Modeling of geochemical processes

Numeric Mathematics Refreshment

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Numeric mathematics

Numeric mathematics

Search of solution by a substitution of exact numerals for variables.

Large number of repeated numeric operation

Personal computers

Iterations and algorithms

- **algorithm** – an instruction how to solve the given task
- **iteration algorithm** – technique of calculation in the repetitious steps, at which the result from the previous step is input into next step[1].
- **iteration** – the step in the iteration algorithm

[1] Algorithm should „converge“ (it should approach solution).

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Example: Calculation of square root $\sqrt{\mathbf{N}}$

It is a solution of the equation $\mathbf{x}^2 = \mathbf{N}$, for $\mathbf{x}$

We have to find, e.g., square root of 16, **N** = 16.

The arrangement of the definitional equation gives $x = \frac{16}{x}$.

Let us calculate **x**.

At first (zero step), we substitute for **x** on the right hand of the equation its estimation (arbitrary number), e.g., $\mathbf{x_0} = 2$, and calculate new value of **x**, i.e., $\mathbf{x_1}$. We substitute the found solution for **x** and repeat the calculation till the solution is not constant.

The solution procedure (algorithm) can be written as

$$\mathbf{x_{(k+1)}} = \frac{\mathbf{N}}{\mathbf{x_k}}$$

where **k** is step number; iteration number (we start by zero step)

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Calculation:

x_o	2
x_1	8
x_2	2
x_3	8
x_4	2

As can be seen, the algorithm does not converge. It must be revised!

We can add **x** to both sides of the equation, $\mathbf{x} + \mathbf{x} = \mathbf{x} + \frac{\mathbf{N}}{\mathbf{x}}$,

and rewrite it as: $$\mathbf{x}_{(\mathbf{k}+1)} = \frac{1}{2}\left(\mathbf{x}_\mathbf{k} + \frac{\mathbf{N}}{\mathbf{x}_\mathbf{k}}\right)$$

The new calculation:

iterace	**x**
0	2
1	5
2	4,1
3	4,00122
4	4,00000

Now, the algorithm does converge!

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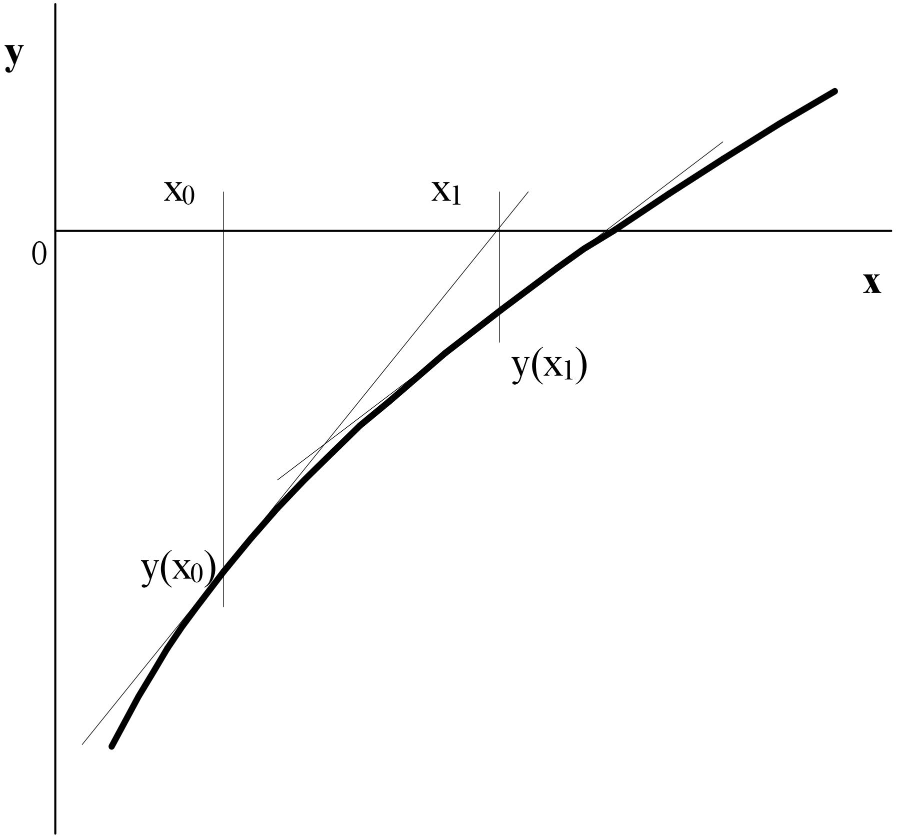
Algorithm formulation

Solution of non-linear equations: *Newton method*



Let the function **y = f(x)** relate to the equation **f(x) = 0,** which root is **x** (the intersection point of **f(x)** and **x**-axis)

(1) we estimate the root $\mathbf{x_0}$,

(2) we keep the tangent through the point $\mathbf{y}(x_0)$

(3) section point of the tangent and **x**-axis, $\mathbf{x}_1$, is the new estimation of root **x**.

(4) the whole procedure is repeated (iterace).

The equation of the tangent in the point

$\mathbf{x_0}, \mathbf{y(x_0)}$ is $\mathbf{y} - y(x_0) = y'(x_0)\,(\mathbf{x} - x_0)$.

Its intersection point with x-axis (y = 0) is

$-\,y(x_0) = y'(x_0)\,(\mathbf{x} - x_0)$

The rearranging yields $$\mathbf{x} = \mathbf{x_0} - \frac{\mathbf{y(x_0)}}{\mathbf{y'(x_0)}}$$

and

$$\mathbf{x_{(k+1)}} = \mathbf{x_k} - \frac{\mathbf{y(x_k)}}{\mathbf{y'(x_k)}}$$

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Example:

Find the roots of the equation

$$\mathbf{x^3 - 4x^2 + 5x - 2 = 0}.$$

The derivation of **f(x)** for **x** is

$$\mathbf{3x^2 - 8x + 5}$$

$$x_{k+1} = x_k - \frac{x^3 - 4x^2 + 5x - 2}{3x^2 - 8x + 5}$$

The roots are

$\mathbf{x}_1 = 2,\ \mathbf{x}_{2,3} = 1$

iteration	x_1	$x_2 = x_3$		iteration	x_1	$x_2 = x_3$
0	5	0		13	2	0,999776
1	3,8	0,4		14	2	0,999888
2	3,0125	0,652632		15	2	0,999944
3	2,507817	0,806483		16	2	0,999972
4	2,204385	0,895986		17	2	0,999986
5	2,051791	0,945653		18	2	0,999993
6	2,004643	0,972144		19	2	0,999997
7	2,000043	0,985886		20	2	0,999998
8	2	0,992894		21	2	0,999999
9	2	0,996435		22	2	1
10	2	0,998214		23	2	1
11	2	0,999106		24	2	1
12	2	0,999553		25	2	1

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Example: Equilibrium in the open system calcite-H_2O-CO_2

system: $CaCO_{3(s)}$, CO_2, H_2O, Ca^{2+}, HCO_3^-, CO_3^{2-}, OH^-, H^+, H_2CO_3 (9 components)

activity coefficient ~ 1, a ~ mol/l,

4 components are given: activity of $CaCO_{3(s)}$ and H_2O, $\mathbf{p}_{CO2}$ = const = 3.10^{-4} atm and $[H_2CO_3]$ = const = $K_H\ p_{CO2}$

5 variables: $x_1 = [H^+]$, $x_2 = [OH^-]$, $x_3 = [Ca^{2+}]$, $x_4 = [HCO_3^-]$, $x_5 = [CO_3^{2-}]$

5 equations: (1) electro-neutrality $[H^+] + 2[Ca^{2+}] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$

and equilibrium equations for:

(2) H_2O, (3) calcite-H_2O system, carbonate dissociation into (4) first and (5) second stage!

5 variables in 5 functions:

$f_1(\mathbf{x}) = x_1 - x_2 + 2\ x_3 - x_4 - 2\ x_5 = 0$ (electro-neutrality)

$f_2(\mathbf{x}) = x_1\ x_2 - K_w = 0$ (water ion product)

$f_3(\mathbf{x}) = x_1\ x_5/x_4 - K_2 = 0$ (dissociation constant K_2)

$f_4(\mathbf{x}) = x_1\ x_4 - K_1\ K_H\ p_{CO2} = 0$ (dissociation constant K_1)

$f_5(\mathbf{x}) = x_3\ x_5 - K_s = 0$ (calcite dissolution product)