## Chemical games to improve communication skills

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In his letter in the April issue of University Chemistry Education White ${ }^{1}$, highlighted his use of a mystery molecule game to encourage students to apply useful conceptsto unknown structures. Business games ${ }^{2}$ are well developed in education as a means of increasing student participation and active thinking, denying them the passive role they so often adopt. Games are adept at reinforcing or revising simple principles, particularly with new undergraduates where an additional aim is to cement group dynamics. Such a situation exists, for example, in the Open University's ST240 Residential School which lasts for only three days, and where many students have to learn quickly in an unfamiliar laboratory situation. One of us has described ${ }^{3}$ a series of experiments which have a significant games element, which requires groups to interact strongly, and are used prior to the main laboratory work. Some games can be quite sophisticated, for example, the elegant Hwuche Hwuche bark, devised by Bailey ${ }^{4}$, which he describes as a business game with real chemical problems ending in student presentations.
One game that we have used is 'The Element Game', which does require some basic know ledge of elemental properties. 'Before you meet your group, w rite the names of selected elements onto post-its or pieces of paper that can be sellotaped onto peoples' backs. Get your group into teams of five or six and firmly attach the element name to each person without their seeing its identity.The rest of the team have to convey the identity of the element by non-verbal means!' Although its use is predominantly in the form of an ice-breaker, when students come together for the first time, it does allow the organiser to gain some useful information about the state of know ledge of students prior to embarking on a course in, say, inorganic chemistry, as well as their ability for lateral thinking. There are obvious variations on the game to fit with other branches of chemistry (using organic structures, analytical techniques etc.)
Comments on the use of games would be appreciated to reinforce or contradict our view that games do have a useful role to play in developing key skills, and a

## Letters

positive attitude to learning. Information about other games will be published in due course.

1. White, HB 1998 Mystery molecules or what's in a name? U Chem Ed 234
2. Gamesand Smulationsfor Business 1995 the Simulation and Gaming Yearbook (ed. D Saunders) 3 (Kogan Page, London)
3. Wallace, RG 1995 Egg races $1-4$ in ScienœSupplementary Material, ST 240 RSER1 Our Chemical Environment(Open University Press, Milton Keynes)
4. Bailey,P 1996 Proceedings,Variety in Chemistry Teaching 1996 (eds. CJ Garratt and T Overton) (Royal Society of Chemistry)

Problems with small numbers
From Dr R Greaves, Department of Chemistry, University of York, York, YO10 5DD

While I was demonstrating in an undergraduate practical I was presented with the following apparent paradox.The student correctly pointed out that the solubility product of $\mathrm{Fe}(\mathrm{OH})_{3}$ is $2 \infty 10^{-39}$. In pure aqueous solution the concentration of hydroxide ions is $10^{-7}$ $\mathrm{mol} \mathrm{dm}{ }^{-3}$ (from the ionic product of water).This would mean that $\left[\mathrm{Fe}^{3+}\right]$ is equal to $2 \infty 10^{-18} \mathrm{~mol} \mathrm{dm}^{-3}$ in a saturated solution. The student further pointed out that in $1 \mu \mathrm{l}$ of solution this would correspond to 1.2 ions of $\mathrm{Fe}^{3+}$. It had occurred to the student that this would mean that $0.5 \mu \mathrm{l}$ of this solution would therefore either contain 0 or 1 ion of $\mathrm{Fe}^{3+}$. With a single $\mathrm{Fe}^{3+}$ ion in $0.5 \mu$ l the solubility product would be exceeded! The student asked me to confirm his conclusion that the $\mathrm{Fe}(\mathrm{OH})_{3}$ would precipitate so that it is impossible to obtain a solution of $0.5 \mu \mathrm{l}$ of $\mathrm{Fe}(\mathrm{OH})_{3}$. 1 thought it more likely that the absence of a nucleation site would prevent precipitation, so that the result would be a super-saturated solution. Was I right? Or is there some other theory which explains why normal laws of chemistry do not apply to very small numbers? There must be other similar
examples. I feel that students would learn something useful about chemistry by thinking about them. But how do we give such apparent paradoxes a meaning?

Titration formulae - a universal approach

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When considering the determination of a titration formula relating the volume of added base to hydrogen ion concentration it is usual to consider four different types of titration, namely strong acid/strong base, strong acid/weak base, etc., as separate cases (e.g. ${ }^{1,2,3,4}$ ). How ever, the concepts of 'strong' and 'weak' acids and bases are limiting cases in a continuum, and therefore this definition of four types of titration is rather arbitrary. It may be that university students find it easier to understand four limiting cases rather than a single general case, but it is important that they appreciate that these are indeed limiting cases of a continuum of titrations, and that all four cases are governed by a universal formula relating $\left[\mathrm{H}^{+}\right]$to the volume of titrant.
For monoprotic acids and bases the universal formula can readily be derived from the following equations:
$K_{a}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}$
$\mathrm{K}_{\mathrm{b}}=\frac{\left.\mathrm{BB}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{BO}^{-} \mathrm{H}\right]}$
$\left[\mathrm{H}^{+}\right]+\left[\mathrm{B}^{+}\right]=\left[\mathrm{OH}^{-}\right]+\left[\mathrm{A}^{-}\right]$
$\left[A^{-}\right]+[H A]=\frac{C_{a} V_{a}}{V_{a}+V_{b}}$
$\left[\mathrm{B}^{+}\right]+[\mathrm{BOH}]=\frac{\mathrm{C}_{\mathrm{b}} \mathrm{V}_{\mathrm{b}}}{\mathrm{V}_{\mathrm{a}}+\mathrm{V}_{\mathrm{b}}}$
$\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]=\mathrm{K}_{\mathrm{w}}$
where $K_{a} C_{a}$ and $V_{a}$ denote the dissociation constant, the concentration and the volume of acid HA, respectively, and similarly for the base BOH , and where $K_{w}$ is the ionic product of $w$ ater. Combining equations (1)-(6) gives the following formula
of added base $\mathrm{V}_{\mathrm{b}}$ (or acid $\mathrm{V}_{\mathrm{a}}$ ) for a given hydrogen ion concentration $\left[\mathrm{H}^{+}\right]$. Alternatively, by rearrangement it can be used to calculate $\left[\mathrm{H}^{+}\right]$for any value of $\mathrm{C}_{\mathrm{a}}$ and $\mathrm{C}_{\mathrm{b}}$.
In the limiting case of a weak acid
$K_{a} \ll 1$, so that the term $1 / K_{a} \gg 1$ in the formula. For the limiting case of a strong acid $K_{a} \gg 1$, so that the term $1 / K_{a} \ll 1$ in the formula. Similar remarks apply to the base, and applying these limiting cases in equation (7) gives the separate cases that are usually quoted. For example, for the limiting case of a strong acid/strong base titration we have $1 / K_{a} \ll 1$ and $1 / K_{b} \ll 1$, and hence equation (7) becomes
$\mathrm{V}_{\mathrm{b}}=\mathrm{V}_{\mathrm{a}} \frac{\left(\mathrm{K}_{\mathrm{w}}-\left[\mathrm{H}^{+}\right]^{2}+\mathrm{C}_{\mathrm{a}}\left[\mathrm{H}^{+}\right]\right)}{\left(\mathrm{C}_{\mathrm{b}}\left[\mathrm{H}^{+}\right]+\left[\mathrm{H}^{+}\right]^{2}-\mathrm{K}_{\mathrm{w}}^{-}\right)}$
Note that equation (8) can be rearranged to give the quadratic equation
$\left[H^{+}\right]^{2} \underset{\left(\mathrm{C}_{\mathrm{a}} \mathrm{V}_{\mathrm{a}}-\mathrm{C}_{\mathrm{b}} \mathrm{V}_{\mathrm{b}}\right)}{\left(\mathrm{V}_{\mathrm{a}}+\mathrm{V}_{\mathrm{b}}\right)}\left[\mathrm{H}^{+}\right]-\mathrm{K}_{\mathrm{w}}=0$

Given that $\mathrm{K}_{\mathrm{w}} \ll 1$ and that $\left[\mathrm{H}^{+}\right]=$
$\mathrm{K}_{\mathrm{w}}$ when $\mathrm{V}_{\mathrm{b}}=\mathrm{C}_{\mathrm{a}} \mathrm{V}_{\mathrm{d}} / \mathrm{C}_{\mathrm{b}}$, the positive root of the quadratic equation approximates to
$\frac{\mathrm{C}_{\mathrm{a}} \mathrm{V}_{\mathrm{a}}-\mathrm{C}_{\mathrm{b}} \mathrm{V}_{\mathrm{b}}}{\mathrm{V}_{\mathrm{a}}+\mathrm{V}_{\mathrm{b}}}$ for $\mathrm{V}_{\mathrm{b}}<\mathrm{C}_{\mathrm{a}} \mathrm{V}_{\mathrm{a}}$
and to
$\underset{\left(C_{b} V_{b}-C_{a} V_{a}\right) /\left(V_{a}+V_{b}\right)}{ }$ for $V_{b}>C_{C_{a} V_{a}}^{C_{b}}$

These expressions are in agreement with the result obtained by calculating $\left[\mathrm{H}^{+}\right]$as the number of moles of excess acid $\mathrm{C}_{\mathrm{a}} \mathrm{V}_{\mathrm{a}}-\mathrm{C}_{\mathrm{b}} \mathrm{V}_{\mathrm{b}}$ divided by the total solution volume $\mathrm{V}_{\mathrm{a}}+\mathrm{V}_{\mathrm{b}}$, or the result obtained by calculating $\left[\mathrm{OH}^{-}\right]$as the number of moles of excess base $\mathrm{C}_{b} \mathrm{~V}_{\mathrm{b}}-\mathrm{C}_{\mathrm{a}} \mathrm{V}_{\mathrm{a}}$ divided by the total solution volume $\mathrm{V}_{\mathrm{a}}+\mathrm{V}_{\mathrm{b}}$, and then using $\left[\mathrm{H}^{+}\right]=\mathrm{K}_{\mathrm{w}} /\left[\mathrm{OH}^{-}\right]$.). Similarly, for the limiting case of a weak acid/strong base titration we have $1 / K_{a} \gg 1$ and $1 / K_{b} \ll 1$, and hence equation (7) becomes
$V_{b}=\frac{V_{a}\left(\left(1+\left[H^{+}\right] / K_{a}\right)\left(K_{w}-\left[H^{+}\right]^{2}+C_{a}\left[H^{+}\right]\right)\right.}{\left(1+\left[\mathrm{H}^{+}\right] / K_{a}\right)\left(\mathrm{C}_{b}\left[\mathrm{H}^{+}\right]+\left[\mathrm{H}^{+}\right]^{2}-\mathrm{K}_{w}\right)}$
(9)

Figure 1: Titration curves for different values of $K_{a}$ and $K_{b}$

(Note that equation (9) can be rearranged as a cubic equation.)
The other two limiting cases follow in a similar way.
For a given $\mathrm{pH},\left[\mathrm{H}^{+}\right]=10^{-\mathrm{pH}}$ can be calculated, and hence the corresponding added volume of base $\mathrm{V}_{\mathrm{b}}$ can be determined from equation (7).
The pH can then be plotted against $\mathrm{V}_{\mathrm{b}}$ (or $\mathrm{V}_{\mathrm{a}}$ ) with pH on the vertical axis in the usual way.The Figure shows three specific examples of titration curve obtained in this way.
I suggest that students benefit from meeting one or more of the limiting cases first, preferably through examples, and including the simplest case of strong acid/ strong base in the usual way.A universal approach can then be considered as outlined above. Similar results are possible for polyprotic cases.
I suggest this approach is of pedagogical value, especially for the theoretical prediction of different titration curves. In
particular, for any value of $\left[\mathrm{H}^{+}\right]$the volume of titrant (acid or base) can be calculated, and $\left[\mathrm{H}^{+}\right]$can be calculated for any value of $C_{a}$ or $C_{b}$. This can provide the student with a better insight in the rather sophisticated topic of different titrations, as well as checking experimental results against the theory.

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2. de Levie, RJ 1997 Principles of QuantitativeChemical Analysis (McGraw -Hill, New York)
3. Atkins, PW 1990 Physical Chemistry (Oxford University Press, Oxford)
4. de Levie, RJ 1993 Explicit expressions of the general form of the titration curve in terms of concentration J Chem Ed 70 209-217
