Solution of polynomial equation

We have seen the method for solving quadratic equation. Now we are going to see how a solution for any polynomial equation can be obtained. The polynomial is of the type.

$f(x) = ax^n + bx^{n-1} + \dots\dots.x + k$ …..(1)

Solution means, the value of x for which f(x) = 0.

In chemistry, we come across many polynomial equations. These are generally simplified by applying assumptions. However, these simplified forms of the equations give approximate results. To get better results, the polynomial equation has to be solved in the exact form.

There are a large number of mathematical methods for solving polynomial equations. We are going to learn a few methods in this paper.

Iterative method

Iterative means something that is repeated a number of times. So Iterative method means a problem solving process in which the steps are repeated more than once before the result is obtained.

In this method the polynomial equation is written as

$x = ax^n + bx^{n-1} + \dots\dots + k$ …..(2)

a,b,….., k are constants with known values.

An approximate value of *x* (known as initial guess) is put in the right hand side of the equation and a new value of *x* (which is taken as x_1) is calculated. x_1 and *x* are compared. If the difference is within the acceptable limit, one of the solution of equation is x_1. If the difference is large, then x_1 is substituted in the right hand side of the equation and second value x_2 is calculated. This procedure is repeated until the difference between two successive values becomes less than the accepted limit. If the difference increases in successive iterations, then the initial choice of *x* is incorrect and a new initial value of *x* has to be taken.

The accepted limit of accuracy =Degree of accuracy DOA

For example, for initial guess $x = 22.314$ After first iteration, the value of *x* is $x_1 = 22.316$

If DOA = 0.01, then the second value is within permitted error. The root is 22.316

If DOA= 0.001, then the second value is not within the permitted error.

$x_1 - x = -0.002$.

$|x_1 - x| = 0.002$ The absolute value of error

Difference = 0.002

$x_1 - x < 0$ but $|x_1 - x| > 0$

Generally, instead of absolute value of difference, relative difference is taken.

Relative difference =$|(x_1 - x)/x|$

If the values of successive iterations come closer then, they are said to converge.

In chemistry, for most of the equations, the initial guess is generally the value of x calculated from the approximate form of the polynomial equation.

The following problem illustrates this.

van der Waals equation of gas is

$$\left(P + \frac{\mathrm{a}n^2}{V^2}\right)(V - n\mathrm{b}) = nRT \qquad \text{....(3)}$$

Writing in cubic form

$$PV^3 - (nRT + nbP)V^2 + an^2V - abn^3 = 0$$

P = pressure of gas
T = temperature of gas in K
n = amount of gas, generally n = 1
$V/n = V_m$

$$PV^3 - (RT + bP)V^2 + aV - ab = 0$$

R = 0.082 atm L^{-1} mol^{-1} K^{-1} or R = 0.083 bar L^{-1} mol^{-1} K^{-1} or R = 8.314 J K^{-1} mol^{-1}

a, b are van der Waal's gas constant

Logic: van der Waal's equation of state is a cubic equation. To solve it using iterative method, the equation is written in the required form $x = ax^n + bx^{n-1} + \ldots\ldots + k$.

$$V = nRT/\left(P + \frac{\mathrm{a}n^2}{V^2}\right) + n\mathrm{b} \qquad \text{.......(4)}$$

The initial value of V is the value of volume calculated using ideal gas equation

$pV = nRT$

$V = nRT/P$ *initial guess*

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Put this value in the RHS of the eq(4). The values of rest of the variables in the equation are known. The LHS V is taken as $V1$, to make it different from initial value, so equation 4 becomes,

$$V1 = nRT/\left(P + \frac{an^2}{V^2}\right) + nb \qquad \text{....(5)}$$

The difference between, $V1$ and V is calculated. Since, this difference can be positive or negative, the value is taken without sign. The difference is divided to get the relative difference.

$|V1 - V|/V$

Let V=0.01, V1=0.011 , V1 − V = 0.001

Percentage difference = (0.001/0.1)x100 = 10%. This difference is large. Therefore we normally find the relative difference.

Calculate |(V1 – V)/V| , compare with DOA

For more accurate result, this relative difference should be small. If the difference is larger than the required accuracy then the procedure is repeated, but now the value of $V1$ is put in the RHS of the equation and a new value of V is calculated.

If $|(V_{i+1} - V_i)/V_i| <= \text{DOA}$, then root is V_{i+1} that is volume of the van der Waal's gas = V_{i+1}

Let's solve the van der Waals gas equation for one mole of a gas with

$a = 1.5$ atm dm^6 mol^{-2}, $n = 1$ mol
$b = 0.02$ dm^3 mol^{-1}, $R = 0.082$ atm dm^3 mol^{-1} K^{-1}, $p = 1$ atm, $T = 273$ K.
DOA = 0.0001 = 1×10^{-4}
Initial guess = $V = nRT/p$ = 1 mol× 0.082 atm L mol^{-1} K^{-1} ×273 K / 1 atm

V = 22.386 dm^3

$$V1 = nRT/\left(P + \frac{an^2}{V^2}\right) + nb = (1 \times 0.082 \times 273)/\{1 + 1.5/(22.386)^2\} + 0.02 = 22.3392$$

$|(V1 - V)/V| = |22.3392 - 22.386|/22.386 = 2.09079 \times 10^{-3}$

2nd iteration , $V2 = nRT/\left(P + \frac{an^2}{V1^2}\right) + nb$

$$= (1 \times 0.082 \times 273)/\{1 + 1.5/(22.3392)^2\} + 0.02 = 22.33891$$

$|(V2 - V1)/V1| = \{|22.33891 - 22.3392|/22.3392\} = 1.255105 \times 10^{-5}$
Since the relative difference is less than DOA, the volume of the gas is $V2$ = 22.33891 dm^3

Next equation is the exact form of dissociation of a weak acid

$$K_a = \frac{[H^+]\left\{[H^+] - \frac{K_w}{[H^+]}\right\}}{C_a - [H^+] + \frac{K_w}{[H^+]}}$$

Exact expression for concentration of H^+ of a weak acid

$[H^+]^3 + K_a[H^+]^2 - (K_w + K_aC_a)[H^+] - K_aK_w = 0$

$K_w = 1 \times 10^{-14}$

$[H^+] = (K_a \times C_a)^{1/2}$

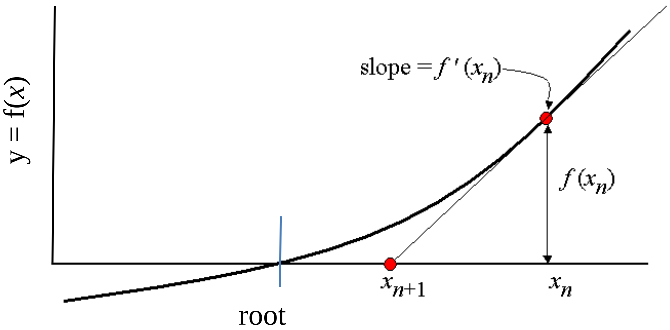
$[H^+]_1 = \{[H^+]^3 + K_a[H^+]^2 + K_aK_w\}/(K_w + K_aC_a)$

Problem: Solve the exact expression for the dissociation of an acid using iterative method to calculate the pH for an acid with $K_a = 1.85 \times 10^{-5}$, $C_a = 0.01$ mol dm^{-3} . pH = − log $[H^+]$

(b) Newton-Raphson method

It is a method of finding real roots of a continuous polynomial equation that can be differentiated.

In this method the polynomial equation is written in the form f(x) = 0.



Let the initial guess of the root is x_n. Draw a tangent to the curve at x_n. This tangent crosses the x-axis at x_{n+1}. If our initial guess is correct then, x_{n+1} is nearer to the actual root. The slope of the tangent is equal to the value of derivative of the function at x_n. The derivative is $f'(x_n)$.

The equation of the tangent is

$y = f'(x_n)(x - x_n) + f(x_n)$ $\quad\quad$ ($y = mx + c$)
m = slope $(y_2 - y_1)/(x_2 - x_1)$ = first derivative of function
c = intercept = value of y when $x = 0$
For root, y = 0. Let $x = x_{n+1}$ when y = 0. Put this in the equation of the line.

y =0 = f ’(x_n)(x_{n+1} –x_n) + f(x_n)

f ’(x_n)(x_{n+1} –x_n) = − f(x_n)

x_{n+1} –x_n = − f(x_n)/ f ’(x_n)

Further solving, we get the recursive formula:

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)} \qquad \text{…..(6)}$$

Put the value of x_n in the equation, if it is the actual solution, the value will come out to be zero, otherwise, it will have a non-zero value.

f '(x_n) is the first derivative of the function at x_n. Iteration is carried out, that is the values of x_n, f(x_n) and f '(x_n) are put in RHS of eq(6). x_{n+1} is calculated and x_{n+1} is compared with x_n. If the two values are not sufficiently close then the value of x_{n+1} is substituted into the right hand side of the recursion equation (Eq. 6) and the computation is repeated.

For example, for solving the van der Waal’s equation using this method.

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

The equation is written in the form f(x) = 0

$$PV - nbP + \frac{an^2}{V} - \frac{abn^3}{V^2} - nRT = 0$$

Multiplying the equation by V^2 we get

$$PV^3 - (nRT + nbP)V^2 + an^2V - abn^3 = 0 \qquad f(x) = 0 \text{ here } x = V$$

Take the derivative with respect to V since we have to find its value.

$$3PV^2 - 2(nRT + nbP)V + an^2 = 0 \qquad f'(x) = 0$$

Initial guess $V = nRT/p$

Similarly, the concentration of H^+ ions in a weak acid can be calculated from the exact expression.

$$K_a = \frac{[H^+]\left\{[H^+] - \frac{K_W}{[H^+]}\right\}}{C_a - [H^+] + \frac{K_W}{[H^+]}} \qquad \text{….(7)}$$

Its form as f(x) = 0 is here x = [H^+]

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$[H^+]^3 + K_a[H^+]^2 - (K_w + K_aC_a)[H^+] - K_aK_w = 0$ …(8) f(x)

Differential form of eq(8) is

$3[H^+]^2 + 2K_a[H^+] - (K_w + K_aC_a)$ ….(9) f '(x)

$K_w = 1\times10^{-14}$ at 25 °C

K_a is acid dissociation constant of acid, C_a is the initial concentration of acid. For weak acid the concentration of H^+ ions is calculated using the following equation

Initial guess = $[H^+] = \sqrt{K_aC_a}$ ….(10)

For $K_a = 1.85 \times 10^{-3}$, $C_a = 0.01$ DOA = 1×10^{-5}

Initial guess = $\sqrt{1.85 \times 10^{-3} \times 0.01} = 4.301163 \times 10^{-4}$

After first iteration, $H_1 = 4.301163\times10^{-4} - \frac{f(4.301163\times10^{-4})}{f'(4.301163\times10^{-4})}$

$= 4.301163 \times 10^{-4} + \frac{3.422492 \times 10^{-12}}{3.8519143 \times 10^{-7}}$

$H_1 = 4.212477 \times 10^{-4}$

Relative difference between H and H_1 is 2.061889×10^{-2}. This is greater than DOA

After 2^{nd} iteration, $H_2 = 4.212477\times10^{-4} - \frac{f(4.212477\times10^{-4})}{f'(4.212477\times10^{-4})}$

$= 4.212477 \times 10^{-4} + \frac{1.02247 \times 10^{-13}}{3.629351 \times 10^{-7}} = 4.20966 \times 10^{-4}$

Relative difference between H_1 and H_2 is 6.687872×10^{-4}. This is greater than DOA

After 3^{rd} iteration, $H_3 = 4.20966 \times 10^{-4} - \frac{f(4.20966\times10^{-4})}{f'(4.20966\times10^{-4})}$

$= 4.20966 \times 10^{-4} + \frac{1.008642 \times 10^{-16}}{3.6221291 \times 10^{-7}} = 4.209657 \times 10^{-4}$

Relative difference the values is 6.913582×10^{-7} which is less than DOA = 1×10^{-5}.

Therefore, the concentration of H^+ ions is 4.209657×10^{-4} and pH is 3.376

Problem: The van der Waals equation for argon at 143 K and 35.0 atm pressure can be written as

$$\overline{V}^3 - 0.3664\overline{V}^2 + 0.03802\overline{V} - 0.001210 = 0$$

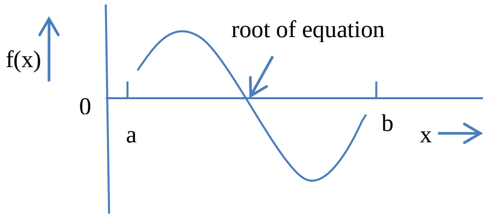
Find the roots to this equation using Newton-Raphson method. Take DOA = 0.001

Hint : Initial guess = $\bar{V} = V_m = \frac{V}{n} = \frac{RT}{p} = \frac{0.082 \times 143}{35}$

(c) Binary bisection method

This method is based on the repeated application of the intermediate value theorem. The polynomial equation is written in the form f(x) = 0. If the root of the equation lies in the interval [a, b] then the sign of the function at the two extremes of the interval is different, that is,

sign of f(a) ≠ sign of f(b)



It is assumed that the root of the equation lies at the midpoint of the interval [a, b]. The mid-point c is calculated as

$$c = \frac{a+b}{2}$$

Calculate the value of function at c, that is , f(c). If f(c) = 0 then c is the required root. Otherwise check the subintervals [a,c] and [c,b].

If the sign of f(c) is same as f(a), that is, f(a).f(c) >0 then the root does not lie in the interval [a,c]. It lies in the interval [b,c].

Otherwise the root lies in the interval [a,c], that is, when f(a).f(c) < 0.

Now find the midpoint of the subinterval in which the root lies. If the interval is [a,c] then the midpoint is

$$c' = \frac{a+c}{2}$$

If the interval is [c,b] then the midpoint is

$$c' = \frac{c+b}{2}$$

Calculate f(c´). Repeat the process until the exact root is obtained.

If the interval [a,b] is large then the method is modified. The entire interval is subdivided into small intervals of range s. For the first step the interval is a and a+s. This interval is checked for the presence of the root. If the root is absent then next interval between a+s and a+2s is taken. This process is continued until either the root is obtained or maximum value of interval, b is reached.

Problem: Solve the equation $x^5 + 2x^4 + 4x = 5$ using binary bisection method for the root that lies between 0 and 1.

Logic:

- Write equation in the form f(x) = 0.
  - $f(x) = x^5 + 2x^4 + 4x – 5$
- In this program, lower limit is a and upper limit is b. So the interval is [a, b]=[0,1].
- Find f(a). If f(a) = 0 then the root is a.
  - $(0)^5 + 2(0)^4 + 4(0) – 5 = -5$
  - f(a) ≠0 so a is not the root.
- Find f(b). If f(b) =0 then the root is b.
  - $(1)^5 + 2(1)^4 + 4(1) – 5 = 1+2+4 – 5 = 2$
  - f(b) ≠0 so b is not the root.
- If the sign of the function at a, that is f(a) and the sign of the function at b, that is f(b) are same that means the root does not lie in the range.
  - f(a) < 0, f(b) > 0
- Since the signs are different then the root lies in the range.
- Find mid-point c = $\frac{0+1}{2} = 0.5$
- Find f(0.5)
  - $(0.5)^5 + 2(0.5)^4 + 4(0.5) – 5 = 0.03125 + 0.125 + 2 – 5 = -2.84375$
  - f(c) < 0
- f(a).f(c) > 0 and f(b).f(c) < 0
  - Since signs of the functions at x = a and x = c are same, root does not lie between a and c.
  - Root lies between c and b.
  - The new interval is [c,b] = [0.5,1]
- Find midpoint of the new interval.
  - $c_1 = \frac{0.5+1}{2} = 0.75$
- Find f(0.75)
  - $(0.75)^5 + 2(0.75)^4 + 4(0.75) – 5 = -1.12988$
  - $f(c_1) < 0$
- $f(c).\ f(c_1) > 0$ and $f(b).\ f(c_1) < 0$
  - Since signs of the functions at $x = c_1$ and x = c are same, root does not lie between c_1 and c.

  - Root lies between c_1 and b.
  - The new interval is $[c_1,b] = [0.75,1]$
- Find midpoint of the new interval.
  - $c_2 = \frac{0.75+1}{2} = 0.875$
- Find f(0.875)
  - $(0.875)^5 + 2(0.875)^4 + 4\,(0.875) - 5 = 0.18527$
  - $f(c_2) > 0$
- $f(c_2).\ f(c_1) < 0$ and $f(b).\ f(c_2) > 0$
  - The root lies between c_1 and c_2
- Find the midpoint of c_1 and c_2
  - $c_3 = \frac{0.875+0.75}{2} = 0.8125$
- $f(c_3) = f(0.8125) = -0.9601$
- $f(c_2).\ f(c_3) < 0$ and $f(c_1).\ f(c_3) > 0$
  - Root lies between 0.8125 and 0.875
- Keep on repeating the process till $f(c_i) = 0$ or very near to 0 or c_i and c_{i-1} are very close to each other.
- For this problem, root is 0.8596191, and $f(c_i) = -5.753974 \times 10^{-5}$ after 12 steps