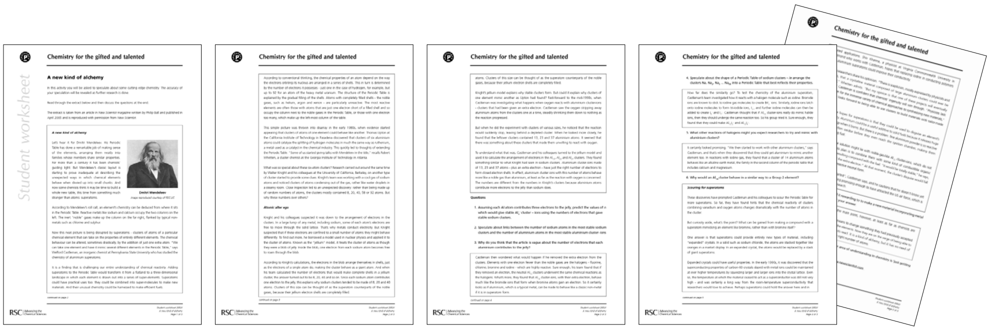
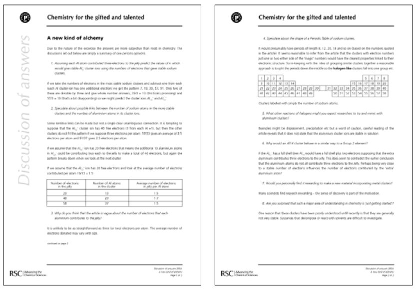
A new kind of alchemy



Student worksheet: CDROM index 20SW



Discussion of answers: CDROM index 20DA

Topic

The Periodic Table.

Level

Able post-16 students.

Prior knowledge

Simple atomic structure and how the Periodic Table relates to electronic configuration.

Rationale

This presents some cutting edge research for post-16 students in a context that they can appreciate. It shows the students there are still big ideas to be explored in chemistry and should promote research as a career choice. The students are asked to speculate about questions where there are no known answers. This is designed to develop their creative thinking skills.

Use

This activity could be given at almost any stage in a post-16 chemistry course but is most appropriate in connection with topics about the Periodic Table. The activity could be done by a whole class but is also very well suited to use as a differentiated activity for the more able or more creative thinkers. When this was trialled, some less able students found it demoralising that there were not definitive answers to some of the questions.

Student worksheet

A new kind of alchemy

In this activity you will be asked to speculate about some cutting edge chemistry. The accuracy of your speculation will be revealed as further research is done.

Read through the extract below and then discuss the questions.

The extract is taken from an article in *New Scientist* magazine written by Philip Ball and published in April 2005 and is reproduced with permission from *New Scientist*.

A new kind of alchemy

Let's hear it for Dmitri Mendeleev. His Periodic Table has done a remarkable job of making sense of the elements, arranging them neatly into families whose members share similar properties. For more than a century it has been chemists' guiding light. But Mendeleev's classic layout is starting to prove inadequate at describing the unexpected ways in which chemical elements behave when divvied up into small chunks. And now some chemists think it may be time to build a whole new table, this time from something much stranger than atoms: superatoms.

Dmitri Mendeleev

image reproduced courtesy of the Library & Information Centre, Royal Society of Chemistry

According to Mendeleev's roll call, an element's chemistry can be deduced from where it sits in the Periodic Table. Reactive metals like sodium and calcium occupy the two columns on the left. The inert "noble" gases make up the column on the far right, flanked by typical non-metals such as chlorine and sulphur.

Now this neat picture is being disrupted by superatoms - clusters of atoms of a particular chemical element that can take on the properties of entirely different elements. The chemical behaviour can be altered, sometimes drastically, by the addition of just one extra atom. "We can take one element and have it mimic several different elements in the Periodic Table," says Welford Castleman, an inorganic chemist at Pennsylvania State University who has studied the chemistry of aluminium superatoms.

It is a finding that is challenging our entire understanding of chemical reactivity. Adding superatoms to the Periodic Table would transform it from a flatland to a three-dimensional landscape in which each element is drawn out into a series of super-elements. Superatoms could have practical uses too: they could be combined into super-molecules to make new materials. And their unusual chemistry could be harnessed to make efficient fuels.

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According to conventional thinking, the chemical properties of an atom depend on the way the electrons orbiting its nucleus are arranged in a series of shells. This in turn is determined by the number of electrons it possesses - just one in the case of hydrogen, for example, but up to 92 for an atom of the heavy metal uranium. The structure of the Periodic Table is explained by the gradual filling of the shells. Atoms with completely filled shells - the noble gases, such as helium, argon and xenon - are particularly unreactive. The most reactive elements are often those with atoms that are just one electron short of a filled shell and so occupy the column next to the noble gases in the Periodic Table, or those with one electron too many, which make up the left-most column of the table.

This simple picture was thrown into disarray in the early 1980s, when evidence started appearing that clusters of atoms of one element could behave like another. Thomas Upton at the California Institute of Technology in Pasadena discovered that clusters of six aluminium atoms could catalyse the splitting of hydrogen molecules in much the same way as ruthenium, a metal used as a catalyst in the chemical industry. This quickly led to thoughts of extending the Periodic Table. "Some of us started giving talks with Mendeleev in the title," recalls Robert Whetten, a cluster chemist at the Georgia Institute of Technology in Atlanta.

What was so special about these six-atom clusters? Research carried out around the same time by Walter Knight and his colleagues at the University of California, Berkeley, on another type of cluster started to provide some clues. Knight's team was working with a cool gas of sodium atoms and noticed clusters of atoms condensing out of the gas, rather like water droplets in a steamy room. Close inspection led to an unexpected discovery: rather than being made up of random numbers of atoms, the clusters mostly contained 8, 20, 40, 58 or 92 atoms. But why these numbers over others?

Atomic alter ego

Knight and his colleagues suspected it was down to the arrangement of electrons in the clusters. In a large lump of any metal, including sodium, some of each atom's electrons are free to move through the solid lattice. That's why metals conduct electricity. But Knight suspected that if these electrons are confined to a small number of atoms they might behave differently. To find out more, he borrowed a model used in nuclear physics and applied it to the cluster of atoms. Known as the "jellium" model, it treats the cluster of atoms as though they were a blob of jelly. Inside the blob, one electron from each sodium atom becomes free to roam through the blob.

According to Knight's calculations, the electrons in the blob arrange themselves in shells, just as the electrons of a single atom do, making the cluster behave as a giant atom. And when his team calculated the number of electrons that would make complete shells in a jellium cluster, the answer turned out to be 8, 20, 40 and so on. Since each sodium atom contributes one electron to the jelly, this explains why sodium clusters tended to be made of 8, 20 and 40 atoms. Clusters of this size can be thought of as the superatom counterparts of the noble gases, because their jellium electron shells are completely filled.

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Knight's jellium model explains why stable clusters form. But could it explain why clusters of one element mimic another as Upton had found? Fast-forward to the mid-1990s, when Castleman was investigating what happens when oxygen reacts with aluminium cluster ions - clusters that had been given an extra electron. Castleman saw the oxygen stripping away aluminium atoms from the clusters one at a time, steadily shrinking them down to nothing as the reaction progressed.

But when he did the experiment with clusters of various sizes, he noticed that the reaction would suddenly stop, leaving behind a depleted cluster. When he looked more closely, he found that the leftover clusters contained 13, 23 and 37 aluminium atoms. It seemed that there was something about these clusters that made them unwilling to react with oxygen.

To understand what that was, Castleman and his colleagues turned to the jellium model and used it to calculate the arrangement of electrons in the Al_{13}, Al_{23} and Al_{37} clusters. They found something similar to what Knight had seen in sodium clusters. Aluminium cluster ions made of 13, 23 and 37 atoms - plus an extra electron - have just the right number of electrons to form closed electron shells. In effect, aluminium cluster ions with this number of atoms behave more like a noble gas than aluminium, at least as far as the reaction with oxygen is concerned. The numbers are different from the numbers in Knight's clusters because aluminium atoms contribute more electrons to the jelly than sodium does.

Questions

1. **Assuming each Al atom contributes three electrons to the jelly, predict the values of *n* which would give stable Al_n^- cluster ions using the numbers of electrons that gave stable sodium clusters.**

2. **Speculate about links between the number of sodium atoms in the most stable sodium clusters and the number of aluminium atoms in the most stable aluminium cluster ions.**

3. **Why do you think that the article is vague about the number of electrons that each aluminium contributes to the jelly?**

Castleman then wondered what would happen if he removed the extra electron from the clusters. Elements with one electron fewer than the noble gases are the halogens - fluorine, chlorine, bromine and iodine - which are highly reactive. Sure enough, his team found that if they removed an electron, the neutral Al_{13} clusters underwent the same chemical reactions as the halogens. What's more, they found that Al_{13} cluster ions, with their extra electron, behave much like the bromide ions that form when bromine atoms gain an electron. So it certainly looks as if aluminium, which is a typical metal, can be made to behave like a classic non-metal if it is in superatom form.

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4. Speculate about the shape of a Periodic Table of sodium clusters – *ie* arrange the clusters Na, Na_2, Na_3 ... Na_{58} into a Periodic Table that best reflects their properties.

How far does the similarity go? To test the chemistry of the aluminium superatom, Castleman's team investigated how it reacts with a halogen molecule such as iodine. Bromide ions are known to stick to iodine gas molecules to create BrI_2^- ions. Similarly, iodine ions latch onto iodine molecules to form tri-iodide ions, I_3^-, and further iodine molecules can then be added to create I_5^- and I_7^-. Castleman thought that if Al_{13} cluster ions really do mimic halide ions, then they should undergo the same reaction too. So his group tried it. Sure enough, they found that they could make $Al_{13}I_2^-$ and $Al_{13}I_4^-$.

5. What other reactions of halogens might you expect researchers to try and mimic with aluminium clusters?

It certainly looked promising. "We then started to work with other aluminium clusters," says Castleman, and that's when they discovered that they could get aluminium to mimic another element too. In reactions with iodine gas, they found that a cluster of 14 aluminium atoms behaves like an alkaline earth metal, the family in the second column of the periodic table that includes calcium and magnesium.

6. Why would an Al_{14} cluster behave in a similar way to a Group 2 element?

Scouring for superatoms

These discoveries have prompted Castleman and his colleagues to scour the Periodic Table for more superatoms. So far, they have found hints that the chemical reactivity of clusters combining vanadium and oxygen atoms changes dramatically with the number of atoms in the cluster.

But curiosity aside, what's the point? What can be gained from making a compound with a superatom mimicking an element like bromine, rather than with bromine itself?

One answer is that superatoms could provide entirely new types of material, including "expanded" crystals. In a solid such as sodium chloride, the atoms are stacked together like oranges in a market display. In an expanded crystal, the atoms would be replaced by a stack of giant superatoms.

Expanded crystals could have useful properties. In the early 1990s, it was discovered that the superconducting properties of carbon-60 crystals doped with metal ions could be maintained at ever higher temperatures by squeezing larger and larger ions into the crystal lattice. Even so, the temperature at which the material ceased to act as a superconductor was still not very high - and was certainly a long way from the room-temperature superconductivity that researchers would love to achieve. Perhaps superatoms could hold the answer here and in

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related applications. Shiv Khanna, a physicist at Virginia Commonwealth University in Richmond who works with Castleman, hopes that replacing iodine in conducting polymers with aluminium superatoms could improve their conductivity.

Not all researchers share his optimism. "There is scepticism, mostly expressed by physicists and theorists, that a crystalline material composed of large aluminium clusters could ever be achieved," Whetten admits. "But my opinion is that one of these projects will eventually succeed." Castleman is confident that chemists' ingenuity will win through. "Physicists lack appreciation for the immense variety of chemical approaches to synthesising new materials," he says. He looks forward to being able to use clusters to build materials with tailor-made properties.

Another of the hopes for superatoms is that they could be used to disguise an element's normal chemistry. Aluminium could be a useful additive to solid fuels because it releases huge amounts of energy when it burns. But there is a problem: fine aluminium powder is so reactive that the grains often oxidise before they even reach the ignition chamber, making them useless for boosting fuel.

Castleman thinks the solution might lie with noble gas-like Al_{13} cluster ions, which do not react with oxygen. His plan is to combine them with some kind of combustible organic molecule and mix the resulting compound with the fuel. "It would be totally stable," he says, "until a flame kicks out the extra electron." At that moment, the cluster's disguise would fall away, returning it to its reactive neutral form.

The idea "is just getting started", Castleman says, and he cautions that he doesn't know yet if it will work. But it is looking promising enough to have attracted the US air force, which is funding him to do further research.

7. **Would you personally find it rewarding to to make a new material incorporating metal clusters? Give a reason for your answer.**

Applications like these are not the main point, however, at least as far as chemists are concerned. For them, superatoms could provide a means to change something they had previously accepted as given: the chemical properties of the elements. Now they are on the verge of being able to control and alter the way the elements react. It is a kind of alchemy, but it has no need of magic. All you have to do is count the right number of atoms.

8. **Are you surprised that such a major area of understanding in chemistry is 'just getting started'?**

For more articles of scientific interest visit *www.newscientist.com*.

A new kind of alchemy

Due to the nature of the excercise, the answers are more subjective than most in chemistry. The discussions set out below are simply a summary of one person's opinions.

1. *Assuming each Al atom contributed three electrons to the jelly, predict the values of n which would give stable Al_n^- cluster ions using the numbers of electrons that gave stable sodium clusters.*

If we take the numbers of electrons in the most stable sodium clusters and subtract one from each (each Al cluster ion has one additional electron) we get the pattern 7, 19, 39, 57, 91. Only two of these are divisible by three and give whole number answers, 39/3 = 13 (which looks promising) and 57/3 = 19 (which is a bit disappointing) so we might predict the cluster ions Al_{13}^- and Al_{19}^-.

2. *Speculate about possible links between the number of sodium atoms in the more stable clusters and the numbers of aluminium atoms in its cluster ions.*

Some tentative links can be made, but not a single clear unambiguous connection. It is tempting to suppose that the Al_{13}^- cluster ion has 40 free electrons (3 from each Al plus one extra to give it the negative charge), but then the other clusters do not fit the pattern if we suppose three electrons per atom. 57/23 gives an average of 2.5 electrons per atom and 91/37 gives 2.5 electrons per atom.

If we assume that the Al_{13}^- ion has 20 free electrons, that means the additional 10 aluminium atoms in Al_{23}^- could be contributing two each to the jelly to make a total of 40 electrons, but again the pattern breaks down when we look at the next cluster.

If we assume that the Al_{13}^- ion has 20 free electrons and look at the average number of electrons contributed per atom 19/13 = 1.5

Number of electrons in the jelly	Number of Al atoms in the cluster	Average number of electrons in jelly per Al atom
20	13	1.5
40	23	1.7
58	37	1.5

3. *Why do you think that the article is vague about the number of electrons that each aluminium contributes to the jelly?*

It is unlikely to be as straightforward as three (or two) electrons per atom. The average number of electrons donated may vary with size.

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4. *Speculate about the shape of a Periodic Table of sodium clusters.*

It would presumably have periods of length 8, 12, 20, 18 and so on (based on the numbers quoted in the article). It seems reasonable to infer from the article that the clusters with electron numbers just one or two either side of the 'magic' numbers would have the clearest properties linked to their electronic structure. So in keeping with the idea of grouping similar clusters together, a reasonable approach is to split the periods down the middle so the **halogen like** clusters fall into one group *etc*.

1	2	3	4														5	6	7	8
9	10	11	12	13	14										15	16	17	18	19	20
21	22	23	24	25	26	27	28	29	30		31	32	33	34	35	36	37	38	39	40
41	42	43	44	45	46	47	48	49				50	51	52	53	54	55	56	57	58

Clusters labelled with simply the number of sodium atoms.

5. *What other reactions of halogens might you expect researchers to try and mimic with aluminium clusters?*

Examples might be displacement, precipitation *etc* but a word of caution, careful reading of the article reveals that it does not state that the aluminium cluster ions are stable in solution.

6. *Why would an Al_{14} cluster behave in a similar way to a Group 2 element?*

If the Al_{13}^- has a full shell then Al_{14} would have a full shell plus two electrons, supposing that the extra aluminium contributes three electrons to the jelly. This does seem to contradict the earlier conclusion that the aluminium atoms do not all contribute three electrons to the jelly. Perhaps being very close to a stable number of electrons influences the number of electrons contributed by the 'extra' aluminium atom?

7. *Would you personally find it rewarding to make a new material incorporating metal clusters? Give a reason for your answer.*

Many scientists find research rewarding – the sense of discovery is part of the motivation.

8. *Are you surprised that such a major area of understanding in chemistry is 'just getting started'?*

One reason that these clusters have been poorly understood until recently is that they are generally not very stable. Substances that decompose or react with solvents are difficult to investigate.