

Chapter 12 continued – Acid / Base Titrations

Things to Remember Concerning Titration Curves

Important regions of titration curve:

- ✓ In buffer region, $\text{pH} = \text{pK}_a$. This occurs at $\frac{1}{2}$ the volume of base needed to reach the equivalence point.
- ✓ The steepest region of the curve is the equivalence point.
- The weaker the acid (smaller K_a or large pK_a), the smaller the equivalence point region.
- The more dilute the acid or the titrant, the smaller the equivalence point region.

Standardizing the Titrant

Strong bases (used to titrate strong and weak acids) are susceptible to changes in concentration in the presence of carbonates (which comes from CO_2 in the air). So they must be standardized with a primary standard to determine the true concentration. They also must be stored to minimize CO_2 exposure once they are standardized.

Strong Acids (used to titrate strong and weak bases) are made up from concentrated acids that do not have a well defined concentration. For example HNO_3 is listed as having a concentration from 69 to 71%. Strong acids used as titrants must be standardized with a primary standard also.

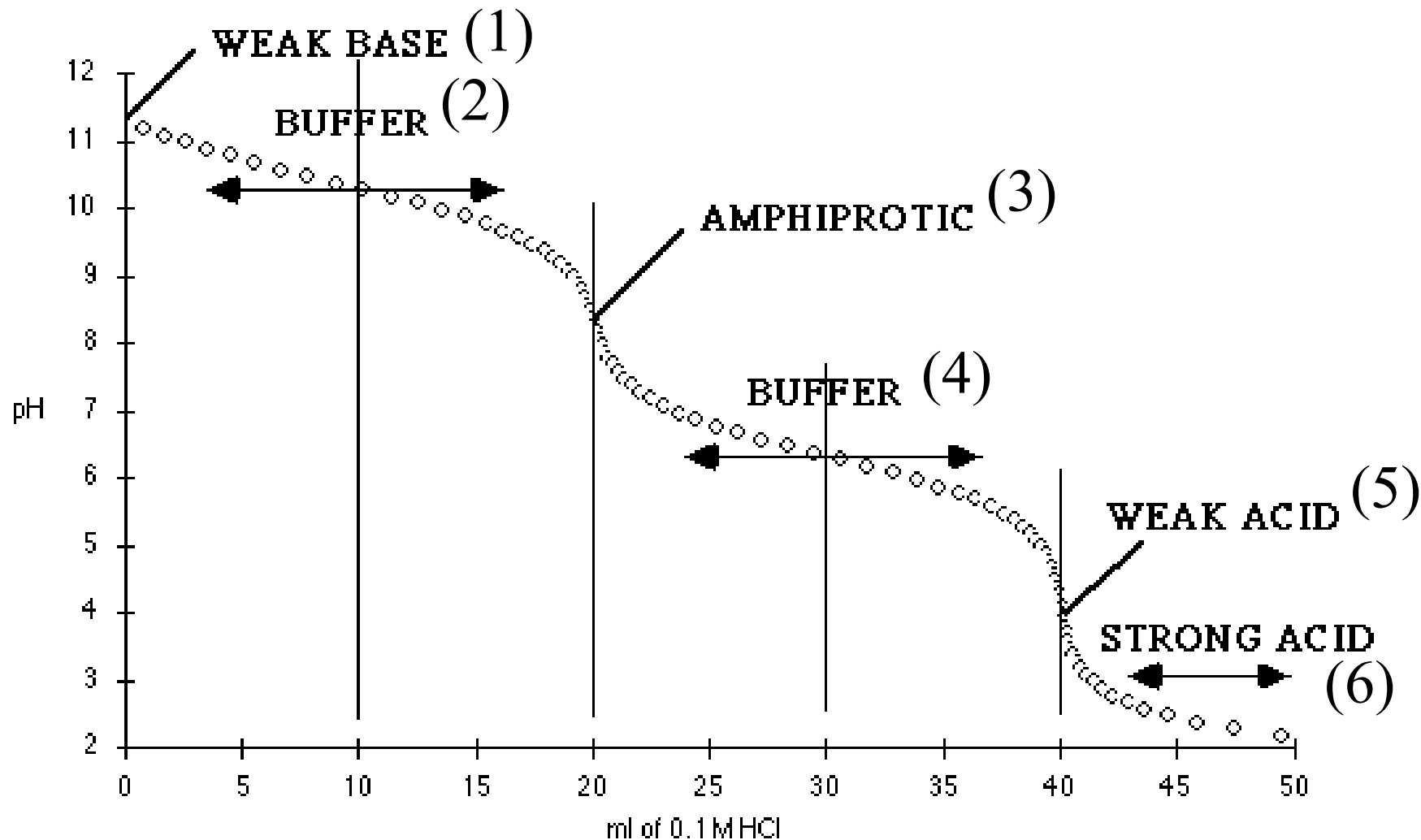
See Harris pg. 244-245 for list of primary standards.

Leveling Effect

The strongest acid that can exist in water is H_3O^+ . The strongest base that can exist in water is OH^- . If an acid stronger than H_3O^+ is dissolved in water, it cannot have a stronger acid group than H_3O^+ ; it is said to be “leveled” by the water. Similarly, the stronger base is also “leveled” by the water.

Example: HClO_4 is a stronger acid than HCl , but in water they have the same strength. If these acids were dissolved in acetic acid, then the difference in acid strength could be observed.

Regions of the Titration Curve a Diprotic Base



Determining pH of Different Regions of the Titration Curve a Diprotic Weak Base

The first step is to determine the volume of base needed to reach the equivalence point. Use the concentration and volume of base.

Region 1: Initial point (no acid added) – The pH is determined from the concentration of the weak base. $x^2/(F-x) = K_b$
 $x = [\text{OH}^-] = K_w / [\text{H}^+]$.

Region 2: Before 1st equivalence point (buffer region) – The pH is determined using the Henderson-Hasselbalch equation (buffer)
 $\text{pH} = \text{p}K_{a2} + \log([\text{base}]/[\text{acid}]) = \text{p}K_w/\text{p}K_{b1} + \log([\text{base}]/[\text{acid}])$.

Region 3: 1st equivalence point – All the most basic form has been converted to the first intermediate form ($\text{B} + \text{H}_2\text{O} \rightarrow \text{BH}^+ + \text{OH}^-$). Since BH^+ can be both an acid and base, the pH is determined either from the equation relating $[\text{H}^+]$ to the K_{a1} , K_{a2} , and F **OR** from the equation $\Rightarrow \text{pH} = \frac{1}{2} (\text{p}K_{a1} + \text{p}K_{a2})$.

Region 4: Before 2nd equivalence point (buffer region) – The pH is determined using the Henderson-Hasselbalch equation (buffer)
$$\text{pH} = \text{pK}_{\text{a}1} + \log([\text{base}]/[\text{acid}]) = \text{pK}_{\text{w}}/\text{pK}_{\text{b}1} + \log([\text{base}]/[\text{acid}]) .$$

Region 5: 2nd equivalence point – All the most base has been converted to the most acidic form ($\text{BH}^+ + \text{H}_2\text{O} \rightarrow \text{BH}^{+2} + \text{OH}^-$). The pH is determined using the initial concentration (F) accounting for the dilution factor to get at F', then using the weak base equation: $x^2/(F' - x) = K_{\text{b}2}$. $x = [\text{OH}^-]$ so $[\text{H}^+] = K_{\text{w}} / x$.

Region 6: After the 2nd equivalence point – The pH is dictated by the excess acid $[\text{H}^+]$ in solution.

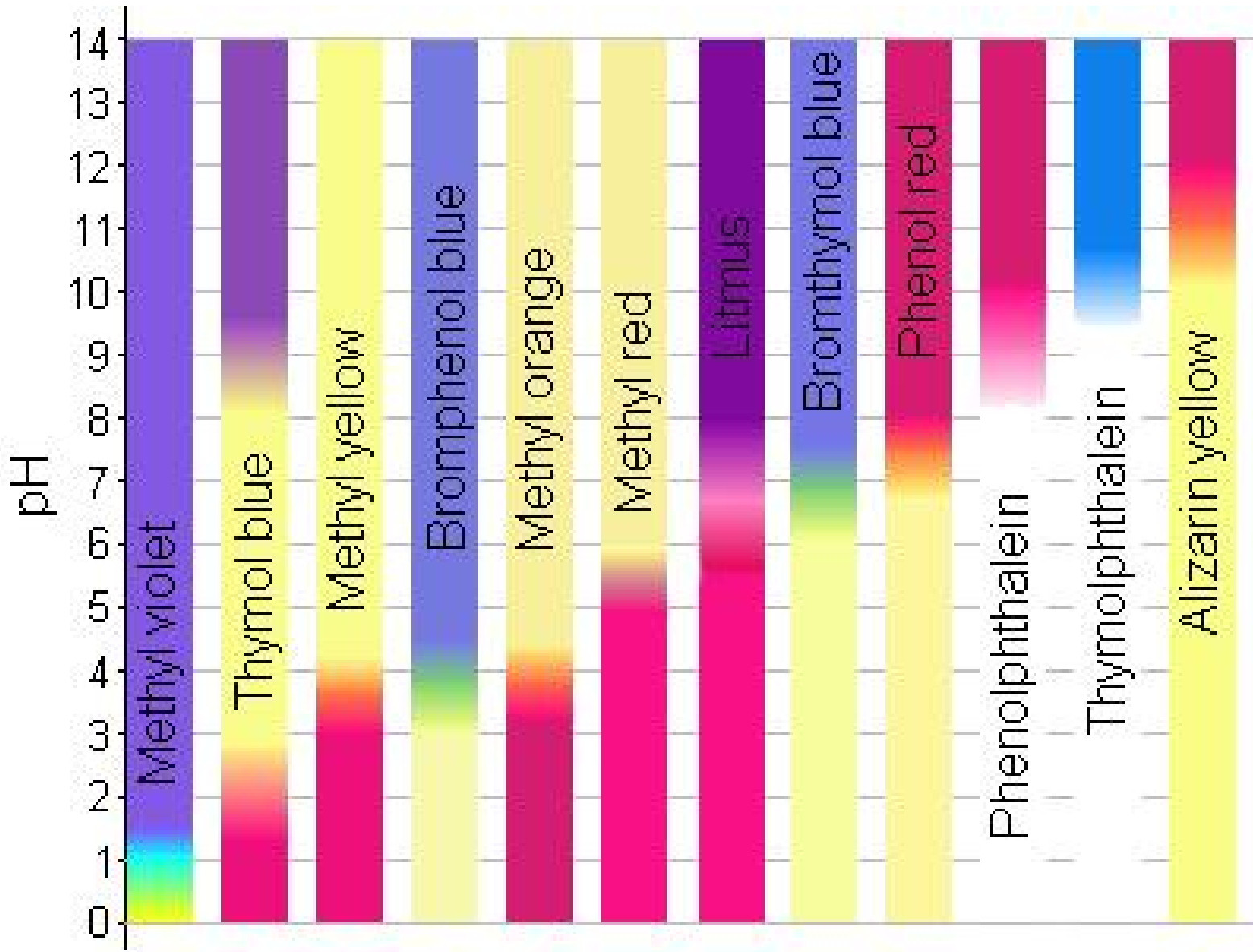
Calculate the pH at each point and sketch the titration curve of the titration of 50.0 mL of 0.0500 M malonic acid with 0.100 M NaOH.
 $V_b = 0.0, 8.0, 12.5, 19.3, 25.0, 37.5, 50.0, 56.3$ mL

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End-point determination with indicators

Acid-Base indicators are dyes that are themselves weak acids and bases. However, the conjugate acid-base forms of the dye have different colors. Different dyes will change color at different pH's (the value can be calculated from the equilibrium constant for the indicator). One of the difficulties with giving a range of colors is that different person's eyes are not all equally sensitive (also different monitors will display colors differently), so these colors are only approximations.

When conducting a titration, one must select the proper indicator so that its pH range will match the equivalence point of the titration. Also, you must use an indicator that changes color obviously, so that it can be detected easily. This is why phenolphthalein is so often used for strong acid-strong base titrations.



How to find the end point of a titration.

End point: Some physical or measured changed showing that all the acid/base site of the analyte has been titrated.

Equivalence point: Actual point along the titration curve that the acid/base site of the analyte has been titrated. Typically thought of as the volume of titrant needed to neutralize the analyte.

We can calculate the equivalence point, but in an experiment we may not have the info to do the calculation, so we need some way to measure the end point.

- Use pH meter. Look for dramatic changes in pH
 - ✓ To get specific end point (closer to equivalence point), use the 1st or 2nd derivative plots.
- Use color indicators
 - ✓ Match the pH where there is a change in color to the pH of the equivalence point.

1st and 2nd derivative plots:

mL NaOH	pH	mL NaOH	1st derivative dpH/dmL	ml NaOH	2nd derivative d(dpH/dmL)
10.679	7.643				
10.696	7.447	10.6875	-11.5294118		
10.713	7.091	10.7045	-20.9411765	10.696	-0.87993313
10.721	6.7	10.717	-48.875	10.71075	-1893.81854
10.725	6.222	10.723	-119.5	10.72	-7635.13514
10.729	5.402	10.727	-205	10.725	-17100
10.733	4.993	10.731	-102.25	10.729	25687.5
10.738	4.761	10.7355	-46.4	10.73325	13141.1765
10.75	4.444	10.744	-26.4166667	10.73975	3074.35897
10.765	4.227	10.7575	-14.4666667	10.75075	1086.36364

