Letters

Activity Series of Metals

With regard to the article "Studying Activity Series of Metals" (*J. Chem. Educ.* **1995**, *72*, 51) in which the authors are intending to explain several properties of metals, its ions and compounds from activity series of metals (derived from reactions with water/steam and dilute acids), the following observations might be of interest for those having decided to use this article in the class:

1. As quite simple arguments are used, statements and conclusions should be regarded as rough guides subjected to numerous exceptions. For example, in *remembering the order of the series* it is stated: "*2. The increase in activity of metals down a group is explained...*". However, what about Zn, Cd, Hg, to mention a familiar group? If a such statement has to be made I suggest a refinement such as "in groups 1 to 3" or "most active" accompanying to metals.

2. The information included in tables should be handled with care. For example, the presence and position of aluminium carbonate in Tables 4 and 5 induces to think that this is a common carbonate, also more resistant to heat than those of Zn, Fe, or Cu; in Table 6 (*properties of metals....*) the inclusion of *I_2 solution* is inappropriate, and the color *blue* associated to *hydrated copper(II)* together with the *green* to *Cu^{2+}* is confusing. I suggest removing from these tables aluminium carbonate, I_2 solution, and hydrated copper(II), moving Cu^{2+} to the position of this last.

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A recent article on the activity series of metals (*1*) contains some interesting points such as the integration of the topic with other topics and the review of previously learned materials. This procedure allows the students to incorporate new knowledge into what they already know, thus leading to significant learning. Nevertheless, the article also contains some mistakes and some inaccurate generalizations. For example, the authors state that the activity of metals increases down a group and that, as a result, the position of Li is below K and Na in the activity series. Nevertheless, if we look at the standard reduction potentials, that put the activity series of metals on a quantitative basis (*2*), we see that Li is the most active metal in the periodic table. Furthermore, although the activity of group 2 metals does increases down the group, the opposite situation is found for group 13 metals. Also, for group 14 metals, Sn is more active than Pb, despite being above in the group. Another mistake is stating that all group 1 metals are more active than group 2 metals. Although this is the general trend, Na is less active than Ca, Sr, and Ba.

The activity series ranks the elements in order of their reducing ability in aqueous solution (*3*). Therefore, the position of a metal in the activity series is a thermodynamic property that is quantified by the standard reduction potential. On the other hand, for metals that are more active than hydrogen, there is an interesting parallel between the ease of oxidation of the metal and the speed with which it reacts with water or aqueous acids with evolution of hydrogen (*4*). However, confusion between the thermodynamic and kinetic properties of a reaction should be avoided. For example, while Ca reacts slowly with water at room temperature, Na reacts violently (*3*). Also, Li reacts less vigorously than the other alkali metals with water. Despite these observations, both Ca and Li are more active (stronger reductors) than Na. It is clear that this is a kinetic effect, probably due to the fact that Na (mp 98 °C) melts during the reaction with water, while Li (mp 180 °C) and Ca (mp 851 °C) don't.

In order to understand that the reducing power of alkali metals increases in the order Na < K < Rb < Cs < Li, we may consider the process $M(s) \rightarrow M^+(aq)$ as divided into steps of sublimation of the metal, ionization, and hydration of the ion. While the energies of sublimation and ionization decrease down the group, the hydration energy follows the opposite trend, and for the small Li^+ ion is high enough to more than compensate the other factors.

Another point that needs to be clarified is the thermal stability of salts such as carbonates. The principal factors affecting the thermal stability of carbonates are the charge and radii of the cations which influence the lattice energies. The anions oxide and carbonate have the same charge, but carbonate has a higher radius. Hence, for the same metal ion, the oxide has a higher lattice energy. Therefore, for cations with a high charge and/or small radius, the oxide becomes increasingly more stable with respect to the carbonate, and the carbonate decomposes at a lower temperature. Thus, Li_2CO_3 is the alkali metal carbonate more easily decomposed. By assuming a link between the ease of decomposition of metal carbonates and the activity series of metals, it has been (wrongfully) concluded that $Al_2(CO_3)_3$ should be less readily decomposed than the carbonates of zinc, iron, and copper (*1*). In fact, the high charge and small radius of the Al^{3+} cation, make $Al_2(CO_3)_3$ so unstable with respect to Al_2O_3 that the carbonate is not known.

Although it is reasonable to relate the activity of the metals with the stability of metal oxides (*1*), it should be remembered that the activity series of metals refers to reactions in aqueous solutions, while the decomposition of oxides into metals plus oxygen is a solid state reaction. In the former case the hydration energy of the ions plays a significant role, while in the second case the lattice energy of the oxide is the magnitude to be considered. Therefore, some discrepancies are found between the activity series of metals and the thermal stability of oxides. Indeed, CaO is the most stable metal oxide in a broad temperature range. The stability of metal oxides at different temperatures is clearly displayed in Ellingham diagrams (*5*). Indeed, the Ellingham diagram shows that Ag_2O is easily decomposed to metallic

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silver on heating. Nevertheless, Ag_2O is thermodynamically stable at room temperature and it is not correct to state that it is so unstable that it may explode (*1*).

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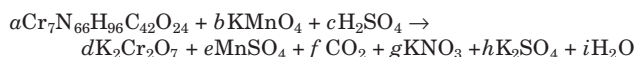5. Sharpe, A. G. *Inorganic Chemistry*, 3rd ed.; Longman: London, 1992; p 307.

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Redox Challenges

A recent article (*J. Chem. Educ.* **1995**, *72*, 1125) challenges students and faculty to balance three oxidation–reduction equations. As pointed out by the author, the first two are relatively easy. The third is more challenging, since several species are changing oxidation number and may well be beyond the ability of most good beginning chemistry students. For the more mathematically inclined among one's beginning students, however, there is a relatively straightforward approach utilizing nothing more complex than the conservation of atoms and the use of integers in balancing chemical equations.

Rewrite the formula of the coordination compound $[Cr(N_2H_4CO)_6]_4[Cr(CN)_6]_3$ as $Cr_7N_{66}H_{96}C_{42}O_{24}$. Let a, b, c, d, e, f, g, h, and i be the coefficients in the equation:

$$aCr_7N_{66}H_{96}C_{42}O_{24} + bKMnO_4 + cH_2SO_4 \rightarrow$$
$$dK_2Cr_2O_7 + eMnSO_4 + f\,CO_2 + gKNO_3 + hK_2SO_4 + iH_2O$$

Write conservation relationships for all atoms as follows:

Element	No. reactant atoms	=	No. product atoms
Cr	$7a$	=	$2d$
N	$66a$	=	g
H	$96a + 2$	=	$2i$
C	$42a$	=	f
O	$24a + 4b + 4c$	=	$7d + 4e + 2f + 3e + 4h + i$
K	b	=	$2d + g + 2h$
Mn	b	=	e
S	c	=	$e + h$

Additional relationships follow:
(1) $a = (2/7)d = (1/66)g = (1/42)f$
(2) $g = (66/42)f$
(3) $d = (7/84)$
(4) $b = 2d + g + 2h = 2(7/84)f + (66/42)f + 2h = (146/84)f + 2h = e$
(5) $c = e + h = (146/84)f + 2h + h = (146/84)f + 3h$
(6) $i = 48a + c = (48/42)f + (146/84)f + 3h = (242/84)f + 3h$
(7) $24a + 4b + 4c = 7d + 4e + 2f + 3g + 4h + i$

Therefore,
$$24(1/42)f + 4e + 4(146/84)f + 4(3h) =$$
$$7(7/84)f + 4e + 2f + 3(66/42)f + 4h + (242/84)f + 3h$$
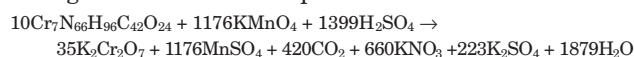
Collecting terms in f and h gives:
(8) 5h = [(855 - 632)/84]f = 223f. Thus, h = (223/420)f.

We can now assign values to the coefficients. If h is to be an integer, the smallest possible value for f is $f = 420$. This gives $h = 223$.

Further,

$a = (1/42)f = (1/42)420$; $a = 10$.
$d = (7/84)f = (7/84)420$; $d = 35$.
$g = (66/42)f = (66/42)420$; $g = 660$.
$b = e = (146/84)f + 2h = (146/84)420 + 2(223)$; $b = e = 1176$.
$c = e + h = (146/84)f + 3h = (146/84)420 + 3(223)$; $c = 1399$.
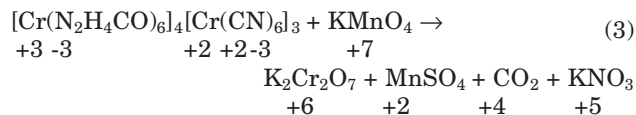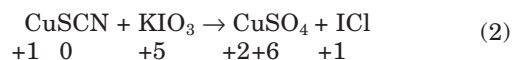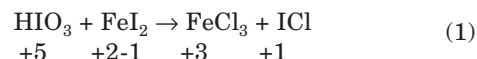$i = (242/84)f + 3h = (242/84)420 + 3(223)$; $i = 1879$.

This gives the balanced equation:
$$10Cr_7N_{66}H_{96}C_{42}O_{24} + 1176KMnO_4 + 1399H_2SO_4 \rightarrow$$
$$35K_2Cr_2O_7 + 1176MnSO_4 + 420CO_2 + 660KNO_3 + 223K_2SO_4 + 1879H_2O$$

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I was intrigued by the article "Redox Challenges" in the December 1995 issue of the *Journal* (*1*). What were described as "difficult" and "incredibly challenging" redox equations turned out to be straightforward and at worst a little tedious when balanced by means of oxidation numbers. I succeeded in balancing all three in less than 20 minutes, even while being interrupted several times to answer students' questions. Partial equations, with only those species shown in which oxidation numbers change, are

$$HIO_3 + FeI_2 \rightarrow FeCl_3 + ICl \qquad (1)$$
$$+5 \qquad +2\text{-}1 \qquad +3 \qquad +1$$

$$CuSCN + KIO_3 \rightarrow CuSO_4 + ICl \qquad (2)$$
$$+1 \ \ 0 \qquad +5 \qquad +2 +6 \qquad +1$$

$$[Cr(N_2H_4CO)_6]_4[Cr(CN)_6]_3 + KMnO_4 \rightarrow \qquad (3)$$
$$+3 \text{ -}3 \qquad\qquad +2 +2\text{-}3 \qquad +7$$
$$K_2Cr_2O_7 + MnSO_4 + CO_2 + KNO_3$$
$$+6 \qquad\quad +2 \qquad +4 \qquad\quad +5$$

In eq 1, a decrease in oxidation number of 4 (1 I, $+5 \rightarrow +1$) is compared to an increase in oxidation number of 5 (1 Fe, $+2 \rightarrow +3$ and 2 I, $-1 \rightarrow +1$ each). This requires coefficients of 5 on HIO_3 and 4 on FeI_2 so that the total increase in oxidation number equals the total decrease in oxidation number. The equation can then be balanced easily by inspection.

In eq 2, a decrease in oxidation number of 4 (1 I, $+5 \rightarrow +1$) is compared to an increase in oxidation number of 7 (1 Cu, $+1 \rightarrow +2$ and 1 S, $0 \rightarrow +6$). This requires coefficients of 4 on CuSCN and 7 on KIO_3, followed by a simple inspection process to finish balancing the equation. Oxidation numbers for CuSCN were chosen so that there is no change in the oxidation numbers of C and N

when compared to the product HCN (not shown above). This illustrates the often arbitrary nature of oxidation number assignments and the fact that they can be assigned in any way we like for the purposes of balancing equations as long as certain basic rules are followed (such as the sum of the oxidation numbers in SCN⁻ must equal -1).

The "exceedingly difficult" Equation 3 is just a little tedious, and has large coefficients, but is no different than Equations 1 and 2. The decrease in oxidation number of 5 (1 Mn, +7 → +2) is compared to an increase in oxidation number of 588 (4 Cr, +3 → +6 each; 3 Cr, +2 _ +6 each; 66 N, -3 → +5 each; and 18 C, +2 → +4 each). This requires coefficients of 588 on $KMnO_4$ and 5 on the reactant being oxidized. The equation can then be balanced with a coefficient of 17.5 on $K_2Cr_2O_7$, and the coefficients can be doubled to eliminate the fraction.

After reading the article, I supposed that the "freshman chemistry methods" mentioned by the author consisted of the ion-electron or half-reaction method. This assumption has since been confirmed (2). I agree wholeheartedly that attempting to balance eq 3 by that method would be exceedingly difficult. The half-reaction method works well for reactions occurring in aqueous solution, especially those already written in net ionic equation format. For equations such as those discussed above, the oxidation number method is clearly superior. It is unfortunate that so few textbooks present it.

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Roland Stout Replies:

Regarding the letter to the Editor from Noel S. Zaugg: He is correct, the method I used in balancing my "Redox Challenges…" (*J. Chem. Educ.* **1995**, 72, 1125) is the half-reaction or ion-electron method. I was remiss in not saying so. As Zaugg says, other methods are easier and more quickly applied, and yield the correct answer. I note, however, that most freshman chemistry texts use oxidation number approach (often called inspection) for simple problems and the half-reaction method for more complex reactions. The half-reaction method is a structured approach which, once learned, can be systematically applied. The oxidation number method looks to many students to be trial and error. It requires more knowledge and insight to apply.

Zaugg points out that oxidation numbers may be assigned in any way we like as long as certain basic rules are followed. I call oxidation numbers bookkeeping devices personally, but their choice is not arbitrary. Oxidation numbers and the changes in them are related to the oxidation state of atoms and how many electrons are transferred in some process. If we choose oxidation numbers merely to balance a reaction we risk loosing sight of the underlying chemistry. If your purpose is purely to balance the reaction, this may be of little consequence. If your purpose is to teach, the choice of oxidation numbers is everything. They are the link between a chemical equation and the chemistry it represents.

Which method to choose? Several will work perfectly well, the choice depends on your purpose in balancing the reaction. In retrospect, perhaps the "Challenge" presented in my paper was in finding an easier, faster way. Zaugg (and others) have done that.

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Undergraduate Research

I was pleased to see the article, "The Past Two Decades of Undergraduate Research" by Spencer and Yoder (*J. Chem. Educ.* **1995**, 72, 146). This work and their earlier contributions are valuable in drawing attention to the state of undergraduate research and its role in educating and motivating chemistry students to pursue a graduate degree. However, I fear that the authors have unintentionally given the impression that they have provided an exhaustive evaluation of the publication records of undergraduate institutions during the past two decades. This impression is related to statements such as "We have continued to monitor the progress in research activity and Ph.D. production at undergraduate institutions." The current paper, in fact, identifies a certain group of institutions that met criteria related to their earlier work and does not freshly evaluate the situation. They do add schools (four) "that were identified as having significant research activity but not meeting the criteria for inclusion in the original survey" and this statement reinforces the view that they have truly monitored the progress in research activity. I was startled to read this since I was fairly confident that two institutions that I worked at during those two decades, Smith and Wellesley, should have comfortably made this current survey. To check my view, I searched *Chemical Abstracts* (through STN) for publications listing both Smith College and chemistry department in the appropriate record field. I found that there were 23 publications from our department during the period 1977–1992. In checking each citation, I found that this quick search missed several publications so that the actual number is somewhat higher. Therefore, it seems that Smith College would have fallen around the middle of the list of fifty-two institutions had it been included at all. In an identical search for the publications of the Wellesley College publications during the period in question. It is especially unfortunate that these excluded schools are both women's colleges.

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My main point here is that some care should be exercised in interpreting this current survey. However, one might also dispute the "conclusion that, in general, undergraduate research has not accelerated significantly (at least as measured by the number of publications) over the past 10–15 years [and this] is a bit disconcerting given national promotion of undergraduate research by the Council of Undergraduate Research and the National Science Foundation in its RUI program." It could be argued that a study that is limited to institutions that have had reasonable records throughout the period in question misses the institutions that are likely to show the most dramatic improvement.

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Phase Diagrams

I read with interest and appreciation the useful article "The Solid–Liquid Phase Diagram Experiment" by K. R. Williams and S. E. Collins in *J. Chem. Educ.* **1994**, *71*, 617. However, a detail in Fig. 5 appears to be wrong: the finite slope of the equilibrium curves as the composition approaches the value corresponding to the congruently melting addition compound StTNF. The slope of the liquidus curve should instead change continuously, and have a value of zero at such a composition; see A. F. Berndt, *J. Chem. Educ.* **1969**, *46*, 594, and the detailed account of the topic by A. F. Berndt and D. J. Diestler, *J. Phys. Chem.* **1968**, *72*, 2263.

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Inner City Students

I would like to take issue with the implications of the article "Comparing Achievement of Inner City High School Students in Tradition versus STS Chemistry Courses" (*J. Chem. Educ.* **1994**, *71*, 501). The last paragraph implies that Afro-American students are incapable of abstract thinking as referred to on page 502 of the article. Also, while it is true that some Afro-American students and other minorities do poorly in schools, the article brands all inner city Afro-American students as underachievers.

This study was one in only one inner city school for one year only. This hardly represents a scientific study. The authors should have done some of the studies that were given in the recommendations before publishing a "scientific" paper that blankets all Afro-American students as incapable of doing "college preparatory work".

I have taught traditional chemistry for over 20 years in a predominately Caucasian suburban school system and I have seen many Caucasian, some Asian, and some Afro-American students who would benefit from the STS approach. I also have had many of all three categories who did well in traditional chemistry and went on to successful scientific careers.

A well respected journal such as yours should avoid publishing such articles until more research is done.

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Visualizing the S_N2 Inversion

Sands, Dressman, and Wyatt (*J. Chem. Educ.* **1995**, *72*, 428) recently presented a simple, clever way to visualize the S_N2 inversion process using an easily constructed paper model. I would like to suggest a slight modification of this construction which allows students to relate the inversion motion to the trajectory of the approaching nucleophile and also allows visualization of the resulting configurational change.

First, align the long end of the model's center strip in the direction of the triangles. Then darken the strip up to the end designated nucleophile (NUC) to indicate a region of minimal interaction. Now, by moving the strip, representing the approaching nucleophile and receding leaving group, in the direction of the flip rather than against it (down in the figure) the inversion process is seen to be induce as the new bond is made. Bond elongation, breaking, and departure of the leaving group are also clearly represented as the dark nonbonding region shifts. By assigning CIP priority numbers to the triangle corners [(NUC) = 3D (LG) = 3D highest priority i.e. halide] the R–S configurational change can also be appreciated.

It should be emphasized to students that, in this model, the atoms (or groups) reside on the triangle corners, which is different from visualizing attached groups at the vertices of a tetrahedron.
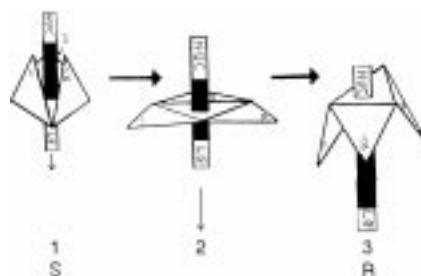
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