

**A reference epistemological model in calculus and kinetics of chemical reaction**

**Un modelo epistemológico de referencia en el cálculo y la cinética de las reacciones químicas**

**Un modèle épistémologique de référence dans le calcul et la cinétique des réactions chimiques**

**Um modelo epistemológico de referência em cálculo e cinética de reações químicas**

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**Abstract**

In this article, we resume discussions about the application of differential and integral calculus in the teaching of chemical kinetics in teacher training. Aspects aimed at demonstrating statements through the resolution of tasks in a course of studies and research as a strategy aimed at appropriating concepts in the domain of reaction kinetics, in the context of activities based specifically on the anthropological theory of the didactic - ATD, based on epistemological models of reference and the dominant one around the object speed laws of chemical reaction. along the way, the importance and reason for being of integral and differential calculus techniques for teacher training and the formulation of didactic organizations that can serve as support for tasks in the exercise of the profession in high school were highlighted, highlighting the use of software, such as Excel, in the construction of these tasks. It was observed that throughout the course the students understood the steps proposed in the reference epistemological model by completing a crucial task, associated with the question that generated the course, which necessarily applies integration and differentiation techniques to obtain ordinary differential equations, associated with the technique analysis of the least squares

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method, for the kinetic characterization of a chemical system, a medicine in the simulation of the experimental determination of its expiration date.

**Keywords:** Teacher training, Chemical kinetics, Calculus.

### **Resumen**

En este artículo retomamos las discusiones sobre la aplicación del Cálculo Diferencial e Integral en la Enseñanza de la Cinética Química en la Formación Docente. Aspectos orientados a demostrar enunciados a través de la resolución de tareas en un curso de estudios e investigaciones como estrategia encaminada a apropiarse de conceptos en el dominio de la cinética de reacción, en el contexto de actividades basadas en la Teoría Antropológica de la Didáctica (TAD), concretamente basados en modelos epistemológicos de referencia y el dominante en torno a las leyes de velocidad del objeto de la reacción química. En el recorrido se resaltó la importancia y razón de ser de las técnicas de Cálculo Integral y Diferencial para la formación docente y la formulación de organizaciones didácticas que puedan servir de apoyo a las tareas en el ejercicio de la profesión en la escuela secundaria, destacando el uso de instrumentos de Las TIC, como Excel, en la construcción de estas tareas. Se observó que a lo largo del curso los estudiantes comprendieron los pasos propuestos en el modelo epistemológico de referencia al completar una tarea crucial, asociada a la pregunta que generó el curso, la cual necesariamente aplica técnicas de integración y diferenciación para la obtención de ecuaciones diferenciales ordinarias, asociadas a la técnica. análisis del método de mínimos cuadrados, para la caracterización cinética de un sistema químico, un medicamento en la simulación de la determinación experimental de su fecha de caducidad.

**Palabras clave:** Formación del profesorado, Cinética química, Cálculo.

### **Résumé**

Dans cet article, nous reprenons les discussions sur l'application du calcul différentiel et intégral dans l'enseignement de la cinétique chimique dans la formation des enseignants. Aspects visant à démontrer des énoncés à travers la résolution de tâches dans un cours d'études et de recherche comme une stratégie visant à s'approprier des concepts dans le domaine de la cinétique de réaction, dans le cadre d'activités basées sur la théorie anthropologique de la didactique (TAD), à savoir, basée sur des modèles épistémologiques de référence et celui dominant autour des lois de vitesse des objets de la réaction chimique. Au cours du parcours, on a souligné l'importance et la raison d'être des techniques de calcul intégral et différentiel pour la formation des

enseignants et la formulation d'organisations didactiques pouvant servir de support aux tâches dans l'exercice de la profession au lycée, en soulignant l'utilisation d'instruments de Les TIC, comme Excel, dans la construction de ces tâches. Il a été observé que tout au long du cours, les étudiants ont compris les étapes proposées dans le modèle épistémologique de référence en accomplissant une tâche cruciale, associée à la question qui a généré le cours, qui applique nécessairement des techniques d'intégration et de différenciation pour obtenir des équations différentielles ordinaires, associées à la technique analyse par la méthode des moindres carrés, pour la caractérisation cinétique d'un système chimique, d'un médicament dans la simulation de la détermination expérimentale de sa date de péremption.

**Mots-clés :** Formation des enseignants, Cinétique chimique, Calcul.

### **Resumo**

Retomamos neste artigo discussões acerca da aplicação do Cálculo Diferencial e Integral no Ensino de Cinética Química na formação de Professores. Aspectos voltados para a demonstração de enunciados mediante resolução de tarefas em um percurso de estudos e pesquisas como uma estratégia visando à apropriação de conceitos no domínio da cinética de reações, no âmbito de atividades embasadas na Teoria Antropológica do Didático (TAD), especificamente, a partir dos modelos epistemológicos de referência e o dominante em torno do objeto leis de velocidade de reação química. Ao longo do percurso foi evidenciada a importância e razão de ser de técnicas do Cálculo Integral e Diferencial para a formação docente e a formulação de organizações didáticas que possam servir de suporte para tarefas no exercício da profissão, no Ensino Médio, destacando o uso de instrumentos das TIC, a exemplo do Excel, na construção dessas tarefas. Foi observado que ao longo do percurso os estudantes compreenderam os passos propostos no modelo epistemológico de referência ao cumprirem uma tarefa crucial, associada à questão geradora do percurso, que necessariamente aplica técnicas de integração e diferenciação para a obtenção de equações diferenciais ordinárias, associada à técnica de análise do método dos mínimos quadrados, para a caracterização cinética de um sistema químico, um medicamento na simulação da determinação experimental de seu prazo de validade.

**Palavras-chave:** Formação de professores, Cinética química, Cálculo.

## **A reference epistemological model in calculus and kinetics of chemical reaction**

In this study, we present observations made in class as part of a project to train chemistry teachers on a chemistry degree course of the State University of Feira de Santana, Uefs, 2019, in which one of the objectives is to address issues related to the teaching of Physical Chemistry and the integration of webbing (Trouche; Drijvers, 2014), with emphasis on mastering the laws of kinetics of chemical reactions.

We emphasize that the integration carried out in the study aimed to solve tasks such as finding a function using calculus techniques as differentiation and integration that could be used to characterize a chemical system whose composition varies over time. The interactions between students and the teaching path conducted throughout a school semester were the object of study during a school semester and the object of didactic analysis from a methodological perspective inspired by modeling according to the framework of the ATD (Chevallard, 2020). The situations were created based on modeling in Chemistry where ordinary differential equations (ODE) were the starting point for their building. Therefore, the epistemological bases of differential and integral calculus justify the theme of this article, which calls for to praxeologies based on differentiation and integration processes as a central element.

The interdisciplinarity required in this course serves the purpose of joint training in Chemistry, Mathematics and webbing, and raises some questions that guided our research: how to propose tasks that consider these three domains; what adaptations should be proposed in the curriculum; would a Mathematics teaching more focused on Chemistry be an alternative? These questions converge to many others: what are the cognitive gaps of students that will be revealed throughout the training process, from contact with objects of chemical kinetics? what epistemological obstacles are involved? and, how could virtuality contribute to more effective training in Chemistry?

Based on these considerations, we propose a theoretical framework as a tool for interpreting and characterizing the epistemological models involved in teacher training.

### **Theoretical-methodological framework: anthropological modeling of the chemical reaction kinetics object**

What is a model? According to Willett (2012), the term model is commonly used in science and raises important philosophical, historical and epistemological questions. It is often a source of confusion even when it should be an anchoring point and a guide for those who practice scientific research. Solutions to a problem also serve as a model (Willett, 2012), that is, sometimes a model is perceived and understood as being a theory.

This is because not only the terms paradigm and theory are present in the face of certain problems. Models also have this characteristic (Willett, 2012). From this debate emerges a theory of didactics that has in the modeling process its own epistemology that opposes the problems that exist in merely formal teaching. (Barquero et al., 2011).

In this sense, based on the raising of a problem that questions *what we must teach in terms of Calculus to Chemistry students?* How can we use webbing to enhance the application of Calculus techniques? What are the Calculus techniques that we should explore with students in the construction of meanings in a domain of chemistry – reaction kinetics?

Based on these reflections, we opted for modeling centered on the theory of praxeologies to clarify what is essential for understanding this teaching problem, proposing reformulations in terms of the reason for being of certain mathematical content in chemistry education. Thus, we were inspired by Barquero *et al.* (2011, p. 554), when they propose the search for didactic organizations that favor the integration of modeling in the teaching of mathematics and physical sciences, as “opposed to the merely formal and isolated teaching of mathematics in higher education” (Fonseca Bon *et al.*, 2014, p. 8).

The ideas of science and theory implicit in this type of modeling go beyond those of the *stricto sensu*. Thus, Chevallard (2020) was inspired by Louis Bourdeau when he adopts the term praxeology and applies it to modeling practices that are part of a science still unfinished, the didactics.

In this way, the interest of praxeology is not the objectives of the action, but the action itself, regardless of the circumstances. This means that the focus is on the means and not the ends - the focus of attention in praxeology is on human action [*anthropos* in Greek], that is, the acting individual. From this principle, Chevallard generates theorems and records of means, which allow him to develop an analysis of the processes of action.

Teaching from the perspective described above raises a research problem: *how can we formulate a didactic model that enables global disciplinary integration, based on local experimentation for the training of chemistry teachers?*

In the construction of the answer to this problem, praxeological modeling can be articulated between calculus and chemistry, according to the paradigm of questioning the world (Chevallard, 2020), whose didactic face translates into a studies and research path (SRP), which is organized around a praxeological reference model (PRM) of the teacher.

It is worth noting that praxeologies serve both the study of the object – didactic praxeologies – and the investigation of the relationships between subjects and between them and the object of study in institutions. Here we have praxeologies of investigation, whose

background is the didactic transposition of a given object. Let's look at the details of the modeling in progress.

In each reference institution, I, the praxeological modeling around an object of knowledge, O, refers to the first theorem of the ATD, expressed by Yves Chevallard as follows:

1) Every institutional practice can be analyzed in different ways in a system of relatively well circumscribed tasks, which is structured during this practice (Bosch & Chevallard, 1999, p. 5).

According to this postulate, teaching practices can be modeled. This is done through the execution of tasks, which brings us to the second postulate of ATD:

2. The accomplishment of every task result(s) in the implementation of a technique (Bosch; Chevallard, 1999, p. 5).

This postulate leads us to look at the techniques used to build an epistemological model aimed at teaching concepts - in this case, techniques specific to calculus and therefore applicable to solving chemistry tasks, according to the institutional position of each actor in the didactic system.

Regarding the aspects related to the *reason for being* of these techniques and the conditions and restrictions for implementing a praxeological model. Here, in a specific way, it focuses on a set of tasks that seek conceptualization in the field of chemical kinetics. We therefore refer to the 3rd postulate of ATD, which deals with the ecology of tasks and their respective techniques, technologies and theories:

3. A discourse justifying tasks and techniques requires a technology, which in turn needs a justification, called a theory of technology, which is its basis. This means that in each institution there is an integrated and justified technique, which guarantees the effectiveness of the task and must be subject to control and participation by various institutional actors.

In this way, we can represent this praxeological model of analysis according to a *Herbacian* scheme, where  $\wp$  = praxeology,  $T$  = type of tasks,  $\tau$  = technique,  $\theta$  = technology and  $\Theta$  = theory. Thus

$$\wp = (T, \tau, \theta, \Theta).$$

Through this scheme we can model the life of teaching objects; they live in an institution, from where we highlight their epistemological, economic and ecological dimensions, when we detect a teaching problem in their surroundings.

Thus, we can highlight two epistemological models analyzed in this study, characterized based on the praxiological approach mentioned above, *i.e.* that of reference and the dominant one.

### **Characterization of epistemological models: the reference model**

In this investigation, the epistemological reference model (MER) gave rise to a PEP composed of conceptual elements that meet the epistemological dimension of the didactic problem around the teaching object. In this model, we highlight the dependence relationships between the kinetic variables and the *habitat* of chemical kinetics in objects of calculus and chemistry that feed each other (Almouloud, 2022; Chevallard, 1999) and are organized around a reference knowledge. Let us see.

Chemical Reaction Kinetics describes the dependence of concentration on time: experimentally, empirical laws are obtained that provide us with the rate laws; another important consequence of kinetics is the establishment of relations that indicate the reversibility of a reaction [reactants (R)  $\rightleftharpoons$  products (P)], which help us to elucidate the mechanism of a reaction, whose inferences clarify the state of reaction equilibrium in which  $R \rightleftharpoons P$ ; from the differential method and the integral operator, the order,  $n$ , of a chemical reaction is obtained, whose kinetics is represented by an ODE in exponential form; Chemical Reaction Kinetics describes the dependence of concentration on time: experimentally, empirical laws are obtained that provide us with the rate laws; another important consequence of kinetics is the establishment of relations that indicate the reversibility of a reaction [reactants (R)  $\rightleftharpoons$  products (P)], which help us to elucidate the mechanism of a reaction, whose inferences clarify the state of reaction equilibrium in which  $R \rightleftharpoons P$ ; from the differential method and the integral operator, the order,  $n$ , of a chemical reaction is obtained, whose kinetics is represented by an ODE in exponential form. In the Figure 1 we have the summary of the MER as a conceptual map.

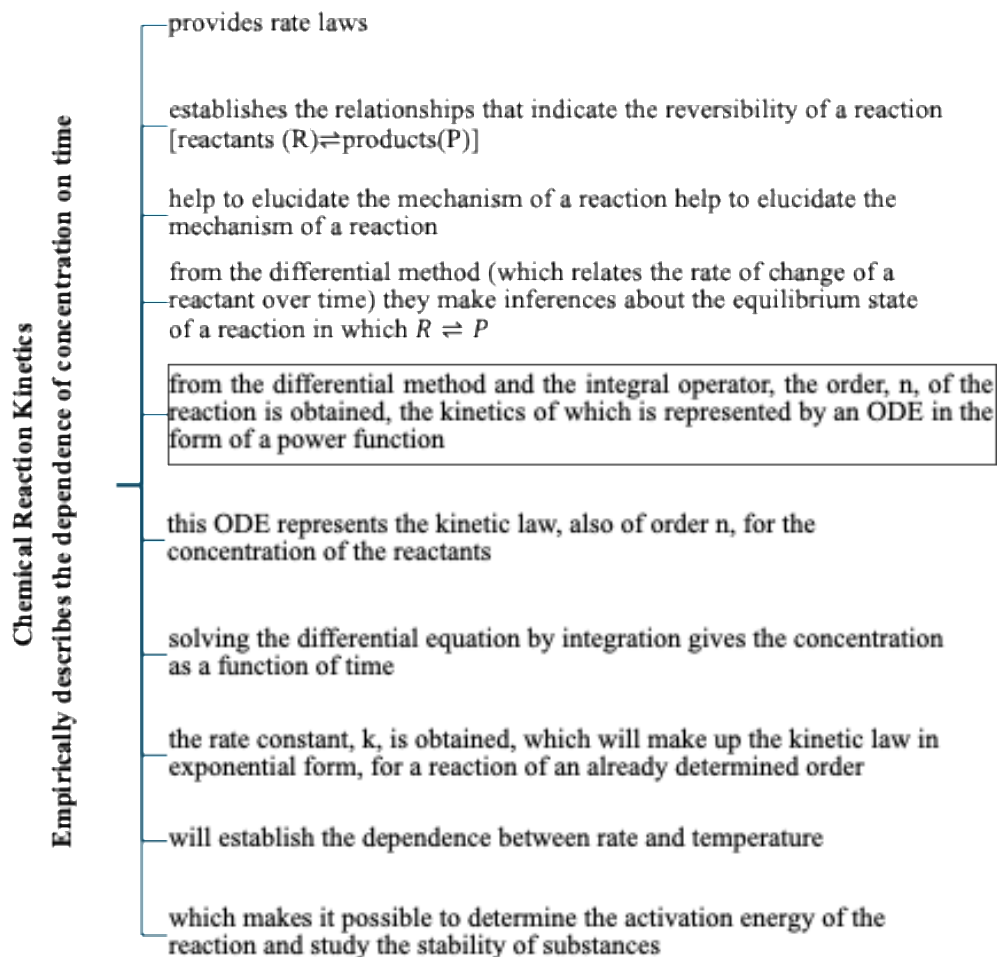


Figure 1.

*Epistemological reference model for chemical kinetics (part I) (Source: the authors)*

The second conceptual map is organized around the differential method (central concept): measuring the rate at the start of the reaction is the empirical basis for applying this method; it is considered that the rate does not vary under these conditions.

The experimental method is applied based on the definition of the derivative of a time-dependent concentration function, t

$$C = C(t) \text{ e } C'(t) = v \text{ (velocidade) para } \Delta t \rightarrow 0$$

$$v = C'(t) = \lim_{\Delta t \rightarrow 0} \frac{C(t + \Delta t) - C(t)}{\Delta t}.$$

If this limit exists,  $C'(t) \rightarrow \infty$  at the start of the reaction remains constant. This is the summary of the initial rate method shown in Figure 2 in concept map format.



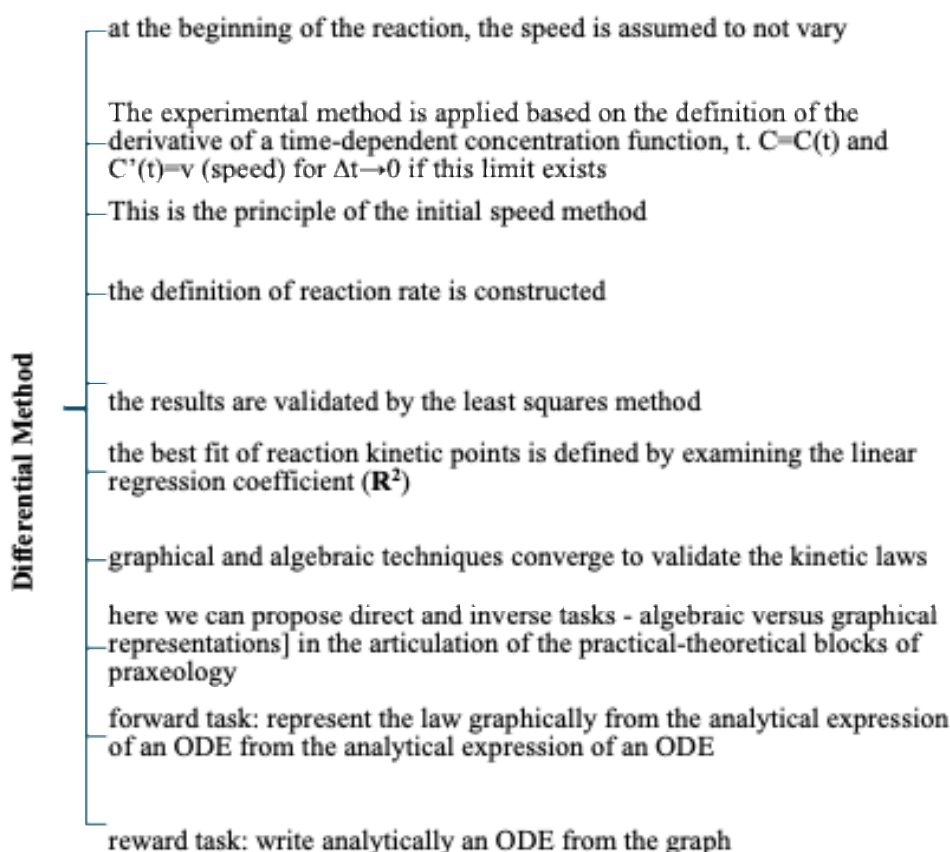


Figure 2.

*Epistemological reference model of chemical kinetics (part II) (Source: the authors)*

It is on the basis of these premises that the definition of reaction rate is constructed as a praxeology: the most common tasks it will involve are the techniques of differentiation and integration; the results arising from the treatment of kinetic data are validated by the least squares method; this helps us to define the best fit of reaction kinetics points by examining the linear regression coefficient ( $R^2$ ) of these data.

In this sense, the Excel software is integrated into the model to validate the experiment by providing the linear regression coefficient of the points in the concentration-time relationship in which the graphical and algebraic techniques converge to validate the speed laws.

Thus, we can propose direct and inverse tasks in the algebraic and graphical frameworks, which interconnect the practical-theoretical blocks of the praxeology  $[T, \tau] \rightleftharpoons [\theta, \Theta]$ :

$T_{forward}$ : represent the law graphically from the analytical expression of an ODE

$T_{dreward}$ : write an ODE analytically from the graph.

Note that an infinite number of relationships are possible between kinetic quantities such as reaction speed, specific rate, reaction order, as well as notions such as molecularity and the theories of state transition and molecular collisions (TST and TMC), among others, which indicate the most diverse didactic organizations and theoretical advances. As we need to delimit our study, we will focus on the institutional conditions and restrictions that make the materialization of a possible SRP, also adding our analysis of the epistemological dominant model in the research institution.

### **The dominant epistemological model**

The epistemological dominant model (EDM from now on) can be characterized based on some institutional elements, provided for in the scale of levels of determinacy (Chevallard, 2020) such as the *Base Nacional Comum Curricular* - BNCC (Brasil, 2017), the political-pedagogical project of the educational institution, the textbook and the social sphere, which determine teacher/knowledge/student relations.

The BNCC expressly recommends reaction kinetics as a sector of study, according to level 3 of the codetermination scale (CHEVALLARD, 2002b, p. 49 *apud* ALMOULOU, 2022). This indicates that an ecological analysis of this object can be made from the analysis of the lower levels,  $n$ , of the discipline ( $n \leq 5$ ), which covers the domain, sector, theme, subject ( $n = 4, 3, 2, 1$ , respectively). There is an equivalence between elements of these lower levels:

$n = 1 \Leftrightarrow \text{task}$ ;  $n = 2 \Leftrightarrow \text{technique}$ ;  $n = 3 \Leftrightarrow \text{technology}$ ;  $n = 4 \Leftrightarrow \text{theory}$ , with levels 2, 3 and 4 aimed at teachers and level 1 at students. In short, the subject is related to the various praxeological organizations corresponding to the various types of tasks, techniques, technologies and theories necessary for teacher training, but also for their work in elementary school in contact with students (Brasil, 2017).

The hierarchical scale of the levels of didactic codetermination and their respective levels in descending order. According to Chevallard (2020) and adapted from Silva (2017, p. 24). These levels are interrelated:

$\text{civilization (9)} \Rightarrow \text{society (8)} \Rightarrow \text{school (7)} \Rightarrow \text{pedagogy (6)} \Rightarrow \text{discipline (5)}$   
 $\Rightarrow \text{domain (4)} \Rightarrow \text{sector (3)} \Rightarrow \text{theme (2)} \Rightarrow \text{subject (1)}.$

It is from the internal interrelationships between these levels that the conditions and restrictions on the functioning of the didactic ecosystem are revealed.

The PPP for the Uefs chemistry teacher training course recommends that kinetics be included as a curricular component as early as the *introduction to matter transformations* course in the 2nd semester. In addition, a specific theoretical-practical subject, *physical chemistry III*, in the 7th semester, is dedicated exclusively to chemical kinetics, adding heterogeneous catalysis, homogeneous catalysis and adsorption to its curriculum.

Teachers graduating from this degree course in chemistry will be expected to teach in natural sciences in basic education. In their professional work, future teachers will have to contextualize kinetics concepts using problems whose representation of concentration variation over time [reaction rate] can be verified in algebraic and graphical form. This approach contributes to the development of skills such as recognizing chemical reactions in students, coded as follows: EM 22CN06 (Brasil, 2017). Knowing how to represent, identify and calculate kinetic quantities through simple experiments, manipulating variables that can modify the speed of a reaction, defining parameters such as temperature, pressure, contact surface, concentration and the presence of catalysts are skills that are expected to be mastered by high school and college students, depending on the level of depth, through the appropriate didactic transposition in each case.

In addition, the profile required of future teachers requires them to understand chemistry as a science and a mastery of specific knowledge. It also requires them to understand the problems surrounding the concepts, laws and principles of chemistry and to know the physical and chemical properties of the main elements in the periodic table, simple substances and compounds, as well as being able to understand and predict their physical and chemical behavior, aspects of reactivity, reaction mechanisms and substance stability.

Faced with the mathematization involved in developing problems with chemical content, students need to develop epistemic skills such as the ability to reflect on their own way of thinking and confront answers with the context that generates the problem. For this reason, it is recommended that calculus be taught in conjunction with chemistry through the construction and exploration of specific tasks for the objects of chemical kinetics (Brasil, 2017, p. 133; Skoog et al., 2006).

The reason of being of differential and integral calculus is justified by the mathematical nature of the definitions and concepts of kinetics.

In this way, the process of mathematization is inherent in the execution of tasks involving the objects of reaction kinetics. This process faces a restriction that Barquero et al. (2007) refer to as the phenomenon of applicationism in mathematics teaching, i.e. the separation between mathematics and experimental science teaching at this and other institutions.

Other restrictions at the level of society and schools in general, such as epistemological purification. More radically, mathematics remaining independent of other disciplines, the prevalence of the logic of models [the teaching of mathematics following deductive logic] and the teaching of the basic tools of mathematics always preceding their application, are restrictions that run counter to the desirable teaching of other disciplines articulated with calculus, although in the subject of calculus I at Uefs - prerequisite - to the subject dedicated to kinetics, the topic “applications” is recommended in the syllabus of the calculus I component, this disarticulation exists and manifests itself in the final years of teacher training.

In view of this situation, we recommend including the topic of dimensional analysis in the tasks, as well as emphasizing the quantities, units and dimensions present in the algebraic foundations of relational calculus, which is widely applied in the experimental sciences such as chemistry and physics (Vergnaud, 2006), which would bring mathematics and the experimental sciences closer together.

In this sense, a praxeological modeling around kinetic variables and their techniques, it is essential to articulate chemistry and mathematics from the inclusion of calculus tasks in the dominant epistemological model in the institution of reference of this study. In this way, a curricular “ecosystem” can be built (Chevallard, 2020, p. 46), where the techniques of differentiation and integration would serve as “food” for the subject of reaction kinetics, which indicates that calculus should “live” in a stable way, feeding and contributing to its survival to help give meaning to chemical concepts, linking the practical-technical  $[T/\tau]$  and theoretical-technological  $[\theta/\Theta]$  blocks of chemical-mathematical praxeological organizations.

These recommendations are observed in the university chemistry textbooks adopted and form the analytical basis of this EDM to develop a ERM that will guide the SRP to be described here.

To deal with the complex articulation between the domains of calculus and kinetics, we opted, among many paths, for the construction and execution of tasks around the objects,  $O$ , or praxeology,  $\wp$ , it is necessary to consider the object universe  $\Omega(u)$  and the cognitive equipment  $\Gamma(u)$  appropriate to the object, both teachers,  $Y$ , and of the students,  $X$ . The object universe of the actors in the institution  $\Omega(u)$  is defined as a praxeology whose relationship between the subject and this object is not empty. In addition, the praxeological equipment  $\Gamma(u)$  is defined as a praxeology whose relationship between the subject and this object is not empty and where this praxeology belongs to the object universe of the subject in the institution under analysis. For the moment, we have finalized the lack of face-to-face training described in this research. This was due to the social isolation necessary to cope with the Covid-19 epidemic, which

affected the education system worldwide, so there was a significant restriction at the level of humanity,  $n = 9$  on the didactic codetermination scale (Chevallard, 2020).

Formally  $\Omega(u) \stackrel{\text{def}}{=} \{o/R(u, o) \neq \emptyset\}$  and  $\Gamma(u) \stackrel{\text{def}}{=} \{(o, R(u, o) \neq \emptyset / o \in \Omega(u))\}$ ; these belonging relations are:  $\Omega^\diamond(u) \stackrel{\text{def}}{=} \{\wp/R(u, \wp) \neq \emptyset\}$  and  $\Gamma^\diamond(u) \stackrel{\text{def}}{=} \{\wp, R(u, \wp)/\wp \in \Omega^\diamond(u)\}$ ; where  $\Omega^\diamond(u) \stackrel{\text{def}}{=} \{\wp/R(u, \wp) \neq \emptyset\}$  means praxeological universe, which is by definition equal to a praxeology such that the relation of a given instance  $\mu$  to that praxeology is not empty.  $\Omega^\diamond(u) \subset \Omega(u)$  means that the praxeological universe of the instance is contained in the object universe of that instance, and  $\Gamma^\diamond(u) \subset \Gamma(u)$ , in which the praxeological equipment of the subject belongs to the cognitive equipment  $\Gamma(u)$  of that subject/actor, according to what is expected of the subject/actor in the institution in terms of their relations with knowledge.

In the next chapter, we demonstrate how the definitions of speed, reaction order and other definitions of kinetics - the body of knowledge in question here - are developed deductively.

### Reaction kinetics

Let's start with a demonstration of how the dependence of a system's composition on time can be described by a velocity law. When developing a kinetic equation in chemistry, we look for a derivative, which represents the rate of change of the concentration of the reactant with time, providing the basis for the differential equation of the kinetic law. Differentiation will express small changes in concentration and time, composing the differential equation, and integration serves to solve the differential equation, providing the function that describes how the concentration of reactants and products varies over time (Leithold, 1994, p. 463). Having made the initial considerations of calculus, let's show how the processes of differentiation and integration can be worked on in the interdisciplinary context of the kinetics of chemical reactions.

Let's consider that we are dealing with closed, homogeneous systems, with defined stoichiometry, according to the model proposed by Connors (1990) and Atkins (2010), which define the reaction progression,  $\xi$ , mentioned above,

$$\xi = \frac{n_i - n_0}{\nu_i}$$

where  $\nu_i$  is the stoichiometric number,  $n_i^0$  as the molar quantity of substance at a specific time ( $t = 0$ ) and  $n_i$  at any given moment ( $t$ ).

Generalizing, we have

$$\xi = \frac{\Delta n_i}{\nu_i} \Leftrightarrow \Delta n_i = \nu_i \xi.$$

Differentiating the above equation member by member by time, we can define the change in the amount of substance over time as the speed of the reaction, so it is  $d\xi/dt$ , or

$$\frac{d\xi}{dt} = \frac{1}{\nu_i} \frac{dn_i}{dt}$$

In solution kinetics, we usually work with systems at constant volume, and we find it convenient to use molar concentration units. Dividing both sides of the equation by the volume  $V$  gives us

$$\frac{d(\xi/V)}{dt} = \frac{1}{\nu_i} \frac{dc_i}{dt} = v$$

because

$$\frac{1}{\nu_i} \frac{dn_i/V}{dt} = \frac{1}{\nu_i} \frac{dc_i}{dt} = v$$

where  $v$  is the reaction rate per unit volume and  $c_i$  is the molar concentration of the  $i$ -th substance. Usually,  $v$  is called the reaction rate, or reaction rate.

Note that the sign of  $v$  indicates that it is always a positive quantity, by convention. These considerations are valid for molecular reactions, which take place in a single step. For reactions in the real world, in the laboratory, we need to consider that the process is more complex. To understand this, let's look at how empirical data is processed in experiments. To do this, some concepts must be appropriate: rate, kinetic constant, reaction order, etc.

### **Determination of the kinetic constant, $k$ and order, $n$ by the experimental initial rate method**

In an overview of the forms of kinetic laws, the differential form of the velocity equation can be seen from two notations for the molar concentration, thus  $C_A \equiv C_i$ . Let's see

$$v = \pm \frac{dC_i}{dt} \quad (1),$$

which allows us to arrive at the integrated form by equating equation (1) with the exponential form of the kinetic law, taking reagent A as a reference, in the form of a polynomial function, equation (2) which is an empirically determined law that allows us to determine the velocity constant,

$$v = kC_A^n \quad (2)$$

$$-\frac{dC_A}{dt} = kC_A^n \Leftrightarrow \frac{dC_A}{C_A^n} = -kdt \quad (3)$$

$$ou C_A^{-n} dC_A = -k dt$$

knowing that

$$\int_1^2 x^{-n} dx = \frac{x_2^{-n+1} - x_1^{-n+1}}{-n+1}$$

we can arrive at the integrated form. Having separated the variables following integration between limits results in

$$\int_1^2 C_A^{-n} dC_A = -k \int_1^2 dt \quad (4)$$

$$\frac{C_A^{-n+1} - C_{A,0}^{-n+1}}{-n+1} = -kt \quad \text{for } n \neq 1$$

$$\left(\frac{C_A}{C_{A,0}}\right)^{-n+1} = 1 + C_{A,0}^{n-1}(n-1)kt \quad \text{for } n \neq 1 \quad (4),$$

which is a general formula.

If  $n = 1$ :

$$-\frac{dC_A}{dt} = kC_A \quad (3)$$

$$\int_{C_{A,0}}^{C_A} \frac{dC_A}{C_A} = -k \int_0^t dt$$

$$\ln\left(\frac{C_A}{C_{A,0}}\right) = -kt \Leftrightarrow \ln C_A - \ln C_{A,0} = -kdt$$

$$\Leftrightarrow C_A = C_{A,0}e^{-kt}$$

if  $n = 1$ .

The reaction described above is of order 1. This can be seen from the graphical representation of the kinetic data according to the rate law [ $n = 0, 1, 2, \dots$ ]. Linearizing the points in these cases is a powerful mathematical tool for obtaining the kinetic parameters. This can easily be done using Excel. Hence the inclusion of this resource as a didactic tool.

The orders and units of the kinetic constants,  $k$ , for different kinetic laws are shown in table 1. Note that in this model we have a reaction between A and B.

The data in Table 1 reflect molecular reactions, which occur in a single step in the mechanism of a chemical reaction. In practice, not everything is as perfect as in Table 1. A

researcher may find that the points on the graph are scattered and need to be adjusted according to the kinetics of the reaction.

As we will see below, we must be careful with this point linearization technique, as the reaction time will be an important variable in this analysis - too short a time can lead to confusion between orders 0 and 1, for example, making it impossible to conclude its kinetic regime (Ball, 2005). These operations involve complex mathematical articulation even for students at the end of their undergraduate studies.

Table 1.

*The orders and units of the kinetic constants, k, for different kinetic laws (McQuarrie & Simon, 1997, p. 1140)*

Rate law	Order	Units of $k$
$v = k$	0	$dm^{-3}mol.s^{-1}$
$v = k[A]$	1	$s^{-1}$
$v = k[A]^2$	2	$dm^3mol^{-1}s^{-1}$
$v = k[A][B]$	1 em [A]	
	1 em [B]	$dm^3mol^{-1}s^{-1}$
	global = 2	$dm^{-3/2}mol^{1/2}s^{-1}$
$v = k[A]^{1/2}$	1/2	
$v = k[A][B]^{1/2}$	1 em [A]	
	1/2 em [B]	$dm^{3/2}mol^{-1/2}s^{-1}$
	global = 3/2	

The construction and application of a model that can change the curriculum by adopting interdisciplinary teaching, which includes an approach to constructing and solving tasks, mathematizing kinetic phenomena, allied to the insertion of webbing, contributes to teacher training and the development of concepts. This hypothesis was proposed in this REM and tested through the study and research path described below, based on its objectives, description and praxeological analysis.



## General objective of the path and General description of the path

The objective is training teachers around situations in chemical kinetics, articulating Calculus techniques, supported by webbing

The choice of these gestures was guided by the scientific knowledge that tells us the answer to the initial question, which is in the field of kinetics, i.e.,  $Q_0$ : “how does the purity of a material vary over time?”. In an investigation praxeology, we propose answers to the following three “big questions”:

- How to study the types of kinetic laws?

The content required to answer this question is the formal definition of rate laws, the kinetic equation in integrated form, the lifetime of a reactant and the kinetic constant and parameters. To do this, the student needs to mobilize techniques from differential and integral calculus. One of the learning objectives is to obtain the kinetic law, which is a function of a single variable,  $C = C(t)$ .

- How to analyze experimentally obtained kinetic data in graphs?

The content required to answer this question is the resolution (graphical and algebraic) of velocity equations. In this respect, we highlight the development of some complementary questions, which were key moments, revealing the techniques mobilized in the tasks that follow.

- How to integrate web resources via experimental simulation and kinetic data processing?

The titrAB.fr software application and the Excel software, whose characteristics and implications were discussed in (Nascimento Júnior et al., 2018; 2019) were used by  $Y$  when teaching the notion of acid-base chemical equilibrium; thus, the treatment of kinetic data that helped in the algebraization and construction of the graphical representations were already known to  $Y$  when teaching acid-base chemical balance  $X$ .

The content covered and needed to answer  $Q_0$  was graph construction, deducing and solving equations and finding the angular coefficient of a line, both graphically and by algebra.

## Experimentation

The research reported here is an excerpt from a longer period of investigation, which began in March 2019 (the research design phase) and is scheduled to end in February 2023, in the Department of Exact Sciences at Uefs. In this section, the period covered was over one academic semester, each theoretical-practical class lasting four (04) hours for a total of 60 hours/class, in the academic semester from February 2021 to July 2021, through the Google

platform and [www.schoology](http://www.schoology). Seven (07) future chemistry teachers took part. Face-to-face classes were planned, but this was not possible due to the persistence of the Covid-19 pandemic during the semester.

The didactic analyses were carried out based on the data generated. They were structured into praxeologies and error analysis, depending on which theory best explained the phenomena observed during the course. In both stages (remote and face-to-face) there was technological training through practices that incorporated web resources, such as in the tasks: simulated titration, data processing, table construction, determining kinetics by linearizing points, among others, using digital resources: computer, platforms, internet access, Office 2019, data-show, the software [www. titrAB.fr](http://www.titrAB.fr). If face-to-face classes were possible, these materials - which are part of the milieu - would include glassware, a pH potentiometer and chemical reagents:  $\text{CH}_3\text{COOH}$  and  $\text{NaOH}$ .

## Results

The SRP was implemented according to three didactic moments: the encounter with the object, the tasks explored, and the elaboration of techniques began, and the elaboration of the theoretical discourse, through articulation between the blocks of knowing and knowing how to do.

1st meeting: in an online environment, it began with an epistemological approach to the object of kinetics, its origin in Physics and its conceptual structure in Chemistry. To initiate the students into the dialectic of questions and answers, the teacher proposed a Task ( $t_1$ ) for the students to search for questions that reflect the kinetic character of a natural phenomenon: answers using the web search technique were presented by the students and discussed from the point of view of kinetics.

The answers came in the form of questions, of which we highlight two:

$r_1$ : *how much H turns into He per second in the Sun?*

$r_2$ : *how much matter is processed every second on the Sun?*

In  $r_1$  the technique adopted was adopted as an answer found on the website: “our star is capable of converting hydrogen atoms into helium, and the numbers are incredible: every second, the Sun fuses about 600 million tons of hydrogen into helium, converting part of this mass into energy in the form of electromagnetic waves, such as gamma rays.” [<https://www.google.com.br/search?>]

The technique and the task are intertwined, as are the question and the answer. At an early level of initial functional modeling, we can seek to “materialize in models that are

expressed through isolated functions of a variable and the corresponding associated equations (and inequalities)” (Ruiz-Munzón et al., 2011, apud Fonseca Bon et al., 2016, p. 11).

To  $r_2$ : how much matter is processed every second on the Sun?

The following explanation was found: “In all, the Sun consumes about 4 million tons of its mass per second, a rate more than enough to keep it shining for the next 6 or 7 billion years, due to its large mass, which is approximately  $1.98.10^{31}$  kg, more than 330,000 times the mass of the Earth.” [ <https://brasilecola.uol.com.br/fisica/sol>].

This moment provided the opportunity to create a mathematical model that represents a mathematical situation that represents the problem situation. From it we proposed a question  $Q_0$ , which met a basic requirement of a SRP - that it be a question with a high degree of generality, but that it be scientific (Lucas, 2015), for example, “*how does the purity of a material vary over time?*”.

We could say that by using didactic techniques (Chevallard, 1999 apud Fonseca Bom et al. 2015), we can encourage students to look for their own questions in different media. In this way, identifying questions from a given science is a skill to be developed. So, we proposed a question describing the time evolution of the concentration of a medicine until it reaches its expiration date. This more specific question was  $Q_1$ .

$Q_1$  According to FDA procedures, the expiry date (maximum time limit for the use of a drug) must correspond to 90% of the active ingredient content indicated on the product label.

According to this information and based on a kinetic study of the stability of commercial Paracetamol, whose data is shown in Table 1, “determine the shelf life of this medicine”.

The aim of this path was to develop the students' praxeologies linked to the topic through the ability to devise questions that help them find the answers to  $R^\heartsuit$  à question  $Q_0$ , thus developing their praxeological equipment by practicing the dialectic of questions and answers in the object of study.

All the students took part in the classes with smartphones and three with computers. They used the software [www.titrAB.fr](http://www.titrAB.fr) - to simulate acid-base titration - Excel ® and the Office text editor to construct the graphs.

During the application of the didactic model, we surveyed the questions derived from the generating question  $Q_0$ , highlighting that throughout the process we built a  $Q - R/map$  (of questions and answers) which shows how the answer  $R^\heartsuit$ , from  $Q_0$ , is arrived at.

In this sense, the students tried to find ways to answer  $R^\heartsuit$ , through the dialectic of questions and answers, formulating provisional answers,  $R^\diamond$ .

At this point, the teacher also proposed a question derived from the initial question, question  $Q_1$ : “According to FDA<sup>3</sup> procedures, the expiration date (maximum time limit for the use of a drug) must correspond to 90% of the active ingredient content indicated on the product label.

According to the above information and based on a kinetic study of the stability of commercial Paracetamol, the data for which is shown in Table 2, determine the shelf life of this medicine.” The aim of this activity was to develop students' praxeologies linked to the topic through the ability to devise questions that help them find the answers  $R^\heartsuit$  à question  $Q_0$ , thus developing their praxeological equipment by practicing the dialectic of questions and answers in the object of study.

Table 2.

*Kinetics of decomposition of pure paracetamol. Adapted from David Ball (Source: 2005, p. 724)*

Time/ month	[A]/mmolL <sup>-1</sup>	Ln [A]	(1/[A])/(mmol <sup>-1</sup> L)
0	2.719	1.000	0.368
1	2.612	0.960	0.383
2	2.586	0.950	0.387
3	2.509	0.920	0.399
4	2.459	0.900	0.407
10	2.138	0.760	0.468
15	1.855	0.618	0.539
20	1.664	0.509	0.601
25	1.448	0.370	0.691
30	1.276	0.244	0.784

To arrive at the answer  $R^\heartsuit$  to question  $Q_0$ , one of the paths comes from the search for the answer to  $Q_1$ . In this process, the student needs to mobilize knowledge of reaction kinetics. These are concepts and definitions that make it possible to understand the complexity of the answer and one of the causes is the mathematization process involved in formulating definitions such as velocity or kinetic law ( $v$ ), reaction order ( $n$ ) - which corresponds to the order of an ODE and specific velocity ( $k$ ) - also called specific speed. One of the challenges is dealing with the units, magnitudes, quantities and units of these chemical entities. The technique we recommend for algebraic manipulation is *dimensional analysis* (Vergnaud, 2006).

<sup>3</sup> <http://www.portalection.com.br/estabilidade-de-medicamentos-rdc-318/prazo-de-validade>.

Among the tasks proposed in the meeting with the praxeological organization with the aim of changing the  $R_I(X,o)$  relationship, we highlight the following:

$t_a$ : demonstrate algebraically how velocity and temperature are related in the radical hydroxylation reaction of chlorobromomethane,  $HO \bullet + CH_2BrCl \rightarrow Product$ . The kinetic data for  $t_a$  are

Ensaio	$T/^{\circ}C$	$k10^{13}/cm^3mol\u00e9culas^{-1}s^{-1}$
1	393.6	6.91
2	127.0	2.54
3	24.6	1.11

$t_{a,1}$ : determine the value of the Activation Energy of the reaction,  $E_A$ , em  $Jmol^{-1}$  by exploring the line obtained.

$t_{a,1,1}$ : organize a table containing the variables  $lnk$  and  $1/T$ .

$t_{a,1,2}$ : with the help of Excel, organize a table with the kinetic variables and represent them in a graph of  $lnk$  as a function of  $1/T$ .

$t_b$ : from the graph in Excel, obtain the equation of the line, its angular coefficient and estimate the values of the activation energy and the Arrhenius pre-exponential factor (A) for the reaction. The choice of technique was free.

Task  $t_b$  served as a task generator when we chose task  $t_{b1}$

$t_{b1}$ : from the graph in Excel, obtain the equation of the line, its angular coefficient and estimate the values of the activation energy and the Arrhenius pre-exponential factor (A) for the reaction. The choice of technique is free.

$t_c$ : construct an acid-base titration curve on [www.titrAB.fr](http://www.titrAB.fr) and compare it with the curve made in Excel from empirical data. Compare the two techniques:  $titrAB-\tau_{ITT}$  and Excel -  $\tau_{Excel}$ .

$t_d$ : from the empirical data, graphically represent the adsorption model of acetic acid on activated carbon

Still in the second moment, the tasks were explored and the development of techniques to solve a given type of task began.

To execute  $t_{a,1}$  the algebraic and Excel techniques were manipulated:  $\tau_a$  and  $\tau_E$ .

In  $t_{a,1,1}$  the  $\tau_E$  technique was mobilized, in which the Excel application was used to represent the  $lnk$  as a function of  $1/T$  on the cartesian plane.

In  $t_{b1}$ , the algebraic technique was the only one possible - in this case we have a punctual praxeology.

To fulfill  $t_c$ , the two techniques were compared: titrAB -  $\tau_{TIT}$  and Excel -  $\tau_{Excel}$ , based on empirical data.

In compliance with  $t_d$ , the algebraic and Excel techniques were manipulated:  $\tau_a$  and  $\tau_E$ , in addition to the elaboration of an experimental protocol to infer about the adsorption model of acetic acid on activated carbon. The findings in this praxeology open perspectives for the advancement in heterogeneous catalytic modeling.

Third moment: among the tasks developed, we highlight the one of a genuinely technological nature, the  $t_c$  task. Its technique, through simulation in titrAB- $\tau_{TitrAB}$ , was used to develop experiment protocols in this application. The acid-base curve and other data from the application page are shown in Figure 3. The development of the protocol made it possible to carry out titrations on site - using the  $\tau_{Excel}$  technique and volumetric method in the experimental laboratory when classes were still held in person in the chemical laboratory.

From the analysis of the two curves obtained and the respective techniques, it was possible to establish the discourses of the techniques and evaluate the theoretical/technological block  $[\theta/\Theta]$  that justified the two techniques  $[\tau_{TitrAB}/\tau_{Excel}]$ , used in the execution of the task  $t_c$  as being at least punctual praxeological organizations - PPO - different techniques for the same task,  $[t_1, \tau_{TitrAB}, \theta_1, \Theta]$  and  $[t_1, \tau_{Excel}, \theta_1, \Theta]$ , forming an LPO  $[t_1, \tau_{1i}, \theta_1, \Theta]$  (Almouloud, 2015).

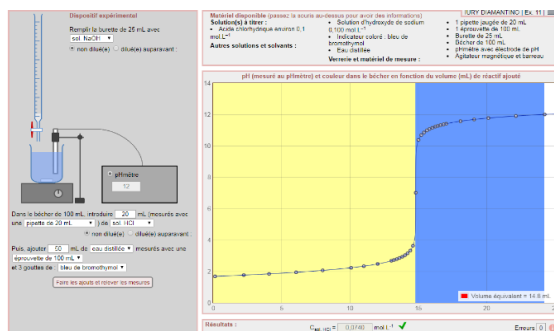


Figure 3.

### *Simulation of titration of acetic acid, $CH_3COOH$ with $NaOH$ in titrAB.fr*

From the  $t_c$  task, it was observed that the students used two volumetric neutralization techniques: the online titrAB.fr technique and the volumetric technique. To perform this technique, the simulator provided information that enabled the elaboration of the experiment protocol. In this sense, previous knowledge of chemistry such as the law of titration dilution and the volume-concentration equivalence at the end point of the titration were used. This was

evident in the reports - in the pre-calculation - when they used the relationship  $C_1V_1 = C_2V_2 = k$  (*constante*); [C = molar concentration; V = volume in mL; 1: acidic solution; 2: basic solution], in addition to expressing themselves using concepts from acid-base theories (Arrhenius, Bronsted-Lowry, Lewis).

These findings reveal that there were articulations between the technical [t/ $\tau$ ] and theoretical [ $\theta/\Theta$ ] blocks in the execution of  $t_c$ . The presence of concepts and definitions such as acid and base strength, pH and molar concentration, in addition to the notion of equivalence and neutralization points was present in 85.6% of the students' responses, confirming that the  $\tau_{TitrAB}$  technique favored access to these theoretical elements in the production of protocols and reports.

### **The search for an answer to the question that generated the SRP**

In the search for  $R^\heartsuit$  we formulate more derived questions beyond  $q_1$ ; we elaborate  $q_{1,1}, q_{1,2}, etc.$  Figure 4 shows the provisional praxeologies,  $R^\diamond$ , posed by students.

q<sub>1,1</sub>: how is the order ( $n$ ) of the decomposition reaction of Paracetamol determined?

q<sub>1,2</sub>: what is the physical meaning of the rate constant ( $k$ )?

q<sub>2</sub>: how is it possible to determine the reaction rate constant?

q<sub>2,1</sub>: how can I determine the expiration date of this medicine  $t_{90}$ , in months, from the values of  $k$  and  $n$ ?

Figure 4.

*Summary with the generating question and the derivative questions in path*

This collective construction helped us to construct tasks whose answers served as elements of analysis and theoretical reflection on the evolution of the students' object universe throughout the semester. From the data in Chart 3 it is possible to construct a map of questions and answers [ $Q-A/map$ ], obtained from the data of the path.

The path to finding the answer to  $Q_1$  was through the linearization of the points in Table 2 in the plane of the molar concentration of the reagent [Paracetamol] versus time in seconds. The points were processed in the Excel software. According to the reaction order of the integrated ODE, we projected three possible orders [ $n = 0, 1$  ou  $2$ ], according to Figure 1. The curve that presented the best adjustment of points, that is, the linear regression coefficient [ $R^2 = 0,9992$ ] closest to 1, which corresponds to a 1st order ODE, if the reaction order,  $n = 1$ .

The graphical representation, obtained with the help of the Excel application, in Figure 5, which follows below.

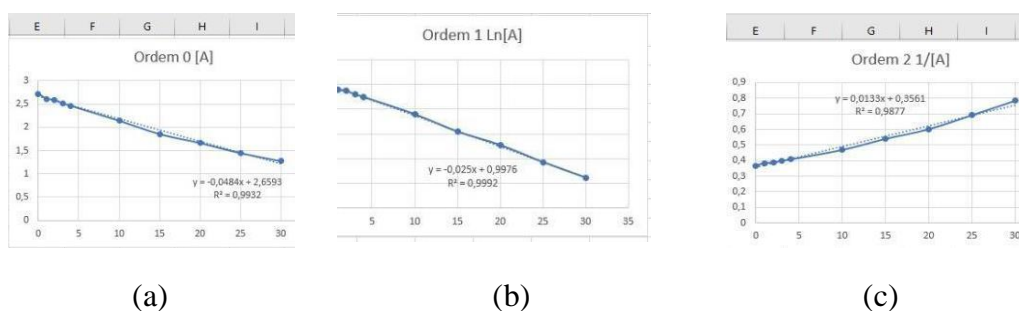


Figure 5

Students' response to  $Q_1$ : graphical representation of ODE of order 0, 1 and 2, respectively

One of the applications of ODEs that deserves to be highlighted is the derived question  $Q_1$  regarding the decomposition reaction of a medicine until it reaches its expiration date. Regarding this, the students unanimously concluded, correctly, that the rate law that best fits the points is of 1st order. Thus, the answer to  $Q_1$  is

$$\ln\left(\frac{C_A}{C_{A,0}}\right) = -kt \Leftrightarrow \ln C_A - \ln C_{A,0} = -kt_{0,9}$$

Substituting for  $t_{0,9}$ , we get

$$\ln 0.9 - \ln 1 = -0.025 t_{0,9} \Rightarrow t = \frac{-(0,105 + 0)}{-0.025} = 4.21 \text{ months.}$$

4.21 months as the shelf life of the medicine, where the kinetic constant  $k = 0.025s^{-1}$  is provided directly by Excel.

The algebraic and graphical elements in this praxeology reveal to us that the expected answer was achieved. This denotes a non-empty relation with the object  $R(u, o) \neq \emptyset$  the personal praxeologies were satisfactory, according to the conditions and restrictions present in the institution.

### Final remarks

The proposed didactic organization allowed the study of an initial question of a SRP, in which students must mobilize calculation techniques with concepts and definitions in Chemical Kinetics. An argument in favor of the didactic organization was the coherence required to fully address a question  $Q_0$ , resorting to reviews, in-depth analysis, raising questions related to the question, searching for the answer in various sources, mobilizing various resources in the web, constructing techniques that lead to the answer  $R^\heartsuit$ , without losing sight of the whole.



The use of digital resources was crucial to continuing the training of chemistry teachers. Although there were restrictions regarding teaching conditions, for example, the short period of time in the Chemical Kinetics discipline, the journey was a learning experience for these future teachers regarding the inclusion of the web in the classroom.

The praxeologies developed in SRP met one of the objectives of the study, which is to provide a reason for the existence of Calculus techniques in the construction of chemical meaning to objects such as specific speed, order and reaction equilibrium, among others.

We noted that an organization of the blocks  $[t/\tau]$  and  $[\theta/\Theta]$  involved in the topic of Chemistry and the didactic organization put into practice adjusted satisfactorily to the conditions and restrictions indicated in the EDM. This was evidenced by the didactic transposition of the Chemical Kinetics object demonstrated in the resolution of question  $Q_1$ , derived from  $Q_0$ , which would not be possible without mobilizing the techniques of differentiation and integration in chemical-mathematical praxeologies.

This organization also allowed us to see that the techniques expressed in graphical, algebraic representations, tables, etc., complement each other, respecting the domain of validity of each of them by future teachers.

They were receptive to working in a praxeological environment in which didactic organizations around the most varied chemical objects.

In this sense, the choice of an epistemological reference model resulted in a didactic model materialized in a SRP adapted to an ecological scenario with the characteristics mentioned above, such as applicationism. This showed that it is possible to break with a teaching model where disciplines are isolated and internally disjointed, which highlighted the reason for the existence of Differential and Integral Calculus in Chemistry training. In this sense, the theoretical option arising from ATD was essential to better understand the teaching conditions that can favor  $X - Y - O$  relationships in chemical kinetics training.

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