Notes on the Titration Curve for a Weak Acid

Adapted from : Skoog, D. A., West, D. M. and Holler, F. J.
"Fundamentals of Analytical Chemistry," 7th Ed.; Ch. 10
Saunders College Publishing: Fort Worth, 1996.

(And from Prof. J. I. Steinfeld's lecture, Oct. 2001.)
Transcribed and considerably expanded from 5.311 lecture, 10/8/02.

- We need to determine the pK_a of the unknown carboxylic acid, as one of the clues in its identification. One way to do this is to determine the pH of the solution when half of the acid has been neutralized:

$$HA + \tfrac{1}{2}\,{}^{-}OH \rightleftarrows \tfrac{1}{2}A^- + \tfrac{1}{2}HA + \tfrac{1}{2}H_2O$$

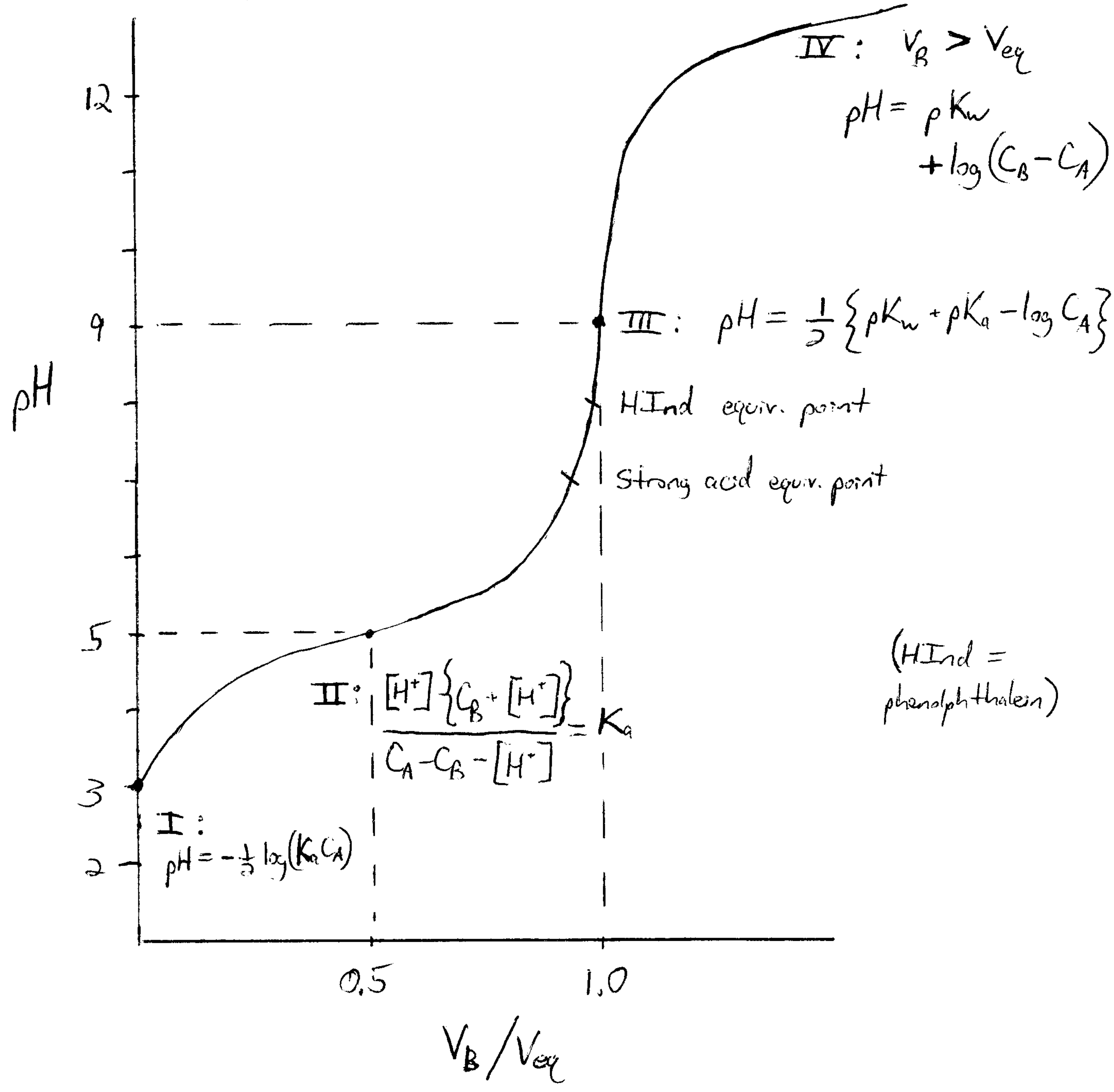
At this point, [HA] and $[A^-]$ are (very nearly) equal.

Recall the Henderson - Hasselbalch equation:

$$pK_a = pH - \log\frac{[A^-]}{[HA]} \quad \text{or} \quad pH = pK_a + \log\frac{[A^-]}{[HA]}$$

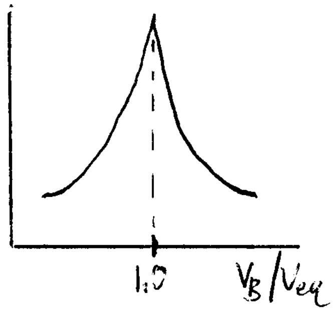
Halfway to the equivalence point, $\frac{[A^-]}{[HA]} = 1$, and the log term disappears ; $pK_a = pH$! So we need to be able to identify that point, and determine the corresponding pH.

Here is a typical titration curve for a weak acid (approximate)



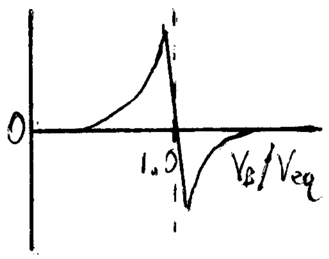
1st deriv.:

$$\frac{d(pH)}{d(V_B/V_{eq})}$$



2nd deriv.:

$$\frac{d^2(pH)}{d(V_B/V_{eq})^2}$$



A few variables will come in handy:

n_A = number of moles of <u>starting</u> acid

$C_A = n_A / (\text{vol. of sol'n})$

n_B = number of moles of base added ; V_B = volume of base added. (proportional to n_B, C_B)

$C_B = n_B / (\text{vol. of sol'n})$

$[HA]$ = current concentration of undissociated acid

$[A^-]$ = anion concentration

$pH = -\log[H^+]$; $pK_a = -\log K_a$; $pK_w = -\log K_w = 14$

Note: At the equivalence point, $C_A = C_B$; $n_A = n_B$. V_{eq} is the volume of base needed to reach this point.

$$V_B / V_{eq} = n_B / n_A = C_B / C_A$$

— We will derive the equations that govern the titration curve for regions I (before any base is added), II (roughly V_B/V_{eq} between 0.2 and 0.8), III (at the equivalence point) and IV (well beyond the equivalence point).

— For now, note that the curve steepens as it approaches the equiv. point, but shallows out after it. If you can calculate (using Excel) the point where the second derivative reaches zero, you have found the equivalence point.

- Again, when half of the base needed to reach the equivalence point has been added ($V_B = \frac{1}{2} V_{eq}$), $[A^-] = [HA]$, and $pH = pK_a$. You can calculate this volume based on V_{eq}, then read (interpolate) the corresponding pH, as the first way to determine pK_a.

- With respect to the volumetric titration, used to calculate molecular weight: Note how steeply pH rises, for a given increment of base, near the equiv. point. Phenolphthalein will actually turn pink at a pH below the equivalence point of most carboxylic acids, but the difference in pH translates to a <u>very</u> small error in volume — a negligible one, for our purposes.

<u>Derivations</u>

— Region I – Before addition of base

Consider: $HA + H_2O \rightleftharpoons H_3O^+ + A^-$

We are using dilute solutions, and the activity coefficients approach 1.

Thus, $K_{eq} = \dfrac{[H_3O^+][A^-]}{[H_2O][HA]}$ simplifies to $K_a = \dfrac{[H^+][A^-]}{[HA]}$.

Let α equal the fraction of [HA] that dissociates.

$1-\alpha$ is by definition the mole fraction that remains.

$$[HA] = C_A(1-\alpha) = C_A - \alpha C_A$$

Let $x = \alpha C_A$

$$HA \rightleftharpoons H^+ + A^-$$

$C_A - x$ $\qquad$ x $\qquad$ x $\qquad$ (concentration of species, in moles $\cdot L^{-1}$)

$$K_a = \frac{x^2}{C_A - x}$$

How to solve this?

1) It's a quadratic equation : $K_a(C_A - x) - x^2 = 0$

2) We can simplify it. For a weak acid, $K_a \ll 1$.

Therefore $\alpha \ll 1$, and $x \ll C_A$.

$$K_a = \frac{x^2}{C_A - x} \approx \frac{x^2}{C_A}$$

$$x^2 = K_a C_A$$

$$x = [H^+] = \sqrt{K_a C_A}$$

$$pH = -\log (K_a C_A)^{1/2}$$

$$= -\frac{1}{2}\log K_a C_A$$

So, for a 0.1 M solution of a carboxylic acid of $pK_a = 5$, the starting pH should be very close to 3.

–Region II : Some base added, but less than V_{eq}.

Adding $Na^+ \, {}^-OH$.

$$\underset{Na^+}{HA + {}^-OH} \rightleftarrows \underset{Na^+}{A^-} + H_2O$$

Cations and anions must be present in equal concentration:

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

This is an acidic solution, however, so $[{}^-OH]$ is very small relative to $[A^-]$.

$$[H^+] + [Na^+] \approx [A^-]$$

Note that $[Na^+] = C_B$ (number of moles NaOH added ÷ sol'n volume)

$$[A^-] = [H^+] + C_B$$

– So we have an expression for the anion concentration, and we're measuring pH (and thus, indirectly, $[H^+]$). What about the concentration of undissociated acid?

$$C_A = [HA] + [A^-]$$

$$[HA] = C_A - [A^-]$$ (We just derived $[A^-]$.)

$$[HA] = C_A - C_B - [H^+]$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]\{C_B + [H^+]\}}{C_A - C_B - [H^+]}$$

- This equation (which is where the lecture left off) may seem an odd way to express the proton concentration, but it allows the convenient derivation of the Gran's plot equation.
- The Gran's plot is the second method to determine the pK$_a$ of your acid. It is a linear plot of quantities you can calculate from part of your titration data (the early part). The slope of the line gives you the acid dissociation constant.
- The assumptions used here work well for $(0.2 < V_B/V_{eq} < 0.8)$ (roughly). Outside this range they break down (think about why).

$[H^+] \ll C_B$

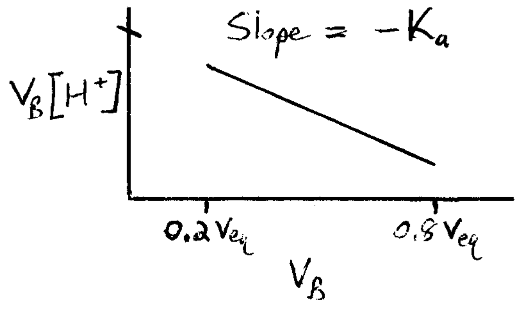
$$K_a = \frac{[H^+]\{C_B + [H^+]\}}{C_A - C_B - [H^+]}$$

$$K_a \approx \frac{[H^+]\,C_B}{C_A - C_B} = \frac{[H^+]\,V_B}{V_{eq} - V_B}$$

$$[H^+]\,V_B = K_a\,(V_{eq} - V_B)$$

$$[H^+]\,V_B = -K_a V_B + K_a V_{eq}$$

This is the equation of a line, since $K_a V_{eq}$ is a constant.



III. The Equivalence Point

$$n_A = n_B$$

The equilibrium that applies here is

$$A^- + H_2O \rightleftarrows HA + {}^-OH$$

Concentrations $C_A - x$ $\quad x \quad x$

$$K_{eq} = \frac{[{}^-OH][HA]}{[H_2O][A^-]}$$

$$K_{eq}[H_2O] = \frac{[{}^-OH][HA]}{[A^-]} = \frac{x^2}{C_A - x}$$

Recall: $K_w = [H^+][{}^-OH]$ (in water) $= 10^{-14}$

We can express $[{}^-OH]$ in terms of $[H^+]$ and a constant:

$$[{}^-OH] = \frac{1}{[H^+]} K_w$$

Substituting: $$\frac{\frac{1}{[H^+]} K_w [HA]}{[A^-]} = \frac{K_w [HA]}{[H^+][A^-]} = \frac{K_w}{K_a} = \frac{x^2}{C_A - x}$$

$x << C_A$, so $$\frac{x^2}{C_A} \approx \frac{K_w}{K_a} \quad ; \quad x^2 = \frac{K_w C_A}{K_a}$$

$$x = [{}^-OH] = \sqrt{C_A K_w / K_A} \quad ; \quad [H^+] = K_w / [{}^-OH]$$

$$[H^+] = \sqrt{K_w K_A / C_A}$$

If $[H^+] = \left(\frac{K_w K_A}{C_A}\right)^{\frac{1}{2}}$, then

$$\log [H^+] = \frac{1}{2}\left(\log K_w + \log K_a - \log C_A\right)$$

$$-\log [H^+] = \frac{1}{2}\left(-\log K_w - \log K_a + \log C_A\right)$$

$$pH = \frac{1}{2}\left(pK_w + pK_a + \log C_A\right)$$

For a 0.1 M starting concentration of acid with $pK_a = 5$, pH at the equivalence point is $\frac{1}{2}(14 + 5 - 1) = 9$.

— For a weak acid, the ability of A^- to deprotonate water results in a pH higher than neutral at the equivalence point.

Region IV : Beyond the equivalence point

$n_B > n_A$ $\qquad [OH] = \frac{n_B - n_A}{\text{volume of soln}} = C_B - C_A$

$$[H^+] = \frac{K_w}{[OH]} = \frac{K_w}{C_B - C_A}$$

$$\log [H^+] = \log K_w - \log (C_B - C_A)$$

$$pH = pK_w + \log (C_B - C_A)$$

Consider why the curve is steepest at the equivalence point.

— Before the equivalence point: Region II

$$K_a = \frac{[H^+]\{C_B + [H^+]\}}{C_A - C_B - [H^+]}$$

$$[H^+] = \frac{K_a(C_A - C_B - [H^+])}{C_B + [H^+]}$$

Let's simplify this $C_B >> [H^+]$. At the equivalence point, $[H^+]$ is about 10^{-8} or 10^{-9} M, So even if $C_A = 0.1000$ M and $C_B = 0.0999$ M, $C_A - C_B - [H^+]$ will be very close to $C_A - C_B$.

So $[H^+] \simeq \dfrac{K_a(C_A - C_B)}{C_B}$; $-\log[H^+] \simeq -\log K_a - \log(C_A - C_B) + \log C_B$

$$pH \simeq pK_a + \log C_B - \log(C_A - C_B)$$

This approximation will break down if taken too near the equivalence point (pH will never actually be undefined). But we can see that as $C_A - C_B$ becomes a smaller fraction, $-\log(C_A - C_B)$ will become a larger positive term — until the equivalence point.

— Similar reasoning works after the equivalence point. The curve follows the equation $pH = pK_w + \log(C_B - C_A)$. Think how little base must be added to change the second term from -5 to -4, and how much more base is needed to change it from -3 to -2.