Numerical (Aqueous) Solutions: Diffusion under Chemical Constraints

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Reaction-Diffusion : when the proton kicks in...

The problem :

- Everybody knows : $\partial_t[\mathrm{H}^+] = D_{\mathrm{H}^+}\Delta[\mathrm{H}^+] + \sigma_{\mathrm{H}^+}$, $\partial_t[\mathrm{HO}^-] = D_{\mathrm{HO}^-}\Delta[\mathrm{HO}^-] + \sigma_{\mathrm{HO}^-}$
- Some people know :
  $\mathrm{H_2O} \underset{k'=1.4\ 10^{11}\mathrm{M}^{-1}\mathrm{s}^{-1}}{\overset{k=2.4\ 10^{-5}\mathrm{s}^{-1}}{\rightleftharpoons}} \mathrm{H}^+ + \mathrm{HO}^-$ $(\Rightarrow \sigma_{\mathrm{H}^+}, \sigma_{\mathrm{HO}^-})$ and $K_w = [\mathrm{H}^+]_{eq}\cdot[\mathrm{HO}^-]_{eq}$
- Almost nobody knows the source terms for species like $\mathrm{H_2CO_3}$, $\mathrm{HCO_3^-}$, LacH...
- We start with an incomplete, multi-scale problem (who said 'chemistry' ?)

A solution :

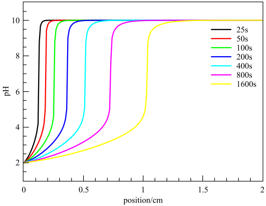
- Typical relaxation time for protic reactions : $\tau \simeq 10\ \mu$s.
- Typical diffusive length : $\leq \sqrt{D_{\mathrm{H}^+}\tau} < 0.5\mu\mathrm{m}$. All right !
- Assumption : diffusion occurs on a chemical manifold for typical length $\geq 1\mu\mathrm{m}$.
- The manifold is defined by the set of equilibrium constants.
- The chemical extents are the "internal forces" that kept the concentrations on that manifold (think "mechanical constraints" for Molecular Dynamics or Robotics).

Tensorizing the Diffusion Equations : Theory and Real Case

- **Theory : a novel set of equations**

$$\partial_t \begin{bmatrix}[\mathrm{H}^+]\\ [\mathrm{HO}^-]\\ \vdots\end{bmatrix} = \left(\mathbf{I} - {}^t\boldsymbol{\nu}(\boldsymbol{\Phi}\boldsymbol{\nu})^{-1}\boldsymbol{\Phi}\right)\cdot\left(\begin{bmatrix} D_{\mathrm{H}^+}\Delta[\mathrm{H}^+]\\ D_{\mathrm{HO}^-}\Delta[\mathrm{HO}^-]\\ \vdots\end{bmatrix} + \vec{\rho}\right), \left\{\begin{array}{ll} \boldsymbol{\nu} & \text{chemical topology}\\ \boldsymbol{\Phi} & \text{equilibria Jacobian}\\ \vec{\rho} & \text{other source terms}\end{array}\right.$$

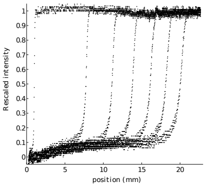
- **Numerical Results with Finite Volumes Code**

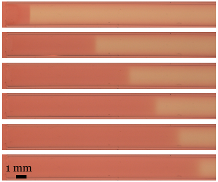


- classical and chemical schemes are **indistinguishable**.
- computational speedup : 100 – 300 **times faster**.

  (OK, we removed the 'high frequencies')
- convenient for physiology, electrochemistry...

- **Experimental support : all uncoupled simulations are wrong (under the previous assumptions, of course)**





- We follow a diffusive pH front.
- Non reactive proton

  $\Rightarrow D_F \simeq 3.6 \cdot 10^{-7} m^2 \cdot s^{-1}$
- Reactive proton : numerical **and** experimental

  $\Rightarrow D_F \simeq 1.2 \cdot 10^{-7} m^2 \cdot s^{-1}$
- Heavily depends on composition...