Modelado en COMSOL Multiphysics de un proceso de microscopía electrónica en fase líquida

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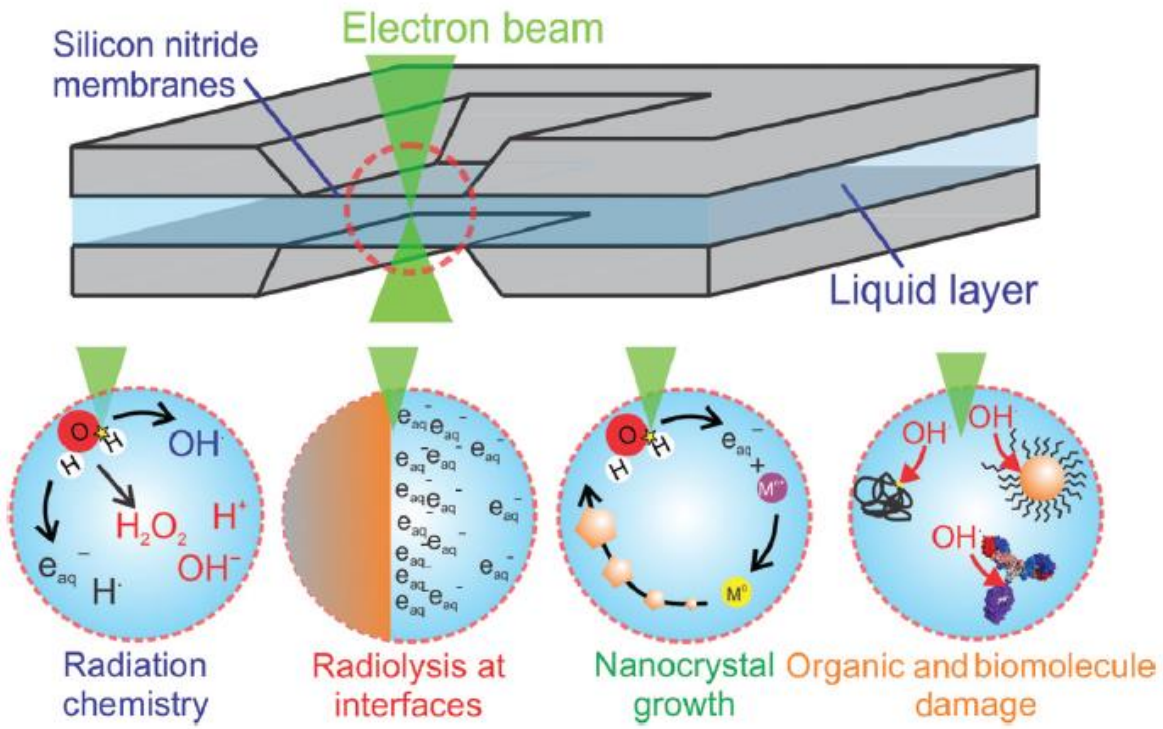
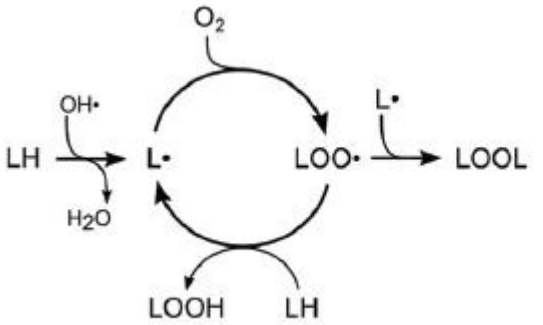
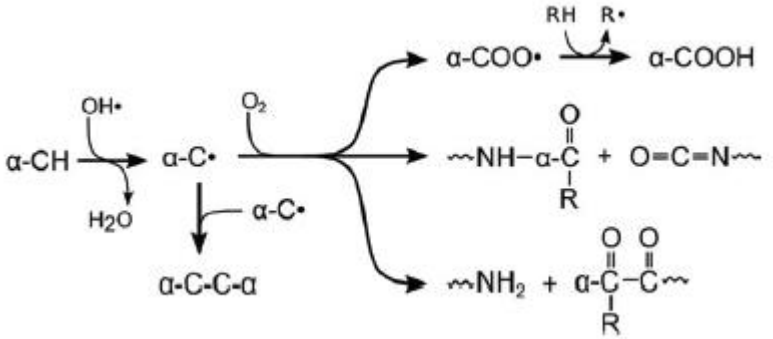
(Curso académico 2020/2021)

Introducción y fundamento teórico:







Introducción y fundamento teórico:

Reaction #	Equilibria	pK_a (25°C)
2	$H_2O \leftrightarrow H^+ + OH^-$	13.999
3	$H_2O_2 \leftrightarrow H^+ + HO_2^-$	11.65
4	$OH \leftrightarrow H^+ + O^-$	11.9
5	$HO_2 \leftrightarrow H^+ + O_2^-$	4.57
6	$H \leftrightarrow H^+ + e_{aq}^-$	9.77
	Chemical Reaction	**Rate Constant (25°C) ($M^{-1}s^{-1}$ unless specified otherwise)**
7	$H^+ + OH^- \rightarrow H_2O$	1.4×10^{11}
8	$H_2O \rightarrow H^+ + OH^-$	$\frac{k_7 \times K_2}{[H_2O]}\ s^{-1}$
9	$H_2O_2 \rightarrow H^+ + HO_2^-$	$k_{10} \times K_3\ s^{-1}$
10	$H^+ + HO_2^- \rightarrow H_2O_2$	5.0×10^{10}
11	$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$	1.3×10^{10}
12	$HO_2^- + H_2O \rightarrow H_2O_2 + OH^-$	$\frac{k_{11} \times K_2}{K_3 \times [H_2O]}$
13	$e_{aq}^- + H_2O \rightarrow H + OH^-$	1.9×10^1
14	$H + OH^- \rightarrow e_{aq}^- + H_2O$	2.2×10^7
15	$H \rightarrow e_{aq}^- + H^+$	$k_{16} \times K_6\ s^{-1}$
16	$e_{aq}^- + H^+ \rightarrow H$	2.3×10^{10}
17	$OH + OH^- \rightarrow O^- + H_2O$	1.3×10^{10}
18	$O^- + H_2O \rightarrow OH + OH^-$	$\frac{k_{17} \times K_2}{K_4 \times [H_2O]}$
19	$OH \rightarrow O^- + H^+$	$k_{20} \times K_4\ s^{-1}$
20	$O^- + H^+ \rightarrow OH$	1.0×10^{11}
21	$HO_2 \rightarrow O_2^- + H^+$	$k_{22} \times K_5\ s^{-1}$
22	$O_2^- + H^+ \rightarrow HO_2$	5.0×10^{10}
23	$HO_2 + OH^- \rightarrow O_2^- + H_2O$	5.0×10^{10}
24	$O_2^- + H_2O \rightarrow HO_2 + OH^-$	$\frac{k_{23} \times K_2}{K_5 \times [H_2O]}$
25	$e_{aq}^- + OH \rightarrow OH^-$	3.0×10^{10}
26	$e_{aq}^- + H_2O_2 \rightarrow OH + OH^-$	1.1×10^{10}
27	$e_{aq}^- + O_2^- + H_2O \rightarrow HO_2^- + OH^-$	$\frac{1.3 \times 10^{10}}{[H_2O]}\ M^{-2}s^{-1}$
28	$e_{aq}^- + HO_2 \rightarrow HO_2^-$	2.0×10^{10}
29	$e_{aq}^- + O_2 \rightarrow O_2^-$	1.9×10^{10}
30	$e_{aq}^- + e_{aq}^- + 2H_2O \rightarrow H_2 + 2OH^-$	$\frac{5.5 \times 10^9}{[H_2O]^2}\ M^{-3}s^{-1}$
31	$e_{aq}^- + H + H_2O \rightarrow H_2 + OH^-$	$\frac{2.5 \times 10^{10}}{[H_2O]}\ M^{-2}s^{-1}$
32	$e_{aq}^- + HO_2 \rightarrow O^- + OH^-$	3.5×10^9
33	$e_{aq}^- + O^- + H_2O \rightarrow OH^- + OH^-$	$\frac{2.2 \times 10^{10}}{[H_2O]}\ M^{-2}s^{-1}$
34	$e_{aq}^- + O_3^- + H_2O \rightarrow O_2 + OH^- + OH^-$	$\frac{1.6 \times 10^{10}}{[H_2O]}\ M^{-2}s^{-1}$
35	$e_{aq}^- + O_3 \rightarrow O_3^-$	3.6×10^{10}
36	$H + H_2O \rightarrow H_2 + OH$	1.1×10^1
37	$H + O^- \rightarrow OH^-$	1.0×10^{10}
38	$H + HO_2^- \rightarrow OH + OH^-$	9.0×10^7
39	$H + O_3^- \rightarrow OH^- + O_2$	1.0×10^{10}
40	$H + H \rightarrow H_2$	7.8×10^9
41	$H + OH \rightarrow H_2O$	7.0×10^9
42	$H + H_2O_2 \rightarrow OH + H_2O$	9.0×10^7
43	$H + O_2 \rightarrow HO_2$	2.1×10^{10}
44	$H + HO_2 \rightarrow H_2O_2$	1.8×10^{10}
45	$H + O_2^- \rightarrow HO_2^-$	1.8×10^{10}
46	$H + O_3 \rightarrow HO_3$	3.8×10^{10}
47	$OH + OH \rightarrow H_2O_2$	3.6×10^9
48	$OH + HO_2 \rightarrow H_2O + O_2$	6.0×10^9
49	$OH + O_2^- \rightarrow OH^- + O_2$	8.2×10^9
50	$OH + H_2 \rightarrow H + H_2O$	4.3×10^7
51	$OH + H_2O_2 \rightarrow HO_2 + H_2O$	2.7×10^7
52	$OH + O^- \rightarrow HO_2^-$	2.5×10^{10}
53	$OH + HO_2^- \rightarrow HO_2 + OH^-$	7.5×10^9
54	$OH + O_3^- \rightarrow O_3 + OH^-$	2.6×10^9
55	$OH + O_3^- \rightarrow O_2^- + O_2^- + H^+$	6.0×10^9
56	$OH + O_3 \rightarrow HO_2 + O_2$	1.1×10^8
57	$HO_2 + O_2^- \rightarrow HO_2^- + O_2$	8.0×10^7
58	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	7.0×10^5
59	$HO_2 + O^- \rightarrow O_2 + OH^-$	6.0×10^9
60	$HO_2 + H_2O_2 \rightarrow OH + O_2 + H_2O$	5.0×10^{-1}
61	$HO_2 + HO_2^- \rightarrow OH + O_2 + OH^-$	5.0×10^{-1}
62	$HO_2 + O_3^- \rightarrow O_2 + O_2 + OH^-$	6.0×10^9
63	$HO_2 + O_3 \rightarrow HO_3 + O_2$	5.0×10^8
64	$O_2^- + O_2^- + 2H_2O \rightarrow H_2O_2 + O_2 + 2OH^-$	$\frac{1.0 \times 10^2}{[H_2O]^2}\ M^{-3}s^{-1}$
65	$O_2^- + O^- + H_2O \rightarrow O_2 + 2OH^-$	$\frac{6.0 \times 10^4}{[H_2O]}\ M^{-2}s^{-1}$
66	$O_2^- + H_2O_2 \rightarrow OH + O_2 + OH^-$	1.3×10^{-1}
67	$O_2^- + HO_2^- \rightarrow O^- + O_2 + OH^-$	1.3×10^{-1}
68	$O_2^- + O_3^- + H_2O \rightarrow O_2 + O_2 + 2OH^-$	$\frac{1.0 \times 10^4}{[H_2O]}\ M^{-2}s^{-1}$
69	$O_2^- + O_3 \rightarrow O_3^- + O_2$	1.5×10^9
70	$O^- + O^- + H_2O \rightarrow HO_2^- + OH^-$	$\frac{1.0 \times 10^9}{[H_2O]}\ M^{-2}s^{-1}$
71	$O^- + O_2 \rightarrow O_3^-$	3.6×10^9
72	$O^- + H_2 \rightarrow H + OH^-$	8.0×10^7
73	$O^- + H_2O_2 \rightarrow O_2^- + H_2O$	5.0×10^8
74	$O^- + HO_2^- \rightarrow O_2^- + OH^-$	4.0×10^8
75	$O^- + O_3^- \rightarrow O_2^- + O_2^-$	7.0×10^8
76	$O^- + O^3 \rightarrow O_2^- + O_2$	5.0×10^9
77	$O_3^- \rightarrow O_2 + O^-$	$3.3 \times 10^3\ s^{-1}$
78	$O_3^- + H^+ \rightarrow O_2 + OH$	9.0×10^{10}
79	$HO_3 \rightarrow O_2 + OH$	$1.1 \times 10^5\ s^{-1}$

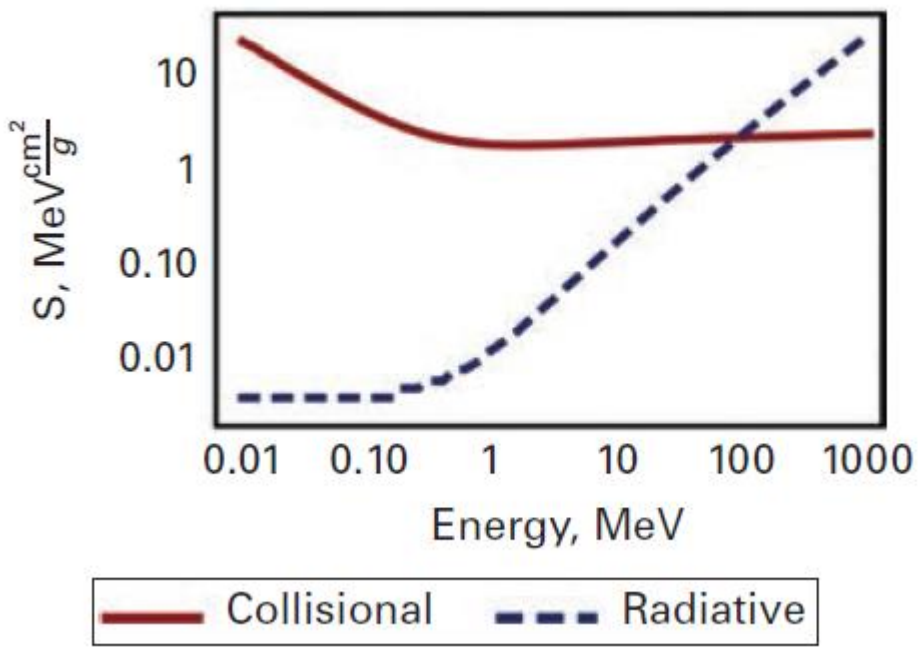
Introducción y fundamento teórico:

- **Productos primarios debidos a la radiación:**

$$H_2O \rightarrow e_h^-, H^\bullet, OH^\bullet, H_2, H_2O_2, H_3O^+, HO_2^\bullet$$

- **Energía perdida por el electrón y su dose rate:**

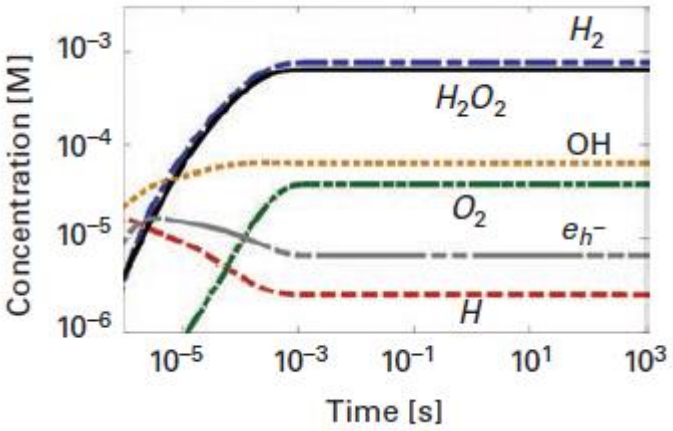
$$S_{Total} = \frac{dE}{ds} = S_R + S_C = \rho S \qquad \psi = \frac{10^5 SI}{\pi a^2} \text{ (Gy/s)}$$

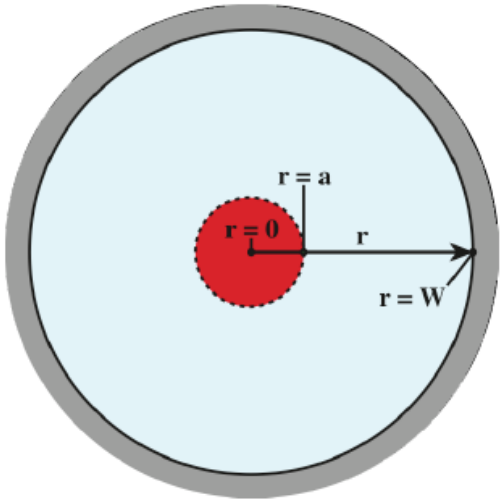


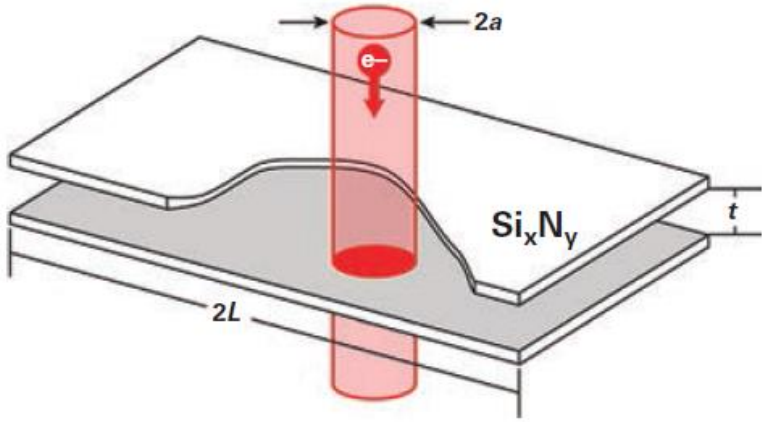
- **Ecuación de la concentración de las especies:**

$$\frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i - \sum_j k_{ij} C_i C_j + \sum_{j,k \neq i} k_{jk} C_j C_k + R_i$$

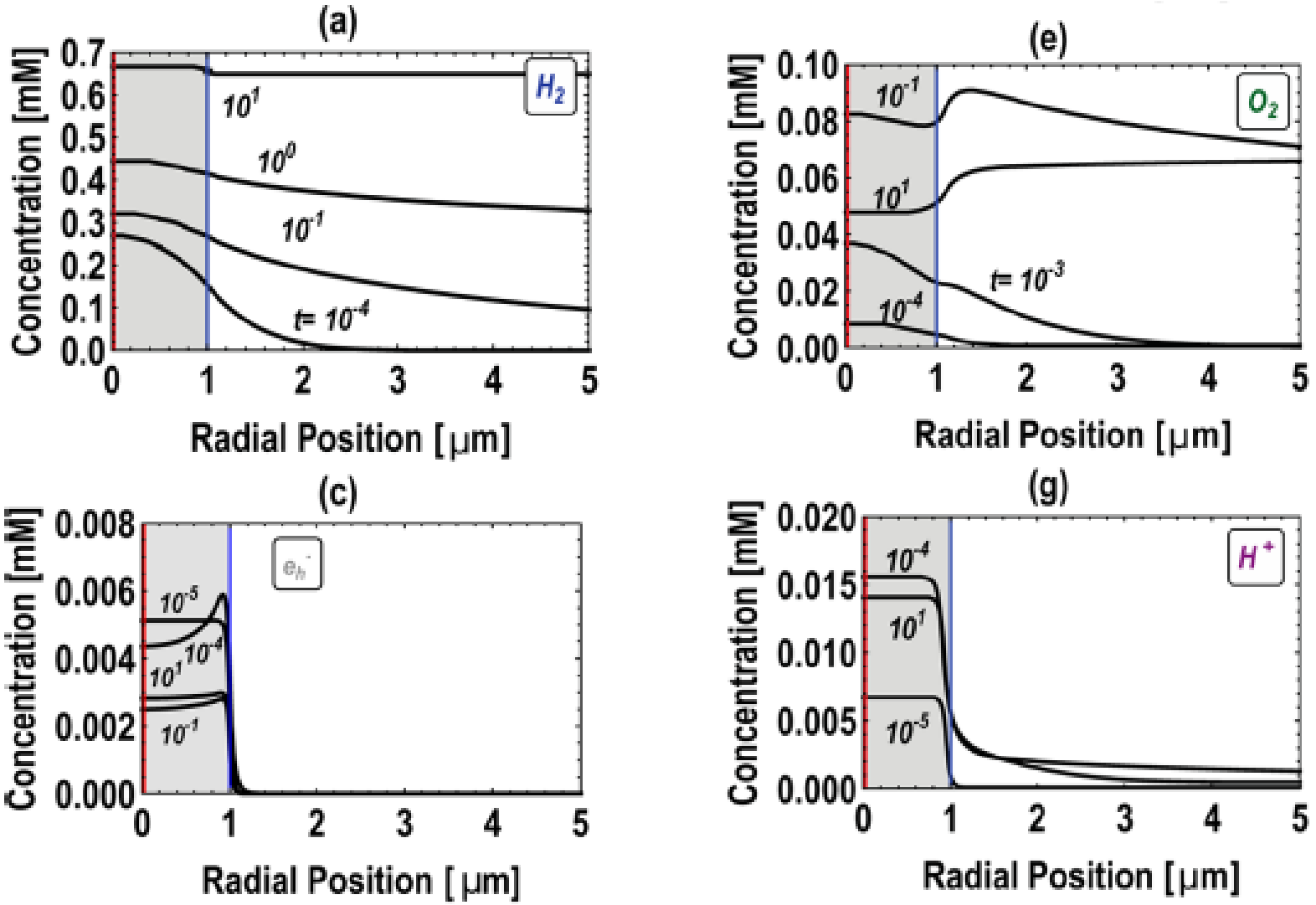
Introducción y fundamento teórico:



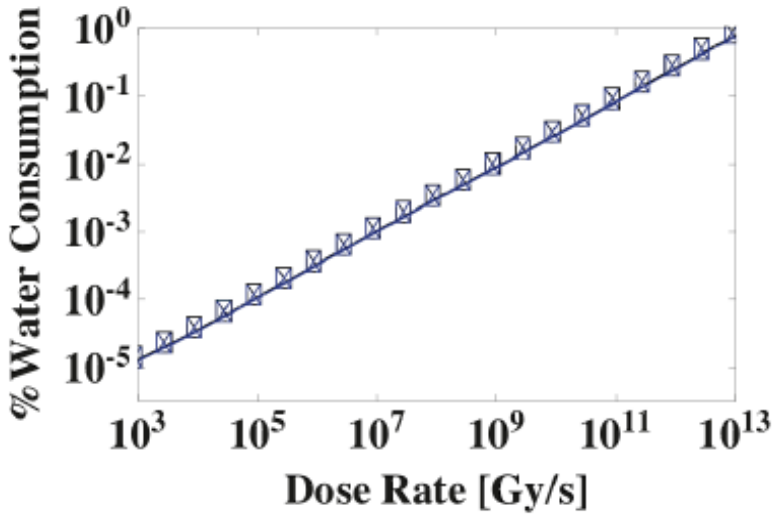


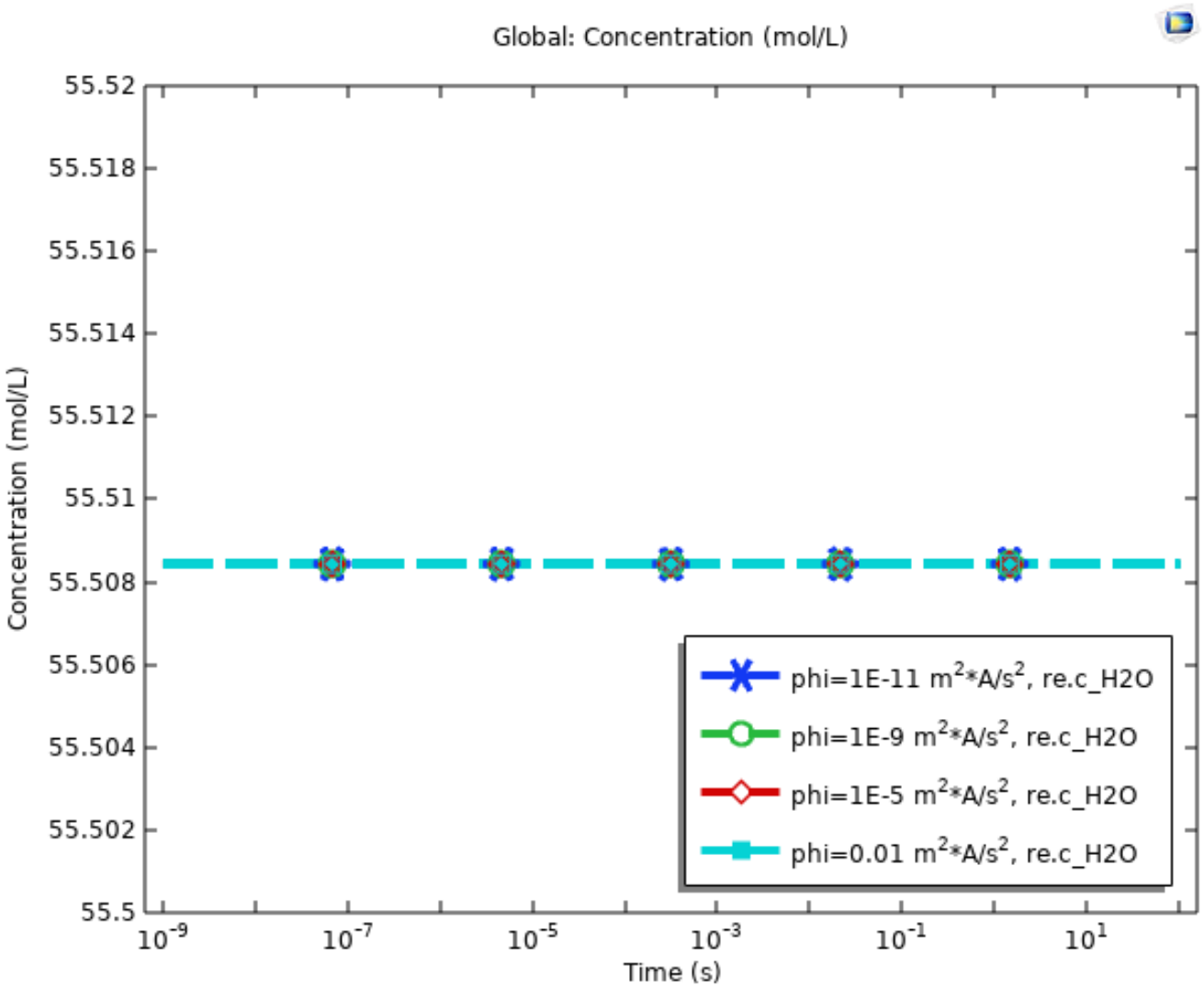


Introducción y fundamento teórico:



Simplificaciones del problema:





Definiciones globales, parámetros:

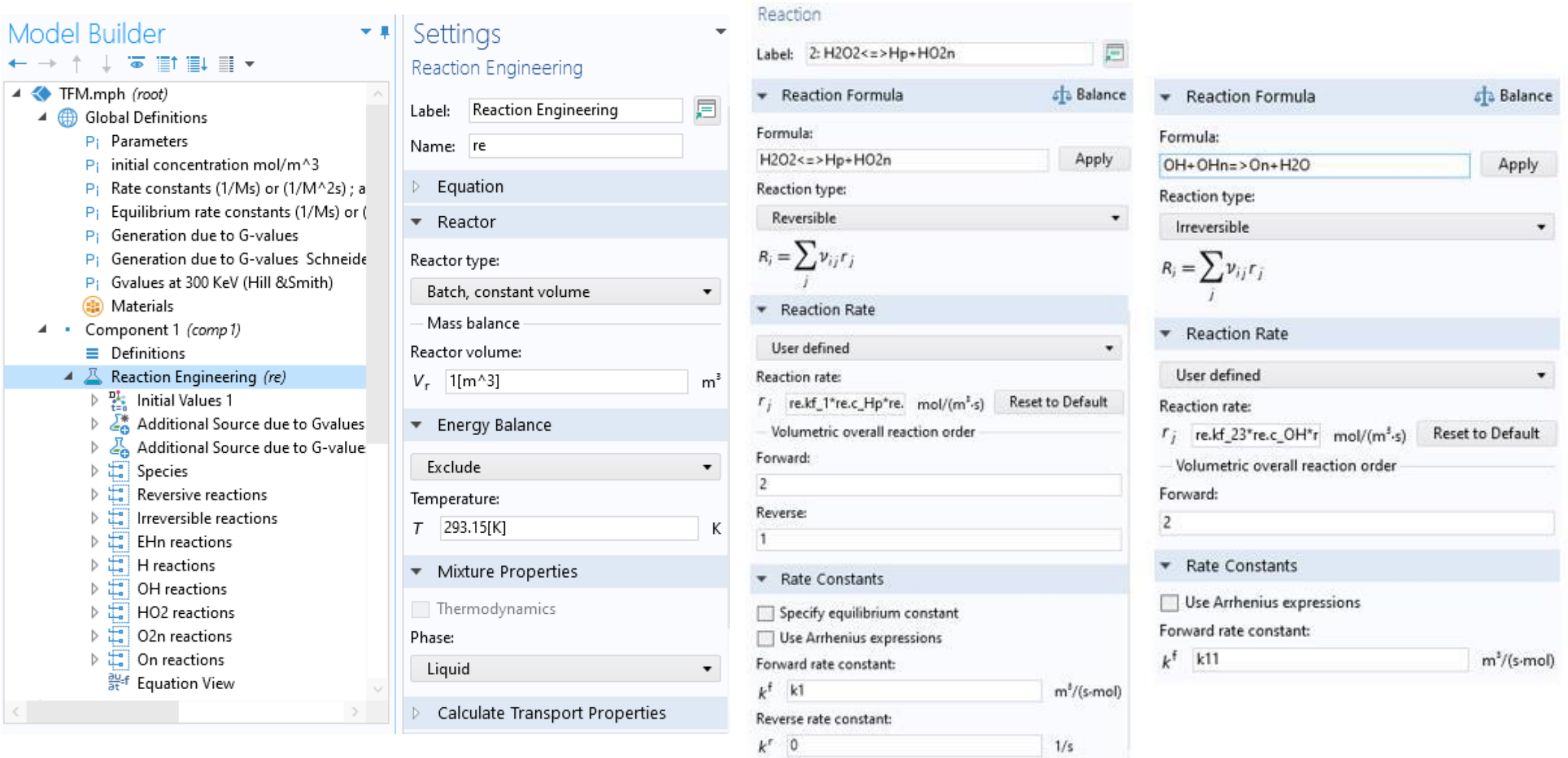
Name	Expression	Value	Description
phi	(S*I)/(pi*a^2)	1.02E-11 $m^2 \cdot A/s^2$	Doserate depending on following values
S	2[(MeV*cm^2)/(g)]	3.2044E-14 m^4/s^2	Stopping power
I	1e-9[A]	1E-9 A	Current
a	1e-4[cm]	1E-6 m	Beam radius
F	F_const	96485 C/mol	Faraday constant
rho	0.997[g/cm^3]	997 kg/m^3	Density of water

Name	Expression	Value	Description
GEHn	2.701033709730987e7[uM/s]	27010 $mol/(m^3 \cdot s)$	generation due to Gvalues
GH2O	-(GOHn+2*GH2O2+GOH+2*GHO2)	-44213 $mol/(m^3 \cdot s)$	
GH2	1.323272999003653e6[uM/s]	1323.3 $mol/(m^3 \cdot s)$	
GHO2	6.227167054134840e5[uM/s]	622.72 $mol/(m^3 \cdot s)$	
GOH	2.825577050813684e7[uM/s]	28256 $mol/(m^3 \cdot s)$	
GH	7.783958817668550e6[uM/s]	7784 $mol/(m^3 \cdot s)$	
GH2O2	3.658460644304218e6[uM/s]	3658.5 $mol/(m^3 \cdot s)$	
GOHn	7.394760876785121e6[uM/s]	7394.8 $mol/(m^3 \cdot s)$	
GHp	3.440509797409499e7[uM/s]	34405 $mol/(m^3 \cdot s)$	

Name	Expression	Value	Description
K1	10^-13.999[(mol/L)^2]	1.0023E-8 mol^2/m^6	equilibrium rate constants (1/Ms) or (1/M^2s)
K2	10^-11.65[(mol/L)]	2.2387E-9 mol/m^3	
K3	10^-11.9[(mol/L)]	1.2589E-9 mol/m^3	
K4	10^-4.57[(mol/L)]	0.026915 mol/m^3	
K5	10^-9.77[(mol/L)]	1.6982E-7 mol/m^3	

Name	Expression	Value	Description
REHn	0[mol/m^3]	0 mol/m^3	initial concentration micromolar/sec
RHp	1e-4[mol/m^3]	1E-4 mol/m^3	
ROHn	1e-4[mol/m^3]	1E-4 mol/m^3	
RH2O2	0[mol/m^3]	0 mol/m^3	
RHO2n	0[mol/m^3]	0 mol/m^3	
RH	0[mol/m^3]	0 mol/m^3	
ROH	0[mol/m^3]	0 mol/m^3	
ROn	0[mol/m^3]	0 mol/m^3	
RHO2	0[mol/m^3]	0 mol/m^3	
RO2n	0[mol/m^3]	0 mol/m^3	
RO2	0[mol/m^3]	0 mol/m^3	
RH2	0[mol/m^3]	0 mol/m^3	
RO3n	0[mol/m^3]	0 mol/m^3	
RO3	0[mol/m^3]	0 mol/m^3	
RHO3	0[mol/m^3]	0 mol/m^3	
RH2O	(1000000/18.01528)[mol/m^3]	55508 mol/m^3	

Interfaz física:



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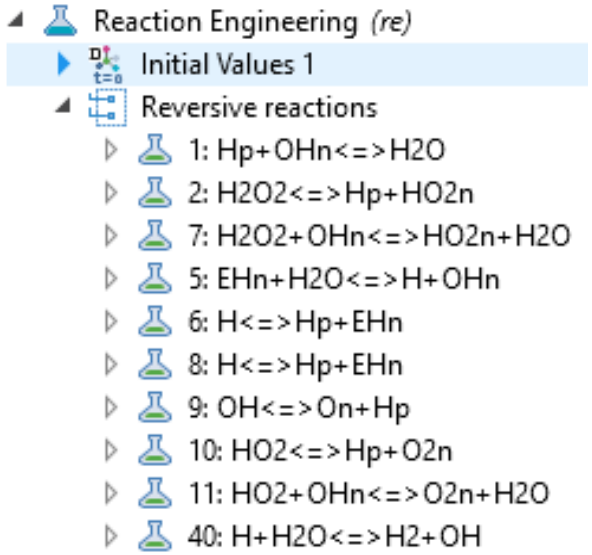
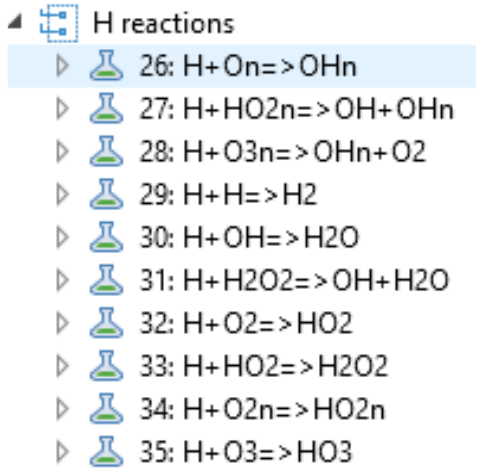
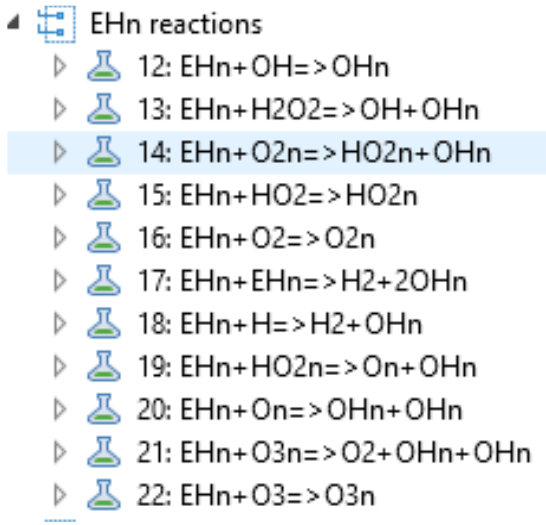
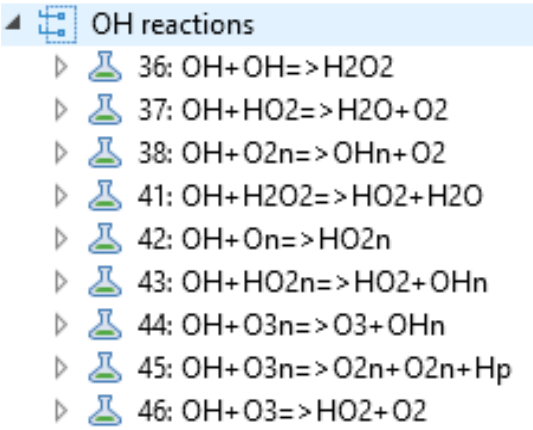
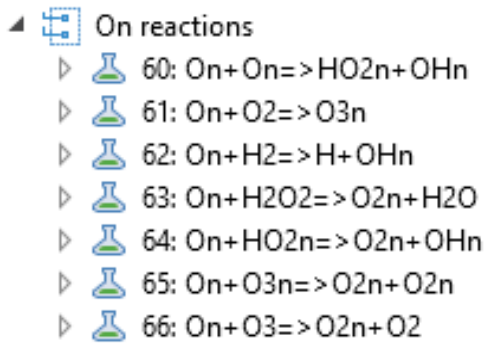
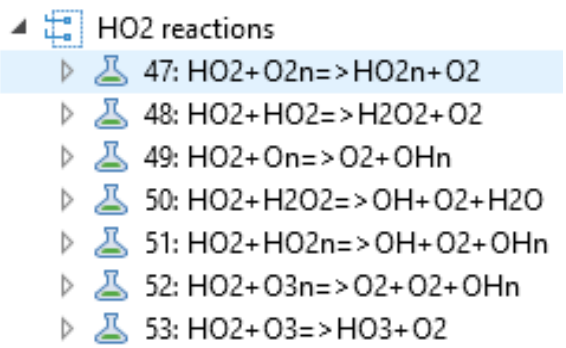


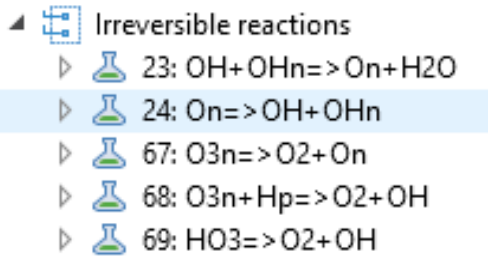


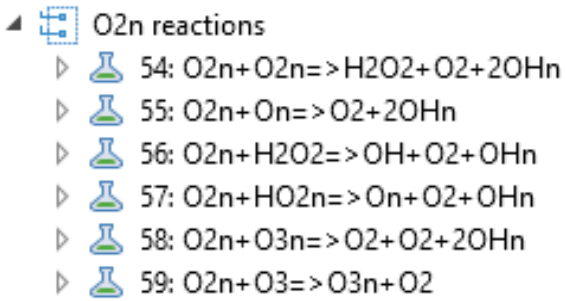




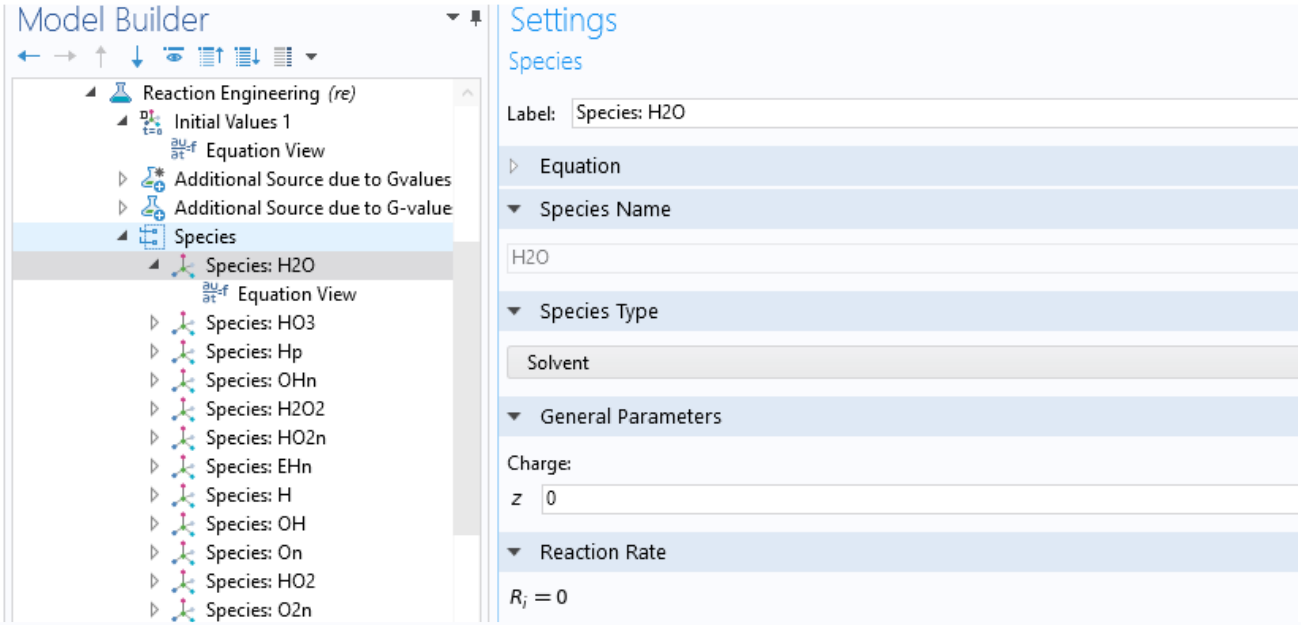


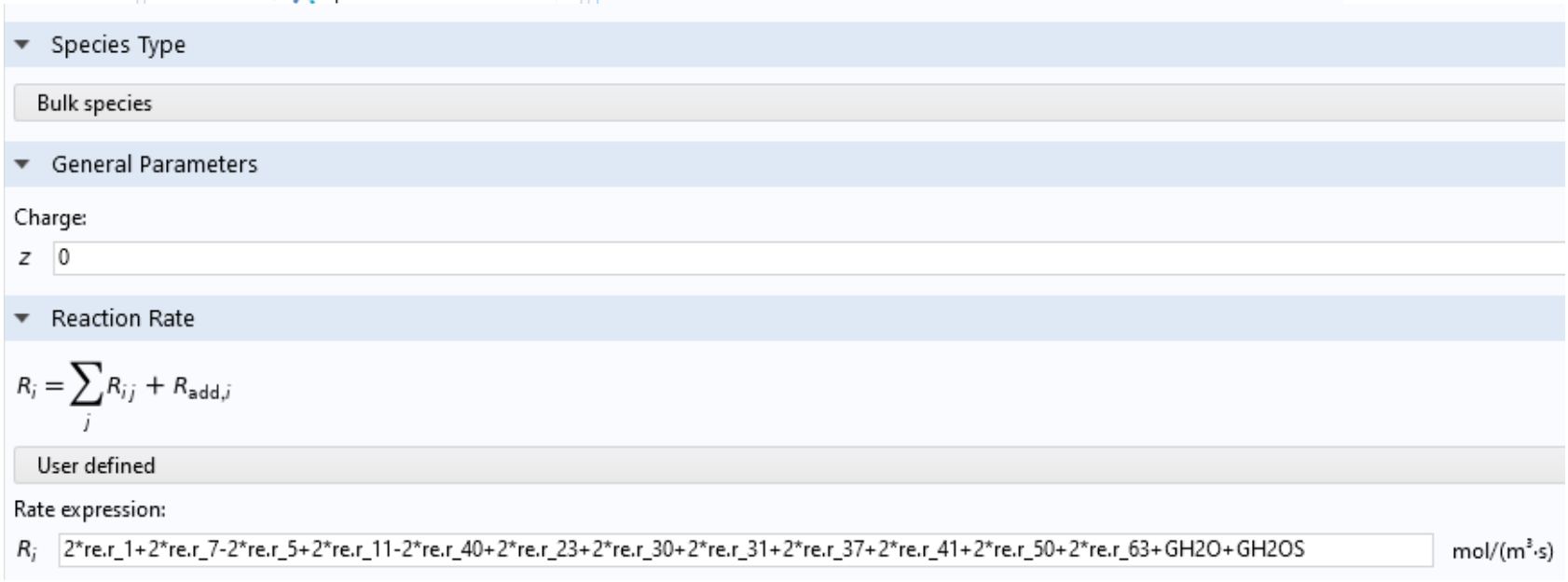




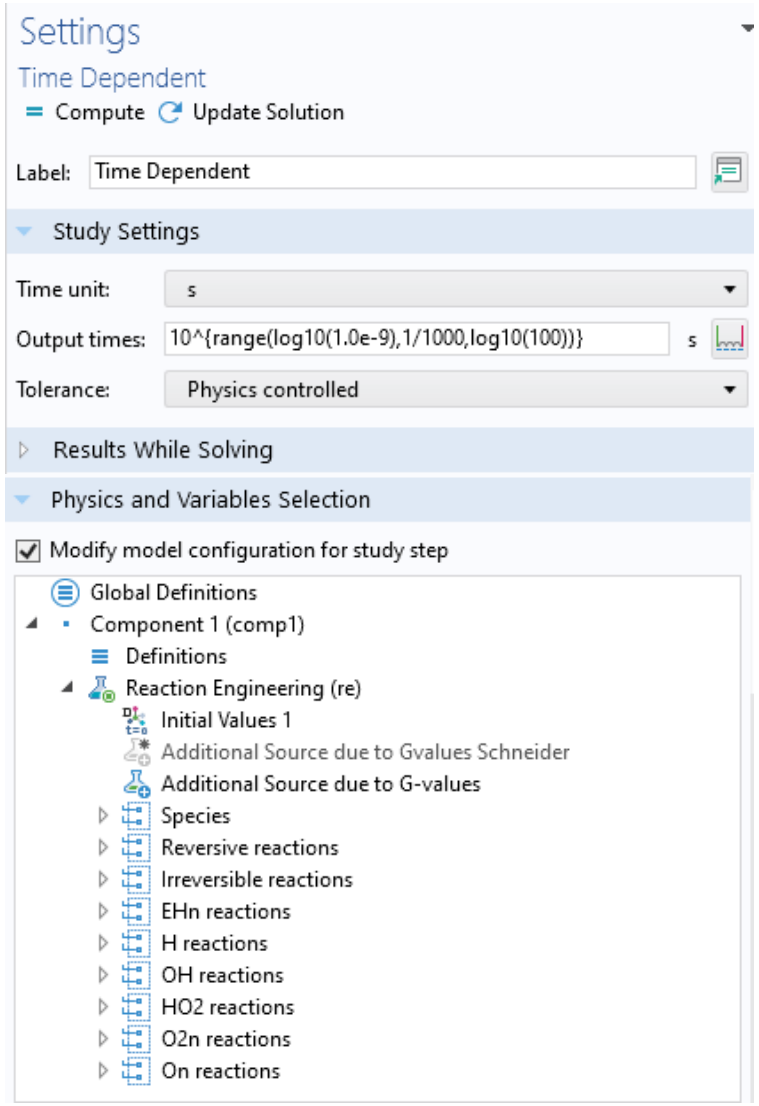


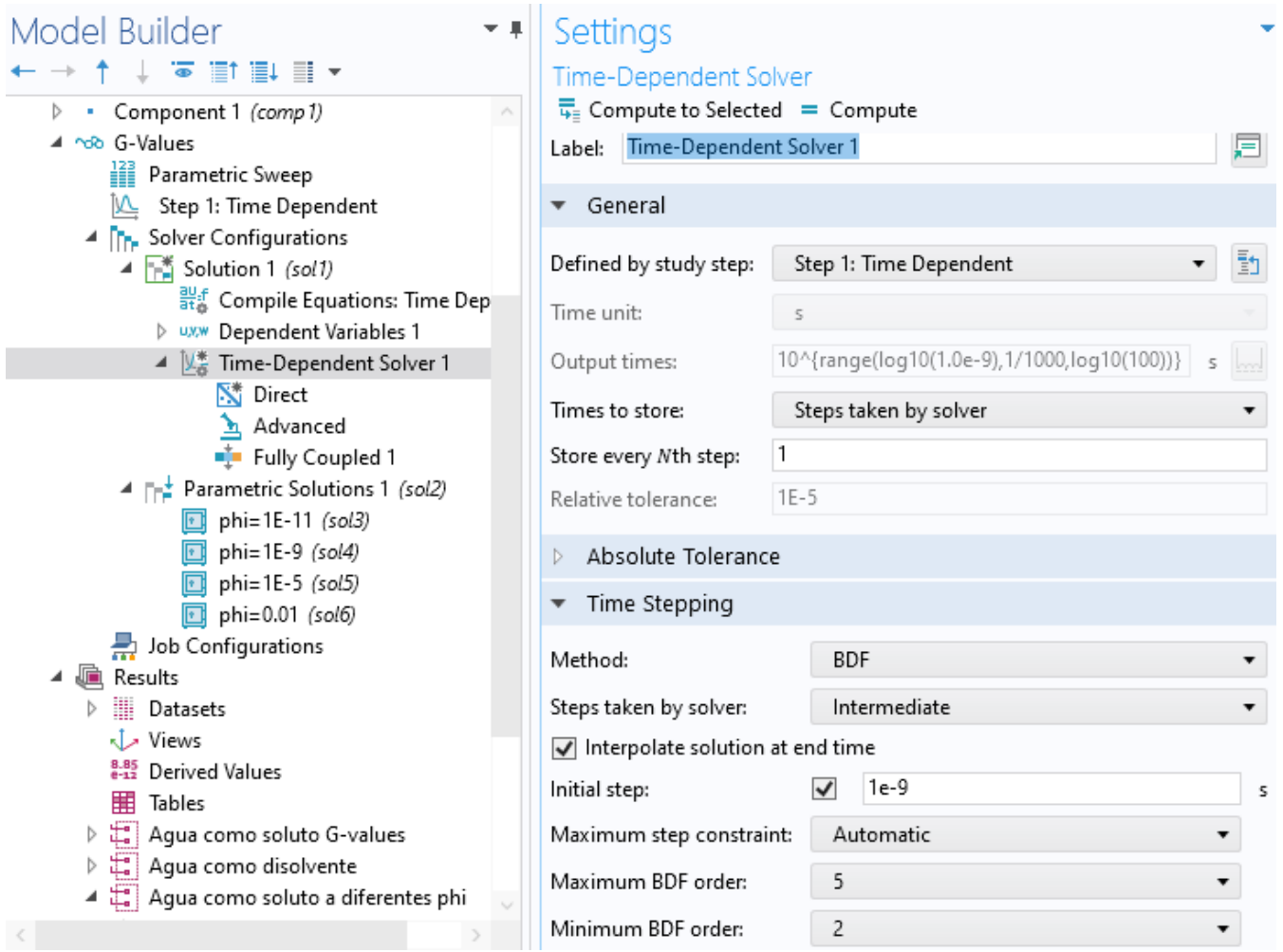
Interfaz física:



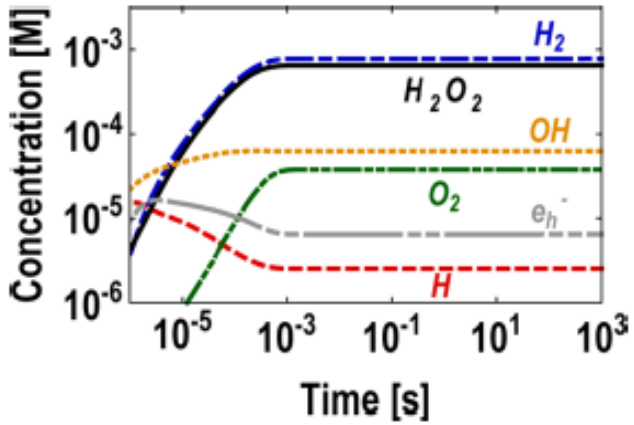


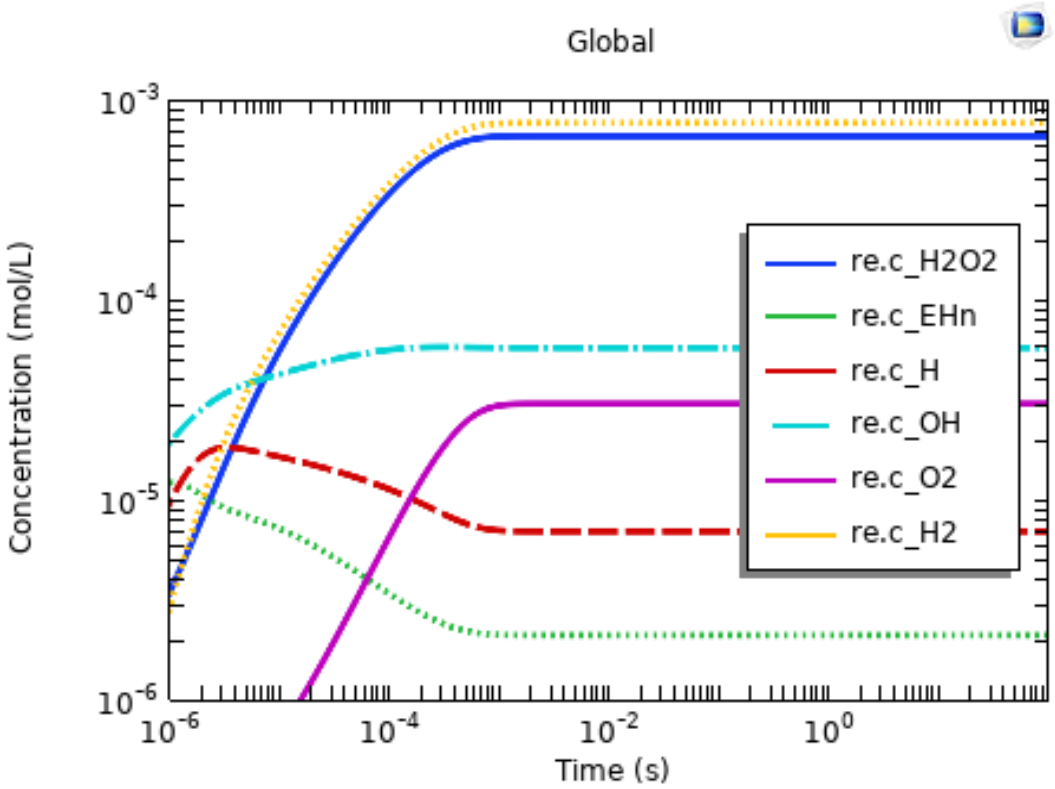
Estudio y resolvedor:

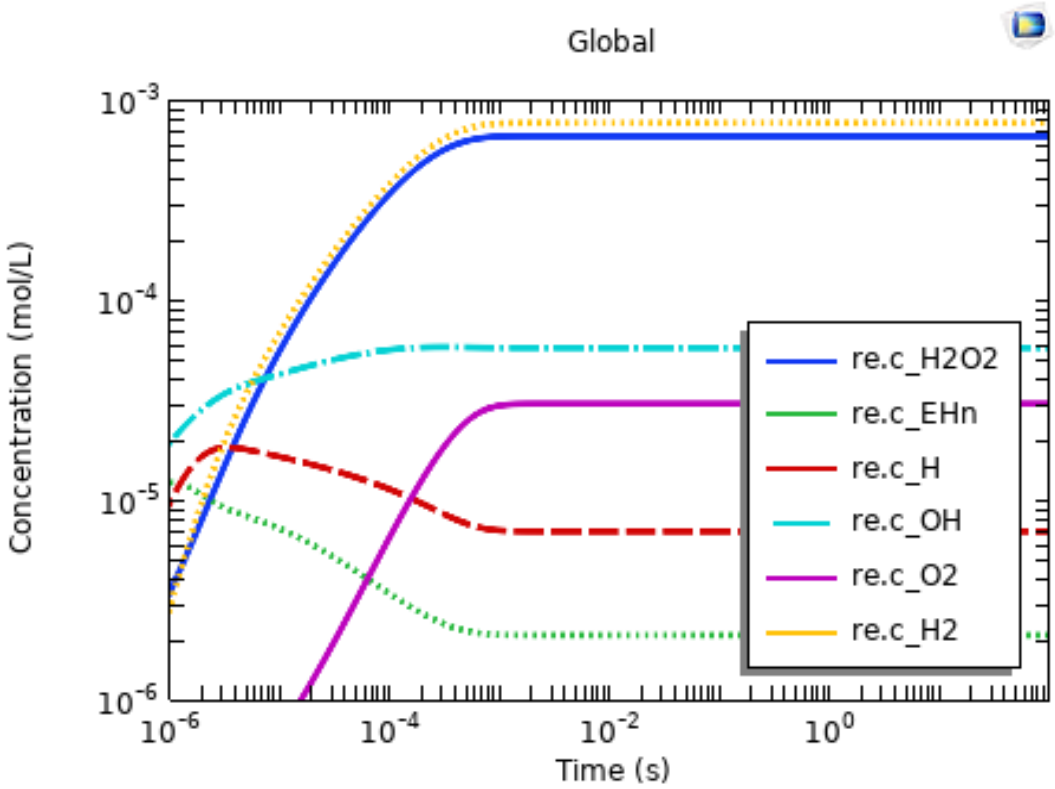




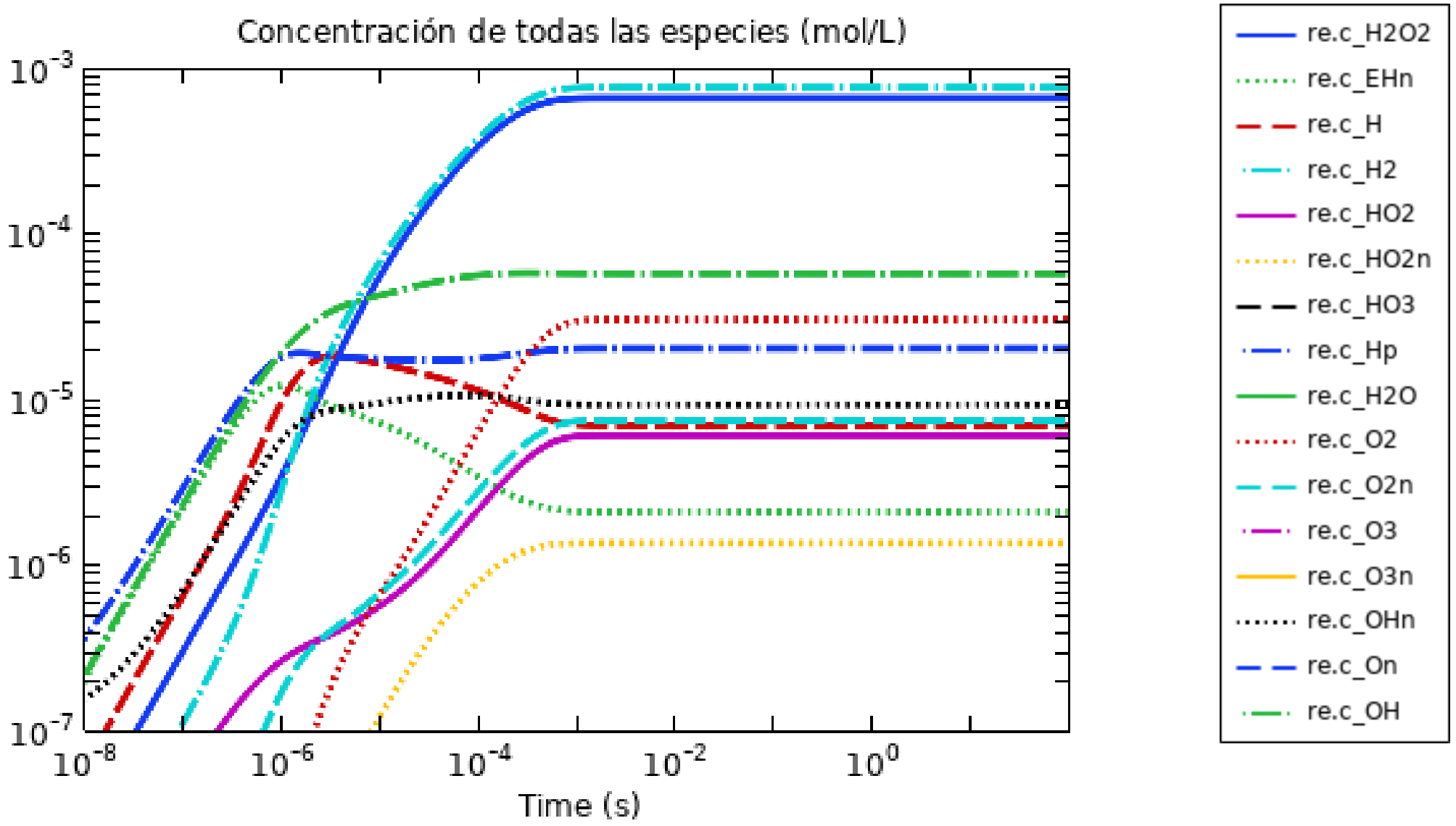
Resultados:


Concentration [M]
10^{-3}
10^{-4}
10^{-5}
10^{-6}
H_2
H_2O_2
OH
O_2
e_h^-
H
10^{-5}
10^{-3}
10^{-1}
10^{1}
10^{3}
Time [s]

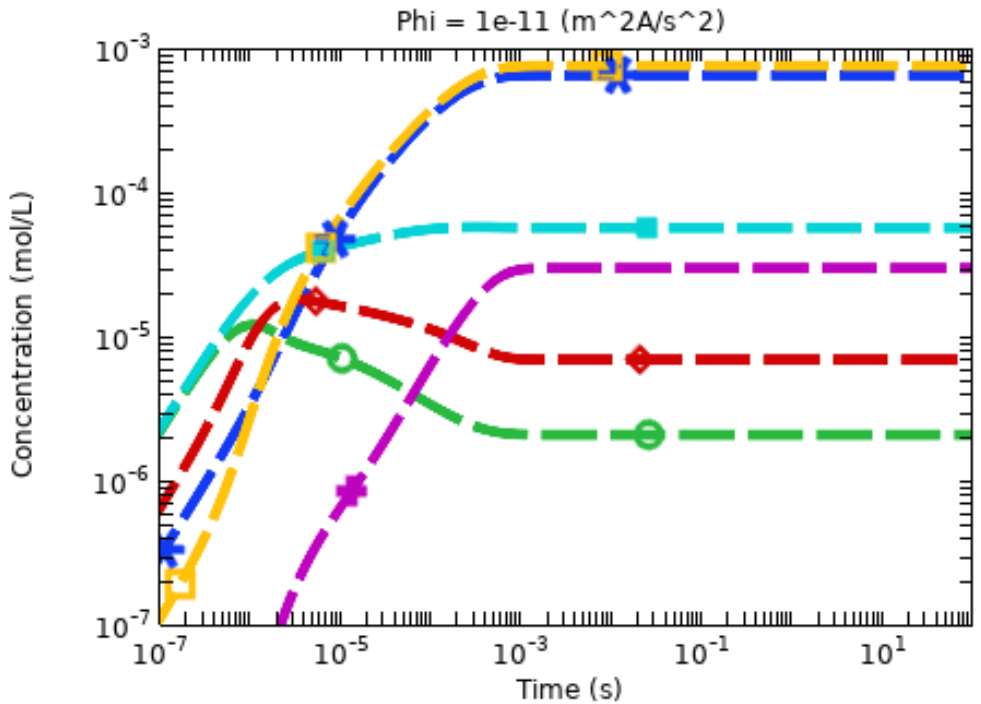

Global
Concentration (mol/L)
10^{-3}
10^{-4}
10^{-5}
10^{-6}
re.c_H2O2
re.c_EHn
re.c_H
re.c_OH
re.c_O2
re.c_H2
10^{-6}
10^{-4}
10^{-2}
10^{0}
Time (s)

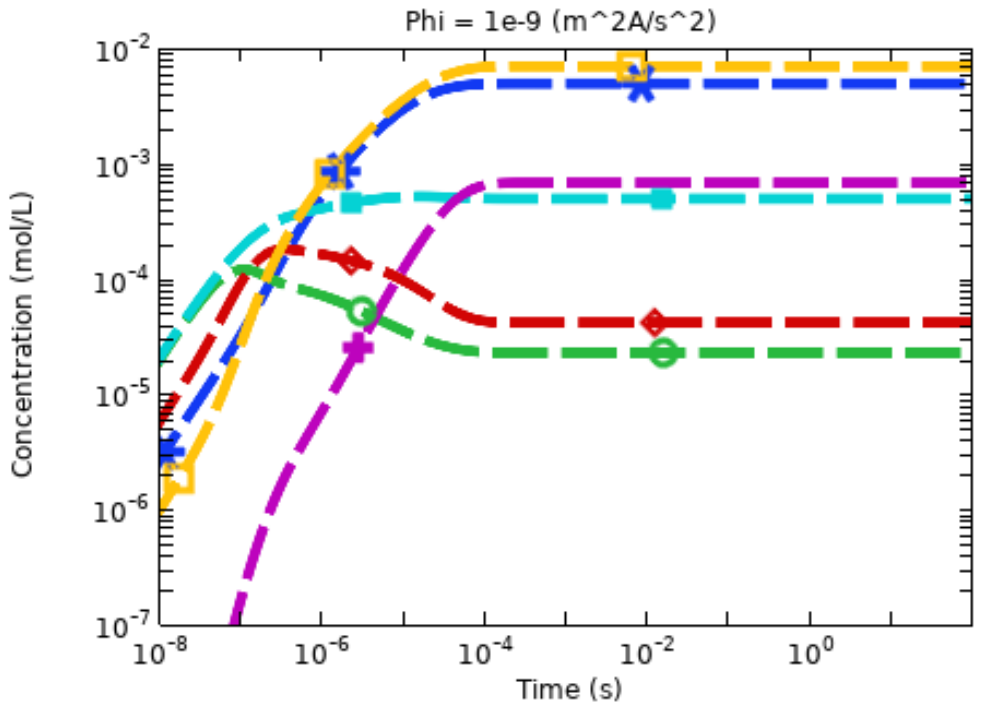

Global
Concentration (mol/L)
10^{-3}
10^{-4}
10^{-5}
10^{-6}
re.c_H2O2
re.c_EHn
re.c_H
re.c_OH
re.c_O2
re.c_H2
10^{-6}
10^{-4}
10^{-2}
10^{0}
Time (s)

Resultados:

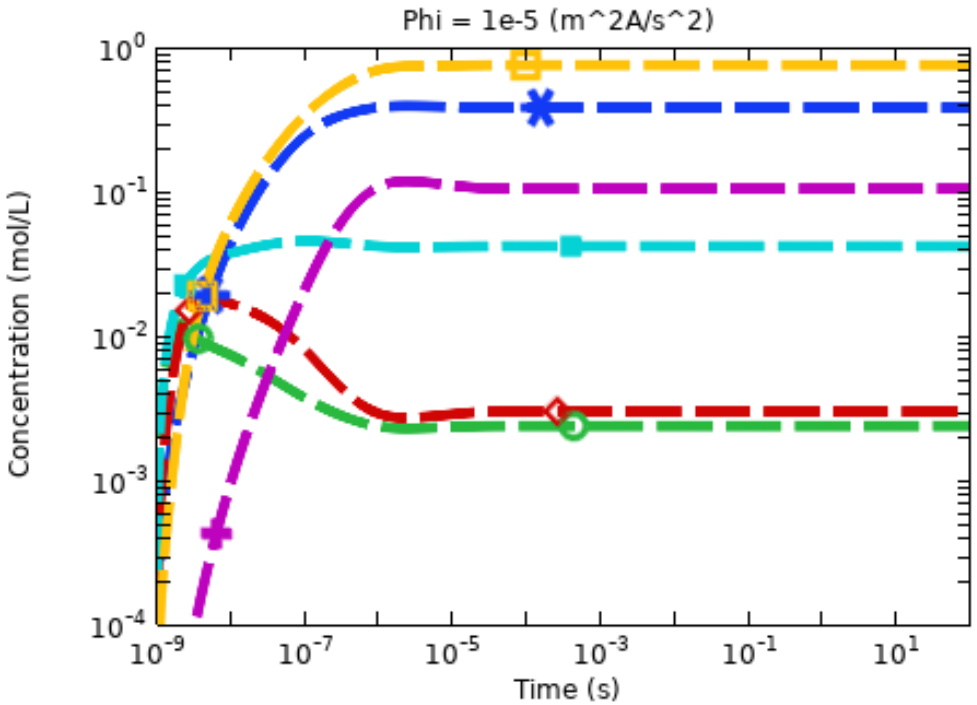

Concentración de todas las especies (mol/L)
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-6}
10^{-4}
10^{-2}
10^{0}
Time (s)
re.c_H2O2
re.c_EHn
re.c_H
re.c_H2
re.c_HO2
re.c_HO2n
re.c_HO3
re.c_Hp
re.c_H2O
re.c_O2
re.c_O2n
re.c_O3
re.c_O3n
re.c_OHn
re.c_On
re.c_OH

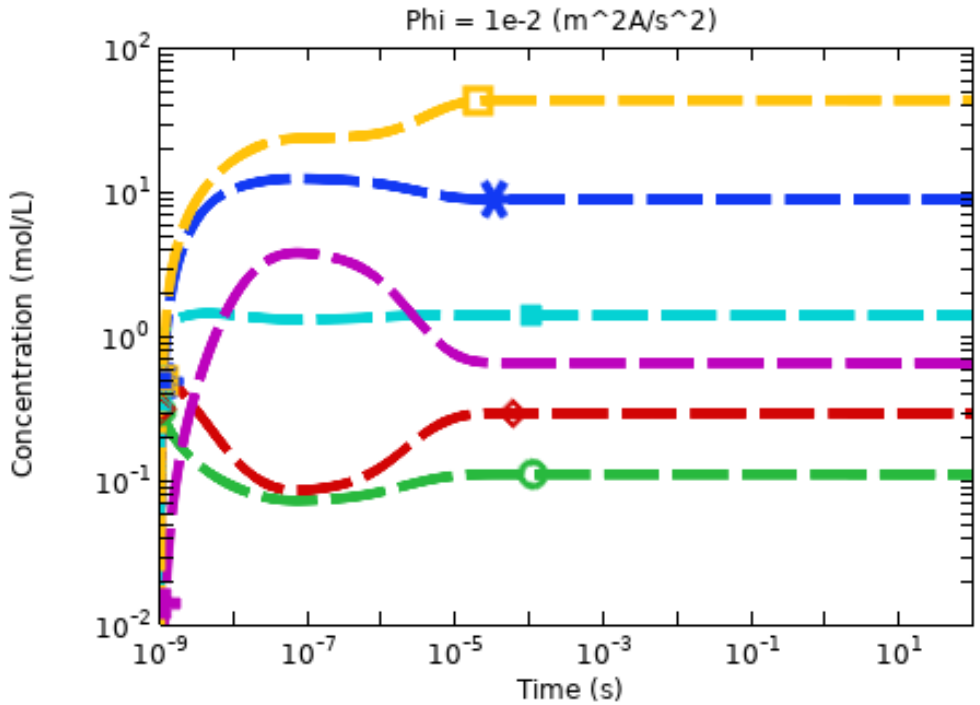
Resultados:


Phi = 1e-11 (m^2A/s^2)
Concentration (mol/L)
Time (s)
10^-3
10^-4
10^-5
10^-6
10^-7
10^-7
10^-5
10^-3
10^-1
10^1


Phi = 1e-9 (m^2A/s^2)
Concentration (mol/L)
Time (s)
10^-2
10^-3
10^-4
10^-5
10^-6
10^-7
10^-8
10^-6
10^-4
10^-2
10^0

Resultados:

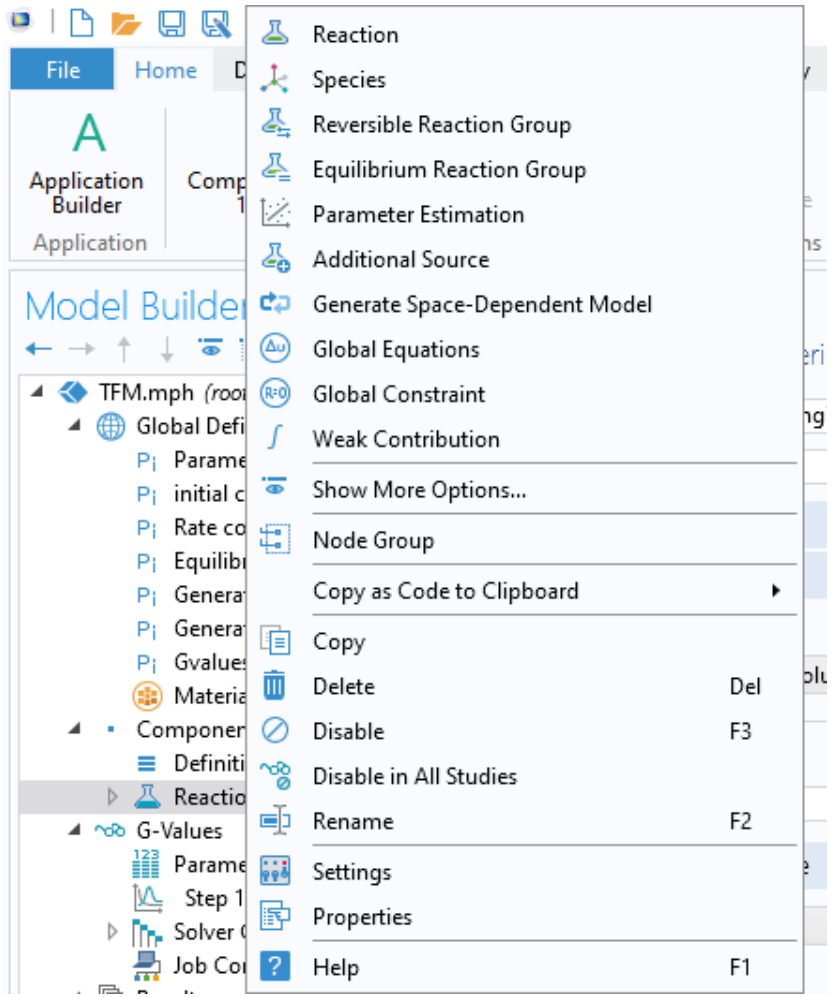

Phi = 1e-5 (m^2A/s^2)
Concentration (mol/L)
Time (s)
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-9}
10^{-7}
10^{-5}
10^{-3}
10^{-1}
10^{1}

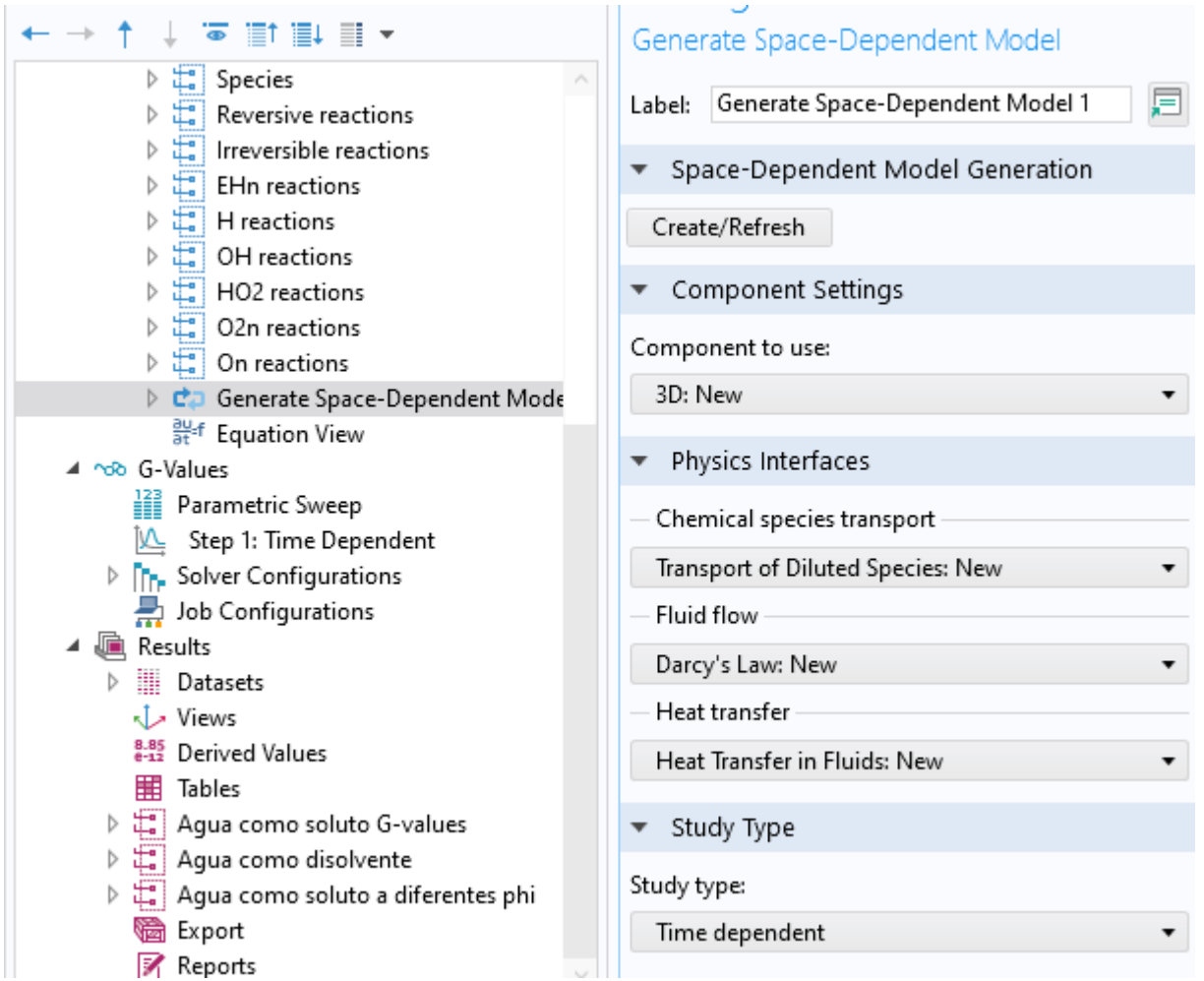

Phi = 1e-2 (m^2A/s^2)
Concentration (mol/L)
Time (s)
10^{2}
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{-9}
10^{-7}
10^{-5}
10^{-3}
10^{-1}
10^{1}

Conclusiones:

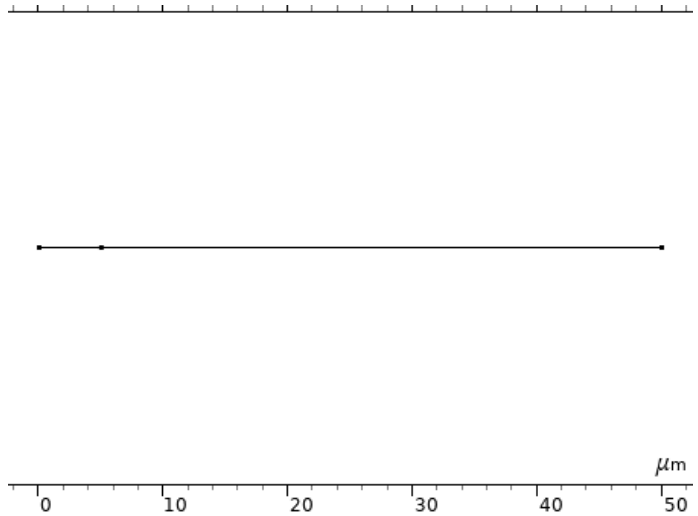
- **Reacciones casi instantáneas → Reactor tipo Bach.**
- **Aumentar el haz de electrones irradiado disminuye el tiempo al que se alcanza el estado estacionario y mayor velocidad cinética.**
- **Interesante ver cuales de las reacciones es más lenta y por tanto suprimible, asimismo cual es tan rápida que podemos tratar como una concentración inicial.**

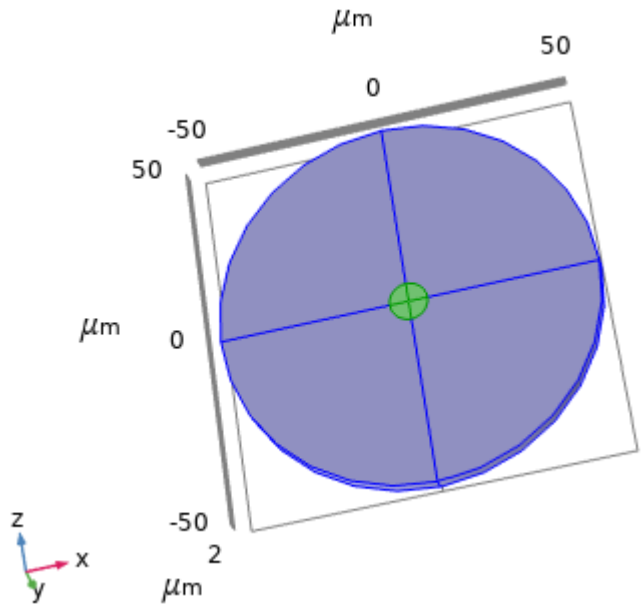
Siguiente reto:

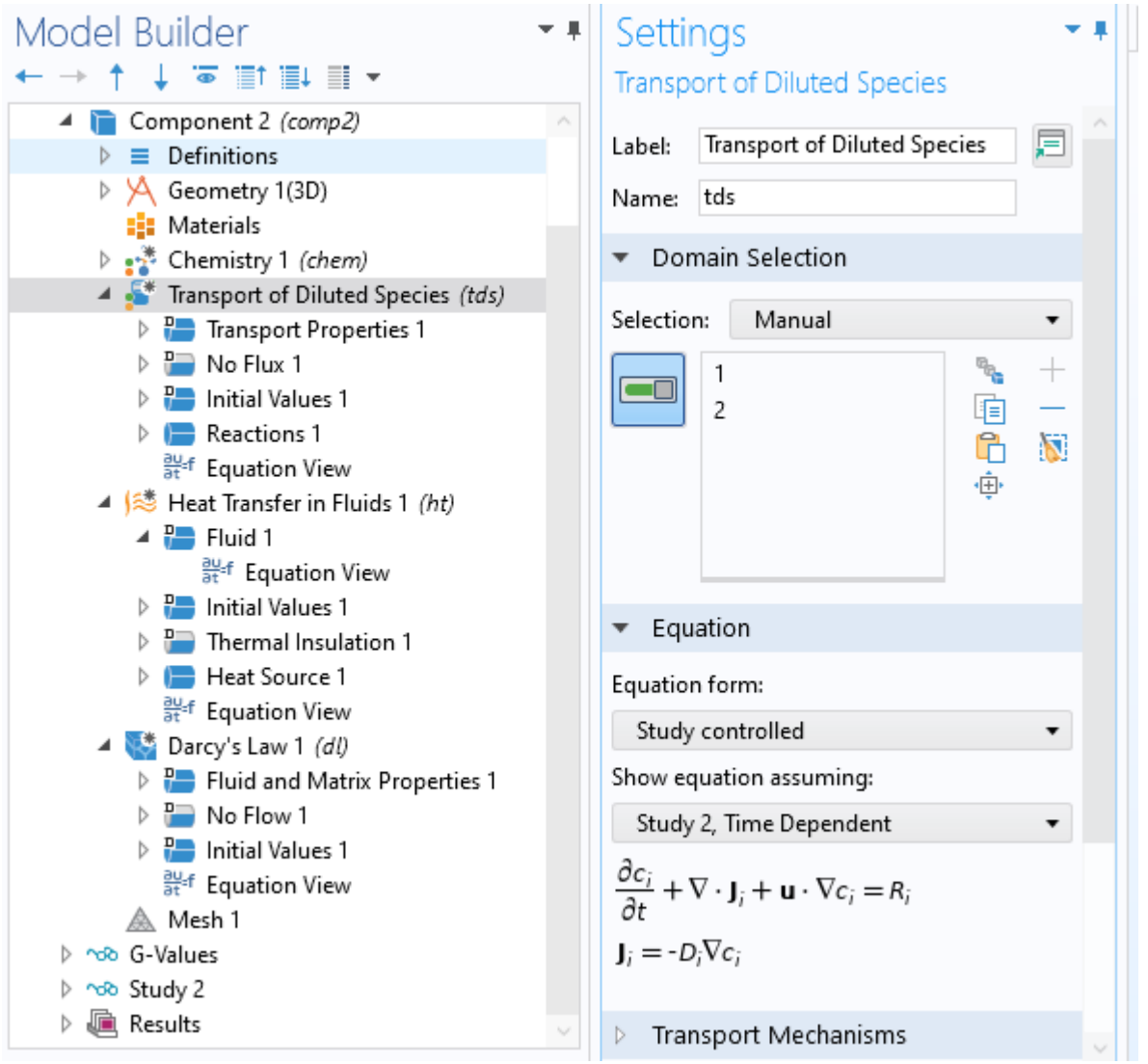




Retos:


μm
0
10
20
30
40
50


μm
50
0
-50
50
μm
0
-50
2
μm
z
x
y


Model Builder
Component 2 (comp2)
Definitions
Geometry 1(3D)
Materials
Chemistry 1 (chem)
Transport of Diluted Species (tds)
Transport Properties 1
No Flux 1
Initial Values 1
Reactions 1
Equation View
Heat Transfer in Fluids 1 (ht)
Fluid 1
Equation View
Initial Values 1
Thermal Insulation 1
Heat Source 1
Equation View
Darcy's Law 1 (dl)
Fluid and Matrix Properties 1
No Flow 1
Initial Values 1
Equation View
Mesh 1
G-Values
Study 2
Results
Settings
Transport of Diluted Species
Label: Transport of Diluted Species
Name: tds
Domain Selection
Selection: Manual
1
2
Equation
Equation form:
Study controlled
Show equation assuming:
Study 2, Time Dependent
$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{J}_i + \mathbf{u} \cdot \nabla c_i = R_i$
$\mathbf{J}_i = -D_i \nabla c_i$
Transport Mechanisms

Referencias:

[1] N.M. Schneider, M.M. Norton, B.J. Mendel, J.M. Grogan, F.M. Ross, H.H. Bau, Electron-Water interactions and implications for liquid cell electron microscopy, J. Phys. Chem. C. 118 (2014) 22373–22382. https://doi.org/10.1021/jp507400n.

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[3] T. Gupta, N.M. Schneider, J.H. Park, D. Steingart, F.M. Ross, Spatially dependent dose rate in liquid cell transmission electron microscopy, Nanoscale. 10 (2018) 7702–7710. https://doi.org/10.1039/c8nr01935e.

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[5] N.M. Schneider, Electron Beam Effects in Liquid Cell TEM and STEM 7.2 Electron Energy Loss in Liquids, (2017) 140–163.

Muchas gracias por su atención