

Agent-based Model of Oxidation Reactions of Ferrous Ions

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Abstract Molecules in comets are formed through chemical oxidation reactions induced by radiation. These reactions can be simulated in laboratory experiments applying gamma radiation to samples at low temperatures. The kinetics of the induced reactions can be modeled by a system of coupled non-linear ordinary differential equations describing the mass balance of all of the species involved. However, finding a traditional solution to this system is difficult because of the large number of reactions involved, the need to solve all of the equations simultaneously, and the strong dependence on the initial conditions due to the non-linear character of the equations. For each species, the mass-balance equation includes all of the reaction rates leading to production (source terms) and to destruction (sink terms). In this sense, each equation is analogous to the prey-predator model, with the sink terms considered to be the “prey” and the source terms as the “predators”. Due to this, we can use an agent-based model to follow the kinetics of the chemical reactions. In this paper, we present a code in Python for an agent-based model of the chemical oxidation of ferrous ions (Fe^{2+}) induced by gamma radiation and in the presence of molecular oxygen. We compare the results that this code produces for molar concentrations of Fe^{3+} over time with those obtained in the laboratory.

Keywords: Chemical reactions; radiation; kinetics of reactions; prey-predator model; Fricke-model.

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1. INTRODUCTION

Chemical oxidation reactions induced by radiation at low temperatures are fundamental in laboratory experiments that simulate the formation of biologically relevant molecules in icy bodies like comets [4, 7, 10, 11]. In these simulated experiments, dose measurements can indicate the amount of energy deposited by the gamma radiation on the samples providing a quantitative measure of the changes induced by ionizing radiation. Chemical analysis, pulse radiolysis, and competition kinetic methods have been employed experimentally to obtain the large number of rate constants involved in the reactions as in [3, 6].

To describe the products generated by the interactions among the different molecules and their chemical reactions under radiation, mathematical models exist that describe the kinetics of the chemical reactions as coupled nonlinear ordinary differential equations (NODEs) [5, 15, 16]. Solving these models is difficult because of the large number of reactions involved, the need to solve all of the equations simultaneously, and the strong dependence on initial conditions due to the non-linear character of the equations [5,9]. To overcome these numerical troubles, it has been used Monte-Carlo simulations [17]. Here, we propose an agent-based model to simulate the chemical evolution of oxidation reactions among ferrous ions under radiation. This is a modified version of the prey-predator model [2, 8, 13, 14], in which each chemical species involved is considered to be an agent that can interact with other species with known reaction rates. The agent-model is programmed in Python. The radiation is considered as a factor that promotes product creation/destruction. This original model can reproduce the formation of products and the consumption of ferrous and oxygen ions in a laboratory reaction [15].

2. EXPERIMENTAL SETUP FOR THE OXIDATION OF FERROUS IONS

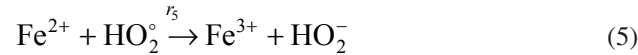
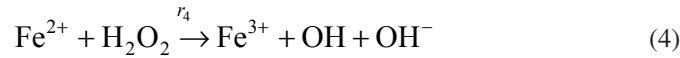
We irradiated oxygenated solutions of iron salt ($1.6 \cdot 10^{-3} \text{M Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$) in sulfuric acid 0.4M in a Cobalt 60 source at a dose rate of 0.93Gy/min (following the setup of [10]). The samples were in Pyrex cells surrounded by a Dewar flask filled with different cooling agents. In the frozen case, the samples were melted after irradiation, and the temperature was adjusted to 25°C prior to the spectroscopic measurement of the Fe^{3+} concentrations. Our first approximation was with the data at 295 K.

3. OXIDATION REACTION MODEL

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3.1. Chemical oxidation reactions: Ferrous ions(Fricke dosimeter)

In the case of the Fricke dosimeter, the chemical oxidation reactions for the Fe^{2+} are well known [15]:



In this case, there are seven chemical reactions that involve 11 species (Fe^{2+} , Fe^{3+} , H_2O , H° , HO_2° , HO_2^- , O_2 , H_3O^+ , OH , OH^- , and H_2O_2), and seven known reaction rates (r_i). We considered H_3O^+ , Fe^{2+} , O_2 , and H_2O to be compounding the pre-irradiated solution, so initially there are no other species (the initial concentrations of Fe^{3+} , H° , HO_2° , HO_2^- , OH , OH^- , and H_2O_2 are zero). We used the standard concentrations for the Fricke dosimeter (from 0.1 to 0.001M for $\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$), in which the oxidation of ferrous ions takes place in an acid medium (H_2SO_4 , 0.4M). The concentration of oxygen is based on its solubility in water, as given by [12]. Then, the values for the initial conditions were 0.0016 M Fe^{2+} , 0.0120 M O_2 , and 0.4000 M H_3O^+ . The reaction rates were: $r_1 \sim 2.0 \cdot 10^{10}$, $r_2 \sim 2.3 \cdot 10^{10}$, $r_3 \sim 3.0 \cdot 10^8$, $r_4 \sim 50$, $r_5 \sim r_6 \sim 7.3 \cdot 10^5$, and $r_7 \sim 10^5$ in $\text{M}^{-1}\text{s}^{-1}$.

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3.2. Mathematical model

We are interested in monitoring the concentration of the 11 species involved as the experiment progresses, to follow the kinetics of the chemical reactions (Eqs. 1-7) induced by the radiation. These chemical reactions can be modeled through differential equations that establish the mass balance for each species involved. The mass balance equations predict the expected change in the molar concentration of the species over time, and take into account all of the reaction rates leading to production (source terms) and to destruction (sink terms). In this sense, it is analogous to the prey-predator model, with the sink terms being considered the “prey” and the source terms as the “predators”. Importantly, a species can be a prey in one of the mass balance equations; and in another equation, the same species can play the role of predator. In this model, we consider that each balance equation reflects the interaction of at most 2 species, and that such a reaction, whatever its rate, must lead to the production or consumption of a certain species. In general, the NODEs are of the form given by [5]:

$$\frac{dN_i(t)}{dt} = f_i + \sum_j \sum_k r_{j,k}^{(i)} N_j(t) N_k(t) - N_i(t) \sum_m r_{i,m}^{(i)} N_m(t), \quad (8)$$

where $N_i(t)$ denotes the molar concentration of the i -species at time t , f_i is the number of molecules of the i -species produced in the radiolysis process induced by the gamma radiation, and $r_{j,k}^{(i)}$ denotes the reaction rate constant for the two reactive species j, k that produce the specie (i) . The radiolysis term, f_i , is an external source in the balance equations (8), which we propose as a linear function of the radiation dose intensity I_d , given in rad/h, and of the temperature T , as in [5]:

$$f_i(I_d, T) = \frac{6.2 \cdot 10^{11}}{3.6 N_A} \frac{M_i}{M_{H_2O}} G_i \lambda(T) I_d,$$

where N_A is the Avogadro number (6.022×10^{23} molecules), M_i is the molecular mass of the species i , M_{H_2O} is the molecular mass of water (18.02g/mol), and G_i is the radiochemical yield that gives the amount of species i produced when 100eV are absorbed by the system, in this case 15.6 molecules of Fe^{3+} .

The system of chemical reactions given by Eqs. (1)-(7) can be rewritten as a system of 11NODEs, Eqs. (8), one for each species involved. For the ferrous ion, Fe^{2+} , the NODE is:

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$$\frac{dN_{\text{Fe}^{2+}}(t)}{dt} = f_{\text{Fe}^{2+}}(I_d, T) - r_3 N_{\text{OH}}(t) N_{\text{Fe}^{2+}}(t) - r_4 N_{\text{H}_2\text{O}_2}(t) N_{\text{Fe}^{2+}}(t) - r_5 N_{\text{HO}_2^\circ}(t) N_{\text{Fe}^{2+}}(t), \quad (9)$$

where only Fe^{2+} is consumed in agreement with Eqs. (3), (4) and (5). This Fe^{2+} is responsible for the production of Fe^{3+} , through equation:

$$\frac{dN_{\text{Fe}^{3+}}(t)}{dt} = f_{\text{Fe}^{3+}}(I_d, T) + r_3 N_{\text{OH}}(t) N_{\text{Fe}^{2+}}(t) + r_4 N_{\text{H}_2\text{O}_2}(t) N_{\text{Fe}^{2+}}(t) + r_5 N_{\text{HO}_2^\circ}(t) N_{\text{Fe}^{2+}}(t). \quad (10)$$

If we consider the radical hydrogen, H° , as the species, the corresponding NODE is:

$$\frac{dN_{\text{H}^\circ}(t)}{dt} = f_{\text{H}^\circ}(I_d, T) + r_2 N_{e_{aq}^-}(t) N_{\text{H}_3\text{O}^+}(t) - r_1 N_{\text{O}_2}(t) N_{\text{H}^\circ}(t), \quad (11)$$

where the production terms involve Eq. (2), and the consumption terms come from eq. (1). Notice that H° is produced at the same rate as H_3O^+ and e_{aq}^- are consumed. In the case of oxygen, O_2 , the corresponding equation only has a loss term that arises from eq. (1):

$$\frac{dN_{\text{O}_2}(t)}{dt} = f_{\text{O}_2}(I_d, T) - r_1 N_{\text{O}_2}(t) N_{\text{H}^\circ}(t). \quad (12)$$

If we continue doing this, we get a system of 11 coupled NODEs, which can be solved numerically through traditional methods, as the one's presented in [16], or by considering an agent-based model [1].

4. NUMERICAL SOLUTION

A numerical solution for the NODEs Eqs. (8) for all of the species can be found by transforming each differential equation to a difference one:

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$$N_i(t) = f_i + \sum_j \sum_k r_{j,k}^{(i)} N_j(t-1) N_k(t-1) + N_i(t-1) \left[1 - \sum_m r_{i,m}^{(i)} N_m(t) \right]. \quad (13)$$

For example, the molar concentration of Fe^{3+} at moment t can be obtained from the molar concentrations of OH , Fe^{2+} , H_2O_2 , and HO_2° at the previous time $t-1$ through:

$$N_{\text{Fe}^{3+}}(t) = N_{\text{Fe}^{3+}}(t-1) + f_{\text{Fe}^{3+}}(I_d, T) + r_3 N_{\text{OH}}(t-1) N_{\text{Fe}^{2+}}(t-1) + r_4 N_{\text{H}_2\text{O}_2}(t-1) N_{\text{Fe}^{2+}}(t-1) + r_5 N_{\text{HO}_2^\circ}(t-1) N_{\text{Fe}^{2+}}(t-1), \quad (14)$$

and Eq. (11) for H° takes the form:

$$N_{\text{H}^\circ}(t) = f_{\text{H}^\circ}(I_d, T) + r_2 N_{e_{aq}^-}(t-1) N_{\text{H}_3\text{O}^+}(t-1) + N_{\text{H}^\circ}(t-1) - r_1 N_{\text{O}_2}(t-1) N_{\text{H}^\circ}(t-1). \quad (15)$$

The coupled system of eqs. (13) can be solved using an agent-based model with sources and sinks that can be interpreted as prey and predators. We made a Python program to follow the molar concentrations of each species. The code initializes a region of $1,000 \times 1,000$ pixels, with 4,000 randomly allocated points associated with H_3O^+ , 120 points of O_2 , and 16 of Fe^{2+} (see Figure 1a). Each position is checked during the next time instant, if two neighbor species can react in accordance to eqs. (1) to (7), the reaction takes place consuming the “prey” elements by the “predators” produced. The rate of reaction is determined by the $r_{j,k}^{(i)}$. After actualizing the entire net, the procedure is repeated until the steady-state is reached (see Figure 1b). In the program we can follow the molar concentration of each species as a function of time. In Figure 2, the molar concentration of Fe^{3+} is plotted and compared with experimental data.

One of the common problems in following the kinetics of many chemical reactions is that the reaction rates are unknown, especially at low temperatures. Our agent-based model can be used to evaluate some of these rates using experimentally determined concentration values. For this, we ran the model with different values of unknown rates until we reached the best experimental approximation. In Figure 3, we plotted the relative error in the evaluation of the different rates when we did not know from one to four rates. Our model had an evaluation error of less than 10% when we did not know the values of one or two parameters. The worst approximation was given to r_4 , the smallest reaction rate.

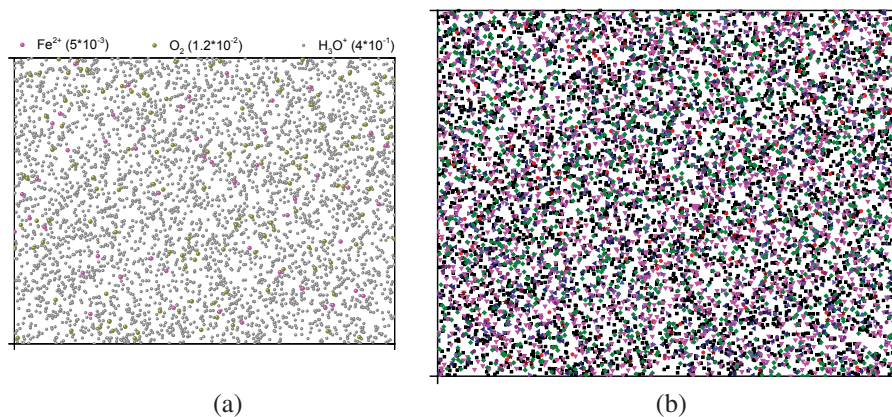


Figure 1: Agent-based spatial distribution of the species (a) initially and (b) at steady-state.

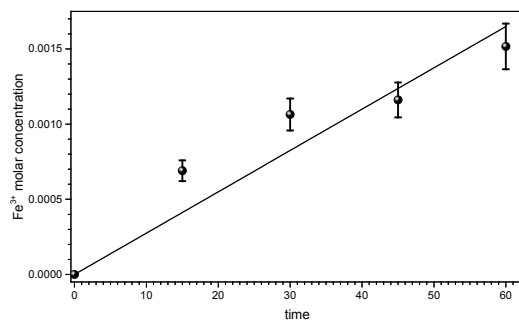


Figure 2: Molar concentration of Fe^{3+} . The points correspond to experimental values and the continuous line to the agent-based results, at room temperature.

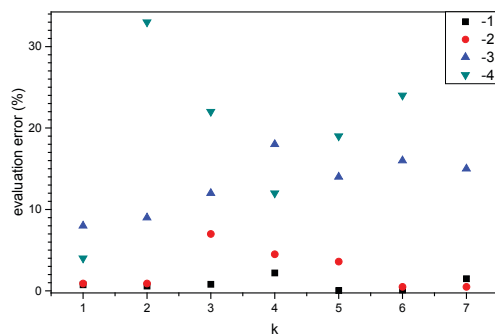


Figure 3: Evaluation error of the reaction rates obtained from the agent-based model.

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5. CONCLUSION

In this paper we described the kinetics of the oxidation of Ferrous ions induced by gamma radiation at room temperature in a Fricke dosimeter. Instead of solving the system of coupled non-linear ordinary differential equations that describe the mass balance of all the species involved (Eqs. 8), here we implemented an original agent based model that includes in Eqs. (13) all of the reaction rates as source and sink terms (like in a prey-predator model). The agreement of the results from our agent-based model developed in Python with the experimental results suggests that the numerical model is reliable for analyzing the kinetics of chemical oxidation reactions induced by radiation. This model is very simple and robust, and maybe could be applied to different chemical reactions. We expect that it can be used to understand the kinetics of reactions induced by radiation when the temperature of the irradiated medium decreases below the freezing point. Further studies and experiments are needed to reveal the utility of our model.

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