Midterm Examination Solution
March 2, 2017
Due: Beginning of Class, Tuesday, March 7, 2017

Consider a system with three anions, A, B and OH, and two cations, C, D and H. The following reactions are possible

$AH \overset{K_1}{\leftrightarrow} A^- + H^+$ reaction 1.

$AC \overset{K_2}{\leftrightarrow} A^- + C^+$ reaction 2.

$AD \overset{K_3}{\leftrightarrow} A^- + D^+$ reaction 3.

$BH \overset{K_4}{\leftrightarrow} B^- + H^+$ reaction 4.

$BC \overset{K_5}{\leftrightarrow} B^- + C^+$ reaction 5.

$BD \overset{K_6}{\leftrightarrow} B^- + D^+$ reaction 6.

$COH \overset{K_7}{\leftrightarrow} OH^- + C^+$ reaction 7.

$DOH \overset{K_8}{\leftrightarrow} OH^- + D^+$ reaction 8.

There are a total of fourteen species: *AH*, *AC*, *AD, BH*, *BC, BD*, *COH*, *DOH*, A^-, B^-, C^+, D^+, H^+, OH^-. Equilibrium coefficients govern the distribution of each of these reactions.

$$K_1 = \frac{[A^-][H^+]}{[AH]} \quad \text{or} \quad [AH] = \frac{[A^-][H^+]}{K_1} \qquad \text{equation 1.}$$

$$K_2 = \frac{[A^-][C^+]}{[AC]} \quad \text{or} \quad [AC] = \frac{[A^-][C^+]}{K_2} \qquad \text{equation 2.}$$

$$K_3 = \frac{[A^-][D^+]}{[AD]} \quad \text{or} \quad [AD] = \frac{[A^-][D^+]}{K_3} \qquad \text{equation 3.}$$

$$K_4 = \frac{[B^-][H^+]}{[BH]} \quad \text{or} \quad [BH] = \frac{[B^-][H^+]}{K_4} \qquad \text{equation 4.}$$

$$K_5 = \frac{[B^-][C^+]}{[BC]} \quad \text{or} \quad [BC] = \frac{[B^-][C^+]}{K_5} \qquad \text{equation 5.}$$

$$K_6 = \frac{[B^-][D^+]}{[BD]} \quad \text{or} \quad [BD] = \frac{[B^-][D^+]}{K_6} \qquad \text{equation 6.}$$

$$K_7 = \frac{[OH^-][C^+]}{[COH]} \quad \text{or} \quad [COH] = \frac{[OH^-][C^+]}{K_7} \qquad \text{equation 7.}$$

$$K_8 = \frac{[OH^-][D^+]}{[DOH]} \quad \text{or} \quad [DOH] = \frac{[OH^-][D^+]}{K_8} \qquad \text{equation 8.}$$

Four more equations come from molar balances on *A*, *B*, *C, D*.

$$[A_{Tot}] = [AH] + [AC] + [AD] + [A^-] \qquad \text{equation 9.}$$

$$[B_{Tot}] = [BH] + [BC] + [BD] + [B^-] \qquad \text{equation 10.}$$

$$[C_{Tot}] = [AC] + [BC] + [COH] + [C^+] \qquad \text{equation 11.}$$
$$[D_{Tot}] = [AD] + [BD] + [DOH] + [D^+] \qquad \text{equation 12.}$$

The pH of the solution is given, which effectively provides the values of both $[H^+]$ and $[OH^-]$.

Solve for the concentration of all fourteen species as a function of pH from 1 to 13 for the following parameter values. Both the equilibrium coefficients and the concentrations have units of $\frac{mol}{\ell}$.

$K_1 = 10^{-1}$, $K_2 = 10^{-2}$, $K_3 = 10^{-7}$, $K_4 = 10^{-3}$, $K_5 = 10^{-4}$, $K_6 = 10^{-4}$, $K_7 = 10^{-6}$ and $K_8 = 10^{-4}$.
$[A_{Tot}] = 1.0 \cdot 10^{-3}$, $[B_{Tot}] = 0.5 \cdot 10^{-4}$, $[C_{Tot}] = 1.0 \cdot 10^{-3}$, and $[D_{Tot}] = 0.5 \cdot 10^{-4}$.

Solution:

To solve this problem I used the following script (based on the script in the notes).

script: paramstep_xm1_s17.m

```
%
%  parameter stepping example 3:  Solution Equilibria
%
clear all;
close all;
format longe;
% make current value of lambda available globally
global pHi
%
% set up pH vector
%
phlo =1.0;
phhi = 13.0;
dph = 0.001;
nph = (phhi - phlo)/dph + 1;
phvec = zeros(nph,1);
phvec=[phlo:dph:phhi]';
%
%  reserve memory for solution matrix
%
nvar = 4;
solmat = zeros(nph,nvar);
%
%  initial guess for low pH
%
A_tot = 1.0e-3;
B_tot = 0.5e-4;
C_tot = 1.0e-3;
D_tot = 0.5e-4;
Aguess = 0.1*A_tot;
Bguess = 0.1*B_tot;
Cguess = 0.1*C_tot;
Dguess = 0.1*D_tot;
x0=[Aguess; Bguess; Cguess; Dguess];
% set the tolerance and printing switch
```

```
tol=1.0e-6;
iprint=0; % 0 is off, 1 is on
%
%  parameter step
%
for i =1:1:nph
% call Newton-Raphson
    pHi = phvec(i);
    [x,err,f] = nrndn_xm01_s17(x0,tol,iprint);
% store result
  solmat(i,1:nvar) = x(1:nvar);
  fmat(i) = f;
% update initial guess
  x0(1:nvar) = x(1:nvar);
end

%
%  plot result
%
figure(1)
semilogy(phvec(1:nph),solmat(1:nph,1),'k-');
hold on;
semilogy(phvec(1:nph),solmat(1:nph,2),'r-');
hold on;
semilogy(phvec(1:nph),solmat(1:nph,3),'b-');
hold on;
semilogy(phvec(1:nph),solmat(1:nph,4),'g-');
hold off;
xlabel('pH');
ylabel('molarity');
legend('A','B','C','D')
%
%  plot error
%
figure(2)
semilogy(phvec(1:nph),fmat(1:nph),'k-');
xlabel('pH');
ylabel('average absolute error on f');

%
%  calculate other variables to Reproduce Figure 4 of reference
%
global K1 K2 K3 K4 K5 K6 K7 K8

solmat2 = zeros(nph,4);
for i = 1:1:nph
    H = 10.0^(-phvec(i));
    OH = 10.0^(-(14.0-phvec(i)));
    A = solmat(i,1);
    B = solmat(i,2);
    C = solmat(i,3);
    D = solmat(i,4);
    AH = A*H/K1;
    AC = A*C/K2;
    AD = A*D/K3;
    BH = B*H/K4;
```

```
    BC = B*C/K5;
    BD = B*D/K6;
    COH = C*OH/K7;
    DOH = D*OH/K8;
    solmat2(i,1) = AH;
    solmat2(i,2) = AC;
    solmat2(i,3) = AD;
    solmat2(i,4) = BH;
    solmat2(i,5) = BC;
    solmat2(i,6) = BD;
    solmat2(i,7) = COH;
    solmat2(i,8) = DOH;
    solmat2(i,9) = OH;
    solmat2(i,10) = H;
end

figure(3)
semilogy(phvec(1:nph),solmat2(1:nph,1),'k-');
hold on;
semilogy(phvec(1:nph),solmat2(1:nph,2),'r-');
hold on;
semilogy(phvec(1:nph),solmat2(1:nph,3),'b-');
hold on;
semilogy(phvec(1:nph),solmat(1:nph,1),'g-');
xlabel('pH')
ylabel('Molarity')
legend('AH','AC','AD','A')
hold off;

figure(4)
semilogy(phvec(1:nph),solmat2(1:nph,4),'k-');
hold on;
semilogy(phvec(1:nph),solmat2(1:nph,5),'r-');
hold on;
semilogy(phvec(1:nph),solmat2(1:nph,6),'b-');
hold on;
semilogy(phvec(1:nph),solmat(1:nph,2),'g-');
xlabel('pH')
ylabel('Molarity')
legend('BH','BC','BD','B')
hold off;

figure(5)
semilogy(phvec(1:nph),solmat2(1:nph,7),'k-');
hold on;
semilogy(phvec(1:nph),solmat2(1:nph,8),'r-');
hold on;
semilogy(phvec(1:nph),solmat(1:nph,3),'b-');
hold on;
semilogy(phvec(1:nph),solmat(1:nph,4),'g-');
xlabel('pH')
ylabel('Molarity')
legend('COH','DOH','C','D')
hold off;
```

```
figure(6)
semilogy(phvec(1:nph),solmat2(1:nph,9),'k-');
hold on;
semilogy(phvec(1:nph),solmat2(1:nph,10),'r-');
xlabel('pH')
ylabel('Molarity')
legend('OH','H')
hold off;
```

I also modified the `nrndn.m` input function as follows:

```
function f = funkeval(x)
%
% these two lines force a column vector of length n
%
n = max(size(x));
f = zeros(n,1);
%
% EDIT BELOW:
%
%global variables for post processing
%
global pHi
global K1 K2 K3 K4 K5 K6 K7 K8
%Setting input variables for solver
A = x(1);
B = x(2);
C = x(3);
D = x(4);
%H and OH calculator
pH = pHi;
pOH= 14.0-pH;
H = 10.0^(-pH);
OH = 10.0^(-pOH);
%equillibrium constants
K1 = 1.0e-1;
K2 = 1.0e-2;
K3 = 1.0e-7;
K4 = 1.0e-3;
K5 = 1.0e-4;
K6 = 1.0e-4;
K7 = 1.0e-6;
K8 = 1.0e-4;
% total amount of material
A_tot = 1.0e-3;
B_tot = 0.5e-4;
C_tot = 1.0e-3;
D_tot = 0.5e-4;
%  equilibrium relations
AH = A*H/K1;
AC = A*C/K2;
AD = A*D/K3;
BH = B*H/K4;
BC = B*C/K5;
BD = B*D/K6;
COH = C*OH/K7;
DOH = D*OH/K8;
```

```
%Molar Balances
% left hand side
A_balance_lhs = A_tot;
B_balance_lhs = B_tot;
C_balance_lhs = C_tot;
D_balance_lhs = D_tot;
% right hand side
A_balance_rhs = AH + AC + AD + A;
B_balance_rhs = BH + BC + BD + B;
C_balance_rhs = AC + BC + COH + C;
D_balance_rhs = AD + BD  + DOH + D;
% Functions = RHS - LHS = 0
f(1) = A_balance_lhs - A_balance_rhs;
f(2) = B_balance_lhs - B_balance_rhs;
f(3) = C_balance_lhs - C_balance_rhs;
f(4) = D_balance_lhs - D_balance_rhs;
```

At the command line prompt, I executed the script:

```
>> paramstep_xm01_s17
```

which generated the following three plots.

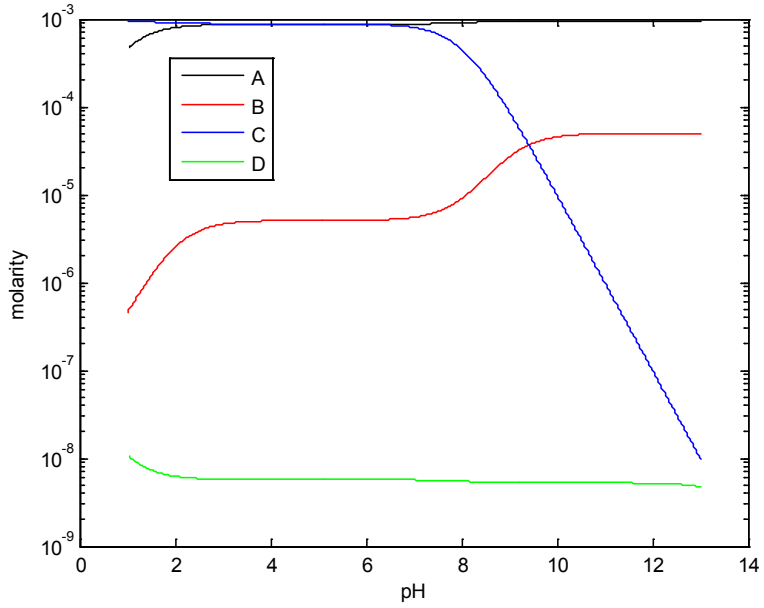

Figure 1. Concentrations of A^-, B^-, C^+ and D^+ as a function of pH.

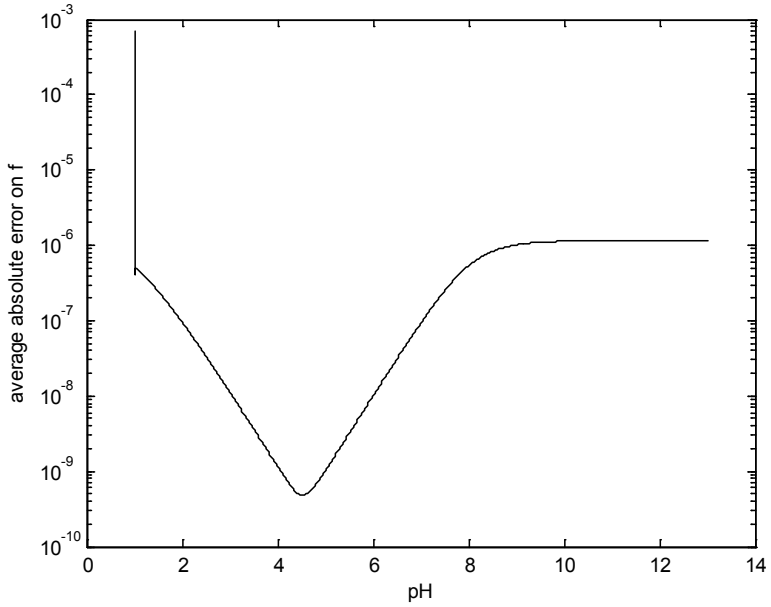

Figure 2. Error as a function of pH. This function shows that the tolerance was always satisfied. (Something peculiar happened at the very first of the 13,001 points.)

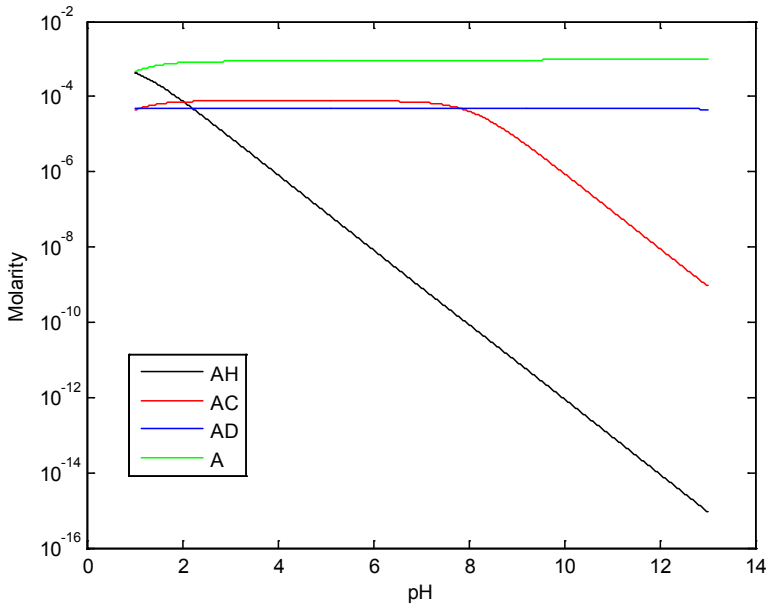

Figure 3. Concentration of *AH*, *AC*, *AD* and A^- as a function of pH.

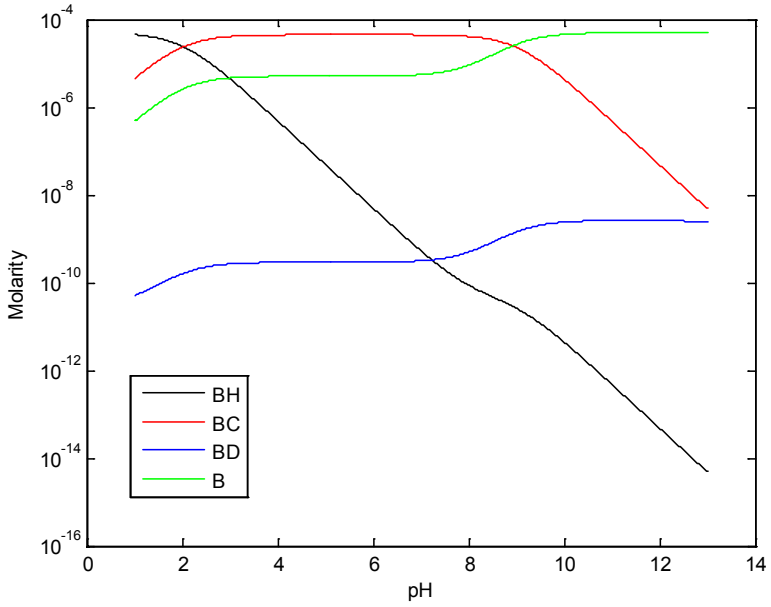

Figure 4. Concentration of *BH*, *BC*, *BD* and B^- as a function of pH.

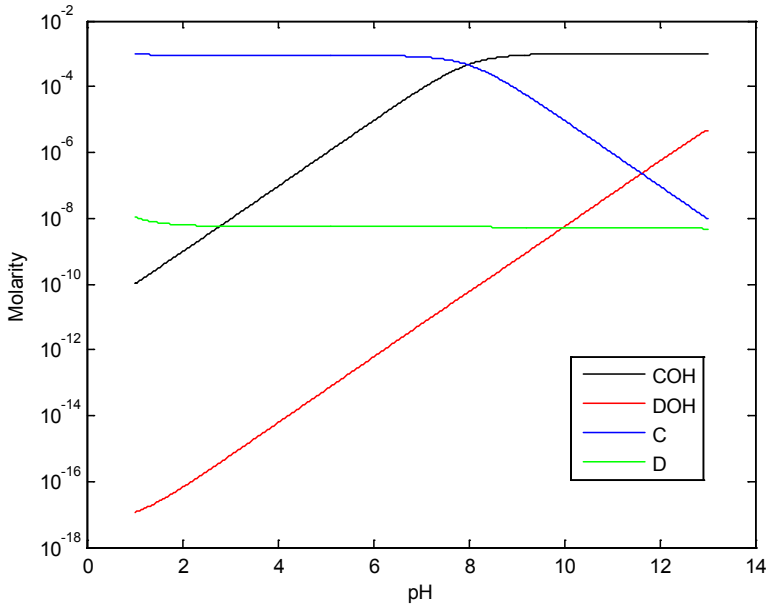

Figure 5. Concentration of *COH*, *DOH*, C^+ and D^+ as a function of pH.

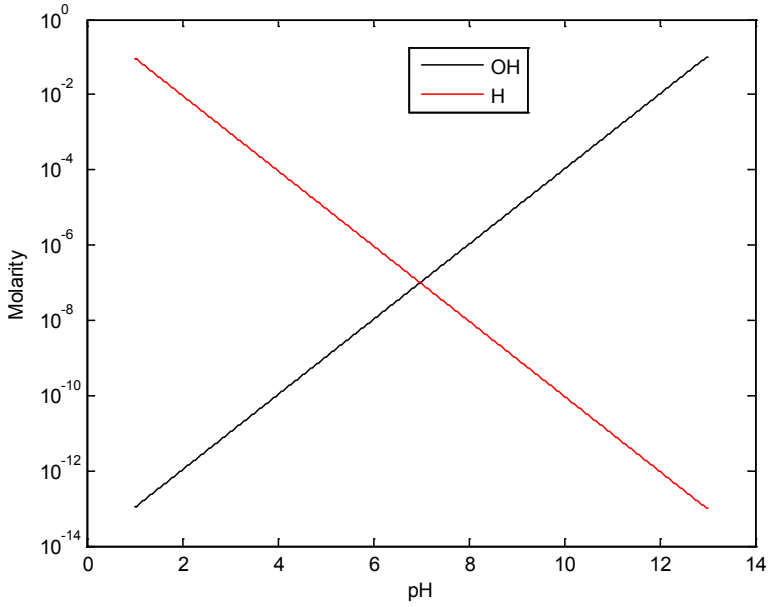

Figure 6. Concentration of OH^- and H^+ as a function of pH.