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Contents

Prospective teachers' conceptual understanding of electrochemistry: Galvanic and electrolytic cells

Paper

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This study investigated prospective chemistry teachers' conceptual difficulties in understanding basic aspects of electrochemistry related to galvanic and electrolytic cells. It was conducted with ninety-two prospective teachers who were students in the final year class at Marmara University, Atatürk Faculty of Education and had received both classroom and laboratory instruction on electrochemistry for about three and a half months (3 hours per week for both classroom and laboratory instruction). Fifteen volunteers from among the group were first interviewed for about 40-45 minutes. After the interviews, a test of 27 multiple-choice questions, consisting of assertion-reason statements and a set of alternative answers, was administered to all subjects. This study was able to identify new electrochemical misconceptions as well as some of those previously reported. The results show that students from different countries and different levels of electrochemistry study have similar difficulties and suggest that concepts are presented to them poorly. It also discusses some of the possible origins of these misconceptions.

Introduction

There have been a large number of studies that reported students' understanding of various science topics. Studies in this area included students as well as teachers. More studies have been conducted with students at secondary schools and universities rather than with teachers and prospective teachers, but there have been a number concerning conceptions of teachers and prospective teachers. Bradley and Mosimege[1] investigated misconceptions of South African prospective teachers about acids and bases through a twenty-item questionnaire divided into twelve multiple-choice items and eight discussion items. They reported that the prospective teachers' performance in these was disappointing. Kokkotas et al.[2] noted that Greek prospective teachers share a number of misconceptions with pupils. Haidar[3] investigated the extent of Yemen prospective teachers' understanding of certain fundamental theoretical concepts such as atoms and mass, the mole, atomic mass, and balancing chemical equations. He reported that their understanding of most of these concepts ranged from a partial understanding with specific misconceptions to no understanding and that their knowledge about the concepts was fragmented and not correlated. The results of his study also showed that they only memorized the concepts without meaningful understanding. Quilezpardo and Solazportoles[4] developed a written

test to diagnose both students' and teachers' alternative conceptions about chemical equilibrium. They stated that misconceptions emerged through:
a) misapplication and misunderstanding of Le Chatelier's principle;
b) the use of rote-learning recall and algorithmic procedures;
c) incorrect control of the variables;
d) limited use of the chemical equilibrium law;
e) a lack of mastery of the principles of chemical equilibrium and difficulty in applying such principles to new situations.

Pardhan and Bano[5] reported on a qualitative research study carried out on science teachers' alternative conceptions about electricity. They also discussed the nature and origin of the alternative conceptions of teachers. Trumper et al.[6] discussed the similarities and differences for Israeli and Argentinian prospective teachers' conceptions about energy. They noted that there was a serious discrepancy between both Israeli and Argentinian student teachers' understanding of energy and the accepted scientific concepts. They concluded that the students' understanding of energy needs to be improved. Chang[7] administered an open-ended, written test to 364 students in a teacher training college and interviewed a representative selection of students in a semi-structured manner to discover their conceptions about evaporation, condensation, and boiling. Examining the students' ideas

carefully, the researcher concluded that learning difficulties regarding these concepts could be a result of poor understanding of what water vapour is. A study reported by Yip[8] revealed that novice biology teachers held a number of conceptual errors about various biology concepts, which were also prevalent among secondary school students. Specific teaching strategies were suggested to prevent the propagation of these misconceptions to students. These studies confirm that students at all levels, and even science teachers, hold misconceptions as well as conceptual and propositional knowledge that is inconsistent with or different from the scientific consensus, and are unable to explain adequately observable scientific phenomena (Nurrenbern;[9] de Jong et al.;[10] Quilezpardo and Solazportolez[4]).

Science educators are paying increasing attention to students' conceptual difficulties in the field of electrochemistry. Several researchers have reported that students find the topic difficult (Bojczuk;[11] Finley et al.;[12] Butts and Smith;[13] de Jong[14]). Allsop and George[15] reported that students have difficulty using standard reduction potentials to predict the direction of chemical reactions and were unable to produce an acceptable diagram of an electrochemical cell. Birss and Truax[16] noted that students who learn electrochemistry from most high school and first-year university textbooks are likely to experience confusion on this subject. They also discussed the most important problems students are likely to encounter. Garnett et al.[17] discussed students' understanding of electrochemistry, with the aim of improving science curricula. In subsequent articles, Garnett and Treagust[18, 19] identified common student misconceptions about oxidation-reduction reactions, electric circuits and galvanic and electrolytic cells by using student interviews, and discussed some probable origins of these misconceptions. Ogude and Bradley[20, 21] investigated pre-college and college students' difficulties regarding the qualitative interpretation of the macroscopic processes that take place in operating electrochemical cells. They stated that although many students can solve quantitative electrochemical problems in exams, few are able to answer qualitative questions that require a deeper conceptual knowledge of electrochemistry. Sanger and Greenbowe[22, 23] applied Garnett and Treagust's interviews[19] on galvanic and electrolytic cells to their own subjects and extended them by adressing student misconceptions about concentration cells. Subsequently, they analyzed college chemistry textbooks as sources of misconceptions and errors in electrochemistry (Sanger and Greenbowe[24]). Huddle et al.[25] reported a concrete model to correct known misconceptions in electrochemistry. Recently, Thompson and Craig[26] investigated the concept of electrochemical equilibrium in relation to thermodynamic functions with the aim of providing pedagogical support for undergraduate analytical chemistry students. The subjects of these studies were either high school or college students.

We could not find a research report in literature on the alternative electrochemistry conceptions of prospective teachers. There are only a few reports on the electrical concepts of science teachers (Webb;[27] Pardhan and Bano[5]). Furthermore, previous studies[15-25] do not investigate electrochemical concepts such as chemical equilibrium, electrochemical equilibrium, and the instrumental requirements for the measurement of cell potential or electromotive force (emf). Therefore, we embarked on a study designed to identify previously reported and new electrochemical misconceptions of prospective chemistry teachers, considering previously uninvestigated concepts.

An earlier paper (Özkaya[28]), concentrated on identifying prospective teachers' new misconceptions, taking into account previously uninvestigated concepts, but reported on only some of these. This paper focuses on misconceptions that are common with those of students from different countries and different levels of electrochemistry. It also discusses new misconceptions not reported in the earlier paper.

The purpose

This study investigated prospective chemistry teachers' conceptual difficulties in understanding basic aspects of electrochemistry related to galvanic and electrolytic cells after they had received a course of electrochemistry instruction. In the study we attempted to answer three questions.

- Which of the common misconceptions about electrochemistry reported by Garnett and Treagust,[18, 19] and Sanger and Greenbowe[22, 23] are held by our student teachers?
- Do they hold new misconceptions not previously reported?
- What are the likely sources of their misconceptions?

The sample

The sample consisted of ninety-two prospective teachers who were students in the final year class at Marmara University, Atatürk Faculty of Education. The study was conducted after they had received both classroom and laboratory instruction on electrochemistry for about three and a half months (2 hours per week for classroom and 3 hours per week for laboratory instruction). The electrochemistry laboratory and classroom instruction covered the following topics: metallic

and electrolytic conductance, conductimetric titration, systematic investigation of cells, thermodynamic functions of galvanic cells, potentiometric titration, Faraday Laws, electrolysis and polarization, electrochemical corrosion, and some electroanalytical methods (amperometry, polarography and cyclic voltammetry). The students were instructed by traditional lecture and quantitative problem-solving approaches.

Methodology

Fifteen volunteers from among the ninety-two were first interviewed for about 40-45 minutes using the protocol of Garnett and Treagust[18, 19] to which the following questions were added:

- How is the emf of a cell measured? Is it possible to use an ordinary voltmeter to measure the emf of a cell precisely?
- Under what conditions is an electrochemical equilibrium established in a galvanic cell?
- Under what conditions is a chemical equilibrium established between the species involving in the cell reaction in a galvanic cell?
- What happens when a metal is immersed into an electrolyte solution involving its ions?

The interview subjects were selected on the basis of their performance in the electrochemistry course, with five students from the top third of the class, five from the middle third, and five from the bottom third. Before the interviews, the students wrote their responses on the question sheets. During each individual interview, the conversation was recorded. The responses were analyzed to identify the students' conceptual difficulties.

After the interviews, a test of 27 multiple-choice questions, consisting of assertion-reason statements and a set of alternative answers, was administered to all subjects. The test items did not cover all the classroom and laboratory topics, only the basic concepts of galvanic and electrolytic cells. Some of the assertion-reason statements were based on students' alternative ideas reported previously in literature.[18, 19, 22] This allowed us to test for previously reported misconceptions. Other assertion-reason statements were based on either the subjects' scientifically incorrect responses during the interviews or on concepts not previously investigated. This made possible the identification of misconceptions not previously reported.

Results and discussion

The students' misconceptions identified in this study are given in the Appendix. These misconceptions were classified into five areas:

- Electrode potentials and cell emf
- Identifying the cathode and anode
- Metallic and electrolytic conduction
- Chemical and electrochemical equilibrium
- Predicting electrode and cell reactions

The results from the analysis of test questions examining each area are discussed below.

Electrode potentials and cell emf

Some questions in the twenty-seven-item test (Questions 1-7) were designed to test the students' understanding of electrode potentials and cell emf. Question 6 and the subjects' responses to it are shown in Table 1 as an example. Of the fifteen subjects interviewed, four stated that standard half-cell potentials can be used to predict the spontaneity of the reaction involving in the half-cells, since some standard half-cell potentials are

Table 1

Question 6

Assertion	because	Reason
Standard half-cell potentials can be used to predict the spontaneity of the reactions involving the half-cells		Some standard half-cell potentials are positive while the others are negative in value

Alternative	Statement 1 *Assertion*	Statement 2 *Reason*
a*	True	True
b*	True	True
c	True	False
d	False	True
e	False	False

*The difference between alternatives *a* and *b* was explained before the test. In both cases statements 1 and 2 are both true, but in *a* the reason statement correctly explains the assertion and in *b* it does not.

Answers to question 6		
Alternative	n	%
a	42	45.7
b	30	32.6
c	0	0
d**	18	19.6
e	2	2.1

**Correct answer

positive while the others are negative in value. Therefore, question 6 with appropriate assertion-reason statements was designed on the basis of this scientifically incorrect idea (Table 1). The results from the analysis of question 6 were consistent with the subjects' responses during the interviews. A significant proportion of the subjects marked either 'a' or 'b'; they held misconception 1 (Appendix). Of the seventy-two subjects, who marked 'a' or 'b', forty-two thought that the reason statement "*Some standard half-cell potentials are positive while the others are negative in value*" correctly explains the assertion statement "*Standard half-cell potentials can be used to predict the spontaneity of the reactions involving in the half-cells*". Therefore, this alternative idea can be expressed as a new misconception (2, Appendix).

In response to a question, nearly all students correctly stated that it is not possible to measure a half-cell potential without using another half-cell; they did not hold the previously reported[19, 22] misconception: "*A standard half-cell is not necessary*". However, in response to another question, half of the subjects believed that the electrode potential is equal to the electrochemical potential difference between the metal and electrolyte in the half-cell, since both can be expressed in volts. This alternative idea was regarded as misconception 3 (Appendix). These subjects were unaware that the electrochemical potential is composed of electrical potential and chemical potential, and that when a metal is immersed into the electrolyte involving its ions, the electrochemical potentials of two phases become equal in a very short time i.e., an electrochemical equillibrium is established between the metal and its ions in the electrolyte.

In the interviews, of the fifteen subjects responding to the question "*Why does $H_2(1\ atm)/H^+(1M)$ standard half-cell have an E^0 value of 0.00 V?*" four could not offer a reason. Eleven correctly stated that it was arbitrarily set at 0.00 V. However, four of those eleven suggested that there should be a relationship between the value of zero and chemistry of H^+ and H_2, and proposed a variety of reasons why the standard hydrogen electrode potential is set at 0.00 V. The most popular reason was the statement "*Hydrogen is in the middle of the activity series for metals*". On the basis of their responses, a question was designed with appropriate assertion-reason statements. The assertion statement was a scientifically incorrect idea: "*The value of zero for the standard reduction potential of the $H_2(1\ atm)/H^+(1M)$ standard half-cell is based on the chemistry of H^+ and H_2*". The results of the test were in accordance with the responses in the interviews; forty-two subjects (46%) thought the statement was true. These subjects held misconception 4 (Appendix). On the other hand, twenty-five of forty-two subjects thought that the reason statement, "*Hydrogen is in the middle of the activity series for metals*", correctly explains the assertion statement. This alternative idea is regarded as a new misconception (5, Appendix).

Identifying the cathode and anode
During the interviews, the students showed widespread uncertainty about the reactions that occur at the electrodes and the assignment of electrodes as (+) and (−) in galvanic and electrolytic cells. Five questions were designed to probe their understanding in this area. Question 9 and the subjects' responses to it are shown in Table 2. The assertion statement "*In galvanic cells, oxidation occurs at the anode and reduction at the cathode,*

Table 2

Question 9

Assertion	because	Reason
In galvanic cells, oxidation occurs at the anode and reduction at the cathode, while in electrolytic cells oxidation occurs at the cathode and reduction at the anode		In galvanic cells, the anode is labelled as (-) and the cathode as (+), while in electrolytic cells the anode is labeled as (+) and the cathode as (-).

Alternative	Statement 1 *Assertion*	Statement 2 *Reason*		Alternative	n	%
a*	True	True		a	27	29.4
b*	True	True		b	13	14.1
c	True	False		c	6	6.5
d	False	True		d**	42	45.7
e	False	False		e	4	4.3

*The difference between alternatives *a* and *b* was explained before the test. In both cases statements 1 and 2 are both true, but in *a* the reason statement correctly explains the assertion and in *b* it does not.

Answers to question 9 (header spanning right n/% columns)

**Correct answer

while in electrolytic cells oxidation occurs at the cathode and reduction at the anode" was thought to be true by half of the respondents who chose either 'a', 'b' or 'c'. They held misconception 6.

Several previous studies[19, 22-24] about the students' understanding of electrochemistry reported that the students have the incorrect idea: "*In galvanic cells, the anode is positively charged because it has lost electrons; the cathode is negatively charged because it has gained electrons*". This alternative idea did not appear as a common misconception among the subjects of this study; the number of students holding this view was only ten. However, responses to a question showed that a significant proportion (41%) believed that in galvanic cells, the electrodes are charged with a high electrical charge. This was regarded as a new misconception (7, Appendix). This finding is consistent with the results of previous research. Sanger and Greenbowe[24] reported that students overestimate the magnitude of the net charge associated with the electrodes. They analyzed ten college-level chemistry textbooks and stated that only one of these books discusses the net charges of the electrodes in a galvanic cell, and it mentions that the net charge on the electrodes is exceedingly small – only about one electron for 10^{14} metal atoms.

In another question, the assertion statement "*In an electrolytic cell, the direction of the applied voltage has no effect on the reaction or the site of the anode and cathode*" was a previously reported misconception (8, Appendix).[19, 22, 24] Half of our subjects showed that they held this misconception by choosing the statement as true. On the other hand, the statement "*In both electrolytic and galvanic cells, oxidation occurs at the anode and reduction at the cathode*" was the reason in the question. Forty-one subjects (45 %) thought the reason statement was false. This is consistent with the subjects' responses to question 9 since the assertion statement in this question was thought to be true by half of the respondents. Forty-one subjects probably had the idea that in electrolytic cells oxidation occurs at the cathode and reduction at the anode. Therefore it may be assumed that they also held misconception 6.[19, 22, 24]

Sanger and Greenbowe[24] reported that the misconception "*The identity of the anode and cathode depends on the placement of the half-cells*" was originally suggested by a student who observed that the textbook and the instructor always drew the anode half-cell on the left and the cathode half-cell on the right. They suggested that while it may seem logical for authors and instructors to consistently place the anode half-cell on the left-side according to the cell notation suggested by IUPAC and

always to connect it to the (–) terminal of the voltmeter, this may mislead students into believing that these are viable methods to identify the anode and cathode in electrochemical cells. They suggested that these conventions might pose problems when students are asked to analyze electrochemical cell diagrams in examinations or build and draw cells in the laboratory. The results of this study are in accordance with their findings. In response to a question, forty-seven subjects believed that the identity of the anode and cathode of a galvanic cell shown in a figure depends on the physical placement of the half-cells (misconception 9). Moreover, of the forty-seven subjects having this idea, twenty-six (55%) believed that the statement "*IUPAC convention requires to place the cathode on the right and the anode on the left in the cell notation*" correctly explained their belief. This alternative idea was regarded as a new misconception (10, Appendix).

Metallic and electrolytic conduction
In response to a question designed to probe the students' understanding of metallic conduction, twenty-three subjects (25%) stated that in a galvanic cell electrons enter the electrolyte at the cathode, move through the electrolyte and emerge at the anode. Fourteen of these subjects believed that the statement "*Electrons move directly from the anode to cathode through the external circuit*" correctly explains their idea. This demonstrated two previously identified misconceptions (11 and 12, Appendix). In response to another question, fifty-two subjects (57%) claimed that in an electrolytic cell free electrons move both in the electrolyte and in the wire connecting the two electrodes because they conduct an electric current through the circuit. This was regarded as a new misconception (13, Appendix).

In Question 15 (Table 3) both statements are false, but thirty-six subjects marked 'a'. They believed that if a metal wire replaces the salt bridge in a galvanic cell, the ammeter connected through the circuit will show a reading because there will be continuous flow of current, since the metal wire conducts electricity. This alternative idea was a new misconception labelled as 14. On the other hand, twelve subjects marked 'b', having the idea that both statements are true, but that there is not an assertion-reason relationship between them. Sixty-seven subjects thought that if a metal wire replaces the salt bridge in the galvanic cell, the ammeter connected through the circuit would show a reading. This misconception was also identified as new (15, Appendix). Those, who thought the reason statement was true, probably had the incorrect idea that in galvanic cells the salt bridge supplies electrons to complete the circuit. Therefore they

Table 3

Question 15

Assertion	because	Reason
The ammeter connected through the circuit in Figure 1 will show a reading		There will be a continuous flow of current since the platinum wire conducts electricity

Alternative	Statement 1 *Assertion*	Statement 2 *Reason*
a*	True	True
b*	True	True
c	True	False
d	False	True
e	False	False

Answers to question 15

Alternative	n	%
a	36	39.1
b	12	13.0
c	19	20.7
d	8	8.7
e**	17	18.5

*The difference between alternatives *a* and *b* was explained before the test. In both cases statements 1 and 2 are both true, but in *a* the reason statement correctly explains the assertion and in *b* it does not.

**Correct answer

Figure 1

Zn —— Ⓐ —— Cu
Pt wire

1M ZnSO$_4$ —— | | —— 1M CuSO$_4$
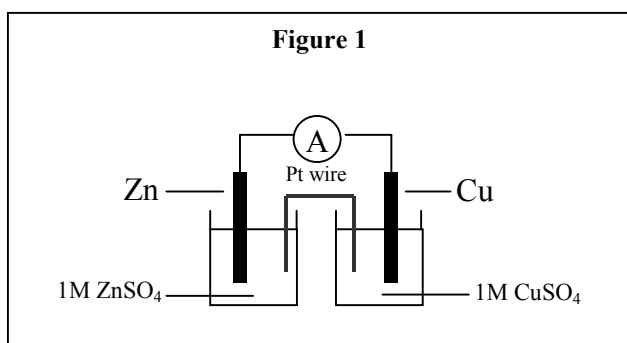
can be assumed to demonstrate misconception 16 (Appendix).

In response to the question "*What does the salt bridge do?*", of the fifteen subjects interviewed, four stated that the salt bridge completes the circuit but this does not necessarily mean that it assists the flow of current; the ions assist the flow of current. The results of the test were in accordance with the responses in the interviews. In a test question, forty-two respondents thought the statement "*the salt bridge assists current flow*" to be false. This resulted in a new, surprising, misconception (17, Appendix).

In a test question, the assertion statement "*In the electrolysis of aqueous Na$_2$SO$_4$ with inert electrodes H$_2$(g) is produced at the cathode and O$_2$(g) at the anode*", was true and the reason statement "*The movement of Na$^+$ and SO$_4^{2-}$ ions in solution does not constitute an electric current*" was false. Unfortunately, forty-three subjects (47%) thought the reason statement to be true. They seemed to believe that the movement of sodium and sulphate ions does not constitute an electric current because they do not react at the electrodes. This led to the identification of a new misconception not previously reported (18).

Chemical and electrochemical equilibrium
Question 18 and the percentage of respondents who chose each alternative in this item are given in Table 4. In this question, the assertion statement "*When a metal is immersed in an electrolyte involving its ions, the electrical potentials of the metal and electrolyte become equal*" was false and the reason statement "*An electrochemical equilibrium is established between the metal and ions in the electrolyte when a metal is immersed into an electrolyte involving its ions*" was true. Forty-nine of the subjects thought the assertion statement to be true by choosing either 'a', 'b', or 'c'. They held a new misconception (19, Appendix). Of the forty-nine who held this misconception, thirty thought that the reason statement correctly explained the assertion statement. Their alternative idea was regarded as another misconception (20). Previous studies did not investigate chemical and electrochemical equilibrium, whereas the present one took these concepts into account. The students' other misconceptions about chemical and electrochemical equilibrium were reported and discussed in detail in the earlier paper.[28]

Predicting the electrode and cell reactions
In the course of the interviews, five of the fifteen subjects surprisingly claimed that the reduction and oxidation of the species in the electrolyte do not occur at the electrodes; these reactions occur at metal/solution interfaces. The results from the analysis of two test questions were consistent with the subjects' responses in the interviews. In response to one of these questions, fifty-two of the subjects chose as true that "*No reaction occurs at the electrodes if inert electrodes are used in a galvanic cell because inert electrodes are not altered chemically in cell reactions*". In response to

Table 4

Question 18

Assertion	because	Reason
When a metal is immersed in an electrolyte containing its ions, the electrical potentials of the metal and the electrolyte become equal	*because*	When a metal is immersed in an electrolyte containing its ions, an electrochemical equilibrium is established between the metal and its ions in the electrolyte

Alternative	Statement 1 *Assertion*	Statement 2 *Reason*
a*	True	True
b*	True	True
c	True	False
d	False	True
e	False	False

*The difference between alternatives *a* and *b* was explained before the test. In both cases statements 1 and 2 are both true, but in *a* the reason statement correctly explains the assertion and in *b* it does not.

Answers to question 18

Alternative	n	%
a	30	32.6
b	3	3.3
c	16	17.3
d**	40	43.5
e	3	3.3

**Correct answer

another question, fifty-six subjects (61%) had the similar idea that "*In electrolytic cells, no reaction occurs at the anode if an inert electrode is used as the anode because inert electrodes are not oxidized in cell reactions*". These led to the identification of a new misconception (21, Appendix). The students who demonstrated misconception 21 presumably recognized only the reactions of the electrode material as electrode reactions. These subjects seemed to be unaware that all electrode reactions, whether they involve the electrode material or not, are considered to occur at the electrodes (i.e. at the interface between the electrode and electrolyte). Textbook authors or instructors should note that the term 'electrode' usually refers to a metallic conductor; however, in some cases it refers to a half-cell and even to the interfacial region. As

discussed before by Sanger and Greenbowe,[24] some textbooks never specify the composition of inert electrodes and fail to mention that, although these electrodes made of inert substances and therefore are unreactive towards oxidation and reduction, it is possible for the other electrodes to react. On the other hand, most of the textbooks do not discuss why some electrodes are inert while others can react. As a result, students have difficulty in determining when an electrode will be reactive or inert. Instructors and textbook authors need to discuss some of the factors that make electrodes inert.

In the course of the interviews, three subjects stated that "*water does not react during the electrolysis of aqueous solutions*". This scientifically incorrect

Figure 5

Question 25

Assertion	because	Reason
If the electrolysis of water is attempted, using inert electrodes, essentially no reaction is observed at the electrodes	*because*	Water does not react during the electrolysis of aqueous solutions

Alternative	Statement 1 *Assertion*	Statement 2 *Reason*
a*	True	True
b*	True	True
c	True	False
d	False	True
e	False	False

*The difference between alternatives *a* and *b* was explained before the test. In both cases statements 1 and 2 are both true, but in *a* the reason statement correctly explains the assertion and in *b* it does not.

Answers to question 25

Alternative	n	%
a	14	15.2
b	28	30.4
c**	24	26.1
d	8	8.7
e	18	19.6

**Correct answer

idea was included in Question 25 (Table 5) as the reason statement. The results of the test are in accordance qualitatively with the responses in the interviews. Fifty subjects who chose 'a', 'b', or 'd' thought the above reason statement was true; this led to the identification of a previously reported[19, 22, 24] misconception (22). Misconception 23, reported previously by Sanger and Greenbowe[24] "*In electrolytic cells with identical electrodes connected to the battery, the same reactions occur at each electrode*" was also held by two of the fifteen students interviewed. Subsequently, this mistaken idea was included in Question 26 (Table 6). However, it did not appear as a common misconception among the subjects of this study; only four subjects marked 'a', 'b', or 'c', as shown in Table 6. This is probably due to the fact that during their practical work in the electrochemistry laboratory, these students had carried out the electrolysis of sulfuric acid solution with inert (Pt) electrodes and determined the Faraday constant from the volume of the electrolysis products [$O_2(g)$ and $H_2(g)$] and the amount of electricity that passed through the electrolyte.

Conclusions

This study was able to identify new student misconceptions concerning electrochemistry related to galvanic and electrolytic cells. In addition, it confirmed some of the previously reported misconceptions. However, the fact that the subjects of this study did not hold some of the previously reported misconceptions does not necessarily mean that the here-unseen misconceptions are not valid or common. Moreover, some of the misconceptions here identified may be specific to this group of students.
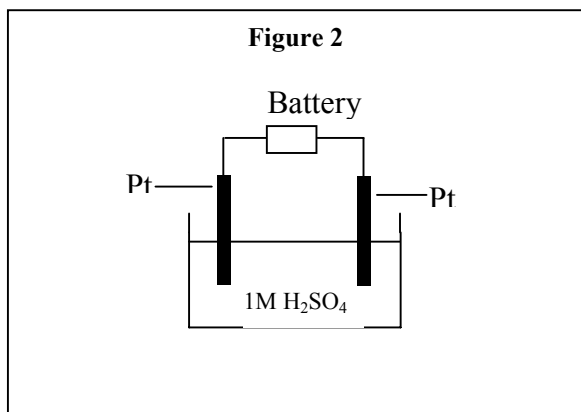
Although the subjects of this study received an intensive classroom and laboratory instruction on electrochemistry for several months, the results of this study demonstrated that the students still had many misconceptions about the basic aspects of electrohemistry. Some of these are similar to those of students at different education levels and countries. This is consistent with the constructivist model of learning, which suggests that the source of

Table 6

Assertion	because	Reason		
In the cell shown in Figure 2 the same reaction occurs at each electrode		The two electrodes in the cell are identical		

Alternative	Statement 1 *Assertion*	Statement 2 *Reason*
a*	True	True
b*	True	True
c	True	False
d	False	True
e	False	False

Answers to question 26		
Alternative	n	%
a	2	2.2
b	2	2.2
c	0	0
d**	86	93.4
e	2	2.2

*The difference between alternatives *a* and *b* was explained before the test. In both cases statements 1 and 2 are both true, but in *a* the reason statement correctly explains the assertion and in *b* it does not.

**Correct answer

Figure 2

Battery

Pt —

— Pt

1M H_2SO_4

students' alternative conceptions lies in how they construct knowledge; when students construct their own meanings they are influenced by their existing (often incorrect) conceptions (Osborne and Wittrock[29]). During the learning process, the students have previously constructed frameworks of conceptions in their memory and recall these to interpret the new knowledge from the lecture.

A significant proportion of our subjects were capable of solving various complex electrochemistry problems during their course. However, they could not demonstrate satisfactory knowledge about the basic concepts of electrochemistry. It was stated in several reports that most of the assessments of chemistry or

electrochemistry courses in various countries are based on quantitative problem-solving abilities (Nurrenbern and Pickering,[30] Pickering,[31] Sawrey,[32] Ogude and Bradley[20]). Unfortunately the situation for the subjects of this study is no different; the electrochemistry course and the examinations emphasized the quantitative and mathematical aspects of the subject. One of the difficulties with this approach is that students learn by rote-application of algorithms the facility to carry out calculations but they do not need to construct proper meanings for the ideas involved in the calculations. Probably there were no opportunities to elicit the students' qualitative explanations, to find out what alternative ideas they had before they started the course and what alternative ideas they developed during the course. Instead, they learnt to manipulate symbols and equations to solve quantitative electrochemistry problems without understanding the concepts they represented. By presenting electrochemical concepts only in terms of mathematical relationships, students are allowed to ignore the conceptual meaning of the equations while they concentrate on using them to perform calculations. This type of presentation may mislead students into believing that conceptual knowledge is not important or even necessary to be successful in an electrochemistry course.

It seems that another influence on the students' learning difficulties is the style of examination questions. Nearly all the students had the same reaction to the assertion-reason questions with true-false alternatives. They said that these questions were very different from those thay had faced in their electrochemistry course and exams. Our results suggest that questions employed in the electrochemistry teaching and assessment process need to be of a kind that requires students demonstrate an understanding of basic concepts and that the teaching should be revised to prepare students for these. The setting of questions involving only numerical calculations gives the impression that competence in manipulating equations is all that is needed to learn the subject. In this study, the disregard of the conceptual knowledge during the teaching and especially assessment processes seemed to be the main reason for the students' misconceptions in electrochemistry. Instructors probably teach, but underemphasize conceptual knowledge and they usually do not assess it. Therefore, students realize that it is the assessment that counts, and concentrate their efforts on improving their problem solving abilities.

As also reported in the earlier paper,[28] the results of this study showed that one of the difficulties experienced by our subjects involved the concept of different potentials. The students have difficulty

understanding that the half-cell potential talked about in electrochemistry is the potential difference between the solution and the electrode immersed in it, and this potential difference can not be measured but the difference between two differences, or the potential difference between two half-cells, can. Therefore, it is strongly recommended that instructors or curriculum developers offer detailed explanation of the origin of half-cell potentials (the interactions between the metal atoms on the electrode and the metal ions in solution, the electrical double layer, and the formation of a potential difference at two metal-solution interfaces during the approach to equilibrium). Moreover, they should explain clearly the instrumental requirements for the measurement of the potential difference between two electrodes under the conditions of no current flow (cell emf) and the changes in circuitry required for current to pass through an electrochemical cell. This explanation should include the relations between the use of a specially designed voltmeter (potentiometer) to measure the cell emf, the current flow in a cell, and chemical and electrochemical equilibrium. In that way, students can be able to understand what the terms 'chemical equilibrium' and 'electrochemical equilibrium' refer to in electrochemical processes, and what the relationship and difference between these are.

Various concepts relevant to cells, such as electrode potential, electrical double layer, cell emf, chemical and electrochemical equilibrium, current, electrical conductance (metallic and electrolytic conductance), electrical neutrality, salt bridge, and electrode processes cannot be understood in isolation from each other. An instructional strategy aimed at alleviating students' misconceptions about these concepts should thus adopt an approach where the cell can be understood in its entirety. For example, the lack of knowledge of what individual components of a galvanic cell do can lead to various misconceptions; a formal description of what a very high resistance voltmeter (potentiometer), ammeter, salt bridge, and external source of current do in a circuit can alleviate this problem.

As stated in the results and discussion part, there was widespread uncertainty about why the potential of standard hydrogen electrode is set at 0.00 V, so the students proposed a variety of reasons during the interviews. Moreover, as identified in this study and previously by Sanger and Greenbowe,[22] many students do not understand that chemists cannot make absolute potential measurements. On the other hand, they think that there is a relationship between the half-cell potentials and the spontaneity of half-cell reactions. On the basis of these findings, we suggest that instructors should

emphasize the role of the standard hydrogen electrode or other reference electrodes in determining half-cell potentials and the relative nature of these potentials. As reported by Sanger and Greenbowe,[22] although all textbooks usually contain explicit statements that absolute half-cell potentials can not be measured, some of these contain statements suggesting that standard reduction potentials are absolute — that is, half-reactions with positive reduction potentials are spontaneous and half-reactions with negative reduction potentials are nonspontaneous and spontaneous in the opposite direction. On the other hand, some textbooks calculate cell potentials using the equation $E^0_{cell} = E^0_{red} + E^0_{ox}$, where E^0_{red} is the reduction potential of the reduction half-reaction and the E^0_{ox} value is determined by taking the reduction potential of the oxidation half-reaction and changing its sign. Although this is technically the same as calculating the cell potential as a potential difference (i.e., $E^0_{cell} = E^0_{cathode} - E^0_{anode}$, where $E^0_{cathode}$ and E^0_{anode} are the standard reduction potentials of the reduction and oxidation half-reactions, respectively), calculating the cell potential as a sum may mislead students into believing that these potentials are absolute. An additional problem may arise from using the additive method. Although the equation, $E^0_{cell} = E^0_{red} + E^0_{ox}$, works only for balanced oxidation-reduction reactions, students may get the impression that the standard oxidation and reduction potentials for any half-reactions are extensive properties that obey Hess's Law, and can be added together. For example, thay may believe that $E^0_{red}(Cu^{2+}/ Cu^+)$ can be calculated by adding $E^0_{red}(Cu^{2+}/ Cu)$ to $E^0_{ox}(Cu/ Cu^+)$. Therefore, using the additive method may reinforce the relevant student misconceptions; it is strongly recommended that instructors calculate cell potentials using the potential difference method.

It may be concluded from the results of this and previous studies[16-22] that an effective teaching strategy aimed at improving students' understanding of galvanic and electrolytic cells should take into consideration documented misconceptions about electrochemistry, their likely origins, and suggestions to overcome these proposed in previous research on the topic. We believe that the application of carefullly designed conceptual explanations based on research findings, while providing students with accurate information, is indispensable in achieving this goal. On the other hand, the use of carefully designed conceptual questions during or after the presentation of conceptual explanations may help them to construct their knowledge properly. Moreover, some assessment at the beginning of the teaching process may be useful to evaluate the nature of the knowledge students bring to the class. This could

give an instructor a focus for where particular instruction will be needed to overcome students' misconceptions. The explicit teaching of structural knowledge of concepts requires the students to actively engage in the teaching-learning process. During this process, conceptual questions can be utilized to create a class discussion, encourage the students to actively engage the discussion, and therefore to facilitate conceptual change. The students should be allowed to express and defend their judgement to the class. Once the students have made their effort to express and defend their alternative ideas, it is the instructor's turn. The instructor's effort should consist in being prepared to promote and steer class discussion by considering students' alternative ideas. He or she should never forget to tie all the loose ends together by providing the authoritative explanation of the events. On the other hand, instructors should use a carefully chosen terminology and avoid insufficient explanation in explaining electrochemical processes. For instance, one of the difficulties students have in dealing with the identification of the correct direction of ion and electron flow in cells using electrode charges. Although the net charges on the electrodes are extremely small and simple electrostatic arguments concerning these charges do not correctly explain the correct direction of ion and electron flow, they routinely apply simple electrostatic arguments to determine the direction of electrically charged species. Therefore, they have difficulty understanding the following points:

- Why do electrons flow away from a positively charged anode toward a negatively charged cathode in electrolytic cells?
- Why do anions flow toward a negatively charged anode and cations move toward a positively charged cathode in galvanic cells?
- Why is the cathode labeled (+) in a galvanic cell although the electrons move from the anode to the cathode?

A detailed description of the net electronic charges on the electrodes, emphasizing that the net charge on each electrode is exceedingly small and simple electrostatic arguments can not be used to determine the direction of ion and electron flow, will probably minimize students' mistaken beliefs about this area. On the other hand, instructors who have the idea that this description is too complex for some students to understand may choose to emphasize the electrode signs as electrode polarities (i.e., the positive electrode has a higher potential than the negative electrode) instead of electronic charges.

Conceptual computer animations that portray the electrochemical processes occurring in the half-cells at the molecular level may be used in conjuction with electrochemistry lectures. In that

way, students may be able to make better connections between the microscopic and macroscopic levels of knowledge and explore specific aspects of the cells in more detail, after viewing a molecular level representation of the dynamics of the cells, such as ion migration in solution in the anode and cathode compartments and the salt bridge, electron movement in the external circuit, reduction at the cathode, and oxidation at the anode. However, it should be noted that using computer animations does take some additional time and may not be practicable in some developing countries, due to economical shortages and/or crowded classes. In the absence of available computer technology, carefully designed models may be developed and used to contribute to students' ability to visualize molecular behaviour in electrochemical processes occurring in a cell.

Because of these findings, the authors of this study plan to change the method of teaching about galvanic and electrolytic cells in a university general chemistry course. An experimental group will be told about the known misconceptions and why these statements are considered incorrect. During the teaching process with this group, conceptual questions carefully designed on the basis of previous research findings will be applied to improve the students' conceptual understanding of electrochemical processes and their problem solving ability. A control group will be taught in the traditional manner. The achievement of two groups both in conceptual knowledge and in problem solving ability will be compared statistically, to assess the ability of this instructional method to prevent and overcome misconceptions. Several reports have shown that when students are taught chemical processes conceptually and assessed accordingly, their conceptual knowledge improves considerably (Pickering,[31] Burke et al.[33]).

References

1. J.D. Bradley and M.D. Mosimege, *South African Journal of Chemistry*, 1998, **51**, 137.
2. P. Kokkotas, I.V lachos and V. Kouladis, *Int. J. Sci. Educ.*, 1998, **20**, 291.
3. A.H. Haidar, *J. Res. Sci. Teaching*, 1997, **34**, 181.
4. J. Quilezpardo and J.J. Solazportoles, *J. Res. Sci. Teach.,* 1995, **32**, 939.
5. H. Pardhan and Y. Bano, *Int. J. Sci. Educ.*, 2001, **23**, 301.
6. R. Trumper, A. Raviola and A.M. Shnersch, *Teaching and Teacher Education*, 2000, **16**, 697.
7. J.Y. Chang, *Sci. Educ.*, 1999, **83**, 511.
8. D. Yip, *Int. J. Sci. Educ.*, 1998, **20**, 461.
9. S.C. Nurrenbern, *Abstracts of Papers of The American Chemical Society,* 1991, **201**, 199.
10. O. de Jong, J. Acampo and A. Verdonk, *J. Res. Sci. Teach.*, 1995, **32**, 1097.
11. M. Bojczuk, *School Sci. Rev.,* 1982, **64**, 545.
12. F.N. Finley, J. Stewart and W.L. Yarroch, *Sci. Educ*, 1982, **66**, 531.
13. B. Butts and R. Smith, *Aust. Sci. Teachers J.*, 1987, **32**, 45.
14. O. de Jong, *Chemisch Weekblad,* 1982, **78**, 90.
15. R.T. Allsop, and N.H. George, *Educ. Chem.*, 1982, **19**, 57.
16. V.I Birss and R. Truax, *J. Chem. Ed.*, 1990, **67**, 403.
17. P.J. Garnett and D.F. Treagust, *Int. J. Sci. Educ.,* 1990, **12**, 147.
18. P.J. Garnett and D.F. Treagust, *J. Res. Sci. Teach.,* 1992, **29**, 121.
19. P.J. Garnett and D.F. Treagust, *J. Res. Sci. Teach.,* 1992, **29**, 1079.
20. N.A.Ogude and J.D. Bradley, *J. Chem. Ed.,* 1994, **71**, 29.
21. N.A.Ogude and J.D. Bradley, *J. Chem. Ed.,* 1996, **73**, 1145.
22. M.J Sanger and T.J. Greenbowe, *J. Res. Sci. Teach.,* 1997, **34**, 377.
23. M.J Sanger and T.J. Greenbowe, *J. Chem. Ed.,* 1997, **74**, 819.
24. M.J Sanger and T.J. Greenbowe, *J. Chem. Ed.,* 1999, **76**, 853.
25. P.A. Huddle, M.D. White and F. Rogers, *J. Chem. Ed.,* 2000, **70**, 104.
26. R.Q. Thompson and N.C. Craig, *J. Chem. Ed.,* 2001, **78**, 928.
27. P. Webb, *Int. J. Sci. Educ.*, 1992, **14**, 423.
28. A.R. Özkaya, *J. Chem.Ed.*, 2002, **79**, 735.
29. R.J. Osborne and M.C. Wittrock, *Studies in Science Education*, 185, **12**, 59.
30. S.C. Nurrenbern and M. Pickering, *J. Chem. Ed.,* 1987, **64**, 508.
31. M. Pickering, *J. Chem. Ed.,* 1990, **67**, 254.
32. B.A. Sawrey, *J. Chem. Ed.,* 1990, **67**, 253.
33. K.A. Burke, T.J. Greenbowe and M.A. Windschitl, *J. Chem. Ed.,* 1998, **75**, 1658.

Appendix

Misconceptions identified in this study[a, b]
   Electrode potentials and cell emf
1.   Half-cell potentials can be used to predict the spontaneity of the half-cell reactions
2.   *Half-cell potentials can be used to predict the spontaneity of the half-cell reactions because some half-cell potentials are positive while the others are negative in value.*
3.   *Electrode potential is equal to the electrochemical potential difference between the metal and electrolyte in the half-cell.*
4.   The value of zero for the standard potential of the H_2(1 atm)/H^+(1M) standard half-cell is zero is somehow based on the chemistry of H^+ and H_2.
5.   *The value of zero for the standard potential of the H_2(1 atm)/H^+(1M) standard half-cell is zero is somehow based on the chemistry of H^+ and H_2 because hydrogen is in the middle of the activity series for metals.*
   Identifying the anode and cathode
6.   Processes at the anode and cathode are reversed in galvanic and electrolytic cells; in galvanic cells oxidation occurs at the anode and reduction at the cathode, while in electrolytic cells oxidation occurs at the cathode and reduction at the anode.
7.   *In galvanic cells, the electrodes are charged with a high electrical charge.*
8.   In an electrolytic cell, the direction of the applied voltage has no effect on the reaction or the site of the anode and cathode.
9.   In galvanic cells, the identity of the anode and cathode depends on the physical placement of the half-cells.
10. *In galvanic cells, the identity of the anode and cathode depends on the physical placement of the half-cells because IUPAC convention requires the placing of the cathode on the right and the anode on the left in the cell notation.*
   Metallic and electrolytic conduction
11. Electrons flow in electrolytes.
12. Electrons enter the electrolyte at the cathode, move through the electrolyte, and emerge at the anode.
13. *In an electrochemical cell free electrons are found both in the electrolyte and in the wire connecting two electrodes because they conduct an electric current throughout the circuit.*
14. *If a metal wire replaces the salt bridge in a galvanic cell, the current continues to flow because the metal wire conducts electricity.*
15. *If a metal wire replaces the salt bridge in a galvanic cell, the ammeter connected through the circuit will show a reading.*
16. In galvanic cells, the salt bridge supplies electrons to complete the circuit.
17. *The salt bridge does not assist current flow.*
18. The movement of an ion in solution does not constitute an electric current if it does not react at the electrodes.
   Chemical and electrochemical equilibrium[c]
19. *When a metal is immersed in an electrolyte involving its ions, the electrical potentials of the metal and electrolyte become equal.*
20. *When a metal is immersed into an electrolyte involving its ions, the electrical potentials of the metal and electrolyte become equal because an electrochemical equilibrium is established between the metal and its ions in the electrolyte.*
   Predicting the electrode and cell reactions
21. *No reaction occurs at the electrodes if inert electrodes are used in a galvanic or an electrolytic cell because inert electrodes are not altered chemically in cell reactions.*
22. Water does not react during the electrolysis of aqueous solutions.
23. In electrolytic cells with identical electrodes connected to the battery, the same reactions occur at each electrode.[d]

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[a] Misconceptions reported by Garnett and Treagust[18, 19] and Sanger and Greenbowe[22-24]
[b] Italicized misconceptions are new ones, reported for the first time in this paper.
[c] The students' other misconceptions about chemical and electrochemical equilibrium were reported and discussed in detail in an earlier paper (Özkaya[28]).
[d] It was expected that a significant proportion of the students would demonstrate this misconception, but they did not.

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Learning from Problem Based Learning

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There is increased interest in Problem Based Learning (PBL) as a teaching and learning method in the sciences. This paper describes the form of PBL currently in use in a medical school where PBL is the main method for learning the content of the course and for generating self-driven, independent learning and for fostering the skills of organisation and communication. The course has been independently evaluated to discover if the claims for PBL can be substantiated. The PBL technique and the evaluation results are presented here and suggestions are made about how this might be applied to the teaching and learning of the sciences.

Introduction

The term Problem Based Learning (PBL) has recently been appearing in Science Education circles, in conferences and in the literature.[1, 2] Even in casual conversation the title PBL is being applied to what used to be called tutorials, problem solving workshops and group exercises and indeed they all involve some measure of PBL They are problem based, but do they necessarily facilitate learning?

Exercises in chemistry designed to promote discussion and group problem-solving have been around for along time [3, 4, 5, 6, 7] and efforts to evaluate them have generally shown positive gains in skills and improvement in attitudes towards the methods themselves and towards chemistry in general.[8, 9]

However, the idea of PBL as the *main* medium for learning in a discipline, or cluster of cognate disciplines, has been addressed by some of our medical colleagues. This paper will be devoted to the description and evaluation of one form of PBL in the medical school in the University of Glasgow. Implications of this for the teaching of chemistry and other sciences will be explored. We believe that this could stimulate thinking in the sciences about PBL and lead to a wider perspective on the teaching and learning of the sciences. The basic sciences of chemistry, physics, biology and biochemistry are being learned through PBL in medical schools, suggesting the possibility of the transference of PBL into the traditional science structures.

Why did medical schools make such a change in their curriculum? They were responding to pressure from the General Medical Council[10] to devise courses to equip students to be effective, self-directed learners throughout their professional life and also to be good listeners and communicators.

'Traditional' undergraduate courses, although not identical in format, have tended to share certain features, for example, teaching methods which rely heavily on large-group lectures and structured laboratory classes; a heavy assessment load, with a reliance on multiple choice tests, and discipline-based, self-standing courses in the basic sciences (e.g., physics, chemistry, biology) during the initial, pre-clinical years.[11] Recommendations for change have highlighted the need to reduce the factual 'load' in undergraduate courses while developing students' critical thinking skills, such as independent enquiry, awareness of different contexts in which decisions are made, and the evaluation of information on the basis of evidence. The need for course designers to address concerns about integrating knowledge of the basic sciences with their practical application in the clinical setting has also been stressed.[10, 12]

In contrast to this picture, PBL has its own characteristic features.

Students are required to assume far greater responsibility for what and how they learn. The student's role, for instance, includes defining issues, identifying learning needs, drawing on self-directed learning in relation to scenarios provided by clinical and research cases, and organising and

integrating learning material from various sources. The PBL process is thought to be facilitated by small-group work and independent study, with other more traditional activities, such as lectures and labs, playing a much reduced role.[11, 12]

Introduction of problem based learning in Glasgow University's medical course

How was PBL implemented in our medical school? The PBL course was devised by writing teams over a two year period. Staff training was undertaken by the university's Teaching and Learning Service in readiness for the changeover. Rather than changes being phased in gradually, the PBL course completely superseded its predecessor; in one academic year, new medical students entered the first year of the traditional course; the next year, new students entered the first year of the PBL course. Small group work was the major method for students to acquire course content in PBL and in the first year they worked in groups of eight. In deliberate contrast to the heavy reliance in the traditional curriculum on frequent class exams and lab reports, the first year in the new curriculum included assessment of independent learning, an objective, structured, clinical examination and a written examination. Course assignments also contributed to final assessment.

A week in the life of a PBL student
Monday: PBL (2 hours). A group of eight students work with a facilitator. The first hour is devoted to discussion of the outcomes of the previous Thursday's tasks. The second hour is for the introduction and analysis of a new scenario and the selection of tasks to be undertaken.
Tuesday and Wednesday: Students work independently on the tasks arising from Monday. There are laboratories, workshops and larger group discussions.
Thursday: PBL (2 hours) as for Monday
Friday: As for Tuesday and Wednesday.

Occasionally (not weekly) there would be a lecture to integrate the work of the previous scenarios or to prepare the context for the forthcoming scenarios.
Almost half the week was earmarked for private study, library work and report writing.

How was a PBL session organised?
The facilitator (a member of staff, drawn from medicine or science, trained to ask questions rather than to provide answers) met with the group of eight students. One student was appointed as chairperson and another as scribe. (These 'posts' were rotated round the group from time to time.) Each student was presented with the scenario on about half a page of A4. This consisted of a description of a situation, part of which might be

familiar from previous work. The facilitator would explain any unfamiliar terms and then the students, under the chairperson, had to decide on the main issues about which they required knowledge. The scribe recorded the ideas on a board in the form of a mind map to show linkages between the issues and to arrive at an agreed analysis of the problems. The facilitator could help with emphasis on main concerns and help to deflect students from pursuing unprofitable lines. The students then left with a short list of about six issues to be pursued. They were obliged to search in textbooks, library texts, papers and computer resources. At the next PBL session, the first hour was devoted to the students' reporting back. They had to communicate their findings, compare them and resolve any conflicts. They also had to report on their information sources. From this interaction, students compiled their response to the scenario along with some input from the facilitator. The second hour of PBL was spent opening up the next scenario.

The method was clearly designed to develop communication skills, independent learning, source seeking and integration of knowledge. The laboratories were closely linked with the scenarios so that some of the issues raised in the PBL session could be answered in the laboratory thus giving added importance and point to them.

This major innovation in PBL had, on the face of it, all the ingredients needed to foster the skills and attitudes thought to be desirable in students and future professionals[13]. However, Rosenthal and Ogden[13] argued that "proponents for change in medical education appear to have given little consideration to the attitudes of students themselves either to the present curricula or to the proposed changes". The innovative changes in the Glasgow curriculum created an opportunity for such an evaluation because the last cohort of the 'traditional' course and the first of the PBL course were available for comparison. The authors, one psychologist (RIFB), one psychologist and specialist in adult education (AMM) and one chemist (AHJ) were invited to carry out an evaluation study, which will make up the remainder of this paper.

Conceptual framework for the present study: Perry's[14] scheme of intellectual and ethical development.

The GMC's document[10] *'Tomorrow's Doctors'*, emphasised the attributes that were required for medical graduates in the twenty-first century: the ability to apply theoretical knowledge in a range of clinical contexts; good communication skills for working with patients and colleagues alike; and the capacity for self-directed, lifelong learning for

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continuing professional development. These attributes are similar to those described by Perry[14] as being at the higher levels in his proposed scheme of intellectual development – reflecting a critical, self-directed student, capable of evaluating information and evidence, and wanting scope to demonstrate understanding of the complexities of a field of study. Also relevant to our study, Perry's developmental scheme has been used to describe how students view their own role and that of their teachers[15, 16, 17].

Perry's[14] initial, longitudinal study investigated changes in thinking among undergraduates and the ways in which they made sense of their educational experience. The outcome of his research was an outline of intellectual and ethical development in which he described a series of nine 'Positions' or stages, together with their associated transitions, in the individual's developmental journey. Each Position reflected the person's way of thinking about the world and self, as well as knowledge and how learning takes place. Perry conceptualised the Positions as representing a hierarchical sequence in which individuals moved from relatively simple ways of thinking to highly complex ways of perceiving and evaluating knowledge and the world. At one extreme ('Dualism') are students who see knowledge consisting of 'right answers', 'taught' by the lecturer, and whose responsibility is to return memorised 'facts' in assessments. At the other extreme ('Contextual Relativism') are students who are analytical, independent learners, who see their task as demonstrating that they can evaluate possible solutions to problems on the basis of evidence. 'Knowledge' is seen as not absolute, and the student copes with this uncertainty by taking into account the settings in which decisions are made. The lecturer is expected to provide knowledge within a context and to demonstrate evidence for a decision or opinion. Within the scheme, the individual's 'ways of seeing the world' are reorganised as the person confronts social and intellectual challenges, either by chance through social situations, or by design through an educational programme.[18]

There have been criticisms of the scheme and Perry's research methodology. For instance, it has been claimed[18] that one Position should not be regarded as 'better' than another. However, it is difficult to view 'Dualist' and 'Contextual Relativist' Positions as equally desirable for students in higher education. Indeed, much of the 'Perry' research in educational settings[17] seemingly has tried to determine how best to challenge students to encourage them to move to 'higher' Positions. Also, participants in Perry's initial study were Harvard undergraduates, not necessarily representative of students in general, with major analyses based on male interviewees, although a quarter of participants were women.

Despite such criticisms, there seems to be agreement in the literature about Perry's important contribution to understanding learning from the student's perspective,[19] and his work has generated copious research in diverse areas of post-school education, including medicine, law, engineering, science and teacher training.[20]

Later researchers have reduced the number of Positions to three or four.[21, 22] We utilised a three stage version of Perry's scheme;[17] 'A' Position or 'Dualism' (representing Perry's Positions 1 and 2); 'B' Position or 'Multiplicity' (representing Positions 3 and 4); 'C' Position, or 'Contextual Relativism' (representing Positions 5-9). Johnstone[23] has summarised these three Positions in relation to students' perceptions of four elements of the learning environment (Table 1).

Method

Two cohorts of medical undergraduates at Glasgow University were invited to take part: *(i)* the final intake of students to the first year in the traditional course (n=237) and *(ii)* in the subsequent year, the first intake of students to the first year in the PBL course (n=235). All students were asked to complete a questionnaire about their learning experience on two occasions – near the *beginning* of first year (five weeks after the course began) and near the *end* of first year (five weeks before the course finished).

Questionnaire to investigate students' learning perceptions

One problematic area in Perry's scheme is the measurement of an individual's Position within it. Originally, Perry used unstructured interviews, as did early follow-up studies. Subsequently other instruments were developed, such as structured interviews, paraphrasing and restatement tasks, and semi-structured essays.[24] Although these produce extremely rich data, many are inappropriate for large groups. Therefore we devised a questionnaire incorporating sentence stems and 'agree/disagree' statements of the kind used in previous Perry-related research,[22, 24] and which had been developed to measure the 'A', 'B', and 'C' positions shown in Table 1.[25, 26] (See the Appendix for sentence stems).

A student in Position 'A' ('Dualist'), for example, might be expected to agree with views about the nature of knowledge and the roles of lecturer and student described in Table 1, column 2. Conversely, a student in Position 'C' ('Contextual Relativist') might be expected to disagree with such views.

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Table 1
Description of 'Positions' in three-stage version of Perry's scheme of intellectual development (Johnstone[23])

Perceptions of:	Student in Position 'A'	Student in Position 'B'	Student in Position 'C'
Student's role	Passively accepts	Realises that some responsibility rests with the student. But what? And how?	Sees student as source of knowledge or is confident of finding it. Discusses, and makes own decisions
Role of lecturer / member of staff	Authority, giving facts and know-how	Authority. Where there are controversies, wants guidance as to which view is favoured by staff	Authority among authorities. Values views of peers. Member of staff as facilitator
Nature of knowledge	Factual; black and white; clear objectives; non-controversial; exceptions unwelcome	Admits 'black-and-white' approach not always appropriate. Feels insecure in the uncertainties this creates	Wants to explore contexts; seeks interconnections; enjoys creativity; scholarly work
Student's task in examinations / assessments	Regurgitation of 'facts'. Exams are objective. Hard work will be rewarded	Quantity is more important than quality. Wants to demonstrate maximum knowledge	Quality is more important than quantity. Wants room to express own ideas and views.

Questionnaire drafts were discussed with student representatives and staff, and then finalised after piloting. Four sentence stems referred to the four elements of learning. In each stem, students were asked to choose one answer from the three provided (representing 'A', 'B' and 'C' positions). Each set of three answers was presented, not in order of progression in the Perry scheme, but randomly. Additionally, in the first term questionnaire, students were asked to respond to each sentence stem as they might have done *prior* to university. It can be argued[27] that retrospective accounts such as these are less valid than concurrent ones, but since students were being asked to reflect on a lengthy period of schooling which, for most, had ended only about four months beforehand, we considered that such retrospective impressions would still be informative.

Clearly it was important for meaningful comparison of students' responses, that the two questionnaires be as similar as possible. Thus, the first term questionnaires were identical. However, about 10%

of respondents in the PBL course provided written feedback, emphasising the need for minor re-wording of several items to take into account more explicitly the nature of their course. The amended wording in the third term questionnaire is also shown in the Appendix.

Results and Discussion

Questionnaire response rates
Although Term 1 and Term 3 response rates were high in both cohorts, it was to be expected that they would be lower for questionnaires returned on *both* occasions (Table 2). These were still acceptable in the context of survey research. The results described below are based on the questionnaires returned on both occasions.

Table 2
Response rates associated with questionnaire on learning perceptions

Time of questionnaire returns	Number returned		Response rate	
	Traditional course	PBL course	Traditional course	PBL course
(Year 1: Middle of Term 1)	*(169)*	*(192)*	*(71% of 237)*	*(82% of 235)*
(Year 1: Middle of Term 3)	*(176)*	*(166)*	*(74% of 237)*	*(71% of 235)*
Returned on both occasions	126	134	53% of 237	57% of 235

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Table 3

Percentage of undergraduates endorsing 'A', 'B' and 'C' responses to the four sentence stems: Comparison of undergraduates in traditional (n=126) and PBL (n=134) courses

Type of response given to sentence stem concerning	Before coming to university (gauged retrospectively)		Middle of first term, first year (5 weeks after course started)		Middle of third term, first year (5 weeks before course ended)	
	Trad. Course %	PBL course %	Trad. Course %	PBL course %	Trad. Course %	PBL course %
1. Student role:						
A	27.8	32.1	0.8	-	4.8	0.8
B	38.1	25.4	41.3	15.7	34.1	17.2
C	28.6	35.8	54.0	83.6	61.1	80.6
Mixed response	-	-	-	-	-	0.8
No response	5.6	6.7	4.0	0.8	-	0.8
Significance level	***χ^2 = 4.93, df = 3, NS		*χ^2 = 24.08, df = 1, $p \leq .001$		*χ^2 = 13.62, df = 1, $p \leq .001$	
2. Staff role:						
A	24.6	34.3	5.6	3.0	7.9	0.8
B	28.6	19.4	11.1	3.7	27.0	8.2
C	39.7	38.8	81.0	88.8	65.1	89.6
Mixed response	0.8	-	-	-	-	0.8
No response	6.3	7.5	2.4	4.5	-	0.8
Significance level	***χ^2 = 4.49, df = 3, NS		**χ^2 = 6.29, df = 2, $p \leq .05$		**χ^2 = 26.14, df = 2, $p \leq .001$	
3. Nature of knowledge:						
A	23.0	20.9	5.6	0.8	8.7	2.2
B	25.4	27.6	27.8	28.4	35.7	28.4
C	45.2	44.0	61.1	70.2	54.8	67.2
Mixed response	-	-	1.6	-	-	0.8
No response	6.3	7.5	4.0	0.8	0.8	1.5
Significance level	***χ^2 = 0.39, df = 3, NS		*χ^2 = 1.03, df = 1, NS		**χ^2 = 7.80, df = 2, $p \leq .05$	
4. Exams/assessment						
A	49.2	46.3	42.9	26.1	44.4	18.7
B	21.4	26.9	22.2	26.1	31.0	18.7
C	23.8	20.2	31.0	44.0	24.6	60.4
Mixed response	-	-	1.6	0.8	-	0.8
No response	5.6	6.7	2.4	3.0	-	1.5
Significance level	***χ^2 = 1.45, df = 3, NS		**χ^2 = 8.67, df = 2, $p \leq .01$		**χ^2 = 31.38, df = 2, $p \leq .001$	
*Chi-square analyses based on: *A &B combined, C: **A, B, C; ***A,B,C, No response*						

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Sentence stem responses: Comparison of students in traditional and PBL courses at three points in time.
Table 3 shows the types of sentence stem responses given by students in the traditional and PBL courses at each of three points in time: *(i)* 'pre-university' (students gauging retrospectively what their responses might have been before university); *(ii)* five weeks after the course began (middle of Term 1); and *(iii)* five weeks before first year ended (middle of Term 3). 'Pre-university', both cohorts reported similar perceptions of all four elements. However, even as early as halfway through the first term of first year, differences between the two cohorts existed in all elements except nature of knowledge. By the end of first year, their perceptions differed significantly in all four elements and, excepting knowledge, were highly significant.

'Pre-university' perceptions.
In both cohorts, views about student and staff roles were fairly evenly spread across 'A', 'B' and 'C' perspectives. The great majority of students in both courses had recently left school and had had no previous experience of higher education. In contrast, perceptions of the nature of knowledge and assessment-related tasks were slightly more polarised in the 'C' and 'A' positions respectively. The two groups showed no significant differences in any of the four elements.

Perceptions early in first year (mid-Term 1).
Although the retrospective reports did not distinguish between the two cohorts, significant differences were demonstrated in three elements after five weeks' experience of undergraduate life. The direction of the differences – 'C' type responses reported by higher proportions of 'PBL' students – might be expected to be more closely associated with a PBL curriculum than a traditional, lecture-based one, especially in terms of the extent to which students see themselves as more independent, analytical learners ('C' position) rather than passive, unquestioning recipients of 'handed down' information ('A' position).

Differences between the two cohorts were especially marked in perceptions of the student role. Most 'PBL' students (83.6%) considered they should take a critical approach to their subjects, check out information from various sources and take responsibility for what and how they learned ('C' position). While this approach was also reported by just over half the students in the traditional course (54.0%), a sizeable proportion (41.3%) were uncertain about what or how they should learn, while accepting that some responsibility for learning lay with them ('B' position). There were also significant differences

between the cohorts in perceptions of staff roles. Here, significantly more 'A' and 'B' responses were given by 'traditional' students, and significantly more 'C' by 'PBL' students.

Similarly, the two cohorts differed significantly in what they thought was expected of them in exams/assessments. 'A' perspectives were more prominent among 'traditional' students (42.9%, compared with only 26.1% of 'PBL' students). Conversely, 'C' type views were more evident among 'PBL' students (44.0%, compared with 31.0% of 'traditional' students). Only in the fourth element – the nature of knowledge – were there no significant differences between the two cohorts. Most students regarded knowledge from a 'C' perspective; almost all the remainder endorsed 'B' type views. Very few students in either course supported 'A' type views.

Perceptions towards the end of first year (mid-Term 3).
At this stage, perceptions of the two cohorts differed significantly in relation to all four elements. A considerable majority of 'PBL' students reported 'C' perceptions of both student and staff roles (80.6% and 89.6% respectively), compared with 61.1% and 65.1% respectively in the traditional course. Even in their perceptions of exams/assessments, a majority of 'PBL' students (60.4%) now reported a 'C' position, considerably higher than the proportion of 'traditional' students (24.6%). In contrast, a relatively high proportion of traditional students (44.4%) reported 'A' type views about assessments, compared with a much lower proportion of 'PBL' students (18.7%).

For the first time, significant differences between the two cohorts were evident in views about the nature of knowledge, the one area where students had shown greatest similarity at earlier stages. Here, more of the 'PBL' students reflected a 'C' stance (67.2%, compared with 54.8% in the traditional course). Conversely, more of the 'traditional' students (44.4% *vs.* 30.6% in the PBL course) gave 'A' and, especially, 'B' perspectives.

From Table 3 it can be seen that, with the exception of the 'traditional' students' response to exams/assessments, more than half in each course reported 'C' perspectives at the end of first year. This was more marked among 'PBL' students, especially in terms of how they saw their own role, as well as that of the staff. However, the largest divergence between the two cohorts related to exams/assessments, where substantially fewer in the traditional course saw them as 'open-ended', allowing scope for their own thinking. Certainly 'pre-university' views about this element indicated that many students in both cohorts had further to

'travel' to reach a 'C' position at the end of first year. The following questionnaire comments may cast some light on possible reasons for the findings:

'Traditional' students:

" used to prefer the open long questions but after what I have experienced during the academic year, I know I prefer clear-cut answers/questions."

"There is no room for thought – all you do is ... regurgitate ... I don't feel that [this] response is what I would like but this appears to be what is expected of me. I don't necessarily agree with the lecturer but I answer exams with his opinion as he will be responsible for the marking scheme."

"Objectives should be provided in all subjects for all sections of the course so students can clearly see what material is examinable and essential. This way there will be no problem with lecturers introducing extra material into lectures."

'PBL' students:

"...much of what we learn makes sense when we stand back and think about the reasoning behind it. It is easy to become overloaded with facts; it is not possible to learn everything but rather get an overview and grasp the basics."

"I enjoy getting to grips with so many different angles and creating my own personal way of understanding."

"The beauty and enjoyment of science lies in the fact that there are many ways to look at things and many options to explore."

Comments from the 'traditional' students embodied a more restricted, syllabus-bound approach to learning, with exams very much regarded as the end towards which they were working. This 'A' stance might be closely associated with perceptions of school exams, and indeed was reflected in 'pre-university' views of many students in both courses. The (relatively) more familiar teaching/learning environment of the traditional course was likely to reinforce this way of thinking about exams. Possibly, many school leavers would find difficulty envisaging alternative forms of 'exams' or assessments. It can be argued, of course, that this was a sound and realistic approach for the 'traditional' students to adopt, and one that had perhaps been validated already by their first year experience. It was also clear from their questionnaire comments that they felt pressure from the numerous exams during the year, that the workload had been heavy, and that it was often difficult to identify what was 'needed' for exams.

By the third term, they had had considerable 'first hand' experience of university exams and many had obviously drawn their own conclusions about what was wanted in exam answers.

The 'PBL' students were also facing their first 'professional' exams soon after completing the Term 3 questionnaire but it was clear from their comments that many felt the course assessments during the year gave inadequate preparation. Two 'PBL' students stated:

"It's right that we take responsibility for our own learning and not be spoon-fed by staff but when push comes to shove, we still have to pass exams so we need SOME idea of what we need to know for the exam."

"It's all very well giving assessments which allow students the opportunity to 'show they have ideas of their own' but the marking of these assessments must reflect this in order for these to be worthwhile."

It was quite apparent, therefore, from sentence stem responses and comments that exams/assessments were areas that students in both courses found especially difficult. In particular, their frequency in the traditional course and their infrequency in the PBL course were mentioned as sources of disquiet.

Maintenance/change in individuals' responses between Terms 1 and 3.
We were interested not only in students' perceptions of the four elements at different points in time but, in particular, whether individual students differed significantly in their patterns of change in perceptions during first year. Table 4 shows, for each sentence stem, the percentages of students in each course who, during first year, moved 'forward', 'back' or showed 'no change' in response. Small expected cell frequencies in the chi-square analyses necessitated the combining of sub-categories under 'No change', 'Moving forward' or 'Moving back'.

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Table 4

Maintenance/change in individuals' sentence stem responses by end of first year: Comparison of undergraduates in traditional (n=126) and PBL (n=134) courses

Type of change in sentence stem responses between first and third terms in first year:	1. Student Role		2. Staff Role		3. Nature of Knowledge		4. Exams/Assessments	
	Traditional Course %	PBL Course %	Traditional Course %	PBL Course %	Traditional Course %	PBL Course %	Traditional Course %	PBL Course %
No change – stayed at:	**57.9**	**76.1**	**65.1**	**84.3**	**58.7**	**72.4**	**45.2**	**52.2**
A	0	0	1.6	0.8	3.2	0	24.6	11.2
B	19.8	5.2	6.4	1.5	14.3	15.7	11.1	7.5
C	38.1	70.9	57.1	82.1	41.3	56.7	9.5	33.6
Moved 'forward':	**20.6**	**9.7**	**7.9**	**4.5**	**12.7**	**10.4**	**23.0**	**29.1**
$A \Rightarrow B$	0	0	1.6	0.8	2.4	0	10.3	3.0
$A \Rightarrow C$	0.8	0	2.4	1.5	0	0.8	7.9	11.9
$B \Rightarrow C$	19.8	9.7	4.0	2.2	10.3	9.7	4.8	14.2
Moved 'back':	**17.5.**	**12.7**	**24.6**	**5.2**	**22.2**	**14.2**	**27.8**	**13.4**
$B \Rightarrow A$	1.6	0	0.8	0	2.4	1.5	6.4	3.7
$C \Rightarrow A$	3.2	0.8	5.6	0	3.2	0.8	12.7	3.0
$C \Rightarrow B$	12.7	11.9	18.2	5.2	16.7	11.9	8.7	6.7
Mixed/no responses given	**4.0**	**1.5**	**2.4**	**6.0**	**6.4**	**3.0**	**4.0**	**5.2**
Significance level	**χ^2=30.6, df=3, p$\leq$0.001*		***χ^2=21.0, df=2, p$\leq$0.001*		****χ^2=10.0, df=4, p$\leq$0.05*		*χ^2=46.2, df=8, p$\leq$0.001*	
Chi-square analysis based on:	* "No change: B", "No change: C", "Moved 'forward' ", "Moved 'back' "							
	** "No change", "Moved 'forward' ", "Moved 'back' "							
	*** "No change: A", "No change: B", "No change: C", "Moved 'forward' ", "Moved 'back' "							

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'Maintenance'.

Table 4 highlights the extent to which individuals in each cohort were characterised, not by *change* during first year, but by *maintenance* of their first term perceptions. In all four elements of the learning environment, a higher percentage of 'PBL' students reported 'C' perceptions at mid-first term of first year and maintained these into the third term. Perceptions of the student's role over the year showed a highly significant difference between the two cohorts (χ^2 = 30.6, df = 3, p< 0.001) especially in maintaining 'C' positions: of those in the PBL course 70.9% maintained this position, compared with just over a third in the traditional course (38.1%). Only a very small proportion of 'PBL' students (5.2%) held 'B' views over the year, compared with a much larger proportion in the traditional course (19.8%). In relation to the role of staff, the difference between the cohorts was also highly significant (χ^2=21.0, *df*=2, *p*≤ 0.001), with 82.1% of 'PBL' students maintaining a 'C' position throughout the year, compared with 57.1% of 'traditional' students. Perceptions of the nature of knowledge, also differed significantly (χ^2=10.0, *df*=4, *p*≤ 0.05), with 56.7% of 'PBL' students and 41.3% 'traditional' students maintaining a 'C' position. Finally, the difference in response to exams/assessments was highly significant (χ^2=46.2, *df*=8, *p*≤ 0.001): 33.6% of 'PBL' students compared with 9.5% of the 'traditional' students remained in a 'C' position throughout the year; twice as many 'traditional' students (24.6%) as 'PBL' students (11.2%) maintained an 'A position.

'Changes'.

Changes in individuals' perceptions that could be interpreted as representing 'backward' movement during first year tended to be reported by more students in the traditional course, mostly to a 'B' position. For instance, with reference to the role of staff, 24.6% of the 'traditional' students appeared to move 'back' compared with 5.2% of 'PBL' students. In the case of exams/assessments, 27.8% of the 'traditional' students appeared to move 'back' (mostly towards 'A'), compared with 13.4% of 'PBL' students (half of whom moved 'back' to 'A').

There was also evidence of what could be described as 'forward' movement for individuals in both cohorts. In their views of the student's role, twice as many in the traditional course as in 'PBL' (20.6% *vs.* 9.7%) reported moving 'forward', and this was towards a 'C' position. Also worth noting was the proportion of students in both courses reporting 'forward' movement in their perceptions of exams/assessments (23.0% of 'traditional' and 29.1% of 'PBL' students). Of these, about half the 'traditional' students (12.7%) moved to 'C' while almost all 'PBL' students (26.1%) did so.

Confidence and uncertainty

The questionnaires, whose results are discussed above, were accompanied by open-ended sections to obtain student views more informally. Analysis of these responses exposed aspects of confidence and uncertainty, which supported and amplified the findings of the main questionnaire.

By the end of first year, there seemed to be some evidence among 'PBL' students of less confidence and more uncertainty about the depth and breadth of course content and about the 'appropriate' approach to take to given topics, and this was more pronounced than for those in the traditional course. Evidence came from 'PBL' students' comments:

"Sometimes it can be scary to do all this work on your own in case what you learn is wrong."

"When you are trying to work independently, this can lead to ... an inability to see the wood for the trees."

"It is difficult to work out what is right or most feasible, as an uneducated student, without guidance from staff. Difficult to evaluate when students' knowledge is not enough to make an informed decision on the relevance of information."

Some 'PBL' students requested some lecture sessions, not in a desire for 'spoon-feeding', it seemed, but as an organisational framework for what they had discovered through their own independent learning:

"More backup lectures to supplement rather than replace PBL would be very helpful."

"I strongly believe there needs to be an increase in 'reinforcement lectures' to consolidate and aid in our understanding of core topics (e.g., coagulation, immunology, neurology)."

[These problems have since been addressed, by the issue of clear objectives for each five-week block of work.]

'Traditional' students, in their unstructured comments, also referred to uncertainty about what was expected of them, especially in knowing what was 'essential' for exams rather than 'merely interesting'. However, this was far less prominent than among 'PBL' students.

Those aspects which 'PBL' students found problematic are identical to those revealed in other studies. Their greater concerns about breadth and depth of knowledge required and ability to identify 'core' information were referred to by Albanese &

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Mitchell[11] in their meta-analysis of studies of PBL in medicine. The fulfillment of pre-course fears about gaps in 'necessary' knowledge and about incorrect information being reinforced by fellow students and 'naïve' (i.e., non-specialist) staff were highlighted by Bernstein et al.[28] Uncertainty about how to tackle preparation for examinations was reported by Birgegård & Lindquist.[29] Uncertainty about what was expected of medical students and a perceived lack of feedback on progress was noted by Kaufman et al,[30] and these were also reported as sources of stress in Moffat et al.'s [31] Glasgow study of the PBL cohort which followed the one in the current study.

Effects of the different courses on students' perceptions

If features associated with a 'C' stance are the qualities desired in medical graduates, it was encouraging to find that, at the end of their first year, more than half the students in each course reported 'C' perspectives in the sentence stems concerning knowledge and the roles of students and staff. 'C' type responses from both cohorts emphasised the importance of setting decisions in appropriate contexts, referring to ethical issues, the complexity of human beings, and the suitability of different treatments for different patients. One 'traditional' student said:

"I think the scientific facts have to be put in the context of treating the patient. Often logic is not applicable and the human body requires individual assessment."

One of the 'PBL' students commented that

"Very few things in medicine are clear cut: drugs have various side effects and many body mechanisms are not known. Ethics are certainly not clear cut ... Few things in medicine are clear cut, if you think about them."

However, more striking were the significant differences in the views reported by the two cohorts about their first year learning experience. These were generally in a consistent direction: to a greater extent, 'PBL' students reported views associated with more critical, self-directed learning, i.e., a 'C' type stance.

The question is whether this resulted directly from the PBL format. It is impossible to say with certainty what produced the differences between the two cohorts, given the likely range of individual differences, even in this highly selected student body. These comprise intrinsic factors, such as motivation, confidence, academic ability and personality, and extrinsic factors likely to impinge

on students in their first year, for example, the transition from school, and often living away from home. The research design did not permit conclusions about cause-and-effect. However, statistically significant perceptions were found to be associated with students enrolled in the two different courses.

It could be argued that 'traditional' and 'PBL' students entered first year from different starting-points – that more of the 'PBL' students held a 'C' perspective before they even began university – and this was the source of the significant differences. However, students' retrospective evaluations of how they viewed learning prior to university lent support to the idea that the two cohorts had started from essentially similar baselines. Recall of 'pre-university' study would have to be consistently faulty across both cohorts to produce no significant differences between them. Very importantly, too, admission requirements had not been altered. The same criteria, based on academic qualifications and interview, applied to students in both cohorts, lending further support to their apparent initial similarity.

Prior knowledge about the forthcoming change in curriculum might have been a source of bias, with advance information about the new PBL course attracting more potentially 'C' type students. Questionnaire comments from 'PBL' students suggested this was unlikely – they reported extremely vague (and, in the event, inaccurate) expectations, 'pre-university', about what PBL would entail. Many, expecting 'group work' akin to school seminars, had been unprepared for the radically different format.

It is impossible to claim that the two cohorts definitely started from similar baselines in their 'pre-university' perceptions. However, it seems likely, from the above, that they were more similar than dissimilar. At least, they were similar in the perceptions they thought they had before university.

Distributing the first questionnaire in mid-first term should have allowed for initial settling-in without substantial adaptation to the new learning environment. Therefore, it was surprising to find significant differences between the cohorts appearing so soon. Obviously, by then the PBL students had experienced the new format in practice, they had observed how staff behaved and they were learning what was expected of them, as students, in this new learning environment – all very different from school. The school to university transition, especially during the first few weeks, can be expected to have an impact on most undergraduates and, indeed, at this early stage, more students in both courses endorsed a 'C' stance

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than had done in the 'pre-university' reports. Apparently, however, in their first few weeks, 'PBL' students encountered a course so different from their expectations or previous experience that it had an even greater impact on them than the traditional course had on its students.

Tracing the ways in which individual students changed or did not change during first year demonstrated that, in both cohorts, end-of-year 'C' positions represented largely, not a movement to 'C', but maintenance of a 'C' stance from first term. Thus, whatever movement to 'C' had occurred seemed to be associated with the first few weeks of the new academic session. This does not mean there was no movement at all by individual students. There was evidence of change both 'forward' and 'back' within each cohort, though change 'back' was more clearly, but not exclusively, associated with students in the traditional course.

Possible reasons for moving 'back' or maintaining 'A'/'B' positions emerged from questionnaire comments. For 'traditional' students, these included the much more onerous workload; the perceived irrelevance of studying the basic sciences, accompanied by decreasing motivation and pressures from frequent exams throughout the first year. For 'PBL' students, likely factors derived largely from the novel nature of the PBL course, such as decreasing confidence and increasing confusion about appropriate depth and breadth of learning material – what constituted 'core' knowledge – and feelings of a lack of preparedness for the forthcoming first 'professional' exams. Indeed, the lowest proportion of 'PBL' students in an end-of-year 'C' position was found in the exam/assessment element. This suggested that changes in assessment formats (or, at least, students' perceptions of assessment demands) were perhaps not keeping pace with the PBL thrust in other aspects of the students' learning environment. The problem of devising appropriate assessments in PBL has been acknowledged elsewhere.[32]

Conclusion

Our findings from this relatively short-term study of the learning experience of first year medical undergraduates provided some evidence that PBL, as implemented here, was fulfilling, with certain qualifications, the General Medical Council's recommendations for change. Compared with the traditional course, the new curriculum seemed to be associated overall with a more critical, self-directed approach to learning among students entering under identical admission criteria and holding similar 'pre-university' perceptions of learning.

Possibilities for the sciences

It could be argued that what is an appropriate teaching and learning experience for highly intelligent and motivated medical students would not be suitable for science students. However, the positive responses obtained from science students participating in limited PBL experiences mentioned at the beginning of this paper might encourage us to go further. If we want the desirable skills and attitudes, which are so often aired in the literature, to develop in our students, we may have something to learn from our medical colleagues.

It might also be argued that the kind of scenarios used in medicine where science, medicine and social problems can be personalised in a 'living' situation, would be difficult to find in the sciences. However the 'case studies' that have been used in chemistry to link academic and industrial and environmental situations are exactly parallel to those in medicine. The laboratory could easily provide the scenario. Wham[33] devised such a situation when he had students analyse water samples taken at different points on the River Kelvin for phosphate and then work in groups to explain the results. The brainstorming raised issues such as: "Where was the phosphate coming from? Who used it and for what? Why did the phosphate concentration rise suddenly at some points and then diminish? Has anyone got a map? What industries are on the tributaries?" This is exactly analogous to the type of scenarios used by our medical colleagues.

Many examples must exist which could be shared within the chemical and inter-science community and so enable us to see new possibilities for the development of the skills of our students and even to gain the bonus of enthusiastic and co-operative learning of chemistry.

References

1. S.T. Belt, E.H. Evans, T. McCreedy, T.L. Overton and S. Summerfield, *U.Chem.Ed.,* 2002, **6**, 65.
2. T.L. Overton, *Problem Based Learning: An introduction*, LTSN Physical Sciences Primer 4, version 1, 2001.
3. F. Percival, *A study of teaching methods in tertiary chemical education*, PhD thesis, University of Glasgow, 1976.
4. A.H. Johnstone (editor) Set of interactive discussion units: '*Nitrogen for the Nineties*', '*To market a drug*', '*Zinc and You*', '*Titanium, the space age metal*', '*Organic liquids containing oxygen*', Royal Society of Chemistry, London, 1982.

5. M.S. Byrne and A.H. Johnstone, *Simulations and games for learning*, 1983, **13**, 95.
6. C.A. Wood, *Creative Problem Solving in Chemistry*, Royal Society of Chemistry, London, 1993.
7. A.T. Schwartz, D.M. Bunce, R.G. Silberman, C.L. Stanitski, W.J. Stratton and A.P. Zipp, *Chemistry in Context*, American Chemical Society, Indiana, W.C. Brown, 1994.
8. N. Reid and M-J. Yang, *Intern. J. of Science Ed.,* 2002, **24** (12).
9. M.S. Byrne and A.H. Johnstone, *Educ. Chem.*, 1987, **24**(3), 75.
10. General Medical Council, *Tomorrow's Doctors*: *Recommendations on undergraduate medical education,* General Medical Council, London, 1993.
11. M.A. Albanese and S. Mitchell, *Academic Medicine,* 1993, **68**(1), 52.
12. S.D. Block, *Academic Psychiatry*, 1996, **20** (2), 65.
13. J. Rosenthal and J. Ogden**,** *Medical Education***,** 1998**, 32**(2), 127.
14. W.G. Perry, *Forms of intellectual and ethical development in the college years: a scheme,* Holt, Rinehart &Winston, New York, 1970.
15. P. Fitch and R.S. Culver, *Educational activities to stimulate intellectual development in Perry's scheme*, Proceedings of the ASEE Annual Conference, 1984.
16. D. Simpson, K. Dalgaard and D.K. O'Brien, *The Journal of Family Practice*, 1986, **23**(5), 46.
17. D.C. Finster, *J. Chem. Ed.,* 1991, **68**(9), 752.
18. M. Salner, *Systems Research,* 1986, **3**(4), 225
19. P. Hettich, *Epistemological approaches to cognitive development in college students*, in: P. Sutherland (ed.) *Adult Learning: A Reader*, Kogan Page, London, 1998
20. W. Moore, *Cumulative bibliography and photocopy service catalogue for the Perry scheme of intellectual and ethical development,* S.W. Olympia, WA, Perry Network, 1990.
21. L.L. Knefelkamp, *Current Issues in Higher Education,* 1980**, 5**, 13.
22. D.C. Finster, *J. Chem. Ed.,* 1989, **66**(8), 659.
23. A.H. Johnstone, *Evaluation of innovation: a case study,* Project Improve *hefce* Fund for the Development of Teaching and Learning, Hull, 1998
24. W. Moore, *Georgia Journal of College Student Affairs,* 1988, **3**(2), 11.
25. J.M. Harvey, *An investigation into ways of encouraging the development of higher level cognitive skills in undergraduate biology students with reference to the Perry scheme of intellectual development,* Ph.D. thesis, Napier University, 1994.
26. M. Katung, A.H. Johnstone and J.R. Downie, *Teaching in Higher Education,* 1999, **4**(1), 43.
27. F. Clark and G. Anderson, *Higher Education,* 1992*,* **24**, 379.
28. P. Bernstein, J. Tipping, K. Bercovitz and H. Skinner, *Academic Medicine,* 1995, **70**(3), 245.
29. G. Birgegard and U. Lindquist, *Medical Education,* 1998, **32**(1), 46.
30. D.M. Kaufman, D. Mensink and V. Day, *Teaching and Learning in Medicine,* 1998, **10**(3), 138.
31. K. Moffat, S. Ross and J. Morrison, *Undergraduate medical student stress and coping in the new Glasgow medical curriculum*, University of Glasgow Department of General Practice, Glasgow, 1998.
32. E. Driessen and C. van der Vleuten, *Studies in Continuing Education,* 2000, **22**(2), 235.
33. A.J.B. Wham, *Innovations in practical work at Tertiary Level*, PhD thesis, University of Glasgow, 1977.

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Appendix   Sentence stems

[The associated 'Perry' Position is shown for each response (Positions were not indicated in the actual questionnaires). The amended wording in the Term 3 questionnaire for students in the PBL course is shown in italics in brackets.]

The statements below are about your views of knowledge and learning. In each case, choose <u>ONE</u> statement which <u>best fits your view at present</u>.

1   My job as a student is:

To accept the information given to me by the lecturer without question and to learn it. *(To accept the information given to me without question and to learn it.)*   **Position 'A'**

To accept that some responsibility rests on me for learning but I am not sure what is expected of me about what or how to learn.   **Position 'B'**

To accept what is given but to think about it critically, to check other sources for myself and to take responsibility for what and how I learn.   **Position 'C'**

2   I think that the lecturer's job *(the job of members of staff)* **is:**

To give me all I need to know for the exams but where there is more than one way of looking at things the lecturer should indicate clearly which way s/he prefers. *(To give me all I need to know but where there is more than one way of looking at things, it should be indicated clearly which way is preferred.)*
                                                    Position 'B'

To provide me with information but I realise that the lecturer is *(members of staff are)* not the only source of information and that I can find things out for myself to supplement what the lecturer has *(they have)* given.
                                                    Position 'C'

To give me all I need to know for the exams *(To give me all I need to know)* and to avoid any extra non-examinable material.   **Position 'A'**

3   I think that knowledge is:

A collection of unchangeable facts which are either right or wrong. I dislike uncertainties and vague statements. I am uncomfortable if I am asked to think for myself. I prefer to be given the facts.
                                                    Position 'A'

Complex and by no means all black and white but I find this exciting and stimulating. It makes me want to explore things for myself.   **Position 'C'**

Not just a collection of black and white facts but that there are shades of grey. Things may be right or wrong depending on circumstances and context. This uncertainty makes me feel uncomfortable.
                                                    Position 'B'

4   My job in my exam *(assessments and exams)* **is:**

To give back the facts I have learned as accurately as possible. I prefer questions with single clear-cut answers rather than open long questions.   **Position 'A'**

To answer the questions, including what I have been taught and what I have found out for myself from reading or other sources. I dislike questions which force me into a fixed answer (such as multiple choice) and prefer open questions in which I have room to show my own thinking.
                                                    Position 'C'

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To give back all I know about the topic and leave the examiner *(marker)* to give me credit for the relevant bits. I quite like open-ended questions, which allow me to show how much I know.

Position 'B'

In the first term, in a separate section of the questionnaire, students were also asked (see below) to say what they thought their answers to each sentence stem might have been prior to entering university.

<u>Before</u> you came to university, you may have held different views from those you hold now. In each case, choose <u>ONE</u> statement which best represents your views then.

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Malpractices in Chemical Calculations

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Abstract
Chemistry undergraduates are frequently guilty of faulty or inefficient practices in performing physicochemical calculations, possibly leading to incorrect answers, both in the processing of laboratory data and in answers to tutorial/examination questions. The purpose of this article is to draw attention to some of the more common malpractices, but more importantly, to provide a framework for good practice in teaching students how to perform chemical calculations.

Introduction

The purpose of this article is to draw attention to improper or inefficient procedures often encountered in chemical calculations performed by higher education students, as perceived by a lecturer with over 40 years of physical chemistry teaching experience at university level. Sometimes these malpractices are encountered in student answers to isolated problems (perhaps in examinations or tutorials) but more commonly, they are encountered in the processing of laboratory data. The author wishes to identify a number of standard approaches that should help to reduce the confusion of students, and might also provide guidelines that could be followed by instructors and authors of textbooks.

Quantity Calculus vs. Measure Calculus

Before discussing some specific malpractices, it is appropriate to outline the general algebraic system that is at the heart of advanced modern calculation techniques in physical science and engineering. This is based upon the concept that natural relationships exist between *quantities* and not between *measures*, the latter being defined by the general relationship: quantity = measure × unit; (for the special case of dimensionless quantities, the unit is 1). For example, in the statement: mass = 2 kg (× is implicit), mass is a quantity, kg is a unit of that quantity and 2 is the corresponding measure; whereas this mass is invariant, the measure and the unit can be varied in tandem: $2 \text{ kg} = 2 \times 10^3 \text{ g} = 2 \times 10^6 \text{ mg}$ = etc. A simple invariant relationship in quantities is density = mass/volume, but there is no *universal* relationship between measures of these quantities; individual relationships will depend on the choice of units for the three quantities involved. It is this invariance that is responsible for the widespread adoption of the algebraic system known as *Quantity Calculus* (or *quantity algebra*),[1] a system pioneered by people such as E. A. Guggenheim,[2] G. N. Copley[3] and M. L. McGlashan.[4] In this system, symbols represent *quantities*; in the example just given, density, mass and volume might be symbolised ρ, m and V; m will not be (for example) the number of kg in the mass (equivalent to saying that mass = m kg).

The method of quantity calculus contrasts with that traditionally used in pure mathematics, which is normally concerned with pure numbers and their algebraic representatives. However, even when mathematicians deal with non-dimensionless quantities, it has been standard practice to let *measures*, rather than quantities, be represented by algebraic symbols. To illustrate, it was not uncommon to start a problem in the following sort of way: "Let the length of the rod be l cm …" or "Let Mr Smith be aged x years and Mr Jones be aged y years…". In these cases, the symbols represent *measures*; the algebra resulting from such symbolism could legitimately be called 'measure calculus'. It *could* be argued that a measure is a *dimensionless quantity* defined as the ratio of a general quantity and a 'standard' value of that quantity. For example, we might have a pressure ratio p/p_c or p/p^o (p = pressure, p_c = critical pressure for the specific substance, p^o is a general standard pressure such as 100 kPa or 1 atm = 101.325 kPa). The first ratio, called reduced pressure, is commonly symbolised p_r. One *could* introduce a single symbol for the second, P perhaps, and if p^o is say 1 atm, then $p = P$ atm and P, formally a measure, has become a *special* quantity symbol. If this argument is valid, we are effectively stating that quantity calculus includes measure calculus as a special case, but the reverse is certainly not true, *i.e.*, measure calculus is standalone. There is one important situation where relationships are ultimately required in terms of measures (whether

written as a quantity/unit ratio or as a single symbol) and this is when a computer (capable of processing only numbers) is to be used. The conversion of a quantity formula to the requisite measure formula can cause problems for students and will be considered towards the end of this article. The majority of it will, however, be concerned with faulty or illogical practices in using algebraic quantity formulae.

Examples of Malpractice

Let us now consider these practices. Here, the emphasis will often be made on the correct practice with the implication that such practice is commonly not followed.

Avoidance of unnecessary repetition
Firstly, one ought to say that in simple calculations, such as those encountered in secondary education, one can completely avoid algebra. To take a simple case of a volumetric analysis calculation, one could proceed as follows (or something like this), using a specific example.[i]
NaOH + HCl → NaCl + H_2O; known [HCl] = 0.1234 mol dm^{-3}; HCl in burette
Pipetted volume of NaOH = 25.00 cm^3; experimental (mean) titre = 23.25 cm^3
Calculation: Amount of substance of HCl = 0.1234 mol dm^{-3} × 23.25 cm^3 = 0.1234 mol dm^{-3} × (23.25/1000) dm^3 = 0.002869 mol
So amount of substance of NaOH = 0.002869 mol
[NaOH] = 0.002869 mol/25.00 cm^3 = 0.002869 × 1000 mol /25.00 dm^3 = 0.1148 mol dm^{-3}

In pre-HE education, there is admittedly substantial advantage in this kind of procedure. Students often say something like "*We are encouraged not to remember formulas that we do not understand, but to proceed stepwise through the calculation without introducing symbols*". There are common student faults with this kind of procedure, in connection with (i) incorrect names for quantities, (ii) non-inclusion of units, and (iii) insignificant figures; these points will be covered later.

Objections arise to this procedure when an identical analysis has to be applied to several NaOH solutions, using the same pipette and the same HCl solution—the extreme situation would arise if a large number of titrations were required over a time range when NaOH is consumed in a kinetic study. Sensibly, in cases like this, one *must* exploit the constancy of both the pipette volume and the HCl concentration; as a consequence, one can deduce the generic relationship: [NaOH] = (0.1234 mol

dm^{-3}/5.00 cm^3) × titre, *i.e.,* [NaOH]/mol dm^{-3} = 0.00494 × titre/cm^3. This formula has but one independent variable, the titre. One would then tabulate titre/cm^3 and [NaOH]/mol dm^{-3} alongside the NaOH sample number/label or time/min, as appropriate. In the case of following the titre (or indeed any other quantity proportional or linearly related to concentration) as a function of reaction time, it may be wasteful of effort to convert each individual titre to a concentration when graphical processing of data is to be used. This point will be discussed again in the section concerned with plotting graphs, below.

Definition of quantity symbols
A statement of a quantity formula should always be accompanied by the definition of its symbols, even if these have a traditional meaning, like *V* commonly signifying volume; quantity symbols are *recommended*, but not fixed, by bodies such as the International Organization for Standardization (ISO),[5] the International Union of Pure and Applied Chemistry (IUPAC)[6] and the International Union of Pure and Applied Physics (IUPAP).[7] An important point is that one should not include units in such definitions, *e.g.*, '*V* = volume', NOT '*V* = volume (m^3)'. The choice of unit for the quantity is completely irrelevant—see below. Needless to say, quantity names should be modern ones, *e.g.*, 'amount of substance' or 'chemical amount', NOT 'number of moles' or just 'moles' (equivalent to miscalling 'mass' 'number of grams' or 'grams'), Avogadro constant (for 6.022 × 10^{23} mol^{-1}) and NOT Avogadro number—incidentally, the addition of the possessive: 's' after a person's name is not current scientific practice.

The need to substitute quantity symbols with both measures and units
Substitution of values into a quantity formula requires that both the measure *and* the corresponding unit be inserted. To take a simple physical chemistry example, consider the perfect (or ideal) gas relationship $V = nRT/p$ to be used to calculate gaseous volume *V* from pressure *p*, amount of substance *n* and thermodynamic (absolute) temperature *T*; *R* is the gas constant. It is essential to replace each of the right side symbols by both the measure AND corresponding unit; furthermore, the units should be there at *all* stages of the calculation—it is an option whether to keep each unit alongside its measure or to isolate the units in a composite unit term. Following this, one should handle the unit manipulation with the same care as the measure simplification; (if the relationship is wrong, unit manipulation will often reveal this). If the units are so-called *coherent*—SI units for example—they will 'cancel' nicely and, using this same example, give a simple, recognisable unit of volume. But, even if they are

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[i] In what follows, there is no specific objection to using M as a synonym of mol dm^{-3}, or litre—safest symbol L — and mL instead of dm^3 and cm^3.

not coherent, one will still get the correct answer (because the rules of substitution have been followed), *e.g.*, one might obtain an answer 1234 J atm^{-1} for the volume and if (as likely) that unit is not liked, it can be converted into m^3 by use of atm = 101 325 Pa and J Pa^{-1} = m^3. Unit prefixes can be manipulated in the same sort of way, *e.g.*, the composite unit m^3 cm^{-3} (produced as such perhaps in some calculation) can be reduced to a number as follows: m^3 cm^{-3} = m^3 (10^{-2} m)$^{-3}$ = m^3 × 10^{+6} m^{-3} = 10^6.

Use of proper functional arguments

If a function (*f*), by its definition, has a non-dimensionless argument [*x* in *f*(*x*)], then this requirement *must* be satisfied. Perhaps the commonest example of such a function in chemistry is the logarithm; one can take logarithms only of *positive numbers*. Physical scientists (textbook writers and, sadly, mathematicians who teach physical science students) should not pretend that terms, such as pH = –log$_{10}$([H$^+$]), ln(*p*) or ln(*k*) (where *k* is a rate constant) are meaningful. The following are all right: pH = –log$_{10}$([H$^+$]/mol dm^{-3}) (/ means 'divided by'), ln(*p*/atm), ln(*p*/*p*^{o}) (*p*^{o} = a chosen standard pressure), ln(*p$_1$*/*p$_2$*), ln(*p$_r$*) (*p$_r$* = a relative pressure, which could be *p*/*p*^{o} or even *p*/atm). The indefinite integral of 1/*p* is ln(*kp*) with *k* a positive integration constant with dimension of reciprocal pressure. The (strictly meaningless) differential coefficient dln(*p*)/d*T* is correctly (but cumbersomely) written dln(*kp*)/d*T*; however, it is also correctly (*and* simply) written (1/*p*) d*p*/d*T*.

Dimensional homogeneity in expressions and equations

Additive/subtractive expressions, and equations generally, should be 'dimensionally homogeneous'. For example, in connection with the thermal expansion of a solid, the following are all examples of correct forms:

V/cm^3 = 1.234 + 2.345 × 10^{-4} *t*/^{o}C (*t* = Celsius temperature)

V = 1.234 cm^3 + 2.345 × 10^{-4} cm^3 ^{o}C^{-1} *t*

V = (1.234 + 2.345 × 10^{-4} *t*/^{o}C) cm^3

but the following are improper:

V = 1.234 + 2.345 × 10^{-4} *t*

V/cm^3 = 1.234 + 2.345 × 10^{-4} *t*

Modern tabulation

Tabulation, for the sake of conciseness, is of numbers and the names of columns and rows should reflect this. For example, we might give a set of volumes as

V/cm^3 1.234 2.456 3.789…

not   *V*(in cm^3) … or *V*(cm^3) …

Formally, *V* 1.234 cm^3 2.456 cm^3 3.789 cm^3…

is correct but clearly cumbersome; transfer of the common unit once and for all to the row designator makes obvious sense. The same point applies to a repetitive power-of-ten multiplier;

V/m^3 1.234 × 10^{-3} 2.456 × 10^{-3} 3.789 × 10^{-3}…

is (deliberately avoiding the prefixes milli and centi to make the point) more concisely written as

V/10^{-3} m^3 1.234 2.456 3.789…

or as 10^3 *V*/m^3 1.234 2.456 3.789…

In this latter case, the first table entry 1.234 is exactly what the row name says it is, *viz.*, 10^{+3} *V*/m^3 (author's + sign emphasis) so that *V* = 1.234 × 10^{-3} m^3. Incidentally, *V*/cm^3 can alternatively be written *V* × cm^{-3} or just *V* cm^{-3}, but the quotient format is usually regarded as clearer.

Plotting graphs

Just as one tabulates numbers, so one also plots *numbers*[8] (just as mathematicians do when symbols such as *x* and *y* represent numbers). However, this is only when we have discrete plot points, corresponding to measured data, say, a set of temperatures and corresponding volumes where we might plot *V*/cm^3 against *T*/K (or perhaps against *T*/kK ≡ *T*/1000 K) with axis tick marks properly labelled as numbers.[ii] It must necessarily follow that graphical intercepts, slopes and areas must also be *numbers* and, furthermore, the algebraic equivalents of these parameters must reflect this. To exemplify (also bringing in the point about proper logarithmic arguments): in the field of reaction kinetics, one encounters the Arrhenius (quantity) relationship *k* = *A* exp(–*E*/*RT*) [*k* = a rate constant (here exemplified by a first order one with dimension [TIME^{-1}]), *A* = pre-exponential factor, *E* = activation energy, *T* = thermodynamic (or absolute) temperature]. Suppose, one has a set of experimental values for *k* and corresponding *T* and one wishes to determine *A* and *E* by graphical means. The proper logical procedure, starting with division by a sensible unit of *k*, is as follows:

k/min^{-1} = (*A*/min^{-1}) exp(–*E*/*RT*)

ln(*k*/min^{-1}) = ln(*A*/min^{-1}) – *E*/*RT* = ln(*A*/min^{-1}) – *E*/(*R* × 1000 K) × 1000 K/*T*

Then plot the *number* ln(*k*/min^{-1}) against the (conveniently sized) *number* 1000 K/*T* to give a straight line of slope –*E*/(*R* × 1000 K) and intercept ln(*A*/min^{-1}) from which *E* can be obtained by multiplying the slope by –*R* × 1000 K and from which *A* can be obtained by taking the natural antilogarithm of the intercept and then multiplying this by min^{-1}. If axes are labelled as numbers, it would be wrong to say that ln(*k*)— meaningless anyway—is plotted against 1/*T* and the slope is –*E*/*R*.

[ii] Formally, there is nothing improper in plotting in a quantity space, *V* against *T* with tick marks tediously labelled as *quantities* (1 cm^3, 2 cm^3, 3 cm^3, …, 290 K, 300 K, 310 K, …).

However, one must distinguish here such number plots from so-called 'sketch graphs' where one merely wants to show *with no experimental points*, for example, the general trend of *V* (for a solid, say) against *T*. Here one plots quantities *V* and *T*, with common implicit assumptions that the axes are linear and cross at the origin.

It is now appropriate to return to the point deferred earlier, concerning the optimum processing of titre vs time data in a kinetics experiment, avoiding the conversion of each individual HCl titre to a NaOH concentration. Suppose that one wishes to test whether the process is first order in NaOH (other reactants being in excess and essentially remaining at constant concentration). The equation to be tested is then $\ln([NaOH]/[NaOH]_o) = -kt$ {subscript o indicates a value at zero time, k = first order rate constant, t = time}. The first point to note is that $[NaOH]_o$ is a constant and division of each [NaOH] by that constant can easily be avoided, but one can go further. Since $[NaOH] \propto$ titre, *T*, the equation to be tested can be transformed as follows:
$\ln(T/T_o) = -kt$; $\ln(T/cm^3) = \ln(T_o/cm^3) - k \times min \times t/min$

Plot $\ln(T/cm^3)$ against t/min and *if* the order is 1 (and the reaction has been followed to high degree of completion), the graph will be a straight line of slope $-k \times min$ from which $k = -slope \times min^{-1}$ can be obtained. Similar arguments will apply to the testing of other kinds of rate equation, *i.e.*, not first order, except that there will then be need for a final *single* use of the proportionality constant in $[NaOH] \propto$ titre when converting a graphical slope into a rate constant. If a *product* rather than a reactant is being monitored, again similar arguments may be used, but there will be a further need to obtain and involve a titre at 'infinite' time.

Unit conversion
Students often find unit conversion difficult. To take a simple example, suppose one had a concentration of 1.234 mol dm^{-3} and wanted to convert this into so many mol m^{-3}. Students would often argue (correctly) as follows: 1 m^3 is 1000 times as big as 1 dm^3, so this would require a 1000 times as much amount of substance, *i.e.*, 1234 mol, so 1.234 mol dm^{-3} = 1234 mol m^{-3}. But the following (taken in more steps than is conventional for emphasis) is simpler and more generally applicable: 1.234 mol $dm^{-3} = 1.234$ mol $(10^{-1}$ m$)^{-3}$ $= 1.234 \times (10^{-1})^{-3}$ mol $m^{-3} = 1.234 \times 10^{+3}$ mol $m^{-3} =$ 1234 mol m^{-3}.

Significant figures
It is very common for students to create far too many figures in a calculation. A simple rule in a multiplicative/divisive calculation is to give the answer to the same *relative* error (roughly the same

number of *significant figures*, but this can be wrong by ±1) as the least accurate datum in the calculation. Additive/subtractive calculations should give an answer to the same number of *decimal places* as the least precise datum, so that $(1.15 - 0.1234)$ cm^3 = 1.03 cm^3, but 1(exactly) – $0.1234 = 0.8766$. As a rough guide, taking a logarithm of a number with *n* significant figures would produce *n* decimal places. One can do better than this by applying statistical considerations, of course, ('cumulation of errors'), and including '± *e*' after the number (preferably, stating whether *e* is a standard error of the mean or a 95% confidence deviation or whatever). In this connection, a simple rule of thumb is to give *e* to one figure (or possibly two if the first figure is a 1) and then round the mean to the same number of *decimal places*. If the last decimal place is a zero, it should be present; the same point applies to the primary data, *i.e.*, significant terminal zeros should be included. A related matter arises when the number of significant figures is less than the number of figures preceding the decimal point (or decimal symbol); 1.234×10^5 is clear in significant figures but 12340 is ambiguous. On a minor issue, it is the author's opinion, that for measures below 1, an initial zero before the decimal point is generally clearer than when that zero is omitted. Two other small points agreed internationally: (1) a comma should not be used to space sets of three digits (either side of a decimal symbol)—when there are more than four digits, one can use a space instead, *e.g.*, 12 345.123 45; (2) the comma can be used instead of a stop for a decimal symbol—this is standard European (but not British) practice

Use of computers
Although the previous emphasis has been on the use of algebraic symbols as quantity representatives, one may have to consider an effective deviation from this if data are to be processed by computers, which cannot (generally) handle units. In this context, it may be that, for example, instead of *c* standing for concentration, it may have to stand for concentration/mol dm^{-3}; strictly speaking *c* would be the name of a register containing the number concentration/mol dm^{-3}, a point more appreciated when one had to write a computer programme to perform the task and less appreciated in the present age of general computer packages. As a precursor to computer processing, some manipulation of the quantity formula to involve units is necessary.

This will be illustrated by the calculation of a gas volume from the perfect gas equation. Suppose that one wanted to (i) calculate the number of cm^3 in the volume, (ii) input the constant R as the number of J K^{-1} mol^{-1} in this quantity, and (ii) input information on quantities n, T and p as the number of moles (symbol mol), the number of K and the number of atm, respectively. Then, we would have to manipulate the original equation $pV = nRT$ as follows:

$$V = \frac{nRT}{p}$$

$$\frac{V}{cm^3} = \frac{(n/mol)(R/J\,K^{-1}\,mol^{-1})(T/K)}{(p/atm)} \times \frac{mol \times J\,K^{-1}\,mol^{-1} \times K}{atm \times cm^3}$$

$$= \frac{(n/mol)(R/J\,K^{-1}\,mol^{-1})(T/K)}{(p/atm)} \times \frac{mol \times J\,K^{-1}\,mol^{-1} \times K}{101\,325\,Pa \times 10^{-6} m^3}$$

$$= \frac{(n/mol)(R/J\,K^{-1}\,mol^{-1})(T/K)}{(p/atm)} \times \frac{J}{101\,325\,Pa \times 10^{-6} m^3}$$

$$= \frac{(n/mol)(R/J\,K^{-1}\,mol^{-1})(T/K)}{(p/atm)} \times \frac{1}{0.101\,325}$$

$$= 9.869 \frac{(n/mol)(R/J\,K^{-1}\,mol^{-1})(T/K)}{(p/atm)}$$

and then assign each measure (= quantity/unit) to a particular computer register (sensibly, given the same name as the quantity, of course). Naturally, if the units involved are coherent, *e.g.*, (unprefixed) SI units, there is no multiplying factor like the 9.869 above.

Unit names and symbols
One should use the correct (mandatory) symbols for units, *e.g.*, s not sec for seconds, h not hr for hour, l or L not lit for litres (L better because of possible confusion of l with the digit 1), atm not atmos for atmospheres. Generally, unit *names* based upon scientists' names have an initial lower case letter, *e.g.* joule, but the corresponding symbols have a capital letter, *e.g.* J; otherwise the symbol is all lower case—litre is the exception to the rule. Unit symbols (which in print are roman, unlike italic symbols for quantities in print) should not be pluralised or followed by an abbreviation point. Of course, there is a severe font problem when writing on paper or a blackboard; italicisation can be simulated by underlining but this is tedious— students could, for example, confuse K (for kelvin) with K (for equilibrium constant). There should be a space between a measure and a unit and between components of a composite unit; compare ms^{-1} = 1/millisecond and m s^{-1} = metre per second. Although a strong supporter of SI units, the author does not believe that students should not use other units.

Use of the solidus
A small point arises in connection with the use of the solidus (/) for division in quantity or unit expressions. The modern convention is that everything that follows the solidus (unless bracketing indicates otherwise) is part of the divisor. Thus a/bc means a divided by the product of b and c; in other words multiplication has priority over division; J/K mol is the same as J K^{-1} mol^{-1}—a second solidus after K would be redundant. This contrasts with the usage in computer programming coding, which is a different matter. However, it is better to add extra bracketing if there is any danger of confusion.

Conclusion

It is my view that students (like us!) must use completely rigorous and consistent methods for performing chemical calculations. Whilst this might seem to necessitate extensive defining of rules and procedures, it is an essential part of gaining an education in chemistry if our students are to understand their subject properly and are to use their knowledge as professional chemists. Although many of the principles underpinning this article have been expounded by others, my experience, and that of virtually all my colleagues, is that students receive conflicting advice from lecturers, tutors, demonstrators and textbooks. Also, it is widely felt that students come to university with a weaker grasp of physics and mathematics than (say) 20 years ago. University chemical educators must be absolutely consistent in the way they expect students to manipulate data if they are to grasp the essential principles, and I hope that the guidelines provided in this article will help both colleagues and students.

References

1. I. Mills, T. Cvitaš, K. Homann, N. Kallay and K. Kuchitsu, *Quantities, Units and Symbols in Physical Chemistry*, 2nd ed., Blackwells, Oxford, 1988, pp 107-9.
2. E.A. Guggenheim, *J. Chem. Ed.*, 1958, **35**, 606.
3. G.N. Copley; *J. Roy. Inst. Chem.*, 1959, **83**, 477.
4. M.L. McGlashan, *Physicochemical Quantities and Units*, Royal Institute of Chemistry Monograph for Teachers No. 15, 1971.
5. *ISO 31-0* to *ISO 31-13*, International Organization for Standardization, Geneva, 1992.

Joe Lee

6. Ref. 1, p 9.
7. E.R. Cohen and P. Giacomo, *Symbols, Units, Nomenclature and Fundamental Constants in Physics* (Document IUPAP-25), International Union of Pure and Applied Physics, 1987.
8. S. Le Vent; *Educ. Chem.*, 1987, **24**, 14.

A simple and general method to draw resonance forms

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Introduction

Knowledge of the most important resonance form(s) of covalent compounds of s- and p-block elements is essential for the application of the VSEPR model or for discussing in such compounds, at the basic level of the Valence Bond Model, bond distances, bond orders, relative bond strengths, dipole moments, orbital hybridization, reactivity, etc. This requires for every particular species: i) the knowledge of all its possible resonance forms and ii) some criteria to predict the most important resonance form(s).

At present there is no simple, systematic and general method to generate all resonance forms. Most reported methods apply only to simple molecules or require the use of mathematical formulae or complex rules. This communication reports a simple and general method to write resonance forms of any molecule or ion, simple or not, linear, branched or cyclic, containing any s– and p–block elements without using mathematical formulae or rules difficult to remember.

Fundamentals

It is necessary to accept some limitations when using any method of writing resonance forms:
1) Hydrogen and the elements of groups 1 and 2 only form σ bonds.
2) Li, Be (2s elements), B, C, N, O or F (2p elements) never exceed the octet. Although the expansion of the octet is a controversial matter, we will consider that the third and subsequent row elements of groups 13 to 18 (>2p elements) can expand the octet
3) π bonds between >2p elements are rare and very weak. Therefore, formation of a π bond requires 2p/2p or 2p/>2p pairs of elements.
4) Elements of the s- and p-block can only form single, double or triple bonds because formation of a quadruple bond requires the use of valence d orbitals (transition elements).
5) In molecules with an odd number of electrons *(e.g.* NO, NO_2) the unpaired electron is non-bonding, *i.e.*, it is a lone electron.

In some cases, it is necessary to calculate the formal charge of all atoms. The formal charge of an atom is the difference between the number of electrons it contributes to the molecule *(i.e.* its valence electrons) and the number of the electrons it 'owns' in the molecule. The latter can be calculated as the sum of its unshared electrons plus half of those it shares with its neighboring atoms (or plus the number of bonds this atom establishes with its connected atoms). The formal charges must always be considered with their mathematical signs. Consequently, the charge on a resonance form is always the algebraic sum of the formal charges of all atoms.

Before applying the method we need:
1) A sketch showing which atoms are bonded to which others (the σ skeleton).
2) To calculate **V** as the total number of pairs of electrons of the compound. This number is equal to the total number of valence electrons of all atoms less the charge (including the sign) of the species, if it is an ion, divided by two.
   For example for OH^-, $V = [(6 + 1) - (-1)]/2 = 4$; for NH_4^+, $V = [(5 + 4 \times 1) - (+1)]/2 = 4$.
3) To count the number (**N**) of σ plus lone electron pairs (*leps*) of the octet representation. This representation is generated by the addition to each element of groups 13 to 18 (np elements) in the σ skeleton the necessary number of *leps* to attain the octet. With some experience, N can be deduced without drawing the octet representation. This is not a true electronic representation of the compound because often N≠V. Thus, for example, the octet representation of O_2 is the Lewis structure of O_2^{2-}.

The Method

*Basic Resonance Form*s.
We will first draw resonance forms trying to ensure, whenever possible, that each np element achieves its octet. We will call these the basic resonance forms. It is obvious that the octet representation will be a basic resonance form if V = N. This is the case for CF_4 because $V = (4 \times 7 + 4)/2 = 16$ and $N = 4\ \sigma + 3 \times 4\ leps = 16$.

Let's analyze the cases where N ≠ V.

N > V.

It will be necessary to remove the excess, E = N – V pairs, from the octet representation. This must be done while maintaining the octet of all np elements. To illustrate the process with the simple case of O_2, we see that its octet representation has N = 1 σ + 3x2 *leps* = 7 pairs while V = (2x6)/2 = 6. Therefore, one pair must be removed from the octet representation. If one *lep* is eliminated from each oxygen and one π pair is added, the resulting representation will have 6 pairs and both oxygen atoms have an octet of electrons. Alternatively, this resonance form also results after establishing E = N – V = 1 π bond and completing the octet of both atoms. This observation can be generalized as a rule:

> *Add to the σ skeleton E = (N – V) π pairs between 2p/2p or 2p/>2p elements in all possible ways to form double or triple bonds without expanding the octet of any atom. Then complete the octet of all np elements.*

Some special cases.

In the absence of 2p elements to form π bonds (*e. g.*, $SnCl_2$) remove E *leps* from some bridging atom in the octet representation.

If possible, avoid formation of π bonds with fluorine (*e. g.*, NSF); if not, consider also the resonance forms resulting after transforming the π pair into a *lep* on fluorine atoms, even if the octet of the donor atom is not complete (*e. g.*, BF_3).

In odd electron species, place the lone electron on any of the atoms in all possible ways, establish (E – 0.5) π pairs as above, and complete the octet of all the atoms except that with the lone electron, that will achieve only 7 electrons (*e. g.*, NO_2).

N < V.

The octet representation will have fewer electrons than those contributed by all atoms. Therefore, to obtain the resonance forms we must add V – N *leps* to the octet representation. Since all atoms of this representation have at least four pairs of electrons, the V – N added pairs will expand the octet of some element(s) which must therefore be >2p elements (*e. g.*, BrF_5). In general, a bridging atom is always the acceptor of *leps* when they must be added to *(e. g.*, BrF_5, [ICl_2]⁻) or removed from *(e.g.*, $SnCl_2$) the octet representation. The rule when N < V will be:

> *Add to the octet representation V – N leps on bridging >2p elements in all possible ways.*

Extra Resonance Forms.

New resonance forms (called 'extra resonance forms') can be created from the basic ones by converting *leps* into π pairs. The new forms will have at least one atom with more than an octet as a consequence of such conversion. Therefore, the acceptor must be a >2p element, because it will need to expand its octet, and the donor atom must be a 2p element, because this is a requirement for the formation of a π bond (see limitation 3 above). This electron shift will result in the adding of one positive charge to the donor and one negative charge to the acceptor. Such a shift of electrons will be favoured (*i. e.*, the resulting resonance form will be more important) if in the basic resonance form the acceptor has formal positive charge and/or the donor a negative charge (SO_2 offers a very good example of this). The rule for drawing extra resonance forms will be:

> *From any basic resonance form, transform* leps *into π pairs in all possible ways to give double or triple bonds. The donor must be a 2p element and the acceptor a >2p element. This transfer of electrons should tend to annul, if possible, the formal charges of all atoms. If not, it should lead to place the negative formal charges into the most electronegative elements and the positive charges into the less electronegative ones.*

Final Remarks.

The reader must be aware that the valence bond model (**VBM**) is too simple to expect from it a description of the electronic structure of molecules as good as that of the molecular orbital model (**MOM**). In spite of this, from a pedagogical point of view, the utility of the VBM is superior to that of the MOM. It should be noted that if one is to describe qualitatively (*i.e.,* without using a computer) some simple molecules by means of the MOM, the knowledge of the best resonance form(s) is necessary, though the resonance forms of some molecules do not describe accurately their electronic structure. Thus, using our method we can only write one resonance form for F_3NO [V = (5 + 6 +3x7)/2 = 16, N = 4 σ + 3 x 4 *leps* = 16] in which the N–O and the three N–F bonds are single bonds because (N = V), while the N–O bond length (1.158 Å) suggests a N=O bond. To solve this problem it has been proposed that three ionic resonance forms [$F_2N=O$]⁺ F⁻ should also be considered.

For extensive illustrations with examples, including those mentioned here, and the complete set of references, the reader is invited to consult the full paper at URL:
http://www.rsc.org/uchemed/papers/2003/vicenteful l03.htm.

Letter

The Mythical Dependence of Boiling Points on Molecular Mass

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The myth that molecular mass, as such, greatly affects boiling points, persists and even seems to gather strength. This conventional 'wisdom' was disposed of long ago[1] but keeps popping up all over, as will be shown below, albeit for brevity, with a narrow set of examples.

Some writers note that gravity is not crucial, but they still allege the importance of mass itself. Others however, even in some secondary physics textbooks, have actually stated that gravity makes the difference.

Is boiling like escaping from gravity?
Laing examined the boiling points of small molecules versus molecular mass.[2] However, a molecule escaping from a liquid is not closely analogous, as claimed, to 'a satellite breaking free from the earth's gravitational field' with the requirement of 'a minimum escape velocity', such that the required kinetic energy is proportional to the mass of the satellite at that escape velocity.

The difference is that all the mass of the satellite is acted upon by the restraining force (or curved space-time) of gravity, while the mass of the boiling molecule is practically irrelevant to the crucial van-der-Waals, London, or mutual-polarization forces in the liquid. Thus germanium tetrachloride, hexafluorobenzene, pentacarbonylruthenium, and tetrapropyltin do not boil appreciably higher than carbon tetrachloride, benzene, pentacarbonyliron, or tetrapropylmethane, respectively, where, in most cases, the additional potentially polarizing and polarizable electrons, not to mention additional nucleons, of the heavier molecules are buried in the center.

Much more information is available elsewhere[3] and in references therein. The unknown boiling points of a great variety of substances are also predicted there.

What does H_2 prove?
In the paper 'A Thermodynamic Analysis to Explain the Boiling-Point Isotope Effect for Molecular Hydrogen'[4] the title is just right, but we need to point out clearly, and perhaps often, that the mass effect, which is mentioned repeatedly and properly throughout the article is very small in the rest of chemistry. Too many otherwise well-prepared chemists still teach and write about a supposed general dependence of boiling point on molecular 'weight' or mass, and some readers may take this article as supporting that.

Even for molecular hydrogen, the difference in boiling points between 20.4 K for H_2 and 23.5 K for D_2, although important at these low temperatures, is perhaps not striking for a mass ratio of 1 to 2.

Does mass directly affect melting points?
For the related variable of melting point, the molecular mass as such is cited currently[5] and repeatedly as a relevant independent variable. This is misleading for melting points too, although the importance of symmetry is well elucidated in that paper.

Let's give students the useful and interesting information in both of these articles[4, 5], together with a perspective[3] that incidentally exposes the uniqueness of molecular hydrogen with regard to the importance of mass.

How decisive is molecular surface area?
Mebane et al. correlate the physical properties of organic molecules with computed molecular surface areas.[6] This should recall the earlier general (not just for organics) correlation of boiling points with the ¾ power of the polarizabilities of the outer atoms.[3] Polarizability, as noted there, is closely related to volume, and of course surface area is proportional to the ⅔ power of volume for any given shape.

The ¾ and ⅔ powers differ only slightly, but the former, applied to polarizability (as London theory suggests and as Mebane et al. mention in passing) rather than to volume itself, covers all types of volatile molecules having low polarity, and over a wider range of boiling temperatures, although it has not yet been used for a great variety of physical properties. Students and teachers may wish to be alerted to this related but different work.[3]

Another point is that entirely different functions had to be chosen to correlate boiling points for different classes of substance, i.e. a logarithmic one for the alkanes, and a second-order polynomial for the alcohols.[6] At least with these related (organic) molecules, we might have expected a single type of function to work if it were potentially more fundamental than empirical.

Conclusion
Students are found to be well able to understand that molecular mass per se has a nearly always negligible influence on boiling temperatures. This result is supported both by theory and by the observations of nearly constant boiling points in various series of both organic and inorganic substances whose masses vary greatly while their polarizabilities at their molecular surfaces are nearly constant. We need to bury once and for all the contrary but false conventional wisdom,

however entrenched it may be. Polarizability is found to be much more useful for the practical prediction of unknown boiling points for all sorts of only slightly polar substances.

References
1) a) D.C. Bradley, *Nature*, 1954, **174**, 323;
   b) R.L. Rich, *Periodic Correlations*; Benjamin-Cummings, Menlo Park, CA, 1965, p 69.
2) M. Laing, *J. Chem. Ed.*, 2001, **78**, 1544.
3) a) R.L. Rich, *J. Chem. Ed.*, 1995, **72**, 9;
   b) R.L. Rich, *Bull. Chem. Soc. Japan*, 1993, **66**, 1065.
4) D.B. Baker and B.K. Christmas, *J. Chem. Ed.*, 2000, **77**, 732.
5) R.J.C. Brown and R.F.C. Brown, *J. Chem. Ed.*, 2000, **77**, 724.
6) R.C. Mebane, S.A. Schanley, T.R. Rybolt and C.D. Bruce, *J. Chem. Ed.*, 1999, **76**, 688.