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Numerical modeling of radiation-induced reactions: Fricke dosimeter at 298 K, 198 K, and 77 K

A. Paredes-Arriaga[a,d,*], A.L. Rivera[b,d], D. Frías[c], S. Ramos[d], and A. Negrón-Mendoza[d]

[a]*Posgrado en Ciencias de la Tierra, Universidad Nacional Autónoma de México.*
[*]*e-mail: ale.paredes.arriaga@gmail.com*
[b]*Instituto de Ciencias de la Complejidad, Universidad Nacional Autónoma de México.*
[c]*Universidade do Estado da Bahia, Salvador-BA., Brazil.*
[d]*Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México.*

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The Fricke dosimeter is a widely used gamma radiation dosimetry system. The system is based on the detection of Fe^{2+} to Fe^{3+} oxidation in an aqueous solution of ferrous sulfate in sulfuric acid, exposed to ionizing radiation in the presence of oxygen. The system is formed by a series of highly dependent chemical reactions. We developed a numerical model of coupled differential equations based on the mass balance; each equation incorporates information about the formation and breakdown of each molecule, as well as a term that represents an external source of radiation. The numerical model can reproduce the behavior of the experimental data at room temperature. We proposed a correction factor to simulate the behavior of the dosimeter at temperatures of 198 K and 77 K, respectively, when the system is in a thermal bath of dry ice or liquid nitrogen. This model could support a variety of experimental challenges for radiation at low temperatures in different fields of industry and could have relevance for astrobiology problems by offering the possibility of simulating reactions in comets and other exoplanetary bodies.

Keywords: Fricke dosimeter; radiation; mathematical model; temperature.

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1. Introduction

Ionizing radiations are energetic electromagnetic waves or particles emitted by radioactive substances, characterized by the ability to excite or ionize atoms of matter with which they interact [1]. Part of the energies involved in nuclear chemical reactions are transmitted to the atoms in the form of recoils and excitation energy, thus strongly affecting chemical bonds [2]. The excited species can also react with neighboring atoms or molecules. The number of ionized species and the means of formation of a specific medium depend on the energy and type of radiation [3].

The two major natural sources of ionizing radiation on a planetary body are the decay of radioactive isotopes present on the surface and the flux of cosmic rays from above [4]. In processes of chemical evolution, the radiation-induced reactions of simple molecules may lead to compounds of prebiotic significance. In these processes, the possible set of chemical reactions is controlled by the thermodynamics and kinetics of each possible prebiotic system [5]. The analysis of radiation-induced reactions is crucial to understanding the formation of biologically-important molecules on planets and icy bodies [6].

The Fricke dosimeter is a standard of dosimetry [7]. It operates by measuring the oxidation of Fe^{2+} to Fe^{3+} in an aqueous solution of ferrous sulfate with free sulfuric acid under ionizing radiation and in the presence of oxygen [8,9]. This system has been used as a standard to test the viability of numerical models, given that its reaction mechanism (which is relatively simple) and reaction rate constants are known [10-12]. We modeled the behavior of the Fricke dosimeter and proposed a corrective function to the system, expanding the model to low temperature conditions.

2. Methodology

Experimental setup. We obtained experimental data from the work of Negron-Mendoza *et al.* (2012) [11]. The initial concentration of Fe^{2+} was 0.0016 mol/L and was irradiated at absorbed dose rate of 0.93 Gy/min. The samples were placed in Pyrex cells inside a Dewar flask with different refrigerants to make a thermal bath: 298 K with water at room temperature, 198 K with dry ice, and 77 K with liquid nitrogen. At 585 mmHg of pressure. The samples were analyzed with a spectrophotometer (UV-Vis Varian Cary 100) at 308 nm.
Reaction kinetics. The reaction mechanism is known and can be summarize as

$$H_2O \xrightarrow{\text{rad}} OH\cdot,\ e^-_{aq}\ ,\ H\cdot,\ \ H_2,\ H_2O_2$$

$$H_3O + e^-_{aq} \xrightarrow{k1} H\cdot$$

$$H\cdot + O_2 \xrightarrow{k2} HO_2$$

$$Fe^{2+} + OH\cdot \xrightarrow{k3} Fe^{3+} + OH^-$$

$$Fe^{2+} + H_2O_2 \xrightarrow{k4} Fe^{3+} + 2OH^-$$

$$Fe^{2+} + HO_2 \xrightarrow{k5} Fe^{3+} + HO_2^-$$

$$\mathrm{H}\cdot + \mathrm{HO}_2^- \xrightarrow{k6} \mathrm{H_2O_2}$$

$$\mathrm{H}\cdot + \mathrm{HO}_2^- \xleftarrow{k7} \mathrm{H_2O_2}$$

The system had 11 chemical species, 7 reactions, and 7 rate constants: $k1 = 1.9 * 10^{10}$, $k2 = 2.3 * 10^{10}$, $k3 = 2.6 * 10^8$, $k4 = 61.9$, $k5 = 7.3 * 10^5$, $k6 = 5 * 10^5$, and $k7 = 1 * 10^5$[11]. The initial concentrations were $Fe^{2+} = 1.6 * 10^{-3} M$, $O_2 = 1.2 * 10^{-2} M$, and $H_3O^+ = 4 * 10^{-1} M$ [13].

Numerical model. We transformed the chemical reactions in differential equations, taking into consideration the formation/destruction of the species involved. Each differential equation comprised three terms: the addition of molecules formed, the subtraction of molecules decomposed, and an external source:

$$\frac{dN_i(t)}{dt} = f_i + \sum_{j\neq i}\sum_{k\neq i} k_{j,k}^{(i)} N_j\,(t)\,N_k\,(t) - N_i\,(t)\sum_m k_{i,m} N_m\,(t), \quad (1)$$

where N_i, N_j, and N_k are the molar concentrations of *i*, *j*, and *k* species at time *t*, $k_{j,k}^i$ is the rate constant for the *j* and *k* species produced by the *i* species, $k_{i,m}$ is the rate constant for the reaction between *i* and *m* chemical species, and f_i is an external energy source.

The source term (f_i) is determined as:

$$f_i\,(I_d, T) = \frac{6.2 * 10^{11}}{3.6\,N_A}\frac{M_i}{M_{\mathrm{H_2O}}} G_i\,[I_d * (6{*}10^3)]\lambda(T), \quad (2)$$

where N_A is the Avogadro number ($6.022 * 10^{23}$ molecules), M_i is the molecular mass of the i species, $M_{(\mathrm{H_2O})}$ is the water's molecular mass (18.02 g/mol), Gi is the radiochemical yield of the i species when the system absorbs 100 eV (specific to each chemical species), I_d is the dose intensity ($Gy/\min$), and $\lambda(T)$ is a temperature correction factor [14].

$\lambda(T)$ is a normalized function between 0 and 1, functioning as a correction factor over the source term to approximate the model's reactions below temperatures of 273 K. In this work, we propose:

$$\lambda\,(T) = \left(\frac{T}{298\ \mathrm{K}}\right)^2 (1 - APF)\,, \quad (3)$$

where T is the temperature (in K) and APF is the atomic packing factor of water ice ($APF = 0.34$).

We computed the root mean square error (RMSE) between the experimental and model data:

$$RMSE = \sqrt{\left(\left[\sum_{i=1}^{N}(x_i - y_i)^2\right] \Big/ N\right)}, \quad (4)$$

where x_i is the observed value, y_i the estimated value, and N the number of observations.

To solve the coupled ordinary differential equations system, we generated a code in $python$ 3 and used the *solve_ivp library*, which computes solutions for stiff and non- stiff ODE systems with diverse methods [15].

3. Results and discussion

The model of the Fricke dosimeter under gamma radiation at room temperature (298 K) shows a progressive reduction of Fe^{2+} molar concentration and the formation of Fe^{3+}. This model reflects the behavior of the experimental results (Fig. 1).

We sought a function to approximate the effect of low temperatures (below 273 K), when the water of the system is in the ice phase. $\lambda(T)$ is a normalized function between 0 and 1 [13]. To develop this function, we analyzed the important factors able to change the transfer of matter in solids: diffusion mechanism, temperature, solvent crystal structure, crystal lattice imperfections, and concentration of diffusing elements [16,17].

This model has two assumptions: a) the crystal lattice imperfections do not represent a significant change and b) molecule are diffused by the same mechanism. Molecule concentration was already considered in the initial conditions of the ODE system. The weight factor is provided by the solvent crystal structure, which, in this case, is the water's APF (0.34). With this information, we propose Eq. (3) for this model.

We used the correction factor $\lambda(T)$ to compute the Fricke dosimeter model at temperatures of 198 K and 77 K. The model follows the behavior of the experimental results (Fig. 2) in the three cases.

The $RMSE$ between the experimental data and the model data is $8.18 * 10^{-5}$ at 298 K, $2.87 * 10^{-5}$ at 198 K, and $2.35 * 10^{-5}$ at 77 K, equivalent to 5.1 %, 1.8%, and 1.5%, respectively. The correlation coefficient (R^2) is higher than 0.98 for the three cases.

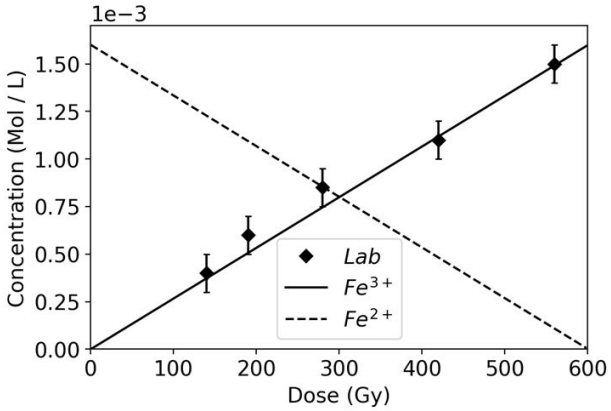

FIGURE 1. Fe^{2+} oxidation and Fe^{3+} formation in the Fricke dosimeter. Lines represent the numerical model, and dots represent laboratory experiments.

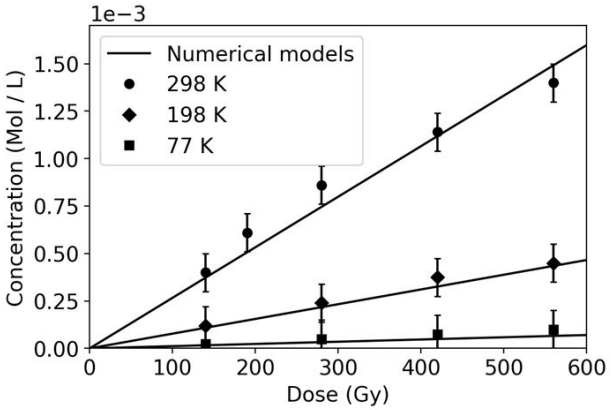

FIGURE 2. Fe^{3+} formation in function of radiation dose at three temperatures, modeled with the temperature correction factor $\lambda(T)$. Lines represent the numerical model and points represent the experimental results.

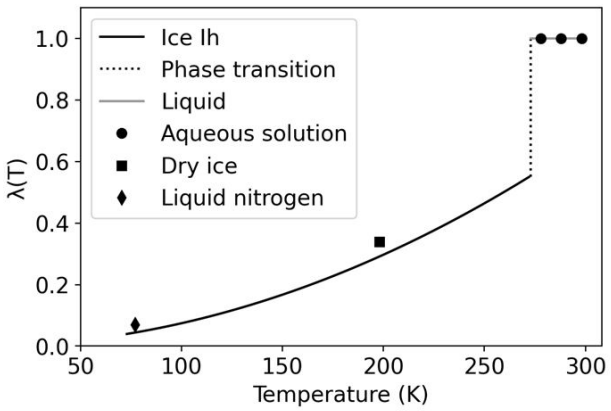

FIGURE 3. Function $\lambda(T)$ is a correction factor that changes the reaction velocity of the molecules in function of the system temperature when irradiated at 198 K and 77 K.

With the correction factor $\lambda(T)$ in the source term $f_i(I_d, T)$, it is possible to approximate the linear behavior of the dosimeter's experimental data at room and cool temperatures (below 273 K), when the system is under dry ice and in a liquid nitrogen thermal bath (Fig. 2).

Figure 3 shows the closeness between the behavior of $\lambda(T)$ from 75 K to 273 K and the collected experimental data. The experimental data show implicitly an abrupt reduction of radiation energy absorption by water ice. It is modeled with a heuristic function. We now propose an unreleased function, also with a heuristic nature, but rather based on the physics of atomic packing processes including a parameter, which has been defined and measured experimentally. It is important to remark that $\lambda(T)$ represents an approximation and simplification for a multi-factorial system and does not involve a complete physical description of the phenomena.

4. Conclusions

Experimental results show the lineal behavior of the Fricke dosimeter. The proposed numerical model reproduced the experimental results at room and cool temperatures. Low temperatures (198 K and 77 K) slowed down the oxidation chemical reaction of Fe^{2+} to Fe^{3+}, and the numerical model can reproduce the experimental results at different temperatures with the function $\lambda(T)$. *Solve_ivp* is an efficient library for solving this coupled ordinary differential equations system. This model is a reductionist approximation that addresses the most general elements of a complex problem with multiple variables.

Due to the possibility of simulating reactions in comets and other extraterrestrial bodies, this model could support a variety of experimental challenges in domains of industry involving radiation at low temperatures, as well as contribute to solutions for astrobiological and astronomical problems.

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