Equilibriums in water - exemplified by inorganic carbon

Ions and compounds are in equilibriums with each other. A typical equilibrium is the one between ammonia (NH_3) and ammonium (NH_4^+) discussed in the section about pK_a and K_a. These types of equilibriums are dependent on pH.

pH determines how much of a compounds or an ion in an equilibrium is dissociated. A simple example is already given in the pK_a / K_a section, so here's a better one:

Consider the equilibrium between carbonic acid, bicarbonate and carbonic ion: H_2CO_3, HCO_3^- and CO_3^{2-}. First of all it should be noted that only approximately 1/400 of the carbonic acid H_2CO_3 is on the form H_2CO_3. The rest is on the form CO_2.

For this reason the carbonic acid in the "inorganic carbon equilibrium" is often denoted CO_2^* even though it at first sight seems unreasonable that CO_2^* can dissociate into HCO_3^-

To calculate the concentration of individual species in the equilibrium one first have to introduce a variable denoting the sum of concentrations of CO_2^*, HCO_3^- and H_2CO_3. This variable should be called TIC - a shortcut for Total Inorganic Carbon.

$$TIC = [CO_2^*] + [HCO_3^-] + [CO_3^{2-}]$$

If we start by finding the $[CO_2^*]$, CO_2^* should be isolated in the above equation. By rearranging the equation above to:

$$TIC = [CO_2^*] \cdot \left(1 + \frac{[HCO_3^-]}{[CO_2^*]} + \frac{[CO_3^{2-}]}{[CO_2^*]}\right)$$

If both sides are divided by $\left(1 + \frac{[HCO_3^-]}{[CO_2^*]} + \frac{[CO_3^{2-}]}{[CO_2^*]}\right)$ we get that:

$$[CO_2^*] = \frac{TIC}{1 + \frac{[HCO_3^-]}{[CO_2^*]} + \frac{[CO_3^{2-}]}{[CO_2^*]}}$$

To move on with this equation and to see how it depend on $[H^+]$ we introduce $[H^+]$ in the denominator:

$$[CO_2^*] = \frac{TIC}{1 + \frac{[HCO_3^-] \cdot [H^+]}{[CO_2^*] \cdot [H^+]} + \frac{[CO_3^{2-}]}{[CO_2^*]}}$$

At this point it is necessary to recall the definition of the dissociation or ionization constant. A more detailed explanation on this subject can be found on the site about pK_a and K_a.

The ionization or dissociation constant of CO_2^* is $\frac{[HCO_3^-]\cdot[H^+]}{[CO_2^*]}$

This ionization constant of CO_2^* ($K_a(CO_2^*)$) can be substituted into denominator of the equation for TIC:

$$[CO_2^*] = \frac{TIC}{1 + \frac{K_a(CO_2^*)}{[H^+]} + \frac{CO_3^{2-}}{CO_2^*}}$$

The calculation is not finished yet. $[CO_3^{2-}]$ and $[CO_2^*]$ are not known and the equation as it is right now is not of much use.

The substitution for $\frac{CO_3^{2-}}{CO_2^*}$ is different from previous. It's more complicated.

The ionization constant of HCO_3^- is $\frac{[H^+]\cdot[CO_3^{2-}]}{[HCO_3^-]}$

If this, the ionization constant of HCO_3^- is multiplied by the ionization constant of CO_2^* we get that:

$$K_a(HCO_3^-)\cdot K_a(CO_2^*) = \frac{[H^+]\cdot[CO_3^{2-}]}{[HCO_3^-]}\cdot\frac{[HCO_3^-]\cdot[H^+]}{[CO_2^*]} = \frac{[CO_3^{2-}]\cdot[H^+]^2}{[CO_2^*]}$$

But this is the same as saying that:

$$\frac{K_a(HCO_3^-)\cdot K_a(CO_2^*)}{[H^+]^2} = \frac{[CO_3^{2-}]}{[CO_2^*]}$$

This can be substituted into the equation for CO_2^* from before:

$$[CO_2^*] = \frac{TIC}{1 + \frac{K_a(CO_2^*)}{[H^+]} + \frac{K_a(HCO_3^-)\cdot K_a(CO_2^*)}{[H^+]^2}}$$

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Nielsen, May 2007