Aquatic Chemistry exercises 1-12

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Exercise 1

The aim of this exercise is to investigate the ionic strengths and ion activity factors in different natural waters.

Water and water cycles are one of the fundamental processes that underpin the chemical, biological and geological processes which create the foundation for life on this planet. As the scope of human activity has expanded so to has anthropogenic effects on water systems. This necessitates a thorough understanding of the chemical properties and processes of water systems. A central concept in chemistry is equilibrium, a stable state in a chemical system where the forward and reverse reactions happen at the same rate.

The concept of equilibrium and equilibrium position allows quantification and modelling of how complex systems react to inputs, sinks and changes in environment. The equilibrium position is given by the equilibrium constant k that for the reaction in the ideal solution $A + xB \leftrightharpoons yC + D$ is defined as $k = \frac{[C]^y \cdot [D]}{[A] \cdot [B]^x}$. For non-ideal solutions the concentration is instead replaced with the species activity a (for species A) where $a_A = \gamma \cdot [A]$ where γ is the activity factor, a solution constant that describes the deviation from an ideal solution.

The ion concentration in natural waters is highly variable and dependent on multiple factors such as the surrounding geology, proximity to oceans, surrounding ecosystems and anthropogenic activity. The ion strength I of a solution, a measure that takes into account both the total ion concentration as well as the ion charges, affects the activity factor of each species according to the Debye-Hückel equation (2) and can therefore have a large influence on equilibrium calculation.

Ion strength of a solution consisting of species with the index i is defined as

$$I = \frac{1}{2}\sum_i C_i \cdot z_i^2 \quad \text{C in mol L}^{-1}, \qquad I = \frac{1}{2}\sum_i C_i \cdot |z_i| \quad \text{C in ekv L}^{-1} \tag{1}$$

where z_i denotes the species charge. Further the activity factor γ of a species i is given by the Debye-Hückel equation where r_i denotes the species hydrated ionic radius.

$$\log \gamma = \frac{-0.51 z_i^2 \sqrt{I}}{1 + 0.33 r_i \sqrt{I}} \Leftrightarrow \gamma = 10^{\frac{-0.51 z_i^2 \sqrt{I}}{1 + 0.33 r_i \sqrt{I}}} \tag{2}$$

The ion concentration and species for the natural waters listed in Table 1 were calculated using the maltlab `script e1.m` and the calculated value can be seen in Table 2.

The locations of the natural waters can be seen in the compendium Figure 3.4 (page 27) with the point marked 'Djup' referring to the location where Deep groundwater was sampled. As is to be expected the

Table 1: Table showing the ion concentrations of five different natural waters.

	Cl$^-$	SO$_4^{2-}$	NO$_3^-$	HCO$_3^-$	Na$^+$	Ca^{2+}	Mg^{2+}	K$^+$	NH$_4^+$	Al^{3+}	H$^+$
	Concentrations in μeq L^{-1}										
Lake Härsvatten	243	102	30	0	240	29	58	11	3	4	$10^{-4.5}$
Lake Sövdesjön	454	503	5	2218	479	2656	346	72	18	0	$10^{-8.16}$
Lake Vemmarsjön	18	29	2	88	53	78	38	8	2	0	$10^{-6.1}$
Deep groundwater	704	500	16	3172	1196	2525	568	97	6	0	$10^{-7.5}$
	Concentrations in meq L^{-1}										
Seawater	547	56	*NA*	2.3	470	21	110	10	*NA*	*NA*	*NA*

Table 2: Table showing the Ionic strength I of five natural waters and the activity factors γ for different ionic species. Activity factors in italics are for species not present or not measured in the sample water.

	Ionic Strength I	Cl$^-$	SO$_4^{2-}$	NO$_3^-$	HCO$_3^-$	Na$^+$	Ca^{2+}	Mg^{2+}	K$^+$	NH$_4^+$	Al^{3+}	H$^+$
					Activity factors γ							
Lake Härsvatten	0.0005	0.98	0.91	0.98	*0.98*	0.98	0.91	0.91	0.98	0.98	0.81	0.98
Lake Vemmarsjön	0.0002	0.98	0.93	0.98	0.98	0.98	0.93	0.93	0.98	0.98	*0.86*	0.98
Lake Sövdesjön	0.0051	0.92	0.74	0.92	0.93	0.93	0.74	0.75	0.92	0.92	*0.54*	0.93
Deep groundwater	0.0062	0.92	0.72	0.92	0.92	0.92	0.73	0.73	0.92	0.92	*0.51*	0.93
Seawater	0.7017	0.58	0.15	*0.58*	0.63	0.63	0.23	0.26	0.58	*0.58*	*0.08*	*0.75*

natural water in the northern inland of Sweden (Lake Vemmarsjön) has the lowest Ionic strength due to it's oligotrophic nature, lack of anthropogenic influences and distance to the sea. The exception is the relatively high concentration of Al^{3+} ions, likely dissolved from the surrounding bedrock due to the relatively low pH of the water. Lake Härsvatten and Sövdesjön are likely influenced by deposition of oceanic ions and Sövdesjön is surrounded by agricultural land which leads to increased concentrations of ammonium and potassium ions. Finally the deep groundwater has generally high ion concentrations - much of this can be explained by leeching from the bedrock.

When performing calculations relating to equilibrium in natural waters one must make a decision whether to use the simplified calculations using concentrations or use the activity or each species. The difference in result will be dependent on how close to an ideal solution the water is. No natural water is completely ideal and thus the question hinges largely on what is considered an acceptable error. Based on the results the authors suggest that for many applications most surface and groundwaters can be considered ideal, especially for monovalent ions. However care should be taken when dealing with ground waters and surface waters that have several factors that increase their ionic content, especially if dealing with highly charged ions with a small radii such as Al^{3+} who's activity factor will start to diverge from ideal at even relatively low ionic strengths. It should be noted that sea water should never be considered ideal.

File: e1.m

```
% Concentration of ions in \mu eq / L in the order of
% % Cl(-), SO4(2-), NO3(-), HCO3(-), Na(+), Ca(2+), Mg(2+), K(+), NH4(+), Al(3+), H(+)
data = [243 102 30 0 240 29 58 11 3 4 31.6;         % harsvatten
        18 29 2 88 53 78 38 8 2 0 0.794;            % vemmarsjon
        454 503 5 2218 479 2656 346 72 18 0 0.001;  % sovdesjon
        704 500 16 3172 1196 2525 568 97 6 0 0.03;  % deep
        547 56 0 2.3 470 21 110 10 0 0 0];          %sea, unit change to meq / L

% Ion constants.
% för varje jon [z r] i ordningen
% Cl(-), SO4(2-), NO3(-), HCO3(-), Na(+), Ca(2+), Mg(2+), K(+), NH4(+), Al(3+), H(+)
ionConst = [[-1 3]; [-2 4]; [-1 3]; [-1 4]; [1 4]; [2 6]; [2 7]; [1 3]; [1 3]; [3 9]; [1 9]];

% Table that will be populated with the results of the calculations
resultTable = [];

for sample = 1:rows(data)
  for i = 1:length(ionConst)
    % convert concentration given in data to eq/L.
    if sample == rows(data)
      concFactor = 10^-3;
     else
      concFactor = 10^-6;
    endif
    cumulativesum(i) = data(sample,i)*concFactor*abs(ionConst(i, 1));
  end
  I = 0.5 * sum(cumulativesum); % ion strength of each sample
  IMatrix(sample,1) = I; % matrix containing the ion strength of each sample

 for i = 1:length(ionConst)
   resultTable(sample, i) = calcAct(IMatrix(sample,1), ionConst(i, 1), ionConst(i, 2));
 end
end
resultTable = cat(2, IMatrix, resultTable);
csvwrite('output.csv', resultTable);
```

File: calcAct.m

```
% Function that returns the activity of a species given the Ionic Strength I,
% the species charge z and the hydrated ionic radius of the species r.
function activity = calcAct(I, z, r)
  activity = 10^((-0.51 * (z^2) * sqrt(I))/(1 + 0.33 * r * sqrt(I)));
end
```

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Exercise 2

As waves in oceans crash against each other, the water, containing different ions, will get launched up and sprayed into the air as an aerosol. This spray upwards is sometimes powerful enough to launch the aerosol up into the atmosphere where it will merge with clouds and thus raising the concentration of different ions in the clouds. As the clouds then precipitate, the ions will follow and get transported to different areas. This is one way out of several modes of transportation of ions. It is important to analyse precipitation in order to track the origin of it's contained ions, as ions affect the environment and ecosystems with their chemical properties. In this exercise, dissolved ion concentrations of the precipitation in four different european locations has been analysed. The concentration of ions vary from location to location, all locations including the ions Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, NO_3^-, SO_4^{2-}, Cl^-, and H^+.

A charge balance was calculated by subtracting the sum of the negative charges from the sum of the positive charges. The results can be seen in table 3.

Table 3: Charge balance for each of the four locations in $\mu eq L^{-1}$

	Charge Balance
Klosterhede, W Jutland	-4,6
Kootwijk, Holland	-1
Höglwald, Bavaria	-4,2
Ballyhooly, Ireland	16,5

Out of the eight different ions found in the precipitation, Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, and Cl^- are of marine origin. Table 3.3 in the compendium gives a relationship of the concentrations in marine waters relative to the Na^+ concentration in the marine water. Using the assumption that all Na^+ ions in the precipitation are from marine origin, the same relationship can then be applied to analyse what amount of the concentrations of K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^- in the precipitation stem from marine origins.

The concentration factors given by the relationship to Na^+ was put in a row vector in Matlab, and then multiplied with a matrix containing the concentrations of ions in the precipitation. This gave us a matrix (displayed in table 4) with the concentrations of ions in the precipitation with marine origin.

Table 4: Concentrations in $\mu eq L^{-1}$ of ions in precipitation with marine origin.

	Na$^+$	K$^+$	Ca^{2+}	Mg^{2+}	NH4$^+$	H$^+$	NO3$^-$	SO4^{2-}	Cl$^-$
Klosterhede, W Jutland	192	4.03	8.45	46.08	0	0	0	23.04	224.64
Kootwijk, Holland	59	1.24	2.60	14.16	0	0	0	7.08	69.03
Höglwald, Bavaria	11	0.23	0.48	2.64	0	0	0	1.32	12.87
Ballyhooly, Ireland	266	5.59	11.70	63.84	0	0	0	31.92	311.22

In table 5 we can see the percentage of each species in the precipitation with marine origin.

When comparing the concentrations between each of the locations, it is interesting to look at what concentrations differ the most, as they may be explained by the surrounding environment. For instance, the

Table 5: Percentage of ions in precipitation with marine origin.

	Na$^+$	K$^+$	Ca^{2+}	Mg^{2+}	NH4$^+$	H$^+$	NO3$^-$	SO4^{2-}	Cl$^-$
Klosterhede, W Jutland	100%	80.64%	56.32%	96%	0	0	0	25.6%	93.99%
Kootwijk, Holland	100%	61.95%	43.27%	88.5%	0	0	0	9.70%	87.38%
Höglwald, Bavaria	100%	23.1%	20.17%	29.33%	0	0	0	1.76%	99%
Ballyhooly, Ireland	100%	79.8%	65.02%	95.28%	0	0	0	76%	98.18%

Table 6: Concentrations of ions dissolved in precipitation of non-marine origin in μeqL^{-1}

	Na$^+$	K$^+$	Ca^{2+}	Mg(2+)	NH4$^+$	H$^+$	NO3$^-$	SO4^{2-}	Cl$^-$
Klosterhede, W Jutland	0	0.97	6.55	1.92	35	79.4	50	66.96	14.36
Kootwijk, Holland	0	0.76	3.40	1.84	86	20	38	65.92	9.97
Höglwald, Bavaria	0	9.77	23.52	6.36	55	15.8	41	73.68	0.13
Ballyhooly, Ireland	0	1.41	6.30	3.16	28	0.50	11	10.08	5.78

concentrations of Mg^{2+} and Na^+ is highest in Klosterhede and Ballyhooly, this is because the two locations are surrounded by sea in most directions, and the origin of these ions are mostly marine (some come from weathering of minerals). The concentrations of K^+ and Ca^{2+} vary according to the mineral composition in the bedrock for each of the four locations. For example, the highest concentration of Ca^{2+} in Höglwald could be explained by a higher presence of limestone rock when compared to the other locations. The highest concentrations of NH_4^+ and SO_4^{2+}, found in Kootwijk and Höglwald, can be explained by the presence of big cities close to these locations. The ions are constituents in air pollutants, which are prevalent in bigger cities. The concentration of NO_3^- is the highest in Klosterhede, the location which also has the lowest pH-value (highest concentration of H^+). These two concentrations affect eachother, a lower pH-value in soil gives rise to more leeching of nutrients, such as NO_3^-.

File: e2.m

```
% Concentrations of ions at the different locations in [mueq/L]
% Pos: Na(+), K(+), Ca(2+), Mg(2+), NH4(+), H(+)
% Neg: NO3(-), SO4(2-), Cl(-)

% Klosterhede, W Jutland:
Klospos=[192 5 15 48 35 79.4];
Klosneg=[50 90 239];
% Kootwijk, Holland:
Kootpos=[59 2 6 16 86 20.0];
Kootneg=[38 73 79];
%H?glwald, Bavaria:
Hoglpos=[11 10 24 9 55 15.8];
Hoglneg=[41 75 13];
%Ballyhooly, Ireland:
Ballpos=[266 7 18 67 28 0.501];
```

```matlab
Ballneg=[11 42 317];

%%
% Charge balances

CBKlos=sum(Klospos)-sum(Klosneg);
CBKoot=sum(Kootpos)-sum(Kootneg);
CBHogl=sum(Hoglpos)-sum(Hoglneg);
CBBall=sum(Ballpos)-sum(Ballneg);

Results=[CBKlos;CBKoot;CBHogl;CBBall]

%%
% Concentrations of ions  relative to Na+ of marine origin.


Data=[Klospos Klosneg;
 Kootpos Kootneg;
 Hoglpos Hoglneg;
 Ballpos Ballneg;]

% Concentration factors

CFm=[1 0.021 0.044 0.24 0 0 0 0.12 1.17];

Results2=[];

for i=1:4
    Results2(i, :)=Data(i,1).*CFm;
end

Results2
percResults2=Results2./Data

Results3=Data-Results2

%%
csvwrite('concentrationmarine.csv',Results2)
csvwrite('percentagemarine.csv', percResults2)
csvwrite('dataprotons.csv', Data)
csvwrite('concentrationnonmarine.csv',Results3)
```

Exercise 3

When doing concentrations and chemical balances for the carbonate system it is important to analyse what components are involved in the independant chemical reactions and how they react. In this exercise we analyze the carbonate system and the chemical reactions involved (5.-IV-5.IX) with an additional equilibrium reaction X:$H_2CO_3 + OH^- \Leftrightarrow HCO_3^- + H_2O$. The total reaction system, with it's component, is put into a reaction matrix. This reaction matrix shows what components are created and lost on either side of the reaction. The reaction matrix is displayed in table 7.

Tabelle 7: Reaction matrix with involving components

Reaction	Components						
	CO2	H2CO3	HCO3$^-$	CO3^{2-}	H20	H$^+$	OH$^-$
5.VI	-1	1	0	0	-1	0	0
5.VII	0	-1	1	0	0	1	0
5.III	0	0	-1	1	0	1	0
5.IX	0	0	0	0	-1	1	1
X	0	-1	1	0	1	0	-1

Using the rank-function in Matlab calculates the amount of independent chemical reactions in the matrix i.e. the amount of reactions who are not linearly dependent of eachother. Utilizing of the rank-function on this matrix gives us the number 4. We can see that, for reactions 5.VI-5.IX, there are components that do not show up in the other reactions; these reactions are linearly independent from eachother. Reaction X is a combination of all the other reactions, and can therefore be excluded from calculations.

The equilibrium constant for reaction X can be calculated by using the relationships between constants and concentrations given by equations 5-15-5.18 in the compendium. The equation for the equilibrium constant of reaction X can be calculated using these relationships as such:

$$K_X = \frac{(K_{H_2CO_3})}{K_W} \tag{3}$$

The equilibrium constants are dependent on temperature, so K_X will vary accordingly.

K_X can also be analysed using the relationship

$$K_X = \frac{\left[HCO_3^-\right]}{[H_2CO_3] \cdot [OH^-]} \tag{4}$$

$$[H_2CO_3] = K_H \cdot P_{CO_2} \tag{5}$$

and we find an expression of the ratio between $\left[HCO_3^-\right]$ and $[OH^-]$ through rearranging the equations like so:

$$\frac{\left[HCO_3^-\right]}{[OH^-]} = K_X \cdot [H_2CO_3] = \frac{K_{H_2CO_3} \cdot K_H \cdot P_{CO_2}}{K_W} \tag{6}$$

Here we can see that the ratio is dependent on temperature and the partial pressure of CO_2. A conclusion can be drawn here: for a constant temperature, increasing partial pressure of CO_2 pushes the equilibrium to the left, increasing the concentration of HCO_3^-, and vice versa.

Exercise 4,5 and 6

At a constant temperature, the carbonate system in natural waters will be in equilibrium with the partial pressure of carbon dioxide in the atmosphere. The molecules exert a pressure on the water surface, several molecules slam against the surface area, some make it through and get solved in the water as H_2CO_3 . When solved, H_2CO_3 can then deprotonate and contribute the system with concentrations of HCO_3^- and CO_3^{2-}. In a pure H_2O and CO_2 system, meaning no other ions present in the water, the pH will land on a fixed value if the temperature and partial pressure of CO_2 is constant. If other acids or bases are added to the system the pH will change and the species present in the carbonate system will change as shown in figure 1.
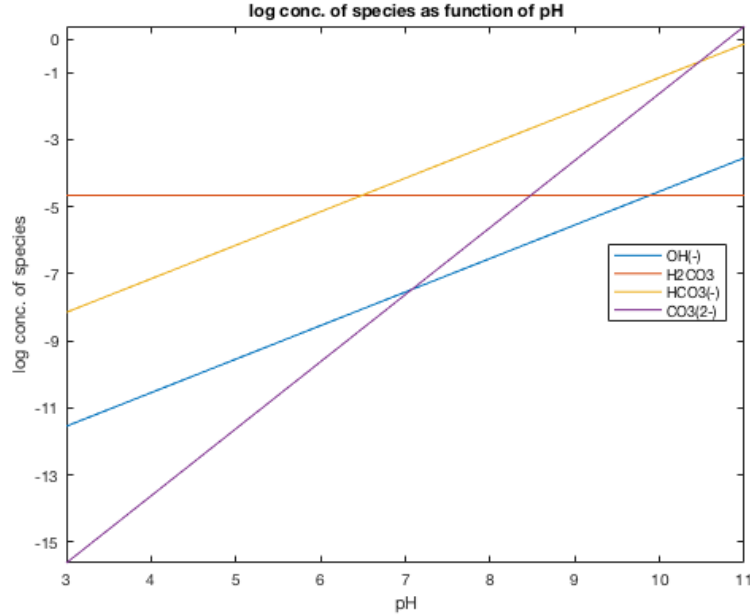

Figure 1: Log concentration of species in a pure carbonate system as a function of pH

The concentration of H_2CO_3 is constant at all pH-values as the concentration is only affected by the partial pressure of carbon dioxide and the temperature dependent solubility. The concentration of OH^- in the carbonate system is coming from the autoprotolysis of water. As the concentrations are logarithmic in the base of ten, two steps on the y-axis equals a difference in concentrations of $\frac{1}{100}$. This means, when comparing two lines, that when they differ with two steps on the y-axis, the concentration shown by the lower line is 1% of the other. Assuming 1% as a negligible percentage, OH^- can be neglected in the interval of pH-values > 9, when compared to concentrations of HCO_3^- and CO_3^{2-}.

Looking at the slope of the HCO_3^- and CO_3^{2-} concentrations, we can see that the concentration of CO_3^{2-} is steeper. The reason for this becomes clear when we analyse the equations for the two concentrations.

$$\left[HCO_3^-\right] = K_{H_2CO_3} \cdot K_H \cdot P_{CO_2} \cdot \frac{1}{[H^+]}$$

$$\left[CO_3^{2-}\right] = K_{HCO_3}K_{H_2CO_3}K_H \cdot P_{CO_2} \cdot \frac{1}{[H^+]^2}$$

The concentration of H^+ is squared when calculating the concentration of CO_3^{2-}, this sets a steeper incline of the curve.
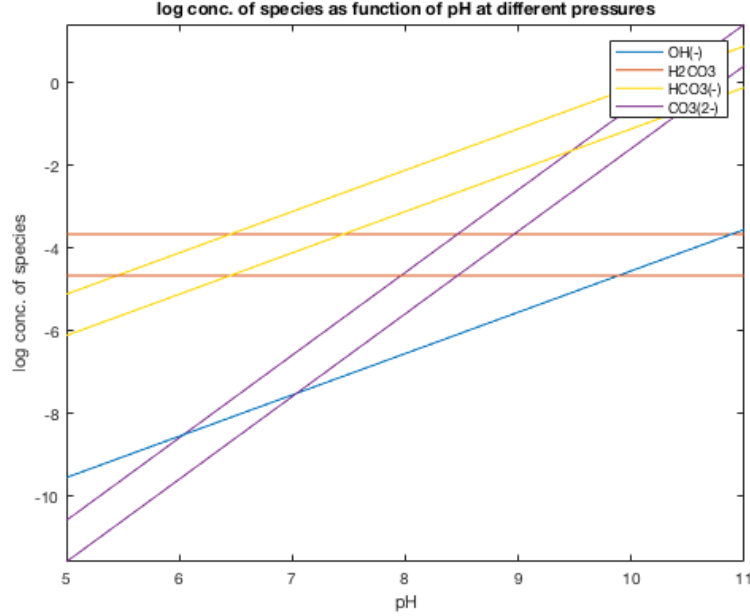

Figure 2: Plot of conc. of species as function of pH at different partial pressures of CO_2. The higher of lines give values from a ten times higher pressure.

In Fig. 2 it can be seen that with a higher partial pressure of CO_2 the concentrations of the different species in the system increase, except for OH^-. The reason for this becomes apparent when looking at the expressions of the concentrations used in the model

$$[H_2CO_3] = K_H \cdot P_{CO_2}$$

$$\left[HCO_3^-\right] = K_{H_2CO_3} \cdot K_H \cdot P_{CO_2} \cdot \frac{1}{[H^+]}$$

$$\left[CO_3^{2-}\right] = K_{HCO_3} \cdot K_{H_2CO_3} \cdot K_H \cdot P_{CO_2} \cdot \frac{1}{[H^+]^2}$$

$$\left[OH^-\right] = K_W \cdot \frac{1}{[H^+]}$$

The exception of the concentration OH^- is due to the fact that the model used for calculating the concentration assumes that it only stems from the autoprotolysis of H_2O. This is not the case in reality, as the increased concentration of H^+ at a higher pressure would in turn shift the equilibrium of the autoprotolysis, decreasing the concentration of OH^-.
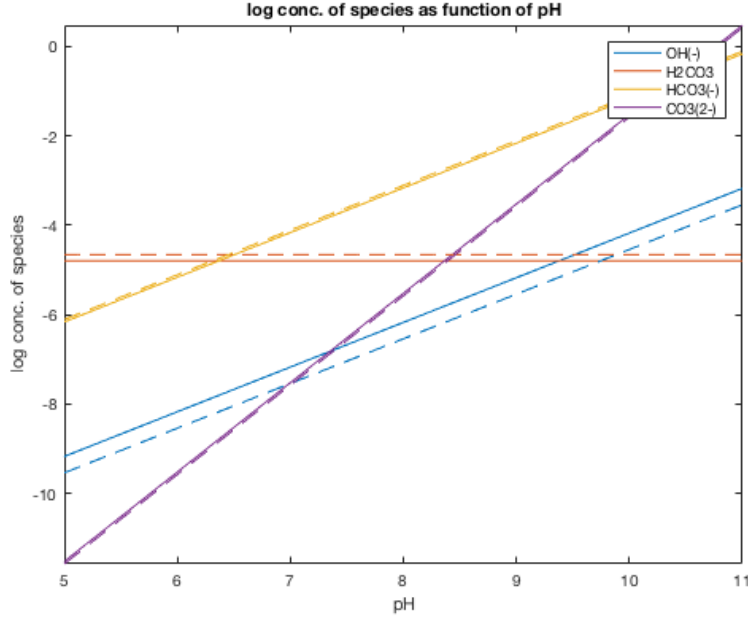
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Figure 3: Plot of conc. of species as a function of pH at different temperatures. Dotted lines are conc. at 10°C, straight lines at 20°C.

In Fig. 3 it can be seen that the different concentrations either increase or decrease during the temperature increase. The solubility of gases in water decreases with increasing temperatures as can be seen by the lower concentration of H_2CO_3. The higher concentration of OH^- is explained by the endothermic character of the autoprotolysis of H_2O; the higher the temperature, more heat energy is supplied to the reaction, pushing equilibrium to higher concentrations of product.

A ratio was then calculated, which shows the relationship between concentrations of $\left[HCO_3^-\right]$ and $\left[CO_3^-\right]$ at 10°C and 20°C. The ratios were calculated as

$$\frac{\left[HCO_3^-\right]_{10C}}{\left[HCO_3^-\right]_{20C}} = \frac{K_{H_2CO_3}^{10C} K_H^{10C}}{K_{H_2CO_3}^{20C} K_H^{20C}} = 1.1378$$

$$\frac{\left[CO_3^{2-}\right]_{10C}}{\left[CO_3^{2-}\right]_{20C}} = \frac{K_{HCO_3}^{10C} \cdot K_{H_2CO_3}^{10C} \cdot K_H^{10C}}{K_{HCO_3}^{20C} \cdot K_{H_2CO_3}^{20C} \cdot K_H^{20C}} = 0.8790$$

We can see that the ratios correlate to the concentrations found in fig. 3. In the case of $\left[HCO_3^-\right]$, the concentration is dependant on the solubility of CO_2 in water and of the dissociation of H_2CO_3. The solubility decreases with increasing temperature, while the dissociation rate increases with rising temperatures. The solubility of H_2CO_3 sets the limit in this case, and the concentration decreases with the 10°C increase. In the case of $\left[CO_3^{2-}\right]$, there is another variable added that affects the concentration - the dissociation rate of HCO_3^-. This dissociation rate increases with increasing temperature, enough so that a 10°C increase will create a higher concentration of CO_3^{2-}.

File: e4plot.m

```
%% log conc. of species as function of pH
figure(1);
fplot(@conc4_ph, [3 11]);
title('log conc. of species as function of pH');
legend('OH(-)','H2CO3','HCO3(-)','CO3(2-)');
xlabel('pH');
ylabel('log conc. of species');
```

File: conc4_ph.m

```
function y=conc4_ph(ph)

%constants and parameters @ 10?C
kh2co3=10^-6.487;
khco3=10^-10.471;
kw=10^-14.540;
kh=10^-1.260;
pco2=4e-4;

h=10^-ph;

y(1)=log10(kw/h); % OH
y(2)=log10(kh*pco2); % h2co3
y(3)=log10(kh*pco2*kh2co3/h); % hco3
y(4)=log10(kh*pco2*kh2co3*khco3/h^2); % co3
end
```

File: e51plot.m

```
% plot of a 10-fold increase in CO2-pressure compared to normal pressure
fplot(@conc5P_ph, [5 11])
title('log conc. of species as function of pH')
legend('OH(-)','H2CO3','HCO3(-)','CO3(2-)')
xlabel('pH')
ylabel('log conc. of species')
hold on
fplot(@conc5_ph, [5 11])
legend('OH(-)','H2CO3','HCO3(-)','CO3(2-)')
hold off
```

File: conc5P_ph.m

```
function y=conc5P_ph(ph)

%constants and parameters @ T?C
T=283.15
kh=10^(-12.59+(2198/T)+0.0126*T);
kh2co3=10^(14.82-(3401/T)-0.0327*T);
khco3=10^(6.53-(2906/T)-0.0238*T);
kw=10^(6.09-(4471/T)-0.0171*T);
pco2=4e-3;

h=10^-ph;
```

```
y(1)=log10(kw/h);
y(2)=log10(kh*pco2);
y(3)=log10(kh*pco2*kh2co3/h);
y(4)=log10(kh*pco2*kh2co3*khco3/h^2);
end
```

File: conc5_ph.m

```
function y=conc5_ph(ph)

%constants and parameters @ T?C
T=283.15
kh=10^(-12.59+(2198/T)+0.0126*T);
kh2co3=10^(14.82-(3401/T)-0.0327*T);
khco3=10^(6.53-(2906/T)-0.0238*T);
kw=10^(6.09-(4471/T)-0.0171*T);
pco2=4e-4;

h=10^-ph;

y(1)=log10(kw/h);
y(2)=log10(kh*pco2);
y(3)=log10(kh*pco2*kh2co3/h);
y(4)=log10(kh*pco2*kh2co3*khco3/h^2);
end
```

File: e52plot.m

```
% plot of a 10?C increase in temperature compared to normal temperature
fplot(@conc5T_ph, [5 11])
title('log conc. of species as function of pH')
legend('OH(-)','H2CO3','HCO3(-)','CO3(2-)')
xlabel('pH')
ylabel('log conc. of species')
hold on
fplot(@conc5_ph, [5 11])
legend('OH(-)','H2CO3','HCO3(-)','CO3(2-)')
hold off
```

File: conc5T_ph

```
function y=conc5T_ph(ph)

%constants and parameters @ T?C
T=293.15
kh=10^(-12.59+(2198/T)+0.0126*T);
kh2co3=10^(14.82-(3401/T)-0.0327*T);
khco3=10^(6.53-(2906/T)-0.0238*T);
kw=10^(6.09-(4471/T)-0.0171*T);
pco2=4e-4;

h=10^-ph;
```

```
y(1)=log10(kw/h);
y(2)=log10(kh*pco2);
y(3)=log10(kh*pco2*kh2co3/h);
y(4)=log10(kh*pco2*kh2co3*khco3/h^2);
end
```
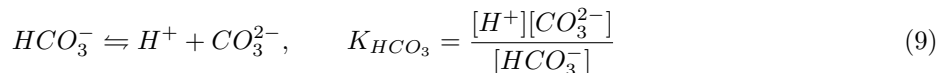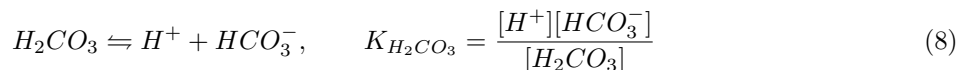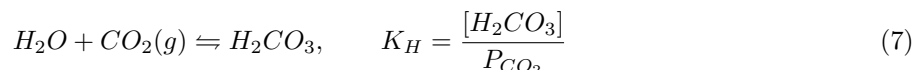
File: e6.m

```
T1=283.15
kh1=10^(-12.59+(2198/T1)+0.0126*T1);
kh2co31=10^(14.82-(3401/T1)-0.0327*T1);
khco31=10^(6.53-(2906/T1)-0.0238*T1);
kw1=10^(6.09-(4471/T1)-0.0171*T1);
%%
T2=293.15
kh2=10^(-12.59+(2198/T2)+0.0126*T2);
kh2co32=10^(14.82-(3401/T2)-0.0327*T2);
khco32=10^(6.53-(2906/T2)-0.0238*T2);
kw2=10^(6.09-(4471/T2)-0.0171*T2);
%%
HCO310=kh2co31*kh1;
HCO320=kh2co32*kh2;
CO310=khco31*kh2co31*kh1;
CO320=khco32*kh2co32*kh2;
%%
HCO310/HCO320
CO310/CO320
```

Exercise 7

Natural waters, especially the oceans contain a massive amount of dissolved inorganic carbon through the carbonate system, a system of equilibrium reactions as can be seen in Equations 7 - 10. As can be seen from Equation 7 this system is in communication with atmospheric CO_2. As anthropogenic activity interacts with environmental processes to increase the CO_2 concentration in the atmosphere a thorough understanding of the carbonate system and how it reacts to changes in the partial pressure of CO_2 is vital to climate modelling. Further the partial pressure of CO_2 influences the acidity of natural waters. This in turn can have large consequences for chemical and biological processes. This exercise aims to determine the pH of a natural, ideal water system at approximately current partial pressures of CO_2 (400ppmv).

The carbonate system is characterised by the following four equilibrium reactions:

$$H_2O + CO_2(g) \leftrightharpoons H_2CO_3, \qquad K_H = \frac{[H_2CO_3]}{P_{CO_2}} \tag{7}$$

$$H_2CO_3 \leftrightharpoons H^+ + HCO_3^-, \qquad K_{H_2CO_3} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \tag{8}$$

$$HCO_3^- \leftrightharpoons H^+ + CO_3^{2-}, \qquad K_{HCO_3} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \tag{9}$$

$$H_2O \leftrightharpoons H^+ + OH^-, \qquad K_W = [H^+][OH^-] \tag{10}$$

To be able to solve this system of equations for a given partial pressure of CO_2 requires an additional equation, namely the charge balance:

$$[H^+] = [OH^-] + [HCO_3^-] + 2 \cdot [CO_3^{2-}] \tag{11}$$

These five equations can then be combined, simplified and written in the form of a polynomial equation:

$$0 = [H^+]^3 - [H^+](K_W + K_{H_2CO_3}K_H P_{CO_2}) - 2K_{H_2CO_3}K_{HCO_3}K_H P_{CO_2} \tag{12}$$

At a given temperature and for an ideal system K_H, K_W, $K_{H_2CO_3}$ and $K_{HCO_3^-}$ are well established constants. For the following calculations values for a temperature of 10 °C , namely $10^{-1.260}$, $10^{-14.540}$, $10^{-6.482}$, $10^{-10.471}$ respectively, as taken from the workbook Appendix 3 (page 110).

The pH of the water at a partial pressure of CO_2 of $P_{CO_2} = 400 \cdot 10^{-6}$ atm was calculated using the `ph_cons.m` and `ph.m` as can be seen below. The only difference is that `ph_cons.m` specifies P_{CO_2} as a constant while `ph.m` accepts it as an argument. Both function use matlabs built in `roots()` function that solves polynomial equations given it's coefficients, in this case the coefficients can be read from Equation 12. The largest non-imaginary root was selected.

These calculations yielded a pH of $5.5699 \approx 5.57$.

This result appears to be congruent with expectations of slightly acidic conditions and in within the range of the measured pHes in several natural Swedish waters as presented in Table 3.2 of the compendium (page 28).

It should be noted however that in natural waters other ions are likely to be present in the water affecting the waters acid neutralizing capacity and hence the pH. The model developed in this exercise can be expanded upon to take this into account, as likely will be explored in future exercises.

File: ph_cons.m

```
function ph=ph_cons
% Constants at 10 degC
  kw = 10^-(14.540);
  kh2co3 = 10^-(6.482);
  khco3 = 10^-(10.471);
  kh = 10^-(1.260);
  pco2 = 400 * 10^(-6); % atm

  a(1) = 1 ; a(2) = 0 ; a(3) = -(kw + kh2co3 * kh * pco2) ; a(4) = 2 * kh2co3 * khco3 * kh * pco2;

  X = roots([a]);
  x = max(X(find(imag(X) == 0))); % conc. h+
  ph = -log10(x);
end
```

File: ph.m

```
function phres=ph(p)
  % Constants at 10 degC
  kw = 10^(-14.540);
  kh2co3 = 10^(-6.482);
  khco3 = 10^(-10.471);
  kh = 10^(-1.260);
  pco2 = p; % atm

  a(1) = 1 ; a(2) = 0 ; a(3) = -(kw + kh2co3 * kh * p) ; a(4) = -2 * kh2co3 * khco3 * kh * p;

  X = roots([a]);
  x = max(X(find(imag(X) == 0))); % conc. h+
  phres = -log10(x);
end
```

Exercise 8

Similarly to Exercise 7, Exercise 8 investigates the affect of the partial pressure of CO_2 on the pH of an ideal water system. A more thorough introduction to why this topic is worthy of study can be seen in the introduction to Exercise 7. The aim of this exercise is to investigate how the pH of an ideal water system changes as a function of of P_{CO_2}.

The calculations utilise the same method as outlined in Exercise 7 (Equation 12) and the ph function outlined in `ph.m`. However this exercise utilises the matlab function `fplot` to plot the result of the ph function (the water pH) across a range of different input values (P_{CO_2}).

The result of plotting the pH versus the partial pressure of CO_2 across a range of P_{CO_2} from $4 \cdot 10^{-4}$ to $3 \cdot 10^{-2}$ atm was can be seen in Figure 4. The exact matlab code that was used to generate this plot can be seen under `e8.m` below.
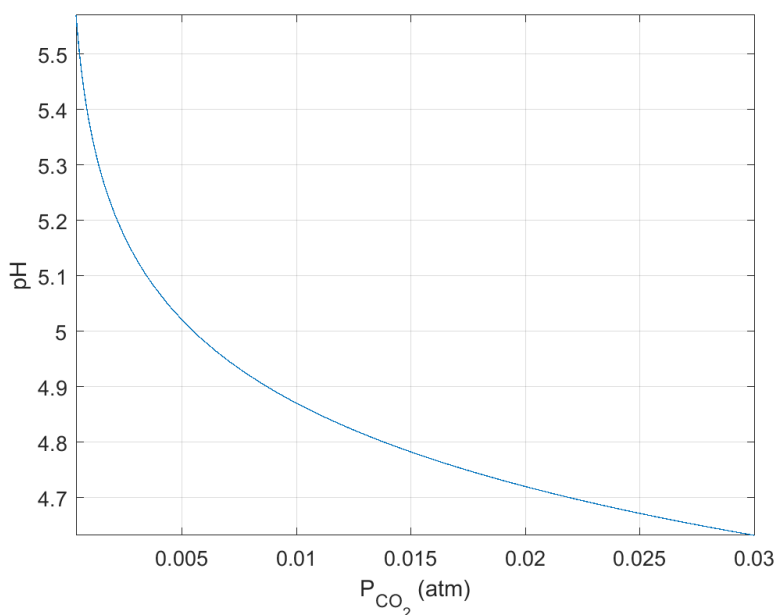

Figure 4: Plot of calculated pH versus P_{CO_2} for $4 \cdot 10^{-4} < P_{CO_2} < 3 \cdot 10^{-2}$ (atm).

This plot can be compared with Figure 5 that shows measured values for pH vs P_{CO_2} across a similar range of P_{CO_2} (10^{-3} to $5 \cdot 10^{-2}$ atm) and calculated trend line. The data is collected from Labaratory exercise 1 performed by the authors.
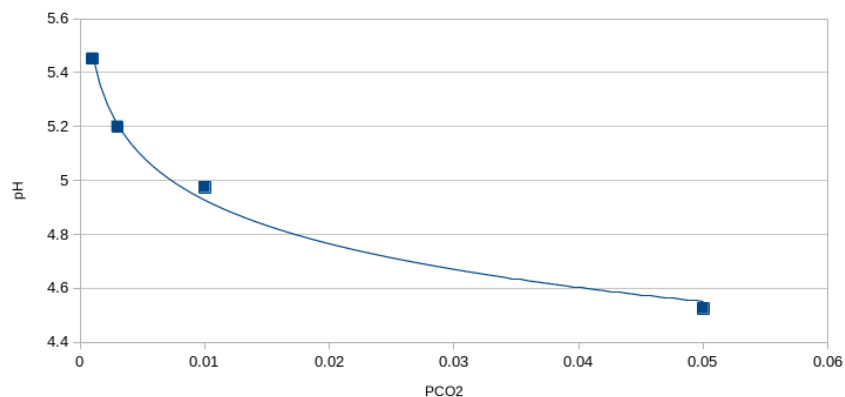
Figure 5: Plot of measured pH versus P_{CO_2} and calculated trend-line for $10^{-3} < P_{CO_2} < 5 \cdot 10^{-2}$ (atm).

Table 8 compares the theoretical and measured pHs at different partial pressures of CO_2. As can be seen from the differences there is a good fit between theoretical and experimental data. This indicates that the model is a good fit to reality for ideal waters.

Table 8: Table comparing the theoretical and measured pH at varying P_{CO_2}. The theoretical values are calculated using the *ph.m* function and measured values are mean sampled values from laboratory exercise 1. The difference is calculated as Theoretical-Measured.

P_{CO_2}	Theoretical pH	Experimental pH	Difference
10^{-3}	5.37	5.36	0.01
$3 \cdot 10^{-3}$	5.13	5.16	-0.03
10^{-2}	4.87	4.94	-0.07
$5 \cdot 10^{-2}$	4.52	4.50	0.02

File: e8.m

```
fplot(@ph, [4*10^(-4) 3*10^(-2)])
xlabel('P_{CO_2} (atm)')
ylabel('pH')
grid on
```

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Exercise 9

In natural waters, such as lakes, the chemical processes mainly discussed in these exercises interact with the biotic processes facilitated by the water biota. These biotic processes will affect chemical outcomes such as water pH and thus may be important when considering the effect of changing atmospheric CO2 levels on natural waters. This exercise aims to discuss, with background in the authors previous knowledge of aquatic ecology, two such chemical/biotic interactions, namely the diurnal pH variation in lake surface water and decrease in surface pH in lakes covered with ice.

Diurnal effects on pH in lake systems are likely caused by respiration and photosynthesis of plankton and algae. During the night respiration is dominant, leading to localised increases in the concentration of inorganic carbon. This, due to the carbonate system discussed in previous exercises leads to a decrease in pH. Conversely during the day photosynthesis decreases the concentration of inorganic carbon, similarly increasing the pH. This effect is contingent on a few assumptions; one assumption is that the time for H_2CO_3 to reach equilibrium with CO_2 in the atmosphere (Equation 7) is not to short. If this time is to short the pH will be constant. It also assumes a significant amount of biotic life and the effect would therefore be expected to be greater in eutrophic lakes without pollutants toxic to aquatic life and less to non-existent in oligotrophic lakes or lakes containing pollutants toxic to aquatic life. Diurnal pH variation also assumes water layer stratification. In a situation with very high water mixing would tend to dilute the effects of biology on pH to the point of not being measurable. As such it would be expected that the effect would be most observable during the summer (in climates with significant seasonal variation) when the combination of high incident solar radiation (leading to increased photosynthesis) and stable water strata and less in autumn and spring (due to water column mixing) and winter (due to decreased solar radiation).

Drop in pH below lake ice is likely caused by respiration of plankton and algae. Though biotic activity can be expected to decrease in times of decreased temperature it will not cease completely. Biotic respiration will cause a localised increase in inorganic carbon. The ice cover will prevent exchange with the atmosphere and prevent the H_2CO_3 - CO_2 equilibrium from stabilising the pH and the typical stably stratified water column will allow localised extremes. Further seasonal decrease in solar radiation combined with the scattering, reflecting and shading qualities of the ice will lead to minimal photosynthesis - the other biotic property that could be expected to increase the pH.

In summary biotic activity can lead to measurable differences in surface water pH in lakes though the effects of respiration and photosynthesis on the concentration of inorganic carbon. It is to be expected that the pH will fall during the night and increase during the day. However the size of the effect will be largely dependent on other environmental factors such as water nutrient content, water layer stratification/stability, incident solar radiation and the presence of pollutants toxic to aquatic life. Drop in pH in lake surface water covered with ice is likewise caused by biotic respiration coupled with the prevention of equalisation by the H_2CO_3 - CO_2 equilibrium system.

Exercise 10

The importance of the carbonate system can be read about in the introduction to Exercise 7. As the P_{CO_2} increases due to anthropogenic activity it is important to be able to predict the affect of future increases on the pH of natural waters. This exercise aims to graphically determine the $[H^+]$ and pH in a natural water system in equilibrium with atmospheric carbon dioxide using a graphical method.

To achieve this, the carbonate system equilibrium reactions (Equations 7 - 11) are first substituted in to the charge balance:

$$0 = [H^+] - [OH^-] - [HCO_3^-] - 2 \cdot [CO_3^{2-}] \tag{13}$$

$$0 = [H^+] - \frac{K_W}{[H^+]} - \frac{K_{H_2CO_3}K_H P_{CO_2}}{[H^+]} - 2 \cdot \frac{K_{H_2CO_3}K_{HCO_3}K_H P_{CO_2}}{[H^+]^2} \tag{14}$$

At a given temperature and for an ideal system K_H, K_W, $K_{H_2CO_3}$ and $K_{HCO_3^-}$ are well established constants. For the following calculations values for a temperature of 10 °C , namely $10^{-1.260}, 10^{-14.540}, 10^{-6.482}, 10^{-10.471}$ respectively, as taken from the workbook Appendix 3 (page 110).

Equation 14 was used to construct the matlab function e10func.m (see below) which accepts $[H^+]$ as an argument, and for a $P_{CO_2} = 400 \cdot 10^{-6}$ atm solves

$$y = [H^+] - \frac{K_W}{[H^+]} - \frac{K_{H_2CO_3}K_H P_{CO_2}}{[H^+]} - 2 \cdot \frac{K_{H_2CO_3}K_{HCO_3}K_H P_{CO_2}}{[H^+]^2} \tag{15}$$

where y is the deviation from charge balance.

The matlab file e10.m (see below) was used to plot the deviation from charge balance for $[H^+]$ in the range of $10^{-6.1}$ to $10^{-4.9}$ (Figure 6). This range was chosen because it corresponds to a pH range of 6.1 - 4.9 and the results of Exercise 7 suggests that charge balance will occur at a pH within this range, namely 5.57. As at equilibrium it is known that the charge balance equals 0, Figure 6 can be used to determine the $[H^+]$ at equilibrium.
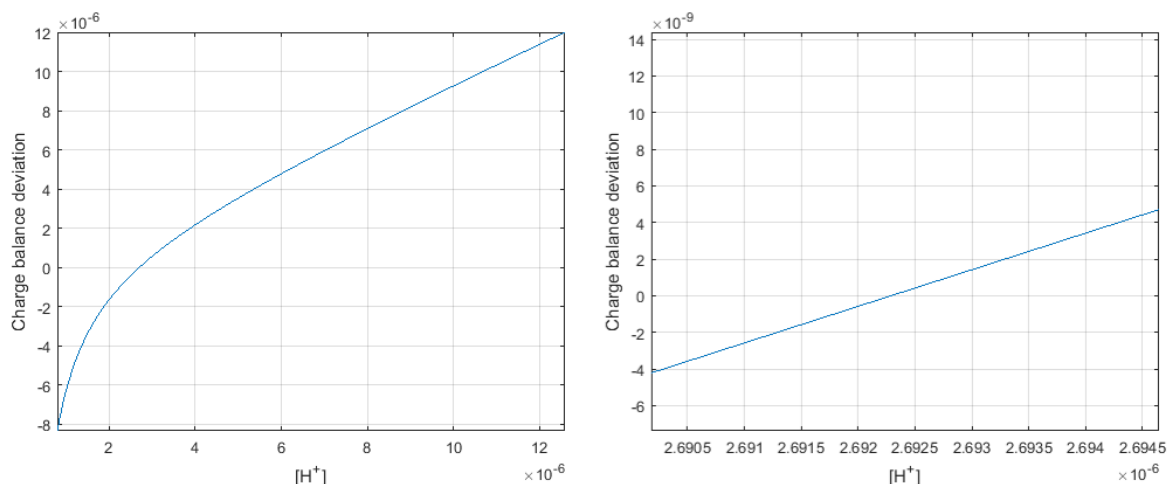
Figure 6: Figure showing the deviation from charge balance versus versus $[H^+]$ for the range of $[H^+]$ from $10^{-6.1}$ to $10^{-4.9}$ at a P_{CO_2} of $400 \cdot 10^{-6}$atm (left) and an enlargement of the section of this figure around the $[H^+]$ when the charge balance deviation equals 0.

As can be read from Figure 6, the $[H^+]$ at equilibrium is approximately $2.6923 \cdot 10^{-6}$ mol/L. This corresponds to a pH of $-\log\left(2.6923 \cdot 10^{-6}\right) = 5.57$.

This result is equal to the result from exercise 7, which is to be expected as it is solving the same equilibrium using the same basic equations and constants, albeit graphically instead of analytically. This shows that the equilibrium pH of an idealised water system can be solved by multiple means.

File: e10func.m

```
function y=e10func(hc)
  kw = 10^(-14.540);
  kh2co3 = 10^(-6.482);
  khco3 = 10^(-10.471);
  kh = 10^(-1.260);
  pco2 = 400*10^-6; % atm
  ph = -log10(hc);

  y = hc - (kw/hc) - ((kh2co3*kh*pco2)/hc) - 2.*((kh2co3*khco3*kh*pco2)/hc^2);
end
```

File: e10.m

```
fplot(@e10func, [10^-6.1 10^-4.9])
xlabel('[H^+]')
ylabel('Charge balance deviation')
grid on
```

Exercise 11

The importance of the carbonate system has been explored in earlier exercises as well as solving the system to determine the pH at different values of P_{CO_2}. The mathematical models that have been analysed so far can however be simplified in order to make calculations easier. The aim of this exercise is to examine one possible simplification and compare it to the models used in previous exercises.

It has been established in earlier exercises that at atmospheric values of P_{CO_2}, the pH of an ideal water system in equilibrium will be 5.57 (at 10°C) and will decrease as the P_{CO_2} increases. The first assumption that will be made in the simplification is then that only pH < 6 are considered. At pH < 6 it can be seen from Figure 1 that $[OH^-] <\;\; [H^+]$ and $\left[HCO_3^-\right]$ with an order of magnitude greater than 3, that $\left[CO_3^{2-}\right] < [H^+]$ and $\left[HCO_3^-\right]$ with an order of magnitude greater than 4. It can be seen from Figures 2 and 3 that these proportions hold true also as the P_{CO_2} and temperature increases. Thus the second assumption made in the simplification is that $[OH^-]$ and $\left[CO_3^{2-}\right]$ can be ignored.

With these two assumptions the charge balance is reduced to

$$[H^+] = [HCO_3^-] \tag{16}$$

Substituting in Equation 8 and 7 and simplifying yields the simplified model for $[H^+]$ as

$$[H^+] = \sqrt{K_{H_2CO_3} \cdot K_H \cdot P_{CO_2}} \tag{17}$$
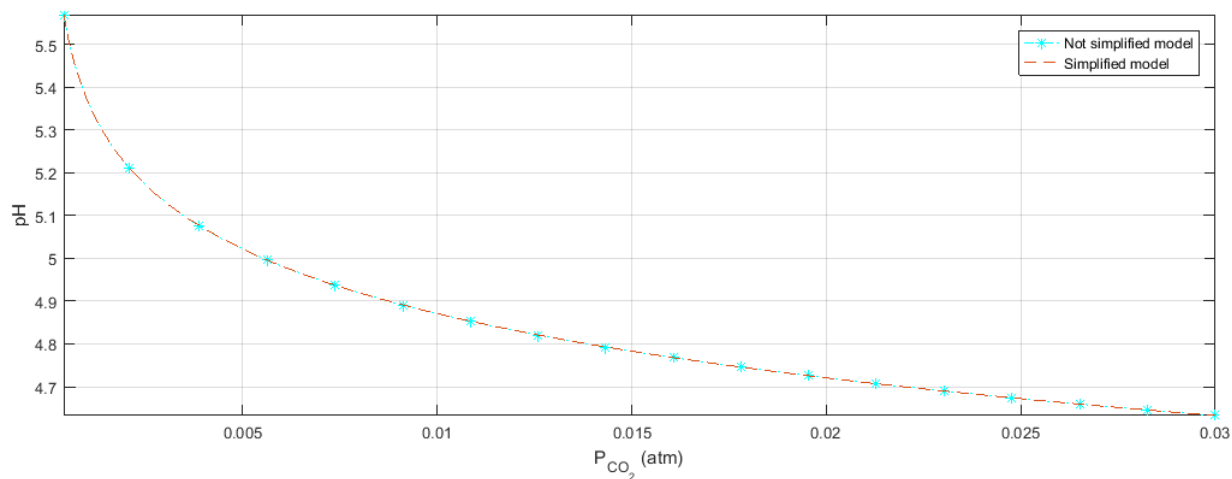

Figure 7: Figure showing the pH of an idealised water system as a function of P_{CO_2} in the range of

Figure 7 was generated using matlab and the `phsim.m` function (see below) the `ph.m` function (see under Exercise 7 above) and the script `e11.m` (see below). The figure shows how pH varies as a function of the partial pressure CO_2 in the range $4 \cdot 10^{-4}$ to $3 \cdot 10^{-2}$ atm using both the simplified and not simplified model. The calculated pH is visually indistinguishable between the two models. This also holds up at relatively large magnifications and holds true across the range of partial pressures. This indicates that the assumptions made in the simplification are valid. Specifically assumption one, that only pHes < 6 are considered is valid

given the starting pH of 5.75 (known from previous exercises) and the decrease of pH with increased P_{CO_2}. Further the assumption that $[OH^-]$ and $\left[CO_3^{2-}\right]$ can be ignored is supported by the results of Exercises 4, 5 and 6 (see Figures 1-3) as well as the high degree of agreement between the pH calculated with the simplified and not simplified models.

File: phsim.m

```
function ph=phsim(p)
  % Constants at 10 degC
  kh2co3 = 10^(-6.482);
  kh = 10^(-1.260);
  pco2 = p; % atm

  h = sqrt(pco2*kh*kh2co3);
  ph = -log10(h);
end
```

File: e11.m

```
fplot(@ph, [4*10^(-4) 3*10^(-2)], '-.*c')
xlabel('P_{CO_2} (atm)')
ylabel('pH')
grid on
hold on

fplot(@phsim, [4*10^(-4) 3*10^(-2)], '--')

legend('Not simplified model', 'Simplified model')
```

Exercise 12

The mole fraction diagram is a useful tool when wanting to know the percentage of a certain chemical species in a system at a certain ... . In this exercise a mole fraction diagram was created for the carbonate system, where the fractions of H_2CO_3, HCO_3^-, and CO_3^{2-} can be derived at a certain pH-value. The mole fraction diagram can be seen in fig. 8.
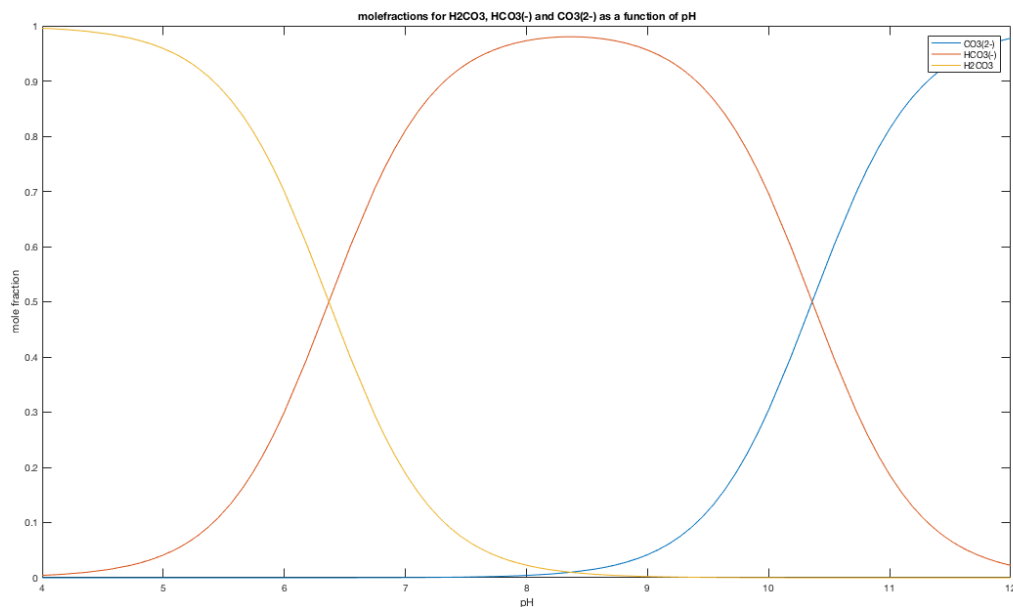

Figure 8: Mole fraction diagram of the carbonate system.

The mole fraction diagram was calculated using the expressions found in the text book. The temperature for the equilibrium constants was set to be 20°C. The three intersections 1, 2 and 3, can be seen from left to right when looking at the diagram. Intersection 2 coincides with a maximum mole fraction of HCO_3^-. The pH value at the different intersections can be calculated by equating the expressions for each mole fraction as such

$$x_{HCO_3^-} = x_{H_2CO_3} \Leftrightarrow \frac{[H^+]_1}{\alpha \cdot K_{HCO_3}} = \frac{[H^+]_1^2}{\alpha \cdot K_{H_2CO_3} \cdot K_{HCO_3}} \Leftrightarrow [H^+]_1 = K_{H_2CO_3} = 4.2897 \cdot 10^{-7}$$

$$x_{H_2CO_3} = x_{HCO_3} \Leftrightarrow \frac{[H^+]_2^2}{\alpha \cdot K_{H_2CO_3} \cdot K_{HCO_3}} = \frac{1}{\alpha} \Leftrightarrow [H^+]_2 = \sqrt{K_{H_2CO_3} \cdot K_{HCO_3}} = 4.3273 \cdot 10^{-9}$$

$$x_{HCO_3^-} = x_{CO_3^{2-}} \Leftrightarrow \frac{[H^+]_3}{\alpha \cdot K_{HCO_3}} = \frac{1}{\alpha} \Leftrightarrow [H^+]_3 = K_{HCO_3} = 4.3653 \cdot 10^{-11}$$

$$pH = -\log\left([H^+]\right)$$
$$pH_1 = 6.3676$$

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$$pH_2 = 8.3638$$

$$pH_3 = 10.3600$$

Intersections 1 and 3 occur at when $[H^+]$ equals the chemical equilibrium constant for the two reactions. By definition of the equilibrium constant, this happens when the concentrations other than $[H^+]$ are equal.

$$[H^+]_1 = K_{H_2CO_3} = \frac{[H^+]_1 \cdot [HCO_3^-]}{[H_2CO_3]} \Leftrightarrow [HCO_3^-] = [H_2CO_3]$$

$$[H^+]_3 = K_{HCO_3} = \frac{[H^+]_3 \cdot [CO_3^{2-}]}{[HCO_3^-]} \Leftrightarrow [HCO_3^-] = [CO_3^{2-}]$$

Intersection 2 and the maximum of $x_{HCO_3^-}$ occur due to the fact that HCO_3^- is being produced and dissociated at the same rate, depleting H_2CO_3 and creating CO_3^{2-}.

$$[H^+]_2^2 = K_{H_2CO_3} \cdot K_{HCO_3} = [H^+]_2^2 \cdot \frac{[HCO_3^-] \cdot [CO_3^{2-}]}{[H_2CO_3] \cdot [HCO_3^-]} \Leftrightarrow [H_2CO_3] = [CO_3^{2-}]$$

File: exercise12.m

```
%% plot of mole fractions as a function of pH
fplot(@molefrac, [4 12]);
title('molefractions for H2CO3, HCO3(-) and CO3(2-) as a function of pH');
legend('CO3(2-)','HCO3(-)','H2CO3');
xlabel('pH');
ylabel('mole fraction');
```

File: molefrac.m

```
function y=molefrac(pH)
%% constants at T
T=293.15
kh=10^(-12.59+(2198./T)+0.0126.*T);
kh2co3=10^(14.82-(3401./T)-0.0327.*T);
khco3=10^(6.53-(2906./T)-0.0238.*T);
kw=10^(6.09-(4471./T)+0.0171.*T);
%%
h=10^-pH;
a=(1+(h/khco3)+(h^2/(kh2co3*khco3)));
%% molefractions xco3,xhco3,xh2co3
y(1)=(1/a)
y(2)=(h/(a*khco3))
y(3)=(h^2/(a*kh2co3*khco3))
end
```