Lecture Modelling of Hydro-systems

Mass Transport Process Part III: Reactive Transport

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Table of Content

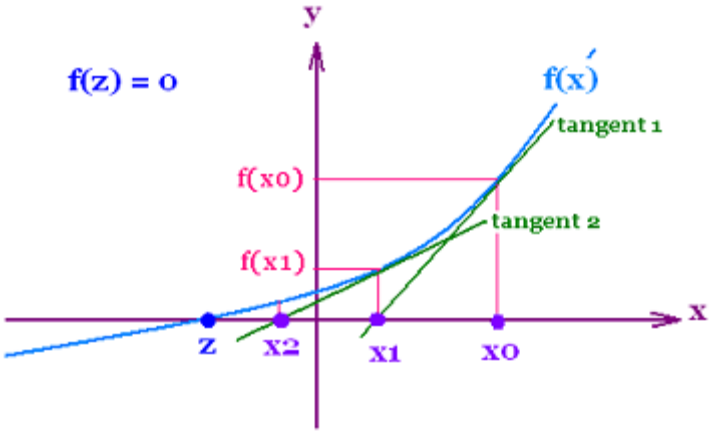
- Newton-Raphson algorithm
- Law of Mass Action based equilibrium reactions
- Matlab Example of carbonate system
- Modelling reactive transport process with OpenGeoSys-PhreeqC (calcite example)

Newton-Raphson Method

Issac Newton

Joseph Raphson

$f(x) = x^3 - 2x^2 - 10x + 4$ $f'(x) = 3x^2 - 4x - 10$



Newton-Raphson Method

The Newton-Raphson Method says:

Choose a starting value x_0

$$x_1 = x_0 - \frac{f(x_0)}{f'(x_0)}.$$

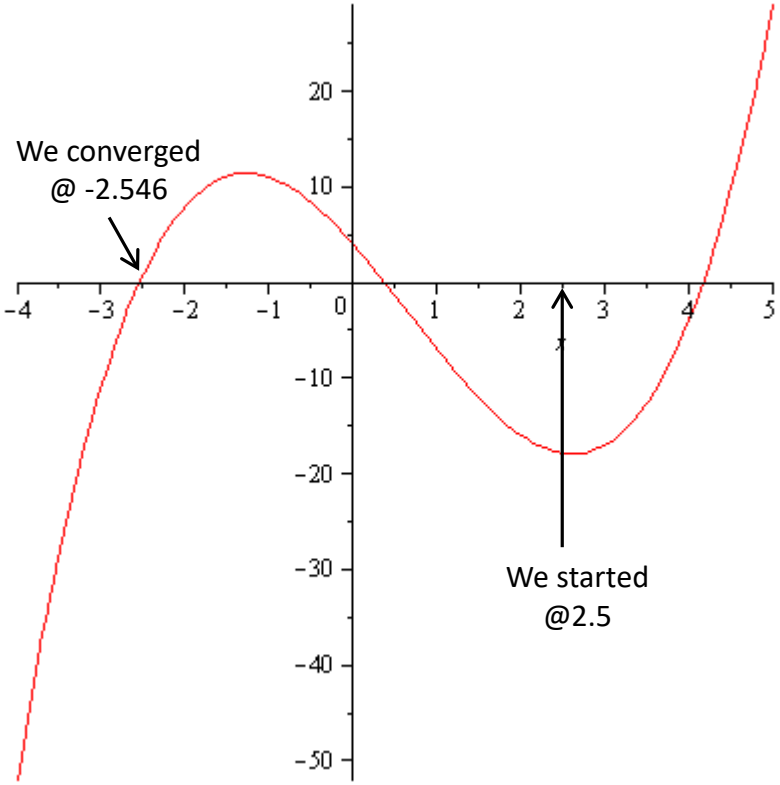
Iterate the process

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}$$

Until $||f(x_{n+1})||$ is approaching zero

Iter#	x_n	f(x)	f'(x)	$x_{n+1} - x_n$	x_{n+1}
0	2.5	-17.88	-1.25	-14.3	-11.8
1	-11.8	-1800	454.9	3.956	-7.844
2	-7.844	-523.3	206	2.541	-5.304
3	-5.304	-148.4	95.6	1.552	-3.751
4	-3.751	-39.42	47.22	0.8348	-2.917
5	-2.917	-8.655	27.18	0.3184	-2.598
6	-2.598	-1.057	20.64	0.0512	-2.547
7	-2.547	-0.0256	… …		

Newton Raphsen Method



Where are all the intermediate points located on the curve?

Iter#	x_n	f(x)	f'(x)	$x_{n+1} - x_n$	x_{n+1}
0	2.5	-17.88	-1.25	-14.3	-11.8
1	-11.8	-1800	454.9	3.956	-7.844
2	… …				

What if we only want the solution that is positive and close to zero?

You could use the so-called

Damped Newton Method

Damped Newton-Raphson Method

Choose a starting value x_0

Iterate the process

Calculate damping factor δ

$$x_{n+1} = x_n + \delta \frac{-f(x_n)}{f'(x_n)}$$

Until $||f(x_{n+1})||$ is approaching zero

For example, if we would like to constrain the solution x to positive values, a popular damping factor formulation would be,

$$\frac{1}{\delta} = \max(1.0, -\frac{\Delta x}{\alpha \cdot x})$$

α

So for our case, if we have damping switched on,

Δx = -14.3

x = 2.5

α = 0.5

δ = ?

$\delta \Delta x$ = ?

After damping factor applied,

Iter#	x_n	f(x)	f'(x)	$x_{n+1} - x_n$	δ	x_{n+1}
0	2.5	-17.88	-1.25	-14.3	0.0874	1.25
1	1.25	-9.672	-10.31	-0.937	-0.6664	0.625
2	0.625	-2.787	-11.33	-0.246	1.0	0.379
3	0.379	-0.022	-11.09	-0.002	1.0	0.377
	… …					

Newton-Raphsen in multiple dimensions

Single Dimension

Choose a starting value x_0

$$x_1 = x_0 - \frac{f(x_0)}{f'(x_0)}.$$

Iterate the process

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}$$

Until $||f(x_{n+1})||$ is approaching zero

Multiple Dimensions

Choose a starting value x_0

Iterate

Evaluate residual $f(x_n)$

Evaluate Jacobi matrix $J(x_n)$

solve $\Delta x = -J^{-1}(x_n) \cdot f(x_n)$

update $x_{n+1} = x_n + \Delta x$

Until $||f(x_{n+1})||$ is approaching zero

$$J_f(a) := \begin{pmatrix} \frac{\partial f_1}{\partial x_1}(a) & \frac{\partial f_1}{\partial x_2}(a) & \dots & \frac{\partial f_1}{\partial x_n}(a) \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial f_m}{\partial x_1}(a) & \frac{\partial f_m}{\partial x_2}(a) & \dots & \frac{\partial f_m}{\partial x_n}(a) \end{pmatrix}$$

Different rows are different functions

Different columns are derivatives over different unknowns

Newton-Raphsen in multiple dimensions

If we do not know
the explicit expression of f(x),

Using 1st order forward Euler approximation

$$J_f(a) := \begin{pmatrix} \frac{\partial f_1}{\partial x_1}(a) & \frac{\partial f_1}{\partial x_2}(a) & \dots & \frac{\partial f_1}{\partial x_n}(a) \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial f_m}{\partial x_1}(a) & \frac{\partial f_m}{\partial x_2}(a) & \dots & \frac{\partial f_m}{\partial x_n}(a) \end{pmatrix}$$

$$\frac{\partial f_i(x)}{\partial x_j} \approx \frac{f_i(x + \Delta x) - f_i(x)}{\Delta x}$$

How do you decide the size of Δx?

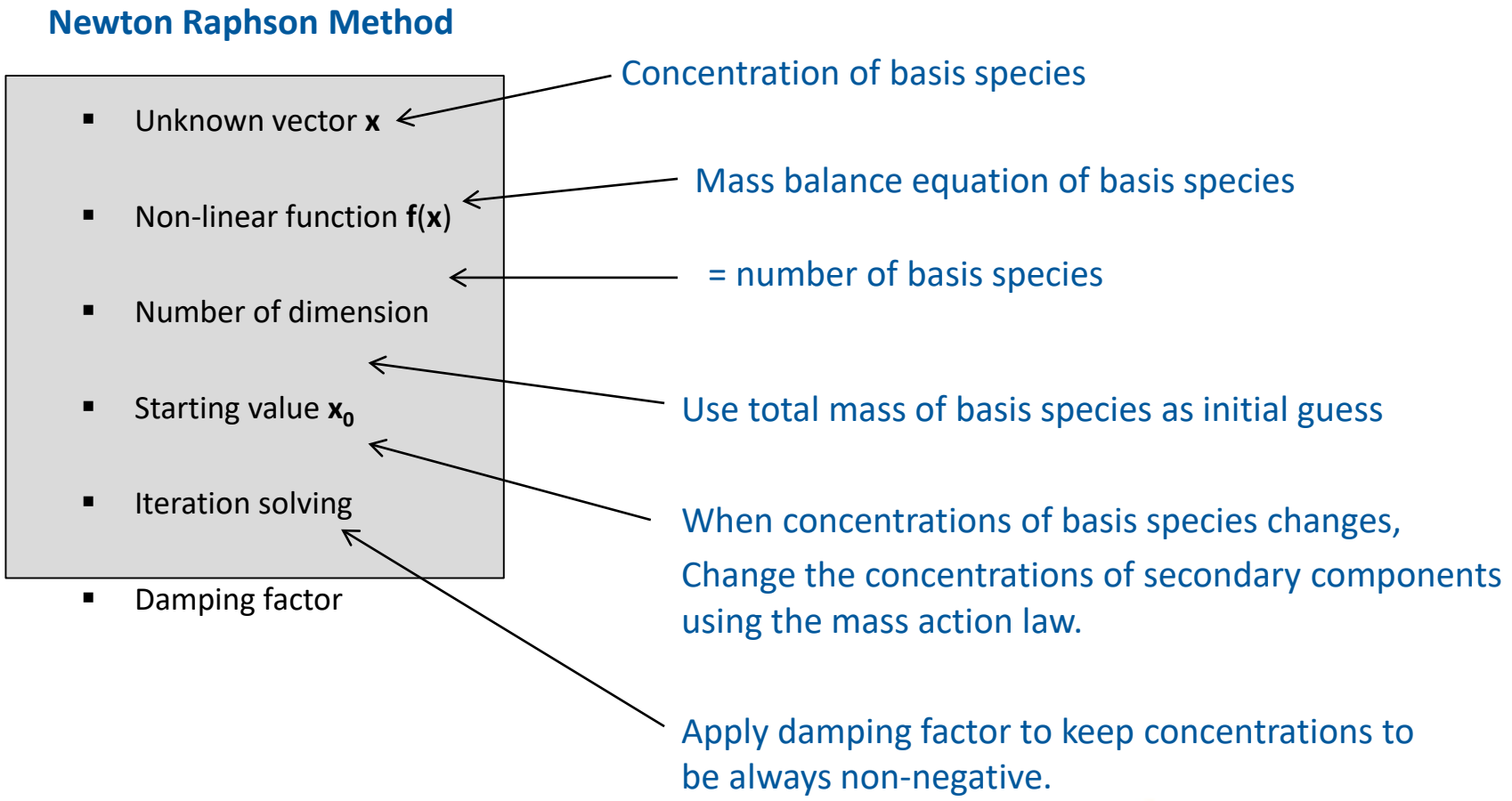
Someone suggests to use 1.0e-6 for Δx, what do you think?

An often adopted technique is to use relative increment.

$$(\nabla_h F)(x)_j = \begin{cases} \dfrac{F(x + h\|x\|e_j) - F(x)}{h\|x\|} & x \neq 0 \\ \dfrac{F(he_j) - F(x)}{h} & x = 0 \end{cases}$$

Normally using 1.0e-6 for h will be appropriate.

Combined with Newton Method



Governing Equations for the Equilibrium Reactions

In mathematical language, the chemical system is always constrained by 2 types of governing equations. They are,

1) **Mass action equations**

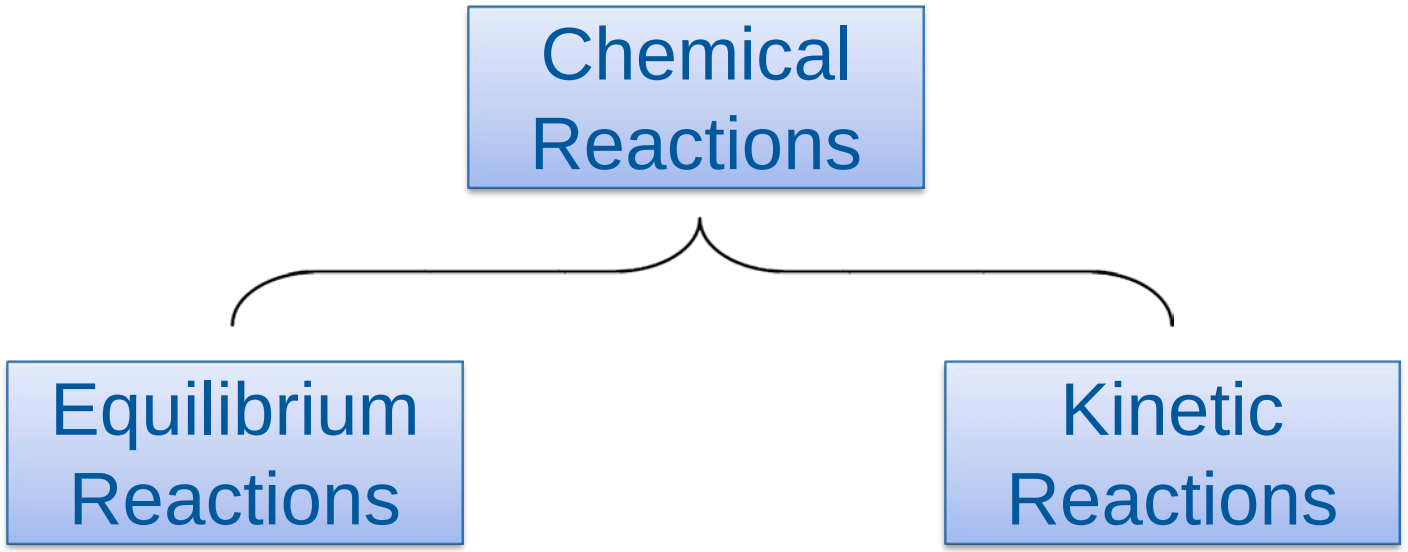
2) **Mass conservation equations (Mass balance)**

In another word,

1) Equilibrium reactions always satisfies the stoichiometric relationship and equilibrium constants.

2) Mass only shifts from one component to the other in chemical reactions. It is never destroyed or created.

Classification of Chemical Reactions



"Instantaneous"

$$\frac{\partial C}{\partial t} = 0$$

Algebraic Equations (AE)

"Gradually"

$$\frac{\partial C}{\partial t} \neq 0$$

Ordinary Differential Equations (ODE)

Basis Species

Secondary Components

flour

water

egg

bread

spätzle

Basis and Secondary Components

Secondary \ Basis			
	0.5	0.5	0
	0.5	0.2	0.3

Basis and Secondary Components

Equations	logK
$CaCO_3 \rightleftharpoons H_2CO_3^* - 2H^+ + Ca^{2+}$	13.46
$HCO_3^- \rightleftharpoons H_2CO_3^* - H^+$	6.35
$CO_3^* \rightleftharpoons H_2CO_3^* - 2H^+$	16.68

Take one example: $CaCO_3 \rightleftharpoons H_2CO_3^* - 2H^+ + Ca^{2+}$

Law of mass action: $K = \frac{\{H_2CO_3^*\} \cdot \{Ca^{2+}\}}{\{H^+\}^2 \cdot \{CaCO_3\}}$

Log on both side.

$$logK = log\{H_2CO_3^*\} - 2log\{H^+\} + log\{Ca^{2+}\} - log\{CaCO_3\}$$

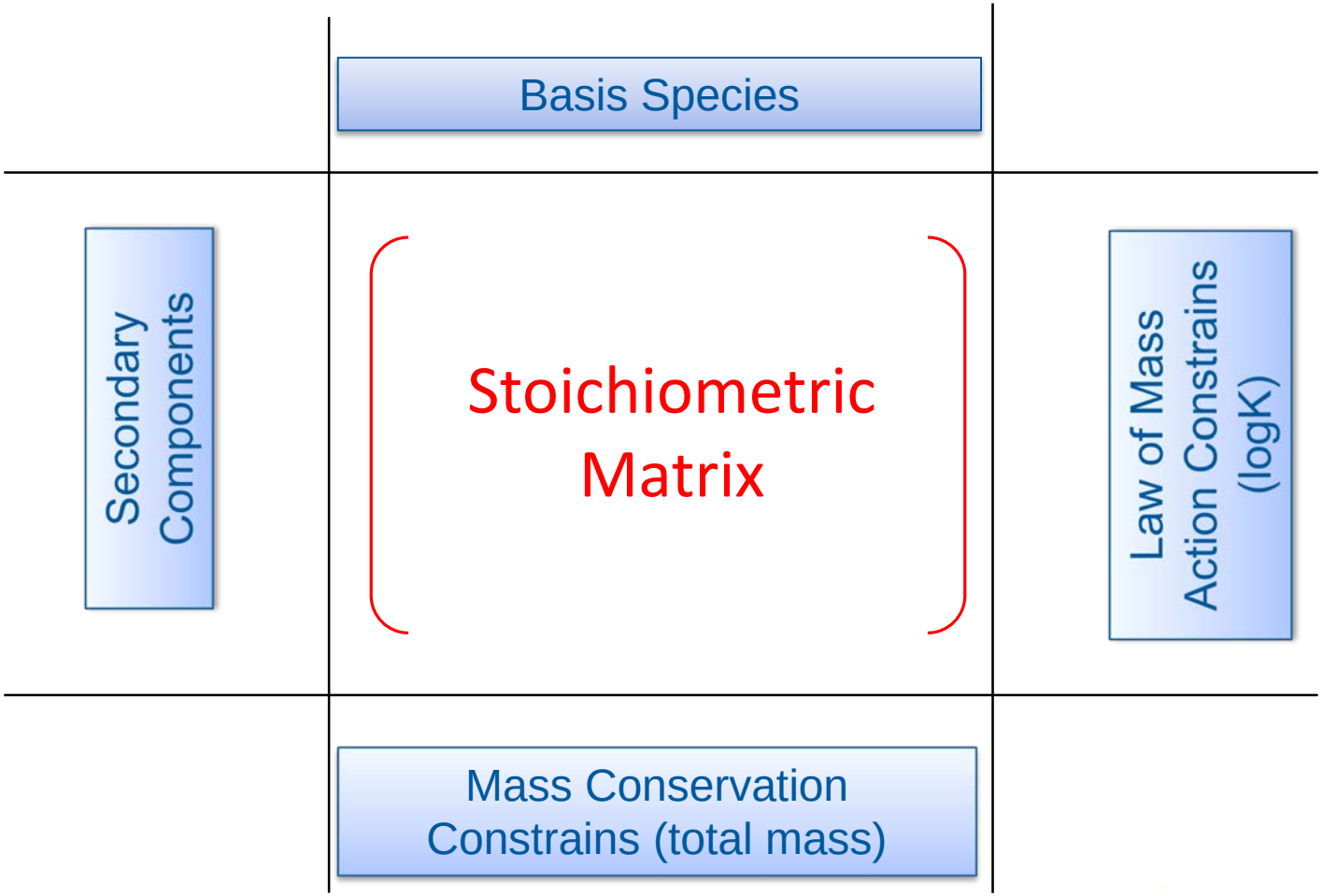
Write in the same sequence as original equation:

$$log\{CaCO_3\} = log\{H_2CO_3^*\} - 2log\{H^+\} + log\{Ca^{2+}\} - logK$$

Basis and Secondary Components

Secondary \ Basis	$Log\{H_2CO_3^*\}$	$Log\{H+\}$	$Log\{Ca_2++\}$
$Log\{CaCO_3\}$			
$Log\{HCO_3-\}$			
$Log\{CO_3--\}$			

Basis and Secondary Components



Following the Law of mass action,

Let’s fill the numbers in...

	H_2CO_3*	H+	Ca_2++	
$CaCO_3$				
HCO_3-				
CO_3--				

Law of Mass Action in Linear Algebraic expression

The mass action law is actually linear:

$$\begin{pmatrix} \text{Log}\{CaCO_3\} \\ \text{Log}\{HCO_3^-\} \\ \text{Log}\{CO_3^{--}\} \end{pmatrix} = \begin{pmatrix} \square & \square & \square \\ \square & \square & \square \\ \square & \square & \square \end{pmatrix} \cdot \begin{pmatrix} \text{Log}\{H_2CO_3^*\} \\ \text{Log}\{H^+\} \\ \text{Log}\{Ca^{++}\} \end{pmatrix} - \begin{pmatrix} \text{Log}K_1 \\ \text{Log}K_2 \\ \text{Log}K_3 \end{pmatrix}$$

Mathematicians likes the vector/Matrix form:

$$\text{Log\_SC} = \text{StoiMatrix} \cdot \text{Log\_BS} - \text{Log\_K}$$

Law of Mass Balance

Total mass of basis species should be balanced:

$$[H_2CO_3^*] + [CaCO_3] + [HCO_3^-] + [CO_3^-] = tot[H_2CO_3^*]$$

$$[H^+] - 2[CaCO_3] - [HCO_3^-] - 2[CO_3^-] = tot[H^+]$$

$$[Ca^{2+}] + [CaCO_3] = tot[Ca^{2+}]$$

In a matrix vector form:

$$BS + StoiMatrix^{T} \cdot SC - tot\_Mass = 0$$

We use numerical method to solve the above Mass Conservation Eq. together with mass action Eq.

$$Log\_SC = StoiMatrix \cdot Log\_BS - Log\_K$$

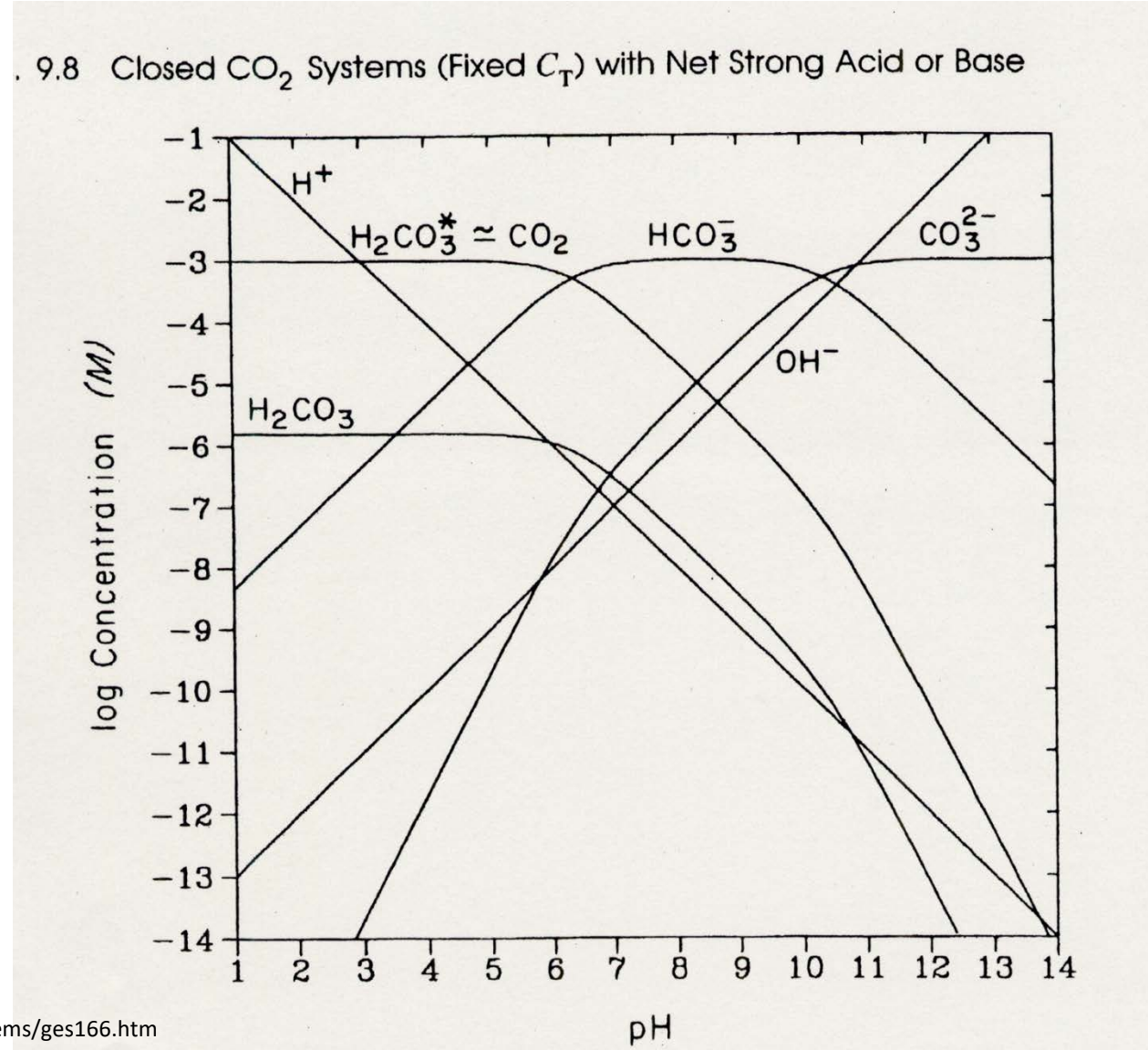
Example: the carbonate system

Let's look at the Ca-carbonate system.

Species / Components are:

- H_2CO_3
- HCO_3-
- CO_3^{2-}
- H^+
- Ca^{2+}
- $CaCO_3(aq)$

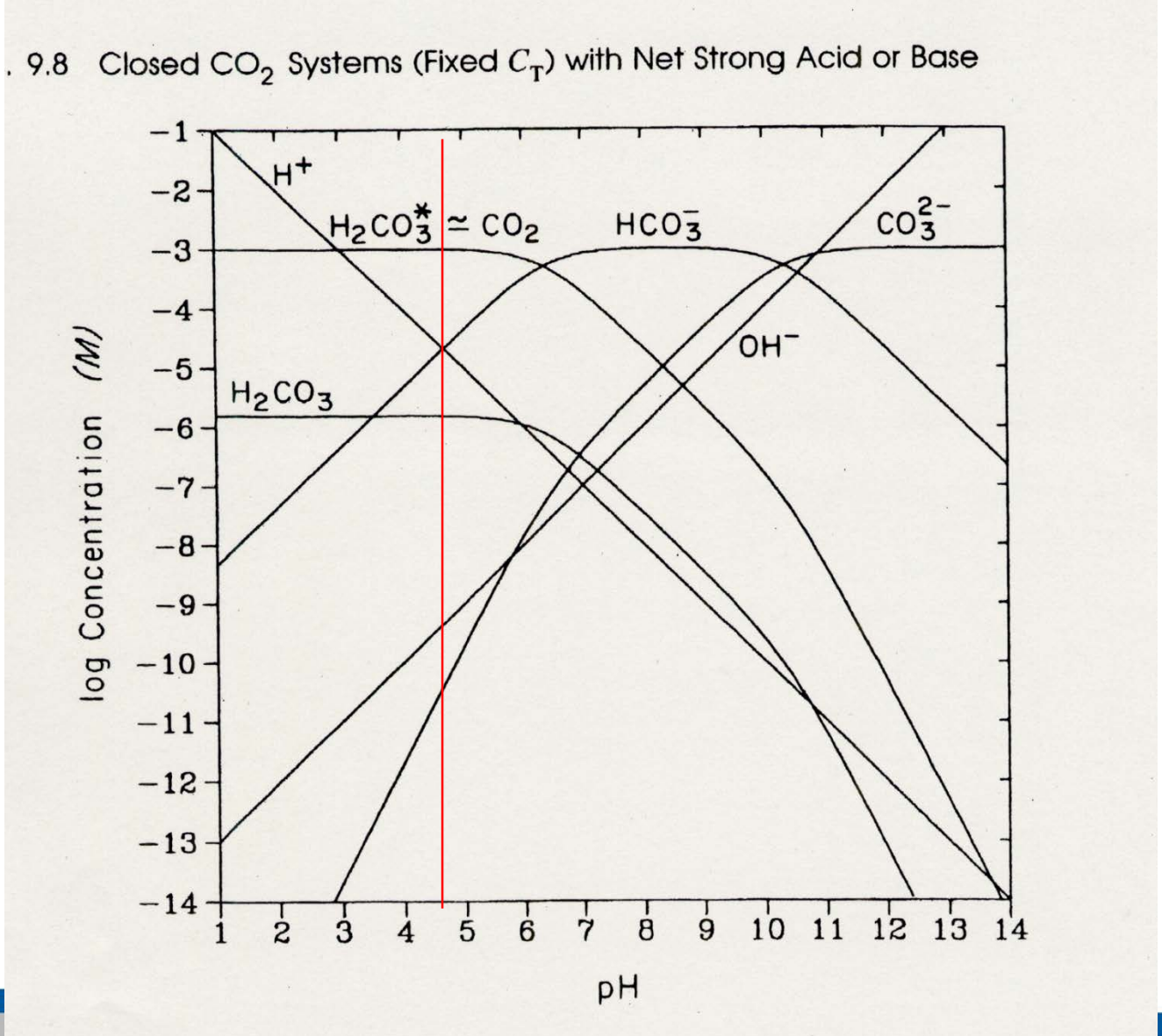
Which are the **basis species** and which are the **secondary components**?



Source: http://soils.stanford.edu/classes/GES166_266items/ges166.htm

Example: the carbonate system

We are about there. The bias in CO3– is because of the $CaCO_3$ presence.



Example: the carbonate system

We will explain the MatLab script.

… …

What's the result values we get?

H_2CO_3*	_____	$CaCO_3$	_____
H+	_____	HCO_3-	_____
Ca_2++	_____	CO_3--	_____

Please compare to the carbonate figure, do we get correct values?

Reactive transport with OGS-6#iPHREEQC

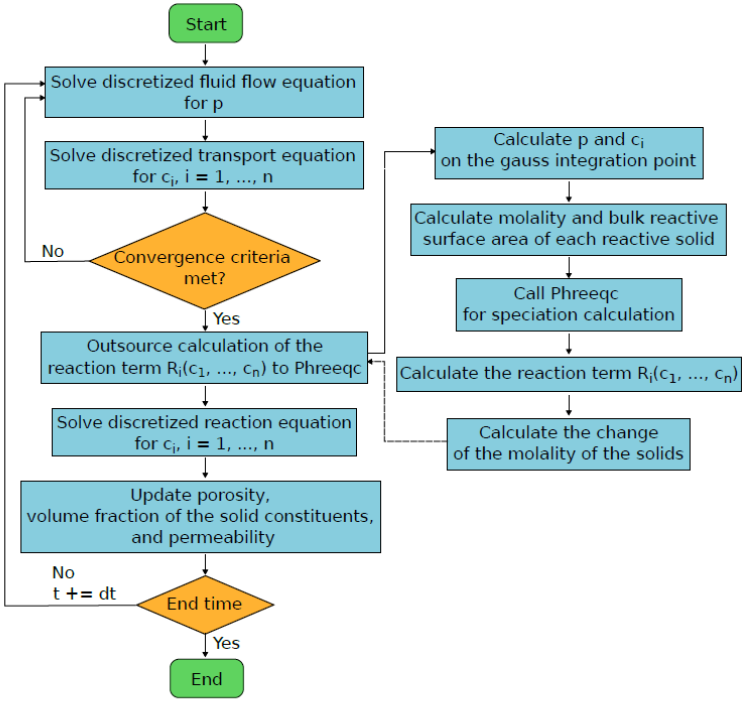


Figure 1. Workflow of solving reactive transport problems using a sequential non-iterative approach. This new computational workflow is implemented in the OpenGeoSys-6#Phreeqc.

Lu et al., 2022 Computers and Geosciences

The operator-splitting approach:

$$\frac{\partial(\phi c_i)}{\partial t} + \nabla \cdot (\mathbf{q} c_i - \phi \mathbf{D} \nabla c_i) + Q_i + R_i(c_1, ..., c_n) = 0, \quad i = 1, .., n.$$

The Phreeqc chemical solver is called over each time-step and mesh cell integration point

CPU time is a direct function of the number of cells in the mesh (with constant int. pts.)

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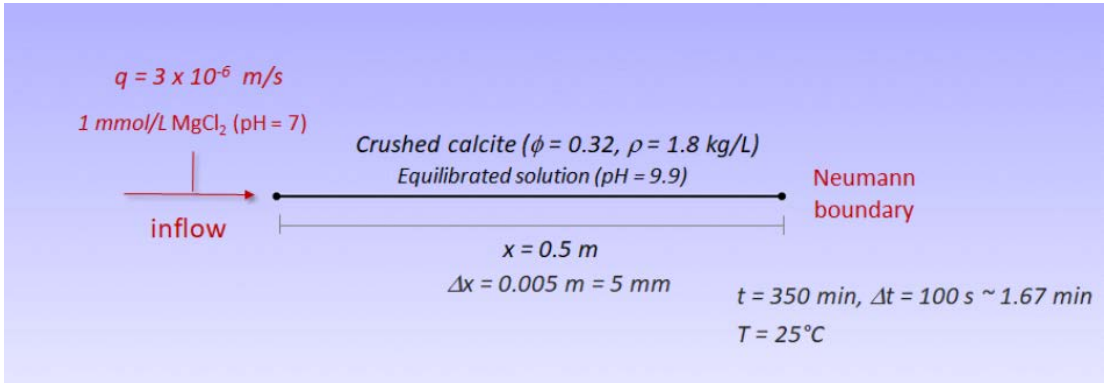
Reactive Transport Example: Calcite Problem

<chemical_system> on the .prj file

```
<chemical_system chemical_solver="Phreeqc">
    <mesh>ReactiveDomain_mesh</mesh>
    <database>phreeqc.dat</database>
    <linear_solver>general_linear_solver</linear_solver>
    <solution>
        <temperature>25</temperature>
        <pressure>1</pressure>
        <pe>4</pe>
        <components>
            <component>Na</component>
            <component>Cl</component>
            <component>Ca</component>
            <component>C(4)</component>
        </components>
    </solution>
    <equilibrium_reactants>
        <phase_component>
        <name>Calcite</name>
            <saturation_index>0.0</saturation_index>
        </phase_component>
    </equilibrium_reactants>
    <knobs>
        <max_iter>500</max_iter>
        <relative_convergence_tolerance>1e-12</relative_convergence_tolerance>
        <tolerance>1e-15</tolerance>
        <step_size>5</step_size>
        <scaling>0</scaling>
    </knobs>
</chemical_system>
```



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<chemical_solver>

```
<chemical_system chemical_solver="Phreeqc">
    <mesh>ReactiveDomain_mesh</mesh>
    <database>phreeqc.dat</database>
    <linear_solver>general_linear_solver</linear_solver>
    <solution>
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        <pe>4</pe>
        <components>
            <component>Na</component>
            <component>Cl</component>
            <component>Ca</component>
            <component>C(4)</component>
        </components>
    </solution>
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    <knobs>
        <max_iter>500</max_iter>
        <relative_convergence_tolerance>1e-12</relative_convergence_tolerance>
        <tolerance>1e-15</tolerance>
        <step_size>5</step_size>
        <scaling>0</scaling>
    </knobs>
</chemical_system>
```

At the moment, only Phreeqc is supported (more solvers, e.g., GEMS, could be added in the future)

https://www.usgs.gov/software/phreeqc-version-3

<mesh>

```
<chemical_system chemical_solver="Phreeqc">
    <mesh>ReactiveDomain_mesh</mesh>
    <database>phreeqc.dat</database>
    <linear_solver>general_linear_solver</linear_solver>
    <solution>
        <temperature>25</temperature>
        <pressure>1</pressure>
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        <components>
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    <knobs>
        <max_iter>500</max_iter>
        <relative_convergence_tolerance>1e-12</relative_convergence_tolerance>
        <tolerance>1e-15</tolerance>
        <step_size>5</step_size>
        <scaling>0</scaling>
    </knobs>
</chemical_system>
```

Mesh needs to be added under <meshes> tag (recall the creation of a reactive domain with the identifySubdomains OGS utility)

Note: name needs to be typed without .vtu extension.

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<database>

```
<chemical_system chemical_solver="Phreeqc">
    <mesh>ReactiveDomain_mesh</mesh>
    <database>phreeqc.dat</database>
    <linear_solver>general_linear_solver</linear_solver>
    <solution>
        <temperature>25</temperature>
        <pressure>1</pressure>
        <pe>4</pe>
        <components>
            <component>Na</component>
            <component>Cl</component>
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            <component>C(4)</component>
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            <saturation_index>0.0</saturation_index>
        </phase_component>
    </equilibrium_reactants>
    <knobs>
        <max_iter>500</max_iter>
        <relative_convergence_tolerance>1e-12</relative_convergence_tolerance>
        <tolerance>1e-15</tolerance>
        <step_size>5</step_size>
        <scaling>0</scaling>
    </knobs>
</chemical_system>
```

We need to provide a valid Phreeqc database here. More details on databases:

https://water.usgs.gov/water-resources/software/PHREEQC/documentation/phreeqc3-html/phreeqc3-5.htm#50593793_39915

In this case, the database needs to have information about the components and the equilibrium reactant

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<solution>

```
<chemical_system chemical_solver="Phreeqc">
    <mesh>ReactiveDomain_mesh</mesh>
    <database>phreeqc.dat</database>
    <linear_solver>general_linear_solver</linear_solver>
    <solution>
        <temperature>25</temperature>
        <pressure>1</pressure>
        <pe>4</pe>
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            <component>Na</component>
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            <component>C(4)</component>
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            <saturation_index>0.0</saturation_index>
        </phase_component>
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        <max_iter>500</max_iter>
        <relative_convergence_tolerance>1e-12</relative_convergence_tolerance>
        <tolerance>1e-15</tolerance>
        <step_size>5</step_size>
        <scaling>0</scaling>
    </knobs>
</chemical_system>
```

How to input pH?

↓

pH is input as H+ concentration

↓

H needs to be added to the list of components for the ComponentTransport process but **not** to the chemical system (this will cause errors)

↓

for pH = 7

H = 10^-7 mol/kgw

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Optional keywords

```
<chemical_system chemical_solver="Phreeqc">
    <mesh>ReactiveDomain_mesh</mesh>
    <database>phreeqc.dat</database>
    <linear_solver>general_linear_solver</linear_solver>
    <solution>
        <temperature>25</temperature>
        <pressure>1</pressure>
        <pe>4</pe>
        <components>
            <component>Na</component>
            <component>Cl</component>
            <component>Ca</component>
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    <knobs>
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        <relative_convergence_tolerance>1e-12</relative_convergence_tolerance>
        <tolerance>1e-15</tolerance>
        <step_size>5</step_size>
        <scaling>0</scaling>
    </knobs>
</chemical_system>
```

<knobs> keyword is used to input Phreeqc numerical settings

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Optional keywords

```
<chemical_system chemical_solver="Phreeqc">
    <mesh>ReactiveDomain_mesh</mesh>
    <database>phreeqc.dat</database>
    <linear_solver>general_linear_solver</linear_solver>
    <solution>
        <temperature>25</temperature>
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    <knobs>
        <max_iter>500</max_iter>
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        <tolerance>1e-15</tolerance>
        <step_size>5</step_size>
        <scaling>0</scaling>
    </knobs>
</chemical_system>
```

Same as equilibrium reactants, other keywords in the chemical system are optional (i.e., <kinetic_reactants>, <surface>, <exchange>)

Note that, in this case, the amount of Calcite is not defined here (it needs to be defined under the <medium> tag by adding a solid phase)

Model Results of Calcite Problem