Acid/base calculations and graphical representations

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September 5, 2016

Contents

1 Acids and bases

1.1 Brönsted acids and Brönsted bases

The definition of acids and bases according to Brönsted can be considered as the standard model for acids and bases in aqueous solutions. However other models (Arrhenius acids and bases) as well as newer more general models (Lewis acids and bases) are used, depending on the context. The traditional definition of a Brönsted acid can be formulated as some specie that releases hydrogen ions to the surrounding as shown with the formula below. Brönsted acid are said to be hydrogen ion donors. The reactions take place in an aqueous environment, thus we add the "(aq)" aggregation state symbol after each specie.

$$HA(aq) \rightleftarrows A^-(aq) + H^+(aq) \tag{1}$$

If one would like to emphasize that the hydrogen ion is not existing as a free specie but rather as bound to a water molecule, the formation of an oxonium ion could be emphasized as shown below.

$$HA(aq) + H_2O(l) \rightleftarrows A^-(aq) + H_3O^+(aq) \tag{2}$$

Similarly a Brönsted base can be defined as a specie that accepts hydrogen ions from the surrounding. Brönsted bases are said to be hydrogen ion acceptors. The specie $A^-(aq)$ above is known as the "corresponding base" to the acid $HA(aq)$. The reaction of a Brönsted base with the solvent water, acting as hydrogen ion donor can be described with the reaction formula below.

$$A^-(aq) + H_2O(l) \rightleftarrows HA(aq) + OH^-(aq) \tag{3}$$

1.2 Arrhenius acids and Arrhenius bases

Another (older) model for acids and bases are due to Svante Arrhenius. He defined acids as compound that released hydrogen ions (or oxonium ions) when mixed with water and bases as substances that released hydroxide ions when mixed with water. The Arrhenius acid concept is quite similar to the Brönsted acid concept, however some conceptual differences occur with the bases. A base according to Arrhenius produces an hydroxide ion while a hydrogen ion is consumed by a Brönsted base.

$$Acid(aq) + H_2O(l) \rightleftarrows (\text{conjugate Base})^-(aq) + H_3O^+(aq) \tag{4}$$

$$Base(aq) + H_2O(l) \rightleftarrows (\text{conjugate Acid})^+(aq) + OH^-(aq) \tag{5}$$

1.3 Lewis acids and bases

Still another acid base model, more general than the previous model, focus on the electron pair ans how it is transferred between species.

A Lewis acid is defined as some specie accepting electron pairs, *e.g.* H^+, Cu^{2+}, BH_3, etc.

A Lewis base is a specie that donates an electron pairs, *e.g.* OH^-, SO_4^{2-}, NH_3 etc.

2 Strong or weak acid or bases, equilibrium constants

The equilibrium constant is defined as the product of activities of the right hand side species divided by the product of activities of the left hand side species. The activity of "pure" liquids are set to unity and the activities of solutes are approximated by the numeric value of the concentrations with units mol/dm^3.

2.1 Acids - acidity constant

The equilibrium constant for the reaction of an acid with the solvent water is termed the acidity constant, K_a for that very acid. Large values of the acidity constant indicates "strong" acids and small values of the acidity constant indicates "weak" acids. An arbitrary value for acidity constants to designate strong or weak acids could be chosen as 1.

$$HA(aq) + H_2O(l) \rightleftarrows A^-(aq) + H_3O^+(aq)$$

$$K_a = \frac{\{A^-(aq)\}\{H_3O^+(aq)\}}{\{HA(aq)\}\{H_2O(l)\}} \approx \frac{[A^-(aq)][H_3O^+(aq)]}{[HA(aq)]} \tag{6}$$

2.2 Bases - base constant

The base constant for a Brönsted base is defined correspondingly as the equilibrium constant for the reaction of a base with water.

$$A^-(aq) + H_2O(l) \rightleftarrows HA(aq) + OH^-(aq)$$

$$K_b = \frac{\{HA(aq)\}\{OH^-(aq)\}}{\{A^-(aq)\}\{H_2O(l)\}} \approx \frac{[HA(aq)][OH^-(aq)]}{[A^-(aq)]} \tag{7}$$

2.3 Corresponding acids and bases and the solvent water

A "strong" acid is an acid with a large acidity constant and must necessarily have a "weak" corresponding base, associated with a small base constant. The "stronger" the acid the i.e. the larger the acidity constant of the acid, the "weaker" the base, i.e the smaller the base constant, and vice versa. Some acid and its corresponding base are related to the acid-base properties of water, as shown below.

$$HA(aq) + H_2O(l) \rightleftarrows A^-(aq) + H_3O^+(aq)$$

$$A^-(aq) + H_2O(l) \rightleftarrows HA(aq) + OH^-(aq)$$

Adding these two reactions we get:

$$HA(aq) + H_2O(l) + A^-(aq) + H_2O(l) \rightleftarrows A^-(aq) + H_3O^+(aq) + HA(aq) + OH^-(aq)$$

Species occurring in both left and right hand side cancel. What's left, is the auto-dissociation (auto-protolysis) of water.

$$2H_2O(l) \rightleftarrows H_3O^+(aq) + OH^-(aq)$$

Adding reactions corresponds to multiplying equilibrium constants. In this case when multiplying the expressions for the acidity constant of *any* Brönsted acid and the base constant for the corresponding Brönsted base, we get the autoprotolysis constant of water.

$$K_a \cdot K_b = \frac{\{H_3O^+(aq)\}\{OH^-(aq)\}}{\{H_2O(l)\}^2} = \{H_3O^+(aq)\}\{OH^-(aq)\} = K_w \tag{8}$$

The corresponding logarithmic relation is shown below.

$$pK_a + pK_b = pK_w \tag{9}$$

Table 1: List of acidity constants and base constants. The acids and bases of each line form corresponding acid base pairs. The values of the acid or base constants corresponds to the thermodynamic equilibrium constants defined with activities of the species. Note that: $pK_a(HA)$ + $pK_b(A^-) = pK_w = 14$ at T = 298K.

Acid	K_a	pK_a	Base	K_b	pK_b
HCl	10^3	-3	Cl^-	10^{-17}	17
H_2SO_4	10^2	-2	HSO_4^-	10^{-16}	16
H_3O^+	1	0	H_2O	10^{-14}	14
HSO_4^-	10^{-2}	2	SO_4^{2-}	10^{-12}	12
H_3PO_4	$7.1 \cdot 10^{-2}$	2.15	$H_2PO_4^-$	$1.4 \cdot 10^{-12}$	11.85
HF	$5.0 \cdot 10^{-4}$	3.3	F^-	$2.0 \cdot 10^{-11}$	10.7
$HOAc$	$1.74 \cdot 10^{-5}$	4.76	OAc^-	$5.75 \cdot 10^{-10}$	9.24
$H_2PO_4^-$	$7.9 \cdot 10^{-8}$	7.10	HPO_4^{2-}	$1.3 \cdot 10^{-7}$	6.90
HPO_4^{2-}	$4.8 \cdot 10^{-13}$	12.32	PO_4^{3-}	$2.1 \cdot 10^{-2}$	1.68
H_2O	10^{-14}	14	OH^-	1	0

2.4 Total concentration

The concept "total concentration" is essential to some of the discussions of equilibria in chemistry and corresponds to the sum of several different concentrations. If a solution contains an acid in an unknown state, say three different states: H_2A, HA^- or A^{2-}, then the total concentration w.r.t. "A", is: $[A]_{tot} = [H_2A] + [HA^-] + [A^{2-}]$. The total concentration is well defined while the concentrations of the individual species are theory dependent.

3 pH or pOH in acids or bases

3.1 Two logarithmic concepts: pH and pOH

A possible reason for the use of the logarithmic quantities pH and pOH is that its considerably easier to talk about a solution with pH = 5, than a solution with $[H^+(aq)] = 10^{-5} mol/dm^3$. The concepts pH and pOH are related by the water autoprotolysis as the following shows.

$$\{H_3O^+(aq)\}\{OH^-(aq)\} = K_w \qquad \text{or} \qquad pH + pOH = pK_w = 14 \tag{10}$$

Note that this does NOT imply that $pH = pK_a$. It *only* means that the sum of pH and pOH always equals 14 in water solutions at 25 ^oC. There is nothing claimed about either pK_a nor pK_b in the above relation, only that their sum is 14. The relation between acidity constant of an arbitrary acid and its corresponding base do look very similarly, but is not equivalent! It is shown below, don't mix pK_a with pH or pK_b with pOH.

$$pK_a(HA) + pK_b(A^-) = pK_w = 14 \tag{11}$$

3.2 Strong acids or strong bases

3.2.1 Strong acid: HCl

Hydrochloric acid, HCl(aq) is an example of an strong acid. Another view of a strong acid is that the hydrogen ion atom is considerably more strongly bound to the water molecules than to the chloride ions. The hydrogen chloride is de-protonated to a very large extent: hydrochloric acid is a strong acid.

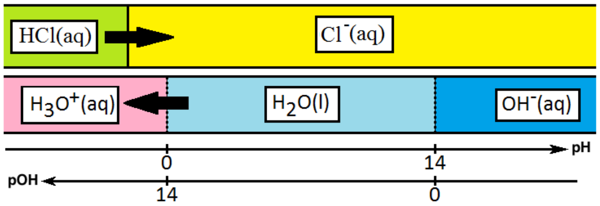
$$HCl(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + Cl^-(aq)$$

3.2.2 Analytical calculation of pH for a strong acid, HCl

The reaction may be assumed to be very heavily shifted to the right side, thus the equilibrium hydrogen ion concentration will be equal to the initial concentration of hydrochloric acid, $[H_3O^+(aq)]_{equilibrium} \approx [HCl(aq)]_{initial}$ and since we know the initial $[HCl(aq)]$, the acid solution will have: $pH = -lg[HCl(aq)]_{initial}$.

3.2.3 Graphic representation of the strong acid, HCl

A sufficient condition for a reaction to take place is that the two different existence areas do not occupy the same region of the pH line. The acid HCl cannot coexist with water, the existence area of HCl is far outside the existence area of $H_2O(l)$, thus the reaction described above will occur.



A graphic representation showing that a mixture of HCl and $H_2O(l)$ cannot coexist, but forms $Cl^-(aq)$ and $H_3O^+(aq)$ when mixed.

3.2.4 Strong base: $NaOH$ or even stronger base: Na_2O

When the solid compound sodium hydroxide, NaOH dissolves in water both sodium ions, $Na^+(aq)$ and hydroxide ions, $OH^-(aq)$ forms in the water solution. The hydroxide ion is the strongest base that can coexist with water. An example of a considerable stronger base is the oxide ion, it cannot coexist with water. If formed it would react with water forming hydroxide ions. Even though the oxide ion may not exist in an aqueous solution we can write $O^{2-}(aq)$ below. If it suit our purposes it can be allowed, even though its not a good representation of what's present in the solution. Instead of an oxide ion we can use a symbolic strong base, B^- that is protonated by water.

$$NaOH(s) \rightleftarrows Na^+(aq) + OH^-(aq)$$

$$Na_2O(s) \rightleftarrows 2Na^+(aq) + O^{2-}(aq)$$

$$O^{2-}(aq) + H_2O(l) \rightleftarrows 2OH^-(aq)$$

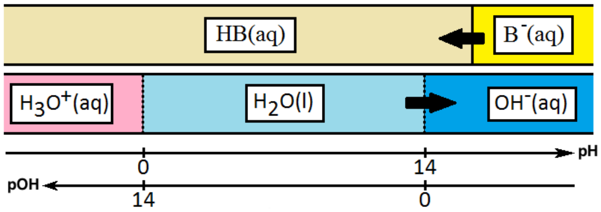
$$B^-(aq) + H_2O(l) \rightleftarrows HB(aq) + OH^-(aq)$$

3.2.5 Analytical calculation of pH (or pOH) for a strong base B^-

If we assume that no ion pairs exist in the solution the $[OH^-(aq)]$ is set by the number of formula units of NaOH (assuming B^- equals OH^-) which gives $pOH = -\log[OH^-(aq)]$ and thus pH = 14-pOH. The number of hydroxide ions formed equals the number of B^- added to the solution. Thus the $pOH = -lg[B^-]$ and pH = 14-pOH.

3.2.6 Graphic representation of the strong base B^-

Assume that the base B^- cannot coexist with water. The is equivalent to that the existence area of B^- is far outside the existence area of $H_2O(l)$. Thus the reaction described above will occur.



A mixture of B^- and $H_2O(l)$ cannot coexist, but forms $HB(aq)$ and $OH^-(aq)$.

3.3 Weak acids or weak bases

Weak acids or weak bases dissociates to a minor degree when dissolved in water and one need to take into account both the dissociated as well as the undissociated species. An arbitrary quantitative rule for some acid or base to be regarded as a "weak" is that the acidity constant or base constant should be (considerably) smaller than unity.

3.3.1 Weak acid: HF

The dissociation of hydrogen fluoride in water make HF a typical example of a weak acid. Note that the solvent water is important, in another solvent, say chloroform, HF may not be acidic, but now we stick to water. The acidity constant of HF = $5 \cdot 10^{-4}$. Assume that 0.1 mole HF is dissolved in 1 dm^3 of water, which will give $C_{tot} = 0.1\ mol/dm^3$. The scheme below shows the initial state and the equilibrium state of a water solution of the acid.

	$HF(aq)$	$+$	$H_2O(l)$	$\rightleftarrows$	$F^-(aq)$	$+$	$H_3O^+(aq)$
$Initial:$	C_{tot}		1		$-$		$-$
$Equilibrium:$	$C_{tot}-x$		1		x		x

3.3.2 Analytical calculation of pH for the weak acid, HF

The equilibrium concentration of oxonium ions is expressed with the symbol "x". Reformulate the equilibrium expression and solve for the value the unknown parameter, x.

$$K_a = \frac{\{H_3O^+(aq)\}\{F^-(aq)\}}{\{HF(aq)\}\{H_2O(l)\}} \approx \frac{[H_3O^+(aq)][F^-(aq)]}{[HF(aq)]} = \frac{x \cdot x}{(C_{tot} - x)}$$

$$K_a \cdot (C_{tot} - x) = x^2$$

$$x^2 + K_a \cdot x - K_a \cdot C_{tot} = 0$$

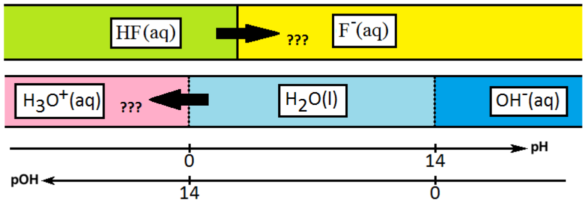
$$x = -\frac{K_a}{2} \pm \sqrt{\frac{K_a^2}{4} + K_a \cdot C_{tot}}$$

A couple of lines with Octave code to evaluate the solutions to the equation above are shown below. First the acidity constant and total concentration are set and then the two different solutions are calculated. Note that only x1 is a reasonable solution as x2 is negative. Negative concentrations are unrealistic, at least presently. The $[H_3O^+(aq)] = x$, thus the pH could also be calculated as shown below.

```
>> Ka = 5e-4
Ka =  5.0000e-04

>> Ctot = 0.1
Ctot =  0.10000

>> x1 = -(Ka/2)+sqrt(Ka^2/4+Ka*Ctot)
x1 =  0.0068255

>> x2 = -(Ka/2)-sqrt(Ka^2/4+Ka*Ctot)
x2 = -0.0073255

>> pH = -log10(x1)
pH =  2.1659
```

3.3.3 Graphic representation of the weak acid, HF

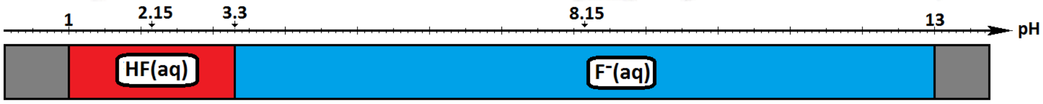
A weak acid such as HF can coexist with water, the existence area of HF overlaps with the existence area of $H_2O(l)$. Thus the dissociation reaction described above will occur only to a minor extent.



A mixture of $HF(aq)$ and $H_2O(l)$ can coexist since the existence areas of H_2O and HF overlap. Only a minor amount of HF forms $F^-(aq)$ and $H_3O^+(aq)$.

3.3.4 Graphic estimation of pH for the weak acid, HF

If the total concentration is known, a graphical method can be used to estimate the pH of the solution of the acid component, $HF(aq)$ as well as of the basic component, $F^-(aq)$.



Simple predominance diagram for $HF(aq)$ - $F^-(aq)$ system with $pK_a = 3.3$.

- With $C_{tot} = 0.1\ mol/dm^3$ the $pH_{min} = 1$ and $pH_{max} = 13$
- pH of a solution of $HF(aq)$ = (1+3.3)/2 = 2.15.
- pH of a solution of $F^-(aq)$ = (3.3+13)/2 = 8.15.

3.3.5 Weak base: NH_3

The aqueous solution of ammonia is a typical example of a weak base. The base constant of NH_3= $2 \cdot 10^{-5}$. Assume that 0.1 mol NH_3 is dissolved in 1 dm^3 of water, which will give C_{tot} = 0.1 mol/dm^3 . The scheme below shows the initial state and the equilibrium state of a water solution of the base.

	$NH_3(aq)$	$+$	$H_2O(l)$	$\rightleftarrows$	$NH_4^+(aq)$	$+$	$OH^-(aq)$
Initial :	C_{tot}		1		$-$		$-$
Equilibrium :	$C_{tot} - x$		1		x		x

3.3.6 Analytical calculation of pH (or pOH) for the weak base NH_3

The equilibrium concentration is expressed with the symbol "x". Reformulate the equilibrium expression and solve for the value the unknown parameter, x.

$$K_b = \frac{\{NH_4^+(aq)\}\{OH^-(aq)\}}{\{NH_3(aq)\}\{H_2O(l)\}} \approx \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]} = \frac{x \cdot x}{(C_{tot} - x)}$$

$$K_b \cdot (C_{tot} - x) = x^2$$

$$x^2 + K_b \cdot x - K_a \cdot C_{tot} = 0$$

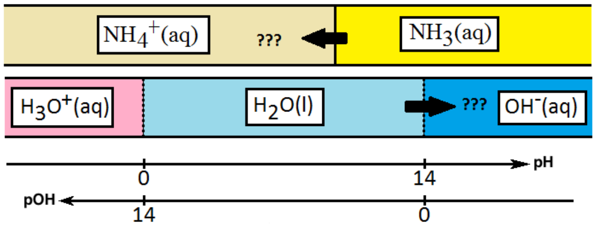
$$x = -\frac{K_b}{2} \pm \sqrt{\frac{K_b^2}{4} + K_a \cdot C_{tot}}$$

A couple of lines with Octave code to evaluate the solutions to the equation above are shown below. First the base constant and total concentration are set and then the two different solutions are calculated. Note that only x1 is a reasonable solution as x2 is negative. Negative concentrations are unrealistic. The $[OH^-(aq)] = x$, thus the pOH (and pH) could also be calculated as shown on line 5 and 6 below.

```
>> Kb = 2e-5
Kb =  2.0000e-05

>> Ctot = 0.1
Ctot =  0.10000

>> x1 = -Kb/2 + sqrt(Kb^2/4+Kb*Ctot)
x1 =  0.0014042

>> x2 = -Kb/2 - sqrt(Kb^2/4+Kb*Ctot)
x2 = -0.0014242

>> pOH = -log10(x1)
pOH =  2.8526

>> pH = 14-pOH
pH =  11.147
```

3.3.7 Graphic representation of the weak base NH_3

The base NH_3 can coexist with water, the existence area of NH_3 is overlapping the existence area of $H_2O(l)$, thus essentially no reaction will occur. To a rather minor degree the base will react with water as shown above, however that equilibrium will be shifted to the left.



A mixture of $NH_3(aq)$ and $H_2O(l)$ can essentially coexist as the existence areas overlap. A minor part of the reactants forms $NH_4^+(aq)$ and $OH^-(aq)$.

4 The role of water in acid or base solutions

Aqueous species, derived from water, could always be considered to be present in the solution either as $H_3O^+(aq)$, $H_2O(l)$ or $OH^-(aq)$. The relative amounts of the different species will vary. Only the total number of hydrogens, summed over all species in the solutions, will remain constant. Instead of several different hydronium ions, H_3O^+, $H_5O_2^+$, $H_7O_3^+$, $H_9O_4^+$, etc. one sometimes write only $H^+(aq)$ to signify a hydrogen ion surrounded by some water molecules. With normal titration methods there are small possibilities to know the relative proportions of the different ions.

5 Different version of the diagrams

One could envisage several versions of distribution diagrams for acids or bases.

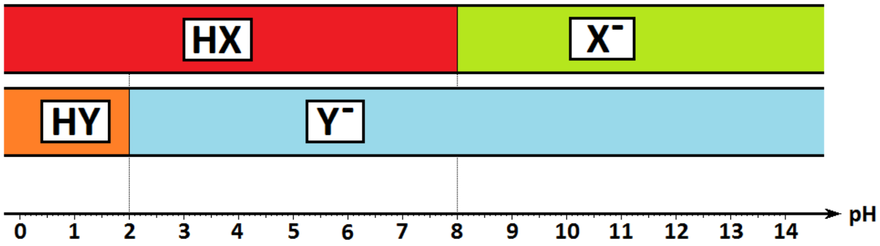
Simple diagrams: a plain figure showing the different pKa (or pKb for bases) points, separating the different predominance areas.

Fraction curve: (α-curve) shows the fraction of each specific specie.

Logarithmic diagram: the logarithmic version of the α-curve, more instructive than the fraction diagram, at least at very low concentrations. The term pHpC diagram are also used.

5.1 Simple predominance diagrams to determine reactions

- If two species should be able to coexist the predominance areas should overlap each other.
- Two species with non-overlapping existence areas cannot coexist, at least both species cannot be the dominant species of each system.



Predominance diagram for two different acid base systems,
HX with a $pK_a = 8$ and HY with $pK_a = 2$.

- The two species HX and HY can coexist as well as the two species X^- and Y^- can coexist. Their existence areas overlap.
- X^- is a stronger base than Y^-.
- The two species Y^- and HX can coexist. Their existence areas overlap. HX is too weak as an acid and X^- is a too weak as a base to react.
- HY and X^- cannot coexist in a solution. Their existence areas do not overlap. They will react, as shown below.

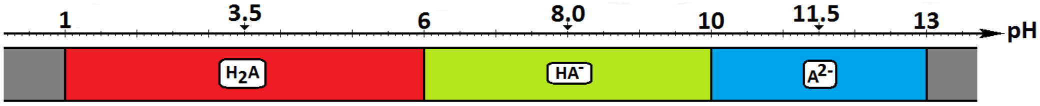
$$HY + X^- \rightleftarrows Y^- + HX$$

5.1.1 Determination of pH of certain solutions

One use of the simple distribution diagrams is to decide what pH a certain solution would have.

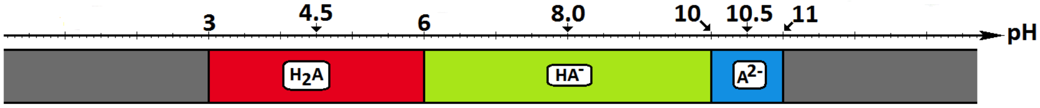
- The idea of minimum and maximum pH of the solution need to be introduced. Assume that the solution contain either a strong acid or a strong base.
- $pH_{min} = -lg(C_{tot})$, i.e. $[H^+(aq)] = [acid(aq)] = C_{tot}$.
- $pOH_{min} = -lg(C_{tot})$ and thus $pH_{max} = 14 + lg(C_{tot})$. If.

All diagrams below show a diprotic acid system: $H_2A \rightleftarrows H^+ + HA^-$; $HA^- \rightleftarrows H^+ + A^{2-}$) with $pK_{a1} = 6$, $pK_{a2} = 10$



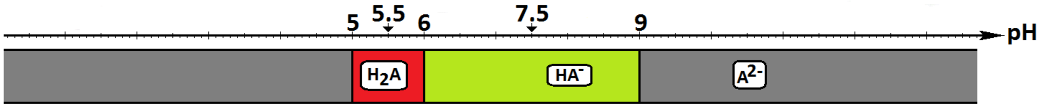
Simple predominance diagram for a diprotic acid system with $C_{tot} = 0.1 mol/dm^3$.

- With $C_{tot} = 0.1\ mol/dm^3$ the $pH_{min} = 1$ and $pH_{max} = 13$
- pH of a solution of $H_2A(aq)$ = (1+6)/2 = 3.5.
- pH of a solution of $HA^-(aq)$ = (6+10)/2 = 8.0.
- pH of a solution of $A^{2-}(aq)$ = (10+13)/2 = 11.5.



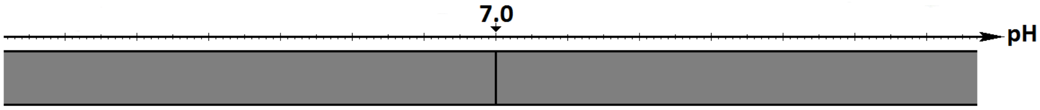
Simple predominance diagram for a diprotic acid system with $C_{tot} = 0.001 mol/dm^3$.

- With $C_{tot} = 0.001 mol/dm^3$ the $pH_{min} = 3$ and $pH_{max} = 11$
- pH of a solution of $H_2A(aq)$ = (3+6)/2 = 4.5.
- pH of a solution of $HA^-(aq)$ = (6+10)/2 = 8.0.
- pH of a solution of $A^{2-}(aq)$ = (10+11)/2 = 10.5.



Simple predominance diagram for a diprotic acid system with $C_{tot} = 10^{-5} mol/dm^3$.

- With $C_{tot} = 10^{-5} mol/dm^3$ the $pH_{min} = 5$ and $pH_{max} = 9$
- pH of a solution of $H_2A(aq)$ = (5+6)/2 = 5.5.
- pH of a solution of $HA^-(aq)$ = (6+9)/2 = 7.5.
- pH of a solution of $A^{2-}(aq) = pH_{max} = 9$. This is a result of that the existence area for A^{2-} is positioned to the right of pH_{max} and thus $A^{2-}(aq)$ can be considered as a strong base which is completely protonated by water.



Simple predominance diagram for a di-protic acid systems, with very low total concentration $C_{tot} = 10^{-7} mol/dm^3$ or even lower. This is nearly pure water! All solutions with that low total concentration will have approximately pH = 7.

5.2 The fraction diagram, α-curve

The fraction diagram, also named the α-curve shows the fraction of each specie compared to the total concentration. At pH $= pK_a$ there is equal amounts of the neighbouring species.

$$C_{tot} = [H_3A(aq)] + [H_2A^-(aq)] + [HA^{2-}(aq)] + [A^{3-}(aq)]$$

5.2.1 mono-protic acids

$$C_{tot} = [HA(aq)] + [A^-(aq)]$$

$$\alpha_0 = \frac{[HA(aq)]}{C_{tot}} = \frac{[H^+(aq)]}{[H^+(aq)] + K_{a1}} \tag{12}$$

$$\alpha_1 = \frac{[A^-(aq)]}{C_{tot}} = \frac{K_{a1}}{[H^+(aq)] + K_{a1}} \tag{13}$$

5.2.2 di-protic acids

$$C_{tot} = [H_2A(aq)] + [HA^-(aq)] + [A^{2-}(aq)]$$

$$\alpha_0 = \frac{[H_2A(aq)]}{C_{tot}} = \frac{[H^+(aq)]^2}{[H^+(aq)]^2 + K_{a1}[H^+(aq)] + K_{a1}K_{a2}} \tag{14}$$

$$\alpha_1 = \frac{[HA^-(aq)]}{C_{tot}} = \frac{K_{a1}[H^+(aq)]}{[H^+(aq)]^2 + K_{a1}[H^+(aq)] + K_{a1}K_{a2}} \tag{15}$$

$$\alpha_2 = \frac{[A^{2-}(aq)]}{C_{tot}} = \frac{K_{a1}K_{a2}}{[H^+(aq)]^2 + K_{a1}[H^+(aq)] + K_{a1}K_{a2}} \tag{16}$$

5.2.3 tri-protic acids

$$C_{tot} = [H_3A(aq)] + [H_2A^-(aq)] + [HA^{2-}(aq)] + [A^{3-}(aq)]$$

$$\alpha_0 = \frac{[H_3A(aq)]}{C_{tot}} = \frac{[H^+(aq)]^3}{[H^+(aq)]^3 + K_{a1}[H^+(aq)]^2 + K_{a1}K_{a2}[H^+(aq)] + K_{a1}K_{a2}K_{a3}} \tag{17}$$

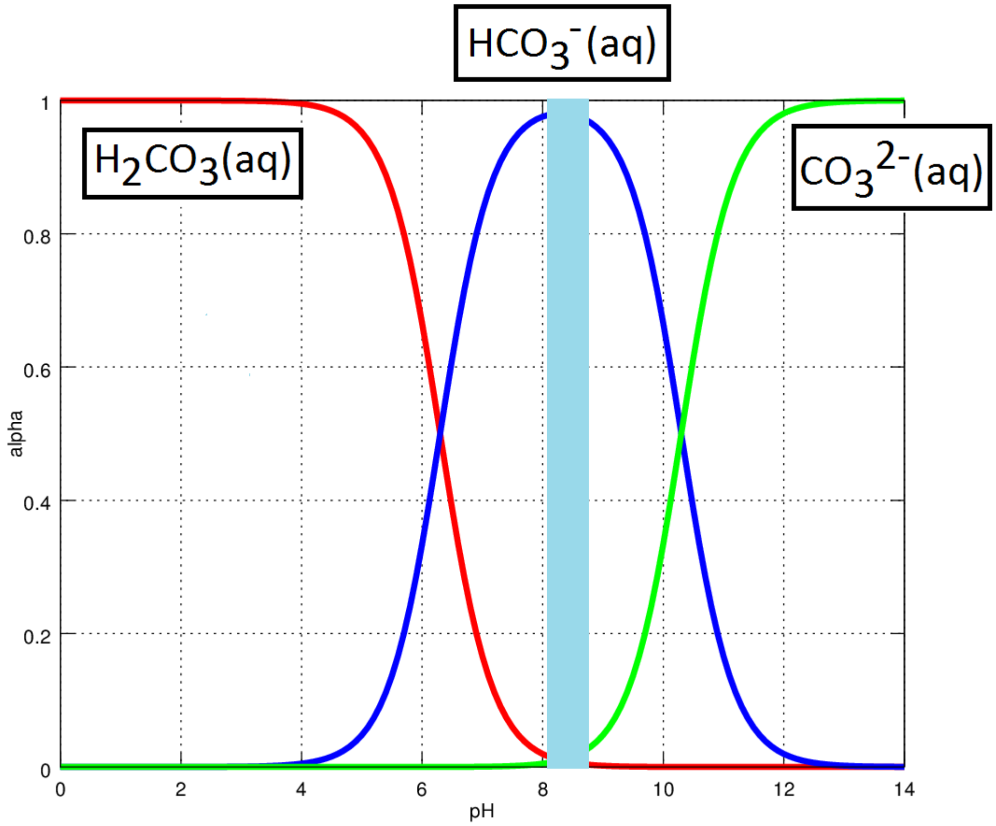
$$\alpha_1 = \frac{[H_2A^-(aq)]}{C_{tot}} = \frac{K_{a1}[H^+(aq)]^2}{[H^+(aq)]^3 + K_{a1}[H^+(aq)]^2 + K_{a1}K_{a2}[H^+(aq)] + K_{a1}K_{a2}K_{a3}} \tag{18}$$

$$\alpha_2 = \frac{[HA^{2-}(aq)]}{C_{tot}} = \frac{K_{a1}K_{a2}[H^+(aq)]}{[H^+(aq)]^3 + K_{a1}[H^+(aq)]^2 + K_{a1}K_{a2}[H^+(aq)] + K_{a1}K_{a2}K_{a3}} \tag{19}$$

$$\alpha_3 = \frac{[A^{3-}(aq)]}{C_{tot}} = \frac{K_{a1}K_{a2}K_{a3}}{[H^+(aq)]^3 + K_{a1}[H^+(aq)]^2 + K_{a1}K_{a2}[H^+(aq)] + K_{a1}K_{a2}K_{a3}} \tag{20}$$

5.2.4 Fraction curve related to sea water

The fraction diagram gives more information about the acid base system compared to the simple distribution diagram in the previous section. The diagram below shows clearly that at pH = 6.3 the fractions of the species $H_2A(aq)$ and $HA^-(aq)$ are equal. Close to each of the pK_a points one can draw conclusions about the fractions of the neighboring species. The middle curve describes the hydrogen carbonate specie at different pH values. It dominates the carbonic acid system at $6.3 < pH < 10.3$.



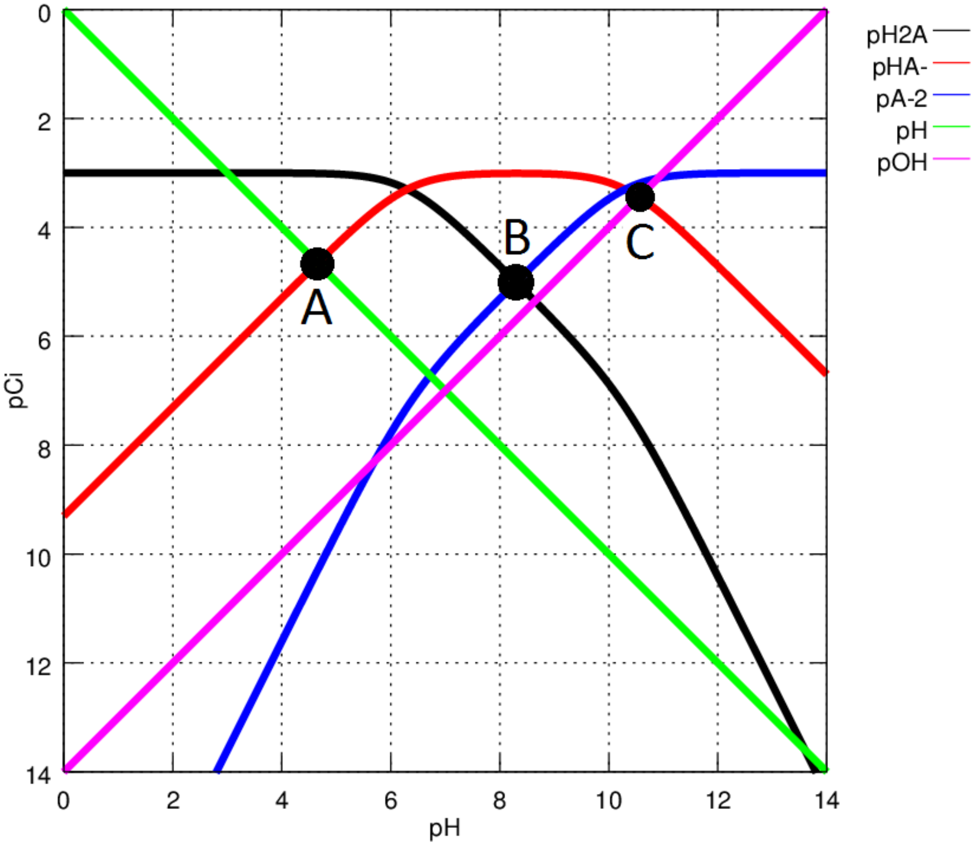
Fraction diagram of carbonic acid system, a diprotic acid with $pK_{a1} = 6.3$ and $pK_{a2} = 10.3$. This is a reasonable model of sea water. The light blue box approximates the existence area of sea water.

5.3 The logarithmic diagram, pHpC

The logarithmic diagram gives information about, not only neighboring species at the pK_a points but also about almost all species in the acid base system. The total concentration and fractions of the species are defined as with the fraction diagram. The simplest logarithmic diag ram is simply a fraction diagram with a logarithmic Y-axis. Normally the total concentration is multiplied with the fractions. In addition to the species of the acid base system two more lines derived from the $[H^+(aq)]$ and $[OH^-(aq)]$ are usually plotted as help lines.

$$C_{tot} = [H_2A(aq)] + [HA^-(aq)] + [A^{2-}(aq)]$$

$$[H_2A(aq)] = \alpha_0 \cdot C_{tot}; \qquad [HA^-(aq)] = \alpha_1 \cdot C_{tot}; \qquad [A^{2-}(aq)] = \alpha_2 \cdot C_{tot}$$



Logarithmic diagram of the carbonic acid system (also called carbonate system), with $pK_{a1} = 6.3$ and $pK_{a2} = 10.3$. The total concentation of is $10^{-3} mol/dm^3$, a close approximation of sea water.

Note the use of pC_{tot} and the direction of the positive Y-axis... The points A, B and C gives the pH values of solutions of $H_2CO_3(aq)$, $HCO_3^-(aq)$ and $CO_3^{2-}(aq)$,

5.4 The proton balance condition - book-keeping hydrogen ions

When some kind of acid or base is dissolved in water a repartition of the hydrogen ions will be the result. If the dissolved species was an acid the hydrogen ions will protonate the solvent and if the dissolved specie was a base the hydrogen ions will be taken from water to protonate the base. It is only a question of book keeping all hydrogens that protonate some species, they must come from some other species. We illustrate with the hydrogen carbonate ion in water, three important questions and the construction of the proton condition.

- Which species do we find initially, before any protolysis reaction has occurred, in the solution?
  Answer: $H_2O(l)$ and $HCO_3^-(aq)$.
- Which new species, not present from the beginning, are formed when accepting hydrogen ions?
  Answer: $H_3O^+(aq)$ and $H_2CO_3(aq)$.
- Which new species, not present from the beginning, are formed when donating hydrogen ions?
  Answer: $OH^-(aq)$ and $CO_3^{2-}(aq)$.

A suitable scheme for book-keeping all of these species can look like the one below. The sum of all species that accepted extra hydrogens, ”$+H^+$” must be equal to the sum of species that have donated hydrogens, ”$-H^+$” . Since all species occur in the same volume one can compare concentrations.

$+H^+$		Initial species		$-H^+$
$H_2CO_3(aq)$	$\leftarrow$	$HCO_3^-(aq)$	$\rightarrow$	$CO_3^{2-}(aq)$
$H_3O^+(aq)$	$\leftarrow$	$H_2O(l)$	$\rightarrow$	$OH^-(aq)$
$[H_2CO_3(aq)] + [H_3O^+(aq)]$		$=$		$[CO_3^{2-}(aq)] + [OH^-(aq)]$

This is the proton condition for the hydrogen carbonate solution. At point B in the diagram above one can neglect one term each on both sides and thus transforms to the equality above to the simpler expression below.

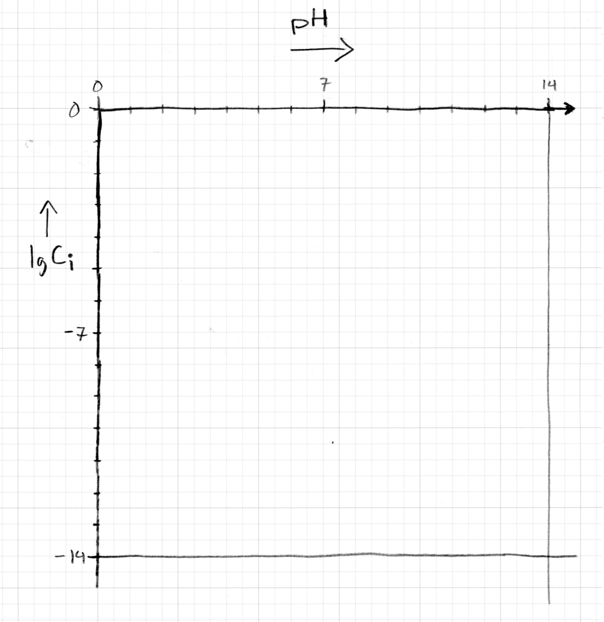
$$[H_2CO_3(aq)] = [CO_3^{2-}(aq)]$$

This is simply the intersection between two lines, thus easily marked in the diagram. Whether one should neglect terms, or not, from the original expression is a delicate question. A pragmatic rule is that if the lower line is one unit below, on the logarithmic scale, that term could easily be neglected. Another more rough rule is that as long as one line is below another it is neglected. One should always have in mind that the solution obtained is approximate. But it is often surprisingly correct when compared with more exact calculations.

6 Recipe for the manual construction of a pHpC-diagram

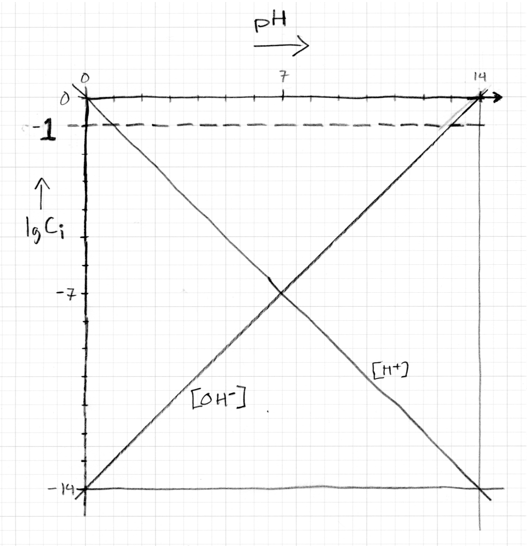
A recipe in seven steps, for the manual construction of a pHpC diagram is given below.

1. Draw a quadratic diagram, 14 by 14 unit boxes on square paper.
2. Label the x-axis as "pH" and the y-axis as "lg(C)".



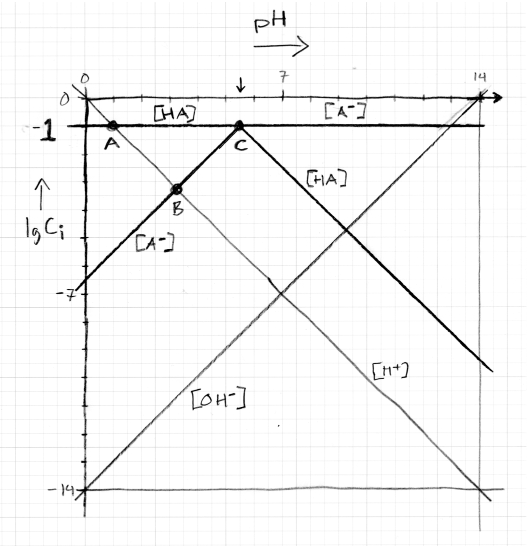
A square diagram with axis labels.

3. Draw $\log(C_{tot})$ as a horizontal line.
4. Draw the lines for the oxonium ion and the hydroxide ion.



$lg(C_{tot})$ marked together with H^+ and OH^- lines.

5. Mark the different pKa points on the C_{tot} line.
6. Draw graphs for all species and remember that upon passage of each pKa point the slope of the line should change one unit downwards.
7. Note: draw the lines all the way to the pKa points but remember that this will be slightly erroneous exactly at the pKa points. A possible correction for this error can be done afterwards.



The finished diagram for an acid with $pK_a = 5.5$ and $C_{tot} = 0.1 mol/dm^3$.

In the logarithmic diagram above, the lines for the acid $[HA]$ and the corresponding base $[A^-]$ has been marked. These two lines cross at pH = pKa (point C). The pH of the acid solution could be evaluated using the proton condition below

$$[H_3O^+(aq)] = [A^-(aq)] + [OH^-(aq)]$$

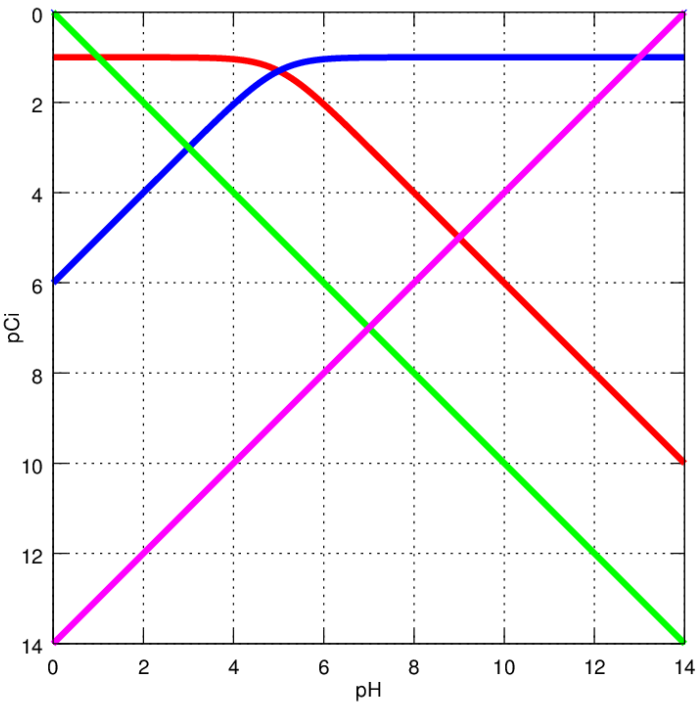
At point B the proton condition is satisfied. The term $[OH^-(aq)]$ can be neglected as it is more than 7 units below the $[A^-(aq)]$ line. Thus the pH of the initial acid solution, (HA(aq)) will be 3.25 which can be calculated from the isosceles triangle (A-B-C).

7 Construction of the diagrams using Octave

The construction is greatly simplified by using a computer program, e.g. the script file `dist1.m`, `dist2.m` or `dist3.m` with Octave. The scripts "dist1.m", "dist2.m" and "dist3.m" are used for mono-protic, di-protic and tri-protic respectively. The only visible difference between the scripts are the number of pK_a points that are requested when choosing option "1" from the menu.

```
>> dist1
----------------------------------------------
Main menu, what do you want to do?

1) Set pKa1 and Ctot.
2) Plot distribution diagram (alpha-curve).
3) Plot logaritmic diagram, pCi = f(pH).
4) Save one of the pCi=f(pH) [ph, pCi] to a file.
5) Save the current plot as a file (graf.jpg).

Enter your choice [1,2,3,4 or 5]: 1
----------------------------------------------
Enter pKa1: 5
Enter Ctot: 0.1
----------------------------------------------
```

The menu is repeated, until any other option than 1,2,3,4 or 5 is used. The construction of a logarithmic diagram is done with option 3 and finally option 5 will save the plot on a file. This plot can then be used , edited, inserted into reports etc.



pHpC diagram with Octave for a mono protic acid with $pK_a = 5$ and $C_{tot} = 0.1 mol/dm^3$.

8 Selected acidity constants

Table 2: Selected, mainly inorganic acids with acidity constants (one or several values)

Name (acid or ion)	Formula	pK_a	Swedish name
Hydrofluoric	HF	3.3; 3.45	Fluorvätesyra, Vätefluorid
Hydrochloric, Muriatic	HCl	-3	Saltsyra, , Väteklorid
Hydrobromic	HBr	-4	Bromvätesyra, Vätebromid
Hydroiodic	HI	-5	Jodvätesyra, Vätejodid
per-Chloric	$HClO_4$	-6	Perklorsyra, Överklorsyra
Chlorous	$HClO_2$	2.0	Klorsyrlighet
hypo-Chlorous	$HClO$	7.4	Underklorsyrlighet
Sulphuric	H_2SO_4	-3	Svavelsyra
Hydrogen Sulphate	HSO_4^-	1.92	Vätesulfatjon
Sulphurous	H_2SO_3	1.81	Svavelsyrlighet
Hydrogen Sulphite	HSO_3^-	6.91; 7.2	Vätesulfitjon
di Hydrogen Sulphide	H_2S	7.04	Divätesulfid, Svavelväte
Hydrogen Sulphide	HS^-	11.96	Vätesulfidjon
Telluric	$Te(OH)_6$	7.68	Tellur(V)syra
poly-meta-Telluric	$H_2(TeO_4)_n$	11.29	
Nitric	HNO_3	-1.4	Salpetersyra
Nitrous	HNO_2	3.37	Salpetersyrlighet
Ammonium	NH_4^+	9.3	Ammoniumjon
Hydrazinium	$NH_2NH_3^+$	8.23	Hydraziniumjon
Hydroxyl Ammonium	NH_3OH^+	6.03	Hydroxylammoniumjon
Phosphoric	H_3PO_4	2.15	Fosforsyra
di-Hydrogen Phosphate	$H_2PO_4^-$	7.10	di-Vätefosfatjon
Hydrogen Phosphate	HPO_4^{2-}	12.32	Vätefosfatjon
Phosphorous	H_3PO_3	2.00; 1.29	Fosforsyrlighet
di-Hydrogen Phosphite	$H_2PO_3^-$	6.74	di-Vätefosfitjon
Carbonic acid	H_2CO_3	6.35	Kolsyra
Hydrogen Carbonate	HCO_3^-	10.33	Vätekarbonatjon, Bikarbonatjon
Ethanoic, Acetic	CH_3COOH	4.8; 4.76	Etansyra, Ättiksyra
tri-Fluoro-Acetic	CF_3COOH	0.5	tri-Fluorättiksyra
tri-Chloro-Acetic	CCl_3COOH	0.7; 0.65	tri-Klorättiksyra
di-Chloro-Acetic	$CHCl_2COOH$	1.3; 1.29	di-Klorättiksyra
Chloro-Acetic	$CH_2ClCOOH$	2.9; 2.86	Klorättiksyra
Bromo-Acetic	$CH_2BrCOOH$	2.69	Bromättiksyra

9 A few examples

A set of examples of different chemical systems are presented in the list below. In all cases the pH of an aqueous solution is sought with the premises given. For the construction of the pHpC diagram the acidity constants may be necessary. Look them up in some chemical data book or search the internet for equilibrium constants. Remember to be suspicious regarding the validity of the equilibrium constants. They do determine what results are obtained from the analysis of the distribution diagrams. In addition to the diagram method, traditional analytical calculations of pH in the solutions are presented.

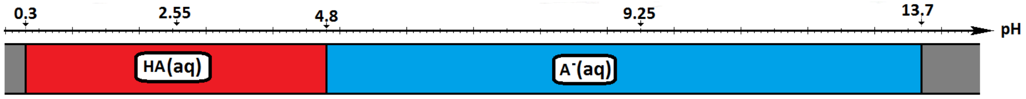
1. The pH of a 0.5 mol/dm^3 aqueous solution of CH_3COOH
2. The pH of a 0.1 mol/dm^3 aqueous solution of NaF
3. The pH of a 0.001 mol/dm^3 aqueous solution of $NaHCO_3$
4. The pH of a 0.01 mol/dm^3 aqueous solution of Na_2CO_3
5. The pH of a 0.001 mol/dm^3 aqueous solution of H_2SO_4

All analytical calculation in the examples below will be done by concentration measures which necessarily will introduce some systematic errors. Activity factors are approximated to unity. In order to obtain more accurate results one should try to use an activity scale with more proper activity coefficients. However this is not done presently in these calculations.

9.1 The pH of a 0.5 mol/dm^3 aqueous solution of CH_3COOH

Necessary parameters are either the acidity constant of CH_3COOH ($pK_a = 4.76$) or the base constant of CH_3COO^- ($pK_b = 9.24$) and the total concentration ($C_{tot} = 0.5 mol/dm^3$ or $pC_{tot} = 0.3$). We assume that the ethanoic acid is partly dissociated in water i.e. the ethanoic acid acts as a weak acid. Thus that the pH should be slightly acidic.

9.1.1 The simple predominance diagram method



Simple predominance diagram for $CH_3COOH(aq)$ - $CH_3COO^-(aq)$ shown as $HA(aq)$ - $A^-(aq)$ system with $pK_a = 4.8$ and $pC_{tot} = -\log 0.5 = 0.3$.

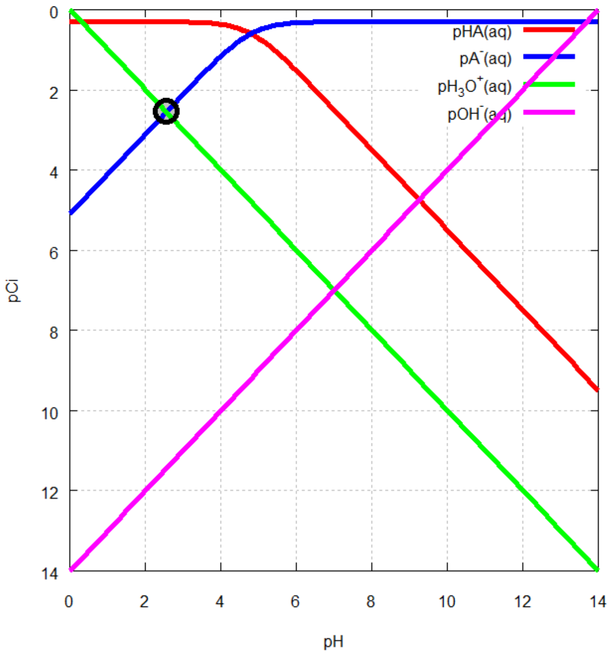
- With $C_{tot} = 0.5\ mol/dm^3$ the $pH_{min} = 0.3$ and $pH_{max} = 13.7$
- pH of a solution of $HOAc(aq)$ = (0.3+4.8)/2 = 2.55.
- pH of a solution of $OAc^-(aq)$ = (4.8+13.7)/2 = 9.25.

Note: $HOAc(aq) = CH_3COOH(aq)$ and $OAc^-(aq) = CH_3COO^-(aq)$.

9.1.2 The logarithmic diagram method

Formulate a proton condition as the one shown below. The initial species in the solution are $CH_3COOH(aq)$ and $H_2O(l)$. Finally construct a pHpC diagram, preferably with some computer program.

$+H^+$		Initial species		$-H^+$
$-$	$\leftarrow$	$CH_3COOH(aq)$	$\rightarrow$	$CH_3COO^-(aq)$
$H_3O^+(aq)$	$\leftarrow$	$H_2O(l)$	$\rightarrow$	$OH^-(aq)$
$[H_3O^+(aq)]$		$=$		$[CH_3COO^-(aq)] + [OH^-(aq)]$



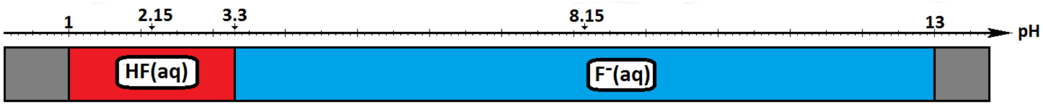
pHpC diagram for the $CH_3COOH(aq)$ - $CH_3COO^-(aq)$ system with $pK_a = 4.8$ and $pC_{tot} = 0.3$

Since there is only one term on the left hand side we check what specie that intersects the oxonium ion line first. Its the CH_3COO^- line. The hydroxide ions could be neglected since the hydroxide ion line is more than 8 units below the CH_3COO^- line. Note that this is more than 8 units on a logarithmic scale. The proton condition is fulfilled at the marked point in the figure above. The pH is the average of 0.3 and 4.8 which gives that pH = 2.55. The pH could also be read from the pH-scale in the figure. This answer fits with the initial estimate that the solution should be slightly acidic.

9.2 The pH of a 0.1 mol/dm^3 aqueous solution of NaF

Necessary parameters are either the acidity constants of HF ($pK_a = 3.3$) or the base constant of F^- ($pK_b = 10.7$) and the total concentration ($C_{tot} = 0.1 mol/dm^3$ or $pC_{tot} = 1$). We assume that the sodium fluoride is completely dissociated in water and that the acidous properties of the sodium ion is negligible. The fluoride ion acts as a weak base, thus some hydrogens from water will perhaps be associated with fluoride ion. An reasonable estimate is thus that the pH should be slightly basic.

9.2.1 The simple predominance diagram method



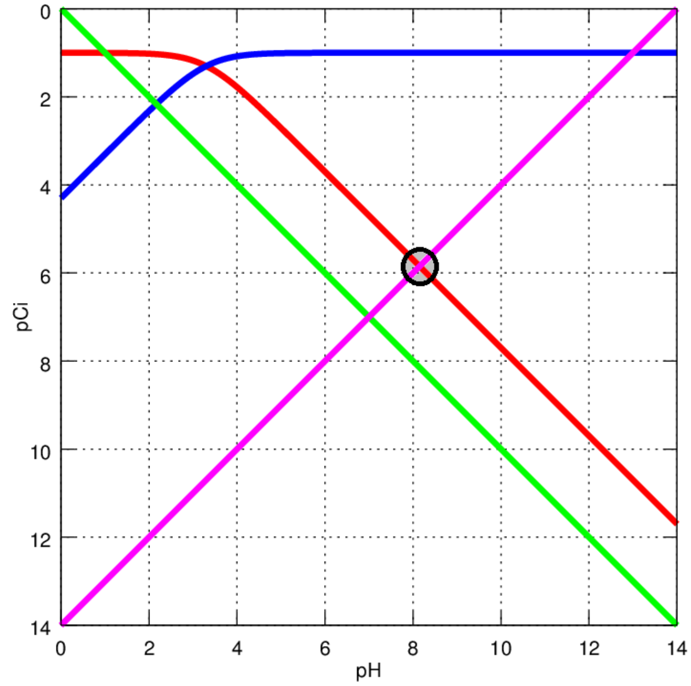
Simple predominance diagram for $HF(aq)$ - $F^-(aq)$ system with $pK_a = 3.3$.

- With $C_{tot} = 0.1\ mol/dm^3$ the $pH_{min} = 1$ and $pH_{max} = 13$
- pH of a solution of $HF(aq)$ = (1+3.3)/2 = 2.15.
- pH of a solution of $F^-(aq)$ = (3.3+13)/2 = 8.15.

9.2.2 The logarithmic diagram method

Formulate a proton condition as the one shown below. The initial species in the solution are $F^-(aq)$ and $H_2O(l)$. Finally construct a pHpC diagram, preferably with some computer program.

$+H^+$		Initial species		$-H^+$
$HF(aq)$	$\leftarrow$	$F^-(aq)$	$\rightarrow$	$-$
$H_3O^+(aq)$	$\leftarrow$	$H_2O(l)$	$\rightarrow$	$OH^-(aq)$
$[HF(aq)] + [H_3O^+(aq)]$		$=$		$[OH^-(aq)]$



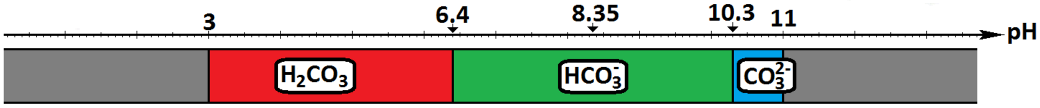
pHpC diagram for $HF(aq)$ - $F^-(aq)$ system with $pK_a = 3.3$.

Since there is only one term on the right hand side we check where this line intersects with the hydroxide line first. The first inersection is the HF line. The oxonium ions could be neglected as the oxonium line is nearly two units below the HF line.The proton condition is fulfilled at the marked point in the figure above. The pH is the average of 3.3 and 13.0 which gives that pH = 8.15. The pH could also be read from the pH-scale in the figure. This answer fits with the initial estimate that the solution should be slightly basic.

9.3 The pH of a 0.001 mol/dm^3 aqueous solution of $NaHCO_3$

Necessary parameters are either the acidity constants of the carbonate system ($pK_{a1} = 6.4$ and $pK_{a2} = 10.3$) and the total concentration ($C_{tot} = 0.001 mol/dm^3$ or $pC_{tot} = 3$). We assume that the sodium hydrogen carbonate is completely dissociated in water and that the acid/base properties of the sodium ion is negligible. The HCO_3^- ion acts as both a weak acid and a weak base. A reasonable estimate of the pH is in the middle of the existence area for the hydrogen carbonate ions as shown below. As a bonus the pH of solutions of carbonic acid and carbonate ions, for similar concentrations, could easily be determined.

9.3.1 The simple predominance diagram method



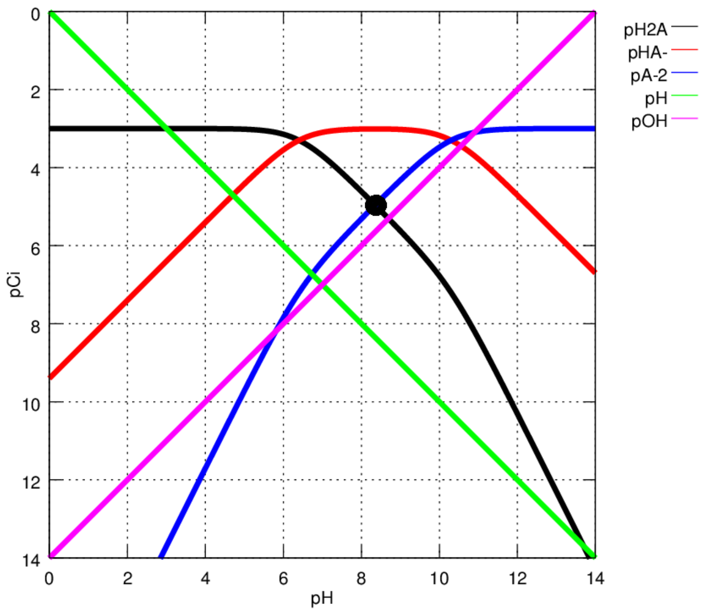
Simple predominance diagram for $H_2CO_3(aq)$ - $HCO_3^-(aq)$ - $CO_3^{2-}(aq)$ system with $pK_{a1} = 6.4$ and $pK_{a2} = 10.3$.

- With $C_{tot} = 0.001\ mol/dm^3$ the $pH_{min} = 3$ and $pH_{max} = 11$
- pH of a solution of $H_2CO_3(aq) = (3.0{+}6.4)/2 = 4.7$.
- pH of a solution of $HCO_3^-(aq) = (6.4{+}10.3)/2 = 8.35 \leftarrow$ this was the sought value!
- pH of a solution of $CO_3^{2-}(aq) = (10.3{+}11.0)/2 = 10.65$.

9.3.2 The logarithmic diagram method

We assume that the sodium hydrogen carbonate is completely dissociated i water and that the acidous properties of the sodium ion are negligible. The hydrogen carbonate ion acts both as a weak base as well as a weak acid. An estimate of pH is rather difficult. The hydrogen carbonate ions conjugated acid is carbonic acid, H_2CO_3 and its conjugated base is the carbonate ion, CO_3^{2-}. Formulate a proton condition as the one shown below. The initial species in the solution are $HCO_3^-(aq)$ and $H_2O(l)$. Finally construct a pHpC diagram, preferably with some computer program. Necessary parameters are the acidity constants of carbonic system ($pK_{a1} = 6.4$ and $pK_{a2} = 10.3$) and the total concentration ($C_{tot} = 0.001 mol/dm^3$ and thus $pC_{tot} = 3$).

$+H^+$		Initial species		$-H^+$
$H_2CO_3(aq)$	$\leftarrow$	$HCO_3^-(aq)$	$\rightarrow$	$CO_3^{2-}(aq)$
$H_3O^+(aq)$	$\leftarrow$	$H_2O(l)$	$\rightarrow$	$OH^-(aq)$
$[H_2CO_3(aq)] + [H_3O^+(aq)]$		$=$		$[CO_3^{2-}(aq)] + [OH^-(aq)]$



pHpC diagram for H_2CO_3 - HCO_3^- - CO_3^{2-} with $pK_{a1} = 6.4$ and $pK_{a2} = 10.3$.

The actual point where the proton condition is true is marked with a point i the pHpC diagram above. At the point we can assume that $[H_2CO_3(aq)] = [CO_3^{2-}(aq)]$ and the other two terms are neglected. The pH at this very point is the average of the two pK_a points, i.e. 8.35. This value fits quite well with the pH in the oceans and since the $[HCO_3^-] \approx 10^{-3} mol/dm^3$ in the oceans its a quite plausible result.

9.4 The pH of a 0.01 mol/dm^3 aqueous solution of Na_2CO_3

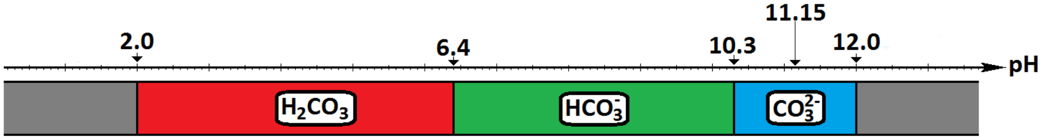
Necessary parameters are the acidity constants of the carbonate system ($pK_{a1} = 6.4$ and $pK_{a2} = 10.3$) and the total concentration ($C_{tot} = 0.01 mol/dm^3$ or $pC_{tot} = 2$). An alternative is the corresponding basicity constants for the carbonate system ($pK_{b1} = 3.7$ and $pK_{b2} = 7.6$) and the total concentration. The relation between the different acidity constants and base constants are shown below.

$$K_{a1} \cdot K_{b2} = K_w \qquad \text{or} \qquad pK_{a1} + pK_{b2} = pK_w$$

$$K_{a2} \cdot K_{b1} = K_w \qquad \text{or} \qquad pK_{a2} + pK_{b1} = pK_w$$

We assume that the sodium carbonate is completely dissociated in water and that the acid/base properties of the sodium ions are negligible. The CO_3^{2-} ion acts as a weak base. A reasonable estimate of the pH is in the middle of the existence area for the carbonate ions as shown below. As a bonus the pH of solutions of carbonic acid and hydrogen carbonate ions, with similar concentrations, could easily be determined. This is quite a similar diagram as in the previous exercise.

9.4.1 The simple predominance diagram method



Simple predominance diagram for $H_2CO_3(aq)$ - $HCO_3^-(aq)$ - $CO_3^{2-}(aq)$ system with $pK_{a1} = 6.4$ and $pK_{a2} = 10.3$.

- With $C_{tot} = 0.01$ mol/dm^3 the $pH_{min} = 2$ and $pH_{max} = 12$
- pH of a solution of $H_2CO_3(aq)$ = (2.0+6.4)/2 = 4.2.
- pH of a solution of $HCO_3^-(aq)$ = (6.4+10.3)/2 = 8.35.
- pH of a solution of $CO_3^{2-}(aq)$ = (10.3+12.0)/2 = 11.15 ← this is the wanted value!

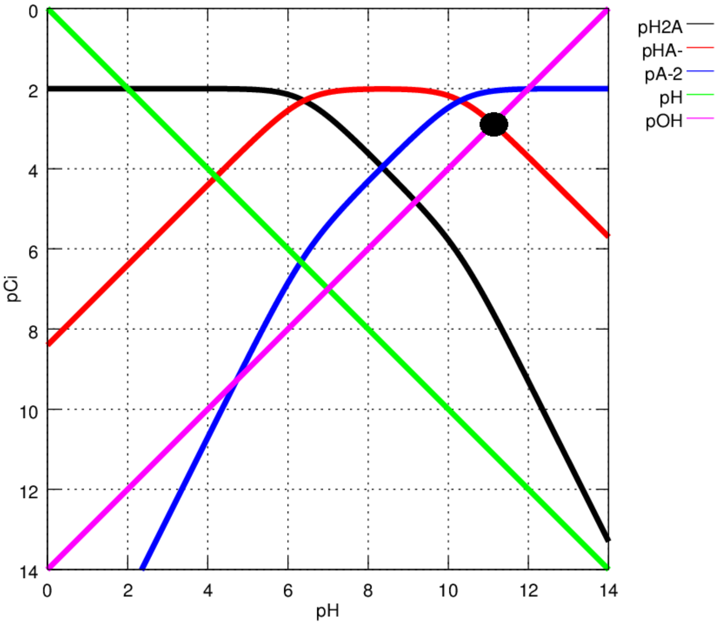
9.4.2 The logarithmic diagram method

We assume that the sodium carbonate is completely dissociated i water and that the acidous properties of the sodium ion are negligible. The carbonate ion acts as a base. The carbonate ion conjugated acid is hydrogen carbonate ion, $HCO_3^-(aq)$. Formulate a proton balance condition as the one shown below. The initial species in the solution are $CO_3^{2-}(aq)$ and $H_2O(l)$. Finally construct a pHpC diagram, preferably with some computer program. Necessary parameters are the acidity constants of carbonic system ($pK_{a1} = 6.4$ and $pK_{a2} = 10.3$) and the total concentration ($C_{tot} = 0.01 mol/dm^3$ and thus $pC_{tot} = 2$).

$+2H^+$		$+H^+$		Initial species		$-H^+$
$H_2CO_3(aq)$	$\leftarrow$	$HCO_3^-(aq)$	$\leftarrow$	$CO_3^-(aq)$	$\rightarrow$	$-$
		$H_3O^+(aq)$	$\leftarrow$	$H_2O(l)$	$\rightarrow$	$OH^-(aq)$

Which will lead to the following proton condition. Note the factor 2 in front of $[H_2CO_3(aq)]$ as there are two hydrogens per H_2CO_3 molecule.

$$2[H_2CO_3(aq)] + [HCO_3^-(aq)] + [H_3O^+(aq)] = [OH^-(aq)]$$



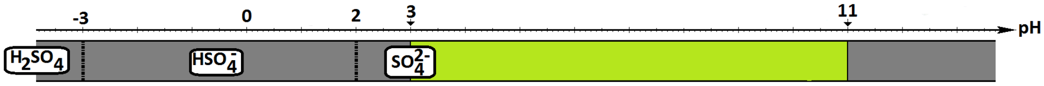
pHpC diagram for H_2CO_3 - HCO_3^- - CO_3^{2-} with $pK_{a1} = 6.4$ and $pK_{a2} = 10.3$.

The proton condition above is fulfilled at the point marked in the figure above. We assume that the $[H_2CO_3(aq)]$ and the $[H_3O^+(aq)]$ terms can be neglected. The pH is the average value of 10.3 and 12.0 i.e. 11.15.

9.5 The pH of a 0.001 mol/dm^3 aqueous solution of H_2SO_4

We assume that sulphuric acid has $pK_{a1} = -3$ and $pK_{a2} = 2.0$. The first protolysis step is very strong, i.e. the first dissociation it is virtually complete while the second protolysis step, i.e. the hydrogen sulphate ions is an example of a weak acid. However at the low concentration as in this case one can note that fully de-protonated sulphate ions dominate the solution. The simplified diagram below shows that the dominating species is $SO_4^{2-}(aq)$.

9.5.1 The simple predominance diagram method



Simple predominance diagram for $H_2SO_4(aq)$ - $HSO_4^-(aq)$ - $SO_4^{2-}(aq)$ system with $pK_{a1} = -3$ and $pK_{a2} = 2$.

- With $C_{tot} = 0.001\ mol/dm^3$ the $pH_{min} = 3$ and $pH_{max} = 11$
- The pH of a solution of monoprotic acid could be expected to be equal to 3 but this is only correct for a monoprotic acid, However the sulphuric acid, $H_2SO_4(aq)$ is a diprotic acid and as seen from the diagram below, even the second dissociation step is fully deprotonated. Thus the hydrogen concentration will be twice as large. Thus pH = 2.7 i.e. pH $= -\log 2 \cdot 10^{-3}$.
- pH = 3 of a solution of $HSO_4^-(aq)$ with the same concentration. This could be obtained from e.g. an aqueous solution of $NaHSO_4$.
- pH = (3+11)/2 = 7 of a solution of $SO_4^{2-}(aq)$ without acidos cations. This could be obtained from e.g. an aqueous solution of Na_2SO_4.

9.5.2 The logarithmic diagram method

Formulate a proton condition as the one shown below. The initial species in the solution are $H_2SO_4(aq)$ and $H_2O(l)$. Finally construct a pHpC diagram.

$+H^+$		Initial species		$-H^+$		$-2H^+$
	$\leftarrow$	$H_2SO_4(aq)$	$\leftarrow$	$HSO_4^-(aq)$	$\rightarrow$	$SO_4^{2-}(aq)$
$H_3O^+(aq)$	$\leftarrow$	$H_2O(l)$	$\rightarrow$	$OH^-(aq)$		

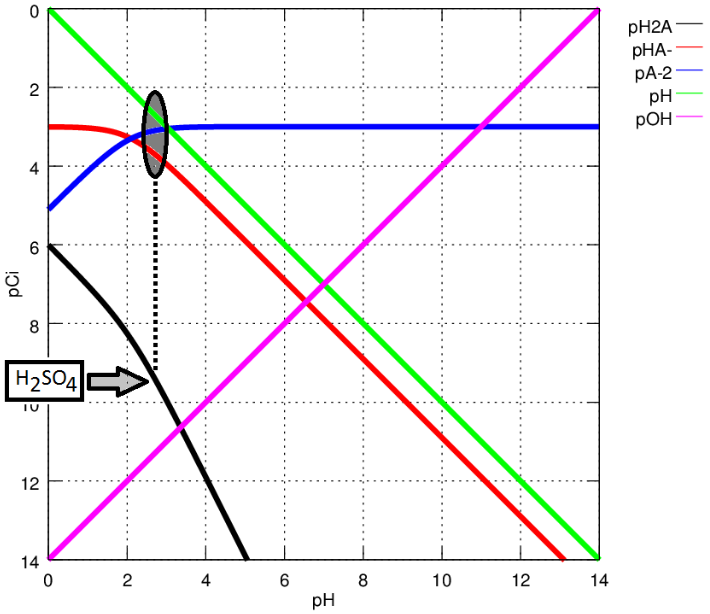
Which will lead to the following proton condition. Note the factor of 2 in front of $[SO_4^{2-}(aq)]$ as two hydrogens have been lost per molecule.

$$[H_3O^+(aq)] = [OH^-(aq)] + [HSO_4^-(aq)] + 2[SO_4^{2-}(aq)]$$

Since the HSO_4^- line is below the H_3O^+ line we neglect the $[HSO_4^-]$. The simplified proton condition is shown below. The area where this proton condition is fulfilled is shown in the figure below.

$$[H_3O^+(aq)] = 2[SO_4^{2-}(aq)]$$

A factor of 2 means a shift of 0.3 with a logarithmic scale. Since the intersection of of the $H_3O^+(aq)$ and $SO_4^{2-}(aq)$ occurs at pH = 3.0 the above proton condition is fulfilled at pH = 2.7. This also fits with the figure. The pH = 2.7 of the sulphuric acid solution.



pHpC diagram for 0.001 mol/dm^3 of H_2SO_4. Note the very low value of $[H_2SO_4(aq)]$, it is totally dissociated, at least according to the present model.