NUMERICAL VALUES OF UNITS AND QUANTITIES IN UNDERSTANDING BASIC CHEMICAL PRINCIPLES

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Abstract

A proposal is made to conduct discussions and carry out simple mathematical tasks in the chemistry laboratory targeting the understanding of the magnitude of various constants and/or quantities which are described and frequently used by first year undergraduate students. Examples are presented about the numeric and/or descriptive procedures utilized to clarify the meaning of expressions and the actual "size" of quantities which are involved in a number of chemical laboratory applications, within the framework of an introductory general chemistry class.

Keywords: *Chemical principles, university students, magnitudes, values of observables*

1. INTRODUCTION

As a follow up to our recent studies concerning the initial formulation and the consecutive retention of chemistry-related misconceptions in the Greek secondary education (Katsikis et al 2015, Vandoulaki et al 2016), we went on to the investigation of the extent to which such ideas are preserved at the higher level of education (Katsikis et al 2017, Kontopoulou et al 2017. We focused our interest on the period just after the initial semester of undergraduate studies which includes both classroom lecturing and laboratory practice on specific topics related to the content of the introductory General Chemistry course. In recent decades, we have established contact with a number of first-year students who are required to study Chemistry to varying degrees, depending on their course objectives and the relative education they receive in the General Chemistry class taught during their first semester of study. Biology, Geology, Pharmacy and occasionally Physics departments incorporate such an introductory course to their curriculum.

It is well documented that students, even at an early age, have acquired some understanding of their environment in a way mainly dictated by their cultural and socio-economic background and try to interpret all their observations within their individually constructed system of arbitrary laws and undefined relationships. Since this procedure is initiated at an early age, when the young students are introduced to science within the secondary education science curriculum, they generally attempt to modify novel aspects they come across to in order to avoid contradiction with their previous ideas and perceptions rather than the opposite. Additionally, it is well documented that the task of conceptual change, whenever it is attempted by the teacher, is never going to be easy, since such preconceptions are safely integrated into the cognitive structure at a relatively young age (Driver & Easley 1978, Gunstone et al 1981). Intense and elaborate teaching at the level of primary and secondary education, which depends partly on the teacher's personality and the receptiveness of the young student and partly on the available textbooks and on the construction of the science educational program, can help towards drifting the early "alternative ideas" into a group consisting mainly of scientifically accepted ideas and secondarily of persistent "preconceptions". These preconceptions become much more difficult to be dealt with at a later age, since it has been argued and to a great extent proved that, in many cases, the length in time and the intensity of teaching a particular subject do not provoke substantial advances (Bodner 1991, Horton 2007).

Furthermore, it has been emphasized that in the absence of specifically and strategically designed curricular models, laudable curriculum goals as they may be formulated by the teacher may not be

sufficient to ensure the intended teaching and learning (Taber 2008). Designed curricular models are generally absent from the Greek education system probably due to the inability of compromising the various ideas and tendencies present within the committees assigned the task of providing them. Besides that, to our knowledge, a detailed and in depth evaluation of the existing model before trying to amend it is not a process normally considered or attempted. In several cases it has been confirmed that the introductory lectures on a specific topic at senior high school are forced to deal with discussion of facts which ought to have been taught (and therefore expected to be mastered by the students) during the three-year span of junior high school. Something analogous occurs in the introductory courses of higher education with respect to knowledge that ought to have been assimilated at senior high school. Typical misconceptions occurring at early high school grades are therefore "transferred" through to the last grade of senior high school and from then on to the undergraduate courses.

A substantial number of students in their last high school grade and consequently of their first-year undergraduate studies have been identified as having difficulty in dealing with some simple mathematical procedures, especially when they involve exponentials. Memorizing is a widespread process in many cases and it is called upon as a means to overcome difficulties arising from the lack of or neglect for critical thinking, however this is not free from errors. For example, many last-grade high school students and consequently first year university students remember the sequence of prefixes used to describe multiples and submultiples of units (i.e. milli-micro - nano - pico and kilo-mega – giga - tera), however a common misconception is widespread that each one of them corresponds to an order of magnitude. Therefore, a quantity two orders of magnitude larger than the unit of the quantity measured is expected to be represented as 10^6 of the unit. Along the same line of lack of understanding exponentials, the order of magnitude is mistaken for a simple multiplication procedure, therefore students informed that the full span of the electromagnetic spectrum is about 15 orders of magnitude and given the energy of the lower end photon as equal to 1 (disregarding any relevant units of energy or the equivalent) tend to believe that the higher energy end photon should possess an energy of 15 units. This represents a typical misconception related to the difficulty of integrating effectively the three distinct realms over which Chemistry expands (Johnstone 1982), in our case mathematical expressions and numbers attempting to correlate the macroscopic observation-measurement to the submicroscopic world of atoms and molecules.

In this respect, we would like to present some minor modifications to the curriculum that entail a series of minor goals and the means to achieve them in the introductory chemistry laboratory, aiming at the better understanding of the magnitude of units and quantities generally used in Chemistry. In our belief, the following process involves several sub-processes, calling for both intuitive and cognitive steps to be taken by the students, under the guidance of the lecturer or tutor, lying within the realm of "classroom flpping" although it lacks some of its typical characteristics (Mazur 2009). However, the inevitable group discussions carried out and the research and calculations required, which are well within the students' abilities (Stefanova 2014) help to promote assimilation of the target knowledge to a better degree (Yip 2004).

1.1 First-year university studies involving General Chemistry

There are several undergraduate courses which require some introductory Chemistry classes, in most of the cases including a series of tutorials and light to medium difficulty laboratory experiments. A typical curriculum consists of several 2- or 3-hour laboratory periods, of which some are devoted to weak electrolytes and pH measurements of electrolyte solutions, while redox reactions and titration of acids and based are also included. The pre-lab introduction includes an extended reference to reactions; stoicheiometry and equilibrium in general, the equilibria related to the dissociation of weak electrolytes. Experiments are carried out for the determination of the dissociation constant, either as K_a or pK_a, of a weak acid via either the measurement of the pH of successively more diluted solutions of the acid or of a series of buffer solutions with acetic acid and sodium acetate, in the course of which the theory and equations about buffers is explained. Furthermore, redox reactions are considered and studied in relation to their spontaneous character and completing a balanced redox reaction is

practised. Finally, both acid-base neutralisation is discussed and appropriate titrations carried out, while in some instances complexometric titrations are also performed.

In most cases simplifications are applied, mainly in order to keep mathematics to a limited extent and also considering that in subsequent classes of Physical Chemistry more detailed discussion of solution phenomena will take place. However, apart from the well-established difficulties that secondary students face when dealing with algebra and its applications in Chemistry, which are transferred to their undergraduate courses, there is a general lack of understanding of the meaning of some quantities, especially when they are expressed in the form of powers.

2. DISCUSSIONS AIMING AT RESULTS

2.1 Big, bigger, vast or small, smaller, miniscule

In the theoretical part of Chemistry as well as in "real life" one crosses the roads of observables well outside the magnitude boundaries that one is used to, i.e. the milli-to-kilo scale of any unit. Although the introduction and use of powers has managed to bypass some problems in carrying out mathematical operations with such numbers, their actual magnitude is not exactly and entirely incorporated into the students' background. A common mistake in any calculation required in a chemical lab is related to poor understanding of powers and the way they transform or merely transfer into the various expressions involved. A further and deeper problem lurks in the unexplored waters of the sub consciousness where even the meaning of the power is challenged. More than once per academic year a teacher has to confront queries like "do we really need the decimals in Avogadro's number?" or "please remind me, the number related to the mole is to the plus or minus 23rd power?". Furthermore, the use of pocket calculators (cell phone applications in the most modern era) prohibits students of understanding basic principles of the way powers are expected to function, i.e. to present magnitudes of measurement. For example, it seems fairly easy to use the LOG key of any computing device in order to transform a given pH value, e.g. 4.35 to the equivalent concentration but what is the meaning of the result which is produced in the form of $10^{-4.35}$? And to what exactly does it transform into? It really takes some effort to let the students understand that this does not give any consistent idea about the concentration of the solution, while its transformation to $4.47x10^{-5}$ does because it may readily be recognized as a typical real number (i.e. a number having digits 4, 4 and 7 in the fifth, sixth and seventh decimal places respectively).

It is well-accepted that acquiring scientific knowledge is not a process involving simple transmission from teacher to student, but rather that it has to be reconstructed by the latter (Taber 2000), through proper genuine activity that will initiate the mechanism for true chemical thinking (Izquierdo-Aymerich 2012). In this respect, exercise is the most productive method of acquiring knowledge that can also be used as a diagnostic tool for misconceptions or misinterpretations on behalf of the students. We have, therefore, introduced our first-year students attending the General Chemistry class a simple task of evaluating, whilst at home, a few numerical values and compare them following a minor discussion in the laboratory where opinions about their individual vastness and relative ordering were expressed.

The first one is directly related to the ancient Shaman rice payment in relation to the chessboard (as presented in Pickover 2009) and may be described as follows: A Shaman revealed the secrets of chess, which is played on an 8x8 board to the Maharaja, whereupon the latter would like to express his thanks in any way described. The Shaman required one grain of rice (in some versions wheat) for the first square of the board, two for the second, four for the third and so on. It even appears to present day students a rather big but not overwhelming payment and they readily undertake the task to find the exact number of grains, having access to computer programs and especially spreadsheets to diminish the calculation time of the series described by the following formula. The initial idea of most students is, that although this sounds like a huge demand it can somehow be met by the Maharaja and the number of grains involved is large but not so large as to render payment impossible.

An observation, parallel but not directly related to the main target of our effort is that almost one third of the students believe that applying the following formula simply means to calculate the final term and not the sum of the series presented.

$$\sum_{i=1}^{64} 2^{i-1}$$

Then, a question is put forward about the time elapsed since the well-known big bang, which marks the beginning of time for our universe. After some general remarks about it and setting down for the rounding-up of the most accurately proposed period (Planck 2015 results) to 15 billion years the students are asked to calculate this period in terms of seconds. In a few cases the need of an Archangel was required in the name of Raphael who is supposed to have been assigned the task of counting the seconds of the existence of the world following its creation. The required numeric value, even taken down in years produces a feeling that it is extremely huge and expressed in seconds appears at first as innumerable. In fact, about half of the students believe it should exceed 10^{50}.

In the final query the students are reminded of the meaning of Avogadro's constant and its significance to the development of Chemistry and as a final task they are urged to compare it with the other two numbers, which initially were thought of being moderately and hugely big respectively. To the amazement of most students, the grains required to pay the Shaman surpass the age of the universe in seconds by two orders of magnitude ($1.85x10^{19}$ vs $4.73x10^{17}$) while none of them are close to the well-known value of Avogadro's constant.

The above discussion and task operation takes place during the preparation of solutions for the typical pH measurements of various weak electrolytes and/or buffer solutions. The next laboratory experiment is concerned with the standard titration method of a base by an acid and it offers an excellent opportunity to move to the realm of the miniscule entities to which Avogadro's constant is related. The task now has to do with the determination of how many hydronium ions have been introduced to the final solution upon the assumption that only a drop of the 0.1 M solution of HCl used was added in excess after complete neutralization was achieved. At this point the scientific thinking of the students has to be sharpened (Izquierdo-Aymerich 2012, Wollman 2014) by taking the action of determining the volume of a single solution drop. After an initial discussion about how it can be done and the reasonable conclusion that a number of drops must be measured instead, a group of students is urged to actually do this measurement in order to have a reasonable and reliable mean value. Then, based on the knowledge of the previously described magnitudes the estimation is made which gives an enormous amount of "loose" protons therefore both unravelling the hypothetical nature of producing a completely neutralised solution and the false argument that "it was just a mere drop in excess". In our laboratory experience an average of 15 drops per mL has been reached which transforms to $4.02x10^{18}$ additional H_3O^+ present in the solution discussed, a value again far beyond any initial expectation.

The aftermath for the students is that one may not jump to early statements about who big or small a numeric value is prior to working it out and that science is not the right place to practice intuition to. Interestingly enough, when a group of final year undergraduate as well as some post graduate students were subjected to the above query, their response was practically identical. Therefore, about 72% predict the lifespan of universe to be huge and at any rate larger than the other numerical values considered and the rice seeds would not exceed a value of about 10^{10} at the most. Interestingly enough, although they are aware of the meaning of molarity about 62% of them also predict that the drop of acid solution represents by far the smallest value of all the numbers considered, not exceeding 10^5.

2.2 Limit up and limit down

In the secondary education curricula and in many of the university ones, effort is placed mainly on the use rather than the derivation of mathematical formulae that are being used to represent the phenomena studied. Mainly due to the background of the teachers, teaching is focused on solving problems of ever-growing difficulty and complexity rather than understanding the basic physical and chemical laws behind the formulae, many students initiate their answers and reasoning to such problems by making a statement like "as the formula tells …" (in free translation from Greek, having

the meaning of "according to the formula…"). Our aim is to provide the students with some background as to understand first that the formula used has been derived from a series of measurements and calculations and second, that a formula simply viewed in its mathematical context may not be very useful or can even be distractive with respect to solving a problem to which it is applied.

The pH value as a property of electrolyte solutions is amongst the key topics covered by the secondary education teaching program and is thought of as being fully understood by students. The scale, when required, is reported as being "from 0 to 14" with the expected simplification that "when referring to relatively dilute solutions" generally omitted. When this assumption is pointed out to the students and they are asked to suggest a range appropriate for any solution it is often infinity that turns out to be the limit of the scale. Disregarding any reference to Bjerrum theory (Bjerrum 1926, Fuoss et al 1935) about ion pairing in condensed solutions and the use of activity coefficients, which is a topic discussed mainly in Physical Chemistry courses, the discussion follows a request about the probability of purchasing at a low cost, pH-metric paper advertised to work in the region -5 to 20. Upon expression of inquiries how to make appropriate estimates, limits are given (or sought out) for the maximum concentration of a strong acid and a strong base solution that can be obtained. Collecting data about NaOH and HCl solutions and their concentrations, the conclusion is reached that a scale of -1 to 16 expresses, at the most, the probable concentrations of acids and bases to be considered.

Electrolyte solutions and especially their pH values and consequently the pH scale form the basis for a few more points about limits that can be and have been considered. Using indicators is a widespread idea of carrying out titrations or other determinations and understanding indicator behavior is therefore of key importance. Students tend to memorise in general that given the pK value of an indicator, it can easily be used to indicate the pH value in its environment in a region of pK±1 units. The point is an excellent chance to discuss the difference between the mathematical perception of a formula and its "imaging" and understanding within the field of Chemistry. The following end-formula, which is being taught at high-school, mathematically presents a case of infinite solutions since one may substitute any real number for the listed concentrations.

$$\mathrm{pH} = \mathrm{pK_a} + \log\frac{\left[A^-\right]}{\left[HA\right]}$$

However, as the previous short discussion may have proved there is a physical limit to the concentration of any compound and furthermore, this point color detection limits as set by human physiology are also included in the data to be considered. It is therefore almost readily accepted and understood why the ratio in the above equation cannot have a meaning if one of the concentrations is dominating the other by two orders of magnitude, limiting the possible solutions to the range between 10 and 0.1. A step further can be taken after considering the Henderson-Hasselbalch equation (Henderson 1908, Hasselbalch, 1917) which is in fact a transcript of the above to the case of a buffer solution. As described in the previous section (and within the curriculum in the preceding laboratory working period) the upper limit for the molar concentration of aqueous solutions has been set as well as the one that is meaningful for the writing and working with the familiar expressions of weak electrolyte dissociation. At this point, the students are firstly asked about the expected pH value of a buffer produced by mixing equimolar amounts of acid and salt and almost promptly respond with the right answer. When they are presented with the dilemma whether a solution bearing 1 M or 0.01 M of each of the two constituents would perform better as buffer, they also promptly give the right answer therefore verifying that they have understood the basic trick for the behavior of buffer solutions and also understand the meaning and the truth of the statement that given a weak acid with a specific pK_a value, one can prepare using it buffers with pH values in the range $pK_a \pm 2$.

Directly related to the above discussion is the inquiry about how to prepare the 0.01 M solutions given their 1 M counterparts, which is rather straightforward since it has been dealt with at school. Since in most cases the idea prevails to perform successive 1:10 dilutions rather than one over several orders of magnitude then the problem is put forward as of which could be molar concentration of the least

possible concentrated solution when prepared by standard laboratory methods, i.e. using the available balances and volumetric flasks, none of which is larger than 1 L. This appears to pose a quite different problem than the above and it is therefore deduced that the true meaning of Avogadro's constant has escaped the notice and understanding of the students. Even when they are given the hint that the least concentrated solution in the laboratory could contain a single molecule per 1 liter of solution, they cannot relate the concentration discussed to the inverse of Avogadro's constant ($1/N = 1.66x10^{-24}$ M).

2.3 Oversimplification side-effects

Simplification is a technique used frequently by teachers in order to facilitate more readily understanding of topics they address. However this procedure too, is not free from flaws, some indicative examples being presented right now. First of all, it appears that although the students know about the temperature scales and especially Celsius used in everyday life and Kelvin used frequently in science, they often forget the meaning and use of the 273 displacement factor. Therefore, when asked about how to slow down a reaction they normally think about lowering the temperature but cannot understand that there is a lower limit to the value of the actual temperature applied and they have to be reminded.

In some cases the actual "phrasing" of a law or mathematical expression provides basis for misunderstandings, a serious example being the definition of pH which is described as the "negative of the logarithm…" provoking students to believe that there exist logarithms for negative numbers. Reformulation of the phrasing as "opposite of the logarithm…" or "logarithm of the reciprocal …" might be more helpful in this sense.

Furthermore, some simplifications in the course of experiments give rise to misunderstandings. A common one relates to the heterogeneous equilibrium where traditionally two solutions of salts are mixed producing a sparingly insoluble product which promptly precipitates. Students are usually asked to calculate the K_{sp} value of the product given the amount of the solid after filtration and the concentrations of the two initial solutions used. However, the two solutions (in our case lead acetate and ammonium sulfate) are provided as equal in molarity making calculations more simple to be carried out and since the example used has, as in our specific case the form of [A][B], it gives the impression that the concentrations of the two entities, A and B have to be equal. We recognized this misconception when during the extension of the K_{sp} topic we required answer to the question whether a soluble compound can be precipitated under specific conditions. Most of the answers were negative, adopting the simplistic approach that a compound is either soluble or insoluble, besides the prior demonstration that there exists a certain degree of dilution of the initial solutions, upon which the expected precipitate after their mixing does not appear. In order to demonstrate the new aspect we used the typical example of addition of concentrated hydrochloric acid to a saturated NaCl solution whereupon, much to the amazement of the students white solid NaCl precipitated. The main conceptual obstacle to overcome was exactly the aforementioned one, i.e. that as the acid is added the concentration of $[Na^+]$ is expected to become less and that of $[Cl^-]$ more than the ones in the initial saturated NaCl solution were they were expected to be equal. Therefore a slightly modified approach to the $PbSO_4$ case presented in the traditional experiment has been adopted, where various solutions of $Pb(OAc)_2$ and $(NH_4)_2SO_4$ are provided and the students, formed in groups are given the solubility product of as $1.6x10^{-8}$ and asked to work out the probability of precipitating the compound by mixing equal amounts of any couple of reactants.

3. CONCLUSIONS

Are there any, or can there be any? We are currently looking forward to it and we are in the process of carrying out a survey which will include third and fourth year students who will be required to answer some simple questions or perform some calculations analogous to the ones described here. Since in the meantime they will have followed several other courses, especially in Analytical and Physical Chemistry we will require statement about which of these courses gave them the means to work out their answers in order to investigate the significance of teaching such aspects within the introductory General Chemistry course.

Whatever the result of this future study maybe, we believe that the set of examples given above form an optimistic step towards promoting active critical thinking among the students taking a general chemistry class, because it incorporates questioning and reasoning, recognising and when appropriate reorganising initial assumptions, seek, evaluate and present numeric data and finally drawing conclusions (Pergiovanni, 2014) about the magnitude of units and quantities and therefore better understanding their meaning and possibly unravelling their mathematical notation.

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