Contents

Contributions on any matter of interest to second-level chemistry teachers are welcome. Normally the results of research (chemical or educational) are **not** published, except in a general form or as a review. Articles should be submitted electronically (email or disc) to **peter.childs@ul.ie** together with a printed copy.
For subscription details etc. see inside back cover.

Cover design: Ray Boyce, Alphaset, Limerick ray@alphaset.ie
Cover photo: **Editor: Peter E. Childs peter.childs@ul.ie**
Assistant editors: Marie Walsh, Maria Sheehan, Sarah Hayes, Anne O'Dwyer

Cover photo: Beulah Mcmanus in action at the 8th Chemistry Demonstration Workshop in UL (Photo: SSPC/UL)

Editorial #102

Change is coming

Since I wrote the last editorial we have a new Minister of Education: Ruari Quinn resigned and was replaced by Jan O'Sullivan.

The new minister inherits a full agenda and some tricky problems, particularly the teachers' boycott of the new junior cycle proposals. This is a major change in the existing system and was being rushed through without regard for the teachers' and parents' views. At the very least the new minister should slow down the process, open the consultation and delay the implementation. The timescales are too short, the CPD provision is inadequate and the concerns of teachers and parents about certification need to be taken on board. There are also resource implications and the problem of introducing a new style of teaching and learning without adequate CPD. The new English course is due to start in September and Science in 2015. The new Science specification is not yet published and so there is less than a year to prepare for its introduction, run CPD courses, get new textbooks written etc. This timescale is much too short. Also the report of the STEM Review Group is not due out until the end of the summer. In any rational system one would wait for the recommendations of this before changing and introducing a new junior Science syllabus. Also until junior Science is sorted out there is no point finalising the new LC science subjects, so that they match with the new Junior Cycle course and ensure a smooth transition. Once again, curriculum development is being done from the top-down rather than from the bottom-up. Some of these issues are taken up later in this issue.

End of an era

The production of second-level science teachers in Thomond College of Education began in 1972, which offered a Physical Education degree, with Chemistry as one of the electives. Dr John O'Halloran was responsible for the Chemistry course and he was joined in 1978 by your editor, and later by Dr Matthew Fanning. The PE + Chemistry courses was followed in the 1980s by General and Rural Science, which later turned into the BSc Biological Sciences (Biology and Ag. Science with Chemistry or Physics) and later followed by the BSc Physical Sciences (Chemistry and Physics). All these courses were taken into the University of Limerick when it merged with Thomond College in 1991. This PE + Chemistry course is thus the reason your editor is in Ireland and why *Chemistry in Action!* exists.

After over 40 years of producing PE teachers who can also teach Chemistry, the elective is being cancelled from Sept. 2015, so this year's intake (Sept. 2014) will be the last one and they will graduate in 2018. The elective was never very popular, attracting between 1 and 10 students a year, as it involved more contact hours and more work, although science with PE is a good combination. The PE course always attracted high calibre students and the points' cut-off is currently 495. Over the years the course has produced some fine teachers, and many of them are in senior positions (including principal) in Irish schools, and around the world.

Outcomes alone are not enough

At the moment the new LC science courses only exist as a set of learning outcomes, despite major concerns being expressed by the ISTA and other bodies. You cannot have a curriculum which is only specified by its outcomes. The new courses have been approved by the NCCA Council and detailed specifications are promised later. The ISTA commissioned a report from Professor Aine Hyland on the issue, which was launched in Galway in April at the ISTA conference. (This is will be discussed in issue #103.) The basic conclusion, based on a small survey of international practice, is that no-one issues a syllabus which is **only** specified by its learning outcomes. To be useful and practicable a curriculum also need the content to be specified, as well as the assessment and the recommended pedagogical approach. What is lacking in all of the three science specifications is the content to flesh out the outcomes. In the past courses were often just a list of content to be covered, indicating the depth of treatment. More recent courses have specified student achievements in terms of learning outcomes (or objectives). In reality courses are developed by an inter-play between content and outcomes, but both are needed for a workable curriculum. It is impossible to judge the outcomes properly unless one also knows the detail of the content and depth of treatment.

Peter E. Childs

Hon.Editor

Education News and Views

The Editor welcomes contributions and news of interest to chemistry teachers in this section.

New Junior Science Team appointed

The draft science specification for the new Junior Cycle Student Award (JCSA) will be published for consultation early in the new school year, after their approval by the NCCA. (http://www.juniorcycle.ie/) There will be a 6 week period for response and comments on the new syllabus, which will then be revised and issued to schools. The new science course is due to start in Sept. 2015, unless it is delayed or derailed by the teachers' boycott. A support team of 5 seconded science teachers has been appointed to start the new course.
(http://www.juniorcycle.ie/JCT-Support-Service)

One day of CPD per year has been allocated for three years to support the new course. This would amount to at most 18 hours of CP in total, which is totally inadequate preparation for a new course, new approach and new form of assessment. International studies suggest that at least 80 hours of CPD is needed to support effectively major curriculum change.

The other major concern about the new course is the speed of introduction and the lack of time for real consultation and preparation. By the time the new syllabus is issued to schools there will be less than a school year before the course is due to start. 6 weeks isn't enough in the middle of the academic year for a proper assessment and response to the new syllabus. This should all have been happening a year ago if the science course is due to be introduced in Sept. 2015. There is also the lead time needed to produce new textbooks to support the new course, although I know that textbook authors are already in action.

There is a strong case for delaying the introduction of the new Junior Cycle Award to allow for proper preparation and resourcing of the new courses. Once again new courses are being rushed in to suit a political timetable, without being properly thought out and prepared for.

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New RSC education support for Ireland

The Royal Society of Chemistry has had an Education Coordinator for Ireland for some time, based in Belfast. The job was initially done by Iris Suitor, who was replaced by Angela McKeown, and you may have met them at ChemEd-Ireland and other events, running RSC workshops. The RSC has now decided to expand their support for chemical education. Angela McKeown has become Programme Coordinator, based in Queen's University Belfast, and the RSC has decided to appoint two Education Coordinators – one based in the North at QUB and one based at a higher education institution in the Republic. Institutions in the Republic were asked to submit an expression of interest to host the Education Coordinator by August 15th. Sometime after October the host institution will be appointed and they will then be responsible for advertising and recruiting an Education Coordinator for the Republic. The appointment will run from 2015 for three years. Watch this space to find out who the Education Coordinators are and where the one will be located in the Republic. The appointment will provide enhanced support and resources for Irish chemistry teachers.

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Stop press:

Due to the large number of articles for the ChemEd-Ireland 2013 Proceedings, one of the largest ever, a number of items of Education News & Views had to be left over for the next issue (#103).

In the next issue we hope to hope to feature the new LC chemistry syllabus and the Hyland Report; details of the new science specification for the junior cycle; and the Report of the STEM Review Group.

In addition there will be a number of other articles and regular features, which had to be left out of this issue due to lack of space.

Proceedings ChemEd-Ireland 2013

In the Spring issue of *Chemistry in Action!* we usually print the Proceedings of the previous year's ChemEd-Ireland conference, both to remind those who attended of the talks and workshops, but also more importantly to provide a permanent record and make the talks available to a much wider audience. There is no beating the personal experience of attending, as Mary Mullaghy's piece below reminds us, but the next best thing is to read the articles. Thanks are due to the speakers who sent in material for the Proceedings and to Marie Walsh, the main organizer of the 2013 conference, for chasing up the articles. She wrote a report on the conference in the last issue of *Chemistry in Action!* (#101). ChemEd-Ireland 2013 had a good mix of talks and workshops and it was a very productive day. The conferences started in 1982 and ran for 25 years in the University of Limerick. Since 2007 it has moved around various third-level institutions (UCC, DCU, UL, DIT and LIT), alternately between the East and West coasts. This year it is back to Dublin and Claire McDonnell at DIT is the main organiser and the conference will be held on Saturday 11th October, a week earlier than usual. In 2015 it is back to Cork and Declan Kennedy and his team in UCC.

If you are reading this and have never been to a ChemEd-Ireland conference then you should put it in your diary for 2014: it is cheap; it is a good day out; it provides an intellectual stimulation at the start of a new school year; it is a great opportunity to meet like-minded colleagues from other schools; there are usually great resources available; the event is a great buzz and it only takes one day out of your life! **Can you afford to miss it?**

It is not always possible to print every talk, as we depend on the goodwill and hard work of the speakers to provide a written text. Over the years the Proceedings have reported and collected some very valuable material on the teaching and learning of chemistry. The talks highlighted below in the programme, can be found in the Proceedings. Thanks to all the authors for their contributions.

Programme ChemEd-Ireland 2013

8.30 a.m. Registration
9.00 a.m. Welcome to LIT - Paschal Meehan, Head of Faculty of Applied Science Engineering and Technology, LIT and Michelle McKeon-Bennett, Head of Department of Applied Science, LIT
SESSION 1: Chair Marie Walsh (LIT)
9.15 - 9.45 a.m. ***Assessment of Leaving Certificate Chemistry***
Fiona Desmond, State Exams Commission, State ExaminationsCommission
9.45 - 10.30 a.m. ***The use of mobile phones in the Chemistry class as a tool for active learning?***
Maria Sheehan & Mick O'Callaghan, PDST
10.30 - 10.45 a.m. ***Resources for Chemistry teaching*** (RSC sponsored)
Peter Hoare, Newcastle University
10.45 - 11.15 a.m. Coffee and information stands
SESSION 2: Workshops and Demonstrations
11.15 - 12.15 p.m. Workshops round 1
12.15 - 1.15 p.m. Workshops round 2
Each participant could do two workshops from the 4 listed below.
1. Lab 8A703 ***Bonding and reactions workshop***, Iris Suitor, Royal Society of Chemistry
2. Lab 8A706 ***Environmental Chemistry,*** David Sutton, Limerick Institute of Technology
3. Lab 8A701 ***Molecular models in organic chemistry,*** Anne O'Dwyer and PeterChilds, University of Limerick
4. Computer lab: ***Chemistry teaching resources***, Peter Hoare, Newcastle University
1.15 - 2.10 p.m. LUNCH in canteen
SESSION 3: Chair Billy Madden (LIT)
2.15 - 3.05 p.m. ***A new method of electrolysing water***, Mike Lyons, Trinity College Dublin
3 - 3.20 p.m. ***Integrating Maths in the Junior Science Curriculum***, Grainne Walshe, University of Limerick
3.20 - 3.40 p.m. **The New Organic Practical for Leaving Cert Chemistry - Oxidation of Phenylmethanol* (with resource sheet developed by Michael Seery DIT), Brendan Duane PDST
3.40 - 4 p.m. *Molecules from the Sea*, Danny Walsh, Limerick Institute of Technology
4 - 4.35 p.m. ***Leaving Cert Chemistry practicals - how might they be assessed*?**, Declan Kennedy, University College Cork
(Talks in ***bold*** are included in these Proceedings.)
* This has already been published in issue # 100

My ChemEd Experience 2013

Mary Mullaghy

On Saturday 19th October I attended the Annual ChemEd Conference in Limerick. This was the first time that Limerick Institute of Technology acted as host. Member of the LIT academic staff and wonder woman, Marie Walsh, who was a key organiser behind the scenes for years, when the conference was run in UL, fronted proceedings on this occasion.

While I stood chatting to the original founder, Dr Peter Childs, about the forthcoming 100th edition of Chemistry in Action, it suddenly dawned on me that it was 20 years ago that I first started coming to this annual get together for chemistry teachers. In that time some things hadn't changed. Inevitably it was a glorious sunny day; there were many familiar faces at the selection of workshops and lots of up to the minute cutting-edge chemistry. However, the format had evolved somewhat, there was no afternoon coffee, but to my surprise that didn't bother me as much as I had anticipated, as the sessions were short and snappy and time just seem to evaporate. In fact it might have been a clever ruse by the organisers, as a lot of people used to slip away after that coffee break, especially those with 3 or more hours driving ahead of them! However this year anyone who left early, also missed out on generously sponsored spot prizes.

All the plenary sessions were informative and interesting. Dr Fiona Desmond, the newly appointed EAM (Examination & Assessment Manager) for Chemistry, spoke about the Leaving Certificate Chemistry examination and drew our attention to the new circular letter, 0047/2013 'Adjustments to the Leaving Certificate Chemistry Syllabus', which are effective from September 2013 for all students who will sit the Leaving Certificate Chemistry examination in 2015 and thereafter. Brendan Duane and the PDST team will be rolling out the details at in-services nationwide in the Education Centres in November and March, along with a plethora of other stuff such as 'Strategies to Engage' and 'Mobile Phone use in the classroom', which are in tune with the this years ChemEd theme 'New Perspectives for Chemistry Teaching in Ireland'. My personal highlights were 'Molecules from the Sea' by Dr Daniel Walsh from LIT, whose talk about Biologically Active Molecules of Marine Based Origin (BAMMBO), appropriately illustrated the everyday applications of chemistry and 'Bringing the hydrogen economy closer; rusty metal electrodes for electrochemical water splitting' by the exuberant Prof Mike Lyons from CRANN/AMBER at Trinity College.

Next year it is the turn of Dublin Institute of Technology and the dynamic duo, Dr Michael Seery and Dr Claire McDonnell to carry on the ChemEd baton, and I have every faith that they will continue to build on the excellent job done by Marie and her team!

□

Some of the crowds in LIT for ChemEd-Ireland 2013.

Assessment of Leaving Certificate Chemistry by the SEC

Fiona Desmond
Chief Examiner for Chemistry, State Examinations Commission

Introduction

Thanks to LIT staff member Marie Walsh for the invitation to speak to you today and to Ann Culhane, another LIT Chemistry Department staff member and former research comrade of mine, for her warm welcome. I am very pleased to have this opportunity to speak to the Chemistry teachers of Ireland about the State Examinations Commission and my (new) role as Chief Examiner for Chemistry. In this lecture I shall address the following:

- Overview of SEC
- The role of the Chief Examiner
- Chemistry participation & performance rates
- Areas of good and poor candidate performance
- Some advice for 2014
- 2015 examination
- The future……

Overview of SEC

The State Examinations Commission (SEC) is the sole provider of state assessment and certification at middle and end of Irish second level education. As such the SEC, established in 2003, is an independent agency of the Minister of the Department of Education & Skills. Under the umbrella of the Department of Education & Skills, the SEC acts as an *implementation* agency and operates closely with the National Council for Curriculum and Assessment (NCCA) the *advisory* agency, and with the Department of Education inspectorate, the *regulatory* body.

The SEC is largely state funded with some finance coming from students' families through examination fees. The SEC is responsible for the operation of all aspects of the Junior Certificate and the Leaving Certificate examinations (including LCVP and LCA) and this includes the written, oral, aural, practical and coursework components of all examinations. The SEC also provides some professional and trades examinations. Annually the SEC provides examinations to about 110,000 candidates in 750 schools. Preparation of the 2.5 million individual examination components involves about 550 people. The examinations are superintended by about 4700 people and are marked by about 6500 examiners. The SEC compiles issues about 1.2 million results. The SEC has a full-time staff of about 120 administrative officers based in SEC headquarters in Athlone and a full-time staff of 27 Chief Examiners based in different locations around the country and who are responsible for developing the tests. The SEC employs on a part-time basis experts including graphic artists, photographers, actors (to make audio and audiovisual material), translators, printers, etc., to have an input into preparation of examination components.

Clearly the SEC cannot function without the cooperation of school management in providing venues for examinations and handling the entries of candidates for examinations. Furthermore the SEC relies heavily on the 9000 or so part-time staff – mostly teachers who are in possession of the unique skill set to be involved in superintending and marking examinations – i.e. to deliver the examinations.

The SEC is committed to fairness, equity, openness, transparency and inclusiveness in its work. Therefore Irish translations and examinations in Braille or modified in other ways are provided. A range of reasonable accommodations are put in place to assist candidates with specific learning needs. In particular, the Leaving Certificate examinations are high stakes exit examinations that are highly determining of candidate's further education and career options. In 2003 these examinations were benchmarked by (University Central Access

System) UCAS for entry to UK universities and the SEC is committed to maintain year-on-year the standard achieved in this benchmarking process. The SEC is aware of the high degree of public confidence it has earned and is protective of this trust. The work of the SEC is open to public scrutiny and is the subject of sometimes intense coverage in the media. The access of candidates to a multi-layered appeal system (including the viewing of Leaving Certificate scripts by candidates after the issue of results) helps deliver fairness and transparency.

The role of the Chief Examiner

As Chief Examiner for Chemistry, I am responsible for all aspects of preparation of the examination papers at Higher and Ordinary level, the marking process, the appeals process and the preparation of a Chief Examiner's report. I am also the SEC representative of the Chemistry subject development group of the NCCA and contribute to syllabus modification and new syllabus development. Incidentally, I am also Chief Examiner for the Leaving Certificate subject Physics & Chemistry and for three LCA subjects and manage examination component preparation, marking, appeals and reporting for these subjects also.

There is in fact a 20 month lifecycle for a particular Chemistry examination paper (either Higher (HL) or Ordinary (OL)). During that period the initial draft paper is redrafted a number of times. It undergoes scrutiny by subject experts from both Trinity College and the National Universities – university bodies that previously held matriculation examinations. This scrutiny serves three valuable purposes. It allows these two university bodies an opportunity to ensure that the standard of the state second-level exit examination is a sufficiently high standard to serve as a matriculation examination. It gives the examination paper the benefit of the input of third-level subject experts. It provides a communication forum for exchange of concerns and ideas between third level and second level. The draft papers are translated into Irish. The English and Irish are compared and checked. The (hopefully) error free proofs are printed. Further proof-reading of the English and Irish versions takes place. Any errors identified are given in *Errata* lists to be read to candidates on the day of the examination.

In parallel with the examination paper preparation, a draft marking scheme has been prepared. The three hour Chemistry examinations (HL and OL) take place in mid June. The marking conferences take place (late June and early July) where the draft marking scheme is redrafted and fine-tuned. The marking scheme is finalised very early on in the marking when the draft from the marking conference has been applied to a significant number of scripts. The final marking scheme is then translated and the final version is applied to *all* scripts. During the marking process the work of examiners is monitored to ensure adherence to the final marking scheme and to ensure inter-candidate equity. The marking is completed at the end of July. The marks are issued as results to candidates in mid-August. The viewing and appeals processes then occur. In a few cases there may be appeals of appeals and at the end of the cycle appeals to independent scrutineers.

Chemistry participation & performance rates

The uptake of Chemistry has increased (in terms of overall candidate numbers and as a percentage of candidature) during the lifetime of the current syllabus as shown in Table 1. The split between Higher Level and Ordinary Level remains steady at about 83% to 17% as shown in Table 2.

Table 1: Participation Rates, Chemistry 2002-2013

Year	Chemistry Candidates	Total LC cohort	% of total LC cohort
2002	6497	55374	11.7
2003	6698	56237	11.9
2004	7227	55185	13.1
2005	7366	54069	13.6
2006	7071	50995	13.9
2007	6926	50870	13.6
2008	7114	52144	13.7
2009	7403	54196	13.7
2010	7548	54481	13.9
2011	7677	54341	14.1
2012	8086	52589	15.4
2013	8155	52767	15.5

Table 2: HL /OL split, Chemistry 2008-2013

Year	Total	OL	HL	% OL	% HL
2008	7114	1210	5904	17.0	83.0
2009	7403	1366	6037	18.5	81.5
2010	7548	1250	6298	16.6	83.4
2011	7677	1405	6272	18.3	81.7
2012	8086	1381	6705	17.1	82.9
2013	8155	1399	6756	17.2	82.8

The number of female candidates at HL is consistently slightly greater than the number of male candidates. At OL the numbers of male and female candidates are close, and fluctuate slightly from year to year such that boys just outnumber girls and vice-versa. See Table 3.

Table 3: Female/Male split, Chemistry 2008-2013

Year	% OL Female	% OL Male	% HL Female	% HL Male
2008	49.2	50.8	57.6	42.4
2009	50.7	49.3	56.7	43.3
2010	51.0	49.0	57.3	42.7
2011	50.7	49.3	56.3	43.7
2012	48.7	51.3	54.8	45.2
2013	47.9	52.1	54.1	45.9

Thus the participation rate is holding and improving slightly, more than 80% take the subject at Higher Level at examination stage and it is gender neutral.

In terms of performance, recall that there are in fact 28 different categories of achievement in LC Chemistry across 14 sub-grades in each of the two levels Higher and Ordinary as shown in Table 4.

Note that for the purposes of scoring CAO points the grades shown in Table 5 had equal values in 2013.

Table 4: Categories of achievement, HL and OL Chemistry

Higher Level	A 1	A 2	B 1	B 2	B 3	C 1	C 2	C 3	D 1	D 2	D 3	E	F	NG
Ordinary Level	A 1	A 2	B 1	B 2	B 3	C 1	C 2	C 3	D 1	D 2	D 3	E	F	NG

Table 5: Grades of equal CAO merit.

CAO points	60	50	45
Higher Level	C3	D2	D3
Ordinary Level	A1	A2	B1

It is also important to note the very good degree of course coverage demonstrated by most Chemistry candidates. The rubrics of the examination paper require candidates to attempt 8 of 11 questions. Most candidates attempt the required 8 questions. Many candidates at Higher Level attempt surplus questions, although candidates rushing through the examination to answer surplus questions is discouraged. The choice on the LC Chemistry examination papers encourages broad subject knowledge and has effectively eliminated the practice (observed during the lifetime of the previously syllabus) of omission of full units of knowledge by some candidates e.g. organic chemistry. Limited choice provides the candidates with some control over maximising their score.

The breakdown of numbers of candidates achieving each sub-grade is given in Tables 6 (Higher Level) and in Table 7 (Ordinary Level).

Table 6: Performance Rates – Higher Level Chemistry 2013

Higher Level Chemistry – sub-grades by percentage														
Year	A1	A2	B1	B2	B3	C1	C2	C3	D1	D2	D3	E	F	NG
2008	13.2	10.5	10.7	10.3	10.0	8.8	8.0	7.3	5.4	4.6	5.6	4.1	1.3	0.3
2009	12.5	9.4	10.4	10.8	10.0	8.4	8.1	8.0	4.5	4.9	6.2	4.6	1.8	0.5
2010	9.7	11.1	9.7	10.2	9.4	8.5	8.6	8.1	5.4	5.0	6.3	5.3	2.2	0.6
2011	11.4	10.5	10.5	10.9	9.1	7.9	8.3	7.4	4.8	4.5	6.1	5.6	2.4	0.6
2012	11.5	8.4	9.9	9.5	9.1	8.2	7.3	8.7	5.3	6.1	7.1	5.9	2.5	0.6
2013	9.4	11.0	8.2	9.7	9.9	8.4	7.9	8.9	6.3	5.6	6.6	5.7	1.8	0.6

Table 7: Performance Rates – Ordinary Level Chemistry 2013

Ordinary Level Chemistry – sub-grades by percentage														
Year	A1	A2	B1	B2	B3	C1	C2	C3	D1	D2	D3	E	F	NG
2008	5.3	6.6	9.0	9.7	11.6	9.8	7.9	7.9	6.4	4.8	7.3	7.8	4.9	1.2
2009	3.0	6.2	5.9	8.6	11.0	10.7	8.6	9.1	5.3	6.8	9.4	8.7	5.6	1.0
2010	2.2	5.4	4.9	8.6	8.7	9.1	9.1	8.1	7.9	7.7	9.8	10.1	6.8	1.6
2011	3.3	5.8	7.5	8.9	10.9	9.3	8.6	10.4	7.8	7.0	7.8	6.8	4.8	1.2
2012	2.0	5.6	4.9	8.2	9.0	10.4	10.0	9.3	7.9	7.4	8.7	9.9	4.8	1.9
2013	2.6	4.5	4.2	7.5	9.7	9.2	10.2	10.3	7.6	6.9	9.1	10.3	6.0	1.9

Figure 1 (Higher level) and Figure 2 (Ordinary Level) depict these percentages graphically. It is obvious from Figure 1 that the distribution of grades is not, as is often thought, a 'bell-shaped curve'. In fact performance at Higher Level is positively skewed with a greater number of Higher sub-grades than would be expected in a normal distribution. Figure 2 depicts a more normal distribution of sub-grades at Ordinary Level.

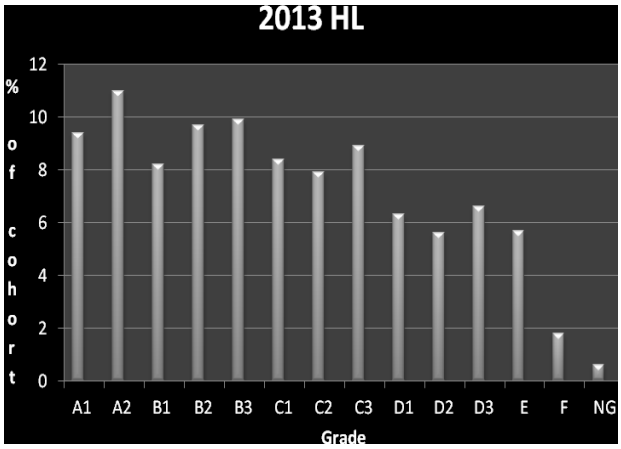


Figure 1: Performance Rates – Higher Level Chemistry 2013

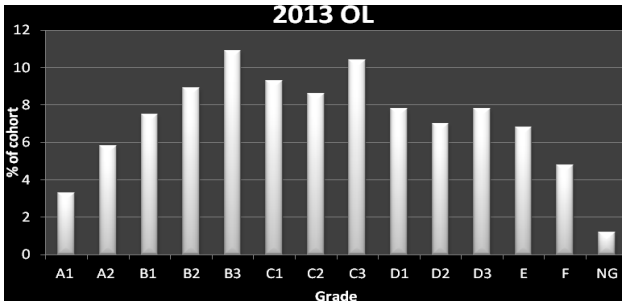


Figure 2: Performance Rates – Ordinary Level Chemistry 2013

Figure 3 (Higher Level) and Figure 4 (Ordinary Level) graphically compare the performance of 2013 candidates across the sub-grades with the 2012 and 2013 cohorts. These charts provide evidence for maintenance of standards of performance at both levels

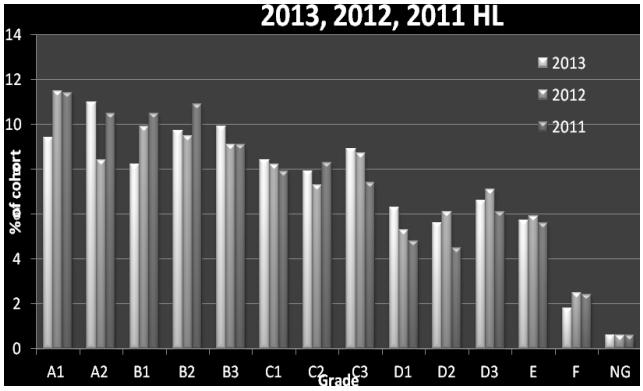


Figure 3: Comparison of Performance Rates – Higher Level Chemistry 2013, 2012, 2011

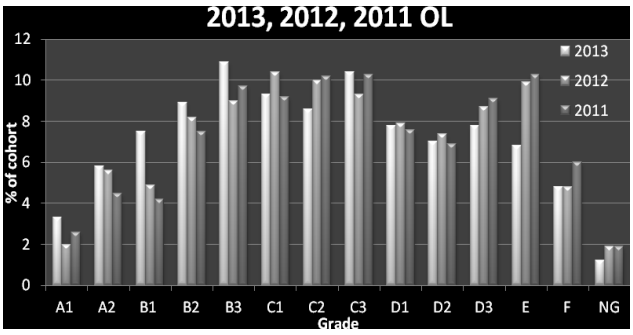


Figure 4: Comparison of Performance Rates – Ordinary Level Chemistry 2013, 2012, 2011

In summary, performance rates are comparable for the last number of years. However, at Higher Level the increased participation of approximately 500 candidates in 2012 and again in 2013 has been accompanied by a decrease in overall performance with a total A rate below the mean, but within one standard deviation of the results in the previous 5 years but with a more significant decrease in the combined ABC rate in 2013 compared to previous years. Performance within the relatively small Ordinary Level cohort tends to fluctuate more from year to year than the larger Higher Level cohort performance does. Results in the combined ABC range this year fell within expected parameters but slightly below the mean. Results in the D range are slightly elevated this year compared to recent years while results in the EFNG bands lie within range of recent results.

At Higher Level, 5.2% of results were appealed of which 0.8% were upheld. There were no downgrades in 2013. Less than 0.1% of Ordinary Level scripts were appealed. In 2013 there were no changes to Ordinary Level results on appeal.

Areas of good candidate performance

Table 8 summarises the popularity of and candidate performance in each of the questions on the 2013 Higher Level paper – the data is based on a sample of scripts. From year to year HL candidates consistently answer well in the following syllabus areas: kinetics (volume versus time graphs), Hess's law calculations, fuels, most titrations, equilibrium calculations, Q4, water and pH calculations. Conversely, candidates struggle every year to explain trends in the periodic table, radioactivity, evidence for energy levels (Bohr atomic model) and mechanisms in organic chemistry especially the evidence and kinetics (other than rate of gas evolution graph).

Those who achieve high grades at this level have demonstrated good course coverage, display a wide range of skills in the cognitive domain, have familiarity with practical work and have knowledge of social and applied chemistry.

Table 8: Popularity and Performance Higher Level Chemistry 2013

Higher Level Chemistry – analysis of questions					
Question	**% of attempts**	**Rank order in terms of popularity**	**Average mark (%)**	**Rank order in terms of mark**	**Topic**
1	86.3	3	33.8 (67.6)	6	Volumetric Analysis (O_2)
2	70.4	5	28.4 (56.7)	11	Organic Practical - General
3	65.6	9	28.9 (57.7)	10	Heat of Reaction
4	88.0	2	34.5 (68.9)	4	Miscellaneous
5	70.0	6, 7	33.1 (66.3)	7	Atom
6	88.9	1	35.3 (70.7)	2	Organic Chemistry
7	50.9	11	31.4 (62.8)	9	Rates of Reaction
8	55.2	10	32.6 (65.2)	8	Organic Chemistry
9	70.0	6, 7	35.4 (70.8)	1	Equilibrium
10	68.7	8	33.9 (67.7)	5	(a) Bonding (b) Redox/Stoichiometry (c) Radioactivity
11	83.0	4	34.6 (69.3)	3	(a) First Ionisation Energy (b) Bases / pH (c) A Electrochemistry B Industrial Chemistry

Table 9 summarises the popularity of and candidate performance in each of the questions on the 2013 Ordinary Level paper – the data is based on a sample of scripts. From year to year OL candidates consistently answer well in the following syllabus areas: kinetics (volume versus time graphs) and usually, but not always, titrations. Ordinary Level candidates struggle with calculations, abstract ideas (energy levels, trends in the periodic table) and organic chemistry. There is a lack of evidence for study and practice in the answering of many candidates.

Table 9: Popularity and Performance Ordinary Level Chemistry 2013

Ordinary Level Chemistry – analysis of questions					
Question	**% of attempts**	**Rank order in terms of popularity**	**Average mark (%)**	**Rank order in terms of mark**	**Topic**
1	80.0	6	29.5 (59.0)	3	Soap Preparation
2	90.0	3	30.2 (60.4)	2	Volumetric Analysis
3	70.0	7	25.6 (51.2)	7	Mandatory Experiments 1.1, 1.2 and 2.1
4	93.8	2	26.3 (52.6)	5, 6	Miscellaneous
5	81.3	5	21.1 (42.2)	11	Atom
6	68.8	8, 9	25.4 (50.8)	8	Organic Chemistry
7	68.8	8, 9	23.2 (46.4)	9	Acid-Base Theory/Water Analysis
8	45.0	11	28.4 (56.8)	4	Organic Chemistry
9	82.5	4	26.3 (52.6)	5, 6	Rates of Reaction
10	65.0	10	22.5 (45.0)	10	(a) Electronegativity (b) Stoichiometry (c) Chromatography
11	97.5	1	31.2 (62.4)	1	(a) Atomic Structure (b) Purification of Water (c) A Atmospheric Chemistry B Materials

Advice for 2014 (and later years)

For teachers and senior cycle students working in collaboration:

- Course coverage is essential
- Use the 2 year cycle
- Understanding not just recall will help
- Engage with the practical work
- Don't omit organic chemistry
- Develop clarity & accuracy of expression by practice
- Make use of past papers
- Use feedback loop of written homework and correction of homework

For all candidates:

- Prepare by studying – take ownership
- Understand in advance the layout of the examination paper and how to allocate your time
- Present work intelligently
- Be wary of rushing to attempt additional questions

- Look at mark allocation as a guideline of how much to write
- Read over what you have written before you finish
- In study practice writing out answers to questions in the past papers with the help of your notes

Specially for Ordinary Level students:

- Do your HOMEWORK
- Use the three hour exam period
- Attempt all parts of at least 8 questions including 2 from Section A
- Write as much as you can
- Attempt the calculations

Please see the Chief Examiners Report (Chemistry) 2013, which will be soon available on the SEC website, www.examinations.ie.

LC Chemistry Examination in 2015

Please see DES Circular 0047/2013 notifying you about changes to the Mandatory Chemistry practicals, which will be examinable in 2015.

The future for LC Chemistry……

My objectives as Chief Examiner for Chemistry are to maintain participation rates in the subject, preserve the integrity of the subject and standards of the examination, balancing academic, social and economic needs/concerns and to preserve confidence in the reliability of the examination team and appeals processes.

The NCCA has brought new syllabuses for all three senior science subjects, Biology, Chemistry and Physics, incorporating direct assessment of practical work, to the advanced draft stage. Chemistry teachers are represented on the NCCA Chemistry subject development group by nominees from the teaching unions and the Irish Science Teachers Association. School Management and Third Level Institutions are also represented. I am the SEC representative on this group and the DES is represented by one of their Chemistry Inspectors. Don't forget to keep informed about developments associated with these new syllabuses and make your opinions about teaching, learning and assessment of Chemistry known through your representatives.

□

The Mobile Phone as a teaching and learning tool in Chemistry

Maria Sheehan* and Michael O'Callaghan[+]

Michael O Callaghan ~

*Advisor with the Professional Development Service for Teachers (PDST) mariasheehan@pdst.ie

[+]Local Facilitator with the PDST mmicdom@gmail.com

Introduction

ICT in the classroom allows the teacher to create innovative, exciting and engaging learning environments for their students. This articles aims to highlight how the mobile phone can become a useful teaching and learning tool in the Chemistry class. Mobile phones are a creative tool which encourage engagement by the pupils. A MOBILE PHONE is a fully working sound and video studio. They can also function as references and encyclopaedias (*Wikipedia* is as accurate as the *Encyclopaedia Britannica*).

Worries that the teacher may have about using the mobile phone in class and how these worries may be overcome:

1. Distraction: Pupils could use the mobile phone to send texts, play games etc.: ***Make cell phones visible.*** Require students to place their cell phones on the top right-hand corner of their desks when they come into class. That way you will know if someone is texting or calling a friend when they're supposed to be learning

2. Non-filtered web access/Access to inappropriate material: The School Wi-Fi can and most probably is filtered at present.
3. Cyber bullying: This will most likely take place outside the class and is not just limited to the mobile phone. The school as a whole would need a very strong policy on how to deal with the issue of cyber bullying.
4. Recording the teacher: The teacher should never be recorded without their permission. However, the teacher should not be engaged in activities in the classroom that would embarrass them. If the threat of recording keeps us professional all times, that's a good thing.

Advantages of using the mobile phone:

- They are cost effective for schools
- They reduce the need for all students to have access to computers in classroom
- There is less equipment needed like digital cameras, camcorders, mics etc
- If pupils are going to have them in schools anyway, irrespective of whether it is officially allowed, they may as well be exploited for learning. Overcomes some of the problems of 'distraction' etc.
- Can be used as creative tool – making podcasts, picture blogs, twittering etc
- Encourages engagement –Socrative.
- Pupils are encouraged to use general reference books so why not phones – as dictionary, spell checker, thesaurus, encyclopaedia etc.
- As specific research tool via web access.
- Supporting locational learning contexts such as field-trips, museums and work-based learning.
- Enhancing interactivity.
- Engaging 'shy' learners through use of familiar, non-threatening.

Figure 1: Keep the mobile phone visible at all times

ICT in general can be used to promote the development of higher order thinking skills. Bloom's Taxonomy was created in 1956 by educational psychologist Dr Benjamin Bloom, in order to promote higher forms of thinking in education, such as analysing and evaluating, rather than just remembering facts (rote learning). (See Figure 2 and Table 1.) There are a lot of ICT-based activities that can help the teacher to do this. Table 1 lists a number of ICT applications that will encourage and promote the development of the different domains of cognition cited by Bloom.

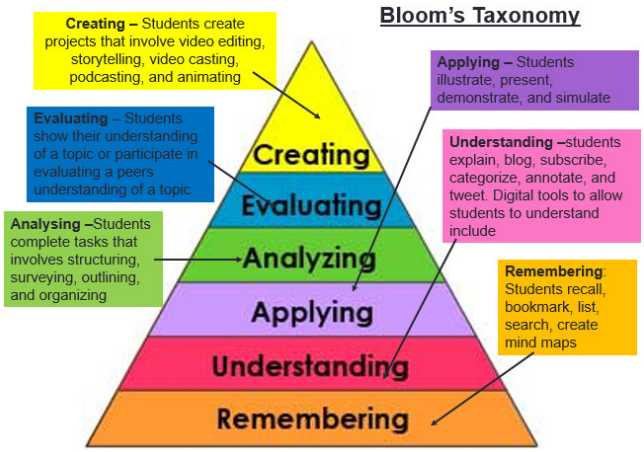


Figure 2: Bloom's Taxonomy

Table 1: Digital Tools That Work With Bloom's Taxonomy (Reference: http://www.edudemic.com/35-digital-tools-that-work-with-blooms-taxonomy/)

Remembering	Understanding	Applying	Analysing	Evaluating	Creating
Pages Google Docs Study Blue Bit.ly Wordle	PowerPoint Google Blogs Fotobabble Bit.ly Twitter neu.Annotate.	ScreenChomp SonicPics QuickVoice Fotobabble Keynote Podomatic Skype	Corkboard SurveyMonkey Study Blue Keynote Stickyboard	Google Docs Poll Everywhere Socrative BrainPOP Today's Meet	Story Kit Comic Life iMovie GoAnimate.com SonicPics Fotobabble Sock Puppet

Specific teaching activities for Chemistry using the mobile phone

Activity 1: Using the mobile phone as a colorimeter:

Before the Class:

1. Download a colour picker programme onto the phone.
    - IOS Examples: ColorAssist or Colorometer.
    - Android Examples: ColorPicker
2. Photocopy results template for each group:

Example:

Solution Conc.	1	4	16	64
R				
G				
B				

During the Class:

1. Make four standard by serial dilution.
2. Set up four standards in the cuvettes as shown in picture.
3. Use the colour picker programme to record the RGB values on results sheet for each cuvette
4. Select which one of the values, R, G, or B to use for graphing the information. This will depend on the colour of the solution you have used.

Figure 3: Experimental set-up for the colorimeter experiment

Activity 2: Studying the effects on reaction rate of (i) concentration and (ii) temperature:

Before the Class:

1. Download a light meter onto the phone:

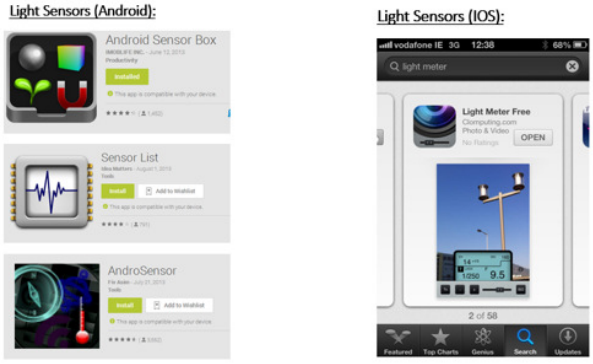


Figure 3: Examples of Light Sensors available for IOS and Android phones

During the Class:

Theory:

1. The precipitate of sulfur formed gradually obscures a cross marked on paper and placed beneath the reaction flask.
2. The rate of reaction, and consequently the time taken to obscure the cross, depends on a number of variables, conc and temp.
3. Measure the rate of sulphur formation by using the exposure meter on a mobile phone camera to calculate transmitted light.

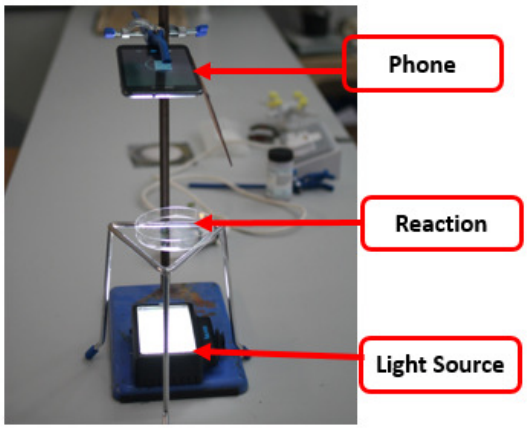


Figure 4: Experimental set up for rates of reaction experiments

NOTE: The phone and the light source should be interchanged with an acetate over the phone at the bottom, as the light meters work from the reverse camera not the forward camera.

Activity 3: Teaching Nomenclature in Organic Chemistry:

During the class:

1. Provide pupils with MolyMod kits and the formula of the organic molecules you would like them to create (see Figure 6)
2. Clip the mobile on to a retort stand, facing down at an A4 page.
3. Take individual photos of each molecule created.
4. Discuss with teacher if the structure is correct.

Note: pupils discover isomers for themselves as they complete this activity.

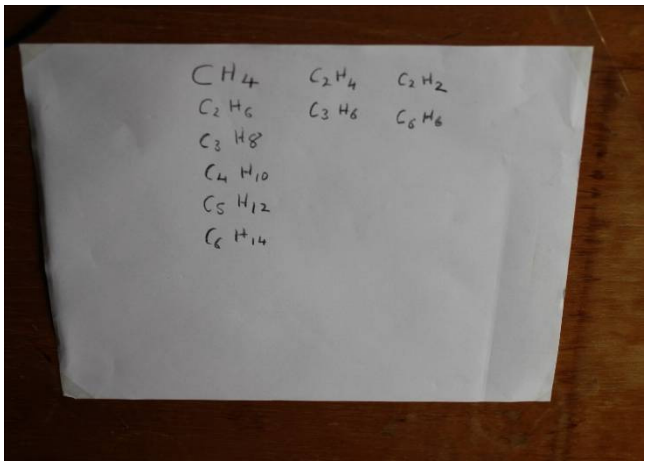


Figure 5: Worksheet for nomenclature assignment)

Other adaptations:

- Pupils can create stop-motion animations to explain reaction mechanisms.

4: Creating QR codes to share information/create worksheets etc.:

QR stands for quick response code. All types of phones have free QR readers, pupils will need to download one. To use the reader pupils need only point their phone at the QR code and the file will download immediately to their phone.

In order to generate a QR code, search online for free QR code generators. Figure 7 shows an example called http://goqr.me/

Copy and paste the url for the website, YouTube clip, document you want students to access and a QR code will be generated. This can then be copied and pasted onto a word document/label etc.

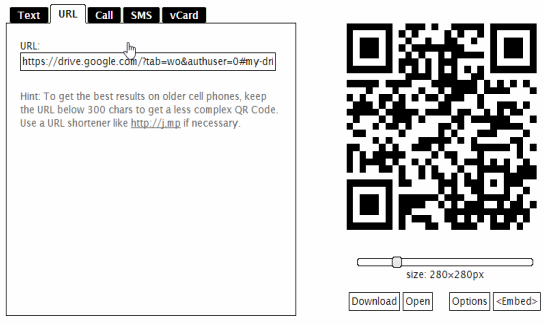


Figure 6: Example of a QR code generator

Possible uses for QR codes in Chemistry:

1. Add them to worksheets to help scaffold pupils to answer questions (See Figure 8)

2. Add them to worksheets to allow for differentiation. You could have question prompts for weaker pupils or deeper thinking exercises for stronger pupils.
3. QR codes directing pupils to video clips of mandatory experiments could be created and printed onto labels. These labels could be placed in the appropriate places in the pupil's text book.
4. QR codes could be place on posters in the laboratory directing pupils to locations where they could find out more information about that content of the poster.
5. QR codes could be placed on equipment in the laboratory to explain what it is and how is it used.

Figure 7: QR codes on Worksheets

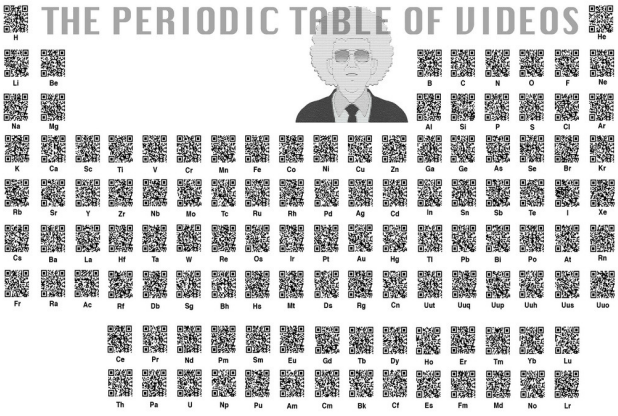


Figure 8: A novel use of QR codes specific to Chemistry

Activity 5: Converting Word documents/PowerPoint into e-books:

E-book's are easy to read on a phone. If you have a word document, PowerPoint presentation or a PDF file that you would like pupils to read, these can be converted to the e-book format using a simple free program such as *calibre*. It is a one click operation. See Figure 10:

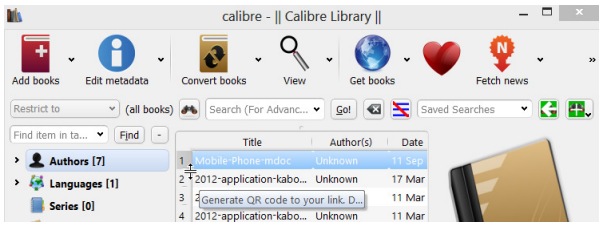


Figure 9: Converting documents to e-books using calibre

Activity 6: Use the mobile phone as a student response system ~ SOCRATIVE:

Socrative is a smart student response system that empowers teachers by engaging their classrooms with a series of educational exercises and games. The app itself takes seconds to login and feedback is instant. Socrative runs on tablets, smartphones, and laptops.

SOCRATIVE can be accessed at www.socrative.com . The teacher and student version of this app can be downloaded onto your smart phone by visiting the appropriate app store. This is a free app. The SOCRATIVE app allows the smartphone to act as a 'clicker' and students responses are collected instantly.

Figure 10: Login screen www.socrative.com

Once you have your teacher account set up you will be able to direct students to your account by issuing them your room number. Figure 12 shows how the students can login on their smart phone.

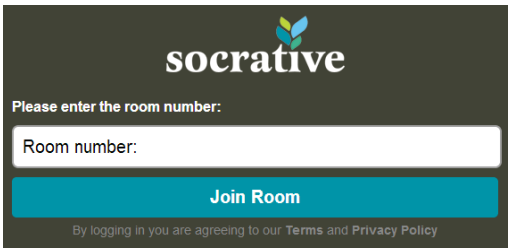


Figure 11: Student Login on smartphone

Facilities on SOCRATIVE which are useful for the Chemistry class:

1. Quick Response: Real-time formative assessment ~ Take a snapshot of student thinking through real time formative assessment. Choose your question type, ask a question, and wait for responses:
   a. Multiple Choice: Present students with a MC question and see the results populate the bar chart as students select their answer.
   b. True or False: Ask a T/F question, see the results, and discuss the choices as they come to life on the screen.
   c. Short Answer: Gather open ended responses to any question you ask. Instantly project the student responses and then let students vote on the content.

2. Exit tickets: Check in on your students' understanding as they head out the door. Gather responses on their comfort with the material as well as answers to questions you create in real time or prepare before class. Figure 13 illustrates how an exit ticket works:

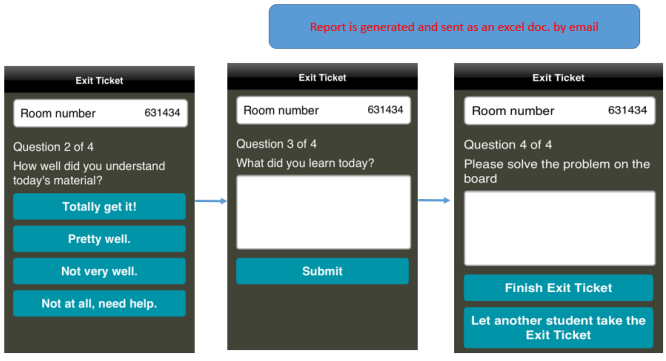


Figure 12: Exit Tickets on Socrative

Other suggested ideas by teachers on how the mobile phone can be used to teach Chemistry:

1. During a practical class, the mobile phone can be used to take pictures of each of the pupils' experimental set-up. At the end of the session these pictures could be displayed on the board and used to discuss examples of good practice. This activity incorporates formative assessment into the practical classroom.

2. When selecting data logging equipment ensure that it is Wi-Fi enabled so that the information can be directly linked to the pupil's mobile phone.

3. Use the mobile phone during the course work B experimental phase so that pupils have a record of what they did.

□

Dr Maria Sheehan and Mr Michael O'Callaghan are science teachers seconded to work with the PDST.

International Conference On
Initiatives In Chemistry Teacher Training
November 29th, 2013
Limerick Institute of Technology, Limerick, Ireland
Proceedings available at:
http://www.lit.ie/ICTT/Papers/Papers/Chemistry%20is%20all%20around%20us%20Conference%20on%20Teacher%20Training%20Limerick%20November%2029th%202013.pdf

Post-16 Chemistry Learning and Teaching Resources Utilising the WebCSD Online Crystallographic Database

Peter Hoare
Chemistry Outreach Officer, Department of Chemistry, Newcastle University, Newcastle on Tyne, UK
peter.hoare@ncl.ac.uk
www.ncl.ac.uk/chemistry/outreach

Editor's note: This brief account is based n the Powerpoint slides of Peter's talk. This was supplemented by a one hour workshop (#4), where teachers were able to access the database and see how the materials could be used. Participants were given a booklet describing the materials and how to use them. This can be obtained on request by contacting Peter Hoare at the email address above.

The Background to the project

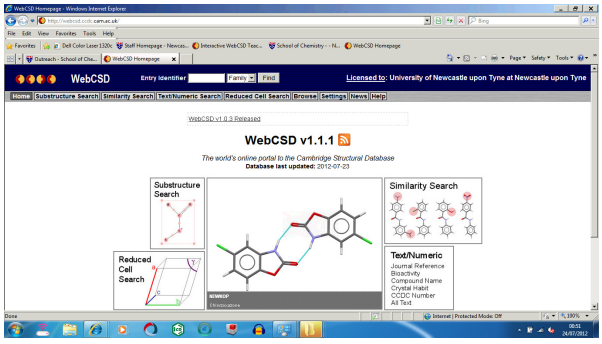
See the CCDC November 2012 Newsletter: *"Crystalline"*. I attended the 2010 ViCE Conference in Loughborough and went to a workshop run by Dr Susan Henderson from the Cambridge Crystallographic Data Centre (CCDC), which was on using WebCSD as an undergraduate teaching resource. I asked the question: "Have you ever thought about using this for Outreach?" Susan answered: "Yes, but we don't know anything about schools….." This was the start of the project to adapt the resources for use in UK schools.

Cambridge Crystallographic Data Centre (CCDC):

CCDC was established in 1965 by the Chemistry Department at Cambridge University and they developed the Cambridge Structural Database (CSD). This is now an independent not-for-profit charitable company – with over 50 employees and their systems are used in over 55 countries worldwide. CSD now contains over 700,000 X-ray crystal structures! These are mainly small molecules – including organics, pharmaceuticals, organometallics and transition metal complexes. They have their own in-house team of software programmers and developers (including of web-based browser platforms). Their objective is "the general advancement and promotion of the science of chemistry and crystallography for the public benefit".

What is WebCSD?

CCDC have an extensive range of software applications to view and manipulate x-ray crystal structures – all developed in-house. But one needs a site licence to access and updates need to be downloaded and installed annually. WebCSD is an internet-based platform which combines some of the main functionalities of CCDC's major applications, but it also needs the site licence!

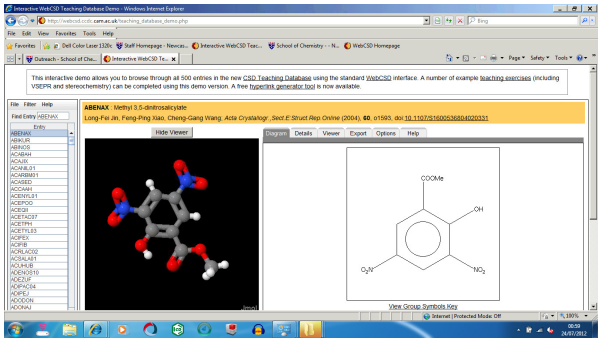


WebCSD Free Teaching Subset:

A free access version of WebCSD was developed in 2008-9 and contains approximately 500 structures, used specifically to deliver 5 undergraduate teaching exercises developed with Dr Greg Ferrence at Illinois State University, USA. No site licence is needed for access and updates can be provided seamlessly. The 5 topics available are: VSEPR, Aromaticity, Optical Isomerism, Hapticity & Ring Conformations.

WebCSD Free Teaching Subset can be accessed at:

http://webcsd.ccdc.cam.ac.uk/teaching_database_demo.php



Key features of the free WebCSD browser:
Using the browser you can:
* View/rotate molecules in Jmol viewer.
* View molecules in 3D with glasses if option selected.
* Measure bond lengths.
* Measure bond angles.
* Measure torsional angles; "planarity".
* Identify Organic Functional Groups;
* Investigate VSEPR;
* Stereochemistry – cis/trans (E/Z);
* Stereochemistry – optical (R/S);
* TM complexes;
* Structure of Benzene/Aromaticity;
* Reaction Mechanisms/Intermediates:
e.g. #1 - electrophilic addition of bromine to alkenes;
e.g. #2 - electrophilic substitution of benzene;
* Intermolecular forces – Hydrogen bonding

Current Topics

Activities format – all worksheets are a maximum of 2 sides A4. Each topic includes:
* Theory/background/information sheet;
* Basic activity which meets (major) A-level specification requirements;
* Extension activities (for e.g. G&T students/St1&2 UG/outreach)

e.g. VSEPR: Basic activity –
#1 - for single-bonded species with no lone pairs;
#2 - single-bonded species with one lone pair;
Extension activities:
a) - species with more than 1 lone pair;
b) - effect of lone pairs on bond angles;
#3 - multiply-bonded species.

Format:

All activity sheets are produced entirely by the Nuffield students and my MChem project student – my role is supervisory. Steve Carman, my MChem student 2012-13, reviewed/revised the original Nuffield worksheets, developed further ones to fill identified topic gaps and collated and evaluated the feedback. The feedback was obtained from 192 people – a mix of teachers, lecturers and students in schools, colleges and universities from all over the world! Steve was employed by CCDC over the summer vacation to edit and proof-read sheets and produced further worksheets and "how to" video clips. Result is a set of peer-produced resources – trialled worldwide!

They can be obtained via our website:
www.ncl.ac.uk/chemistry/outreach/ccdc
Freely accessible/downloadable as pdf files.
Online feedback/comment form available. Further new trial resources at can b accessed at:www.ncl.ac.uk/chemistry/outreach/trial.

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Mumena Ali; Sacred Heart RC High School, Newcastle
Emma Burnett; St John's RC College, Bishop Auckland
Gabriel Bramley; St Robert of Newminster RC School, Washington

Newcastle University, School of Chemistry:
Steven Carman; MChem stage 4 project student 2012-13
Prof Bill Clegg, Dr Ulrich Baisch & colleagues in X-ray Crystallography
www.ncl.ac.uk/chemistry/outreach

□

Environmental Chemistry - Acid Rain Simulation

Oonagh Quin and David Sutton
Department of Applied Science, Limerick Institute of Technology, Limerick, Ireland.
Oonagh.quin@lit.ie and david.sutton@lit.ie

Abstract
This simulation creates samples of "acid rain" in a controlled environment via a double displacement reaction and a subsequent reaction with water vapour in the 'atmosphere'. The workshop informs the learner about double displacement reactions. Furthermore, the workshop identifies the source and formation of a primary pollutant (SO_2) and consequent formation of a secondary pollutant (H_2SO_4) within the environment in the form of acid rain. The dispersal and re-concentration of the pollutant as acid rain and subsequent collection for analysis is realised. Time related pH sensor data is employed to quantify the change in pH of a water body in the simulate environment (optional). The resultant data can be employed to understand the effects of weather conditions on the dispersal and formation of the acid rain. The product acid rain is collected and tested to determine what effects acid rain has on common substances.

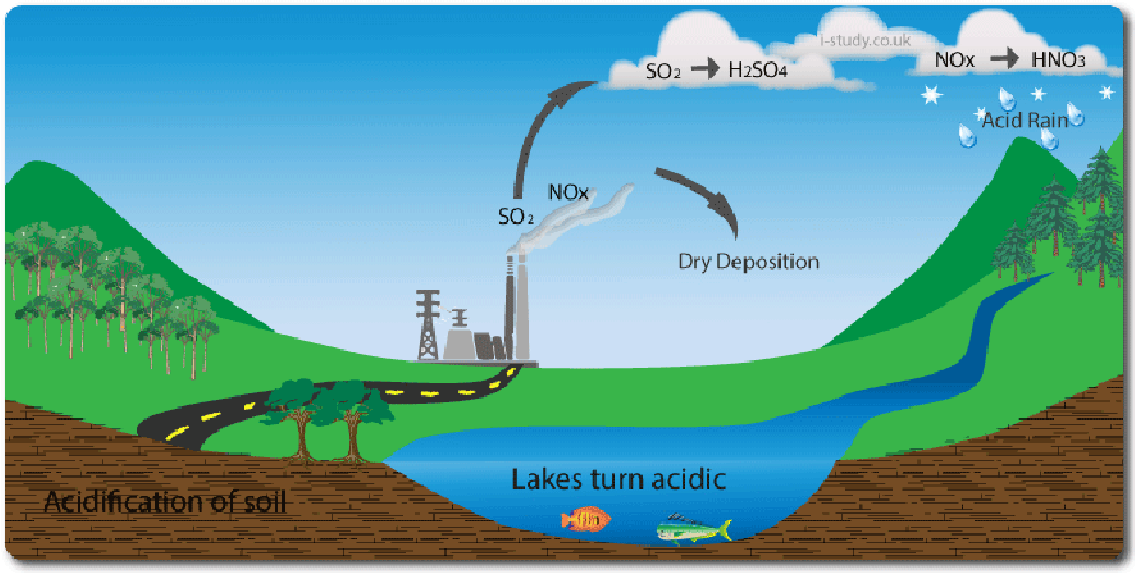

Figure 1: Diagram of the pathways leading to the formation of acid rain in our atmosphere.

1. Introduction
Before falling to Earth as precipitation, water vapour in the atmosphere normally reacts with carbon dioxide gas to form a weak acid - carbonic acid (H_2CO_3). Consequently, the pH of rainwater is roughly 5.6, making typical rainwater slightly acidic. However, water vapour in the atmosphere will also react in a similar manner with other gases. Acidic gases in the atmosphere include sulphur dioxide (SO_2), nitrogen dioxide (NO_2), and nitrogen trioxide (NO_3). The anthropogenic presence of these gases is primarily as a result of the combustion of fossil fuels as a source of energy: for example, combustion of petrol in the internal combustion engine and coal burning power station. The analogous reactions of these gases produces acids stronger than that of carbonic acid, including sulphuric acid (H_2SO_4), nitric acid (HNO_3), and sulphurous acid (H_2SO_3) as represented in Figure 1 above. If the concentration of these acids in the atmosphere is appreciable, the pH of rainwater can be lowered considerably. Rain with a pH lower than 5.6 is considered "acid rain" and can have significant environmental effects on natural cycles, ecosystems and on physical structures such as bridges and statues.

(see http://channel.nationalgeographic.com/channel/videos/acid-rain-invisible-menace/)

2. Chemistry of the workshop

The first reaction of this workshop generates sulphur dioxide via a ***double displacement reaction***. A double displacement reaction is a chemical reaction where two reactant ionic compounds exchange ions to form two new product compounds with the same ions.

$A^+B^- + C^+D^- \rightarrow A^+D^- + C^+B^-$ **Eq. 1**

The reaction $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$ is a classic double replacement reaction. The silver 'traded' its nitrite ion for the sodium's chloride ion.

The products of the double displacement reaction for the reaction of sodium sulphite with hydrochloric acid are sulphurous acid and sodium chloride. However, the sulphurous acid is not stable and decomposes to form water and sulphur dioxide; the sulphur dioxide escapes from the solution and is liberated into the atmosphere.

Intermediate

$Na_2SO_{3\,(s)} + HCl_{\,(aq)} \rightarrow (H_2SO_3)$

$\rightarrow SO_{2\,(g)} + H_2O_{\,(l)} + NaCl_{\,(aq)}$ **Eq. 2**

In a coal burning power plant sulphur is a natural inclusion is some coal and burns with a blue flame. Generally, the cheaper the coal, the higher the sulphur content. The sulphur as an inclusion in coal is a result of underlying geology from where extraction took place.

A gas, sulphur dioxide is the main product of the combustion of sulphur contained within the coal. On occasion a little sulphur trioxide is also formed, which makes the gas slightly cloudy. These gases are known as **primary pollutants** and as such have a polluting effect themselves (primary pollutant - first to pollute).

$S + O_2 \rightarrow SO_2$ **Eq. 3**

OR/AND

$2\,S + 3\,O_2 \rightarrow 2\,SO_3$ **Eq. 4**

If these primary pollutant gases escape into the atmosphere they can react with water vapour, thus forming secondary pollutants which are acidic. A **secondary pollutant** is the product of a primary pollutant and another compound in the environment.

$SO_2 + H_2O \rightarrow H_2SO_3$ **Eq. 5**

$SO_3 + H_2O \rightarrow H_2SO_4$ **Eq. 6**

For the purposes of the simulation the contents of a sealed plastic bag are considered to be an environmental scenario similar to that of Figure 2. A coal burning power plant is represented by the test tube and its contents and will produce sulphur dioxide. The test-tube itself is very similar to a chimney stack in its role of being the point source for the emission of the sulphur dioxide. The water in the bottom of the bag represents a nearby lake which is of a neutral pH. Within the sealed bag there will be a positive water vapour pressure.

Through the double displacement reaction in the test tube and the subsequent evolution of sulphurous gases, acid rain is created which will 'rain' and contaminate the distilled water in the bag. The equipment for this simulation is basic and can be adapted for any level of student.

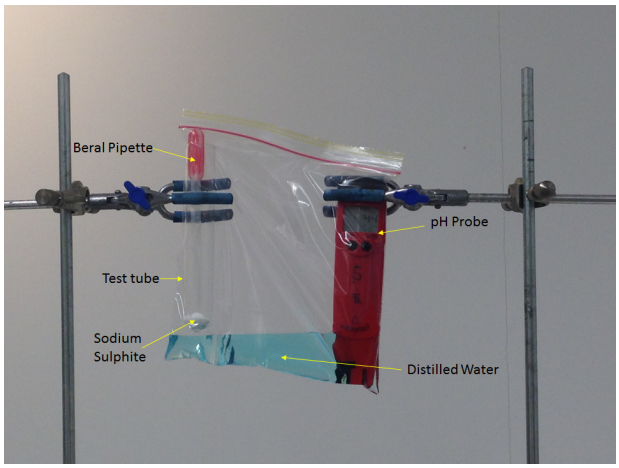

Figure 2: Experimental set-up for the simulation of acid rain

3. Materials

pH Sensor (Litmus paper/pH Paper/ Universal Indicator Solution)
6 M hydrochloric acid (HCl) -- approximately 2 cm^3
Sodium sulphite (Na_2SO_3), solid crystals – 1-2 g
Test tubes, 20 x 150 mm (4)
Disposable plastic Beral-type pipettes (2)
Zip-seal plastic bag, 500 cm^3
Plastic wash bottle containing distilled water

Small (25 cm^3) graduated cylinder
Small strip of magnesium ribbon, dried soil etc.
Stopwatch

4. Procedure

1. Add 50-100 cm^3 of distilled water to the plastic bag. Use a retort stand to hold the bag while carrying out the next steps. (See Figure 2)

2. To generate acid rain: Obtain a 1-2 g sample of sodium sulphite (Na_2SO_3) in a test tube. Place the test tube inside the plastic zip-seal bag, holding the test tube upright from outside the bag and clamp on the stand.

3. Carefully fill a disposable beral pipette with 6 M hydrochloric acid (HCl).
(CAUTION: 6 M hydrochloric acid (HCl) is corrosive. Avoid spilling, and avoid breathing fumes.)

4. WITHOUT squeezing the bulb of the beral pipette, so that no acid is released from it, place the pipette filled with acid inside the test tube which is inside the plastic bag. Be sure the tip of the pipette does not contact the sodium sulphite - do not start the reaction yet! Also make sure that the water in the plastic bag *does not* come into contact with either the acid or the sodium sulphite.

5. Place the portable pH sensor in the other corner of the plastic bag and hold in position or clamp. Be sure that the sensor is immersed in the water and note the pH – it should be roughly 5.6 if you use distilled water (Why so low? Distilled water is condensed in the atmosphere just like rainwater.) and 6.6 for tap water. While a pH sensor is ideal any monitoring system is suitable e.g. universal indicator solution gives technicolour display.

6. While one lab partner holds the test tube / plastic bag assembly in place with the pipette inside the test-tube, a second person should seal the bag as tightly as possible.

7. The plastic bag "environment" should now be closed, with the sensor ready to record the pH of the water – note the "weather" in the bag it should be clear!

8. Once you start the experiment record the pH of the water every 30 seconds – the experiment starts once you add the first drops of acid.

9. Keeping the pH sensor in place, slowly and carefully squeeze the pipette bulb so that all of the acid drips onto the solid sodium sulphite in the test tube drop the acid over a period of 1-2 minutes.

10. Keep the test tube upright so that the contents do not spill, and keep the bag sealed.

11. Allow the reaction in the test tube to proceed for 3.5-4 minutes, tapping gently on the test tube as needed. (You may need to continue to hold the pipette above the test tube while the reaction proceeds so that fumes can escape the test tube.)

12. After 4 minutes, remove the set up from the clamp and gently swirl the water in the bottom of the bag for 2 additional minutes while continuing to record the pH. Be careful the water does not come into contact with the contents of the test tube, but that the sensor tip stays submerged.

13. End data collection after the pH level stabilizes this will be at around a pH of 2.

14. In the fume hood (or well-ventilated area) carefully open the top corner of the plastic bag and remove the assembly from the pH Sensor. Rinse the tip of the sensor with distilled water from the wash bottle. Do not breathe the fumes from the bag.

15. You should now have your contaminated water in the bag; transfer the liquid into the 3 remaining test tubes, label them A, B, or C.

16. The subsequent samples of acid rain can be tested against various substrates. Reaction with magnesium ribbon, calcium carbonate, soil, vegetation etc.

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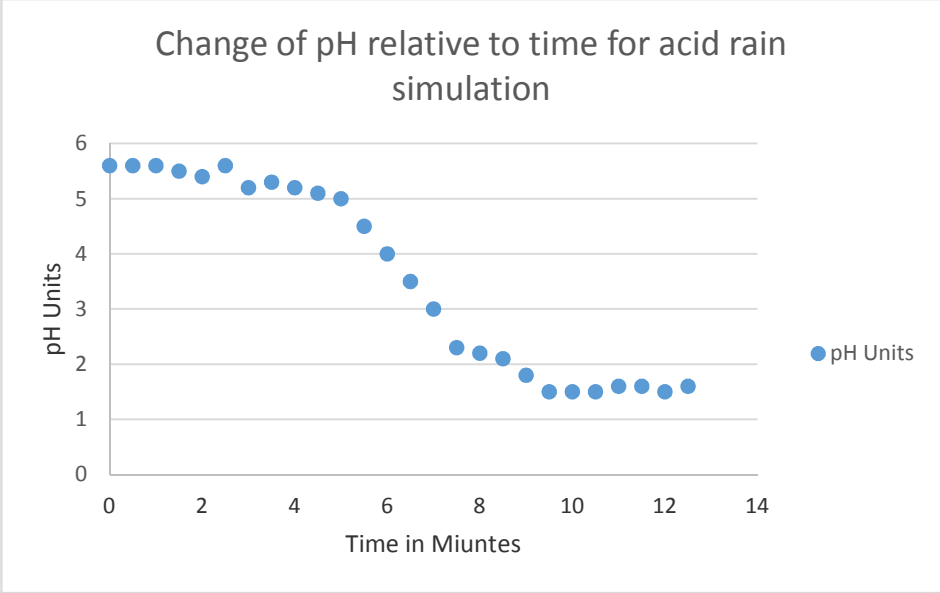

Figure 3: Typical results for the change of pH for the water body in the bag against time for the simulation of acid rain.

5. Data analysis and observation

The data for the pH vs time can be plotted (see Figure 3). The point of commencement and cessation of dropping of acid should be noted (T=0 and T = 2 min). The point of removal of the assembly from the stand and the gentle swirling of the bag is noted at ~4 minutes in Figure 3. At this point on the graph there is a dramatic rate of change of pH for the 'lake' until 9.5 minutes. This activity in the procedure simulates transportation of the primary pollutant from the point source to dispersal in the environment by 'weather' (wind) and subsequent reaction to form acid rain – the secondary pollutant. The subsequent rain can be observed as the misting of the atmosphere in the plastic bag as condensation rolls down the inside of the bag to contaminate the water in the bag.

*Remember at no point did the HCl come in contact with the water in the bag, so that what is being observed is exactly as it would occur in the natural environment.

Testing of the acid rain can be along the lines of that for any weak acid. However, in keeping with the environmental theme it is often appropriate to investigate the following reactions. The reaction with magnesium ribbon which has had its oxide layer removed with some sandpaper will yield (albeit very slowly) hydrogen gas. If left for a few minutes the bubbles of hydrogen are observed at nucleation points created by the roughening of the surface of the metal. Alternatively, calcium carbonate chips (or even some antacid tablets) will also produce a reaction with the liberation of carbon dioxide thus simulating the effect on sedimentary rock in the environment.

The pH of soil is easily investigated using some soil and distilled water and a pH probe. For the purposed of demonstration the 1-2 g of soil mixed with 25 cm^3 of distilled water is allowed to stand. Reading its pH after 5 minutes using as probe or some universal indicator paper will give a rough pH of the soil. The same procedure repeated using the 'acid rain' in place of the soil can be used to demonstrate the buffering capacity of the soil i.e. the pH of the soil is changed by the reaction of alkaline compound with in the soil with the acid rain. Effects on plant growth and on vegetation can be investigated but may require a collection of a large volume of the product 'acid rain' collectively from a class. One dramatic effect can be observed for a simple seed germination experiment.

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Molecular Models in Organic Chemistry

Anne O' Dwyer [1,2] and Peter Childs[1,2,3]

1. National Centre for Excellence in Mathematics and Science Teaching and Learning (NCE-MSTL), University of Limerick. 2. Chemistry Education Research Group (CERG), University of Limerick. 3. Department of Chemical & Environmental Sciences, University of Limerick.
anne.m.odwyer@ul.ie and peter.childs@ul.ie

Introduction

Organic Chemistry requires learners to understand many abstract concepts. This workshop highlighted the importance of the use of models and concrete explanations in the teaching of Organic Chemistry. The workshop included the use of commercial and home-made models and demonstrated how they that can be used for different representations in a number of abstract Chemistry topics, in particular the teaching of Organic Chemistry.

Cognitive Development of the Learner

There are four key stages of cognitive development: sensorimotor (0-2 years), pre-operational (2-6 years) concrete operational (7-11 years) and formal operational (12-15 years). The ages included in brackets here are the predicted ages for each stage of development (Piaget 1964). Formal operational learners are able to understand abstract ideas and systematic thinking. Johnstone (1991) has described the multi-dimensional nature of Chemistry as one of the factors contributing to learners' difficulty with the subject. Chemistry requires the learner to understand at the macroscopic level (concrete materials that the learner can see, feel, smell, touch), the submicroscpic level (abstract concepts such as atoms and molecules) and the symbolic level (equations, molecular formulae). Learners can understand the macroscopic (visible and tangible) content of Chemistry when operating at the concrete stage of cognitive development. However, to understand the sub-microscopic and symbolic nature of Chemistry, learners need to be at the formal stage of cognitive development. Problem solving in Mathematics and Chemistry requires formal operations. Research carried out in Ireland has found that less than 20% of Second-Level pupils are operating at the formal stage of cognitive development (Childs and Sheehan 2010).

Cognitive Demand of Organic Chemistry

Shayer and Adey (1981) devised a Curriculum Analysis Taxonomy (CAT) to analyse the cognitive demand of school Chemistry. This CAT was designed using the structure of Piaget's work to classify curriculum objectives according to the schema and reasoning patterns employed as well as the stage of cognitive development at which they are characteristic. This was done by using two taxonomies. The first taxonomy looked at the different aspects of the development of the child's interaction with the world. The second taxonomy looked at different schema required for the understanding of the Sciences.

Using these taxonomies, Shayer and Adey (1981) analysed the curriculum content of the O-Level Chemistry syllabus. The properties of organic compounds according to their functionality, organic reactions and integration between organic families require the highest level of abstract thought (late formal stage of cognitive development) and intellectual ability. The content of the Organic Chemistry topics on the O-Level syllabus is the same as those included in the current Irish Leaving Certificate syllabus (DES, 1999) Table 1 which follows shows the proposed stages of cognitive development that Irish Second-Level pupils need to be at in order to learn and understand the complex nature of Organic Chemistry.

It can be seen from Table 1 that much of the Organic Chemistry in the current Leaving Certificate syllabus requires pupils to be operating at the early and late formal stages of cognitive development. The topics listed in italics in Table 1 are Higher Level content only. The other topics are common to Ordinary and Higher Level. While much of the Higher Level material requires learners to operate at the late formal stage of development, most of the Ordinary Level content also requires formal operational thinking.

Table 1: Cognitive analysis of Leaving Certificate Chemistry (adapted from Shayer & Adey, 1981)

Organic Chemistry (DES, 1999)	Late Concrete	Early Formal	Late Formal
5.2 **Structure of Aliphatic Hydrocarbons**	Nomenclature and physical properties of alkanes, alkenes, alkynes.	Recognition of alkanes, alkenes, alkynes as homologous series	How the functional group and structure affects the physical state of aliphatic hydrocarbons and their solubility in water and non-polar solvents.
5.3 **Aromatic Hydrocarbons**	Nomenclature of benzene and examples of aromatic compounds. Physical properties of benzene	Recognition of examples of aromatic compounds.	How the functional group and structure affects the physical state of aromatic hydrocarbons and their solubility in water and non-polar solvents
7.1 **Tetrahedral Carbon**	Nomenclature and physical properties of alkanes, *chloroalkanes*, alcohols.	Recognition of alcohols as a family due to the functional group.	How the functional group and tetrahedral shape affect the physical state of aromatic hydrocarbons and their solubility in water and non-polar solvents
7.2 **Planar Carbon**	Nomenclature and physical properties of alkenes, *ketones*, aldehydes, carboxylic acids, *esters*.	Recognition of *benzaldehyde*, alkenes, *ketones*, aldehydes, carboxylic acids and *esters* as families of compounds due to their functional groups.	How the functional group and planar shape affect the physical state of *benzene*, alkenes, aldehydes, *ketones*, carboxylic acids and *esters* and their solubility in water and non-polar solvents
7.3 **Organic Chemical Reaction types**			Addition reactions. *Ionic addition mechanism.* Substitution reactions. *Free radical substitution mechanism.* *Esterification.* *Base hydrolysis of esters.* Elimination reactions. Redox reactions (*of ketones*). Reactions as acids. *Acidic nature of carboxylic acids.* Organic synthesis.

Is Organic Chemistry too difficult?

It is easy to understand how and why Chemistry is often described as an elitist subject. Learners need to be at the formal stage of cognitive development in order to learn and understand core Organic Chemistry ideas (Ingle and Shayer, 1971, Shayer and Adey, 1981). Most of the topics in Chemistry courses are developed on an abstract, conceptual level even though most of the learners are only operating at a lower cognitive level. If the majority of Second-Level pupils in Ireland have not yet reached this stage of cognitive development, it is not surprising that these topics are difficult for them. Organic Chemistry has a high cognitive demand, hence this subject is often over-whelming for novice learners operating at the concrete stage of cognitive ability.

Using models to facilitate Cognitive Development

The Leaving Certificate Organic Chemistry syllabus requires the pupils to learn a large amount of content in short time. This situation does not facilitate, and can hinder, cognitive development. Learners revert to concrete operational or pre-operational thinking whenever they encounter a new concept or problem (Bodner, 1986). Learning requires an active framework and new material must be familiar or concrete so that it can manipulated and understood (Libby, 1995). Learners need to become more aware of their own thought patterns and develop the ability to abandon the concrete external supports to develop and improve their self-concept. Improved teaching strategies with the use of visual aids and molecular models can help to reduce memory overload and encourage true understanding for the concrete operational learner in allowing them to develop abstract thought. Programmes such as CASE (Cognitive Acceleration in Science Education) (Adey, 1999)

and ITS Chemistry (Sheehan, 2010) have been effective in facilitating the cognitive development of the learner.

Different types of models can be used in all levels of Science to explain a number of different concepts. The use of models helps to bridge the gap from the concrete level of cognitive ability to the formal operational stage necessary to understand many concepts in Chemistry. Many student difficulties and misconceptions in Chemistry result from inadequate or inaccurate mental models at the molecular level. Molecular modelling representations can be compelling and effective learning resources (Tasker and Dalton, 2006). However, they must be designed and presented with great care to encourage students to focus on the intended 'key features', and to avoid generating or reinforcing misconceptions. Learners need time to become familiar with whatever type of molecular models are being used (Taber, 2002). There is much evidence that many learners are not able to interpret scientific models as intended. Learners need to move backwards and forwards between two-dimensional and three-dimensional representations using physical models and paper representations (Hassan *et al.,* 2004).

Molecular models

Molecular models facilitate the pupils' understanding of molecules: their three-dimensional shape and structure, their bond angles, isomerism and their properties. Molecular models provide the concrete learner with a more tangible understanding than could be explained through two-dimensional diagrams, which can be incorrectly perceived as 'flat' molecules. Models allow the pupils to visualise how molecules fill a certain shape in space, and also allow them to 'experiment' with molecules. As well as being useful in teaching functional groups, nomenclature, isomerism etc., the molecular models can also be integrated into practical and experimental work. Figure 1 illustrates how the learner can use the molecular models to represent the oxidation of an alcohol at a sub-microscopic level. This helps the learner to 'see the oxidation' as hydrogen atoms are removed and oxygen is added.

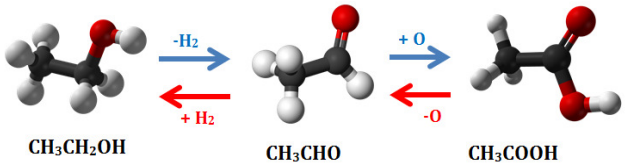

Figure 1: Sub-microscopic representation of macroscopic oxidation of ethanol.

Alternative visual representations

As well as commercial model kits, many other simple and cheap resources can be used to illustrate sub-microscopic representations:

- Plastic building blocks - to represent elements, compounds and mixtures.
- Physical examples of elements to introduce elements in the Periodic Table.
- Plastic building blocks- to introduce the concept of isomerism. This is described in detail in Issue 98 of *Chemistry in Action!* (O' Dwyer & Childs, 2012).
- Balloons- to illustrate the VSEPR theory: shapes of alkanes, alkenes and alkynes.
- Straws, cocktail sticks & plasticine - to build molecular models of organic compounds.
- Beads on a chain / poppit beads- to represent monomers and polymers.
- Different size spheres e.g. polystyrene / marbles etc. can be used to represent a homologous series.

There are some benefits of using homemade models rather than conventional model kits:

- Conventional model kits tend to lead pupils towards the correct answer, with a fixed number of holes and a fixed geometry inherent in each piece of the kit.
- Conventional model kits do not allow pupils the freedom they may desire to represent different types of models.
- Pupils can still build their own, potentially unconventional, representations of molecules.
- Not all pupils are positively affected by the use of the conventional modelling kits. Nicoll, 2003)

In contrast to textbook illustrations, animations can show the dynamic, interactive, and multi-particulate nature of chemical reactions explicitly (Tasker and Dalton,2006). Computer modelling makes three-dimensional molecular structures visual and mobile in a manner that hand-held models cannot.

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Dr Anne O'Dwyer works for the National Centre for Excellence in Mathematics and Science Teaching and Learning, University of Limerick and this article is based on of her PhD work, which was supervised by Dr. Peter E. Childs.

Diary

2014

32nd ChemEd-Ireland
11th October
DIT, Dublin
Claire.mcdonnell@dit.ie

2015

ISTA Conference
27-29 March
UCC, Cork
www.ista.ie

1st International Baltic Symposium on Science and Technology Education (BalticSTE2015)
15-18 June
Siauliai, Lithuania

6th Eurovariety 2015
29 June – 1 July
Tartu, Estonia

ChemEd
28 July – 1 August
Kenneaw, Georgia, USA
http://ccpe.kennesaw.edu/chemed/

11th ESERA
31 August – 4 September
University of Helsinki, Finland

45th IUPAC World Chemistry Congress
9 - 14 August
Busan, S. Korea (KR)

ChemEd-Ireland
17 October (tbc)
UCC, Cork
d.kenendy@ucc.ie

If you know of any relevant conferences or events of interest to chemistry teachers, please send in details to:
peter.childs@ul.ie

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Bringing the hydrogen economy closer: rusty metal electrodes for electrochemical water splitting

Michael E.G. Lyons*, Richard L. Doyle, Damaris Fernández, Ian J. Godwin, Michelle P. Browne and Aurélie Rovetta

Trinity Electrochemical Energy Conversion & Electrocatalysis (TEECE) Group, School of Chemistry & AMBER, CRANN Research Institute, Trinity College, Dublin 2, Ireland.

*To whom correspondence should be addressed.

Email: melyons@tcd.ie

Introduction

The use of hydrogen gas produced by the electrolysis of water is the basis of a long term energy conversion and storage option that has been, and still continues to be, the subject of considerable research and development, albeit occuring in fits and starts depending on current research funding priorities, fashions and directions. Alkaline water electrolysis, using electricity generated by renewable sources has been proposed as an environmentally inoffensive route to the production of the large volumes of hydrogen gas from non fossil fuel sources required by a possible hydrogen economy[1-5] as illustrated in Fig.1. In practice the efficiency of water electrolysis is limited by the large anodic overpotential of the oxygen evolution reaction (OER)[6].

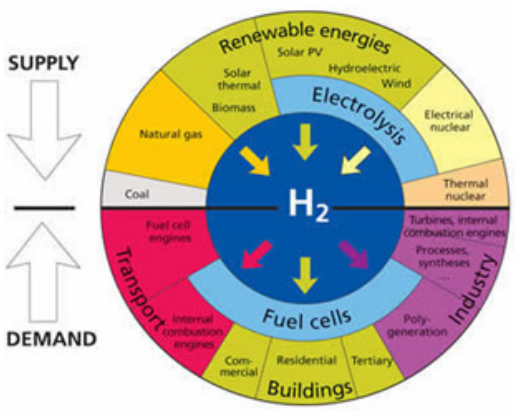


Figure 1: Electrochemical Ying/Yang. Schematic representation of hydrogen used as energy vector. Hydrogen can be generated via water electrolysis, and consumed as a fuel in a fuel cell for electricity generation.

Over the past thirty years, considerable research effort has been devoted to the design, synthesis and characterization of anode materials, with the aim of achieving useful rates of the OER at the lowest possible overpotential, in order to optimize the overall electrolysis process. This is one of the remaining grand challenges in Physical Electrochemistry and Energy Science.

Currently, the optimal OER anode materials are RuO_2 and IrO_2 since these oxides exhibit the lowest overpotentials for the OER at practical current densities[5]. However the high cost of these materials and their poor long term stability in alkaline water electrolysis cells renders their widespread commercial utilization both uneconomical and impractical[6], however they have been shown to be quite stable in polymer electrolyte membrane (PEM) cells. In light of these limitations, the oxides of the first row transition metals offer a compromise solution. Iron and nickel electrodes are interesting candidates. Although they possess inferior electrocatalytic activity for the OER, their relatively low cost and long term corrosion resistance in alkaline solution make them attractive OER anode materials[7].

The mechanism of the OER at first row transition metal oxide surfaces remains controversial and the important question of whether a possible common mechanism can be formulated, which would facilitate a theory of electrocatalysis for oxygen evolution is currently unresolved. It is our opinion that a systematic and consistent study of the OER at the oxidized surfaces of electrodes of adjacent first row transition metals should prove useful in elucidating whether a common reaction mechanism prevails.

In the present paper we review some basic electrochemical ideas which will serve to set the

scene, and also report on recent studies performed within the TEECE Group on using cutting edge electrochemical techniques to interrogate the mechanism of oxygen evolution at iron and nickel oxyhydroxide film coated electrodes and on thermally prepared Fe_2O_3 and RuO_2/NiO mixed oxides coated on Ti support surfaces in aqueous base . We propose a mechanism for the OER reaction which specifically takes into account the nature of the active sites which we label surfaquo-groups which are present in the latter oxide thin film materials during active oxygen evolution. A more technically advanced presentation on the ideas proposed in this article have been recently published elsewhere[8].

Basic Electrochemical Ideas

Electrochemical Science is a venerable discipline drawing its roots and inspiration from the work of Galvani, Volta and especially, Faraday. Yet the subject also forms the basis for a feasible solution to the major issue of cheap environmentally friendly energy production underpinning the future sustainability of 21st century life. Electrochemistry is the science of electron transfer processes at interfaces in which electrical energy inputted from outside the system is used to perform chemistry, or spontaneously occuring chemical reactions combine to produce a flow of electrical current which can flow through an external load thereby enabling useful work to be accomplished.

Interfacial electron transfer processes are of two types: oxidation or de-electronation and reduction or electronation (Fig.2). In oxidation, a species present in the electrolyte (termed a reductant or electron donor) may donate an electron to the electrode and in so doing become chemically transformed. The electrode acts as an electron sink and is termed an anode. In reduction, an oxidant species present in the electrolyte accepts an electron from the adjacent electrode, and in so doing becomes chemically transformed. In this case the electrode acts as an electron source and is termed a cathode . Hence interfacial electron transfer has a chemical implication. Substances may be transformed and chemistry done at interfaces via application of an external electrical potential.

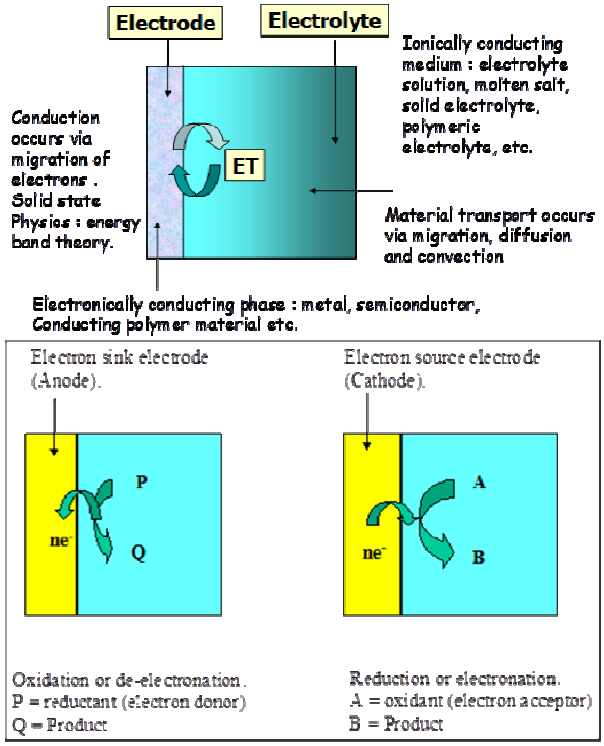


Figure 2: (a) Schematic representation of electrode/solution interface. (b) Schematic representation of an oxidation and a reduction process at an electrode/solution interface.

We present some typical examples of oxidation and reduction reactions in Table 1. We note from Table 1 that redox reactions may be of many different types, and can vary from simple single step processes involving the transfer of a single electron, to complex multistep processes involving the transfer of many electrons. A further point should be noted here. Besides the elementary act of electron transfer itself, one must in many cases consider further complicating processes such as the occurrence of chemical reactions preceding or following the electron transfer step (CE or EC processes), adsorption processes involving reactants, intermediates or products, and electrochemical nucleation and phase formation reactions. Furthermore the process of reactant transport to the electrode and product transport from the electrode will be important especially when the rate of electron transport is high. This idea becomes very important when the important application of electrochemical sensing is considered. In such applications electron transfer is very rapid and getting to the site of electron transfer from the bulk solution, i.e. transport, will be slow and rate determining.

In short, one may classify electrode processes into two general classes: simple single step charge transfer processes involving inorganic complex ions, and complex multistep multi-electron transfer reactions which consist of a number of elementary electron transfer and chemical reactions which can occur either in a consecutive or a parallel manner. Parallel electrode reactions are not common and are usually encountered in the anodic oxidation of certain organic compounds such as methanol in acidic or alkaline media. Consecutive processes are much more common. Typical examples of the latter type of processes are the cathodic oxygen reduction reaction, metal dissolution processes and various electro-organic transformations. Now analysis of the kinetics of simple single step reactions (i.e. outer sphere reactions involving inorganic complex ions which do not involve bond breaking) at a phenomenological level is relatively simple and is well understood. In contrast, the kinetics of multistep processes is generally complicated particularly for the case of electro-organic reactions. However some consecutive electrode reactions are particularly suitable for detailed attention since the number of steps involved is not too large. A particular example of the latter is the cathodic hydrogen evolution reaction (example b in Table 1). Of course the anodic oxygen evolution reaction (example c, Table 1) involving the transfer of four electrons, is the reaction of focus in the present paper.

Table 1. Representative oxidation and reduction reactions.

Cathodic reduction process	Anodic oxidation process
$Fe^{3+}(aq)+e^- \rightarrow Fe^{2+}(aq)$ (a)	$Ce^{3+}(aq) \rightarrow Ce^{4+}(aq)+e^-$ (a)
$2H_2O+2e^- \rightarrow H_2(g)+2OH^-$ (b)	$Pt+H_2O \rightarrow PtO+2H^++2e^-$ (f)
$O_2(g)+4H^+(aq)+4e^- \rightarrow 2H_2O$ (c)	$2Cl^-(aq) \rightarrow Cl_2(g)+2e^-$ (g)
$Cu^{2+}(aq)+2e^- \rightarrow Cu(s)$ (d)	$Fe(s) \rightarrow Fe^{2+}(aq)+2e^-$ (h)
$2CH_2=CHCN+2H_2O+2e^- \rightarrow (CH_2CH_2CN)_2+2OH^-$ (e)	$CH_3OH+H_2O \rightarrow CO_2+6H^++6e^-$ (i)

(a) Simple outer sphere single step single electron transfer reaction. This reaction type serves as a prototype in fundamental kinetic studies.
(b) The cathodic evolution of hydrogen. A much studied multistep, multielectron transfer reaction which involves the formation of intermediate species adsorbed on the electrode surface.
(c) The electrochemical reduction of dioxygen. Much studied in fuel cell technology. Again a complex reaction involving multiple electron transfer and the involvement of adsorbed intermediates.
(d) Metal electro deposition. An example of an electrochemical phase formation reaction involving nucleation and growth processes.
(e) Conversion of acrylonitrile (AN) to adiponitrile (ADN). An example of electrochemistry applied to organic synthesis.
(f) Metal oxidation. An example of a surface electrochemical redox transformation. Again this involves the generation of transient intermediates.
(g) Chlorine gas evolution. Important in the chlor-alkali industry. This is the anodic analogue to hydrogen evolution. Again adsorbed intermediates are involved in the reaction mechanism.
(h) Metal dissolution reaction. Fundamental basis of low temperature corrosion.
(i) Oxidation of methanol. Much studied in fuel cell research. Typical example of a complex multistep , multielectron transfer process.

An important point to note from Table 1 and from the previous discussion, is that many redox processes which underline important technological applications are complex ranging from the reduction of molecular oxygen to water of interest in hydrogen/oxygen fuel cells and metal/air batteries to the oxidation of metallic iron which forms the basis of rusting, and the oxidation of methanol to form carbon dioxide. Hence their study requires considerable ingenuity and the use of a broad arsenal of electrochemical and in situ spectroscopic techniques which are surface specific. Hence the modern approach to the study of electrode kinetics involves the use of electrochemical and non-electrochemical techniques. Indeed one may state that the examination of the kinetics and mechanisms of electrochemical reactions is one specific aspect of the broader area of surface science. An important take-home message from table 1 is that Electrochemical Science underpins many important industrial processes.

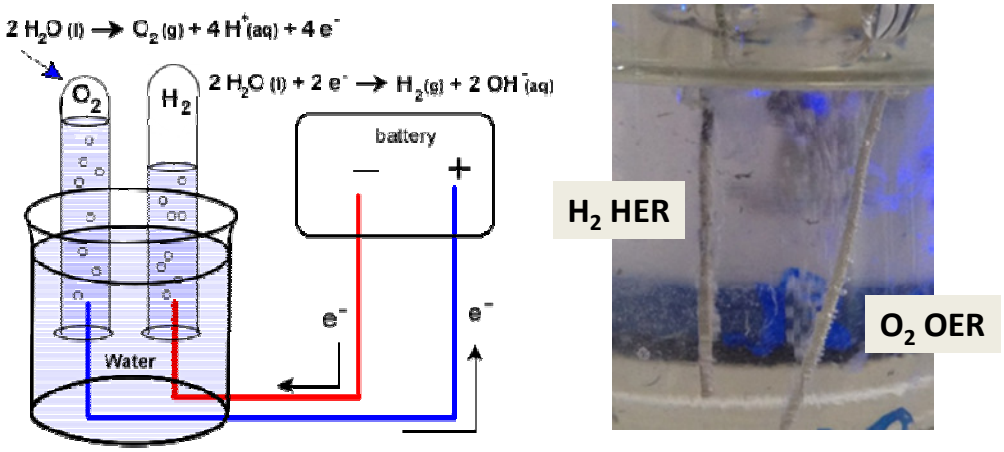


Figure 3: Schematic representation of water electrolysis cell showing constituent anode (Oxygen Evolution Reaction OER) and cathode (Hydrogen Evolution Reaction HER) reactions. Electrolyte typically aqueous NaOH or KOH.

The basic chemistry underpinning alkaline electrochemical water splitting which occurs according to:
$2H_2O$ (l) → $2H_2(g)+ O_2(g)$ is outlined in Fig.3. The latter process does not occur in a thermodynamically spontaneous manner. An energy input in the form of an electrical potential is required in order to split water into its constituent parts, H_2 and O_2 in the ratio of 2:1. A good modern overview of the technological aspects of alkaline water electrolysis has been recently provided by Marini and co-workers[9]. This is the most mature technology currently available for the electrolytic production of hydrogen. Polymer Electrolyte Membrane electrolysis systems are also extensively used. [10] The two systems are compared in Fig.4. Although of undoubted technical utility, we will not dwell on the latter PEM systems in this paper but refer the reader to some modern discussions[10]. The minimum potential required to split water is that determined by the Nernst equation, the so called Nernst or equilibrium potential E_N which has a value of 1.23 V. This value is never observed in practice. In order to generate hydrogen or oxygen at an appreciable rate expressed in terms of a current density j (say at 30- 100 $mAcm^{-2}$) one needs to apply a potential in excess of the Nernst potential. The difference between the applied potential and the Nernst value is termed the overpotential $\eta = E(j) - E_N$. The overpotential can be significant, typically 400-600 mV at room temperature, and is related to the activation energy barrier for the electron transfer process. Both the cathode and the anode reaction have an overpotential (the activation overpotential) contribution to the net energy cost for performing chemistry using the electrolysis cell. A contribution also arises due to the conductivity of the solution between the anode and the cathode. This term is called the Ohmic overpotential and has the form $\eta_\Omega = IR_S$ where I denotes the current flowing through the cell and RS denotes the electrolyte resistance. Hence the total electrical energy cost is given by: $E = E_N + \eta_A + |\eta_C| + IR_S$.

The cathode reaction is the HER which involves the transfer of two electrons: $2\ H_2O + 2e^- \rightarrow H_2 + 2OH^-$. Now electrons transfer one at a time and so the HER involves the formation of one or more adsorbed intermediate species at the electrode surface. This can involve three possible steps named Volmer (V), Tafel (T) and Heyrovsky (H) named after the founding fathers of Physical Electrochemistry. These steps take the following form in aqueous alkaline solution:

$S + H_2O + e^- \rightarrow SH + OH^-$ (V) (1)
$SH \rightarrow 2S + H_2$ (T) (2)
$H_2O + SH + e^- \rightarrow S + H_2 + OH^-$ (H) (3)

Hence we can envisage either a VT or a VH mechanism for the HER.

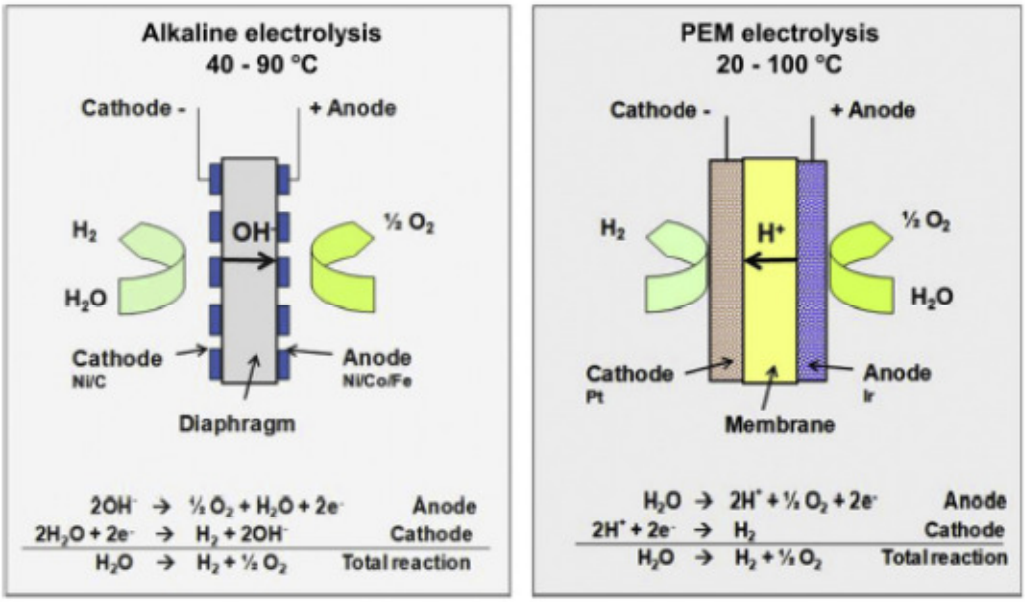


Figure 4: Typical water electrolysis cells : Alkaline electrolysis and PEM electrolysis.

The oxygen evolution reaction is even more complicated since it involves the transfer of four electrons: $4\ OH^- \rightarrow O_2 + 2H_2O + 4e^-$. Hence the number of possible mechanisms is quite large. One common pathway quoted is the Krasil'shchikov path which takes the form:

$S + OH^- \rightarrow SOH + e^-$ (4)

$SOH + OH^- \rightarrow SO^- + H_2O$ (5)

$SO^- \rightarrow SO + e^-$ (6)

$2\ SO \rightarrow 2\ S + O_2$ (7)

In the latter mechanistic schemes, S denotes a catalytically active surface group which we term a surfaquo-group, of which more later. Hence we see that one can have electron transfer steps (E steps) and purely chemical steps (C steps) which do not involve electron transfer in a multistep reaction sequence. The important point to note here is that these complex surface reactions are activated processes. They require an activation energy in order to proceed at a measured rate, or in electrochemical terms, proceed at a finite current density (current and rate being directly related via the Faraday Law of electrolysis). The reaction rate (current density j) depends increases with increasing electrochemical driving force (overpotential η according to the following relationship: $j = j^0 \exp\left[\mp \alpha F\eta / RT\right]$ where j^0 is the exchange current density which is a measure of the catalytic facility of the reaction either at the cathode or the anode, and which includes pertinent reactant concentrations . Furthermore, α is the transfer coefficient, the numerical value of which depends on the detailed steps in the reaction mechanism. The negative sign in the exponential term corresponds to a cathodic reaction (such as the HER) and the positive sign to the anodic reaction (such as the OER). The anodic and cathodic activation overpotentials are given by: $\eta_k = \frac{RT}{\alpha_k F} \ln\left\{\frac{j}{j_k^0}\right\} \cong \frac{RT}{\alpha_k F} \sinh^{-1}\left[\frac{j}{2j_k^0}\right]$ where k denotes the anode or cathode reaction respectively. Typically $\alpha_A \cong 2$ and $\alpha_C \cong 0.5$. The value adopted for the exchange current densities depends on the nature of the electrode material. The better the electrocatalyst, the higher the value of the exchange current density.

One can show that the transfer coefficient is related to mechanism via: $\alpha = \frac{n'}{\upsilon} + n_r\beta$, where n' denotes the number of electrons prior to the slow rate determining step of the reaction sequence. The latter designated rds is the step with the highest energy barrier and represents the kinetic bottleneck. Furthermore, n_r represents the number of electrons transferred during the rate determining step. For an E step $n_r = 1$ always since the probability for the simultaneous transfer of more than one electron is very small[11], and for a C step (such as eqn.5) $n_r = 0$. The quantity υ is the stoichiometric factor and is the number of times the rate determining step occurs per one act

of the overall reaction. Hence for the VT mechanism of the HER $\upsilon = 2$. Finally β is the symmetry factor and usually takes the numerical value close to 0.5. It tells us about the nature of the transition state in the rate determining E step. A factor close to 0.5 implies that the transition state is midway between reactants and products. Typically, the potential applied to the electrode is swept in a controlled manner either in the region where active hydrogen or oxygen evolution occurs and resultant current density measured. A plot of current density versus applied potential is obtained which can be subjected to subsequent analysis. One such form of analysis is a Tafel plot. Here a plot of logarithm of current density versus overpotential is constructed and is usually linear over a defined potential range. The slope of the latter affords the Tafel slope b which is related to the transfer coefficient via: $b = \left(\frac{d\eta}{d \log j} \right)_{a_X} = 2.303 \frac{RT}{\alpha F}$. The Tafel plot is recorded under conditions where the activity (or concentration) of the reactant species X, a_X (where for example X = OH^- in alkaline solution)is kept constant during the experiment. The numerical value of the Tafel slope is a good indicator of mechanism. For instance when T = 298 K one can show that if the first E step in a sequence is rate limiting then b = 120 mV dec^{-1}. In contrast if the first C step is rate limiting then b = 60 $mVdec^{-1}$. If the second E step is rate limiting then b = 40 $mVdec^{-1}$. The latter slopes would be observed if the steps 4, 5 or 6 were rate determining in the OER mechanism presented previously. One further piece of mechanistic data can be elucidated. We can measure the electrochemical reaction order m_X. The latter is measured at constant overpotential from a series of Tafel plots recorded at different activities of the reactant species X such as OH^-. The reaction order is given by: $m_X = \left(\frac{d \log j}{d \log a_X} \right)_\eta$. Hence step 4 rate determining implies that m = 1 and step 5 rate limiting m = 2 . Hence the set of parameters (b, m_X) when taken together can serve to pin down a mechanism quite well. This is an approach we have used with profit in our recent studies on the OER at transition metal oxide electrodes in aqueous base. One final point in this whistlestop summary of electrochemical kinetics: the lower the value of the Tafel slope the more effective the electrocatalyst. Hence in summary kinetic happiness resides in a combination of a large exchange current density and a low value of Tafel slope. We will discuss these aspects more later on in the paper.

We now follow the discussion of Millet and co-workers[12] and discuss some figures of merit for water electrolysis cells. The efficiency of a water electrolysis cell relates the theoretical amount of energy W_T required to split one mole of water to the real amount of energy required W_R, hence we write:

$$\varepsilon = W_T / W_R = \left(\frac{E_N It}{n_{H_2}} \right) \Big/ \left(\frac{E_{cell} It}{n_{H_2}} \right) = E_N / E_{cell} .$$

Hence the conversion efficiency of the electrolytic cell is given by the ratio of the Nernst Potential divided by the actual cell potential E_{cell} at the operating current density (typically 100 mA/cm^2). At low current densities, cell efficiencies close to 100% are obtained. The efficiency of a water electrolysis cell is a critical parameter responsible for the energy cost of the process. Operation at high current density is necessary to reduce investiment costs, but since efficiency decreases when current density increases, a compromise has to be struck between energy and investiment costs. The specific energy consumption E_S is the amount of electricity (in kWh) required for the production of a given volume (say 1 m^3) of hydrogen. It is expressed in units of kWh/Nm^3. It is a function of operating temperature, pressure and current density and is given by: $E_S(T, P, j) = \frac{E_{cell}(T, P, j) I}{\dot{m}_{H_2}}$ where I is the cell current (in A) and $\dot{m}_{H_2}$ is the hydrogen production rate (in Nm^3/h. Under standard conditions E_S^0 = 2.94 kWh/Nm^3. The system efficiency is defined as the ratio between the theoretical energy demand to produce 1 Nm^3 of H_2 at E_N = 1.23 V (ca. 3.0 kWh) and the energy required by the overall system (typically 5.0 kWh) and so we write: $\varepsilon_S = E_S^{\,0} / E_S(T, P, j)$. Finally the Faradaic yield or current efficiency is defined as the dimensionless ratio of the hydrogen mole number n_{H_2} formed during a given time interval Δt to the quantity of electricity passed through the cell during the same time period times the

Faraday constant F (ca. 96,500 C/mol). Hence $\varepsilon_j = 2Fn_{H_2} / jA\Delta t$ where A is the electrode area. Electrolysis cells are operated at elevated temperature usually close to 80°C and at high current density to optimize efficiency. There have been some useful papers published which attempt to make system wide models of the electrolysis cell[13].

The most important way of optimizing device efficiency is in optimizing the type of materials used in both the cathode and the anode. This involves optimizing the materials chemistry in order to reduce the expensive noble metal catalytic materials presently used by less expensive but equally catalytically effective substitutes.

Electrochemically induced generation of metal oxy-hydroxide thin films on electrode surfaces

We classify metal oxides into two groups[14]. The first are termed compact, anhydrous oxides such as rutile, perovskite and spinel in which oxygen is present only as a bridging species between two metal cations and ideal crystals constitute tightly packed giant molecules. The second class are dispersed, hydrous oxides where oxygen is present not just as a bridging species between metal ions, but also as O^-, OH and OH_2 species in co-ordinated terminal group form. In many cases, the latter materials when in contact with aqueous media, contain considerable quantities of loosely bound and trapped water plus, on occasion electrolyte species. It should be noted[14] that with microdispersed species the boundary between the solid and aqueous phase may be nebulous as the two phases virtually intermingle. This will be important when a simple physical model is developed to aid the understanding of the redox switching behaviour observed in thin films of the latter materials[15].

Furthermore, while compact oxides are usually prepared by thermal techniques such as for example decomposition of an inorganic salt precursor in air at elevated temperatures (RuO_2 and IrO_2 are typically formed at 450°C), the dispersed oxides are almost invariably prepared in an aqueous environment using base precipitation or electrochemical potential cycling techniques. We focus attention on both preparation methods here. In the latter methodology, the potential applied to the parent metal (or indeed to an inert metal support if film formation is accomplished via electro-precipitation from a metal salt solution) is cycled (or pulsed) in a repetitive manner between suitable upper and lower limits in an aqueous solution of appropriate pH. It is important to emphasise here that the oxide materials deposited via such procedures are deposited in the kinetically most accessible, rather than the thermodynamically most stable form. As a consequence the redox behaviour of the film will exhibit time varying effects. The deposited films are often amorphous or only poorly crystalline and will be prone to rearrangement in a manner that is directly influenced by factors such as temperature, pH and ionic strength. Microdispersion is usually due to the presence of strand, layer, tunnel or cage structures which facilitate not just small ions, but also in many cases solvent molecules to permeate the oxide or oxy-hydroxide phase.

One of the most versatile and convenient techniques used to generate hydrous metal oxy-hydroxide modified electrodes in a form suitable for the real time determination of their redox switching and electrocatalytic behaviour is that of repetitive potential multicycling (RPM). Here the electrode of the parent metal is cycled repetitively between suitable lower and upper limits in an aqueous alkaline or indeed acid solution. The RPM technique has been used to form oxide layers on many metals such as Fe, Ni, Co, Rh, Ir, Pt, Pd, Mn, and Cu. The type of potential perturbation used for oxide growth –sinusoidal, square or triangular wave- apparently makes little difference. Indeed the triangular wave is the most convenient, as changes in the current vs potential response profile (termed the cyclic voltammogram) can be employed during the oxide deposition reaction to monitor changes in redox behaviour associated with the latter as illustrated below in Fig.5 for the growth of hydrous oxy-hydroxide films on Fe electrodes in aqueous 0.5 M NaOH.

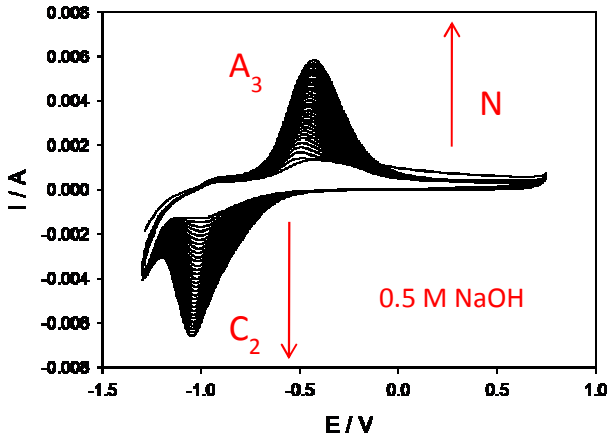


Figure 5: Growth of hydrous iron oxy-hydroxide thin film on Fe support electrode monitored via analysis of the real time voltammogram in 0.5 M NaOH. Potential swept between – 1.30 V and 0.75 V (vs Hg/HgO) at a sweep rate of 400 mV/s.

The growth of the hydrous oxide film on the Fe electrode can be readily monitored by following the development of the set of redox peaks labelled A_3,C_2 as a function either of the time or the number of potential cycles N. The variation of the integrated redox charge capacity Q (the latter is directly related to the hydrous oxide layer thickness L) as a function of number of cycles N is outlined in Fig.6 below.

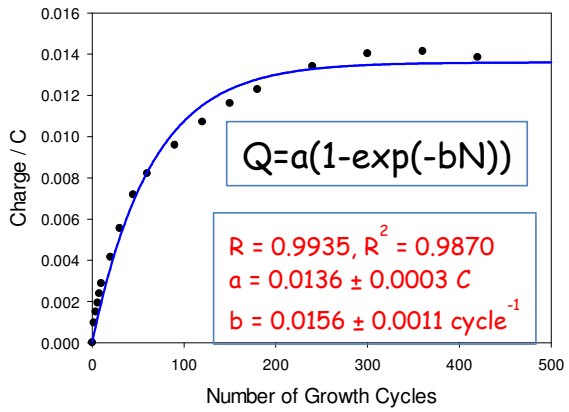


Figure 6: Growth of hydrous iron oxy-hydroxide thin film on Fe support electrode monitored via analysis of the real time voltammogram in 0.5 M NaOH. Potential swept between – 1.30 V and 0.75 V (vs Hg/HgO) at a sweep rate of 400 mV/s.

In Fig.6 the experimental data can be fit adequately to the latter kinetic expression $: Q = a\{1-\exp[-bN]\} = a\{1-\exp[b\upsilon t]\}$, where υ denotes the sweep rate in V/s. This expression implies that as $N \to \infty$, $Q \to a$ which is a constant limiting value. Furthermore the rate of increase of oxide growth dQ/dN decreases in a regular manner with increasing number of cycles N or with increasing time t.

As illustrated in Fig.7 the RPM technique can also be applied to deposit a hydrous nickel oxy-hydroxide thin film on either a Ni metal electrode in aqueous base or on a Au support electrode from a buffer solution containing Ni^{2+} ion (Pt and GC electrodes are also good supports). The developing redox behaviour of the immobilized nickel ion sites in the film can be readily monitored in real time by examination of the developing voltammograms.

The mechanism of hydrous oxide growth via RPM is now reasonably well understood, at least at a qualitative level[16,17]. It may be assumed that the initial oxidation process involves the formation of reversibly adsorbed OH and O moieties on the metal surface. With increasing degree of surface coverage adsorption assumes a more irreversible character accompanied by the formation, via a place exchange mechanism, of a thin, largely anhydrous, compact passivating phase oxide layer. Under conventional steady state anodization conditions where a steady oxidizing potential is applied to the metal surface such layers are of limited thickness as the activation energy for atom or ion migration in the compact film is usually quite large.

Even though it is directly produced in the initial electrochemical oxidation process, the anhydrous film is probably not the most stable metal oxidation product in the aqueous medium, but it may be regarded as an intermediate or metastable product in the formation of the hydrous oxide layer. In the anhydrous film ions are held in a rigid manner in an extended network of polar covalent bonds which drastically reduce ion transport through (and consequently extension of) the surface layer. The next stage of the film thickening reaction is the hydration process, and is generally very slow. This is because as in phase transformation reactions, it involves rupture of primary coordination metal-oxygen bonds. We have established in previous studies that the extent of hydrous oxide growth depends on the value chosen for the upper and lower limit of the potential sweep. As well as on the cycling

frequency adopted and the solution temperature and pH employed during the RPM procedure.

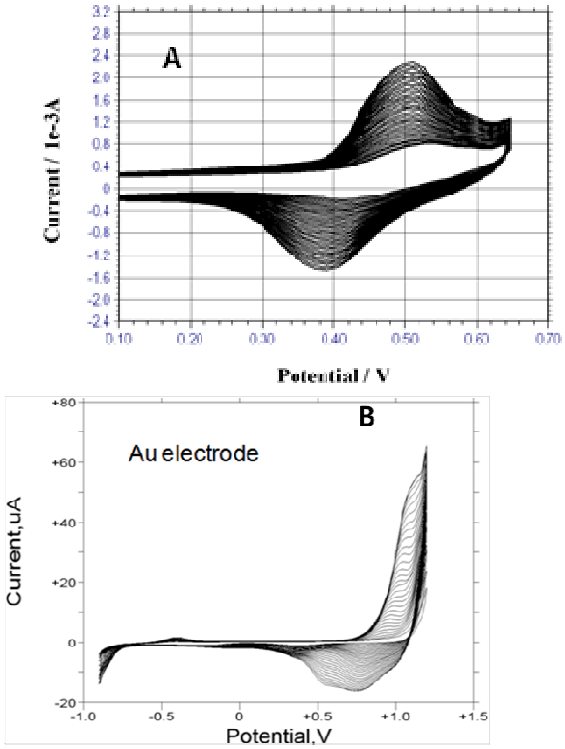


Figure 7: (A) Growth of nickel oxy-hydroxide thin film on Ni metal support electrode in 1.0 M NaOH. Growth potential limits: - 1.45 V to 0.65 V (vs Hg/HgO), sweep rate 150 mV/s, N = 30 cycles. . (B) Growth of nickel oxy-hydroxide thin film on Au support electrode monitored via analysis of the real time voltammogram in Ni2+ containing aqueous acetate buffer solution, pH 7.6. The potential was cycled from – 900 mV to + 1200 mV (the latter potentials were measured with respect to a SCE in the acetate buffer medium) at a potential sweep rate of 50 mV/s.

Note that the chemistry involved in film formation can be complex. For example referring to the data outlined in Fig.7(B) for nickel oxy-hydroxide film deposition in aqueous buffer We note that the electro-deposition process may proceed as follows:

$Ni^{2+}(aq) + 2OH^- \rightarrow Ni(OH)_2$ (8)

The following process may also occur as the applied potential becomes more anodic:

$OH^- \rightarrow OH_{ads} + e^-$ (9)

$Ni^{2+}(aq) + H_2O + OH_{ads} \rightarrow NiOOH + 2H^+(aq)$ (10)

The following process may also occur in the solution:

$Ac^- + H_2O \rightarrow HAc + OH^-$ (11)

$Ni^{2+}(aq) + OH^- \rightarrow NiOH^+(aq)$ (12)

$NiOH^+ + OH_{ads} \rightarrow NiOOH + 2H^+$ (13)

Hence we infer that both $Ni(OH)_2$ and NiOOH may well be formed during the course of the potential sweep perturbation. Unravelling the details of the redox chemistry which underlie the oxide film deposition can indeed be complex, and one needs to apply a combination of gravimetric and spectroscopic techniques to fully elucidate the mechanism[18].

Hence under conditions of thick film growth produced via potential cycling the interfacial region may be represented by the following: $M/MO_x/(MO)_a(OH)_b(OH_2)_c$/aqueous phase, as outlined in fig.8 below. This is the Duplex Layer Model of the oxide/solution interface region first proposed by Burke et al[19] some time ago.

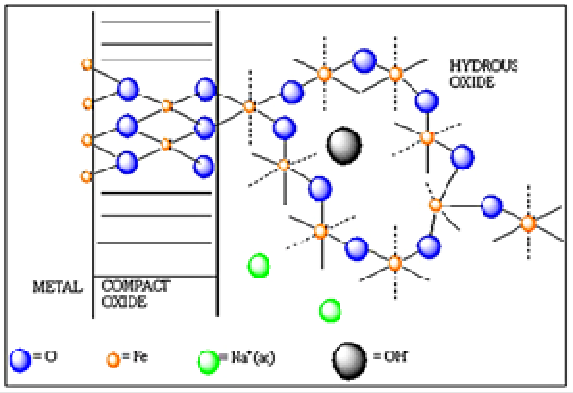


Figure 8: Schematic representation of Duplex Layer Model of oxide/solution interface.

The inner compact oxide layer is usually extremely thin, typically 1-5 monolayers in extent. The outer hydrous layer is regarded as extensively hydrated with both bound and trapped water present, as well as anions and cations. Hence we conclude that the hydrous oxide film can be regarded as an extended surface bonded polynuclear species. Metal cations in the polymer network are held together by a sequence of oxy and hydroxyl bridges. In short we can regard the microdispersed hydrous oxide layer as an open porous mesh of interconnected octahedrally coordinated surfaquo metal oxy groups. Burke and O'Sullivan[19] have suggested that the compact film component of the duplex oxide is highly conducting, with little potential drop across the inner layer. The major potential drop is assumed to occur at the outer surface of the compact film where the hydrous oxide is located (Fig.8). As noted in Fig.5 and indeed in Fig.7 the growth of the hydrous oxide layer on cycling is not accompanied by any notable increase in charge associated with the double layer region. This

suggests that the electrode area remains constant despite the formation of a thick, quite visible porous oxide film. A possible explanation of the observed constancy of the double layer currents exhibited in Fig.5 and Fig.7 is that the compact oxide/hydrous oxide interface (the region of maximum potential drop) is the only region where a faradaic electron transfer reaction occurs. The material in the hydrous layer is so dispersed that it does not behave as a separate bulk phase distinct from the electrolyte solution. Hence the hydrous oxide strands and solution do not form separate phases. The oxide might well not exhibit such bulk characteristics as a distinct three dimensional electronic band structure or a well defined oxide/solution phase boundary. This concept is borne out by ellipsometric measurements where the apparent refractive index exhibits a very low value and the film density is low.

The marked dependence of oxide growth rate on the lower limit of the potential sweep is indicative of the essential role that partial reduction of the anhydrous oxide plays in the production of a thick deposit. Partial reduction of the compact oxide layer apparently facilitates rearrangement of oxy-cation species at the metal surface, leaving it in a somewhat disrupted state. It has been established for a number of metals that the anhydrous film is reduced much more readily than the hydrated film. The greater stability of the latter is probably due to reasons such as (i) lower repulsion between cations owing to greater separation, (ii) decreased net charge arising from hydroxyl ion coordination by cations present and (iii) polymer formation. On subsequent re-oxidation of the partially reduced metal surface the compact layer is restored but the outer region of the compact film is present in a more dispersed form. On further reduction the latter material becomes incorporated into the outer hydrated layer. It is not clear whether this rearrangement process involves the detachment of oxycations, i.e. a dissolution/re-precipitation mechanism, or a certain weakening, with only a partial detachment of oxycation binding in the compact oxide layer. In the latter case the partially reduced cations are assumed to be displaced from normal lattice sites, and, as such, are more susceptible to oxidation in the subsequent anodic sweep during which they complete their oxygen coordination shell of six oxygen atoms to form a rather open polymeric inorganic bronze or zeolite type structure.

The upper limit of the potential sweep also has an important effect on the rate of oxide growth. The importance of this parameter lies in the fact that it extends oxygen penetration into the outer regions of the metal lattice, and may also help to generate a slight expansion and stress associated disruption of the metal/oxide interface. The upper potential limit may also facilitate uptake of a slight excess of oxygen by the oxide phase. A common observation in our studies is that there is an optimum value of upper limit. The fall of in oxide growth efficiency at more anodic values of applied potential may be associated with the increasing difficulty of reduction of the passivated surface film at lower potentials when the potential sweep is subject to reversal. Hence the optimum upper limit corresponds to a potential which represents the best compromise between two opposing effects. In short the compact layer must attain a reasonable thickness (hence the need for a relatively high anodic potential), but too high an upper limit results in a very un-reactive layer which does not reduce readily at the lower potential limit.

Hence for most metals, but especially for the noble metals such as Au, Pt, Ir and Rh, extension of oxide growth beyond the monolayer level under conventional galvanostatic or potentiostatic (constant current or potential) conditions is usually quite slow. This is obviously due to the presence of the initial compact oxide product layer which acts as a passivating diffusive barrier to further growth via ion migration (such compact oxides often exhibit parabolic growth kinetics). In contrast under potential cycling conditions the upper limit plays a significant role. There is probably a combination of thermodynamic and kinetic factors involved, but evidently the upper limit must be sufficiently anodic that compact oxide formation exceeds significantly the single monolayer level so that on subsequent reduction, a disturbed, highly disordered layer of metal atoms is prepared on the metal surface (see Fig.8). Thus with Pt and Au, two metals where oxide monolayer behaviour is well defined[20], the optimum lower limit lies at a potential value at, or below, the value of the monolayer oxide reduction peak. On subsequent re-oxidation the disturbed layer of metal atoms is converted to hydrated or partially hydrated oxide – complete hydration under these circumstances may involve several

redox cycles- with a fresh inner compact layer being regenerated at the metal surface on each anodic sweep. On repetitive potential cycling, the porous outer layer increases in thickness at the expense of the underlying metal.

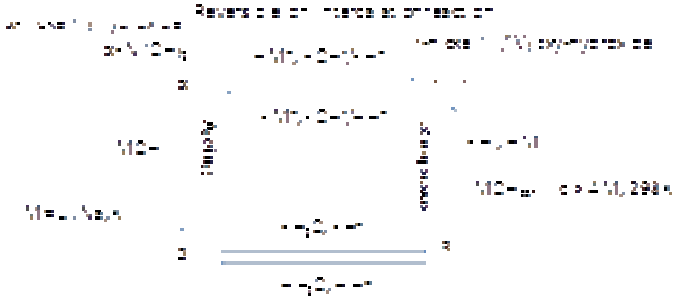
Finally the decrease in oxide growth rate with number of cycles, time (or equivalently with increasing film thickness expressed quantitatively via $dQ/dN = ab\exp[-bN]$, can be attributed to the increasing inhibition of water and hydroxide ion transfer to the inner region of the oxide layer, with increasing hydrous oxide thickness. We have observed that this effect is more marked with increasing base concentration. Evidently, increased hydroxide ion activity suppresses hydroxide ion dissociation and/or favours adsorption of this species. This will result in the inhibition of crystallization of the hydrous oxide layer, and the resulting more amorphous film will be more effective in excluding water from the inner region of the oxide film, thereby inhibiting growth of the microdisperse hydrous layer.

Redox switching in multilayer hydrous oxide films

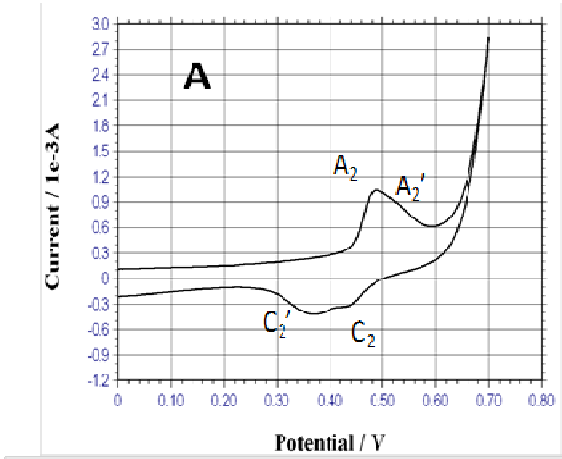
We now describe the electrochemical properties of hydrous oxyhydroxide thin film modified electrodes which are formed via potential cycling in aqueous base. We focus particular attention on nickel oxy-hydroxide films in which the metal oxide is deposited electrochemically on either a Ni or Au support surface. The discussion will focus on the redox switching reaction within the hydrous oxide layer in which the oxymetal sites charge oxidation state via potential induced topotactic redox reactions involving electron transfer between adjacent metal ion sites along the polymeric oxide strand and charge compensating counter ion transport within the solution region between the oxide strands. We focus attention on the latter process since it defines many of the practical applications of the oxide electrode such as its capacity to store charge (useful in supercapacitor applications), to change colour when the oxidation state is changed (electrochromic behaviour) and to serve as an effective pH and chemical sensor.

Typical cyclic voltammetric profiles recorded for multicycled (N = 30 cycles in both cases) Ni and Au electrodes modified with a nickel oxy-hydroxide film in contact with aqueous 1.0 M NaOH are outlined in Fig.9. In Fig .9(a) the oxide layer was grown on a Ni electrode in 1.0 M NaOH by cycling the potential between limits of – 1.45 V to 0.65 V (vs Hg/HgO) at a sweep rate of 150 mV/s. In fig.9(b) the oxide layer was deposited on an Au support surface from a deposition solution of 0.1 M $NiSO_4$, 0.1 M NaAc and 0.001 M NaOH between limits of – 0.90 to 1.20 V (vs SCE) at a sweep rate of 20 mV/s.

It is clear from Fig. 9 that the voltammetric behaviour recorded for the nickel oxy-hydroxide thin films grown both on Ni and Au support electrodes is similar in that two sets of peaks may be observed in the potential region 0.30 – 0.60 V (vs Hg/HgO) prior to the onset of active water oxidation to generate molecular oxygen. These peaks correspond to redox reactions involving the transfer both of electrons and ions within the microdispersed oxide film. The interfacial redox chemistry of the multicycled nickel oxide electrode in aqueous alkaline solution can be readily understood in terms of the Bode scheme of squares[21] as presented in scheme 1 and Fig.10 below.



Scheme 1. Bode square scheme for redox switching in nickel oxy-hydroxide thin films .



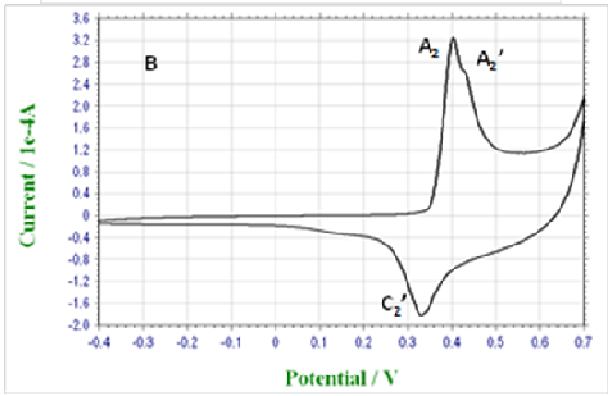


Figure 9: (a) Typical voltammetric response recorded for a hydrous nickel oxy-hydroxide thin film on Ni support electrode in 1.0 M NaOH. Sweep rate, 40 mV/s. Layer grown for N = 30 cycles. (b) Voltammetric response recorded for an electroprecipitated nickel oxyhydroxide modified Au electrode in 1.0 M NaOH. Sweep rate, 40 mV/s.

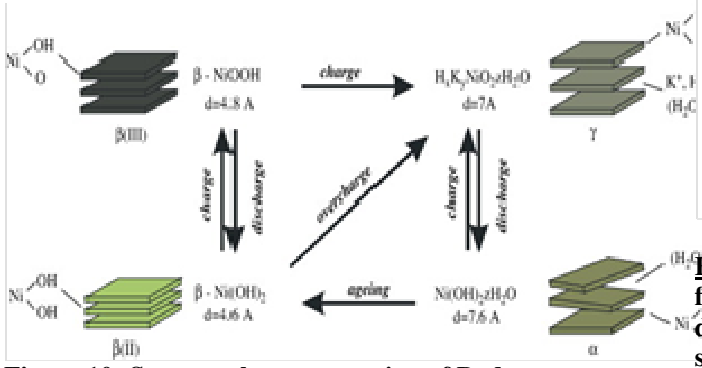


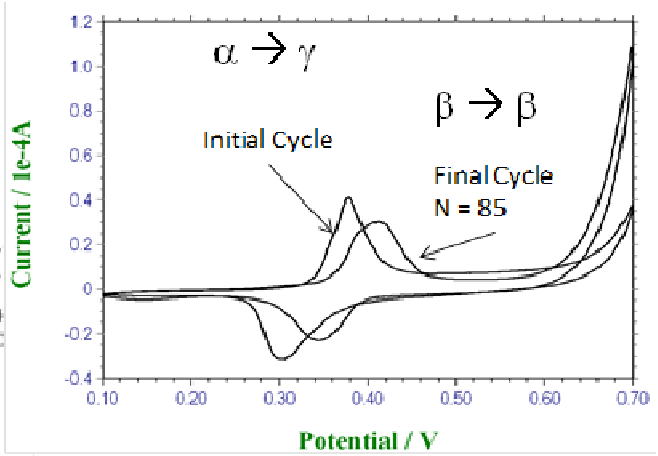
Figure 10: Structural representation of Bode square scheme.

The redox chemistry has been largely elucidated using electrogravimetric methods such as the Electrochemical Quartz Crystal microbalance which enables tiny mass changes which occur in the deposited thin film during redox switching to be monitored in real time[16]. Here the redox switching behaviour of electrochemically generated nickel oxide films was rationalized in terms of four phases as outlined in fig. 10. The discharged or reduced $Ni(OH)_2$ material can exist either as a largely anhydrous phase designated as β – $Ni(OH)_2$ (denoted β-Ni(II)) or as a hydrated phase denoted as α-$Ni(OH)_2$ (in short represented as α-Ni(II)). Oxidation of the β-Ni(II) material is envisaged to produce a phase referred to as β-NiOOH or β-Ni(III). In contrast oxidation of the α-Ni(II) material produces γ-Ni(III) or γ-NiOOH. Hence one expects two distinct redox transitions : α(II)/γ(III) which we label RT1 and β(II)/β(III) which is RT2. The corresponding redox peaks are designated A_2'/C_2' and A_2/C_2 respectively. A general representation of the RT1 and RT2 stoichiometry are outlined in Scheme 2 below.

$$\left[(1+x)\alpha - Ni(OH)_2 w_\alpha OH_2 \bullet (\delta_\alpha NO_3^-, \sigma_\alpha CO_3^{2-})\right] + y\left(Na^+ + OH^-\right) + (1+2x)OH^-$$
$$\square \quad \left[\gamma - NiOOH.xNiO_2.w_\gamma OH_2 \bullet \left(\delta_\gamma NO_3^-, \sigma_\gamma CO_3^{2-}\right)\right] + \left(1+2x+w_\alpha - w_\gamma\right)OH_2 + (1+2x)e^-$$

$$\beta - Ni(OH)_2 \bullet w_\beta OH_2 + OH^- \square \quad \beta - NiOOH + \left(1-w_\beta\right)OH_2 + e^-$$

<u>Scheme 2.</u> The redox stoichiometry of nickel oxide explained.



<u>Figure 11</u>. Typical voltammetric response recorded for an electroprecipitated nickel oxide film deposited on a polycrystalline gold substrate subjected to slow multicycling (sweep rate 10 mV/s) between 0.1 and 0.7 V (vs Hg/HgO) in 5.0 M NaOH. The initial and final response profiles are presented.

We note that the redox potentials of RT1 is typically some 60-100 mV less positive than those of RT2. It can be noted from fig. 11 that upon ageing the α-$Ni(OH)_2$ can dehydrate and re-crystallize as β-$Ni(OH)_2$. This is especially prevalent in more concentrated alkali solution. In addition, overcharging β-NiOOH (which occurs at more elevated potentials) can convert it to γ-

NiOOH. The non-stoichiometric nature of both the discharged and charged material is indicated by the average oxidation state of Ni in each phase as indicated in the structural representation of the various phases in fig. 10. It is important to note that while there is a general acceptance for the general features of the Bode scheme, one must understand that it is inappropriate to think about the formation of a compound or a phase with definite stoichiometry during the chemically complex $Ni(OH)_2$/NiOOH transformation. Instead the four phases mentioned in the Bode scheme should be considered as the limiting forms of the divalent and trivalent materials – the actual composition of the oxide at a given potential depending on a range of factors including its history, method of preparation, degree of hydration, defect concentration etc.

Burke and Lyons[22] and more lately, Lyons *et al.* [23] have shown that, for an ideal oxide electrode system in aqueous solution at 25°C, the potential decreases with increasing pH by ca. 59 mV/pH unit with respect to a pH independent reference electrode such as the NHE or the saturated calomel electrode (SCE). Such a potential-pH shift is referred to as a *Nernstian shift*, since it is predicted by the Nernst equation. Alternatively, if the reference electrode is pH dependent, such as the reversible hydrogen electrode (RHE) or the Hg/HgO electrode, no potential pH shift will be observed, since the potential of this type of electrode also alters by ca. 59 mV per unit change in pH at 25°C. Furthermore, Burke and Lyons[22] have discussed super-Nernstian shifts that have been observed for various hydrous oxide systems – in these cases the potential/pH shift differs from the expected 0.059V/pH unit at 25°C. The mathematical treatment of this situation is beyond the scope of the present paper, but suffice to say, the phenomena have recently been qualitatively summarized[23]. Thus, a zero potential shift (with respect to a pH dependent reference electrode) implies that both the reactants and the product possess the same net charge. A positive potential shift with pH, is indicative of an oxidised state that is more positive than the reduced state, whereas the converse is true in the case of an observed negative potential/pH shift.

As previously shown[22,23] that the anhydrous A_2'/C'_2 peaks exhibit a regular Nernstian shift whereas the hydrous counterparts A_2/C_2 exhibit the characteristic of a hydrous or hyper-extended oxide i.e. *a super-nernstian potential-pH shift*, which typically has the value of $dE/dpH = -2.303(3RT/2F) = -0.088$V/pH unit at T = 298 K. Accordingly, by analogy with a scheme produced by Burke and Whelan[24] for redox switching of iridium oxide films, it has been proposed that the main redox switching reaction (corresponding to the peak set A_2/C_2) may be written as:

$$[Ni_2(OH)_6(OH_2)_3]_n^{2-} + 3nOH^- \rightarrow [Ni_2O_3(OH)_3(OH_2)_3]_n^{3-} + 3nH_2O + 2ne^- \quad (14)$$

corresponding to an Ni(II)/Ni(III) redox transition in a polymeric microdispersed hydrous oxide layer. This redox switching reaction is illustrated schematically in Scheme 3.

The redox switching reaction (associated with the A_2/C_2 voltammetric peaks) reflects the change in oxidation state of the film as a result of a potential perturbation. Redox centres immediately adjacent to the support electrode are directly affected by the electrode potential, whereas charge is further propagated along the oxy-nickel polymer strands in the hydrous layer via a sequence of electron self exchange reactions between neighbouring oxy-metal sites. This process is envisaged to be analogous to redox conduction exhibited by electroactive polymer films. In the simplest terms this electron "hopping" may be modelled in terms of a diffusional process, and so the charge percolation rate may be quantified in terms of a *charge transport diffusion coefficient*, D_{CT} or in terms of a diffusive frequency $\tau = D_{CT}/L^2$ where L denotes the thickness of the oxide film. In the case of hydrous nickel oxide, the latter may reflect either the electron hopping rate or the diffusion of of OH^- (or equivalently H_3O^+) ions via a rapid Grotthuss type mechanism. The charge transport diffusion coefficient may be quantitatively estimated using cyclic voltammetry [25]. The important point to note is that redox switching in the oxide involves electron and ion transport. The Ni(II)/Ni(III) redox transition occurs within a polymeric microdispersed oxide consisting of polymer strands comprising of interlinked octahedrally coordinated surfaquo groups. The assembly can be regarded as a dual rail electrical transmission line of the type presented in fig.12 for porous modified electrodes[26]. Hence the charge transport through the layer can be characterized in terms of characteristic resistances for electron and counter-ion motion along the oxide polymer strands and within the solution filled pores between the oxide strands. This type of conductivity characterization can be best accomplished using Electrochemical Impedance

Spectroscopy[26]. The latter technique is very powerful and has been applied to mixed conducting systems in thin film form such as metal oxides and electronically conducting polymers[27].

Scheme 3: Topotactic redox reaction in hydrated layer in hydrous nickel oxy-hydroxide.

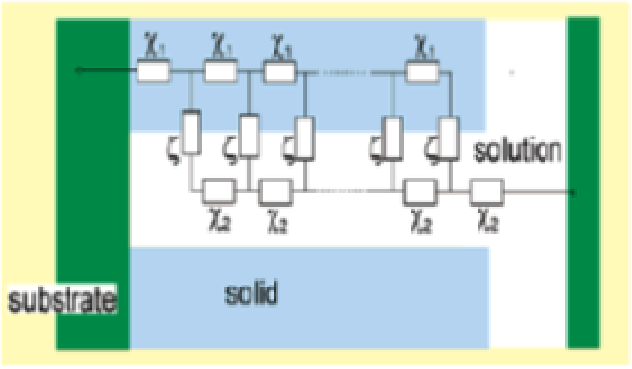


Figure 12: Dual rail transmission line model for porous thin film mixed electronic/ionic conductor. Note that χ_1 and χ_2 corresponds to the specific conductivity of the solid oxide phase and electrolyte solution respectively and ζ represents the specific polarization/charge transfer element at the solid/solution interface.

Multilayer hydrous oxide films as potential pH sensors

The fact that nickel oxy-hydroxide films exhibit a Super-Nernstian decrease in the peak potential associated with the Ni(II)/Ni(III) surface redox switching with increasing solution pH is significant for two reasons. The first signifier is that the oxy metal species must be anionic [22,23]. The second is that the oxide film may prove useful for pH detection. The variation is open circuit potential with solution pH for an electroprecipitated nickel oxy-hydroxide film on a gold substrate is presented schematically in figure 13. The open circuit potential was recorded for a range of time scales varying from 200 to 15,000 seconds. A good linear response of potential to changes in solution pH was recorded. The slope or super-Nernstian with $dE_{OC}/d\ pH = -0.080$ V/dec and $r^2 = 0.95$. The behaviour of the oxide pH sensor was examined by monitoring the response of the latter to the rapid changes in solution pH encountered during the course of a pH titration (fig.14). The titration of 1M sulphuric acid H_2SO_4 with a strong base (50 mL 1 M NaOH) was monitored in real time using both a conventional glass electrode and the metal oxide modified electrode. The open circuit of the latter was determined as a function of volume of strong acid added to the reaction mixture.

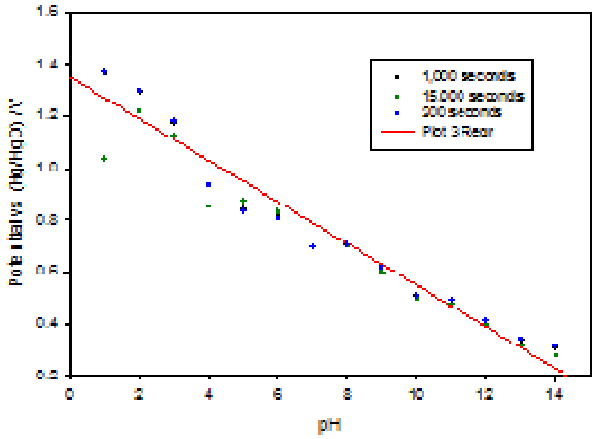


Figure 13: Variation of open circuit potential recorded at an electroprecipitated nickel oxyhydroxide modified gold electrode as a function of solution pH (the latter measured using a glass electrode).

It is indeed gratifying to note that the metal oxide wire electrode potential (measured with respect to a SCE reference electrode) monitors accurately the change in solution pH (measured using a commercial glass electrode system). The solid state pH sensor responds very rapidly to the rapid changes in pH recorded near the equivalence point. As the solution becomes more alkaline the open circuit potential of the oxide electrodes increases in a well defined manner. The metal oxide electrode accurately predicts the position of the equivalence point. Furthermore we have shown that an excellent correlation exists between the pH value calculated from the E_{OC} magnitude and that experimentally measured using a commercial glass electrode. Hence we conclude that electro-precipitated nickel oxyhydroxide thin film electrodes offer potential as novel pH sensors[29] .

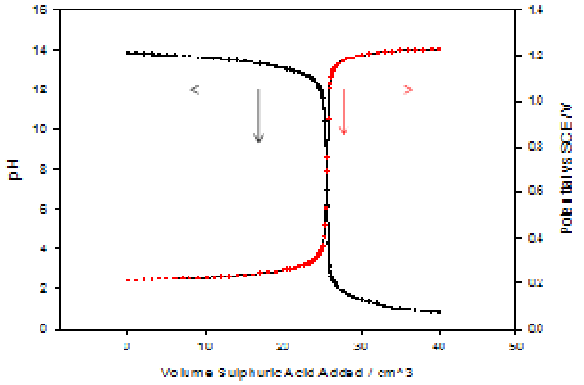


Figure 14: Variation of open circuit potential recorded at an electroprecipitated nickel oxyhydroxide modified gold electrode as a function of solution pH (the latter measured using a glass electrode) during the course of a strong acid/strong base titration.

The kinetics and mechanism of electrolytic water oxidation to generate molecular oxygen

The generation of molecular oxygen via electrolysis of water (OER) is a complex and energetically demanding reaction. The reversible potential in alkaline solution is 0.303 V (vs Hg/HgO). However in order to generate oxygen at an appreciable rate an overpotential of several hundred millivolts may be required. The net reaction takes the following form

$4OH^- \leftrightarrows O_2 + 2H_2O + 4e^-$ (15)

Hence the process may be regarded as a proton coupled electron transfer process which occurs over a number of steps which will include both electron transfer and chemical steps, and will also involve adsorbed intermediates. The surface coverage of reaction intermediates may well vary with electrode potential. Consequently the analysis of the oxygen evolution reaction thermodynamics and kinetics is challenging. In recent years the TEECE group at Trinity College have made significant progress in the understanding of the OER. First it must be noted that the OER at oxidized metal and metal oxide electrodes involves the active participation of the oxide. Second, the acid/base behaviour of the oxide layer is an important factor : the oxide is anionic (as noted previously when discussing super-Nernstian behaviour (see Fig. 15 for nickel oxy-hydroxide thin films grown on Ni metal support surfaces), and, as illustrated in fig.16 for nickel oxy-hydroxide thin films grown on nickel electrodes in aqueous base the OER onset potential decreases in a linear manner to less positive potentials with increasing solution pH which mirrors the variation of the redox switching peaks. Third, the activity of the oxide film can be ascribed to the presence of active surface or surfaquo groups which are octahedrally co-ordinated and interlinked throughout the hydrous oxide matrix. Hence the catalysis of oxidative water splitting is three dimensional. These ideas have been recently reviewed by Lyons and co-workers[29].

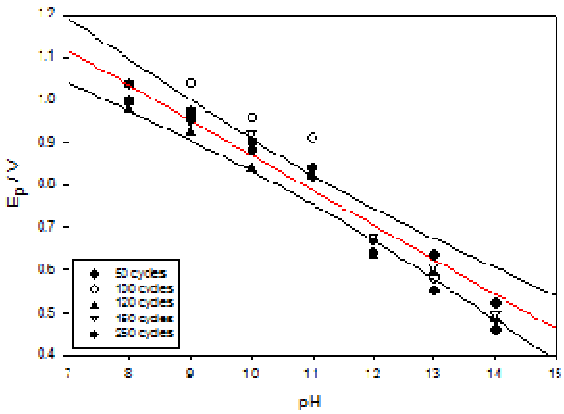


Figure 15: Variation of anodic A_2 peak potential with solution pH. Slope = - 0.082 V, r^2 = 0.96. Data measured for layers of various thickness. Nickel oxy-hydroxide layer grown via potential cycling in 1.0 M NaOH on Ni support electrodes.

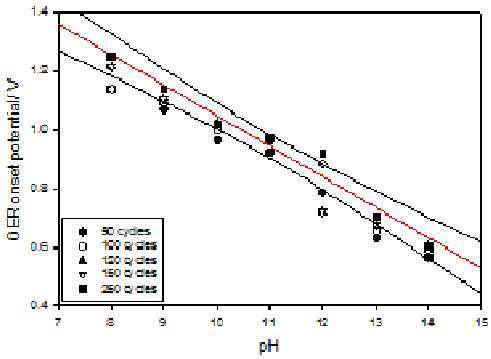


Figure 16: Variation of oxygen evolution onset potential with solution pH. Slope = - 0.104 V/dec, r^2 = 0.97. Data measured for layers of various thickness. Nickel oxy-hydroxide layer grown via potential cycling in 1.0 M NaOH on Ni support electrodes.

The classic approach adopted to examine the kinetics of the OER at metal oxide and oxidized metal electrodes has been the use of an ensemble of steady state and transient electrochemical techniques such as Tafel Plot Polarization, Open Circuit Potential Decay (OCPD) and Electrochemical Impedance Spectroscopy[27]. These measurements yield key parameters such as the Tafel slope b and the reaction order m of the

mechanistically significant reactant such as the hydroxide ion when studies are conducted in alkaline solution. The latter data are of mechanistic significance and can be used to propose a chemically meaningful step by step mechanism for the multistep OER. Electrochemical impedance spectroscopy data can be directly fitted to a proposed electrical equivalent circuit which is developed from a mathematical analysis of the proposed OER mechanistic sequence. The components of the equivalent circuit (resistors, capacitors etc) can in many cases be assigned to physically meaningful parameters and processes such as rate constants (via Faradaic impedance), film resistances, and ionic and electronic transport rates.

Typical Tafel plots for oxygen evolution at hydrous nickel oxy-hydroxide thin films grown via potential cycling (N = 120 cycles) on Ni support electrodes are presented in Fig.17.

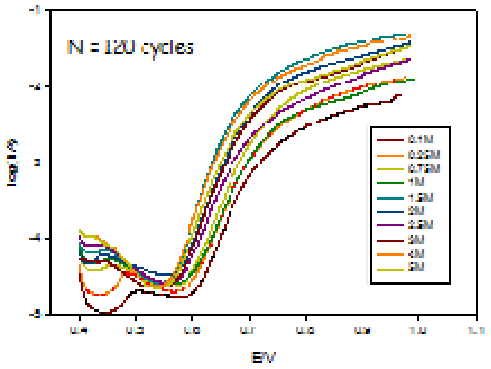


Figure 17: Typical Tafel plots for OER at multicycled nickel oxy-hydroxide thin films grown for N = 120 cycles in 1 M NaOH. Plots were recorded as function of base concentration.

The latter data is expressed in conventional Tafel format where the OER rate is expressed as the logarithm of the current and the reaction driving force is the electrode potential. According to the Tafel equation the OER rate is exponentially dependent of the applied potential. The Tafel slope b is given by b = dE/d log i. We note dual Tafel slope behaviour with a slope of 60 mV/dec at low potentials and 120 mV/dec at higher potentials. The latter values are mechanistically significant. The reaction order is obtained by plotting the logarithm of the oxygen evolution current density recorded at a fixed electrode potential as a function of the logarithm of the hydroxide ion activity. This was done for potentials located in the low and high Tafel slope region at typical values of reaction order were $m_{OH^-} \approx 0.9$. Similar results were obtained for electro-precipitated nickel oxy-hydroxide films grown on gold support electrodes.

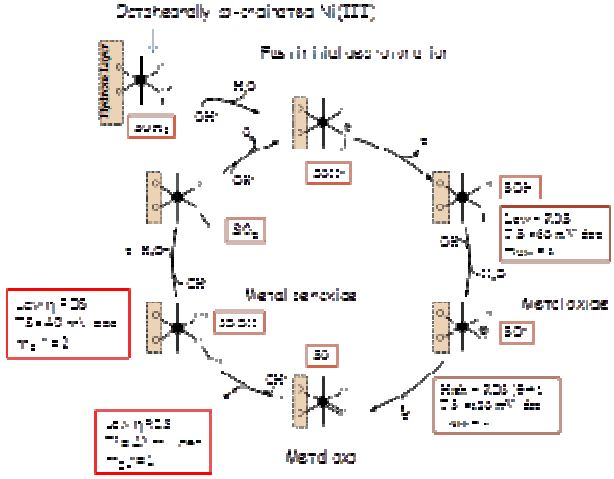
We have recently proposed[30] that the following set of reaction steps may be proposed to account for the mechanism of electrochemical oxygen evolution at nickel oxy-hydroxide electrodes in aqueous alkaline solution. Our mechanistic thinking is guided by the earlier work of Kobussen and Broers[31] . The mechanism is presented in schematic form in scheme B. Note that octahedrally co-ordinated oxy-nickel surfaquo groups are identified as the catalytically active species and are located within the hydrous layer. The following reaction sequence based on scheme 4 may be outlined:

$$SOH_2 + OH^- \rightarrow SOH^- + H_2O \quad (16)$$
$$SOH^- \rightarrow SOH + e^- \quad (17)$$
$$SOH + OH^- \rightarrow SO^- + H_2O \quad (18)$$
$$SO^- \rightarrow SO + e^- \quad (19)$$
$$SO + OH^- \rightarrow SOOH + e^- \quad (20)$$
$$SOOH + OH^- \rightarrow SO_2 + H_2O + e^- \quad (21)$$
$$SO_2 + OH^- \rightarrow SOH^- + O_2 \quad (22)$$

In the latter scheme S represents the surfaquo group which is attached to the hydrous oxide surface by bridging oxygen ligands.

The Lyons-Doyle reaction sequence[30] is presented schematically in Scheme 4. The initial deprotonation step involves a bound water molecule attached to an octahedrally co-ordinated Ni(III) surfaquo group located within the hydrous layer. A common feature of these schemes is that the starting point for the OER catalytic cycle is usually represented as a metal coordinated water molecule. However, in the strongly alkaline conditions used in this system it is likely that a significant proportion of these coordinated water molecules will be deprotonated. The pK_a value for a water molecule coordinated to a highly charged metal atom is generally in the range pK_a 5-9 [32]. In light of this, it is more reasonable to assume that the initial deprotonation step expressed in eqn.16 is facile and will occur outside of the catalytic cycle.

Hence, the initial deprotonation step is depicted as a pre-step in Scheme 4 and the OER catalytic cycle begins with the resultant coordinated OH^- ion which we label SOH^-. A second point of note regarding Scheme 4 is that the formation of the metal oxide SO^- (eqn.18) and metal oxo SO (eqn. 19) species are designated as rate determining. Interestingly, in a recent theoretical study Muckermann *et al.* [33] showed, through the use of DFT calculations, that for a GaN/ZnO surface with high coverage of adsorbed OH^- ions the intermediate associated with the highest energy was an oxide radical. Similarly, Rossmeisl *et al.* [34] performed a DFT study of the OER at RuO_2 surfaces. They too found, for a surface saturated with adsorbed OH, that the highest energy intermediate was a surface oxygen species, in this case an oxo species. Considering these studies, the present mechanistic interpretation brings together a number of strands in the current understanding of the OER at metal oxides, and resonates with recent work proposed for water oxidation using transition metal complexes in homogeneous solution. The 60 mV/dec Tafel slope and associated reaction order of unity is associated with rate determining generation of metal oxide species (eqn.18) whereas the Tafel slope of 120 mV/dec observed for all base concentrations at high potentials and associated unity reaction order with respect to hydroxide ion activity is rationalized by assuming that the decomposition of metal oxide to form metal oxo-species is slow and rate determining (eqn.19). We also note from Scheme 4 that rate determining decomposition of the nickel oxo species or indeed rate determining decomposition of the nickel peroxide moiety would suggest a different set of diagnostic parameters, namely low potential Tafel slope values of ca. 40 mV/dec for both options and reaction orders wrt hydroxide ion activity of 1 and 2 for oxo decomposition (eqn.20) and peroxide decomposition (eqn.21) respectively. The catalytic cycle illustrated in scheme 3 has been used to rationalize the OER kinetics and mechanism both at hydrous Fe and Ni oxy-hydroxide thin film modified electrodes. One of the key steps in our proposed mechanism involves the formation of a surface bound metal oxo-species (SO). In scheme 4 above this species is depicted as M=O suggesting a M(V) metal centre. However, this species could also be represented as a metal oxyl moiety M(IV)-O· . Indeed the degree of radical character has been shown to depend on the length of the metal oxo bond with M(V)=O being more stable for shorter bond lengths[35]. In the case of Fe the metal oxo species possibly involves Fe(V) [36] as inferred from recent variable temperature mass spectrometry data obtained for a biomimetic non-heme Fe complex with an Fe(V) oxo as the catalytic centre. The situation in the case of Ni is less clear. The Ni-O bond may be longer and have a greater radical character and a Ni(IV) oxyl intermediate may be the better descriptor of the situation.



Scheme 4: Lyons-Doyle reaction sequence for electrolytic generation of molecular di-oxygen at nickel oxygroups located within the hydrous oxide layer in aqueous alkaline solution

The important point to note is that the surfaquo group structures outlined in the catalytic cycle presented in Scheme 4 reflects current thinking in the allied field of water oxidation in homogeneous solution via molecular catalysts [37]. This is not unexpected given the very dispersed and somewhat tenuous nature of the catalytically active hydrous oxide layer which we postulate to be formed electrochemically on the electrode surface after cyclic polarization of the support electrode in aqueous alkaline solution.

Concluding Remarks and Future Outlook

In this paper we have presented a survey of some recent work on electrochemically prepared metal oxy-hydroxide materials deposited as thin films on either the parent metal, or on conductive gold support surfaces. The redox chemistry of the latter materials has been described in terms of electron transfer along connected surfaquo groups located within a microdispersed polymeric matrix of oxide strands immobilized on the support electrode surface. The application of these films

as new generation solid state pH sensors and as efficient electrocatalysts for the electrolytic generation of molecular di-oxygen gas has been demonstrated. We have noted that the acid/base behaviour of the electrochemically prepared films is an important factor to take into account when considering the mechanism of oxygen evolution. An important new mechanism has been proposed for the OER at nickel oxide modified electrodes based on electrochemical, spectroscopic and DFT studies both in our laboratory and in others. We conclude that metal oxide and oxo species are active intermediates in the multistep OER under electrochemical conditions in aqueous solution. Indeed we can conclude that the chemistry of the surfaquo group determines the chemistry of the OER catalytic cycle.

Acknowledgements

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Biography

Mike Lyons is currently Professor in Physical Chemistry and SFI Principal Investigator in the School of Chemistry & CRANN, and Investigator within the recently formed AMBER Centre, Trinity College Dublin, Ireland. He was born in Cork city in 1956 and is a graduate of University College Cork (1979) where he read Chemistry and Mathematical Physics. He obtained his Ph.D degree from the same University in 1983 under the supervision of the late Prof. Declan Burke in metal oxide electrochemistry. He worked with the late Prof. John Albery and Prof. Brian Steele at Imperial College London on metal oxide electrocatalysis before being appointed to a lectureship in Physical Chemistry at Trinity College Dublin in 1984. He was elected to Fellowship, Trinity College Dublin, in 1992 on the basis of publication and research. Mike has served both on the University Academic Council and Governing Body (Board) of Trinity College, and has been Director of Undergraduate Teaching & Learning and Head of Physical, Computational and Materials Chemistry within the School of Chemistry. His research interests encompass Physical and Analytical Electrochemistry and in a publication output of two books and more than 115 papers, he has made significant contributions to electrode kinetics, metal oxide electro-catalysis, electroactive polymer electrochemistry, mathematical modelling of electrochemical systems, electrochemical biosensors, and carbon nanotube electrochemistry. His H-index is 27. His current interests in collaboration with the recently formed SFI funded Trinity Electrochemical Energy Conversion and Electrocatalysis Group, is in revisiting and finally understanding the redox and electrocatalytic behaviour with respect to oxygen evolution, oxygen reduction and hydrogen evolution of hydrous oxide coated metal and metal oxide electrodes for use in energy conversion and storage device applications. His group is also developing non enzymatic electrochemical biosensors based on metal oxide modified electrodes for bio-diagnostic applications and examining the use of metal oxide electrodes as new generation pH sensors.

Integrating Mathematics into Junior Science

Gráinne Walshe, Jennifer Johnston and George McClelland
National Centre for Excellence in Mathematics and Science Teaching and Learning,University of Limerick, Limerick grainne.walshe@ul.ie

Introduction

Science and mathematics are closely related in the physical world, yet as school subjects they can be quite separate, even where they share overlapping content (McBride and Silverman cited in Czerniak 2007). Science and mathematics integration has been recommended as a way to increase student conceptual understanding of, interest in, and motivation to learn both subjects (Pang and Good 2000). Moreover, STEM education (involving the purposeful integration of science, technology, engineering and mathematics) is receiving increasing emphasis in Ireland and elsewhere (Breiner *et al.* 2012). This article describes some key aspects which it is useful to be aware of so that meaningful teaching and learning of the important overlaps and interactions between the subjects can occur. The ideas have emerged from our research into the design, development and evaluation of a model for science and mathematics integration in Ireland. The model consists of three elements: a syllabus map of the overlapping content on the Junior Cycle science and mathematics curricula, a Teaching and Learning Sequence for overlapping science and mathematics content and skills, and a series of Critical Integrated Skills Activities (CISA) for science classrooms.

The CISA Model for Developing Integrated Mathematics into Science Lessons

The first stage of the research was to develop and evaluate a Syllabus Map and Teaching Sequence for integrated learning. The Sequence included the identification of six CISA mini-schemes. These are based on significant overlapping areas between science and mathematics, as found from the Syllabus Map, but also coordinated with the likely stage of learning of students in both subjects through the Sequence. Exemplar lessons have been developed based on a CISA lesson template (see Fig. 1). These provide teachers with guidelines for developing further mathematics integrated into science lessons, based on topics that work with their preferred teaching sequences, and their students' needs.

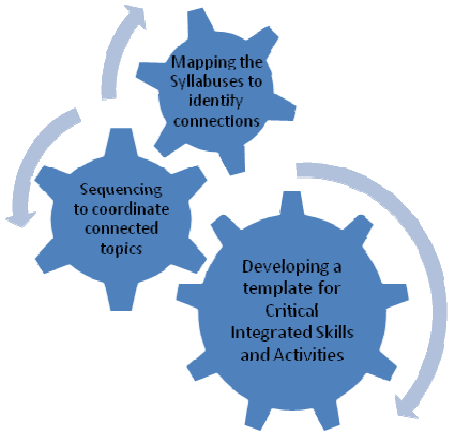


Figure 1: The CISA Model for Developing Integrated Mathematics into Junior Science Lessons

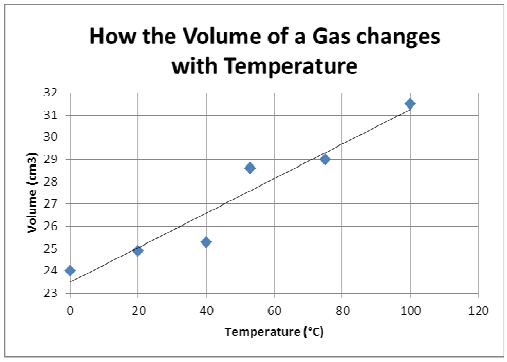
Literacy and Numeracy versus Integration

Literacy and Numeracy are an important aspect of lessons in all subjects in Irish education in recent years (DES 2011). It is sometimes thought that integration of mathematics into science is solely concerned with developing student numeracy within science. However, from an integration perspective you cannot separate out numeracy and literacy: integration involves utilising mathematical skills, concepts and knowledge transferred into science contexts; and for this to be successful, science teachers and their students have to be aware of mathematical language as well as procedures (Offer and Mireles 2009). When students are asked to draw a graph, should they draw a scatter plot, a trend graph or a bar chart? The variety of terminology used for the concept of slope is another case in point: gradient, rise over run, tan theta, rate of change. Students could encounter the five terms in five different subjects, and may be justifiably confused.

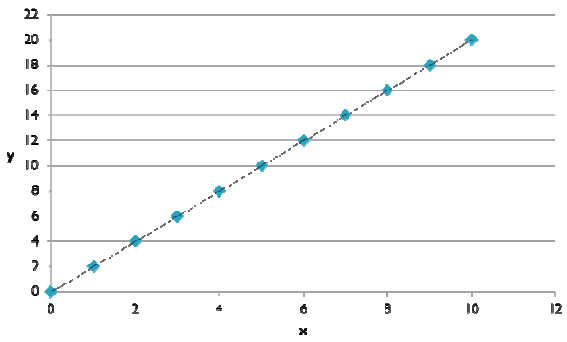
Integration therefore, could involve either a common approach across subjects and/or an explanation by science teachers that these different words refer to the same idea, thereby making the connections clear for students.

STEM Literacy

In this article the focus is on integrating mathematics into Junior Science, but equally the same process could be used to integrate science into mathematics lessons. A major element of an integrated lesson is not just developing literacy in general, but also developing STEM literacy. STEM Literacy involves contextualised interdisciplinary knowledge and the development of the ability to transfer skills between STEM subjects and between school and real-life contexts (Breiner *et al.* 2012). In this case this is through interdisciplinary science teaching and learning. At the most basic level of scientific literacy, we expect that students will learn about, for example, linear relations in mathematics class, and apply that knowledge where appropriate in science, for example in drawing graphs of experimental data. However, as Figure 2 below indicates, representations of linear relations can look very different in science and in mathematics.



a) Linear graph from science



b) Linear graph from mathematics

Figure 2: Representations of Linear Relationships can look very different in Science and Mathematics

Students may not therefore easily make the connection between what they learn in mathematics and how this is applied in science. Teachers can help students to utilise their mathematical reasoning more effectively by using the same language and techniques in science class, but also by acknowledging the differences as well as similarities across the subjects.

Identifying Mathematics to integrate into Junior Science

There are many ways in which mathematics and science overlap, and the choice of topics will depend on both the teacher's teaching sequence and the students' learning needs. Some of the more significant overlaps relevant to Junior Science are mentioned here. In broad terms, the three different areas of biology, chemistry and physics have their own mathematical emphases:

- Statistical reasoning in Biology: e.g. investigations into class pulse rates and other investigations that involve counts of a single variable
- Ratio and Proportion in Chemistry: working out proportions, concentrations, dilutions and balancing equations
- Relating two variables in Physics, e.g. time and speed or voltage and current

An integrated 'Big Idea' forms the backbone of the CISA lessons (Ainley *et al.* 2011). This is a significant overlapping concept between the science and mathematics syllabuses, such as those above, e.g., the overlap between data analysis in science and relating two variables in mathematics. The lesson can be based on specific science topics (for example, relating the amount of solute that will dissolve to the temperature of the solution), but the same overlapping concept is relevant to all science topics where students analyse what happens to one variable when the other is changed. Hence students are learning a set of integrated skills that will carry them through Junior Cycle Science, and beyond. Clearly, these integrated Big Ideas will also be developed in complexity over time. First years may need to know how and why they draw straight line graphs, but they will not need to know about finding a slope and equation until third year.

In addition to overlapping content, instructional approaches such as inquiry-based teaching and problem solving, in the case of science and mathematics, and design in the case of technology and engineering, are also recommended for an integrated lesson (Johnson 2013).

Making a Start

A good place to start with developing student STEM literacy is to make a direct connection with how they learn about data in mathematics and how they will use that learning in Science. In the Statistics Strand in Project Maths students learn about the data-handling cycle and the different types of data and how they are represented from early in first year. In Science students are often unaware of why they would choose to represent their experimental data in a histogram, a trend graph, a bar chart or a pie chart, for example. In mathematics they now learn the reason for this. The diagram in Figure 3 from Project Maths Development Team material outlines the different types of data.

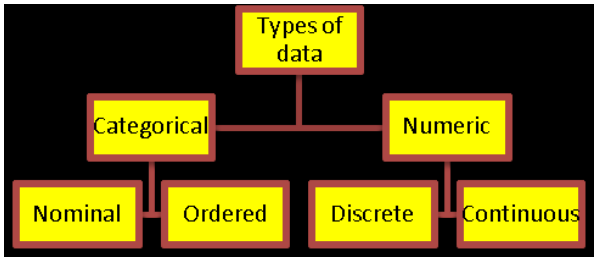


Figure 3: The types of data. Data representation and analysis relates to data type. (Image from Project Maths Development Team: http://www.projectmaths.ie/documents/data_handling_cycle_2011.pdf)

This is a simple but powerful concept for students. It permits them to look at any data, for example, heights of seedlings, know immediately it is numeric data and therefore can be represented in a histogram. They will know that categorical data, such as different types of plant found in a habitat, should rather be represented in a bar chart. This is beginning of understanding that data analysis usually consists of representation in different forms and of numerical analysis. Through well-timed integrated lessons or activities, science teachers can encourage students to make such connections with their mathematical learning. This should help students to make the leap between the subject silos in order to transfer their mathematical learning into science in a meaningful way, and to become truly STEM-literate.

For further information please email Grainne.Walshe@ul.ie

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Grainne Walshe is a PhD student at the University of Limerick under the supervision of Dr Jennifer Johnston and Dr George McClelland.

Devising a model for the Assessment of Practical Work in the Revised Chemistry Syllabus

Declan Kennedy
School of Education, University College, Cork d.kennedy@ucc.ie

Introduction

Many science teachers will be aware that draft syllabi in Biology, Chemistry and Physics have been prepared by the NCCA subject development committees. It is proposed that students be given credit for carrying out practical work as part of these new syllabi. In this article I will attempt to give some background to this proposal as it applies to Leaving Certificate chemistry and outline some possible tasks on which students' ability to perform practical work could be assessed.

The importance of practical work was clearly stressed in the introduction to the chemistry syllabus that was introduced in 1983:

> *'The development of appropriate experimental and manipulative skills and abilities is an integral part of this course…….The fostering of these experimental skills, along with abilities to evaluate and express procedures, hypotheses, data and results in a concise and comprehensive manner is strongly urged. Because laboratory work is seen as an intrinsic part of the syllabus, it is recommended that 40% of time allocated to the subject be devoted to laboratory activity'.*

(Department of Education, 1983)

In addition, the Department of Education specified that students had to maintain records of their practical work in laboratory notebooks and these notebooks were to be available for inspection by the science inspectorate. If an inspector felt that an adequate course of laboratory work had not been followed, then the student could be refused admission to the Leaving Certificate examination.

In order to ascertain the level of success on the emphasis placed on the 1983 Leaving Certificate Chemistry syllabus, a survey of chemistry teachers was carried out in the 1985–86 academic year by Smyth and Childs (1990). This survey found that 54.76% of teachers reported that around 40% of their teaching time was devoted to practical work and 11.91% reported that they spent more than 40% of their time. When questioned about difficulties encountered with the practical component of the syllabus, teachers gave examples such as lack of equipment, large class sizes, lack of technical assistance, and difficulty with accessing laboratories as being the main impediments. Whilst the survey was carried out only two years after the introduction of the syllabus, it is clear that despite encountering many problems, the majority of teachers (66.66%) appear to have embraced the practical work involved in the 1983 Leaving Certificate chemistry syllabus.

New Leaving Certificate syllabi in physics and chemistry were introduced in 2000 and a new Leaving Certificate biology syllabus was introduced in 2002. These syllabi broke new ground as, for the first time, mandatory practical work was introduced for all students undertaking these Leaving Certificate subjects.

Practical Work in Science Education

The aims of practical work were clearly laid out by Kerr (1963) who carried out a landmark survey of science teachers in the UK in order to find out why they carried out practical work with their students. The 10 aims proposed by Kerr are listed in Table 1.

Table 1. Aims of Practical Work (Kerr 1963)

1. To encourage accurate observation and careful recording. 2. To promote simple, common-sense, scientific methods of thought. 3. To develop manipulative skills. 4. To give training in problem-solving. 5. To fit the requirements of practical examination regulations. 6. To elucidate the theoretical work so as to aid comprehension. 7. To verify facts and principles already taught. 8. To be an integral part of the process of finding facts by investigation and arriving at principles. 9. To arouse and maintain interest in the subject. 10. To make biological, chemical and physical phenomena more real through actual experience.

Since Kerr's original work was carried out, various other science educators have carried out similar research work which showed that the most popular aims of practical work among science teachers were:

- To encourage accurate observation and description;
- To make scientific phenomena more real.
- To arouse and maintain interest in the subject.
- To promote a logical and scientific method of thought.

Whilst it is clear that practical work is held in high esteem by science teachers, it is unfortunate that, at the present time, this practical work is assessed at Leaving Certificate chemistry level only by means of a written terminal examination. Hence, it is proposed to introduce a new mode of assessment of practical work in the revised Leaving Certificate Chemistry syllabus which will be worth 30% of the overall mark awarded.

Before describing this assessment of practical work, it may be helpful to clarify the meaning of some terms:

- **Direct Assessment of Practical Skills (DAPS).** In this situation students' skills are assessed in the presence of the person who is awarding marks, e.g. observing the student's ability to carry out certain procedures, manipulate apparatus, etc.
- **Indirect Assessment of Practical Skills (IAPS).** In this situation students' skills are inferred in a written examination or some other secondary source of assessment.
- **Process skills**. These are generic skills, e.g. planning, observation, measurement, classifying, analysing, etc.
- **Practical skills**. These are skills necessary for performing a non-written task, e.g. performing a titration, measuring melting point, collecting a gas, etc.

It is proposed that the assessment of laboratory practical work in the new Leaving Certificate Chemistry syllabus will involve both DAPS and IAPS. A comparison of these two aspects of assessment of practical work has been carried out by Reiss, Abrahams and Sharpe (2012) and this is summarised in Table 2.

Table 2. Comparing Direct Assessment of Practical Skills (DAPS) and Indirect Assessment of Practical Skills (IAPS)

	DAPS (Direct Assessment)	**IAPS (Indirect Assessment**
What is the principle of the assessment?	• A student's ability at performing practical tasks is directly measured as they demonstrate the skill.	• A student's ability at performing practical tasks is *inferred* from his / her data and/or reports of the practical work they undertook
How is the assessment undertaken?	• Observations of students as they undertake a piece of practical work	• Marking of student's reports that have been written up during the practical activity or immediately after wards or marking of a written examination paper subsequently taken by students
Advantages	• High validity • Encourages teachers to ensure that students gain expertise in the practical skills that will be assessed	• More straightforward for those who are undertaking the assessment
Disadvantages	• More costly • Requires teachers to be trained to undertake the assessment • Has greater moderation requirements	• Lower validity • Less likely to raise students' level of practical skills

Whilst the details of the proposed Leaving Certificate practical examination in Chemistry have not been finalised, one proposal is that the examination would consist of a 90 minute performance assessment involving a combination of direct and indirect assessment. Students carrying out a set of laboratory tasks are observed by an external examiner who could award up to 15% of the overall mark for direct assessment and a further 15% of the overall mark for indirect assessment. The indirect assessment could be based on the data collected and observations noted by the students and this would be marked by the State Examinations Commission along with the written paper. Thus, as stated above, the practical component would be worth 30% of the overall mark assigned to the student for his or her performance in Leaving Certificate Chemistry.

One of the advantages of the above system is that the students' abilities at performing a particular laboratory task is assessed directly by DAPS whereas the students' understanding of a process is assessed by IAPS. This is in keeping with what is recommended in the literature on the assessment of practical work (Reiss, Abrahams and Sharpe, 2012).

Feasibility Study on Assessment of Practical Work

In Ireland we are fortunate that we are not starting with a blank page to design a system of assessment of practical work since four years prior to the implementation of the Leaving Certificate chemistry syllabus being taught in our schools at present, the Department of Education and Science set up a Steering Committee to investigate if a system could be devised to give students credit for practical work which they would perform over the two-year Leaving Certificate chemistry and physics courses. This project became known as the 'Feasibility Study on Practical Assessment for Leaving Certificate Physics and Chemistry'. The main thrust of the Feasibility Study was to provide a reliable and valid means of assessing practical abilities and, in doing so, to raise the profile of practical work in schools by giving both students and teachers more confidence in undertaking practical work.

A 5% sample of the schools offering physics and chemistry were chosen for participation in the Feasibility Study. These schools were chosen from the 193 schools that applied to participate in the study. A total of 29 schools in chemistry and 30 schools in physics were selected to participate in the study. Selection of the examiners for physics and chemistry (12 in each subject) was made by the Inspectorate of the Department of Education. These examiners were highly experienced teachers with a good track record in using practical work in their teaching. An intensive training course was provided for these examiners on all aspects of the assessment of practical work. Additionally, during the two-week period in which the assessment of students was undertaken, three examiners took on the role of moderators. Each examiner was visited by a moderator to ensure (i) that the assessment was carried out in accordance with the guidelines and (ii) that standards were correctly applied. Examination centres were also visited by the Inspectorate and by the project officer appointed by the Steering Committee.

Full details of the outcomes and evaluation of the Feasibility Study are reported elsewhere (Bennett and Kennedy, 2001). Overall, analysis of the data gathered during the Feasibility Study convinced the Steering Committee of the successful nature of the project in terms of reliability and validity and a recommendation was made that this mode of assessment of practical work should be implemented. In this mode of assessment, emphasis was placed on the assessment of three main skills: Measuring Skills, Manipulative Skills and Observational Skills. Some examples of these are given in Table 3.

Table 3. Some examples of skills assessed in the Feasibility Study on assessment of practical work.

1. **Measurement Skills**
   - Use of lab balance to measure out a given quantity.
   - Reading the volume of liquid in a burette.
   - Reading the volume of liquid in a graduated cylinder.
   - Reading the temperature of a liquid.
   - Reading the volume of gas collected.

2. **Manipulative Skills**
   - Correct procedure for filling a pipette and burette.
   - Correct use of volumetric flask.
   - Correct procedure for carrying out a titration.
   - Correct procedure for preparation of ethene, ethyne, soap.

- Correct procedure for carrying out a recrystallisation experiment.
- Correct procedure for melting point determination.
- Correct procedure for monitoring rate of production of gas and following rate of precipitation.
- Correct procedure for measurement of heat of reaction.

3. **Observational Skills**

- Observations noted in flame tests.
- Observations noted in tests for anions.
- Observations noted in the reaction of acidified potassium permanganate solution with iron(II) sulfate solution.
- Observations noted in reaction of sodium thiosulfate solution and dilute hydrochloric acid.
- Observations noted when steel wool is added to copper sulfate solution.
- Observations noted when ethanal reacts with Fehling's reagent and ammonical silver nitrate.

Conclusions

It is clear that practical work plays a central role in science education and that the assessment of practical work will have to be an important component of the proposed new Leaving Certificate chemistry syllabus. The Feasibility Study on the assessment of practical work has laid a good foundation to help plan for the future assessment of practical work in the Leaving Certificate chemistry examinations. There is a clear need for changes to be made in the assessment procedure as it stands at present (i.e. assessment only by means of a written examination) in order to give a more valid and fairer assessment of students' ability at practical work. On the basis of the research evidence which emerged from the Feasibility Study, the Steering Committee felt confident in recommending the introduction on a national basis of the model that was trialled in the Feasibility Study. It would be very important that, at least in the initial stages of finalising the model of practical assessment, that the experiments be drawn from the list of Mandatory Experiments rather than expect students to be assessed on laboratory work which they have not encountered in the past. Let us hope that the proposed new Leaving Certificate Chemistry syllabus will adopt a model that will reward our students in a fair and valid way for their ability to carry out laboratory practical work.

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Dr Declan Kennedy is a Senior lecturer in Education at University College Cork, a well-known textbook author and former science teacher.

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Editorial correspondence

If you want to communicate with the editor for any reason, please use the following information:

Dr.Peter E. Childs
Hon. Editor
Chemistry in Action!
University of Limerick,
Limerick, Ireland.
Tel. +353-61-202075 (direct)
Fax. +353-61-202568
E-mail: peter.childs@ul.ie

Communications in writing/e-mail are preferred rather than phone calls!

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TY Science Modules

These modules for TY Science are available from the University of Limerick @ €10 each plus p&p. The titles are:

- **Forensic Science**
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University of Limerick,
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Peter.childs@ul.ie

In the next issue:

- **The new LC Chemistry syllabus**
- **The Hyland Report**
- **Conference reports**
- **Climate change activities**
- **Parabens as preservatives**
- **Junior science specification**
- **STEM Review Group Report**