Acid-Base and Buffer Notes

Approaching a problem:
Determine what type of compound(s) is/are present. Strong or weak acid? Strong or weak base? Ionic compound which is acidic or basic?

For reactions which go to completion:
Set up a chart in moles to determine which is limiting and what will be left over.
Look at what is left over and determine what types of compounds are present.
Determine which of the following situations fits your mixture. If needed, determine the new concentrations (dividing #moles by the total volume). If you are dealing with an equilibrium, set up the next chart in molarities.

Single compounds

1. Strong acid by itself in water. Calculate pH by first calculating the $[H_3O^+]$ in the acid solution. Strong acids: HCl, HBr, HI, HNO_3, H_2SO_4 (first ionization), $HClO_3$, $HClO_4$.

2. Strong base by itself in water: Calculate pH by first calculating the $[OH^-]$ in the solution. Strong bases: NaOH, KOH, $Ba(OH)_2$, any soluble metal hydroxide.

3*. Weak acid by itself in water: Write the K_a reaction and the K_a expression. Use equilibrium concepts to solve the problem. Check any assumptions made. You might want to use the method of successive approximations. Weak acids: any acid which is not one of the strong acids above; cations of weak bases (meaning: conjugate acids of weak bases); some metal ions.

4*. Weak base by itself in water: Write the K_b reaction and the K_b expression. Use equilibrium concepts to solve the problem. Check any assumptions made. You might want to use the method of successive approximations. Weak bases: neutral weak bases often contain nitrogen. Look for a $-NH_2$ group, an -NH, or just a nitrogen somewhere. Anions of weak acids are also weak bases (meaning: conjugate bases of weak acids are weak bases.) Look for an ionic compound which contains an anion other than Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, ClO_3^-, or ClO_4^-. Example: NaF contains F^-, a weak base.

5. Neutral compound by itself in water: solution will be neutral. pH = 7.00 at 25°C. Example: $KNO_{3\,(aq)}$: both ions are neutral.

Combinations of compounds

6. Strong acid and strong base: Will react with each other. The reaction goes to completion. Determine the number of moles of each, which is the limiting reactant, and how much of which ion (H_3O^+ or OH^-) remains after the reaction. Use the total volume to calculate the concentration of the ion in excess after the reaction, then calculate pH.

7*. Weak acid and strong base: Will react with each other. The reaction goes to completion. Write the chemical equation for the reaction. Determine the number of moles of each, which is the limiting reactant, and how much of which species (HA, A^-, or OH^-) remains after the reaction. Use the total volume to calculate the concentration of each species left after the reaction. Then: what type of compound(s) is/are left?
(a) just A^-: to finish calculation, treat as a weak base problem. See **4** above.

(b) A^- and HA: if the ratio of these two species is between 1/10 and 10/1, treat as a buffer. To finish the calculation, see **9** below.
(c) A^- and OH^-: Depending on the relative amounts of these two species, either treat as a weak base in the presence of a common ion, or if the amount of hydroxide is significantly greater, calculate the $[H_3O^+]$ and pH based on just the hydroxide. See **12** below.

8*. <u>Weak base and strong acid</u>: Will react with each other. The reaction goes to completion. Write the chemical equation for the reaction. Determine the number of moles of each, which is the limiting reactant, and how much of which species (HA, A^-, or H_3O^+) remains after the reaction. Use the total volume to calculate the concentration of each species left after the reaction. Then: what type of compound(s) is/are left?
(a) just HA: to finish calculation, treat as a weak acid problem. See **3** above.
(b) A^- and HA: if the ratio of these two species is between 1/10 and 10/1, treat as a buffer. To finish the calculation, see **9** below.
(c) HA and H_3O^+: Depending on the relative amounts of these two species, either treat as a weak acid in the presence of a common ion, or if the amount of hydronium ion is significantly greater, calculate the pH based on just the $[H_3O^+]$. See **11** below.

9*. <u>Weak acid and weak base which are conjugates of each other</u>: Determine the number of moles of each. If the ratio of these two species is between 1/10 and 10/1, it is a buffer. Write either the K_a or the K_b reaction and the corresponding equilibrium constant expression. Once you have determined that the solution is a buffer, it is the ratio of A^- to HA that determines the pH. This can be either the ratio of concentrations or the ratio of <u>moles</u>. The expression can turn into: $K_a = [H_3O^+](\text{moles } A^-/\text{moles HA})$ or $K_b = [OH^-](\text{moles HA}/\text{moles } A^-)$. This is a very important shortcut!!
You don't even have to know the actual number of moles as long as you know the ratio. Also, for a buffer, it is almost always safe to assume that the initial concentrations of the conjugate acid and base are equal to the concentrations at equilibrium (so once you know it's a buffer, you don't have to make a chart showing how things change as they go to equilibrium). Check any assumptions made, just to be safe.

10. Weak acid and weak base which are not conjugates of each other: will react, but the reaction will not necessarily go to completion. Use the K_a and the K_b reactions to find the overall equilibrium constant for the entire reaction. Consider the size of the resulting K_c in determining how to proceed. (If K is very large, it goes to completion. If K is medium or small, treat it as an equilibrium problem.) This type of reaction is not very important compared to the other types.

11. Strong acid and weak acid: Will not react. Probably, the pH and the $[H_3O^+]$ will be determined by the strong acid in the solution. Be sure to take into account the change in volume when determining the concentrations.

12. Strong base and weak base: Will not react. Probably, the pOH and the $[OH^-]$ will be determined by the strong base in the solution. Be sure to take into account the change in volume when determining the concentrations.

<u>**13**.* Strong acid added to a buffer</u>: The SA will react with the conjugate base in the buffer. Write the equation for the reaction, find moles of all species: H_3O^+, A^-, and HA initially and after the reaction. What's left? The analysis will be similar to **8** above.

14.* Strong base added to a buffer: The SB will react with the conjugate acid in the buffer. Write the equation for the reaction and find the moles of all species: OH^-, HA, and A^- initially and after the reaction. What's left? Analyze similar to **7** above.

15. Making a buffer of a specific pH: from the given pH, choose a system so that the pK_a of the conjugate acid of the system is as close as possible to the desired pH. Once this system is chosen, determine the ratio of A^-/HA needed in the buffer (plug in the K_a and the $[H_3O^+]$ into the K_a expression and solve for the ratio of A^-/HA). Any solution with that ratio of A^-/HA will work, but choose relatively high concentrations of each so that the solution has a reasonable buffer capacity. Are there any other constraints on the problem?

a. If the least (or most) concentrated buffer component must have a certain concentration: from the ratio of A-/HA, figure out which is the least (or most) concentrated component. Use the ratio of A-/HA to determine the concentration or moles of the other component, and then from the total volume, determine grams of solid or volumes of solution needed to give these concentrations.

b. If you have to start with just HA and OH- to make the buffer: Some of the initial HA will be converted to A-. The number of moles of HA to start with is equal to the number of moles of HA and A- added together in the final buffer. The number of moles of OH- to add is equal to the number of moles of A- needed in the final buffer. (Every 1 mole of OH- added converts 1 mole of HA to A^-).

c. If you have to start with just A^- and H_3O^+ to make the buffer: Some of the initial A- will be converted to HA. The number of moles of A- to start with is equal to the number of moles of HA and A- added together in the final buffer. The number of moles of H_3O^+ to add is equal to the number of moles of HA needed in the final buffer. (Every 1 mole of H_3O^+ added converts 1 mole of A^- to HA.)

d. If you are starting with a buffer and you need to change its pH to a specified pH: If the pH is increasing, you need to add base (either OH^- or A^-). If the pH is decreasing, you must add acid (either H_3O^+ or HA). First, from the needed pH, determine the mole ratio of A-/HA needed in the new buffer solution. Remember that adding OH^- to the buffer will convert HA to A-. Adding A^- will not cause a reaction, it will just increase the amount of A^- present. Adding H_3O^+ to the buffer will convert A^- to HA. Adding HA will not cause a reaction, it will just increase the amount of HA present.

From the old mole ratio, the type of change, and the new mole ratio, determine the amount of strong base, weak base, strong acid, or weak acid to add.