

## “Thinking” chemistry...

One of the common difficulties is that we consider acid/base equilibrium predominantly through the addition of a weak acid or base to neutral water at 298 K. However, there are many situations where acid/base chemistry must be applied that do not meet these narrow conditions. Working with buffer systems, mixtures of strong and weak acids, acid/base indicators, lactic acid/lactate in foods or the human body, whether the preservative in diet sodas should be called benzoic acid or sodium benzoate... It can be difficult reasoning through the dominant species in solution at various pH levels when an acid/base equilibrium is involved. Reasoning based on pKa vs pH can make this easier.

Fundamental idea: for a mixture containing weak acid HA (or weak base A-)...

when  $[HA] = [A^-]$ ,  $[A^-]/[HA] = 1$ , so  $pH = pK_a + \log 1$  (but  $\log 1 = 0$ , so)

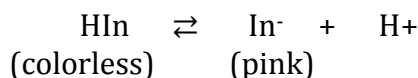
$$pH = pK_a$$

and therefore...

- if the pH of the mixture is lower than the pKa of the weak acid,  $[HA] > [A^-]$
- if the pH of the mixture is greater than the pKa of the weak acid,  $[HA] < [A^-]$

Taking an acid/base titration with an indicator as an example:

Indicators are often solutions of weak acids, with the un-ionized (we'll represent as HIn) and ionized forms (In<sup>-</sup>) transmitting different colors of light. Phenolphthalein, for example, is colorless in its “acid” or un-ionized form, but its ionized form appears pink.

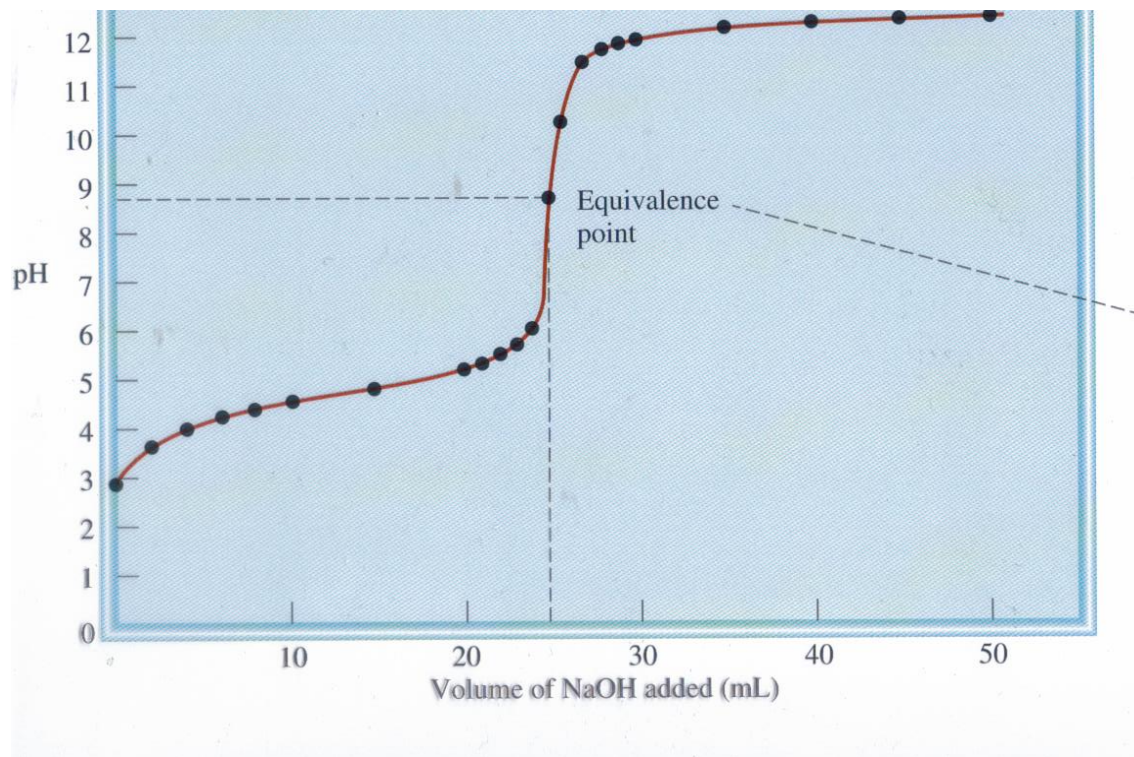


Phenolphthalein has a pKa of 9.3. When conducting a titration of an acid analyte with a base titrant using phenolphthalein as the indicator, the pH will be low at the beginning, so the phenolphthalein will be mostly in the un-ionized or “protonated” “acid” form (we'll refer to as HIn). As the pH increases over the course of the titration, the pH will eventually get close to the pKa of phenolphthalein, and when  $pH = pK_a$ , there will be roughly equivalent amounts of the un-ionized form (HIn) and the deprotonated, or ionized form (In<sup>-</sup>). Since the deprotonated form is colored, the characteristic color of the deprotonated phenolphthalein is evident at pH 9.3. However, the human eye can detect color well below the 50% threshold, so most textbooks give a rule of 10% deprotonation as sufficient for color to be noticed, or 1 pH unit prior to the pKa of the indicator. As such, phenolphthalein is usually given an indicator range of just above pH 8 → pH 10 for use in titrations. So when  $pH < pK_a$  of phenolphthalein, it will be mostly colorless because it will be un-ionized. If pH is close to pKa, then there will be a mixture of protonated (HIn) and deprotonated (In<sup>-</sup>) forms of the indicator. If pH is greater than pKa, then the phenolphthalein will be mostly deprotonated (In<sup>-</sup>) and appear pink. This can be confirmed with calculations, the Henderson-Hasselbach equation, and/or conceptual reasoning through Le Chatelier's Principle.

If we can reason quickly that if  $pH < pK_a$  then the protonated or unionized form is dominant, then we can estimate an approximate value prior to (or instead of) calculating a value. Alternatively, we can check at the end if our answer makes sense. If asked a simple question of “is pentanoic acid mostly ionized or un-ionized in a buffer of  $pH = 6$ ,” we should be able to do that estimation in our heads given the pKa for pentanoic acid. If we have to set up an ICE chart and solve for the equilibrium concentrations, that will take a lot of time for something that can be easily estimated through a comparison of pH and pKa. We often are asked questions about “what will the pH be” or “what is the equilibrium concentration of the acid.” It's also important to consider the relative concentrations of the acid compared to the conjugate base in a variety of situations, and well as when that balance inverts.

Moving into future coursework, for example, Biochemistry, we can more easily reason through the complexities of amino acids and which form of the amino acid is present at different pH levels. Even in Biology, we are exposed to lactic acid fermentation and metabolism of the lactate ion, and we should be able to easily reason (without calculation) that the human body's pH is significantly higher than the pKa of lactic acid (3.86), so the lactate ion is dominant, even though biologists typically refer to both as “lactic acid.” However, during lactic acid fermentation, the pH of the surroundings gradually decreases as the bacteria convert sugars into lactic acid/lactate, producing mostly lactate (with an equal amount of hydrogen ion). However, the proportion of lactic acid increases as the fermentation continues, since the pH of the surroundings gradually decreases with the release of so many hydrogen ions. This explains why milk which tastes slightly sweet becomes sour and tangy yogurt, and why *lactate* is produced from “*lactic acid*” fermentation.

Weak acid titrated with strong base...



Weak base titrated with strong acid

