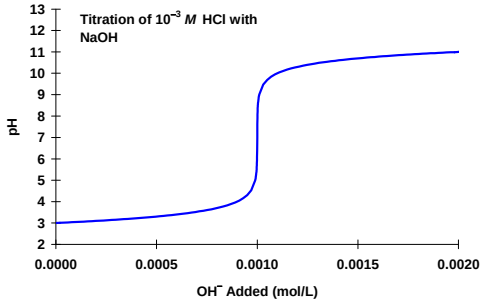
## Acid/Base Titrations

- Experimental procedure in which incremental amounts of a solution of known composition are added to a solution of unknown composition. The pH (or other) response provides information about the unknown composition.
- For addition of strong acid, a "real-life" implementation of the imaginary procedure used to determine the likely dominant species, except that the titration starts in the middle of the imaginary process (with some bases already protonated).
- Can equally well be carried out using a weak acid, or a strong or weak base, as the titrant.

## Titration with Strong Base)

- In a titration with base, each increment of titrant adds $OH^-$ and inert salt. Some added $OH^-$ remains "free", and some combines with $H_3O^+$ and other acids to form their conjugate bases.

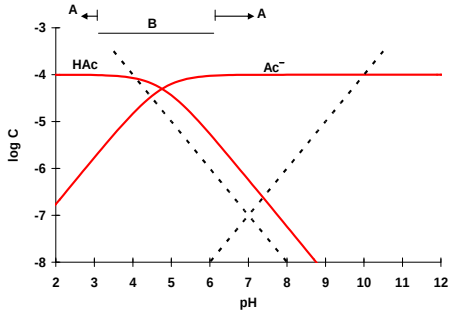
Because of the logarithmic relationship between $[H^+]$ and pH, much more $OH^-$ must be added for a given $\Delta$pH at high or low pH than at near-neutral pH



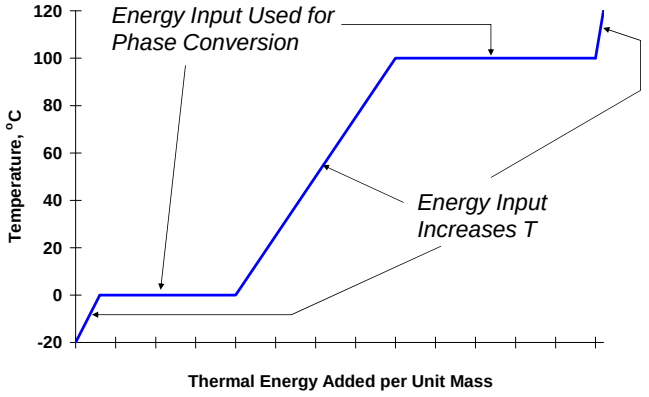

## Titration with Strong Acid or Base

- Consider two solutions that are identical, except that one contains *TOT*A of a weak acid/base pair

- If pH is in range where speciation of the *TOT*A is almost constant, the two solutions will have almost identical responses to titrant additions
- If pH is in range where speciation of the *TOT*A is changing rapidly, the acid/base will react with much of the added $OH^-$/$H^+$, and pH will change more slowly in the system with *TOT*A




## Titration with Strong Acid or Base: Analogy to a "Thermal" Titration



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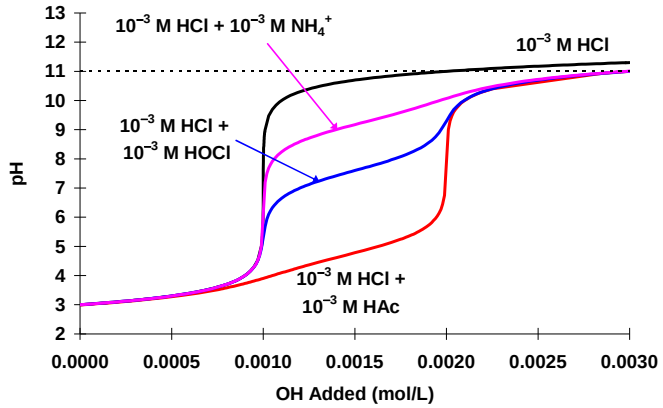
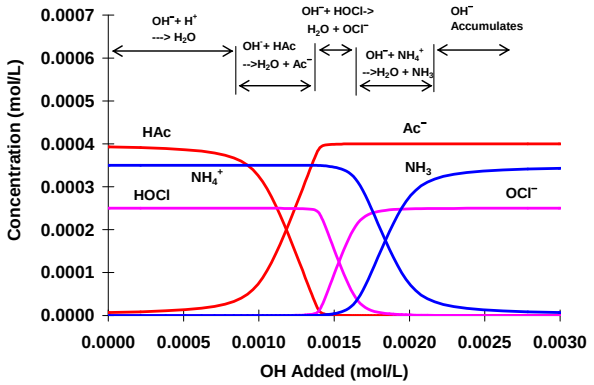



## Titration with Strong Acid or Base

$10^{-3}$ HCl + 0.4x$10^{-3}$ HAc + 0.25x$10^{-3}$ HOCl + 0.35x$10^{-3}$ $NH_4Cl$

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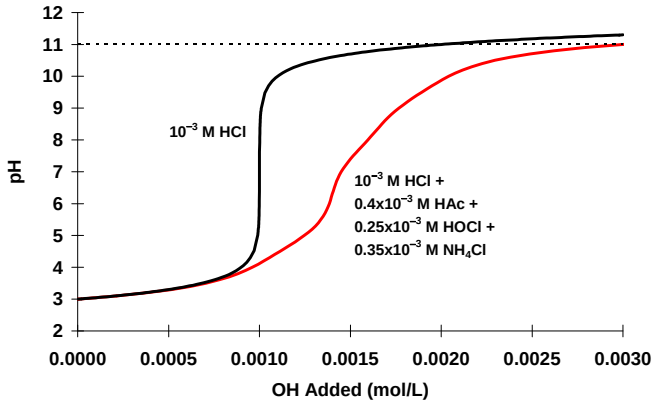


- When plotted as pH vs. conc'n of strong acid or base added, titration curves have "flat" regions in the vicinity of the p$K_a$ of each conjugate acid/base group in the solution. The extra width in the flat region indicates the concentration of $H^+$ released (or acquired) by the group as it is converted from acid to conjugate base (or vice versa).
- The additional amounts of strong acid or base needed to achieve a given ΔpH (compared to a control system with no weak acids or bases) are additive, considering all the weak acid/base groups in the system.
- Because all reactions are reversible, titrations with strong acid can be exactly reversed by titrations with strong bases (except for changes in activity coefficients induced by the salt addition).
- 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**.

## Titration with Strong Acid or Base