

Modeling Chemical Kinetics Graphically

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Abstract In literature on chemistry education it has often been suggested that students, at high school level and beyond, can benefit in their studies of chemical kinetics from computer supported activities. Use of system dynamics modeling software is one of the suggested quantitative approaches that could help to develop students' knowledge about chemical kinetics and chemical equilibrium and to remediate alternative conceptions. The methodology, strengths, and weaknesses of the implementation of graphical system dynamics software for modeling chemical kinetics are presented in this paper. An extension of classical graphical modeling is proposed that is closer to how chemists think about chemical reactions and that could make it easier for students to investigate chemical kinetics, especially in cases of non-trivial reaction mechanisms. The proposed approach has also useful applications in other subject areas. Illustrative examples are given throughout the paper.

Keywords Chemical kinetics · Graphical, system dynamics based modeling · computer based learning

1 Introduction

Chemical equilibrium and chemical kinetics are important concepts in general chemistry, both in secondary education (e.g., UK and the Netherlands) as well as in higher education. The study of chemical equilibrium aims at a better understanding of incomplete, reversible chemical reactions that lead to a stable mixture of reactants and products and of the factors that influence

the stability of this dynamic equilibrium. The study of chemical kinetics seeks to provide insight into the way chemical reactions proceed, both regarding the observed relationships between reaction rate and the variables that exert influence on them as well as the reaction mechanisms that could explain an experimentally determined rate law. These topics are related to each other and a kinetic approach to chemical equilibrium is quite popular in education.

Chemical equilibrium and chemical kinetics are on the other hand considered difficult topics to teach and to learn, no matter whether a qualitative or (semi-)quantitative approach has been adopted. A short review of common students' alternative conceptions and instructional strategies is included in Section 2. This is done for the purpose of underpinning the potential of graphical computer modeling of chemical kinetics with regard to addressing some of these alternative conceptions.

It has often been suggested that students can benefit in their studies of chemical kinetics and chemical equilibrium from computer supported activities. Proposed activities range from computer-assisted instruction (Hameed et al 1993; Reid et al 2000), data logging (Chairam et al 2009; Choi and Wong 2004; Cortés-Figueroa and Moore 1999), use of dedicated packages (Allendoerfer 2003; Halpern 2006; Lee and Briggs 1978), modeling with computer algebra systems and other scientific computing environments (Alberty 2004; Ferreira et al 1999; Harvey and Sweeney 1999; Maher et al 2003; Mira et al 2004; Mulquiney and Kuchel 2003; Ogilvie and Monagan 2007; Zielinski 1995), use of a graphical calculator (Cortés-Figueroa and Moore 1999, 2002) and a spreadsheet program (Blickensderfer 1990; Bruist 1998; de Levie 2002) to computer simulations (Fermann et al 2000; Halkides and Herman 2007; Huddle and White 2000; Seybold et al 1997; Solomonidou and Stavridou 2001; Stieff and Wilensky 2003) and system dynam-

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ics based computer modeling (Chonacki 2004; Kosinsky 2001; Ricci and van Doren 1997; Steffen and Holt 1993). All of these approaches attempt to make the chemical concepts accessible or comprehensive for students, for example by giving students first-hand experience with reactions through laboratory work or by simulating and visualizing the reaction dynamics and/or the dynamic nature of chemical equilibrium. Although the possibility of using system dynamics software like STELLA (www.iseesystems.com) has been advocated in the past for a quantitative approach to chemical kinetics, it seems that it has never expanded enormously and that the use of spreadsheets in kinetics courses is dominant (at least at American college chemistry faculties around the year 2000, as Miles Jr. and Francis (2002) reported).

This paper puts forward the point that one of the reasons for the unpopularity of system dynamics modeling software may be that teachers and students quickly find out that the underlying model of graphical modeling in these software environments is not so suitable for easy investigation of chemical kinetics beyond the level of studying very simple reaction systems. The methodology, strengths and weaknesses of the implementation of graphical system dynamics modeling software for mathematical modeling of chemical kinetics are discussed in Section 3.

By thinking in terms of kinetic graph theory and by introducing a new component in the graphical modeling language, which handles stoichiometric relationships, a new look of chemical reaction dynamics in the graphical interface is achieved that is on the one hand as simple as the associated system of coupled mathematical equations looks classically, but that is on the other hand expected to be more accessible to students who are less mathematically oriented or skilled. Early experiences with prototypes and discussions with Dutch chemistry teachers at secondary school level about the proposed graphical modeling approach keep this prospect upright, but systematic research into the use and evaluation of the proposed method is still lacking.

In addition, the incorporation of an easy-to-use, built-in possibility of instant change of a computer model due to a discrete-time event or of user interaction with a model ‘in real time,’ by adjusting the size of an influential variable while the model is still running, is considered an affordance of a modeling tool that promotes a better understanding of the behavior of equilibrium system when conditions change.

As examples will illustrate in Section 4, these extensions of classical graphical system dynamics based modeling could make a quantitative approach to chemical equilibrium and chemical kinetics, in which some of

the known alternative conceptions about chemical equilibrium and chemical kinetics are directly addressed, viable in chemistry education at an earlier level than higher education.

In Section 5 it is briefly illustrated that the new graphical modeling approach has applications in other scientific areas, too. This is considered essential for a general purpose system for mathematics, science, and technology education, when integration of tools is high on the list of design criteria.

Illustrative examples are given throughout the paper. The modeling tool of the computer learning environment Coach 6 is used for this purpose. Coach 6 is a versatile computer learning and authoring environment for mathematics, science and technology education at secondary level and beyond (Heck et al 2009). It provides integrated tools for measurement with sensors, control activities, digital image and video analysis, modeling, simulation, and animation. It has been translated into many languages, it is used in many countries, and the CMA Foundation (www.cma.science.uva.nl) distributes it. For this paper it is only relevant that the selected software environment supports the classical STELLA-like graphical system dynamics modeling approach as well as the proposed extensions.

2 Teaching and Learning Chemical Kinetics

All over the world, chemical equilibrium and chemical kinetics are considered difficult topics to teach and to learn, no matter whether a qualitative or (semi-)quantitative approach has been adopted. In literature on chemistry education (Banerjee 1991; Cheung et al 2009; van Driel and Gräber 2002; Ganares et al 2008; Justi 2002; Özmen 2008; Pedrosa and Diaz 2000; Quílez 2004a; Quílez-Pardo and Solaz-Portolés 1995) it is frequently discussed that teachers lack good subject matter knowledge and pedagogical content knowledge, and that many students have learning difficulties because of prevailing alternative conceptions linked to macroscopic perspectives, difficulties with the abstract and unobservable particulate/submicroscopic basis of chemistry, problems with the different meanings of terms in everyday and chemistry contexts, and insufficient mathematical abilities to cope with rate equations and computations involving the equilibrium equation. A short review of common students’ alternative conceptions and instructional strategies is given in the next two subsections.

2.1 Alternative Conceptions

Problematic concepts of chemical equilibrium appear to be all over the world the same and the most difficult ones are the dynamic and reversible nature of chemical equilibrium, the integration of several concepts concerning various domains of chemistry (structure of matter, thermodynamics, kinetics, etc.) at different levels (macroscopic, submicroscopic, symbolic), the shift of an equilibrium as a consequence of changing conditions (concentration, temperature, pressure), the equilibrium constant, and the effect of a catalyst. Numerous research studies in secondary and early tertiary education, see for example (Bergquist and Heikkinen 1990; Garnett et al 1995; Gorodetsky and Gussarsky 1986; Griffiths 1994; Hackling and Garnett 1985; Huddle and Pillay 1996; Kousathana and Tsapalis 2002; Voska and Heikkinen 2000), repeatedly showed the following alternative conceptions about the characteristics of a chemical equilibrium and the involved reaction rates:

- The rate of the forward reaction increases with time from the mixing of the reactants until equilibrium is established;
 - The forward reaction is completed before the reverse reaction commences;
 - The forward reaction rate always equals the reverse reaction rate;
 - A simple arithmetic relationship, for example concentrations of substances with equal stoichiometric coefficients are equal or $[\text{reactants}] = [\text{products}]$, exists between the concentrations of reactants and products at equilibrium;
 - When a system is at equilibrium and a change is made in the conditions, the rate of the favored reaction increases but the rate of the other reaction decreases (i.e., an equilibrium consists of two independent parts rather than one whole system);
 - Chemical equilibrium involves oscillating behavior as the concentrations of the reactants and products fluctuate;
 - Students' prior experience of reactions that proceed to completion appears to have influenced their conception of equilibrium reactions. Many students fail to discriminate clearly between the characteristics of completion reactions and reversible reactions and they often characterize chemical equilibrium as a static, balanced condition;
 - Failure to distinguish between rate (how fast) and extent (how far) of a reaction;
 - Confusion regarding amount (moles) and concentration (molarity) in an equilibrium expression or rate equation;
 - Failure to take the stoichiometry of a reaction into account when setting up an equilibrium expression or rate equation;
 - Catalysts have no effect on or decrease the reverse rate in an equilibrium reaction;
 - A catalyst only speeds up the forward reaction;
 - The equilibrium constant is independent of the temperature, but changes when the concentration of one the components in an equilibrium system is altered or when the volume of a gaseous equilibrium system is changed;
 - An increase (decrease) of temperature always means an increase (decrease) of the value of the equilibrium constant.
- Compared to chemical equilibrium, remarkably less educational research has been reported on chemical kinetics. However, the main commonly identified alternative conceptions are again linked to the fact that the introduction of reaction rate requires students to revise their initial concepts of chemical reaction and their related corpuscular ideas (van Driel 2002; Garnett et al 1995; Justi 2002):
- Every reaction occurs instantaneously and continues until all reactants are exhausted;
 - The reaction rate increases as the reaction 'gets going';
 - All reaction steps are in essence rate determining;
 - Reactions between two chemical species in a solution may be analyzed without considering the effects of other species present;
 - Failure to distinguish between rate (how fast) and extent (how far) of a reaction;
 - Amount and concentration mean the same thing for species involved in a rate equation;
 - Lack of understanding of the meaning of stoichiometry in chemical kinetics. for example, the 'lowest stoichiometry' in a chemical reaction gives the limiting reactant;
 - Difficulties in relating empirical data and mathematical models for chemical kinetics;
 - Aspects of chemical kinetics (the rate of the reaction) and thermodynamics (does reaction occur) are separate and mutually exclusive;
 - When fast moving particles collide with each other, it is very likely that these particles will bounce back, without a change or reaction occurring. The molecules simply do not have enough time to exchange atoms;
 - An increase (decrease) of temperature always means an increase (decrease) of the reaction rate;
 - A catalyst is not consumed during a chemical reaction but remains unchanged.

2.2 Instructional Strategies

Several effective ways to address and remediate students' alternative conceptions and several qualitative approaches to teach chemical equilibrium and chemical kinetics in secondary and higher education have been proposed and researched. Piquette (2001) identified four successful conceptual change instructional strategies that explicitly attempt to incorporate the four necessary conditions for conceptual change established by Posner et al (1982), that is, the dissatisfaction of the student with the currently held concept and the intelligibility, plausibility, and fruitfulness of the new concept from the student's point view. These classroom strategies include use of cooperative groups, refutational texts, analogies, and stepwise models. However, Piquette and Heikkinen (2005) concluded from self-reported strategies of teachers to address and remediate students' alternative conceptions during their lessons in the classroom that these strategies rarely included all four necessary conditions of (Posner et al 1982). Bilgin (2006) compared the effectiveness of small group discussions and traditionally designed chemistry instruction, and he concluded that the Turkish teacher students in his study gained more from group discussion compared to traditional, teacher-driven instruction. Canpolat et al (2006) also reported about the success of conceptual change approach to chemical equilibrium compared to a traditional teaching approach for Turkish undergraduate chemistry students enrolled in an introductory chemistry course. Locaylocay et al (2005) reported that the use of small group discussions, predict-observe-explain (POE) activities and other experiments, simulations, and explanations through analogies and metaphors, as suggested by (van Driel et al 1998, 1999) for upper secondary chemistry education in The Netherlands, contributed positively to the conceptual development on chemical equilibrium of their 17-18 years old Philippine bachelor students in chemistry and engineering taking a second course in general chemistry. Quílez (2004b) proposed a historical reconstruction in parallel with an experimental approach as an appropriate sequence of learning in the introduction and development of chemical equilibrium. Maia and Justi (2009) recently proposed and did empirical research on a modeling-based approach to this topic in which understanding of chemical equilibrium as a process is emphasized and secondary school students engage in making explanatory models of chemical phenomena.

All previously mentioned instructional strategies try to minimize alternative conceptions, to overcome conceptual difficulties, and to facilitate conceptual change

through the creation of an authentic learning environment that promotes active engagement of students and values 'learning how' rather than 'learning what'. The qualitative nature of these approaches is prevalent. This does not mean that there is an introduction of chemical equilibrium and chemical kinetics no role for studying quantitative aspects. Hackling and Garnett (1986) suggested that greater emphasis on the quantitative aspects of equilibrium through a variety of well-chosen examples may help students gain a clearer picture of the relationship between the concentrations of reactants and products in equilibrium. Concentration-time graphs may help students to visualize what is happening when a change is made to a system at equilibrium. All this becomes more relevant to students when modeling results can be compared with experimental data, preferably from experiments carried out by the students themselves in the laboratory, but otherwise from given data sets.

The concluding words of van Driel et al (1999) in their paper about introducing dynamic equilibrium as an explanatory model through a conceptual change approach, which treats the topic at both macroscopic and corpuscular level, includes assignments that challenge students' existing alternative conceptions, and stimulates active student engagement through small-group discussions and hands-on experiments, are in the same line of thought. The authors wrote in their discussion to anticipate students' difficulties with the idea that chemical reactions take place simultaneously in a state of equilibrium the following sentences (emphasis by the author):

"To anticipate such difficulties, teachers may engage students in a discussion, carefully addressing students' specific conceptions with respect to (i) the possibility that chemical reactions may occur even though this is not indicated by observable changes; (ii) the idea that two opposite reactions may take place at the same time and at equal rates; and, eventually, (iii) the notion that different particles of the same species may engage in different processes at the same time. *Additionally, simulations or computer animations may be used to visualize the dynamic nature of chemical equilibrium. Preferably, the relation of these simulations or animations with the chemical experiments the students have performed is discussed explicitly.*"

A few examples in this paper will illustrate this point of view about the use of computer models as a complement to an introduction of kinetic ideas about chemical reactions in which the focus is on basic understanding of the concept of reaction rate, at both a macroscopic and

a corpuscular level, as outlined by van Driel (2002). In short, the focus of this paper is to contribute to the realization of simulations of chemical kinetics that can easily be understood, used and created by students and/or teachers. It is noted that empirical studies are needed to investigate its impact, certainly because it is notoriously difficult to counteract alternative conceptions of students.

3 Studying Chemical Kinetics with Graphical System Dynamics Modeling Tools

The methodology, strengths, and weaknesses of the implementation of classical graphical system dynamics modeling software for modeling chemical kinetics is discussed in the next three subsections. The following chemical reactions and reaction mechanism are the main examples:

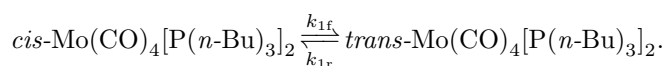
- A unimolecular chemical equilibrium system;
- A termolecular chemical reaction;
- The Michaelis-Menten reaction mechanism.

The last two examples are also used in Section 4 to exemplify the new approach.

3.1 Basics of Graphical System Dynamics Modeling

System dynamics modeling environments like STELLA and Coach 6 are examples of so-called aggregate-focused modeling tools that allow students to construct executable models of dynamics systems. Such tools use aggregated amounts, i.e., quantities (commonly called levels or stocks) that change over time through physical inflows and outflows, as the core components of a specific system. Not only flow of material, but also information flow determines the system's behavior over time. Information flow is best understood as an indication of dependencies or influences between variables in the model. These relations are made explicit in the form of mathematical formulas and graphical or tabular relationships. The variables involved can be levels, flows, parameters, and auxiliary variables.

The level-flow modeling language has a graphical representation in which a user can express his or her thoughts about the behavior of a dynamic system and these ideas are then translated into more formal mathematical representations. An example of a graphical model, implemented in the modeling tool of Coach 6, is depicted in Fig. 1. It represents the chemical kinetics of the isomerization



Four types of variables are present in this graphical model and they are differently iconified:

1. A parameter (temperature T);
2. Auxiliary variables (reaction rate constants k_{1f} , k_{1r});
3. Levels (concentrations $[cis]$, $[trans]$);
4. Flows (rates of change of concentrations r_{1f} , k_{1r}).

Information arrows indicate dependencies between these variables: For example, the arrows from T to k_{1f} and k_{1r} indicate that the author of the model wanted to express that the forward rate constant k_{1f} and the reverse rate constant k_{1r} both depend on the temperature T at which the reaction takes place. The following mathematical expressions have been derived from (Bengali and Mooney 2003) and used in the simulation:

$$k_{1f} = T \cdot 10^{8.87 - \frac{5195}{T}}, \quad k_{1r} = T \cdot 10^{8.78 - \frac{5394}{T}}, \quad (1)$$

where temperature T has been specified here in Kelvin (instead of $^{\circ}\text{C}$) and rate constants are in s^{-1} .

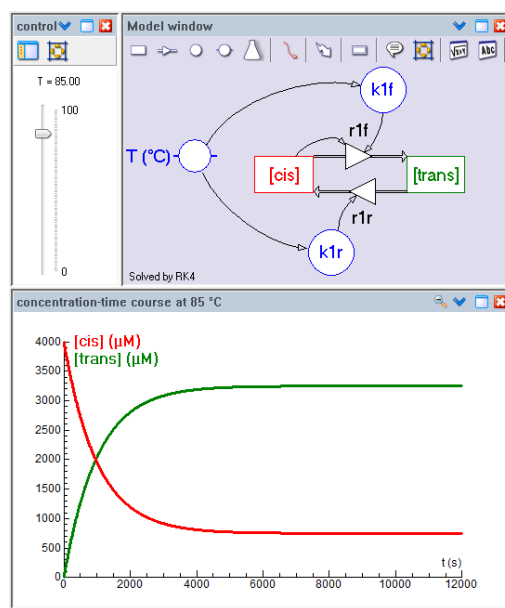


Fig. 1 Screen shot of the graphical model of cis-trans isomerization, and concentration-time graphs in a simulation starting from pure *cis*- $\text{Mo}(\text{CO})_4[\text{P}(n\text{-Bu})_3]_2$ at 85°C .

The model window in the upper part of the screenshot in Fig. 1 illustrates what graphical modeling is all about: an author (curriculum designer, teacher, or student) literally ‘draws’ variables representing physical quantities or mathematical entities and the relations between them. The graphical model can be considered as a representation at conceptual level of the system dynamics, where physical flows represent rates of changes and information arrows indicate dependencies between quantities. Once the sketch of the model

had been made, the details of a model, that is, the algebraic formulas needed to build up the system of equations, can be filled in by clicking on the icons and be hidden again. The general picture of the model is considered most important for understanding. In this particular example, the graphical model almost literally presents a chemical equilibrium.

A graphical system dynamics model corresponds in mathematical terms with a system of differential equations or finite difference equations. Under the assumption that only elementary, unimolecular reaction steps are involved, the graphical model of Fig. 1 represents the following coupled differential equations for the rate of change in the concentrations of the three species involved:

$$\frac{d[cis]}{dt} = -r_{1f} + r_{1r}, \quad \frac{d[trans]}{dt} = r_{1f} - r_{1r}, \quad (2)$$

where $r_{1f} = k_{1f} \cdot [cis]$, $r_{1r} = k_{1r} \cdot [trans]$. But the graphical model represents in fact more: it also represents an automatically generated computer program that solves this system numerically and allows the user to simulate the behavior of the modeled reaction system and to interpret the modeling results.

3.2 Strengths of Classical Graphical Modeling Tools

Research indicates the following:

- Despite the apparent difficulties of computer modeling in an inquiry approach, students can overcome the problems in a modeling task (Jacobson and Wilensky 2006; Sins 2006; Stratford et al 1998);
- A graphical modeling tool supports novice modelers better in constructing their own models and in understanding other people’s models than modeling tools that require their users to work with textual representations in which they have to explicitly write down a sort of equation or a piece of programming code (Löhner 2005).
- “Creating dynamic models has great potential for the use in classrooms to engage students in thought about science content, particularly in those thinking strategies best fostered by dynamic modeling: analysis, relational reasoning, synthesis, testing and debugging, and making explanations.” (Stratford et al 1998, p. 229) Through modeling, students can acquire model-based scientific reasoning skills (Milrad et al 2003) and learn about the specific domain (Ergazaki et al 2005; Schecker 1998);
- Students can get more insight in the behavior of a dynamic system by running an executable model (Wilensky and Resnick 1999; Westra 2008);

- Valid, feasible, and effective learning and teaching strategies about dynamic behavior using modeling and systems thinking in authentic practices can be realized (Spector 2000; Westra 2008).

In the context of chemical kinetics, students are immediately confronted in a simulation of a reaction system with potential alternative conceptions. In the first example of cis-trans isomerization, a student can for instance observe in the graphs of the lower part of Fig. 1 that (i) it takes time before the equilibrium is reached; and (ii) at equilibrium, the concentrations of cis- and trans-complexes are not necessarily equal.

More alternative conceptions about chemical equilibrium, which were listed in Subsection 2.1, can be addressed when one looks at rate-time and net rate-time graphs of the chemical equilibrium shown in Fig. 2.

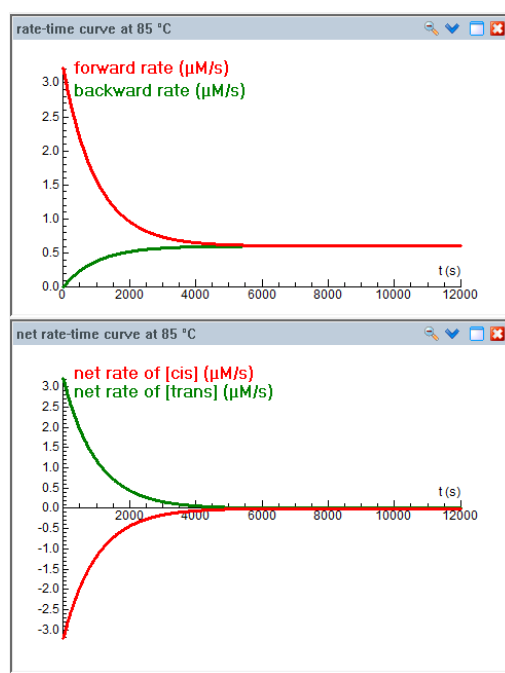


Fig. 2 Rate-time and net rate-time graphs for cis-trans isomerization at 85 °C.

Some of the points that a student could notice in the graphs displayed in Fig. 2 are:

- The rate of the forward reaction decreases with time until equilibrium is reached (and not to completion);
- The rate of the reverse reaction increases with time until equilibrium is reached;
- The forward and reverse reaction rates are not always the same;
- The forward and reverse reaction start at the same time;

- A system in equilibrium does not mean that the reactions ceased;
- A system in equilibrium means that the net rate of concentrations is zero and that the forward- and reverse-reaction rates are equal.

Executable models offer students the opportunity to observe the effects of changing the model or, less dramatically, of changing the parameter values and initial conditions. In fact, this has already been anticipated in the model shown in Fig. 1: The introduction of temperature T , the change of which has been simplified by the incorporation of a corresponding slider in the activity, is motivated by the wish to investigate the effect of temperature on the reaction system. Fig. 3 shows the results of a simulation of the isomerization at a lower temperature, namely at 80 °C. The graphs of the previous simulation at a temperature of 85 °C are shown in gray at the background to support easy comparison.

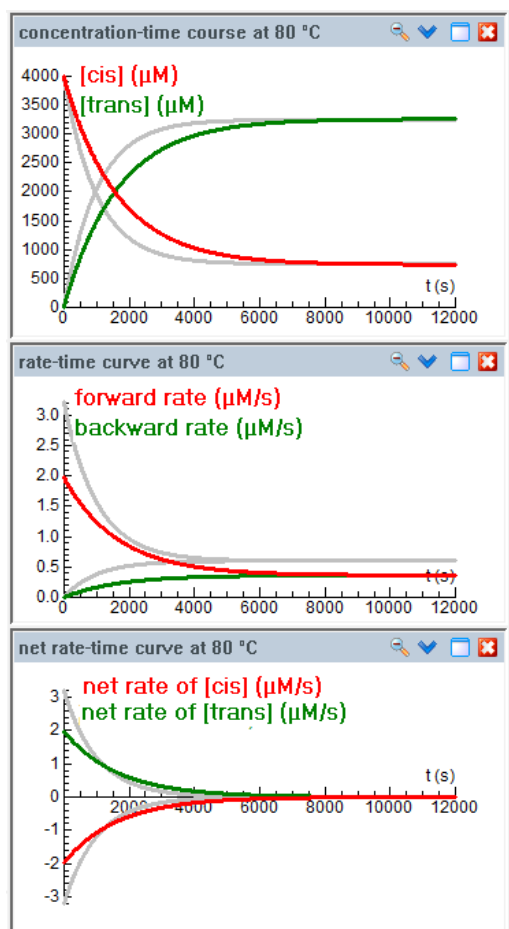


Fig. 3 concentration-time, rate-time, and net rate-time graphs for cis-trans isomerization at 80 °C.

A student could discover from the graphs in Fig. 3 that changing the temperature

- does not necessarily mean that the concentrations at equilibrium are affected. In other words, changing the temperature does not mean that the equilibrium constant is affected.
- may change the magnitudes of the reaction rate constants without changing their ratio. In such case it only affects the time needed for the system to reach equilibrium;
- may change the absolute magnitudes of the forward and reverse rates, also at equilibrium.

It must be emphasized that these conclusions only hold because the isomerization is almost thermoneutral. It is actually a misconception to believe that the equilibrium constant is independent of temperature. When a chemical equilibrium is chosen in which activation energies of the forward and backward reactions differ substantially, a change in temperature will lead to a noticeable shift of the equilibrium.

By changing the initial concentrations of the cis- and trans-complex it can easily be verified that the system will always reach the same equilibrium concentrations, no matter what the starting concentrations are. By playing with the forward and reverse reaction rate constants, a student could discover that while the absolute magnitudes of the forward and reverse rate constants do not control the final equilibrium, equilibrium concentrations are controlled by the ratio of the rate constants.

3.3 Weaknesses of Classical Graphical Modeling Tools

The graphical modeling of chemical kinetics illustrated by the example of cis-trans isomerization is rather simple. Other examples of reaction systems that can be dealt with in this way are unimolecular. Any other type of reaction system would lead for stoichiometric reasons to a disconnected, from chemical point of view incomprehensible graphical model. The basic example used in the paper to illustrate this is the gas-phase oxidation of nitric oxide: $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$. This example of a third-order rate reaction system has been chosen because it is a classical illustration of the fact that reaction rate data alone are not sufficient to determine the underlying reaction mechanism. The following three mechanisms have been identified by Tsukuhara et al (1999), which all lead to third-order reaction kinetics:

- A termolecular reaction, i.e., two molecules of NO and one O_2 collide and form a transient complex, which in a single step forms two molecules of NO_2 ;

- A pre-equilibrium mechanism with dimer of NO as an intermediate;
- A pre-equilibrium mechanism with NO_3 as an intermediate.

The graphical model in Fig. 4 represents the termolecular reaction mechanism through the following coupled differential equations for the rate of change in the concentrations of the three species involved:

$$\frac{d[\text{NO}]}{dt} = -2r, \quad \frac{d[\text{O}_2]}{dt} = -r, \quad \frac{d[\text{NO}_2]}{dt} = 2r, \quad (3)$$

where $r = k \cdot [\text{NO}]^2 \cdot [\text{O}_2]$ and the rate constant is given by the Arrhenius-type equation $k = 1.2 \times 10^3 \times 10^{230/T}$. It also gives information about the units used.

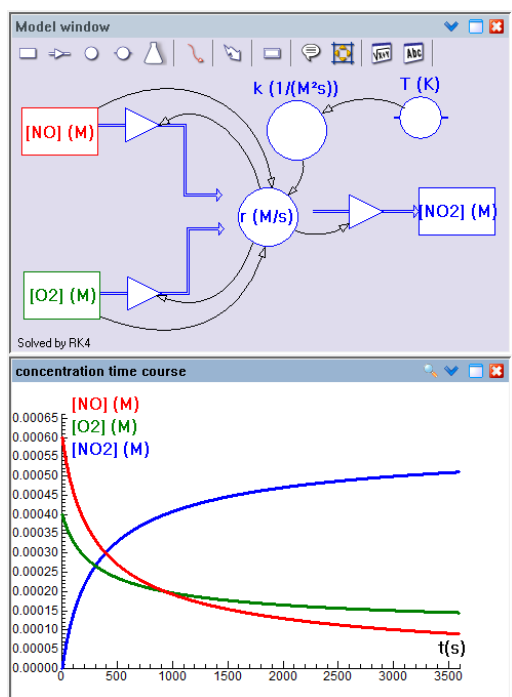


Fig. 4 Screen shot of the graphical model and simulation of the termolecular reaction $2\text{NO} + \text{O}_2 \xrightarrow{k} 2\text{NO}_2$.

Although the flow arrows, which represent the rate of change of concentrations, have been drawn in the graphical model such that the reader is given the impression of a chemical reaction in the form of a chemical network or a metabolic network, all of a sudden the icons that represent concentrations have become disconnected. The reason that one cannot directly draw physical flow arrows from reactants toward products is that the meaning of the graphical modeling tool, which is based on the level-flow model in which the sum of inflows in a level variable is by definition equal to the sum of outflows of this level variable (the so-called ‘principle

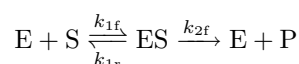
of flow balance’), does not lead to the correct coupled differential equations. In other words, if both an arrow from $[\text{NO}]$ toward $[\text{NO}_2]$ and an arrow from $[\text{O}_2]$ toward $[\text{NO}_2]$ were drawn, this would mean that the increase in concentration of NO_2 over time is equal to the sum of the decrease in concentration of NO over time and the decrease in concentration of O_2 over time. This is from chemical point of view incorrect for the given reaction. Moreover, the implication that both flows can be independently regulated is not true in chemical kinetics.

In fact, due to the selected graphical modeling approach of level-flow diagrams, which is based on a metaphor of water tanks and valves, the diagrams for bi- and termolecular chemical reactions are inevitably disconnected. Forrester, the founder of the system dynamics and level-flow modeling approach in the context of socio-economic systems, was aware of this limitation and wrote (Forrester 1961, p. 70):

“It should be noted that flow rates transport the content of one level to another. Therefore, the levels within one network must all have the same kind of content. Inflows and outflows connecting to a level must transport the same kind of items that are stored in the level. Items of one type must not flow into levels that store another type. For example, the network of materials deals only with material and accounts for the transport of the material from one inventory to another. Items of one type must not flow into levels that store another type.”

Clearly, chemical reactions do not meet this ‘principle of material consistency’ in the structure of a graphical model that is written in terms of levels interconnected by rates of flow: In a bimolecular reaction, two molecules may react to result in one molecule, that’s chemistry! On the other hand, it must be stressed that the problem only lies in the translation of the graphical model into the coupled differential equations that describe the kinetics of the chemical reaction.

The fact that the conventions of a classical graphical system dynamics modeling tool, which state how the coupled differential equations or difference equations are to be generated from the graphical representation, are inconvenient for chemical kinetics comes even more to the fore when complex chemical reaction networks are modeled instead of elementary reactions. The following example, which is the simplest (‘Michaelis-Menten’ and ‘Briggs-Haldane’) mechanism for a two-step enzyme-catalyzed reaction, will illustrate this:



where E, S, ES, and P are the unbound enzyme, substrate, intermediate enzyme-substrate, and product, respectively. One of the things students learn from or need to accept in this mechanism is that a species can simultaneously be involved in more than one reaction: the intermediate enzyme-substrate can both form a product as well as the original substrate. All reaction steps are considered as elementary reactions. See (Bruist 1998) and (Halkides and Herman 2007) for simulations of the reaction system with a spreadsheet, and (Mulquiney and Kuchel 2003) for simulations with a computer algebra system. A steady-state approximation is used in most cases to simplify the algebraic and computational work. The graphical model that represents this enzyme-catalyzed reaction without using this approximation is shown in Fig. 5.

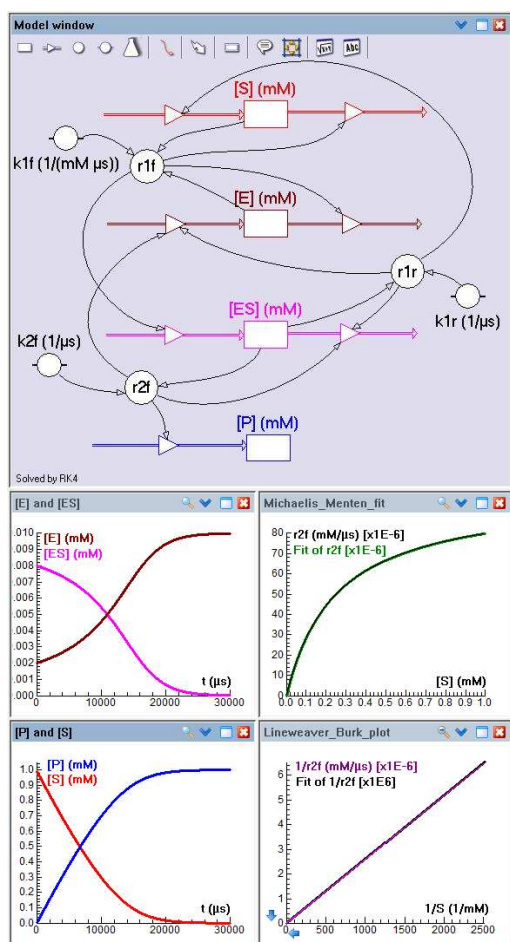


Fig. 5 Screen shot of the graphical model and simulation of the $E + S \xrightleftharpoons[k_{1r}]{k_{1f}} ES \xrightarrow{k_{2f}} E + P$ reaction system.

The graphical model represents the following coupled differential equations for the rate of change in the

concentrations of the four species involved and it also gives the reader information about the units used for concentration and rate of change of concentration:

$$\begin{aligned} \frac{d[S]}{dt} &= -r_{1f} + r_{1r}, & \frac{d[E]}{dt} &= -r_{1f} + r_{1r} + r_{2f}, \\ \frac{d[ES]}{dt} &= r_{1f} - r_{1r} - r_{2f}, & \frac{d[P]}{dt} &= r_{2f}, \end{aligned} \quad (4)$$

where $r_{1f} = k_{1f} \cdot [E] \cdot [S]$, $r_{1r} = k_{1r} \cdot [ES]$, $r_{2f} = k_{2f} \cdot [ES]$.

Values of kinetic parameters have been taken from (Halkides and Herman 2007), which presents in fact a toy model of enzyme kinetics. Its unrealistic character is taken for granted because the graphical model of the reaction mechanism can still be used to convince students that the steady-state approximation makes sense. For example, using the computed time course of the enzyme-catalyzed reaction one can apply the regression tool in Coach 6 to find values of the Michaelis-Menten constant K_m and of the maximum velocity V_{max} by nonlinear regression and one can verify that these values are close to the theoretical values $K_m = (k_{1r} + k_{2f})/k_{1f}$ and $V_{max} = k_{1f} \cdot [E]|_{t=0}$. Values of kinetic parameters found by nonlinear regression can also be compared with values obtained from a Lineweaver-Burk plot. Furthermore, the simulation tool can be used to discuss the validity of the steady-state approximation in the kinetic model.

This example makes clear that a standard, rather simple chemical reaction network already leads to a disconnected graphical model in which the chemical reaction mechanism is obscured by the spaghetti (and meatballs) tangle of arrows and boxes. When the reaction mechanism of the enzyme-catalyzed reaction becomes more complicated, the corresponding graphical model that represents the chemical kinetics readily gets snarled up, to put it mildly. This happens, for example, when the urea cycle (Mulquiney and Kuchel 2003) is studied, a reaction network in which more than one substrate is available for the enzyme, more than one product is formed, and more than one enzyme may be involved.

In summary, the following weaknesses have been identified and exemplified in using the classical graphical system dynamics modeling and simulation approach to chemical kinetics:

- Except for simple unimolecular reaction systems, the graphical models based on the traditional level-flow metaphor do not present a clear overview of the chemical reaction mechanism, but instead they have often an incomprehensible spaghetti (and meatballs) tangle of arrows and boxes. Especially the number of information arrows can be overwhelming.

- In most graphical models of chemical reaction systems levels represent concentrations of chemical species and flows represent rates of change of the species. Because the principle of flow balance holds in the level-flow metaphor, this means that graphical models of chemical reactions must be predominantly models in which levels are disconnected. Such a graphical model does not give any indication anymore of which species are reactants and which species are products of chemical reactions or reaction steps. The reaction mechanism is not clearly revealed in the graphical model.
- Although many graphical modeling tools offer user interface elements such as knobs and sliders to set parameter values and initial conditions, not all of them allow their users to change values during a simulation run. Thus, many modeling tools do not offer much to investigate external effects on the kinetics of a chemical reaction system such as addition of extra reactants, depletion of products, and so on, in an exploratory approach.

These difficulties in graphical modeling of chemical kinetics with level-flow based system dynamics modeling and simulation software are known and suggestions for improvement have been made. For example, the key ideas of chemical kinetics and thermodynamics have been expressed in a bond graph approach (Cellier 1991, ch. 9) and the level-flow metaphor has been replaced in (Elhamdi 2005; LeFèvre 2002, 2004) by the so-called kinetic process metaphor, which was inspired by graphical models of biochemical reaction networks and metabolic pathway systems. But these alternatives for and extensions of the traditional level-flow metaphor are at the level of system dynamics specialists and they are too complicated for use in chemistry education at high school level or first-year undergraduate level. In the next section, a much simpler graphical approach to modeling of chemical reactions is presented that covers the basics of chemical kinetics.

4 Improved Graphical Modeling of Chemical Reaction Systems

A solution to most of the previously identified problems with classical graphical system dynamics modeling is presented in the form of an improved approach of chemical reactions based on a graph theoretic description of reaction kinetics. To this end, a new icon, viz. the Erlenmeyer flask symbol, is added to the graphical modeling tool. After a formal underpinning of the proposed extension, examples will illustrate the new approach to chemical kinetics. In Section 5, other applications of the

Erlenmeyer icon will be presented and this motivates the more general reference to this icon as a ‘process’ instead of a more chemistry related name like ‘reaction.’ In Subsection 4.3, the usefulness of adding interactivity elements such as sliders, buttons, and event controls to the graphical model tool will be illustrated.

4.1 Adding a Process Element to the Modeling Tool

The improved graphical modeling approach of chemical reactions is based on a graph theoretic description of reaction kinetics that is similar to the oriented species-reaction graph introduced in (Craciun and Feinberg 2006) and the directed bipartite graph of a reaction network developed by Vol’pert and Ivanova (1987) [see also (Vol’pert and Hudjaev 1985, ch. 12)], more thoroughly analyzed in (Ermakov and Goldstein 2002; Mincheva and Roussel 2007), and for example implemented in a computer simulation and visualization environment for metabolic engineering (Qeli 2007). The graphical approach will be exemplified by the termolecular gas-phase oxidation of nitric oxide, which was also discussed in Subsection 3.3, $2\text{NO} + \text{O}_2 \xrightarrow{k} 2\text{NO}_2$, with the associated system of differential equations:

$$\frac{d[\text{NO}]}{dt} = -2r, \quad \frac{d[\text{O}_2]}{dt} = -r, \quad \frac{d[\text{NO}_2]}{dt} = 2r, \quad (5)$$

where for a given reaction rate constant k holds

$$r = k \cdot [\text{NO}]^2 \cdot [\text{O}_2]. \quad (6)$$

For a thorough description of the improved graphical approach it is wise to linger over chemical notation of reactions and reaction networks and its meaning. A *chemical reaction network* is formally defined (Feinberg 1979) as a triple $(\mathcal{S}, \mathcal{C}, \mathcal{R})$ that consists of a finite set of chemical species (reactants and products of the reaction steps) \mathcal{S} , a finite set of complexes (the objects before and after the reaction arrows) \mathcal{C} , and a set of reactions $\mathcal{R} \subset \mathcal{C} \times \mathcal{C}$ with the properties that $(y, y) \notin \mathcal{R}$ for any $y \in \mathcal{C}$ and that for each $y \in \mathcal{C}$ there exists a $y' \in \mathcal{C}$ such that $(y, y') \in \mathcal{R}$ or such that $(y', y) \in \mathcal{R}$. In plain words this means that each species must appear on the left- or right-hand side of at least one reaction step, that there are no superfluous species, that no complex reacts to itself, and that no complex is isolated. Henceforth the more suggestive $y \rightarrow y'$ is used in place of (y, y') when $(y, y') \in \mathcal{R}$ and equilibrium reactions are considered as two separate irreversible reaction steps. In case of the reaction $2\text{NO} + \text{O}_2 \xrightarrow{k} 2\text{NO}_2$ the sets are equal to $\mathcal{S} = \{\text{NO}, \text{O}_2, \text{NO}_2\}$, $\mathcal{C} = \{2\text{NO} + \text{O}_2, 2\text{NO}_2\}$, and $\mathcal{R} = \{2\text{NO} + \text{O}_2 \xrightarrow{k} 2\text{NO}_2\}$. The *stoichiometric coefficient* of a species s in a complex y is the positive

integer in front of the species if it is contained in the complex and it is equal to zero otherwise. For example, in the complex $2\text{NO} + \text{O}_2$ the stoichiometric coefficients of NO , O_2 , and NO_2 are 2, 1, and 2, respectively. The *kinetic graph* of the chemical reaction network (\mathcal{S} , \mathcal{C} , \mathcal{R}) is a directed graph in which the set of vertices is partitioned into two sets, namely, a set of species nodes and a set of reaction nodes. There is one species node for each species in the network and one reaction node for each (irreversible) reaction in the network. Each directed edge of the kinetic graph joins a species node to a reaction node or a reaction node to a species node (so the kinetic graph is a directed bipartite graph) according to the following prescription: Consider some reaction $y \rightarrow y'$ in \mathcal{R} . There is one directed edge toward the reaction node $y \rightarrow y'$ coming from each node of a species present in the complex y of the reaction. There is one directed edge from the reaction $y \rightarrow y'$ toward each node of a species present in the complex y' . Otherwise stated, arrows are drawn for each reaction in the network from the reactants toward the reaction node and from the reaction node toward the products created in the reaction. The kinetic graph of the reaction $2\text{NO} + \text{O}_2 \xrightarrow{k} 2\text{NO}_2$ is shown in Fig. 6.

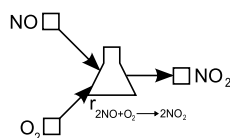
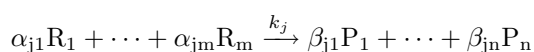


Fig. 6 The kinetic graph of the reaction $2\text{NO} + \text{O}_2 \xrightarrow{k} 2\text{NO}_2$.

Here, a species node is represented by a square and a reaction node is suggestively represented by an Erlenmeyer flask symbol. The directed bipartite graph is called a kinetic graph because it also incorporates by definition information about the kinetics of the chemical reaction. This information is about (contributions to) rates of change of species involved in the given reaction, based on the stoichiometric coefficients associated with the reaction: In this particular example, Formula (6) holds. In general, the elementary j^{th} reaction in a reaction network



has a reaction rate

$$r_j = k_j \cdot [\text{R}_1]^{\alpha_{j1}} \cdot \cdots \cdot [\text{R}_m]^{\alpha_{jm}}, \quad (7)$$

where k_j is the kinetic coefficient and $[\text{R}_i]$ is the concentration of reactant R_i . Normally $\sum_m \alpha_{jm}$, which is the number of reactants involved in the j^{th} reaction step, is a natural number less than or equal to 3. The time

course of the concentrations depends on the reaction rates r_j : For example, the dynamics of $[\text{R}_i]$ and $[\text{P}_i]$ in the above reaction depends on rate r_j in the form

$$\frac{d}{dt}[\text{R}_i] = -\alpha_{ji}r_j, \quad \frac{d}{dt}[\text{P}_i] = \beta_{ji}r_j. \quad (8)$$

In the kinetic graph, there exists a directed edge from the species node R_k toward the j^{th} reaction node if $\alpha_{jk} > 0$ and similarly a directed edge from the j^{th} reaction node toward the species node P_k if $\beta_{jk} > 0$. Note that this formalism does not exclude the situation that reactants and products involve the same species (for example, in auto-catalytic reactions).

The kinetic graph of a chemical reaction network clearly suggests how the classical level-flow formalism of graphical system dynamics modeling tools could be extended to function well for chemical reaction networks: A graphical icon for a reaction, say an Erlenmeyer flask symbol, must be added to the formalism and then levels can represent concentrations of species involved in the reaction network, provided that flows are between level icons and Erlenmeyer symbols. Inflows of an Erlenmeyer symbol originate from reactants and outflows of an Erlenmeyer symbol point at products in the chemical reaction that is symbolized by the Erlenmeyer flask. The Erlenmeyer symbol also represents the dynamics of the levels connected with it via the stoichiometry of the reaction: The Erlenmeyer symbol is linked to a formula for the reaction rate, which depends on the kinetic coefficient, the concentrations of reactants and their stoichiometric coefficients, and the stoichiometric coefficients determine the formulas for the inflows and outflows of the Erlenmeyer symbol.

The improved graphical modeling of chemical reaction, based on kinetic graphs, leads to much clearer visual representations of chemical reaction networks for the following reasons:

- Levels, flows, and process elements give a visual overview of the reaction mechanism;
- The stoichiometry of a reaction already determines the formulas for the inflows and outflows so that there is no need to use information arrows from the reaction node toward these flows.

The examples in the next subsection will illustrate that the new graphical models resemble more the pictures that chemists already draw for ages to illustrate reaction mechanisms. This is also the reason that students do not need to be introduced the kinetic graphs in the same formal way as was done in this subsection to underpin the proposed approach; a more informal introduction suffices to work with it in a sensible way.

4.2 Some Illustrative Examples

The improved graphical modeling approach has been implemented in Coach 6 and the first example in this subsection is the same as the last example discussed in Subsection 3.3, namely, the two-step enzyme-catalyzed reaction $E + S \xrightleftharpoons[k_{1r}]{k_{1f}} ES \xrightarrow{k_{2f}} E + P$. This offers the reader the opportunity to compare the graphical model presented in Subsection 3.3 (Fig. 5) with the model based on the improved formalism (Fig. 7). The reader can also compare the graphical model of enzyme kinetics in Fig. 7 with the equivalent graphical model in Fig. 8, taken from (Lee and Yang 2008), that has been implemented in Powersim (www.powersim.no), another classical graphical modeling tool, and that does not reflect anymore the underlying reaction mechanism.

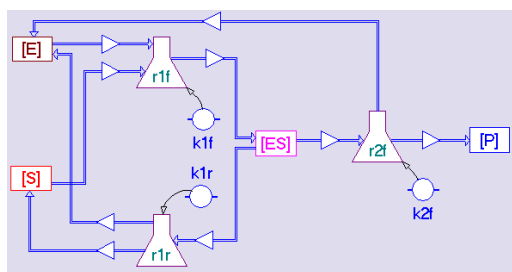


Fig. 7 Screen shot from the improved graphical model of the $E + S \xrightleftharpoons[k_{1r}]{k_{1f}} ES \xrightarrow{k_{2f}} E + P$ network.

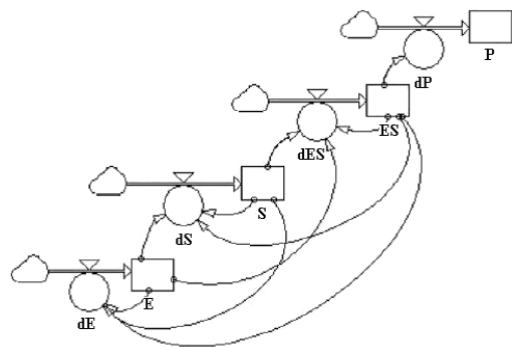
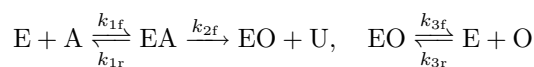


Fig. 8 A model of $E + S \xrightleftharpoons[k_{1r}]{k_{1f}} ES \xrightarrow{k_{2f}} E + P$ in Powersim.

Because one of the goals was to make graphical system dynamics modeling of chemical kinetics viable in cases of more complicated reaction mechanisms, a second example is shown in Fig. 9, which would not be as comprehensible in a classical system dynamics graphical approach. It is the following enzyme-catalyzed reaction mechanism, taken from (Kuchel et al 1977; Maher et al 2003; Mulquiney and Kuchel 2003), for the hydroly-

ysis of arginine to ornithine and urea catalyzed by the hydrolytic enzyme arginase, which is only one step of the urea cycle:



where A, U, and O denote arginine, urea, and ornithine, respectively. The graphical model represents the following coupled differential equations for the rate of change in the concentrations of the species involved:

$$\begin{aligned} \frac{d[A]}{dt} &= -r_{1f} + r_{1r}, & \frac{d[E]}{dt} &= -r_{1f} + r_{1r} - r_{3r} + r_{3f}, \\ \frac{d[EA]}{dt} &= r_{1f} - r_{1r} - r_{2f}, & \frac{d[EO]}{dt} &= r_{2f} - r_{3f} + r_{3r}, \\ \frac{d[U]}{dt} &= r_{2f}, & \frac{d[O]}{dt} &= r_{3f} - r_{3r}, \end{aligned} \quad (9)$$

where

$$\begin{aligned} r_{1f} &= k_{1f} \cdot [E] \cdot [A], & r_{1r} &= k_{1r} \cdot [EA], & r_{2f} &= k_{2f} \cdot [EA], \\ r_{3f} &= k_{3f} \cdot [EO], & r_{3r} &= k_{3r} \cdot [E] \cdot [O]. \end{aligned}$$

Values of kinetic parameters can be taken from (Kuchel et al 1977). The graphical model, the construction of which is envisioned to be doable by upper secondary school chemistry students or first-year undergraduate chemistry students, is very informative about the reaction mechanism. Thus, chemical kinetics of more realistic reaction mechanisms is not expected to be beyond the level of students anymore.

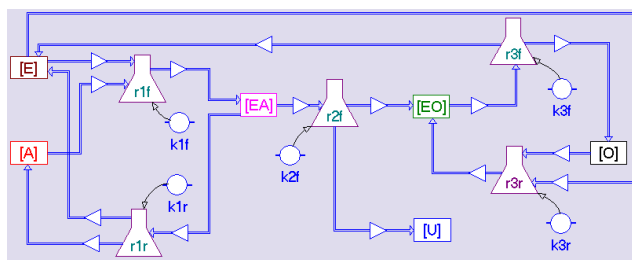


Fig. 9 Screen shot of the graphical model of $E + A \xrightleftharpoons[k_{1r}]{k_{1f}} EA \xrightarrow{k_{2f}} EO + U, EO \xrightleftharpoons[k_{3r}]{k_{3f}} E + O$ network.

4.3 Interactivity in Chemical Kinetics Modeling

Le Châtelier's Principle is often used in textbooks to explain how a system in equilibrium responds to an external perturbation such as addition of a reactant, depletion of a product, change in pressure or temperature, and so on. Many research studies (Canpolat et al 2006; Cheung et al 2009; Quílez 2004a; Quílez-Pardo and Solaz-Portolés 1995; Tyson et al 1999; Voska and

Heikkinen 2000) reported that teachers and students have difficulties in applying this principle appropriately and accurately. A common mistake is to reason that increasing the concentration of one of the reactants will result in an increase of the forward rate and a decrease of the reverse rate, because the forward reaction is favored over the reverse one. Such misinterpretations and misapplications of Le Châtelier's Principle have brought Cheung et al (2009) and others (Allsop and George 1984; Quílez 2004a) to question the appropriateness of this principle in chemistry education for predicting the direction in which a chemical equilibrium will shift when it is disturbed. In a qualitative or semi-quantitative approach to chemical equilibrium phenomena there is hardly any other instructional strategy than applying Le Châtelier's Principle or reasoning with the Equilibrium Law. But then one better resists the temptation to combine this thermodynamic approach to chemical equilibrium, which does not make statements about forward or backward reactions, with a kinetic approach to chemical equilibrium based on the 'law of mass action.' A quantitative approach seems more suitable for discussing how chemical equilibrium is reached or how it changes when conditions change. This holds especially when a modeling and simulation environment offers tools to interactively change conditions during a simulation and/or allows an easy implementation of event-handling such as response to a sudden change in concentration, temperature, and so on. Furthermore, Solomonidou and Stavridou (2001) pointed at the potential of computer simulations and animations to help students construct appropriate conceptions about Le Châtelier's Principle and the equilibrium constant law.

Interactive change of initial conditions as well as event-handling of sudden changes during a simulation run have been implemented in the Coach 6 environment and are exemplified with the equilibrium shift of a gas mixture of hydrogen, iodine, and hydrogen as a response to a sudden change in hydrogen concentration and temperature. The reaction system under consideration is $\text{H}_2 + \text{I}_2 \xrightleftharpoons[k_{1r}]{k_{1f}} 2\text{HI}$, where second-order rate kinetics is assumed given by the following coupled differential equations for the rate of change in the concentrations of the three species involved:

$$\begin{aligned} \frac{d[\text{H}_2]}{dt} &= -r_{1f} + r_{1r}, & \frac{d[\text{I}_2]}{dt} &= -r_{1f} + r_{1r}, \\ \frac{d[\text{HI}]}{dt} &= r_{1f} - r_{1r}, \end{aligned} \quad (10)$$

where $r_f = k_f \cdot [\text{H}_2] \cdot [\text{I}_2]$, $r_r = k_r \cdot [\text{HI}]^2$, and the Arrhenius equations for the rate constants are given (Graven 1956) for temperature T (in $^\circ\text{K}$) by $k_r =$

$7.18 \times 10^{12} \times e^{-24775/T}$ and $k_f = 1.23 \times 10^{12} \times e^{-20646/T}$. It follows from these equations that the forward gas phase reaction is exothermic. Figure 10 is a screenshot of a simulation run based on this kinetic model.

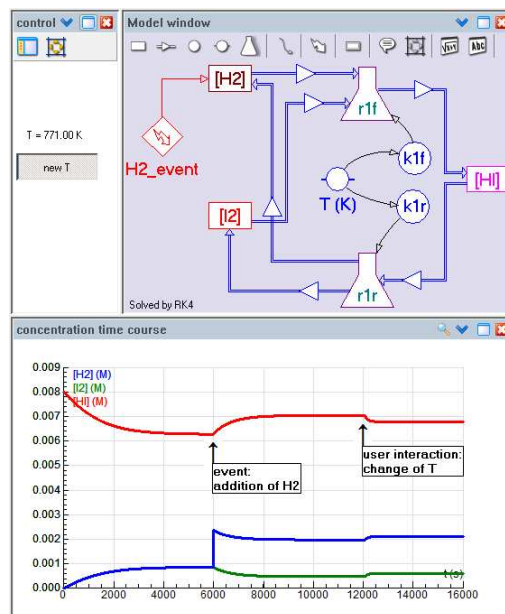


Fig. 10 Screen shot of the graphical model of the $\text{H}_2 + \text{I}_2 \xrightleftharpoons[k_{1r}]{k_{1f}} 2\text{HI}$ equilibrium reaction and a simulation with user interaction and an event during execution of the model.

Figure 10 shows a simulation run starting with only a nonzero concentration of HI at a temperature $T = 721^\circ\text{K}$. After 6000 seconds the concentration of H_2 is suddenly raised by 0.002 M, which has an immediate effect on the concentration time course. This sudden change is realized in the graphical model by introduction of an event (iconized by the thunderbolt symbol). The code behind this event icon is very simple: `Once t>6000 then [H2] := [H2] + 0.002`. The effect is that the equilibrium which was almost established is shifted right to less dissociation of hydrogen iodine. After a new equilibrium has been established established equilibrium, the user has pressed about 12000 seconds after the start of the reaction the button in the control panel to cause a sudden raise in temperature of 50°K . The effect is that the equilibrium shifts to the left, that is, more hydrogen iodide dissociates again. This is in agreement with the Le Châtelier Principle that states that increasing the temperature will shift the equilibrium to the left because the forward reaction is exothermic. Although the kinetic and thermodynamic approaches to chemical equilibrium phenomena are of different nature, results obtained by either method complement each other.

5 Other Applications

Graphical modeling and simulation tools have other applications in chemistry education, for example in modeling and simulating acid-base titration curves (Heck et al 2010), and in other science fields [see for example (van den Berg et al 2008)]. Although no attention has been paid to it in this article so far, it is worth mentioning that the improved graphical modeling approach also has applications beyond chemical kinetics. This aspect is important in education because it would most probably not be worth the effort to add new elements to a general purpose graphical modeling tool if they were only relevant for a small part of the science curriculum. Students and teachers have to use their time effectively and economically. Much is won when students and teachers can use one and the same modeling environment for many science subjects. Then they have ample opportunities to grow into their roles of knowledgeable and skilled modelers of natural phenomena.

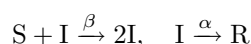
We discuss two examples of usage of the new graphical formalism that are conceptually rather close to the chemical context of this paper. But one must realize that examples of completely different nature, such as for instance the modeling of the height of beer foam (Heck 2010), could be presented as well.

The first example illustrates that quantitative pharmacokinetic models can be conveniently treated through the new graphical formalism. Fig. 11 shows a graphical model and simulation of the pharmacokinetics of the metabolism of ecstasy in the human body [taken from high school lesson materials “Swilling, Shooting, and Swallowing,” see also (Heck 2007)]: The improved graphical modeling approach provides a connected diagram that indicates the flow of the pharmacoin in the body over time.

The second example is the classical SIR (susceptible-infected-recovered) epidemic model, also known as the Kermack and McKendrick (1927) model:

$$S' = -\beta IS, \quad I' = \beta IS - \alpha I, \quad R' = \alpha I. \quad (11)$$

The origin of the above system of differential equations can be a description of an epidemic though a compartmental model. Alternatively, the SIR model can be considered, like a chemical reaction network, as a two-step process with the following mechanism:



The first step in the process is linked with contact between healthy and infected persons, which leads to two infected persons. When an infected person has on average β contacts per day and infected persons are on

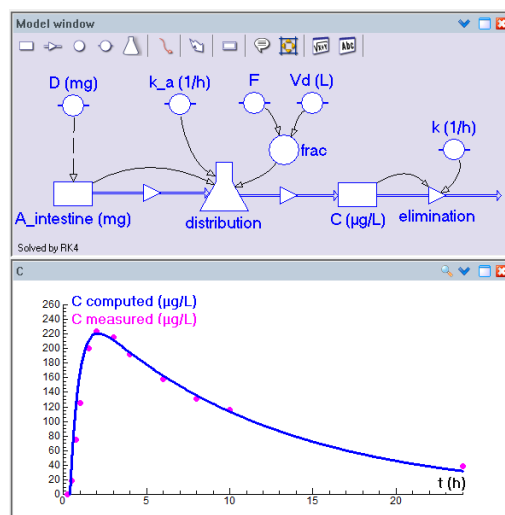


Fig. 11 Screen shot of a graphical model of pharmacokinetics of ecstasy in the human body and a simulation run with real data in the background.

average $1/\alpha$ days ill, then the above system of differential equations follows from probabilistic considerations. Fig. 12 shows a graphical model based on a process network (the non-default stoichiometric coefficient has been added in the graphical model as an annotation).

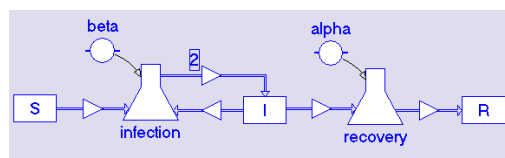


Fig. 12 Screen shot of a process network based graphical model of the Kermack-McKendrick model of epidemics.

6 Conclusion

A central aspect of inquiry learning is that the learners must develop their own models and in particular their own executable computer models of real world phenomena. Classroom experience and case studies indicate that this is possible at secondary school level when graphical system dynamics based software is used. Subsections 3.1 and 3.2 showed the potentiality of graphical system dynamics based modeling environments like STELLA in the context of chemical equilibrium and chemical kinetics. However, as was illustrated in Subsection 3.3, level-flow based modeling tools are of limited use in studying chemical kinetics when bi- or trimolecular reactions or chemical reaction networks come into play. It is tempting to associate in these graphical

models levels with concentrations of species in a reaction and physical flows with chemical reaction arrows, representing at the same time the kinetics of the reactions. But stoichiometry and plurimolecular reaction types are a spoil-sport. The graphical representation of a chemical reaction network in the form of a kinetic graph, as it has been introduced in Subsection 4.1, is more suitable. Only one thing is needed for this in the graphical level-flow formalism, namely, inclusion of a new icon for a reaction step. Then, levels can indeed represent concentrations of species and flows can represent changes in concentrations of species provided that these flows are between levels and reaction icons (the Erlenmeyer flask symbols in this paper). Each reaction icon is linked with a formula that describes the reaction rate and the stoichiometry of the reaction determines the formulas for the inflows and outflows of the reaction icon. In this way the graphical model gives a clear overview of the reaction mechanism (as was exemplified in Subsection 4.2).

Another improvement comes from the addition of user interaction tools like sliders and button to influence simulation run while they are going on and of a special icon for discrete time event handling. This offers students the opportunity to explore “what if?” questions. An example of such an investigation of the influence of external effects on a chemical equilibrium was given in Subsection 4.3.

Both improvements have been exemplified in this paper by the computer implementation in Coach 6. Furthermore, the examples in Sections 3 and 4 illustrated that alternative conceptions of students about chemical equilibrium and chemical kinetics, which were reviewed in Section 2, can be directly addressed with the (extended) graphical modeling approach. Section 5 contained some examples to briefly illustrate that this improved approach has applications beyond chemical kinetics and helps to clarify the dynamics of all kinds of real world phenomena.

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