

Forbidden reactions

Chemistry is a messy business. The elements are so diverse that their interactions can be unpredictable and sometimes bizarre. Often, chemists rely on nothing more than intuition to tell them what may or may not be possible.

Sometimes that leads them astray. History is littered with ideas that were derided or dismissed at first, but eventually changed the rules of the game. **Philip Ball** tells five stories of chemistry they said could never happen



IMPOSSIBLE SYMMETRY

The crystal patterns that broke all the rules

Of all people, chemist Linus Pauling should have appreciated boldness in a scientist, even if they turn out to be wrong. After all, the Nobel laureate jumped ahead of the evidence to propose a triple-helix structure for DNA early in 1953, shortly before Francis Crick and James Watson announced the real answer. Yet when in 1984 Israeli chemist Dan Shechtman claimed to have found a “quasicrystalline” form of atomic symmetry in certain solids, Pauling sniped: “There is no such thing as quasicrystals, only quasi-scientists.”

So Shechtman had more cause for

satisfaction than usual as he stepped up to the podium in Stockholm in December last year to receive the 2011 Nobel prize in chemistry. He had been bold – and right.

In the early 1980s, Shechtman was firing beams of electrons at metal alloys at the then National Bureau of Standards in Gaithersburg, Maryland. He analysed the interference patterns formed as the beams reflected off layers of the material, and this allowed him to determine the packing of the atoms inside.

A pattern of sharply defined interference spots is a sign of regular crystalline order. But among the alloys Shechtman studied, a beautifully sharp pattern from a blend of aluminium and manganese made no sense. It suggested a crystal with fivefold symmetry, like that of a pentagon. Crystallographic rules dictate, however, that atoms can't be packed into a regular, repeating arrangement with this sort of symmetry, just as pentagons can't tile a floor in a periodic way with no gaps.

Pauling was not the only fierce critic. When Shechtman persisted with his claim, he was asked to leave the research group, and had great difficulty getting the result published.

In fact, the answer to the riddle was already out there. In the 1970s, mathematician Roger Penrose had discovered that two rhombus-shaped tiles could cover a flat plane without leaving gaps and without the pattern ever repeating. In 1981, crystallographer Alan Mackay at Birkbeck College in London found that atoms sitting at every corner of such a Penrose tiling would produce a diffraction pattern with fivefold symmetry, even though the arrangement was not perfectly periodic. The atomic packing in Shechtman's alloy was analogous to a three-dimensional Penrose tiling. It never repeated exactly, and so did not make a perfect crystal; it was a “quasicrystal”.

Since then, many other quasicrystalline alloys have been found. Similar structures exist in polymers and assemblies of soap-like molecules called micelles, and quasicrystalline order has been seen in a fragment of meteorite recovered from Siberia. In 2010, a team led by Valeria Molinero at the University of Utah in Salt Lake City even suggested that water, when confined in very narrow slits, can freeze into quasicrystalline ice (*Journal of Chemical Physics*, vol 133, p 154516).

CHEMICAL PENDULUM

Reactions go one way – and not back and forth

For Boris Belousov, vindication came too late. When the Soviet biochemist was awarded his country's prestigious Lenin prize in 1980, he had been dead for 10 years.

At least he lived long enough to see the scorn heaped on his work give way to grudging acceptance. In the 1950s, he had devised a cocktail of chemical ingredients that provided a simple analogue of glycolysis, the process by which enzymes break down sugars. The mixture changed from colourless to yellow as the reaction proceeded.

But then something astonishing happened: the cocktail went colourless again. Then yellow. Then colourless. It began to oscillate repeatedly between these two states.

This was unacceptable. A reaction that went spontaneously in both directions seemed to go against one of science's most cherished dictums, the second law of thermodynamics. This states that all change in the universe is accompanied by an increase in entropy – put crudely, it must leave things less ordered than they were before. Entropy cannot possibly increase in both directions in a chemical reaction. Belousov was proposing something that only cranks would suggest.

In fact, Belousov was not the first to observe the effect. In 1921, American chemist William Bray had reported similar oscillations when hydrogen peroxide reacted with iodate ions. No one had believed him, either. As for Belousov, he couldn't get his findings published. In the end, he appended them to a Soviet conference paper on a different topic, where they languished in obscurity.

Or at least they did until a compatriot of Belousov's, Anatoly Zhabotinsky, modified the original reaction mixture in the 1960s to make it change colour between red and blue – too dramatic a change to ignore. As news of the "Belousov-Zhabotinsky" (BZ) reaction and other similar oscillating reactions percolated through to the west from 1967 onwards, an explanation began to crystallise. The oscillations come about because the initial reaction generates intermediate compounds that are autocatalytic, speeding up their own production. At the same time, some of the resulting compounds kick-start a second autocatalytic cycle that restores the ingredients of the first. The overall reaction thus flip-flops between the two cycles.

Crucially, these oscillations don't last forever: left to their own devices, they slowly die away and the mixture settles into an unchanging state. They are an example of a transitory "non-equilibrium" phenomenon. Thermodynamics only deals with equilibrium states, not what happens en route to them, and so the second law is not threatened.

If the BZ reaction is constantly fed fresh reagents and the final products are removed, the oscillations can be sustained indefinitely. Such oscillations happen in industrially important reactions using metal catalysts and even in real glycolysis. In an unstirred mixture, they can spread as chemical waves, giving rise to complex patterns; related biochemical reactions are thought to create pigmentation markings in animals from wildcats to ladybirds. The waves are also

analogues of the electrical pulses that pass through heart tissue. Their dynamics have been widely studied to get a better understanding of the factors that might induce irregular heartbeats.

Andrew Adamatsky at the University of the West of England in Bristol, UK, is even using BZ-based chemical wave interactions to create logic gates. He and collaborators in Germany and Poland are aiming to create "wet" chemical circuits that will crudely mimic the behaviour of neurons, including their capacity for self-repair.

"Entropy could not possibly increase in both directions in a chemical reaction – that was something only cranks would propose"

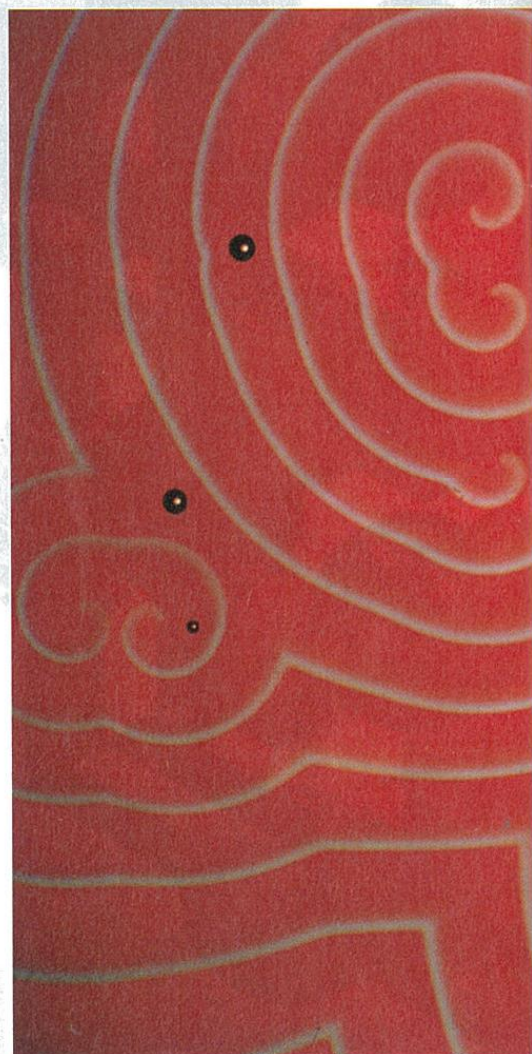
FLIRTING WITH THE LAW

In its choice of language, chemistry sometimes flirts with its own law-breaking inclinations.

Take "symmetry-forbidden" reactions. These break rules that chemists Roald Hoffmann and Robert Woodward laid down in 1965, based on the mathematical symmetry of electron orbitals as they are rearranged or recombined by light or heat. Or "spin-forbidden" reactions, which involve the flipping of the quantum-mechanical "spin" of the electron configurations in the reactants.

Neither of these types of reactions is in fact impossible – they just proceed at slower rates than "allowed" reactions. According to Hoffmann, the choice of word was deliberate: on Woodward's insistence they asserted in their 1965 paper that there were no exceptions to their rules to spur others on to finding them.

Two-way reactions spread through a mixture as chemical waves



SCAPE TUNNEL

“you can't go over the barrier, use quantum rules to smash through it

's very cold in space. So the origin of some of the rather complex molecules found there, such as polymers, is a puzzle.

Most chemical reactions proceed through the formation of high-energy intermediate molecules, which then rearrange themselves into lower-energy products. Energy, usually in the form of heat, is needed to get the reactants over this barrier. According to standard “kinetic” theory, almost all molecules meeting each other in the frigid gas clouds that pepper the interstellar void would lack the energy to react.

In the 1970s, a Soviet chemist named Vitali Goldanski challenged that dogma. His experiments showed that certain molecules involved in polymerisation reactions would keep on reacting even when chilled to 4 kelvin, only slightly warmer than the coldest parts of space. Formaldehyde, a common component of molecular clouds, could come together in polymer chains several hundred molecules long with a little help from gamma rays or high-energy

electrons – the sort of things often found zipping around in space.

How was this possible? Goldanski argued that the conventional picture was missing a crucial element. Quantum rules dictate that particles such as the atoms and electrons involved in chemical reactions can get across energy barriers even if they don't appear to have enough energy using the process known as tunnelling. Goldanski suggested that in the frigid environment of space, tunnelling keeps things going – perhaps even allowing the molecular building blocks of life to assemble on interstellar dust grains from simple ingredients such as hydrogen cyanide, ammonia and water.

Goldanski's work was a curiosity at the time, but the principle of the quantum assist is now well established. Some biological reactions catalysed by enzymes are more efficient than kinetic theory predicts because they involve the movement of hydrogen ions – lone protons that are particularly prone to quantum tunnelling.

Yet we can still be taken by surprise. In June last year, Wesley Allen of the University of Georgia in Athens and his co-workers trapped a highly reactive free-radical molecule called methylhydroxycarbene in an inert matrix of solid argon at 11 kelvin. It has unpaired electrons that predispose it to react fast – although supposedly not at such low temperatures.

Not only did the methylhydroxycarbene react, though, it also formed the wrong product. The molecule can rearrange its atoms to form either acetaldehyde or vinyl alcohol, but the energy barrier to making vinyl alcohol is lower, so more of this product would be expected. Instead, the reaction delivered a large amount of acetaldehyde (*Science*, vol 332, p 1300).

Allen proposes that although the barrier to making acetaldehyde is higher, it is also narrower, making it easier to tunnel through. That tunnelling could happen through such high barriers “was quite a shock to most chemists”, he says.

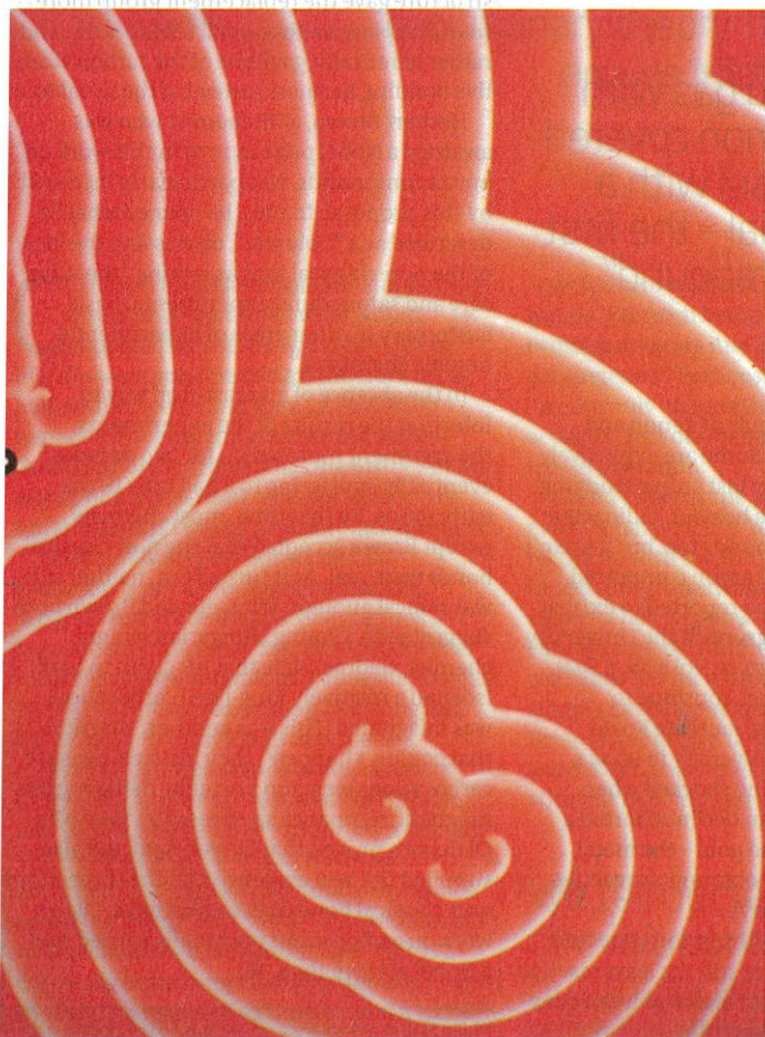
FORCED INTO ACTION

Noble gases don't react, except when they do

If there is one half-remembered chemical fact that most of us carry from our schooldays, it is that the inert or “noble” gases do not react.

The early history of these elements, ranged in the right-hand column of the periodic table, provided ample support for that view. Just after the noble gas argon was discovered in 1894, the French chemist Henri Moissan mixed it with fluorine, the viciously reactive element that he had isolated in 1886, and sent sparks through the mixture for good measure. Result: nothing. In 1924, the Austrian Friedrich Paneth pronounced the consensus. “The unreactivity of the noble gas elements belongs to the surest of all experimental results,” he wrote. The theory of chemical bonding explained why. The noble gases have full outer shells of electrons, and so cannot share other atoms' electrons to form bonds.

The influential chemist Linus Pauling (see “Impossible symmetry”, page 31) was one of the chief architects of that theory, yet he didn't give up on the noble gases immediately. In the 1930s, he managed to get hold of a rare sample of xenon and persuaded his colleague Don Yost at the California Institute of Technology in Pasadena to try to get it to react with fluorine. After much cooking and sparking, Yost succeeded only in corroding the walls of



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MÉNAGE À TROIS

There's room in this bond for three

A chemical bond is a union between two atoms. The idea that, on occasions, a third atom might hop into the bed was so offensive when it was first proposed that it provoked a decades-long flame war.

It all started in the 1940s, with attempts to explain certain reactions of organic molecules that involved the swapping of negatively charged dangling groups. If one such group fell off, that left the rest of the molecule as a “carbocation”, an ion containing a positively charged carbon atom. By rights the replacement group should have attached itself at the same place, at the positively charged atom. But it didn't always.

Some chemists, in particular Sam Winstein of the University of California, Los Angeles, championed a startling explanation: that the positive charge was smeared between a triangular array of three carbon atoms in the carbocation. This “non-classical” bonding structure gave the replacement group more than one place to dock – and temporarily, and rather heretically, gave one of the carbon atoms five bonding partners instead of the usual four.

Herbert Brown, a US chemist who was awarded a Nobel prize in 1979 for his work on boron compounds, was particularly incensed by this proposal. In 1961, he opened what he described as a “holy war”, dismissing the idea of the non-classical ions as lacking “the same care and same sound experimental basis ... customary in other areas of experimental organic chemistry”.

In the absence of any cast-iron way to interpret the results of the experiments, the argument motored on for two decades, eventually sputtering to a halt only in the early 1980s. By that time, most chemists except Brown accepted that the non-classical bonds were real. As it turned out, neither side was radical enough: Winstein and Brown both suggested to a young Hungarian emigré chemist, George Olah, that his claim to have isolated a relatively long-lived carbocation was misguided. This was another “reaction that couldn't happen”, they insisted, because carbocations were too unstable. Using nuclear magnetic resonance spectroscopy, however, Olah both proved that he was right and also supplied the best evidence that the three-atom non-classical bond does indeed exist. Olah's work on carbocations eventually earned him a Nobel prize in 1994. ■

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noble-gas compound.

Many other compounds of xenon and then krypton followed. Some are explosively unstable: Bartlett nearly lost an eye studying xenon dioxide. Radon, a heavier, radioactive noble gas, forms compounds too, but it wasn't until 2000 that the first argon compound, argon fluorohydride, was reported to exist at low temperatures by a group at the University of Helsinki, Finland (*Nature*, vol 406, p 874). Even now, the noble gases continue to produce surprises. Nobel laureate Roald Hoffmann of Cornell University in Ithaca, New York, admits to being shocked when, also in 2000, chemists in Berlin reported a compound of xenon and gold – the metal gold is supposed to be noble and unreactive too (*Science*, vol 290, p 117).

So don't believe everything you were told at school. Noble gases are still the least reactive elements out there; but it seems you can coax elements to do almost anything.

his supposedly inert quartz flasks.

After that, it was a brave or foolish soul who still tried to make noble-gas compounds. British chemist Neil Bartlett, working at the University of British Columbia in Vancouver, Canada, was not trying to defy conventional wisdom, he was just following common logic.

In 1961, he discovered that the compound platinum hexafluoride (PtF_6), first made three years earlier by US chemists, was an eye-wateringly powerful oxidant. Oxidation, the process of removing electrons from a chemical element or compound, bears oxygen's name because oxygen has an almost unparalleled ability to perform the deed. But Bartlett found that PtF_6 could even oxidise oxygen, ripping away its electrons to create a positively charged ion.

Early the next year, Bartlett was preparing a lecture and happened to glance at a textbook graph of “ionisation potentials”. These numbers quantify the amount of energy required to remove an electron from various substances. He noticed that xenon's ionisation potential was almost exactly the same as oxygen's. If PtF_6 could oxidise oxygen, might it oxidise xenon, too?

Mixing red gaseous PtF_6 and colourless xenon supplied the answer. The glass vessel was immediately covered with a yellow material. Bartlett found it to have the formula XePtF_6 – xenon hexafluoroplatinate, the first