

# Gregarious gallium

Trick cutlery and mobile phones have one peculiar element in common, as **Marshall Brennan** explains.

The periodic table is arguably the most recognizable tool in chemistry. In 1869, Dmitri Mendeleev arranged the elements known at the time from lightest to heaviest, starting a new row whenever the properties of the elements appeared to resemble those in the row above. Mendeleev was by no means the first to try and organize the elements like this, but perhaps the reason his table is the one that hangs in classrooms and laboratories worldwide comes from the fact that he initially left gaps in it to be filled later. Wherever he reasoned that there should be an as-yet undiscovered element that better emulated the members of a given group than those known, he left placeholders named after congeners of the closest element in their group — ekaboron, ekaaluminium, ekamanganese and ekasilicon — and predicted some of their properties and characteristics based on their position in the table.

In 1875, the French chemist Paul-Émile Lecoq de Boisbaudran detected the first of these hypothetical elements in a sample of the mineral sphalerite. Spectroscopic examination revealed a pair of violet lines, which denoted the signature of ekaaluminium. De Boisbaudran collected the first pure sample of the element by electrolysis later that year, naming it 'gallium' after his home country of France. He went on to describe the element and its properties, and so similar were most of the experimental findings to the predicted properties of ekaaluminium that Mendeleev felt compelled to write to de Boisbaudran to suggest that his measured density of  $4.5 \text{ g ml}^{-1}$  for the metal was incorrect (Mendeleev had predicted a density of  $6 \text{ g ml}^{-1}$ ). Indeed, the value was subsequently corrected to  $5.9 \text{ g ml}^{-1}$ , in stunning agreement with Mendeleev's prediction, and vindicating his placement of the eka- elements in his periodic table.

Gallium is a soft, silvery metal with modest conductivity; its properties are intermediate between those of aluminium and indium, as expected given its place in the fourth period<sup>1</sup>. Due to poorer shielding from its  $3d$  shell compared with aluminium's filled  $2p$  shell,



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gallium's ionization energies are greater than those of aluminium, and, perhaps more importantly, its atomic radius is much smaller than might be expected — at 130 pm, it is nearly identical in size to aluminium. This unusually small atomic radius is one factor that gives rise to gallium's most familiar property: at room temperature, gallium is a soft metal, but a mere  $9^\circ \text{C}$  higher — the equivalent of a warm day in Illinois, or a few degrees below body temperature — the metal melts. This property was the subject of a classic prank among nineteenth century chemists, where a spoon would be fashioned from gallium and given to an unsuspecting guest with his or her tea (pictured). Upon stirring the tea, the spoon rapidly melts, much to the victim's surprise. More practically, its low melting point means that gallium exhibits metallic properties in the liquid phase across a useful and accessible temperature range.

Perhaps the most important characteristic of gallium is the ease with which it can alloy with various metals, as its small radius allows it to diffuse relatively easily into the lattice of many metals. Gallium's low melting point is often conferred on the final alloy, which makes the resulting material more easily workable, more stable and, as a result, more cost-effective. Most applications for gallium are in the semiconductor industry. GaAs — far and away gallium's most

common alloy — is used in high-speed logic chips and preamplifiers in mobile phones, while AlGaAs and InGaAs are the light-emitting materials in the 405 nm laser diodes for Blu-ray disc players.

In addition to enabling technological advances, gallium chemistry has started tackling fundamental problems in fuel and energy science. Early work showed that gallium-doped zeolites effectively catalyse the ring opening and scission of methylcyclohexane into small alkanes<sup>2</sup> — used to recycle the pyrolysis products of gasoline. Gallium zeolites can also aromatize *n*-decane<sup>3</sup> and emerging work indicates that nanowires of GaN can even catalyse the production of benzene from methane<sup>4</sup>. Cleaving a C–H bond in methane is no small feat, and these reactions are important steps to convert relatively unreactive methane deposits and unwanted byproducts of gasoline production into useful petrochemicals, which has important implications for fuel storage and fine chemical synthesis.

Gallium itself holds few records on the periodic table, with middle-of-the-road properties including its melting point and density. It is likely to be these characteristics that allow it to be so fundamentally important in the semiconductor industry, where its cohesion with other elements and phase transition properties are highly valued. From its role in confirming early chemical theories to the most cutting-edge technologies, gallium has had a profound impact on all of chemistry, and perhaps its importance will only increase as further applications are explored. □

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