

## What makes a metal?

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In the age of the internet, the periodic table has taken on a life of its own. Periodic tables of everything from meat<sup>1</sup> to the characters of the Lord of the Rings<sup>2</sup> have been constructed, though they rarely serve to demonstrate anything more than their creators' lack of understanding of the concept of periodicity. The powerful connections between elements provided by their electronic shell structure is rarely better demonstrated than by the periodic table in its usual form; some exceptions exist, including the recent construction of a map of the elements modelled on the London Underground.<sup>3</sup> This manages to include the links between properties such as nuclear stability and phase under standard conditions, albeit it with the loss of the left-right ordering of the periodic groups.

So what exactly makes the periodic table in its usual form so powerful?

A good place to start is with the ability to make predictions about the behaviour of elements based on the chemical behaviour of their congeners. John Newlands and Lothar Meyer had contributed to the description of periodicity before Dmitri Mendeleev assembled the modern version; the attribution of the discovery to Mendeleev is in large part supported because he had the audacity to make predictions based on his table. No known element could be made to fit in the space after zinc, or between aluminium and indium in group 3: this observation was enough for Mendeleev to suggest the existence of gallium, though it was only given that name later by its experimental discoverer, Paul Emile Lecoq de Boisbaudran.<sup>4</sup>

Fig. 1 presents the elements of the periodic table coloured according to their date of discovery. It is clear that most activity in this respect occurred in the 19<sup>th</sup> century, which should be no surprise. Less obvious to many chemists, perhaps, is the extent of development that occurred in the 20<sup>th</sup> and into the 21<sup>st</sup> century. But with respect to the periodicity of the elements, there is little to remark; the probability of an element having been known before the introduction of modern chemical science relates primarily to the abundance of the element on earth, and its ability to occur in a solid elemental form under standard conditions of temperature and pressure. The coinage metals present an exception, as demonstrated by their ability to appear in native metallic form, such as the familiar nuggets of gold. This is clearly related to their chemical properties; in particular, their relative resistance to oxidation. But the chemistry is certainly not the whole story.

More commonly, we colour in elements according to their group in the periodic table, as shown in Fig. 2. The chemical groups are defined by a particular number and type of valence electrons – one *s*-electron in group one, five *p*-electrons in group 17. However, for convenience,

we group the elements not only vertically but also horizontally – the transition metals, the lanthanides and the actinides all have more in common with each other than with the left or right hand sides of the periodic table, which it makes sense to acknowledge. However, in general, their chemical behavior still varies from one column to the next.

There are a few regions of the periodic table where the group that an element belongs to is not the primary predictor of its behaviour; in particular, the left half of the *p*-block, where the elements change from metallic to non-metallic both as a function of electron configuration and mass. An excellent example is gallium, which has the same crystal structure as the solid halogens, composed of pairs of atoms, but retains a metallic electronic structure.<sup>5</sup> Referred to as a 'molecular metal', the relationship between the curious structure of gallium and its low melting temperature is an area of current research interest.<sup>6,7</sup> A few other examples are notable: despite common usage, zinc and cadmium do not meet the criterion for belonging to the transition metals, which are defined as those elements which use their *d*-electrons in chemical reactions and bonds. Or in the IUPAC definition "an element whose atom has a partially filled *d* sub-shell, or which can give rise to cations with an incomplete *d* sub-shell".<sup>8</sup>

However, mercury has been shown to exist in oxidation state +4, and therefore may be referred to as a transition metal.<sup>9</sup> The reason for this deviation from periodicity is the influence of relativity on the inner electrons of a heavy atom such as mercury: this increases the binding of *s*-electrons which have a high probability of being near the nucleus, and deshields the *d*-electrons which consequently become more able to participate in chemical reactions.

The presence of the actinides and lanthanides at the bottom of the periodic table seems to imply that we treat them differently. This is not quite true: it is a matter of simple convenience to leave them outside of the main block of the table, to avoid the elongated form of the table shown in Fig. 3.

On the other hand, the chemistry of the lanthanides and actinides is more consistent within each row than if considered by column: this is not a bad reason to treat these *f*-elements outside of the block of 18 groups.

In a very real sense, the periodic table represents simply the ordering of the elements imposed by the Pauli exclusion principle: that each element with an additional electron must occupy the next rung on the ladder – or box in the periodic table.

Fig. 4 presents a slightly different version of the periodic table, focused on a single property: the lattice structure.

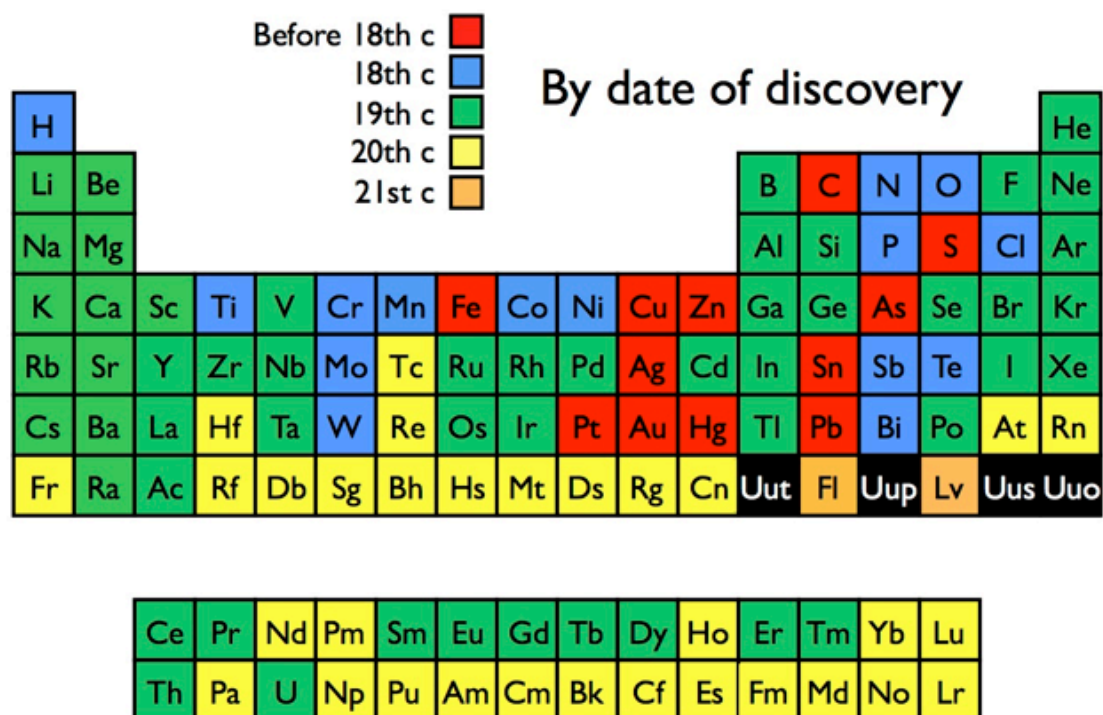


Fig. 1. The date of discovery of the elements

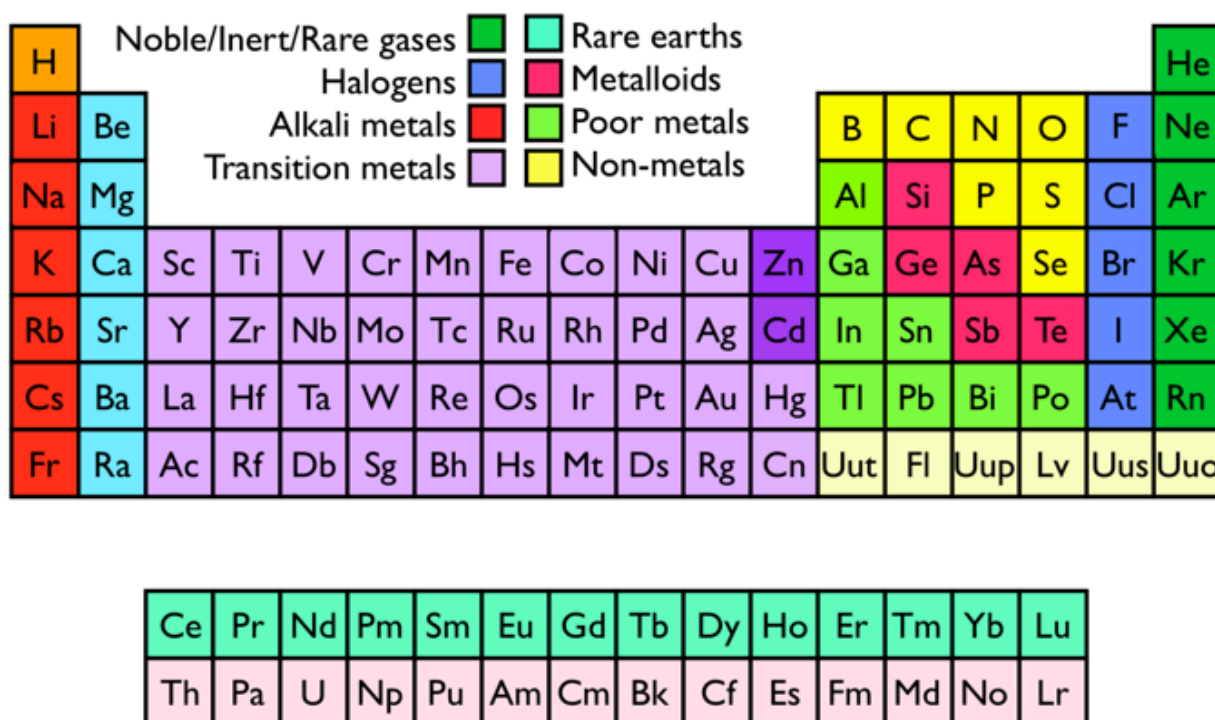


Fig. 2. The groups of the elements

Restricted to the metallic elements, due to the significantly more complex structures adopted by the non-metals, there is nonetheless significant variation in structure.

There is certainly some periodicity in the structures of the metallic elements. The alkali metals are robustly body-centred cubic (bcc); the overwhelming majority of metals (80%) fall into either bcc, or one of the two close-packed structures, face-centred cubic (fcc), or hexagonal close-packed (hcp). If we include the lanthanides, which crystallize in a hybrid fcc/hcp lattice, where the packing alternates between ABA... (hcp) and ABC... (fcc), this proportion goes up to 88%. The alternating prefer-

ence along the series of transition metals for bcc and fcc structures has been successfully explained in terms of a Jahn-Teller distortion<sup>10</sup> which changes the structural preference of the transition metals based on the filling of the *d*-orbitals; no such model to date can account for the preference for the hcp structure, which in any case should be close in energy to the fcc structure, which has the same density. The magnetic 3d transition metals, manganese, iron, and copper, are understood to deviate from the periodic trend due to their magnetic ordering. It is however in the *p*-block - the region of the periodic table known as the 'poor metals', that a complete absence of periodicity in structure is observed.

The rhombohedral structure of mercury has been shown to be due to relativity.<sup>11</sup> The mercury-mercury bond in the dimer is very weak, due to the inert nature of the closed  $6s^2$  valence shell, which means binding is due entirely to dispersion interaction.<sup>12</sup> The closing of the band gap between the occupied  $s$ -shell and the valence  $p$ -orbitals happens as a function of size, at around 400 atoms. The metallic nature of bonding changes the mercury-mercury interaction significantly, reducing the bond length from 3.7 Å in the dimer to 3 Å in the bulk. The inertness of the  $s$ -shell is a relativistic effect due to the proximity of these electrons to the heavy nucleus, and results in a destabilisation of the underlying  $d$ -orbitals due to deshielding. Thus, at the short distances between mercury atoms in the bulk metal, the  $d$ -orbitals are able to interact strongly enough to cause modification of the lattice structure away from close-packing. It is also straightforward to show that the inclusion of relativity reduces the cohesive energy of bulk mercury, going some way to explaining its low melting temperature.<sup>11</sup> Recent simulations have demonstrated that the influence of relativity lowers the melting temperature by 105 K.<sup>13</sup>

A more extreme version of this relativistic effect on both structure and properties has been shown in calculations of the lattice and band structure of copernicium, the element

formerly known as eka-mercury. The stabilisation of the valence  $s$ -electrons and corresponding destabilisation of the  $d$ -electrons is so significant that they change order of occupation, meaning that the valence band of the solid is primarily of  $d$ -character. The unoccupied  $p$ -shell remains high enough in energy that a small band gap opens up, transforming this element into a semi-conductor: the first one to be known in the  $d$ -block.<sup>14</sup>

But is the metallicity of an element as fundamental a property as we like to think? It is certainly one of the most basic categorisations of the elements that we are used to making – but it deserves some further thought. Just as we think of the phases of the elements – such as the essential liquidity of mercury – as the phases that they exist in under standard conditions of temperature and pressure, so are the structural phases of the elements – their preferred allotropes – simply the ones which are most stable under standard conditions. Under high pressure, the properties of the elements have been shown to change in remarkable fashion: hydrogen has been predicted to become metallic<sup>15</sup> though the experimental evidence remains controversial.<sup>16-21</sup> In no less surprising a manner, simple metals such as sodium and lithium, which define the metallic paradigm in most solid-state texts, have been shown to adopt dimeric structures which become insulat-

Fig. 3. An alternative way to include the lanthanides and actinides in the periodic table

		Hexagonal (HCP)		Cubic (BCC)		Cubic (FCC)		Hybrid HCP/FCC		Rhombohedral		Simple cubic		Tetragonal		Orthorhombic			
H																			He
Li	Be																		
Na	Mg																		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo		

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Fig. 4. Periodicity in the structures of the metallic elements

ing.<sup>21,22</sup> Thus, even the position of the boundary between non-metals and metals in the periodic table needs to be understood as contingent on conditions such as pressure and temperature.

Another variable, that is of equal importance, though which perhaps offers more promise for practical application, is that of size. As mentioned previously in the case of mercury, the overlap of bands necessary for the existence of the metallic state relies on bonding between a sufficient number of atoms. Additionally, the structures preferred at small sizes are often quite different to those familiar to us in the bulk: when the surface area to volume ratio is large, the preferred structures will be those that achieve close-packed surfaces, based on icosahedral symmetry, rather than the familiar close-packed cubic and hexagonal structures. Structure-property relationships – in particular, the interactions between structure and the electronic structure that determines metallicity – are highly sensitive, and thus contribute to the broad range of anomalous phenomena that may be observed at the nanoscale.

An excellent example of such anomalous behavior is the greater than bulk melting temperatures found for small gallium clusters, at sizes below a hundred atoms.<sup>23-25</sup> At these sizes, we know that the structures are very different from the paired structure of the bulk; it is however necessary that the cohesive energy per atom of these small clusters must be considerably lower than that of the bulk, due to the large number of atoms at the surface of the cluster, where they are under-coordinated. The normal paradigm of melting in small particles is that of melting point depression: as the surface area increases relative to the particle volume, the melting temperature should decrease – and so it does, for the vast majority of substances. Gallium is the only substance in which the melting temperature is systematically elevated across a range of particle sizes, from 17 to around 80 atoms, according to experiment.

In thermodynamic terms, we can think of size at the nanoscale having an effect similar but opposite to that of pressure in the bulk: smaller particles have a lower effective pressure, due to the dominance of the surface. The lowering of pressure should increase the relative stability of the less dense phase: and gallium is indeed one substance which, like water, has a greater density in the liquid phase than in the solid. Whether this argument is sufficient to explain the higher melting temperatures is, however, questionable without detailed simulation of the melting transition. Simulations to date have shown that there is certainly more to the argument: for example, it is not easy at these sizes to quantify a difference in density.<sup>6,7</sup>

All of these examples demonstrate just how many degrees of freedom affect the behavior of the elements, and their most basic properties. Whether an element is metallic or not can change, and it can change greatly.

One of the first lessons of science is that even the question that you are asking is up for questioning. Outside the paradigm of standard conditions of temperature and pressure; far from the thermodynamic limit; the difference between liquid and solid, metal and non-metal, is open to question: and the answers both threaten and promise to be full of surprises.

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