

Research Article

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Chemistry students' conceptual difficulties and problem solving behavior in chemical kinetics, as a component of an introductory physical chemistry course

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Abstract: The identification of undergraduate chemistry students' conceptual difficulties and common mistakes with basic concepts and problems in chemical kinetics provided the aim for this study, which involved 2nd-year/4th semester students who had passed the chemical kinetics component of a physical chemistry course. The study involved the analysis, evaluation and interpretation of students' answers to the final examination in chemical kinetics. Three achievement groups, for the various topics, were identified: Group A, high achievement (mean $\approx 85\%$): (a) the steps in a chain-reaction mechanism, (b) integrated 1st- and 2nd-order rate laws; and (c) the Lindemann–Hinshelwood mechanism. Group B, intermediate achievement (mean $\approx 74\%$): (a) half-life, (b) instantaneous rate and the extent of reaction variable (ξ), (c) the Michaelis–Menten mechanism, and (d) theoretical rate law not asking for a final formula. Group C, low achievement (mean $\approx 54\%$): (a) experimental rate law and the reaction rate constant on the basis of an experimental-data table, (b) extracting the theoretical rate law, and (c) the Arrhenius equation. Students' errors and misconceptions have also been identified. Successful students tended to respond well to straightforward questions on the theory of the subject, but had difficulties when solving problems. It is essential that teachers understand the potential of their students, especially possible misconceptions they may hold, and the teaching approaches that may contribute to overcoming the student difficulties. Problems in chemical kinetics can be very demanding both in terms of algebraic manipulations and conceptually. Teaching should focus on problem solving, with the emphasis on students themselves trying to solve the problems.

Keywords: chemical kinetics; misconceptions; students' errors; teaching and learning; undergraduate chemistry education.

Introduction

The study of physical chemistry plays an important part in the education of chemists and many other scientists and engineers, but students consider it as a complex and difficult course (Moore & Schwenz, 1992). According to Vemulapalli (2010) “physical chemistry has a reputation for being fascinating and fearsome”. Several studies have considered the general aspects of teaching and learning physical chemistry (Derrick & Derrick, 2002; Hahn & Polik, 2004; Nicoll & Francisco, 2001; Sözbilir, 2004) as well as students' misconceptions and difficulties of understanding in its various areas. Historically, physical chemistry made great progress in

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chemical thermodynamics, electrochemistry, and chemical kinetics by approaching these areas from a phenomenological perspective, that is, by considering only directly observable and measurable entities, without the use of submicroscopic entities, such as electrons, atoms, molecules, and chemical bonds. Macroscopic chemical kinetics provides the focus for the present study.

The German scientist Wilhelm Ostwald (1853–1932) received the Nobel prize in chemistry in 1909 for his work on catalysis, chemical equilibria, and reaction rates, areas that are central in the study of phenomenological chemical kinetics.¹ In 1864, the Norwegians Peter Waage (a chemist) and Cato Guldberg (a mathematician) formulated the law of mass action, which has had a great influence on the development of chemical kinetics. The law was later elucidated by the Dutch chemist Jacobus van't Hoff in 1877.

Aim of the present study

A recent review article in the literature on the teaching and learning of chemical kinetics concluded with suggestions for future research and implications for practice (Bain & Towns, 2016). According to the authors, more research at the undergraduate level was needed on more advanced kinetics concepts, such as reaction order, mechanism, steady-state approximation, and enzyme kinetics.

The teaching and learning of chemical kinetics has been the subject of the present study, which focused on the teaching of a university course of chemical kinetics in a department of chemistry at a Greek university as part of a physical chemistry course. Note that in tertiary education, chemical kinetics is taught not only to chemistry majors, but also to many other STEM majors (biology, biochemistry, pharmacy, and other life sciences, as well as to students in chemical and metallurgical engineering). The kinetics course was placed in the 2nd-year/4th-semester. The aim was to spot the difficult topics in the course and to identify common mistakes and misconceptions among the students. The study involved the analysis, evaluation and interpretation of students' answers to the final examination questions in kinetics. Results from the marking and analysing of students' scripts from eight (8) consecutive final examinations are presented,² and students' errors and conceptual difficulties/misconceptions, and problem solving behavior are considered. The following were the research questions of the study:

1. What levels of achievement according to the taught and examined topics were observed in the students' answers to the exam questions?
2. Which were the students' most common errors and conceptual difficulties about the taught and examined topics?
3. What explanations could be offered for the observed errors and difficulties?
4. How do our findings compare to previous relevant findings in the education literature?

The ultimate aim was to articulate a number of proposals for the better teaching of kinetics at the undergraduate physical chemistry level.

The topics covered in the study include: instantaneous rate of formation and extent of reaction variables; half-life of a reaction; integrated 1st- and 2nd-order rate laws; calculation of the reaction rate constant on the basis of experimental rate data; experimental and theoretical reaction rate laws; the pre-equilibrium and the steady-state approximations; the Michaelis–Menten mechanism; the Lindemann–Hinshelwood mechanism; chain-reaction mechanisms; the Arrhenius equation.

¹ For a long time, Ostwald denied the existence of submicroscopic entities, insisting that atoms and molecules, being not directly observable, were hypothetical entities (Sutton, 2003). Only in 1909, did Ostwald finally accept the reality of atoms.

² The first exam was set in July 2012 (actually it should have taken place in June 2012) and the eighth exam in September 2014. Note that in Greek universities, a semester system is followed, with exams taken place twice a year, once in January for the autumn semester or June for the spring semester, and a resit in the following September. Note also that because of a change in the placement of the course in the autumn term of the 1st year, for our study, exams have taken place both in June and in January, but all our students had attended the 2nd-year/4th semester course.

Before proceeding, it is essential to note that despite the fact that the data analysed were collected 8–10 years ago, the study is still relevant for the following reasons: The content of the kinetics course, the teaching style, and the form and demand posed by the examinations have remained essentially unchanged. In addition, the exams described were partly written by the instructor and partly were taken from the literature (the latter often with changes made by the instructor).

Rationale: the logical and psychological structure of physical chemistry and of chemical kinetics

In principle, phenomenological physical chemistry deals with observable and concrete entities, and yet it is a conceptually demanding subject, involving abstract physical reasoning and the use of complex mathematics, such as calculus and differential equations. Relevant to this is Jensen's scheme for the logical structure of chemistry (Jensen, 1998), which distinguishes three dimensions: D1: Composition and structure; D2: Energy; D3: Time. Each dimension can be treated at one of the three levels: L1: Molar level; L2: Molecular level; L3: Electrical level. This scheme leads to $3 \times 3 = 9$ subdivisions, of which the simplest is the treatment of composition at the molar level (D1L1) (see Figure 1).

Applying Jensen's scheme to the various areas of physical chemistry, we should place phenomenological thermodynamics at the energy dimension/molar level (D2L1), while quantum chemistry is at the structure dimension/electrical level (D1L3), and statistical thermodynamics is at the energy dimension/electrical level (D2L3). The positioning of chemical kinetics depends on the level at which it is studied: the simplest approach (definition of reaction rates and experimental elementary kinetics) is at the D3L1 level, while the study of reaction mechanisms may require the D3L2 and the D3L3 levels. Treating kinetics at the electrical level (D3L3) is the most complicated case, involving both a quantum mechanical and a statistical mechanical approach. It follows from the above rationale that the study of chemical kinetics must start from the simpler phenomenological approaches, and this approach was adopted in the course that is the subject of the present study. But even this approach requires abstract reasoning and the use of complex mathematics, such as differential equations, hence the complexity and the difficulties of the subject.

Review of education literature

This section starts with the review article by Bain and Towns (2016) of the literature on the teaching and learning of chemical kinetics at both the secondary and tertiary level. Justi (2002) had previously reviewed this topic. Thirty four studies from various science education research journals were included in the 2016 review article. Research at both the secondary level and the introductory tertiary level was included. A basic difference with the current study should be noted at the outset, namely the fact that the present study focuses on the higher *physical chemistry* level.

The studies examined basic concepts and aspects, such as defining reaction rate, explaining effects of variables (e.g., temperature, concentration, and catalyst), and understanding activation energy. Some studies investigated more complex concepts involving multi-step reaction mechanisms and reaction order, but

Dimensions (D) →	Composition and structure dimension	Energy dimension	Time dimension
Levels (L) ↓			
Molar level	D1L1	D2L1	D3L1
Molecular level	D1L2	D2L2	D3L2
Electrical level	D1L3	D2L3	D3L3

Figure 1: Jensen's scheme for the logical structure of chemistry (Jensen, 1998).

at a relatively simple level (due to the context of the studies, largely being at the secondary or introductory tertiary levels). Two areas of work emerged from the Bain and Towns review: (a) student understanding and misconceptions, and (b) instructional approaches to teaching. It is noteworthy that issues concerning concepts of kinetics have often arisen during studies on chemical equilibrium and thermodynamics, with students often conflating the two areas, for instance, they believe that a catalyst would speed up only the forward reaction (and not the reverse), while there is also confusion between reaction yield and reaction rate (see also below).

Since the time of the publication of the Bain and Towns (2016) review article, many studies (including many by the Towns group) that deal with kinetics topics have been published. Below we refer to some of these studies, leaving other studies that are more relevant to the present study for inclusion in the conclusions, discussion, and recommendations sections.

First, we refer to three diagnostic instruments, which have been constructed respectively for: (1) assessing 12th-grade students' understanding of reaction kinetics (Yan & Subramaniam, 2016), (2) exploring the nature of 12th-grade students' alternative conceptions on reaction kinetics (Yan & Subramaniam, 2018), and (3) a four-tier diagnostic instrument for exploring first year undergraduate students' understanding of chemical kinetics (Habiddin & Page, 2019).

Cheng (2017) used students' visualization of chemical reactions with emphasis on the particle model to support the learning of advanced concepts such as energetics and collision theory. Sweeder, Herrington and Vanden Plas (2019) used visualizations such as screencasts and simulations, which can illustrate how particles interact to yield successful reactions and how changes in concentration and temperature impact the number and success of individual collisions. Gegios, Salta and Koinis (2017) analysed how the school textbook approaches the concepts of chemical kinetics, and investigated 11th-grade students' relevant difficulties. Lamichhane, Meltese and Reck (2018) introduced an instrument for detecting undergraduate chemistry students' misconceptions about reaction coordinate diagrams (or "energy diagrams"). Atkinson and Bretz (2021) developed the "Reaction Coordinate Diagram Inventory" to measure chemistry students' thinking and confidence when interpreting the kinetic and thermodynamic information encoded within reaction coordinate diagrams.

Warfa and Odowas (2015) used creative exercises to examine how often students in an upper-division undergraduate biochemistry course linked prior chemical concepts to biochemical ones, such as enzyme kinetics and biomolecular structures. Rodriguez and Towns (2019a) reviewed the teaching of kinetics with analogies in the context of enzyme kinetics. Rodriguez, Bain, and Towns (2019) characterized how 2nd-year students enrolled in an introductory biochemistry course interpreted graphs in the context of enzyme kinetics, and reported that students typically focused on surface features related to reaction order and rate laws, which limited their understanding of the Michaelis–Menten model of enzyme kinetics (see also Rodriguez & Towns, 2019b). Rodriguez et al. (2019) studied further 1st-year, nonmajors chemistry students' graphical reasoning as they responded to a kinetics prompt at a Swedish university.

Bain, Rodriguez, and Towns (2018) tested zero-order systems as an opportunity for students to think about the underlying mechanism behind the physical phenomena being modeled. General chemistry, physical chemistry, and chemical engineering students were asked to think aloud about the half-life of a catalyst-driven zero-order reaction. Students often described zero-order in mathematical terms (i.e., the zero-order rate law, integrated rate law, and graphical representation), but lacked a clear understanding of the particulate nature of zero-order systems.

Bain, Rodriguez, and Towns (2019) considered the way students reason about the information encoded in rate constants, which is important for developing a deep understanding of chemical kinetics at the molecular level. During semi-structured interviews, general chemistry, physical chemistry, and chemical engineering students worked through kinetics problems and were asked to discuss equations used in kinetics, yielding rich data that provided insight regarding students' understanding of rate constants. Students often conflated ideas from kinetics and equilibrium, such as rate constants and equilibrium constants, as well as rate and rate constants. Misconceptions about reaction rate and their impact on misconceptions in chemical equilibrium was also the subject of the study by Jusniar, Effendy, Budiasih, and Sutrisno (2020). The following

misconceptions were detected: misconceptions related to changes in the reaction rate with time; the effect of temperature on the reaction rate; the effect of adding catalysts on the activation energy; and the mathematical relationship between the rate of reaction and the number of moles.

Finkenstaedt-Quinn et al. (2020) considered the relationship of thermodynamics and kinetics, with students struggling to make conceptually correct connections, sometimes seeing them as two separate topics with no relationship and other times conflating their meanings and explanatory powers. It was found that peer review and revision played an important role in supporting students to describe relevant concepts, for instance distinguishing between spontaneity and rate, and appropriately relating activation energy and rate.

Next we turn to consider papers that deal specifically with problem solving in chemical kinetics. Becker, Rupp and Brandriet (2017) studied the role of using conceptual reasoning and reflecting on one's work during an initial rates task. Bain, Rodriguez, Moon, and Towns (2018) explored undergraduate student integration of chemistry and mathematics by asking students to make their reasoning and thinking explicit as they described provided equations and as they worked through chemical kinetics problems. According to Rodriguez, Bain, Hux, and Towns (2019), in order to solve a problem, students must cue into relevant features, ignore irrelevant features, and choose among potential problem-solving approaches. However, what is considered appropriate or productive for problem solving is highly context-dependent. Analysis focused on characterizing the productive and unproductive problem-solving routes used by students, while the findings emphasized the role of using conceptual reasoning and reflecting on one's work during problem solving. Finally, Atabek-Yigit (2018) examined the relationship between two cognitive styles (field dependence/independence and convergent/divergent thinking) and cognitive structure outcomes in chemical kinetics. Field independent students tended to have more extensive and richer cognitive structure outcomes, while the convergence/divergence dimension did not show any correlation with cognitive structure outcomes.

Methods

Eight (8) consecutive examination occasions for the course "Physical Chemistry II" were selected, starting with the examination that took place in July 2012 and ending with the examination that took place in September 2014. The course was taught in the 2nd-year/4th-semester and was divided into two parts: (1) electrochemistry and (2) chemical kinetics. As an example, Appendix 1 (in the Supplementary material to this article) shows the chemical kinetics part of the examination paper with was set in September 2012. The lecturer was one of the authors of this paper (GT). As is the case with all theoretical courses (lectures) in Greek universities, attending the course was not mandatory. All students used as textbook Atkins' (1989) 3rd edition of "Physical Chemistry" (translated into Greek), which was distributed freely to all students by the Greek Ministry of Education. The course closely followed this text.

Teaching methodology

The method of teaching was traditional-teacher-centered, using a chalkboard as well as overhead transparencies. However, due to the lecturer's expertise in science education, a teaching methodology was employed in accordance with recommendations from research literature in science education. In particular, the lecturer often entered into a dialogue with the students and invited individual students or pairs of students to the board in order to work, with his guidance and help, either topics of theory or exercises and problems. This methodology was not intended to assess students' knowledge and skills, but simply to encourage them to think and thus be led to the desired answer/solution. This did not develop a competitive environment but a constructivist one. The ultimate goal was for the students at the end of the course to feel that they had succeeded and not that they had failed. Additional features of a constructivist approach were the emphasis on common errors, misunderstandings, and misconceptions of the students.

Despite the above, the fact that attendance at lectures was not compulsory resulted in a large number of students not benefiting from the teaching and thus facing the exams on their own, with only the help of

various notes circulating from private photocopying shops, and answers by past students to questions from previous exams that are not always complete or even correct.

Final examinations

In all the final exams, the examination items were set by the course lecturer, with the items usually having a similar structure: two of the topics (often the first two) were questions on the theory of the subject, with the next two or three being problems. The theoretical questions required just the reproduction of knowledge from the textbook, that is, they were at the lowest level of the Bloom taxonomy. On the other hand, the ‘problems’ often required for their solution the application of learned procedures and several similar topics had been taught during the course. Therefore these ‘problems’ belonged to so-called algorithmic problems or just ‘exercises’ (Bodner, 1987). In some cases, however, the problems were real/authentic problems, requiring for their solution the contribution of a number of mental resources (Johnstone, 1993) (see also Appendix 2 in the Supplementary material to this article). It is worth noting at this point that Peter Atkins in his ‘Physical Chemistry’ textbook has at the end of each chapter first “Exercises” and then “Problems” [The “Exercises” were called previously (e.g. in the 3rd edition) “Introductory Problems”].

The kinetics topics contributed 40 or 45 out of a maximum of 100 marks (with the remaining 60 or 55% respectively being assigned to the electrochemistry part). For the total course “Physical Chemistry II” (electrochemistry + chemical kinetics), the duration of each examination was three (3) hours. The examination was of the closed-book type, and throughout it the lecturer and additional laboratory personnel and post-graduate students acted as invigilators. The marks allocated to each item and/or questions were shown on the examination paper (see Appendix 1). The examination items can be categorized as follows:

- instantaneous rate of formation (dP/dt) of the product P and the extent of reaction (ξ) variables;
- differential and integrated 1st- and 2nd-order rate laws;
- calculation of the reaction rate constant on the basis of experimental rate data;
- half-life of a 1st-order and of a 2nd-order reaction;
- calculation of the reaction rate constant on the basis of experimental rate data;
- experimental and theoretical reaction rate laws;
- the Arrhenius equation.
- the pre-equilibrium condition and the steady-state approximation;
- the Michaelis–Menten mechanism;
- the Lindemann–Hinshelwood mechanism;
- definition of mechanism, characterization of steps in the mechanism (elementary reactions, including chain-reaction mechanisms);
- determining a theoretical rate law (without concluding into a final mathematical formula)
- determining a theoretical rate law (concluding into a final mathematical formula).

Examples of simple examination questions

(Note: Examples of more demanding questions and comments can be found in Appendix 2 in the Supplementary material to this article, and in other places in this paper).

Defining reaction rate: For the following chemical reaction $3A + 2B \rightarrow 4C$, write how the (instantaneous) reaction rate is defined with respect to A, with respect to B, with respect to C, and with respect to the extent of reaction variable ξ .

Experimental rate law: For the reaction $\text{NO(g)} + \text{NO}_2\text{(g)} + \text{O}_2 \rightarrow \text{N}_2\text{O}_5\text{(g)}$, the following experimental data are given:

# Experiment	[NO] ₀	[NO ₂] ₀	[O ₂] ₀	Initial rate, mol L ⁻¹ s ⁻¹
1	0.10 M	0.10 M	0.10 M	2.1×10^{-2}
2	0.20 M	0.10 M	0.10 M	4.2×10^{-2}
3	0.20 M	0.30 M	0.20 M	1.26×10^{-1}
4	0.10 M	0.10 M	0.20 M	2.1×10^{-2}

Calculate the experimental rate law and the reaction rate constant.

Integrated rate law: Derive the formula that gives the integrated rate law for a 1st-order reaction (alternatively: for a 2nd-order reaction with one reactant).

Half-life of reaction: The half-life of a radioisotope is 4.55 min. If the radioactive decay follows 1st-order kinetics, calculate the percentage of radioisotope that will remain after 2.00 h.

The Arrhenius equation: Write the equation that gives the dependence of the reaction rate constant on the temperature, state which parameters we can determine from it and explain how they can be determined.

The Michaelis–Menten mechanism: Refer to the Michaelis–Menten mechanism.

At other times, the question statement was more demanding (see exam item K2 in Appendix 1).

The Lindemann–Hinshelwood mechanism: Refer to the Lindemann–Hinshelwood mechanism.

Theoretical rate law: See exam item K4 in Appendix 1.

Many of the theoretical topics as well as the exercises/problems had been duplicated from previous exams, some with exactly the same and others with different wording. The ultimate goal was to enable the diligent students to succeed in the exam and obtain high grades commensurate with their application and ability. In some exams the students were given the choice of answering one question from two. In fact, in one case, one of the two topics to be selected was very demanding and had additional bonus marks assigned (see item K.3 in Appendix 1). It is not then surprising that this item was selected by only one student. This student obtained a mark on this question of 83.5% and gained a considerable part of the bonus points.

Grading of the students' answers

In all cases, the students' answers were graded by the lecturer at the time of the exam, on the basis of his long experience. A marking scheme, based on a comparison of the answers with the considered complete and correct answers by subtracting marks because of deviations, omissions and errors in the answers, was consistently followed. Correct statements or problem steps as well as erroneous ones were marked by the lecturer on the student scripts with color pen, so that it was easy for someone else to follow the logic of the assigned mark to each item or question. For the purpose of this study (that is, for recording the student errors), these marks were checked by the graduate student (the first author of this paper).

Reliability

A small number (10) of student scripts were re-marked by the graduate student based on the marking scheme indicated by the lecturer. For this task, the student used copies of exam papers, which had already been graded by the lecturer, with the individual and total grades masked, so that they were not apparent. The two scores (the initial marks by the lecturer and the marks by the graduate student) were then compared and agreements and disagreements were identified. An agreement on the disagreements was reached after discussion. Spearman's correlation coefficients ρ and Pearson's r were used to test the reliability of the scores. The Pearson coefficient is parametric and suitable for (relatively) large samples (>30) following the normal distribution. For small samples, such as ours, which are usually not following the normal distribution, Spearman's non-parametric correlation ρ is more suitable. Here we use both coefficients, with the reasoning that if both

lead to the same statistical conclusion, this is a booster of statistical analysis, regardless of whether or not the normal distribution is followed. The initial values found were $\rho = 0.867$ and $r = 0.8998$, and after discussion we found $\rho = 0.979$ and $r = 0.992$, that is, there is a significant positive correlation.

The students were categorized into achievement groups according to their degree of success in the kinetics part only. The groups based on the degree of achievement were as follows: group A: 30–39%; group B: 40–54%; group C: 55–69%; group D: 70–79%; group E: 80–100%. This was followed by the recording, on an excel sheet, of the individual mark per topic for each student, by the graduate student. In addition, a recording of the errors observed was made, with similar errors being grouped together.

Results I – descriptive statistics

From a total of 662 students who participated in the eight (8) examination occasions, 584 (88.2%) participated in the kinetics part, and from these only 328 students (56.2%) achieved a score $\geq 30.0\%$. It is these 328 students who were taken into account in the results reported below. The distribution of exam scores is shown in Table 1. It is observed that about half (50.9%) of the students performed below or just above the baseline 50%, while over 1/4 of the students achieved high or relative high marks ($\geq 70\%$).

Results II – comparison of different categories of examination topics

In this section we group the exam topics and questions into categories according to level of achievement. Three broader groups resulted. Before proceeding to the results, let us explain how we have worked with the results of each exam item, using as example the questions about the integrated 1st- and 2nd-order rate laws. Table 2 shows the detailed data.

The questions for the first three exams were the same (with one slightly differently worded), so we grouped these together, by taking the weighted average achievement, according to the sample sizes: $(12 \times 70.8 + 24 \times 81.2 + 31 \times 71.6)/67 = 74.9$. On the other hand, the last two questions were different, so we left the relevant data intact. In this way the condensed data in Table 3 resulted. Note that for the total mark in Table 3, we simply took the average of the three set of data (that is, without taking a weighted average: $(74.9 + 83.4 + 91.3)/3 = 83.2$). It is this total that we report for each exam topic in the results below. In this way, achievement in related questions was treated on an equal footing, independently of the sample size.

The classification into the three broader groups is as follows:

Group A, high achievement. This includes three groups of topics:

- Characterization of the stages of a chain reaction mechanism [this item was set only once and was answered by a small number of students ($N = 26$)]. Average achievement: 88.5%, SD = 18.0%];
- Integrated 1st- and 2nd-order rate laws ($N = 117$, $M = 83.2\%$ SD = 8.2%); and
- The Lindemann–Hinshelwood mechanism ($N = 24$, $M = 82.2\%$, SD = 6.2%)

Table 1: Distribution of exam scores.

		Mark				
		30–39%	40–54%	55–69%	70–79%	80–100%
N	328	71 (21.6%)	96 (29.3%)	75 (22.9%)	46 (14.0%)	40 (12.2%)
Mean (standard deviation ^a)		34.1% (2.7%)	46.8% (4.3%)	61.5% (3.9%)	73.6% (2.3%)	87.0% (6.3%)

^aStandard deviation was calculated on the basis of the sample.

Table 2: Data for questions about the integrated 1st- and 2nd-order rate laws.

No. of exams	Topic	<i>N</i>	<i>M</i>	<i>SD</i>
1	1st-order	12	70.8	43.8
1	1st-order	24	81.2	33.5
1	1st-order	31	71.6	19.3
1	2nd-order	19	83.4	31.9
1	1st-order and 2nd-order	31	91.3	16.5

Table 3: Condensed data for questions about the integrated 1st- and 2nd-order rate laws.

No. of exams	Topic	<i>N</i>	<i>M</i>	<i>SD</i>
3	1st-order	67	74.9	30.0
1	2nd-order	19	83.4	31.9
1	1st- and 2nd-order	31	91.3	16.5
Total		117	83.2	8.2

The average of the three of these groups was 84.6% ($N_{A,\text{total}} = 167$).

Group B, intermediate achievement. It includes four groups of topics:

- Half-life of a reaction ($N = 62$, $M = 77.9\%$, $SD = 17.4\%$)
- Instantaneous rate of formation and the extent of reaction variable ($N = 60$, $M = 75.3\%$, $SD = 21.5\%$),
- The Michaelis–Menten mechanism ($N = 93$, $M = 74.0\%$, $SD = 6.0\%$), and
- Theoretical rate law not asking for a final formula ($N = 120$, $M = 67.7\%$, $SD = 8.0\%$).

The average achievement of these four groups was 73.7% ($N_{B,\text{total}} = 335$).

Group C, low achievement:

- Determining the experimental reaction rate law and calculating the reaction rate constant on the basis of an experimental-data table ($N = 10$, $M = 59.5\%$, $SD = 43.7\%$),
- Extracting the theoretical rate law ($N = 258$, $M = 53.5\%$, $SD = 11.1$), and
- The Arrhenius equation ($N = 60$, $M = 50.3\%$, $SD = 16.1$).

The average achievement of these three groups was 54.4% ($N_{C,\text{total}} = 328$).

We observe that the difference between the averages of groups A and B is ca. 11 percentage points, while between the averages of groups B and C is ca. 20 percentage points. It is noteworthy that all the above average achievements are over 50%. However, the above classification is completely schematic and is made to facilitate the distinction/difficulty of the subjects and the study of the findings.

Specific comments about various topics/questions

Group B, intermediate achievement, (a) half-life of a reaction ($N = 62$, $M = 77.9\%$, $SD = 17.4\%$)

One question (Atkins, 1998, Problem 25.10(a), p. 788) required the age of an archaeological specimen based on ^{14}C radioactivity to be determined ($N = 25$, $M = 93.7\%$, $SD = 10.0\%$). Another question (see Appendix 2) referred to radioactive ^{131}I in relation to the thyroid gland and asked how much ^{131}I will remain in the human

body after 30 days ($N = 24$, $M = 83.2\%$, $SD = 29.3\%$). A third question (Atkins, 1998, Problem 25.10(b), p. 788) referred to radioactive ^{90}Sr in relation to metabolism and its deposition in bone instead of Ca. It asked how much ^{90}Sr will remain in the human body after 70 years ($N = 8$, $M = 81.9\%$, $SD = 23.9\%$). Finally, a fourth question referred *generally* to a radioactive isotope and also provided the information that radioactive decay follows 1st-order kinetics ($N = 5$, $M = 53.0\%$, $SD = 40.6\%$). The last question, despite being very simple in its description, had the lowest achievement, and this could be attributed to the fact that it asked for the *percentage* of radioisotope that will remain after 2.00 h. Note also the small samples for the last two questions.

Group B, intermediate achievement, (c) the Michaelis–Menten mechanism ($N = 93$, $M = 74.0\%$, $SD = 6.0\%$)

There were two similar questions, asking for reference to the mechanism, and in addition giving the Michaelis–Menten equation and asking what happens at the maximum reaction rate ($N = 9$, $M = 82.6\%$, $SD = 22.1\%$ / $N = 23$, $M = 69.2\%$, $SD = 29.8\%$). Another question, asked specifically for a reference to the Michaelis constant, as well as an investigation of the equation ($N = 30$, $M = 70.6\%$, $SD = 28.7\%$) (see also item K2 in Appendix 1).

Group B, intermediate achievement, (b) instantaneous rate of formation and the extent of reaction variable ($N = 60$, $M = 75.3\%$, $SD = 21.5\%$)

In this case we excluded the results of a critical question, which asked students to write down the formula that expresses the experimental rate law for the reaction $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{aq}) + \text{O}_2(\text{g})$ (see item K1 in Appendix 1). The correct answer is that without experimental data, we cannot know the experimental rate law. Here some students directly applied the law of mass action to the above stoichiometric equation and provided the answer $d[\text{O}_2]/dt = k_{\text{exp}}[\text{H}_2\text{O}_2]^2$, but this is not an acceptable approach.

Group C, low achievement, (b) extracting the theoretical rate law ($N = 258$, $M = 53.5\%$, $SD = 11.1$)

The detailed results are shown in Table 4, where the problems are placed in order of difficulty – first the easiest and then the most difficult. We observe four groups of problems: the easiest is the first problem with M.O. 72% followed by two problems with a score of $\approx 60\%$. Finally, we have the most difficult problems with scores from 50 to 41%. The most difficult problems are characterized by a more complex structure, e.g. more steps in the mechanism or more outcomes sought, e.g. in addition to deriving the theoretical rate law, they also seek to justify the approximations used (the pre-equilibrium condition and the steady-state approximation). In fact, for a large majority of students, the argumentation concerning the conditions for the application of the two conditions appears conceptually very demanding (see also Appendix 2).

Students encountered a question asking for the overall (stoichiometric equation for the) reaction, for which a mechanism was supplied. For the answer to this question, see Appendix 1. Here we have the case of a question with an unusual element, the answer to which requires the employment of *higher-order thinking skills* (HOTS) (Eklund & Prat-Resina, 2014; Tsaparlis, 2020; Zoller et al., 1995; Zoller & Tsaparlis, 1997). Such questions present great difficulties to many students.

Table 4: Detailed results for the low-achievement group: Extracting the theoretical rate law. (Problems are placed according to order of difficulty.)

No. of exams	Topic	<i>N</i>	<i>M</i>	<i>SD</i>
1	(A → P)	30	71.8	19.6
3	(2NO + O ₂)	82	60.9	22.7
1	(HOOH + I ⁻)	10	60.4	32.5
1	(C ₂ H ₄ + H ₂)	31	49.8	25.5
3	(O ₃ →)	50	45.5	27.3
2	(C ₂ H ₆ + H ₂ → 2CH ₄)	36	45.1	32.6
1	(N ₂ O ₅ →)	19	41.2	30.2
Total		258	53.5	11.1

Group C, low achievement, (c) the Arrhenius equation (*N* = 60, *M* = 50.3%, *SD* = 16.1)

Here one question proved more demanding than the other: The easier one (*N* = 48, *M* = 61.7%, *SD* = 31.4) gives the rate constant at two temperatures and asks students to calculate (a) the activation energy and (b) the rate constant at a third temperature. Data and outcomes are clear. On the other hand, the difficult question (*N* = 12, *M* = 38.9%, *SD* = 31.5) asks students to write the equation that gives the dependence of the rate constant on temperature, and to state which parameters can be determined from the data and explain how we can determine them. This problem is general, and, while it is based directly on taught/known theory, it seems to have confused many students, who most likely did not understand exactly what the problem is asking for (e.g. what is a “parameter”?)

Results III: common errors and misconceptions

Errors and misconceptions

Let us start by considering the meanings we attach to the terms “Error” and “Misconception”.

- “Systematic” errors are caused by learning difficulties or failures in understanding the underlying theory, concepts or procedures. This is commonly referred to by the term “alternative conceptions” or “alternative ideas” or simply as “misconceptions”.
- “Random” errors are caused not by lack of knowledge or misunderstanding, but by haste or carelessness or overload of “working memory” or by the “field effect” (or by a combination of the above factors).

We assume that the overload of the “working memory” and “field dependence” contribute not only to random errors, but also to incomplete knowledge and to wrong knowledge/misconceptions. We must also recognize that what may be a random error for one student can be a systematic error for another.

In the data presented below we attempt to characterize the errors according to the following features: random error (RE); systematic error/misconception) (M); lack of knowledge (LK); Lack of understanding (LU). Of course a lack of understanding can be due to or associated with an underlying misconception.

Findings

Table 5 lists the basic errors with their frequency among the students’ answers for the following topics: Instantaneous rate of formation and the extent of reaction variable, integrated 1st-order rate law, half-life, Arrhenius equation. Regarding the integrated 1st-order rate law, the students had been taught the differential

Table 5: Students' basic errors for the following topics: Instantaneous rate of formation and the extent of reaction variable, integrated 1st-order rate law, half-life, Arrhenius equation.

Topic	Errors	Frequency ^a
<i>Instantaneous rate of formation and the extent of reaction variable</i>	– Using the wrong definition of the extent of reaction variable (LK, LU)	46.0%
Total no. of answers 107	– Deriving a rate law on the basis of the total, stoichiometric equation and not on the basis of the given mechanism (M)	42.0%
Total no. of errors 50 (46.7%)		
<i>Integrated 1st-order rate law</i>	– Mathematical errors with employing logarithmic operations (RE, LK, LU)	28.0%
Total no. of answers 166	– Wrong sign in the rate law (RE, LK)	20.0%
Total no. of errors 25 (15.1%)		
<i>Half-life</i>	– Wrong numerical substitution in the formula for the half-life (RE)	50.0%
Total no. of answers 69	– Erroneous logarithmic operations (LK, LU)	35.7%
Total no. of errors 14 (20.3%)	– Wrong formula at the outset (LK)	14.0%
<i>Arrhenius equation</i>	– Exponential factor A in the equation wrongly interpreted (LK, LU)	31.3%
Total no. of answers 59	– Perceiving the equation just as a mathematical expression (LU)	25.0%
Total no. of errors 16 (27.1%)	– Inappropriate/not required comments (LK, LU)	18.8%
	– Wrong logarithmic operations (LK, LU)	12.5%

^aFrequency refers to percentage of the students in the exam(s) concerned, who committed the stated error.

rate law and how to integrate it to arrive at the integrated formula. Regarding the half-life, they were expected to know the half-life formulas for both the 1st- and 2nd-order reactions, but they should also know how to derive them from the corresponding integrated rate equation. Regarding the Arrhenius equation, they were aware of both the exponential and the logarithmic forms of the equation.

Comments

Instantaneous rate of formation and the extent of reaction variable: The extent of reaction variable appeared to cause a severe conceptual difficulty. On the other hand, many students seem to be able to apply the logic of the law of mass action when directly writing an experimental rate law on the basis of the stoichiometric equation for the reaction. Quite often, the stoichiometric coefficient (such as $-1/3 d[\text{H}_2]/dt$) is not used for the definition of the reaction rate in terms of a reactant or a product. Often the plus sign (+) (for a product) or the minus sign (–) (for a reactant) were missing or confused.

Integrated 1st-order rate law: A higher frequency (28%) of errors related to mathematical errors when employing logarithmic operations, while 20% of the errors related to wrong sign in the rate law (wrong application, possibly due to inattention).

Half-life: Most frequent (50%) errors concerned a wrong numerical substitution in the formula for the half-life. A further 35.7% of errors concerned erroneous logarithmic operations.

Arrhenius equation: The highest frequency (31.3%) was observed regarding the exponential factor A , which was wrongly defined. Wrong operations with logarithms also appeared here.

Table 6 lists the basic errors with their frequency among the students' answers for the following topics: The Michaelis–Menten mechanism, the Lindemann–Hinshelwood mechanism, and the characterization/naming of the steps in a chain reaction mechanism.

Comments

The Michaelis–Menten mechanism: The Michaelis constant K_M , the investigation of the equation and the maximum reaction rate appeared to cause problems.

Table 6: Students' basic errors for the following topics: The Michaelis–Menten mechanism, the Lindemann–Hinshelwood mechanism, and the characterization/naming of the steps in a chain reaction mechanism.

Topic	Errors	Frequency
<i>The Michaelis–Menten Mechanism</i>	– Either lack of investigation of the equation or arriving at a wrong conclusion about the maximum reaction rate (LK, LU)	42.4%
Total no. of answers 119	– Wrong definition for the Michaelis constant K_M (or they did not employ K_M at all) (LK, LU)	24.0%
Total no. errors 92 (77.3%)	– Did not use the steady-state approximation (LK, LU)	15.2%
	– Jumping to a conclusion without explanation or adequate explanation (LK, LU)	12.0%
<i>The Lindemann–Hinshelwood Mechanism</i>	– Jumping to a conclusion without explanation or adequate explanation (LK, LU)	55.2%
Total no. of answers 35	– Neglected to apply the right approximations or made errors in the approximations and simplifications in the application (LK, LU)	24.1%
Total no. of errors 29 (82.9%)	– Omission of a stoichiometric coefficient in the rate law (RE, LK, LU)	15.3%
<i>Definition of reaction mechanism, characterization of the steps in a chain reaction mechanism</i>	– Omission of an exponent for a concentration that participates in the expression for the reaction rate (RE, LK), or for not taking into account elementary reaction steps, usually the fast step (LK, LU)	13.3%
Total no. of answers 94		
Total no. of errors 98 (104.3%)		

The Lindemann–Hinshelwood Mechanism: The approximations used and the changing of the kinetics (from monomolecular to bimolecular, depending on the conditions: high or low gas pressure) caused problems in conceptual understanding.

Definition of reaction mechanism, characterization of the steps of a chain reaction mechanism: Regarding the definition of reaction mechanism, the comments above about the instantaneous rate of formation apply here too. Regarding the characterization of the steps of a chain reaction mechanism, the question concerned the use of labels such as initiation, propagation, inhibition, and termination steps.

Table 7 lists the basic errors with their frequency among the students' answers for the following topics: The theoretical rate law not asking for a final formula, and the relevant topic of deriving the theoretical rate law.

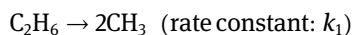
Table 7: Students' basic errors for the following topics: The theoretical rate law not asking for a final formula, and deriving the theoretical rate law.

Topic	Errors	Frequency
<i>Theoretical rate law not asking for a final formula</i>	– Omissions in writing down the kinetic equations (RE, LK, LU)	33.6%
Total no. of answers 168	– Errors in writing down the reaction-rate law (RE, LK)	29.6%
Total no. of errors 226 (134.5%)	– Errors about both approximation methods employed, namely the pre-equilibrium condition and the steady-state approximation (LK, LU)	22.5%
	– Omission of a stoichiometric coefficient in the expression of the rate law (RE, LK)	15.9%
	– Errors in the approximations or the simplifications in the theoretical rate law (LK, LU)	15.0%
	– Confusion about kinetic equations and the total reaction equation (M)	13.3%
<i>Deriving the theoretical rate law</i>	– Errors about the choice of the method or comparison to be followed, as well as of justification (LK, LU)	48.1%
Total no. of answers 322	– Confusion about the kinetic equation(s) and the overall reaction (M)	27.2%
Total no. of errors 445 (134.0%)	– Errors about the expression of the rate law (RE, LK, LU)	17.8%
	– Lack of justification of assumptions for the implementation of the steady-state approximation (LK, LU)	10.8%
	– Derivation of a wrong final formula, either because of mathematical errors(s) or of lack of using the right assumptions that lead to a simplification (RE, LK, LU)	10.6%

Comments

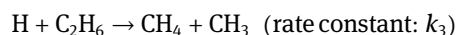
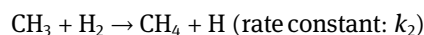
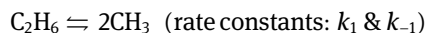
The following lists the frequent errors related to writing down a theoretical kinetic equation:

- (1) Failing to include in the rate equation the product of concentrations of *reactants* only (with each concentration raised to the proper exponent, according to the number of molecules in the elementary equation). This error was more likely to occur when writing the rate equation for the backward reaction in an equilibrium reaction. For such a reaction it might be preferable to write two separate elementary reactions instead of one, with the second reaction being the backward reaction in the equilibrium, for instance: instead of the equilibrium $\text{C}_2\text{H}_6 \rightleftharpoons 2\text{CH}_3$ (with rate constants k_1 & k_{-1} respectively), write:



- (2) Taking the correct sign for each contribution to the theoretical rate law: plus (+) for a product, minus (–) for a reactant.
- (3) Not expressing the rate for a chemical entity taking into account all elementary reactions in which the entity enters but only one reaction.

Example: Given the mechanism for the reaction $\text{C}_2\text{H}_6(\text{g}) + \text{H}_2(\text{g}) \rightarrow 2\text{CH}_4(\text{g})$:



the correct kinetic equation is:

$$d[\text{CH}_4]/dt = k_2[\text{CH}_3][\text{H}_2] + k_3[\text{H}][\text{C}_2\text{H}_6]$$

Instead, they defined the rate with respect to the product CH_4 based on one elementary reaction alone:

$$d[\text{CH}_4]/dt = k_2[\text{CH}_3][\text{H}_2] \quad \text{or}$$

$$d[\text{CH}_4]/dt = k_3[\text{H}][\text{C}_2\text{H}_6]$$

For a detailed solution to this problem and further comments, see Appendix 2.

- (4) Taking reactants or products as intermediates.

A mathematical misconception in deriving the theoretical rate law from a mechanism

Let us consider the above problem, which is asking students to derive the theoretical rate law, by assuming that for the first reaction the pre-equilibrium condition applies, while the intermediate H is in a steady state. Here, some students did not use the two conditions at all, and made the following fundamental error (which is surely a misconception): From the mechanism, we get respectively:

$$d[\text{CH}_4]/dt = k_2[\text{CH}_3][\text{H}_2]$$

$$d[\text{CH}_4]/dt = k_3[\text{H}][\text{C}_2\text{H}_6]$$

On the other hand, some students assumed that since the left sides of eqs. (7) and (8) are equal, the right sides must also be equal. This is a wrong deduction – for further comments, see Appendix 2.

Conclusions, discussion, and recommendations

As discussed at the beginning of this paper, students consider physical chemistry as a complex and difficult topic. Chemical kinetics, which involves abstract physical reasoning and the use of complex mathematics even at the macroscopic/phenomenological level, is no exception. Using Jensen's scheme for the various areas of physical chemistry, we placed chemical kinetics at its simplest approach (definition of reaction rates and experimental elementary kinetics) at the D3L1 level, while the study of reaction mechanisms may require the D3L2 and the D3L3 levels.

This study was about 2nd-year undergraduate chemistry students' conceptual difficulties and misconceptions in basic concepts and problems of chemical kinetics as part of the physical chemistry course. The study involved the analysis, evaluation and interpretation of students' answers to the final examination questions in chemical kinetics. The course followed closely Peter Atkins's approach from a Greek translation of Atkins's 3rd edition of the textbook "Physical Chemistry". The study involved only students who had passed the chemical kinetics component of the course. The results of the study of students' errors and conceptual difficulties were reported. The course had adopted macroscopic modeling (rather than theoretical or particulate modeling) when solving kinetics problems. This was also the case with the studies included in the (Bain & Towns, 2016) review.

Regarding research question (1), three achievement groups were identified, each including the listed topics: Group A, high achievement: (a) characterization of the steps in a chain-reaction mechanism, (b) integrated 1st- and 2nd-order rate laws; and (c) the Lindemann–Hinshelwood mechanism. The average achievement of these three groups was $\approx 85\%$. Group B, intermediate achievement. (a) half-life of a reaction, (b) instantaneous rate of formation and the extent of reaction variable, (c) the Michaelis–Menten mechanism, and (d) theoretical rate law not asking for a final formula. The average achievement of these four groups was $\approx 74\%$. Group C, low achievement: (a) determining the experimental reaction rate law and calculating the reaction rate constant on the basis of an experimental-data table, (b) extracting the theoretical rate law, and (c) the Arrhenius equation. The average achievement of these three groups was $\approx 54\%$. It is pertinent to note that Atkinson and Bretz (2021) have reported a persistent student difficulty in accepting the extent of reaction variable ξ as a time unit.

To answer research question (2), students' errors and misconceptions have been identified. The distinction of the errors into random and systematic ones was made, with the latter being also identified as misconceptions. The achievement of successful students shows that they tend to respond better to the questions on the theory of the subject, but have difficulties in solving problems. The basic errors detected were about:

- The definition of reaction rate and integrated rate laws (1st and 2nd order).
- The instantaneous formation rate and the extent of reaction variable.
- 1st-order reaction rate law – Mathematical errors in logarithmic operations.
- Half-life – Errors in the numerical substitution and wrong logarithmic operations.
- The Arrhenius equation – Mainly lack of knowledge.
- The Michaelis–Menten equation – Wrong definition or not using the Michaelis K_M constant. To a lesser extent, the steady-state approximation is not applied. More frequent: students come to the wrong conclusion about the maximum reaction rate. Note that enzyme kinetics, especially Michaelis–Menten kinetics and enzyme inhibition, was the topic of studies by the Towns group (Rodriguez & Towns, 2019a, 2019b, 2020; Rodriguez et al., 2021).
- Definition of reaction mechanism and characterization of steps in a chain reaction mechanism.
- The theoretical rate law calculation (without arriving at final formula) – A significant percentage of errors: Omission of a stoichiometric coefficient in the expression of the rate law. Most errors: Omissions when writing the kinetic equation, followed by errors in formulating the rate law. Confusion between the kinetic equation and the total reaction; and errors relating to the two approximation methods, the pre-equilibrium condition and the steady-state approximation.

- The theoretical rate law calculation (arriving at a final formula) – Errors in the formulation of the rate law, confusion of the kinetic equation and the overall reaction, and choosing the appropriate method or comparison as well as justification.

From the findings of the present study it is confirmed that the teaching of chemical kinetics presents students with significant difficulties in understanding and/or confusion with basic concepts. Students' errors and misconceptions have been identified.

Research question (3) concerns explanations that could be offered for the observed errors and difficulties. According to Bain and Towns (2016), research in undergraduate mathematics education has shown that many students struggled with the basic mathematical concepts that lay the foundation for rate-related problems. The role of mathematics in chemical kinetics has been the subject of a chapter by Bain, Rodriguez, Moon, and Towns (2019) in a collective volume about mathematics and chemistry. This chapter presents the results from a large project about how students understand and use mathematics in chemical kinetics, with an emphasis on the "blending" of chemistry and mathematics during problem solving. During interviews, the students were prompted to reason about kinetics equations and work through kinetics problems. The chapter discusses student engagement in modelling, mathematical reasoning (i.e., symbolic and graphical forms), reasoning regarding the role of mathematics in chemical kinetics, understanding of rate constants, conceptions of zero-order and half-life, and problem-solving approaches.

Page, Escott, Silva, and Barding Jr. (2018) investigated the effect of teaching the entire academic year of high school chemistry utilizing abstract reasoning. The methodology reinforced key proportional relationships featured in the balanced chemical equation and related topics such as acids and bases, reaction rates, equilibrium, and conservation of matter. A statistically significant difference was detected between students receiving instruction based on concrete reasoning and students receiving instruction rich in abstract reasoning, in favor of the latter.

In the preceding discussion, where appropriate, we set our findings against the relevant education literature, in an attempt to answer research question (4). In any case, we must take into account that the present study considered chemical kinetics at the undergraduate physical chemistry level, while most of the published work at the tertiary level is approaching the topics from the general chemistry perspective, which places the emphasis on qualitative relationships, explanations, and predictions about reaction rates and mechanisms, and less so on mathematical kinetics.

Finally, it is important to consider general guidelines for the teaching of physical chemistry at the undergraduate level. According to Marzabal et al. (2018), the difficulties of learning the key concepts of chemical kinetics are due, in part, to the fact that traditional teaching does not consider the findings of research on students' learning in this particular domain of chemistry, and proposed a teaching strategy that favors the evolution of students' intuitive conceptions. It is essential that teachers know the potential of their students, especially the possible misconceptions, but also the teaching approaches that may contribute to overcoming such student difficulties. On the other hand, while successful students tended to respond well to straightforward questions on the theory of the subject, they still tended to have difficulties when solving problems. There are problems in chemical kinetics that are very demanding in terms of both algebraic manipulations and conceptually.

A great emphasis must then be placed on problem solving, with the students themselves trying to solve the problems. On the other hand, exercises and home assignments should also be used (with encouragement and collaboration among students), so that students are taking their studies seriously.

It is also important that teachers help students with appropriate guidance and suggestions, as well as to encourage collaborative learning in groups. In addition, laboratory experience can cause cognitive conflict and lead students to the desired conceptual change – finding out for themselves their errors through conducting the experiment (a constructivist learning model). Finally, attendance at the lectures by the students should be regular/compulsory and NOT minimal or even non-existent. This is an old problem for theoretical courses (lectures) in the Greek universities. The system of organization and operation of university

departments must therefore be drastically changed. In other words, there must not only be a radical change in the organization of the teaching methods, but also in the way the students themselves deal with the lectures.

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Supplementary Material: The Supplementary Information includes two Appendices:

Appendix 1: An example of an examination paper with the chemical kinetics part (set in September 2012)

Appendix 2: Examples and comments on more demanding examination questions

The online version of this article offers supplementary material (<https://doi.org/10.1515/cti-2022-0005>).