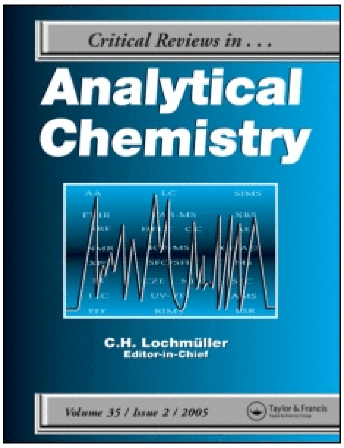

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A More Rational Treatment of the Acid-Base Equilibria Applying the Proton Condition in Equilibrium. How the Protons in Equilibria are Additive: Dissolutions of Acids

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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

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The calculus of the acid-base equilibria can be rationalized applying the proton condition in every case, on solutions of strong acids, weak acids, and their possible mixtures. Futhermore, applying the proton condition in equilibrium, it is clearly pointed out that the protons in equilibrium are additive, in solutions of strong acids as well as those of weak acids.

Keywords proton condition, acid-base equilibria, the protons are additive

INTRODUCTION

In the textbooks of the last decade, for the calculation of H^+ in equilibrium we usually resort to make a balance of masses and a balance of charges, which combining with the constants of the equilibria that take part in the system, leads to protons in equilibrium (1–7). When the species are simple the solution is easy, but when the species at work are more complicated the solution is more laborious, and at the end it leads to confusions. Furthermore, the students do not understand what happens in the bosom of the dissolution and at the end what they do are mathematics and not chemistry (what the matter is).

More than 30 years ago, Kolthoff, Sandell, Meehan and Bruckenstein (8), proposed and developed the proton condition as the most convenient way to treat the acid-base equilibria, where they include every protolitic reaction between the solvent and the acids and bases dissolved. Their statement of the proton condition is:

$$[H^+] = a + \Sigma n_i[\mathrm{base}]_i - b - \Sigma m_j[\mathrm{acid}]_j$$

where a and b represent the concentrations of strong acid and strong base, $[\mathrm{base}]_i$ represents the concentration in equilibrium of the ith base produced by the reaction $H_{ni}\ base_i \rightarrow n_i H^+ + base_i$. On a similar way, $[\mathrm{acid}]_j$ represents the concentration of the jth acid produced by the reaction of the base_j, $base_j + m_j H^+ \rightarrow acid_j$.

Later on, Hulanicki (9), in the chapter dedicated to the calculations of pH in dissolutions of acids and bases, used a similar treatment to the proton condition, but without an explicit mention to it.

More recently, Robert de Levie (10) used the proton balance equation for calculi of pH, but in the IX part "Applications to mixtures" he recommended to make a balance of charges and masses to obtain the proton balance equation. In the book (11), the same author proposed to sum up the proton balance equation as proton condition. This author (12) refers to Butler's book (13), and he says word by word: "Use of the proton balance (also called proton condition) was promoted specially by Butler."

Certainly, Butler proposes the proton condition to solve the acid-base equilibria, but he frequently resorts to the balance of charges and balance of masses to reach it. That is what happens in the case of salts of strong acid and strong base, in the calculus of the salt of strong acid and weak base, in the mixture of a strong and weak acid, and in the salt of polyprotic acids.

In this work something similar is proposed: the *proton condition in equilibrium* is proposed. It is called the proton condition in equilibrium because the H^+ are the ones that the acids provide to or the bases remove from *that dissolution in equilibrium*, and not the H^+ that the acids provide independently as if they were alone. Furthermore, it is said the proton condition is in equilibrium because there are situations of mixtures that initially are not in equilibrium due to the presence of acids and bases, and the dissolution in equilibrium may have nothing in common with the initial one.

The proton condition in equilibrium is a balance of protons, balance between protons that are provided to and removed from the dissolution (gained and lost protons in the dissolution), and which result is the same one obtained when the balance of masses and the balance of charges are applied, but is easier and more didactic.

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Actually, in the proton condition proposed, we do not write the protons that appear or disappear, but "the consequences" of the protons that appear or disappear in the dissolution in equilibrium. As Kolthoff and collaborator say, the weak acids develop as many niH^+ as base i, and the weak bases use as many protons as acids appear.

Proton condition in equilibrium:

$$[\mathrm{H}^+]_{\text{equilibrium}} = \Sigma[\mathrm{H}^+]_{\text{are provided}} - \Sigma[\mathrm{H}^+]_{\text{are removed}}$$

Balance that can be applied to any solution as we will see on the following.

If we start from a aqueous solutions, we take it for granted that the dissolvent fulfils the equilibrium:

$$\mathrm{H_2O + H_2O \overset{10^{-14}}{\rightleftharpoons} H_3O^+ + OH^-}$$

From now, on we will write:

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

In a pure water dissolution, the only contribution of protons is that of the same dissolvent, and as a consequence of the equilibrium of H_2O, as many protons as hydroxyls are provided.

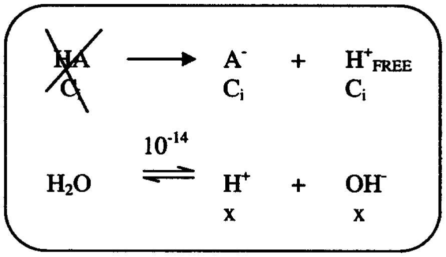
Thus, the proton condition for H_2O is $[\mathrm{H}^+] = [\mathrm{OH}^-]$, and writing the OH^- according to the H^+ that the dissolution in equilibrium has, $[\mathrm{OH}^-] = \frac{\mathrm{K_w}}{[\mathrm{H}^+]}$, the proton condition for water would be:

$$[\mathrm{H}^+] = \frac{K_w}{[H^+]}, \text{ from which } [\mathrm{H}^+]^2 = \mathrm{K_w} \Rightarrow [\mathrm{H}^+] = 10^{-7}\mathrm{M} = [\mathrm{OH}^-]$$

SOLUTIONS OF ACIDS

Strong Acid HA

The strong acid is completely dissociated providing A^- and H^+ to the dissolution in similar concentrations to the initial concentration of HA. So we will come across the next solution:



This solution is in equilibrium. There is no possibility to any reaction. What there is here is a common ion effect of the $\mathrm{H^+_{FREE}}$ with the H^+ of the H_2O.

We have two species that provide protons, the strong acid HA and the H_2O. In the dissolution, as many protons as HA added appear, which are free protons because they are not subject to any equilibrium. Furthermore, as many protons as OH^- appear due to water (and they won't be 10^{-7} as they were when water was alone).

Applying the proton condition in equilibrium:

$$[\mathrm{H}^+] = \mathrm{Ci} + [\mathrm{OH}^-]$$

Why that emphasis on the proton condition *in equilibrium*? Because if the dissolution of the acid HA were mixed with one of a base, for instance BOH, the concentration of $\mathrm{H^+_{FREE}}$ would not be equal to the initial concentration of HA = Ci.

- Here it is proposed that the H^+ the strong acids provide to the dissolution will be called *H^+ free*, as they are not subject to any equilibrium (differing from the H^+ the weak acids provide that are subject to equilibrium).

Then the proton condition would be:

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

and writing the OH^- according to the H^+ that the dissolution in equilibrium has, $[\mathrm{OH}^-] = \frac{\mathrm{K_w}}{[\mathrm{H}^+]}$, it becomes:

$$[\mathrm{H}^+] = [\mathrm{H}^+]_{\mathrm{FREE}} + \frac{\mathrm{K_w}}{[\mathrm{H}^+]} \qquad [1]$$

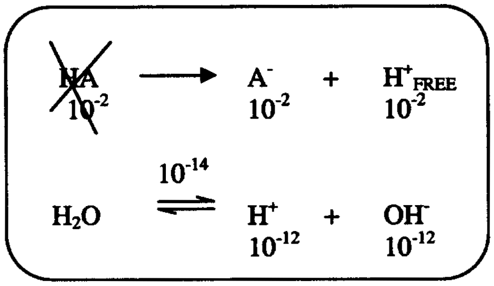
This is a general equation for strong acid that can be simplified, depending on the conditions.

The Strong Acid is Lightly Concentrated. Dissolution of strong acid HA = 10^{-2} M.

Applying the proton condition it leads to the general equation, we would get $[\mathrm{H}^+] = 10^{-2} + \frac{10^{-14}}{[\mathrm{H}^+]}$, from where $[\mathrm{H}^+] = 10^{-2}$M. The protons of the dissolution are the ones that come from the strong acid, as expected, and the contribution of H_2O is negligible. The OH^- that water provides to the dissolution will be 10^{-12}M, that will be the same as H^+ that provides to that dissolution (because it provides as many proton as hydroxyl ions).

- If we had looked carefully at our dissolution instead of doing mathematics, that is what we have done instead of resolving the second grade equation . . . Let us come back to our dissolution and think again:

$[\mathrm{H}^+] = [\mathrm{H}^+]_{\mathrm{FREE}} + \frac{\mathrm{K_w}}{[\mathrm{H}^+]} = 10^{-2} + \frac{10^{-14}}{[\mathrm{H}^+]}$, if we pay attention to the dissolution it seems that at least the H^+ will be the ones of the strong acid, 10^{-2} M, so that we get that the protons are $10^{-2} + \frac{10^{-14}}{\approx 10^{-2}} = 10^{-2} + \cancel{10}^{-12}$ where it is show that the protons provided by H_2O are negligible to the ones that the strong acid HA provides. Then the dissolution will be formed by:



The protons in equilibrium are: $[\mathrm{H}^+] = 10^{-2} + \cancel{10}^{12} = 10^{-2}$ M

In the case of strong acid lightly concentrated, the general equation is simplified:

$$[H^+] = [H^+]_{FREE} \quad [2]$$

The Strong Acid is Very Diluted. As has been observed previously if the acid is lightly concentrated, the contribution of H_2O is negligible. Logically, we have to think that as the added acid is more diluted, its contribution will be smaller, and consequently, the contribution of protons by the H_2O will be more important. We have to state a limit to decide when a term is negligible or not.

- Here it is proposed that a term is negligible when it is 100 times smaller than another is, so that the error made will be less than 1% at most.

Following this criterion, the concentration of the limit acid is 10^{-6} M, because there we will have at least 10^{-6} M protons, so that $[H^+] = 10^{-6} + \frac{10^{-14}}{\approx 10^{-6}} = 10^{-6} + \approx 10^{-8}$ where the contribution of H_2O is just 100 times smaller. As we are just in the limit, let us solve the general equation $[H^+] = 10^{-6} + \frac{K_w}{[H^+]}$, where the protons that H_2O provides are not yet negligible, and once solved leads us to $[H^+] = 1.01 \times 10^{-6}$ M. If we had neglected the contribution of the water, the answer would have been $[H^+] = 1.00 \times 10^{-6}$M, so the error made would be –1%.

Then, for concentrations of strong acid equal or less than 10^{-6} M, what the H_2O provides is not negligible, and the equation that solves the protons in equilibrium in this dissolution is the general equation:

$$[H^+] = [H^+]_{FREE} + \frac{K_w}{[H^+]}$$

On the following we will have to think that if the strong acid dilutes more, there will be a moment in which its contribution will be negligible to water. That is what happens with acid concentrations less than 10^{-8} M.

In a dissolution of strong acid 10^{-8} M protons, at least there are 10^{-8} M of free protons due to the strong acid added, so that we would have

$$[H^+] = [H^+]_{LIB} + \frac{K_w}{[H^+]} = 10^{-8} + \frac{10^{-14}}{\approx 10^{-8}} = 10^{-8} + \approx 10^{-6},$$

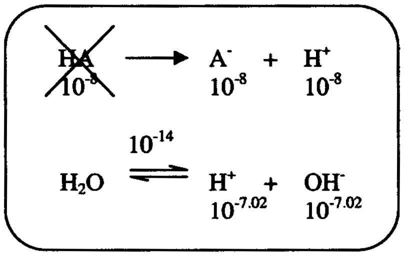
where it is showed that the protons that water provides are more than those of the acid, but the ones the strongly diluted acid provides are not yet negligible.

The complete equation will have to be solved, $[H^+] = 10^{-8} + \frac{K_w}{[H^+]}$, from where $[H^+] = 10^{-6.98}$ M were indeed the contribution of the acid in concentration 10^{-8} M is observed. The dissolution is lightly acidic; the pH is 6.98.

At this point it has to be pointed out that the H^+ of the dissolution of strong acid 10^{-8} M are not due to the acid 10^{-8}, plus those of the water 10^{-7}, because $10^{-8} + 10^{-7} = 10^{-6.96} \neq 10^{-6.98}$.

The equilibrium of water has had to be adapted to the situation of that small concentration of acid added. The OH^- that water provides to the dissolution with some protons in equilibrium of $10^{-6.98}$ will be, $[OH^-] = \frac{10^{-14}}{10^{-6.98}} = 10^{-7.02}$ M, that will be the same as the H^+ that it provides to that dissolution because it provides as many proton as hydroxyl ions.

Then the dissolution will be formed by:



$[H^+]_{equilibrium} = 10^{-8} + 10^{-7.02} = 10^{-6.98}$M
The equilibrium of the dissolution continue fulfilling
$[H^+][OH^-] = 10^{-6.98} \times 10^{-7.02} = 10^{-14} = K_w$

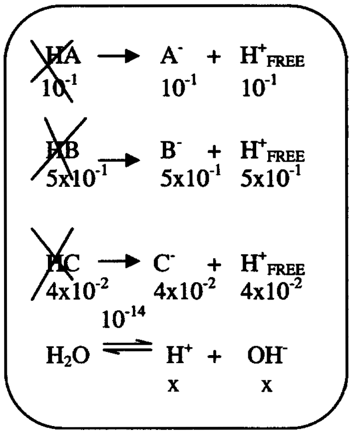
Dissolution that shows that the H^+ that the acid provides, 10^{-8}, plus the ones that the water in equilibrium in that dissolution provides, $10^{-7.02}$, are $10^{-6.98}$.

We have discovered something new: The protons in equilibrium are additive

Finally, if we dilute more the strong acid, we conclude that for concentrations of strong acid smaller than 10^{-8} M, the contribution of the acid is negligible, so that the proton condition becomes: $[H^+] = [OH^-]$, from were $[H^+] = \frac{Kw}{[H^+]}$, that is $[H^+] = 10^{-7}$ M. The protons in this dissolution are only due to the contribution of H_2O.

Mixture of Strong Acids. Let us suppose we have a mixture of strong acids HA 10^{-1} M, HB 5×10^{-1} M and HC 4×10^{-2} M, from which we want to know the concentrations of all species in equilibrium.

The situation of the dissolution would be:



The dissolution is a mixture of strong acids that provide free protons to the dissolution and make the equilibrium of water retrograde.

Applying the proton condition in equilibrium:

$$[H^+] = [H^+]_{FREE} + [H^+]_{FREE} + [H^+]_{FREE} + [OH^-]$$
$$= 6.4 \times 10^{-1} + \frac{K_w}{[H^+]}$$

The protons in this dissolution are at least the sum of all the free protons, that is, 6.4×10^{-1} M.

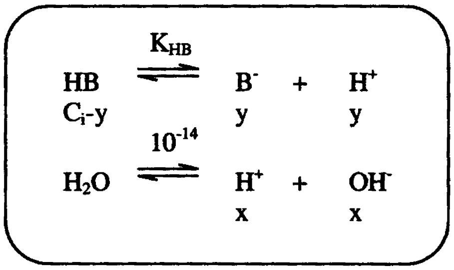
This way the proton condition becomes $[H^+] = 6.4 \times 10^{-1} + \frac{10^{-14}}{\approx 6.4\times 10^{-1}} = 6.4 \times 10^{-1} + \approx \cancel{10}^{-13.8} = 6.4 \times 10^{-1}$ M.

The protons in equilibrium are the sum of the free protons of the strong acids. What water provides is negligible, but it has to be adapted to the situation of $[H^+] = 6.4 \times 10^{-1}$ M. Them, the OH^- due to water in equilibrium are $\frac{10^{-14}}{6.4\times 10^{-1}} = 10^{-13.8}$ M, that will be the same as the H^+ that water provides to that dissolution.

The protons of the dissolution will be: $[H^+] = 6.4 \times 10^{-1} + \cancel{10}^{-13.8} = 6.4 \times 10^{-1}$ M.

Monoprotic Weak Acid

Let us state the situation of a weak acid HB in concentration Ci and with a constant K_{HB}, that in the dissolution would be:



We have a dissolution that contains the weak acid HB and water, and that is in equilibrium.

We expect that most of the protons are due to the acid, but everything will depend on its initial concentration and on the value of its constant.

If we apply the proton condition to this dissolution in equilibrium, we will observe that as protons as B^- appear due to the acid HB, and as many protons as OH^- due to H_2O:

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

And everything we have to do is to write $[B^-]$ according to [HB] and the protons that the dissolution in equilibrium has, and the $[OH^-]$ according to the protons. Replacing it in the proton condition we get:

$$[H^+] = \frac{K_{HB}[HB]}{K_{HB} + [H^+]} + \frac{K_w}{[H^+]} \qquad [3]$$

A general equation for monoprotic weak acid that can be simplified depending on the conditions.

- Here is proposed "to suppose" that what the acid dissociates is negligible to what there was initially ($C_i - y = C_i$), and once solved to prove that the supposition is true.

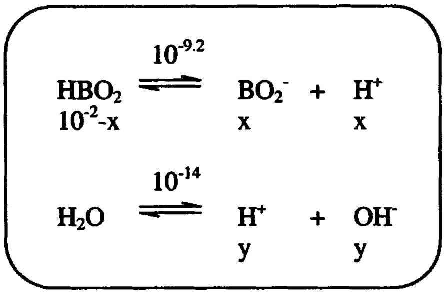
This proposition is made because the majority of cases the supposition is true, so that resolving it is easier, and because the systematic to follow is to solve every case being influenced by the equilibria that fulfil in every dissolution. Do not learn formulae by heart.

Thus, Eq. [3] simplifies to: $[H^+] = \frac{K_{HB}[HB]}{[H^+]} + \frac{K_w}{[H^+]}$ and it leads to

$$[H^+] = \sqrt{K_{HB}[HB] + K_w} \qquad [4]$$

What the Acid Dissociates is Negligible Compared to What There was Initially. Dissolution of metaboric acid, HBO_2, in concentration 10^{-2} M and pK = 9.2.

We will have in the dissolution:



Dissolution that is in equilibrium and we will be able to apply the proton condition to it. As many protons as BO_2^- and as many protons as OH^- will appear:

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

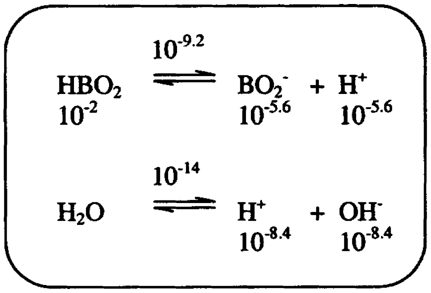
where replacing $[BO_2^-] = \frac{K_{HBO_2}[HBO_2]}{[H^+]}$

and $[OH^-] = \frac{K_w}{[H^+]}$, it leads us to the general equation:

$$[H^+] = \sqrt{K_{HBO_2}[HBO_2] + K_w} = \sqrt{10^{-9.2} \times 10^{-2} + 10^{-14}}$$
$$= \sqrt{10^{-11.2} + \cancel{10}^{-14}} = 10^{-5.6}\,\text{M}.$$

Following the criterion that every term 100 times smaller is negligible, it is observed that the protons that water provides are negligible to the ones the acid provides. Thus, the protons in equilibrium are $10^{-5.6}$ M, and the OH^- will be $10^{-8.4}$ M, which are the same as the H^+ that water provides in that dissolution. The main equilibrium is the one of the boric acid, what imply that $[H^+] = [BO_2^-]$. The $[BO_2^-]$ is also $10^{-5.6}$ M.

To prove that the supposition made about that the acid dissociates is negligible, we will have that $10^{-2} - 10^{-5.6} = 10^{-2}$. The supposition is true, so that we have avoided to solve the quadratic equation general. If this is so, the dissolution will be formed as follows:



There is a main equilibrium that is the one that predominates in the dissolution, and the rest of the equilibria have to adapt to it.

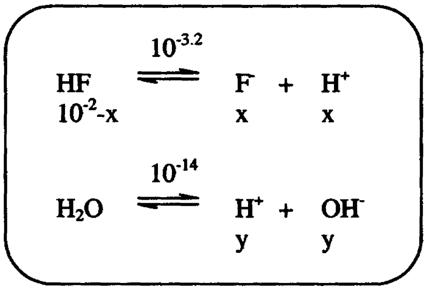
The protons in equilibrium are those of the HBO_2, and the equilibrium of water has to be adapted to that situation.

$$[H^+] = 10^{-5.6} + \cancel{10}^{-8.4} = 10^{-5.6}\,\text{M}$$

where the protons in equilibrium continue being additive and all the equilibria continue being fulfilled:

$$\frac{10^{-5.6}\times 10^{-5.6}}{10^{-2}} = 10^{-9.2} = K_{HBO_2},\ \textit{and}\ 10^{-5.6}\times 10^{-8.4} = 10^{-14} = K_w$$

What the Acid Dissociates to is not Negligible Compared to What There was Initially. Dissolution of HF in concentration 10^{-2} M and pK = 3.2. We continue having a weak acid, but stronger than in the previous case:



Applying the proton condition we will have:

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

where writing F^- and OH^- according to the H^+ and the concentration of HF, we reach the general equation on the following way:

$$[H^+] = \sqrt{K_{HF}[HF] + K_w} = \sqrt{10^{-3.2}\times 10^{-2} + 10^{-14}} = \sqrt{10^{-5.2} + \cancel{10}^{-14}} = 10^{-2.6}\,M$$

It is pointed out again that there is a main equilibrium, that is the one that prevails in the dissolution. But if we prove that the assumption made to solve it is fulfilled, we find that $10^{-2} - 10^{-2.6} \neq 10^{-2}$, that is, what is dissociated is not negligible to what there was initially, so we will have to take it into account.

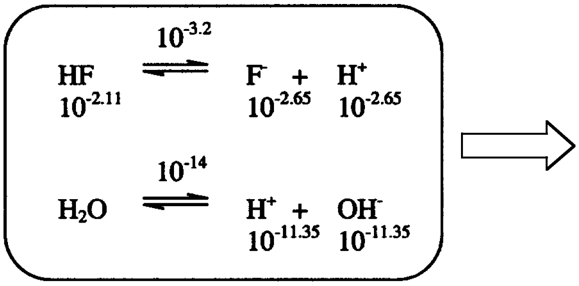
If what the HF dissociates into is not negligible, $[HF] = C_i - [F^-]$. From $K_{HF} = \frac{[F^-][H^+]}{C_i - [F^-]}$ we obtain the $[F^-] = \frac{K_{HF}C_i}{K_{HF}+[H^+]}$ that replaced in the proton condition $[H^+] = [F^-] + [OH^-]$ leads to the expression $[H^+] = \frac{K_{HF}C_i}{K_{HF}+[H^+]} + \frac{K_w}{[H^+]}$, similar to Eq. (3).

As we have already observed that what H_2O provides is negligible, what we get is $[H^+] = \frac{K_{HF}C_i}{K_{HF}+[H^+]}$. Solving it we have that $[H^+] = 10^{-2.65}$ M, what will also be $[F^-]$, because the equilibrium of HF is the main equilibrium and $[F^-] = [H^+]$.

The, $[H^+] = 10^{-2.65}$ M, obtained value seems to be similar to the one obtained without taking into account what the acid dissociates, $[H^+] = 10^{-2.60}$ M, but if we calculate the error that would be made Er = +12%. The error made would be considerable, and higher than the 1% that we have fixed as a criterion.

The dissolution in equilibrium contains: $[H^+] = 10^{-2.65}M = [F^-]$, $[HF] = 10^{-2} - 10^{-2.65} = 10^{-2.11}$ M, $[OH^-] = 10^{-11.35}$ M $= [H^+]$ that H_2O provides to that dissolution and that are negligible compared to the ones the acid provides.

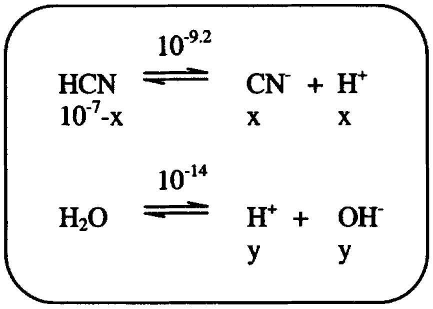
The different species in dissolution are fulfilling their respective equilibria on the following way:



$$[H^+] = 10^{-2.65} + \cancel{10}^{-11.35} = 10^{-2.65}M$$

$$\frac{10^{-2.65}\times 10^{-2.65}}{10^{-2.11}} = 10^{-3.2} = K_{HF},\ \text{and}\ 10^{-2.65}\times 10^{-11.35} = 10^{-14} = K_w$$

What the Acid Provides is Negligible to What the Solvent Provides. Dissolution of acid HCN 10^{-7} M and pK = 9.2. We have a very weak acid and very diluted acid:



Applying the proton condition we will have:

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

where writing CN^- and OH^- according to the H^+ and the concentration of HCN, we reach the general equation on the way:

$$[H^+] = \sqrt{K_{HCN}[HCN] + K_w} = \sqrt{10^{-9.2}\times 10^{-7} + 10^{-14}} = \sqrt{\cancel{10}^{-16.2} + 10^{-14}} = 10^{-7.0}\,M$$

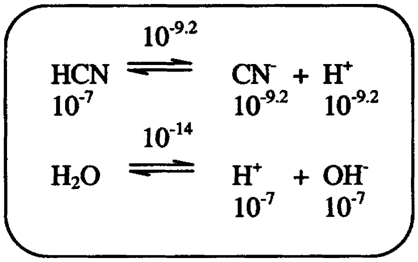
It is pointed out that the contribution of the acid is negligible, as it is a very weak acid and it is very diluted. In this case the concentration of CN^- that the acid leaves will have to be taken from its constant, taking into account the H^+ that there are in equilibrium (the protons of the dissolution in equilibrium are not equal to CN^- yet):

$$[CN^-] = \frac{[HCN]K_{HCN}}{[H^+]} = \frac{10^{-7}\times 10^{-9.2}}{10^{-7}} = 10^{-9.2}\,M$$

which will be also the H^+ that the acid HCN provides.

If we prove what is dissociated to what was initially, $10^{-7} - 10^{-9.2} = 10^{-7}$, it becomes negligible.

Then the dissolution in equilibrium would be on the following way:



$$\begin{array}{lcccc} & 10^{-9.2} & & & \\ HCN & \rightleftharpoons & CN^- & + & H^+ \\ 10^{-7} & & 10^{-9.2} & & 10^{-9.2} \\ & 10^{-14} & & & \\ H_2O & \rightleftharpoons & H^+ & + & OH^- \\ & & 10^{-7} & & 10^{-7} \end{array}$$

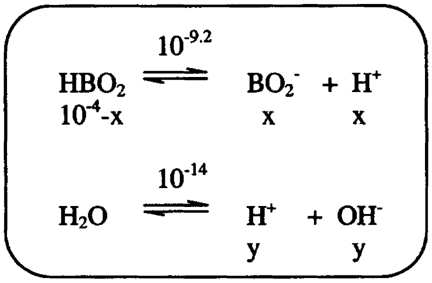
$$[H^+] = \cancel{10}^{-9.2} + 10^{-7} = 10^{-7}\ M$$

The protons continue being additive, although the ones that the HCN provides are negligible. And all the equilibria continue being fulfilled.

$$\frac{10^{-9.2} \times 10^{-7}}{10^{-7}} = 10^{-9.2} = K_{HCN}, \text{ and}$$
$$10^{-7} \times 10^{-7} = 10^{-14} = K_w$$

The Contribution of any Species is not Negligible. Dissolution of acid HBO_2 in concentration 10^{-4} M and pK = 9.2.

The dissolution contains a very weak and diluted acid:



$$\begin{array}{lcccc} & 10^{-9.2} & & & \\ HBO_2 & \rightleftharpoons & BO_2^- & + & H^+ \\ 10^{-4}\text{-}x & & x & & x \\ & 10^{-14} & & & \\ H_2O & \rightleftharpoons & H^+ & + & OH^- \\ & & y & & y \end{array}$$

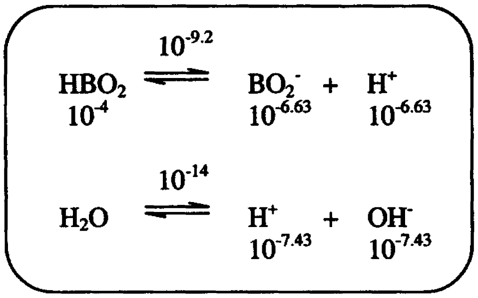
Proton condition:

$$[H^+] = [BO_2^-] + [OH^-]$$
$$\Downarrow$$
$$[H^+] = \sqrt{K_{HBO_2}[HBO_2] + K_w} = \sqrt{10^{-9.2} \times 10^{-4} + 10^{-14}}$$
$$= \sqrt{10^{-13.2} + 10^{-14}} = 10^{-6.57}\ M$$

It can be observed that the contribution of the acid is not negligible, and neither is the contribution of the solvent. The OH^- in equilibrium will be $\frac{10^{-14}}{10^{-6.57}} = 10^{-7.43}$ M (that will be also the H^+ that H_2O provides), and taking out the borates by means of their constant to pH in equilibrium $[BO_2^-] = \frac{K_{HBO_2}[HBO_2]}{[H^+]} = \frac{10^{-9.2} \times 10^{-4}}{10^{-6.57}} = 10^{-6.63}$ M (that is also the H^+ that the acid HBO_2 provides to that dissolution)

Once again the supposition that what the acid dissociates is negligible to its initial concentration, $10^{-4} - 10^{-6.63} = 10^{-4}$.

We can show what provides each equilibrium to the dissolution:



$$\begin{array}{lcccc} & 10^{-9.2} & & & \\ HBO_2 & \rightleftharpoons & BO_2^- & + & H^+ \\ 10^{-4} & & 10^{-6.63} & & 10^{-6.63} \\ & 10^{-14} & & & \\ H_2O & \rightleftharpoons & H^+ & + & OH^- \\ & & 10^{-7.43} & & 10^{-7.43} \end{array}$$

$$[H^+] = 10^{-6.63} + 10^{-7.43} = 10^{-6.57}\ M$$

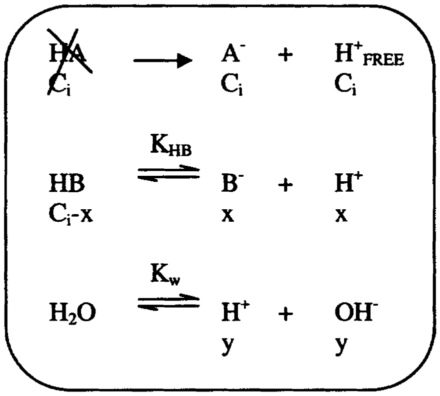
The protons in equilibrium are additive.

and all the equilibria continue fulfilling:

$$\frac{10^{-6.63} \times 10^{-6.57}}{10^{-4}} = 10^{-9.2} = K_{HBO_2}, \text{ and } 10^{-6.57} \times 10^{-7.43}$$
$$= 10^{-14} = K_w$$

Mixture of Strong Acid and Weak Acid

Let us suppose a mixture of strong acid HA and weak acid HB with a constant K_{HB} and in concentration Ci.



$$\begin{array}{lcccc} \cancel{HA} & \longrightarrow & A^- & + & H^+_{FREE} \\ \cancel{C_i} & & C_i & & C_i \\ & K_{HB} & & & \\ HB & \rightleftharpoons & B^- & + & H^+ \\ C_i\text{-}x & & x & & x \\ & K_w & & & \\ H_2O & \rightleftharpoons & H^+ & + & OH^- \\ & & y & & y \end{array}$$

We have a dissolution that contains the strong acid, the weak acid and water, and that is in equilibrium. Proton condition in equilibrium:

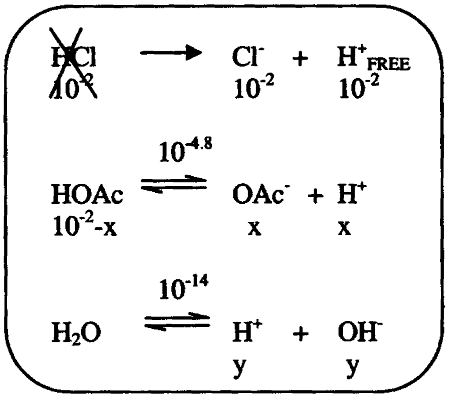
$$[H^+] = [H^+]_{FREE} + [B^-] + [OH^-]$$

where writing each term according to the concentrations and the $[H^+]$ in equilibrium, it leads to:

$$[H^+] = [H^+]_{FREE} + \frac{K_{HB}[HB]}{[H^+]} + \frac{K_w}{[H^+]} \qquad [5]$$

General Equation for Mixture of Strong Acid and Weak Acid

The Contribution of the Weak Acid is Negligible. For a mixture of acid HCL 10^{-2} M and HOAc 10^{-2} M with pK = 4.8.



Applying the proton condition in equilibrium:

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

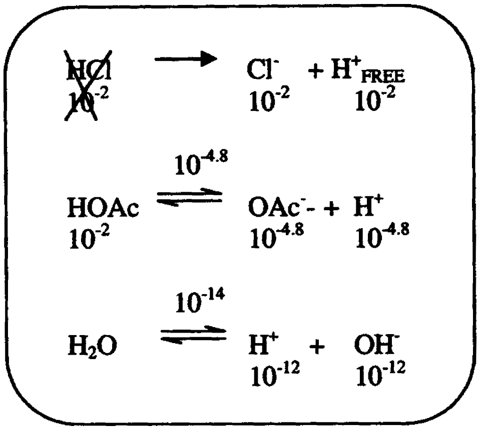
Writing $[OAc^-]$ and $[OH^-]$ according to the concentration of HOAc and $[H^+]$ in equilibrium, the following expression is obtained:

$$[H^+] = [H^+]_{FREE} + \frac{K_{HOAc}[HOAc]}{[H^+]} + \frac{K_w}{[H^+]},$$

where taking into account that at least there are 10^{-2} M protons due to the H^+_{FREE}, $[H^+] = 10^{-2} + \frac{10^{-4.8}\times 10^{-2}}{\approx 10^{-2}} + \frac{10^{-14}}{\approx 10^{-2}} = 10^{-2} + \approx \cancel{10}^{-4.8} + \approx \cancel{10}^{-12} = 10^{-2}$ M, where it is shown that the protons provided by weak acid and by the solvent are negligible to the ones that the strong acid provides.

The protons in equilibrium are the ones that HCL provides, as is was expected. The rest of the equilibria have adapted to that situation. From their respective constants and the H^+ in equilibrium, we obtain the concentrations: $[OAc^-] = 10^{-4.8}$ M and $[OH^-] = 10^{-12}$ M.

The dissolution will be formed as follows:



The protons in equilibrium continue being additive:

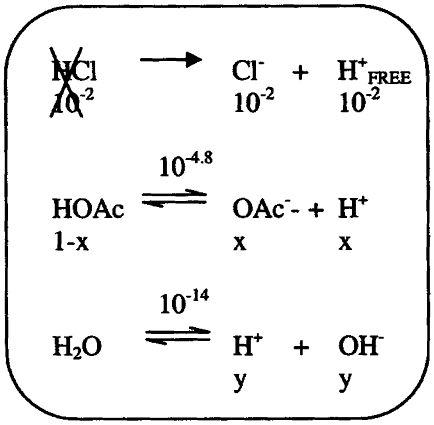
$$[H^+] = 10^{-2} + \cancel{10}^{-4.8} + \cancel{10}^{-12} = 10^{-2}\,M$$

Every equilibrium fulfilled the pH in equilibrium and what the HOAc dissociates is negligible to the initial concentration.

$$\frac{10^{-4.8}\times 10^{-2}}{10^{-2}} = 10^{-4.8} = K_{HOAc},\ 10^{-2}\times 10^{-12} = 10^{-14} = K_w,\ \text{and}\ 10^{-2} - 10^{-4.8} = 10^{-2}\,M$$

The Contribution of the Weak Acid is Not Negligible. For a mixture of HCL 10^{-2} M and acid HOAc 1 M with pK = 4.8.

The dissolution in equilibrium contains:



Proton condition in equilibrium:

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

which leads to the same expression that in the previous case:

$$[H^+] = [H^+]_{FREE} + \frac{K_{HOAc}[HOAc]}{[H^+]} + \frac{K_w}{[H^+]}$$

Following the same reasoning as in the previous part:

$$[H^+] = 10^{-2} + \frac{10^{-4.8}\times 1}{\approx 10^{-2}} + \frac{10^{-14}}{\approx 10^{-2}} = 10^{-2} + \approx 10^{-2.8} + \approx \cancel{10}^{-12}$$

It is observed that the contribution of protons by the strong acid is higher than the of the weak acid, although none of them is negligible, and what the water provides continues being negligible.

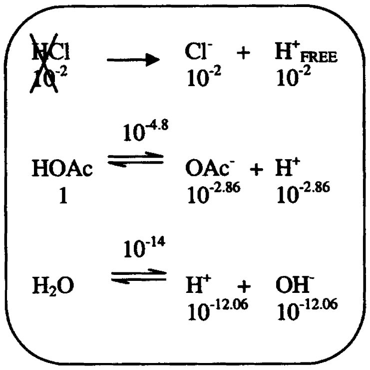
With the obtained result, we have to work in terms of the two acids:

$$[H^+] = [H^+]_{FREE} + \frac{K_{HOAc}[HOAc]}{[H^+]}$$

from where $[H^+]^2 = 10^{-2}[H^+] + 10^{-4.8}$ and once solved leads to $[H^+] = 10^{-1.94}$ M.

Know the concentration of protons in equilibrium, the concentrations of the rest of the species can be calculated: $[OAc^-] = 10^{-2.86}$ M $= [H^+]$ that the acetic acid provides to that dissolution, and the $[OH^-] = 10^{-12.06}$ M $= [H^+]$ that water provides.

The dissolution in equilibrium would be on the following way:



$$\begin{array}{llll} \cancel{HCl} & \longrightarrow & Cl^- \; + & H^+_{FREE} \\ \cancel{10^{-2}} & & 10^{-2} & 10^{-2} \\ HOAc & \overset{10^{-4.8}}{\rightleftharpoons} & OAc^- \; + & H^+ \\ 1 & & 10^{-2.86} & 10^{-2.86} \\ H_2O & \overset{10^{-14}}{\rightleftharpoons} & H^+ \; + & OH^- \\ & & 10^{-12.06} & 10^{-12.06} \end{array}$$

The protons in equilibrium continue being additive:

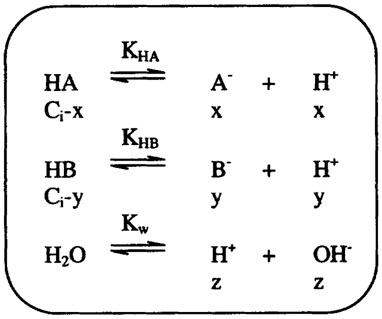
$$[H^+] = 10^{-2} + 10^{-2.86} + \cancel{10}^{-12.06} = 10^{-1.94}\,M$$

What HOAc dissociates is negligible to the initial concentration, and all the equilibria are fulfilled in the dissolution.

$$1 - 10^{-2.86} = 1M, \quad \frac{10^{-2.86} \times 10^{-1.94}}{1} = 10^{-4.8} = K_{HOAc,}$$
$$\text{and } 10^{-1.94} \times 10^{-12.06} = 10^{-14} = K_w$$

Mixture of Weak Monoprotic Acids

Let us suppose a mixture of two weak acids whatever HA and HB in concentrations C_i , and with constants K_{HA} and K_{HB} respectively:



$$\begin{array}{llll} HA & \overset{K_{HA}}{\rightleftharpoons} & A^- \; + & H^+ \\ C_i\text{-}x & & x & x \\ HB & \overset{K_{HB}}{\rightleftharpoons} & B^- \; + & H^+ \\ C_i\text{-}y & & y & y \\ H_2O & \overset{K_w}{\rightleftharpoons} & H^+ \; + & OH^- \\ & & z & z \end{array}$$

We have a dissolution that contains two weak acids and water in equilibrium, and to which we can apply the proton condition:

$$[H^+] = [A^-] + [B^-] + [OH^-]$$

where everything we have to do is to write the $[A^-]$, $[B^-]$ and $[OH^-]$ according to the concentrations of the species we know from the dissolution and the $[H^+]$ in equilibrium.

$$[A^-] = \frac{K_{HA}[HA]}{[H^+]}, [B^-] = \frac{K_{HB}[HB]}{[H^+]}, \text{y } [OH^-] = \frac{K_w}{[H^+]},$$

that replacing in the proton condition:

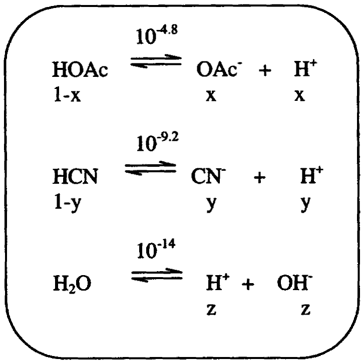
$$[H^+] = \frac{K_{HA}[HA]}{[H^+]} + \frac{K_{HB}[HB]}{[H^+]} + \frac{K_w}{[H^+]}$$

where operating we reach the corresponding equation

$$[H^+] = \sqrt{K_{HA}[HA] + K_{HB}[HB] + K_w} \qquad [6]$$

That is the general equation for a mixture of weak monoprotic acids, and in which giving the corresponding values to the constants and the concentrations, the contribution of every species to the dissolution can be observed.

Mixture of Two Weak Monoprotic Acids with Rather Different Constants. Let us observe a mixture of HOAc 1 M with pK = 4.8 and HCN 1 M with pK = 9.2.



$$\begin{array}{llll} HOAc & \overset{10^{-4.8}}{\rightleftharpoons} & OAc^- \; + & H^+ \\ 1\text{-}x & & x & x \\ HCN & \overset{10^{-9.2}}{\rightleftharpoons} & CN^- \; + & H^+ \\ 1\text{-}y & & y & y \\ H_2O & \overset{10^{-14}}{\rightleftharpoons} & H^+ \; + & OH^- \\ & & z & z \end{array}$$

The dissolution is in equilibrium, so that we can apply the proton condition:

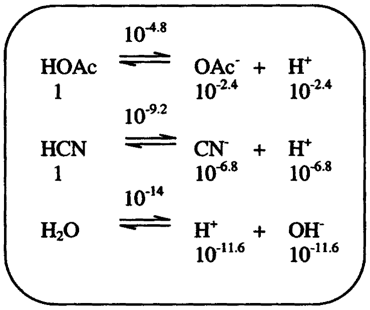
$$[H^+] = [OAc^-] + [CN^-] + [OH^-]$$

where replacing every term by the concentrations we know and by the protons in equilibrium, it leads us to:

$$[H^+] = \sqrt{K_{HOAc}[HOAc] + K_{HCN}[HCN] + K_w}$$
$$= \sqrt{10^{-4.8} \times 1 + \cancel{10}^{-9.2} \times 1 + \cancel{10}^{-14}} = 10^{-2.4}\,M$$

The equilibrium of HOAc prevails over the equilibria of HCN and H_2O, and what is dissociated is negligible $(1 - 10^{-2.4} = 1)$. Logically, what the HCN dissociates will be negligible because its constant of dissociation is much smaller.

From the constant of HCN and with the protons in equilibrium, we get that $[CN^-] = 10^{-6.8}$ M; and from the K_w that $[OH^-] = 10^{-11.6}$ M. Thus, the dissolution in equilibrium will be formed by:



$$\begin{array}{llll} HOAc & \overset{10^{-4.8}}{\rightleftharpoons} & OAc^- \; + & H^+ \\ 1 & & 10^{-2.4} & 10^{-2.4} \\ HCN & \overset{10^{-9.2}}{\rightleftharpoons} & CN^- \; + & H^+ \\ 1 & & 10^{-6.8} & 10^{-6.8} \\ H_2O & \overset{10^{-14}}{\rightleftharpoons} & H^+ \; + & OH^- \\ & & 10^{-11.6} & 10^{-11.6} \end{array}$$

Main equilibrium to which the rest of the equilibria of the dissolution has to be adapted.

The protons in equilibrium are $10^{-2.4}$ M , as the condition explains:

$$[H^+] = 10^{-2.4} + \cancel{10}^{-6.8} + \cancel{10}^{-11.6} = 10^{-2.4}\,M$$

and all the equilibria are fulfilled with those protons in dissolution:

$$\frac{10^{-2.4}\times 10^{-2.4}}{1} = 10^{-4.8} = K_{HOAc},$$

$$\frac{10^{-6.8}\times 10^{-2.4}}{1} = 10^{-9.2} = K_{HCN},$$

$$\text{and } 10^{-2.4}\times 10^{-11.6} = 10^{-14} = K_w$$

Mixture of Two Monoprotic Weak Acids with Similar Constants. Let us suppose a mixture of HCN 10^{-2} M with pK = 9.2 and HBO_2 10^{-2} M with pK = 9.2.

$$\begin{array}{llll}
 & 10^{-9.2} & & \\
HCN & \rightleftharpoons & CN^- + & H^+ \\
10^{-2}\text{-}x & & x & x \\
 & 10^{-9.2} & & \\
HBO_2 & \rightleftharpoons & BO_2^- + & H^+ \\
10^{-2}\text{-}y & & y & y \\
 & 10^{-14} & & \\
H_2O & \rightleftharpoons & H^+ \ + & OH^- \\
 & & z & z
\end{array}$$

The dissolution contains the two acids and the solvent fulfilling its respective equilibria.

Applying the proton condition:

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

Writing every species according to the know concentrations and the $[H^+]$ in equilibrium it leads to $[H^+] = \sqrt{K_{HCN}[HCN] + K_{HBO_2}[HBO_2] + K_w} = \sqrt{10^{-9.2}\times 10^{-2} + 10^{-9.2}\times 10^{-2} + \cancel{10}^{-14}} = 10^{-5.45}$ M where it is observed that the protons in equilibrium are due to the contribution of both acids, and what the solvent provides is negligible. From the respective constants and with the calculated protons in equilibrium, we obtain $[CN^-] = 10^{-5.75}$ M, that will be also the protons that HCN provides; and $[BO_2^-] = 10^{-5.75}$ M, that will be the protons HBO_2 provides. Logically, the contribution of HCN and HBO_2 is identical as their constants and concentrations are equal.

What water provides with those protons in equilibrium will be:

$$[OH^-] = \frac{10^{-14}}{10^{-5.45}} = 10^{-8.55}\,\text{M}.$$

As we have solved our problem assuming that the acids dissociate is negligible to the initial concentrations, we have to prove that the assumption is true: $10^{-2} - 10^{-5.75} = 10^{-2}$. We have assumed well, and can state that the dissolution is in equilibrium on the following way:

$$\begin{array}{llll}
 & 10^{-9.2} & & \\
HCN & \rightleftharpoons & CN^- \ + & H^+ \\
10^{-2} & & 10^{-5.75} & 10^{-5.75} \\
 & 10^{-9.2} & & \\
HBO_2 & \rightleftharpoons & BO_2^- \ + & H^+ \\
10^{-2} & & 10^{-5.75} & 10^{-5.75} \\
 & 10^{-14} & & \\
H_2O & \rightleftharpoons & H^+ \ + & OH^- \\
 & & 10^{-8.55} & 10^{-8.55}
\end{array}$$

The protons in equilibrium are the protons that the HCN provides, plus the protons that the HBO_2 provides, plus the ones that the H_2O in that dissolution provides

$$[H^+] = 10^{-5.75} + 10^{-5.75} + \cancel{10}^{-8.55} = 10^{-5.45}\,\text{M}$$

Dissolution in which all the equilibria are being fulfilled:

$$\frac{10^{-5.75}\times 10^{-5.45}}{10^{-2}} = 10^{-9.2} = K_{HCN},\ \frac{10^{-5.75}\times 10^{-5.45}}{10^{-2}}$$

$$= 10^{-9.2} = K_{HBO_2},$$

$$10^{-5.45}\times 10^{-8.55} = 10^{-14} = K_w$$

Polyprotic Acids

Polyprotic acids are weak electrolytes, except for some cases where the first dissociation constant refers to the complete dissociation. In most cases, the dissociation constants, $K_1, K_2, K_3, \ldots$ differ greatly and $K_1 >> K_2 >> K_3 \ldots$ Thus, only the first two dissociation steps will be taking into account in the dissolution of polyprotic acids.

Let us state the situation of a polyprotic acid H_2A in concentration C_i and with the equilibrium constants K_1 and K_2, that in the dissolution will be:

$$\begin{array}{llll}
 & K_1 & & \\
H_2A & \rightleftharpoons & HA^- \ + & H^+ \\
C_i\text{-}(x+y) & & x & x+y \\
 & K_2 & & \\
HA^- & \rightleftharpoons & A^{2-} \ + & H^+ \\
x & & y & y \\
 & K_w & & \\
H_2O & \rightleftharpoons & H^+ \ + & OH^- \\
 & & z & z
\end{array}$$

From the first dissociation of H_2A acid, as many protons as HA^- appear, but the HA^- not dissociated, that is HA^- plus A^{-2}.

From the second dissociation, as many protons as A^{-2} appear, and as many protons as OH^- appear due to water.

Applying the proton condition to this dissolution:

$$[H^+] = [HA^-] + [A^{2-}] + [A^{2-}] + [OH^-] = [HA^-] + 2[A^{2-}] + [OH^-]$$

- Here again it is proposed "to suppose" that what the acid dissociates is negligible to what there was initially, $C_i - (x + y) = C_i$, and once solved, to prove that the supposition is true.

Writing every species according to the H_2A concentration and to the protons in equilibrium, it leads us to:

$$[H^+] = \frac{K_1[H_2A]}{[H^+]} + \frac{2K_1K_2[H_2A]}{[H^+]^2} + \frac{K_w}{[H^+]} \qquad [7]$$

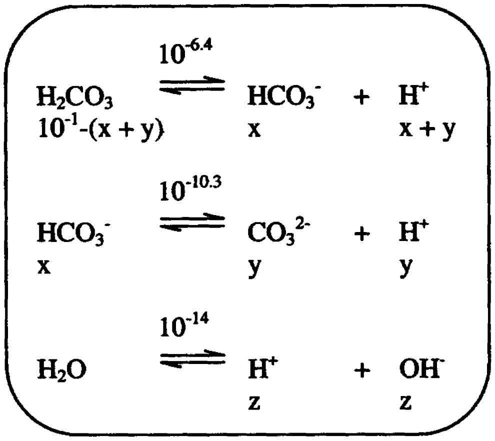
that is the general equation of polyprotic acids.

Generally, the dissociation constants differ greatly, $K_1 >> K_2$, and the protons provided by water are negligible. Thus, Eq. [7] is simplified:

$$[H^+] = \frac{K_1[H_2A]}{[H^+]} \qquad [8]$$

which is identical to the equation for weak monoprotic acids.

Diprotic Weak Acids. Carbonic acid 10^{-1} M with $pK_1 = 6.4$ and $pK_2 = 10.3$



The dissolution is in equilibrium, so we can apply the proton condition:

$$[H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$$

When replacing every term by the initial concentration of H_2CO_3 and by the protons in equilibrium, we have:

$$[H^+] = \frac{K_1[H_2CO_3]}{[H^+]} + \frac{2K_1K_2[H_2CO_3]}{[H^+]^2} + \frac{K_w}{[H^+]}$$

If we suppose that the first term prevails over the other ones, we obtain

$$[H^+] = \frac{K_1[H_2CO_3]}{[H^+]},$$

and once solved it leads us to

$$[H^+] = 10^{-3.7}\,M.$$

To prove that the supposition is true, we substitute the numerical values in the general equation

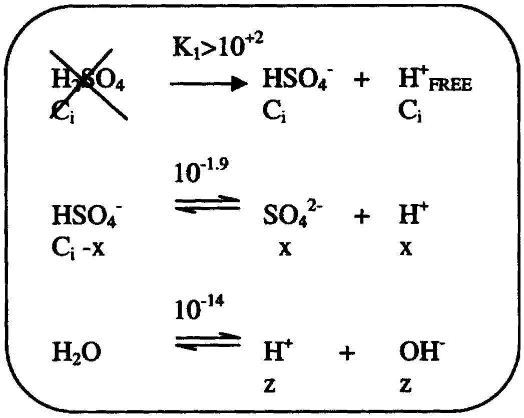
$$[H^+] = \frac{10^{-6.4}\times 10^{-1}}{10^{-3.7}} + \frac{2\times 10^{-6.4}\times 10^{-10.3}\times 10^{-1}}{(10^{-3.7})^2} + \frac{10^{-14}}{10^{-3.7}} = 10^{-3.7} + \cancel{10}^{-10.0} + \cancel{10}^{-10.3} = 10^{-3.7}\,M,$$

where it is proved that the first term is the one that prevails.

From the respective constants and with the calculated protons in equilibrium, we obtain:

$$[H^+] = 10^{-3.7}\,M = [HCO_3^-]\,[CO_3^{2-}] = 10^{-10.3}\,M,\ [H_2CO_3] = 10^{-1} - 10^{-3.7} - 10^{-10.3} = 10^{-1}\,M$$

Diprotic Acid Where the First Equilibrium is Completely Dissociated. Sulphuric acid in concentration C_i and with $pK_1 < -2$ and $pK_2 = 1.9$.



The solution is in equilibrium and we will be able to apply the proton condition:

$$[H^+] = [H^+]_{FREE} + [SO_4^{-2}] + [OH^-]$$

There is a strong acid and a weak acid, but the contribution of no species is negligible. However, the protons that H_2O provides to the dissolution are negligible.

Furthermore, what the weak acid dissociates to is not negligible to what there was initially, due to the high value of its constant, the sulphate will be

$$[SO_4^{2-}] = \frac{K_aC_i}{K_a + [H^+]}.$$

If we replace this expression in the proton condition we obtain:

$$[H^+] = [H^+]_{FREE} + \frac{K_aC_i}{K_a + [H^+]} + \frac{K_w}{[H^+]} \qquad [9]$$

That will be the general equation for mixture of strong acid and weak acid if what the acid dissociates is not negligible to what there was initially, and if the concentration of protons produced by the dissociation of water can be neglected, we obtain the simplified equation:

$$[H^+] = [H^+]_{FREE} + \frac{K_aC_i}{K_a + [H^+]} \qquad [10]$$

from where

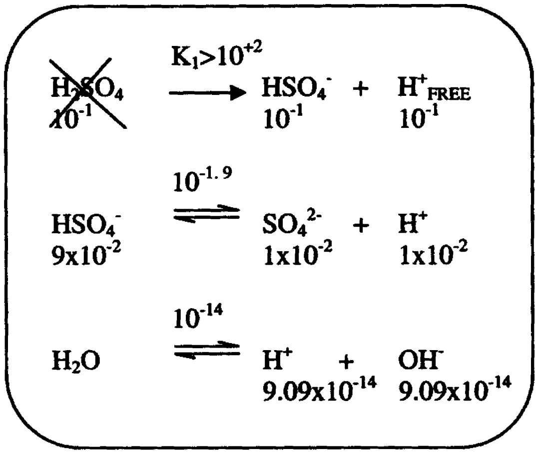
$$[\mathrm{H}^+] = \frac{\mathrm{C_i - K_a} + \sqrt{(\mathrm{K_a - C_i})^2 + 8\mathrm{K_aCi}}}{2}$$

Let us suppose a 10^{-1} M solution of H_2SO_4 from which we want to know the concentrations of all species in equilibrium. The protons of the dissolution will be:

$$[\mathrm{H}^+] = \frac{10^{-1} - 10^{-1.9} + \sqrt{(10^{-1.9} - 10^{-1})^2 + 8 \times 10^{-1.9} \times 10^{-1}}}{2}$$
$$= 1.1 \times 10^{-1}\,\mathrm{M}$$

From the respective constants and with the calculated protons in equilibrium, we obtain $[SO_4^{2-}] = 0.010\,M = [H^+]$ that HSO_4^- provides, $[HSO_4^-] = 0.090$ M, $[OH^-] = 9.09 \times 10^{-14}$ M that will be the protons H_2O provides and that are negligible to the ones the acids provide. The simplified Eq. [10] is true.

The dissolution in equilibrium will be formed by:



Once again, the protons in equilibrium continue being additive:

$$[\mathrm{H}^+] = 1 \times 10^{-1} + 1 \times 10^{-2} + 9.0\cancel{9} \times 10^{-14} = 1.1 \times 10^{-1}\,\mathrm{M}.$$

CONCLUSION

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

The treatment of the acid-base equilibria that is proposed could become immersed in the dissolution and to look at the equilibria that are fulfilled in each case. The matter is not to get a general formula, but in each case the proton condition in equilibrium will be applied, and it will lead us to the solution of our particular problem.

We want the students not to study the formulae by heart, but to know to rationalize what happens in a dissolution and how that dissolution will be in equilibrium. Every new dissolution is a new problem, a new problem to think about. The important question is not to get a more- or less-complicated formula; what is important is to know to reach to an understanding of what each of the species of the dissolution provides. In this way, when moment of solving an acid-base problem, it is proposed that the protons that at least are present in the dissolution are taken into account, so that we will be able to observe which species are negligible according to the contribution of protons, and as a consequence, to be able to simplify the equation that leads us to the solution.

Furthermore, using the proton condition we reach the conclusion that the protons in equilibrium are additive, for strong acids as well as weak acids.

In this article, the acid-base equilibria have been solved algebraically; using the proton condition, they can be solved graphically in the same way.

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