Project 8 Solutions

In this project, we set up a system of nonlinear equations to calculate the pH of a solution containing three weak acids. The acids in question are the following: Acetic acid, Phenol and Chloroacetic acid.

Start by letting HX = Acetic Acid, HY = Phenol and HZ = Choloroacetic acid. Also, define [ ] as the concentration of a chemical species.

We can then form the following system of equations. Start with an overall ion balance

$[H^+] = [X^-] + [Y^-] + [Z^-] + [OH^-]$

Second, we perform mole balances for all the species present in solution.

$[HX] + [X^-] = [HX]_0$

$[HY] + [Y^-] = [HY]_0$

$[HZ] + [Z^-] = [HZ]_0$

where $[]_0$ is defined as the initial concentration of a species.

Finally, we define the equilibrium constants for all species.

$[H^+][X^-] = K_x[HX]$

$[H^+][Y^-] = K_y[HY]$

$[H^+][Z^-] = K_z[HZ]$

Also, it is important not to forget that dissociation of water plays a role in this problem too.

$[H^+][OH^-] = K_w$

Contents

Part 1. Specify the parameters for the problem.

```
% Per our standard approach, we define all known constants for the
% problem.
echo off
clear
clc

% Dissociation constants.
Kac = 1.75e-05; % Acetic acid
Kph = 1e-10; % Phenol
Kch = 0.0014; % Chloroacetic acid
Kw = 1e-14; % Water

% Initial concentration of the acids in the solution.
Cac = 0.1; % [mol/L]
Cph = 0.2; % [mol/L]
Cch = 0.001; % [mol/L]
```

Part 2. Construct the system of nonlinear equations.

In this part we construct an anonymous function which we will pass to the command fsolve to calculate concentrations. We shall make no efforts to properly condition or renormalize the variables.

```
Eqns = @(x) [x(1) - x(2) - x(3) - x(4) - x(5) ; x(6) + x(2) - Cac; ...
             x(7) + x(3) - Cph; x(8) + x(4) - Cch; x(1)*x(2) - Kac * x(6); ...
             x(1)*x(3) - Kph * x(7); x(1)*x(4) - Kch * x(8); x(1)*x(5) - Kw ];

% Specify an initial guess for the ion concentrations and solve the problem.
x0 = 0.5 * ones(1,8);
[x,fval] = fsolve(Eqns,x0);
pH = -log10(x(1));
format short e
left=str2mat('Acetic Acid ','Phenol ','Chloroacetic Acid ');
concs=[left,num2str([[Cac,Cph,Cch]',x(2:4)',x(6:8)'])];
ctable=str2mat('                  Total      Dissoc  non-Dissoc',concs);
waterprod=x(1)*x(5);

% Display the results.
disp(['The pH of the solution is ', num2str(pH)])
disp(' ')
disp('The calculated concentrations are')
disp(ctable)
disp(' ')
disp(['The [H+][OH-] product is ' num2str(waterprod)])
disp(' ')
disp('The final function evaluations are')
fval
```

```
Equation solved.

fsolve completed because the vector of function values is near zero
as measured by the default value of the function tolerance, and
the problem appears regular as measured by the gradient.



The pH of the solution is 2.1563

The calculated concentrations are
                  Total      Dissoc  non-Dissoc
Acetic Acid         0.1   0.0015244    0.098476
Phenol              0.2   0.0015223     0.19848
Chloroacetic Acid 0.001   0.0011083 -0.00010831

The [H+][OH-] product is 1.9692e-05

The final function evaluations are

fval =

  -4.3368e-19
  -1.3878e-17
   2.7756e-17
            0
```

```
    8.9126e-06
    1.0622e-05
    7.8847e-06
    1.9692e-05
```

Part 3. Renormalization of the equations and variables.

Examination of the results above show that all the calculated values are incorrect: while the mass balances are reasonably satisfied, the concentration of the non-dissociated chloroacetic acid is actually negative! Most significantly, the [H+][OH-] product is off by 9 orders of magnitude! We must fix this by renormalization of the problem.

Here we renormalize the variables and equations so that all of the equations are of O(1), as are the variables (concentrations) and the concentrations can never be negative. We work with the log of the concentrations and take the log of the equilibrium relations. Thus:

```
% Define the system of equations that you are trying to solve as an
% anonymous function .
Eqns = @(x) [(exp(x(1)) - exp(x(2)) - exp(x(3)) - exp(x(4)) - exp(x(5))) ; (exp(x(6
             (exp(x(7)) + exp(x(3)))/Cph - 1; (exp(x(8)) + exp(x(4)))/Cch - 1; x(1)+
             x(1)+x(3) - log(Kph) - x(7); x(1)+x(4) - log(Kch) - x(8); x(1)+x(5) - l

% Specify an initial guess for the concentrations and solve the problem.
x0 = - ones(1,8);
[x,fval] = fsolve(Eqns,x0);
% Determining the pH.
pH = -log10(exp(x(1)));
format short e
left=str2mat('Acetic Acid ','Phenol ','Chloroacetic Acid ');
concs=[left,num2str([[Cac,Cph,Cch]',exp(x(2:4))',exp(x(6:8)')])];
ctable=str2mat('                    Total      Dissoc   non-Dissoc',concs);
waterprod=exp(x(1))*exp(x(5));

% Display the results.
disp(['The pH of the solution is ', num2str(pH)])
disp(' ')
disp('The calculated concentrations are')
disp(ctable)
disp(' ')
disp(['The [H+][OH-] product is ' num2str(waterprod)])
disp(' ')
disp('The final function evaluations are')
fval
```

```
Equation solved.

fsolve completed because the vector of function values is near zero
as measured by the default value of the function tolerance, and
the problem appears regular as measured by the gradient.



The pH of the solution is 2.8035
```

```
The calculated concentrations are
                  Total      Dissoc  non-Dissoc
Acetic Acid         0.1    0.001101    0.098899
Phenol              0.2  1.2722e-08         0.2
Chloroacetic Acid 0.001  0.00047106  0.00052894

The [H+][OH-] product is 1e-14

The final function evaluations are

fval =

  -1.3696e-14
  -1.1102e-16
            0
   2.8672e-11
  -8.8818e-16
   3.1086e-15
   8.4377e-14
            0
```

Conclusion:

Thus, even though the solver appeared to converge, the answer yielded to the mathematically identical second problem was very much different (and more correct!). The pH differed by an nearly an order of magnitude (remember that pH is logarithmic in base 10), and none of the concentrations are negative. The value of the function at convergence has decreased by 10 orders of magnitude as well, and is now right on roundoff error. All this points up the importance of having your equations and variables properly normalized! Note that the (incorrect) solution to the first set of equations depended on exactly how you set it up: some ways of writing the equations even yielded complex pH's due to negative [H+] concentrations! Yet if you took the exact solution as your starting point, even that code would work - but the domain of starting points over which you would converge to the correct answer is -very-small!