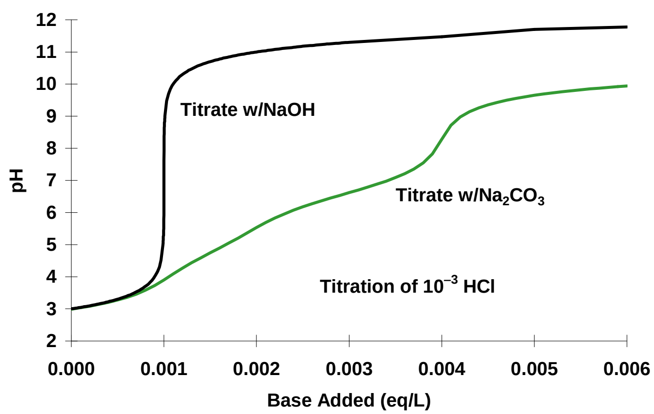
Acid/Base Titrations

- Note: Acid or base added in a titration is often expressed in equiv/L. 1 equiv is 1 mole of H^+ or an amount of some other species that ***can*** provide (or, in the case of bases, consume) 1 mole of H^+.
- The fact that a species ***can*** provide or consume one H^+ does not mean that it necessarily ***will*** do so under a given set of circumstances (specifically, at a given pH). Therefore, the basis for defining "equivalency" must be clearly stated to avoid confusion.
- Universally, H_2CO_3 and CO_3^{2-} are treated as having 2 equiv/mol; for other species, the assignment is not always consistent or obvious.

Titration with a Weak Base



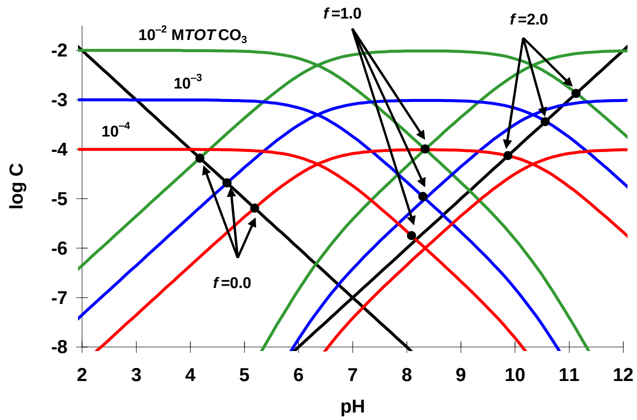
Acid/Base Titrations

- Titrations with weak acids or bases change the pH less than those with strong acids or bases, because they don't exchange all possible H^+ and because they themselves must be titrated.
- The amount of strong acid or base needed to change pH from one value to another equals the difference in *TOT*H of the solution at the two pH values, where *TOT*H can be computed using any consistent set of **components**.

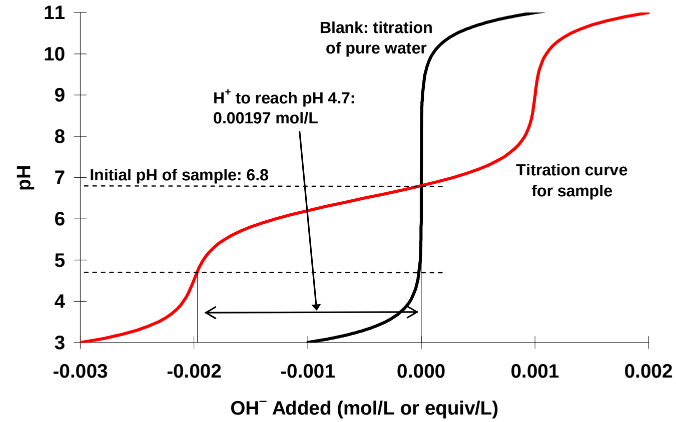
Alkalinity and Acidity

- Generic descriptors of the capacity of the solution to acquire H^+ or OH^- without reaching some limiting or undesirable condition, specified as a particular pH.
- For experimental measurements, pH endpoint for Alk titration is chosen to be 4.5±0.2. Conceptually justified as the pH of a solution made by adding $TOTCO_3$ to pure water, entirely as H_2CO_3.
- Alk frequently approximated as deriving entirely from $H_2CO_3/HCO_3^-/CO_3^{2-}$ and $H^+/H_2O/OH^-$ groups. In reality, ***all weak bases contribute to Alk***, because all consume some H^+ between initial condition and titration endpoint.
- Can be quantified as net proton excess at endpoint minus net proton excess prior to titration (i.e., $TOTH_{endpt} - TOTH_{init}$). Therefore, a ***conservative*** property.

Alkalinity and Acidity



Alkalinity and Acidity



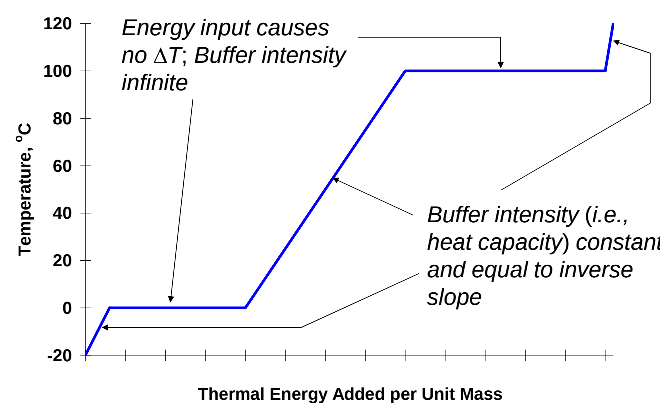
Buffer Intensity

- Generic descriptor of the tendency of the solution to resist a pH change in response to addition of strong acid or base. Defined mathematically as:

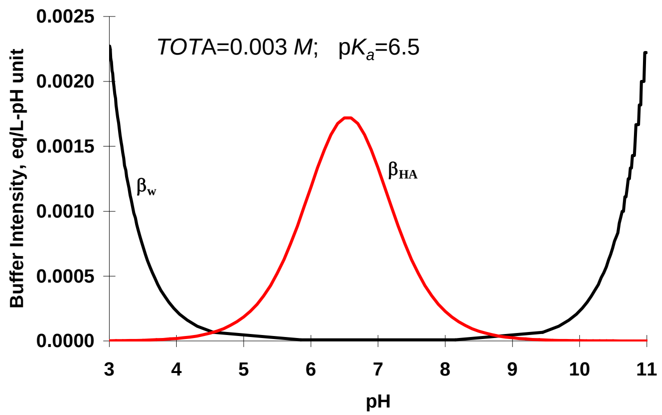
$$\beta = \frac{d\left[\mathrm{OH}^-\right]_{added}}{d\mathrm{pH}} = -\frac{dTOT\mathrm{H}}{d\mathrm{pH}}$$

- Includes contributions required to:
  - increase $[OH^-]$ and decrease $[H^+]$, defined as β_w;
  - react with H^+ released by weak acids, defined as β_a.
- Contributions of different acid/base groups are additive
- Analogous to heat capacity of a solution, which quantifies tendency to resist a temperature change

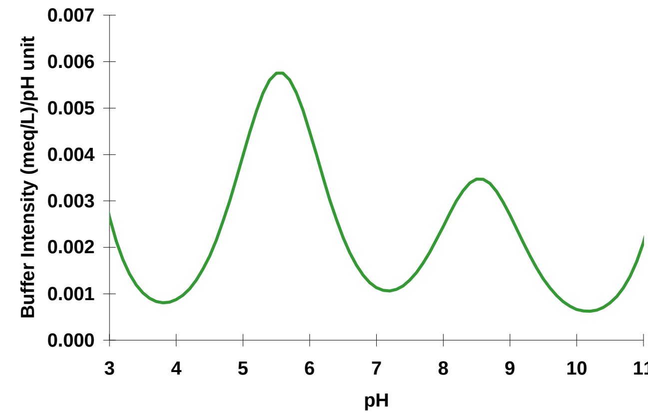
Temperature Buffering Intensity



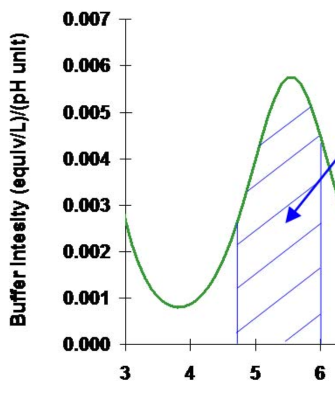
Buffer Intensity



Buffer Intensity



Buffer Intensity



$$\int_{pH_1}^{pH_2} \beta\, dpH = \int_{pH_1}^{pH_2} \frac{d\left[OH^-\right]_{added}}{dpH}\, dpH = \Delta\left[OH^-\right]_{added}$$

Buffer Intensity