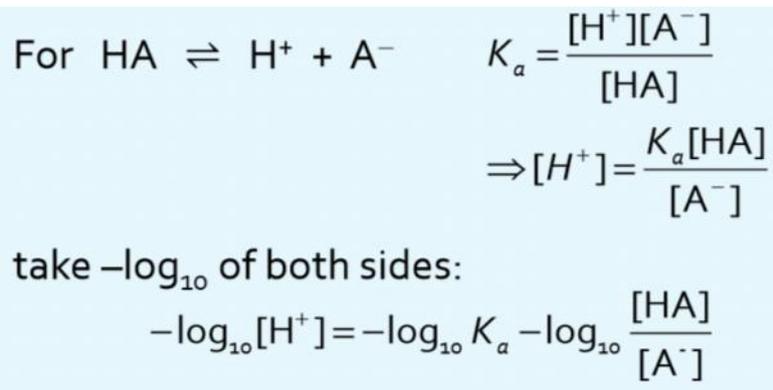


Lecture 1, 2 & 3 - Acid-Base Chemistry

Monday, 27 July 2015 1:59 PM

Revision:

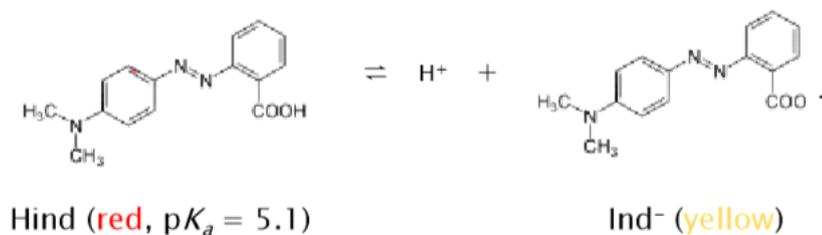
- Acid - proton donor, produces H^+ in aqueous solutions
 - Base - proton acceptor, produces OH^- in aqueous solutions
 - $K_W = [H^+][OH^-] = 10^{-14}$
 - $pH + pOH = 14$
 - Strong acids - HCl, HBr, HI, HNO_3 , H_2SO_4 , $HClO_4$ (perchloric) - all dissociate completely in water
 - Strong bases - NaOH, LiOH, KOH etc. (all group 1 metal hydroxides)
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- For weak base dissociation, an example equation is:
 $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
The OH^- ion comes from the water molecule
 - The equilibrium constant for weak base dissociation is K_b , and its size tells us about the strength of the base
 - e.g. $K_b = [NH_4^+][OH^-] / [NH_3]$
 - A small K_b indicates a weak base
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- Most cations (except Group 1 and some Group 2 metal ions) are weak acids, and undergo **acid hydrolysis** (hydrolysis = reaction with water)
 - This is why transition metal ion solutions precipitate unless acid is added - precipitation is seen as cloudiness, and adding acid clarifies the solution
 - Group 1 metal ions don't hydrolyse in water, so they have no effect on pH, therefore they are **pH-neutral ions**
 - The anion (A^-) of a weak acid (HA) is a weak base because it will react with water (hydrolyse) to produce a small amount of OH^- ($A^- + H_2O \rightleftharpoons HA + OH^-$)
 - So most anions (except OH^- , HSO_4^- , Cl^- , Br^- , I^- , NO_3^- , ClO_4^- - anions of strong bases) are weak bases
 - Most are pH neutral
 - With anions that could be acidic or basic (e.g. $H_2PO_4^-$), we have to look at the pK_a and pK_b to see which is smaller (which K is bigger)
 - e.g. $pK_b(H_2PO_4^-) = 11.88$
 $pK_a(H_2PO_4^-) = 7.21$
therefore, $H_2PO_4^-$ is acidic because $pK_a < pK_b$
 - Given the formula of many salts, we can decide if they will produce acidic, basic or neutral solutions in water
 - e.g. NaF - Na^+ is neutral (group 1 metal ion), F^- is the anion of a weak acid, and is basic. Therefore the overall salt solution will be basic
 - e.g. KCN - K^+ is neutral (group 1 metal ion), CN^- is the anion of a weak acid, and is basic. Therefore the overall salt solution will be basic
 - e.g. $NaNO_3$ - both ions are neutral, so solution will be pH 7 (neutral)
 - If the cation is acidic and the anion is basic (e.g. NH_4F), we look at pK_a for the acidic ion, and pK_b for the basic ion, and the smallest pK (biggest K) wins
e.g. $pK_a(NH_4^+) = 9.24$, $pK_b(F^-) = 10.83$, so the salt is slightly acidic in water
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- Buffer - a solution that resists change in pH
 - A buffer is a mixture of a weak acid and its conjugate weak base
 - The conjugate base consumes any added H^+ , while the conjugate acid consumes any added OH^-
 - Best buffering occurs at pH values near the pK_a of the conjugate acid
 - Different conjugate acid/base pairs give buffering at different pH values
 - In order to determine the pH of a particular buffer system (or determine the amount of each substance needed to create a buffer for a specific pH), we use the Henderson-Hasselbalch Equation



$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]}$$

- The best buffer solutions will have a ratio of $[\text{A}^-]/[\text{HA}]$ which is close to 1
- The buffer capacity is the amount of added acid or base a buffer can tolerate before its pH changes significantly
- Buffers are usually made by titrating either the appropriate conjugate acid with a small volume of conc. NaOH or the conjugate base with (say) conc. HCl until the desired pH is obtained (indicated by pH meter)
- Graphs can be used to detect the equivalence point in a titration - there is a very steep rise in pH around the equivalence point, while the volume does not change
- At the titration mid-point (halfway between beginning and equivalence point), $\text{pH} = \text{p}K_a$ (conjugate acid)
- An indicator is usually a weak acid or base that undergoes a dramatic colour change over a reasonably narrow pH range
- The indicator endpoint should be as close as possible to the equivalence point
- A good indicator therefore changes colour in the steepest part of the titration curve
- The pH range of an indicator should correspond with the estimated pH of the equivalence point of your reaction
- Most indicators are organic dyes that have differently coloured base (Ind^-) and acid (Hind) forms

■ e.g. Methyl red



- Methyl red is red if ratio is $<1/10$, yellow if ratio $>10/1$ and orange in between
- Colour change will occur roughly between $\text{pH} = \text{p}K_a(\text{Ind}) - 1$ and $\text{pH} = \text{p}K_a(\text{Ind}) + 1$
- So if you know the $\text{p}K_a(\text{Ind})$ (look up), you can estimate it will change colour in the range **$\text{pH} = \text{p}K_a(\text{Ind}) \pm 1$**