On the Mathematical Iteration Principle and its Application to Chemical Equilibrium Calculations

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The practical application of the method of iteration for the numerical calculation of roots in equations which cannot be solved is discussed.

It is shown that the theoretical condition of iteration convergence is to be substituted with a practical condition which makes the method appropriate for actual calculation. The method is demonstrated on chemical equilibrium calculations.

The importance of a particular "sensitive" variable is stressed.

In his work with chemical equilibrium expressions the chemist very often has to determine a root in an equation which cannot be solved or which can be solved only with difficulty. In the following the method of successive approximation (iteration) will briefly be mentioned. This method seems to be very useful for determination of approximate root values.

Suppose the given equation is $F(x) = 0$, and that r is the unknown root of interest. If it is possible to rewrite the equation $F(x) = 0$ in the form:

$$x = f(x)$$

where $f(x)$ is differentiable and $|f'(x)| \leq c < 1$ in the interval to be considered containing the root r , then the series

$$x_0, x_1 = f(x_0), x_2 = f(x_1), \dots, x_n = f(x_{n-1}), \dots$$

where x_0 is an estimated value for the root r , will be convergent with the limit

$$r = f(r)$$

This follows by repeated application of the meanvalue theorem:

$$\begin{aligned} |x_n - r| &= |f(x_{n-1}) - f(r)| \\ &= |f'(u)| |x_{n-1} - r| \\ &\leq c |x_{n-1} - r| = c |f(x_{n-2}) - f(r)| \\ &= c |f'(v)| |x_{n-2} - r| \\ &\leq c^2 |x_{n-2} - r| = \dots \\ &\leq c^n |x_0 - r| \rightarrow 0 \\ &\text{when } n \rightarrow \infty, \text{ q.e.d.} \end{aligned}$$

Fig. 1. A and B: condition of iteration is fulfilled, i. e. convergence.
C and D: condition of iteration is not fulfilled, i. e. divergence.
A and C: $f' > 0$, i. e. steady motion.
B and D: $f' < 0$, i. e. oscillating motion.

Further and analogous considerations in the case: $|f'(x)| \geq c \geq 1$ make clear, that the condition of iteration convergence

$$|f'(x)| < 1$$

in the neighbourhood of r , in theoretical respect is necessary and sufficient for the series convergence, but it must be emphasised that this condition is *not* sufficient for practical purposes, as will be seen in the following example: If $1 \cong |f'(x)| < 1$, then n must be large if $x_n \cong r$. This is tantamount to the necessity of calculation of many $f(x)$ -values, which follows from:
 $|x_n - r| \leq c^n |x_0 - r|$ where $1 \cong c < 1$. It is also evident from A, B-type diagrams (see Fig. 1).

Consequently the practical condition of iteration convergence must be:

$$|f'(x)| < c,$$

where c is essentially less than 1. Or otherwise expressed: The nearer $f(x)$ is by constancy in the interval containing the root, the faster the iteration process will progress (consider A,B-type diagrams for $f'(x) \cong$ or $= 0$).

In many cases it is possible and appropriate first to rewrite the $F(x)$ given, so that the $F(x)$ function is mainly (and preferably strongly) depending on a

certain, single $x = x_s$ (the most "sensitive" x) in the $F(x)$ expression. Then this x_s is to be isolated in the equation given, *i.e.* $F(x) = 0$ is rewritten as $x_s = f(x)$. This $f(x)$ will fulfill the practical condition of iteration.

The principle of this successive approximation method is shown graphically in four characteristic cases where the condition of iteration: $|f'(x)| < 1$ partly is and partly is not fulfilled (diagrams A and B, and C and D, respectively).

Mathematical example

Suppose that calculations on a mass action expression has given the equation:

$$F(x) = x^4 + 10^{-2}x^3 - 10^{-4} = 0$$

where x is the degree of reaction. Consequently $0 < r < 1$. It is evident that the equation $F(x) = 0$ can be rewritten in many other forms. On account of the practical condition of iteration, it is appropriate to select an $f(x)$ function which depends only slightly on x ($f'(x)$ near 0).

Hence $F(x) = 0$ is rewritten in the form:

$$(x + 10^{-2})x^3 = 10^{-4} = 0$$

The greater x -exponent difference in this equation causes one of the two $f(x)$ functions, ($f_B(x)$), which is the most natural to select here, to be only slightly dependent on x , while the other, ($f_D(x)$), contrary to the condition of iteration, varies strongly with x . Obviously the most "sensitive" $x (= x_s)$ is contained in the factor x^3 . Consequently

$$x_s = f_B(x) = \left(\frac{10^{-4}}{x + 10^{-2}} \right)^{1/3}$$

$$(x = f_D(x) = \frac{10^{-4}}{x_s^3} - 10^{-2}),$$

where $f'_B(x)$ and $f'_D(x)$ is < 0 , and subscripts B and D refer to diagrams B and D. Notice that it is neither convenient nor necessary in general to calculate $f'(x)$. As $f(x)$, $f_B(x)$ is chosen because it is only a slightly varying function.

Now it only remains to choose a suitable x_0 (preferably in the neighbourhood of the root r). The general method for selection of x_0 is that the equation given is first solved qualitatively, with more or less good approximation. In most cases one can be helped through chemical considerations (pH-diagrams etc; see also "chemical example"). But in this and other cases one must try to estimate the root directly from the equation given. Thus it is often convenient to try the insertion of probable powers of ten for x_0 . From $F(x) = 0$ rewritten in the form:

$$g(x) = (x + 10^{-2})x^3 = 10^{-4}$$

is estimated, that $r = 10^{-1}$, which gives:

$$g(10^{-1}) = 1.1 \times 10^{-4} \simeq 10^{-4}$$

i.e., 10^{-1} is an applicable value for x_0 .

Consequently the convergence series is:

		error (%)
$x_0 = 10^{-1} =$	0.10000	2.4
$x_1 = f_a(x_0) = \left(\frac{10^{-4}}{10^{-1} + 10^{-2}} \right)^{1/3} =$	0.09688	0.7
$x_2 = f_a(x_1) =$	0.09781	0.2
$x_3 = f_a(x_2) =$	0.09752	0.07
$x_4 = f_a(x_3) =$	0.09761	0.02
$x_5 = f_a(x_4) =$	0.09759	0.01
$x_6 = f_a(x_5) =$	0.09759	0.01
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Notice that even $x_1 = f(x_0)$ is a good approximation to $r = 0.09759 \dots$. Hence continuation of the iteration process for $n > 2$ generally will be superfluous in cases like the present.

Chemical example 1

Given is a gaseous mixture having the following composition

SO ₂	7.8 vol %
O ₂	10.8 vol %
N ₂	81.4 vol %
	100.0 vol %

This gaseous mixture is passed into a converter where in the presence of a catalyst the SO₂ is oxidized to SO₃. The temperature in the converter is maintained at 500°C and the pressure at 1 atm, which is corresponding to $K_c = 177$ 800 l/st* for the equilibrium:

Calculate the composition of the gases leaving the converter, assuming that equilibrium conditions are reached. It may be assumed that the fugacity coefficients are equal to unity.

Qualitative solution. Notice that $K_c \gg 1$ and the amount of O₂ equivalent to the 7.8 vol % SO₂ (in the gas mixture given) is $1/2 \times 7.8 = 3.9 < 10.8$ vol % (= vol % O₂ in the mixture). Consequently the composition of the equilibrium mixture must approximately be:

SO ₂	0 vol %	SO ₃	8 vol %
O ₂	7 "	N ₂	85 "

Quantitative solution

$n_{\text{total}} = n_{\text{SO}_2} + n_{\text{O}_2} + n_{\text{SO}_3} + n_{\text{N}_2}$	moles of equilibrium mixture
$n_{\text{total}} = (a - 2x) + (b - x) + (0 + 2x) + c$	" " "
$n_{\text{total}} = a + b + c - x$	" " "

* st is by definition the number of moles equal to the stoichiometrical coefficients in the given scheme of reaction.

where a , b , 0 and c is the initial number of moles of SO_2 , O_2 , SO_3 and N_2 , and x is the equilibrium conversion of SO_2 .

Suppose $a + b + c = 100$ moles; then we get $n_{\text{total}} = 100 - x$ moles.

If by definition

$$K_n = \prod n_i^{\nu_i} = \frac{(n_{\text{SO}_3})^2}{(n_{\text{SO}_2})^2 (n_{\text{O}_2})}$$

where ν_i is the stoichiometrical coefficient of the i -th component, then:

$$K_c = K_n v^{-\Sigma \nu_i} = K_n v \quad (\text{for } -\Sigma \nu_i = -(2-2-1) = 1).$$

If the ideal gas laws are valid

$$v = n_{\text{total}} RT/p = (100-x)RT/p$$

i.e.,

$$K_c = \frac{(2x)^2(100-x)}{(a-2x)^2(b-x)} \frac{RT}{p}, \quad \text{or}$$

$$\frac{x^2(100-x)}{(a/2-x)^2(b-x)} = \frac{pK_c}{RT}$$

Now

$$\begin{array}{llll} a & = 7.8 & \text{mole} & p = 1 \text{ atm} \\ b & = 10.8 & \text{"} & R = 0.08205 \text{ l.atm/K.mole} \\ K_c & = 177\,800 & \text{l.atm/K.mole} & T = 773.2 \text{ K} \end{array}$$

Hence the equation $F(x) = 0$ is

$$\frac{x^2(100-x)}{(3.9-x)^2(10.8-x)} - 2802.6 = 0$$

From the qualitative solution we have:

$$n_{\text{SO}_3} = a - 2x \simeq 0 \quad (\text{almost complete reaction}), \text{ i.e.}$$

$$x \simeq \frac{a}{2} = 3.9.$$

Consequently 3.9 must be suitable as the initial value x_0 . The qualitative result, $x \simeq 3.9$, also makes clear that it is the $x (= x_s)$ in the group $3.9-x$ which is the most "sensitive". Hence we rewrite $F(x) = 0$ in the form

$$x_s = 3.9 - \frac{x}{53} \sqrt{\frac{100-x}{10.8-x}}$$

We now use the iteration principle

$$x_{n+1} = 3.9 - \frac{x_n}{53} \sqrt{\frac{100-x_n}{10.8-x_n}}$$

and get the following convergence series

$$\begin{array}{ll} x_0 = & 3.900 \\ x_1 = 2.9 - \frac{3.9}{53} \sqrt{\frac{100-3.9}{10.8-3.9}} = & 3.63 \\ x_2 = & 3.649 \\ x_3 = & 3.647 \\ \text{---} & \\ \text{---} & \end{array}$$

i.e.

$$x = r \simeq 3.647 \simeq 3.65.$$

Consequently

$n_{\text{SO}_2} = 2x$	$= 2 \times 3.65$	$= 7.30$	mole or	7.58	vol %
$n_{\text{O}_2} = b - x$	$= 10.8 - 3.65$	$= 7.15$	" "	7.42	" "
$n_{\text{SO}_2} = a - 2x$	$= 7.8 - 7.30$	$= 0.50$	" "	0.52	" "
$n_{\text{N}_2} =$		81.40	" "	84.47	" "
		<hr/>			
		96.35	mole or	100.00	vol %

which is in agreement with the qualitative solution.

Simultaneous equations

In the general case, with simultaneous equations in several unknowns, the method of iteration is given by the following two-equation example:

Suppose the given equations are

$$F(x, y) = 0 \text{ and } G(x, y) = 0.$$

In general the two independent variables are asymmetrical in the equations, and this is to be utilized for a fast working iteration process.

Assume that a certain $x = x_s$ in $F(x, y)$ is the relatively most "sensitive" of all the x 's and y 's in the two (eventually rewritten) functions given, and that y_s is the most "sensitive" of the y 's only in the other function $G(x, y)$. Then isolate x_s in $F(x, y) = 0$ and y_s in $G(x, y) = 0$:

$$x_s = f(x, y) \text{ and } y_s = g(x, y).$$

Now the two iteration principles are

$$x_{n+1} = f(x_n, y_n)$$

and

$$y_{n+1} = g(x_{n+1}, y_n)$$

i.e.

$$y_{n+1} = u(x_n, y_n) = g(f(x_n, y_n), y_n).$$

The initial values x_0 and y_0 are also in this case to be selected by qualitative solution of the problem considered.

Chemical example 2

Calculate c_{H^+} and $c_{\text{H}_2\text{Ox}}$ in a 0.1 M solution of potassium hydrogen oxalate in water. Assume that the activity coefficients are equal to unity, and that

$$K_1 = 10^{-1.19} \text{ and } K_2 = 10^{-4.21}$$

The schemes of significant reactions are

Qualitative solution

$$\text{pH} = 1/2(\text{p}K_1 + \text{p}K_2) = 2.7, \text{ i.e. } C_{\text{H}^+} = x = 0.002 \text{ and } y = 0.003$$

Quantitative solution

Hence

$$K_1 = 10^{-1.19} = \frac{x}{y} (0.1 - x - 2y)$$

$$K_2 = 10^{-4.21} = \frac{x(x+y)}{0.1-x-2y}$$

rewritten as

$$F(x,y) = x^2 \left(1 + \frac{10^{-1.19}}{0.1-x-2y} \right) = 10^{-5.40} = 0$$

$$G(x,y) = x \frac{0.1-x-2y}{y} - 10^{-1.19} = 0$$

It is to be seen that " x_s " is contained in the group x^2 in the F function. Hence

$$x_{n+1} = f(x_n, y_n) = \left(\frac{10^{-5.40}}{1 + \frac{10^{-1.19}}{0.1-x_n-2y_n}} \right)^{1/2}$$

and analogously

$$y_{n+1} = g(x_{n+1}, y_n) = x_{n+1} \frac{0.1 - x_{n+1} - 2y_n}{10^{-1.19}}$$

From the qualitative solution we choose $x_0 = y_0 = 0$. Consequently the two convergence series are derived as follows:

$$\begin{array}{ll} x_0 = 0 & y_0 = 0 \\ x_1 = f(x_0, y_0) & y_1 = g(x_1, y_0) \\ \quad = 1.556 \cdot 10^{-3} & \quad = 2.371 \cdot 10^{-3} \\ x_2 = f(x_1, y_1) & y_2 = g(x_2, y_1) \\ \quad = 1.535 \cdot 10^{-3} & \quad = 2.229 \cdot 10^{-3} \\ x_3 = f(x_2, y_2) & y_3 = g(x_3, y_2) \\ \quad = 1.536 \cdot 10^{-3} & \quad = 2.237 \cdot 10^{-3} \\ - & y_4 = g(x_3, y_3) \\ - & \quad = 2.236 \cdot 10^{-3} \end{array}$$

i.e.

$$x = 1.54 \cdot 10^{-3} \text{ and } y = 2.24 \cdot 10^{-3} \text{ (mole/l)}$$

It is a matter of course that the practical condition of iteration convergence is also well applicable to the approximative solution of transcendental equations as, for instance, $F(x) = 2 \lg x - x = 0$.

Finally it is noticed that the iteration process can easily be accelerated, if by the calculation of say x^{n+1} , it is possible, from the foregoing series values to estimate a better value x'_n than the x_n , and then insert this x'_n instead of x_n .

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