

Announcements

- Turn on the Clicker (the red LED comes on).
- Push “Join” button followed by “20” followed by the “Send” button (switches to flashing green LED if successful).
- Exam 3 on on Thursday.
- Please do not enter room until asked to.
- Discussion will begin with short review worksheet.
- Bring questions for the rest of discussion.

Review

- pH, pOH, pK_w
- relation between K_a and K_b of conjugates: $K_w = K_a K_b$
- pH of salt solutions
 - Salts of conjugates of weak acids make basic solutions (examples: NaF, KF, NaNO_2 , KHSO_4)
 - Salts of conjugates of weak bases make acidic solutions (example: NH_4Cl)
 - Salts of conjugates of strong acids and bases do not affect pH (example: NaCl)

Review

- Buffers
 - Buffer = a solution that resists a change in its pH when either an acid or base is added.
 - Can calculate pH using standard equilibrium calculations
 - If salt and acid reasonably high easier to use Henderson-Hasselbach: $\text{pH} = \text{pK}_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) = \text{pK}_a + \log\left(\frac{[\text{salt}]}{[\text{acid}]}\right)$
 - As seen in lab Henderson-Hasselbach is only approximate.
 - Calculation of approximate new pH if you add an acid or base using Henderson-Hasselbach.

Strong Acid-Strong Base Titration Curve

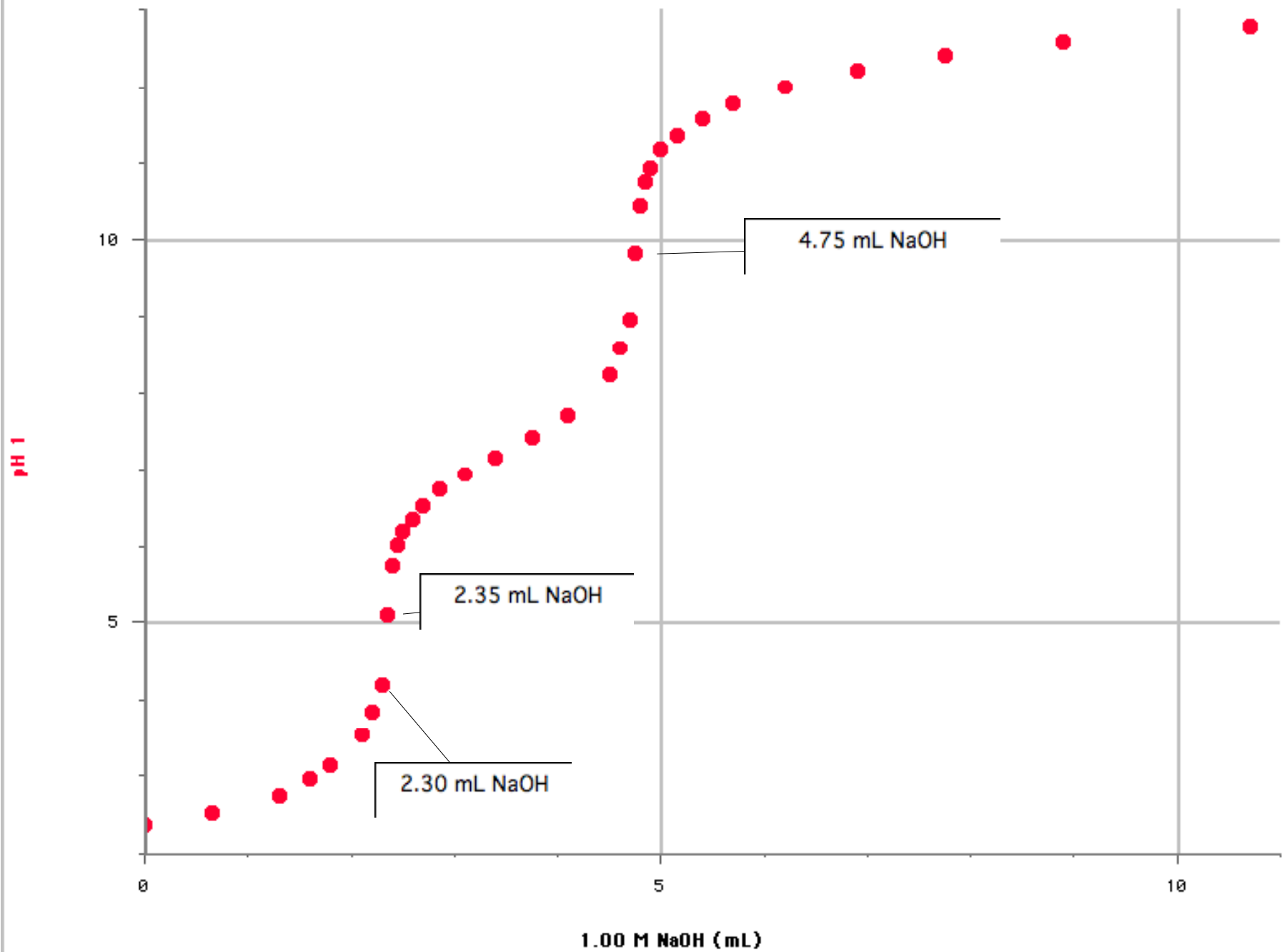
Chang Fig 17.4

Weak Acid-Strong Base and Strong Acid-Weak Base Titrations

Weak Acid-Strong Base
Chang Fig. 17.5

Weak Base-Strong Acid
Chang Fig. 17.6

Phosphoric acid titrated with NaOH



Review

- Chemical equilibria are dynamic equilibria
 - the forward reaction rate exactly balances the reverse reaction rate. ($R_f = R_r$)
- Considered RXN: $N_2 + O_2 \rightleftharpoons 2NO$
 - $R_f = R_r \Rightarrow k_f [N_2][O_2]^{-1/2} = k_r [NO]^2/[O_2]^{1/2}$
 - Where all [..] are the equilibrium concentrations.

Review

- Writing equilibrium constant mass action expressions:
 - $aA + bB \rightleftharpoons cC + dD$
 - $K_{eq} = [C]^c[D]^d / \{[A]^a[B]^b\}$ where all concentrations (or partial pressures are at equilibrium).
 - If not at equilibrium this ratio is called Q, the reaction quotient.
 - $Q > K \Rightarrow$ reaction will run in reverse.
 - $Q < K \Rightarrow$ reaction will run forward.
- $K_{reverse} = K^{-1}$
- $K_P = K_C(RT)^{\Delta n}$
 - R must be in L atm mol⁻¹K⁻¹ if partial P's have units of atm.
 - R must be in Jmol⁻¹K⁻¹ if partial P's in Pa.

Review

- Quadratic in solving equilibria
- Relation between K and ΔG
 - $K = \exp(-\Delta G^\circ / (RT))$
 - $\Delta G^\circ = -RT \ln K$
- Le Châtelier's principle:
 - If a system at equilibrium is subjected to a stress, the position of the equilibrium will shift in the direction that will relieve that stress.
 - Examples: effect of changes of concentration, pressure and temperature.
 - Catalysts have no effect since they do not change ΔG° .
- Heterogeneous equilibria: pure solids and solvents do not appear in mass action expression.

Review

- Acid-Base equilibria.
 - Strong acids: HNO_3 , HCl and first proton on H_2SO_4 dissociate completely when mixed with water.
 - For weak acids $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ does not go 100%.
 - $K_a = [\text{H}^+][\text{A}^-]/[\text{HA}]$ is tabulated for many of these.
 - Can use K_a in normal equilibrium calculations.
- Important acid-base equilibrium situation is buffers.
 - Buffer = a solution that resists having its pH changed when acid or base is added.
 - Made by mixing a weak acid and a salt containing the same negative ion.

Review

- $\text{pH} = -\log_{10}[\text{H}^+]$, generally $\text{pX} = -\log_{10}X$, $10^{-\text{pX}} = X$
- Showed that when the [acid] and [salt] in a buffer are near 1.0 M we can use the Henderson-Hasselbach equation to estimate $\text{pH} = \text{pK}_a + \log[\text{salt}]/[\text{acid}]$. The [..] are assumed to be the initial values.
 - When making a buffer pick $\text{pK}_a \approx$ desired pH.
 - Solve $\text{pH} = \text{pK}_a + \log[\text{salt}]/[\text{acid}]$ for ratio [salt]/[acid].
 - For ratio < 1 set minimum [salt]•(L sol'n) $>$ # moles of acid to buffer.
 - For ratio > 1 set minimum [acid]•(L sol'n) $>$ # moles of base to buffer.

Review

- Brønsted-Lowry
 - acid = a proton donor
 - base = a proton acceptor
- Lewis
 - acid=electron pair acceptor
 - base = electron pair donor
- Conjugate pairs
 - Acids and bases which interconvert during an acid-base reaction.
 - Conjugate bases of weak acids are strong bases.
 - Conjugate acids of weak bases are strong acids.
- Acid dissociation equilibria just like any other.
 - $\text{HA(aq)} \rightleftharpoons \text{H}^{\text{+}}(\text{aq}) + \text{A}^{-}(\text{aq})$ $-K_{\text{a}} = [\text{H}^{\text{+}}][\text{A}^{-}]/[\text{HA}]$
 - Given numerical value for K_{a} and initial $[\text{HA}]$ can find final equilibrium concentrations.
- Likewise for bases
 - $\text{MOH(aq)} \rightleftharpoons \text{M}^{\text{+}}(\text{aq}) + \text{OH}^{-}(\text{aq})$ $-K_{\text{b}} = [\text{M}^{\text{+}}][\text{OH}^{-}]/[\text{MOH}]$

Review Con't

- Acid Rain (pH < 5.3)
 - Multiple coupled acid dissociation equilibria
 - Large K_{a1} , assume first dissociation goes to completion and then equilibrate second step (K_{a2}).
 - Small K_{a1} , equilibrate first dissociation, use result to as start to equilibrate second dissociation, then iterate. You are not expected to iterate, but must show that second step change is small enough that you do not need to.
 - Acids causing acid rain H_2SO_4 , HNO_3 , HNO_2 .
 - Natural rain slightly acidic from carbonic acid (H_2CO_3) equilibria. The carbonic acid comes from dissolved CO_2 .
- Judging relative strength of oxo and halogen acids. (More oxygen on conjugate base = more acidic, for halogens acids stronger as go down group).
- $pH = -\log_{10}[H^+] = -\log_{10}[H_3O^+]$ (pH < 7 = acid, pH > 7 = base)

pH, pOH, pK_w

- $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$
 - $K_w (25^\circ \text{C}) = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$
 - in pure water $[\text{H}^+] = [\text{OH}^-] = x$
 - $x^2 = 1.0 \times 10^{-14}$
 - $x = 1.0 \times 10^{-7} = [\text{H}^+] = [\text{OH}^-]$
- $\text{p}K_w = -\log(1.0 \times 10^{-14}) = 14.00$
 - $\text{p}K_w = -\log[\text{H}^+][\text{OH}^-] = -\log[\text{H}^+] + -\log[\text{OH}^-]$
 $= \text{pH} + \text{pOH} = 14.00$
 - For conjugate pairs: $K_a K_b = K_w$ or $\text{p}K_a + \text{p}K_b = \text{p}K_w$