. 107; License: CC BY 4.0.)

parts per billion in 2018, 22% above levels around the year 1750.¹¹⁸ N₂O in the exhausts from internal combustion engines is removed using catalytic converters.¹¹⁹ Some attention has been given to development of methods (e.g., use of metal oxides on activated carbon) for the removal of N₂O from industrial exhausts, such as in the adipic acid production process (for nylon production) using HNO₃ as oxidizing agent, where the N₂O content in tail gas is as high as 38%.¹²⁰

Shifts in the use of land can release GHGs, particularly CO₂, CH₄ and N₂O, including through deforestation, changes to soil conditions in agriculture and commercial forestry, and conversions to other land uses such as mining and industry. Chemistry contributions are needed across all these areas, including for new knowledge and innovations to promote soil retention of carbon, prevent conversion of nitrogen fertilizers to N₂O and capture/recapture GHGs.^{121–123}

3. Carbon capture: from sinks to renewable/reusable carbon sources

The net zero goal requires that global emissions of GHGs are brought as close to zero as possible by 2050. However, the complementary approach of removing or re-absorbing GHGs present in the atmosphere must also play a key role. Sequestration will be vital both in helping bring global efforts on track to limit global warming to 1.5 °C by 2050 and helping sustain the net zero balance beyond this point, given that there will likely remain significant GHG emissions continuing from indispensable sectors such as agriculture.

Three natural processes contribute to the major planetary mechanisms by which CO₂ is absorbed from the atmosphere: dissolution in seawater, uptake by plants and especially trees, and retention in soils. However, during the last couple of centuries these mechanisms have become increasingly unable to sustain a steady atmospheric CO₂ level within the planetary carbon cycle. Deforestation and changes in land use have led to simultaneous

release of CO₂ from long-term storage and reduction in the size of these reservoirs, while global warming has itself accelerated the pace of CO₂ release (e.g., from permafrost soil) and has reduced the CO₂-absorptive capacity of oceans as they have warmed.

3.1 Sequestration

Anthropogenic processes for absorption of atmospheric CO₂ are becoming critically important in efforts to rebalance the carbon cycle. While reforestation and improved approaches to land use may play a role, it is also clear that S&T solutions with a core contribution by chemistry are vital.¹²⁴ According to a McKinsey report,¹²⁵ achieving CO₂ removals, or 'negative emissions', will take significant investment to build markets and infrastructure to the scale required for net zero balance. The report highlights three technologies that are currently ready to go to the necessary scale of removing gigatons of carbon: (1) 'natural' climate solutions, in which plants are grown to capture CO₂ and the plant materials are subsequently transformed into long-term carbon storage forms; (2) bioenergy carbon capture and storage, in which CO₂ generated by combustion of bio-materials is captured by technology installed at the site of production;¹²⁶ and (3) direct air capture (DAC) and storage, in which CO₂ is taken out of the atmosphere and stored permanently, safely and securely, deep underground.¹²⁷

A key input needed from chemistry is the development of affordable, efficient, and sustainable processes to capture CO₂ either at the point of production or from the atmosphere. Once sequestered, the CO₂ may be pumped directly into geological storage sites deep underground, or mineralised (e.g., as solid carbonates) for underground storage.¹²⁸ A range of physical, chemical, electrochemical and biochemical methods is being explored.^{129–131} While CO₂ capture from concentrated streams in flue gases is itself challenging in terms of efficiency and cost,¹³² an additional challenge with DAC approaches is that the ultra-low atmospheric CO₂ concentration [c. 400 ppm by volume] is considered a major obstacle due to low CO₂ sorption capacities.



A hybrid sorbent containing polyamine-Cu(II) complex, Polyam-N-Cu²⁺, has now been shown to exhibit two to three times greater CO₂ capture capacity than most of the DAC sorbents reported to date, at the ultra-dilute concentration of CO₂ in the atmosphere. The sorbent is mechanically strong, chemically stable, and amenable to efficient regeneration by salt solutions at an ambient temperature, including seawater. This hybrid sorbent can be regenerated with waste heat or thermal energy at <90 °C, and the captured CO₂, sequestered as NaHCO₃, can be recovered and stored.¹³³

It is estimated that the oceans are a sink for around 25% of the atmospheric CO₂ emitted by human activities each year.¹³⁴ Concepts for increasing ocean-based carbon removal have been proposed, but most are at early stages of development. Among approaches under exploration are the pumping of ocean acidity from the surface to deep waters,¹³⁵ and ocean 'fertilization' in which iron compounds would be dispersed to stimulate massive blooms of phytoplankton and other photosynthetic algae, which would soak up carbon and sequester it when the algae die and sink.¹³⁶ Ocean 'liming' with calcium oxide or hydroxide is also being investigated.¹³⁷ Such options illustrate the importance of taking a comprehensive systems approach to the evaluation of possible solutions. For example, the production of lime is currently based on thermal decomposition of calcium carbonate, liberating CO₂ (see discussion of concrete in Section 2.1) and in the absence of alternative large-scale, low-carbon manufacturing processes, its use in ocean liming would not lead to a net reduction in atmospheric CO₂.

3.2 CO₂ reuse

The very large quantities of CO₂ generated by anthropogenic processes represent a chemical resource which can be used for diverse processes^{138–141} which, however, should not lead to emission into the atmosphere. Examples of CO₂ utilization include its use to make a wide variety of chemicals and plastics, fuel production, concrete enrichment and power generation.^{142,143} A review of ten pathways for the utilization of CO₂, each of which was potentially scalable to over 0.5 gigatonnes of carbon dioxide utilization annually, suggested that the most promising are pathways that involve construction materials, which can both utilize and remove CO₂.¹⁴⁴

4. Broadening criteria for sustainability: systems perspectives on chemistry for net zero

Historically, large-scale transformations of matter and generation of useful products and processes did not generally require consideration of environmental impacts that were distant in time and space. However, the dramatically increasing extent and pace of transformations of matter have now forced a rethink, a reconceptualization of the parameters to be considered of vital importance to the sustainability of people and planet when the development of any new process or product is being contemplated. A clear signal that this can no longer be delayed came when it was assessed that the

production of anthropogenic mass (the global total dry mass of material contained in inanimate solid objects made by humanity) had been doubling every 20 years since 1900 and had reached 30 Gt per year and totalled c. 1.1 trillion tonnes present on the planet in 2020.¹⁴⁵ For the first time, in 2020 this accumulated amount equalled the dry weight of total biomass on Earth and, on current trends, total anthropogenic mass will be triple the dry weight of biomass by 2040.

With business-as-usual no longer an option,^{146,147} radical changes are very urgently needed in how humanity sources, transforms, uses and disposes of the material resources available. The required shifts in approach cut across many spheres, including economics, policy, science, social behaviour and ways of thinking and are highly relevant to chemistry as well to all other sectors.

Particularly important dimensions of the reconceptualization of the transformation of matter at large scale include the adoption of systems perspectives and the combination of these with circular economy and planetary boundary frameworks. For chemistry, these need to be complemented by a reorientation that prioritises the leading role it can play in the stewardship of the Earth's material resources. The interplay among these in relation to production, consumption and disposal is illustrated in Fig. 4.

Chemists are used to regarding the reaction vessel and its connected devices, whether at micro-scale in the laboratory or production scale in the chemical plant, as a reaction system. Adding the factor of sustainability through the goal of net zero confers the need to consider the sourcing, extraction, refining, transportation and final preparation of every reagent, catalyst, solvent and piece of equipment, as well as the chain of energy production, transmission and consumption, used in transformations; and the fate of every product, co- and by-product, solvent and waste material, whether these are generated in solid, liquid or gas form. Chemists also need to be aware of different kinds of hazards to the environment and life forms in it; and the impacts of the intended use and of other possible uses and the fate of the product. The systems perspective connects the production/consumption/disposal system with the physical/environmental and biological/ecological systems of the planet and with human systems which mediate the context in which materials are made, used and disposed of.

Many of the components needed to construct such a comprehensive multisystem-based understanding are already available. In particular, extending the 'chemistry for sustainability' pyramid presented by Whalen *et al.*,¹⁴⁸ chemistry's contribution to sustainability is seen as being mediated through orientations that prioritise its interactions with Earth and societal systems, using sustainability tools and frameworks (Fig. 5).

While Fig. 4 develops a comprehensive 'systems thinking' picture of actors and factors to be considered, Fig. 5 indicates how the information required to operationalise this approach can be sought, combined and filtered in the overall evaluation. Nevertheless, it is important to emphasise that (1) not all the frameworks (*e.g.* planetary boundaries,¹⁰ human security,¹⁴⁹ resilience¹⁵⁰) and tools are as yet fully developed with regard to their chemistry dimension; (2) not all the data required (*e.g.*, for



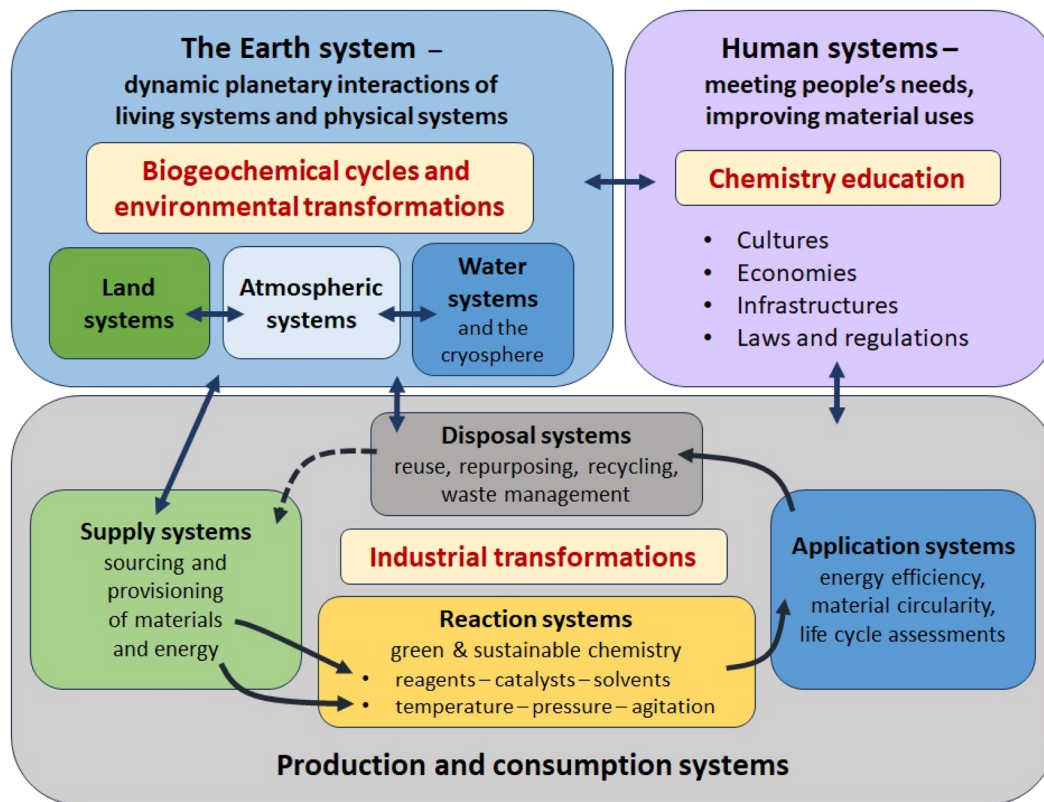


Fig. 4 Production, consumption and disposal in the context of Earth and societal systems.

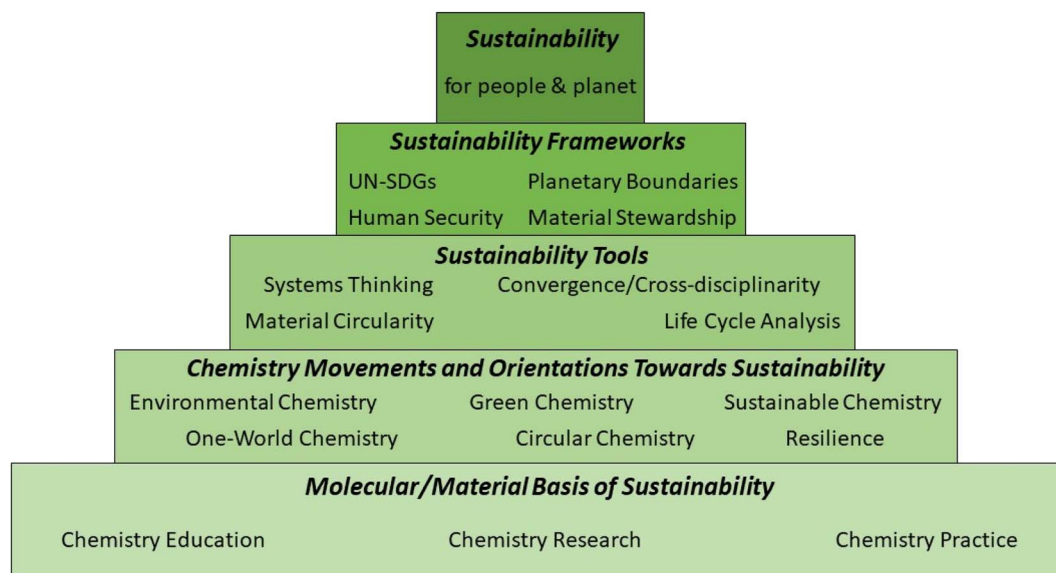


Fig. 5 'Chemistry for sustainability' pyramid.

the application of material circularity^{151–153} and life cycle analysis and for the definition of planetary boundaries for all materials produced at large scale⁹) is available as yet; and (3) the practical integration of frameworks (e.g., planetary boundaries) with sustainability tools (e.g., material circularity) and orientations (e.g. material stewardship) has yet to be achieved.

Importantly, both Fig. 4 and 5 embody the appreciation that sustainability is an emergent property of the whole system – it is not simply a property of individual components of that system. This insight, which requires a process-based, multi-scale and systemic approach,¹⁵⁴ provides a valuable perspective from which to evaluate partial solutions to sustainability challenges



such as 'net zero', when a breakthrough in one aspect (e.g., development of a new catalyst, process, material or policy) is heralded as a 'green' solution, in isolation from a comprehensive analysis of the total material and energy balances. Examples that illustrate this in relation to net zero include:

- Much emphasis is placed on the switch from fossil fuels to renewable forms of energy, but it is extremely important to conduct comprehensive assessments of the matter and energy inputs necessary to greatly expand the scale of production of the hardware necessary to achieve the clean energy transition. For example, in the most ambitious climate action scenarios, nearly 2 billion metric tons of steel and 1.3 billion metric tons of cement could be needed for energy infrastructure between now and 2050. Large increases will also be needed in production of rare-earth metals like dysprosium and neodymium used in wind turbine magnets and of high-grade polycrystalline silicon used in solar energy devices. One analysis of 17 of the key materials needed from 2020 to 2050 for the infrastructure to generate low-emissions electricity¹⁵⁵ estimated that, while material demands increase, cumulatively they do not exceed the geological reserves. The substantial cumulative CO₂ emissions due to the large quantities of materials needing to be mobilized during progressive power sector decarbonization would consume only a minor share of global carbon budgets (1–9%), with technological choices strongly influencing the spectrum of future material requirements.

- A major net zero challenge concerns the need for energy carriers that can be used in remote and mobile settings, where fuel/power lines are not practical. The main approaches (see Section 2.1) involve either use of batteries to store and deliver electricity on demand or chemical carriers of energy that can be sourced and used sustainably. For the expansion of use of batteries in critical areas like transport, major constraints include the design of better batteries that can store and deliver energy at practical levels of power and duration, speed of recharging, the sourcing and delivery of sustainable energy for recharging, and the sustainable and resilient sourcing and recycling of battery components.¹⁵⁶

- Exploration of chemical carriers of energy to provide viable alternatives to fossil fuels, particularly for transport requirements, include intensive investigations of the potentials for use of H₂ and NH₃. (a) Hydrogen-based approaches to net zero and sustainable energy have been widely advocated, but since more than 95% of the hydrogen currently produced is derived from fossil fuels, primarily through steam reforming of methane, alternative production methods that use other materials and renewable energy sources are essential.¹⁵⁷ Options, including splitting water by heterogeneous catalytic, electrochemical and photochemical methods, need to be evaluated comprehensively for overall sustainability, including in relation to the sourcing of materials and input energies for splitting processes and the fates and potentials for recycling of the hardware employed as well as of the primary products of the splitting reaction itself.¹⁵⁸ (b) Ammonia is also being intensively investigated as a potential energy carrier, especially for transport settings. It can be used directly as a fuel in internal combustion engines, or indirectly as a carrier of hydrogen in fuel cells. However, the synthesis of

ammonia employed for the last century (Haber–Bosch process) consumes large amounts of hydrogen and energy, both of which are currently derived mainly from fossil fuel sources. Chemistry's major role in developing alternative processes for NH₃ synthesis must be guided by the totality of sustainability considerations outlined above.¹³⁴

5. Stewardship of planetary resources – an essential role for chemistry

The idea of human responsibility to tend the Earth can be found in human cultures throughout history.¹⁵⁹ Planetary stewardship in general and especially in an environmental context has been recognized as essential in the face of Anthropocene challenges.^{160,161} It has been mentioned in relation to specific resources including fossil fuels, phosphorus, metals, and other materials derived from Earth's geological deposits,³⁸ as well as in the context of Earth system processes such as atmospheric and oceanic chemistry and control of air pollution.¹⁶² From a commercial perspective, it has been emphasised that product stewardship and sustainable chemistry principles apply across cradle-to-grave product cycles.¹⁶³ However, only recently have there been preliminary signposts to the overall central role of chemistry in the comprehensive stewardship of the planet's chemical resources,¹⁰ recognizing that the planet's elemental resources are finite and, in a growing number of cases, in short supply,^{164,165} but the implications for chemistry have not yet been elaborated in detail.

The positioning of material stewardship of planetary resource among the overarching frameworks in the highest levels of the sustainability pyramid (Fig. 5) projects the strong contribution it can make to guiding chemistry education, research and practice in their orientations, attention to movements, and adoption of tools aiming at sustainability. In relation to net zero, it importantly expands the scope of attention beyond a focus on keeping materials, products, and components in the market for as long as possible through repair, reuse, re-manufacture, and recycling (technical material circularity). It also requires attention to the scale of global operation (respecting planetary boundaries) and accounting for total balances of material flows (life-cycle analysis) and energy characteristics and the intersections of all these factors with Earth and societal systems (systems thinking and convergence). As well as attending to the implications of physical scale in the transformations of matter, material stewardship incorporates temporal and locational perspectives on the sourcing and redistribution of elements and compounds, with implications for resilience of supplies and the impact of material dispersal on the environment. Net zero must be aligned with broader sustainable development objectives, which implies an equitable net-zero transition, socio-ecological sustainability and the pursuit of broad economic opportunities.

The overarching ambition of material stewardship of planetary resources not only encompasses chemistry's role in achieving net zero, but frames it within a broader landscape of sustainability goals. Among other issues, critiques^{27,166,167} of net



zero argue that, as well as becoming over-focused on aspirational and politically negotiated numerical targets, it can become a distraction from a wider and more comprehensive approach to sustainability, with a result that other critical areas are neglected or even made worse. Material stewardship requires that chemists take a planet-wide view of the stocks and flows of all material resources in the context that sustainability is a property of the whole system.

An example of where this is important concerns the fate of CO₂ captured as it is emitted or sequestered from the atmosphere. Net zero necessitates that this CO₂ is held long-term in forms from which it is not released to the atmosphere, and much attention has been focused on mineralisation and storage deep under land or oceans. However, principles of material circularity and stewardship point to the very large quantities of CO₂ involved being viewed as a chemical resource to be managed. This requires that, in reorienting the carbon reuse economy that has been developing CO₂ as a feedstock for fuels, chemicals, materials and food,^{168,169} two critical criteria are met: (1) ensuring that during transformations to products and their use and recycling, the lock on preventing CO₂ release is maintained; and (2) that the transformations and uses are fully analysed using the best knowledge and methods available to ensure that the processes and uses are sustainable from energy, matter and environment perspectives. One area where synergies can be exploited in elaborating the material circularity/stewardship approach is the case of plastics. The damage caused by environmentally persistent plastic wastes has reached such levels of concern that negotiations are now in progress for a UN treaty to address the global plastics crisis.¹⁷⁰ Conversion of CO₂ into recyclable plastics¹⁷¹ *via* sustainable chemistry/biochemistry and environmentally benign processes offers a convergent way to deal with two major challenges.

6. Conclusion and next steps

The challenge of achieving net zero as a means of driving effective action to limit climate change, and more broadly the challenge of sustainability for people and planet, infiltrate many of the current polycrises. They involve a confluence of factors within the nexus of science, society and policy. Solutions that are purely technological in nature, that only focus on behaviour change or that depend exclusively on setting policies at national and global levels are likely to have limited impact. It is only when all three are able to act in a coordinated manner that decisive shifts take place globally. The strikingly rapid Vienna-Montreal process which ended the use of CFCs that were severely damaging Earth's stratospheric ozone layer (see Section 2.2) demonstrated what is possible when the interests of science, society and policy intersect and result in far-ranging scientific, political, and economic cooperation.⁹⁵ This contrasts with the slow pace of advance on the more broadly threatening issue of climate change.¹⁷² Likewise, the commitment made by countries in 2002, to minimize by 2020 the adverse effects of chemicals and pollutants passing into the environment, was not achieved.¹⁷³

These lessons from history show that chemistry's role as an innovative source of solutions to problems such as net zero is necessary but not sufficient. Innovation in industrial processes is essential, shifting the frame of reference to a more comprehensive, planetary-scale approach to sustainability. It must originate in well-oriented research that is rooted in an educational foundation creating knowledge and skills that enable professional chemists to apply their creative impulses to seeking pathways to solutions in the context of Earth and societal systems. It must be complemented by chemistry's engagement in the societal, policy and diplomacy processes that lead to systems change, which requires action by individuals, professional bodies and industry associations working together. There is need for greater incentives within all these areas at the nexus of science, society and policy, to accelerate action towards net zero with increased urgency. Incentives along the whole of the S&T pathway are required, including investments in research, development and commercialisation, as well as resources to encourage identification, piloting and large-scale implementation of improved practices. The new process mandated¹⁷⁴ by the UN World Environment Assembly and administered through UNEP has established a science-policy panel to contribute further to the sound management of chemicals and waste and to prevent pollution. This represents a major opportunity for the chemistry profession to engage at this critical interface, beginning with participation in the ad hoc open-ended Working Group¹⁷⁵ established to develop the process.

Adopting the mission of planetary stewardship of material resources as a human responsibility is vital to ensure that technically sound and sustainable solutions developed are implemented and that trade-offs do not result in ineffective policies or even make global warming worse – especially in the setting of specific targets where competition between net zero and other sustainability goals may arise.^{27,167,176} The centralization of the stewardship of planetary material resources as a core chemistry mission will require strong leadership from key chemistry bodies, especially those representing the chemistry profession such as the national and international chemistry societies and industry associations.

Author contributions

GM conceived the study. SM wrote the first draft of the manuscript and prepared Fig. 2, 3 and 5. SM SC and AK prepared Fig. 4. All authors reviewed, inputted to and edited the final manuscript. All authors have read and approved the final version of this manuscript for publication.

Conflicts of interest

There are no conflicts to declare.

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