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 students develop knowledge about chemical kinetics and chemical equilibrium and remediate alternative conceptions. The methodology, strengths, and weaknesses of the implementation of graphical system dynamics software for modeling chemical kinetics are presented. An extension of classical graphical modeling is proposed that could make it easier for students to investigate chemical kinetics, especially in cases of non-trivial reaction mechanisms. Illustrative examples are given throughout the paper.*

Introduction

Chemical equilibrium and chemical kinetics are important concepts in general chemistry and therefore included in both secondary school and university curriculum in most countries [1]. 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 [2-11], no matter whether a qualitative or (semi-)quantitative approach has been adopted. Some common students' alternative conceptions and instructional strategies are discussed in order to underpin the potential of graphical computer modeling of chemical kinetics for addressing some 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 include data logging [12-14] and the use of dedicated packages [15,16], scientific computing environments [17-19], spreadsheet programs [20-22], computer simulations [23-25], and system dynamics modeling software [26-29]. 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 has been advocated in the past for a quantitative approach to chemical kinetics, it seems that it has never expanded enormously.

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 computer 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.

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 possibility of instant change of a computer model due to a discrete-time event or 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, 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.

It is also 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 is a versatile computer learning and authoring environment for mathematics, science and technology education at primary level and beyond [30], developed for more than twenty years at the University of Amsterdam and distributed by the CMA Foundation [31]. It provides integrated tools for measurement with sensors, control activities, digital image and video analysis, modeling, simulation, and animation. For this paper it is only relevant that the selected computer learning environment supports the classical graphical system dynamics modeling approach as well as the proposed extensions.

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 [2-7] 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. Some common students’ alternative conceptions and instructional strategies are discussed in the next two subsections.

Alternative Conceptions. Problematic concepts of chemical equilibrium appear to be the same all over the world, see for example [7-10], with the greatest difficulties being concerned with 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 difference between rate constants and equilibrium constants, and the effect of a catalyst. One of the main messages in this paper is that the use of graphical computer modeling of chemical kinetics may help address alternative conceptions about the characteristics of a chemical equilibrium and the involved reactions. I illustrate this in the next section for the following alterative conceptions:

- The rate of the forward reaction increases with time from the mixing of the reactants equilibrium is established;
- The forward reaction is completed before the reverse reaction commences;
- The forward reaction rate always equals the reverse reaction rate;
- The rate (how fast) and extent (how far) of a reaction have the same meaning;
- 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, a few of which are listed below, 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 [1,10,11]:

- Every reaction occurs instantaneously and continues until all reactants are exhausted;
- The reaction rate increases as the reaction ‘gets going;’
- 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.

Instructional Strategies. Numerous 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 [12-25,32-39]. Many 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 in an introduction of chemical equilibrium and chemical kinetics no role for studying quantitative aspects. Hackling and Garnett [40] 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, preferbly 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* [41] in their paper about introducing dynamic equilibrium as an explanatory model through a conceptual change approach are in the same line of thought:

> “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 introducetion 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 [11]. 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 teachers, and that help improve the teaching and learning of the subject. It is noted that empirical studies are needed to investigate its impact, certainly because it is notoriously difficult to counteract alternative conceptions of students and because the use of modeling can just as easily introduce new alternative conceptions as remove existing ones.

Graphical System Dynamics Modeling of Chemical Kinetics

I discuss the methodology, strengths, and weaknesses of the implementation of classical graphical system dynamics modeling software for modeling chemical kinetics through the following examples: (1) a unimolecular chemical equilibrium system; (2) a termolecular chemical reaction; and (3) the Michaelis-Menten reaction mechanism. The last two examples are also used in the next section to exemplify the new approach.

Basics of Graphical System Dynamics Modeling. Graphical system dynamics modeling environments like STELLA, Powersim, 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 relationships are made explicit in the form of mathematical formulas and graphical or tabular relationships. The variables involved can be levels, flows, parameters, or 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 Figure 1. It represents the chemical kinetics of the isomerization

$$\textit{cis}\text{-Mo(CO)}_4[\text{P}(n\text{-Bu})_3]_2 \underset{k_{1r}}{\overset{k_{1f}}{\rightleftharpoons}} \textit{trans}\text{-Mo(CO)}_4[\text{P}(n\text{-Bu})_3]_2\ .$$

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*]); and (4) flows (rates of change of concentrations r_{1f}, r_{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 k1f 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 reference [42] and used in the simulation:

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

where temperature T has been specified here in Kelvin and rate constants are in s^{-1}.

The model window in the upper part of the screenshot in Figure 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. This contrasts with computer simulations in which only the parameters of a given model can be altered and not the underlying model. 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, i.e, 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 Figure 1 represents the following coupled differential equations for the rate of change in the concentrations of the two species involved:

$$\frac{d[cis]}{dt} = -r_{1f} + r_{1r}, \qquad \frac{d[trans]}{dt} = r_{1f} - r_{1r} ,$$

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.

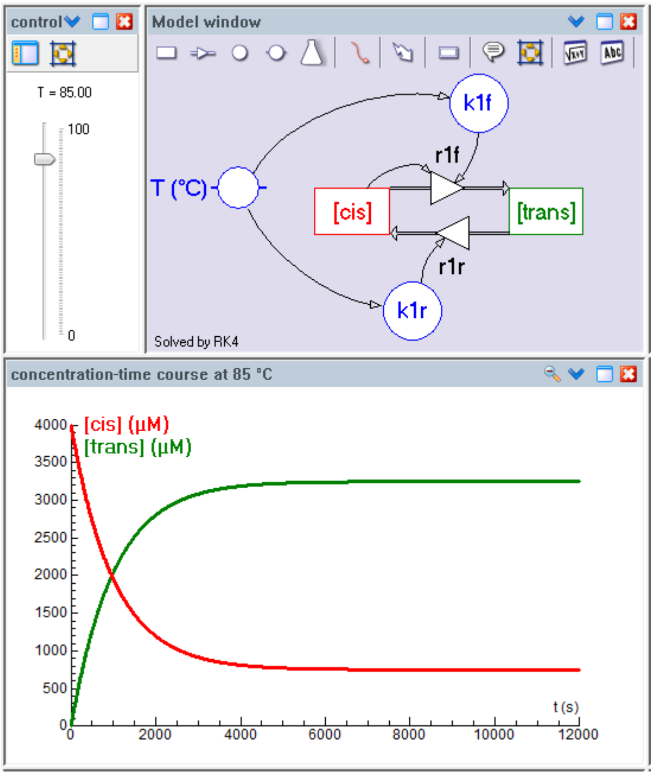

Figure 1. Screen shot of the graphical system dynamics model of cis-trans isomerization and concentration-time graphs in a computer simulation starting from pure *cis*-$Mo(CO)_4[P(n\text{-}Bu)_3]_2$.

Strengths of Classical Graphical Modeling Tools. In the context of chemical kinetics, students are immediately confronted in a computer 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 Figure 1 that (1) it takes time before the equilibrium is reached; and (2) at equilibrium, the concentrations of cis- and trans-complexes are not necessarily equal.

More alternative conceptions about chemical equilibrium can be addressed by looking at rate-time and net rate-time graphs of the chemical equilibrium shown in Figure 2. Some of the points that a student could notice in the graphs are:

- The forward and reverse reaction start at the same time and the rates of both reactions are not always the same;
- 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 change in the rates of both reactions with respect to time tends to zero as equilibrium is approached, i.e., the slopes of both rate curves become equal to each other and to zero when equilibrium is reached;
- A system in equilibrium does not mean that the reactions have ceased. It only means that the net rate of concentrations is zero and that the forward- and reverse-reaction rates are equal.

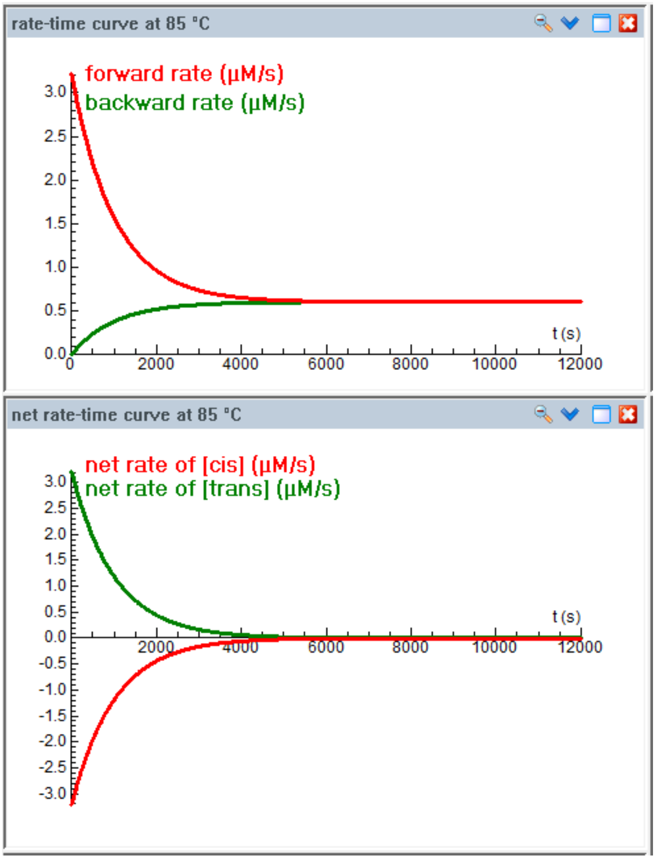

Figure 2. Rate-time and net rate-time graphs for cis-trans isomerization at 85 ºC.

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. For example, by changing the initial concentrations of the cis- and trans-complex it can easily be verified that the system will always reach the same ratio of 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. In fact, this kind of exploration has already been anticipated in the model shown in Figure 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.

Figure 3 shows the results of a simulation of the isomerization at a lower temperature, namely at 80 ºC. The graphs of the previous simulation at a temperature of 85 ºC are shown in gray at the background to support easy comparison. A student could discover from the graphs 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.

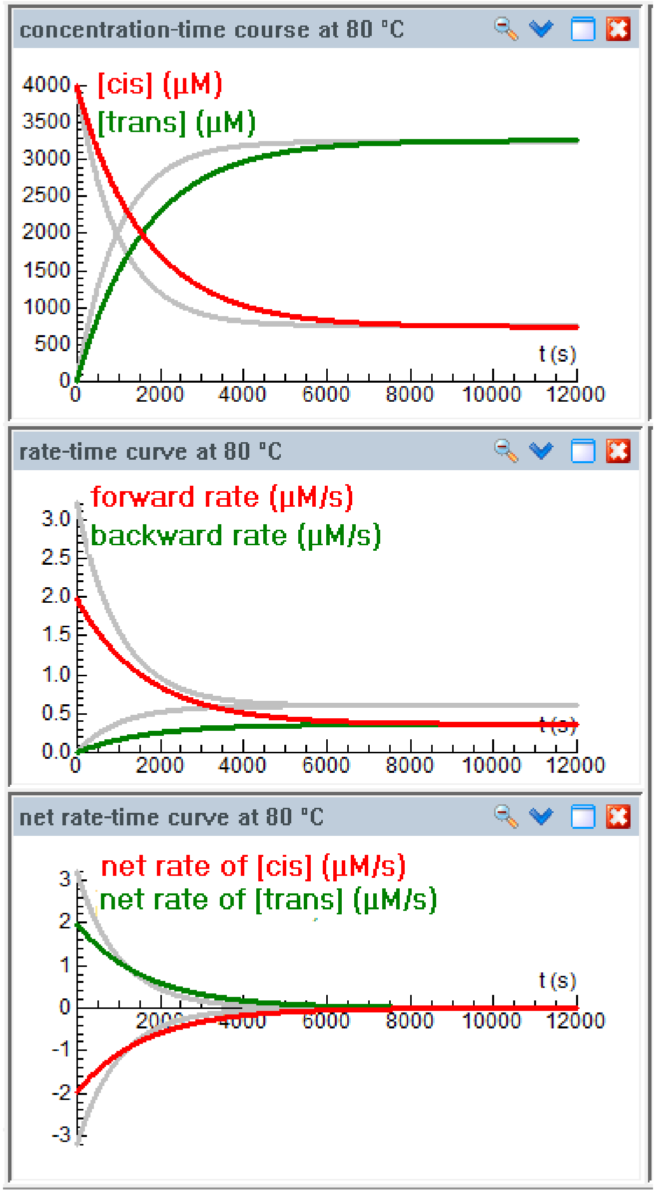

Figure 3. Concentration-time, rate-time, and net rate-time graphs for cis-trans isomerisation at 85 ºC.

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. Consider for example, the gas-phase oxidation of nitric oxide: $2\mathrm{NO} + \mathrm{O_2} \rightarrow 2\mathrm{NO_2}$. 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. Although there exist more than one mechanism that leads to third-order reaction kinetics [43], the simplest one, namely a termolecular reaction mechanism, would already lead in a classical graphical system dynamics modeling approach to a disconnected picture as shown in Figure 4, because one could not simply draw physical flow arrows from reactants to products.

The graphical model in Figure 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:

$$\frac{d[\mathrm{NO}]}{dt} = -2r, \quad \frac{d[\mathrm{O_2}]}{dt} = -r, \quad \frac{d[\mathrm{NO_2}]}{dt} = 2r \ ,$$

where $r = k \cdot [\mathrm{NO}]^2 \cdot [\mathrm{O_2}]$ for some rate constant *k*. It also displays the units used.

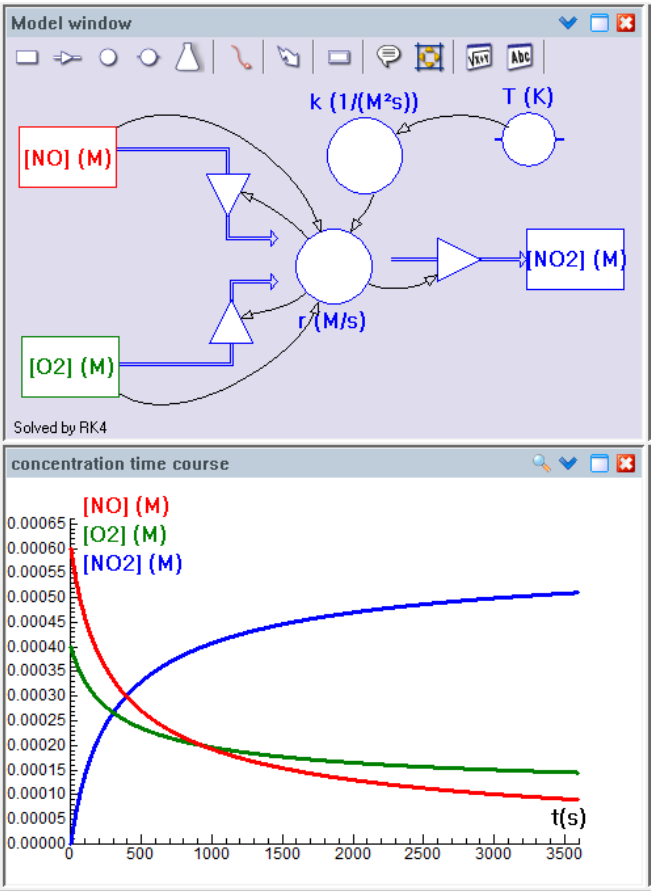

Figure 4. Screen shot of the graphical system dynamics model and computer simulation of the termolecular reaction $2\mathrm{NO} + \mathrm{O_2} \xrightarrow{k} 2\mathrm{NO_2}$.

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, all of a sudden the icons that represent concentrations have become disconnected. The reason 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 [NO] toward [NO2] and an arrow from [O2] toward [NO2] were drawn, this would mean that the increase in concentration of $\mathrm{NO_2}$ over time is equal to the sum of the decrease in concentration of NO over time and the decrease in concentration of $\mathrm{O_2}$ over time. This, from a chemical point of view, is 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 ([44], 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 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, illustrates this:

$$\mathrm{E}+\mathrm{S} \underset{k_{1\mathrm{r}}}{\overset{k_{1\mathrm{f}}}{\rightleftharpoons}} \mathrm{ES} \xrightarrow{k_{2\mathrm{f}}} \mathrm{E}+\mathrm{P}\,,$$

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. A steady-state approximation is used in most cases to simplify the algebraic and computational work. The classical graphical system dynamics model that represents this enzyme-catalyzed reaction without using this approximation is shown in Figure 5.

The graphical model in Figure 5 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:

$$\frac{d[\mathrm{S}]}{dt} = -r_{1\mathrm{f}} + r_{1\mathrm{r}}\,, \quad \frac{d\left[E\right]}{dt} = -r_{1\mathrm{f}} + r_{1\mathrm{r}} + r_{2\mathrm{f}}\,,$$

$$\frac{d[\mathrm{ES}]}{dt} = r_{1\mathrm{f}} - r_{1\mathrm{r}} - r_{2\mathrm{f}}\,, \quad \frac{d[\mathrm{P}]}{dt} = r_{2\mathrm{f}}\,,$$

where

$$r_{1\mathrm{f}} = k_{1\mathrm{f}} \cdot \left[\mathrm{E}\right] \cdot \left[\mathrm{S}\right], \quad r_{1\mathrm{r}} = k_{1\mathrm{r}} \cdot \left[\mathrm{ES}\right], \quad r_{2\mathrm{f}} = k_{2\mathrm{f}} \cdot \left[\mathrm{ES}\right].$$

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.

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 often result in 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 [45] and the level-flow metaphor has been replaced in references [46-48] 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 to 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.

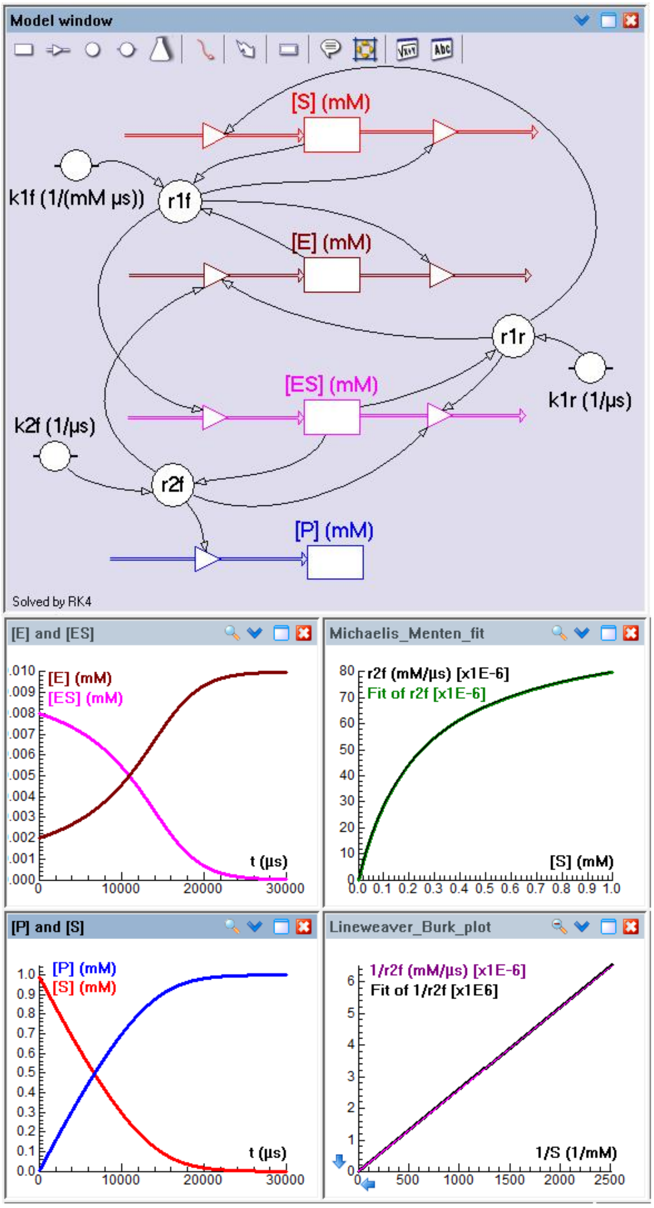

Figure 5. Screen shot of the graphical system dynamics model and computer simulation of the $\mathrm{E}+\mathrm{S} \underset{k_{1\mathrm{r}}}{\overset{k_{1\mathrm{f}}}{\rightleftharpoons}} \mathrm{ES} \xrightarrow{k_{2\mathrm{f}}} \mathrm{E}+\mathrm{P}$ reaction system.

Improved Graphical Modeling of Chemical Reaction Systems

Solutions to most of the previously identified problems with classical graphical system dynamics modeling are presented in the form of an improved approach to chemical reactions based on a graph theoretic description of reaction kinetics. To this end, a new icon, namely, the Erlenmeyer flask symbol, is added to the graphical modeling tool. Examples illustrate the new approach to chemical kinetics. The usefulness of adding interactivity elements such as sliders, buttons, and event controls to the graphical modeling tool is also discussed.

Adding a New Element to the Graphical 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 reference [49] and the directed bipartite graph of a reaction network developed by Vol'pert and Ivanova [50] (see also [51]), more thoroughly analyzed in [52,53]. In short, it is based on the principle that a chemical reaction network can be represented by 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. 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. This directed bipartite graph is called a kinetic graph because it also incorporates information about the kinetics of the chemical reaction, i.e., information about (contributions to) rates of change of species involved in the given reaction, based on the stoichiometric coefficients associated with the reaction. The kinetic graph of the termolecular gas-phase oxidation of nitric oxide discussed before, $2\mathrm{NO}+\mathrm{O}_2\xrightarrow{k}2\mathrm{NO}_2$, is shown in Figure 6.

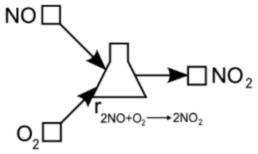

Figure 6. The kinetic graph of the reaction $2\mathrm{NO}+\mathrm{O}_2\xrightarrow{k}2\mathrm{NO}_2$.

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 flask symbols. Inflows of an Erlenmeyer flask symbol originate from reactants and outflows of an Erlenmeyer flask symbol point at products in the chemical reaction that is symbolized by the Erlenmeyer flask. The Erlenmeyer flask symbol also represents the dynamics of the levels connected with it via the stoichiometry of the reaction: The Erlenmeyer flask symbol is linked to a formula for the reaction rate, which depends on the kinetic coefficient, the concentrations of reactants and their stoichiometric coefficients (in this example $r=k\cdot[\mathrm{NO}]^2\cdot[\mathrm{O}_2]$), and the stoichiometric coefficients determine the formulas for the inflows and outflows of the Erlenmeyer flask 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 reaction icons 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 illustrate that the new graphical models more closely resemble the pictures that chemists already use to represent reaction mechanisms. This is also the reason that students do not need to be rigorously introduced to the theory of kinetic graphs; a more informal introduction should permit students to work with it in a sensible way.

Some Illustrative Examples. The improved graphical modeling approach has been implemented in Coach 6 and the first example in this subsection is the two-step enzyme-catalyzed reaction

$$\mathrm{E}+\mathrm{S}\underset{k_{1r}}{\overset{k_{1f}}{\rightleftharpoons}}\mathrm{ES}\xrightarrow{k_{2f}}\mathrm{E}+\mathrm{P}\,,$$

which has been discussed before. This offers the reader the opportunity to compare the classical graphical system dynamics model (Figure 5) with the model based on the improved formalism (Figure 7), which reflects the underlying reaction mechanism much better.

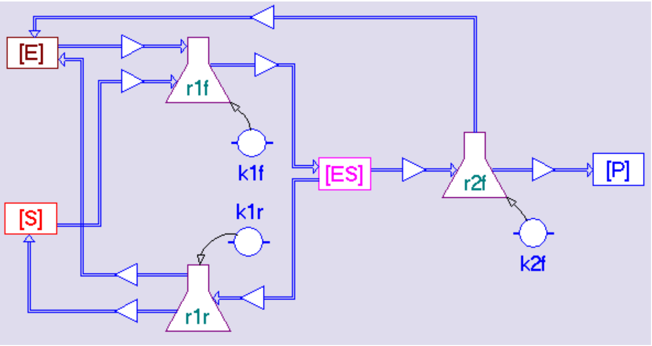

Figure 7. Screen shot of the improved graphical system dynamics model of the $\mathrm{E}+\mathrm{S}\underset{k_{1r}}{\overset{k_{1f}}{\rightleftharpoons}}\mathrm{ES}\xrightarrow{k_{2f}}\mathrm{E}+\mathrm{P}$ network.

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 Figure 8, which would not be as comprehensible in a classical graphical system dynamics approach. It is the following enzyme-catalyzed reaction mechanism, taken from [54-56], for the hydrolysis of arginine to ornithine and urea catalyzed by the hydrolytic enzyme arginase, which is only one step of the urea cycle:

$$\mathrm{E}+\mathrm{A}\underset{k_{1r}}{\overset{k_{1f}}{\rightleftharpoons}}\mathrm{EA}\xrightarrow{k_{2f}}\mathrm{EO}+\mathrm{U},\quad \mathrm{EO}\underset{k_{3r}}{\overset{k_{3f}}{\rightleftharpoons}}\mathrm{E}+\mathrm{O}\,,$$

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:

$$\frac{d[\mathrm{A}]}{dt}=-r_{1\mathrm{f}}+r_{1\mathrm{r}},\quad \frac{d[E]}{dt}=-r_{1\mathrm{f}}+r_{1\mathrm{r}}-r_{3\mathrm{r}}+r_{3\mathrm{f}},$$
$$\frac{d[\mathrm{EA}]}{dt}=r_{1\mathrm{f}}-r_{1\mathrm{r}}-r_{2\mathrm{f}},\quad \frac{d[\mathrm{EA}]}{dt}=r_{2\mathrm{f}}-r_{3\mathrm{f}}+r_{3\mathrm{r}},$$
$$\frac{d[\mathrm{U}]}{dt}=r_{2\mathrm{f}},\quad \frac{d[\mathrm{O}]}{dt}=r_{3\mathrm{f}}-r_{3\mathrm{r}},$$

where

$$r_{1\mathrm{f}}=k_{1\mathrm{f}}\cdot[\mathrm{E}]\cdot[\mathrm{A}],\quad r_{1\mathrm{r}}=k_{1\mathrm{r}}\cdot[\mathrm{EA}],\quad r_{2\mathrm{f}}=k_{2\mathrm{f}}\cdot[\mathrm{EA}],$$
$$r_{3\mathrm{f}}=k_{3\mathrm{f}}\cdot[\mathrm{EO}],\quad r_{3\mathrm{r}}=k_{3\mathrm{r}}\cdot[\mathrm{E}]\cdot[\mathrm{O}].$$

Values of kinetic parameters can be taken from [54]. In the improved graphical system dynamics approach, modeling and simulation of chemical kinetics of more realistic reaction mechanisms is not expected to be beyond the level of secondary school students or first-year undergraduate chemistry students anymore.

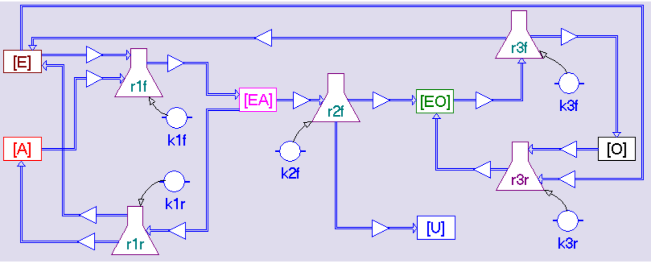

Figure 8. Screen shot of the improved graphical system dynamics model of the $\mathrm{E}+\mathrm{A}\underset{k_{1r}}{\overset{k_{1f}}{\rightleftharpoons}}\mathrm{EA}\xrightarrow{k_{2f}}\mathrm{EO}+\mathrm{U},\quad \mathrm{EO}\underset{k_{3r}}{\overset{k_{3f}}{\rightleftharpoons}}\mathrm{E}+\mathrm{O}$ network.

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, volume or temperature, and so on. Many research studies [3,6,8,34,57,58] 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* [3] and others [57,59] 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 to explain how a system in equilibrium responds to a perturbation. 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 allows an easy implementation of event-handling such as response to a sudden change in concentration, temperature, and so on. Solomonidou and Stavridou [24] 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 Coach 6 and are exemplified with the equilibrium shift of a gas mixture of hydrogen, iodine, and hydrogen iodine as a response to a sudden change in hydrogen concentration and temperature. The reaction system under consideration is $H_2 + I_2 \underset{k_{1r}}{\overset{k_{1f}}{\rightleftharpoons}} 2HI$, 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:

$$\frac{d[H_2]}{dt} = -r_{1f} + r_{1r}, \quad \frac{d[I_2]}{dt} = -r_{1f} + r_{1r}, \quad \frac{d[HI]}{dt} = r_{1f} - r_{1r},$$

where $r_{1f} = k_{1f} \cdot [H_2] \cdot [I_2]$, $r_{1r} = k_{1r} \cdot [HI]^2$, and the Arrhenius equations for the rate constants are given [60] for temperature T (in ºK) by $k_{1f} = 7.18 \times 10^{12} \times e^{-24775/T}$, $k_{1r} = 1.23 \times 10^{12} \times e^{-20646/T}$. It follows that the forward gas phase reaction is exothermic.

Figure 9 is a screenshot of a simulation run based on this kinetic model and starting with only a nonzero concentration of HI at a temperature of 721 ºK. 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 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, 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 ºK. The effect is that the equilibrium shifts to the left, that is, more hydrogen iodine dissociates again. This is in agreement with Le Châtelier's Principle that states that increasing the temperature will shift the equlibrium to the left because the forward reaction is exothermic. Although kinetic and thermodynamic approaches to chemical equilibrium phenomena are of different nature, results obtained by either method complement each other.

Other Applications

Graphical modeling and simulation tools have other applications in chemistry education, for example in modeling and simulating acid-base titration curves [61], and in other science fields (see for example [62,63]). Although no attention has been paid to it in this article so far, it is worth mentioning and it 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 they 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. I mention here only one context of usage of the improved graphical formalism that is conceptually rather close to the chemical context of this paper, namely quantitative pharmacokinetic modeling. But one must realize that examples of completely different nature, such as for instance the modeling of the height of beer foam [64], could be presented as well. Figure 10 shows a graphical model and computer 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 reference [65]): The improved graphical modeling approach provides a connected diagram that indicates the flow of the pharmacon in the body over time.

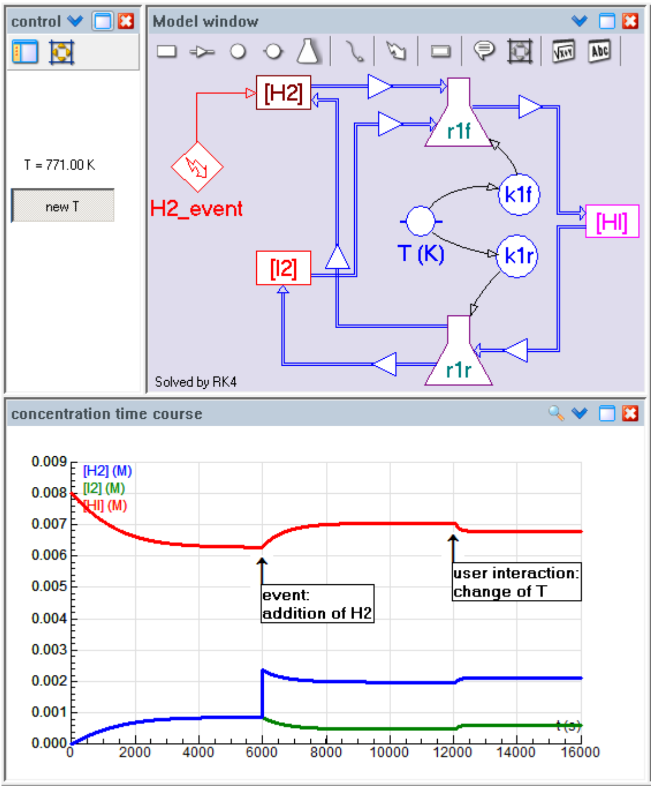

Figure 9. Screen shot of the improved graphical system dynamics model of the $H_2 + I_2 \underset{k_{1r}}{\overset{k_{1f}}{\rightleftharpoons}} 2HI$ equilibrium reaction and a computer simulation with user interaction and an event during execution of the model.

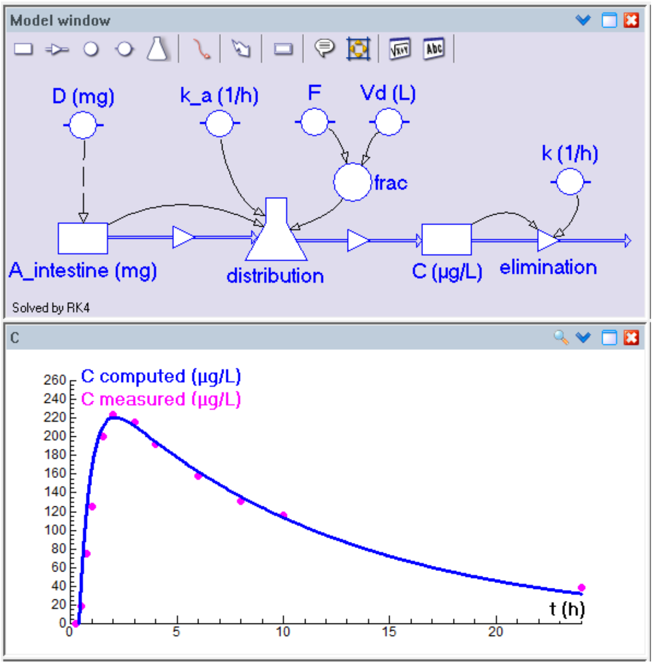

Figure 10. Screen shot of a graphical model of pharmacokinetics of ecstasy in the human body and a simulation run with real data in the background.

Conclusion

In this paper it is advocated that it is a good learning experience for students to 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 already possible at secondary school level when graphical system dynamics based software is used. The potentiality of classical graphical system dynamics based modeling environments in the context of chemical equilibrium and chemical kinetics was discussed. One of the conclusions was that the 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. The graphical representation of a chemical reaction network in the form of a kinetic graph 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 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.

Another improvement comes from the addition of user interaction tools like sliders and button to influence simulation runs 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 presented.

Both improvements have been exemplified in this paper by the computer implementation in Coach 6. Furthermore, the examples illustrated that alternative conceptions of students about chemical equilibrium and chemical kinetics can be directly addressed with the (improved) graphical modeling approach. It was noted 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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