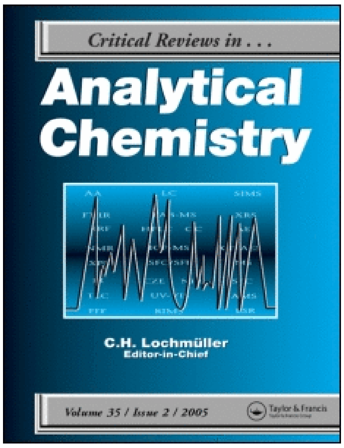

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A More Rational Treatment of the Acid-Base Equilibria Applying the Proton Condition, or the Hydroxyl Condition, in Equilibrium. How the Hydroxyls are Additive in Equilibrium: Dissolutions of Bases, Salts and Mixtures

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San Sebastián, Spain

The calculus of the acid-base equilibria can be rationalized by applying the proton condition or the hydroxyl condition in every case, on solutions of strong bases, mixtures of bases, mixtures of acids and bases, and different salts. Furthermore, applying the proton condition or the hydroxyl condition in equilibrium, it is clearly pointed out that the hydroxyls in equilibrium are additive in solutions of strong bases as well as in those of weak bases.

Keywords Proton condition, hydroxyl condition, the hydroxyls are additive

INTRODUCTION

The system procedure followed in the textbooks of the last decade for the treatment of the equilibria in dissolutions of bases, salts and mixtures, is identical to the one used for the solution of acids. They make a balance of masses and a balance of charges that, combined with their respective constants of equilibria that take part on the system, guide us to the hydroxyls in equilibrium (1–7).

In a similar way to how the dissolutions of acids have been treated (8), in this work the dissolutions of bases will be treated, too, using *the proton condition in equilibrium*. And as the bases provide hydroxyls to the dissolution, we will be able to solve them, too, applying *the hydroxyl condition in equilibrium,* that as we will observe, guides to the same solution.

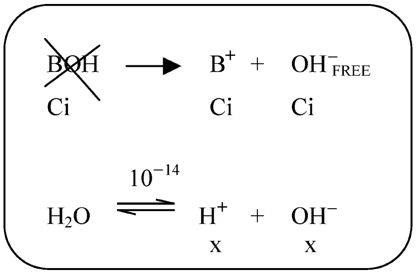
Here we will solve several cases of dissolutions of bases, although the same situations we set out for the dissolutions of acids can be set out now, and we will use the same system and the same criteria we used in the case of the acids:

- We will consider every term that is a hundred times smaller than another one to be negligible.
- We will suppose that what weak bases dissociate is negligible compared to their initial concentrations, and later we will prove if the supposition made is valid.
- Here it is proposed that the OH^- that come from strong bases will be called OH^-_{FREE} because they are not subject to any equilibrium, on a similar way to what was described with the strong acids.

DISSOLUTIONS OF BASES

Strong Base BOH

The strong base is completely dissociated providing B^+ and OH^-_{FREE} to the dissolution on equal concentrations to the initial concentration of BOH. We would have a dissolution:



This is a dissolution that is in equilibrium and to which we can apply the proton condition.

$$\text{Proton condition in equilibrium}: [H^+]_{equilibrium} = \sum[H^+]_{provide} - \sum[H^+]_{remove}$$

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In the dissolution as many protons as OH^- appear due to the equilibrium of H_2O, and as many protons as OH^-_{FREE} that the dissolution of strong base provides will disappear (the OH^- are $-H^+$). This way we would get $[H^+] = [OH^-] - [OH^-]_{FREE}$, that putting it in order leads us to:

$$[OH^-] = [OH^-]_{FREE} + [H^+]$$

and if we fix carefully on the solution we have reached, we will notice that what we have obtained is the balance of hydroxyls of the dissolution, the hydroxyl condition.

In any dissolution we can reach the situation of equilibrium through the H^+ in equilibrium or through the OH^- in equilibrium. Thus, we can propose the *hydroxyl condition in equilibrium* making the corresponding balance of OH^-, balance that will be given by the hydroxyls that are provided and removed from the dissolution.

$$\text{Hydroxyl condition in equilibrium:}[OH^-]_{\text{equilibriuum}} = \sum[OH^-]_{\text{provide}} - \sum[OH^-]_{\text{remove}}$$

In the dissolution as many OH^- as $[OH^-]_{FREE}$ are provided due to the strong base, and furthermore, as many OH^- as H^+ due to water (in this dissolution $OH^-$are not removed). Then we will get:

$$[OH^-] = [OH^-]_{FREE} + [H^+]$$

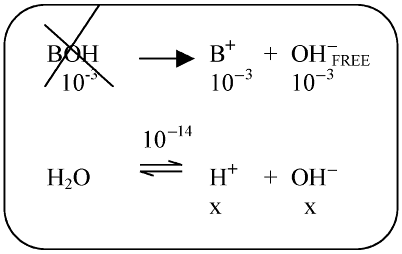
Exactly the same as with the proton condition, and where writing the H^+ according to the OH^- in equilibrium, it guides us to the *general equation for strong base:*

$$[OH^-] = [OH^-]_{FREE} + \frac{Kw}{[OH^-]} \qquad [1]$$

It is a similar equation to the one obtained for strong acids, that solves the same way with different situations of more or less concentrated bases, and that is simplified in a similar way depending on the case we find.

Moderately Concentrated Strong Base

For instance, let us suppose a strong base BOH 10^{-3} M, so that in the dissolution we would have:



This is a dissolution that is in equilibrium, as there is no possibility of any reaction. The OH^- of the strong base are OH^-_{FREE}, that play like common ions with those of H_2O.

Applying the OH^-condition, we would find that as many hydroxyls as OH^-_{FREE} appear due to the strong base, plus as many OH^- as protons due to water: $[OH^-] = [OH^-]_{FREE} + [H^+]$, and where writing the H^+ according to the OH^- we would get: $[OH^-] = [OH^-]_{FREE} + \frac{Kw}{[OH^-]}$.

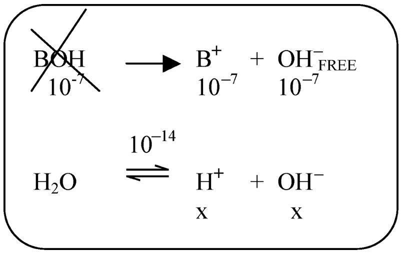
Arguing the same way we did for the acids (8), we observe that as a minimum there are 10^{-3}M of OH^-, so that $[OH^-] = 10^{-3} + \frac{10^{-14}}{\approx 10^{-3}} = 10^{-3} + \approx \cancel{10}^{-11} = 10^{-3}$ M. In the dissolution, the OH^- of the strong base prevail, as it was expected, and what water provides is negligible.

We continue assuming that every term 100 times less than another one is negligible.

For concentrations of strong base higher than 10^{-6}M, the contribution of water is negligible comparing with the contribution of the base, so that $[OH^-] = [OH^-]_{FREE}$.

Very Diluted Strong Base

Let us suppose a dissolution of strong base BOH with concentration 10^{-7} M, so that initially in the dissolution we will have:

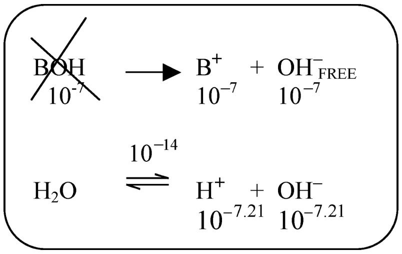


Applying the hydroxyl condition we will have:

$$[OH^-] = [OH^-]_{FREE} + [H^+].$$

That will guide us to the Eq. [1], $[OH^-] = [OH^-]_{FREE} + \frac{Kw}{[OH^-]}$, where substituting the OH^- that are in the dissolution due to the base forms the equation $[OH^-] = 10^{-7} + \frac{10^{-14}}{\approx 10^{-7}} = 10^{-7} + \approx 10^{-7}$. The contribution of water is not negligible yet, so we will have to take it into account solving the complete equation $[OH^-] = 10^{-7} + \frac{10^{-14}}{[OH^-]}$, from where it is obtained that $[OH^-] = 10^{-6.79}$M. With these hydroxyls in equilibrium, the H^+ that H_2O provides will be $10^{-7.21}$ M, that will also be the OH^- that H_2O provides to that dissolution.

Thus, the dissolution in equilibrium will be formed by:



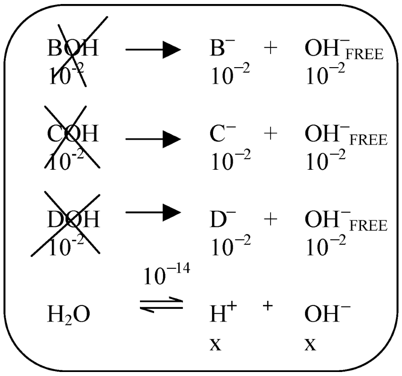
As the hydroxyl condition said, $[OH^-] = 10^{-7} + 10^{-7.21} = 10^{-6.79}$ M. Where the contribution of water is not negligible, it seems that something else happens: *The hydroxyls in equilibrium are additive*, as well as they were the H^+ in equilibrium in the case of the acids.

Following the same reasoning as with the acids, we reach the conclusion that for concentrations of strong base between 10^{-6} and 10^{-8} M the contribution of water is not negligible, so that the complete Eq. [1] will have to be solved.

Finally, for concentrations of base less than 10^{-8} M, the contribution of the base will be negligible, and the hydroxyls in equilibrium are the ones that water provides. That is: $[OH^-] = 10^{-7}$ M.

Mixture of Strong Bases

Let us suppose a dissolution that contains strong bases BOH, COH, and DOH on 10^{-2} M concentrations.



We have a dissolution of strong bases in equilibrium, and we can apply the proton condition:

$$[H^+] = [OH^-] - [OH^-]_{FREE} - [OH^-]_{FREE} - [OH^-]_{FREE}$$

that written in order will lead us to:

$$[OH^-] = [OH^-]_{FREE} + [OH^-]_{FREE} + [OH^-]_{FREE} + [H^+]$$

that would be the same result if we applied the hydroxyl condition. In the dissolution there appear as many OH^- as the sum of free hydroxyls, plus as many OH^- as H^+ due to water.

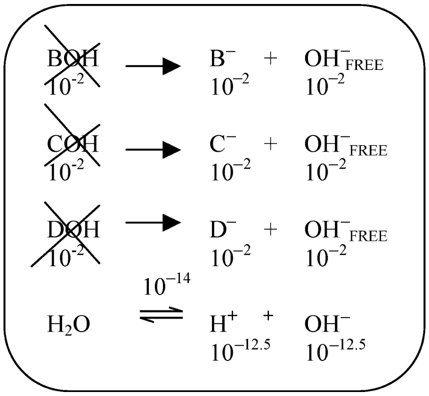
Substituting the concentrations of OH^-_{FREE} and writing the protons of water according to the OH^- that the dissolution has in equilibrium:

$$[OH^-] = \sum [OH^-]_{FREE} + \frac{Kw}{[OH^-]} \qquad [2]$$

that is the *general equation for mixture of strong bases*

In this case we will have $[OH^-] = 3 \times 10^{-2} + \frac{10^{-14}}{[OH^-]}$, and if we take into account that in the dissolution there are at least 3×10^{-2} M hydroxyls, we will get $[OH^-] = 3 \times 10^{-2} + \frac{10^{-14}}{\approx 3\times 10^{-2}} = 3 \times 10^{-2} + \approx \cancel{10}^{-12.5} = 3 \times 10^{-2}$ M. The hydroxyls of the dissolution are due to the strong base, and what water provides to this dissolution, from H^+ and from OH^-, will be $10^{-12.5}$ M.

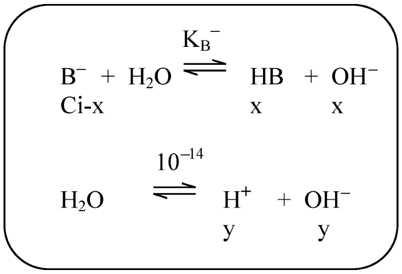
Thus, the dissolution in equilibrium will be formed in the following way:



where the hydroxyls in equilibrium are: $[OH^-] = [OH^-]_{FREE} + [OH^-]_{FREE} + [OH^-]_{FREE} + [H^+] = 10^{-2} + 10^{-2} + 10^{-2} + \cancel{10}^{-12.5} = 3 \times 10^{-2}$ M

Monoprotic Weak Base

Let us suppose a weak B^-in concentration Ci and K_B^- that in dissolution will be:



Applying the proton condition, we observe that as many H^+ as OH^- appear due to the equilibrium of H_2O. And as many H^+ disappear as HB appear, that will be the same as the OH^- that appear: $[H^+] = [OH^-] - [HB]$. Writing it in order will be:

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

that is really the hydroxyl condition; as many OH^- as HB appear due to base B^-, plus as many OH^- as H^+ due to water.

Writing the concentration of HB according to the initial concentration of B^- and of the OH^- that the dissolution has in equilibrium, and the H^+ according to the OH^- in equilibrium leads to:

$$[OH^-] = \frac{K_{B^-}[B^-]}{K_{B^-} + [OH^-]} + \frac{K_w}{[OH^-]} \qquad [3]$$

that is the *general equation for weak monoprotic base* that will be able to be applied to any dissolution of weak base, and that will be simplified, depending on the cases, in a similar way to what was observed in the dissolutions of weak monoprotic acids. Thus, we will suppose that what the weak base dissociates is negligible in contrast with the initial concentration, so that we will get the simplified equation:

$$[OH^-] = \frac{K_{B^-}[B^-]}{[OH^-]} + \frac{K_w}{[OH^-]}, \qquad \text{from where we get that:}$$

$$[OH^-] = \sqrt{K_{B^-}[B^-] + K_w} \qquad [4]$$

What the Weak Base Dissociates is Negligible in Contrast With its Initial Cconcentration

Let us suppose a dissolution of NH_3 with pK = 4.8 and concentration 1 M. We will have in dissolution:

$$\begin{array}{lllll}
NH_3 & + H_2O & \overset{10^{-4.8}}{\rightleftharpoons} & NH_4^+ & + OH^- \\
1\text{-}x & & & x & x \\
 & & & & \\
H_2O & & \overset{10^{-14}}{\rightleftharpoons} & H^+ & + OH^- \\
 & & & y & y
\end{array}$$

In the dissolution as many protons as OH^- will appear due to water, and as protons disappear NH_4^+ appear due to the ammonia:

$$[H^+] = [OH^-] - [NH_4^+]$$

that putting it in order guides us to the hydroxyl condition:

$$[OH^-] = [NH_4^+] + [H^+]$$

and that leads us to a similar equation to the Eq. [3]:

$$[OH^-] = \frac{K_{NH_3}[NH_3]}{K_{NH_3} + [OH^-]} + \frac{K_w}{[OH^-]} \qquad [5]$$

and where supposing that what the ammonia dissociates is negligible in contrast with its initial concentration, we get that:

$$[OH^-] = \sqrt{K_{NH_3}[NH_3] + K_w} = \sqrt{10^{-4.8} \times 1 + \xcancel{10}^{-14}}$$
$$= 10^{-2.4}\ \text{M.Thus,} [OH^-] = 10^{-2.4}\ \text{M} = [NH_4^+].$$

The supposition made is valid, $1 - 10^{-2.4} = 1$. The $[OH^-]$ that water provides to that dissolution will be $10^{-11.6}$ M, that will be the same quantity as the protons that water provides. The dissolution in equilibrium will be.

$$\begin{array}{lllll}
NH_3 & + H_2O & \overset{10^{-4.8}}{\rightleftharpoons} & NH_4^+ & + OH^- \\
1 & & & 10^{-2.4} & 10^{-2.4} \\
 & & & & \\
H_2O & & \overset{10^{-14}}{\rightleftharpoons} & H^+ & + OH^- \\
 & & & 10^{-11.6} & 10^{-11.6}
\end{array}$$

where it is pointed out that the OH^- in equilibrium are additive, although the contribution of water is negligible in contrast with the contribution of ammonia: $[OH^-] = 10^{-2.4} + \xcancel{10}^{-11.6} = 10^{-2.4}$ M. And where every equilibria continue being fulfilled: $\frac{10^{-2.4} \times 10^{-2.4}}{1} = 10^{-4.8} = K_{NH_3}$, and $10^{-2.4} \times 10^{-11.6} = 10^{-14} = K_w$.

The Contribution of the Dissolvent is Not Negligible

Let us suppose a dissolution of o-Phenanthroline (Phen) 10^{-4} M and with pK = 9.0.

$$\begin{array}{lllll}
Phen & + H_2O & \overset{10^{-9.0}}{\rightleftharpoons} & Phen\text{-}H^+ & + OH^- \\
10^{-4}\text{-}x & & & x & x \\
 & & & & \\
H_2O & & \overset{10^{-14}}{\rightleftharpoons} & H^+ & + OH^- \\
 & & & y & y
\end{array}$$

Dissolution that is in equilibrium and to which we can apply the proton condition:

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

that written in order leads us to the hydroxyl condition:

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

Substituting $[H^+]$ and $[Phen\text{-}H^+]$ by $[OH^-]$ in equilibrium and by the initial concentration of Phen we reach: $[OH^-] = \sqrt{K_{fen}[Phen] + K_w} = \sqrt{10^{-9.0} \times 10^{-4} + 10^{-14}} = \sqrt{10^{-13} + 10^{-14}} = 10^{-6.48}$M, where it is observed that the contribution of water is not negligible. With these hydroxyls in equilibrium we will obtain $[Phen\text{-}H^+]$ and $[H^+]$ that are in that dissolution in equilibrium, $[Phen\text{-}H^+] = 10^{-6.52}$ M and $[H^+] = [OH^-] = 10^{-7.52}$ M due to the equilibrium of water. Again, what the base dissociates is negligible comparing with the initial concentration, $10^{-4} - 10^{-6.52} = 10^{-4}$ M.

Then the dissolution in equilibrium will be:

$$\begin{array}{llll} \text{Phen} + H_2O & \overset{10^{-9.0}}{\rightleftharpoons} & \text{Phen-H}^+ & + OH^- \\ 10^{-4} & & 10^{-6.52} & 10^{-6.52} \\ \\ H_2O & \overset{10^{-14}}{\rightleftharpoons} & H^+ \; + & OH^- \\ & & 10^{-7.52} & 10^{-7.52} \end{array}$$

As the proton condition in equilibriums, or the hydroxyl condition, states is the same: $[OH^-] = [H^+] + [\text{Phen-H}^+] = 10^{-7.52} + 10^{-6.52} = 10^{-6.48}$ M. That is, the OH^- that the base o-Phenanthroline in equilibrium provides, $10^{-6.52}$, plus the OH^- that water in equilibrium provides, $10^{-7.52}$, are $10^{-6.48}$ M. *The hydroxyls in equilibrium are additive.*

And as the dissolution is in equilibrium, all the equilibria are being fulfilled: $\frac{10^{-6.52}\times 10^{-6.48}}{10^{-4}} = 10^{-9.0} = K_{\text{Phen}}$, and $10^{-6.48} \times 10^{-7.52} = 10^{-14} = K_w$.

Mixture of Strong Base and Weak Base

Let us suppose a dissolution that contains a strong base AOH and a weak base B^- with a constant K_B—and concentrations Ci.

The dissolution in equilibrium will be:

$$\begin{array}{llll} \cancel{\text{AOH}} & \longrightarrow & A^- \; + & OH^-_{\text{FREE}} \\ \cancel{\text{Ci}} & & \text{Ci} & \text{Ci} \\ \\ B^- + H_2O & \overset{K_{B^-}}{\rightleftharpoons} & HB + & OH^- \\ \text{Ci-x} & & x & x \\ \\ H_2O & \overset{10^{-14}}{\rightleftharpoons} & H^+ & + OH^- \\ & & y & y \end{array}$$

from where it can be obtained that:

$$[OH^-] = [OH^-]_{\text{FREE}} + [HB] + [H^+]$$

where writing every term according to the initial concentrations and to the OH^- in equilibrium it leads to:

$$[OH^-] = [OH^-]_{\text{FREE}} + \frac{K_{B^-}[HB]}{K_{B^-} + [OH^-]} + \frac{Kw}{[OH^-]} \qquad [6]$$

that is the *general equation for mixture of strong base and weak base,* and that can be simplified depending on the conditions of the dissolution.

The Contribution of Weak Base is Negligible

Let us suppose a mixture of NaOH 10^{-2} M and OAc^- 10^{-2} M with $pK_{OAc^-} = 9.2$.

The dissolution in equilibrium contains:

$$\begin{array}{llll} \cancel{\text{NaOH}} & \longrightarrow & Na+ \; + & OH^-_{\text{FREE}} \\ 10^{-2} & & 10^{-2} & 10^{-2} \\ \\ OAc^- + H_2O & \overset{10^{-9.2}}{\rightleftharpoons} & HOAc & + OH^- \\ 10^{-2}\text{-x} & & x & x \\ \\ H_2O & \overset{10^{-14}}{\rightleftharpoons} & H^+ \; + & OH^- \\ & & y & y \end{array}$$

We have a dissolution that contains two bases and water in equilibrium, and to which we apply the hydroxyl condition:

$$[OH^-]=[OH^-]_{\text{FREE}}+[HOAc]+[H^+].$$

Supposing that what OAc^-dissociates is negligible comparing to the initial concentration, it leads to the expression: $[OH^-] = [OH^-]_{\text{FREE}} + \frac{K_{OAc^-}[OAc^-]}{[OH^-]} + \frac{K_w}{[OH^-]}$.Substituting the values of the constants, and taking into account that in the dissolution there are at least 10^{-2} M of OH^- due to NaOH, it is obtained that $[OH^-] = 10^{-2} + \frac{10^{-9.2}\times 10^{-2}}{\approx 10^{-2}} + \frac{10^{-14}}{\approx 10^{-2}} = 10^{-2} + \approx \cancel{10}^{-9.2} + \approx \cancel{10}^{-12} = 10^{-2}$M where it is showed that the hydroxyls provided by weak base and by water are negligible to the ones that the strong base provides.

The hydroxyls in equilibrium are the ones that the NaOH provides, as it was expected. From their respective constants and the OH^- in equilibrium, we obtain the concentrations: $[HOAc] = 10^{-9.2}$ M, $[H^+] = 10^{-12}$ M and $[OAc^-] = 10^{-2} - 10^{-9.2} = 10^{-2}$ M; the hydrolysis of the OAc^- is negligible.

The dissolution in equilibrium will be:

$$\begin{array}{llll} \cancel{\text{NaOH}} & \longrightarrow & Na+ \; + & OH^-_{\text{FREE}} \\ \cancel{10^{-2}} & & 10^{-2} & 10^{-2} \\ \\ OAc^- + H_2O & \overset{10^{-9.2}}{\rightleftharpoons} & HOAc & + OH^- \\ 10^{-2} & & 10^{-9.2} & 10^{-9.2} \\ \\ H_2O & \overset{10^{-14}}{\rightleftharpoons} & H^+ \; + & OH^- \\ & & 10^{-12} & 10^{-12} \end{array}$$

The OH^- in equilibrium are additive: $[OH^-] = 10^{-2} + \cancel{10}^{-9.2} + \cancel{10}^{-12} = 10^{-2}$ M, and all the equilibria are fulfilled in the dissolution.

The Contribution of the Weak Base is not Negligible. Let us suppose a mixture of NaOH 10^{-2} M and NH_3 1 M with $pK = 4.8$.

The dissolution in equilibrium contains:

$$\begin{array}{lclll}
\cancel{\mathrm{NaOH}} & \longrightarrow & \mathrm{Na+} & + & \mathrm{OH^-_{FREE}} \\
\cancel{10^{-2}} & & 10^{-2} & & 10^{-2} \\[2ex]
\mathrm{NH_3 + H_2O} & \overset{10^{-4.8}}{\rightleftharpoons} & \mathrm{NH_4^+} & + & \mathrm{OH^-} \\
1\text{- } x & & x & & x \\[2ex]
\mathrm{H_2O} & \overset{10^{-14}}{\rightleftharpoons} & \mathrm{H^+} & + & \mathrm{OH^-} \\
 & & y & & y
\end{array}$$

from where it is obtained that:

$$[OH^-] = [OH^-]_{FREE} + [NH_4^+] + [H^+]$$

and supposing that what NH_3 dissociates is negligible comparing to the initial concentration, it leads to the expression: $[OH^-] = [OH^-]_{FREE} + \frac{K_{NH_3}[NH_3]}{[OH^-]} + \frac{K_w}{[OH^-]}$.Substituting the values of the constants, and taking into account that in the dissolution there are at least 10^{-2} M of OH^- due to NaOH, it is obtained that $[OH^-] = 10^{-2} + \frac{10^{-4.8}\times 1}{\approx 10^{-2}} + \frac{10^{-14}}{\approx 10^{-2}} = 10^{-2} + \approx 10^{-2.8} + \approx \cancel{10}^{-12}$, where it is pointed out that the contribution of water is negligible, though the contribution of ammonia is not negligible yet. Thus, we will have to solve our problem taking into account the contribution of the strong base and the contribution of the weak base: $[OH^-] = [OH^-]_{FREE} + \frac{K_{NH_3}[NH_3]}{[OH^-]} = 10^{-2} + \frac{10^{-4.8}\times 1}{[OH^-]}$,from where we get the second grade equation $[OH^-]^2 - 10^{-2}[OH^-] - 10^{-4.8} = 0$ that once solved gives us $[OH^-] = 10^{-1.94}$ M.

Once known the concentration of OH^- in equilibrium, we can obtain the concentration of all the other species of the dissolution: $[NH_4^+] = 10^{-2.86}$ M $= [OH^-]$ that the equilibrium of ammonia provides, $[NH_3] = 1 - 10^{-2.86} = 1$ M (the supposition made of what the NH_3 dissociates is negligible is valid), and the concentration of protons that water provides to that dissolution will be $[H^+] = 10^{-12.06}$ M $= [OH^-]$ that water also provides.

Then the dissolution in equilibrium will be:

$$\begin{array}{lclll}
\cancel{\mathrm{NaOH}} & \longrightarrow & \mathrm{Na^+} & + & \mathrm{OH^-_{FREE}} \\
\cancel{10^{-2}} & & 10^{-2} & & 10^{-2} \\[2ex]
\mathrm{NH_3 + H_2O} & \overset{10^{-4.8}}{\rightleftharpoons} & \mathrm{NH_4^+} & + & \mathrm{OH^-} \\
1 & & 10^{-2.86} & & 10^{-2.86} \\[2ex]
\mathrm{H_2O} & \overset{10^{-14}}{\rightleftharpoons} & \mathrm{H^+} & + & \mathrm{OH^-} \\
 & & 10^{-12.06} & & 10^{-12.06}
\end{array}$$

The hydroxyls in equilibrium continue being additive: $[OH^-] = 10^{-2} + 10^{-2.86} + \cancel{10}^{-12.06} = 10^{-1.94}$ M. And in the dissolution all the equilibria are being fulfilled: $\frac{10^{-2.86}\times 10^{-1.94}}{1} = 10^{-4.8} = K_{NH_3}$, and $10^{-12.06} \times 10^{-1.94} = 10^{-14} = K_w$.

Mixture of Weak Bases

Let us suppose a mixture of OAc^- 1 M with $pK_{OAc^-} = 9.2$ and BO_2^- 1 M with $pK_{BO_2^-} = 4.8$.

$$\begin{array}{lclll}
\mathrm{OAc^- + H_2O} & \overset{10^{-9.2}}{\rightleftharpoons} & \mathrm{HOAc} & + & \mathrm{OH^-} \\
1\text{-}x & & x & & x \\[2ex]
\mathrm{BO_2^- + H_2O} & \overset{10^{-4.8}}{\rightleftharpoons} & \mathrm{HBO_2} & + & \mathrm{OH^-} \\
1\text{-}y & & y & & y \\[2ex]
\mathrm{H_2O} & \overset{10^{-14}}{\rightleftharpoons} & \mathrm{H^+} & + & \mathrm{OH^-} \\
 & & z & & z
\end{array}$$

Applying the hydroxyl condition we will have:

$$[OH^-] = [HOAc] + [HBO_2] + [H^+]$$

where substituting every term by the initial concentrations and the OH^- in equilibrium, the following equation is reached:

$$[OH^-] = \frac{K_{OAc^-}[OAc^-]}{[OH^-]} + \frac{K_{BO_2^-}[BO_2^-]}{[OH^-]} + \frac{K_w}{[OH^-]} \qquad [7]$$

that is the *general equation for mixture of two weak bases*, and operating it is obtained:

$$\begin{aligned}
[OH^-] &= \sqrt{K_{OAc^-}[OAc^-] + K_{BO_2^-}[BO_2^-] + K_w} \\
&= \sqrt{\cancel{10}^{-9.2}\times 1 + 10^{-4.8}\times 1 + \cancel{10}^{-14}} = 10^{-}2.4\ \text{M}.
\end{aligned}$$

The hydroxyls of the dissolution in equilibrium are due to the strongest base BO_2^-, and the contributions of H_2O and OAc^- are negligible. Once the OH^- in equilibrium is known, we will obtain the concentrations of the rest of the species in the dissolution: $[HBO_2] = [OH^-] = 10^{-2.4}$ M as it is the main equilibrium, so the supposition made is valid $(1 - 10^{-2.4} = 1)$, $[HOAc] = 10^{-6.8}$ M $= [OH^-]$ that OAc^- provides to the dissolution, and the $[OH^-]$ that H_2O provides will be $10^{-11.6}$ M (that will be equal to $[H^+]$).

The dissolution in equilibrium will be formed by:

$$\begin{array}{lcccc} OAc^- + H_2O & \overset{10^{-9.2}}{\rightleftharpoons} & HOAc & + & OH^- \\ 1 & & 10^{-6.8} & & 10^{-6.8} \\ BO_2{}^- + H_2O & \overset{10^{-4.8}}{\rightleftharpoons} & HBO_2 & + & OH^- \\ 1 & & 10^{-2.4} & & 10^{-2.4} \\ H_2O & \overset{10^{-14}}{\rightleftharpoons} & H^+ & + & OH^- \\ & & 10^{-11.6} & & 10^{-11.6} \end{array}$$

The hydroxyls in the dissolution continue being additive: $[OH^-] = \cancel{10}^{-6.8} + 10^{-2.4} + \cancel{10}^{-11.6} = 10^{-2.4}$ M and all the equilibria are being fulfilled.

DISSOLUTIONS OF SALTS

To solve problems of dissolutions of salts, we will have to take into account that they are strong electrolytes and as a consequence, they are completely dissociated in the dissolvent H_2O. Once dissociated in the ions, we will apply to the ions that provide the dissolution the possible equilibria that take place with the dissolvent to reach the dissolution in equilibrium. To the dissolution in equilibrium we will apply the proton condition or the hydroxyl condition.

Salt of Strong Acid and Strong Base

Let us suppose a dissolution of NaCl 10^{-2} M.

As a consequence of the dissociation of NaCl, in the dissolution we will have Na^+ 10^{-2} M and Cl^- 10^{-2} M; as Na^+ comes from a strong base, it is a neutral cation (it doesn't give any acid-base reaction), and as the anion Cl^-comes from a strong acid, it will also be neutral. Then, in the dissolution in equilibrium we will have:

$$\begin{array}{lcccc} \cancel{Na^+} + H_2O & \longrightarrow & Na^+ & + & H_2O \\ \cancel{C_i} & & C_i & & \\ \cancel{Cl^-} + H_2O & \longrightarrow & Cl^- & + & H_2O \\ \cancel{C_i} & & C_i & & \\ H_2O & \overset{10^{-14}}{\rightleftharpoons} & H^+ & + & OH^- \\ & & x & & x \end{array}$$

The only species with acid-base properties is water, so that applying the proton condition we will have: $[H^+] = [OH^-] = 10^{-7}$ M. If we had applied the hydroxyl condition, the solution would have been the same: $[OH^-] = [H^+] = 10^{-7}$M.

Salt of Weak Acid and Strong Base

Let us suppose a salt of NaOAc 10^{-2} M and with $pK_{OAc^-} = 9.2$. NaOAc is completely dissociated to give ions Na^+ 10^{-2} M and OAc^- 10^{-2} M, that in the dissolution will be:

$$\begin{array}{lcccc} \cancel{Na^+} + H_2O & \longrightarrow & Na^+ & + & H_2O \\ \cancel{10^{-2}} & & 10^{-2} & & \\ OAc^- + H_2O & \overset{10^{-9.2}}{\rightleftharpoons} & HOAc & + & OH^- \\ 10^{-2}\text{-}x & & x & & x \\ H_2O & \overset{10^{-14}}{\rightleftharpoons} & H^+ & + & OH^- \\ & & y & & y \end{array}$$

In the dissolution there appear as many protons as OH^- due to H_2O, and disappear as many protons as HOAc appear due to the equilibrium of OAc^-. Na^+, a neutral cation, does not have an effect on the acid-base equilibrium of the dissolution (it has an effect on the ionic force, but that is not a matter of concern now).

Applying the proton condition we have:

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

that written in order leads us to the hydroxyl condition:

$$[OH^-] = [HOAc] + [H^+].$$

As can be observed, the solution of a dissolution of salt of weak acid and strong base is exactly the same as that of a dissolution of the weak base OAc^- in water. Substituting [HOAc] and $[H^+]$ by the initial concentrations and the hydroxyls in equilibrium leads to:

$[OH^-] = \frac{10^{-9.2}[OAc^-]}{[OH^-]} + \frac{10^{-14}}{[OH^-]}$, that is similar to the Eq. [4] that was obtained for weak base and that leads us to $[OH^-] = \sqrt{10^{-9.2} \times 10^{-2} + 10^{-14}} = \sqrt{10^{-11.2} + \cancel{10}^{-14}} = 10^{-5.6}$ M $=$ [HOAc], $[OAc^-] = 10^{-2} - 10^{-5.6} = 10^{-2}$M, y and $[H^+] = 10^{-8.4}$M.

Salt of Strong Acid and Weak Base

Let us suppose a dissolution of NH_4NO_3 10^{-2} M and with $pK_{NH_4^+} = 9.2$.

We will have in the dissolution NH_4^+ 10^{-2} M and NO_3^- 10^{-2} M that will be fulfilling their respective equilibria in the following way:

$$\begin{array}{lcll}
\cancel{\mathrm{NO_3^-}} + \mathrm{H_2O} & \longrightarrow & \mathrm{NO_3^-} + \mathrm{H_2O} & \\
\cancel{10^{-2}} & & 10^{-2} & \\[1em]
\mathrm{NH_4^+} & \xrightleftharpoons{10^{-9.2}} & \mathrm{NH_3} \ + & \mathrm{H^+} \\
10^{-2}\text{-}x & & x & x \\[1em]
\mathrm{H_2O} & \xrightleftharpoons{10^{-14}} & \mathrm{H^+} \ + & \mathrm{OH^-} \\
 & & y & y
\end{array}$$

The anion NO_3^- doesn't have any influence on the equilibrium because it is neutral, so that we are in front of a dissolution of weak acid, NH_4^+, in water:

$[H^+] = [NH_3] + [OH^-]$

that we already know how to solve (8).

Salt of Weak acid and Weak Base

Let us suppose a dissolution of NH_4F 10^{-1} M, with $pK_{NH_4^+} = 9.2$ and $pK_{F^-} = 10.8$.

In the dissolution, we will have NH_4^+ 10^{-1} M and F^- 10^{-1} M fulfilling their corresponding equilibria:

$$\begin{array}{lcll}
\mathrm{NH_4^+} & \xrightleftharpoons{10^{-9.2}} & \mathrm{NH_3} \ + & \mathrm{H^+} \\
10^{-1}\text{-}x & & x & x \\[1em]
\mathrm{F^-} + \mathrm{H_2O} & \xrightleftharpoons{10^{-10.8}} & \mathrm{HF} \ + & \mathrm{OH^-} \\
10^{-1}-y & & y & y
\end{array}$$

As we have an acid, NH_4^+, that provides H^+ to the dissolution and a base, F^- that provides OH^-, it will have to be questioned if the dissolution is in equilibrium (if what prevails in the dissolution in equilibrium are the species of the beginning).

In this dissolution, what will happen is that the H^+ will react with the OH^- to form H_2O. And if they were H^+_{FREE} and OH^-_{FREE}, $K = 10^{+14}$. But as they come from weak acid and weak base, they are subject to their corresponding equilibria and they will have to be taken into account. Thus, traditionally in the dissolution the following equilibria will be formed:

$$\begin{array}{lcll}
\mathrm{NH_4^+} & \xrightleftharpoons{10^{-9.2}} & \mathrm{NH_3} \ + & \mathrm{H^+} \\
10^{-1}\text{-}x & & x & x \\[1em]
\mathrm{F^-} + \mathrm{H_2O} & \xrightleftharpoons{10^{-10.8}} & \mathrm{HF} \ + & \mathrm{OH^-} \\
10^{-1}-y & & y & y \\[1em]
\mathrm{H^+} + \mathrm{OH^-} & \xrightleftharpoons{10^{+14}} & \mathrm{H_2O} & \\
x \quad\ y & & & \\
\hline
\mathrm{NH_4^+} + \mathrm{F^-} & \xrightleftharpoons{K = 10^{-6.0}} & \mathrm{NH_3} + \mathrm{HF} &
\end{array}$$

The value of the K of the reaction of NH_4^+ with F^- will be the product of the constants:

$K = 10^{-9.2} \times 10^{-10.8} \times 10^{+14} = 10^{-6.0}$. The value that points out that the ammonium reacts with the fluoride, but in a small extension, so that we can assure that the dissolution is in equilibrium, and prevails NH_4^+ 10^{-1} M and F^- 10^{-1} M.

Personally, I think what really happens is that the F^- directly reacts with the H^+ of NH_4^+, that are freer protons than those of H_2O, as it is a stronger acid. Then, the reaction will be:

$$\begin{array}{lcll}
\mathrm{NH_4^+} & \xrightleftharpoons{10^{-9.2}} & \mathrm{NH_3} \ + & \mathrm{H^+} \\
10^{-1}\text{-}x & & x & x \\[1em]
\mathrm{F^-} \ + \ \mathrm{H^+} & \xrightleftharpoons{10^{+3.2}} & \mathrm{HF} & \\
10^{-1}\text{-}x \quad x & & x & \\
\hline
\mathrm{NH_4^+} + \mathrm{F^-} & \xrightleftharpoons{K} & \mathrm{NH_3} + \mathrm{HF} &
\end{array}$$

where the value of the constant continues being the same: $K = 10^{-9.2} \times 10^{+3.2} = 10^{-6.0}$.

Anyway, the same dissolution in equilibrium is reached:

A)

$$\begin{array}{lcll}
\mathrm{NH_4^+} & \xrightleftharpoons{10^{-9.2}} & \mathrm{NH_3} \ + & \mathrm{H^+} \\
\mathrm{F^-} + \mathrm{H_2O} & \xrightleftharpoons{10^{-10.8}} & \mathrm{HF} \ + & \mathrm{OH^-} \\
\mathrm{H_2O} & \xrightleftharpoons{10^{-14}} & \mathrm{H^+} \ + & \mathrm{OH^-}
\end{array}$$

B)

$$\begin{array}{lcll}
\mathrm{NH_4^+} & \xrightleftharpoons{10^{-9.2}} & \mathrm{NH_3} \ + & \mathrm{H^+} \\
\mathrm{F^-} + \mathrm{H^+} & \xrightleftharpoons{10^{+3.2}} & \mathrm{HF} & \\
\mathrm{H_2O} & \xrightleftharpoons{10^{-14}} & \mathrm{H^+} \ + & \mathrm{OH^-}
\end{array}$$

However, by means of Scheme A it can be anticipated how the dissolution in equilibrium will end, acid or basic. In this case, the dissolution has to be acid because with the constants observed, the acid, NH_4^+, is slightly stronger than the base, F^-. To any of the two schemes we can apply the proton condition in equilibrium, getting the same solution:

$$[H^+] = [NH_3] + [OH^-] - [HF]$$

that once written in order becomes: $[H^+] + [HF] = [NH_3] + [OH^-]$.

Substituting every term by the initial concentrations and the protons in equilibrium, and supposing that what both reactions move towards the right is negligible in contrast with the initial concentrations, leads to: $[H^+] + \frac{[H^+]\times[F^-]}{K_{HF}} = \frac{K_{NH_4^+}\times[NH_4^+]}{[H^+]} + \frac{K_w}{[H^+]}$, where operating it leads to the expression:

$$[H^+] = \sqrt{\frac{K_{NH_4^+}[NH_4^+] + K_w}{1 + \frac{[F^-]}{K_{HF}}}} \qquad [8]$$

that is the *general equation for salt of weak acid and weak base*, and that can be simplified depending on the conditions:

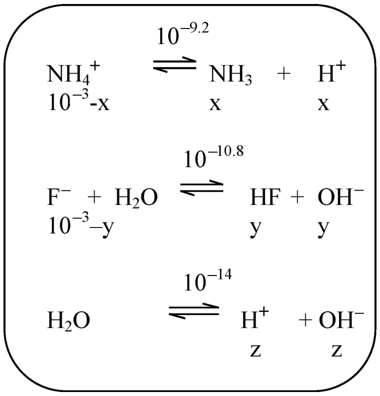
- If $K_{NH_4^+} \times [NH_4^+] >> K_w \Rightarrow K_w$ is negligible.
- If $[F^-] >> K_{HF} \Rightarrow 1$ is negligible.

We get the simplified equation: $[H^+] = \sqrt{K_{NH_4^+} \times K_{HF}} = \sqrt{10^{-9.2} \times 10^{-3.2}} = 10^{-6.2}$ M, because in equilibrium $[NH_4^+] = [F^-]$. And as we had expected, the dissolution in equilibrium is lightly acid. From the corresponding constants, it is obtained: $[HF] = \frac{10^{-6.2}\times10^{-1}}{10^{-3.2}} = 10^{-4}$M, $[OH^-] = 10^{-7.8}$ M, and $[NH_3] = \frac{10^{-9.2}\times10^{-1}}{10^{-6.2}} = 10^{-4}$ M. What both species react is negligible in contrast with the initial concentration (10^{-1}-10^{-4} = 10^{-1}), and $[NH_4^+] = [F^-] = 10^{-1}$ M.

It can attract someone's attention the fact that the H^+ that the NH_4^+ provides are not the same as the NH_3, and that the OH^- that the F^- provides are not the same as the HF. Well, initially the NH_4^+ will provide $[H^+] = 10^{-4}$ M and F^- will provide $[OH^-] = 10^{-4}$ M. But these protons and these hydroxyls would not be in equilibrium because $10^{-4} \times 10^{-4} > Kw$, so that they will react until they reach the situation of equilibrium. In fact, a dissolution that contains NH_4^+ 10^{-1} M and NH_3 10^{-4} M has to have $10^{-6.2}$ M of H^+ in equilibrium, and a dissolution that contains F^- 10^{-1} M and HF 10^{-4} M has to have $10^{-7.8}$ M of OH^- in equilibrium.

What happens in this dissolution is that the equilibrium that prevails is: $NH_4^+ + F^- \rightleftharpoons NH_3 + HF$; this determines conditions that in the dissolution in equilibrium are $[NH_4^+] = [F^-] = 10^{-1}$ M and $[NH_3] = [HF] = 10^{-4}$ M, that works as a buffer dissolution, as Butler said (9).

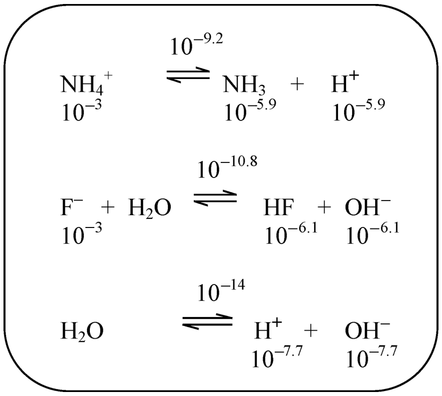
Let us see what happens if we dilute the dissolution of the beginning. Let us suppose a dissolution of salt NH_4F 10^{-3} M. We will have in dissolution:



Applying the proton condition, we reach:

$$[H^+] = \sqrt{\frac{10^{-9.2} \times 10^{-3} + 10^{-14}}{1 + \frac{10^{-3}}{10^{-3.2}}}} = \sqrt{\frac{10^{-12.2} + 10^{-14}}{1 + 10^{+0.2}}} = 10^{-6.3} \text{ M.}$$

In the general expression it is observed that no term is negligible yet, and the protons in equilibrium are $10^{-6.3}$ M. With these protons in equilibrium and from their respective constants, the concentrations of all the species in the dissolution are obtained: $[NH_3] = 10^{-5.9}$ M, $[HF] = 10^{-6.1}$ M, $[NH_4^+] = 10^{-3} - 10^{-5.9} = 10^{-3}$M, $[F^-] = 10^{-3} - 10^{-6.1} = 10^{-3}$ M, and $[OH^-] = 10^{-7.7}$ M, so that the dissolution in equilibrium will be:



The protons in equilibrium will be $[H^+] = 10^{-5.9} - 10^{-6.1} + 10^{-7.7} = 10^{-6.3}$ M, and as a consequence of the dilution, the buffer effect does not prevail yet. The H^+ that the NH_4^+ provides are the same as the NH_3, and the OH^- that the F^- provides are the same as the HF. Furthermore, the contribution of H_2O is not negligible yet.

Solutions of Amphiprotic Substances

Let us suppose a dissolution of $NaHCO_3$ of concentration 10^{-1} M and with the following constants for H_2CO_3: $pK_1 = 6.4$ and $pK_2 = 10.3$.

We will have in dissolution Na^+ 10^{-1} M and HCO_3^- 10^{-1} M that will be fulfilling their respective equilibria. As it has been observed on the previous parts, Na^+ doesn't produce any acid-base reaction, so we won't take it into account. Thus, the dissolution will contain HCO_3^- that will be able to work as acid or base, as amphiprotic substance, that is:

$$\begin{array}{lllcll}
 & HCO_3^- & & \overset{10^{-10.3}}{\rightleftharpoons} & CO_3^{2-} + & H^+ \\
 & -x & & & x & x \\
10^{-1} & & & & & \\
 & HCO_3^- & + H_2O & \overset{10^{-7.6}}{\rightleftharpoons} & H_2CO_3 + & OH^- \\
 & -y & & & y & y \\
 & & & & & \\
 & H^+ & + OH^- & \overset{10^{+14}}{\rightleftharpoons} & H_2O & \\
 & x & \;\; y & & & \\
\hline
 & HCO_3^- & + HCO_3^- & \overset{K=10^{-3.9}}{\rightleftharpoons} & CO_3^{2-} + & H_2CO_3
\end{array}$$

The value of K of the reaction of HCO_3^- as acid with HCO_3^- as base, will be the product of the constants: $K = 10^{-10.3} \times 10^{-7.6} \times 10^{+14} = 10^{-3.9}$. This value that points out that HCO_3^- reacts with itself but in a small extension, so that we can assume that in the dissolution in equilibrium what prevails is HCO_3^- 10^{-1} M. With the constants observed, the dissolution in equilibrium must be alkaline.

- If we fix on the dissolution, we will take into account that we are in the same case as in the previous part, a weak acid and a weak base, that can be solved exactly the same way.
- In a similar way to what was observed in the previous case, it is expected that HCO_3^- as base reacts with the H^+ that HCO_3^- gives as acid, as the protons are freer than the ones that H_2O provides.

Anyway, applying the proton condition in equilibrium, the same solution is reached:

$$[H^+] = [CO_3^{2-}] + [OH^-] - [H_2CO_3]$$

that leads us to a similar equation to Eq. [8]

$$[H^+] = \sqrt{\frac{K_2[HCO_3^-] + K_w}{1 + \frac{[HCO_3^-]}{K_1}}} \qquad [9]$$

that is the **general equation for amphiprotic substances**.

And as $K_2 \times [HCO_3^-] >> K_w \Rightarrow$ that K_w is negligible, and as $[HCO_3^-] >> K_1 \Rightarrow$ that 1 is negligible, we get the simplified equation: $[H^+] = \sqrt{K_{H_2CO_3} \times K_{HCO_3^-}} = \sqrt{10^{-6.4} \times 10^{-10.3}} = 10^{-8.35}$ M. Once the protons in equilibrium are known, the concentrations of the rest of the species in the dissolution can be calculated: $[CO_3^{2-}] = 10^{-2.95}$ M, $[H_2CO_3] = 10^{-2.95}$ M, $[HCO_3^-] = 10^{-1} - 2 \times 10^{-2.95} = 10^{-1.01}$ M, and $[OH^-] = 10^{-5.65}$ M.

Once again, we are in front of a stopped up dissolution $[HCO_3^-] = 10^{-1.01}$ M in equilibrium with $[CO_3^{2-}] = [H_2CO_3] = 10^{-2.95}$ M that works as a buffer (10). And if we dilute it enough, it will stop being a buffer in a similar way to what was observed in the previous case.

MIXTURES OF ACIDS AND BASES

Here we will lay out the different possibilities of mixtures of acids and bases.

Mixture of Strong Acid and Strong Base on Equivalent Quantities

Let us suppose the resultant dissolution of mixing 100 mL of HCl 2×10^{-2} M with 100 mL of NaOH 2×10^{-2} M.

The resultant mixture will have 200 mL that initially contains HCl 10^{-2} M and NaOH 10^{-2} M and that in the dissolution will be:

$$\begin{array}{lcll}
\cancel{HCl} & \longrightarrow & Cl^- + & H^+_{FREE} \\
\cancel{10^{-2}} & & 10^{-2} & 10^{-2} \\
\cancel{NaOH} & \longrightarrow & Na+ + & OH^-_{FREE} \\
\cancel{10^{-2}} & & 10^{-2} & 10^{-2}
\end{array}$$

This dissolution is not in equilibrium because $10^{-2} \times 10^{-2} >> K_w$. The H^+_{FREE} will react with the OH^-_{FREE} to give water.

$$\begin{array}{llll}
 & H^+{}_{FREE} + & OH^-{}_{FREE} & \overset{10^{+14}}{\rightleftharpoons} H_2O \\
\text{Initial} & 10^{-2} & 10^{-2} & \\
\text{Equil.} & x & x &
\end{array}$$

The dissolution in equilibrium contains Na^+ 10^{-2} M, Cl^- 10^{-2} M and H_2O that has nothing to do with the initial dissolution.

$$\underset{10^{-2}}{\cancel{Cl^-}} + H_2O \longrightarrow \underset{10^{-2}}{Cl^-} + H_2O$$

$$\underset{10^{-2}}{\cancel{Na^+}} + H_2O \longrightarrow \underset{10^{-2}}{Na^+} + H_2O$$

$$H_2O \overset{10^{-14}}{\rightleftharpoons} \underset{x}{H^+} + \underset{x}{OH^-}$$

where the only species with acid-base properties is water, so that applying the proton condition, we will have: $[H^+] = [OH^-] = 10^{-7}$ M.

Mixture of Strong Acid and Strong Base in no Equivalent Quantities

Let us suppose a dissolution of the result of mixing 100 mL of HCl 4×10^{-2} M with 100 mL of NaOH 2×10^{-2} M.

The resultant mixture will have 200 mL that initially contains HCl 2×10^{-2} M and NaOH 10^{-2} M and that in dissolution will be:

$$\underset{2\cdot10^{-2}}{\cancel{HCl}} \longrightarrow \underset{2\cdot10^{-2}}{Cl^-} + \underset{2\cdot10^{-2}}{H^+_{FREE}}$$

$$\underset{10^{-2}}{\cancel{NaOH}} \longrightarrow \underset{10^{-2}}{Na+} + \underset{10^{-2}}{OH^-_{FREE}}$$

The dissolution is not in equilibrium because $2{\cdot}10^{-2} \times 10^{-2} >> K_w$. The $H^+{}_{FREE}$ will react with the $OH^-{}_{FREE}$ to give water:

$$H^+{}_{FREE} + OH^-{}_{FREE} \overset{10^{+14}}{\rightleftharpoons} H_2O$$

$$\begin{array}{lll} \text{Initial} & 2{\cdot}10^{-2} & 10^{-2} \\ \text{Equil.} & 10^{-2} & x \end{array}$$

The dissolution in equilibrium contains Na^+ 10^{-2} M, Cl^- $2{\cdot}10^{-2}$ M, $H^+{}_{FREE}$ 10^{-2} M and H_2O, and it will be:

$$H^+_{FREE} \quad 10^{-2}$$

$$\underset{2\cdot10^{-2}}{\cancel{Cl^-}} + H_2O \longrightarrow \underset{2\cdot10^{-2}}{Cl^-} + H_2O$$

$$\underset{10^{-2}}{\cancel{Na^+}} + H_2O \longrightarrow \underset{10^{-2}}{Na^+} + H_2O$$

$$H_2O \overset{10^{-14}}{\rightleftharpoons} \underset{x}{H^+} + \underset{x}{OH^-}$$

Applying the proton condition we will have:

$$[H^+] = [H^+{}_{FREE}] + [OH^-]$$

that we already know how to solve (8).

It can be pointed out that in the dissolution in equilibrium the $[H^+]_{FREE}$ is not the same as the [HCl] initially written.

Mixture of Strong Acid and Weak Base on Equivalent Quantities

Let us suppose the mixture of 100 mL of HCl 2×10^{-1} M plus 100 mL of NH_3 2×10^{-1} M, $pK_{NH_3} = 4.8$.

The resultant dissolution is 200 mL that initially contains HCl 10^{-1} M and NH_3 10^{-1} M and that will be in dissolution:

$$\cancel{HCl} \longrightarrow Cl^- + H^+_{FREE}$$

$$NH_3 + H^+_{FREE} \overset{10^{+9.2}}{\rightleftharpoons} NH_4^+$$

$$H_2O \overset{10^{-14}}{\rightleftharpoons} H^+ + OH^-$$

The dissolution will not be in equilibrium because the $H^+{}_{FREE}$ will react with the base NH_3 to give NH_4^+.

We will have to observe what happens with the dissolution in equilibrium; according to the concentrations of acid and base we have:

$$H^+{}_{FREE} + NH_3 \overset{10^{+92}}{\rightleftharpoons} NH_4^+ \qquad [10]$$

$$\begin{array}{lll} \text{Initial} & 10^{-1} & 10^{-1} \\ \text{Equil.} & \times & \times 10^{-1} \end{array}$$

The dissolution in equilibrium contains NH_4^+ 10^{-1}M, Cl^- 10^{-1}M y H_2O, and they will be fulfilling their respective equilibria in the following way:

$$\underset{10^{-1}}{\cancel{Cl^-}} + H_2O \longrightarrow \underset{10^{-1}}{Cl^-} + H_2O$$

$$\underset{10^{-1}\text{-}x}{NH_4^+} \overset{10^{-9.2}}{\rightleftharpoons} \underset{x}{NH_3} + \underset{x}{H^+}$$

$$H_2O \overset{10^{-14}}{\rightleftharpoons} \underset{y}{H^+} + \underset{y}{OH^-}$$

We are in front of a dissolution of weak acid that has nothing to do with the initial dissolution. Applying the proton condition, we reach:

$$[H^+] = [NH_3] + [OH^-]$$

that we already know how to solve (8).

Mixture of Strong Acid and Weak Base on no Equivalent Quantities

Let us suppose a mixture of 100 mL of HCl 4×10^{-1} M plus 100 mL of NH_3 2×10^{-1} M, $pK_{NH_3} = 4.8$.

The resultant dissolution is 200 mL that initially contains HCl 2×10^{-1} M and NH_3 10^{-1} M, and as in the previous case, the $H^+{}_{FREE}$ will react with NH_3 to give NH_4^+, although in this case there is an excess of $H^+{}_{FREE}$.

The dissolution in equilibrium will be:

$$\begin{array}{lcl}
H^+{}_{FREE} \quad 10^{-1} & & \\
\cancel{Cl^-} + H_2O & \longrightarrow & Cl^- + H_2O \\
2 \times 10^{-1} & & 2 \times 10^{-1} \\
NH_4^+ & \overset{10^{-9.2}}{\rightleftharpoons} & NH_3 \;+\; H^+ \\
10^{-1} & & x \qquad\;\; x \\
H_2O & \overset{10^{-14}}{\rightleftharpoons} & H^+ \;+\; OH^- \\
 & & y \qquad\;\; y
\end{array}$$

That way we are in front of a dissolution in equilibrium of mixture of strong acid and weak acid, to which we will be able to apply the proton condition:

$$[H^+] = [H^+]_{FREE} + [NH_3] + [OH^-]$$

that we already know how to solve (8).

Mixture of Weak Acid and Weak Base that Lightly React with Each Other

Let us suppose a resultant dissolution of mixing 100 mL of HBO_2 2×10^{-1} M + 100 mL of NaF 2×10^{-1} M, pK of $HBO_2 = 9.2$ and pK of HF = 3.2.

Initially, in the 200 mL of dissolution we will have HBO_2 0.1 M, Na^+ 10^{-1} M and F^- 10^{-1} M due to the dissociation of salt, that will be fulfilling their respective equilibria:

$$\begin{array}{lcl}
HBO_2 & \overset{10^{-9.2}}{\rightleftharpoons} & BO_2^- + H^+ \\
F^- + H_2O & \overset{10^{-10.8}}{\rightleftharpoons} & HF + OH^- \\
\cancel{Na^+} + H_2O & \longrightarrow & Na^+ + H_2O
\end{array}$$

The Na^+ does not provide or remove protons from the dissolution, and as we have an acid and a base, we will have to observe if the dissolution is in equilibrium.

$$\begin{array}{lcl}
HBO_2 & \overset{10^{-9.2}}{\rightleftharpoons} & BO_2^- + H^+ \\
F^- + H_2O & \overset{10^{-10.8}}{\rightleftharpoons} & HF + OH^- \\
H^+ + OH^- & \overset{10^{+14}}{\rightleftharpoons} & H_2O \\
\hline
HBO_2 + F^- & \overset{K = 10^{-6.0}}{\rightleftharpoons} & BO_2^- + HF
\end{array}$$

The constant of the reaction will be the product of the constants $10^{-9.2} \times 10^{-10.8} \times 10^{+14} = 10^{-6.0}$. The value of the K points out that the dissolution is in equilibrium and that the species that prevail in the dissolution are the initial ones. Thus, the dissolution in equilibrium will be:

$$\begin{array}{lcl}
HBO_2 & \overset{10^{-9.2}}{\rightleftharpoons} & BO_2^- \;+\; H^+ \\
10^{-1} - x & & x \qquad\;\; x \\
F^- + H_2O & \overset{10^{-10.8}}{\rightleftharpoons} & HF \;+\; OH^- \\
10^{-1} - y & & y \qquad\;\; y \\
H_2O & \overset{10^{-14}}{\rightleftharpoons} & H^+ \;+\; OH^- \\
 & & z \qquad\;\; z
\end{array}$$

Applying the proton condition, we reach:

$$[H^+] = [BO_2^-] - [HF] + [OH^-]$$

where, if we pay attention, we will take into account that we are in the same case as in the dissolution of weak acid and weak base salt.

Substituting $[BO_2^-]$ by $[HBO_2]$ and the protons in equilibrium, [HF] by $[F^-]$ and the protons in equilibrium, and $[OH^-]$ by the protons in equilibrium, a similar equation to Eq. [7] is obtained:

$$[H^+] = \sqrt{\frac{K_{HBO_2}[HBO_2] + K_w}{1 + \frac{[F^-]}{K_{HF}}}} \qquad [11]$$

that is the *general equation for a mixture of weak acid and weak base when they lightly react*, and it will be simplified in a similar way to what was seen for the salt of weak acid and weak base:

- If $K_{HBO_2}[HBO_2] >> K_w \Rightarrow K_w$ is negligible.
- If $[F^-] >> K_{HF} \Rightarrow 1$ is negligible.

So that we get the simplified equation: $[H^+] = \sqrt{K_{HBO_2} \times K_{HF}} = \sqrt{10^{-9.2} \times 10^{-3.2}} = 10^{-6.2}$M.

Mixture of Weak Acid and Weak Base that Mostly React with Each Other

Let us suppose a mixture of 100 mL of HF 2×10^{-1} M + 100 mL of $NaBO_2$ 2×10^{-1} M, pK of $HBO_2 = 9.2$ and pK of $HF = 3.2$.

Initially in the 200 mL of dissolution we will have HF 10^{-1} M, Na^+ 10^{-1} M and BO_2^- 0.1 M, that will be fulfilling their respective equilibria:

$$\begin{array}{l}
HF \overset{10^{-3.2}}{\rightleftharpoons} F^- + H^+ \\
BO_2^- + H^+ \overset{10^{+9.2}}{\rightleftharpoons} HBO_2 \\
\cancel{Na^+} + H_2O \longrightarrow Na^+ + H_2O
\end{array}$$

As we have an acid and a base, we will have to observe how the dissolution in equilibrium is.

$$\begin{array}{l}
HF \overset{10^{-3.2}}{\rightleftharpoons} F^- + H^+ \\
BO_2^- + H^+ \overset{10^{+9.2}}{\rightleftharpoons} HBO_2 \\
\hline
HF + BO_2^- \overset{K = 10^{+6.0}}{\rightleftharpoons} F^- + HBO_2
\end{array}$$

The constant of the reaction will be the product of the constants $10^{-3.2} \times 10^{+9.2} = 10^{+6.0}$. The value of K points out that the reaction is moved towards the right, or what is the same, that it is not in equilibrium and the dissolution in equilibrium have nothing in common with the initial one.

The acid HF will react with BO_2^- to give F^- and acid HBO_2 in the following way:

$$\begin{array}{lcccc}
 & HF & + BO_2^- \overset{10^{+6.0}}{\rightleftharpoons} & F^- & + HBO_2 \\
\text{Initial} & 10^{-1} & 10^{-1} & & \\
\text{Equil.} & x & x & 10^{-1} & 10^{-1}
\end{array}$$

So that in the dissolution in equilibrium what prevails is F^- 10^{-1} M and HBO_2 10^{-1} M, that will be fulfilling their respective equilibria in the following way:

$$\begin{array}{l}
\underset{10^{-1}-x}{HBO_2} \overset{10^{-9.2}}{\rightleftharpoons} \underset{x}{BO_2^-} + \underset{x}{H^+} \\
\underset{10^{-1}-y}{F^-} + H_2O \overset{10^{-10.8}}{\rightleftharpoons} \underset{y}{HF} + \underset{y}{OH^-} \\
H_2O \overset{10^{-14}}{\rightleftharpoons} \underset{z}{H^+} + \underset{z}{OH^-}
\end{array}$$

Applying the proton condition in equilibrium, we reach:

$$[H^+] = [BO_2^-] - [HF] + [OH^-].$$

This is a similar solution to the one obtained on the previous part, and where once again we have to point out that the dissolution in equilibrium has nothing to do with the initial dissolution.

CONCLUSION

Applying the proton condition or the hydroxyl condition in equilibrium, all the acid-base equilibria can be solved, including their mixtures and salts, without need of making balance of masses and balance of charges.

Newly, what we try is to become immersed in the dissolution to visualize the different equilibria that are being fulfilled, and to get to solve it by means of the proton condition in equilibrium or the hydroxyl condition, what at the end is the same. It is necessary to insist on the fact that it is a dissolution in equilibrium, proton condition or hydroxyl condition in equilibrium, because there are cases of dissolutions that initially contain acids and bases that logically react getting dissolutions that have nothing to do with the initial dissolutions.

Again, in this work we do not intend for the students to learn the formulae by heart, but to know to rationalize what happens in a dissolution and how every species that forms that dissolution in equilibrium will be. The important question is not to get a more or less complicated formula; what is important is to know how to reach an understanding of what each of the species' dissolution provides.

Using the hydroxyl condition, we reach the conclusion that the hydroxyls in equilibrium are additive, not only the ones of strong bases but also those of weak bases. It happened the same way with the protons in the case of dissolutions of acids (8).

In a similar way to what was seen with the dissolutions of acids, the equilibria of dissolutions of bases, mixtures and salts have been solved algebraically, though they can also be solved graphically using the proton condition or the hydroxyl condition in equilibrium.

REFERENCES

1. D. A. Skoog, D. M. West, F. J. Holler, and S. R. Crouch, *Fundamentos de Química Analítica* (Thomson, Madrid, 2005), Resolución de problemas de equilibrio en sistemas complejos. 286–290.
2. J. F. Rubinson and K. A. Rubinson, *Contemporary Chemical Analysis* (Prentice Hall, New Jersey, 1998), Simple and competitive Chemical Equilibria. 169–180.
3. M. Aguilar, *Introducción a los Equilibrios Químicos* (Reverté, Barcelona, 1999), Cálculo de equilibrios ácido-base. 18–39.
4. D. A. Skoog, D. M. West, F. J. Holler, and S. R. Crouch, *Analytical Chemistry: An Introduction* (Harcourt College Publishers, Orlando, 2000), How Equilibrium Calculations Can Be Applied to Complex Systems. 222.
5. F. M. Burriel, F. C. Lucena, S. J. Arribas, and J. M. Hernández, *Química Analítica Cualitativa,* (Paraninfo, Madrid, 2001), Reacciones ácido-base. 45–86.
6. D. Harvey, *Modern Analytical Chemistry* (McGrawHill, Boston, 2000), Equilibrium Chemistry. 159–164.
7. D. C. Harris, *Quantitative Chemical Analysis* (W. H. Freeman, New York, 2003), Monoprotic Acid-Base Equilibria, 178–223.
8. A. Casado, A more rational treatment of the acid-base equilibria applying the proton condition in equilibrium. How the protons in equilibria are additive: Dissolutions of acids. *Critical Reviews in Analytical Chemistry* 35 (2005):289–299.
9. J. N. Butler, *Ionic Equilibrium, a Mathematical Approach* (Addison-Wesley, Reading, MA, 1964), Polyprotic Acids. 238.
10. J. N. Butler, *Ionic Equilibrium, a Mathematical Approach* (Addison-Wesley, Reading, MA 1964), Polyprotic Acids, 216.