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Five ideas in chemical education that must die

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Abstract
The article concerns five traditionally difficult issues that chemical educators encounter and how they should be resolved. In some cases I propose the examination of necessary and sufficient conditions in order to cast light on the relationships under discussion. The five educational issues are, the notion that a pH value of seven implies a neutral solution of water and vice versa, the use of Le Châtelier's Principle, the relative occupation and ionization of $4s$ and $3d$ orbitals, the explanation of anomalous electronic configurations and the elements that make up group 3 of the periodic table.

Keywords Chemical education · pH and neutrality · Le Châtelier Principle · Electronic configurations · Anomalous configurations · Group 3

This article was inspired by the recent book "This Idea Must Die", in which 175 leading thinkers have expounded on ideas, theories and concepts that they believe are unproductive and should be retired.[1] Remarkably, there is not a single chemist among the authors, thus reinforcing the misconception that chemistry lacks any philosophical substance or profound intellectual content. The steady growth in interest in the philosophy of chemistry since the early 1990s demands that this situation be rectified by considering what chemical ideas may also be in need of 'killing off'. Having spent a good deal of my career attempting to promote the philosophical aspects of chemistry and the value of taking a more reflective view in chemical education, I feel compelled to make up for the deficit in the book.[2] I will therefore discuss what I consider to be the five most obstructive and confused ideas that exist among teachers and authors of chemistry textbooks.

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[1] *This Idea Must Die,* ed J. Brockman, Harper Perennial, New York, 2015.

[2] *Philosophy of Chemistry: Synthesis of a New Discipline*, Boston Studies in the Philosophy of Science, ed D. Baird, E.R. Scerri and L. McIntyre, Springer, Dordrecht, 2006, vol 242; *Philosophy of Chemistry: Growth of a New Discipline*, Boston Studies in the Philosophy and History of Science, ed E.R. Scerri and L. McIntyre, Springer, Berlin, 2015, vol 306; E.R. Scerri, *Collected Papers on the Philosophy of Chemistry*, Imperial College Press, London, 2008; Foundations of Chemistry, Springer, https://link.springer.com/journal/10698.

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Solutions with a pH of 7 are neutral and vice versa

The notion that a solution with pH 7 is always neutral and that neutral implies a pH value of 7 is prevalent in the classroom, especially when the subject is treated qualitatively. But once the concept of K_w and its value of 10^{-14} is introduced, it becomes problematic. K_w is the dissociation constant for water is given by the concentration of hydrogen ions multiplied by that of hydroxide ions ($K_w = [H^+][OH^-]$) which at room temperature has a value of 1×10^{-14} mol^{-2} dm^{-6}. pH is calculated by taking the square root of this value since the ionization of water produces equal amounts of H^+ and OH^- ions. Using the formula that $pH = -\log_{10}[H^+]$ it follows that the pH of water at room temperature has a value of 7.

The problem lies with the implied notion that having a pH of 7 is both necessary and sufficient for neutrality to occur. In fact, it is neither necessary nor sufficient for a solution to be pH 7 for it to be neutral. Establishing necessary and sufficient conditions ensures that a causal link between any two concepts can be specified.

For example, one may ask if the act of smoking cigarettes is necessary and/or sufficient for contracting lung cancer. If smoking led to lung cancer, it would mean that smoking is sufficient to cause the disease in anyone, but this is not the case. Conversely, one could ask whether people with lung cancer must be smokers, but there can be many possible causes of the disease and smoking is of course only one of them. So smoking is neither a necessary or sufficient cause, although there is a high correlation between a person smoking and the probability of their contracting the disease.

Another chemistry-based example consists in the notion that if an atom contains 79 protons, it must be gold. Conversely, for any atom to be gold its nucleus must contain 79 protons. Having a particular number of protons is thus both necessary and sufficient to ensure the identity of any element.

Returning to pH values and the issue of neutrality or otherwise, the lack of sufficiency is easy to establish by determining whether a pH of seven implies that a solution is neutral. The answer is no, since what defines a neutral solution is the presence of an equal number of moles of H^+ and OH^- ions, a situation that may occur at any pH value. For example, a solution can consist solely of H^+ ions at a concentration of 10^{-7} mol L^{-1} but this would clearly not be neutral.

We must abandon the idea that it is sufficient for a solution to be pH 7 for it to be neutral. Conversely, if a solution is neutral, that does not guarantee that it is also at pH 7. For example, at a temperature of 50 °C, $K_w = 5.47 \times 10^{-14}$, thus giving a pH of 6.63. Temperature affects the equilibrium of the reaction of water dissociating into hydrogen and hydroxide ions. The process is endothermic, and so the forward reaction absorbs heat. Increasing the water's temperature favors the forward reaction. As a result, more hydrogen ions and hydroxide ions are formed, raising the value of K_w and lowering the pH. Nevertheless, the solution is still neutral, since whatever the temperature, the self-ionization of water results in equal amounts of H^+ and OH^- ions. The implicit notion that it is also necessary for a solution to be pH 7 for it to be neutral is inherited from elementary chemistry and must be unlearned at college level.[3]

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[3] Another related false notion to do with pH is that the range of possible values runs from 1 to 14. These limits can easily be exceeded in cases of 1 M or 10 M solutions of strong acids (pH = 0 and −1 respectively) or 10^{-15} M, which yields a pH of 15, all of which values that novice chemistry students initially find rather shocking.

Although the points I am making here are not particularly original, I believe that the use of necessary and sufficient conditions to clarify the situation may represent a new contribution to teaching about pH and neutrality.

Le Châtelier's principle

The second idea that must die is the principle that 'a system in equilibrium that is subjected to a stress will react in such a way as to counteract the stress'.[4] This is a qualitative principle that is supposed to predict the outcome of any change made in pressure, concentration or temperature to a system that is in a state of equilibrium. The problem is that it can fail to make the correct prediction in two out of the three cases that it is intended for, namely pressure and temperature changes.

To predict what happens when the pressure of a system is increased, a student might imagine a balloon filled with gas whose pressure is being increased by squeezing the balloon down to a smaller volume. The student might be justified in thinking that the system would react by increasing its volume to *oppose* the initial reduction in volume. This would of course be an incorrect prediction since it is known that systems at equilibrium proceed in the direction of volume decrease, following any increase in total pressure. To educators, it might appear as a legitimate maneuver to rescue the wording in the supposedly guiding principle, by informing students that what was intended was a pressure increase without a change in volume and that this has been the cause of the incorrect prediction. But this might only serve to confuse students further.

When the temperature is raised in a reaction at equilibrium, students might be excused for thinking that the reaction should proceed in the exothermic direction to literally oppose the applied increase in heat energy. Again, this is an incorrect prediction since it is endothermic, rather than exothermic, reactions that are favored by temperature increases. Part of the problem lies in the precise wording of the principle. Many textbook authors attempt to solve the problem by changing the wording to say precisely the opposite of Le Châtelier's principle, as that the equilibrium shifts to 'accommodate' the change.[5] To make matters worse, no two textbooks give the same statement. Admittedly, this alternative wording seems to fix the problems in that students can now argue that an increase in pressure on the balloon, by means of reducing the volume, will indeed result in volume decrease being favored. Similarly, in the case of raising the temperature, the student is now supposed to argue that raising the temperature will result in favoring whichever direction results in an uptake of the added heat, namely the endothermic direction, in full accordance with the experimental facts.

Perhaps it is time to retire Le Châtelier's principle as a whole. Instead, one can make unambiguous and correct predictions by calculating the equilibrium constant for pressure, K_p, of a gaseous reaction. Substituting for the partial pressures of each component gas in the equation—the product of the mole fraction for each component and the total pressure—shows unequivocally that increasing the total pressure results in a greater mole fraction of the substances that accompany a volume decrease, on moving from left to right in the

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[4] D. W. Oxtoby, H. P. Gillis and A Campion, *Principles of Modern Chemistry,* 7th edition, Brooks/Cole, Belmont, 2012, p. 642.

[5] M. Munowitz, *Principles of Chemistry*, Norton, 2000. P. 454.

reaction equation. This is done in many university level textbooks and owes nothing to the confusing Le Châtelier's principle.[6]

For temperature increases, a different approach is needed since the equilibrium constant itself varies with temperature. Instead, thermodynamic formulas relating the equilibrium constant to temperature can be used, such as the one that applies to exothermic changes:

$$\ln K \propto 1/T$$

It follows from this expression that, for exothermic reactions, the equilibrium constant decreases as the temperature is increased and as a result, the reaction, as written from left to right, is not favored by raising the temperature. Again, this is being done without appeal to Le Châtelier's highly unreliable principle.

While on the subject of temperature changes let me pause to mention a completely ad hoc approach that appears to be entrenched among some chemical educators. It consists of treating heat as a reactant in the case of endothermic reactions and as a product for exothermic reactions. Next one uses the same approach as though one was making a change to a reactant and product (see following section) and, low and behold, the correct prediction is arrived at for the wrong reason. Two immediate objections to this all too common ploy are that (a) we have known for more than 200 years that heat is not in fact a material substance and (b) the raising of lowering of heat energy is made to an entire reaction at equilibrium and so it is completely meaningless to arbitrarily choose to add heat as a substance to one or other side of the reaction.

Curiously, in the case of concentration changes, the wording in the principle seems to work well, adding even further to the confusion. Consider what happens when the concentration of substance A is increased in this reaction:

$$A + B \rightleftharpoons C + D$$
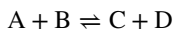
According to Le Châtelier's principle, the system should act to oppose the increase, consuming the additional amount of A, which it does. In this case, the observed change does indeed seem to be a genuine opposition to the applied change. But a principle that claims to predict what happens on the application of three types of changes, and only succeeds clearly in one of the three types, would seem to be rather counter-productive.

That 4*s* orbitals are preferentially occupied in transition metal atoms

The third idea, that I believe should be jettisoned, is the notion that 4*s* atomic orbitals are preferentially occupied and preferentially ionized with respect to 3*d* orbitals in transition metal atoms. This idea is extremely pervasive even though it has occasionally been corrected in the scientific and chemistry education literature.[7]

As many chemistry students are quick to realize, the notion that 4*s* orbitals are preferentially occupied and also ionized makes little sense since the preferential occupation of 4*s* orbitals seems to suggest that the electrons falling into these orbitals should *not* be the first

[6] A. Thompson, J. Stephens and A. Lainchbury, *Advanced Chemistry Calculations*, 2nd edition, Hodder Education, 1998, p. 116; M. Lewis and G. Waller, *Advancing Chemistry*, Oxford University Press, 1982, p. 263.

[7] S-G Wang and W H E Schwarz, *Angew. Chem., Int. Ed.*, 2009, 48, 3404 (DOI: https://doi.org/10.1002/anie.200800827); E.R. Scerri, The trouble with the aufbau, *Education in Chemistry*, November 2013, 24–26, E R Scerri, *A tale of seven elements.* Oxford University Press, 2013.

to be ionized. The relative occupation of orbitals, just like the opposite energetic process of ionization, is governed by the stability of atoms. If the $3d$ electrons are the last to enter the atom, students correctly reason that they should be the first to depart, when ionization energies are considered. But the experimental ionization energies for transition metal atoms show unequivocally that it is the $4s$ electrons, or the ns electrons if we consider the transition metals in general, that are the first to be removed.

Textbook authors and instructors react to this apparent conundrum by appealing to all kinds of contorted arguments that are intended to pacify students and lead them to think that the solution lies in the higher reaches of quantum mechanics, which are beyond their level of understanding.[8] There are some plausible reasons why this view persists. One factor is that in the case of potassium and calcium atoms, the $4s$ orbitals are genuinely preferentially occupied. But for these two atoms, the question of the relative occupation and ionization of $4s$ and $3d$ orbitals does not even arise, for the simple reason that there are no $3d$ electrons present. Also, it would seem natural to suppose that the configuration of scandium should consist of what already exists in the calcium atom plus an additional electron, which one might expect would enter a $3d$ orbital. But this view is incorrect.

What should be done in every case is to consider the relative order in the energies of all the orbitals for each particular atom in question. In the case of the scandium atom, the relevant ordering is that the energy of the $3d$ orbitals falls below that of the $4s$. Consequently, it is the $3d$ orbitals that are preferentially occupied, contrary to what is stated in 99% of textbooks.[9] The $4s$ orbital is occupied last, in terms of an energetic order, and consequently, it is perfectly consistent that it should also be preferentially ionized when the reverse energetic process is considered. The initial student intuition turns out to have been correct. If $4s$ fills first, it cannot possibly also ionize first.

But there is one remaining problem to solve. As mentioned, the $3d$ orbitals have energies lower than those of $4s$ for the metals in the first transition series. So why is the configuration of scandium [Ar] $3d^1 4s^2$, instead of [Ar] $3d^3$? The answer to this puzzle is that the final two electrons that enter the scandium atom can experience less electron–electron repulsion by making their way into the larger, more diffuse $4s$ orbital. This arrangement is more stable. Despite this state of affairs, the fact remains that $3d$ fills before $4s$ and $4s$ ionizes preferentially. Or, more generally, experimental evidence for transition metals from any of the first three series points to the preferential occupation of $(n − 1)d$ orbitals and the preferential ionization of the corresponding ns orbital.

The anomalous configuration of the chromium atom

The fourth idea that should be killed off, is that chromium displays an anomalous configuration of [Ar] $3d^5 4s^1$ *because* of the stability of its half-filled sub-shell. Many chemistry textbook authors make this claim. My response is that there is nothing intrinsically stable about half-filled shells or sub-shells and that this is an ad hoc notion that should be abandoned. After all, why should the possession of a half-filled sub-shell confer any additional stability? What principle of physics is supposed to justify such a claim?

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[8] R. Chang, *Physical Chemistry for the Chemical and Biological Sciences*, University Science Books, 2000, p. 602..

[9] One notable exception is the textbook by D.W. Oxtoby, H.P. Gillis and P. Campion, *Principles of Modern Chemistry* (7th ed.), Brooks/Cole, 2012, p. 219.

As a matter of fact, there is no such justification and it is just another myth that seems to be embraced by many chemical educators. As in the case of my earlier remarks concerning the concept of a solution having a pH of seven and whether it is neutral, there is an implication that having a half-filled sub-shell is somehow both necessary and sufficient for an atom to display an anomalous configuration.

This implication can easily be demolished by answering two questions. Does a half-filled sub-shell lead to an anomalous configuration, in the sense of having an outer shell of ns^1? The answer is no, since atoms such as manganese and technetium possess half-filled d sub-shells, yet they do not have outer shells consisting of ns^1 configurations. Conversely, if a metal atom has an anomalous configuration, is this always accompanied by a half-filled sub-shell configuration? Once again, the answer is no. There are several metal atoms, especially in the second transition metal series, that are anomalous in displaying a $5s^1$ outer shell, that lack a half-filled $4d$ sub-shell. These atoms are niobium, ruthenium and rhodium with the following configurations respectively: [Kr] $4d^4\,5s^1$, [Kr] $4d^7\,5s^1$ and [Kr] $4d^8\,5s^1$. There is a lack of any direct causal link in both directions. Possessing half-filled sub-shells is neither sufficient nor necessary for there to be an anomalous configuration in any particular case. All that does exist is the coincidence that two atoms, namely chromium and molybdenum, among eleven atoms with anomalous configurations in the d-block, happen to display both attributes.

Why then do chemical educators continue to make such a 'song and dance' out of half-filled sub-shell stability in this context? Students still need an explanation for the anomalous configuration in atoms such as chromium. I suggest that given the choice between the following configurations [Ar] $3d^5\,4s^1$ and [Ar] $3d^4\,4s^2$ one can say that the first of these is observed because it is more stable overall. Better still, the second of these options is less stable because of the additional electron–electron repulsion between the two electrons in the 4s orbital. So, rather than falsely implying that there is something intrinsically stable about the half-filled sub-shell configuration, it is more accurate to say that this configuration occurs by default, since the other option represents a less stable arrangement of electrons.

The careful reader will note an apparent contradiction with what was stated in the earlier discussion about atoms such as scandium that favor having two electrons in the 4s orbital in order to achieve maximum stability. But each atom must be considered on its own terms. If anything, this emphasizes the fact that simple general rules concerning electronic configurations frequently break down. A fuller explanation of why s^1 configurations ever occur in preference to the more typical s^2 configurations can be found, again, in the work of Eugen Schwarz who has done so much to clarify the 4s, 3d question.[10]

That group 3 of the periodic table should consist of Sc, Y, La and Ac

The fifth idea in our series is the view that group 3 of the periodic table consists of Sc, Y, La and Ac. There is now enough evidence to show this is incorrect. In 1982, an article in the *Journal of Chemical Education* argued group 3 should instead consist of Sc, Y, Lu and Lr.[11]

[10] W H E Schwarz et al., *Chem. Eur. J.* 2006, 12, 4101, (DOI: https://doi.org/10.1002/chem.20050 0945) (see figure 8 and accompanying text).

[11] W.B. Jensen, *J. Chem. Educ.*, 1982, **59**, 634 (DOI: https://doi.org/10.1021/ed059p634).

H 1																															He 2
Li 3	Be 4																									B 5	C 6	N 7	O 8	F 9	Ne 10
Na 11	Mg 12																									Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
K 19	Ca 20																Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38																Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	*Lu 71*	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Fr 87	Ra 88	Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	*Lr 103*	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Ds 110	Rg 111	Cn 112	Nh 113	Fl 114	Mc 115	Lv 116	Ts 117	Og 118

Fig. 1 Long-form periodic table showing all elements in order of increasing atomic number

Some textbook authors have taken this up, but the majority seem reluctant to do so.[12] The author of the 1982 article was not the first to group the elements of group 3 in this way, and many earlier periodic tables showed the same grouping. Several physicists in the 1950s and 60s also suggested lutetium should be in group 3 rather than the final member of the first row of the *f*-block.[13]

In the 1982 article, Jensen suggested that an incorrect assignment of the ytterbium atom's electronic configuration had led to the placement of lanthanum, rather than lutetium, directly below yttrium in group 3. Ytterbium was assumed to have a configuration of $[Xe] 4f^{13}5d^16s^2$ and lutetium's was assumed to be $[Xe] 4f^{14}5d^16s^2$. As a result, the differentiating $4f$ electron in lutetium implied that it should be the last member of the first row of the *f*-block. However, spectroscopic measurements revealed that both elements possess 14 *f*-electrons.[14] This meant that both elements had an equal claim to be the last member of the first row of the *f*-block. If ytterbium occupied this position, the subsequent element, lutetium, would have to be the first element in the third row of the transition metals.

Similarly, because lanthanum and lutetium have the configurations $[Xe] 5d^16s^2$ and $[Xe] 4f^{14} 5d^16s^2$ respectively, both could occupy the first place in the third row of the transition metal series below scandium and yttrium, in principle. If lutetium occupies this position, following its removal from the *f*-block as discussed above, lanthanum becomes the first member of the *f*-block elements. Some authors object to this placement because lanthanum lacks *f*-orbital electrons. But, this is not an anomaly since more serious cases are tolerated. For example, thorium's atom possesses no *f*-orbital electrons, yet there is no dispute that it belongs in the *f*-block.

Electronic configurations are ultimately approximations to what is more fundamentally described as a superposition of several closely lying configurations. Atoms do not require a

[12] D.W. Oxtoby, H.P. Gillis and A. Campion, *Principles of Modern Chemistry*, Brooks/Cole, 7th ed, 2012, p. 71. However, on the inside cover, the table shows lanthanum and actinium in group 3.

[13] L. Landau and E.M. Lifshitz, *Quantum mechanics*, Pergamon, 1959, p. 245; D.C. Hamilton and M.A. Jensen, *Phys. Rev. Lett.*, 1963, **11**, 205 (DOI: https://doi.org/10.1103/physrevlett.11.205); D.C. Hamilton, *Am. J. Phys.*, 1965, **33**, 637 (DOI: https://doi.org/10.1119/1.1972042).

[14] Jensen implies that this reassignment of the configuration of ytterbium has been a 'recent' change. As a matter of fact, it was first made in 1937.

Fig. 2 Long-form periodic table showing alternative placements of Lu and Lr. The continuous sequence of atomic numbers shown in Fig. 1 is lost—lanthanum, element 57, appears between elements 71 and 72, while actinium, 89, appears between elements 103 and 104

Fig. 3 Third option for presenting the long-form periodic table in which the *d*-block is split into two uneven portions of one and nine groups

particular kind of differentiating electron in order to belong to the corresponding block of the periodic table. For example, helium, whose atoms have a differentiating s-orbital electron, is almost always placed in the *p*-block.[15]

There is a different reason why placing lutetium and lawrencium, rather than lanthanum and actinium, in group 3 is the better option.[16] If we incorporate either lutetium and lawrencium or lanthanum and actinium into group 3 of the long-form periodic table, only the first placement is consistent, because it results in a continuously increasing sequence of atomic numbers (Fig. 1). Conversely, incorporating lanthanum and actinium into group 3 of the long-form table results in two glaring anomalies in terms of sequences of increasing atomic numbers (Fig. 2).

For me, this is a virtually conclusive argument in favor of group 3 consisting of Sc, Y, Lu and Lr. The only fly in the ointment is a third possibility, but this involves an awkward

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[15] This is not the case in the Janet or left-step periodic table, however, in which helium is placed in the s-block.

[16] E.R. Scerri, Mendeleev's Periodic Table Is Finally Completed and What To Do about Group 3? *Chemistry International,* July–August 2012, 3, 28.

A very short introduction to the periodic table, Oxford University Press, 2008, Ch. 10.

sub-division of the *d*-block elements (Fig. 3). As such, it is not a fatal objection to the group 3 assignment that is being proposed in this article.

A recent article in *Nature* magazine was reported in the popular science press as having contributed to the resolution of the group 3 conundrum.[17] Unfortunately, various members of the large team of authors appear to have used the same data to arrive at opposite conclusions. This highlights the need for a categorical means of settling the issue, which I claim to have provided in my article in *Chemistry International*.[18] In any case, it is high time that the idea of group 3 consisting of Sc, Y, La and Ac be abandoned.

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[17] T.K. Sato *et al.*, *Nature*, 2015, **520**, 209 (DOI: https://doi.org/10.1038/nature14342).

[18] The proposal was first made in E R Scerri, *Chem. Int.*, July–August 2012, 34, 28. Also see, E. Scerri, *A Very Short Introduction to the Periodic Table*, Oxford University Press, 2011, chapter 10.