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ORIGINAL ARTICLE

Proportional reasoning in the learning of chemistry: levels of complexity

Ajay Ramful · Fawzia Bibi Narod

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Abstract This interdisciplinary study sketches the ways in which proportional reasoning is involved in the solution of chemistry problems, more specifically, problems involving quantities in chemical reactions (commonly referred to as stoichiometry problems). By building on the expertise of both mathematics and chemistry education research, the present paper shows how the theoretical constructs in proportional reasoning in mathematics education offer rich explanatory accounts of the complexities involved in solving stoichiometry problems. Using Vergnaud's concept of measure spaces, the theoretical analysis shows that proportionality situations are relatively more intricate, involving various layers of complexity in chemistry as compared to those in the mathematics curriculum. Knowledge of proportionality and chemistry are simultaneously required to provide solutions to chemical reactions. Our analysis of a range of stoichiometry situations led us to propose a problem analysis framework involving five levels of difficulty. Further, the specificity of proportionality in stoichiometry is that it can only be established when quantities are interpreted in the unit “mole,” a unit which does not have any physical embodiment in terms of a measure of quantity unlike mass and volume. Our analysis of student-teachers' solution to the stoichiometry problems, shows that they tend to incorrectly (probably intuitively) set proportional relationships when two quantities in a reaction are expressed in non-molar quantities such as mass. The data also bring to the fore the primarily formulaic approach that student-teachers use in setting inherent proportionality relationships. An important finding is the interpretation of a chemical equation as a mathematical equation, rather than a statement of proportionality.

Keywords Proportional reasoning · Transfer · Vergnaud · Stoichiometry · Mole

A. Ramful (✉) · F. B. Narod
Mauritius Institute of Education, Reduit, Mauritius
e-mail: a.ramful@mieonline.org

A. Ramful
Research Institute for Professional Practice Learning and Education, Charles Sturt University, Waga Waga, Australia

Introduction

It is generally acknowledged that chemistry students encounter difficulties when dealing with mathematics in a chemistry context, and according to Hoban (2011), possible reasons include students' lack of sufficient mathematical knowledge, students' inability to apply and interpret relevant mathematical knowledge, or to transfer mathematical knowledge to chemistry. Further, mathematics and chemistry educators tend to work separately, focusing on their respective subject areas. While the mathematics education literature abounds with findings in terms of number sense, proportional reasoning, measurement sense, and algebraic reasoning (National Research Council, 2001), the implications of such findings in other subject areas such as in chemistry tend to be outside the focus of educational researchers. Similarly, the literature in the teaching and learning of chemistry has highlighted a number of mathematically related issues (Hoban, 2011) and the relevance of these findings has not always been considered from a mathematics education point of view. Nevertheless, both chemistry education and mathematics education, as fields of study, have developed a range of theoretical constructs, which can be productive in understanding the fine-grained sense that students make of chemistry concepts. Looking at the interface between mathematics and chemistry can be mutually beneficial in terms of pedagogy to both mathematics and chemistry educators. Such collaborative endeavor is expected to open new doors of opportunities to adjust instructional strategies for the teaching of chemistry as far as the transfer of mathematical knowledge is concerned. Looking at mathematical knowledge in the context of learning chemistry is both theoretically relevant and practically important at the level of the classrooms. While there has been a number of attempts to tease out the mathematical knowledge used in the learning of Physics (diSessa, 1993), it was deemed fitting to try such an endeavor regarding the use of proportional reasoning in chemistry. This type of analysis is specifically important as proportional reasoning is known to be cognitively demanding (Litwiller & Bright, 2002). Thus, the first objective of this study was to identify the type of proportionality situations in stoichiometry, a branch of chemistry that deals with the relative quantities of reactants and products in chemical reactions. We analyze proportionality situations in terms of their levels of complexity, using theoretical constructs from the field of mathematics education. The second objective of the study was to identify the approaches used by student-teachers in solving proportional problems in stoichiometry as well as the hurdles that they encounter.

The present paper is thus organized as follows. The first part surveys the literature in the field of mathematics education to identify the critical variables known to influence proportional reasoning. The second part outlines the findings from the chemistry education literature in relation to stoichiometry and the related mole concept. Further, because the paper is meant for both mathematics and chemistry educators, we explicitly provide definitions of key terms or concepts. The conceptual framework is then outlined to describe the tools used in the analysis. In the succeeding section, the theoretical analysis is presented based on an extensive set of problems from common chemistry textbooks and papers from the Cambridge International Examinations board. Finally, the discussions and conclusions are presented.

Proportional reasoning in mathematics education

A large body of research has been directed towards students' understanding of proportion (Tourniaire & Pulos, 1985; Harel et al., 1991; Behr et al., 1992; Lamon, 2007) and different theories (Vergnaud, 1983; Lamon, 1994; Kaput & West, 1994) have been put forward in the domain of mathematics education to explain the development of proportional reasoning and the nature of difficulties that students encounter. As succinctly highlighted by Lamon (2007):

> Proportional reasoning means supplying reasons in support of claims made about the structural relationships among four quantities (say a, b, c, d) in a context simultaneously involving covariance of quantities and invariance of ratios or products; this would consist of the ability to discern a multiplicative relationship between two quantities as well as the ability to extend the same relationship to the other pair of quantities (p. 637).

In general, proportional situations are categorized as missing value and comparison problems. In missing value problems, three of the four values in the proportion $a/b = c/d$ are known and the objective is to find the fourth missing value. In a comparison problem, four values are given (a, b, c, and d) and the objective is to determine the order relation between the ratios a/b and c/d, that is," Is a/b (<, =, >) than c/d?"

Proportional reasoning has been shown to be influenced by variables such as the physical context of the problem situation (e.g., mixture or non-mixture problems), the type of multiplicative relations that exist among the problem parameters, the numerical aspect of the problem parameters, type of ratios, as well as the order of missing value (Harel et al., 1991; Kaput & West, 1994). For instance, mixture problems have been shown to be more demanding than other proportion problems (Tourniaire & Pulos, 1985). Divisibility relationships, integral ratios, and unit rates usually facilitate symbolic solutions of proportions (Lamon, 1993). In general, proportional problems involving integer quantities are more accessible to students than those involving decimals or fractions. At this point, it needs to be highlighted that four methods are commonly used in solving proportional problems, namely the unit-rate method, factor-of-change method, fraction strategy, and cross-product strategy (Cramer & Post, 1993).

While previous studies such as Heller et al. (1989) highlight the importance of proportional reasoning in chemistry, they do not show explicitly how this form of reasoning occurs practically in actual problems in chemistry. Further, research in chemistry education has focused more on the mole (a particular unit as described in the next section) rather than the ways in which proportional relationships are articulated from a mathematical perspective. On the other hand, the accumulated understanding of proportional reasoning in mathematics education, as summarized in the foregoing section, provides us with a rich knowledge base to interpret proportionality in chemistry. In what way is proportionality involved in the solution of stoichiometry problems? This is the first research question that motivated the present study. The second research question emerged as an ancillary question in the process of answering the first one. We attempted to identify the strategies that student-teachers use and the difficulties that they encounter in articulating proportionality relationships in stoichiometry problems.

At the secondary school level, when stoichiometry is generally introduced, students (about 14 years old) studying chemistry are required to solve proportional situations in chemical reactions. As an illustrative example, consider the following chemical reaction: Methane (CH_4) reacts with steam (H_2O) to form hydrogen (H_2) and carbon monoxide (CO) according to the following equation: $CH_4 + H_2O \rightarrow CO + 3H_2$. This equation shows that 1 mol of methane reacts with 1 mol of steam to produce 1 mol of carbon monoxide and 3 mol of hydrogen. As will be explained later, the unit mole is a particular unit of measurement commonly used in chemistry. A typical stoichiometry problem may require the determination of the volume of hydrogen produced from say 100 cm^3 of methane.

More generally, stoichiometry problems involve essentially two reactants (say R_1 and R_2) and one or two products (say P_1 and P_2). However, the quantitative calculations often involve only two quantities at a time, e.g., the two reactants R_1 and R_2 or one reactant and one product say R_1 and P_1. Consider a chemical reaction involving two reactants and two products according to the following equation:

$$k_1R_1 + k_2R_2 \rightarrow k_3P_1 + k_4P_2, \quad (1)$$

where k_1, k_2, k_3, and k_4 are integer constants to balance the chemical equation. Two of the constants k_i, i=1, 2, 3, and 4 are used to generate a ratio and to construct an equivalent ratio (i.e., a proportion). Different types of proportionality situations can be generated depending on the type of quantities in which the reactants and products are specified, the type of relationship given as well as the physical states (solid, liquid, or gas) of the reactants and products. Quantities may be specified in terms of mole, volume, mass, percentage, concentration, or a combination thereof to formulate problem situations in stoichiometric calculations.

Stoichiometry problems may also be formulated in such a way that instead of specifying the measure of the individual quantities or reactants and products explicitly in terms of standard measures, parameters are given in terms of relationships between two reactants or between a reactant and a product expressed as ratio, proportion, or percentage (e.g., when iron is heated in a stream of dry chlorine, it produces a chloride that contains 34.5 % by mass of iron). It should also be noted that some chemistry educators advocate the use of dimensional analysis (DeLorenzo, 1994) to solve stoichiometry problems rather than proportional reasoning.

Transfer of mathematical knowledge to chemistry: the challenge

In this section, we give an overview of some conceptual aspects of chemistry to provide the necessary background for the later interpretation of proportional reasoning in the paper. Conceptual understanding in chemistry requires students to operate on three different levels of thought (Johnstone, 2000), namely, the macroscopic and tangible level (involving solids, liquids, metals, non-metals, acids, bases, fuels, etc.), the microscopic (involving molecules, atoms, and electrons) and the symbolic (involving symbols, formula, equations, measurement, mathematical manipulation, and graphs). The schema in Fig. 1 specifically exemplifies this triad (i.e., macroscopic, microscopic, and symbolic) for stoichiometry as this is the main object of the current study. It is at the symbolic stage that mathematical reasoning (or more specifically, proportional reasoning in chemical reactions) is required. According to Johnstone (2000), one of the challenges of learning chemistry relates to working with all three different levels simultaneously since humans have very limited working memory. It is also reported (Desjardins, 2008) that the use of mathematics in chemistry can create pedagogical difficulties as many fundamental chemistry concepts are expressed in mathematical terms. DeMeo (2008) not only claims that almost all chemistry courses include

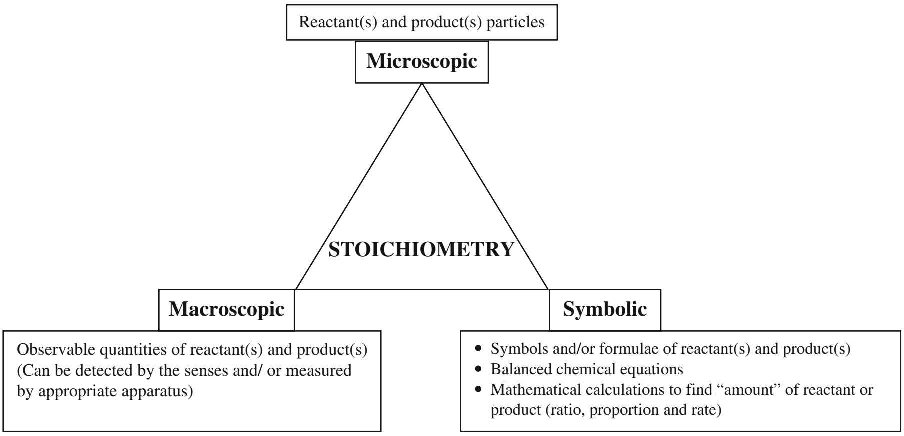

Fig. 1 Stoichiometry interpreted in the interplay of three levels of representations

concepts that necessitate mathematical solutions but he also acknowledges that mathematical problems represent a challenge to chemistry teaching.

The mole as a measuring unit

The mole (Krishnan & Howe, 1994; Gorin, 1994) is an indisputably important unit in chemistry. It allows chemists to comfortably work with the amount of substances reacting and of those being produced at the microscopic level by making use of macroscopically observable quantities like mass and volume in the International System of Units. This unit measures the relative number of particles present in a substance. Figure 2 illustrates the relationship between the number of moles of a substance (reactant or product), its number of microscopic particles, and its macroscopic quantities (volume, mass, and concentration).

The stp and rtp refer to "standard temperature and pressure" and "room temperature and pressure." These differential physical conditions determine the volume of 1 mol of a gas. Thus, 1 mol of a gas occupies 22,400 cm^3 at stp and 24,000 cm^3 at rtp.

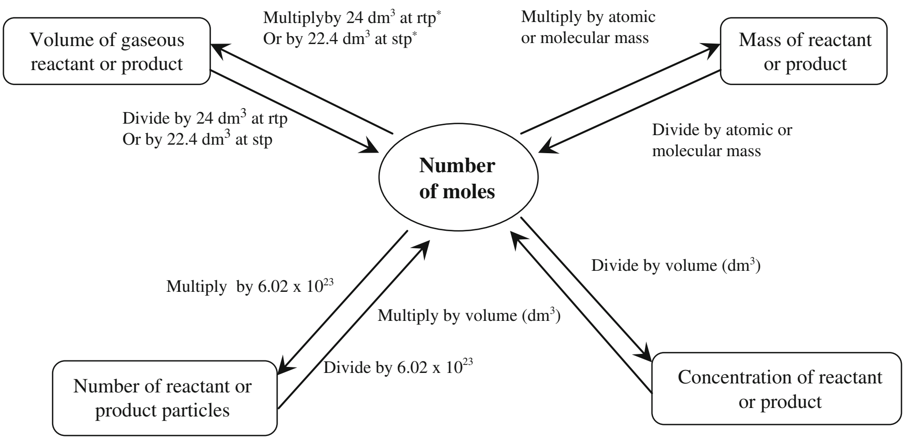

Fig. 2 Mathematical relationship among volume, mass, concentration, number of particles, and mole

The "mole" has been reported to be a challenging concept for students, mainly because of its abstract nature (Furio et al. 2002; Gorin, 1994). The mole, as a measure of the amount of substance, does not have a physical representation unlike quantities such as mass and volume. The survey of literature conducted by Furio et al. (2002) on students' understanding of the mole concept shows that students tend to confuse the unit mole with number of particles and mass in grams.

Another concept from the mathematics education literature related to the current discussion is the notion of intensive and extensive quantities as clarified by Singer et al. (1997):

> Extensives quantify *how much* of a substance or *how many* of a class of objects are present. Extensive quantities behave additively; that is, they can be combined and partitioned in ways that match the combination and partitioning of amounts of physical material in the world … Intensives, by contrast, are relational quantities that describe how two different extensives are related to one another. Rates, such as 5 apples per box, $3 per hour, or 30 miles per gallon, are all intensive quantities. So too are rates that do not specify a base unit of 1, such as 5 apples for every 3 dollars or 5 pencils for 2 dollars. Intensives do not behave additively. (p. 116).

In stoichiometry, reactants and products are either measured in terms of mass and volume which are extensive quantities, while concentration (e.g., mole per cubic decimetre or gram per cubic decimetre) constitutes an intensive quantity. The critical quantity mole is an intensive quantity as it the ratio of mass to atomic or molecular mass of a substance.

The mathematics education literature has empirically analyzed a range of proportional situations to understand the variables that affect proportional reasoning. Harel et al. (1991) shows that not only do the mathematical nature of a proportional situation (such as the numeric aspect of the problem) influence proportional reasoning, but also that the physical context of the problem also matters. This study attempted to understand the ways in which different types of proportional situations occur in a specific problem context, namely stoichiometry. Fundamentally, a chemical equation is a statement of proportionality, not only between the reactants but equally between the reactants and the products. This is where the gist of proportionality lies in stoichiometry. By analyzing a range of stoichiometry problems, we identify five categories of proportionality situations which require increasing levels of thinking. The contribution of this study is essentially in the insightful analysis of proportional situations in chemistry using explanatory constructs from the proportional reasoning literature in mathematics education. In this sense, our study can be regarded more as an application of proportional reasoning findings to another content domain, that is, chemistry.

Conceptual framework

Mathematical concepts exist in relation to each other and draw their meaning from a variety of situations. To analyze the complexity of the interrelatedness of concepts, Vergnaud (1988) introduced the theory of *conceptual fields*. He defines a conceptual field as "a set of situations, the mastering of which requires the mastery of several

Boxes	Pencils
1	3
4	x

Fig. 3 Representation of a multiplicative relationship in terms of proportion

concepts of different natures" (p. 141). He considers the *conceptual field of multiplicative structures* as "all situations that can be analyzed as simple and multiple proportion problems and for which one usually needs to multiply and divide" (p. 141). Vergnaud (1988) interprets a multiplicative situation in terms of a proportion. Consider the following example: "Paul has four boxes of pencils. There are three pencils in each box. How many pencils does Paul have altogether?" The parameters of the problem and proportional relationship are made explicit in terms of measure spaces in Fig. 3.

This problem can be reformulated in terms of other unknowns: Paul has 12 pencils. They are packed in boxes such that each box has three pencils. How many boxes of pencils does he have? or Paul has 12 pencils. He distributes them equally in four boxes. How many pencils are there per box? (Fig. 4)

This type of analysis in terms of the measure space diagrams makes the proportional structure of problems explicit, especially when quantities are prescribed in different units as is the case in the present study. Further, the measure space diagrams permits the analysis of their hierarchical structure and levels of complexity. As pointed out by Vergnaud (1996), the theory of conceptual fields provides "a way to identify the similarities and differences between situations, their hierarchical structure, and also the continuities and discontinuities that organize the repertoire of schemes that is progressively developed to master these situations" (p. 225).

Method

As pointed out earlier, the main objective of the present study is to conduct a theoretical analysis of the type of proportionality situations involved in stoichiometry using the constructs available from research on proportional reasoning in the field of mathematics education. The value of theoretical analyses in understanding mathematical concepts has been demonstrated by Vergnaud (1988), Behr et al. (1992), and Lamon (2007). Further, according to Nesher (1988), "the significance of any theoretical analysis is that it enables us to hypothesize the major parameters that have explanatory power for the observed phenomena" (p. 38). To meet the first objective, we consulted a range of stoichiometry problems from chemistry textbooks and past examination papers (1985–2010) in international examination boards (primarily Cambridge International

Boxes	Pencils
1	3
x	12

Boxes	Pencils
1	x
4	12

Fig. 4 Unknown quantities in a simple proportion problem

Examinations) wherever these could be accessed. We analyzed a variety of problems in terms of problem structure (focusing on proportion) and the knowledge that may be required to solve them. This led us to develop a hierarchy of proportional situations in stoichiometry, which we described in terms of levels, on the basis of the complexity required to set the proportion. In our theoretical analysis and collection of data, we have considered only the mathematical (proportional) aspect of the problems. Thus, in selecting the stoichiometry problems for analysis, we have focused only on those which require the application of proportional reasoning.

We also present a snapshot of the strategies used and difficulties encountered by four student teachers (denoted by students 1, 2, 3, and 4) in solving some of the problems presented in the hierarchy. The student-teachers were enrolled in the second year of the Teacher's Diploma program, which is meant to prepare teachers to teach chemistry up to Grade 10 at the secondary level. The problems presented in the hierarchy were presented in a worksheet and the four student-teachers were given about 45 min to complete it. We would like to highlight that they voluntarily participated in the study. Their writings in the worksheet were analyzed to identify the strategies used and difficulties encountered.

Theoretical analysis

As depicted in Figs. 1 and 2, the topic stoichiometry involves a range of concepts which are defined or quantified in terms of mathematical relations. For instance, some of the commonly used concepts in chemical reactions are relative atomic mass and relative molecular mass, percentage composition of an element in a compound, and percentage purity of a substance. These concepts are often defined on the basis of ratio, rate, or percentage and expressed in terms of decimal or fractional representations which we know from the literature in mathematics education are demanding for many students. These initial observations underline the complexity of stoichiometry situations and when proportionality is superimposed on these, the conceptual field becomes even more extensive. Added to these mathematical requirements are the subtle differences between apparently related concepts such as mass and atomic mass or molecular mass.

A hierarchy of proportional situations in stoichiometry

We started the study by collecting as many stoichiometry problems as we could from past examination papers and commonly used textbooks. We scrutinized the problems specifically focusing on the proportionality aspect. We analyzed each problem using the measure space diagram from Vergnaud's theory. The analytic process led us to identify different categories of problems based on their proportional structure. We were motivated to create this categorization to be able to show how the stoichiometry problems became more and more demanding in terms of setting the proportional relationship. In level 1 problems, the proportionality relationship between the chemicals can be set directly (as in a common missing value problem in mathematics) since the two quantities involved are stated in the unit "mole." In level 2, the quantities defining the proportion are prescribed in different units and as such require unit conversions.

However, all the units used are extensive quantities such as mass and volume. In level 3, the proportionality relation is given between intensive quantities (i.e., quantities measured in units such as mole per cubic decimetre). Level 4 situations involve more than one chemical reaction, i.e., more than one proportionality relationship. This requires the problem solver to work with a given proportion to find the amount of an intermediate quantity. The intermediate quantity is in turn used to find another quantity. The type of units used may be intensive or extensive. The most complex stoichiometry situations that we analyzed involved the determination of an element in a compound using the proportionality relationship. This constitutes level 5 problems. As we move from level 1 to 5, it necessarily implies that more steps are required to solve the problems. Table 1 shows how the complexity of the proportional situation increases from level 1 to 5 in terms of setting the proportionality relationship.

What may be the use of such a theoretical analysis and categorization of problems? We believe that such a hierarchy may be beneficial to chemistry teachers to explicitly look at the variation in proportional situations emanating from stoichiometry, a fundamental tool in the learning of chemistry. A chemistry teacher may not necessarily understand the cognitive demand of proportionality, an area which mathematics education researchers have already shown to be challenging for many students. The analysis carried out in terms of measure spaces makes the inherent proportionality in stoichiometry explicit. In exploring a particular proportional context, i.e., stoichiometry, from a domain different from the mathematics curriculum, our study contributes in analyzing a set of proportionality situations that have not been given attention by mathematics educators. The knowledge generated from our analysis adds to the database on proportional reasoning which is of interest to mathematics education researchers.

Our theoretical analysis has revealed that stoichiometry situations essentially involve missing value problems, where three parameters in the proportion are given and one has to find a fourth parameter. Such problems involve different levels of proportional reasoning, depending on the quantities used and relationships defined in the chemical equations of the reactions. Quantities may be given in intensive or extensive units as highlighted earlier. We have categorized the proportional situations in stoichiometry in terms of their assumed level of complexities. The construction of the different levels has been guided by the number of steps required to find the missing value in the proportion. This categorization is meant to portray the increasing level of cognitive load that may be required to articulate the proportional relationship. Our analysis reveals five

Table 1 Levels of complexity in stoichiometry problems in terms of proportionality

Level	Description
1	The proportional relation is used directly without the necessity for unit conversion.
2	Quantities are given in different units and require conversion to the unit mole to set proportional relationship.
3	Proportional relationship involving quantities specified in intensive units.
4	Two or more proportional relationships are given (as specified by different chemical equations). It may involve intensive quantities and unit conversions.
5	Proportional relationship between two quantities where one of the quantities is unknown or involves an unknown element. It may involve intensive quantities and unit conversions.

levels of complexity in stoichiometry problems requiring proportional reasoning as elaborated below.

Level 1 Level 1 involves the simplest type of proportional situations where the ratio between two quantities is given and one has to determine the missing value of one of the two quantities. In this level, the two quantities are stated in the same units (i.e., there is no necessity for unit conversion). Two sub-levels were defined depending on whether one or more chemical equations are involved.

Level 1a Consider Eq. (1) as defined earlier, that is, $k_1R_1+k_2R_2\rightarrow k_3P_1+k_4P_2$. In the first level, the ratio of two reactants (e.g., k_1:k_2) or one reactant and one product (e.g., k_1:k_4) is obtained from the balanced equation and one has to determine the missing value of one of the quantities.

Example 1a: Butane (C_4H_{10}) reacts with oxygen (O_2) according to the following equation:

$$2\ C_4H_{10} + 13\ O_2 \rightarrow 8\ CO_2 + 10H_2O.$$

How many moles of oxygen O_2 are required for the complete combustion of 3 mol of butane?

We can set up the measure space diagram as follows to deduce that 3 mol of butane requires $\left(\frac{13}{2}\times 3\right)$ moles of oxygen.

C_4H_{10}	O_2
2 moles	13 moles
3 moles	x

Level 1b As in Level 1a, here, the two quantities are stated in the same units. Additionally, it involves two equations such that one has to work with more than one ratio.

Example 1b: Nitrogen is formed according to the following equations:

$$2NaN_3 \rightarrow 2Na + 3N_2 \quad (1.1)$$

$$10Na + 2\ KNO_3 \rightarrow K_2O + 5Na_2O + N_2 \quad (1.2)$$

How many moles of nitrogen gas are produced from one mole of sodium azide, NaN_3?

NaN_3	N_2
2 moles	3 moles
1 mole	3/2 moles

NaN_3	Na
2 moles	2 moles
1 mole	1 mole

Na	N_2
10 moles	1 mole
1 mole	1/10 mole

Fig. 5 A situation involving more than one ratio

This situation can be analyzed in terms of measure spaces as shown in Fig. 5.

From the Eq. (1.1), 2 mol of NaN_3 produces 3 mol of N_2 and from Eq. (1.2), 10 mol of Na produce 1 mol of N_2. Thus, a total of $\left(\frac{3}{2}+\frac{1}{10}=\frac{16}{10}\right)$ moles of N_2 are produced.

Level 2 Level 2 situations involve an additional step compared to level 1 problems in that they require the conversion from one unit to the other. The quantities are stated in different units. One has to use the ratio from the balanced equation to determine the unknown quantity. The complexity of problems at level 2 can be interpreted in terms of two categories: levels 2a and 2b. In level 2a, the proportional relationship arises from only one chemical equation while in level 2b, such relationships are constructed from more than one equation.

Level 2a *Example 2a*: When zinc blende (*ZnS*) is heated in air, the reaction is represented by the following equation $2ZnS+3O_2 \rightarrow 2ZnO+2SO_2$. What volume of oxygen (in cubic centimeter) would be needed to react completely with 388 g of ZnS (at room temperature and pressure, rtp)?

ZnS	O_2
2 moles	3 moles
388 g	x cm^3

Before deploying the proportion, one has to use his/her chemistry knowledge to reason that a proportionality relationship can only be set for a chemical reaction in terms of mole ratios as per the given stoichiometric equation. In other words, proportional relationships cannot be defined directly by using quantities such as mass (in gram) or volume (in cubic centimeter). To allow for comparability, the unit "gram" has to be converted to the unit "mole" by dividing by the relative molecular mass. Here, the relative molecular mass of *ZnS* is 97.

ZnS	O_2
2 moles	3 moles
388/97 = 4 (moles)	x

Thus, 4 mol of *ZnS* will produce 6 mol of oxygen. At this point, another conversion factor is required, namely converting moles to volume by making use of the concept "molar volume." In other words, since one mole of any gas occupies a volume of 24,000 cm^3 at rtp, 6 mol of oxygen occupy $6\times24{,}000$ cm^3$=144{,}000$ cm^3.

Level 2a In level 2b, a sequence of reactions occurs and one has to transfer the ratio from one equation to the other to determine the quantity of an unknown reactant or product. An example is given below.

Example 2b: During the production of nitric acid (HNO_3), three processes take place according to the following equations:

$$4NH_3 + 5\,O_2 \rightarrow 4\,NO + 6H_2O \tag{2.1}$$

$$2NO + O_2 \rightarrow 2NO_2 \tag{2.2}$$

$$4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3 \tag{2.3}$$

Calculate the mass of nitric acid that can be obtained from 1 tonne of ammonia. The following stoichiometric ratios can be set from Eqs. (2.1), (2.2), and (2.3) to deduce that 1 mol of ammonia (NH_3) produces 1 mol of nitric acid (HNO_3).

NH_3	NO
4 moles	4 moles
1 mole	1 mole

NO	NO_2
2 moles	2 moles
1 mole	1 mole

NO_2	HNO_3
4 moles	4 moles
1 mole	1 mole

Given that 1 mol of ammonia (NH_3) and 1 mol of nitric acid (HNO_3) have relative molecular masses 17 and 63 g, respectively, the following proportional relationship can be set up to find the mass of (HNO_3) that can be obtained from one tonne, that is (1×10^6)g of NH_3.

NH_3	HNO_3
1 mole	1 mole
17 g	63 g
1000 000 g	$\frac{63 \times 1\ 000\ 000}{17}\ g$

It should be noted that in this problem, the measure of the quantities (i.e., 17, 63, and 1,000000 g) are not integer multiples of the other. Thus, additional flexibility to work with proportion is required here.

Level 3 The level of complexity of the proportional situations in stoichiometry increases when two intensive quantities are specified. It is common practice in chemistry to state the concentration of a solution in terms of the intensive unit “mole per dm^3” or “mol/dm^3”. In level 3 situations, one is required to work with proportional relationships involving quantities specified in intensive units (e.g., mole per cubic decimetre) as exemplified below.

Example 3: What volume of 0.5 mol/dm^3 hydrochloric acid (*HCl*) is required to neutralize 20.0 cm^3 of 0.4 mol/dm^3 sodium carbonate (Na_2CO_3) as per the following equation:

$$Na_2CO_3 + 2\ HCl \rightarrow 2NaCl + H_2O + CO_2 \tag{3.0}$$

Na_2CO_3	HCl
1 mole	2 moles
0.4 mol/dm^3	0.5 mol/dm^3
(20 cm^3)	(x cm^3)

First, one has to deduce that since 1000 cm^3 of Na_2CO_3 contains 0.4 mol, 20 cm^3 contains $\left(\frac{0.4\times 20}{1000}\right) = 0.008\ \ \mathrm{mol}$. Next, the ratio (1 : 2) suggests that 0.008 mol of Na_2CO_3 will react with 2×0.008=0.016 mol of HCl. At this point, one uses the concentration of HCl to find its volume. In other words, since 0.5 mol of HCl is contained in 1000 cm^3, 0.016 mol would be contained in $\left(\frac{1000\times 0.016}{0.5}\right) = 32\ \ \mathrm{cm}^3$. The complexity of this situation equally lies in the intermediate conversion from one unit of measurement to the other.

Level 4 In this category, a sequence of equations is given and one has to determine the measure of intermediate quantities (based on proportions) to find the measure of the required end (product) or starting (reactant) quantity. Further, it may involve intensive quantities and multiple intermediate unit conversions.

Example 4: The carbon monoxide in a sample of polluted air can readily be determined by passing it over solid iodine (V) oxide, I_2O_5, to give carbon dioxide and iodine according to the following equation:

$$I_2O_5 + 5\ CO \rightarrow 5CO_2 + I_2 \tag{4.1}$$

The iodine produced is removed and titrated with aqueous sodium thiosulfate as follows:

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI \tag{4.2}$$

A 1.0-dm^3 sample of air produced iodine that required 20.0 cm^3 of 0.10-mol/dm^3 sodium thiosulfate to discharge the iodine color. Calculate the mass of carbon monoxide (in gram) in this sample of polluted air.

Note: The Roman numeral “V” represents the valency of iodine in the compound, iodine (V) oxide, I_2O_5. The valency is a technical chemistry term which denotes the combining power of one atom to another. Many elements have only one valency, that is, their combining power is always same when they combine with other elements.

However, when an element can have variable valencies, then its valency needs to be specified as in the above case for iodine.

Using Eq. (4.2), the following proportion is set:

$Na_2S_2O_3$	I_2
2 moles	1 mole
0.10 mol/dm^3 (20 cm^3)	$x = \frac{1}{2} \times \frac{0.10 \times 20}{1000} = 0.001$ mole

From Eq. (4.1),

CO	I_2
5 moles	1 mole
$y = 5 \times 0.001 = 0.005$ mole	0.001 mole
$= 0.005 \times (12 + 16) = 0.14g$	

One is first required to apply proportional reasoning using the second Eq. (4.2) to find the amount of iodine (x) produced from the unknown amount of carbon monoxide. Then, one has to use the calculated amount of iodine (x=0.001 mol) and the proportional relationship given in the first Eq. (4.1) to obtain the amount of carbon monoxide in terms of the mole unit (y) present in the sample of air. Finally, the number of moles of CO is converted to mass in gram by multiplying by the molecular mass of CO (i.e., 28).

Level 5 Stoichiometry problems are often set where a particular element in a compound is not known (say X) and one has to use the given quantity of reactants or products and the balanced equation to determine it. This type of situation also involves proportional reasoning as illustrated by the following example.

Example 5: A 5.00-g sample of the metal nitrate $X(NO_3)_2$ loses 3.29 g in mass (as a result of the release of NO_2 and O_2 gases) on strong heating. The reaction occurs according to the following equation:

$$2X(NO_3)_2 \rightarrow 2XO + 4NO_2 + O_2 \tag{5.1}$$

Use the information given to calculate the atomic mass of metal X.

From Eq. (5.1), 2 mol of $X(NO_3)_2$ produce 2 mol of XO. Moreover, the mass of XO left after heating is 1.71 g (i.e., 5.00–3.29 g). Thus, 5 g of $X(NO_3)_2$ produce 1.71 g of XO. We have to convert the masses (5 and 1.71 g) of the two quantities in terms of moles by dividing by the relative molecular mass to be able to set the proportion. However, we do not know the mass of unknown quantity X. We assume the mass to be m g, where m is a number to be determined. The atomic mass of oxygen and nitrogen are 16 and 14 g, respectively. Thus, the molecular mass of $X(NO_3)_2$ is m+(14+[3×

16])×2=m+124 and that of XO is m+16. Now, we can represent the proportion in the measure space diagram as follows:

$X(NO_3)_2$	XO
2	2
$\frac{5}{m+124}$	$\frac{1.71}{m+16}$

Since the mole ratio of $X(NO_3)_2$:XO is 2:2=1:1, the following equality can be established:

$$\frac{5}{m+124}=\frac{1.71}{m+16}.$$

On solving this equation, we have m=40, i.e., the mass of the unknown quantity X is 40 g.

We acknowledge that students may use different pathways in solving the problem situations presented in each level. The rationale behind this hierarchy is to show the level of complexities in these situations from the point of view of setting the proportionality. This hierarchy is theoretical and need empirical testing.

A glimpse of proportional reasoning in stoichiometry from student-teachers' perspective: some empirical illustrations

The theoretical analysis that we made in terms of the five levels were based on our experience as teacher educators. We wanted to make a first assessment of whether the

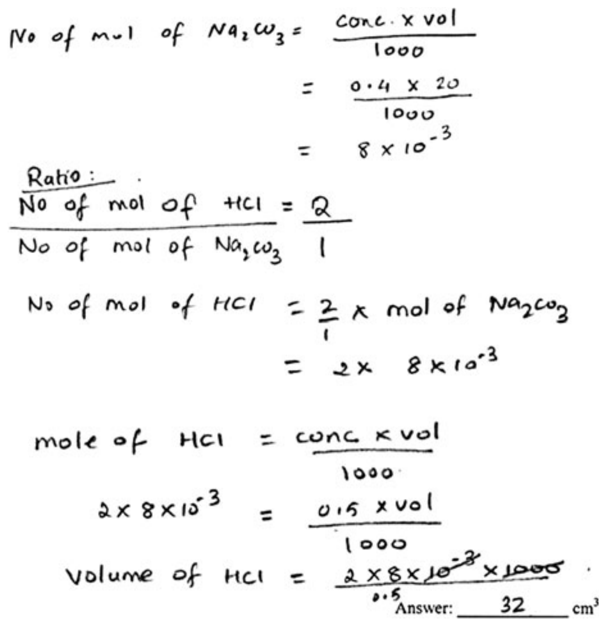

Fig. 6 Use of formula to articulate proportionality relationship in stoichiometry

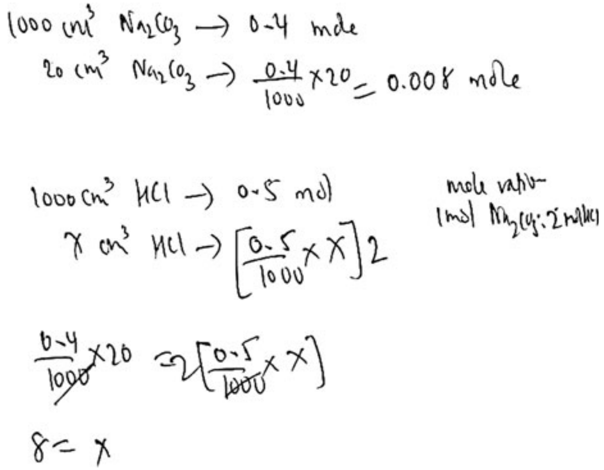

Fig. 7 Representation of the unknown quantity by a letter (*x*)

assumed increasing level of difficulty has some empirical evidence. At the time the study was conducted, there were only five pre-service teachers available in the Chemistry department and four of them agreed to work out the problems for us. We acknowledge that this is a limited sample and the inferences we made are bound to their written work only. Our small data set limit us from making generalizations in terms of patterns of solution or common students' difficulties. However, the difficulties that they encountered (detailed later) as they worked out the problems from level 1 to 5, do support the increasing level of complexity of the proposed hierarchy.

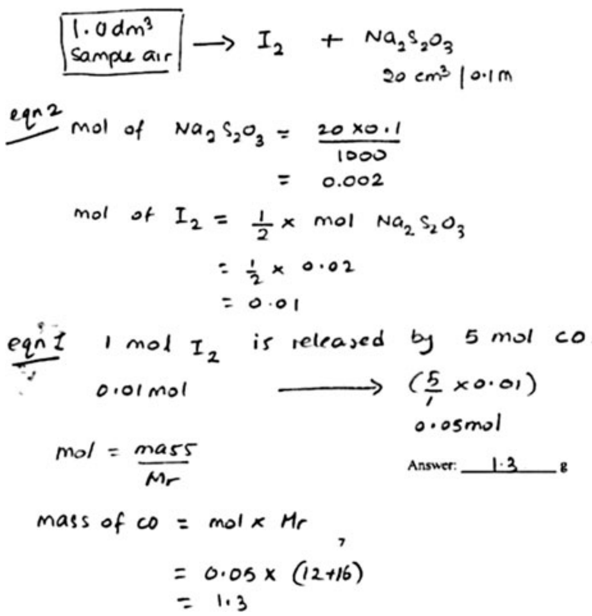

Fig. 8 Solution presented by student 2

In this section, we illustrate the strategies and difficulties that the student-teachers displayed in solving some of the illustrative problems that we used in the hierarchy that we constructed. One of the first observations from the written work of the students is that they tend to carry ready-made formula and plug in given numbers. For instance, in Fig. 6 (Example 3), to find the number of moles Na_2CO_3, the student used the formula, no.of moles $= \frac{\text{concentration} \times \text{volume}}{1000}$. The same formula can be seen when the student found the number of moles of *HCl*. In fact, our experience as teacher educators indicates that this approach tend to be favored by some teachers. To facilitate the articulation of the proportionality relationship associated with chemical reactions, teachers tend to follow a procedural approach where students can readily plug in appropriate values to determine unknown quantities. Such algorithmic approach to stoichiometry problems has been pointed out by Beall & Prescott (1994). The limitation of such an approach is that a formula remains a crutch and may not attain the status of a meaningful procedure. Our experience shows that the stereotypic application of learnt procedures may be constraining when problem formulations are altered.

Positing an unknown quantity

Another solution strategy that could be observed is the positing of a letter such as x as a place holder in the determination of the unknown quantity in the proportional relation. Such a labeling of the unknown quantity allows the setting up of the proportion to proceed algebraically, somewhat similar to the well-known cross multiplication strategy in proportion. An algebraic solution to example 3 from a student-teacher is presented in Fig. 7. The solution given by the student-teacher is flawed as will be discussed in the last part of this section.

Multiple ratios

In level 4 of the proposed strata, different ratios are involved as one has to work with different chemical reactions. We compare the solution provided by two student-teachers

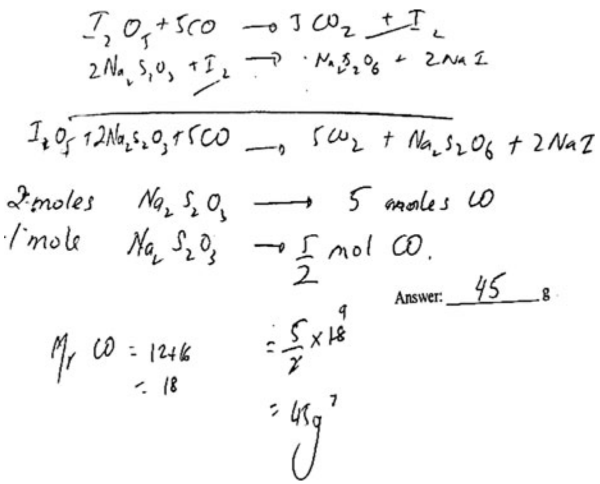

Fig. 9 Solution presented by student 3

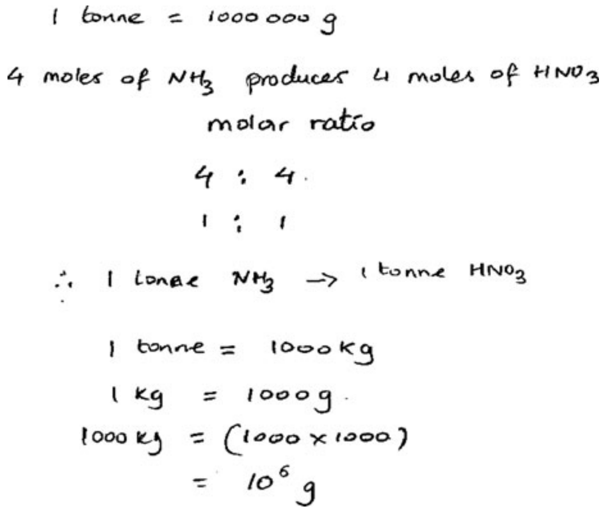

Fig. 10 Incorrect application of molar ratio to relate masses proportionally

to illustrate the different strategies they used to deal with the proportionality requirements. In the first case, in Fig. 8 (example 4), the student worked with each of the two equations separately. Using Eq. (4.2), she calculated the number of moles of iodine and then determined the number of moles of carbon monoxide from Eq. (4.1). Note that she transferred 0.002 as 0.02 in the third step of her calculation in Fig. 8. Further, the final step contains a computational mistake, that is, $0.05\times(12+16)=0.14$ rather than 1.3.

Another student-teacher (student 3) combined the two equations into a single equation such that the ratio of the concerned chemicals could be set directly as shown in Fig. 9. Such a curtailment reduces the multiple steps in the problem but it demands that one maintains the proportionality requirements. In this case, although the student could set the ratio $Na_2S_2O_3$:CO=2:5, she worked with one mole of $Na_2S_2O_3$ rather than $\left(\frac{0.1\times 20}{1000}\right)$ moles. Note that student 3 made a computational mistake in calculating the molecular mass of carbon monoxide, that is, $12+16=18$, instead of the correct value 28 (Fig. 9).

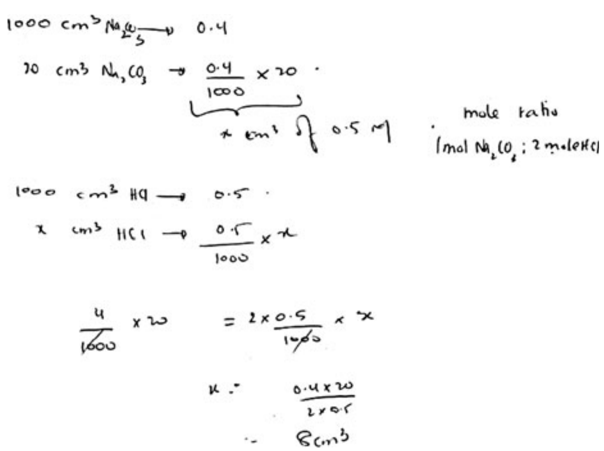

Fig. 11 Incorrect extension of molar ratio to relate quantities proportionally

A misconception: applying proportionality among reactants and products in terms of non-molar quantities

Proportionality is distinct in stoichiometry in that such type of multiplicative relationships between two quantities can only be ascertained when the molar ratio (also called stoichiometric relationship) is considered. In other words, in the equation $k_1R_1 + k_2R_2 \rightarrow k_3P_1 + k_4P_2$, the proportional relationship between R_1 and R_2 holds only in terms of moles, that is, k_1 moles of R_1 react with k_2 moles of R_2, but this does not imply that k_1x gram of R_1 react with k_2x gram of R_2. Two cases could be identified where the student-teachers incorrectly set the proportionality relationship as illustrated below.

Case 1: The solution presented in Fig. 10 to example 2b illustrate how the student-teacher incorrectly applied the proportional relationship on masses rather than molar quantities. From the molar ratio, NH_3:HNO_3=1:1, she deduced that 1 tonne of NH_3 produces 1 tonne of HNO_3.

Case 2: In example 3, a student-teacher used the molar ratio 1:2 to incorrectly infer that the volumes of the two quantities are in the ratio 1:2 (Fig. 11).

The student-teacher first calculated the number of moles of Na_2CO_3 from the given concentration (20.0 cm^3 of 0.4 mol/dm^3) as $\left(\frac{0.4\times20}{1000}\right)$. Then, she calculated the number of moles of HCl from the given concentration 0.5 mol/dm^3 as $\left(\frac{0.5\times x}{1000}\right)$, after denoting the volume of HCl used by x cubic centimeter. Using the molar ratio 1:2, she equated the two quantities as shown in Fig. 11. Here, the student-teacher translated a chemical equation into a mathematical equation: $\left(\frac{0.4\times20}{1000}\right) = 2\left(\frac{0.5\times x}{1000}\right)$. The flaw in the setting of this equation is an issue of proportionality. Admittedly, one mole of Na_2CO_3 reacts with two moles of HCl but it is erroneous to equate k_1 moles of Na_2CO_3 to $2\times k_2$ moles of HCl. Rather, k_1 moles of Na_2CO_3 with $2\times k_1$ moles of HCl. Note that a similar observation can be made in Fig. 7. The equality set by the student-teacher leads us to realize the necessity to highlight the difference between a chemical equation (equation representing the proportionality in a chemical reaction) and a mathematical equation. A chemical equation can only be interpreted in terms of molar ratio while a mathematical equation represents equality. The term "equation" in the conventionally used jargon "chemical equation" is a misnomer. It is justifiable why an arrow is used rather than an "equal to" sign in a chemical reaction. By setting the equality between the two reactants, the student-teacher interpreted the chemical equation as a mathematical equation. Such an interpretation does not respect the proportionality requirement.

Although we do not have verbatim data from the student-teachers, it appears to us that it may be intuitive to make such generalizations from molar ratio to mass (as in case 1) or to incorrectly set proportionality relations (as in case 2). These generalizations seem to be similar to the well-known interference of intuitive additive reasoning (Hart, 1984) in proportional situations. Understanding that proportionality holds only under molar ratio and not in terms of other measures is a realization that is crucial in articulating proportional relationships in stoichiometry problems.

Conclusions

Two research questions guided the present study. In response to the first question with regard to the ways in which proportionality is involved in the solution of stoichiometry problems in chemistry, we developed a five-level hierarchy with gradually increasing levels of proportionality requirements. This hierarchy captures different ways in which stoichiometry problems involving proportionality may be posed. It delineates the type of variations that may be effected based on the units used to quantify the reactants and products, and the level of complexity of the stoichiometry problems. For instance, multiple proportions may be required when two or more chemical equations are involved in the stoichiometry problems.

A consistent observation is that compared to conventional mathematics syllabi, proportional reasoning is more intricate in chemistry in that it involves several layers of complexity. This can be accounted for by a number of dimensions. Firstly, proportionality in stoichiometry is defined in terms of the unit "mole," which is based on a quantity which has no physical meaning (or which is defined at the microscopic level). Secondly, the units of the quantities used in the proportionality relationship may be both extensive as well as intensive (e.g., concentration is expressed in mole per cubic decimetre). Similarly, a problem in stoichiometry may simultaneously involve fraction, ratio, rate, proportion or percentage, and these variations require much flexibility with numbers. Further, proportional situations in stoichiometry may involve several conversions or steps (e.g., converting mole to mass). In addition, it is important to distinguish between an equation representing a chemical reaction and a mathematical equation. A chemical equation does not involve equality in terms of quantities but rather it involves proportionality in terms of molar ratio only.

In our analysis, we also came across stoichiometry situations where the formulation of the problem (i.e., the syntactic structure) demanded significant conceptual leap in terms of applying mathematical principles on the part of the problem solver. For instance, problems involving impurity, excess reactants, or loss in mass, demand higher order mathematical thinking and teachers need to be aware of this. In other problems (as in level 5 situations), one is required to determine an unknown element in a particular compound by using both proportional reasoning and algebraic thinking. Similar to the analysis of word problems in mathematics, the examination of stoichiometry problems on the basis of their syntactic and semantic structure can be an object of future research.

Simultaneous use of chemistry knowledge and mathematical knowledge

In the present analysis, we have focused mainly on the mathematical dimension of the stoichiometry problems. But in actual chemistry problems in the laboratory, in textbooks and past examination papers, students often have to write the chemical equations themselves from the given word problems and balance those equations before applying proportionality. Secondly, conceptual knowledge of chemistry is essential for students to be able to work through the various steps in solving the stoichiometry problems involving proportionality.

The second research question was set to investigate the strategies that students use, and the difficulties that they encounter in articulating proportionality relationships in stoichiometry problems. With regards to the strategies used in setting the proportionality between two quantities, the formulaic approach (Beall & Prescott, 1994) was much apparent in the students' work. The unit-rate method was also a preferred strategy.

In terms of constraints, two of the student-teachers set the proportionality relationship using masses on the basis of the molar ratio. In other words, since the molar ratio was 1:1, they assumed that 1 tonne of the first reactant needs 1 tonne of the second reactant. This is a notable misconception since proportionality can only be set when the relative atomic (or molecular) mass of the individual quantities are taken into consideration. In some cases, proportionality requirements were not respected, that is, instead of working with the computed number of moles, they worked with 1 mol.

A consistent observation

In analyzing the chemistry textbooks and examination papers, we could observe that the numbers used in the formulation of the problems were chosen such that divisibility relationships readily hold. Further, in most cases, the ratios between two quantities in the stoichiometry problems were specified in terms of simple integer ratios such as 1:1 or 1:2. Such divisibility relationships and reduced numeric fluctuations may facilitate the determination of the missing value in the proportional situations in chemistry. It is known that numeric variations impede proportional reasoning in mathematics. In terms of strategies to solve the proportions, we could observe that the four student-teachers were more familiar with the unit-rate method rather than the factor-of-change method.

Implications of the study

This study brings to light that collegial collaboration between mathematics and chemistry education researchers can offer insightful understanding of the knowledge that may be required to solve mathematically oriented problems in chemistry. In the current study, the analytical tools and understanding of children's knowledge of proportionality acquired in the field of mathematics education have been used to systematically analyze the proportionality elements in stoichiometry situations. The analysis revealed the complexities involved in solving the proportional situations in stoichiometry as one moves from level 1 to 5 in the proposed framework. Such type of information is important for chemistry educators who may not always view the proportionality requirements from a mathematical angle. Teacher education programs need to be more sensitive to the mathematical (proportional) dimension of stoichiometry. Students may not readily transfer knowledge of proportion from mathematics (where these ideas are first introduced) to chemistry (Hoban, 2011). More explicit pedagogical attention is required for concepts related to proportionality in chemistry education. Similarly, curriculum writers need to boldly underline the mathematical dimension of chemistry concepts.

References

Beall, H., & Prescott, S. (1994). Concepts and calculations in chemistry teaching and learning. *Journal of Chemical Education, 71*(2), 111–112.

Behr, M., Harel, G., Post, T., & Lesh, R. (1992). Rational number, ratio and proportion. In D. Grouws (Ed.), *Handbook of research on mathematics teaching and learning* (pp. 296–333). NY: Macmillan Publishing.

Cramer, K., & Post, T. (1993). Connecting research to teaching proportional reasoning. *Mathematics Teacher, 86*(5), 404–407. Retrieved December 21, 2012 from http://www.cehd.umn.edu/rationalnumberproject/89_6.html.
DeMeo, S. (2008). *Multiple solution methods for teaching science in the classrooms: improving quantitative problem solving using dimensional analysis and proportional reasoning*. Boca Raton: Universal Publishers.
diSessa, A. A. (1993). Toward an epistemology of physics. *Cognition and Instruction, 10*, 105–225.
Desjardins, S. G. (2008). Disorder and chaos: Developing and teaching an interdisciplinary course on chemical dynamics. *Journal of Chemical Education, 85*(8), 1078–1082.
DeLorenzo, R. (1994). Expanded dimensional analysis: a blending of english and math. *Journal of Chemical Education, 71*(9), 789–791.
Furio, C., Azcona, R., & Guisasola, J. (2002). The learning and teaching of the concepts 'amount of substance' and 'mole': A review of the literature. *Chemistry Education: Research and Practice in Europe, 3*(3), 277–292. Retrieved December 22, 2012 from http://www.uoi.gr/cerp/2002_October/pdf/02Furio.pdf.
Harel, G., Behr, M., Post, T., & Lesh, R., (1991). Variables affecting proportionality: Understanding of physical principles, formation of quantitative relations and multiplicative invariance. In F. Furinghetti (Ed.) *Proceedings of the PME XV Conference,* (pp. 125-133). Assisi, Italy. Retrieved from http://www.cehd.umn.edu/rationalnumberproject/91_2.html. Accessed 12 Nov 2012.
Gorin, G. (1994). Mole and chemical amount: a discussion of the fundamental measurements of chemistry. *Journal of Chemical Education, 71*(2), 114–116.
Hart, K. M. (1984). *Ratio: children's strategies and errors—a report of the strategies and errors in secondary mathematics project*. Windsor: Nfer-Nelson.
Heller, P., Ahlgren, A., Post, T., Behr, M., Lesh, R. (1989). Proportional reasoning: The effect of two context variables, rate type, and problem setting. *Journal for Research in Science Teaching*, 26(1), pp. 205-220. Retrieved from http://www.cehd.umn.edu/rationalnumberproject/89_6.html. Accessed 21 Dec 2012.
Hoban, R. (2011). *Mathematical transfer by chemistry undergraduate students*. Dublin: Dublin City University.
Johnstone, A. H. (2000). Teaching of chemistry—logical or psychological? *Chemistry education: research and practice in Europe, 1*(1), 9–15. Retrieved December 21, 2012 from http://pubs.rsc.org.
Kaput, J. J., & West, M. M. (1994). Missing-value proportional reasoning problems: factors affecting informal reasoning patterns. In G. Harel & J. Confrey (Eds.), *The development of multiplicative reasoning in the learning of Mathematics* (pp. 235–287). Albany: State University of New York Press.
Krishnan, S. R., & Howe, A. C. (1994). Developing an instrument to assess conceptual understanding. *Journal of Chemical Education, 71*(8), 653–655.
Lamon, S. J. (1993). Ratio and proportion: connecting content and children's thinking. *Journal for Research in Mathematics Education, 24*(1), 41–61.
Lamon, S. J. (1994). Ratio and proportion: cognitive foundations in unitizing and norming. In G. Harel & J. Confrey (Eds.), *The development of multiplicative reasoning in the learning of mathematics* (pp. 89–120). Albany: State University of New York Press.
Lamon, S. J. (2007). Rational numbers and proportional reasoning: towards a theoretical framework for research. In F. K. Lester (Ed.), *Second handbook of research on mathematics teaching and learning: a project of the National Council of Teachers of Mathematics* (pp. 629–667). Charlotte: Information Age Publishing.
Litwiller, B., & Bright, G. (Eds.). (2002). *Making sense of fractions, ratios, and proportion*. Reston: The National Council of Teachers of Mathematics.
Jeremy, K., Jane, S., Bradford, F., & National Research Council (US) Mathematics Learning Study Committee (Eds.). (2001). *Adding it up: helping children learn mathematics*. Washington: National Academy.
Nesher, P. (1988). Multiplicative school word problems: theoretical approaches and empirical findings. In J. Hiebert & M. Behr (Eds.), *Number concepts and operations in the middle grades* (Vol. 2, pp. 19–40). Reston: Lawrence Erlbaum Associates and National Council of Teachers of Mathematics.
Singer, J. A., Kohn, A. M., & Resnick, L. B. (1997). Knowing about proportions in different contexts. In T. T. Nunes & P. P. Bryant (Eds.), *Learning and teaching mathematics: an international perspective* (pp. 115–132). Sussex: Psychology Press.
Tourniaire, F., & Pulos, S. (1985). Proportional reasoning: of the literature. *Educational Studies in Mathematics: a review , 16*(2), 181–204.
Vergnaud, G. (1983). Multiplicative structures. In R. Lesh & M. Landau (Eds.), *Acquisition of mathematics concepts and processes* (pp. 127–174). New York: Academic.
Vergnaud, G. (1988). Multiplicative structures. In J. Hiebert & M. Behr (Eds.), *Number concepts and operations in the middle grades* (Vol. 2, pp. 141–161). Reston: National Council of Teachers of Mathematics.
Vergnaud, G. (1996). The theory of conceptual fields. In L. P. Steffe & P. Nesher (Eds.), *Theories of mathematical learning* (pp. 219–239). Mahwah: Lawrence Erlbaum Associates.